Inorganica Chimica Acta, 41 (1980) 155–159

Synthesis of Binuclear Copper(II) Complexes with μ-Oxamido, μ-Oxamato, and μ-Oxalato-bridges

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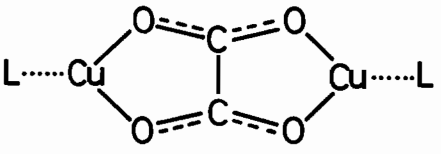
Received December 28, 1979

μ-Oxamido-, μ-oxamato-, and μ-oxalato-bridged binuclear copper(II) complexes $[Cu_2(bridge)L_2]^{2+}$ *coordinated with another ligand (L) such as 2,2'-bipyridine, 2,2'-dipyridylamine, N,N,N',N'-tetramethylethylenediamine, 2-(2-aminoethyl)pyridine, N,N,N',N'',N''-pentamethyldiethylenetriamine, N,N, N'',N''-tetraethyldiethylenetriamine, and N,N,N',N'', N''-pentaethyldiethylenetriamine have been prepared and characterized by infrared and electronic spectra, and magnetic moments at room temperature The complexes are square-planar or tetragonal octahedral for the bidentate L s, while they are five coordinate for the terdentate L s The magnetic moments of these complexes depend upon the bridges as well as L s The moments of the complexes with the bidentate L s are all subnormal and decrease in the order μ-oxalato- > μ-oxamato- > μ-oxamido- bridge The moments of the complexes with the terdentate L s are normal for a μ-oxalato-bridge but subnormal for a μ-oxamido-bridge Magnetic copper-copper interaction seems to be more effective through a μ-oxamido bridge than through μ-oxamato- and μ-oxalato-bridges*

Introduction

A variety of ligands are known to bridge metal ions to form binuclear complexes and an oxalate ion is one such ligand The oxalate ion bridges metal ions in various fashions [1] to form binuclear complexes Binuclear copper(II) complexes bridged by a oxalate



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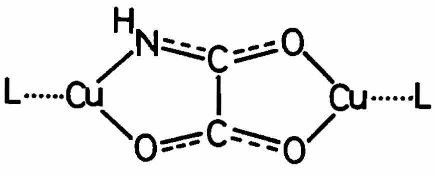

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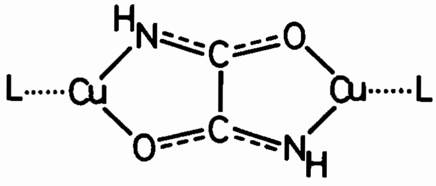

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TABLE 1. Colours, Magnetic Moments, and Analytical Results for the Complexes[a].

