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Binuclear Copper(II) Complexes Bridged by N,N′-Disubstituted Oxamides Containing Thioether Donor Groups

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The title complexes were prepared and characterized spectroscopically and magnetically. In the complexes of the type Cu_2L^{2+} *(*H_2L *= N,N′-disubstituted oxamide, sulfur donor atoms being contained in the substituents) the deprotonated oxamides bridge two copper(II) ions symmetrically and the complexes are all magnetically subnormal at room temperature. The properties of these new complexes are compared with those of copper(II) complexes of similar substituted oxamides containing no sulfur donor.*

Introduction

Binuclear and polynuclear copper(II) complexes attract much attention because of their interesting magnetic properties and enzyme activities [1–3]. Copper(II) ions can be bridged by a variety of ligands such as hydroxo, alkoxo, halogeno, azido, carboxylato groups (ions) *etc.* Magnetic interactions among such copper ions depend upon both the bridging ligand and the stereochemistry around copper ions [2, 3]. As we have shown [4, 5], an oxamide anion ($HNCOCONH^{2-}$) and N,N′-disubstituted derivatives ($RNCOCONR^{2-}$: R = substituent with nitrogen donor atoms) serve as a bridging group.

Sulfur atoms are different in donor properties from nitrogen atoms and are frequently found as donors in the active site of metal enzymes [6, 7]. It is interesting to see the effect of thioether-S donors of N,N′-disubstituted oxamides upon the properties of their copper(II) complexes. In this paper copper(II) complexes of new oxamide derivatives containing thioether-S atoms in the N-substituents are studied. The abbreviations used for the oxamides are given in Table I.

TABLE I. Abbreviations Used for the N,N′-Disubstituted Oxamides, RNHCOCONHR.

N-Substituent, R	Abbreviation
$CH_2CH_2SC_2H_5$	H_2(5S)
$CH_2CH_2CH_2SC_2H_5$	H_2(6S)
$CH_2CH_2CH_2NHCH_2CH_2OC_2H_5$	H_2(65O)
$CH_2CH_2NHCH_2CH_2SC_2H_5$	H_2(55S)
$CH_2CH_2CH_2NHCH_2CH_2SC_2H_5$	H_2(65S)
$CH_2CH_2SCH_2CH_2N(CH_3)_2$	H_2(5S5)
$CH_2CH_2SCH_2CH_2CH_2N(CH_3)_2$	H_2(5S6)
$CH_2CH_2CH_2SCH_2CH_2N(CH_3)_2$	H_2(6S5)
$CH_2CH_2SCH_2C_5H_4N$-2[a]	H_2(5SP)

[a] 2-Pyridyl-group.

Results and Discussion

The oxamide derivatives RNHCOCONHR (H_2L, Table I) are easily obtained by the reactions of diethyl oxalate with appropriate substituted amines, but the products are not crystallized in a high yield. They were therefore used without isolation for the preparation of the complexes, assuming the quantitative yield. The isolated complexes are given in Table II together with the colours and analytical results. The values of the electric conductivities (Table III) support the formulations [8] but some complexes show ambiguous values indicating partial dissociation and/or coordination of anions in solution.

The infrared spectra of the complexes $Cu_2LX_2 \cdot nH_2O$ (Table IV) show strong amide bands between 1606 and 1655 cm^{-1} and between 1302 and 1330 cm^{-1}, characteristic of the dimer skeleton bridged by an oxamide moiety [5] (Structure I: Y, Z = donor atom or group).

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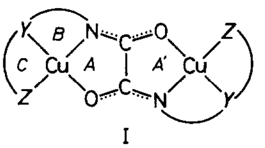
TABLE II. Colours and Analytical Results for the Complexes[a].

