

Donor-Acceptor Properties of *N*- and *O*-Donor Ligands in $\text{Cu}_4\text{OX}_6\text{L}_4$ Complexes as Indicated by Infrared Spectra

G. ONDREJOVIČ and A. KOTOČOVÁ

*Department of Inorganic Chemistry, Faculty of Chemical Technology,
Slovak University of Technology, SK-812 37 Bratislava
e-mail: ondrejov@chtf.stuba.sk*

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Dedicated to Professor Smiljko Ašperger in honour of his 80th birthday

Donor-acceptor properties of ligands L in $\text{Cu}_4\text{OX}_6\text{L}_4$ complexes were deduced from experimental Mulliken electronegativity parameters a_L and b_L and partial charges estimated by the electronegativity equalization method. Four groups of ligands L were examined, a) *N*-donor ligands with saturated ring: pyrrolidine (pyr), *N*-cyanopyrrolidine (cnpyr), piperidine (pi), *N*-cyanopiperidine (cnpi), morpholine (mor), quinuclidine (qu), and 3-quinuclidinone (3-quin); b) *N*-donor ligands with pyridine ring: pyridine (py), 3-methylpyridine (3-mepy), 4-methylpyridine (4-mepy), 3-hydroxymethylpyridine (3-hmpy), 4-hydroxymethylpyridine (4-hmpy), quinoline (quinol), isoquinoline (iquinol), and pyrazine (pyz); c) *N*-donor ligands with imidazole ring: imidazole (im), 1-methylimidazole (1-meim), 1-ethylimidazole (1-etim), and benzimidazole (bzim); d) acyclic *N*- or *O*-donor ligands: NH_3 , 1,3-diisopropylcarbodiimide (cd), dimethylformamide (dmf), dimethyl sulfoxide (dmsO), and triphenylphosphine oxide (OPPh₃). Calculated partial charges on the ligands L indicate that 3-mepy, quinol, iquinol, 1-meim, 1-etim, and bzim are stronger electron acceptors than electron donors and 4-hmpy, 3-hmpy, pyz, py, 4-mepy, im, cd, dmf, dmsO, and OPPh₃ are stronger electron donors than electron acceptors. The partial charges calculated for pyr, pi, mor, cnpi, qu, cnpyr, 3-quin, and NH_3 indicate the donor properties of these ligands. The ligands in the individual groups were ordered according to the electronegativity parameter b_L as follows: a) $b_L(\text{pyr}) > b_L(\text{pi}) > b_L(\text{mor}) > b_L(\text{cnpi}) > b_L(\text{qu}) > b_L(\text{cnpyr})$, $b_L(3\text{-quin})$; b) $b_L(\text{iquinol}) \gg b_L(\text{quinol}) > b_L(3\text{-mepy}) > b_L(4\text{-hmpy})$, $b_L(3\text{-hmpy}) > b_L(\text{pyz}) > b_L(\text{py}) > b_L(4\text{-mepy})$; c) $b_L(1\text{-meim}) > b_L(\text{bzim}) > b_L(1\text{-etim}) \gg b_L(\text{im})$; d) $b_L(\text{NH}_3) > b_L(\text{dmf}) > b_L(\text{dmsO}) > b_L(\text{OPPh}_3) > b_L(\text{cd})$. The ligands with high b_L values are hard, especially 1-meim and iquinol. NH_3 , dmf, dmsO, and OPPh₃ are classified as rather hard ligands. However, py, im, cnpyr, 3-quin, and especially 4-mepy are significantly soft ligands.

The $\text{Cu}_4\text{OX}_6\text{L}_4$ complexes are interesting for their structural distortion tolerance [1], spectral and magnetic properties [2, 3], redox stability [4], and transmetallation reactions [5]. These properties are considerably affected by nature of ligands X and L which take part in building a characteristic structure [6] consisting of three mutually penetrating polyhedra, a tetrahedron OCu_4 , an octahedron OX_6 , and four trigonal bipyramids CuOX_3L . The central oxygen atom is bound to four tetrahedrally arranged copper(II) atoms which are in trigonal bipyramidal coordination geometry, the trigonal planes being occupied by bridging halide atoms, while axial positions are occupied by common oxygen atom and by four terminal ligands L.

Recently we analyzed wavenumbers of an intense band between 500 cm^{-1} and 600 cm^{-1} in infrared spectra of the $\text{Cu}_4\text{OCl}_x\text{Br}_{(6-x)}(\text{OPPh}_3)_4$ complexes [1] which indicates [2, 7] the presence of a tetrahedral

OCu_4 unit in the structure. The position of the band is remarkably affected by both, bridging X and terminal ligands L. It was found that there is a linear correlation between wavenumbers of the Cu_4O bands and the number of halides x . As the number of chloro ligands x in the $\text{Cu}_4\text{OCl}_x\text{Br}_{(6-x)}(\text{OPPh}_3)_4$ complexes increases, the wavenumber of the corresponding Cu_4O band linearly increases, while the value of a cubic lattice parameter linearly decreases. Analogous linear correlation was observed for related morpholine, piperidine [8], ammin [9], and pyrazine [10] $\text{Cu}_4\text{OCl}_x\text{Br}_{(6-x)}\text{L}_4$ complexes. Such correlation clearly involves the effect of ligand electronegativities. It can be extended to all $\text{Cu}_4\text{OX}_6\text{L}_4$ complexes.

In this paper the wavenumbers of the Cu_4O bands for a number of the $\text{Cu}_4\text{OCl}_x\text{Br}_{(6-x)}\text{L}_4$ complexes are correlated with the parameters of Mulliken group electronegativities in order to characterize the electronic

properties of the coordinate ligands L. The distribution of partial charges in the $\text{Cu}_4\text{OX}_6\text{L}_4$ molecules, which was estimated by electronegativity equalization method is also presented.

