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

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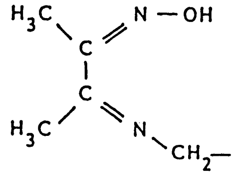
Reaction of copper(I) thiocyanate with imino oximes 3-[[2-(alkylamino)ethyl]imino]-2-butanone oximes or 3-[[2-(dialkylamino)ethyl]imino]-2-butanone oximes, (abbreviated as Hdox-enRR′), gave a series of copper(II) complexes which consist of binuclear complexes [Cu_2(dox-enRR′)$_2$(NCS)$_2$] with a thiocyanate anion coordinated to the copper(II) ion. The magnetic susceptibilities over the temperature range 77—320 K show a strong antiferromagnetic spin coupling through the N-O bridge for these complexes. The magnetic behavior can be explained by using the Bleaney-Bowers equation.

It has been shown previously that imino oximes (Hdox-enRR′ **1**) form various transition metal complexes, in which they function in various manners, namely as bidentate, terdentate or bridging quadridentate ligands, depending upon the nature of the central metal ion on one hand and the substituents R and R′ on the other.[1-4] We have reported that the reactions of nickel(II) thiocyanate with imino oximes **1** yield paramagnetic nickel(II) complexes, which are hexa-coordinated with two thiocyanate ions bonded to the metal ion in cis-positions.[1] This result is in contrast to the results on the corresponding nickel(II) halides and perchlorate complexes with the same ligands.[2-4] Examination has been extended to the corresponding copper(II) thiocyanate complexes in the present study. Since the stereochemistry of copper(II) complexes is known to be significantly different from, although similar in many ways to, that of nickel(II) complexes, it is interesting to compare the copper(II) imino oxime complexes with the corresponding nickel(II) complexes. For example, the behavior of the thiocyanate ion in the copper(II) complexes may be different from that in the nickel(II) complexes. Although copper(II) perchlorate complexes with these ligands were reported previously,[4] there remain important problems about related complexes. Moreover, it is worthwhile to investigate the effects of the anions on the structure and the bonding of copper(II) complexes formed. Another important feature often observed with the copper(II) complexes is the spin-spin interaction between copper(II) ions, whereas the interaction of a similar type rarely occurs in the corresponding nickel(II) complexes. The present paper describes synthesis and characterization of the copper(II) thiocyanato complexes, including examination of their magnetic properties.



Hdox-enRR′
1

Experimental

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

Synthesis. Cu(dox-enMe)NCS (R′=H, R=Me; 2a). A mixture of biacetyl monoxime (1.11 g, 0.011 mol) and copper(I) thiocyanate (0.61 g, 0.005 mol) in 2-propanol (40 cm^3) was heated at 70 °C for 1 h. To the solution was added *N*-methylethylenediamine (0.74 g, 0.01 mol) at 60 °C and stirred for 2 h. Filtration and subsequent washing with ethanol gave dark-green crystalline complex (0.45 g) in 32% yield, which appeared green when ground. Mp 151 °C. Found: C, 34.55; H, 5.04; N, 20.05%. Calcd for $C_7H_{14}N_3OCuNCS$: C, 34.57; H, 5.07; N, 20.16%.

Cu(dox-enEt)NCS (R′=H, R=Et; 2b). A mixture of biacetyl monoxime (1.11 g, 0.011 mol) and copper(I) thiocyanate (0.61 g, 0.005 mol) in 2-propanol (40 cm^3) was heated at 70 °C for 1 h. To the solution was added *N*-ethylethylenediamine (0.88 g, 0.01 mol) at 60 °C and stirred for 2 h. The filtered solution was allowed to stand in a refrigerator. Dark-green crystalline complex (0.57 g) was obtained in 39% yield. Mp 143 °C. Found: C, 37.32; H, 5.68; N, 19.09%. Calcd for $C_8H_{16}N_3OCuNCS$: C, 37.04; H, 5.53; N, 19.29%.

Cu(dox-enPr)NCS (R′=H, R=Pr; 2c). A mixture of biacetyl monoxime (1.11 g, 0.011 mol) and copper(I) thiocyanate (0.61 g, 0.005 mol) in 2-propanol (40 cm^3) was heated at 70 °C for 1 h. To the solution was added *N*-propylethylenediamine (1.01 g, 0.01 mol) at 60 °C and stirred for 2 h. The reaction solution was evaporated spontaneously at room temperature and dark-green crystals were collected by filtration and washed with ethanol to give the complex (0.40 g) in 26% yield. Mp 145 °C. Found: C, 39.26; H, 5.88; N, 18.27%. Calcd for $C_9H_{18}N_3OCuNCS$: C, 39.26; H, 5.93; N, 18.32%.

