

Copper(II) complexes with organic ligands

XXIII. 4-Nitrophenoxyacetatocopper(II) complexes

^aA. VALENT, ^aB. LUČANSKÁ, ^aO. ŠVAJLENOVÁ, ^aV. SERESSOVÁ,
^aM. BLAHOVÁ, ^aJ. SOKOLÍK, ^aM. ŽEMLIČKA, ^aV. HARTELOVÁ, and ^bG. PLESCH

^aDepartment of Inorganic and Organic Chemistry, Faculty of Pharmacy, Comenius University,
CS-832 32 Bratislava

^bInstitute of Inorganic Chemistry, Centre for Chemical Research, Slovak Academy of Sciences,
CS-842 36 Bratislava

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*Dedicated to Associate Professor Dr. J. Krätšmár-Šmogrovič,
in honour of his 60th birthday*

4-Nitrophenoxyacetatocopper(II) complexes containing pyridine-*N*-oxide, quinoline-*N*-oxide and their substituted derivatives were prepared and studied by physical methods. As a parent compound diaqua-bis(4-nitrophenoxyacetato)copper(II) complex was used. In this compound the 4-nitrophenoxyacetato ions act as chelating ligands and the two molecules of water complete the coordination polyhedron of Cu(II) ions. Dimeric complexes of the composition $[\text{Cu}_2(4\text{-NO}_2\text{PhOAc})_4\text{L}_2]$ with bridging carboxyl groups were prepared by the reactions of this complex with *N*-oxide ligands. On the basis of the results of EPR and electronic spectra and magnetic measurements at room temperature conclusions on the coordination geometries of the complexes under examination were drawn.

Были приготовлены и затем охарактеризованы физическими методами комплексы 4-нитрофеноксиацетата меди содержащие *N*-оксиды пиридина, хинолина и их производных. В качестве исходного соединения использовался комплекс диакво-бис(4-нитрофеноксиацетат)меди. Были получены димерные комплексы состава $[\text{Cu}_2(4\text{-NO}_2\text{PhOAc})_4\text{L}_2]$ с мостиковыми карбоксильными группами посредством реакций этого комплекса с *N*-оксидными лигандами. На основе изучения ЭПР- и электронных спектров, а также магнитных измерений при комнатной температуре были сделаны выводы о координационной геометрии изучаемых комплексов.

In recent years there is a considerable interest in the research of carboxylatocopper(II) complexes. Beside the studies of their physical properties also much attention has been paid to the examination of their biological activities. Some bioinorganic aspects of the properties of carboxylatocopper(II) complexes are connected with the biological activity of the bound Cu(II) ions. A combination of the activity of Cu(II) ions with the biological activity of bound ligand is also

possible. Since the nitrophenoxyacetic acids are highly biologically active (growth stimulators, fungicides) [1—5], we focused our attention to the study of copper(II) complexes with these ligands, first of all 4-nitrophenoxyacetatocopper(II) complexes.

The aqua complexes $\text{Cu}(4\text{-NO}_2\text{PhOAc})_2 \cdot 3\text{H}_2\text{O}$ and $\text{Cu}(4\text{-NO}_2\text{PhOAc})_2 \cdot 2\text{H}_2\text{O}$ ($4\text{-NO}_2\text{PhOAc} = 4\text{-nitrophenoxyacetato anion}$) have been described [6]. On the basis of the subnormal value of the magnetic moment ($\mu_{\text{eff}}(298\text{ K}) = 1.57 \mu_{\text{B}}$) as well as of its dependence on temperature a polymeric structure for the complex $\text{Cu}(4\text{-NO}_2\text{PhOAc})_2 \cdot 3\text{H}_2\text{O}$ has been assumed. On the other hand, diaqua-bis(4-nitrophenoxyacetato)copper(II) complex is monomeric with tetragonal symmetry. Its molecular structure is almost the same as of the diaqua-bis(4-methoxyphenoxyacetato)copper(II) complex [7] and diaqua-bis(phenoxyacetato)copper(II) complex [8].

