

Binuclear Copper(II) and Nickel(II) Complexes of *N,N'*-Bis(dimethylaminoalkyl)aminoalkyl)oxamides

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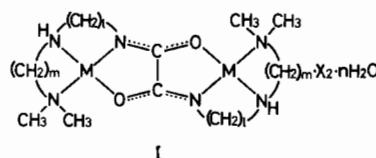
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N,N'-Disubstituted oxamides (H_2L), $[(CH_3)_2N(CH_2)_mNH(CH_2)_lNHCO]_2$ ($m = 2, 3; l = 2, 3, 4, 6$) form binuclear copper(II) and nickel(II) complexes $[M_2L]X_2 \cdot nH_2O$ ($X = Cl, ClO_4, Ph_4B$). The oxamide moiety is deprotonated and bridged between two metal ions coordinating through two oxygen and two deprotonated nitrogen atoms. The diamagnetic, square planar nickel complexes are obtained for the ligands with $m, l = 2, 3$. The magnetic moments of all the copper complexes at room temperature are subnormal and the values vary with chelate ring sizes and counter anions X . The antiferromagnetic interaction through the oxamide moiety decreases with increasing sizes of chelate rings (with the exception of $l = 6$). The electronic spectra are also affected by these factors.

Introduction

Metal complexes of binucleating ligands are attractive as models for the coordination environments of metalloproteins such as hemocyanin, cytochrome *c* oxidase, and bovine erythrocyte superoxide dismutase, and in Type 3 Copper-proteins a pair of copper ions are strongly coupled magnetically [1]. Oxamide is interesting, for it acts as a binucleating ligand and copper(II) complexes with a μ -oxamide bridge show antiferromagnetic interaction [2]. The extent of the interaction is strongly dependent upon the geometries of the complexes. Oxamide is further intriguing since a wide variety of substituted derivatives can be designed according to an object. In order to obtain further insight into the properties of the complexes bridged by a μ -oxamide moiety, copper(II) and nickel(II) complexes have been prepared for several new ligands, *N,N'*-disubstituted oxamides (shown in Structure I and Table I),

which form five to nine membered chelate rings. The sizes of chelate rings are expected to affect the geometries and hence the properties of the complexes. This investigation is a part of our continuing research on the complexes of oxamide and its derivatives [2].



Results and Discussion

The disubstituted oxamides (H_2L), $[(CH_3)_2N(CH_2)_mNH(CH_2)_lNHCO]_2$ ($m = 2, 3; l = 2, 3, 4, 6$) are prepared from diethyl oxalate and an appropriate triamine, and used without isolation. The copper(II) complexes (Table I) are synthesized under basic conditions and isolated as chlorides or perchlorates. The nickel(II) complexes are obtained only for a few ligands as shown in Table I. These complexes have a general formula, $[M_2L]X_2 \cdot nH_2O$. The electric conductivities of the complexes are consistent with this formulation (Table II) [3].

The infrared spectra of the complexes show that the amide groups are deprotonated and coordinated through the nitrogen and oxygen atoms since the characteristic bands of this mode of coordination of an amide group are observed (Table III) [4]. The positions of the higher frequency bands, $\nu_{as}(O-C-N)$ are sensitive to the length of polymethylene chains adjacent to the amide groups and may reflect strains of fused chelate rings. The bands are at higher frequencies when $l = 2$, where the fused chelate ring

TABLE I. Colours, Magnetic Moments, and Analytical Results for the Complexes (see Structure I).

