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Synthesis and Characterization of Cobalt(II), Nickel(II), and Copper(II) Complexes with 2-Furancarbaldehyde Oxime

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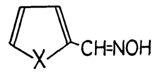
Cobalt(II), nickel(II), and copper(II) complexes with 2-furancarbaldehyde oxime have been prepared and characterized mainly on the basis of electronic spectra and magnetic data. The cobalt(II) and nickel(II) complexes of the formula $MX_2(oxime)_4$ (X=Cl, Br) have been isolated. They are all six-coordinated, the oxime being coordinated as a unidentate through the nitrogen atom. Copper(II) forms complexes of the formula $CuX_2(oxime)_2$ (X=Cl, Br). Possible structures for these complexes are discussed.

It has recently been concluded that 2-thiophenecarbaldehyde oxime (Ia, abbreviated as tox in the present paper) forms metal complexes of the type $MCl_2(tox)_4$ and $MBr_2(tox)_4$, M being Co(II), Ni(II), and Zn(II). The ligand tox in these complexes is coordinated as a unidentate through the nitrogen atom,[1] contrary to the previous claim[2] that only complexes of the type $MCl_2(tox)_2$ could be isolated, *tox* in these complexes functioning as a bidentate through its nitrogen and sulfur atoms.



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a: X=S , b: X=O

It was also claimed previously that 2-furancarbaldehyde oxime (Ib, abbreviated as *fox*) formed metal complexes of the type $MCl_2(fox)_2$, in which the ligand fox was coordinated as a bidentate through two oxygen atoms.[3,4] In view of our isolation of $MX_2(tox)_4$ instead of $MX_2(tox)_2$, reexamination of the metal complexes with fox is thought to be rewarding and significant. It is also interesting to examine whether or not the furan oxygen atom of fox may be coordinated with the metal ion.

Experimental

Materials. *syn*(α)- and *anti*(β)-2-Furancarbaldehyde oxime were prepared as reported previously.[5]

With *anti*-2-furancarbaldehyde oxime, all the metal complexes described below were synthesized successfully, their analytical data being given in Table1 . With *syn*-2-furancarbaldehyde oxime, however, the cobalt(II) and copper(II) complexes were synthesized in a similar manner, while attempts to isolate the nickel(II) complexes have so far been unsuccessful.

Dihalogenotetrakis(2-furancarbaldehyde oxime)cobalt(II), $CoX_2(fox)_4$ *(X=Cl, Br).* Cobalt(II) halide hexahydrate (10 mmol) was added to a solution of 2-furancarbaldehyde oxime (40 mmol) in ethanol (100 cm³) at 50 °C. The reaction was continued for 2 h. A brown precipitate was recrystallized from methanol to give orange (X=Cl) and red-orange (X=Br) crystals.

$Co(NCS)_2(fox)_2$. A method similar to the dihalogeno complexes yielded only $Co(NCS)_2(fox)_2$ instead of $Co(NCS)_2(fox)_4$. The precipitate was recrystallized from methanol to give red-brown crystals. Attempts to isolate $Co(NCS)_2(fox)_4$ have so far been unsuccessful.

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

$Ni(NCS)_2(fox)_4$. A solution of nickel(II) thiocyanate (10 mmol) and fox (40 mmol) in ethanol (100 cm³) was heated at 60 °C with stirring under reflux for 3 h. The solution was filtered and evaporated to about half the volume. A pale green precipitate was recrystallized from methanol–chloroform (3:7) to give green crystals.

The nickel(II) and cobalt(II) complexes described above are soluble in methanol, ethanol, and chloroform, but insoluble in benzene.

$CuX_2(fox)_2$ *(X=Cl, Br).* A suspension of anhydrous copper(II) halide (10 mmol) and fox (20 mmol) in ethanol (100 cm³) was heated at 50 °C for 1 h. A brown precipitate was recrystallized from ethanol to yield red-brown (X=Cl) and dark brown (X=Br) needle-like crystals.

