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

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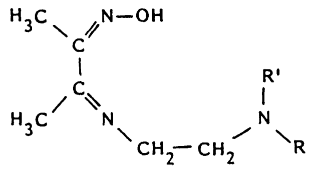
Two types of imino oxime copper(II) complexes were obtained by the reactions of copper(I) halides CuX (X=Br, I) with imino oximes (3-[2-[(alkylamino)ethyl]imino]-2-butanone oximes or 3-[2-[(dialkylamino)ethyl]-imino]-2-butanone oximes, abbreviated as Hdox-enRR′). One type contains the binuclear complexes $[Cu_2(dox\text{-}enRR')_2]^{2+}$ and uncoordinated halide anions. The magnetic susceptibilities measured over the temperature range 77—320 K show 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. It is assumed that the complexes of the other type consist of copper(I) and copper(II) in 2 : 1 ratio without spin-coupling interaction between the copper ions. The plot of the reciprocal magnetic susceptibilities versus temperatures is linear.

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 nickel(II) with imino oximes **1** gave two types of complexes, namely hexa-coordinated and tetra-coordinated nickel(II) complexes. These results show a significant effect of the counter anions.[1] We have extended similar studies to several other metals and found that 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 binuclear copper(II) complexes.[4] It is worthwhile to investigate the effect of the anions on the structure and the bonding of copper(II) complexes formed. Reported here are the results of some of our work with the copper(II) halide complexes, together with their comparison with the corresponding nickel(II) complexes and thiocyanato copper(II) complexes.



**1a** Hdox-enR(R′=H,R=alkyl)
**1b** Hdox-enR$_2$(R′=R=alkyl)
**1**

## Experimental

**Materials.** Biacetyl monoxime, *N*-alkylethylenediamine, *N,N*-dialkylethylenediamine, and copper halides CuX (X=Br, I) were commercially available and used as received.

**Synthesis. Cu(dox-enMe)I (R′=H,R=Me; 2a).** A mixture of biacetyl monoxime (1.01 g, 0.01 mol) and *N*-methylethylenediamine (0.74 g, 0.01 mol) in ethanol (40 cm$^3$) was heated at 60 °C for 2.5 h. Copper(I) iodide (0.95 g, 0.005 mol) was added to the solution at 50 °C, stirred for several hours and filtered off. The solution was evaporated spontaneously at room temperature and a dark-green precipitate was collected by filtration and washed with ethanol to give the complex (0.5 g) in 27% yield. Mp: 147 °C. Found: C, 25.99; H, 4.91; N, 11.37%. Calcd for $C_7H_{14}N_3OCuI\cdot 1/2EtOH$: C, 25.74; H, 4.55; N, 11.29%.

**Cu(dox-enR$_2$)I (R′=R=Me, Et; 2b, 2c).** These complexes were prepared by the method similar to that for Cu(dox-enMe)I except that *N,N*-dimethylethylenediamine and *N,N*-diethylethylenediamine, respectively, were used instead of *N*-methylethylenediamine. On adding a small amount of ether and ethanol when the reaction solution was almost evaporated nearly to dryness, complex **2b** (0.6 g) and complex **2c** (0.6 g) were obtained as dark-green crystals in 33% yield and 31% yield, respectively. Mp: **2b**, 141 °C; **2c**, 142 °C. Found: C, 26.40; H, 4.48; N, 11.42%. Calcd for $C_8H_{16}N_3OCuI$ (**2b**): C, 26.64; H, 4.47; N, 11.65%. Found: C, 31.20; H, 5.24; N, 10.70%. Calcd for $C_{10}H_{20}N_3OCuI$ (**2c**): C, 30.90; H, 5.19; N, 10.81%.

**Cu(dox-enBu$_2$)I (R′=R=Bu; 2d).** A mixture of biacetyl monoxime (1.11 g, 0.011 mol) and copper(I) iodide (0.95 g, 0.005 mol) in methanol (40 cm$^3$) was heated at 70 °C for 1 h. *N,N*-dibutylethylenediamine (1.72 g, 0.01 mol) was added and the mixture was stirred for 1 h. Addition of a small amount of ether and ethanol, followed by evaporation of the solvent almost to dryness, gave dark-green crystals (0.5 g) of the complex **2d** in 23% yield. Mp: 124 °C. Found: C, 37.90; H, 6.39; N, 9.44%. Calcd for $C_{14}H_{28}N_3OCuI$: C, 37.80; H, 6.34; N, 9.45%.