In this work the reactions of 4-nitrophenoxyacetato anions with $\text{Cu}(\text{II})$ ions were performed at conditions usual for the preparation of carboxylatocopper(II) complexes. A series of twelve 4-nitrophenoxyacetatocopper(II) complexes with pyridine-*N*-oxide, quinoline-*N*-oxide, and their substituted derivatives were prepared. Conclusions on the structure of the prepared copper(II) complexes were drawn from the results of electronic and EPR spectra and from their magnetic properties at room temperature.

Experimental

4-Nitrophenoxyacetic acid was prepared according to Ref. [9]. Instead of triethylene glycol ethanol and instead of ethyl ester of monochloroacetic acid ethyl ester of monobromoacetic acid were used. The yield of the final product was by 10 % higher than in the original procedure. The melting temperature of 4-nitrophenoxyacetic acid according to Ref. [9] is 187.2—187.5°C, our product showed a melting temperature 186—187°C.

The reaction of $\text{Cu}(\text{II})$ ions with 4-nitrophenoxyacetato ions was performed in aqueous solutions at room temperature. Various concentrations of equimolar mixtures of $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ and $4\text{-NO}_2\text{PhOAcNa}$ were used. The pH value of the reaction medium was adjusted to the value 4—5 by addition of 4-nitrophenoxyacetic acid. As a final product a complex of composition $\text{Cu}(4\text{-NO}_2\text{PhOAc})_2 \cdot 2\text{H}_2\text{O}$ was obtained in all cases.

By the reactions of the parent aqua complex with the corresponding *N*-oxides ($L = \text{pyridine-}N\text{-oxide}$, 2-methylpyridine-*N*-oxide, 3-methylpyridine-*N*-oxide, 2,6-dimethylpyridine-*N*-oxide, 2,4,6-trimethylpyridine-*N*-oxide, 4-chloropyridine-*N*-oxide, 4-nitropyridine-*N*-oxide, quinoline-*N*-oxide, 4-methylquinoline-*N*-oxide, 4-chloroquinoline-*N*-oxide, and 4-nitroquinoline-*N*-oxide) in hot acetone solutions in amounts of substances ratios $n(\text{Cu}(\text{II})) : n(N\text{-oxide})$ ranging from 1 : 1 to 1 : 4 compounds of the stoichiometric composition $\text{Cu}(4\text{-NO}_2\text{PhOAc})_2 L$ were obtained. The complex with 4-methylpyridine-*N*-oxide was prepared in hot methanol. The final products crystallized

when the reaction medium was cooled down. The collected crystals were washed with ether and dried freely in air. The results of the elemental analysis of the prepared complexes are given in Table 1.

Table 1

Analytical data of 4-nitrophenoxyacetatocopper(II) complexes (w/mass %)

Cu(4-NO ₂ PhOAc) ₂ L L =	M _r	w _i (calc.)/% w _i (found)/%			
		Cu	C	H	N
(H ₂ O) ₂	491.85	12.92	39.07	3.28	5.70
		12.90	38.90	3.30	5.80
Pyox	550.92	11.53	45.78	3.11	7.63
		11.58	45.75	3.31	7.47
2-Me-Pyox	564.95	11.23	46.77	3.39	7.44
		11.18	46.59	3.43	7.31
3-Me-Pyox	564.95	11.23	46.77	3.39	7.44
		11.30	46.61	3.54	7.53
4-Me-Pyox	564.95	11.23	46.77	3.39	7.44
		11.38	46.80	3.31	7.34
2,6-Me ₂ -Pyox	578.98	10.98	47.71	3.66	7.26
		10.81	47.59	3.88	7.31
2,4,6-Me ₃ -Pyox	593.00	10.72	48.61	3.91	7.09
		10.80	48.53	3.70	7.11
4-Cl-Pyox	585.37	10.86	43.09	2.76	7.18
		10.99	43.30	2.98	7.01
4-NO ₂ -Pyox	595.91	10.66	42.33	2.71	9.40
		10.81	42.49	2.90	9.49
Quinox	600.98	10.57	49.96	3.19	6.99
		10.41	49.71	3.31	7.10
4-Me-Quinox	615.00	10.33	50.77	3.44	6.83
		10.40	51.20	3.70	6.58
4-Cl-Quinox	635.42	9.99	47.26	2.86	7.61
		10.14	47.57	3.17	7.50
4-NO ₂ -Quinox	645.97	9.83	46.48	2.81	8.67
		9.68	46.79	3.00	8.36

