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Synthesis of Copper(II) and Nickel(II) Complexes of Several N-Monosubstituted Oxamide Derivatives

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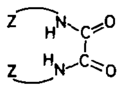
Some nickel(II) and copper(II) complexes have been prepared with N-monosubstituted oxamide derivatives: $HO(CH_2)_nNHCOCONH_2$ *[n = 2(*H_3*heo) and n = 3(*H_3*hto)],* $2\text{-}C_5H_4N\text{-}(CH_2)_n\text{-}NHCOCONH_2$ *[n = 1(*H_2*pmo) and n = 2(*H_2*peo)], and* $NH_2COCONH(CH_2)_nNHCOCONH_2$ *[n = 2(*H_4*edo) and n = 3(*H_4*tdo)]. In the diamagnetic, square-planar* $Na_2[Ni(Hheo)_2]\cdot H_2O$, $Na_2[Ni(Hhto)_2]\cdot 2H_2O$, $Na_2[Ni(tdo)]\cdot 4H_2O$, *and* $Na_2[Ni(edo)]$*, the bidentate Hheo and Hhto are coordinated via two deprotonated amide-N atoms without coordination of a terminal alcohol group and the quadridentate tdo and edo via all four deprotonated amide-N atoms. In* $[Cu(Hpmo)X]\cdot mH_2O$ *and* $[Cu(Hpeo)X]\cdot mH_2O$ *(X = Cl, Br) coordination atoms are pyridyl-N, primary amide-O, and deprotonated secondary amide-N atoms, while all the three nitrogen atoms of pmo are coordinated in* $Na[Cu(pmo)OH]\cdot 4H_2O$*. The magnetically subnormal* $Na[Cu(hto)]\cdot 2H_2O$ *alone seems to be a dimer bridged by an alkoxide-O atom.*

Introduction

Symmetrically N,N′-disubstituted oxamide derivatives [I] (Z = donor atom) are very interesting ligands forming the following three types of complexes: in the monomeric complexes [II] (M = Cu, Ni) these oxamides coordinate as simple linear quadridentate ligands, while in the complexes [III] and [IV] (M, M′ = Cu, Ni) they bridge two metal ions either symmetrically or unsymmetrically [1].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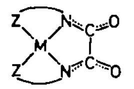
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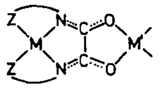
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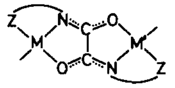
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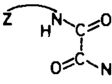
The oxamide moiety bridging two metal ions as in [III] and [IV] serves as a pathway through which electron spin interaction takes place and their copper complexes (M = M′ = Cu) are magnetically subnormal. It is interesting to investigate how N-monosubstituted oxamide derivatives [V] and [VI] behave as ligands in their copper(II) and nickel(II) complexes.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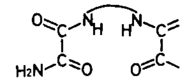
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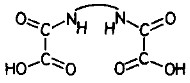

VII

Several new complexes are, therefore, synthesized and characterized, but the ligands are found to be less capable of bridging metal ions.

The abbreviations used in this report are given below:

The ligands of the type V.	
N-(2-hydroxyethyl)oxamide	H_3heo
N-(3-hydroxypropyl)oxamide	H_3hto
N-(2-pyridylmethyl)oxamide	H_2pmo
N-[2-(2-pyridyl)ethyl]oxamide	H_2peo
The ligands of the type VI	
1,3-trimethylenebis(oxamide)	H_4tdo
1,2-ethylenebis(oxamide)	H_4edo
The ligand of the type VII	
1,3-trimethylenebis(oxamic acid)	H_4tba

Experimental

Synthesis of the Ligands

Melting points and analytical data are given in Table I.

An ethanol solution of an appropriate amine and of ethyl oxamate was mixed in a required molar ratio and the mixture was heated on a steam bath for a few hours. A white precipitate was collected and washed with ethanol, and then dried in air. The ligands except H_4tdo and H_4edo were recrystallized from ethanol. The yiled was 80–95%.

TABLE I. Melting Points and Analytical Data for the Ligands.

