Copper(II) complexes containing organic ligands. XIX. 2-Isopropyl-5-methylphenoxyacetatocopper(II) complexes

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The thymoxyacetate ions react in aqueous solution with the Cu^{2+} ions to give anhydrous copper(II) thymoxyacetate which shows magnetic and spectral properties typical of the binuclear carboxylatocopper(II) complexes with bridge structure. $Cu(TOAc)_2$ (TOAc = thymoxyacetate ion) reacts with *N*- and *O*-donor molecular ligands (L) to yield complexes $Cu_2(TOAc)_4L_2$ or $Cu(TOAc)_2L_2$. The magnetic and spectral properties of the complexes $Cu_2(TOAc)_4L_2$ thus prepared confirm that they belong to the carboxylatocopper(II) complexes with binuclear bridge structure of the type of copper(II) acetate monohydrate. On the other hand, the complexes $Cu(TOAc)_2L_2$ exhibit magnetic and spectral properties typical of the mononuclear copper(II) complexes with tetragonal symmetry.

Тимоксиацетатные ионы реагируют в водной среде с ионами Cu^{2+} при образовании безводного тимоксиацетата меди, который проявляет магнитные и спектральные свойства типичные для двухядерных карбоксилатных комплексов меди с мостиковой структурой. $Cu(TOAc)_2$ (TOAc = тимоксиацетатный ион) реагирует с *N*- и *O*-донорными молекулярными лигандами (L) с образованием комплексов $Cu_2(TOAc)_4L_2$ или $Cu(TOAc)_2L_2$. Магнитные и спектральные свойства полученных комплексов состава $Cu_2(TOAc)_4L_2$ подтверждают их принадлежность среди карбоксилатные комплексы меди с двухядерной мостиковой структурой типа моногидрата ацетата меди. Напротив этого комплексы состава $Cu(TOAc)_2L_2$ характеризуются магнитными и спектральными свойствами типичными для одноядерных комплексов меди с тетрагональной симметрией.

The information on the alkyl and aryl oxyacetatocopper(II) complexes has shown a possible formation of copper(II) complexes of different structures due not only to different kinds of coordination of the donor carboxyl group of anionic ligand but also to participation of its etheric *O*-atom in the construction of the inner sphere of copper(II) complexes [1—9]. A more detailed study of this problem has demonstrated that the substituents in the aromatic ring of phenoxyacetate ion are also able (by induction and steric effects) to influence the structure of the arising copper(II) complexes [10—13]. From this view-point, the thymoxyacetatocopper(II) complexes have not been studied yet. In the literature there is only a mention of the preparation of the copper(II) salt of thymoxyacetic acid [14].

The knowledge of the composition and properties of the thymoxyacetatocopper(II) complexes has been obtained by preparative study of the reactions between the thymoxyacetate (2-isopropyl-5-methylphenoxyacetate) ions and Cu^{2+} ions under conditions which usually favour the formation of the corresponding hydrates of the copper(II) salts of carboxylic acids.

Under these conditions, the anhydrous salt of copper(II) thymoxyacetate is separated from an aqueous solution. Therefore, the reactions of $Cu(TOAc)_2$ with molecular ligands of the type of aromatic (heterocyclic) nitrogen-containing bases or aromatic *N*-oxides were studied. On the basis of different composition, the isolated compounds $Cu_2(TOAc)_4L_2$ and $Cu(TOAc)_2L_2$ could be classified and put in the groups of carboxylatocopper(II) complexes with different structures, which was also confirmed by the investigation of their magnetic properties (room temperature), electronic spectra, and in some cases e.p.r. spectra.

Experimental

Preparation of complexes

The copper(II) thymoxyacetate of the composition $Cu(TOAc)_2$ was prepared by the reaction of $TOAc^-$ ions with Cu^{2+} ions in aqueous solution at $pH \approx 5$. The reacting system was prepared by mixing the aqueous solution containing 6×10^{-2} moles of sodium thymoxyacetate (acidified with excess thymoxyacetic acid) and the aqueous solution containing 3×10^{-2} moles of $CuSO_4 \cdot 5H_2O$ at laboratory temperature. After isolation and washing with water, the crystallized green-coloured complex was dried in air at laboratory temperature (Table 1).

The reactions between the complex $Cu(TOAc)_2$ and organic molecular *N*- or *O*-donor ligands in solutions resulted in the formation of the compounds $Cu(TOAc)_2L$ or $Cu(TOAc)_2L_2$.

