# Nitrate Group as a Ligand in Solid Copper(II) Complexes. The Structure of Cu(NO₃)₂ · 2.5H₂O

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The structure of copper(II) nitrate hydrate, which has been assumed to be a trihydrate, has been solved by X-ray structural analysis. The correct composition of this substance is $Cu(NO_3)_2 \cdot 2.5H_2O$ where only two molecules of water coordinate Cu(II) while the remainder is bound merely by hydrogen bonds. The pith of this study is an interpretation of X-ray structural analysis informations about $Cu(NO_3)_2 \cdot 2.5H_2O$ and correlation of this interpretation to the knowledge gathered from the investigation of solutions as well as to the results obtained by other authors in an analogous region.

The subject of this study is the nitrate group and its chemical bonding in Cu(II) compounds. We have started to go into this problem in connection with three facts:

We stated the existence of copper(II) nitrato complexes [1—6] on the basis of physico-chemical analysis. From these results we considered the most interesting the data that indicated the ability of nitrate group to act as a bridge in relatively very stable heterogeneous complexes in solutions. The second fact concerned the knowledge of the properties and structure of anhydrous copper(II) nitrate and especially the disputable character of structure interpretation of this substance [7—14] as well as other information about the structure in this subject matter [5, 6, 15]. The third impuls ensued from our information about the influence of nitrate group acting as a ligand on the intracomplex redox processes which resulted in the reduction of bivalent copper [4].

We took interest in the matter of fact that the structure of one of commonly used substances, copper(II) nitrate hydrate taken for $Cu(NO_3)_2 \cdot 3H_2O$, was not known up to that time.

Copper(II) nitrate forms several hydrates [16—20]. Only two of them. namely $Cu(NO_3)_2 \cdot 1.5H_2O$ and $Cu(NO_3)_2 \cdot 2.5H_2O$, have been investigated with respect to their structure till now. There are only some basic data on the symmetry of the first one [21]. A short communication on some preliminary X-ray structural analysis results of the second one has been published by us [22, 23].

The aim of this study is to contribute some new information and ideas on the bonding properties of nitrate group in copper(II) compounds by determining the structure of one of copper(II) nitrate hydrates. It is a topical problem because the ability of nitrate group to act as a ligand has been discussed in some papers on the basis of modern theories of chemical bonding, recently [24].

## Experimental

The fundamental diffraction data were obtained for two copper(II) nitrate hydrates, namely the commercial trihydrate and the $Cu(NO_3)_2 \cdot 2.5H_2O$, prepared according to [18]. Copper and nitrate content were determined in both substances. Hydrogen and nitrogen were determined by elementary analysis.

For $Cu(NO_3)_2 \cdot 3H_2O$ (241.60) calculated: 26.30% Cu, 51.33% $NO_3$, 2.50% H, 11.59% N; found: 27.12% Cu, 46.88% $NO_3$, 2.42% H, 11.39% N.

For $Cu(NO_3)_2 \cdot 2.5H_2O$ (232.59) calculated: 27.86% Cu, 53.20% $NO_3$, 2.15% H, 12.17% N; found: 27.50% Cu, 48.02% $NO_3$, 2.30% H, 11.19% N.

Both powder and Weissenberg X-ray diffraction patterns showed that both hydrates were identical as regards these two methods. The space groups $I2/c$ and $Ic$, respectively, were deduced from the symmetry of diffraction patterns (the systematically absent reflections were: $h + k + l \neq 2n$ and $h0l$ with $h \neq 2n, l \neq 2n$).

The transformation of axes: $\bar{a}' = \bar{a} + \bar{c}$, $\bar{b}' = \bar{b}$, $\bar{c}' = \bar{c}$ leads to $C2/c$ and $Cc$ space groups what agrees with *International Tables for X-Ray Crystallography*.

The lattice parameters were determined on the basis of Guinier powder patterns. The photographies were calibrated with $Pb(NO_3)_2$ by using $CuK_\alpha$ radiation, $\lambda = 1.54051$ Å. To refine the lattice parameters, the program developed by *Lindquist* [25] was used. The refined values for the space centered symmetry group were: $a = 16.455 \pm 0.003$ Å, $b = 4.041 \pm 0.001$ Å, $c = 15.962 \pm 0.003$ Å, $\beta = 93.75 \pm 0.01°$; $V_0 = 1295.00$ Å³. The density, measured by the flotation technique, was found to be 2.28 g cm⁻³ ($t = 23°C$). The density corresponding to eight formula units of $Cu(NO_3)_2 \cdot 2.5H_2O$ per unit cell was 2.37 g cm⁻³.

A crystal measuring $0.15 \times 0.4 \times 0.15$ mm³ was rotated about the monoclinic $b$ axis. Three-dimensional intensity data were obtained from equi-inclination of Weissenberg photographs (up to the 4th layer). The crystals were deliquescing in the contact with air humidity and therefore they had to be isolated from air by a layer of nitrocellulose lacquer. The substance gave very good diffraction patterns, the expositions did not exceed 30 hours. The films were estimated photometrically. Intensities were corrected for Lorentz and polarization factors. No absorption correction was applied ($\mu R = 0.79$).

### Determination and refinement of the structure

Weissenberg photographs (excepting zero layer) show pseudoquenching. Intensities for which $l = 2n$ are more intense than those for which $l = 2n + 1$. This fact was used for the determination of crystal structure. At first, only the superposition structure was assumed but all structure factors observed were applied in the last phase of refining. The superposition structure had the symmetry $C2/m$ with the $c'$ axis $1/2c$ from which it followed that the $y$ coordinate of Cu atom was equal or close to zero.

The structure was determined using 668 reflections from which 292 reflections were systematically weaker ($l = 2n + 1$). The statistic intensity distribution [22] was calculated for the systematically weaker intensities of type $F(hll)$ which exceeded the values given for a structure with the centre of symmetry. The crystal structure of $Cu(NO_3)_2 \cdot 2.5H_2O$ was solved in $I2/c$ space group.

The position of copper(II) atom was found on the basis of the three-dimensional Patterson analysis. All large peaks could be interpreted by assumption of general position of $I2/c$ space group. The O and C atoms were found by computer search of an electron-density synthesis phased an the Cu atom.
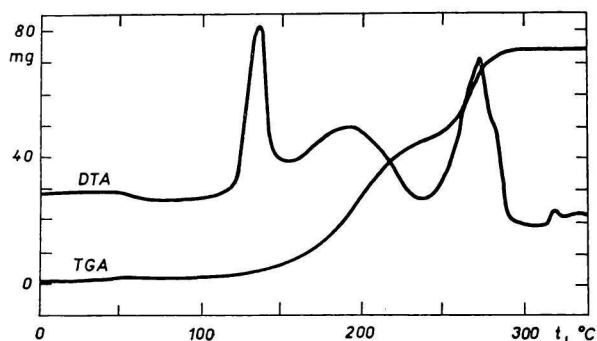
*Fig. 1.* Thermal decomposition record of the commercially produced hydrate, usually denoted as $Cu(NO_3)_2 \cdot 3H_2O$.

Refinement was performed by the least-square method and the value of 0.15 for the $R$-factor was obtained on the basis of the systematically heavy structure factors $F_0$. In these calculations the $y$ coordinates of all atoms were fixed provided these coordinates were close to zero. Besides copper atoms, it refers to all molecules of water, atoms of nitrogen and one oxygen atom of nitrate group. Another two positions of oxygen atoms of this group were fixed already in the superposition structure unambiguously. Fourier synthesis with systematically more intense coefficients $F(hkl)$ doubled the second nitrate group. In principle, it was possible to select two models for this second nitrate group.
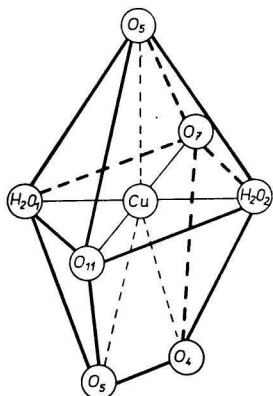


*Fig. 2.* Coordination of the central Cu(II) atom in crystals of $Cu(NO_3)_2 \cdot 2.5H_2O$.
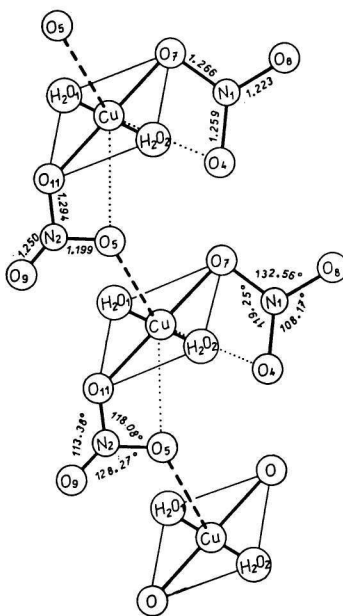
*Fig. 3.* The kind of coupling of coordination polyhedrons in the direction of $b$ axis.

The rightness of one of these models was ascertained by correcting the coordinates of both models according to all observed structural factors. Provided $l = 2n + 1$, $F_o$ and $F_c$ were in conformity one to another in single case only.

Refinement of the atomic positions, the scale factors for systematically heavy and weaker $F_o(hkl)$ and individual isotropic temperature coefficients determined by the full matrix least-square method, yielded the $R$ value of 0.105, defined as $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. The *Cruickshank* [26] weighting scheme was applied for the refinement where $w\Delta^2 = $ const and $w = (A + F_o + CF_o^2)^{-1/2}$. During the last cycle of refinement the constants of $A$ and $C$ had the values of 13.40 and 0.0076, respectively. The structure factors were calculated from the atomic factor values according to *Ibers* [27]. At last the differential Fourier synthesis has been calculated. The maximum electron density in this calculation reached the value of 1.59 e/Å³ and the maximum value of the function $\varrho(xyz)$ was 79.00 e/Å³.

Fourier syntheses were calculated according to the program of Zalkin. The least-square program developed by Gantzel, Sparkson, and Trueblood was used. Both programs were adapted for the computer IBM 360/50 by Lindgren.

In the last cycle of refinement the changes of atom coordinates were smaller than their standard deviations. The refined atom positions and temperature coefficients are given in Table 1. The observed and calculated structure factors are presented in Table 2. The unobserved reflections were omitted in calculations.

*Table 1*

Atomic positions and isotropic thermal parameters with their standard deviations for $Cu(NO_3)_2 \cdot 2.5H_2O$

| Atom | $x$ | $x$ | $y$ | $y$ | $z$ | $z$ | $B$ |
|------|-----|-----|-----|-----|-----|-----|-----|
| Cu | 0.1261 | 1 | 0.0084 | 4 | 0.1139 | 0 | 0.738 |
| $O_3$ | 0.5000 | 0 | 0.0511 | 32 | 0.2500 | 0 | 1.317 |
| $O_1$ | 0.2415 | 6 | 0.0043 | 19 | 0.0893 | 6 | 1.383 |
| $O_2$ | 0.0108 | 6 | 0.0370 | 24 | 0.1406 | 7 | 1.601 |
| $O_4$ | 0.1567 | 6 | 0.7485 | 22 | 0.2573 | 7 | 1.115 |
| $O_{11}$ | 0.4091 | 6 | 0.3382 | 20 | 0.0045 | 6 | 0.909 |
| $O_5$ | 0.3707 | 5 | 0.0034 | 17 | 0.4208 | 0 | 0.908 |
| $O_7$ | 0.1585 | 5 | 0.1784 | 19 | 0.2271 | 6 | 0.751 |
| $O_8$ | 0.1916 | 6 | —0.0118 | 20 | 0.3548 | 7 | 1.572 |
| $O_9$ | 0.4225 | 6 | —0.0520 | 26 | 0.0508 | 7 | 1.935 |
| $N_1$ | 0.1691 | 6 | —0.0104 | 20 | 0.2803 | 6 | 0.261 |
| $N_2$ | 0.0984 | 6 | 0.5792 | 26 | 0.0140 | 6 | 0.288 |

## Results and Discussion

The interatomic distances and their standard deviations are given for $Cu(NO_3)_2 \cdot 2.5H_2O$ in Table 3. In the following Table 4 bond angles and their standard deviations are summarized.