Ligand	M.P.(°C)[a]	Analysis, Found (Calcd.) %		
		C	H	N
H_3heo	167–169	36.18(36.36)	5.90(6.10)	21.12(21.20)
H_3hto	168–169.5	41.03(41.09)	6.81(6.90)	19.51(19.17)
H_2pmo·1/4H_2O	152–153	52.27(52.31)	5.05(5.21)	22.78(22.87)
H_2peo	194–195	55.91(55.95)	5.99(5.74)	21.63(21.75)
H_4edo	330(dec)	35.67(35.65)	5.05(4.99)	26.89(27.71)
H_4tdo	314(dec)	38.62(38.89)	5.54(5.59)	26.08(25.91)

[a]dec = decomposition.

TABLE II. Colours and Analytical Data for the Complexes.

Complex	Colour	Analysis, Found(Calcd.) %				
		M	N	H_2O	Other	
1 $Na_2[Ni(Hheo)_2]\cdot H_2O$	Yellow–Orange	15.25 (15.33)	14.71 (14.63)	4.87 (4.70)		
2 $Na_2[Ni(Hhto)_2]\cdot 2H_2O$	Yellow–Orange	13.50 (13.68)	13.28 (13.06)	8.66 (8.40)		
3 $Na[Cu(hto)]\cdot 2H_2O$	Reddish Violet	23.61 (23.92)	10.38 (10.54)	13.34 (13.56)		
4 $[Cu(Hpmo)Cl]\cdot 3/2H_2O$	Blue	20.92 (20.89)	13.70 (13.81)	8.99 (8.88)	Cl: 11.95 (11.65)	
5 $[Cu(Hpmo)Br]\cdot H_2O$	Greenish Blue	18.75 (18.71)	12.45 (12.37)	5.12 (5.30)	Br: 23.74 (23.53)	
6 $[Cu(Hpeo)Cl]\cdot H_2O$	Blue	20.57 (20.55)	13.35 (13.59)	[a] (5.83)	Cl: 11.27 (11.47)	
7 $[Cu(Hpeo)Br]$	Bluish Green	18.96 (18.93)	12.75 (12.52)		Br: 24.11 (24.81)	
8 $Na[Cu(pmo)OH]\cdot 4H_2O$	Violet	17.81 (18.01)	11.94 (11.91)	21.19 (20.43)		
9 $[H(H_2peo)]_2[CuBr_4]\cdot 2H_2O$	Dark Violet	7.89 (7.89)	10.31 (10.43)	4.50 (4.47)	Br: 40.76 (39.68)	
10 $Na_2[Ni(edo)]\cdot 4H_2O$	Yellow	19.19 (19.38)	18.33 (18.50)			
11 $Na_2[Ni(tdo)]\cdot 4H_2O$	Orange–Yellow	14.90 (15.09)	14.47 (14.41)	18.67 (18.53)		
12 $Na_2[Cu(tba)]\cdot 6H_2O$	Reddish Violet	14.80 (14.72)	6.77 (6.49)	25.13 (25.03)	C: 19.23 (19.47)	H: 4.03 (4.20)
13 "$Na_2[Cu(edo)]\cdot 3/2H_2O$"[b]	Violet	18.65 (18.99)	14.94 (16.74)	8.20 (8.07)		

[a]Decomposed without dehydration. [b]Impure and an approximate composition.

Synthesis of the Complexes

Colours and analytical data are given in Table II.

$[Cu(Hpmo)Cl]\cdot 3/2H_2O$.

To an ethanol solution (150 ml) of H_2pmo (1.0 g) was added an ethanol solution (50 ml) of copper chloride (0.85 g) and the mixture was allowed to stand at room temperature for a few hours. Blue crystals were collected and recrystallized from water to give 0.82 g.

The two complexes, $[Cu(Hpmo)Br]\cdot H_2O$ and $[Cu(Hpeo)Cl]\cdot H_2O$ were prepared in a similar manner but could not be recrystallized from water.