No.	Complex	Colour	μ_{eff}[b] (B.M.)	Analysis, found (calcd.) %		
				Cu	N	H_2O
1	$[Cu_2(oa)(dpa)_2(NO_3)_2]$	Green	1.14	18.84 (18.70)	20.84 (20.61)	
2	$[Cu_2(oa)(dpa)_2](NO_3)_2 \cdot 4H_2O$	Blue	1.07	16.91 (16.91)	18.36 (18.64)	9.57 (9.59)
3	$[Cu_2(oa)(Me_4en)_2](NO_3)_2 \cdot 2H_2O$	Deep blue	1.00	21.23 (20.99)	18.44 (18.50)	5.86 (5.95)
4	$[Cu_2(oa)(aep)_2](NO_3)_2$	Deep blue	1.04	21.87 (21.86)	19.30 (19.27)	
5	$[Cu_2(oa)(bipy)_2](NO_3)_2 \cdot 3H_2O$	Greenish blue	1.00	17.95 (18.06)	15.94 (15.93)	7.60 (7.68)
6	$[Cu_2(oa)(Me_5dien)_2](PF_6)_2$	Greenish blue	1.54	14.84 (14.96)	12.89 (13.19)	
7	$[Cu_2(oa)(Et_4dien)_2](PF_6)_2 \cdot H_2O$	Greenish blue	1.72	13.34 (13.35)	11.61 (11.77)	1.98 (1.89)
8	$[Cu_2(oa)(Et_5dien)_2](PF_6)_2$	Green	1.42	13.27 (13.21)	11.45 (11.65)	
9	$[Cu_2(om)(dpa)_2](NO_3)_2$	Green	1.26	18.62 (18.68)	18.51 (18.52)	
10	$[Cu_2(om)(Me_4en)_2](PF_6)_2 \cdot 3H_2O$	Blue	1.34	16.12 (16.08)	9.06 (8.86)	7.08 (6.84)
11	$[Cu_2(om)(aep)_2](NO_3)_2$	Blue	1.30	21.67 (21.82)	16.82 (16.83)	
12	$[Cu_2(om)(bipy)_2](NO_3)_2 \cdot H_2O$	Blue	1.34	19.04 (19.01)	14.81 (14.67)	2.68 (2.69)
13	$[Cu_2(om)(Me_5dien)_2](PF_6)_2$	Violet-blue	1.85	14.79 (14.94)	11.40 (11.53)	
14	$[Cu_2(om)(Et_4dien)_2](PF_6)_2 \cdot 1/2H_2O$	Blue	1.74	13.67 (13.47)	10.28 (10.39)	1.00 (0.95)
15	$[Cu_2(om)(Et_5dien)_2](PF_6)_2 \cdot H_2O$	Bluish green	1.65	12.98 (12.96)	10.06 (10.00)	1.82 (1.84)
16	$[Cu_2(ox)(dpa)_2(NO_3)_2]$	Green	1.40	18.54 (18.65)	16.31 (16.44)	
17	$[Cu_2(ox)(Me_4en)_2](PF_6)_2 \cdot 4H_2O$	Blue	1.47	15.61 (15.70)	6.99 (6.92)	8.79 (8.90)
18	$[Cu_2(ox)(aep)_2](NO_3)_2 \cdot 2H_2O$	Blue	1.44	20.33 (20.52)	13.65 (13.57)	5.82 (5.82)
19	$[Cu_2(ox)(Me_5dien)_2](PF_6)_2$[c]	Bluish violet	1.88	14.86 (14.92)	9.86 (9.87)	
20	$[Cu_2(ox)(Et_4dien)_2](PF_6)_2$	Blue	1.85	13.61 (13.58)	8.90 (8.98)	
21	$[Cu_2(ox)(Et_5dien)_2](PF_6)_2$[c]	Blue	1.82	13.09 (13.19)	8.91 (8.72)	

[a] The following abbreviations are used. H_2oa = oxamide, H_2om = oxamic acid, H_2ox = oxalic acid, dpa = 2,2'-dipyridylamine, Me_4en = N,N,N',N'-tetramethylethylenediamine, aep = 2-(2-aminoethyl)pyridine, bipy = 2,2'-bipyridyl, Me_5dien = N,N,N',N'',N''-pentamethyldiethylenetriamine, Et_4dien = N,N,N'',N''-tetraethyldiethylenetriamine, and Et_5dien = N,N,N',N'',N''-pentaethyldiethylenetriamine. [b] At room temperature. [c] These complexes are reported in ref. 2.

TABLE II. Electronic Spectra[a] and Electrical Conductances[b].

No.	Solution Spectra			Nujol Mull Spectra Maximum			Λ_M
	Solvent	Maximum (ϵ)[c]					
1	CH_3OH	16.4(100)		14.7	26.3sh[d]		175
2	H_2O	16.5(70)		16.7	25.9sh		175
3	H_2O	16.8(117)		17.5	27.8		186
4	CH_3OH	16.5(112)		16.8	26.5sh		187
5	H_2O	16.1(54)		16.7	27.0sh		179
6	H_2O	14.5(238)	17.5sh	12.4	26.7sh		192
7	CH_3OH	13.2(332)	16.0sh	13.3	16.5sh		201
8	CH_3OH	13.0(305)	15.5sh	13.1	26.0sh		198
9	CH_3OH	15.7(62)		16.1	27.4sh		168
10	H_2O	16.0(104)		16.3	29.0sh		203
11	CH_3OH	15.5(78)		16.0	28.5sh		173
12	H_2O	15.7(49)		16.3	28.6sh		181
13	H_2O	15.0(235)	17.8sh	14.8	16.8sh		220[e]
14	CH_3OH	13.6(331)	16.0sh	14.1	16.5sh		204
15	CH_3OH	13.4(299)	16.0sh	13.2	28.0sh		196
16	CH_3OH	15.0(47)		15.1	23.8sh	29.9sh	170
17	H_2O	15.7(87)		15.5	30.3sh		192
18	CH_3OH	15.1(68)		15.3	30.0sh		179
19	H_2O	14.9(231)	17.5sh	14.8	16.8sh		218[f]
20	CH_3OH	14.2(320)	16.0sh	14.6	16.5sh		202
21	CH_3OH	13.7(280)	16.0sh	13.7			193