Except for one water molecule, all other atoms occupy general positions in the $I2/c$ space group. The oxygen atom of one water molecule is situated in a special fourfold position on the twofold rotation axis. According to the data of structural analysis the stoichiometric formula of the commercial copper(II) nitrate hydrate is

## Table 2

### Observed and calculated structure factors

| H | K | L | Fo | Fc |
|---|---|---|----|----|
| 0 | 0 | 2 | 27.0 | 26.7 |
| 0 | 0 | 4 | 77.2 | 80.4 |
| 0 | 0 | 6 | 158.1 | 159.4 |
| 0 | 0 | 8 | 237.1 | 250.9 |
| 0 | 0 | 10 | 54.9 | 52.4 |
| 0 | 0 | 12 | - | 19.4 |
| 0 | 0 | 14 | - | 22.5 |
| 0 | 0 | 16 | - | 33.1 |
| 0 | 0 | 18 | 50.2 | 62.8 |
| 0 | 0 | 20 | - | 4.5 |
| 2 | 0 | 18 | 66.9 | 55.3 |
| 2 | 0 | 16 | 89.3 | 80.9 |
| 2 | 0 | 14 | 23.1 | 12.0 |
| 2 | 0 | 12 | 148.8 | 142.2 |
| 2 | 0 | 10 | 139.5 | 126.5 |
| 2 | 0 | 8 | 147.8 | 137.3 |
| 2 | 0 | 6 | 231.5 | 243.8 |
| 2 | 0 | 4 | 66.9 | 72.8 |
| 2 | 0 | 2 | 139.5 | 137.8 |
| 2 | 0 | 0 | 23.2 | 21.1 |
| 2 | 0 | -2 | 239.9 | 299.8 |
| 2 | 0 | -4 | 167.4 | 148.7 |
| 2 | 0 | -6 | 78.1 | 81.5 |
| 2 | 0 | -8 | 93.0 | 96.7 |
| 2 | 0 | -10 | 70.7 | 66.3 |
| 2 | 0 | -12 | 116.2 | 121.2 |
| 2 | 0 | -14 | - | 18.0 |
| 2 | 0 | -16 | - | 3.6 |
| 2 | 0 | -18 | 60.4 | 54.8 |
| 2 | 0 | -20 | 53.0 | 89.7 |
| 4 | 0 | 20 | 27.9 | 22.9 |
| 4 | 0 | 18 | 93.9 | 104.9 |
| 4 | 0 | 16 | 94.8 | 83.1 |
| 4 | 0 | 14 | 43.7 | 34.4 |
| 4 | 0 | 10 | 164.6 | 149.2 |
| 4 | 0 | 8 | 187.8 | 169.4 |
| 4 | 0 | 6 | 118.1 | 120.7 |
| 4 | 0 | 4 | 93.0 | 96.6 |
| 4 | 0 | 2 | 106.9 | 95.3 |
| 4 | 0 | 0 | 273.1 | 313.2 |
| 4 | 0 | -2 | 40.9 | 38.6 |
| 4 | 0 | -4 | 111.6 | 67.9 |
| 4 | 0 | -6 | 40.9 | 47.1 |
| 4 | 0 | -8 | 98.6 | 102.4 |
| 4 | 0 | -10 | 79.0 | 75.6 |
| 4 | 0 | -12 | 48.3 | 53.7 |
| 4 | 0 | 12 | 72.5 | 63.6 |
| 4 | 0 | -14 | 93.0 | 94.0 |
| 4 | 0 | -16 | - | 11.1 |
| 4 | 0 | -18 | 97.6 | 93.9 |
| 4 | 0 | -20 | 25.1 | 38.4 |
| 6 | 0 | 18 | - | 20.2 |
| 6 | 0 | 16 | 79.0 | 65.6 |
| 6 | 0 | 14 | 35.3 | 30.2 |
| 6 | 0 | 12 | 50.2 | 24.2 |
| 6 | 0 | 10 | 27.9 | 11.9 |
| 6 | 0 | 8 | - | 5.3 |
| 6 | 0 | 6 | 183.2 | 193.3 |
| 6 | 0 | 4 | 93.0 | 72.6 |
| 6 | 0 | 2 | 62.3 | 34.5 |
| 6 | 0 | 0 | 74.4 | 69.1 |
| 6 | 0 | -2 | 499.3 | 519.8 |
| 6 | 0 | -4 | 94.8 | 78.5 |
| 6 | 0 | -6 | 63.4 | 52.5 |
| 6 | 0 | -8 | 130.2 | 143.7 |
| 6 | 0 | -10 | 199.2 | 184.5 |
| 6 | 0 | -12 | 80.9 | 96.7 |
| 6 | 0 | -14 | 55.8 | 42.6 |
| 6 | 0 | -16 | 50.2 | 37.6 |
| 6 | 0 | -18 | 45.6 | 42.8 |
| 8 | 0 | 18 | 35.3 | 42.7 |
| 8 | 0 | 16 | 54.9 | 57.1 |
| 8 | 0 | 14 | 55.8 | 43.0 |
| 8 | 0 | 12 | - | 14.9 |
| 8 | 0 | 10 | 106.9 | 106.1 |
| 8 | 0 | 8 | 111.6 | 106.5 |
| 8 | 0 | 6 | 88.3 | 92.9 |
| 8 | 0 | 4 | 173.9 | 182.4 |
| 8 | 0 | 2 | - | 11.8 |
| 8 | 0 | 0 | 218.5 | 204.9 |
| 8 | 0 | -2 | 88.3 | 78.4 |
| 8 | 0 | -4 | 210.1 | 190.6 |
| 8 | 0 | -6 | 162.7 | 145.0 |
| 8 | 0 | -8 | 134.8 | 126.8 |
| 8 | 0 | -10 | 102.3 | 94.8 |
| 8 | 0 | -12 | 65.1 | 58.0 |
| 8 | 0 | -14 | 120.9 | 117.0 |
| 8 | 0 | -16 | - | 19.2 |
| 10 | 0 | 16 | 65.1 | 71.4 |
| 10 | 0 | 14 | 76.2 | 68.8 |
| 10 | 0 | 12 | 32.5 | 31.7 |
| 10 | 0 | 10 | 85.5 | 79.3 |
| 10 | 0 | 8 | 111.6 | 104.8 |
| 10 | 0 | 6 | 218.5 | 221.9 |
| 10 | 0 | 4 | 87.4 | 75.9 |
| 10 | 0 | 2 | 175.7 | 158.4 |
| 10 | 0 | 0 | 11.2 | 8.8 |
| 10 | 0 | -2 | 309.9 | 306.9 |
| 10 | 0 | -4 | 72.5 | 70.0 |
| 10 | 0 | -6 | 27.9 | 11.4 |
| 10 | 0 | -8 | 41.8 | 42.2 |
| 10 | 0 | -10 | 61.4 | 58.3 |
| 10 | 0 | -12 | 56.7 | 39.1 |
| 10 | 0 | -14 | - | 14.5 |
| 10 | 0 | -16 | 14.4 | 10.8 |
| 12 | 0 | 14 | 76.2 | 67.6 |
| 12 | 0 | 12 | 49.3 | 46.0 |
| 12 | 0 | 10 | 83.7 | 77.8 |
| 12 | 0 | 8 | 89.7 | 73.3 |
| 12 | 0 | 6 | 17.7 | 8.2 |
| 12 | 0 | 4 | 182.2 | 184.2 |
| 12 | 0 | 2 | 22.3 | 18.0 |
| 12 | 0 | 0 | 0.0 | 4.7 |
| 12 | 0 | -4 | 72.5 | 76.1 |
| 12 | 0 | -2 | 199.9 | 205.8 |
| 12 | 0 | -6 | 43.7 | 50.3 |
| 12 | 0 | -8 | - | 2.0 |
| 12 | 0 | -10 | 63.4 | 61.3 |
| 12 | 0 | -12 | 74.4 | 75.9 |
| 12 | 0 | -14 | 65.1 | 69.4 |
| 14 | 0 | 14 | 59.5 | 71.2 |
| 14 | 0 | 12 | 51.1 | 41.7 |
| 14 | 0 | 10 | - | 5.1 |
| 14 | 0 | 8 | 81.8 | 70.8 |
| 14 | 0 | 6 | 97.6 | 88.9 |
| 14 | 0 | 4 | 51.1 | 39.2 |
| 14 | 0 | 2 | 53.9 | 71.0 |
| 14 | 0 | 0 | - | 15.5 |
| 14 | 0 | -4 | 94.8 | 98.1 |
| 14 | 0 | -2 | 56.7 | 56.7 |
| 14 | 0 | -6 | 49.3 | 39.1 |
| 14 | 0 | -8 | 80.9 | 82.3 |
| 14 | 0 | -10 | 69.7 | 74.0 |
| 14 | 0 | -12 | 55.8 | 62.2 |
| 14 | 0 | -14 | 36.3 | 34.8 |
| 16 | 0 | 8 | 48.3 | 47.2 |
| 16 | 0 | 6 | 39.1 | 35.5 |
| 16 | 0 | 4 | 130.2 | 138.4 |
| 16 | 0 | 2 | - | 12.8 |
| 16 | 0 | 0 | 68.8 | 79.7 |
| 16 | 0 | -2 | 32.5 | 30.6 |
| 16 | 0 | -4 | 185.9 | 190.0 |
| 16 | 0 | -6 | 58.6 | 66.7 |
| 16 | 0 | -8 | 23.2 | 17.5 |
| 16 | 0 | -10 | 40.0 | 49.0 |
| 16 | 0 | -12 | 43.7 | 57.4 |
| 18 | 0 | 8 | 48.3 | 57.9 |
| 18 | 0 | 6 | 78.1 | 77.5 |
| 18 | 0 | 4 | 21.4 | 8.0 |
| 18 | 0 | 2 | 130.2 | 142.2 |
| 18 | 0 | -2 | 30.7 | 43.6 |
| 18 | 0 | -4 | 64.2 | 73.6 |
| 18 | 0 | -6 | 93.0 | 110.5 |
| 18 | 0 | 0 | - | 46.5 |
| 1 | 1 | 18 | 48.0 | 46.5 |
| 1 | 1 | 16 | 90.3 | 93.5 |
| 1 | 1 | 14 | 52.3 | 22.6 |
| 1 | 1 | 12 | 192.1 | 166.2 |
| 1 | 1 | 10 | - | 9.9 |
| 1 | 1 | 8 | 240.3 | 230.9 |
| 1 | 1 | 6 | 134.5 | 131.0 |
| 1 | 1 | 4 | 230.5 | 287.5 |
| 1 | 1 | 2 | 133.5 | 184.5 |
| 1 | 1 | 0 | 100.9 | 142.3 |
| 1 | 1 | -2 | 57.6 | 52.9 |
| 1 | 1 | -4 | 98.9 | 101.3 |
| 1 | 1 | -6 | 74.0 | 87.9 |
| 1 | 1 | -8 | 69.2 | 63.7 |
| 1 | 1 | -10 | 139.3 | 123.1 |
| 1 | 1 | -12 | 16.3 | 7.6 |
| 1 | 1 | -14 | 76.8 | 73.9 |
| 1 | 1 | -16 | 144.1 | 74.6 |
| 1 | 1 | -18 | 79.7 | 67.9 |
| 3 | 1 | 18 | 91.2 | 76.0 |
| 3 | 1 | 16 | 82.6 | 68.9 |
| 3 | 1 | 14 | 155.6 | 141.5 |
| 3 | 1 | 12 | 69.2 | 47.8 |
| 3 | 1 | 10 | 174.8 | 147.2 |
| 3 | 1 | 8 | 144.1 | 125.6 |
| 3 | 1 | 6 | 149.8 | 166.3 |
| 3 | 1 | 4 | 61.5 | 65.4 |
| 3 | 1 | 2 | 28.8 | 34.7 |
| 3 | 1 | 0 | 172.9 | 202.4 |
| 3 | 1 | -2 | 193.1 | 208.8 |
| 3 | 1 | -4 | 31.7 | 43.6 |
| 3 | 1 | -6 | 20.2 | 25.2 |
| 3 | 1 | -8 | 110.5 | 112.8 |
| 3 | 1 | -10 | 81.6 | 53.3 |
| 3 | 1 | -12 | 101.8 | 90.7 |
| 3 | 1 | -14 | - | 20.2 |
| 3 | 1 | -16 | 90.3 | 91.9 |