These copper(II) complexes are soluble in hot methanol and ethanol, but insoluble in chloroform.

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 susceptibilities of the cobalt(II) and nickel(II) complexes were measured by the Gouy method at room temperature. Magnetic measurements with the copper(II) complexes were carried out in the temperature range of 4.2—300 K by the Faraday method using a Cahn balance.

Powder X-ray diffraction patterns were obtained with a Rigakudenki 4001-A2 diffractometer using Co $K\alpha$ radiation and an iron filter.

Results and Discussion

Nickel(II) Complexes. Previously a compound of composition $NiCl_2(fox)_2$ was reported and was claimed to contain the molecules of fox functioning as bidentate ligands.[3,4] In the present work, however, this complex could not be isolated, but compounds of the formula $NiX_2(fox)_4$ only were obtained, X being Cl, Br, and NCS.

The nickel(II) complexes prepared are paramagnetic and of a high spin type (Table 1). Their magnetic moments are in the range expected for the six-coordinate nickel(II) complexes.

The electronic absorption spectra of $NiCl_2(fox)_4$ and $NiBr_2(fox)_4$ are very similar to those of *trans*-$NiX_2(tox)_4$ (Fig. 1). Hence, it is presumed that $NiX_2(fox)_4$ (X=Cl, Br) have a six-coordinate *trans*-dihalogeno structure, in which the oxime molecules are bound through their nitrogen atoms as unidentate ligands with the nickel-

Table 1. Analytical data of nickel(II), cobalt(II), and copper(II) complexes with 2-furancarbaldehyde oxime

Compound	Found, %			Calcd, %			$\mu^{a)}$
	C	H	N	C	H	N	
$NiCl_2(fox)_4$	41.57	3.65	9.90	41.85	3.51	9.76	3.23
$NiBr_2(fox)_4$	36.61	3.30	8.51	36.24	3.04	8.46	3.22
$Ni(NCS)_2(fox)_4$	42.82	3.26	13.57	42.67	3.22	13.52	3.23
$CoCl_2(fox)_4$	41.45	3.47	9.74	41.83	3.51	9.76	5.03
$CoBr_2(fox)_4$	36.22	3.28	8.54	36.24	3.04	8.45	5.11
$Co(NCS)_2(fox)_2$	36.03	2.81	13.90	36.27	2.54	14.10	4.90
$CuCl_2(fox)_2$	33.40	3.14	7.82	33.67	2.83	7.86	1.86
$CuBr_2(fox)_2$	27.17	2.58	6.48	26.95	2.23	6.29	1.88

a) μ: BM at room temperature.

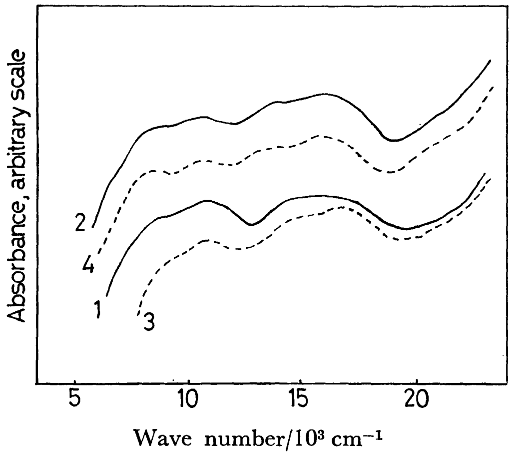

Fig. 1. Electronic absorption spectra of *trans*-$NiX_2(fox)_4$ (——) and *trans*-$NiX_2(tox)_4$ (----) in Nujol. 1: X=Cl, 2: X=Br, 3: X=Cl, 4: X=Br.