$[H(H_2peo)]_2[CuBr_4]\cdot 2H_2O$ and $[Cu(Hpeo)Br]$

A warm ethanol solution (200 ml) of H_2peo (2.0

TABLE III. Magnetic Moments and Solid Electronic Spectra of the Complexes.

Complex	μ_{eff} (B.M.)[a]	Absorption Maxima, × 10^3 cm^{-1}
1 $Na_2[Ni(Hheo)_2]\cdot H_2O$	Dia.[b]	22.5sh[c] 28.4
2 $Na_2[Ni(Hhto)_2]\cdot 2H_2O$	Dia.	22.5sh 29.2
3 $Na[Cu(hto)]\cdot 2H_2O$	0.45	18.5 21.0sh 28.5
4 $[Cu(Hpmo)Br]\cdot H_2O$	1.86	14.3 31sh
5 $[Cu(Hpmo)Cl]\cdot 3/2H_2O$	1.82	14.2 30sh
6 $[Cu(Hpeo)Cl]\cdot H_2O$	1.85	14.2 31sh
7 $[Cu(Hpeo)Br]$	1.78	14.6 28sh
8 $Na[Cu(pmo)OH]\cdot 4H_2O$	1.78	17.1 27.0sh
9 $[H(H_2peo)]_2[CuBr_4]\cdot 2H_2O$	1.84	9.5br 16.4 18.6 23.5sh 29br
10 $Na_2[Ni(edo)]$	Dia.	23.0sh 24.2sh 27.5sh 28.7
11 $Na_2[Ni(tdo)]\cdot 4H_2O$	Dia.	23.0sh 26.5sh 29.2
12 $Na_2[Cu(tba)]\cdot 6H_2O$	1.85	18.5 20.5sh
13 "$Na_2[Cu(edo)]\cdot 3/2H_2O$"	1.8[d]	18.4

[a] At room temperature. [b] Dia. = diamagnetic. [c] sh = shoulder and br = broad. [d] An approximate value.

g) was mixed with an ethanol solution (50 ml) of copper bromide (2.23 g) and the mixture was filtered. After the filtrate was allowed to stand at room temperature, dark violet crystals (1.15 g) were separated, which were washed with ethanol and dried under vacuum.

The mother liquor afforded bluish green second crops (0.83 g) on standing overnight. The product was washed with ethanol and dried in air.

$Na[Cu(pmo)OH]\cdot 4H_2O$

To an aqueous solution (30 ml) of 1.0 g of H_2pmo and 0.85 g of copper chloride was added 0.8 g of sodium hydroxide dissolved in water (10 ml). The mixture was filtered and allowed to stand at room temperature. Violet crystals (1.0 g) were obtained.

$Na_2[Cu(tba)]\cdot 6H_2O$

To an aqueous solution (200 ml) of H_4tdo (2.16 g) and copper sulfate (2.5 g) was added dropwise an aqueous solution (50 ml) of sodium hydroxide (1.6 g) on a steam bath and the mixture was heated for 30 minutes to complete reaction. The resulting solution was filtered while hot and the residual solid was extracted twice with hot water (50 ml). The combined aqueous extracts and filtrate were concentrated under reduced pressure to give reddish purple crystals, which were recrystallized from hot water to give 2.3 g.

$Na_2[Ni(tdo)]\cdot 4H_2O$ and $Na_2[Ni(edo)]$ were prepared by this method. The yield was *ca.* 1.9 g.

$Na[Cu(hto)]\cdot 2H_2O$

To an aqueous solution (150 ml) of copper sulfate (3.2 g) and H_3hto (1.9 g) was slowly added with stirring an aqueous solution (20 ml) of sodium hydroxide (2.0 g) to give red crystals (3.0 g). The product was washed with water and dried in air.

$Na_2[Ni(Hhto)_2]\cdot 2H_2O$

Nickel(II) acetate (2.5 g) and H_3hto(3.0 g) were dissolved in hot water (50 ml), and to the solution was added sodium hydroxide (2.0 g) dissolved in a small amount of water. The resulting mixture was filtered and addition of ethanol (25 ml) to the filtrate gave yellow crystals (2.0 g), which were dried in air.