| 5 | 1 | 18 | 76.8 | 70.9 |
| 5 | 1 | 16 | 124.9 | 121.8 |
| 5 | 1 | 14 | 105.7 | 106.9 |
| 5 | 1 | 12 | - | 7.2 |
| 5 | 1 | 10 | 126.8 | 114.6 |
| 5 | 1 | 8 | 56.7 | 60.1 |
| 5 | 1 | 6 | 9.6 | 17.8 |
| 5 | 1 | 2 | 35.5 | 34.3 |
| 5 | 1 | 0 | 65.3 | 44.9 |
| 5 | 1 | -2 | 19.1 | 2.9 |
| 5 | 1 | -4 | 76.8 | 74.1 |
| 5 | 1 | -6 | 156.5 | 180.2 |
| 5 | 1 | -8 | 74.0 | 67.6 |
| 5 | 1 | -10 | 175.8 | 185.4 |
| 5 | 1 | -12 | 57.6 | 45.3 |
| 5 | 1 | -14 | 165.2 | 157.4 |
| 5 | 1 | -16 | 28.8 | 26.4 |
| 5 | 1 | -18 | 78.8 | 87.3 |
| 7 | 1 | 18 | 70.1 | 56.9 |
| 7 | 1 | 16 | 42.3 | 35.8 |
| 7 | 1 | 14 | 94.1 | 83.8 |
| 7 | 1 | 12 | 80.7 | 64.8 |
| 7 | 1 | 10 | 96.1 | 92.5 |
| 7 | 1 | 8 | - | 11.1 |
| 7 | 1 | 6 | 105.7 | 106.2 |
| 7 | 1 | 4 | 76.8 | 79.3 |
| 7 | 1 | 2 | 145.0 | 156.6 |
| 7 | 1 | 0 | 134.5 | 130.9 |
| 7 | 1 | -2 | 138.3 | 138.6 |
| 7 | 1 | -4 | 120.1 | 116.3 |
| 7 | 1 | -6 | 82.6 | 81.6 |
| 7 | 1 | -8 | 151.8 | 151.4 |
| 7 | 1 | -10 | 48.0 | 29.9 |
| 7 | 1 | -12 | 146.0 | 147.4 |
| 7 | 1 | -14 | 27.9 | 21.0 |
| 7 | 1 | -16 | 74.9 | 77.4 |
| 7 | 1 | -18 | 81.6 | 85.6 |
| 9 | 1 | 16 | 62.2 | 61.2 |
| 9 | 1 | 14 | 57.6 | 40.1 |
| 9 | 1 | 12 | 98.9 | 96.1 |
| 9 | 1 | 10 | 57.6 | 52.3 |
| 9 | 1 | 8 | 101.8 | 94.7 |
| 9 | 1 | 6 | 120.1 | 125.1 |
| 9 | 1 | 4 | 124.9 | 134.5 |
| 9 | 1 | 2 | 94.1 | 91.3 |
| 9 | 1 | 0 | 62.4 | 62.9 |
| 9 | 1 | -2 | 199.0 | 202.3 |
| 9 | 1 | -4 | 177.7 | 176.7 |
| 9 | 1 | -6 | 148.9 | 147.9 |
| 9 | 1 | -8 | 25.0 | 21.2 |
| 9 | 1 | -10 | 146.0 | 133.0 |
| 9 | 1 | -12 | - | 0.1 |
| 9 | 1 | -14 | 70.1 | 69.4 |
| 9 | 1 | -16 | - | 0.8 |
| 9 | 1 | -18 | 28.8 | 39.5 |
| 11 | 1 | 14 | 134.5 | 126.7 |
| 11 | 1 | 12 | - | 2.5 |
| 11 | 1 | 10 | 129.7 | 112.7 |
| 11 | 1 | 8 | 48.0 | 21.2 |
| 11 | 1 | 6 | 129.7 | 131.5 |
| 11 | 1 | 4 | 75.9 | 75.8 |
| 11 | 1 | 2 | 72.0 | 75.8 |
| 11 | 1 | 0 | 67.2 | 69.8 |
| 11 | 1 | -2 | 14.4 | 19.2 |
| 11 | 1 | -4 | 30.7 | 29.0 |
| 11 | 1 | -6 | 32.7 | 27.6 |
| 11 | 1 | -8 | 120.1 | 100.3 |
| 11 | 1 | -10 | 13.5 | 15.8 |
| 11 | 1 | -12 | 75.9 | 83.5 |
| 11 | 1 | -14 | 50.9 | 49.1 |
| 11 | 1 | -16 | 71.1 | 79.9 |
| 13 | 1 | 14 | 23.1 | 21.3 |
| 13 | 1 | 12 | 96.1 | 92.9 |
| 13 | 1 | 10 | 83.6 | 80.2 |
| 13 | 1 | 8 | 78.8 | 75.0 |
| 13 | 1 | 6 | 35.5 | 30.3 |
| 13 | 1 | 4 | 64.4 | 59.4 |
| 13 | 1 | 2 | 66.3 | 63.4 |
| 13 | 1 | 0 | 66.3 | 61.4 |
| 13 | 1 | -2 | 56.7 | 59.5 |
| 13 | 1 | -4 | 82.6 | 73.2 |
| 13 | 1 | -6 | 82.6 | 62.6 |
| 13 | 1 | -8 | - | 20.5 |
| 13 | 1 | -10 | 83.6 | 85.9 |
| 13 | 1 | -12 | - | 8.0 |
| 13 | 1 | -14 | 74.0 | 88.4 |
| 13 | 1 | -16 | 18.3 | 23.2 |
| 15 | 1 | 12 | - | 13.1 |
| 15 | 1 | 10 | 48.0 | 48.7 |
| 15 | 1 | 8 | 41.3 | 30.4 |
| 15 | 1 | 6 | - | 25.4 |
| 15 | 1 | 4 | 72.9 | 76.5 |
| 15 | 1 | 2 | 52.8 | 58.7 |
| 15 | 1 | 0 | 62.4 | 66.4 |
| 15 | 1 | -2 | - | 11.7 |
| 15 | 1 | -4 | 110.5 | 115.6 |
| 15 | 1 | -6 | 88.4 | 86.0 |
| 15 | 1 | -8 | 134.5 | 124.2 |
| 15 | 1 | -10 | 24.0 | 4.0 |
| 15 | 1 | -12 | 104.7 | 113.1 |
| 15 | 1 | -14 | 25.0 | 29.1 |
| 17 | 1 | 10 | 35.5 | 26.0 |
| 17 | 1 | 8 | 49.0 | 54.1 |
| 17 | 1 | 6 | 79.7 | 76.5 |
| 17 | 1 | 4 | 52.8 | 58.7 |
| 17 | 1 | 2 | 62.4 | 66.1 |
| 17 | 1 | 0 | 61.6 | 79.1 |
| 17 | 1 | -4 | 39.4 | 36.2 |
| 17 | 1 | -6 | 60.5 | 66.7 |
| 17 | 1 | -8 | - | 7.4 |
| 17 | 1 | -10 | 86.4 | 94.5 |
| 19 | 1 | 6 | 44.2 | 59.7 |
| 19 | 1 | 4 | 39.4 | 42.5 |
| 19 | 1 | 2 | 48.0 | 57.5 |
| 19 | 1 | 0 | 59.6 | 55.2 |
| 19 | 1 | -2 | 46.1 | 40.0 |
| 19 | 1 | -4 | 58.6 | 63.8 |
| 19 | 1 | -6 | 55.7 | 48.6 |
| 19 | 1 | -8 | 45.1 | 52.9 |
| 0 | 1 | 1 | 15.3 | 6.2 |
| 0 | 1 | 3 | - | 4.1 |
| 0 | 1 | 5 | 58.5 | 45.0 |
| 0 | 1 | 7 | 25.5 | 22.3 |
| 0 | 1 | 9 | 29.7 | 29.0 |
| 0 | 1 | 11 | - | 11.7 |
| 0 | 1 | 13 | 31.4 | 29.1 |
| 0 | 1 | 15 | - | 6.7 |
| 0 | 1 | 17 | 24.0 | 26.0 |
| 0 | 1 | 19 | - | 7.1 |
| 2 | 1 | 19 | 30.0 | 28.0 |
| 2 | 1 | 17 | - | 19.6 |
| 2 | 1 | 15 | 52.6 | 43.8 |
| 2 | 1 | 13 | - | 7.3 |
| 2 | 1 | 11 | 84.8 | 78.9 |
| 2 | 1 | 9 | 13.0 | 20.8 |
| 2 | 1 | 7 | 101.8 | 100.2 |
| 2 | 1 | 5 | 33.9 | 36.4 |
| 2 | 1 | 3 | 84.8 | 101.6 |
| 2 | 1 | 1 | - | 6.8 |
| 2 | 1 | -1 | 52.0 | 46.4 |
| 2 | 1 | -3 | 63.6 | 68.0 |
| 2 | 1 | -5 | 8.5 | 11.9 |
| 2 | 1 | -7 | 54.3 | 57.3 |
| 2 | 1 | -9 | - | 7.7 |
| 2 | 1 | -11 | 51.8 | 44.9 |
| 2 | 1 | -13 | - | 0.9 |
| 2 | 1 | -15 | 21.0 | 24.6 |
| 2 | 1 | -17 | - | 3.5 |
| 2 | 1 | -19 | - | 0.9 |
| 4 | 1 | 15 | - | 5.1 |
| 4 | 1 | 13 | 21.2 | 15.2 |
| 4 | 1 | 11 | 31.4 | 13.5 |
| 4 | 1 | 9 | 25.5 | 23.9 |
| 4 | 1 | 7 | 8.5 | 2.5 |
| 4 | 1 | 5 | 32.2 | 35.6 |
| 4 | 1 | 3 | 37.3 | 21.0 |
| 4 | 1 | 1 | 9.3 | 18.5 |
| 4 | 1 | -1 | 63.0 | 57.5 |
| 4 | 1 | -3 | - | 5.2 |
| 4 | 1 | -5 | 78.1 | 87.8 |
| 4 | 1 | -7 | - | 7.8 |
| 4 | 1 | -9 | 89.0 | 93.4 |
| 4 | 1 | -11 | - | 18.7 |
| 4 | 1 | -13 | 62.0 | 59.6 |
| 4 | 1 | -15 | - | 9.7 |
| 4 | 1 | -17 | 38.0 | 43.2 |
| 6 | 1 | 15 | 33.9 | 34.9 |
| 6 | 1 | 13 | - | 7.5 |
| 6 | 1 | 11 | 35.6 | 34.9 |
| 6 | 1 | 9 | - | 3.9 |
| 6 | 1 | 7 | 49.2 | 48.4 |
| 6 | 1 | 5 | 25.5 | 21.0 |
| 6 | 1 | 3 | 45.0 | 44.1 |
| 6 | 1 | 1 | 28.0 | 27.9 |
| 6 | 1 | -1 | - | 3.2 |
| 6 | 1 | -3 | - | 3.6 |
| 6 | 1 | -5 | 16.7 | 3.5 |
| 6 | 1 | -7 | - | 1.4 |
| 6 | 1 | -9 | 14.0 | 16.1 |
| 6 | 1 | -11 | - | 9.8 |
| 6 | 1 | -13 | - | 14.2 |
| 8 | 1 | 17 | 21.0 | 22.6 |
| 8 | 1 | 15 | 42.4 | 36.7 |
| 8 | 1 | 13 | - | 8.3 |
| 8 | 1 | 11 | 64.5 | 65.1 |
| 8 | 1 | 9 | - | 3.2 |
| 8 | 1 | 7 | 53.5 | 58.0 |
| 8 | 1 | 5 | 29.7 | 28.1 |
| 8 | 1 | 3 | 61.1 | 63.6 |
| 8 | 1 | 1 | 24.0 | 25.2 |
| 8 | 1 | -3 | - | 0.9 |
| 8 | 1 | -5 | 57.7 | 62.9 |
| 8 | 1 | -7 | 12.0 | 12.5 |
| 8 | 1 | -9 | 56.0 | 51.9 |
| 8 | 1 | -11 | - | 5.8 |
| 8 | 1 | -13 | 46.0 | 45.8 |
| 8 | 1 | -15 | - | 0.2 |
| 10 | 1 | 11 | - | 0.6 |
| 10 | 1 | 9 | 12.0 | 13.9 |
| 10 | 1 | 7 | - | 8.3 |
| 10 | 1 | 5 | - | 5.4 |
| 10 | 1 | 3 | - | 4.5 |
| 10 | 1 | 1 | 31.4 | 20.0 |
| 10 | 1 | -1 | - | 3.6 |
| 10 | 1 | -3 | 21.0 | 25.6 |
| 10 | 1 | -5 | - | 7.8 |
| 10 | 1 | -7 | 47.0 | 55.3 |
| 10 | 1 | -9 | - | 1.8 |
| 10 | 1 | -11 | 23.0 | 51.0 |
| 10 | 1 | -13 | - | 12.3 |
| 12 | 1 | 15 | - | 15.6 |
| 12 | 1 | 13 | 28.9 | 29.6 |

