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Preparation and Properties of Copper(II) Complexes with N,N-disubstituted-2-aminoethanol-N-oxides

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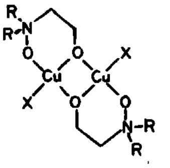
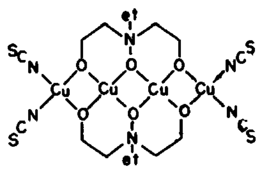
Ten new copper(II) complexes with N,N-disubstituted-2-aminoethanol-N-oxide (HRR'-O) were synthesized. With one exception, they were formulated as Cu(RR'-O)X, (where X = Cl, Br, NCS), on the basis of elemental analyses. They and some similar complexes already reported were investigated by IR, UV and magnetic measurements, and were concluded to be of the binuclear structure I. N-Ethyl-N-2-hydroxyethyl-2-aminoethanol-N-oxide (et·H_2eta-O) forms two types of copper(II) complexes; one is a homologue of the above mentioned complexes, and the other is formulated as Cu_2(et·eta-O)$(NCS)_2$, for which the tetranuclear structure II was proposed.

Introduction

The preparation of copper(II) complexes with N,N-dialkyl-2-aminoethanol-N-oxides and chloride or bromide ions was already reported, and the binuclear structure I was proposed for these complexes.[1]



Structure I



Structure II

In the present study, using the same ligands, we prepared a series of SCN-coordinated copper(II) complexes. We also obtained new copper(II) complexes with N-alkyl-N-2-hydroxyethyl-2-aminoethanol-N-oxide and a mononegative ion (Cl^-, Br^- and NCS^-). Since magnetic susceptibilities were measured only at room temperature in the previous study[1], the measurements were carried out in the present study over the temperature range from liquid nitrogen temperature to room temperature, in order to confirm the binuclear structure and to investigate the spin exchange interaction between copper ions.

Experimental

N-Alkyl-N-2-hydroxyethyl-2-aminoethanol-N-oxide (abbreviated at R·H_2eta-O, where R = CH_3, C_2H_5). Five grams of N-alkyl-N-2-hydroxyethyl-2-aminoethanol was dissolved in 3% aqueous hydrogen peroxide, and allowed to stand overnight at room temperature. The solution was evaporated under reduced pressure until almost colorless syrup was obtained. This was used for the preparation of complexes without further purification.

Cu(me·Heta-O)Cl (me·H_2eta-O represents $CH_3N(O)(CH_2CH_2OH)_2$; hereafter similar abbreviations are used)

One gram of $CuCl_2\cdot2H_2O$ was dissolved in 20 ml of DMF, and warmed at 50°C. To this solution 1.6 g of $CH_3N(O)(CH_2CH_2OH)_2$ was added with stirring. When the solution was allowed to stand at room temperature for several hours, green fine crystals were separated out, which were filtered and washed with DMF several times. The temperature of the solution should not be raised above 65°C, otherwise dissociation of the N-oxide would take place.

Cu(me·Heta-O)Br

This compound was prepared by a method similar to that for the chloro homologue, except for using $CuBr_2$ instead of $CuCl_2\cdot2H_2O$ and 1:1 mixture of methanol and DMF instead of pure DMF.

Cu(R·Heta-O)NCS (R = CH_3, C_2H_5)

A warmed methanol solution containing 0.4 g of NH_4SCN was mixed with a methanol solution of 1.0 g $Cu(CH_3COO)_2\cdot H_2O$ and 1.4 g R-$N(O)(CH_2CH_2OH)_2$. The mixture was left at room temperature for several hours, from which the grayish–blue powder (in the case of R = CH_3) or deep blue fine prisms (in the case of R = C_2H_5) was separated out. In the case of R = CH_3, a slight change in the ratio of the starting materials may bring about the formation of the deep green fine crystals of Cu_2(et·eta-O)$(NCS)_2$.

Cu_2(et·eta-O)$(NCS)_2$ (et = C_2H_5)

The procedure is similar to that for Cu(et·Heta-O) NCS except for using 1.0 g of $Cu(ClO_4)_2 \cdot 6H_2O$ (instead of $Cu(CH_3COO)_2 \cdot H_2O$), 0.8 g $C_2H_5N(O)(CH_2CH_2OH)_2$ and 0.2 g NH_4NCS as starting materials. Deep green fine crystals were obtained.

Cu(me_2-O)NCS (me_2-O represents $(CH_3)_2N(O)CH_2CH_2O^-$; hereafter similar abbreviations are used)

A DMF solution containing 0.5 g of $Cu(CH_3COO)_2 \cdot H_2O$ and 0.3 g of $(CH_3)_2N(O)CH_2CH_2OH$ was mixed with a DMF solution of 0.2 g NH_4SCN. After the mixture was kept at room temperature, the blue fine crystals which separated were filtered. For purification the crystals were suspended in methanol and refluxed for 9 hours. Without this procedure, the cryomagnetic data did not fit the theoretical χ_A–T curve.