Complex		Colour	Prepn.[b]	Analysis, Found (Calcd.), %			
				Cu	N	H_2O	Cl
1	$Cu_2(5S)(NO_3)_2$	Dark green	G	24.50 (24.75)	10.61 (10.91)		
2	$Cu_2(5S)Cl_2$	Yellowish green	A	27.51 (27.61)	5.93 (6.08)		15.16 (15.40)
3	$Cu_2(6S)(NO_3)_2$	Green	G	23.39 (23.47)	10.54 (10.35)		
4	$Cu_2(65O)(ClO_4)_2$	Blue	B	18.68 (18.96)	8.30 (8.36)		
5	$Cu_2(65O)Cl_2 \cdot 1/4H_2O$	Green	A	23.00 (23.24)	10.15 (10.24)	0.77 (0.83)	
6	$Cu_2(55S)(ClO_4)_2 \cdot 1\frac{1}{2}H_2O$	Greenish blue	B	18.19 (18.12)	7.85 (7.99)	3.97 (3.85)	
7	$Cu_2(55S)Cl_2$	Green	D	23.19 (23.25)	10.18 (10.25)		12.83 (12.97)
8	$Cu_2(65S)(ClO_4)_2 \cdot 4H_2O$	Greenish blue	B	16.31 (16.41)	7.20 (7.23)	9.02 (9.30)	
9	$Cu_2(65S)Cl_2$	Bluish green	D	22.00 (22.12)	9.63 (9.75)		12.29 (12.34)
10	$Cu_2(H_2(5S5))Cl_4 \cdot 2H_2O$	Yellowish green	A	19.38 (19.39)	8.23 (8.55)	5.55 (5.50)	21.23 (21.63)
11	$Cu_2(5S6)(BPh_4)_2 \cdot 2H_2O$[c]	Dark green	C	10.89 (10.79)	4.85 (4.76)	2.97 (3.06)	
12	$Cu_2(6S5)(ClO_4)_2 \cdot 2H_2O$	Bluish green	B	16.97 (17.21)	7.66 (7.57)	4.97[d] (4.88)	
13	$Cu_2(6S5)Cl_2$	Green	D	21.86 (22.12)	9.63 (9.75)		12.23 (12.34)
14	$Cu_2(6S5)(BPh_4)_2 \cdot 2H_2O$	Yellowish green	C	10.76 (10.79)	4.39 (4.76)	2.95 (3.06)	
15	$Cu_2(5SP)(ClO_4)_2 \cdot 3H_2O$	Dark green	H	16.54 (16.54)	7.41 (7.29)	6.76 (7.03)	
16	$Cu(H(5SP))ClO_4 \cdot 1\frac{1}{2}H_2O$	Green	F	11.04 (10.97)	9.75 (9.67)	4.38 (4.66)	
17	$Cu(H(5SP))PF_6 \cdot H_2O$	Yellowish green	E	10.32 (10.32)	8.82 (9.09)	2.76 (2.92)	
18	$Cu_2(H_2(5SP))Cl_4 \cdot H_2O$	Yellowish green	A	18.77 (18.76)	7.90 (8.27)	2.20 (2.66)	20.78 (20.93)

[a] Nitrogen analysis for some free ligands isolated in the solid state: $H_2(65O)$, 16.45 (16.17); $H_2(55S)$, 16.29 (15.98); $H_2(5S6)$, 14.71 (14.45); and $H_2(5SP)$, 14.35 (14.35)%. [b] The methods of preparation of the complexes are given in the Experimental. [c] BPh_4 = Tetraphenylborate anion. [d] C: 25.86 (26.02) and H: 5.09 (4.91)%.



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The bands of the three *16*, *17*, and *18*, are exceptional and are observed out of this range, as discussed below. In complexes *1* and *3* coordination of NO_3 is suggested by the bands at 1279 and 1494 (for *1*), and at 1278 and 1500 cm^{-1} (for *3*). Complexes *1*–*3* all show the band due to ν(Cu–X) (Table IV) and coordination of NO_3 and Cl is supported (Structure I: Y = SC_2H_5, Z = ONO_2 or Cl, and chelate ring C is absent).