**Cu(dox-enRR′)Br (R′=R=Me, Et; 2e, 2f).** To a solution of copper(I) bromide (0.36 g, 0.0025 mol) in ethanol (20 cm$^3$) was added the ligand Hdox-enRR′ (0.005 mol) which was prepared beforehand.[1] The mixture was stirred at 70 °C for 1.5 h. The solution was filtered and evaporated spontaneously at room temperature. On adding a small amount of ether when the solution was almost evaporated nearly to dryness, the complex **2e** (0.2 g) and complex **2f** (0.63 g) were obtained as dark-green crystals in 24% yield and 66% yield respectively. Mp: **2e**, 150 °C; **2f**, 137 °C. Found: C, 29.12; H, 5.45; N, 12.65%. Calcd for $C_8H_{16}N_3OCuBr\cdot H_2O$ (**2e**): C, 28.91; H, 5.47; N, 12.67%. Found: C, 34.50; H, 6.03; N, 12.04%. Calcd for $C_{10}H_{20}N_3OCuBr\cdot 1/2H_2O$ (**2f**): C, 34.24; H, 6.03; N, 11.98%.

**Cu$_3$(dox-enPr$^i_2$)$_3$I (R′=R=Pr$^i$; 3a).** A mixture of biacetyl monoxime (1.11 g. 0.011 mol) and copper(I) iodide (0.95 g, 0.005 mol) in ethanol (40 cm$^3$) was heated at 60 °C for 2 h. *N,N*-Diisopropylethylenediamine (1.44 g, 0.01 mol) was added to the solution and the mixture was stirred for 1 h. On concentrating the solution to 20 cm$^3$, a green precipitate (0.1 g) was obtained in a very low yield. Mp>300 °C. Found: C, 41.19; H, 7.09; N, 11.64%. Calcd for $C_{36}H_{72}N_9O_3Cu_3I\cdot 3H_2O$ C, 41.15; H, 7.48; N, 12,00%.

**$Cu_3(dox\text{-}enPr^i{}_2)_3Br$ (R′=R=Pr$^i$; 3b).** A mixture of biacetyl monoxime (1.11 g, 0.011 mol) and CuBr (0.72 g, 0.005 mol) in methanol (50 cm$^3$) was heated at 60 °C for 3 h. At room temperature a solution of *N,N*-diisopropylethylenediamine (1.44 g, 0.01 mol) in ethanol (10 cm$^3$) was added to the reaction mixture above, and the mixture was heated at 60 °C for several hours. Evaporation of the filtered solution at room temperature gave a green precipitate (0.7 g) in 14% yield. Mp>300 °C. Found: C, 44.49; H, 7.55; N, 12.73%. Calcd for $C_{36}H_{72}N_9O_3Cu_3Br\cdot H_2O$: C, 44.69; H, 7.60; N, 13.03%.

**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 with the Gouy-method using $H_2O$ as a susceptibility standard, and magnetic susceptibilities at temperatures 77 K to 320 K were measured by the Faraday method in a manner as described previously.[6] Pascal's constants were used to estimate the diamagnetic corrections for imino oximes, Br, I, and Cu.[7]

## Results and Discussion

**Synthesis of the Copper(II) Halide Complexes with Imino Oximes.** In the present work, the reactions of copper(I) salts CuX (X=I, Br) with the imino oximes (Hdox-enRR′; **1**) gave two types of copper(II) complexes depending on the nature of R and R′:

i) Cu(dox-enRR′)X (**2**; R′=H, R=Me, X=I; R′=R=Me, Et, X=I, Br; R′=R=Bu, X=I).

ii) $Cu_3(dox\text{-}enPr^i{}_2)_3X$ (**3**; X=I, Br)