Table 2. Absorption maxima of metal(II) complexes with 2-furancarbaldehyde oxime

Compound	d-d bands 10^{-3} cm^{-1}
$Ni(NCS)_2(fox)_4$	8.9, 14.8, 25.6
$Ni(NCS)_2(py)_4$[a]	10.1, 16.7, 26.7
$Ni(NCS)_2(NH_3)_4$[b]	10.8, 17.4, 28.0
$CoCl_2(fox)_4$	9.1, 15.6 sh, 18.5
$CoBr_2(fox)_4$	8.8, 15.4 sh, 18.1
$CoCl_2(tox)_4$[c]	8.8, 15.3 sh, 18.6
$CoBr_2(tox)_4$[c]	8.7, 14.8 sh, 18.3
$Co(NCS)_2(fox)_2$	9.6, 15.1 sh, 19.2
$Co(NCS)_2(tox)_2$	9.1, 15.5 sh, 18.7

sh: Shoulder. a) O. Piovesana and C. Furlani, *J. Inorg. Nucl. Chem.*, **30**, 1249 (1968). b) Ref. 7. c) Ref. 1.

Table 3. Infrared ν(OH) and ν(C=N) frequencies of metal complexes with 2-furancarbaldehyde oxime

Compound	ν(OH) cm^{-1}	ν(C=N) cm^{-1}
$NiCl_2(fox)_4$	3225	1662
$NiBr_2(fox)_4$	3250	1662
$Ni(NCS)_2(fox)_4$	3210	1660
$CoCl_2(fox)_4$	3250	1660
$CoBr_2(fox)_4$	3260	1655
$Co(NCS)_2(fox)_2$	3430	1655
$CuCl_2(fox)_2$	3250	1660
$CuBr_2(fox)_2$	3260	1660
fox(anti-form)	3155	1645

(II) ion. The powder X-ray diffraction pattern of $NiCl_2(fox)_4$ is similar to that of $NiBr_2(fox)_4$. The Ni–O (furan) vibration around 400—500 cm^{-1} previously reported for $NiCl_2(fox)_2$[4] was not observed for $NiCl_2(fox)_4$ prepared in the present work.

The approximate symmetry of *trans*-$NiX_2(fox)_4$ 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 observed flat absorption curves are regarded as due to overlapping of split components of the d-d bands.

The complex $Ni(NCS)_2(fox)_4$ is paramagnetic with a moment of 3.2 BM, and its electronic absorption spectrum is typical of the six-coordinate nickel(II) complex (Table 2). Infrared O–N stretching, C–S stretching, and NCS bending vibrations occur at 2108, 830, and 470 cm^{-1}, respectively, indicating that the NCS^- ions are bound through the nitrogen atoms with the nickel(II) ion. Each of these bands appears as a single symmetrical peak, in agreement with the *trans*-diisothiocyanato structure.[6]

The d-d band splitting for *trans*-$Ni(NCS)_2(fox)_4$ may be small, since fox lies close to NCS^- in the spectrochemical series, both the ligands being coordinated through the nitrogen atom, The electronic spectrum of this complex is similar, in the shape of the whole curve as well as in the band maxima, to that of *trans*-$Ni(NCS)_2(NH_3)_4$, which also shows very slight splitting of the d-d bands.[7]

Just like the nickel(II) complexes with such a nitrogen-coordinating unidentate as tox,[1] the nickel(II) complexes with fox show hydrogen-bonded OH stretching vibrations at about 3200—3300 cm^{-1} (Table 3).

Cobalt(II) Complexes. Previously reported $CoCl_2(fox)_2$[3,4] has not been isolated, but $CoX_2(fox)_4$, X being Cl and Br, have been obtained in the present

Table 4. Maxima of main d-d bands of copper(II) complexes with 2-furancarbaldehyde oxime and related ligands

Compound	d-d band 10^3 cm^{-1}
$CuCl_2(\mathit{fox})_2$	14.3
$CuBr_2(\mathit{fox})_2$	14.4
$CuCl_2(\mathit{tox})_2$	14.3
$CuBr_2(\mathit{tox})_2$	14.3
$CuCl_2(\mathit{py})_2$	14.5
$CuBr_2(\mathit{py})_2$	14.6