TABLE III. Absorption Spectra and Molar Conductivities of the Complexes.

Complex		Absorption spectra[a]				Λ_M/Mho, cm^2, mol^{-1} (Concentration)
		Solvent	νmax/10^3 cm^{-1} (log ϵ)			
1	$Cu_2(5S)(NO_3)_2$	EtOH	14.8(2.43)	26.5sh	31.0(3.43)	46.5(1.08)[b]
2	$Cu_2(5S)Cl_2$	EtOH	14.3(2.53)	25.5sh	30.3(3.41)	27.2(0.22)
3	$Cu_2(6S)(NO_3)_2$	EtOH	14.6(2.28)	27.5sh	30.3(3.38)	47.6(0.78)
4	$Cu_2(65O)(ClO_4)_2$	EtOH	15.8(2.00)	31.0(3.00)		64.1(0.82)
5	$Cu_2(65O)Cl_2 \cdot 1/4H_2O$	EtOH	14.8(2.09)	28.5(2.96)		30.5(1.26)
6	$Cu_2(55S)(ClO_4)_2 \cdot 1^1/_2H_2O$	H_2O	16.5(2.47)	27.2sh	31.5(3.45)	207(1.26)
7	$Cu_2(55S)Cl_2$	H_2O	16.5(2.49)	27.0sh	31.5(3.57)	211(1.09)
8	$Cu_2(65S)(ClO_4)_2 \cdot 4H_2O$	MeOH	16.7(2.25)	26.5sh	31.5(3.57)	165(1.13)
9	$Cu_2(65S)Cl_2$	H_2O	16.7(2.26)	26.2sh	31.5(3.57)	218(1.70)
10	$Cu_2(H_2(5S5))Cl_4 \cdot 2H_2O$	MeOH	14.0(2.08)	26.0sh	31.0(3.22)	163(1.42)
12	$Cu_2(6S5)(ClO_4)_2 \cdot 2H_2O$	H_2O	16.5(2.41)	25.0(3.16)	30.5(3.56)	193(1.32)
13	$Cu_2(6S5)Cl_2$	MeOH	16.3(2.39)	25.5sh	31.5(3.54)	161(1.01)
15	$Cu_2(5Sp)(ClO_4)_2 \cdot 3H_2O$	EtOH	16.0(2.51)	25.8(3.21)	31.4(3.38)	64.4(0.87)
16	$Cu(H(5SP))ClO_4 \cdot 1^1/_2H_2O$	c	15.7(2.13)	25.5sh	31.2(3.29)	64.9(0.64)
17	$Cu(H(5SP))PF_4 \cdot H_2O$	MeOH	16.0(2.43)	25.8sh	30.8(3.36)	100(1.06)
18	$Cu_2(H_2(5SP))Cl_4 \cdot H_2O$	MeOH	13.0sh	15.3(2.00)	25.5sh	193(0.66)

[a] sh = shoulder. The two complexes *11* and *14* are not soluble in suitable solvents for the measurements. [b] At 25 °C and figures in parentheses are concentration in 10^{-3} mol/dm^3. The same solvents were used for the measurements of absorption spectra and electric conductivities. [c] A 1:1 mixture of water and ethanol. EtOH = ethanol, MeOH = methanol.

The free ligand H_2 (65O) shows fairly strong bands at 1130 and 1144 cm^{-1}, which are assigned to ν(C–O) of an ether group [10]. In complex *5* these bands shift below 1110 cm^{-1} indicating participation of the ether-O atom in coordination. The corresponding bands of *4* are obscured by those of ClO_4. Complex *4* shows two strong bands at 1064 and 1117 cm^{-1}, suggesting coordination of ClO_4 [9], while a single, broad, strong band near at 1100 cm^{-1} was observed for the other perchlorate complexes indicating no coordination of ClO_4. Identification of ν(C–S) is difficult because of the complicated spectral patterns in the region where ν(C–S) is expected to appear.