The following features are to be noted about the synthesis of these complexes:

i) By the reactions of copper(I) halides CuX (X=I, Br) with 3-[[2-(alkylamino)ethyl]imino]-2-butanone oximes (**1a**), the complex Cu(dox-enMe)I (**2a**) was obtained exclusively. Attempts to isolate copper(II) complexes by the reactions of copper(I) chloride with imino oximes (Hdox-enRR′) have so far been unsuccessful. It seems to be difficult to crystallize out the desirable copper(II) complexes because of their high solubilities in an organic solvent.

ii) Using copper(I) halide salts CuX (X=I, Br) as a starting material, we succeeded in preparing the imino oxime copper(II) complexes (**2**). In this method, the copper(I) ion was oxidized by atmospheric oxygen under the reaction conditions employed. This method has been applied with success to the preparation of other copper(II) complexes.[4] By similar procedures, using copper(II) bromide in place of copper(I) bromide, the desirable copper(II) complex could not be isolated as solid. The following equations can be considered:

$$\mathrm{CuX + Hdox\text{-}enRR' \xrightarrow{O_2} Cu(dox\text{-}enRR')X + H_2O} \quad (1)$$

$$\mathrm{CuX_2 + Hdox\text{-}enRR' \longrightarrow Cu(dox\text{-}enRR')X + HX} \quad (2)$$

According to the Eq. 2, the reaction of copper(II) salt with imino oximes produces HX, which induced the decomposition of ligand Hdox-enRR′ and hence the formation of the complexes Cu(dox-enRR′)X becomes unfavorable; however using copper(I) salt as starting substance, beside the desirable complexes only $H_2O$ is formed as shown in Eq. 1.

iii) As shown in the experimental section, the crystals of complexes were obtained by adding a small amount of ether when the reaction solution was evaporated nearly to dryness. It also reflects the high solubility of these complexes in alcohol.

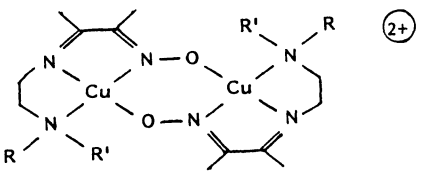
**Characterization of the Copper(II) Halide Complexes (2) of Imino Oximes.** As discussed later in more detail, d-d bands and magnetic properties indicate that the complexes **2** isolated are copper(II) complexes. The composition determined by the elemental analysis indicates that the imino oximes lose 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, 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.

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 be occur.[8,9] Since the magnetic moments of these coeper(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 thiocyanato copper(II) complexes,[4,5] a similar binuclear structure $[Cu_2(dox\text{-}enRR')_2]^{2+}$ (shown in **2**) may

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

| | R | R′ | X | $\mu$/BM | d-d/10$^3$cm$^{-1}$ | $\nu_{C=N}$/cm$^{-1}$ |
|---|---|---|---|---|---|---|
| **2a** | Me | H | I | 0.79 | 18.4 | 1654 |
| **2b** | Me | Me | I | 0.73 | 18.0 | 1642 |
| **2c** | Et | Et | I | 0.60 | 16.1 | 1637 |
| **2d** | Bu | Bu | I | 0.59 | 16.8 | 1636 |
| **2e** | Me | Me | Br | 0.70 | 16.7 | 1642 |
| **2f** | Et | Et | Br | 0.60 | 15.8 | 1641 |
| **3a** | Pr$^i$ | Pr$^i$ | I | 1.08 | 17.0 | 1624 |
| **3b** | Pr$^i$ | Pr$^i$ | Br | 1.06 | 16.9 | 1624 |



$[Cu_2(\text{dox-enRR}')_2]^{2+}$
**2**

also be proposed for the copper(II) halide complexes in the present work. Since the coordination ability of halide anions, particularly iodide anion, is much lower than that of thiocyanate, it is reasonable to assume that the halide anions are not coordinated to copper(II) ion in the complexes **2**. In agreement with this seems to be the finding in the present work that the d-d bands of the copper(II) halide complexes shift to higher energy region, as compared with those of thiocyanato copper(II) 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.[8,9]

