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Synthesis and Properties of Cobalt(II), Nickel(II), and Copper(II) Complexes with Acetaldehyde Oxime and Benzaldehyde Oxime

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Cobalt(II), nickel(II), and copper(II) complexes with acetaldehyde oxime and benzaldehyde oxime have been prepared and characterized by vibrational and electronic spectroscopy, magnetism, and other methods. The cobalt(II) and nickel(II) complexes isolated are of the general formulae: (A) $MX_2(oxime)_4$ ($X=Cl$, Br, I, NO_3, NCS and CH_3COO); (B) $M(NCS)_2(oxime)_2$; (C) MSO_4 $(oxime)_3 \cdot 3H_2O$. They are all six-coordinate, and the complexes (B) are probably multinuclear. Copper(II) forms complexes of the formulae: (A) $CuX_2(oxime)_4$ ($X=Cl$, Br), (B) $CuX_2(oxime)_2$ ($X=Cl$, Br, NCS); (C) $CuSO_4(oxime)_4 \cdot H_2O$. Possible structures for these copper(II) complexes are also discussed. Acetaldehyde oxime and benzaldehyde oxime are unidentates in all these complexes, being coordinated through their nitrogen atom.

Some complexes of cobalt, nickel, and copper with acetaldehyde oxime and benzaldehyde oxime were prepared fifty years ago.[1] However, little work has been done on the more detailed examination of their stereochemistries based upon physicochemical measurements.[2,3] Such studies are thought to be highly desirable in order to elucidate the nature of interaction between the oximes and transition metal ions.

In the present work cobalt(II), nickel(II), and copper(II) complexes with acetaldehyde oxime and benzaldehyde oxime, including previously reported ones, have been synthesized and their stereochemistries have been examined on the basis of vibrational and electronic spectra, magnetism, conductivities, and powder X-ray diffraction patterns. Acetaldehyde oxime and benzaldehyde oxime are abbreviated in the present paper as acox and bzox, respectively.

Experimental

Materials. Acetaldehyde oxime and benzaldehyde oxime were obtained commercially and used as received.

Analytical data of the metal complexes prepared in the present work are given in Tables 1 and 2.

Dichloro- and Dibromotetrakis(acetaldehyde oxime)nickel(II), $NiX_2(acox)_4$ ($X=Cl$, Br) were prepared as reported previously.[1]

Diiodotetrakis(acetaldehyde oxime)nickel(II) Hydrate, $NiI_2(acox)_4 \cdot H_2O$. A suspension of $NiI_2 \cdot 6H_2O$ (0.01 mol) in chloroform (50 ml) was heated under stirring at 40 °C for 15 min and acetaldehyde oxime (0.04 mol) was added to the suspension. The mixture was heated at 40 °C for 1 h and filtered. The filtrate was concentrated to 10 ml with a rotary evaporator at 40 °C and allowed to stand in a refrigerator overnight. A crystalline precipitate was collected by filtration and recrystallized from chloroform to yield olive-green, prismatic crystals.