-The magnetic moments of the dimers Cu_2L^{2+} are all subnormal at room temperature and depend upon the amides and anions. The moments of the perchlorate complexes are usually smaller than those of the corresponding chloride complexes. The complexes where the chelate ring adjacent to the amide N atom (ring B in Structure I) is five membered have more reduced moments than those where the ring is six membered (for instance, *1* vs. *3* and *6* vs. *8*). These trends are the same as those of the previously-studied copper(II) complexes of the oxamides with substituents containing only nitrogen donors. The presence of S-donor on the N-substituents of oxamide affects the magnetic moments in a reserved manner.

The electronic spectral data for the complexes in the solid state and solutions are given in Tables III and IV and in Fig. 1. All the complexes have one broad ligand field transition in the visible region. The energies of the transition depend upon the anions in the solid state. The peak positions of the transitions are generally observed at lower energies for the chloride complexes than for the corresponding other-ion complexes. The chloride ions seem to interact with copper(II) ions (Table IV, ν(Cu–X)), which results in a tetragonal or square pyramidal geometry and then in a lower energy d–d transition. It is also accompanied by a decrease in the magnetic interaction between the copper ions. Higher energy shifts of the transitions of the solution spectra observed for

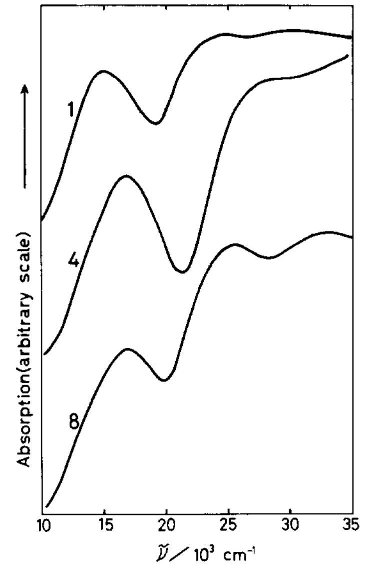

Fig. 1. Electronic spectra of the complexes in the solid state (nujol mulls); 1: $Cu_2(5S)(NO_3)_2$, 4: $Cu_2(65O)(ClO_4)_2$, and 8: $Cu_2(65S)(ClO_4)_2 \cdot 4H_2O$.

TABLE IV. Magnetic Moments, Electronic and Infrared Spectra of the Complexes.

Complex		μ_{eff}[a] (B.M.)	Electronic[b]				Infrared[c], cm^{-1}		
			$\nu_{max}/10^3$ cm^{-1}				ν(CO)	ν(CN)	ν(Cu–X)
1	$Cu_2(5S)(NO_3)_2$	0.84	14.9	24.8	30.6		1633 1638sh	1330	363
2	$Cu_2(5S)Cl_2$	0.86	14.0	23.6	28.7		1616 1641	1320	348
3	$Cu_2(6S)(NO_3)_2$	1.17	14.5	23.8sh	28.6		1606	1326	334
4	$Cu_2(65O)(ClO_4)_2$	1.23	16.8	28.6			1623	1326	
5	$Cu_2(65O)Cl_2 \cdot 1/4H_2O$	1.17	14.7	27.5			1619	1327	313
6	$Cu_2(55S)(ClO_4)_2 \cdot 1^1/_2H_2O$	0.89	16.5	26.2	32.5		1662	1302	
7	$Cu_2(55S)Cl_2$	1.29	15.0	26.2	32.0sh		1655	1318	251
8	$Cu_2(65S)(ClO_4)_2 \cdot 4H_2O$	1.07	16.8	25.4	33.2		1625	1324	
9	$Cu_2(65S)Cl_2$	1.30	15.6	24.8	29.7		1610	1315 1324	190
10	$Cu_2(H_2(5S5))Cl_4 \cdot 2H_2O$	1.21	14.0	24.0	30.0		1630	1324	357
11	$Cu_2(5S6)(BPh_4)_2 \cdot 2H_2O$	0.96	17.2	24.0	31.0		1642	1325	
12	$Cu_2(6S5)(ClO_4)_2 \cdot 2H_2O$	1.10	16.7	24.3	32.0		1611	1326	
13	$Cu_2(6S5)Cl_2$	1.40	12.7	24.5sh	28.0sh		1610	1321	312
14	$Cu_2(6S5)(BPh_4)_2 \cdot 2H_2O$	1.18	16.9	23.9	31.7		1609	1321	
15	$Cu_2(5SP)(ClO_4)_2 \cdot 3H_2O$	0.81	17.1	24.2	30.0		1639	1325	
16	$Cu(H(5SP))ClO_4 \cdot 1^1/_2H_2O$	1.31	15.6 10.5sh	25.0sh	30.5		1629 1672	1325 1504	
17	$Cu(H(5SP))PF_6 \cdot H_2O$	1.20	8.3	14.9	25.0	30.0	1620 1672	1323 1501	
18	$Cu_2(H_2(5SP))Cl_4 \cdot H_2O$	1.89	13.5	21.4	28.5		1663 1695	1512	292

