Synthesis and Properties of Metal Complexes with 2-Thiophenealdehyde Oxime

Hiro KUMA, Kyoji MOTOBE, and Shoichiro YAMADA

Institute of Chemistry, College of General Education, Osaka University, Toyonaka, Osaka 560

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Cobalt(II), nickel(II), copper(II), zinc(II), and manganese(II) complexes with 2-thiophenealdehyde oxime have been prepared and characterized mainly on the basis of electronic spectra and magnetic data. The cobalt(II) and nickel(II) complexes isolated are of the general formulae: (A) $MX_2(oxime)_4$ (X=Cl, Br); (B) $M(NCS)_2(oxime)_2$. These compounds and $ZnCl_2(oxime)_4$ are all six-coordinated, and the complexes (B) are probably multinuclear. Copper(II) and manganese(II) form complexes of the formula $MX_2(oxime)_2$ (X=Cl, Br). Possible structures for these complexes are also discussed. 2-Thiophenealdehyde oxime is unidentate in all these complexes, being coordinated through the nitrogen atom.

In the course of studies on metal complexes with oximes,[1] the present authors happened to obtain cobalt(II), nickel(II), and zinc(II) complexes with 2-thiophenealdehyde oxime, which had composition different from that of previously reported complexes with this ligand.[2] Reinvestigation, therefore, was undertaken in order to examine these and related complexes in more detail. The present paper describes synthesis and characterization of 3d transition metal complexes with 2-thiophenealdehyde oxime, which is abbreviated as tox in the present paper.

Experimental

Materials. 2-Thiophenealdehyde oxime was prepared as reported previously.[3]

Analytical data of the metal complexes prepared in the present work are given in Table 1.

Dihalogenotetrakis(2-thiophenealdehyde oxime)cobalt(II), $CoX_2(tox)_4$ (X=Cl, Br). Cobalt(II) halide hexahydrate (0.01 mol) was added to a solution of 2-thiophenealdehyde oxime (0.04 mol) in ethanol (100 ml) at 65—70 °C. The reaction was continued with stirring under reflux for about two hours. The solution was filtered and allowed to stand overnight at room temperature. Yellow-brown (X=Cl) or brown (X=Br) crystals were collected by filtration and recrystallized from methanol.

$Co(NCS)_2(tox)_2$ was prepared in a manner analogous to the dihalogeno-complexes. A yellow-brown crystalline precipitate was washed with chloroform. The compound is insoluble in common organic solvents.

Dihalogenotetrakis(2-thiophenealdehyde oxime)nickel(II). *$NiX_2(tox)_4$ (X=Cl, Br)* were prepared as yellow-green crystals in a manner similar to the corresponding cobalt(II) complexes. Recrystallization was carried out from methanol.

$Ni(NCS)_2(tox)_2$. 2-Thiophenealdehyde oxime (0.03 mol) was added to a solution of $Ni(NCS)_2$ (0.01 mol) in ethanol (100 ml). The reaction was continued with stirring under reflux for about 2 h at 65—70 °C. A pale green crystalline precipitate was washed with chloroform. The compound is almost insoluble in common organic solvents.

Dichlorotetrakis(2-thiophenealdehyde oxime)zinc(II) was prepared as colorless microcrystals by a method similar to the correspoding cobalt(II) complex.

$CuX_2(tox)_2$ (X=Cl, Br) were obtained as yellow-brown (X=Cl) and brown (X=Br) crystals in a manner analogous to $CoX_2(tox)_4$. The product was recrystallized from methanol.

$MnCl_2(tox)_2$ was obtained as pale-yellow crystals in a manner analogous to the corresponding copper(II) complex. Recrystallization was carried out from methanol.

$MnBr_2(tox)_2$ was prepared as pale-yellow microcrystals in a manner similar to the chloride analogue.

Measurements. Electronic absorption spectra of the complexes were measured on a Shimadzu MPS-50L spectrophotometer. Infrared spectra were recorded as Nujol mulls using a Hitachi EPI-S2 infrared spectrophotometer and a Hitachi 215 infrared spectrophotometer.

Magnetic mesurements were carried out at room temperature by the Gouy method. Powder X-ray diffraction patterns were obtained with a Rigakudenki 4001-A2 diffractometer using Co K_α radiation and an iron filter.