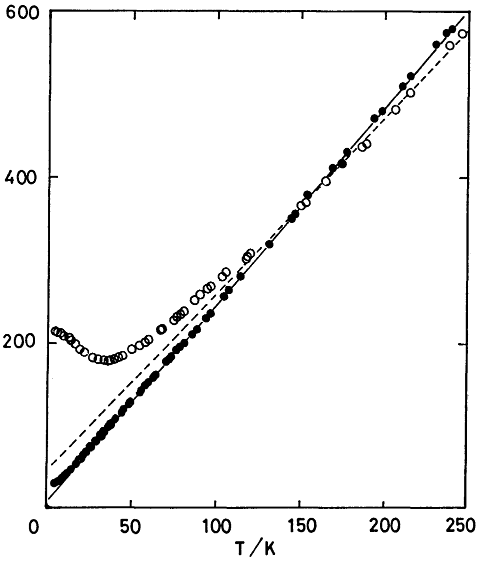

Fig. 2. Plots of reciprocal magnetic susceptibilities (corrected for the temperature-independent paramagnetism) of $CuX_2(\mathit{fox})_2$ against absolute temperature. ●: Experimental for X=Cl, ○: experimental for X=Br. The solid line (X=Cl) and dashed line (X=Br) were derived theoretically from the Curie-Weiss law, θ and g being 4 K and 2.12 for X=Cl and 20 K and 2.25 for X=Br. The value for $N\alpha$ was assumed to be 60×10^{-6} cgs emu.

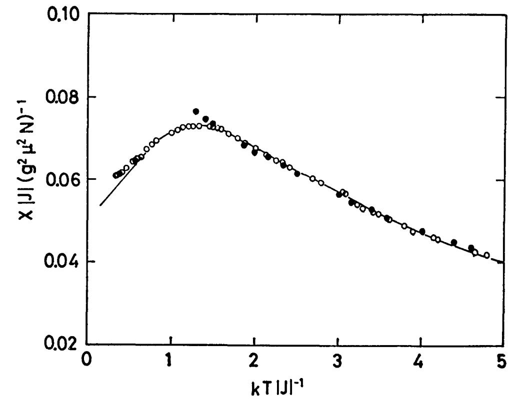

Fig. 3. Magnetic susceptibilities (corrected for the temperature-independent paramagnetism) of $CuX_2(\mathit{fox})_2$. ●: Experimental for X=Cl, ○: experimental for X=Br. The solid curve was obtained by the method of Bonner and Fisher assuming the antiferromagnetic linear chain and on the basis of the Heisenberg model for the interaction between spins with $S=1/2$. For $CuCl_2(\mathit{fox})_2$ $J/k=-3.5$ K, $g=2.06$, $N\alpha=60\times10^{-6}$ cgs emu and for $CuBr_2(\mathit{fox})_2$ $J/k=-25$ K, $g=2.27$, $N\alpha=60\times10^{-6}$ cgs emu.

work. On the other hand, the complex $Co(NCS)_2(\mathit{fox})_2$ has been isolated instead of $Co(NCS)_2(\mathit{fox})_4$.

The complexes $CoX_2(\mathit{fox})_4$ are paramagnetic with magnetic moments of 5.0—5.1 BM, which are in the range expected for the six-coordinate cobalt(II) complexes (Table 1), the d-d band maxima being nearly equal to those of *trans*-$CoX_2(\mathit{tox})_4$ (Table 2). The powder X-ray pattern of $CoCl_2(\mathit{fox})_4$ is very similar to that of $NiCl_2(\mathit{fox})_4$, which has been presumed to have a *trans*-dihalogeno structure. It is very likely, therefore, that the complexes $CoX_2(\mathit{fox})_4$ have a six-coordinate *trans*-dihalogeno structure, in which the ligands *fox* are coordinated as unidentate ligands to the cobalt(II) ion through the nitrogen atom, the oxygen atom in *fox* not being bound to the metal ion.