[a] At room temperature. [b] Nujol mull. sh = Shoulder. [c] Nujol mull. ν(CO) = Asymmetric stretching vibration of an amide group and ν(CN) = symmetric one. X = Cl, ONO_2.

some cases indicate dissociation of the coordinated anions and the geometries of complexes in solutions are almost square planar. These properties are not significantly different from those of the copper complexes containing no sulfur donors [5].

In the near ultraviolet region the complexes (except *4*, *5*, and *18*) show two bands (Tables III and IV and Fig. 1), in contrast with the previously-reported complexes containing no sulfur donors (Structure I: Y, Z = nitrogen donor) [5]. In this region the copper(II) complexes with structure I show, usually, one characteristic band due to the oxamide bridged copper(II) skeleton [5] (structure I; the part of fused twin chelate rings A and A′) and those coordinated with sulfur donors show S to Cu charge transfer transitions [11]. The two bands observed for the new complexes are therefore caused by the above two origins. The two complexes *4* and *5* (containing no S donor, Fig. 1) show only one band in this region and the band should originate in a dimeric copper(II) skeleton bridged by an oxamide moiety (Structure I).

So far we have discussed general properties of the complexes Cu_2L^{2+}, but as indicated above there are some exceptions. The analytical results of the complex *10* give the composition $Cu_2(H_2(5S5))Cl_4 \cdot 2H_2O$ but the amide bands are similar to those of the Cu_2L^{2+} type complexes (Table IV) and no ν(NH) band of an amide group is present. The electronic and magnetic properties are also consistent with those of the complexes of structure I. The electronic spectrum is similar to the complex *2*, indicating a similar chromophore. The formulation $Cu_2[\text{-}CONCH_2CH_2SCH_2CH_2\text{-}NH(CH_3)_2Cl^-]_2Cl_2 \cdot 2H_2O$ should be more proper where the terminal tertially amino groups are protonated and the ligand behaves like $H_2(5S)$. A band at 2710 cm^{-1} may be $\nu(\overset{+}{N}-H)$ and arise from the $\text{-}CH_2\text{-}\overset{+}{N}H(CH_3)_2$ group [13].

There is a problem for complexes *16* and *17*, which are formulated as monomers on the basis of the analytical data. The subnormal magnetic moments suggest the presence of Cu–Cu interaction and the electronic spectra show two bands in the near ultraviolet region like the Cu_2L^{2+} type complexes with structure I. The infrared spectra suggest the presence of a protonated amide group (Table IV and ν(NH) at 3345 (for *16*) or 3337 cm^{-1} (for *17*)) and of the deprotonated groups coordinating in the mode of structure I. One plausible formulation is $Cu_2(5SP)(ClO_4)_2(H_2(5SP))\cdot 3H_2O$ (*16*) or a similar one (*17*) where the deprotonated ligand forms a dimeric skeleton (structure I) and the other protonated one is either coordinated through pyridine-N and/or thioether-S, or merely incorporated in a crystal lattice.