The EPR spectra were recorded on Varian E-4 spectrometer at temperature -160°C in X band ($\nu = 9.1$ GHz). Varian strong pitch was used as a standard for the determination of g values. The parameters of the EPR spectra are given in Table 2.

The electronic absorption spectra were recorded on Specred UV VIS (Zeiss, Jena) spectrometer in the range of $\tilde{\nu} = 12\,500\text{--}30\,000\text{ cm}^{-1}$. Spectra of the solid samples were obtained from nujol mulls using filter paper as a support. The maxima of the $d\text{--}d$ absorption bands are given in Table 3.

Table 2

EPR spectra of 4-nitrophenoxyacetatocopper(II) complexes

$\text{Cu}(4\text{-NO}_2\text{PhOAc})_2\text{L}$ L =	g	g_{\perp}	\bar{g}^*	$\frac{D/hc}{\text{cm}^{-1}}$	$\frac{E/hc}{\text{cm}^{-1}}$	$\frac{A/c}{\text{cm}^{-1}}$
Pyox	2.391	2.089	2.194	0.380	<0.002	—
2-Me-Pyox	2.396	2.086	2.194	0.367	<0.002	—
3-Me-Pyox	2.387	2.094	2.196	0.378	<0.002	—
4-Me-Pyox	2.391	2.091	2.196	0.376	<0.002	—
2,6-Me ₂ -Pyox	2.387	2.072	2.182	0.384	0.004	0.007
2,4,6-Me ₃ -Pyox	2.389	2.071	2.182	0.379	0.003	0.007
4-Cl-Pyox	2.378	2.091	2.191	0.373	<0.002	—
4-NO ₂ -Pyox	2.361	2.080	2.178	0.366	<0.002	—
Quinox	2.382	2.088	2.191	0.380	<0.002	—
4-Me-Quinox	2.396	2.090	2.196	0.369	<0.002	—
4-Cl-Quinox	2.387	2.096	2.197	0.373	<0.002	—
4-NO ₂ -Quinox	2.365	2.074	2.175	0.370	<0.002	0.007

$$*\bar{g} = [(g^2 + 2g_{\perp}^2)/3]^{1/2}$$

Table 3

Magnetic and spectral properties of 4-nitrophenoxyacetatocopper (II) complexes

$\text{Cu}(4\text{-NO}_2\text{PhOAc})_2\text{L}$ L =	T/K	$\frac{\chi_m \cdot 10^{11}}{\text{m}^3 \text{mol}^{-1}}$	$\frac{\mu_{\text{eff}}}{\mu_B}$	$\frac{\tilde{\nu}_{\text{max}} \cdot 10^{-3}}{\text{cm}^{-1}}$
(H ₂ O) ₂	299	1898.18	1.87	14.2
Pyox	299	1136.19	1.41	13.3
2-Me-Pyox	298	1088.43	1.38	13.3
3-Me-Pyox	297	967.61	1.30	13.1
4-Me-Pyox	300	1068.59	1.36	13.5
2,6-Me ₂ -Pyox	298	987.20	1.29	13.3
2,4,6-Me ₃ -Pyox	299	1150.70	1.42	13.4
4-Cl-Pyox	299	1203.68	1.47	13.7
4-NO ₂ -Pyox	296	1100.39	1.39	13.4
Quinox	297	1122.55	1.41	13.8
4-Me-Quinox	296	1168.30	1.44	13.2
4-Cl-Quinox	296	1073.50	1.37	13.6
4-NO ₂ -Quinox	296	923.50	1.26	13.4