EXPERIMENTAL

Except for two cases, already published wavenumbers of the Cu_4O bands have been taken in this work (see Table 1). They refer to $\text{Cu}_4\text{OX}_6\text{L}_4$ complexes ($X = \text{Cl}, \text{Br}$) with four groups of ligands L:

a) *N*-donor ligands with saturated ring: pyrrolidine (pyr) [11], *N*-cyanopyrrolidine (cnpyr) [7], piperidine (pi) [8], *N*-cyanopiperidine (cnpi) [7], morpholine (mor) [8], quinuclidine (qu) [12], and 3-quinuclidinone (3-quin) [12].

b) *N*-donor ligands with unsaturated pyridine ring: pyridine (py) [2, 7, 13, 14], 3-methylpyridine (3-mepy) [7], 4-methylpyridine (4-mepy) [7], 3-hydroxymethylpyridine (3-hmpy) (this work), 4-hydroxymethylpyridine (4-hmpy) (this work), quinoline (quinol) [13], isoquinoline (iquinol) [13], and pyrazine (pyz) [10].

c) *N*-donor ligands with unsaturated imidazole ring: imidazole (im) [12], 1-methylimidazole (1-meim) [15], 1-ethylimidazole (1-etim) [15], and benzimidazole (bzim) [12].

d) Acyclic *N*- and *O*-donor ligands: NH_3 [9], 1,3-diisopropylcarbodiimide (cd) [7], dimethylformamide (dmf) [2], dimethyl sulfoxide (dmsO) [2], and triphenylphosphine oxide (OPPh₃) [1].

The Cu_4O bands recorded by Nujol mull technique were preferred to avoid the ligand replacement during KBr disk pressing. Except for a triple split Cu_4O band recorded for the $\text{Cu}_4\text{OBr}_6(\text{dmf})_4$ complex, only the complexes providing nonsplit Cu_4O bands have been considered.

Some of the calculated values are given with more decimal places than usual in order to minimize the round-off errors.

RESULTS AND DISCUSSION

The $\text{Cu}_4\text{OCl}_x\text{Br}_{(6-x)}\text{L}_4$ molecules can be regarded as those composed of the same central oxygen atom which is bonded to four copper atoms of different $\text{Cu}_4\text{Cl}_x\text{Br}_{(6-x)}\text{L}_4$ groups. Then the $\nu(\text{Cu}_4\text{O})$ vibration will be affected by electronic and structural effects of the ligands occupying the bridging and terminal positions around the copper(II) atoms. A few available structural and infrared data on $\text{Cu}_4\text{OX}_6\text{L}_4$ complexes do not provide a reliable correlation between the Cu—O bond lengths and $\bar{\nu}(\text{Cu}_4\text{O})$ wavenumbers. Structure and infrared spectra of two couples of pyridine [16, 17] and morpholine [3, 18] $\text{Cu}_4\text{OX}_6\text{L}_4$ complexes showed longer Cu—O bonds and at the same time lower $\bar{\nu}(\text{Cu}_4\text{O})$ wavenumbers for bromo than for chloro complexes due to a different electronegativity and size of the bromo and chloro ligands. Unfortu-

nately, structural parameters for other similar couples of the $\text{Cu}_4\text{OX}_6\text{L}_4$ complexes are not available.

The infrared stretching frequency is a function of the force constant and the reduced mass of the molecule. The central oxygen atoms are vibrating inside the $\text{Cu}_4\text{Cl}_x\text{Br}_{(6-x)}\text{L}_4$ structural units which have substantially larger mass than a single oxygen atom. From this fact it follows that the reduced mass is almost constant and hence changes in wavenumber of the Cu_4O band will reflect corresponding changes in the force constant. For similar complexes the force constant will be related to the total Cu—O bond energy. Under these assumptions the squared ratio of the Cu_4O wavenumbers for chloro and bromo complexes $(\bar{\nu}_{\text{Cl}}/\bar{\nu}_{\text{Br}})^2$ represents the corresponding ratio of the Cu—O force constants $k_{\text{f}}^{\text{Cl}}/k_{\text{f}}^{\text{Br}}$ which clearly depends on the nature of the ligands L. It monotonically increases as shown by arrangement of the $\text{Cu}_4\text{OX}_6\text{L}_4$ complexes in Table 1.

Between the $\bar{\nu}(\text{Cu}_4\text{O})$ wavenumbers and the number of chlorides x for the triphenylphosphine oxide [1], ammin [9], morpholine [8], and piperidine [8] $\text{Cu}_4\text{OCl}_x\text{Br}_{(6-x)}\text{L}_4$ complexes there exists a linear correlation as seen in Fig. 1. It can be expressed by the relation

$$\bar{\nu}(\text{Cu}_4\text{O}) \approx k_x x + q_x \quad (1)$$

Each experimental straight line for the complexes of the above-mentioned ligands L consists of seven experimental points, the first ($x = 0$) and the last points ($x = 6$) correspond to $\text{Cu}_4\text{OBr}_6\text{L}_4$ and $\text{Cu}_4\text{OCl}_6\text{L}_4$ complexes, respectively. The parameter x obviously involves two factors affecting the $\bar{\nu}(\text{Cu}_4\text{O})$ wavenumbers, the variation in the charge distribution and at the same time the pertinent changes in the bond lengths. Since ammin, piperidine, morpholine, and triphenylphosphine oxide ligands L in the $\text{Cu}_4\text{OCl}_x\text{Br}_{(6-x)}\text{L}_4$ complexes are structurally and electronically significantly different, eqn (1) may be extended to such complexes of any ligand L. With respect to the linear correlations presented in Fig. 1 the $\bar{\nu}(\text{Cu}_4\text{O})$ wavenumbers for two complexes of each ligand L, $\text{Cu}_4\text{OCl}_6\text{L}_4$ and $\text{Cu}_4\text{OBr}_6\text{L}_4$ were considered to be sufficient for obtaining the parameters k_x and q_x (Table 1).