Cu(R_2-O)NCS (R = C_2H_5, C_3H_7)

The procedures are similar to that for the methyl homologue.

Cu(R_2-O)X (R = CH_3, C_2H_5; X = Cl, Br)

These compounds were prepared according to the method described in the previous paper[1].

Magnetic Measurement

Magnetic susceptibilities were measured by the Faraday method over the temperature range from 77°K to room temperature. All the susceptibilities were corrected for the diamagnetism of the constituting atoms by use of the Pascal constants.

Results and Discussion

The elemental analyses of the new compounds are listed in Table I. All the data, except those for the compound (7), agree with the values calculated for Cu(RR′-O)X (where HRR′-O represents N,N-RR′-2-aminoethanol-N-oxide and X is Cl, Br or NCS), for which the binuclear structure I can be assumed as a possible basic structure. The analytical data of the compound (7) fit the formula Cu_2(et·eta-O)$(NCS)_2$, which is compatible with the tetranuclear structure II.

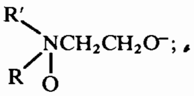
The IR data are shown in Table II. It has been known that the N–O stretching vibration due to a tertiary alkylamine oxide is generally observed around 950 cm^{-1}.[1,3] The present complexes show several bands in the 900~1000 cm^{-1} region with various intensities. This makes it difficult to make definite assignments of ν(N–O). The bands due to the NCS group were observed at 2080~2090 cm^{-1} and 812~821 cm^{-1} for the Cu(RR′-O)NCS type complexes, and at 2105 cm^{-1} and 798 cm^{-1} for Cu_2(et·eta-O)$(NCS)_2$ as shown in Table II. This clearly indicates that NCS is coordinated through nitrogen in both cases[5].

All the complexes show subnormal magnetic moments at room temperature as can be seen in Table II. These values are very low even when compared with other oxygen bridged copper(II) complexes so far reported. The temperature dependence of the magnetic susceptibilities can be interpreted in terms of the Bleaney–Bowers equation based on a binuclear model[4]. Some typical examples are shown in Figure 1. The best fit values of –2J are listed in Table II, where –2J represents an energy difference between the lowest

TABLE I. Elemental Analyses.[a]

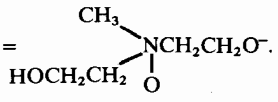
No.	Compound	C (%)		H (%)		N (%)		Cu (%)	
		Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.
(1)	Cu(me·Heta-O)Cl	26.25	25.75	5.28	5.19	6.40	6.01	26.67	27.25
(2)	Cu(et·Heta-O)Cl	29.29	29.16	5.73	5.71	5.80	5.67	25.05	25.71
(3)	Cu(me·Heta-O)Br	21.59	21.63	4.40	4.36	5.10	5.05	23.34	22.89
(4)	Cu(et·Heta-O)Br	24.64	24.71	4.76	4.84	4.85	4.80	21.86	21.79
(5)	Cu(me·Heta-O)NCS	27.64	28.17	4.61	4.73	10.92	10.95	25.32	24.82
(6)	Cu(et·Heta-O)NCS	31.20	31.16	5.57	5.23	9.80	10.38	23.54	23.55
(7)	Cu_2(et·eta-O)$(NCS)_2$	24.51	24.61	3.76	3.36	10.71	10.76	32.48	32.55
(8)	Cu(me_2-O)NCS	26.78	26.60	4.48	4.47	12.45	12.41	29.08	28.15
(9)	Cu(et_2-O)NCS	32.83	33.13	5.55	5.56	11.06	11.04	25.93	25.04
(10)	Cu(pr_2-O)NCS	38.28	38.35	6.43	6.44	9.97	9.94	23.53	22.55

[a] Abbreviations: me = CH_3, et = C_2H_5, pr = C_3H_7, Heta = $HOCH_2CH_2$. (RR′-O) represents



$R'R\overset{}{N}(\to O)CH_2CH_2O^-$;

for example me·Heta-O =



$(CH_3)(HOCH_2CH_2)N(\to O)CH_2CH_2O^-$.

TABLE II. Spectral and Magnetic Data.