TABLE 1. ANALYTICAL DATA OF METAL COMPLEXES WITH 2-THIOPHENEALDEHYDE OXIME

Compound	Found, %			Calcd, %			μ
	C	H	N	C	H	N	
$NiCl_2(tox)_4$	37.33	3.50	8.68	37.63	3.16	8.78	3.21
$NiBr_2(tox)_4$	32.90	2.95	8.02	33.05	2.77	7.71	3.15
$Ni(NCS)_2(tox)_2$	33.48	2.42	13.25	33.60	2.35	13.31	3.22
$CoCl_2(tox)_4$	37.26	3.35	8.64	37.61	3.15	8.78	5.14
$CoBr_2(tox)_4$	32.63	3.06	7.76	33.04	2.77	7.71	5.15
$Co(NCS)_2(tox)_2$	33.38	2.38	13.28	33.58	2.35	13.06	4.95
$ZnCl_2(tox)_4$	36.94	3.26	8.91	37.28	3.13	8.70	dia
$CuCl_2(tox)_2$	30.99	2.54	7.12	30.89	2.59	7.20	1.92
$CuBr_2(tox)_2$	25.15	2.26	5.86	25.15	2.11	5.86	1.85
$MnCl_2(tox)_2$	31.72	2.85	7.44	31.59	2.65	7.37	6.05
$MnBr_2(tox)_2$	25.60	2.15	6.01	25.61	2.15	5.98	5.96

μ: BM at room temperature

Results and Discussion

Nickel(II) Complexes. A compound of composition $NiCl_2(tox)_2$ was reported previously.[2] In the present work, however, this complex could not be isolated, but instead complexes of the formula $NiX_2(tox)_4$, X being Cl and Br, were obtained.

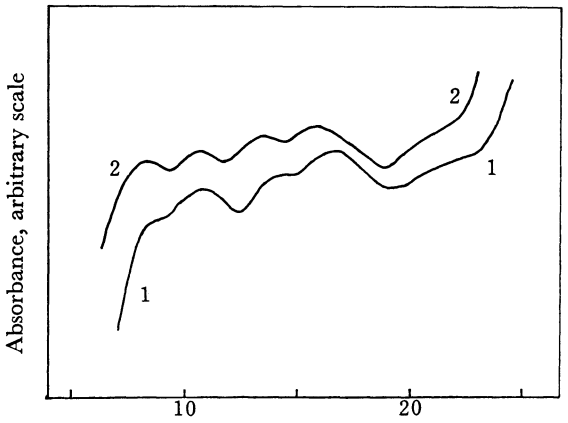

Fig. 1. Electronic absorption spectra of *trans*-dihalogenotetrakis(2-thiophenaldehyde oxime)nickel(II), *trans*-$[NiX_2(tox)_4]$, in Nujol: 1, X=Cl; 2, X=Br.

These nickel(II) complexes prepared are paramagnetic and of a high spin type (Table 1). The electronic absorption spectrum of $NiCl_2(tox)_4$ is very similar to those of *trans*-$NiCl_2(acox)_4$ and *trans*-$NiCl_2(bzox)_4$,[1] where acox and bzox denote acetaldehyde oxime and benzaldehyde oxime, respectively (Fig. 1). It is presumed that $NiCl_2(tox)_4$ has a similar structure to that of *trans*-$NiCl_2(acox)_4$, namely a six-coordinate *trans*-dichloro-structure, in which the oxime molecules are bound as unidentate ligands with the nickel(II) ion through the nitrogen atom.[1,4] It is also concluded that $NiBr_2(tox)_4$ has a six-coordinate *trans*-dibromo-structure, since its powder X-ray diffraction pattern is very similar to that of $NiCl_2(tox)_4$. In agreement with this, electronic absorption spectrum of $NiBr_2(tox)_4$ bears a close resemblance to that of *trans*-$NiBr_2(acox)_4$ (Fig. 1).[1] It is thus found that in these dihalogeno-nickel(II) complexes the ligands tox are bound with the nickel(II) ion as unidentate ligands through their nitrogen atom.

