# Synthesis and Properties of Copper(II) Perchlorate Complexes with Imino Oximes

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Three types of imino oxime copper(II) complexes were obtained by the reactions of copper(II) perchlorate with imino oximes (3-[2-[(alkylamino)ethyl]imino]-2-butanone oximes or 3-[2-[(dialkylamino)ethyl]imino]-2-butanone oximes, abbreviated as Hdox-enRR'). One type contains the dinuclear complexes [Cu$_2$(dox-enRR')$_2$]$^{2+}$ and uncoordinated perchlorate anions. The magnetic susceptibilities measured over the temperature range 77—320 K indicate that there exists a strong antiferromagnetic spin coupling interaction through the N-O bridge in these complexes. The magnetic behavior can be explained by using the Bleaney–Bowers equation. Complexes of the second type probably contain a square-tetranuclear complex. The copper(II) ions assume a penta-coordinated configuration with perchlorate anion coordinated at the axial coordination site. It is assumed that the dinuclear and mononuclear magnetic units coexist in the complexes of the third type. The plot of the magnetic susceptibilities versus temperature is linear in the two temperature ranges ($T > 250$ K, < 100 K).

Previous reports on the metal complexes with imino oximes 1 have shown a variety of structural and magnetic properties, which depend upon the substituents R and R', metal ions and counter anions.[1-5] For example, the reactions of
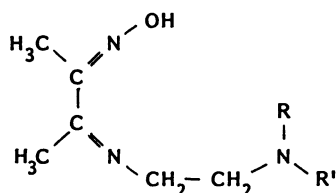
1a Hdox-enR(R' = H, R = alkyl)
1b Hdox-enR$_2$(R' = R = alkyl)

1

nickel(II) salts with imino oximes 1 gave two types of complexes, namely hexa-coordinated octahedral and tetra-coordinated planar nickel(II) complexes. Significant effects of the counter anions[1] are also found in these studies. We have extended similar studies to copper(II) complexes. In the copper(II) thiocyanato complexes, imino oximes 1 are coordinated to copper (II) ion as a bridging quadridentate ligand, and the thiocyanate anion is coordinated through nitrogen atom to form a group of penta-coordinated dinuclear copper(II) complexes.[4] In copper(II) halide complexes with imino oximes, the main skeleton of complexes is similar to that of the copper(II) thiocyanato complexes, in which imino oximes act as a bridging quadridentate ligand. However, halide anions are not coordinated, in contrast to the thiocyanato complexes, showing their weaker coordination ability than that of thiocyanate anion.[5] Although some copper(II) perchlorate complexes with this ligand which were concluded to have a penta-coordinated dinuclear structure have been reported previously,[6] there remain important problems about related complexes with ligands having different steric condi-

tions. In the present work more detailed examination has been carried out on copper(II) perchlorate complexes with a series of imino oximes. The study has shown that tetranuclear complexes and complexes consisting of mononuclear and dinuclear magnetic units, in addition to simple dinuclear one, occur in these copper(II) perchlorate complexes. Reported here are the results of our work on the polynuclear copper(II) perchlorate complexes with imino oximes.

Experimental

Materials. Biacetyl monoxime, *N*-alkylethylenediamine, *N,N*-dialkylethylenediamine, and copper(II) perchlorate hexahydrate were commercially available and used as received.

Synthesis. **Cu(Hdox-enMe)(ClO$_4$)$_2$ (R' = H, R = Me; 4a).** A mixture of biacetyl monoxime (1.01 g, 0.01 mol) and *N*-methylethylenediamine (0.74 g, 0.01 mol) in 2-propanol (20 cm^3) was heated at 70 °C for 2 h. The resulting solution was added to a suspension of copper(II) perchlorate (3.70 g, 0.010 mol) in ethanol (30 cm^3) at 50 °C and stirred for 2 h. Filtration and subsequent washing with ethanol gave green powder of complex (2.52 g) in 56% yield. Mp : 217 °C. Found : C, 22.85; H, 4.07; N, 9.19%. Calcd for C$_7$H$_{15}$N$_3$OCu(ClO$_4$)$_2$ · 1/2PrOH : C, 22.70; H, 4.26; N, 9.34%.