## Table 2

### (Continued)

| H | K | L | Fo | Fc | H | K | L | Fo | Fc | H | K | L | Fo | Fc | H | K | L | Fo | Fc | Fo | Fc |
|---|---|---|----|----|---|---|---|----|----|---|---|---|----|----|---|---|---|----|----|----|----|
| 1 | 3 | -10 | 51.7 | 51.9 | 17 | 3 | 0 | 72.3 | 71.5 | 14 | 3 | -3 | - | 9.7 | 12 | 4 | -8 | 51.8 | 50.0 | | |
| 1 | 3 | -12 | 16.0 | 16.4 | 17 | 3 | -2 | 73.3 | 67.2 | 14 | 3 | -5 | - | 4.3 | 12 | 4 | -10 | 54.6 | 51.5 | | |
| 1 | 3 | -14 | 103.3 | 97.9 | 17 | 3 | -4 | 25.4 | 24.5 | 14 | 3 | -7 | - | 3.8 | 14 | 4 | -2 | 55.6 | 58.0 | | |
| 1 | 3 | 16 | 45.1 | 42.6 | 17 | 3 | -6 | 44.1 | 41.6 | 14 | 3 | -9 | 46.8 | 44.7 | 14 | 4 | -4 | 19.2 | 22.4 | | |
| 1 | 3 | 14 | 112.7 | 114.2 | 0 | 3 | 1 | 44.9 | 48.3 | 14 | 3 | -11 | 19.1 | 7.3 | 14 | 4 | -6 | 13.6 | 31.1 | | |
| 1 | 3 | 12 | 28.2 | 27.3 | 0 | 3 | 3 | 19.1 | 26.2 | 16 | 3 | 5 | 12.4 | 4.4 | 14 | 4 | -8 | 65.2 | 65.6 | | |
| 1 | 3 | 10 | 110.8 | 111.9 | 0 | 3 | 5 | 19.1 | 16.8 | 16 | 3 | 3 | 19.1 | 22.5 | 14 | 4 | -2 | 38.3 | 43.6 | | |
| 1 | 3 | 8 | 59.2 | 71.5 | 0 | 3 | 7 | 75.5 | 75.7 | 16 | 3 | 1 | 23.9 | 22.3 | 16 | 4 | -4 | 69.0 | 83.1 | | |
| 1 | 3 | 6 | 93.9 | 103.1 | 0 | 3 | 9 | 14.3 | 17.2 | 16 | 3 | -1 | 10.5 | 11.7 | 1 | 4 | 13 | 9.1 | 9.6 | | |
| 1 | 3 | 4 | 87.4 | 96.1 | 0 | 3 | 11 | 22.9 | 19.2 | 16 | 3 | -3 | 14.3 | 15.0 | 1 | 4 | 11 | 47.4 | 44.4 | | |
| 1 | 3 | 2 | 75.1 | 72.6 | 0 | 3 | 13 | - | 13.7 | 16 | 3 | -5 | - | 6.2 | 1 | 4 | 9 | - | 36.5 | | |
| 1 | 3 | 0 | 72.3 | 87.9 | 0 | 3 | 15 | 29.6 | 32.3 | 16 | 3 | -7 | - | 8.1 | 1 | 4 | 7 | 47.4 | 53.2 | | |
| 1 | 3 | -2 | 68.6 | 81.1 | 2 | 3 | 11 | 11.5 | 17.9 | 16 | 3 | -9 | - | 7.1 | 1 | 4 | 5 | 28.3 | 23.4 | | |
| 1 | 3 | -4 | 74.2 | 84.8 | 2 | 3 | 9 | - | 7.0 | 18 | 3 | 1 | 38.2 | 36.5 | 1 | 4 | 3 | 36.5 | 60.1 | | |
| 1 | 3 | -6 | 51.7 | 60.7 | 2 | 3 | 7 | 39.2 | 21.2 | 0 | 4 | 2 | 26.8 | 22.2 | 1 | 4 | 1 | - | 29.6 | | |
| 1 | 3 | -8 | 61.1 | 74.7 | 2 | 3 | 5 | 67.9 | 78.0 | 0 | 4 | 4 | 138.0 | 134.2 | 1 | 4 | -1 | - | 22.9 | | |
| 1 | 3 | -10 | 11.0 | 30.4 | 2 | 3 | 3 | 26.8 | 36.2 | 0 | 4 | 6 | 105.4 | 101.8 | 1 | 4 | -3 | 58.4 | 54.0 | | |
| 1 | 3 | -12 | 87.4 | 84.3 | 2 | 3 | 1 | 38.2 | 30.8 | 0 | 4 | 8 | 81.5 | 78.7 | 1 | 4 | -5 | - | 8.4 | | |
| 1 | 3 | -14 | - | 6.2 | 2 | 3 | -1 | 9.6 | 2.3 | 0 | 4 | 10 | 26.8 | 26.4 | 1 | 4 | -7 | 17.3 | 18.9 | | |
| 3 | 3 | -16 | 78.0 | 76.1 | 2 | 3 | -3 | 17.2 | 17.6 | 0 | 4 | 12 | 38.3 | 38.3 | 1 | 4 | -9 | 11.0 | 4.4 | | |
| 3 | 3 | 16 | 62.0 | 24.1 | 2 | 3 | -5 | 22.0 | 18.9 | 0 | 4 | 14 | 44.1 | 43.8 | 1 | 4 | -11 | - | 3.5 | | |
| 3 | 3 | 14 | 26.3 | 24.1 | 2 | 3 | -7 | 9.6 | 4.2 | 2 | 4 | 12 | 42.2 | 42.3 | 1 | 4 | -13 | 9.1 | 5.3 | | |
| 3 | 3 | 12 | 136.1 | 127.1 | 2 | 3 | -9 | - | 27.6 | 2 | 4 | 10 | 83.4 | 86.7 | 3 | 4 | -15 | 11.0 | 12.0 | | |
| 5 | 3 | 10 | - | 5.4 | 2 | 3 | -11 | - | 6.0 | 2 | 4 | 8 | 41.2 | 35.8 | 3 | 4 | 15 | 27.4 | 33.9 | | |
| 5 | 3 | 8 | 40.4 | 37.9 | 2 | 3 | -13 | 22.0 | 21.1 | 2 | 4 | 6 | 52.7 | 48.9 | 3 | 4 | 13 | 21.0 | 21.2 | | |
| 5 | 3 | 6 | 51.7 | 45.4 | 4 | 3 | 15 | 9.6 | 18.1 | 2 | 4 | 4 | 119.8 | 124.9 | 3 | 4 | 11 | 19.2 | 11.8 | | |
| 5 | 3 | 4 | 81.7 | 74.9 | 4 | 3 | 13 | - | 7.6 | 2 | 4 | 2 | 76.7 | 63.6 | 3 | 4 | 9 | 47.4 | 16.5 | | |
| 5 | 3 | 2 | 58.2 | 52.1 | 4 | 3 | 11 | 28.7 | 25.5 | 2 | 4 | 0 | 109.3 | 107.3 | 3 | 4 | 7 | 56.6 | 49.1 | | |
| 5 | 3 | 0 | 14.1 | 8.7 | 4 | 3 | 9 | - | 0.3 | 2 | 4 | -2 | 44.1 | 41.7 | 3 | 4 | 5 | 24.6 | 13.0 | | |
| 5 | 3 | -2 | 12.2 | 1.2 | 4 | 3 | 7 | 26.8 | 7.6 | 2 | 4 | -4 | 57.5 | 104.9 | 3 | 4 | 3 | 18.2 | 5.0 | | |
| 5 | 3 | -4 | 55.4 | 49.9 | 4 | 3 | 5 | 21.0 | 3.5 | 2 | 4 | -6 | 70.0 | 61.0 | 3 | 4 | 1 | - | 45.3 | | |
| 5 | 3 | -6 | 153.1 | 168.6 | 4 | 3 | 3 | 19.1 | 2.3 | 2 | 4 | -8 | 108.3 | 96.2 | 3 | 4 | -1 | 4.6 | 4.3 | | |
| 5 | 3 | -8 | 61.1 | 58.9 | 4 | 3 | 1 | 23.9 | 2.1 | 2 | 4 | -10 | 65.2 | 64.1 | 3 | 4 | -3 | 39.2 | 31.2 | | |
| 5 | 3 | -10 | 87.4 | 90.9 | 4 | 3 | -1 | 8.6 | 8.2 | 4 | 4 | -10 | - | 7.6 | 3 | 4 | -5 | 27.4 | 14.8 | | |
| 5 | 3 | -12 | 37.6 | 31.5 | 4 | 3 | -3 | 16.3 | 14.7 | 4 | 4 | -12 | 56.6 | 56.5 | 3 | 4 | -7 | 35.5 | 32.8 | | |
| 5 | 3 | -14 | 145.6 | 151.3 | 4 | 3 | -5 | 47.8 | 59.6 | 4 | 4 | -14 | 52.7 | 57.0 | 3 | 4 | -9 | 42.0 | 36.8 | | |
| 5 | 3 | -16 | 23.5 | 25.3 | 4 | 3 | -7 | 47.8 | 28.8 | 4 | 4 | 14 | 47.9 | 49.9 | 3 | 4 | -11 | 34.7 | 39.5 | | |
| 7 | 3 | 16 | 17.8 | 16.7 | 4 | 3 | -9 | 20.1 | 19.4 | 4 | 4 | 12 | 75.7 | 81.0 | 3 | 4 | -13 | 27.4 | 28.3 | | |
| 7 | 3 | 14 | 51.7 | 54.0 | 4 | 3 | -11 | - | 1.7 | 4 | 4 | 10 | 58.5 | 59.6 | 3 | 4 | -15 | 14.6 | 16.4 | | |
| 7 | 3 | 12 | 49.8 | 40.3 | 4 | 3 | -13 | 37.3 | 35.9 | 4 | 4 | 8 | 59.4 | 52.9 | 5 | 4 | 13 | 9.1 | 11.0 | | |
| 7 | 3 | 10 | 114.6 | 111.9 | 4 | 3 | -15 | 16.3 | 37.3 | 4 | 4 | 6 | 70.9 | 67.1 | 5 | 4 | 11 | 27.4 | 19.6 | | |
| 7 | 3 | 8 | - | 9.1 | 6 | 3 | 11 | 19.1 | 20.1 | 4 | 4 | 4 | 118.9 | 118.2 | 5 | 4 | 9 | - | 10.1 | | |
| 7 | 3 | 6 | 34.8 | 42.3 | 6 | 3 | 9 | 38.2 | 33.8 | 4 | 4 | 2 | - | 5.5 | 5 | 4 | 7 | 22.8 | | | |
| 7 | 3 | 4 | 69.5 | 70.3 | 6 | 3 | 7 | - | 2.0 | 4 | 4 | 0 | 104.5 | 102.2 | 5 | 4 | 5 | - | 7.7 | | |
| 7 | 3 | 2 | 122.1 | 147.9 | 6 | 3 | 5 | 66.9 | 64.5 | 4 | 4 | -2 | 28.8 | 21.5 | 5 | 4 | 3 | - | 6.8 | | |
| 7 | 3 | 0 | 76.1 | 77.6 | 6 | 3 | 3 | 43.0 | 12.1 | 4 | 4 | -4 | 67.1 | 50.2 | 5 | 4 | 1 | - | 34.9 | | |
| 7 | 3 | -2 | 67.6 | 71.4 | 6 | 3 | 1 | 41.8 | 45.7 | 4 | 4 | -6 | 89.1 | 72.4 | 5 | 4 | -1 | 28.3 | 14.8 | | |
| 7 | 3 | -4 | 78.0 | 73.9 | 6 | 3 | -1 | 45.9 | 33.3 | 4 | 4 | -8 | 75.7 | 87.8 | 5 | 4 | -3 | - | 5.9 | | |
| 7 | 3 | -6 | 71.4 | 70.0 | 6 | 3 | -3 | 18.2 | 14.2 | 4 | 4 | -10 | 23.0 | 20.6 | 5 | 4 | -5 | 54.7 | 55.6 | | |
| 7 | 3 | -8 | 145.6 | 141.7 | 6 | 3 | -5 | 20.1 | 8.5 | 4 | 4 | -12 | 24.9 | 17.6 | 5 | 4 | -7 | - | 0.2 | | |
| 7 | 3 | -10 | 21.6 | 21.9 | 6 | 3 | -7 | 16.3 | 10.3 | 4 | 4 | -14 | 67.1 | 68.3 | 5 | 4 | -9 | - | 27.1 | | |
| 7 | 3 | -12 | 77.0 | 82.1 | 6 | 3 | -9 | 47.3 | 53.4 | 6 | 4 | 14 | 25.9 | 20.9 | 5 | 4 | -11 | 19.2 | 16.4 | | |
| 7 | 3 | -14 | 44.3 | 31.1 | 6 | 3 | -11 | 7.7 | 7.6 | 6 | 4 | 12 | 47.9 | 43.3 | 5 | 4 | -13 | 45.6 | 44.4 | | |
| 7 | 3 | -16 | 86.4 | 85.8 | 6 | 3 | -13 | - | 4.6 | 6 | 4 | 10 | 33.6 | 32.6 | 7 | 4 | 13 | 11.0 | 3.9 | | |
| 9 | 3 | 14 | 24.4 | 24.0 | 6 | 3 | -15 | 17.2 | 15.8 | 6 | 4 | 8 | - | 5.5 | 7 | 4 | 11 | 39.2 | 39.8 | | |
| 9 | 3 | 12 | 93.0 | 87.9 | 8 | 3 | 15 | 9.6 | 0.5 | 6 | 4 | 6 | 79.6 | 75.1 | 7 | 4 | 9 | - | 22.9 | | |
| 9 | 3 | 10 | 39.5 | 35.1 | 8 | 3 | 13 | - | 7.4 | 6 | 4 | 4 | 74.8 | 63.1 | 7 | 4 | 7 | 64.8 | 65.6 | | |
| 9 | 3 | 8 | 69.5 | 71.2 | 8 | 3 | 11 | 19.1 | 19.1 | 6 | 4 | 2 | 101.6 | 91.6 | 7 | 4 | 5 | 10.0 | 7.5 | | |
| 9 | 3 | 6 | 70.4 | 70.1 | 8 | 3 | 9 | 25.8 | 26.7 | 6 | 4 | 0 | 61.4 | 53.3 | 7 | 4 | 1 | 45.6 | 35.4 | | |
| 9 | 3 | 4 | 100.5 | 92.4 | 8 | 3 | -2 | - | 11.7 | 6 | 4 | -2 | 142.8 | 145.1 | 7 | 4 | -1 | 21.0 | 17.5 | | |
| 9 | 3 | 2 | 96.7 | 97.5 | 8 | 3 | 5 | 14.3 | 7.7 | 6 | 4 | -4 | - | 5.8 | 7 | 4 | -3 | 51.1 | 45.9 | | |
| 9 | 3 | 0 | 66.7 | 70.8 | 8 | 3 | 3 | 11.5 | 33.6 | 6 | 4 | -6 | 115.9 | 103.7 | 7 | 4 | -5 | 42.0 | 39.0 | | |
| 9 | 3 | -2 | 99.6 | 107.6 | 8 | 3 | 1 | 57.3 | 52.6 | 6 | 4 | -8 | 97.8 | 90.1 | 7 | 4 | -7 | 9.1 | 1.5 | | |
| 9 | 3 | -4 | 81.7 | 83.8 | 8 | 3 | -1 | 22.9 | 27.4 | 6 | 4 | -10 | 61.4 | 60.4 | 7 | 4 | -9 | 25.5 | 34.2 | | |
| 9 | 3 | -6 | 139.1 | 133.6 | 8 | 3 | -3 | 23.9 | 11.9 | 6 | 4 | -12 | 38.1 | 40.2 | 7 | 4 | -11 | 34.7 | 28.1 | | |
| 9 | 3 | -8 | 39.5 | 36.1 | 8 | 3 | -5 | - | 11.9 | 6 | 4 | -14 | 18.6 | 17.7 | 7 | 4 | -13 | - | 2.9 | | |
| 9 | 3 | -10 | 89.2 | 87.5 | 8 | 3 | -7 | 60.2 | 52.6 | 6 | 4 | 12 | 38.1 | 37.4 | 9 | 4 | 9 | - | 1.9 | | |
| 9 | 3 | -12 | - | 6.7 | 8 | 3 | -9 | 11.5 | 5.2 | 8 | 4 | 10 | - | 66.9 | 9 | 4 | 7 | 38.3 | 20.3 | | |
| 9 | 3 | -14 | 63.9 | 69.4 | 8 | 3 | -11 | - | 20.3 | 8 | 4 | 8 | 32.6 | 28.2 | 9 | 4 | 5 | 42.9 | 42.3 | | |
| 11 | 3 | 10 | 122.1 | 128.1 | 8 | 3 | -13 | 11.5 | 9.7 | 8 | 4 | 6 | 52.7 | 44.7 | 9 | 4 | 3 | 18.2 | 14.3 | | |
| 11 | 3 | 8 | 31.9 | 22.6 | 8 | 3 | -15 | 38.2 | 29.2 | 8 | 4 | 4 | 122.7 | 116.3 | 9 | 4 | 1 | 27.4 | 29.8 | | |
| 11 | 3 | 6 | 60.1 | 53.6 | 10 | 3 | 13 | 17.2 | 21.8 | 8 | 4 | 2 | 38.1 | 28.0 | 9 | 4 | -1 | 27.4 | 24.8 | | |
| 11 | 3 | 4 | 49.5 | 58.5 | 10 | 3 | 11 | - | 1.1 | 8 | 4 | 0 | 114.1 | 109.9 | 9 | 4 | -3 | 24.8 | 24.8 | | |
| 11 | 3 | 2 | 91.1 | 87.0 | 10 | 3 | 9 | 6.7 | 13.0 | 8 | 4 | -2 | 92.0 | 40.0 | 9 | 4 | -5 | 35.4 | 13.1 | | |
| 11 | 3 | 0 | 79.8 | 66.4 | 10 | 3 | 7 | 9.6 | 10.9 | 8 | 4 | -4 | 95.9 | 88.1 | 9 | 4 | -7 | 22.8 | 0.1 | | |
| 11 | 3 | -2 | - | 11.7 | 10 | 3 | 5 | 33.5 | 32.8 | 8 | 4 | -6 | 83.9 | 83.9 | 9 | 4 | -9 | 27.4 | 29.1 | | |
| 11 | 3 | -4 | 12.2 | 14.3 | 10 | 3 | 3 | 22.0 | 18.5 | 8 | 4 | -8 | 99.7 | 89.9 | 9 | 4 | -11 | 36.5 | 39.0 | | |
| 11 | 3 | -6 | 17.8 | 17.0 | 10 | 3 | 1 | 14.3 | 2.7 | 8 | 4 | -10 | 51.8 | 51.7 | 9 | 4 | -13 | 21.9 | 26.2 | | |
| 11 | 3 | -8 | 118.1 | 113.1 | 10 | 3 | -1 | 14.3 | 13.0 | 8 | 4 | -12 | - | 3.7 | 11 | 4 | 9 | 27.4 | 22.1 | | |
| 11 | 3 | -10 | 24.4 | 19.3 | 10 | 3 | -5 | 19.1 | 18.3 | 8 | 4 | -14 | 61.3 | 65.6 | 11 | 4 | 7 | 28.3 | 31.2 | | |
| 11 | 3 | -12 | 37.6 | 39.5 | 10 | 3 | -7 | 19.1 | 18.3 | 10 | 4 | 12 | 49.8 | 86.9 | 11 | 4 | 5 | 11.9 | 8.8 | | |
| 13 | 3 | 8 | 92.0 | 86.7 | 10 | 3 | -9 | 34.4 | 38.9 | 10 | 4 | 8 | 71.9 | 79.4 | 11 | 4 | 3 | - | 9.1 | | |
| 13 | 3 | 6 | 35.7 | 23.8 | 10 | 3 | -11 | 11.5 | 10.0 | 10 | 4 | 8 | 48.9 | 47.9 | 11 | 4 | 1 | 11.0 | 18.5 | | |
| 13 | 3 | 4 | 30.1 | 20.5 | 10 | 3 | -13 | 19.1 | 19.2 | 10 | 4 | 6 | 81.5 | 85.2 | 11 | 4 | -1 | 13.7 | 38.5 | | |
| 13 | 3 | 2 | 63.9 | 50.2 | 12 | 3 | 11 | - | 13.2 | 10 | 4 | 4 | 56.6 | 52.8 | 11 | 4 | -3 | 13.7 | 15.2 | | |
| 13 | 3 | 0 | 77.0 | 75.1 | 12 | 3 | 7 | 5.7 | 8.1 | 10 | 4 | 2 | 122.7 | 132.2 | 11 | 4 | -5 | - | 5.8 | | |
| 13 | 3 | -2 | 46.0 | 43.9 | 12 | 3 | 5 | 19.1 | 16.3 | 10 | 4 | 0 | 41.2 | 31.8 | 11 | 4 | -7 | 28.3 | 25.3 | | |
| 13 | 3 | -4 | 45.1 | 41.5 | 12 | 3 | 3 | 7.6 | 7.7 | 10 | 4 | -2 | 119.8 | 112.2 | 11 | 4 | -9 | 9.1 | 7.8 | | |
| 13 | 3 | -6 | 46.0 | 45.4 | 12 | 3 | 1 | 64.0 | 57.8 | 10 | 4 | -4 | - | 4.8 | 13 | 4 | 9 | - | 0.8 | | |
| 13 | 3 | -8 | 30.1 | 26.4 | 12 | 3 | -1 | 12.4 | 9.1 | 10 | 4 | -6 | 58.8 | 38.1 | 13 | 4 | 7 | 41.1 | 42.0 | | |
| 13 | 3 | -10 | 87.4 | 88.4 | 12 | 3 | -3 | - | 18.6 | 10 | 4 | -8 | 76.7 | 76.7 | 13 | 4 | 5 | 28.3 | 15.1 | | |
| 15 | 3 | 6 | 11.0 | 27.4 | 12 | 3 | -5 | 9.6 | 9.1 | 10 | 4 | -10 | 33.6 | 34.2 | 13 | 4 | 3 | 34.7 | 40.7 | | |
| 15 | 3 | 4 | 16.9 | 17.9 | 12 | 3 | -7 | 10.5 | 6.3 | 10 | 4 | -12 | 7.7 | 7.5 | 13 | 4 | 1 | - | 0.3 | | |
| 15 | 3 | 2 | 44.1 | 38.6 | 12 | 3 | -9 | 14.3 | 13.7 | 12 | 4 | 10 | 52.7 | 49.8 | 13 | 4 | -1 | 15.5 | 32.4 | | |
| 15 | 3 | 0 | 59.2 | 45.1 | 12 | 3 | -11 | 14.3 | 11.8 | 12 | 4 | 8 | 48.9 | 51.1 | 13 | 4 | -3 | - | 10.4 | | |
| 15 | 3 | -2 | 59.2 | 52.4 | 14 | 3 | 1 | 11.5 | 8.7 | 12 | 4 | 6 | 10.5 | 2.1 | 13 | 4 | -5 | - | 6.6 | | |
| 15 | 3 | -4 | 32.9 | 29.0 | 14 | 3 | 3 | 5.7 | 13.2 | 12 | 4 | 4 | 19.1 | 9.4 | 15 | 4 | -1 | 21.9 | 18.7 | | |
| 15 | 3 | -6 | 73.3 | 69.8 | 14 | 3 | -1 | 30.6 | 29.8 | 12 | 4 | 2 | 25.9 | 20.0 | 15 | 4 | -3 | - | 5.8 | | |
| 15 | 3 | -8 | 49.8 | 47.3 | | | | | | 12 | 4 | 0 | 27.8 | 65.4 | 15 | 4 | -5 | 29.2 | 13.8 | | |
| 15 | 3 | -10 | 122.1 | 114.3 | | | | | | 12 | 4 | -2 | 64.2 | 63.5 | 15 | 4 | -7 | 26.5 | 33.9 | | |
| 15 | 3 | -12 | 12.2 | 11.1 | | | | | | 12 | 4 | -4 | 70.9 | 72.1 | | | | | | | |
| 17 | 3 | 2 | 35.7 | 30.6 | | | | | | 12 | 4 | -6 | 19.2 | 20.3 | | | | | | | |
| 17 | 3 | 4 | 51.7 | 46.0 | | | | | | | | | | | | | | | | | |