TABLE 2. BAND SPLITTING AND CRYSTAL FIELD PARAMETERS OF *trans*-$[NiX_2(tox)_4]$ IN 10^3 cm^{-1}

	X=Cl	X=Br
ν ($^3E_g{}^a \leftarrow {}^3B_{1g}$)	8.7	8.2
ν ($^3B_{2g} \leftarrow {}^3B_{1g}$)	10.8	10.7
ν ($^3A_{2g} \leftarrow {}^3B_{1g}$)	14.3	13.4
ν ($^3E_g{}^b \leftarrow {}^3B_{1g}$)	16.6	16.0
Dq^{xy}	1.08	1.07
Dq^z	0.66	0.57
Dt	0.24	0.29
Ds	0.43	0.49

The approximate symmetry of *trans*-$NiX_2(tox)_4$ is D_{4h}. Six-coordinate nickel(II) complexes of O_h symmetry show three spin-allowed d-d bands, each of which is split into two components as the symmetry of the complexes changes from O_h to D_{4h}. The band splitting observed in the spectra of $NiX_2(tox)_4$ is so remarkable that it is possible to obtain the components of the two main d-d bands from the magnitude of the splitting. The maxima of the components are shown in Table 2. From these data and using expressions derived on the basis of crystal field approximation,[5,6] values for Dq^{xy}, Dq^z, Ds, and Dt were estimated and shown in Table 2.

Comparison of the results with previous data[1,5,6] gives the following order as to the in-plane crystal field parameter: py>tox>acox>bzal$\gg$tu, where py and tu denote pyridine and thiourea, respectively. It is thus found that tox, acox, and bzox are close to py and much higher than tu in the spectrochemical series. A marked difference between tox and tu seems to be in agreement with the assumption that tox is coordinated as a unidentate ligand through its nitrogen atom with the nickel(II) ion; tu is known to be coordinated through the sulfur atom.

TABLE 3. ABSORPTION MAXIMA (in 10^3 cm^{-1}) OF METAL(II) COMPLEXES WITH 2-THIOPHENEALDEHYDE OXIME IN NUJOL

Compound	ν
$Ni(NCS)_2(tox)_2$	8.7, 16.4
$Ni(NCS)_2(acox)_2$	8.6, 16.5
$CoCl_2(tox)_4$	8.8, 15.3 sh, 18.6
$CoBr_2(tox)_4$	8.7, 14.8 sh, 18.3
$Co(NCS)_2(tox)_2$	9.1, 15.5 sh, 18.7

sh: shoulder. Band assignment may be made as previously reported in Ref. 1 in the text.

The complex $Ni(NCS)_2(tox)_2$ is paramagnetic with a moment of 3.2 BM, and its electronic absorption spectrum is typical of the six-coordinate nickel(II) complex (Table 3). This complex shows infrared ν(C–N) and ν(C–S) vibration at 2120 and 770 cm^{-1}, respectively. These values, which are close to those of $Ni(NCS)_2(acox)_2$, lie in the range expected for the bridging NCS group.[7] It is most likely that $Ni(NCS)_2(tox)_2$ has a similar structure to that of $Ni(NCS)_2(acox)_2$, which was concluded to have a multinuclear structure with six-coordinate nickel(II) ions and bridging NCS ions.[1]

Just as in the nickel(II) complexes with acetaldehyde oxime and benzaldehyde oxime,[1] the dihalogeno-nickel(II) complexes with 2-thiophenealdehyde oxime show hydrogen-bonded OH stretching vibrations at about 3180—3200 cm^{-1}, while $Ni(NCS)_2(tox)_2$ shows a sharp OH band at a much higher frequency, indicative of the presence of the non-hydrogen-bonded NOH group.

Cobalt(II) and Zinc(II) Complexes. Previously reported $CoCl_2(tox)_2$ and $ZnCl_2(tox)_2$[2] were not isolated, but only $CoX_2(tox)_4$ and $ZnCl_2(tox)_4$, X being Cl and Br, were obtained in the present work. The complexes $CoX_2(tox)_4$ are paramagnetic with magnetic

moments of about 5.1 BM, which are in the range expected for the six-coordinate cobalt(II) complexes. Their electronic absorption spectra are also typical of the six-coordinate cobalt(II) complexes (Table 3).

The powder X-ray diffraction patterns of $CoCl_2(tox)_4$ and $CoBr_2(tox)_4$ are very similar to those of the corresponding dichloro- and dibromo-nickel(II) analogues, respectively. Therefore, the complexes $CoX_2(tox)_4$ have a six-coordinate *trans*-dihalogeno-structure, in which the ligands tox are coordinated as unidentate ligands to the metal ion through the nitrogen atom, the sulfur atom in tox not being bound to the metal ion.

In a similar way $ZnCl_2(tox)_4$ has a *trans*-dihalogeno-structure, since its powder X-ray diffraction pattern is very similar to those of $CoCl_2(tox)_4$ and $NiCl_2(tox)_4$.