TABLE 1. ANALYTICAL DATA OF NICKEL(II) AND COBALT(II) COMPLEXES WITH ACETALDEHYDE OXIME AND BENZALDEHYDE OXIME

Compound	Found, %			Calcd, %			μ
	C	H	N	C	H	N	
$NiCl_2(acox)_4$	26.09	5.60	15.33	26.26	5.51	15.31	3.22
$NiBr_2(acox)_4$	20.72	4.65	12.37	21.13	4.43	12.32	3.18
$NiI_2(acox)_4 \cdot H_2O$	16.95	3.82	9.94	16.95	3.91	9.89	3.14
$Ni(NO_3)_2(acox)_4 \cdot H_2O$	21.77	4.95	19.14	21.99	5.07	19.23	3.16
$Ni(CH_3COO)_2(acox)_4$	34.62	6.25	13.32	34.90	6.34	13.57	3.13
$NiSO_4(acox)_3 \cdot 3H_2O$	18.43	5.16	10.74	18.67	5.48	10.89	3.17
$Ni(NCS)_2(acox)_4$	29.14	4.97	20.57	29.21	4.90	20.44	3.02
$Ni(NCS)_2(acox)_2$	24.90	3.60	19.58	24.59	3.44	19.12	3.23
$NiCl_2(bzox)_4$	54.76	4.68	9.13	54.30	4.60	13.43	3.17
$NiBr_2(bzox)_4$	47.83	4.16	7.95	47.83	4.01	7.97	3.08
$NiI_2(bzox)_4 \cdot H_2O$	41.26	3.65	6.78	41.26	3.71	6.87	3.07
$Ni(NCS)_2(bzox)_2$	45.90	3.53	13.42	46.07	3.38	13.43	3.17
$CoCl_2(acox)_4$	25.87	5.72	15.23	26.24	5.51	15.30	4.86
$CoBr_2(acox)_4$	21.04	4.59	12.40	21.12	4.43	12.31	4.93
$CoSO_4(acox)_3 \cdot 3H_2O$	19.01	5.13	11.06	18.66	5.48	10.88	5.15
$Co(NCS)_2(acox)_2$	24.30	3.63	19.19	24.57	3.44	19.11	4.85
$CoCl_2(bzox)_4$	54.62	4.66	9.22	54.73	4.59	9.12	5.11
$CoBr_2(bzox)_4$	47.81	4.01	8.02	47.81	4.01	7.97	5.04
$Co(NCS)_2(bzox)_2$	45.62	3.54	13.24	46.04	3.38	13.42	4.90

μ: BM at room temperature.

TABLE 2. ANALYTICAL DATA OF COPPER(II) COMPLEXES WITH ACETALDEHYDE OXIME AND BENZALDEHYDE OXIME

Compound	Found, % C	Found, % H	Found, % N	Calcd, % C	Calcd, % H	Calcd, % N	μ
$CuCl_2(acox)_4$	25.71	5.48	15.04	25.92	5.44	15.11	1.80
$CuBr_2(acox)_4$	20.62	4.44	12.18	21.03	4.39	12.19	1.88
$CuCl_2(acox)_2$	19.18	4.14	10.98	19.02	4.00	11.09	1.88
$CuBr_2(acox)_2$	13.69	3.06	8.03	14.07	2.95	8.20	1.82
$CuSO_4(acox)_4\cdot H_2O$	23.62	5.13	13.82	23.21	5.36	13.54	1.92
$CuCl_2(bzox)_2$	44.32	3.88	7.43	44.63	3.75	7.44	1.99
$CuBr_2(bzox)_2$	36.11	3.03	6.06	36.11	3.03	6.02	1.87

μ: BM at room temperature.

Dinitratotetrakis(acetaldehyde oxime)nickel(II) Hydrate, $Ni(NO_3)_2(acex)_4\cdot H_2O$, was prepared from $Ni(NO_3)_2\cdot 6H_2O$(0.01 mol) and acetaldehyde oxime (0.04 mol) in a manner analogous to the diiodo-complex.

$Ni(NCS)_2(acox)_4$ and $Ni(NCS)_2(acox)_2$. A suspension of $Ni(NCS)_2$ (0.01 mol) in ethanol (50 ml) was heated at 60 °C under stirring for 2 h, until the solution turned green, and filtered. To the filtrate was added acetaldehyde oxime (0.04 mol) and stirred for 1 h at room temperature. On evaporating the solution spontaneously, blue crystals of $Ni(NCS)_2(acox)_4$ appeared in the solution. They were collected by filtration and washed with ethanol. The filtrate was heated for 2 h at room temperature. A crystalline powder of $Ni(NCS)_2(acox)_2$ formed in the solution was filtered, washed with ethanol, and dried in a desiccator over silica gel.

$NiSO_4(acox)_3\cdot 3H_2O$ was prepared as blue microcrystals from $NiSO_4\cdot 7H_2O$ (0.01 mol) and acetaldehyde oxime (0.04 mol) in a manner analogous to the dinitrato-complex.

Dichloro- and Dibromotetrakis(benzaldehyde oxime)nickel(II), $NiX_2(bzox)_4$ (X=Cl, Br), were prepared by the literature method.[1)]

Diiodotetrakis(benzaldehyde oxime)nickel(II) Hydrate, $NiI_2(bzox)_4\cdot H_2O$, was prepared as olive-green crystals in a manner similar to the corresponding acetaldehyde oxime complex.