The linear correlation represented by relation (1) evidently indicates that the parameter x implies electronegativity effects due to variation of the two different bridging halides in the $\text{Cu}_4\text{Cl}_x\text{Br}_{(6-x)}\text{L}_4$ complex group. Electronegativity effects can be quantified by Mulliken group electronegativity parameters a_G and b_G [19]. They remind well-known dependences of carbonyl [20], phosphoryl and sulfonyl [21] infrared absorptions on electronegativities of the attached groups.

The Mulliken group electronegativity parameters [19], the inherent electronegativity a_G and the charge

Table 1. Wavelengths of Cu₄O Bands of Chloro and Bromo Cu₄OX₆L₄ Complexes, Linear Slope k_x , Ratio of Force Constants k_f^{Cl}/k_f^{Br} , and Converted Parameters k_a , k_b , q_a , and q_b

| Ligand L | $\tilde{\nu}(\text{Cu}_4\text{O})/\text{cm}^{-1}$ | | k_f^{Cl}/k_f^{Br} | k_x | k_a | k_b | q_a | q_b |
|-------------------|---|------------------|---------------------|--------|---------|-------|--------|-------|
| | Cl | Br(q_x) | | | | | | |
| OPPh ₃ | 586 | 552 | 1.1270 | 5.6667 | 855.44 | 14191 | -4007 | -1590 |
| dmf | 583 | 549 ^a | 1.1277 | 5.6667 | 855.44 | 14191 | -4765 | -1947 |
| NH ₃ | 578 ^b | 544 | 1.1289 | 5.6667 | 855.44 | 14191 | -6028 | -2543 |
| 1-meim | 571 | 537 | 1.1306 | 5.6667 | 855.44 | 14191 | -7797 | -3377 |
| dmsO | 583 | 548 | 1.1318 | 5.8333 | 925.87 | 16862 | -5018 | -2066 |
| iquinol | 570 | 535 | 1.1351 | 5.8333 | 925.87 | 16862 | -8302 | -3615 |
| pyr | 575 | 538 | 1.1423 | 6.1667 | 1066.72 | 22203 | -7544 | -3258 |
| 3-mepy | 574 | 537 | 1.1425 | 6.1667 | 1066.72 | 22203 | -7797 | -3377 |
| quinol | 573 | 536 | 1.1428 | 6.1667 | 1066.72 | 22203 | -8049 | -3496 |
| cnpi | 580 | 542 | 1.1451 | 6.3333 | 1137.14 | 24874 | -6534 | -2781 |
| bmim | 568 | 530 | 1.1485 | 6.3333 | 1137.14 | 24874 | -9565 | -4211 |
| mor | 576 | 537 | 1.1505 | 6.5000 | 1207.57 | 27544 | -7797 | -3377 |
| 4-hmpy | 575 | 536 | 1.1508 | 6.5000 | 1207.57 | 27544 | -8049 | -3496 |
| 1-etim | 568 | 529 | 1.1529 | 6.5000 | 1207.57 | 27544 | -9818 | -4330 |
| pyz | 576 ^b | 536 | 1.1548 | 6.6667 | 1277.99 | 30215 | -8049 | -3496 |
| cd | 572 | 532 | 1.1560 | 6.6667 | 1277.99 | 30215 | -9060 | -3972 |
| pi | 571 | 531 | 1.1563 | 6.6667 | 1277.99 | 30215 | -9312 | -4092 |
| cnpyr | 581 | 540 | 1.1576 | 6.8333 | 1348.42 | 32885 | -7039 | -3019 |
| py | 577 | 536 | 1.1588 | 6.8333 | 1348.42 | 32885 | -8049 | -3496 |
| 3-hmpy | 573 | 532 | 1.1601 | 6.8333 | 1348.42 | 32885 | -9060 | -3972 |
| 4-mepy | 576 | 526 | 1.1991 | 8.3333 | 1982.24 | 56921 | -10576 | -4687 |
| im | 568 | 518 | 1.2024 | 8.3333 | 1982.24 | 56921 | -12597 | -5640 |
| qu | 560 | 510 | 1.2057 | 8.3333 | 1982.24 | 56921 | -14618 | -6593 |
| 3-quin | 567 | 515 | 1.2121 | 8.6667 | 2123.09 | 62262 | -13355 | -5997 |

a) Mean value for triply split band. b) Obtained by linear extrapolation based on Cu₄OCl_xBr_(6-x)(NH₃)₄, $x = 0-4$ and Cu₄OCl_xBr_(6-x)(pyz)₄, $x = 0, 2, 3$ complexes.

coefficient b_G of the Cu₄Cl_xBr_(6-x)L₄ complex groups were calculated by eqns (2) and (3) [22]

$$a_G = \sum(na/b) / \sum(n/b) \quad (2)$$

$$b_G = 1 / \sum(n/b) \quad (3)$$

where a represents the Mulliken atomic or ligand group inherent electronegativity, b represents the Mulliken atomic or ligand group charge coefficient, and n represents the number of atoms in a ligand L or the number of atoms and ligands in the Cu₄Cl_xBr_(6-x)L₄ complex group.

