Copper(II) complexes with organic ligands. XV.
Magnetic properties of copper(II) benzoate complexes of heterocyclic N-oxides

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Copper(II) benzoate complexes of composition $Cu(C_6H_5COO)_2L$ (L = = pyridine-N-oxide, quinoline-N-oxide, or some their methyl derivatives) have even at room temperature markedly lower magnetic moments than are the spin values corresponding to Cu^{2+} ions. Their magnetic behaviour studied in the temperature range 93—303 K is typical for antiferromagnetism, with the Néel temperature $T_m = 268 \pm 12$ K. From equilibrium constants of the singlet-triplet interaction the values of enthalpy (ΔH^0) and entropy (ΔS^0) were estimated. Magnetic properties of the studied complexes indicate that they belong to the copper(II) carboxylate complexes with a binuclear bridged structure. Copper(II) acetate monohydrate is a typical example of this type.

The donor oxygen atom of heterocyclic N-oxides often acts as a monoatomic bridge enabling the strong magnetic interaction of the superexchange type between Cu^{2+} ions [1—3]. For example, the binuclear complex $[Cu_2Cl_4(pyox)_2]$ (pyox = pyridine-N-oxide) has magnetic moment $\mu_{eff} = 0.62$ B.M. ($T = 293$ K) and the value of the singlet-triplet separation $|2J| = 720$ cm^{-1} (2.06 kcal mol^{-1}) [4] derived from the temperature dependence of its magnetic susceptibility. However, the copper(II) acetate complexes $Cu(Ac)_2(pyox)$ and $Cu(Ac)_2(quinox)$ (quinox = quinoline-N-oxide) [3, 5] have the values of the room-temperature magnetic moments and the singlet-triplet separation common to binuclear copper(II) carboxylate complexes [1] of the copper(II) acetate monohydrate type [6]. Therefore the bridge function of acetate ions and the monodentate bond of pyox or quinox at terminal positions of the binuclear structural unit have been assumed in these complexes [4, 5].

Recently [7] we described the preparation of copper(II) benzoate complexes $Cu(benz)_2L$. where L = pyridine-N-oxide, quinoline-N-oxide, or some their methyl derivatives. The observed magnetic moments of the complexes were $\mu_{eff} = 1.40 \pm 0.02$ B.M. (room temperature), absorption bands of their electronic spectra were at $\lambda = 370—380$ nm (shoulder) and at $\lambda = 720—750$ nm [7]. From their mentioned properties we assumed that the prepared complexes $Cu(benz)_2L$ belong to the group of copper(II) carboxylate binuclear complexes with the bridged structure of the copper(II) acetate monohydrate type. To verify our conclusions we further studied the temperature dependence ($T = = 93—303$ K) of the magnetic behaviour of the complexes $Cu(benz)_2L$.

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Experimental

The copper(II) benzoate complexes of composition $Cu(benz)_2L$ (L = pyridine-N-oxide, isomeric picoline-N-oxides, 2,6-lutidine-N-oxide, 2,4,6-collidine-N-oxide, quinoline-N--oxide, quinaldine-N-oxide, and lepidine-N-oxide) were prepared by treating the corresponding N-oxide (in excess) with the adduct of copper(II) benzoate and benzoic acid $(Cu(benz)_2 \cdot Hbenz)$, in the hot n-butanol solution [7].

Magnetic susceptibilities of the prepared complexes were determined by the Gouy method in the temperature range 93—303 K, intensities of magnetic field between 1600 and 6000 Oe, using an available instrument (Newport Instruments Ltd.). Copper(II) sulfate pentahydrate was used as a standard [8] and the determined molar susceptibilities were corrected for diamagnetism by means of Pascal's constants [9]. Magnetic moments were calculated from the formula

$$\mu_{\text{eff}} = 2.83 \, [(\chi'_M - N\alpha)T]^{1/2},$$

where $N\alpha$ is the temperature independent contribution to the paramagnetism per gramion of Cu^{2+}. The "best fit" values, resulting from the *Bleaney—Bowers* equation [10], were inserted for $N\alpha$ (Table 2). The found magnetic data of the complexes $Cu(benz)_2L$ are summarized in Table 1.

Results and discussion

The magnetic properties of the studied copper(II) benzoate complexes with heterocyclic N-oxides are in general very much alike. The magnetic moments at room temperature (≈ 1.4 B.M.) indicate marked magnetic interaction between Cu^{2+}. The found molar susceptibilities are independent of the magnetic field intensity but dependent on temperature, which is typical for antiferromagnetism. The paramagnetic triplet level increases, the diamagnetic singlet level decreases; therefore the values of χ'_M increase with increasing temperature, reaching their maxima (Néel temperature) at $T_m = 268 \pm 12$ K (Table 2). For copper(II) acetate monohydrate $T_m = 255$ K [8, 11]. Further rise of temperature above T_m results in a decrease of χ'_M of the complexes.