## Table 2

### (Continued)

| H | K | L | Fo | Fc |
|---|---|---|----|----|
| 12 | 1 | 11 | - | 0.5 |
| 12 | 1 | 9 | 35.6 | 32.8 |
| 12 | 1 | 7 | 3.7 | 3.7 |
| 12 | 1 | 5 | 33.9 | 36.0 |
| 12 | 1 | 3 | 29.7 | 27.6 |
| 12 | 1 | 1 | 22.1 | 22.8 |
| 12 | 1 | -1 | 18.0 | 20.3 |
| 12 | 1 | -3 | 4.6 | 4.6 |
| 12 | 1 | -5 | 16.0 | 17.1 |
| 12 | 1 | -7 | 4.4 | 4.4 |
| 12 | 1 | -9 | 15.6 | 15.6 |
| 12 | 1 | -11 | 4.1 | 4.1 |
| 14 | 1 | 9 | 1.9 | 1.9 |
| 14 | 1 | 7 | 35.0 | 32.9 |
| 14 | 1 | 5 | 3.9 | 3.9 |
| 14 | 1 | 3 | 29.0 | 27.1 |
| 14 | 1 | 1 | 15.9 | 15.9 |
| 14 | 1 | -1 | 16.0 | 20.1 |
| 14 | 1 | -3 | 20.0 | 27.4 |
| 14 | 1 | -5 | 4.8 | 4.8 |
| 14 | 1 | -7 | 23.0 | 38.3 |
| 14 | 1 | -9 | 4.8 | 4.8 |
| 14 | 1 | -11 | 35.0 | 43.2 |
| 16 | 1 | 9 | 9.5 | 9.5 |
| 16 | 1 | 7 | 3.7 | 3.7 |
| 16 | 1 | 5 | 3.5 | 3.5 |
| 16 | 1 | 3 | 3.0 | 3.0 |
| 16 | 1 | 1 | 10.0 | 13.3 |
| 16 | 1 | -1 | 3.8 | 3.8 |
| 16 | 1 | -3 | - | - |
| 16 | 1 | -5 | 13.3 | 13.3 |
| 16 | 1 | -7 | 11.5 | 11.5 |
| 16 | 1 | -9 | 29.0 | 25.4 |
| 18 | 1 | 7 | 32.0 | 26.0 |
| 18 | 1 | 5 | 2.3 | 2.3 |
| 18 | 1 | 3 | 11.0 | 15.6 |
| 18 | 1 | 1 | 22.0 | 23.3 |
| 18 | 1 | -1 | 14.8 | 14.8 |
| 18 | 1 | -3 | 18.0 | 16.1 |
| 18 | 1 | -5 | 2.1 | 2.1 |
| 18 | 1 | -7 | 23.0 | 22.1 |
| 0 | 2 | 2 | 101.2 | 93.3 |
| 0 | 2 | 4 | 215.9 | 278.3 |
| 0 | 2 | 6 | 94.0 | 79.0 |
| 0 | 2 | 8 | 92.2 | 82.8 |
| 0 | 2 | 10 | 75.9 | 68.2 |
| 0 | 2 | 12 | 90.3 | 76.4 |
| 0 | 2 | 14 | 31.6 | 29.6 |
| 0 | 2 | 16 | - | 4.5 |
| 0 | 2 | 18 | - | 43.8 |
| 2 | 2 | 16 | 87.6 | 80.6 |
| 2 | 2 | 14 | 33.4 | 18.1 |
| 2 | 2 | 12 | 151.8 | 117.3 |
| 2 | 2 | 10 | - | 103.6 |
| 2 | 2 | 8 | 136.4 | 111.4 |
| 2 | 2 | 6 | 171.7 | 165.7 |
| 2 | 2 | 4 | 50.6 | 50.1 |
| 2 | 2 | 2 | 198.8 | 195.5 |
| 2 | 2 | 0 | 12.7 | 2.5 |
| 2 | 2 | -2 | 126.5 | 132.3 |
| 2 | 2 | -4 | 141.8 | 147.3 |
| 2 | 2 | -6 | 180.7 | 164.5 |
| 2 | 2 | -8 | 80.4 | 65.6 |
| 2 | 2 | -10 | - | 1.5 |
| 2 | 2 | -12 | 94.0 | 99.8 |
| 2 | 2 | -14 | - | 52.1 |
| 2 | 2 | -16 | - | 27.2 |
| 2 | 2 | -18 | 37.9 | 39.0 |
| 4 | 2 | 16 | 56.9 | 48.6 |
| 4 | 2 | 14 | 52.4 | 43.4 |
| 4 | 2 | 12 | 125.6 | 111.5 |
| 4 | 2 | 10 | 145.5 | 133.9 |
| 4 | 2 | 8 | 59.6 | 49.7 |
| 4 | 2 | 6 | 58.7 | 56.6 |
| 4 | 2 | 4 | 195.1 | 223.6 |
| 4 | 2 | 2 | 111.1 | 115.2 |
| 4 | 2 | 0 | 105.7 | 103.5 |
| 4 | 2 | -2 | 69.6 | 63.5 |
| 4 | 2 | -4 | 83.1 | 81.6 |
| 4 | 2 | -6 | 28.9 | 30.1 |
| 4 | 2 | -8 | 42.5 | 43.5 |
| 4 | 2 | -10 | 71.4 | 69.5 |
| 4 | 2 | -12 | 59.6 | 63.1 |
| 4 | 2 | -14 | 72.3 | 79.4 |
| 4 | 2 | -16 | - | 7.4 |
| 4 | 2 | -18 | 77.7 | 87.4 |
| 6 | 2 | 14 | - | 2.2 |
| 6 | 2 | 12 | 46.1 | 35.7 |
| 6 | 2 | 10 | 86.7 | 73.4 |
| 6 | 2 | 8 | 39.8 | 37.2 |
| 6 | 2 | 6 | 52.4 | 54.5 |
| 6 | 2 | 4 | 23.5 | 14.5 |
| 6 | 2 | 2 | 158.1 | 164.8 |
| 6 | 2 | 0 | 14.5 | 8.0 |
| 6 | 2 | -2 | 168.0 | 215.6 |
| 6 | 2 | -4 | 108.4 | 108.3 |
| 6 | 2 | -6 | 189.7 | 187.3 |
| 6 | 2 | -8 | 101.2 | 90.9 |
| 6 | 2 | -10 | 77.7 | 75.7 |
| 6 | 2 | -12 | 87.0 | 84.5 |
| 6 | 2 | -14 | 63.2 | 75.4 |
| 6 | 2 | -16 | 47.0 | 51.0 |
| 6 | 2 | -18 | 17.2 | 22.3 |