The nature of eqns (1-3) indicates that besides the parameter x the $\tilde{\nu}(\text{Cu}_4\text{O})$ wavenumbers can as well be expressed in the scale of the Mulliken electronegativity a_G and b_G parameters as shown by the relation

$$\tilde{\nu}(\text{Cu}_4\text{O}) \approx k_x x + q_x \approx k_a a_G + q_a \approx k_b b_G + q_b \quad (4)$$

It can be easily demonstrated that between the parameters a_G and b_G calculated for Cu₄Cl_xBr_(6-x)L₄ groups a linear relationship (5) exists, where $k_{ab} = k_b/k_a$.

$$a_G = k_{ab} b_G + 4.0527 \quad (5)$$

The tests performed for the ammin, piperidine, and morpholine Cu₄Cl_xBr_(6-x)L₄ complex groups showed that the relationships between the $\tilde{\nu}(\text{Cu}_4\text{O})$ wavenumbers and the calculated a_G and b_G parameters using eqns (2) and (3) are in fact linear, as expected according to the relation (4). The values of the correlation coefficients are 0.9969, 0.9801, and 0.9740 for the ammin, piperidine, and morpholine Cu₄Cl_xBr_(6-x)L₄ groups, respectively.

The relation (4) indicates that the experimental parameters k_x and q_x for each of the Cu₄X₆L₄ complex groups can be converted to the corresponding electronegativity parameters k_a , q_a , k_b , and q_b . The factors of conversion are based on the reference a_G^0 and b_G^0 parameters calculated for pyrrolidine, piperidine, and quinuclidine Cu₄X₆L₄ complex groups. Cyclic *N*-donor pyrrolidine, piperidine, and quinuclidine molecules have been selected as the reference ligands since they do not contain substituents, π -bonding, and the atoms with *d*-orbitals, hence their atoms can be assigned to less uncertain valence states. Moreover, the Cu₄OX₆L₄ complexes of the reference ligands cover rather large range of k_x values, ranging from 6.1667 to 8.3333 (Table 1).

The Mulliken atomic electronegativity a and b parameters [23] used for the calculation of the reference and current Mulliken group electronegativity a_G and b_G parameters (eqns (2) and (3)) are presented in

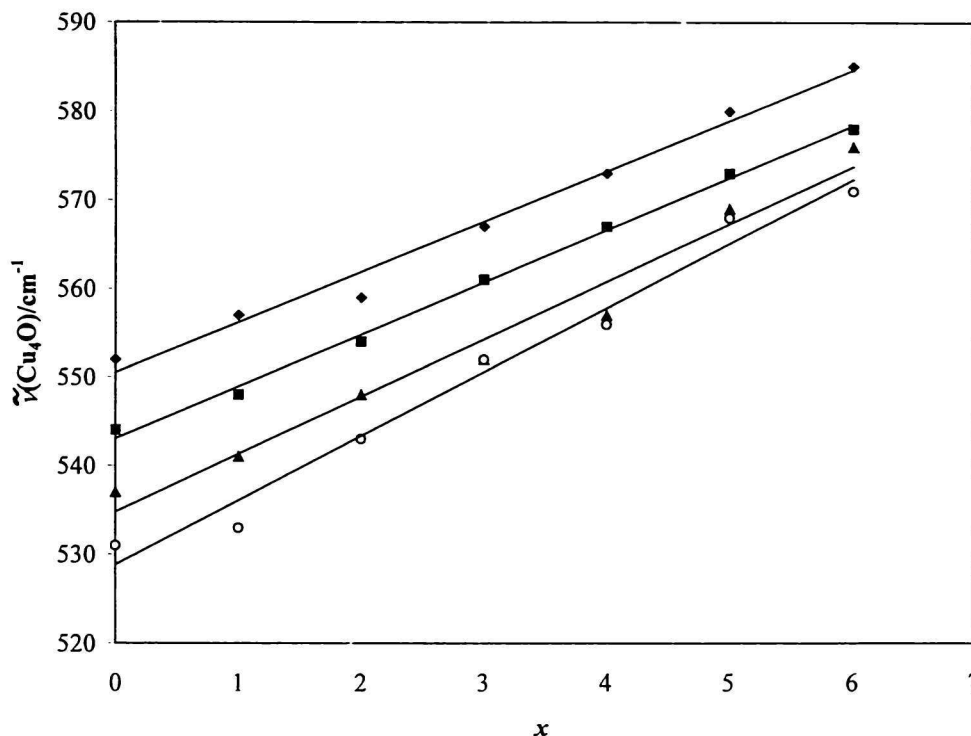


Fig. 1. Linear relationship between $\bar{\nu}(\text{Cu}_4\text{O})$ wavenumbers and parameter x for triphenylphosphine oxide (◆) ($R = 0.9860$), ammin (■) ($R = 0.9923$), morpholine (▲) ($R = 0.9733$), and piperidine (○) ($R = 0.9860$) $\text{Cu}_4\text{OCl}_x\text{Br}_{(6-x)}\text{L}_4$ complexes.

Table 2. Mulliken Atomic Electronegativity Parameters^a Applied for Calculation of Group Electronegativity Parameters

| Atom | Valence state | a/V | b/Ve^{-1} |
|------|--------------------|-------|-------------|
| Cu | 1, s | 4.477 | 6.498 |
| Br | μ , 16.7 % s | 10.52 | 10.44 |
| Cl | μ , 16.7 % s | 11.22 | 11.57 |
| C | tetrahedral | 8.15 | 11.39 |
| H | s | 7.176 | 12.844 |
| N | tetrahedral | 10.66 | 13.16 |
| O | μ , 16.7 % s | 12.55 | 15.47 |
| O | tetrahedral | 14.02 | 15.55 |

a) Ref. [24].