Investigation on the temperature dependence of the magnetic susceptibility of copper(II) complex is very important and useful for understanding the nature of spin-coupling interaction and the structure of complexes. There have been many studies on the magnetic properties of copper(II) complexes, which have binuclear structures and show spin-coupling interaction between two copper(II) ions through the bridging oxygen atom[10-12] or bridging group N-O.[13,14] As discussed above, the magnetic moments of the complexes **2** are much smaller than that of the normal $3d^9$ system, showing that there exists a spin-coupling interaction between two copper(II) ions. Magnetic susceptibilities of complexes **2** were measured over the temperature range 77—320 K. One of the examples is shown in Fig. 1. The temperature dependence of the magnetic susceptibility shows the presence of a strong spin-coupling interaction between copper(II) ions in these binuclear complexes. The magnetic behaviors can be explained using the Bleaney-Bowers equation (Eq. 3)

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

or its modification (Eq. 4)

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

The symbols in Eqs. 3 and 4 have their usual meanings. Figure 1 exhibits the good agreement between the experimental and calculated values. The exchange parameters for the halide copper(II) complexes **2** are given in Table 2. It is interesting that the values of $-2J$ of the halide copper(II) 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 halide 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 binuclear structure $[Cu_2(\text{dox-enRR}')_2]^{2+}$ and that there exists a strong antiferromagnetic interaction between two copper(II) ions through two bridging N-O groups. This result is in contrast to that of similar nickel(II) complexes, in which there is little interaction between two nickel(II) ions having $d^8$ system.[1]

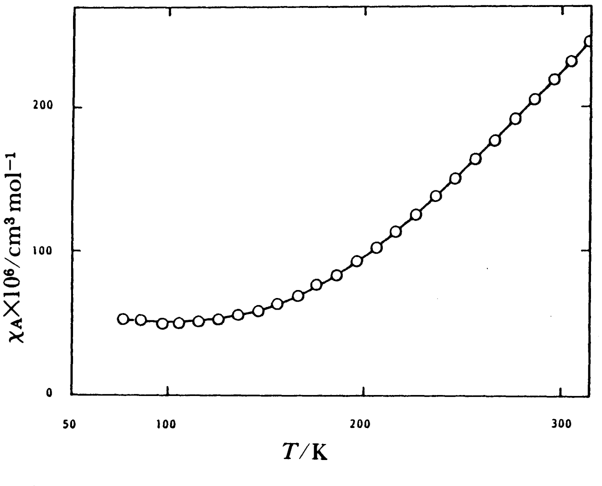


Fig. 1. Temperature dependence of the magnetic susceptibilities for $Cu(\text{dox-enMe}_2)Br$. The solid line was calculated from Eq. 3 with $2J/k = -1060$ K, $N\alpha = 46 \times 10^{-6}$ $cm^3mol^{-1}$.

Depending upon the nature of ligand and the steric conditions, copper(II) ion would form various complexes with different coordination numbers and different structures. The results of the present work show that although the main skeleton of copper(II) complexes was determined by imino oximes used, the different anions form the complexes with different coordination numbers and structures.[4,5,15]

**Characterization of Complexes 3.** The characterization of complexes **3** was investigated in the same way as that for complexes **2**. The composition of the elemental analysis leads to the empirical formula

Table 2. Magnetic Susceptibilities at Room Temperature and Magnetic Parameters of Copper(II) Halide Complexes of Imino Oximes

| | $\chi_g$ <br> $cm^3g^{-1}$ | $g$ | $-2Jk^{-1}$ <br> K | $N\alpha \times 10^6$ <br> $cm^3mol^{-1}$ | $p$ |
|---|---|---|---|---|---|
| **2a** | 0.26 | 2.02 | 861 | 57 | |
| **2b** | 0.14 | 2.21 | 972 | 31 | |
| **2c** | −0.11 | 2.29 | 1160 | 44 | 0.01 |
| **2d** | −0.22 | 2.21 | 1130 | 18 | 0.06 |
| **2e** | 0.12 | 2.29 | 1060 | 46 | 0.01 |
| **2f** | −0.09 | 2.26 | 1240 | 68 | |