Dihalogenotetrakis(acetaldehyde oxime)- and Dihalogenotetrakis(benzaldehyde oxime)cobalt(II), $CoX_2(acox)_4$ and $CoX_2(bzox)_4$ (X=Cl, Br), were prepared as reported previously.[1)]

$Co(NCS)_2(acox)_2$. To a suspension of $Co(NCS)_2\cdot 4H_2O$ (0.01 mol) in chloroform (50 ml) was added acetaldehyde oxime (0.04 mol) at 60 °C, and the mixture was refluxed for 2 h. A pink crystalline precipitate was filtered and washed with chloroform several times.

$Co(NCS)_2(bzox)_2$ was prepared as red-brown crystals in a manner analogous to the corresponding complex with benzaldehyde oxime.

$CoSO_4(acox)_3\cdot 3H_2O$ was prepared as wine-red crystals from $CoSO_4\cdot 7H_2O$ (0.01 mol) and acetaldehyde oxime (0.04 mol) in a manner analogous to the corresponding nickel(II) complex.

$CuCl_2(acox)_2$. To a solution of $CuCl_2\cdot 2H_2O$ (0.015 mol) in ethanol (50 ml) was added acetaldehyde oxime (0.02 mol), and the solution was stirred at room temperature for 3 h. Light-blue flaky crystals of $CuCl_2(acox)_2$ formed in the solution were filtered and washed with ether. The *filtrate* was used for preparing $CuCl_2(acox)_4$. The crystals thus obtained are highly hygroscopic. When left in a desiccator over silica gel for a long time, the blue form of $CuCl_2(acox)_2$ transformed into a green substance of the same composition.

Dichlorotetrakis(acetaldehyde oxime)copper(II), $CuCl_2(acox)_4$. Acetaldehyde oxime (0.05 mol) was added to the *filtrate* obtained in the preparation of $CuCl_2(acox)_2$. Stirring the solution at room temperature for 15 min yielded blue prismatic crystals. They are hygroscopic and are readily decomposed even in the solid state. When kept in a desiccator over silica gel, they gradually lose acetaldehyde oxime, turning green. The composition of the green final product was close to $CuCl_2(acox)_2$.

$CuBr_2(acox)_4$ and *$CuBr_2(acox)_2$* were prepared as blue and yellow-green crystals, respectively, by methods similar to the corresponding dichloro-complexes. They are hygroscopic. When left in a desiccator, $CuBr_2(acox)_4$ loses acetaldehyde oxime to yield $CuBr_2(acox)_2$.

$CuCl_2(bzox)_2$ was prepared as yellow-green crystals by the literature method.[1)] Purification was carried out by recrystallization from chloroform or acetone.

$CuBr_2(bzox)_2$ was prepared as brown crystals from $CuBr_2$ and benzaldehyde oxime in a manner analogous to the corresponding dichloro-complex.

$CuSO_4(acox)_4\cdot H_2O$. To a suspension of $CuSO_4\cdot 5H_2O$ (0.01 mol) in chloroform was added acetaldehyde oxime (0.06 mol), and the mixture was stirred at room temperature for a few hours. The precipitate was recrystallized from chloroform to yield a blue crystalline powder.

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

Magnetic measurements at room temperature were carried out by the Gouy method using $CoHg(SCN)_4$ as a calibrant.

Powder X-ray diffraction patterns were obtained with a Toshiba DX-103 X-ray diffractometer equipped with a Geiger-Müller counter, using Co $K\alpha$ radiation and an iron filter.

Conductivity measurements were carried out using a calibrated Toa-Electronics CG 201 PL conductivity cell and a Toa-Electronics Model CM-1DB conductivity bridge.