Table 2. Carbon and nitrogen atoms in the coordinated reference ligands are assigned by tetrahedral hybridization valence states (25 % s -character), hydrogen atoms by s -character, and the central oxygen atom by tetrahedral hybridization. The oxygen atom in morpholine ligand is assigned by 16.7 % s -character. The electronegativity parameters of the $\text{Cu}_4\text{Cl}_x\text{Br}_{(6-x)}\text{L}_4$ complex groups were calculated using available atomic electronegativity parameters for copper(I) atom. It was assumed that the electronegativity parameters of copper(I) and copper(II) atoms do not differ significantly. Bridging bromides and chlorides are assigned by 16.7 % s -character. The values of atomic electronegativity parameters for a given va-

lence state are regarded to be the same for all complexes. Constant values of atomic electronegativity parameters for copper, halides, and tetrahedral oxygen atom were taken throughout the calculation. Nevertheless, the electronegativity of these atoms must be somewhat affected by varying electronegativity of ligands L.

The $\bar{\nu}(\text{Cu}_4\text{O})$ wavenumbers refer to real structures of the $\text{Cu}_4\text{OX}_6\text{L}_4$ complexes. A few and incomplete structural data are known for the $\text{Cu}_4\text{OX}_6\text{L}_4$ complexes with reference ligands. Structures of the pyrrolidine $\text{Cu}_4\text{OX}_6\text{L}_4$ complexes are not known. The X-ray structure of a piperidine $\text{Cu}_4\text{OCl}_6\text{L}_4$ complex showed the piperidine ligand in a chair conformation, the Cu—N bond being in equatorial position with respect to the equatorial fragment of the coordinate piperidine molecule [12]. Coordination polyhedron of the complex is considerably distorted [1]. However, a $\text{Cu}_4\text{OCl}_6\text{L}_4$ complex with bulky 3-quinuclidinone ligand [24] which is structurally close to related quinuclidine complex is much less distorted [1].

Substituting from the $\bar{\nu}(\text{Cu}_4\text{O})$ wavenumbers and the reference a_G^0 and b_G^0 data into the relation (4) gives reference k_a^0 , q_a^0 , k_b^0 , and q_b^0 parameters, which are summarized in Table 3. The plots of both k_a^0 and k_b^0 vs. k_x , and both q_a^0 and q_b^0 vs. q_x provide regression straight lines and corresponding eqns (6–9). These equations were used for conversion of the experimental k_x and q_x parameters to corresponding experimental electronegativity parameters k_a , k_b and q_a , q_b , respec-

Table 3. Values of Reference Parameters, Standard Error (SE), and Coefficient of Correlation (*R*) Calculated for Reference Pyrrolidine, Piperidine, and Quinuclidine Cu₄Cl₆L₄ and Cu₄Br₆L₄ Complex Groups

| Parameter | Reference ligand | | | SE | <i>R</i> |
|---------------------------------------|------------------|--------|--------|------|----------|
| | pyr | pi | qu | | |
| <i>k_x</i> | 6.1667 | 6.6667 | 8.3333 | – | – |
| <i>q_x</i> | 538 | 531 | 510 | – | – |
| <i>k_a^o</i> | 1035 | 1319 | 1973 | 52 | 0.9970 |
| <i>k_b^o</i> | 21220 | 31493 | 56626 | 1639 | 0.9980 |
| <i>q_a^o</i> | –7379 | –9531 | –14563 | 279 | 0.9986 |
| <i>q_b^o</i> | –3184 | –4186 | –6567 | 123 | 0.9987 |
| <i>a_L^o</i> | 7.7140 | 7.6808 | 7.6830 | – | – |
| <i>b_L^o</i> | 0.8866 | 0.7292 | 0.5873 | – | – |
| <i>a_G^o</i> (Cl) | 7.6831 | 7.6601 | 7.6655 | – | – |
| <i>a_G^o</i> (Br) | 7.6474 | 7.6298 | 7.6402 | – | – |
| <i>b_G^o</i> (Cl) | 0.1771 | 0.1511 | 0.1259 | – | – |
| <i>b_G^o</i> (Br) | 0.1754 | 0.1498 | 0.1250 | – | – |

Table 4. Electronegativity Parameters of Cu₄Cl₆L₄ and Cu₄Br₆L₄ Complex Groups and Mean Values of Partial Charges and Ligand Electronegativity Parameters