Cu(Hdox-enPr)(ClO$_4$)$_2$ (R'=H, R=Pr; 4b). A mixture of biacetyl monoxime (1.01 g, 0.010 mol) and *N*-propylethylenediamine (1.02 g, 0.01 mol) in ethanol(30 cm^3) was heated at 60 °C for 1.5 h. The resulting solution was added to a solution of copper(II) perchlorate (3.70 g, 0.01 mol) in 2-propanol (20 cm^3) at room temperature, and the mixture was stirred for several hours. Slow evaporation of the reaction mixture at room temperature gave green powder of complex (1.18 g) in 24% yield. Mp>300 °C. Found : C, 26.74; H, 5.13; N, 8.92%. Calcd for C$_7$H$_{15}$N$_3$OCu(ClO$_4$)$_2$ · EtOH: C, 26.75; H, 5.10; N, 8.51%.

Cu(dox-enRR')ClO$_4$ (R'=H, R=Ph, 2a; R'=R=Pr^i, 2b). These complexes were prepared by a similar method to that for Cu(dox-enPr)ClO$_4$ (4b), except that *N*-phenylethylenediamine (1.36 g, 0.01 mol) or *N,N*-diisopropylethylenediamine (1.44 g, 0.01 mol) was used in place of *N*-

propylethylenediamine. Dark-green crystalline complexes 2a (2.83 g) and 2b (1.40 g) were obtained in 72% yield and 36% yield respectively. Mp: 2a, 254 °C and 2b, 229 °C (all accompanied by explosion). Found: C, 38.08; H, 4.25; N, 10.85%. Calcd for $C_{12}H_{16}N_3OCuClO_4 \cdot 1/4EtOH$ (2a): C, 38.16; H, 4.48; N, 10.68%. Found: C, 37.08; H, 6.15; N, 10.64%. Calcd for $C_{12}H_{24}N_3OCuClO_4$ (2b): C, 37.02; H, 6.21; N, 10.79%.

Cu(dox-enMe)ClO$_4$ (R'=H, R=Me; 3a). This complex was prepared by a similar method to that for Cu(dox-enPr)ClO$_4$ (4b), except that N-methylethylenediamine (0.74 g, 0.01 mol) was used in place of N-propylethylenediamine. Complex 3a (0.76 g) as dark green crystals was obtained in 23% yield. Mp: 225 °C. Found: C, 26.89; H, 4.57; N, 12.58%. Calcd for $C_8H_{16}N_3OCuClO_4 \cdot 1/4EtOH$: C, 27.24; H, 4.72; N, 12.71%.

Cu(dox-enEt)ClO$_4$ (R'=H, R=Et; 3b). This complex was prepared by a method similar to that for complex Cu(dox-enMe)ClO$_4$, except that N-ethylethylenediamine was used instead of N-propylethylenediamine. Filtration and recrystallization with ethanol gave dark-green crystals of complex 3b (1.90 g) in 57% yield. Mp: 240 °C. Found: C, 28.93; H, 4.76; N, 12.78% Calcd for $C_8H_{16}N_3OCuClO_4$: C, 28.83; H, 4.84; N, 12.61%.

Measurements. Electronic absorption spectra were measured at room temperature with a Shimadzu MPS 5000 spectrophotometer. Infrared absorption spectra were recorded as Nujol mulls on a Perkin-Elmer 938G infrared spectrophotometer. Room temperature magnetic moments were determined by the Gouy method using H$_2$O as a susceptibility standard, and magnetic susceptibilities at temperatures 4 K to 320 K were measured by the Faraday method in a manner as described previously.[11] Pascal's constants were used to estimate the diamagnetic corrections for imino oximes, ClO$_4$, and Cu.[12]

Results and Discussion

Synthesis of the Copper(II) Perchlorate Complexes with Imino Oximes. In the present work, two types of copper(II) complexes were obtained, depending upon the nature of R and R', by reactions of copper (II) perchlorate with one equivalent of imino oximes (Hdox-enRR', 1). From their magnetic properties, as discussed later in more detail, these complexes can be classified into the following three groups:

i) Cu(dox-enRR')ClO$_4$ (2; R'=H, R=Ph; R'=R=Pr^i)
ii) Cu(dox-enR)ClO$_4$ (3; R=Me, Et)
iii) Cu(Hdox-enR)(ClO$_4$)$_2$ (4; R=Me, Pr)

Characterization of the Copper(II) Perchlorate Complexes 2. In these complexes 2, the copper(II) ion is assumed to have a quadri-coordinated square-planar geometry, similar to that in copper(II) halide complexes.[5] The composition determined by the elemental analysis indicates that the imino oximes lose a proton on coordination to the copper(II) ion.