$Na_2[Ni(Hheo)_2]\cdot H_2O$ was obtained by this method.

Measurements

The methods and apparatus of measurements were reported in a previous paper [2].

Results and Discussion

The complexes of H_3hto and H_3heo

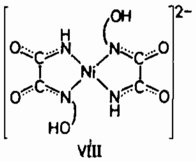
The nickel(II) complexes $Na_2[Ni(Hheo)_2]\cdot H_2O$ and $Na_2[Ni(Hhto)_2]\cdot 2H_2O$ are diamagnetic and show electronic spectra characteristic of square-planar nickel(II) complexes (Table III) [3]. The spectra are fairly identical to that of $Na_2[Ni(tdo)]\cdot 4H_2O$ discussed below (see Figure).

The infrared spectra of the two free ligands show the bands due to ν(NH) and ν(OH) at 3220, 3317, and 3383(H_3heo) and at 3215, 3322, and 3395-H_3hto) cm^{-1}, and these bands shifted to lower frequencies upon deuteration by *ca.* 800 cm^{-1}. The complexes show a sharp band assignable to ν(NH) at 3371(Hheo) and 3377(Hhto) cm^{-1} of a deprotonated N-coordinated primary amide group, the latter band of which shifted to 2489 cm^{-1} upon deuteration [4, 5]. Another broad bands at 3195(Hheo) and 3170(Hhto) cm^{-1} may be due to ν(OH) of alcohol groups and water.

The bands mainly due to ν(C–O) of an alcohol group in the complexes are at 1063(Hheo) and 1050-(Hhto) cm^{-1}, and the positions are close to 1051 cm^{-1} of H$_3$heo and 1043 of H$_3$hto, respectively. Therefore, the alcohol groups seem to be not coordinated to nickel ions.

Both the ligands have two different types of amide groups: a primary and a secondary amide group in the molecules. In the infrared spectra, the amide groups show characteristic bands useful to deduce the mode of coordination of the groups [4–6]. In the region where ν(C=O) and δ(NH$_2$) of the primary, and the amide I band of the secondary amide group are expected to appear, broad bands at 1653 and 1601 (H$_3$heo), and at 1656, 1612sh, and 1601(H$_3$hto) cm^{-1} are observed. The amide II bands of the secondary group are at 1543(H$_3$heo) and at 1545 (H$_3$hto), and the amide III band at 1253(H$_3$heo) and at 1245 cm^{-1} (H$_3$hto). The bands of ν(C–N) of the primary group were observed at 1416(H$_3$heo) and 1415(H$_3$hto) cm^{-1}. In the complexes these bands changed as shown below.

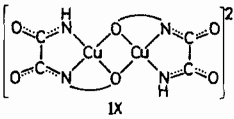
In the region of the amide I and ν(C=O) bands the complexes show broad bands at 1614 and 1599-(Hheo), and at 1612 and 1598sh cm^{-1}(Hhto). The ν(C–N) bands shifted to higher frequencies at 1433-(Hheo) and 1436(Hhto), and the secondary groups show characteristic bands at 1358(Hheo), and at 1356(Hhto) cm^{-1} instead of the amide II and III bands. These spectral changes of the amide groups indicate that both the primary and the secondary amide groups are coordinate through the N atoms with deprotonation [4–6]. Therefore, structures VIII are proposed for the two nickel(II) complexes.



VIII

Different from nickel(II), copper(II) formed only the complex Na[Cu(hto)]·2H$_2$O with the fully deprotonated ligand, hto, and no corresponding complex of heo was isolated. This fact agrees with the experimental rule that bridging of copper(II) with a terminal alkoxide-O atom of a ligand is more favourable for a fused 5-6 than for a similar 5-5 membered chelate ring [7].