The complex $Co(NCS)_2(tox)_2$ shows a powder X-ray diffraction pattern, which is very similar to that of $Ni(NCS)_2(tox)_2$. Therefore, the cobalt(II) complex probably has a similar structure to that of the nickel(II) analogue, namely a multinuclear structure, in which the metal ions assume six-coordination with the NCS groups as bridges, just as in $Ni(NCS)_2(acox)_2$.[1] The cobalt(II) complex $Co(NCS)_2(tox)_2$ is paramagnetic with a magnetic moment of 4.95 BM, which lies in the range expected for the six-coordinate cobalt(II) complex. Its electronic spectrum is also in agreement with the six-coordinate stereochemistry. Its infrared ν(C–N) and ν(C–S) vibrations appear at 2110 and 775 cm^{-1}, respectively. The values indicate the presence of the bridging NCS group on the basis of the previously proposed criteria.[7]

Exactly like the corresponding nickel(II) complex, $CoX_2(tox)_4$ exhibit hydrogen-bonded OH stretching vibrations at about 3190—3200 cm^{-1}, while $Co(NCS)_2(tox)_2$ shows a sharp OH band at a much higher frequency, suggesting the presence of the non-hydrogen-bonded NOH group. This finding is similar to that of the corresponding complexes with acox and bzox.[1]

Copper(II) and Manganese(II) Complexes. Two copper(II) complexes $CuX_2(tox)_2$ were obtained in the present work, X being Cl and Br. One of them (X=Cl) had been reported previously.[2] In view of the results on the corresponding cobalt(II) and nickel(II) complexes, it may be reasonable to assume that tox is coordinated as a unidentate ligand through its nitrogen atom in the complexes $CuX_2(tox)_2$. Billing and Underhill[8] examined correlation between electronic absorption spectra and stereochemistry of complexes of the type CuX_2L_2, L being pyridine and its derivatives. On the basis of their conclusions, the stereochemistry of $CuX_2(acox)_2$ and $CuX_2(bzox)_2$ was discussed in a previous paper.[1]

The electronic spectra of $CuX_2(tox)_2$ have the first d-d band at about 14.3×10^3 cm^{-1}. The maxima are close to those of the multinuclear complexes $CuX_2(acox)_2$, $CuX_2(bzox)_2$, and $CuX_2(py)_2$.[1,8] According to the criteria reported previously,[1,8] and in view of the present finding that tox lies close to acox, bzox, and py in the spectrochemical series, the electronic spectra seem to indicate that $CuX_2(tox)_2$ most probably have a structure similar to that of the multinuclear forms of $CuX_2(acox)_2$, $CuX_2(bzox)_2$, and $CuX_2(py)_2$, in which the copper(II) ions are six-coordinated with halide ions as bridges.

The powder X-ray diffraction patterns of $MnCl_2(tox)_2$ and $MnBr_2(tox)_2$ are very similar to those of the corresponding dichloro- and dibromo-copper(II) analogues, respectively. It is most likely that the complexes $MnX_2(tox)_2$ may have a structure similar to that of the multinuclear $CuX_2(tox)_2$, the manganese(II) ions being in the six-coordinated environment with the halide ions as bridges. A similar structure was reported previously for $MnX_2(py)_2$.[9]

Table 4. Maxima of main d-d absorption bands and of some infrared bands of copper(II) complexes with 2-thiophenealdehyde oxime

Compound	d-d band, 10^3 cm^{-1}	Infrared bands, cm^{-1}	
		ν (M–L)	ν (M–X)
$CuCl_2(tox)_2$	14.3	272	310, 223
$CuBr_2(tox)_2$	14.3	262	221, 203
$CuCl_2(acox)_2$	14.8	272	296, 235
$CuBr_2(acox)_2$	14.8	259	243, 208
$CuCl_2(py)_2$	14.5	268	294, 235[a]
$CuBr_2(py)_2$	14.6	269	255, 202[a]
$MnCl_2(tox)_2$		213	232
$MnBr_2(tox)_2$		210	<200
$MnCl_2(py)_2$		212	233[a]
$MnBr_2(py)_2$		212	<200[a]

a) Infrared data are taken from Ref. 9 in the text.

Their infrared ν(M–X) and ν(M–L) bands also seem to correspond well to those of multinuclear $CuX_2(py)_2$, $CuX_2(acox)_2$, and $MnX_2(py)_2$ (Table 4).

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