| H | K | L | Fo | Fc |
|---|---|---|----|----|
| 8 | 2 | 14 | 48.8 | 45.8 |
| 8 | 2 | 12 | - | 12.8 |
| 8 | 2 | 10 | 107.5 | 96.3 |
| 8 | 2 | 8 | 67.8 | 67.6 |
| 8 | 2 | 6 | 70.5 | 68.7 |
| 8 | 2 | 4 | 158.1 | 163.0 |
| 8 | 2 | 2 | 33.4 | 22.2 |
| 8 | 2 | 0 | 178.9 | 179.9 |
| 8 | 2 | -2 | 67.8 | 58.3 |
| 8 | 2 | -4 | 121.9 | 130.7 |
| 8 | 2 | -6 | 149.8 | 129.3 |
| 8 | 2 | -8 | 160.8 | 135.6 |
| 8 | 2 | -10 | 77.7 | 80.8 |
| 8 | 2 | -12 | 36.1 | 26.2 |
| 8 | 2 | -14 | 84.0 | 92.0 |
| 8 | 2 | -16 | 27.1 | 30.1 |
| 10 | 2 | 14 | 38.9 | 27.9 |
| 10 | 2 | 12 | 11.6 | 28.6 |
| 10 | 2 | 10 | 135.5 | 128.9 |
| 10 | 2 | 8 | 116.5 | 112.5 |
| 10 | 2 | 6 | 102.1 | 96.4 |
| 10 | 2 | 4 | 28.0 | 22.1 |
| 10 | 2 | 2 | 214.9 | 245.4 |
| 10 | 2 | 0 | 45.2 | 42.1 |
| 10 | 2 | -2 | 159.9 | 141.4 |
| 10 | 2 | -4 | 89.4 | 81.4 |
| 10 | 2 | -6 | 77.7 | 75.8 |
| 10 | 2 | -8 | 37.0 | 33.6 |
| 10 | 2 | -10 | 11.8 | 11.8 |
| 10 | 2 | -12 | 33.4 | 36.8 |
| 10 | 2 | -14 | 28.0 | 29.8 |
| 10 | 2 | -16 | 11.6 | 33.7 |
| 12 | 2 | 14 | 66.9 | 62.3 |
| 12 | 2 | 12 | 40.7 | 23.9 |
| 12 | 2 | 10 | 72.3 | 59.1 |
| 12 | 2 | 8 | 105.7 | 101.7 |
| 12 | 2 | 6 | 36.1 | 27.0 |
| 12 | 2 | 4 | 99.4 | 95.3 |
| 12 | 2 | 2 | - | 12.8 |
| 12 | 2 | 0 | 99.4 | 101.6 |
| 12 | 2 | -2 | 45.2 | 37.8 |
| 12 | 2 | -4 | 94.0 | 88.7 |
| 12 | 2 | -6 | 64.1 | 65.8 |
| 12 | 2 | -8 | 68.7 | 69.1 |
| 12 | 2 | -10 | 50.6 | 48.2 |
| 12 | 2 | -12 | 30.7 | 28.6 |
| 12 | 2 | -14 | 44.3 | 52.1 |
| 14 | 2 | 12 | 37.9 | 36.2 |
| 14 | 2 | 10 | 48.8 | 39.8 |
| 14 | 2 | 8 | 80.4 | 73.6 |
| 14 | 2 | 6 | 44.3 | 44.4 |
| 14 | 2 | 4 | - | 17.4 |
| 14 | 2 | 2 | 90.3 | 96.5 |
| 14 | 2 | 0 | - | 1.6 |
| 14 | 2 | -2 | 68.7 | 70.9 |
| 14 | 2 | -4 | 53.3 | 52.7 |
| 14 | 2 | -6 | 41.6 | 43.7 |
| 14 | 2 | -8 | 61.4 | 73.0 |
| 14 | 2 | -10 | 54.2 | 68.9 |
| 14 | 2 | -12 | 44.3 | 57.5 |
| 16 | 2 | 8 | 86.7 | 92.8 |
| 16 | 2 | 6 | 53.3 | 56.0 |
| 16 | 2 | 4 | 54.2 | 57.5 |
| 16 | 2 | 2 | - | 16.2 |
| 16 | 2 | 0 | 135.5 | 145.1 |
| 16 | 2 | -2 | - | 3.7 |
| 16 | 2 | -4 | 84.9 | 99.4 |
| 16 | 2 | -6 | 63.2 | 70.3 |
| 16 | 2 | -8 | 59.6 | 62.9 |
| 16 | 2 | -10 | 40.7 | 44.3 |
| 18 | 2 | 2 | 82.2 | 98.3 |
| 18 | 2 | 0 | 19.9 | 21.9 |
| 18 | 2 | -2 | 71.4 | 70.3 |
| 18 | 2 | -4 | 55.1 | 55.4 |
| 18 | 2 | -6 | 50.6 | 60.3 |
| 18 | 2 | -8 | 43.4 | 50.0 |
| 1 | 2 | 11 | - | 3.8 |
| 1 | 2 | 7 | - | 46.4 |
| 1 | 2 | 5 | - | 4.2 |
| 1 | 2 | 3 | - | 6.2 |
| 1 | 2 | 1 | - | 1.9 |
| 1 | 2 | 1 | 24.5 | 38.4 |
| 1 | 2 | -1 | 53.5 | 27.5 |
| 1 | 2 | -3 | 68.8 | 71.8 |
| 1 | 2 | -5 | 22.9 | 3.2 |
| 1 | 2 | -7 | 22.2 | 19.7 |
| 1 | 2 | -9 | 21.7 | 13.4 |
| 1 | 2 | -11 | 34.0 | 32.9 |
| 1 | 2 | -13 | - | 17.1 |
| 1 | 2 | -15 | - | 16.9 |
| 3 | 2 | 15 | - | 23.9 |
| 3 | 2 | 13 | - | 12.3 |
| 3 | 2 | 11 | - | 10.7 |
| 3 | 2 | 9 | 34.4 | 34.8 |
| 3 | 2 | 7 | 52.7 | 55.5 |
| 3 | 2 | 5 | 13.0 | 9.0 |
| 3 | 2 | 3 | 58.1 | 53.3 |
| 3 | 2 | 1 | 19.1 | 7.3 |
| 3 | 2 | -1 | 61.2 | 67.4 |
| 3 | 2 | -3 | - | 26.8 |
| 3 | 2 | -5 | 32.9 | 26.4 |
| 3 | 2 | -7 | - | 20.9 |

| H | K | L | Fo | Fc |
|---|---|---|----|----|
| 3 | 2 | -11 | - | 5.2 |
| 3 | 2 | -13 | - | 3.7 |
| 3 | 2 | 15 | 19.4 | 19.4 |
| 5 | 2 | 15 | - | 19.0 |
| 5 | 2 | 13 | - | 15.6 |
| 5 | 2 | 11 | - | 9.7 |
| 5 | 2 | 9 | 36.7 | 35.5 |
| 5 | 2 | 7 | 29.1 | 15.0 |
| 5 | 2 | 5 | 32.9 | 43.0 |
| 5 | 2 | 3 | 6.9 | 12.8 |
| 5 | 2 | 1 | 37.5 | 40.5 |
| 5 | 2 | -1 | 38.2 | 18.8 |
| 5 | 2 | -3 | - | 15.5 |
| 5 | 2 | -5 | 26.8 | 9.1 |
| 5 | 2 | -7 | - | 21.3 |
| 5 | 2 | -9 | - | 15.8 |
| 5 | 2 | -11 | - | 26.9 |
| 5 | 2 | -13 | - | 5.6 |
| 5 | 2 | -15 | - | 2.1 |
| 7 | 2 | 13 | 20.6 | 14.4 |
| 7 | 2 | 11 | - | 1.7 |
| 7 | 2 | 9 | - | 8.9 |
| 7 | 2 | 7 | 39.8 | 27.9 |
| 7 | 2 | 5 | - | 6.5 |
| 7 | 2 | 3 | - | 13.2 |
| 7 | 2 | 1 | 29.1 | 27.5 |
| 7 | 2 | -1 | 30.6 | 15.7 |
| 7 | 2 | -3 | 9.2 | 0.9 |
| 7 | 2 | -5 | 50.5 | 49.9 |
| 7 | 2 | -7 | - | 15.1 |
| 7 | 2 | -9 | - | 2.1 |
| 7 | 2 | -11 | 30.6 | 27.5 |
| 7 | 2 | -13 | - | 26.1 |
| 7 | 2 | -15 | - | 6.0 |
| 9 | 2 | 13 | - | 4.4 |
| 9 | 2 | 11 | - | 10.5 |
| 9 | 2 | 7 | - | 8.2 |
| 9 | 2 | 5 | 26.8 | 26.1 |
| 9 | 2 | 3 | 19.1 | 37.4 |
| 9 | 2 | 1 | 11.3 | 22.3 |
| 9 | 2 | -1 | 45.9 | 44.9 |
| 9 | 2 | -3 | 34.4 | 28.5 |
| 9 | 2 | -5 | 39.0 | 34.8 |
| 9 | 2 | -7 | 19.1 | 7.3 |
| 9 | 2 | -9 | - | 12.0 |
| 9 | 2 | -11 | 30.6 | 30.2 |
| 11 | 2 | 13 | - | 17.1 |
| 11 | 2 | 11 | - | 5.1 |
| 11 | 2 | 9 | - | 7.4 |
| 11 | 2 | 7 | 40.5 | 44.3 |
| 11 | 2 | 5 | 11.5 | 10.5 |
| 11 | 2 | 3 | 23.7 | 19.3 |
| 11 | 2 | 1 | 20.6 | 14.9 |
| 11 | 2 | -1 | 34.4 | 32.6 |
| 11 | 2 | -3 | - | 0.5 |
| 11 | 2 | -5 | - | 16.2 |
| 11 | 2 | -7 | - | 3.4 |
| 13 | 2 | 11 | 22.9 | 19.2 |
| 13 | 2 | 9 | - | 1.7 |
| 13 | 2 | 7 | - | 0.4 |
| 13 | 2 | 5 | - | 15.7 |
| 13 | 2 | 3 | - | 8.0 |
| 13 | 2 | 1 | - | 10.3 |
| 13 | 2 | -1 | - | 14.1 |
| 13 | 2 | -3 | - | 2.6 |
| 13 | 2 | -5 | - | 0.8 |
| 13 | 2 | -7 | - | 13.3 |
| 15 | 2 | 9 | - | 8.1 |
| 15 | 2 | 7 | 21.4 | 9.4 |
| 15 | 2 | 5 | - | 12.5 |
| 15 | 2 | 3 | - | 2.6 |
| 15 | 2 | 1 | - | 20.9 |
| 15 | 2 | -1 | - | 9.9 |
| 15 | 2 | -3 | 26.8 | 32.6 |
| 15 | 2 | -5 | - | 16.8 |
| 17 | 2 | 3 | 26.8 | 32.4 |
| 17 | 2 | 3 | - | 2.3 |
| 17 | 2 | 1 | - | 9.3 |
| 17 | 2 | -1 | - | 0.5 |
| 17 | 2 | -3 | 17.6 | 24.5 |
| 17 | 2 | -5 | - | 6.3 |
| 0 | 3 | 11 | 44.9 | 48.3 |
| 0 | 3 | 9 | 19.1 | 26.2 |
| 0 | 3 | 7 | 75.7 | 75.7 |
| 0 | 3 | 9 | 14.3 | 17.2 |
| 0 | 3 | 11 | 22.9 | 19.2 |
| 0 | 3 | 13 | - | 13.7 |
| 0 | 3 | 15 | 29.6 | 32.3 |
| 0 | 3 | 13 | 47.8 | 40.6 |
| 0 | 3 | 11 | 11.5 | 17.9 |
| 0 | 3 | 5 | 67.9 | 78.0 |
| 0 | 3 | 3 | 26.8 | 36.2 |
| 0 | 3 | 1 | 38.2 | 30.8 |
| 0 | 3 | -1 | 9.6 | 2.3 |
| 0 | 3 | -3 | 17.2 | 17.6 |
| 0 | 3 | -5 | 18.9 | 18.9 |
| 0 | 3 | -7 | 9.6 | 4.2 |
| 0 | 3 | -9 | - | 27.6 |
| 0 | 3 | -11 | - | 6.0 |
| 0 | 3 | -13 | 22.0 | 21.1 |
| 4 | 3 | 15 | 9.6 | 18.1 |