Infrared spectra of the complexes 2 exhibit no vibrations in 3140—3253 cm^{-1}, showing that the deprotonated imino oxime monoanions are coordinated to the copper(II) ion, in agreement with the assumption that the complexes 2 are copper(II) complexes. Moreover,

Table 1. The Main Data for Copper(II) Perchlorate Complexes of Imino Oximes

Complex	R	R'	μ/BM	d-d/10^3cm^{-1}	$\nu_{C=N}$/cm^{-1}
2a	Ph	H	0.51	17.0	1654
2b	Pr^i	Pr^i	0.68	16.8	1642
3a	Me	H	1.62	16.1	1637
3b	Et	H	1.62	15.2	1636
4a	Me	H	1.43	15.9	1642
4b	Pr	H	1.34	15.7	1641

the bands due to imino oxime C=N (Table 1) are shifted from the vibration of the free ligand at 1623—1630 cm^{-1}, indicating that the nitrogen atom of imino oxime C=N is bound to the copper(II) ion. The perchlorate anion is not bound to the copper(II) ion, since an unsplit band due to the perchlorate anion appears at about 1080 cm^{-1}.

Electronic absorption spectra of the copper(II) complexes 2 show one broad band in the visible region (Table 1), where d-d bands of square planar copper(II) complexes are expected to occur.[13,14] Since the magnetic moments of these copper(II) complexes at room temperature are subnormal, the spin-coupling interaction between copper(II) ions is presumed to be present. In the light of previous studies on the corresponding copper(II) halide complexes,[5] a similar dinuclear structure [Cu$_2$(dox-enRR')$_2$]$^{2+}$ (shown in 2) may also be proposed for the copper(II) perchlorate complexes 2 in the present work. This is supported by the finding in the present work that d-d bands, like those of copper(II) halide complexes,[5] are shifted to higher energy region, as compared with those of thiocyanato copper(II)

2a, R'=H, R=Ph
2b, R'=Pr^i
[Cu$_2$(dox-enRR')$_2$]$^{2+}$
2
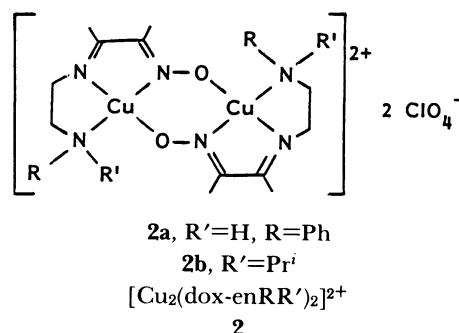
complexes.[4] It is well known that the d-d bands of the square-planar copper(II) complex undergo a bathochromic shift when the fifth ligand is bound to the planar copper(II) ion.[13,14]

Consistent with the assumption about the dinuclear structure, the temperature dependence of the magnetic susceptibilities of copper(II) perchlorate complexes shows that there exists a spin-coupling interaction between two copper(II) ions of dinuclear complexes. Magnetic susceptibilities of complexes 2 measured over the temperature range 77—320 K, which are shown in Fig. 1, indicate the presence of a