[a] In 10^3 cm^{-1}. [b] In mho·cm^2/mol: 10^{-3} *M* CH_3OH solutions at 25 °C. [c] Molar extinction coefficient per copper ion. [d] sh = shoulder. [e] 5×10^{-4} *M*. [f] 3.5×10^{-4} *M*.

ion (abbreviated as 'ox', Structure I) show interesting magnetic properties and the magnetic interaction through the bridge depend markedly upon co-ordinated ligands(L) and also upon counter ions [2]. Oxamic acid(H_2om) and oxamide(H_2oa) have a similar skeleton to that of oxalic acid(H_2ox) and they are expected to bridge copper(II) ions to form binuclear complexes (Structures II and III). Although the monomeric complexes of these ligands, $K_2[Cu(oa)_2]$ and $K_2[Cu(om)_2]$, have been reported [3, 4], there is no investigation of binuclear complexes bridged by these ligands. To compare coordination properties of the three similar bridging ligands, H_2oa, H_2om, and H_2ox, several new μ-oxamido, μ-oxamato, and μ-oxalato copper(II) complexes with another ligand (L: abbreviations used for L are given in the footnotes of Table I) have been prepared and characterized. This investigation is a part of our continuing study on complexes of oxamide derivatives [5].

Results and Discussion

Deprotonated oxamide(oa), oxamic acid(om), and oxalic acid(ox) form complexes of the type $[Cu_2(bridge)L_2]^{2+}$ (bridge = oa, om, and ox) (Table I) and magnetic moments and spectral data are given in Tables I and II. The electric conductances of 10^{-3} *M* methanol solutions at 25 °C are in the range expected for 1:2 electrolytes [6]. The infrared spectra show that counter anions, NO_3 and PF_6, are not coordinated in most of the complexes. In the spectra of $[Cu_2(oa)(dpa)_2(NO_3)_2]$ (green form) and $[Cu_2(ox)(dpa)_2(NO_3)_2]$, however, $\nu(NO_3)$ are observed at 1306 and 1420 cm^{-1} (for the former) and at 1287 and 1431 cm^{-1} (for the latter), suggesting coordination of NO_3.

The infrared spectrum [7, 8] of $K_2[Cu(ox)_2]\cdot 2H_2O$ (where ox is an O,O-chelating ligand) is reported to show $\nu(C{=}O)$ at 1720sh, 1672, and 1645 cm^{-1} and the band is at 1650 cm^{-1} for $[Cu_2(ox)(dien)_2](ClO_4)_2\cdot 2H_2O$ (Structure I; dien = diethylenetriamine), where ox is a bridging ligand. The oxalato complexes prepared in this study (Nos. 16–21) show the bands in the region between 1635 and 1670 cm^{-1}, and the coordination mode of ox is suggested to be similar to that of $[Cu_2(ox)(dien)_2](ClO_4)_2\cdot 2H_2O$, the structure of which is determined [8]. The oxamido complexes (Nos. 1–8) show $\nu(C{=}O)$ due to amide groups in the region between 1605 and 1650 cm^{-1}. The band is reported [3] for the N,N'-bidentate oxamido complex $K_2[Cu(oa)_2]$ at 1620 and 1590 cm^{-1}. The oxamato complexes (Nos. 9–15) show similar bands between 1612 and 1655 cm^{-1}, while for the N,O-chelating oxamato complex [4] $K_2[Cu(om)_2]$ the bands are observed at 1690 and 1660 cm^{-1}. The differences in frequencies of $\nu(C{=}O)$ between the new complexes and those reported may suggest a different mode of coordination of oa, om, and ox. Structures I, II, and III are proposed. The bands ν(N–H) are in the normal region between 3250 and 3360 cm^{-1}.