The experimental values of χ'_M of the studied complexes at several temperatures were compared with the values calculated by the least-squares method from the singlet--triplet equation [10]:

$$\chi'_M = \frac{g^2 N\beta^2}{3kT} \cdot \frac{1}{1 + \frac{1}{3} \exp{(-2J/kT)}} + N\alpha.$$

Calculations were performed on an ELLIOTT 803 B computer with ALGOL programme. In the course of the "best fitting" procedure the values of singlet-triplet separation $-2J$, the electronic splitting factor g, and the temperature independent paramagnetism of copper(II) ion $N\alpha$ were used as variable quantities (Table 2).

Good agreement between the experimental and calculated molar susceptibilities of the studied complexes in the whole temperature range was achieved by the described method (Table 1).

The found values of singlet-triplet separation of the studied copper(II) benzoate complexes $|2J| = 298 \pm 14$ cm^{-1} are in a range characteristic of the binuclear copper(II) carboxylate complexes of the bridged structure [1, 12]. For copper(II) acetate monohydrate the value $|2J| = 286$ cm^{-1} was found from magnetic data [13].

Table 1

Magnetic properties of the copper(II) benzoate complexes Cu(benz)$_2$L in the range 93—303 K

L	T [K]	$\chi_g \cdot 10^6$	$\chi_M' \cdot 10^6$ exp.	$\chi_M' \cdot 10^6$ calc.	μ_{eff} [B.M.]	K_{eq}
Pyridine-*N*-oxide	93	0.13	246	243	0.40	0.035
	123	0.70	474	471	0.65	0.098
	153	1.16	660	662	0.87	0.191
	183	1.47	786	786	1.04	0.297
	213	1.64	852	853	1.17	0.409
	243	1.72	885	881	1.28	0.533
	273	1.74	889	884	1.36	0.644
	293	1.69	873	877	1.39	0.693
	303	1.67	865	872	1.41	0.727
2-Methylpyridine- -*N*-oxide	93	0.23	304	290	0.36	0.029
	123	0.62	469	483	0.57	0.078
	153	1.08	656	659	0.78	0.156
	183	1.39	784	782	0.96	0.258
	213	1.55	853	854	1.10	0.368
	243	1.64	890	890	1.21	0.481
	273	1.66	901	900	1.29	0.586
	293	1.64	893	899	1.33	0.647
	303	1.63	886	895	1.35	0.675
3-Methylpyridine- -*N*-oxide	93	0.22	300	289	0.36	0.030
	123	0.64	474	477	0.57	0.078
	153	1.06	649	649	0.78	0.157
	183	1.39	784	772	0.96	0.261
	213	1.53	846	846	1.09	0.362
	243	1.63	886	883	1.20	0.475
	273	1.65	894	895	1.28	0.580
	293	1.63	886	894	1.32	0.639
	303	1.61	878	890	1.33	0.658
4-Methylpyridi -*N*-oxide	93	0.24	306	292	0.36	0.030
	123	0.63	470	479	0.56	0.075
	153	1.06	650	651	0.77	0.153
	183	1.36	775	774	0.95	0.254
	213	1.54	850	848	1.09	0.366
	243	1.64	888	885	1.20	0.476
	273	1.66	900	897	1.28	0.580
	293	1.64	890	896	1.32	0.637
	303	1.62	886	893	1.34	0.675
2,6-Lutidine-*N*-oxide	93	0.07	253	252	0.42	0.037
	123	0.66	508	503	0.69	0.107
	153	1.13	708	706	0.92	0.206
	183	1.41	828	834	·1.09	0.317
	213	1.58	900	899	1.23	0.442
	243	1.63	924	923	1.33	0.559
	273	1.62	920	922	1.41	0.675
	293	1.60	912	912	1.45	0.743
	303	1.58	900	908	1.47	0.763

Table 1 (Continued)

L	T [K]	$\chi_g \cdot 10^6$	$\chi'_M \cdot 10^6$ exp.	$\chi'_M \cdot 10^6$ calc.	μ_{eff} [B.M.]	K_{eq}
2,4,6-Collidine- -N-oxide	93	0.06	266	265	0.42	0.037
	123	0.64	523	519	0.70	0.109
	153	1.06	708	723	0.91	0.199
	183	1.39	855	852	1.10	0.321
	213	1.55	925	918	1.24	0.443
	243	1.58	938	942	1.33	0.550
	273	1.59	942	941	1.41	0.672
	293	1.57	934	932	1.46	0.745
	303	1.55	925	927	1.48	0.766
Quinoline-N-oxide	93	−0.12	224	231	0.41	0.035
	123	0.58	494	483	0.69	0.109
	153	1.01	687	687	0.92	0.205
	183	1.28	809	814	1.09	0.317
	213	1.42	870	879	1.22	0.431
	243	1.47	896	903	1.32	0.545
	273	1.49	902	902	1.40	0.658
	293	1.47	895	892	1.44	0.739
	303	1.46	890	888	1.45	0.743
Quinaldine-N-oxide	93	−0.03	229	227	0.41	0.035
	123	0.48	470	475	0.68	0.102
	153	0.92	672	680	0.91	0.199
	183	1.22	815	810	1.09	0.312
	213	1.36	877	879	1.22	0.427
	243	1.42	908	906	1.33	0.551
	273	1.41	905	907	1.41	0.661
	293	1.40	897	898	1.45	0.732
	303	1.39	893	894	1.47	0.767
Lepidine-N-oxide	93	0.10	292	291	0.38	0.032
	123	0.55	500	501	0.61	0.088
	153	0.87	652	684	0.80	0.162
	183	1.21	807	807	1.01	0.283
	213	1.35	873	877	1.14	0.395
	243	1.44	905	908	1.24	0.504
	273	1.45	918	914	1.32	0.615
	293	1.43	909	910	1.36	0.675
	303	1.41	900	907	1.38	0.697