| Ligand L | <i>a_G</i> (Cl) | <i>a_G</i> (Br) | <i>b_G</i> (Cl) | <i>b_G</i> (Br) | <i>a_L</i> | <i>b_L</i> | <i>δ_L</i> | <i>δ_O</i> | <i>δ_{Cu}</i> |
|-------------------|---------------------------|---------------------------|---------------------------|---------------------------|----------------------|----------------------|----------------------|----------------------|-----------------------|
| OPPh ₃ | 5.3694 | 5.3297 | 0.1533 | 0.1509 | 4.89 | 0.74 | 0.73 | –0.55 | 0.15 |
| dmf | 6.2519 | 6.2121 | 0.1783 | 0.1759 | 5.91 | 0.89 | 0.46 | –0.50 | 0.28 |
| NH ₃ | 7.7226 | 7.6829 | 0.2199 | 0.2175 | 7.78 | 1.17 | 0.01 | –0.40 | 0.51 |
| 1-meim | 9.7817 | 9.7420 | 0.2782 | 0.2758 | 10.85 | 1.63 | –0.62 | –0.27 | 0.82 |
| dmsO | 6.0492 | 6.0114 | 0.1571 | 0.1551 | 5.71 | 0.76 | 0.52 | –0.51 | 0.25 |
| quinol | 9.5823 | 9.5445 | 0.2482 | 0.2461 | 10.40 | 1.39 | –0.56 | –0.28 | 0.79 |
| pyr | 7.6112 | 7.5766 | 0.1726 | 0.1710 | 7.62 | 0.86 | 0.05 | –0.41 | 0.49 |
| 3-mepy | 7.8471 | 7.8125 | 0.1779 | 0.1763 | 7.92 | 0.89 | –0.02 | –0.39 | 0.53 |
| quinol | 8.0830 | 8.0483 | 0.1833 | 0.1816 | 8.22 | 0.93 | –0.10 | –0.38 | 0.56 |
| cnpi | 6.2556 | 6.2222 | 0.1351 | 0.1336 | 6.01 | 0.64 | 0.46 | –0.50 | 0.28 |
| bzim | 8.9110 | 8.8776 | 0.1921 | 0.1906 | 9.30 | 0.98 | –0.35 | –0.33 | 0.69 |
| mor | 6.9335 | 6.9012 | 0.1435 | 0.1421 | 6.81 | 0.68 | 0.26 | –0.45 | 0.39 |
| 4-hmpy | 7.1419 | 7.1096 | 0.1478 | 0.1464 | 7.05 | 0.71 | 0.19 | –0.44 | 0.42 |
| 1-etim | 8.6005 | 8.5682 | 0.1778 | 0.1764 | 8.87 | 0.89 | –0.25 | –0.35 | 0.64 |
| pyz | 6.7491 | 6.7178 | 0.1348 | 0.1334 | 6.60 | 0.64 | 0.31 | –0.46 | 0.36 |
| cd | 7.5367 | 7.5054 | 0.1504 | 0.1491 | 7.53 | 0.73 | 0.07 | –0.41 | 0.48 |
| pi | 7.7336 | 7.7023 | 0.1543 | 0.1530 | 7.77 | 0.75 | 0.01 | –0.40 | 0.51 |
| cnpyr | 5.6509 | 5.6205 | 0.1095 | 0.1082 | 5.37 | 0.50 | 0.65 | –0.54 | 0.19 |
| py | 6.3974 | 6.3669 | 0.1239 | 0.1226 | 6.20 | 0.58 | 0.42 | –0.49 | 0.30 |
| 3-hmpy | 7.1438 | 7.1134 | 0.1382 | 0.1370 | 7.06 | 0.66 | 0.19 | –0.44 | 0.42 |
| 4-mepy | 5.6258 | 5.6005 | 0.0925 | 0.0916 | 5.39 | 0.41 | 0.66 | –0.54 | 0.18 |
| im | 6.6413 | 6.6161 | 0.1091 | 0.1082 | 6.51 | 0.50 | 0.35 | –0.47 | 0.34 |
| qu | 7.6568 | 7.6316 | 0.1257 | 0.1248 | 7.67 | 0.59 | 0.04 | –0.41 | 0.50 |
| 3-quin | 6.5572 | 6.5327 | 0.1054 | 0.1046 | 6.42 | 0.48 | 0.38 | –0.48 | 0.33 |

tively (Table 1).

$$k_a = 423k_x - 1539 \quad (6)$$

$$k_b = 16024k_x - 76611 \quad (7)$$

$$q_a = 253q_x - 143460 \quad (8)$$

$$q_b = 119q_x - 67344 \quad (9)$$

Each of the regression straight lines (6–9) is constructed only of three points due to a low number of suitable reference ligands L. To consider the errors in-

involved in the conversion procedure, the reference values, together with the corresponding standard errors and the Pearson correlation coefficients were calculated (Table 3). In this connection the relative error is considered to be a difference between the converted and corresponding reference value divided by the reference value. Such relative errors of the converted *k_a*, *k_b*, *q_a*, and *q_b* values are 0.4–0.6 % for quinuclidine and 3–5 % for pyrrolidine and piperidine Cu₄X₆L₄ complex groups. The relative errors of the converted *a_L* values do not exceed 1.5 % and those of converted *b_L* values are below 3.5 %.

Substituting *k_a*, *k_b*, *q_a*, and *q_b* values into the rela-

tion (4) gives experimental electronegativity parameters a_G and b_G for each of the $Cu_4X_6L_4$ complex groups (Table 4). Parameters a_G and b_G imply ligand electronegativity parameters a_L and b_L as it is defined by eqns (2) and (3). Therefore, these equations were rearranged and used for calculation of the ligand parameters a_L and b_L (Table 4).

The classification of donor-acceptor properties of ligands L in the $Cu_4OX_6L_4$ molecules is based on partial charges. The partial charges δ on the ligands L and on the central oxygen and copper atoms as well were estimated by the electronegativity equalization method [22] using eqns (10) and (11)

$$a_{eq} = \left[\sum (na/b) + q \right] / \sum (n/b) \quad (10)$$

$$\delta = (a_{eq} - a)/b \quad (11)$$

where a_{eq} represents the equalized electronegativity parameter a , q represents the net charge on the species, n , a , and b have the same meaning as in eqn (2). The calculated partial charges are presented in Table 4.

The values of the experimental ligand electronegativity parameters a_L and b_L as well as the partial charges δ calculated for both bromo and chloro $Cu_4OX_6L_4$ complexes are only slightly different. The mean values of these parameters describe overall electron donor-acceptor properties of the ligands L in the $Cu_4OX_6L_4$ molecules with respect to the reference pyrrolidine, piperidine, and quinuclidine ligands.

The a_L parameter indicates the ability of a ligand L to hold or attract electrons when combining with a Cu_4OX_6 group [22]. It also represents the measure of a driving potential of a ligand L for the electron flow [25]. The direction of the electron flow is indicated by the partial charge on a ligand L.

In general, the parameter b is interpreted as the resistance of the electronegativity of a chemical species to change in the number of electrons and as a quantitative measure of hardness [26]. A typical hard chemical species tends to have large b parameter and a low electron capacity. The b_L parameter can be interpreted as a measure to which the electron drift resists in both directions, from the ligand L towards the copper(II) atom and backwards [25]. Large, soft, polarizable ligands have low values of b_L , and small, hard, nonpolarizable ligands tend to have higher value [19].