Complex *18* gives the amide bands at unusually high frequencies (Table IV and ν(NH) at 3384 cm^{-1}) (free $H_2(5SP)$ gives the amide bands at 1654 and 1530 cm^{-1} and ν(NH) at 3308 cm^{-1}) and this is magnetically-normal at room temperature. The electronic spectrum differs significantly from those of the others: in solution only one band is present in the near ultraviolet region. On the basis of these data it can be proposed that the amide group of $H_2(5SP)$ is not involved in coordination. The copper(II) ion seems to be coordinated through pyridine-N and thioether-S atoms: the higher frequency shifts of the bands due to the pyridine ring (at 1600, 646, and 429 cm^{-1}) are observed (the bands are at 1591, 629, and 404 cm^{-1} for free $H_2(5SP)$). The two bands at 21.4 and 28.5 $\times 10^3$ cm^{-1} of the electronic spectrum of the solid state may be due to S to Cu and/or Cl to Cu charge transfer bands. The band ν(Cu–Cl) also exists (Table IV).

Experimental

Measurements

Measurements were carried out by the methods reported previously [4, 5].

Synthesis of the Ligands

An ethanol solution (10 ml) of 0.05 mol of diethyl oxalate was added dropwise to an ethanol solution (20 ml) of 0.10 mol of an appropriate amine, and the mixture was heated on a steam bath for 2 h. The resulting solution was divided into ten portions and used for the preparation of further complexes. Upon cooling the reaction mixture, a small amount of a white solid was obtained for some cases. The isolation resulted in low yields, and therefore was not further studied.

Synthesis of the Complexes

(A) An ethanol solution (50 ml) of 0.01 mol of copper(II) chloride was added with stirring to an ethanol solution (50 ml) of 0.005 mol of the ligand to precipitate a micro-crystalline powder. The precipitate was washed with ethanol and dried *in vacuo* over calcium chloride.

(B) An aqueous solution (50 ml) of 0.01 mol of copper(II) nitrate was added with stirring to an aqueous solution (20 ml) of 0.005 mol of the ligand; to the mixture was added an aqueous solution (10 ml) of 0.01 mol of sodium hydroxide. A small amount of copper hydroxide precipitated and was removed by filtration. To the filtrate (warmed to 60 °C) was added a solution of 0.02 mol of sodium perchlorate dissolved in the minimum amount of water. Upon cooling the complex crystallized. The filtered complex was dried in air.

(C) The perchlorate complex (0.01 mol) prepared above was dissolved in a mixture of water and ethanol (1:2, 200 ml) and to the solution was added 0.02 mol of sodium tetraphenylborate dissolved in 10 ml of ethanol. An aqueous solution of the intermediate nitrate prepared in (B) could be used. The product was recrystallized by dissolving it in a mixture of acetone, ethanol, and water (1:1:1) and then cooling the solution.

(D) A mixture of 0.01 mol of copper(II) chloride and 0.005 mol of the ligand in 100 ml of water was warmed to 70 °C and to this was added 0.01 mol of sodium hydroxide dissolved in 10 ml of water. The solution was filtered while hot and allowed to cool. The crystals formed were recrystallized from water.

(E) To the solution of the intermediate nitrate prepared as (B) was added 0.02 mol of sodium hexafluorophosphate dissolved in the minimum amount of water to give immediately a precipitate. The precipitate was recrystallized from methanol.

(F) A similar procedure as for (A) was employed, using copper(II) perchlorate.

(G) A similar procedure as for (A) was employed, using copper(II) nitrate.

(H) Sodium hydroxide was added cautiously, with stirring, to a mixture of 0.01 mol of copper(II) perchlorate and 0.005 mol of the ligand in 200 ml of ethanol until the cloud formed was retained for a few seconds. The solution was filtered and the filtrate was allowed to stand. Crystals obtained were dried in air.

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