Magnetic susceptibilities were measured by the Gouy method at room temperature on a commercial device (Newport Instruments, Ltd.). Measurements were performed at four intensities of magnetic field. The values of molar susceptibilities were corrected for the diamagnetism of the components (χ_m') [10, 11]. The magnetic moments were calculated according to the equation

$$\mu_{\text{eff}} = F[(\chi'_m - N_a) T]^{1/2}$$

where $F = 798 \text{ m}^{-3/2} \text{ K}^{-1/2} \text{ mol}^{1/2}$

The temperature-independent paramagnetism was taken as $N_a = 75 \cdot 10^{-11} \text{ m}^3 \text{ mol}^{-1}$ for the parent magnetically diluted aqua complex. For all other complexes with magnetic interactions $N_a = 94 \cdot 10^{-11} \text{ m}^3 \text{ mol}^{-1}$ [12, 13]. The corrected molar susceptibilities and magnetic moments at room temperature are given in Table 3.

Results and discussion

Regarding the coordination chemistry of divalent copper, carboxylatocopper(II) complexes containing aryloxyacetato ions bound as anionic ligands are interesting not only from the point of view of the possibility of different ways of coordination of the carboxylato group, but also from the point of view of participation of etheric oxygen in the formation of inner coordination sphere of copper(II) complexes. The formation of chelates is the reason for higher stability of monomeric aryloxyacetatocopper(II) complexes [14]. In this group of complexes a less frequent occurrence of dimeric copper(II) compounds with bridging carboxyl groups can be observed. The specific influence of the neutral molecular ligand on the structure of aryloxyacetatocopper(II) complexes is also of great importance in this respect.

By the reactions of Cu(II) and 4-nitrophenoxyacetato ions at the conditions given in Experimental diaqua-bis(4-nitrophenoxyacetato)copper(II) complex was prepared (Table 1). The observed μ_{eff} value of magnetic moment $\mu_{\text{eff}} = 1.87 \mu_B$ at $T = 300 \text{ K}$ (Table 3) and the parameters of its axial EPR spectrum $g_{\parallel} = 2.341$, $g_{\perp} = 2.086$ allow us to classify this complex as a magnetically diluted system with a ground state $d_{x^2-y^2}$. The value of $G = 4.0$ ($G = [(g_{\parallel} - 2)/(g_{\perp} - 2)]$) shows that the local tetragonal axes are aligned parallel and the experimental g values reflect satisfactorily the local microsymmetry of the complex unit [15]. In the electronic spectra a non-split band corresponding to $d-d$ transitions with a maximum at $\tilde{\nu}_{\text{max}} = 14.2 \times 10^3 \text{ cm}^{-1}$ can be observed. These results are in accordance with the data on the structure of this compound [7] with a distorted octahedral coordination of Cu(II) with oxygen ions (elongated square bipyramid). Such coordination is realized by the bonding of two 4-nitrophenoxyacetato anions acting as chelating ligands (bonding through oxygen atoms of carboxylato group and etheric group) and by bonding of two molecules of water.

By the reactions of diaqua-bis(4-nitrophenoxyacetato)copper(II) complex with N -oxide ligands in acetone (or methanol) solutions in amounts of substances ratios $n(\text{Cu(II)}):n(N\text{-oxide})$ varying from 1:1 to 1:4 green crystals of the stoichiometric composition $\text{Cu}(4\text{-NO}_2\text{PhOAc})_2\text{L}$ were obtained in all cases. An addition of small amount of 4-nitrophenoxyacetic acid was necessary for adjust-

ing the optimal pH value and suppressing the solvolysis of the complexes. It was remarkable that the composition of all prepared complexes was $\text{Cu}(4\text{-NO}_2\text{PhOAc})_2\text{L}$. Also in the cases, when the reaction systems contained an excess of molecular ligand, no formation of complexes with higher content of bound ligand L was observed.