Results and Discussion

Nickel(II) Complexes. The following types of nickel(II) complexes were isolated, L being acox or bzox: (1) NiX_2L_4 (X=Cl, Br, I, NO_3, CH_3COO); (2) $Ni(NCS)_2L_2$; (3) $NiSO_4(acox)_3\cdot 3H_2O$. All these nickel(II) complexes are paramagnetic with magnetic moments of 3.0—3.2 BM (Table 1). The dichloro- and dibromo-nickel(II) complexes were reported previously by Hieber and Leutert.[1)]

All the dihalogeno-complexes are non-electrolytes in nitrobenzene, indicating that the halide ions are bound to the nickel(II) ion. According to a previous X-ray study,[3] $NiCl_2(acox)_4$ in the crystalline state has a six-coordinate *trans*-dichloro-structure. The acetaldehyde oxime molecules are coordinated to the nickel(II) ion through their nitrogen atom, and the OH group is hydrogen-bonded to Cl. It is presumed that $NiX_2(acox)_4$ (X=Br, I) and $NiX_2(bzox)_4$ (X=Cl, Br, I) also have a six-coordinate *trans*-dihalogeno-structure, since their electronic absorption spectra are similar to that of *trans*-$NiCl_2(acox)_4$. They all show a significantly large tetragonal splitting in the d-d bands. This *trans*-structure is retained in chloroform, since the spectra of the chloroform solutions are essentially the same as the solid state spectra. On the contrary, they undergo decomposition in water, methanol, and ethanol. For instance, the spectra of the ethanolic solutions differ appreciably from the spectra of the chloroform solutions as well as from the solid state spectra.

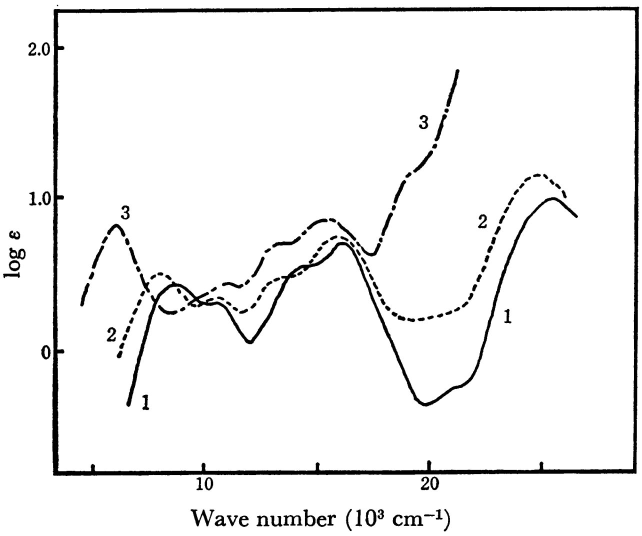

Fig. 1. Electronic absorption spectra of *trans*-dihalogenotetrakis(acetaldehyde oxime)nickel(II), *trans*-$NiX_2(acox)_4$, in chloroform: 1, X=Cl; 2, X=Br; 3, X=I.

As representative examples, the spectra of the acetaldehyde oxime complexes are shown in Fig. 1. It is predicted theoretically that regularly octahedral nickel(II) complexes 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}. If the splitting is considerably large, the components are likely to be well resolved in the observed spectrum. The band splitting in the spectra of the present dihalogeno-complexes is large enough to enable us to resolve the three main d-d bands into their components with reasonable accuracy. The maxima of the components obtained are shown in Table 3. From these data and using expressions derived on the basis of the crystal field approximation,[4] the tetragonal splitting parameters were estimated. The results are shown in Table 3. For *trans*-$NiCl_2(acox)_4$ a similar analysis was made previously using solid state spectrum.[2] The results roughly agree with the present ones. Comparison of the present results with previous studies[4a] on $NiX_2(py)_4$, py being pyridine, gives the following order as to the in-plane crystal field parameter: bzox<acox<py. It is thus found that bzox and acox are close to, though slightly lower than, py in the spectrochemical series.

Table 3. Split components of d-d bands and crystal field parameters in 10^3 cm^{-1} of *trans*-NiX_2L_4

	L=acox (=bzox)		
	X=Cl	X=Br	X=I
$\nu(^3E_g{}^a \leftarrow {}^3B_{1g})$	8.7	8.2	7.3
	(8.5	8.2	7.5)
$\nu(^3B_{2g} \leftarrow {}^3B_{1g})$	10.6	10.6	10.4
	(10.4	10.5	10.4)
$\nu(^3A_{2g} \leftarrow {}^3B_{1g})$	14.2	13.5	12.2
	(13.6	13.5	13.4)
$\nu(^3E_g{}^b \leftarrow {}^3B_{1g})$	16.3	16.2	15.7
	(16.2	15.9	16.1)
Dq^{xy}	1.06	1.06	1.04
	(1.04	1.04	1.05)
Dq^z	0.62	0.57	0.42
	(0.62	0.59	0.46)
Dt	0.24	0.27	0.35
	(0.24	0.26	0.33)
Ds	0.30	0.51	0.66
	(0.48	0.46	0.55)