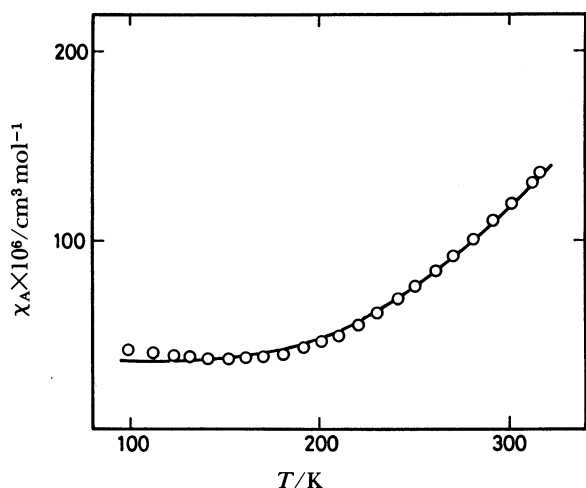Fig. 1. Temperature dependence of the magnetic susceptibilities for Cu(dox-enPh)ClO$_4$ (2a). The solid line was calculated from Eq. 1 with g=2.29, $2J/k$=$-$1300 K, $N\alpha$=35$\times$10^{-6} cm^3 mol^{-1}.

strong spin-coupling interaction between copper(II) ions in these dinuclear complexes, in the same way as in copper(II) thiocyanato and copper(II) halide complexes. The magnetic behaviors can be explained using the Bleaney–Bowers equation (Eq. 1)

$$\chi_A = \frac{Ng^2\beta^2}{kT} \frac{1}{3+\exp(-2J/kT)} + N\alpha \qquad (1)$$

The symbols in Eq. 1 have their usual meanings. Figure 1 exhibits good agreement between the experimental and calculated values. The exchange parameters for the copper(II) perchlorate complexes 2 are given in Table 2. The values of $-2J$ of the copper(II) perchlorate complexes 2, just like the copper(II) halide complexes, are greater than those of the thiocyanato copper(II) complexes. This result implies that the spin-coupling interaction between two copper(II) ions is stronger in the perchlorate complexes than that in the thiocyanato complexes, and may be considered to arise from the apical bonding of the thiocyanate anion to the copper(II) ion in the latter. Thus all the findings combined are consistent with the assumption that the complexes 2 adopts a dinuclear structure [Cu$_2$(dox-enRR$'$)$_2$]$^{2+}$ and that

there exists a strong antiferromagnetic interaction between two copper(II) ions through two bridging N–O groups.
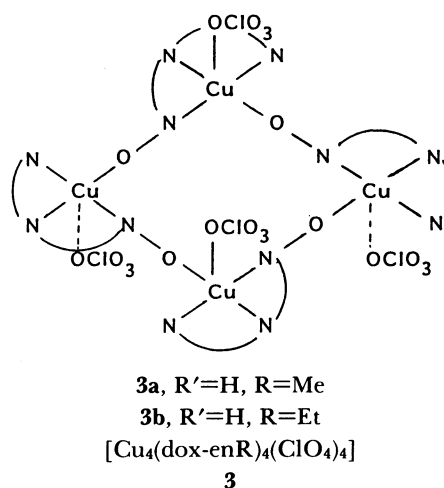
Characterization of Copper(II) Perchlorate Complexes 3. The composition of the elemental analysis shows the same empirical formula as that of complexes 2 though, the magnetic moments (1.62 BM) at room temperature are much higher than those of complexes 2, indicating that the structure of complexes 3 is significantly different from that of complexes 2. Similar to complexes 2, infrared spectra of complexes 3 show that deprotonated imino oximate monoanion is coordinated to the copper(II) ion. A perchlorate anion is coordinated to copper(II) ion (Table 1), which is different from complexes 2. The d–d bands of complexes 3 (Table 1) appear at a lower wavenumber than those of the copper(II) halides complexes. Therefore, it is likely that copper(II) ion in complexes 3 may be penta-coordinated, in a similar way to copper(II) thiocyanato complexes.

Although the subnormal magnetic moments of complexes 3 indicate the presence of antiferromagnetic spin-interaction, their variable temperature magnetic susceptibilities do not obey the Bleaney–Bowers equation for the dinuclear model. Investigation of variable temperature magnetic susceptibilities shows that complexes 3 have a tetranuclear structure, in which there exist an antiferromagnetic interactions. Over the temperature range 4—300 K, the best fit curve of susceptibilities versus temperature shows a clear peak at about 100 K (Fig. 2). The magnetic behaviors can be explained using Eq. 2 for the square-tetranuclear structure :[15]