The EPR spectra of all prepared 4-nitrophenoxyacetatocopper(II) complexes with aromatic *N*-oxides are typical of spin-spin interacting dimeric copper(II) complexes, where the ground state is a singlet ($S = 0$), while the excited, thermally populated state is a triplet ($S = 1$). The following spin Hamiltonian [16]

$$\hat{\mathcal{H}}_S = g_{\parallel}\beta B_z \hat{S}_z + g_{\perp}\beta(B_x \hat{S}_x + B_y \hat{S}_y) + D[\hat{S}_z^2 - (1/3)S(S+1)] + E(\hat{S}_x^2 - \hat{S}_y^2) + A_{\parallel}\hat{I}_z \hat{S}_z \quad (1)$$

where $S = S_1 + S_2 = 1$ and $I = I_1 + I_2 = 3$ was used for the interpretation of the triplet state EPR spectra (Table 2). Its parameters are similar to the values usually found for dimeric copper(II) complexes of a structural type of diaqua-tetrakis(μ -*O,O'*-acetato)dicopper(II) complex [17–20]. In the cases when L = 2,6-Me₂-Pyox and 2,4,6-Me₃-Pyox the perpendicular component of the EPR spectrum at $B \approx 460$ mT is split, which indicates a nonzero value of the *E* parameter in the spin Hamiltonian (Table 2) and a deviation from axial symmetry (rhombic distortion). The seven-line hyperfine splitting of the parallel components of the EPR spectrum from two equivalent copper nuclei is clearly resolved only in the cases of complexes containing bound 2,6-Me₂-Pyox, 2,4,6-Me₃-Pyox, and 4-NO₂-Quinox (Table 2). In all other cases the hyperfine structure is smeared, probably as a result of interdimer exchange interactions. Besides the triplet state EPR spectra also weak absorptions near $B \approx 330$ mT are present. They can be assigned to a small percentage of structural impurities of magnetically diluted ($S = 1/2$) monomeric complexes. Such impurities have been found in most dimeric copper(II) carboxylates [16].

The subnormal values of magnetic moments of the complexes under investigation are in the range $\mu_{\text{eff}} = 1.26\text{--}1.47 \mu_B$ at room temperature (Table 3). These values show that the complexes are magnetically condensed with exchange interactions operating between the spins of the unpaired electrons. The electronic spectra are in good correlation with the results of magnetic measurements. The ligand field transitions are in the range $13.1 \times 10^3\text{--}14.4 \times 10^3 \text{ cm}^{-1}$ (Table 3). The absorption band in the near UV region ($\tilde{\nu}_{\text{sh}} \approx 28 \times 10^3 \text{ cm}^{-1}$) can be also taken as an evidence for a spin-spin interaction [21]. The obtained results together with the parameters of the EPR spectra justify to classify these compounds as dimeric Cu(II) complexes with bridging carboxyl groups. Their composition is then $[\text{Cu}_2(4\text{-NO}_2\text{PhOAc})_4\text{L}_2]$ and the *N*-oxide ligands are bound in axial positions of the dimeric complex unit.

A substitution of coordinated water molecules by aromatic *N*-oxide molecules causes significant structural changes in the inner coordination sphere of diaqua-bis(4-nitrophenoxyacetato)copper(II) complex. The 4-nitrophenoxyacetato anion, originally acting as a chelating ligand, changes to a bridging ligand of a similar type as it has been found in copper(II) acetate monohydrate and related dimeric copper(II) complexes. A magnetic exchange in pairs of Cu(II) ions is then made possible *via* the bridging system of carboxyl groups.

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