The electronic spectra of $[Cu_2(bridge)L_2]^{2+}$ with bidentate L s both in the solid state and in solutions show that the complexes are square-planar or tetragonal octahedral [9]. The absorption maxima of the spectra shift to lower frequencies in the order of the bridges; oa > om > ox, when L is the same. This fact agrees with the chromophore change based on the proposed Structures I, II, and III; $[CuN_2O_2]_2$, ($[CuN_2O_2]$ + $[CuN_3O]$) $[CuN_3O]_2$. The molar extinction coefficients (per copper ion, ϵ) also decrease in this order; oa > om > ox (Table II). The deprotonated amide groups are suggested to have larger hyperchromic effect than the carboxylate groups. Only the spectrum of the solid $[Cu_2(oa)(dpa)_2(NO_3)_2]$ (green form) is exceptional ($\bar{\nu}_{max}$ at 14.7 × 10^3 cm^{-1}) and reveals that it may be five coordinate. This may result from coordination of NO_3 as indicated by the infrared spectrum.

The room temperature magnetic moments of these planar or tetragonal octahedral complexes are all subnormal suggesting the presence of magnetic interaction between copper ions. The proposed Structures I, II, and III are consistent with this fact and the presence of peaks or pronounced shoulders in the near ultraviolet region of the spectra of the solid complexes (Table II) also supports this fact [5, 10]. Although the bidentate ligands (L) have only minor effect on the magnetic moments (Table I), the values depend markedly upon the bridging groups. The antiferro magnetic interaction decreases in the order of the bridges; oa > om > ox.

The electronic spectra of $[Cu_2(bridge)L_2]^{2+}$ with terdentate L s are very different from those of the complexes with bidentate L s discussed above (Table II and Fig. 1). The solid spectrum of $[Cu_2(ox)(Me_5dien)_2](PF_6)_2$ is similar to that of the five-coordinate, square-pyramidal $[Cu_2(ox)(dien)_2](ClO_4)_2$ [8] and the structure of the former should be square-pyramidal [2]. The spectra of $[Cu_2(om)(Me_5dien)_2](PF_6)_2$ and $[Cu_2(bridge)(Et_4dien)_2]^{2+}$ (bridge = oa, om and ox) in the solid state are also similar to that of $[Cu_2(ox)(dien)_2](ClO_4)_2$ suggesting that these complexes are square-pyramidal. The absorption spectra of these complexes in solutions are intense (Table II) and the spectral patterns resemble that of the solid $[Cu_2(ox)(Me_5dien)_2](PF_6)_2$ implying that a five-coordinate, square-pyramidal structure is retained.

The three Et_5dien complexes (Nos. 8, 15, and 21) and $[Cu_2(oa)(Me_5dien)_2](PF_6)_2$ in the solid state have a different type of electronic spectra which show a broad maximum in the d-electron transition region. The structure is assumed to be trigonal bipyramidal like the structure of $[Cu_2(ox)(Et_5dien)_2](BPh_4)_2$ determined by X-ray [2]. A pronounced shoulder is observed for $[Cu_2(oa)L_2]^{2+}$ (L = Me_5dien and Et_5dien) in the near ultraviolet region and a less distinct one for $[Cu_2(om)(Et_5dien)_2]^{2+}$ (Fig. 1).

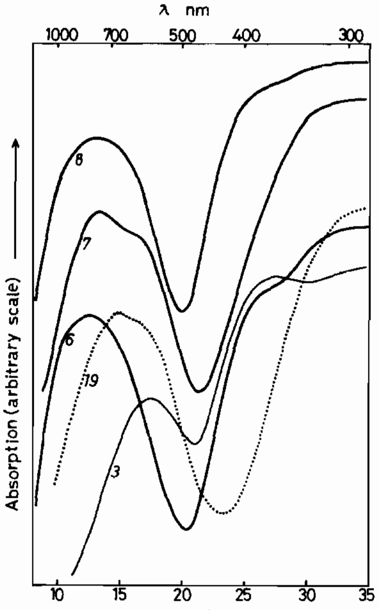

Fig. 1. Electronic spectra of the complexes (Nujol mulls). 3: $[Cu_2(oa)(Me_4en)_2](NO_3)_2 \cdot 2H_2O$, 6: $[Cu_2(oa)(Me_5dien)_2](PF_6)_2$, 7: $[Cu_2(oa)(Et_4dien)_2](PF_6)_2 \cdot H_2O$, 8: $[Cu_2(oa)(Et_5dien)_2](PF_6)_2$, and 19: $[Cu_2(ox)(Me_5dien)_2](PF_6)_2$.