The reference N -donor ligands with saturated rings, pyrrolidine, piperidine, and quinuclidine, in the $Cu_4OCl_6L_4$ complexes showed approximately the same parameter a_L , small positive partial charges, and expected lowering of the b_L values with the decreasing number of atoms in the molecules. The oxygen atoms in morpholine and 3-quinuclidinone ligands significantly lower the electronegativities of these ligands and make them softer as compared with the piperidine and quinuclidine. Dramatically reduced values

of a_L and b_L parameters of N -cyanopyrrolidine and N -cyanopiperidine reveal an intriguing effect when a strong electron-withdrawing N -cyano group substantially increases the donor abilities of pyrrolidine and piperidine ligands. In general, N -donor atoms, as members of saturated rings, are pure σ -donors, since they do not possess any acceptor orbital. It corresponds to the fact that each of the N -donor ligands with saturated ring presented in Table 4 gains a positive charge upon coordination. In this regard, the effective electron donor abilities of N -cyanopyrrolidine and N -cyanopiperidine can be explained by the field effect of N -cyano groups. The relation among the ligands formed by saturated rings can be qualitatively demonstrated by increasing effective electron donor abilities reciprocally indicated by decreasing b_L values in the order

$$b_L(\text{pyr}) > b_L(\text{pi}) > b_L(\text{mor}) > b_L(\text{cnpi}) > b_L(\text{qu}) > b_L(\text{cnpyr}), b_L(3\text{-quin}) \quad (12)$$

The ligands of pyridine group can be ordered according to their electronegativity parameter $\alpha_L = a_L$ or b_L in the row

$$\alpha_L(\text{iquinol}) \gg \alpha_L(\text{quinol}) > \alpha_L(3\text{-mepy}) > \alpha_L(4\text{-hmpy}), \alpha_L(3\text{-hmpy}) > \alpha_L(\text{pyz}) > \alpha_L(\text{py}) > \alpha_L(4\text{-mepy}) \quad (13)$$

It is obvious that the electron donor-acceptor properties of the pyridine ligand are significantly modified by substituents. The 3-methylpyridine and benzo derivatives of pyridine, isoquinoline, and quinoline exhibit relatively high electronegativity parameters. These ligands accommodate negative partial charges indicating poor electron acceptor abilities of 3-methylpyridine and quinoline and a strong electron acceptor ability of isoquinoline. However, the capacity of the ligands for the electron transfer is appreciably low, especially for isoquinoline, as indicated by relatively high values of b_L parameter.

Pyridine ligand is represented by low values of electronegativity parameters. The 3-methylpyridine ligand is significantly more electronegative and 4-methylpyridine less electronegative than pyridine. The ligand partial charges indicate much stronger donor ability of 4-methylpyridine than pyridine. The 4-methylpyridine is the softest ligand of the pyridine group and its electron donor potential is most effective for the electron transfer. This corresponds to well known electron-donating induction effect of a methyl group occupying *para* position. The methyl group in *meta* position reduces the potential of the pyridine ligand for an electron donation and makes negligibly stronger acceptor abilities. Electronegativity of 3-hydroxymethylpyridine and 4-hydroxymethylpyridine was found practically the same. Both substituents a little enhance the elec-

tronegativity and especially hardness of pyridine ligand and reduce its positive charge. The formal replacement of CH group by nitrogen atom in pyridine ring provides a pyrazine molecule. Monodentate pyrazine is more electronegative and somewhat harder than pyridine alone. The 4-hydroxymethylpyridine, 3-hydroxymethylpyridine, pyrazine, pyridine, and especially 4-methylpyridine can be considered to be strong and effective donors.

The values of the α_L parameter indicate that the group of the most electronegative ligands L consists of imidazole derivatives, 1-methylimidazole, benzimidazole, and 1-ethylimidazole, while imidazole alone showed remarkably low electronegativity. The b_L values follow the same order.

High electronegativity of the substituted imidazole ligands is obviously connected with an effect of the substituents. Negative partial charges on these substituted ligands (Table 4) indicate prevailing electron acceptor properties over electron donor abilities. However, the b_L values indicate a fast charge capacity decreasing when substituting imidazole, especially with methyl group. Then, the smallest imidazole that is theoretically the hardest ligand of the group becomes the softest ligand and acts as an effective electron donor. These relations can be expressed by decreasing electron acceptor abilities of the substituted imidazole ligands expressed by the order of $\alpha_L = a_L$ or b_L (14),

imidazole alone being an effective electron donor

$$\alpha_L(1\text{-meim}) > \alpha_L(\text{bzim}) > \alpha_L(1\text{-etim}) \gg \alpha_L(\text{im}) \quad (14)$$

Positive partial charges of 0.35 ecu and 0.42 ecu (ecu \equiv electron charge unit) on imidazole and pyridine ligands, respectively, as well as their relatively low values of the b_L parameter indicate an effective strong electron donor potential of the ligands. Similar effect has been observed in metal-substituted bacteriochlorophylls. Following the principle of electronegativity equalization 0.30 ecu and 0.27 ecu migrated from imidazole and pyridine, respectively, into the nickel-substituted bacteriochlorophyll central core upon monoligation [27].