Complex ^a						Colour	μ_{eff}^b (B.M.)	Analysis, found (calcd.) %				
No.	M	l	m	X	n			M	N	H ₂ O	C	H
1a	Cu	2	2	Cl	2.5	Greenish blue	1.16	22.82 (22.80)	14.84 (15.08)	7.93 (8.08)		
1b	Cu	2	2	ClO ₄	0	Reddish violet	0.89	19.89 (19.85)	12.98 (13.12)		26.12 (26.26)	4.76 (4.72)
1c	Ni	2	2	Ph ₄ B	0	Orange-yellow	dia.	10.93 (10.97)	7.65 (7.85)			
2a	Cu	2	3	Cl	1	Blue	1.00	22.32 (22.76)	15.16 (15.05)	2.92 (3.23)		
2b	Cu	2	3	ClO ₄	2	Bluish violet	0.92	17.94 (18.04)	11.88 (11.93)	5.21 (5.11)	27.21 (27.28)	5.21 (5.44)
2c	Ni	2	3	Ph ₄ B	0	Red	dia.	10.52 (10.69)	7.49 (7.65)			
3a	Cu	3	2	Cl	¼	Bluish green	1.29	22.95 (23.32)	15.32 (15.42)	0.89 (0.83)	35.02 (35.33)	6.22 (6.38)
3b	Cu	3	2	ClO ₄	0	Reddish violet	1.19	18.96 (19.01)	12.57 (12.57)			
3c	Ni	3	2	ClO ₄	0	Red	dia.	17.75 (17.82)	12.77 (12.76)		29.17 (29.17)	5.32 (5.20)
4a	Cu	3	3	Cl	½	Green	1.28	21.82 (22.01)	14.39 (14.55)	1.48 (1.56)		
4b	Cu	3	3	ClO ₄	2	Greenish blue	1.22	17.39 (17.35)	11.37 (11.47)	4.83 (4.92)	30.38 (29.51)	5.58 (5.78)
5a	Cu	4	2	Cl	2	Bluish green	1.35	20.72 (21.02)	13.92 (13.90)	5.97 (5.96)		
5b [*]	Cu	4	2	ClO ₄	¼	Violet	1.25	18.01 (18.13)	11.96 (11.99)	0.81 (0.64)	31.16 (30.84)	5.39 (5.54)
6a	Cu	4	3	Cl	½	Green	1.36	20.69 (20.99)	13.64 (13.88)	1.56 (1.49)		
6b	Cu	4	3	ClO ₄	1	Deep green	1.20	16.97 (17.11)	11.31 (11.32)	2.25 (2.43)	32.36 (32.35)	6.06 (5.97)
7a	Cu	6	2	Cl	5/4	Green	1.18	19.61 (19.64)	13.13 (12.99)	3.65 (3.48)	41.02 (40.83)	7.45 (7.55)
7b	Cu	6	2	ClO ₄	2	Deep green	1.40	16.27 (16.11)	10.65 (10.66)	4.80 (4.57)		
8a	Cu	6	3	Cl	0	Green	1.15	19.21 (19.47)	12.73 (12.88)		44.22 (44.17)	7.72 (7.72)

^aPh₄B = tetraphenylborate ion. Yields are, in general, about 50–70%. ^bAt room temperature, dia = diamagnetic.

is a 5–5–(3 + m) membered one, than when l = 3, 4, and 6, where the fused chelate ring is a 5–6 (or 7 and 9)–(3 + m) membered one (m = 2 and 3). The bands $\nu(\text{N-H})$ of a secondary amino group are observed in the normal region, 3100–3265 cm⁻¹. Non-coordination of ClO₄ is suggested but strong bands between 200–350 cm⁻¹ may be assigned to $\nu(\text{Cu-Cl})$ indicating coordination of Cl.

The electronic spectra in the solid state are given in Table III and Fig. 1. The diamagnetic nickel complexes show a single absorption maximum in the d–d transition region characteristic of square planar nickel(II) complexes. All the copper complexes show strong absorption peaks or pronounced shoulders in the near ultraviolet region 26–30 × 10³ cm⁻¹.

Similar bands have been observed for other binuclear copper(II) complexes bridged by a μ -oxamide moiety which exhibit subnormal magnetic moments [1, 4, 5]. The origin of the bands may be similar. The ligand field d–d transitions are dependent upon both the substituents of oxamide and anions(X). The electronic spectra of the perchlorates suggest that the structures are tetragonal or square planar [6].

The absorption maxima of the d–d bands of [Cu₂L]Cl₂·nH₂O are located at lower frequencies than those of [Cu₂L](ClO₄)₂·nH₂O and the origin may be due to apical coordination of Cl as suggested by the infrared spectra. The shapes of the spectra become progressively broad as chelate ring sizes increase (Fig. 1). In the case of [Cu₂L]Cl₂·

TABLE II. Absorption Spectra and Electric Conductivities of the Complexes.

No.	Solvent	Electronic Spectra ^a		Conductivity Λ_M^b
		$\bar{\nu}_{\max}$ in 10^3 cm^{-1} (log ϵ)		
1b	Water	16.2(2.36)	28.0(3.10)	202
1c	Acetone	22.3(2.27)		206
2b	Water	16.7(2.37)	28.8(3.02)	203
2c	Acetone	20.7(2.21)		213
3b	Water	17.4(2.09)	29.5(3.06)	202
3c	Acetone-water (9:1)	21.3(1.88)		178
4b	Water	16.1(2.15)	28.5sh(3.1)	208
5b	Water	16.8(2.02)	29.0sh(3.1)	192
6b	Water-methanol(1:1)	15.7(2.17)	29.0sh(3.2)	212
7b	Water-methanol(1:4)	16.0(1.95)	29.0sh(2.9)	233

^ash = shoulder. ^bMho, cm^2/mol ; ca. $1 \times 10^{-3} M$ solution at 25 °C.