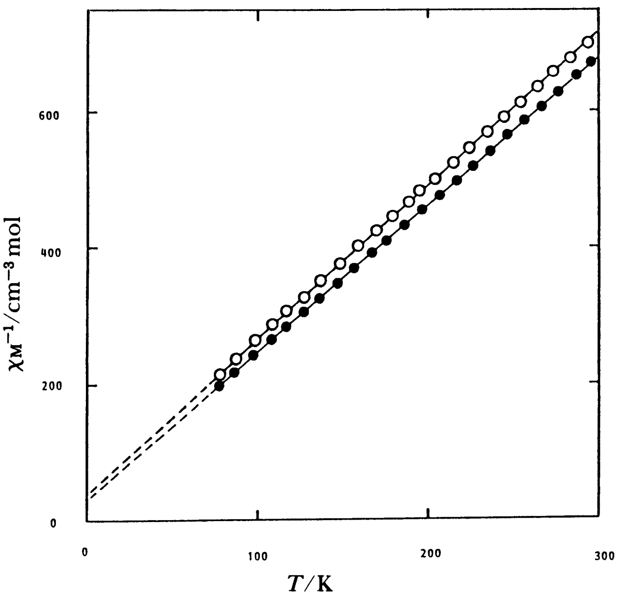


Fig. 2. Reciprocal susceptibility vs. temperature for $Cu_3(dox\text{-}enPr^i_2)_3$ Br (○) and $Cu_3(dox\text{-}enPr^i_2)_3$ I (●). The susceptibility is calculated per formula unit, e.g., for three copper ions. The curves show the theoretical susceptibilities calculated by the Curie–Weiss equation with the parameters described in the text.

$Cu_3(dox\text{-}enPr^i_2)_3X\cdot nH_2O$ (X=I, Br), which is significantly different from that of the complexes **2**. This formulation, which involves the imino oxime monoanion as ligand, requires that copper be present as a mixture in 1+ and 2+ oxidation states. It is also noted that the imino oxime C=N infrared vibrations of complexes **3** occur at wavenumbers around 1624 $cm^{-1}$ distant from the corresponding ones of **2** showing that the structure of **3** differs from that of **2**. The d–d bands (Table 1) indicate that the coordination geometry around copper(II) ion is square-planar. No specific feature of the electronic spectrum could be assigned as an intervalence transfer transition. This difference between complexes **2** and **3** probably arises from the presence of the bulky diisopropylamino groups $-N(Pr^i)_2$ in **3**, which may interfere with the coordination of the $-N(Pr^i)_2$ part. More direct evidence for the existence of a mixed-valence copper complex comes from measurements of the magnetic susceptibility. The magnetic moment calculated per copper ion is $\mu_{eff}=1.06$—1.08 BM (BM=$9.274\times10^{-24}$ $JT^{-1}$). This value is consistent with the presence of Cu(I) and Cu(II) in 2 : 1 ratio without spin-coupling interaction between the copper ions. Variable temperature magnetic susceptibility measurements are also consistent with the existence of copper(I) and almost magnetically independent copper(II) centers. Over the temperature range 77—300 K the plot of reciprocal susceptibility versus temperature is linear (Fig. 2). The data fit well to the Curie-Weiss law (Eq. 5), with $C=0.443$ emu K mol$^{-1}$ and $\theta=-18$ K for X=Br, and $C=0.462$ emu K mol$^{-1}$ and $\theta=-14$ K for X=I, where $C$ and $\theta$ are Curie and Weiss constant, respectively.

$$\chi^{-1}=C^{-1}(T-\theta) \qquad (5)$$

Thus the present compounds are considered to be class I mixed-valence compounds, which contain noninteracting copper(I) and copper(II) sites.[16] Precise structure for these complexes must await further studies using X-ray methods. In any case, however, it is evident that the structure of copper complexes with imino oxime Hdox-enPr$^i_2$ is different from that of the corresponding dialkylamino analogues. The present study thus demonstrates one of those cases, in which the *N*-isopropyl-substituted ligands tend to form metal complexes with structure different from that of the corresponding normal alkyl analogues, owing to the bulky isopropyl groups.[17]

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