Cu(dox-enMe$_2$)NCS (R′=R=Me; 2d). This complex was prepared by a similar method which was used for the preparation of Cu(dox-enMe)NCS, except that *N*,*N*-dimethylethylenediamine (0.88 g, 0.01 mol) was used in place of *N*-methylethylenediamine. Complex **2d** (1.36 g) was obtained in 93% yield. Mp 153 °C. Found: C, 37.32; H, 5.46; N,

Table 1. Main Spectral Data of Copper(II) Complexes

Complex	d-d band	IR(oxime)		IR(NCS)	
	10^3 cm^{-1}	cm^{-1}		cm^{-1}	
		ν(C=N)	ν(C-N)	ν(C-S)	δ(N-C-S)
2a	15.8	1642	2077	793	432
2b	15.4	1645	2080	797	425
2c	15.2	1648	2072	805	425
2d	15.9	1648	2077	776	457
2e	15.2	1643	2096	775	452
2f	16.3	1649	2087	786	453

19.44%. Calcd for $C_8H_{16}N_3OCuNCS$: C, 37.04; H, 5.53; N, 19.29%.

Cu(dox-enEt$_2$)NCS (R′=R=Et; 2e). To a solution of copper(I) thiocyanate (0.61 g, 0.005 mol) in ethanol (40 cm^3) was added a ligand (Hdox-enEt$_2$ 1.99 g, 0.01 mol) which was prepared beforehand.[1] The mixture was stirred at 60 °C for about 1 h. Filtration and washing with ethanol gave dark-green crystalline complex (1.52 g) in 95% yield. Mp 146 °C. Found: C, 41.51; H, 6.34; N, 17.63%. Calcd for $C_{10}H_{20}N_3OCuNCS$: C, 41.29; H, 6.30; N, 17.51%.

Cu(dox-enBu$_2$)NCS (R′=R=Bu; 2f). A suspension of biacetyl monoxime (1.01 g, 0.01 mol) and *N*,*N*-dibutylethylenediamine (1.72 g, 0.01 mol) in 2-propanol (20 cm^3) was refluxed at 70 °C for 2 h. The resulting solution was added dropwise to a suspension of copper(I) thiocyanate (0.61 g, 0.005 mol) in ethanol (30 cm^3) and stirred at 60 °C for several hours. The solution was allowed to evaporate spontaneously at room temperature nearly to dryness. Dark needle-like crystals were filtered and washed with ethanol to yield 1.76 g (94%) of complex. Mp 115 °C. Found: C, 46.47; H, 7.21; N, 14.77%. Calcd for $C_{14}H_{28}N_3ONCS \cdot 1/2H_2O$: C, 46.79; H, 7.33; N, 14.55%.

Measurements. Electronic absorption spectra and infrared spectra were measured at room temperature on a Shimadzu MPS 5000 spectrophotometer and a Perkin-Elmer 938G infrared spectrophotometer, and all samples were mulled with Nujol. Magnetic susceptibilities were measured by the Gouy method at room temperature and by the Faraday method in a manner as described previously[5] at temperatures between 77K and 320K.

Results and Discussion

Synthesis and Characterization of the Thiocyanato (imino oximato)copper(II) Complexes. A possibility was explored in the present work to employ copper(I) thiocyanate as a starting compound for the preparation of copper(II) complexes with the imino oximes, partly because copper(II) thiocyanate was not available in the stable form. Reactions of copper(I) thiocyanate with the imino oximes yielded copper(II) complexes of the type Cu(dox-enRR′)NCS, copper(I) being oxidized to copper(II) by the atmospheric oxygen under the reaction conditions.

As discussed later in more detail, d-d bands and magnetic properties indicate that the products isolated are copper(II) complexes. It is important to note that this method using a copper(I) salt as a starting substance may be applied to the preparation of other copper(II) complexes, in case the copper(II) salts as a starting compounds are not available or do not give successful results.

Table 2. Magnetic Moments and Exchange Parameters of Copper(II) Complexes

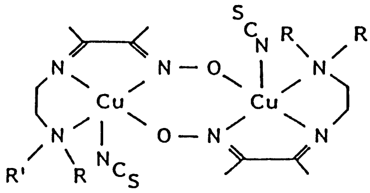
Complex	μ	g	$-2J$	$N\alpha \times 10^6$	p[a)]
	BM		K	cm^{3}mol^{-1}	
2a	0.96	2.33	822	20	0.08
2b	1.05	2.23	719	65	
2c	0.99	2.34	792	37	
2d	0.92	2.24	830	65	
2e	0.76	2.32	938	18	
2f	0.66	2.32	1100	55	0.05

a) the percentage of the impurity species.

The composition determined from elemental analysis indicates that the imino oximes lose a proton on coordination to the copper(II) ion. This assumption is borne out by infrared spectra of these complexes, which exhibit no absorption bands due to the free oxime OH group in the region between 3000 and 3500 cm^{-1}. In other words, the imino oximes are coordinated to the copper(II) ion as monoanions. Moreover, the bands due to imino oxime C=N (Table 1) shift from the vibration 1623—1630 cm^{-1} of the free ligand indicating that imino oxime C=N is bound to the copper(II) ion. Infrared bands due to thiocyanate ions, as shown in Table 1 also indicate that the thiocyanate anion is coordinated to the copper(II) ion through the nitrogen atom.[6,7] Tentative assignments[8,9] are given in Table 1.