| H | K | L | Fo | Fc |
|---|---|---|----|----|
| 4 | 3 | 13 | - | 7.6 |
| 4 | 3 | 11 | 28.7 | 25.5 |
| 4 | 3 | 9 | - | 0.3 |
| 4 | 3 | 7 | 26.8 | 7.6 |
| 4 | 3 | 5 | 21.0 | 3.5 |
| 4 | 3 | 3 | 19.1 | 2.3 |
| 4 | 3 | 1 | 23.9 | 2.1 |
| 4 | 3 | -1 | 8.6 | 8.2 |
| 4 | 3 | -3 | 16.3 | 14.7 |
| 4 | 3 | -5 | 47.8 | 59.6 |
| 4 | 3 | -7 | 47.8 | 28.8 |
| 4 | 3 | -9 | 20.1 | 19.4 |
| 4 | 3 | -11 | 1.7 | 1.7 |
| 4 | 3 | -13 | 37.3 | 35.9 |
| 4 | 3 | -15 | 36.3 | 37.3 |
| 6 | 3 | 13 | 19.1 | 20.1 |
| 6 | 3 | 11 | 38.2 | 33.8 |
| 6 | 3 | 9 | 66.9 | 64.5 |
| 6 | 3 | 7 | - | 2.0 |
| 6 | 3 | 5 | 43.0 | 12.1 |
| 6 | 3 | 3 | 41.1 | 45.7 |
| 6 | 3 | 1 | 45.9 | 33.3 |
| 6 | 3 | -1 | 18.2 | 14.2 |
| 6 | 3 | -3 | 8.5 | 8.5 |
| 6 | 3 | -5 | 16.3 | 10.3 |
| 6 | 3 | -7 | 47.8 | 53.4 |
| 6 | 3 | -9 | 7.7 | 7.6 |
| 6 | 3 | -11 | - | 4.6 |
| 6 | 3 | -13 | 17.2 | 15.8 |
| 6 | 3 | -15 | 9.6 | 0.5 |
| 8 | 3 | 15 | - | 7.4 |
| 8 | 3 | 13 | 19.1 | 19.1 |
| 8 | 3 | 11 | 25.8 | 26.7 |
| 8 | 3 | 9 | - | 13.7 |
| 8 | 3 | 7 | 14.3 | 7.7 |
| 8 | 3 | 5 | 33.5 | 33.6 |
| 8 | 3 | 3 | 57.3 | 52.6 |
| 8 | 3 | 1 | 22.9 | 27.4 |
| 8 | 3 | -1 | 23.9 | 11.9 |
| 8 | 3 | -3 | - | 5.2 |
| 8 | 3 | -5 | 60.2 | 52.6 |
| 8 | 3 | -7 | 11.5 | 5.2 |
| 8 | 3 | -9 | - | 20.3 |
| 8 | 3 | -11 | 11.5 | 9.7 |
| 8 | 3 | -13 | 30.2 | 29.2 |
| 8 | 3 | -15 | 17.2 | 21.8 |
| 10 | 3 | 11 | - | 1.1 |
| 10 | 3 | 9 | 6.7 | 13.0 |
| 10 | 3 | 7 | 9.6 | 10.9 |
| 10 | 3 | 5 | 33.5 | 32.8 |
| 10 | 3 | 3 | 22.0 | 19.5 |
| 10 | 3 | 1 | 14.3 | 2.7 |
| 10 | 3 | -1 | 19.1 | 13.0 |
| 10 | 3 | -3 | - | 18.3 |
| 10 | 3 | -5 | - | 5.2 |
| 10 | 3 | -7 | 19.1 | 18.3 |
| 10 | 3 | -9 | 34.4 | 38.9 |
| 10 | 3 | -11 | 11.5 | 10.0 |
| 10 | 3 | -13 | 11.5 | 19.2 |
| 12 | 3 | 11 | 46.8 | 43.2 |
| 12 | 3 | 9 | 5.7 | 8.1 |
| 12 | 3 | 7 | 19.1 | 16.3 |
| 12 | 3 | 5 | 7.7 | 7.7 |
| 12 | 3 | 3 | 47.8 | 57.8 |
| 12 | 3 | 1 | 12.4 | 9.1 |
| 12 | 3 | -1 | - | 18.6 |
| 12 | 3 | -3 | - | 4.9 |
| 12 | 3 | -5 | 9.6 | 9.1 |
| 12 | 3 | -7 | 10.5 | 6.7 |
| 12 | 3 | -9 | 14.3 | 13.7 |
| 12 | 3 | -11 | 14.3 | 11.8 |
| 14 | 3 | 7 | 7.7 | 15.5 |
| 14 | 3 | 3 | 5.7 | 1.2 |
| 14 | 3 | 3 | 8.6 | 13.2 |
| 14 | 3 | -1 | 10.6 | 29.8 |
| 14 | 3 | -3 | - | 9.7 |
| 14 | 3 | -5 | - | 4.3 |
| 14 | 3 | -7 | - | 3.8 |
| 14 | 3 | -9 | 46.8 | 44.7 |
| 14 | 3 | -11 | 19.1 | 7.3 |
| 16 | 3 | 5 | 12.4 | 4.4 |
| 16 | 3 | 3 | 14.3 | 22.5 |
| 16 | 3 | 1 | 23.9 | 22.3 |
| 16 | 3 | -1 | 10.5 | 11.7 |
| 16 | 3 | -3 | 14.3 | 15.0 |
| 16 | 3 | -5 | - | 6.2 |
| 16 | 3 | -7 | 11.5 | 8.1 |
| 16 | 3 | -9 | - | 7.6 |
| 18 | 3 | 1 | 38.2 | 36.5 |
| 1 | 3 | 14 | - | 5.5 |
| 1 | 3 | 12 | 154.9 | 162.2 |
| 1 | 3 | 10 | 12.2 | 7.2 |
| 1 | 3 | 8 | 99.5 | 107.1 |
| 1 | 3 | 6 | 93.0 | 94.5 |
| 1 | 3 | 4 | 216.0 | 221.5 |
| 1 | 3 | 2 | 103.3 | 100.7 |
| 1 | 3 | 0 | 65.7 | 61.6 |
| 1 | 3 | -2 | 41.8 | 45.8 |
| 1 | 3 | -4 | 75.1 | 81.0 |
| 1 | 3 | -6 | 105.2 | 118.6 |
| 1 | 3 | -8 | 42.3 | 39.2 |

*Table 3*

Bond distances (Å) for $Cu(NO_3)_2 \cdot 2.5H_2O$

|  | Distance | E.S.D. |  | Distance | E.S.D. |
|---|---|---|---|---|---|
| $Cu-O_1$ | 1.963 | 0.010 | $O_5-N_2$ | 1.199 | 0.011 |
| $Cu-O_2$ | 1.977 | 0.010 | $O_5-O_{11}$ | 2.138 | 0.012 |
| $Cu-O_{11}$ | 1.989 | 0.010 | $O_5-O_9$ | 2.204 | 0.011 |
| $Cu-O_7$ | 2.032 | 0.009 | $O_5-O_7$ | 2.850 | 0.010 |
| $Cu-O_5$ | 2.476 | 0.008 | $O_5-O_8$ | 3.064 | 0.013 |
| $Cu-O_6$ | 2.590 | 0.008 |  |  |  |
| $Cu-O_4$ | 2.644 | 0.010 | $O_7-N_1$ | 1.266 | 0.014 |
| $Cu-N_2$ | 2.674 | 0.012 | $O_7-O_8$ | 2.279 | 0.014 |
| $Cu-N_1$ | 2.706 | 0.010 | $O_7-O_7$ | 3.134 | 0.018 |
|  |  |  |  |  |  |
| $O_1-O_8$ | 2.793 | 0.014 | $O_8-N_1$ | 1.223 | 0.014 |
| $O_1-O_7$ | 2.800 | 0.013 | $O_8-O_{11}$ | 3.116 | 0.014 |
| $O_1-O_8$ | 2.858 | 0.014 | $O_8-O_9$ | 3.288 | 0.015 |
| $O_1-O_{11}$ | 2.864 | 0.014 |  |  |  |
| $O_1-O_5$ | 3.051 | 0.013 | $O_9-N_2$ | 1.250 | 0.016 |
| $O_1-O_9$ | 3.092 | 0.014 | $O_9-O_{11}$ | 2.126 | 0.016 |
| $O_1-O_5$ | 3.112 | 0.013 | $O_9-N_2$ | 2.995 | 0.014 |
| $O_1-O_4$ | 3.135 | 0.014 | $O_9-O_{11}$ | 3.143 | 0.016 |
|  |  |  | $O_9-O_9$ | 3.154 | 0.021 |
| $O_2-O_{11}$ | 2.792 | 0.014 | $O_9-O_{11}$ | 3.239 | 0.014 |
| $O_2-O_7$ | 2.803 | 0.014 |  |  |  |
| $O_2-O_{11}$ | 2.836 | 0.014 | $O_{11}-N_2$ | 1.294 | 0.016 |
| $O_2-O_9$ | 3.105 | 0.017 |  |  |  |
| $O_2-O_5$ | 3.189 | 0.014 |  |  |  |
| $O_2-O_9$ | 3.221 | 0.017 |  |  |  |
| $O_2-O_4$ | 3.268 | 0.015 |  |  |  |
|  |  |  |  |  |  |
| $O_3-O_2$ | 2.695 | 0.017 |  |  |  |
| $O_3-O_4$ | 2.969 | 0.013 |  |  |  |
| $O_3-O_7$ | 2.974 | 0.011 |  |  |  |
|  |  |  |  |  |  |
| $O_4-N_1$ | 1.259 | 0.014 |  |  |  |
| $O_4-O_8$ | 2.010 | 0.015 |  |  |  |
| $O_4-O_7$ | 2.179 | 0.014 |  |  |  |
| $O_4-O_7$ | 2.858 | 0.014 |  |  |  |
| $O_4-O_4$ | 3.094 | 0.020 |  |  |  |
| $O_4-O_5$ | 3.109 | 0.011 |  |  |  |
| $O_4-N_1$ | 3.192 | 0.014 |  |  |  |

$Cu(NO_3)_2 \cdot 2.5H_2O$. Another water molecule can be only adsorbed, this adsorption being dependent on the water vapour tension in the medium where the crystals are present. The crystals deliquesce in atmosphere with high relative humidity and the situation in the inner sphere of copper(II) complex changes principally.

To corroborate the X-ray structural analysis results, the crystals of commercially produced copper(II) nitrate hydrate, commonly denoted $Cu(NO_3)_2 \cdot 3H_2O$, were investigated by thermal methods (Fig. 1).

The curve of weight decrease and especially the DTA curve indicates that all water is not bound in the same way. The first part of water in the amount corresponding to 3.94 % starts to escape at 107°C. With increasing temperature the decom-

Bond angles (°) for structure of $Cu(NO_3)_2 \cdot 2.5H_2O$

| | | | | | |
|---|---|---|---|---|---|
| $O_1-Cu-O_4$ | 92.0 | 0.3 | $O_2-O_3-O_2$ | 81.9 | 0.6 |
| $O_1-Cu-O_2$ | 176.3 | 0.4 | $O_2-O_3-O_4$ | 107.9 | 0.3 |
| $O_1-Cu-O_{11}$ | 92.8 | 0.4 | $O_2-O_3-O_4$ | 116.4 | 0.3 |
| $O_1-Cu-O_5$ | 86.0 | 0.3 | $O_2-O_3-O_7$ | 59.0 | 0.3 |
| $O_1-Cu-O_5$ | 85.0 | 0.3 | $O_2-O_3-O_7$ | 80.5 | 0.4 |
| $O_1-Cu-O_7$ | 88.9 | 0.3 | $O_4-O_3-O_4$ | 120.1 | 0.6 |
| $O_2-Cu-O_4$ | 88.7 | 0.3 | $O_4-O_3-O_7$ | 57.4 | 0.2 |
| $O_2-Cu-O_{11}$ | 89.4 | 0.4 | $O_4-O_3-O_7$ | 170.2 | 0.3 |
| $O_2-Cu-O_5$ | 90.7 | 0.4 | $O_7-O_3-O_7$ | 126.5 | 0.6 |
| $O_2-Cu-O_5$ | 98.5 | 0.4 | $O_8-O_1-O_8$ | 121.9 | 0.5 |
| $O_2-Cu-O_7$ | 88.7 | 0.4 | $O_{11}-O_1-O_7$ | 90.4 | 0.3 |
| $O_4-Cu-O_{11}$ | 125.6 | 0.3 | $O_{11}-O_1-O_8$ | 102.2 | 0.4 |
| $O_4-Cu-O_5$ | 131.3 | 0.2 | $O_{11}-O_1-O_8$ | 134.6 | 0.4 |
| $O_4-Cu-O_5$ | 72.8 | 0.2 | $O_7-O_1-O_8$ | 102.6 | 0.4 |
| $O_4-Cu-O_7$ | 53.6 | 0.3 | $O_7-O_1-O_8$ | 71.5 | 0.3 |
| $O_5-Cu-O_5$ | 154.4 | 0.1 | $Cu-O_1-O_8$ | 108.1 | 0.4 |
| $O_5-Cu-O_7$ | 125.8 | 0.2 | $Cu-O_1-O_8$ | 106.6 | 0.4 |
| $O_5-Cu-O_7$ | 77.7 | 0.2 | | | |
| $O_5-Cu-O_9$ | 39.3 | 0.2 | $Cu-O_2-O_3$ | 107.3 | 0.4 |
| $O_{11}-Cu-O_5$ | 102.9 | 0.2 | $Cu-O_2-O_{11}$ | 111.2 | 0.4 |
| $O_{11}-Cu-O_5$ | 53.7 | 0.2 | $O_3-O_2-O_{11}$ | 107.7 | 0.4 |
| $O_{11}-Cu-O_7$ | 178.0 | 0.3 | $O_{11}-O_2-N_2$ | 21.1 | 0.2 |
| $O_{11}-Cu-O_9$ | 63.8 | 0.3 | $O_{11}-O_2-O_7$ | 91.8 | 0.4 |

position of copper(II) salt and formation of CuO sets in. The endothermic processes follow one after another and they cannot be separated properly. Theoretically, the lost of a half water molecule corresponds to 3.72% for $Cu(NO_3)_2 \cdot 3H_2O$ and to 3.87% for $Cu(NO_3)_2 \cdot 2.5H_2O$. These results are, therefore, in a good agreement with X-ray structural analysis results as it will be shown later.