The complex $Co(NCS)_2(\mathit{fox})_2$ is paramagnetic with a magnetic moment of 4.9 BM, which lies in the range expected for the six-coordinate cobalt(II) complex, Its electronic spectrum (Table 2) is also in agreement with this stereochemistry. Its infrared C–N stretching, C–S stretching, and NCS bending vibrations appear at 2100, 780, and 484 and 475 cm^{-1}. These values indicate the presence of the bridging NCS group on the basis of the previously proposed criteria.[8]

Exactly like the corresponding nickel(II) complexes,[1] $CoX_2(\mathit{fox})_4$ exhibit hydrogen-bonded OH stretching vibrations at about 3200—3300 cm^{-1}, while $Co(NCS)_2(\mathit{fox})_2$ shows a sharp OH band at a much higher frequency, indicative of the presence of the non-hydrogen-bonded NOH group (Table 3). When *fox* is bound with the metal ion, ν(C=N) and ν(N–O) frequencies of *fox* are found to shift toward higher frequencies. These findings are similar to those of the corresponding complexes with *acox* and *tox*, *acox* being acetaldehyde oxime. The Co–O(furan) vibration at about 400—500 cm^{-1}, which was reported previously for $CoCl_2(\mathit{fox})_2$,[4] has not been observed with $CoX_2(\mathit{fox})_4$ prepared in the present work.

Copper(II) Complexes. Two copper(II) complexes $CuX_2(\mathit{fox})_2$, X being Cl and Br, have been obtained in the present work. In view of the results on the corresponding cobalt(II) and nickel(II) complexes and also on the metal complexes with related oximes,[1,9] it may be reasonable to assume that *fox* is coordinated as a unidentate ligand through its nitrogen atom in $CuX_2(\mathit{fox})_2$.

Billing and Underhill examined correlation between electronic absorption spectra and stereochemistry of complexes of the type CuX_2L_2, L being pyridine and its derivatives.[10] On the basis of their conclusions, the stereochemistry of $CuX_2(\mathit{tox})_2$ and $CuX_2(\mathit{acox})_2$ was discussed with reasonable success in previous papers.[1,9] The d-d band maxima of $CuX_2(\mathit{fox})_2$ are close to those of the multinuclear complexes $CuX_2(\mathit{tox})_2$ and $CuX_2(\mathit{py})_2$ (Table 4).[1] According to the criteria reported previously,[1,10] and in view of the present finding that *fox* lies very close to *tox*, *acox*, and *py* in the spectrochemical series, the electronic spectra seem to indicate that $CuX_2(\textit{fox})_2$ most probably have a multinuclear structure similar to that of $CuX_2(\textit{tox})_2$, $CuX_2(\textit{acox})_2$, and $CuX_2(\textit{py})_2$, in which the copper(II) ions are six-coordinated with halide ions as bridges. The two complexes $CuCl_2(\textit{fox})_2$ and $CuBr_2(\textit{fox})_2$ have a similar structure, since they show similar powder X-ray diffraction patterns.

The copper(II) complexes with such a structure as assumed above are expected to exhibit the antiferromagnetism characteristic of the chain structure with bridges, –Cu–X–Cu–X–Cu–. Room temperature moments of $CuX_2(\textit{fox})_2$, which are 1.86 (X=Cl) and 1.88 BM (X=Br), differ very little from the normal moments. As shown in Fig. 2, the susceptibilities obey the Curie-Weiss law in the higher temperature range, the Curie-Weiss constants θ being 4 K for $CuCl_2(\textit{fox})_2$ and 20 K for $CuBr_2(\textit{fox})_2$. The temperature dependence of magnetic susceptibilities below 5 K is shown in Fig. 3. Except for deviation below 1.5 K for the chloro complex, the data are in good coincidence with the theoretical curves derived by the method of Bonner and Fisher,11) which is based upon the assumption of an infinite one-dimensional Heisenberg spin lattice with $S=1/2$.

These findings combined may be regarded as supporting the assumption of the antiferromagnetic interaction through halide ions between copper ions in the proposed structure.

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