Their magnetic moments (0.66—1.05 BM) at room temperature are much lower than the spin-only moment (1.73 BM) for the d^9 system, as shown in Table 2. The subnormal magnetic moments imply that a sort of spin-spin interaction is present between copper(II) ions in these complexes.

All the findings discussed above indicate that one of the most probable structures for these copper(II) complexes is a binuclear one, as shown in **2**, in analogy to a copper(II) complex with a similar composition, Cu(dox-enMe$_2$)ClO$_4 \cdot H_2O$ having a subnormal magnetic moment (0.6 BM at room temperatuire).[10] Thus the copper(II) ion has a square-pyramidal coordination geometry, with one thiocyanate ion at the apex, as also presumed from the infrared bands. This is also in agreement with the crystal structure analysis of one of the present complexes. According to preliminary results of the X-ray analysis,[11] Cu(dox-enPr)NCS in the crystalline state consists of binuclear complexes, represented by structure **2**. The coordination polyhedron around the copper(II) ion is square-pyramidal with one thiocyanate ion at the apex, and the binuclear skeleton is somewhat distorted from the strictly planar structure. A similar binuclear structure may be assumed for the other complexes of the type Cu(dox-enRR′)NCS.



Cu(dox-enRR′)(NCS)
2

The maxima of the first d-d bands of the copper(II) complexes, as shown in Table 1, are consistent with the structure in which copper(II) ion is in the square-pyramidal environment with one thiocyanate ion at the apex.[12,13]

The discussion outlined above shows that copper(II) has a higher tendency to form binuclear complexes with the imino oximate N-O bridges in comparion with nickel(II). In this regard, it is interesting to note a marked difference in the structure between the copper(II) and nickel(II) complexes with these imino oximes. Hexa-coordinate copper(II) complexes have not been isolated in the present work, whereas nickel(II) forms hexa-coordinated complexes of the type *cis*-[Ni(NCS)$_2$(Hdox-enRR′)$_2$].[1] The present work indicates that the capacity of copper(II) ion with a 3d^9 configuration to form hexa-coordinated complexes is obviously lower than that of nickel(II) ion having a 3d^8 configuration. One of the main reasons for this may be the Jahn-Teller effect, which is operative in copper(II) complexes having a 3d^9 configuration.

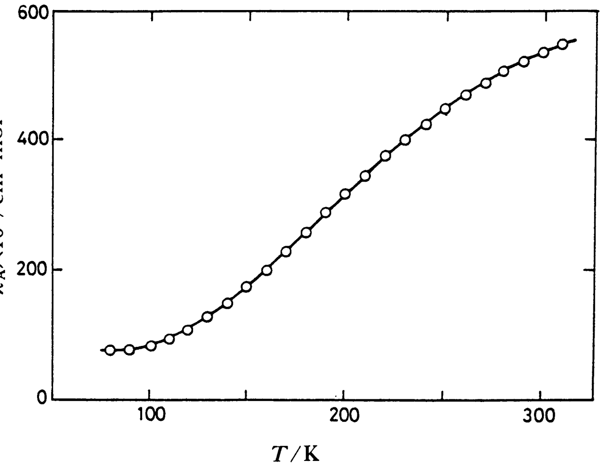


Fig. 1. Temperature dependence of the magnetic susceptibilities for Cu(dox-enEt)(NCS). The solid line was calculated from Eq. 1 with $2J = -719$ K, $N\alpha = 65 \times 10^{-6}$ cm^3 mol^{-1}.

Magnetic Properties of Thiocyanato(imino oximato)-copper(II) Complexes. Variable-temperature magnetic susceptibilities of all the copper(II) complexes obey the Bleaney-Bowers equation for the pair of $S=1/2$ metal ions, Eq. 1,

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

or its modification, Eq. 2,

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

where g, J, $N\alpha$, and p are, respectively, g factor, exchange integral, T. I. P. and percentage of the impurity species.

A typical example of the data is shown in Fig. 1. The figure shows that the experimental data fit to the theoretical expression given above. In Table 2 are also given the magnetic moments of the complexes and the values for the main parameters estimated from the variable-temperature data. All the copper(II) complexes in the present work exhibit large negative J values, showing antiferromagnetic interaction between copper(II) ions. The interaction is considered to arise from superexchange through the bridging N-O groups. The $|J|$ values of these copper(II) complexes are in the range reported for the related binuclear complex, for example, Cu(dox-enMe$_2$)ClO$_4 \cdot$H$_2$O,[10] which also contain similar bridging N-O groups.

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