There are four oxygen atoms next to the central copper(II) atom in the structure of investigated crystals. Two of them belong to water molecules in *trans*-positions (in Fig. 2 and 3 designated $H_2O_1$ and $H_2O_2$, respectively) and are at a distance of 1.963 or 1.977 Å from Cu(II) atom. Other two — belonging to nitrate groups — are at a distance 1.989 and 2.032 Å, respectively, from the central atom. All four atoms are situated on the same plane the equation of which has been found by the least-square method and has the form

$$-0.0509\,X + 0.9072\,Y - 0.4177\,Z = -0.8116,$$

where $X$, $Y$, and $Z$ are orthogonal coordinates in Å. The deviations of oxygen and copper atoms from above-given plane (in Å) are:

$$O_1 = 0.029 \qquad\qquad O_7 = -0.030$$
$$O_2 = 0.030 \qquad\qquad O_{11} = -0.029$$
$$Cu = -0.018$$

Every nitrate group coordinates the central atom still with another oxygen atom. These chemical bonds are, however, weaker. The interatomic distances $Cu-O_{11}$ and $Cu-O_7$ have the values of 2.476 and 2.590 Å, respectively. Moreover, the $O_5$ atom is situated on the other side of the $O_7$ atom and creates a bond between two
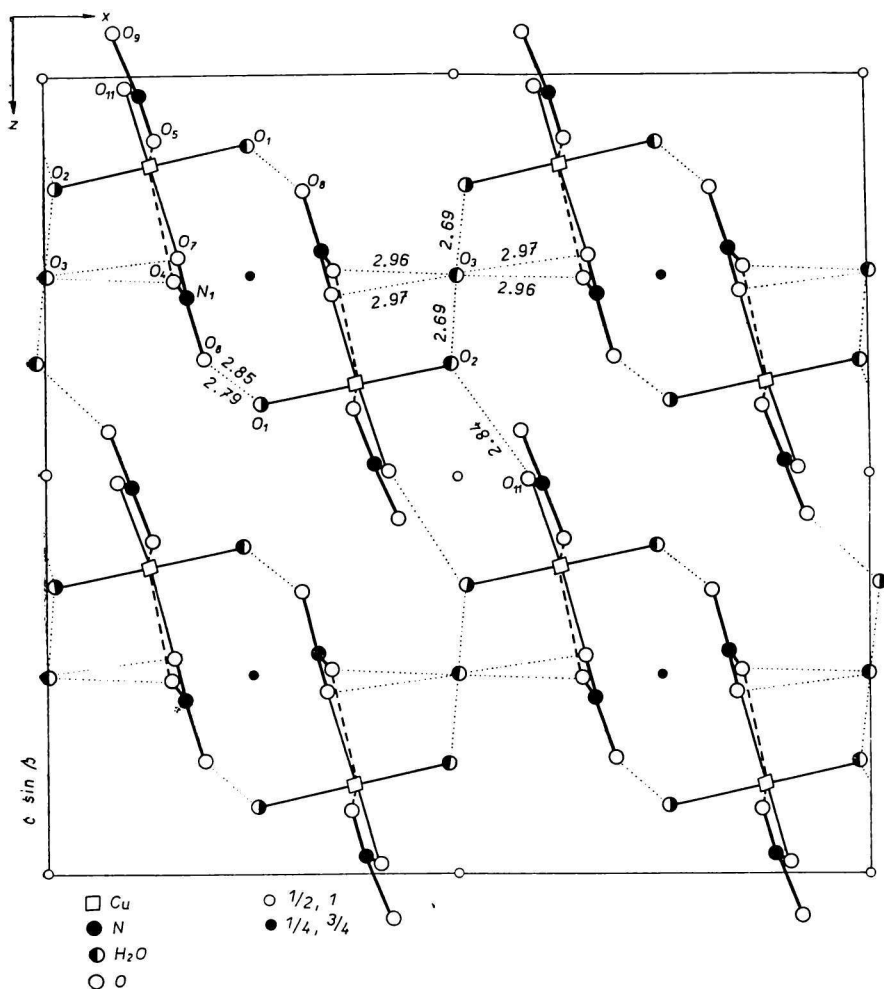
*Fig. 4.* The projection of $Cu(NO_3)_2 \cdot 2.5H_2O$ structure in the direction of $b$ axis. Hydrogen bonds are marked with dotted lines.

copper atoms. Its distance from the second Cu(II) atom is 2.640 Å. The $O_5$ atom is still more than $O_7$ leaned from the axis joining the copper atoms in vertical positions (Fig. 3). All longer Cu—O bonds correspond to weaker but not negligible chemical interactions which are, as regards the length, comparable to the total of the covalent copper atomic radius (1.17 Å) and van der Waals oxygen atomic radius (1.40 Å) [28]. The coordination number of the central atom may thus be expressed as 4 + + 1 + 1 + 1.

The nitrate groups are liable to be bonded as chelates to the metal atom in $Cu(NO_3)_2 \cdot 2.5H_2O$. Each of two independent $NO_3$ groups is bonded to the central atom with a covalent bond (1.989 and 2.032 Å). Likewise, each nitrate group forms

a weaker chemical link with the same copper atom. The function of both nitrate groups in the crystal structure is different in this respect that the oxygen atom of one is bonded to two copper atoms with two weaker chemical links what results in the formation of infinite chains oriented in the direction of axis [0 1 0] (Fig. 3).

In this connection, it is worth mentioning the conclusions of other authors.

*Berger* and co-workers [29] have studied the dependence of the magnetic susceptibility of $Cu(NO_3)_2 \cdot 2.5H_2O$ on temperature. They have found that this substance is antiferromagnetic. By comparing the measured values of magnetic susceptibility at different temperatures with calculated ones, the above author draw conclusion that the copper(II) ions form linear chains with Cu—Cu interactions or that the Cu—Cu dimers are formed.

On the basis of heat capacity measurements at different temperatures *Friedberg* and *Raquet* [30] conclude that a dimer model of $Cu(NO_3)_2 \cdot 2.5H_2O$ structure comes into existence.

*Meyers* and co-workers have measured [31] the intensity of $Cu(NO_3)_2 \cdot 2.5H_2O$ magnetization at different temperatures and from these measurements they have gathered that the $Cu(NO_3)_2 \cdot 2.5H_2O$ structure is dimer with force interactions between individual complex dimer units. These experiments have been carried out at very low temperatures ($T < 5°K$) alike in preceding studies.

From these facts, certain differences between the results of indirect methods and X-ray structural analysis can be observed.

The nitrate groups are planar within limits of the method accuracy. The equation of the plane put through the atoms of nitrate groups expressed in Å is in orthogonal coordinates

$$0.9691\,X - 0.0799\,Y - 0.2335\,Z = 1.3797.$$

The deviations of atoms from this plane are:

$$O_4 = 0.002 \qquad\qquad O_7 = \phantom{-}0.002$$
$$O_8 = 0.002 \qquad\qquad N_1 = -0.006$$

The equation of plane for the second nitrate group is given in terms

$$0.9400\,X + 0.0722\,Y - 0.3333\,Z = 1.3118.$$

The deviations of atoms (in Å) are:

$$O_{11} = 0.008 \qquad\qquad O_5 = \phantom{-}0.010$$
$$O_9 = 0.009 \qquad\qquad N_2 = -0.028$$

The bond angles (Table 4) are close to the values found in other nitrate structures [11, 13, 32, 33]. The interatomic distances N—O are also within the range of values observed (Table 5). Exception is the $N—O_5$ length (1.199 Å) which is distinctly shorter than other chemical bonds of this kind and corresponds to the length of a double chemical bond $N=O$ (1.19 Å). This fact is remarkable because the oxygen $O_5$ forms two weaker links with central atom.

The $Cu(NO_3)_2 \cdot 2.5H_2O$ structure is very compact. The polyhedron chains are linked together with hydrogen bonds. The oxygen atom occuring in a special position forms four hydrogen bonds with neighbouring water molecules and oxygen atoms of $NO_3^-$ groups. The hydrogen bonds and their lengths are presented in Fig. 4. The bond angles of these linkages are given in Table 4.

*Table 5*

Interatomic distances (Å) and angles (°) for the nitrate groups

|  | Distance | E.S.D. |  | Distance | E.S.D. |
|---|---|---|---|---|---|
| $N_1-O_8$ | 1.223 | 0.014 | $O_4-N_1-O_7$ | 119.2 | 1.0 |
| $N_1-O_4$ | 1.259 | 0.014 | $O_4-N_1-O_8$ | 108.2 | 1.0 |
| $N_1-O_7$ | 1.266 | 0.014 | $O_7-N_1-O_8$ | 132.5 | 2.0 |
| $N_2-O_5$ | 1.199 | 0.011 | $O_5-N_2-O_9$ | 128.2 | 1.2 |
| $N_2-O_9$ | 1.250 | 0.016 | $O_5-N_2-O_{11}$ | 118.1 | 1.0 |
| $N_2-O_{11}$ | 1.294 | 0.014 | $O_9-N_2-O_{11}$ | 113.4 | 1.0 |

The Cu(II) coordination in the structure solved as well as the function of nitrate groups are very similar to those in the structure of $Cu(NO_3)_2(CH_3CN)_2$ determined by *Duffin* [33]. Besides four short chemical bonds Cu(II)—ligand, the author mentions two weaker Cu—O links with interatomic distances 2.31 and 2.50 Å, respectively. But he does not state the interatomic distance Cu(II)—$O_5$ which equals 2.66 Å. This distance too is smaller than the total of van der Waals radii what is conform to the Cu(II) $(NO_3)_2 \cdot 2.5H_2O$ structure. Both nitrate groups in the structure determined by Duffin are prone to form chelates too.

The results of X-ray structural analysis of $Cu(NO_3)_2 \cdot 2.5H_2O$ have proved the covalent kind of bonding for the nitrate group bound to the bivalent copper. Moreover, they have given information about the bonding function of this group and its ability to act as a ligand in chelates. The correlation between the structural analysis results and our knowledge achieved by the investigation of solutions is quite good. We bear in mind mainly the ability of nitrate groups to take on the bonding function in copper(II) chloronitrato complexes dissolved in acetone and the piece of knowledge concerning the relative stability of these complexes in this solvent [1—3]. Our data have not confirmed the existence of sandwich structures but only the assumption of multivalency of nitrate group [6, 34]. The principal knowledge achieved implies the tendency of nitrate group to utilize the oxygen atoms for bonding the central Cu(II) atom ($\sigma$-bond, chelate, hydrogen bond). That indicates the necessity to correct our opinion concerning the ability of this group to enter into the inner sphere of complexes. The older point of view has, of course, been deduced from the behaviour of water solutions where the high hydration energy plays an important part. However, the structure determination suggests that the nitrate group takes priority even over water molecules in bonding the central atom in solid state where the conditions for complex utilization of all bonding possibilities of nitrate group are more favourable. This information agrees well with the results of physico-chemical analysis of the $Cu(NO_3)_2 \cdot 3H_2O$ —LiCl—$CH_3COCH_3$ systems where solid copper(II) nitrato complexes are formed independently of the fact that those systems contain water in molar concentration exceeding the nitrate concentration [1—3].

These experimental facts are in a certain degree in contradiction to theoretical considerations about the mutual relation between nitrate group and water molecules as regards their entering the inner sphere of nickel complexes [24]. These differences merely suggest the necessity to bear in mind the specific nature of central atom with respect to the formation and stability of nitrato complexes.

As to the bonding properties, the magnetic properties of some copper(II) nitrato complexes in solution have appeared especially interesting to us. EPR measurements have shown that the paramagnetism of some copper(II) complexes decreases considerably if the nitrate groups form bridges [35]. It bears obviously on the antiferromagnetism of copper complexes containing several nuclei as well as the peculiarity of nitrate group bonding to transition metal elements, especially in view of the possibility of $\pi$-bond formation. The unsaturation of the nitrate group bonds as well as the opportunity of $d$-electrons in $n-1$ shell to form dative $\pi$-bonds may be responsible for a different stability of nitrato complexes in the presence of organic nitrato substances as well as for the influence of nitrate group on the redox properties of copper(II) complexes what seems to be a paradox effect. The entrance of nitrate group into the inner sphere of some complexes results in speeding up the intracomplex redox process which is responsible for the reduction of bivalent copper to univalent [4, 36].

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