The room temperature magnetic moments of the complexes with terdentate L s are higher than those of the corresponding complexes with bidentate L s and some are around the border-line between the normal and subnormal values. The three ox complexes (Nos. 19, 20, and 21) are all normal [2] but $[Cu_2(om)(Et_5dien)_2](PF_6)_2 \cdot H_2O$ and $[Cu_2(oa)L_2](PF_6)_2$ (L = Me_5dien and Et_5dien) are subnormal. The absence of absorption in the near ultaviolet region is a feature for the former type complexes, while there are shoulders in the spectra of the latters (Fig. 1). Similar shoulders in the near ultraviolet region are observed for the magnetically subnormal complexes with bidentate L s mentioned above. Comparison of the magnetic moments of the five coordinate complexes reveals that the N-substituents of diethylenetriamine define the precise structures which affect magnetic interaction between copper(II) ions. To the contrary, the magnetic moments of the complexes with bidentate L s (Table I) are less sensitive to a nature of L.

Magnetic interaction through μ-oxalato, μ-oxamato, and μ-oxamido bridges is more favourable to square-planar or tetragonal octahedral complexes than to trigonal bipyramidal or square-pyramidal complexes. The μ-oxamido group mediates magnetic interaction between copper ions more strongly than the μ-oxamato and μ-oxalato groups, so that even in the five coordinate complexes with a μ-oxamido bridge the interaction persists. It is also noted that the μ-oxamido bridge forces a copper(II) ion to have a trigonal bipyramidal geometry in such a case where μ-oxamato and μ-oxalato bridges form square pyramidal complexes.

More precise interpretation of these magnetic properties will require measurements of magnetic susceptibilities at various temperature over a wide range and electron spin resonance spectra, as well as determination of the structures. These are, however, out of our present purpose.

Experimental

Measurements

Measurements were carried out by the methods reported previously [11].

Synthesis of the Complexes

Colours and analytical results for the complexes are shown in Table I. Yields of the following complexes were 75–80% in all cases.

$[Cu_2(oa)(dpa)_2(NO_3)_2]$(No. 1): To a warm mixture of 2.42 g of $Cu(NO_3)_2 \cdot 3H_2O$, 0.44 g of H_2oa, and 1.71 g of dpa in 200 ml of water was added 0.42 g of $LiOH \cdot H_2O$ dissolved in a small amount of water to give a deep blue solution. The solution was filtered and allowed to stand at room temperature to give blue crystals. Recrystallization of the crystals from methanol gave the green complex No. 1, while upon recrystallization from water the blue complex No. 2 was obtained. The complex No. 2 did not turn to the green complex No. 1 upon dehydration.

The complexes Nos. 3, 4, 5, 9, 11, and 12 were synthesized by the above method using 10 mmol of $Cu(NO_3)_2 \cdot 3H_2O$, 5 mmol of a bridging ligand, 10 mmol of an appropriate ligand L, and 10 mmol of $LiOH \cdot H_2O$. The product was recrystallized from warm water.

The ox complexes Nos. 16 and 18: To a solution of 10 mmol of $Cu(NO_3)_2 \cdot 3H_2O$ and 10 mmol of L in 200 ml of water was added 5 mmol of Li_2ox dissolved in a small amount of water. The mixture was warmed to 60 °C to give clear solution. The solution was filtered while hot and allowed to cool to room temperature to give the crystalline product.

The remaining complexes Nos. 6, 7, 8, 10, 13, 14, 15, 17, 19, 20, and 21 were crystallized upon addition of 10 mmol of $NaPF_6$ in a small amount of water and allowing to cool to room temperature. These complexes were recrystallized from a mixture of water and methanol.

Acknowledgement

The authors are indebted to Miss T. Yamazaki for her collaboration in the preparation and characterization of a few complexes.

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