K_{eq} is the equilibrium constant of the singlet-triplet interaction.

The values of $g = 2.11-2.23$ and $N\alpha = 0-150 \times 10^{-6}$ cgs mol$^-$ for complexes Cu(benz)$_2$L (Table 2) obtained by the "best fitting" procedure from the temperature dependence of their magnetic data show a relatively large variance. Such a variability of these quantities is rather improbable with regard to the assumed identical structure of the studied Cu(benz)$_2$L complexes, all of them being formed by the same anionic and very similar molecular ligands. However, we have to take into account that the

Table 2

Values of the Néel temperature, the singlet $\rightleftarrows$ triplet separation, the electronic splitting factor, the temperature independent paramagnetism of Cu^{2+}, enthalpy and entropy of the $Cu(benz)_2L$ complexes

L	T_m	$|2J|$		g	$N\alpha \cdot 10^6$	ΔH^0	ΔS^0
		[cm^{-1}]	[kcal mol^{-1}]		[cgs mol^{-1}]	[cm^{-1}]	[e.u.]
Pyridine-N-oxide	264	293	0.84	2.17	42	285	2.1
2-Picoline-N-oxide	277	308	0.88	2.12	140	296	2.1
3-Picoline-N-oxide	280	312	0.89	2.11	145	292	2.1
4-Picoline-N-oxide	280	312	0.89	2.11	150	296	2.1
2,6-Lutidine-N-oxide	256	285	0.815	2.22	16	284	2.2
2,4,6-Collidine-N-oxide	256	285	0.815	2.23	28	284	2.2
Quinoline-N-oxide	256	285	0.815	2.22	0	285	2.1
Quinaldine-N-oxide	260	289	0.83	2.23	0	288	2.2
Lepidine-N-oxide	268	299	0.855	2.14	115	293	2.1

experimental magnetic data may be inaccurate due to the presence of mononuclear paramagnetic impurities, often proved in similar complexes by e.p.r. method [12]. Thus it seems to be of no use to seek a physical meaning of the observed variability of g and $N\alpha$; similar conclusion has been drawn in connection with the applicability of the "best fitting" procedure using several variables also in another work [14]. In spite of this limitation the found g and $N\alpha$ values are not at variance with the assumed binuclear bridged structure [7] of the studied $Cu(benz)_2L$ complexes. The next subject of our work will be to verify the reliability of the g and $N\alpha$ values by other methods.

Equilibrium constants of the singlet $\rightleftarrows$ triplet interaction of the studied complexes were calculated from magnetic data as described in [15]. Molar fraction of both the singlet and the triplet states of $Cu(benz)_2L$ molecule were calculated from the experimental magnetic moments, since the actual magnetic moment of the singlet state ($S = 0$) is 0.0 B.M. and magnetic moment of the triplet state is given by the formula $\mu_{eff} = g[S(S + 1)]^{\frac{1}{2}}$. The found values of equilibrium constants for all the complexes are summarized in Table 1.

The values of enthalpy (ΔH^0) and entropy (ΔS^0) were estimated from diagrams of equilibrium constants of the singlet-triplet interaction, in which $\ln K_{eq}$ was plotted against T^{-1} or $RT \ln K_{eq}$ against T. The results are listed in Table 2. Graphically estimated ΔH^0 are in very good agreement with the values of the singlet $\rightleftarrows$ triplet separation $|2J|$ of the complexes $Cu(benz)_2L$ evaluated by means of the Bleaney — Bowers equation from magnetic data. The found entropies (ΔS^0) are also in fair agreement with the expected value $R \ln 3 = 2.2$ e.u., where 3 is the degeneracy ratio assuming that the only contribution is that from the electronic entropy. The magnetic properties of the complexes together with their temperature dependences thus support the assumption that the studied $Cu(benz)_2L$ complexes belong to a group of copper(II) carboxylate complexes characterized by binuclear structure of the type of copper(II) acetate monohydrate. After this scheme, copper(II) ions in the structural units $[Cu_2(benz)_4L_2]$ are bridged in pairs by carboxylic groups of benzoate ions while the molecules of heterocyclic N-oxides are bonded through oxygen donor atoms in the axial terminal positions.

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