No.	Compound	Absorption in DMSO(10^3 cm^{-1})(logε)		Reflectance (10^3 cm^{-1})			ν(NCS) in KBr (cm^{-1})		μ_{eff}[a] (BM)	–2J[b] (cm^{-1})
(1)	Cu(me·Heta-O)Cl	14.4(1.98)	28.3 (3.37)	14.3		28.2			0.70	665[c]
(2)	Cu(et·Heta-O)Cl	14.5(1.98)	28.3 (3.37)	15.2	18.9sh	28.2			0.38	935[c]
(3)	Cu(me·Heta-O)Br	13.7(1.98)	30.3sh (3.30)	14.3		28.6			0.47	840
(4)	Cu(et·Heta-O)Br	14.2(1.99)	39.3sh (3.32)	14.3		27.7			0.59	750
(5)	Cu(me·Heta-O)NCS	14.5(2.05)	29.5 (3.35)	15.6		29.4	2090	820	0.40	925
(6)	Cu(et·Heta-O)NCS	14.7(2.06)	29.4 (3.39)	15.1		29.0	2080	820	0.61	735
(7)	Cu_2(et·eta-O)$(NCS)_2$	14.1(1.97)	30.7sh (3.42)	15.7		28.6	2105	798	0.33	
(8)	Cu(me_2-O)NCS	insoluble		15.6		29.1	2090	820	0.41	910
(9)	Cu(et_2-O)NCS	14.7(2.07)	29.5 (3.50)	15.7		29.1	2080	821	0.26	
(10)	Cu(pr_2-O)NCS	14.7(2.08)	29.7 (3.38)	15.3		29.4	2090	812	0.48	850
(11)	Cu(me_2-O)Cl	14.6(2.09)	28.3 (3.07)	15.1	18.3sh	28.9			0.33	1030
(12)	Cu(et_2-O)Cl	14.5(1.78)	28.5 (3.18)	15.4	18.6sh	28.1			0.30	1030
(13)	Cu(pr_2-O)Cl	14.5(1.84)	28.4 (3.24)	14.9	18.2sh	28.2			0.36	960
(14)	Cu(me_2-O)Br	14.0(1.85)	29.9 (3.02)	15.1	17.9sh	27.5			0.37	955
(15)	Cu(et_2-O)Br	14.2(1.83)	29.5 (3.19)	15.7	18.1sh	27.2			0.31	1030
(16)	Cu(pr_2-O)Br	14.1(1.80)	29.6 (3.12)	14.9	18.2sh	27.0			0.34	990

[a] Calculated according to the equation $\sqrt{8(\chi_A - N\alpha)T}$. [b] $N\alpha = 60 \times 10^{-6}$ and g = 2.10 were assumed unless otherwise noted. [c] $N\alpha = 50 \times 10^{-6}$ was assumed.

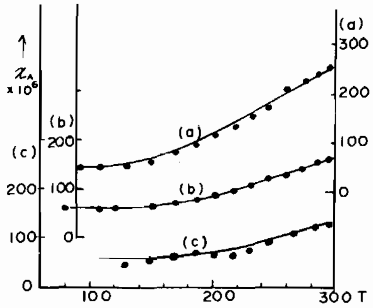
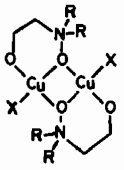


Figure 1. Magnetic susceptibility as a function of temperature: (a) Cu(me·Heta-O)Cl, (b) Cu(me·Heta-O)Br, (c) Cu(me·Heta-O)NCS.

singlet and triplet states. The large –2J values indicate the strong antiferromagnetic interaction between copper ions. It should be noted here that for the complexes where antiferromagnetic interaction is so strong as the present ones the χ_A–T curve may be fitted to a theoretical one based on a tetranuclear and/or poly-(even number)-nuclear model as well as the binuclear model. However, it was already demonstrated in the previous paper[6] that tetranuclear or polynuclear complexes formed by the interaction between binuclear units generally show much higher magnetic moments (>1.4 BM at room temperature) than the present ones (<0.8 BM). Accordingly, it can be concluded that all the complexes (except compound (7)) are essentially binuclear. Thus, the most probable structure is to be assigned to structure I. The alternative structure III seems to be improbable, because the basicity of the N-oxide oxygen is much weaker than that of the alkoxide oxygen.



Structure III

Each of the complexes show a band in the 27~30 kK region in addition to the *d–d* band of copper(II). This band should be the characteric band of oxo-bridged copper complexes with antiferromagnetic interaction, and can be attributed to the charge transfer from 2*pπ* orbital of bridging oxygen to the vacant *d* orbital of copper[6, 7].

The result of magnetic measurements for Cu_2(et·eta-O)$(NCS)_2$ over the temperature range has shown that its ground state is of spin-singlet, excluding the possibility of mononuclear and odd-number-polynuclear structures, but diagnosis of tetranuclear or binuclear structure by the magnetic data is difficult, since the magnetic interaction is very strong (μ_{eff} = 0.33 BM at room temperature). The HCB mull spectrum of this compound shows no absorption at 3000~3500 cm^{-1}, whereas other complexes with similar ligands (compound (1)–(6)) in HCB mull display strong absorptions at 3400 cm^{-1}. This fact indicates that this compound has no alcoholic hydrogen, being in harmony with the structure II. Furthermore, the band due to the coordinated NCS is observed at 2105 and 797 cm^{-1} with no splitting, suggesting that all the NCS groups are equivalent, which is also compatible with the proposed structure II.

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