The reaction systems were prepared in hot organic solvents (methanol, ethanol, acetone) by using the corresponding molecular ligand (always in fourfold excess) and $Cu(TOAc)_2$ as parent compound. Pyridine (py), isomeric picolines (2-pic, 3-pic, 4-pic), lutidines (2,4-lut and 2,6-lut), and 2,4,6-colidine (2,4,6-col) were used as *N*-donor ligands. The chemicals used were pure or very pure or anal. grade reagents (Lachema, or imported chemicals). They were purified by usual laboratory procedures before use. The *N*-oxides of the above *N*-ligands except 2,4-lutidine-*N*-oxide (pyox, 2-picox, 3-picox, 4-picox, 2,6-lutox, and 2,4,6-colox) were used as *O*-donor molecular ligands. All aromatic *N*-oxides were prepared

Table 1. Analytical characteristics, electronic spectra, and magnetic properties of the copper(II) thymoxyacetate complexes

Compound	M	Calculated/found		Electronic spectra			Magnetic properties	
		% Cu	% N	$\tilde{\nu}\cdot 10^{-3}$ cm^{-1}			$\chi'_M\cdot 10^{11}$ m^3 mol^{-1}	μ_{ef} B. M.
Cu(TOAc)$_2$^{a}	478.04	13.29 13.25	— —	14.4		≈26.7 sh	912	1.24
Cu(TOAc)$_2$(py)	557.14	11.40 11.41	2.51 2.69	13.0		≈26.7 sh	1271	1.48
Cu(TOAc)$_2$(2-pic)	571.10	11.11 11.07	2.45 2.60	12.9		≈27.0 sh	1107	1.37
Cu(TOAc)$_2$(3-pic)	571.10	11.11 11.03	2.45 2.58	13.0		≈26.5 sh	914	1.24
Cu(TOAc)$_2$(4-pic)	571.10	11.11 11.07	2.45 2.42	13.2		≈26.7 sh	908	1.24
Cu(TOAc)$_2$(2,4-lut)	585.20	10.85 10.88	2.39 2.50	12.9		≈26.9 sh	933	1.26
Cu(TOAc)$_2$(2,6-lut)$_2$	692.35	9.18 9.29	4.05 4.16	18.0	≈14.0 sh	≈26.9 sh	1810	1.80
Cu(TOAc)$_2$(2,4,6-col)$_2$	720.40	8.82 8.71	3.89 4.06	18.3	≈14.0 sh	≈27.0 sh	2286	2.03
Cu(TOAc)$_2$(pyox)	571.14	11.09 11.09	2.42 2.37	13.2		≈26.6 sh	990	1.30
Cu(TOAc)$_2$(2-picox)	587.17	10.82 10.86	2.38 2.32	13.4		≈26.9 sh	1286	1.49
Cu(TOAc)$_2$(3-picox)	587.17	10.82 10.80	2.38 2.42	13.5		≈27.4 sh	1209	1.45
Cu(TOAc)$_2$(4-picox)	587.17	10.82 10.76	2.38 2.50	13.4		≈26.8 sh	984	1.30
Cu(TOAc)$_2$(2,6-lutox)	601.19	10.57 10.52	2.32 2.22	13.2		≈26.6 sh	996	1.31
Cu(TOAc)$_2$(2,4,6-colox)$_2$	752.40	8.44 8.36	3.72 3.67	16.1	≈12.8 sh	≈26.9 sh	2096	1.96

a) Calculated: 60.30% C, 6.32% H; found: 60.00% C, 6.13% H; sh — shoulder.

and purified according to [15]. The prepared complexes which spontaneously crystallized from cooled reaction systems were washed with ether after isolation and dried in air at laboratory temperature (Table 1).

Magnetic measurements

The magnetic susceptibilities of the complexes prepared were measured by the Gouy method on a commercial instrument (Newport Instruments Ltd.) at laboratory temperature. The measurements were carried out at four different intensities of magnetic field in the range 160—640 $\mathrm{kA^{-1}}$. The molar susceptibilities were corrected with respect to the diamagnetism of individual components by means of the corresponding Pascal constants [16]. The magnetic moment was calculated from the expression $\mu_{\mathrm{ef}} = D[(\chi'_{\mathrm{M}} - N\alpha)T]^{\frac{1}{2}}$ while $D = 798\ \mathrm{m^{-\frac{3}{2}}\,K^{-\frac{1}{2}}\,mol^{-\frac{1}{2}}}$ [17]. In the case of magnetically dilute copper(II) complexes, the value $N\alpha = 75 \times 10^{-11}\ \mathrm{m^3\,mol^{-1}}$ [18] was substituted for temperature independent paramagnetism, whereas in other cases the value $94 \times 10^{-11}\ \mathrm{m^3\,mol^{-1}}$ found for copper(II) acetate monohydrate was used [19] (Table 1).