TABLE III. Infrared and Electronic Spectra of the Complexes (Nujol mulls).

No.	Infrared Spectra (cm^{-1}) ^a				Electronic Spectra (10^3 cm^{-1})		
	$\nu(\text{NH})^b$	$\nu_{\text{as}}(\text{OCN})^c$	$\nu_{\text{s}}(\text{OCN})^c$	$\nu(\text{CuCl})$	$\bar{\nu}_{\max}$		
1a	3205	1659	1309		28.2	15.3	
1b	3265	1660	1315		28.9	17.9	
1c	3165	1672	1310		32.6br	22.0	
2a	3105	1648	1314	278	26.7	15.8	
	3130						
2b	3250	1663	1316		27.4	17.0	
2c	3165	1672	1319		31.7sh	20.5	
3a	3170	1609	1319	297	27.8	15.7	
3b	3240	1622	1322		27.9	18.3	
3c	3200	1636	1326		32.3	20.5	
4a	3120	1619	1328	207	27.0sh	14.5	10.8sh
4b	3240	1633	1328		28.0sh	16.2	
5a	3180	1599	1317	306	27.8	15.1	10.5sh
5b	3235	1617	1324		29.4sh	18.0	
	3260sh						
6a	3150	1614	1340	349	26.5	13.4	10.5sh
6b	3205	1620	1326		27.9	16.7sh	16.0
7a	3205	1614	1336	341	27.6	14.6	10.9sh
	3243						
7b	3240	1610	1340		27.0sh	18.2br	
8a	3220	1614	1339	276	27.2	14.4	

^ash = shoulder, br = broad. ^b $\nu(\text{N-H})$ of secondary amino groups. ^cAsymmetric and symmetric vibrations of amide groups, respectively.

$n\text{H}_2\text{O}$, a pronounced shoulder is observed at lower energy sides of main peaks when the chelate ring sizes are larger (Table III and Fig. 1). The broadening or splitting may suggest that the structures become more distorted with increasing sizes of the chelate rings. The complex 8a, however, shows no shoulder on a lower energy side of a main peak and is different from the successive members of the series $[\text{Cu}_2\text{L}]\cdot\text{Cl}_2\cdot n\text{H}_2\text{O}$.

The perchlorates and tetraphenylborates (Ph_4B) are soluble (mixed solvents are used for 3c, 6b, and 7b because of low solubilities in pure solvents) and absorption spectra are measured (Table II). The spectra are essentially similar to those of the solid complexes but some red-shifts of the d-d bands are observed for the copper complexes. This may result from apical interaction of solvent molecules. The persistence of the peaks or shoulders in the near

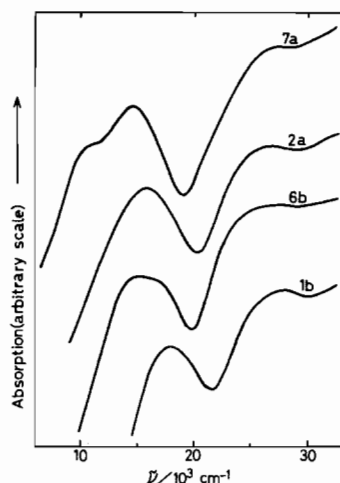


Fig. 1. Electronic spectra of the complexes in the solid state.

ultraviolet region suggests the retention of the dimeric structure(I). The d-d transitions of 1b and 2b are more intense and located at lower frequencies than those of 3b (Fig. 2, $\log \epsilon$, $\tilde{\nu}_{\max}$). In the former two the fused chelate rings are a 5-5-(m+3) (m = 2 and 3) system, while in the latter it is a 5-6-5 system. It has been pointed out that a fused 5-5 membered chelate ring produces an appreciable strain but the strain is released in a 5-6 system [7]. The strain is reflected in the energy and molar extinction coefficient (ϵ) of d-d transitions [7]. This is the case observed here (Table II and Fig. 2). The frequencies of ν_{as} (O-C-N) discussed above give a similar judgment. A similar argument suggests that the fused chelate rings, 5-6-6 (4b) and 5-7-6 (6b) are more strained than 5-6-5 (3b) and 5-7-5 (5b), respectively.

The magnetic moments of all the copper complexes are subnormal at room temperature. The complexes 1a, 1b, 2a, and 2b show more reduced values than the others. In the former the fused chelate rings are a 5-5-(m+3), while in the latter they are a 5-(l+3)-(m+3) system (l = 3, 4, and 6; m = 2, 3). The moments are usually larger for X = Cl than X = ClO₄ except for l = 6 where a nine membered chelate ring is expected to be formed. The structures of the complexes 7a, 7b, and 8a may deviate severely from a square-planar or a tetragonal one, so that their properties are not in line with those of the others.