$$\chi_A = \frac{Ng^2\beta^2}{2kT} \frac{2+5\ \exp(-2x)+\exp(2x)}{7+5\ \exp(-2x)+3\ \exp(2x)+\exp(4x)} + N\alpha \qquad (2)$$

$$(x=-J/kT)$$

where g, J, and $N\alpha$ are g factor, exchange integral, and T. I. P. respectively. The exchange parameters for the copper(II) perchlorate complexes 3 are given in
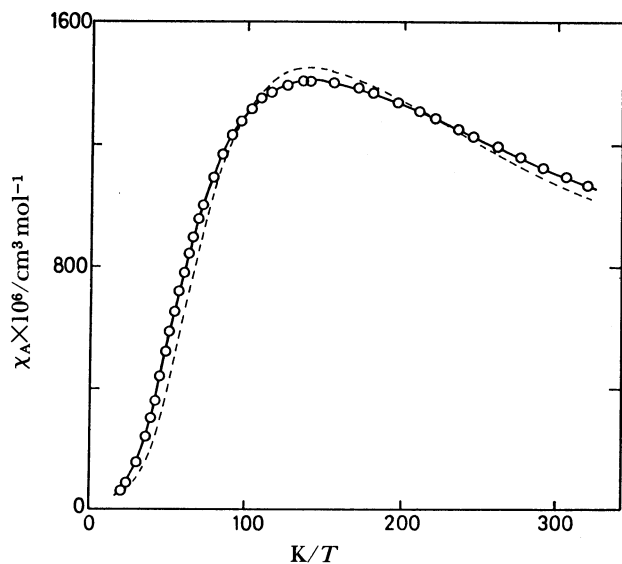
Table 2. Magnetic Susceptibilities at Room Temperature and Magnetic Parameters of Copper(II) Perchlorate Complexes of Imion Oximes

Complex	$\dfrac{\chi_g}{\text{cm}^3\,\text{g}^{-1}}$	g	$\dfrac{-2J k^{-1}}{\text{K}}$	$\dfrac{N\alpha\times10^6}{\text{cm}^3\,\text{mol}^{-1}}$
2a	0.18	2.29	1300	35
2b	−0.09	2.33	1300	50
3a	3.05	2.00	128	60
3b	2.84	2.17	180	60
4a	1.55	2.10	960	60
4b	1.14	2.00	860	60

3a, R$'$=H, R=Me
3b, R$'$=H, R=Et
[Cu$_4$(dox-enR)$_4$(ClO$_4$)$_4$]
3

Fig. 2. Temperature dependence of the magnetic susceptibilities for Cu(dox-enEt)ClO₄ (3b). The solid line was calculated from Eq. 2 with $g=2.17$, $2J/k=-180$ K, $N\alpha=60\times10^{-6}$ cm³ mol⁻¹. The broken line shows the best fit curve for dinuclear structure with $g=2.04$, $2J/k=-255$ K, $N\alpha=60\times10^{-6}$ cm³ mol⁻¹.

Fig. 3. Reciprocal susceptibility vs. temperature for Cu(Hdox-enMe)(ClO₄)₂ (4a). The solid line shows the theoretical susceptibilities calculated from Eq. 4 with $g=2.10$, $2J/k=-960$ K, $N\alpha=60\times10^{-6}$ cm³ mol⁻¹. The broken lines show the Curie-Weiss law.

Table 2. Figure 2 exhibits good agreement between the experimental and calculated values, giving support to the assumption that complexes 3 consist of tetranuclear units.[16] One of most possible structures is shown in 3.