Spectral measurements

The electronic spectra of the complexes in solid state were measured in the wavenumber region $\tilde{\nu} = 13.0 \times 10^3 - 30.0 \times 10^3\ \mathrm{cm^{-1}}$ on an instrument UV VIS Specord by nujol technique.

The positions of the maximum and shoulder of the ligand field band as well as the positions of the shoulder assigned to spin—spin interaction (eventually CT bands of usual type) are given in Table 1 for all complexes studied.

The e.p.r. spectrum of the compound $\mathrm{Cu(TOAc)_2}$ was taken on a spectrometer Varian E-4 in zone X (modulation 100 kHz) by using a powdered preparation. The spectrum was measured in the temperature interval 393—103 K (temperature variator Varian E-257). DPPH was used for calibration as an internal standard.

The e.p.r. spectra of magnetically dilute complexes of the composition $\mathrm{Cu(TOAc)_2L_2}$ were obtained at laboratory temperature in zone X by using polycrystalline preparations (spectrometer ER-9, Zeiss, Jena). DPPH was used as an internal standard. The derivative absorption curves were evaluated by using the approximation according to *Kneubühl* [20].

Results and discussion

A complex of the composition $\mathrm{Cu(TOAc)_2}$ was formed by the reaction between the copper(II) and thymoxyacetate ions (under experimental conditions). This compound distinctly exhibits a subspin value of the magnetic moment — 1.24 B. M. even at room temperature. That indicates the presence of a magnetically condensed system in which an exchange interaction between the spins of the unpaired electrons belonging to pairs of the Cu^{2+} ions is likely to be effective. A magnetic coupling of the central Cu^{2+} ions is also manifested by the character of the electronic spectrum of this complex, namely by the position of the absorption band of ligand field ($\tilde{\nu}_{max} = 14.4 \times 10^3\ cm^{-1}$) as well as by the presence of another absorption band in near ultraviolet region which, in harmony with magnetic properties, may be assigned to spin—spin interaction ($\tilde{\nu}_{max} = 26.7 \times 10^3\ cm^{-1}$). *Dubicki* and *Martin* [21] interpret this absorption band as a result of the charge transfer mechanism consisting in the transition $\sigma^*_{x^2-y^2} \leftarrow n\ p\ \pi$ forbidden by local symmetry.

The e.p.r. spectrum of $Cu(TOAc)_2$ is in agreement with the information on magnetically condensed system in the structure of this complex (magnetic properties, electronic spectra). The character of e.p.r. spectrum investigated as a function of temperature is typical of the binuclear carboxylatocopper(II) complexes of bridge type which are without any particular axial ligand (the so-called anhydrous copper(II) carboxylates) [22, 23]. One broad little intensive band is evident at room temperature. It is centred at $H \approx 239\ kA^{-1}$ ($g \approx 2$) and gradually vanishes with decreasing temperature. Simultaneously, the lines typical of the transitions $\Delta m \pm 1$ (for $D > h\nu$) start to appear at $H_{\parallel}^{(1)}$, $H_{\parallel}^{(2)}$, and $H_{\perp}$ with decreasing temperature. At the temperature of 103 K, the lines are already very well developed and provide the following values of the spin Hamiltonian operator ($S = 1$) [24, 25]: $g_{\perp} = 2.070$, $g_{\parallel} = 2.365$, $\bar{g} = 2.173$, $D = 0.358\ cm^{-1}$, $E = 0.011\ cm^{-1}$. However, even at this temperature, the lines at $H_{\parallel}^{(1)}$ and $H_{\parallel}^{(2)}$ do not exhibit hyperfine splitting. On the other hand, the line at $H_{\perp}$ is distinctly split into two components, which results in a relatively high value of the fine structure parameter E and is connected with the degree of distortion of the coordination polyhedron in the xy plane.

In the region $g \approx 2$, the e.p.r. spectrum of this complex exhibits a relatively intense anisotropic signal of axial type corresponding to the presence of paramagnetic centres ($S = 1/2$). The signal exhibits hyperfine splitting in the region $g_{\parallel}$ and $g_{\perp}$, the values of the constants of hyperfine splitting being $A_{\parallel} = 148.0 \times 10^{-4}\ cm^{-1}$, $A_{\perp} = 14.4 \times 10^{-4}\ cm^{-1}$. The values of g factors of the identified mononuclear admixture are: $g_{\perp} = 2.051$, $g_{\parallel} = 2.348$, $\bar{g} = 2.155$.