The α_L parameter of the O-donor ligands shows a low electronegativity and a strong donor ability of triphenylphosphine oxide, dimethylformamide, and dimethyl sulfoxide. However, the electron flow from the ligands to the central atom and backwards is significantly resisted as indicated by the relatively high values of b_L parameter. The behaviour of these ligands can be connected with π -bonding of O-donor atoms with the rest of the ligand molecules. The structure determination of the Cu₄OCl₆(OPPh₃)₄ complex revealed linear Cu—O—P arrangements indicating a diagonal hybridization and the π -bonding of the oxygen donor atoms. High P—O stretching frequency

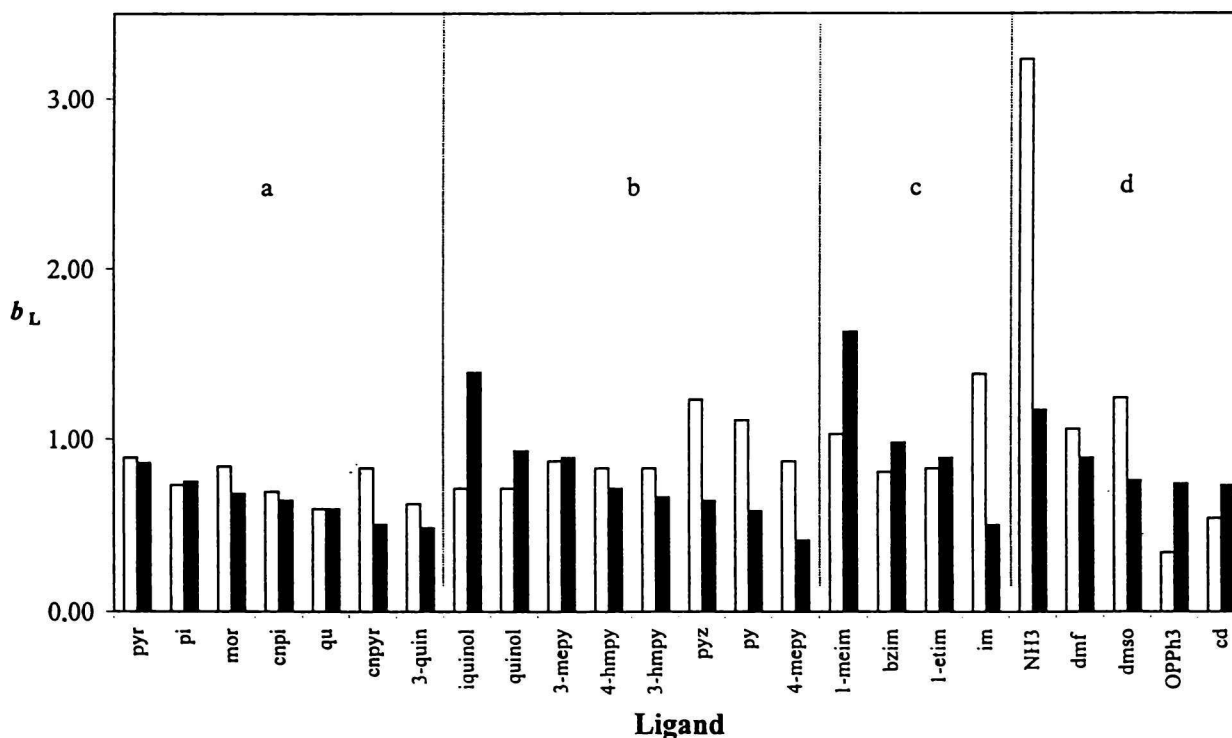


Fig. 2. Comparison of theoretical (white columns) and experimental values (black columns) of b_L parameter for ligands L in Cu₄Ox₆L₄ complexes. a) N-donor ligands with saturated ring, b) N-donor ligands with pyridine ring, c) N-donor ligands with imidazole ring, d) acyclic N- or O-donor ligands.

($\bar{\nu} = 1194 \text{ cm}^{-1}$) found for this complex also indicates a higher bond order than in other phosphine oxide complexes [6]. The angles at *O*-donor oxygen atoms in dimethylformamide [28] and dimethyl sulfoxide [29] ligands coordinated in $\text{Cu}_4\text{OCl}_6\text{L}_4$ complexes are $\text{Cu—O—C} = 125^\circ$ and $\text{Cu—O—S} = 119.5^\circ$ approaching the value of 120° . Then, the oxygen atoms are assigned by trigonal hybridization and dispose of π -orbital.

For some of the $\text{Cu}_4\text{OX}_6\text{L}_4$ complexes a considerable difference between the experimental and theoretical values of a_L and b_L has been found. For illustration there are shown in Fig. 2 the experimental and theoretical values of b_L parameter for all of the ligands L. The theoretical b_L values were calculated using the atomic electronegativity parameters determined by theoretically assigned valence states of atoms. However, these valence states can be to some extent different from those occurring in the real complexes. Moreover, the isomeric ligands, which are substituted by the same group but in different positions of the ring, cannot be distinguished by theoretical b_L parameter. As expected, the reference pyrrolidine, piperidine, and quinuclidine ligands must have practically the same theoretical and experimental b_L values. The *N*-cyanopiperidine, 3-methylpyridine, and 1-ethylimidazole ligands exhibit almost the same theoretical and experimental b_L values. Somewhat larger differences between the theoretical and experimental b_L values are characteristic of 3-quinuclidinone, morpholine, 3-hydroxymethylpyridine, 4-hydroxymethylpyridine, benzimidazole, 1,3-diisopropylcarbodiimide, and dimethylformamide ligands. If the b_L parameter is taken as a measure of hardness, then amin, imidazole, pyrazine, pyridine, dimethyl sulfoxide, 4-methylpyridine, and *N*-cyanopyrrolidine ligands are much softer and isoquinoline, 1-methylimidazole, triphenylphosphine oxide, and quinoline ligands are much harder than expected, considering the theoretical b_L values.

The electronic and steric properties of ligands L in the $\text{Cu}_4\text{OX}_6\text{L}_4$ complexes obviously affect the distribution of partial charges on the central oxygen and copper(II) atoms. The ligands L characterized by low values of a_L and low values of b_L saturate the oxygen and copper(II) atoms by electrons most effectively, as indicated by the mean values of partial charges δ_O and δ_{Cu} presented in Table 4.

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