The infrared spectrum of anhydrous Na[Cu(hto)] shows only one sharp band at 3338 cm^{-1} (for the deuterated complex at 2462), characteristic ν(N–H) of a deprotonated, N-coordinated primary amide group [4]. The other amide bands are very similar to those of the above nickel(II) complex, and the coordination mode of the groups is identical to that in the nickel(II) complex (Structure VIII). The absence of ν(O–H) of the alcohol group and the appearance of ν(C–O) at a lower frequency (at 1005 cm^{-1}) suggest Structure IX containing an alkoxide-O bridge, because bridge-formation by an alkoxide-O atom results in lowering of the ν(C–O) frequency [8].



IX

This is in consistent with the fact that the ν(C–O) of a phenol group shifts to a lower frequency when the O atom is involved in bridges between copper atoms [2]. Structure IX is also confirmed by a subnormal magnetic moment (0.45 B.M.) (Table III).

The *d–d* transition at a fairly high energy (18.5 X 10^3 cm^{-1}) of Na[Cu(hto)]·2H$_2$O suggests nearly square-planar coordination [9] and a pronounced absorption at 28.5 X 10^3 cm^{-1} (Fig. and Table III) is indicative of the presence of an alkoxide-O bridge between copper atoms (Structure IX). The band is attributed to a charge transfer transition between the copper and bridged oxygen atoms [10].

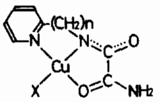
The Complexes of H$_2$pmo and H$_2$peo

The two ligands formed only copper(II) complexes and from ethanol solutions [Cu(Hpmo)X]·mH$_2$O and [Cu(Hpeo)X]·mH$_2$O (X = Cl, Br), and [H(H$_2$-peo)]$_2$[CuBr$_4$]·2H$_2$O were easily obtained. From a basic aqueous solution Na[Cu(pmo)OH]·4H$_2$O was obtained but no peo complex was isolated purely. All these complexes are magnetically normal (Table III) and show electronic spectra observed for common six-coordinate copper(II) complexes [11] except [H(H$_2$peo)]$_2$[CuBr$_4$]·2H$_2$O. [Cu(Hpmo)X]·mH$_2$O and [Cu(Hpeo)X]·mH$_2$O (X = Cl, Br) show a shoulder in the near ultraviolet region (Table III), which may be a charge transfer transition between halogen and copper atoms, suggesting coordination of a halogen atom (X) [12]. This is also suggested by the presence of several halogen-sensitive infrared spectral bands [12] in the region 400–200 cm^{-1}.

The exceptional complex [H(H$_2$peo)]$_2$[CuBr$_4$]·-2H$_2$O has an electronic spectrum similar to that of distorted tetrahedral [Bu$_4^n$N]$_2$[CuBr$_4$] [13]. The tetrahedral structure of [H(H$_2$peo)]$_2$[CuBr$_4$]·2H$_2$O is also supported by ν(Cu–Br) observed at 218 cm^{-1}, a frequency characteristic [14] of tetrahedral [CuBr$_4$]$^{2-}$.

In the infrared spectra, the amide bands of H$_2$pmo and H$_2$peo are similar to those of H$_3$heo and H$_3$hto. For [H(H$_2$peo)]$_2$[CuBr$_4$]·2H$_2$O, non-coordination of H$_2$peo was confirmed by the characteristic amide bands observed at 1663, 1632, 1620 [amide I, ν(C=O), and δ(NH$_2$)], 1534(amide II), 1409[ν(C–N)], and 1247(amide III) cm^{-1}, which are close to those of free H$_2$peo at 1659(very broad), 1544, 1410, and 1239 cm^{-1}. In [Cu(Hpeo)Cl]·H$_2$O the amide I was observed at 1642 and the amide II and III bands disappeared, instead of which a new band at 1366 cm^{-1} was observed to show N-coordination of the secondary amide group [5].

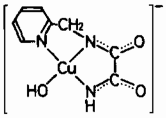
The bands due to the primary amide group are found as follows: ν(N–H) at 3385 and 3272, ν(C=O) at 1679, $\delta(NH_2)$ at 1594, and ν(C–N) at 1450 cm^{-1} to show O-coordination of the group and they shifted to 2560 and 2403 [ν(N–D)], 1669 [ν(C=O)], and 1448 cm^{-1} [ν(C–N)] in the amide-N deuterated complex. In addition, coordination of pyridine-N atom was confirmed by the higher frequency shifts of the bands at 408, 633, 1596 cm^{-1} of free H_2peo to 426, 650sh, 1609 cm^{-1} in the complex [15]. Thus Structure X was assumed.