The information obtained allows to suppose that the complex $Cu(TOAc)_2$ spontaneously separating from the reaction system in aqueous solution shows "polymer" structure like other anhydrous copper(II) carboxylates. In these cases, the fundamental structural units are, however, represented by the binuclear molecules $[Cu_2(R—COO)_4]$ in which the pairs of the Cu^{2+} ions are bound by four carboxylate bridges ensuring magnetic connection between the Cu^{2+} ions. Thus, the axial coordination positions in the binuclear structural units evidently complete themselves according to the crystal structure of the complex. It means that a part of the *O*-atoms in the carboxylate bridges of a binuclear molecule is also coordinated as an axial ligand in the vicinal structural unit, which, as a matter of fact, results in the polymeric character of this compound [23].

The compounds obtained by the reactions of $Cu(TOAc)_2$ with molecular ligands may be divided into two groups. One group is represented by the complexes of the composition $Cu(TOAc)_2L$ with clearly subspin magnetic moments ($\mu_{ef} =$ 1.24—1.49 B. M.). Thus, the ascertained magnetic moment reflects the equilibrium involving the energically higher paramagnetic level ($S = 1$) and lower diamagnetic singlet level ($S = 0$). This equilibrium is shifted in favour of a certain level owing to differently efficient magnetic connections in individual compounds. The character of electronic spectra is also in agreement with magnetic properties. Besides the band of ligand field corresponding to the *d—d* transitions ($\tilde{\nu}_{max} = 12.9 \times 10^3 - 13.5 \times 10^3\ cm^{-1}$), these spectra also show a band of spin—spin interaction appearing as a shoulder in the region $\approx 27 \times 10^3\ cm^{-1}$.

The similarity between magnetic and spectral properties of the discussed group of compounds and these properties of the complex $Cu(TOAc)_2$ enables us to classify these complexes as binuclear carboxylatocopper(II) complexes of the bridge structure where the thymoxyacetate ion functions as a bridge ligand. Since the complexes $Cu(TOAc)_2L$ contain a molecular ligand, there is no reason to assume a "polymer" structure (in contrast to the complex $Cu(TOAc)_2$) because the axial end positions in a dimeric unit $[Cu_2(TOAc)_4L_2]$ are evidently engaged by the *N*- or *O*-donor atom of the corresponding L.

On the other hand, the compounds $Cu(TOAc)_2L_2$ exhibit the composition and properties of magnetically dilute copper(II) complexes. At room temperature they show a superspin value of magnetic moment (1.80—2.03 B. M.), which is evidence of a different orbital contribution. In agreement with this fact, the band of ligand field in their electronic spectrum exhibits a maximum at higher energies ($\tilde{\nu}_{max} = 16.1 \times 10^3 - 18.3 \times 10^3\ cm^{-1}$), which may be attributed to the transition ^2E_g, $^2B_{2g} \leftarrow {}^2B_{1g}$ and the shoulder on the lower energy side ($\tilde{\nu}_{sh} \approx 12.8 \times 10^3 - 14.0 \times 10^3\ cm^{-1}$) may be assigned to the transition $^2A_{1g} \leftarrow {}^2B_{1g}$. Because of magnetic properties, another absorption band appearing in the spectrum in the form of a shoulder at $\tilde{\nu}_{sh} \approx 27.0 \times 10^3\ cm^{-1}$ may be assigned to some of the usual charge transfer mechanisms ligand—metal which are not connected with spin—spin interaction.

Such spectra are characteristic of the tetragonal symmetry of the coordination polyhedron with a transplanar chromophore CuO_2N_2 (or CuO_4) completed with weakly bonded *O*-atoms in axial direction.

The e.p.r. spectra of the compounds $Cu(TOAc)_2L_2$ are typical of the axial symmetry with $g_\perp > 2.04$ in all cases, which points out that the ground state of the Cu^{2+} ions in ligand sphere is $^2B_{1g}(d_{x^2-y^2})$. For the complexes $Cu(TOAc)_2L_2$ where L = 2,6-lut and 2,4,6-col, the spectra are asymmetrical ($g_\perp = 2.048$ or 2.047) but without any resolved $g_{\parallel}$ value. The e.p.r. spectrum of the complex $Cu(TOAc)_2(2,4,6\text{-colox})_2$ is of the normal axial type with the values $g_{\parallel} = 2.316$, $g_{\perp} = 2.054$, $\bar{g} = 2.14$, $G = 5.8$. The fact that the factor $G > 4$ indicates that the Cu^{2+} ions occupy at least approximately equivalent crystallographic positions in the crystal structures.

From the magnetic and spectral properties of the complexes $Cu(TOAc)_2L_2$ it may be deduced that these substances are mononuclear copper(II) complexes of the tetragonal bipyramidal coordination with different extent of axial distortion.

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