Characterization of Copper(II) Perchlorate Complexes 4. The elemental analysis leads to the empirical formula Cu(Hdox-enR)(ClO₄)₂, which is significantly different from those of the complexes 2 and 3. This formulation, requires that molecules of the imino oximes are coordinated to copper(II) ion in complexes 4. Infrared spectra show that perchlorate anion, as in complexes 3, is coordinated to the copper(II) ion. The d-d bands (Table 1) indicate that the coordination geometry around copper(II) ion is penta-coordinated. The magnetic moment calculated per copper(II) ion (1.34—1.43 BM) is smaller than the spin-only value, showing the presence of spin-coupling interaction between copper(II) ion in these complexes 4. Magnetic susceptibilities were measured over the temperature range 4—300 K. The plot of reciprocal susceptibility versus temperature is linear in two temperature ranges, namely, $T<100$ K and $T>250$ K (Fig.3). The data fit to the Curie-Weiss law (Eq.3) with $C_h=0.313$ emu K mol⁻¹ and $\theta_h=-140$ K, $C_l=0.226$ emu K mol⁻¹ and $\theta_l=-10$ K for complex 4a, and $C_h=0.302$ emu K mol⁻¹ and $\theta_h=-100$ K, $C_l=0.185$ emu K mol⁻¹ and $\theta_l=-10$ K for complex 4b, where C_h and θ_h are Curie and Weiss constant of the high temperature range, and C_l and θ_l are Curie and Weiss constant of the low temperature range.
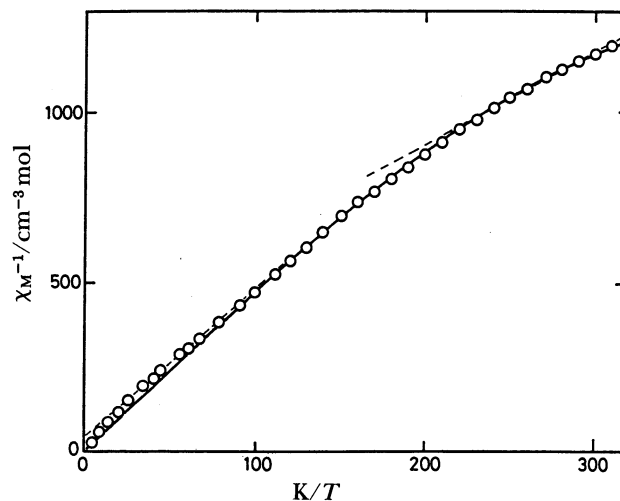
$$\chi^{-1}=C^{-1}(T-\theta) \qquad (3)$$

It is thus clear that there exists a strong antiferromagnetic interaction between copper(II) ions in these complexes 4. The ratio C_h/C_l (1.6 for 4a and 1.4 for 4b) suggests centered-triangular tetranuclear unit or coexistence of dinuclear and mononuclear magnetic units (1:1 ratio) in complexes 4. The magnetic susceptibility for the model of coexisting dinuclear and mononuclear copper(II) complexes in 1:1 ratio can be formulated as Eq. 4:

$$\chi_A=\frac{1}{2}\frac{Ng^2\beta^2}{kT}\frac{1}{3+\exp(-2J/kT)}+\frac{1}{2}\frac{Ng^2\beta^2}{4kT}+N\alpha \quad (4)$$

This equation reproduces the observed susceptibilities well with $2J/k=-960$ K, $g=2.10$ and $N\alpha=60\times10^{-6}$ cm³ mol⁻¹ for complex 4a (Fig.3), and $2J/k=-860$ K, $g=2.00$ and $N\alpha=60\times10^{-6}$ cm³ mol⁻¹ for complex 4b. The agreement between calculated and observed susceptibility for the centered-triangular tetranuclear model is much poorer than for the model of coexisting dinuclear and mononuclear units. Therefore, the latter models more likely for complexes 4. It may be possible that there exists an antiferromagnetic spin interaction between two copper(II) ions in the tetranuclear clusters, but the third and fourth copper(II) ions in the cluster are not involved in spin-coupling with the other copper(II) ions.** Although the precise structure can be determined by the single crystal X-ray study, attempts to grow crystals of the complexes suitable for X-ray studies have not so far been successful.

As discussed above, the present work has revealed

** A referee has questioned whether there would be bridging groups in the proposed formula. It is true that the alcoholato oxygen atom most frequently occurs as a bridge. However, it may also be possible that the alcoholic hydroxyl group functions as a bridge.

that various skeletal structures have been found in copper(II) perchlorate complexes with imino oximes, the result which shows that the structure of copper(II) complexes is quite versatile. It is noteworthy that according to the nature of ligand and the steric condition, copper(II) ion forms various complexes with a different coordination number and a different structure. In consequence of the Jahn–Teller effect, copper(II) complexes show various structures which rarely occur in the corresponding nickel(II) complexes.

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