X

The other complexes of this type show similar infrared spectral features indicating a similar structure.

The anhydrous Na[Cu(pmo)OH] obtained by dehydration of Na[Cu(pmo)OH]·$4H_2O$ at 110 °C has ν(OH) at 3615 and ν(NH) at 3330 cm^{-1} as a very sharp band [16], and the amide I and ν(C = O) at 1642 and 1595 cm^{-1}. However, other bands are difficult to be assigned because of the complicated spectral pattern very different from those of the free ligand and the complexes discussed above. In the electronic spectrum the absorption maximum of this complex (Table III) is at a higher frequency by *ca.* 2.7×10^3 cm^{-1} than that of [Cu(Hpmo)Cl]·$3/2H_2O$ to suggest coordination of strong field amide-N atoms and no pronounced shoulder in the near ultraviolet region is present. Structure XI is, therefore, the most probable one.



XI

The Complexes of H_4tdo and H_4edo

The infrared spectral bands of amide groups of the free ligands are close to those of the other free ligands discussed above and the spectral changes caused by coordination to nickel are similar to those observed for the above nickel complexes. Therefore, both the primary and the secondary amide groups are coordinated via the deprotonated amide-N atoms. The electronic spectra of diamagnetic Na_2[Ni(edo)] and Na_2[Ni(tdo)]·$4H_2O$ in the solid state are those of square-planar nickel(II) complexes (Table III and Figure) and Structure XII is proposed [3].

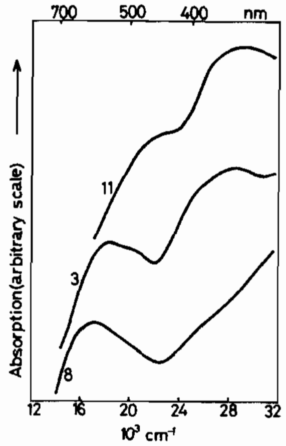
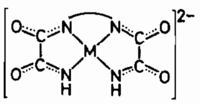
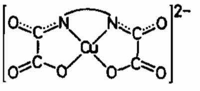


Figure. Electronic spectra of the solid complexes: 3, Na[Cu(hto)]·$2H_2O$; 8, Na[Cu(pmo)OH]·$4H_2O$; and 11, Na_2[Ni(tdo)]·$4H_2O$.



XII

The reaction of H_4tdo with copper(II) sulfate in water resulted in hydrolysis of the terminal primary amide groups and the copper complex coordinated with 1,3-trimethylenebis(oxamate) (tba), Na_2[Cu(tba)]·$6H_2O$ was obtained, which is characterized as follows. This complex was also prepared from diethyl 1,3-trimethylenebis(oxamate) [17]. The magnetic moment is normal and the electronic spectrum shows that it is nearly square-planar [9]. The infrared spectrum shows no band assignable to ν(N–H), which is observed at 3293 cm^{-1} for Na_2[Ni(tdo)] (anhydrous). The infrared spectra of the two complexes differ from each other in other regions. Structure XIII is, therefore, borne out.



XIII

The ligand H_4edo could not give any pure copper(II) complex and the precipitate obtained approximates to Na_2[Cu(edo)]·$3/2H_2O$ (Tables II and III).

Conclusion

The oxamide ligands studied here are very different from those previously reported [1], symmetrically N,N′-disubstituted oxamides (Formula I), in that the latter ligands form binuclear complexes where the oxamide moiety acts as a bridge between two metal ions (Formulae III and IV), whereas the former N-monosubstituted derivatives cannot act as a bridge. The difference may be due to the number of potential chelate rings formed, since N-monosubstituted derivatives have only one arm forming a fused chelate ring and may lack the ability to chelate with a second metal ion.

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