The unpaired electron of tetragonal or square-planar Cu(II) usually lies in a $d_{x^2-y^2}$ orbital which directed toward four donor atoms in the square plane [8]. In this case the plane is defined by terminal dimethylamino-N, central secondary amino-N, and deprotonated amido-N and -O atoms. The unpaired electrons of the two copper ions bridged by a oxamide moiety interact efficiently through the oxamide bridge when the two copper ions and

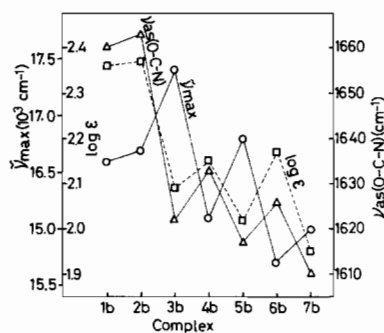


Fig. 2. Schematic representations of $\tilde{\nu}_{\max}$ (○) and $\log \epsilon$ (□) of the absorption spectra, and ν_{as} (O-C-N) (△) of the infrared spectra of the complexes.

oxamide group are in the same plane [2, 8]. The complexes with larger chelate rings are distorted and the copper ions may be displaced away from the plane of the oxamide group. In this case the overlap between the $d_{x^2-y^2}$ orbitals and oxamide orbitals is, therefore, diminished resulting in weak antiferromagnetic interaction (less reduced values of magnetic moments). Apical coordination of Cl may induce a similar unfavourable displacement of copper ions. More detailed interpretation of the electronic and magnetic properties will require determination of molecular structures.

Experimental

Measurements

Measurements were carried out by the methods reported previously [2].

Synthesis of the Ligands

To a solution of 0.1 mol of N,N-dimethylaminoalkylaminoalkylamine in 20 ml of ethanol was added dropwise, with stirring a mixture of 10 ml of ethanol and 0.05 mol of diethyl oxalate. After exothermal reaction had ceased the resultant solution was heated at reflux for 2 h to complete the reaction. The cooled solution was used to prepare the following complexes by assuming quantitative yield of the oxamide ligands.

Synthesis of the Copper(II) Complexes

Chloride Complexes

1a, 2a, 3a, and 5a: A mixture of 0.01 mol of copper chloride and 0.005 mol of the ligand (one-fifth of the ligand solution prepared above) in 20 ml of water was neutralized with a solution of 0.01 mol of sodium hydroxide in 10 ml of water to produce a deep blue solution. The solution was evaporated to dryness under reduced pressure and the residue was extracted with hot methanol. The

hot extract was filtered and cooled after addition of a small amount of water. Crystals precipitated were recrystallized from methanol.

4a and 6a: The two were similarly prepared by using 200 ml of water as solvent. A mixture of methanol and water (5:95) was used for recrystallization.

7a and 8a: The two were also prepared similarly from 200 ml of a mixture of methanol and water (95:5). Recrystallization was impossible because of instability in solution.

Perchlorate Complexes

1b, 2b, and 3b: To a mixture of 0.005 mol of oxamide and 0.01 mol of copper nitrate in 150 ml of water was added with stirring a solution of 0.01 mol of sodium hydroxide in 10 ml of water. Undissolved materials were filtered off and to the filtrate warmed at 80 °C was added 0.02 mol of sodium perchlorate dissolved in 10 ml of water. Upon cooling the perchlorate was precipitated and recrystallized from hot water.

4b and 5b: These were prepared similarly by using a mixture of methanol and water (1:1) as solvent and recrystallized from the same solvent mixture.

6b and 7b: A mixture of methanol and water (95:5) was used for preparation and recrystallization.

Synthesis of the Nickel(II) Complexes

2c: To a solution of 0.005 mol of oxamide and 0.01 mol of nickel nitrate in 100 ml of water was added 0.01 mol of sodium hydroxide dissolved in 10 ml of water and the resulting solution was warmed to 80 °C. The hot solution was filtered and to the hot filtrate was added 0.02 mol of sodium per-

chlorate dissolved in a minimum amount of water to afford red crystals. The crystals were recrystallized from acetone.

1c and 3c: To a solution containing the nickel complex prepared as above was added 0.01 mol of sodium tetraphenylborate dissolved in a minimum amount of ethanol to give a yellow crystalline powder. The powder was collected and washed with hot water and then with hot ethanol. 1c was recrystallized from acetone and the orange crystals were dried in air. 3c was recrystallized from acetonitrile and yellow brown crystals obtained were dried at 110 °C under reduced pressure to give red crystals. The two complexes were impossible to be crystallized as perchlorates, so that they were isolated as tetraphenylborates.

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