In $Ni(NO_3)_2(acox)_4$ the nitrate ions are not free but coordinated to the nickel(II) ion, since infared bands due to the nitrate ions occur at 1290, and 1495 cm^{-1}.[5] The complex is paramagnetic and its electronic spectrum is typical of the six-coordinate nickel(II) complex (Table 4). The broad d-d bands at about 10 and 17×10^3 cm^{-1} have a shoulder at higher frequencies in the former band and at lower frequencies in the latter, indicating

Table 4. Maxima of main d-d absorption bands of nickel(II) complexes with acetaldehyde oxime and benzaldehyde oxime

Compound	Medium	ν_1(log ε)	ν_2(log ε)	ν_3(log ε)
$Ni(CH_3COO)_2(acox)_4$	Nujol	9.9	16.7	27.1
	$CHCl_3$	9.8 (0.62)	16.6 (0.76)	26.3 (1.20)
$Ni(NO_3)_2(acox)_4 \cdot H_2O$	Nujol	9.3	17.0	26.9
	$CHCl_3$	9.3 (0.59)	16.6 (0.85)	26.9 (1.17)
$NiSO_4(acox)_3 \cdot 3HO_2$	Nujol	8.3, 10.7	16.7	26.7
$Ni(NCS)_2(acox)_4$	Nujol	9.9	16.9	26.9
	$CHCl_3$	10.1 (1.08)	16.6 (1.15)	26.7 (1.74)
$Ni(NCS)_2(acox)_2$	Nujol	8.6, 11.2 sh	16.6	27.1
$Ni(NCS)_2(bzox)_2$	Nujol	8.5, 10.9 sh	16.2	27.1

ν_1 $^3T_{2g} \leftarrow {}^3A_{2g}$; ν_2 $^3T_{1g} \leftarrow {}^3A_{2g}$; ν_3 $^3T_{1g}(P) \leftarrow {}^3A_{2g}$ or components thereof. sh: shoulder.

an apparent band splitting, in agreement with the model of the six-coordinate *trans*-dinitrato-complex.

The complex $Ni(CH_3COO)_2(acox)_4$ exhibits CO stretching vibrations at 1580 and 1340 cm^{-1}, showing that the acetate ions are not free but coordinated to the nickel(II) ion as unidentate ligands.[5] The complex is paramagnetic and shows an electronic absorption spectrum typical of the six-coordinate nickel(II) complex.

In $NiSO_4(acox)_3 \cdot 3H_2O$, the ν_1 stretching vibration due to the sulfate group appears at 993 cm^{-1} and ν_3 is split into three bands at 1040, 1085, and 1200 cm^{-1}. Based on the criteria proposed previously,[5] these results indicate that the sulfate group in this complex is coordinated as a bidentate ligand to the nickel(II) ion. Its electronic spectrum is typical of the six-coordinate nickel(II) complex (Table 4). It is, therefore, most likely that the nickel(II) ion forms a six-coordinate complex with three acetaldehyde oxime molecules, a bidentate sulfate ion and a water molecule coordinated. A multinuclear structure, however, may not be eliminated.

$Ni(NCS)_2(acox)_4$ is paramagnetic with a moment of about 3 BM, indicative of a six-coordinate structure for this complex. Its Nujol spectrum is similar to the spectrum of its chloroform solution, showing that the configuration in the solid state is retained in the chloroform solution. The spectra are typical of the six-coordinate nickel(II) complex, and resemble that of *trans*-$Ni(NCS)_2(NH_3)_4$,[6] although slightly displaced towards lower frequencies. It is highly probable that $Ni(NCS)_2(acox)_4$ has a similar structure to that of *trans*-$Ni(NCS)_2(NH_3)_4$ with the thiocyanate ions coordinated through their nitrogen atom to the nickel(II) ion. Any appreciable splitting was not observed in the d-d bands for $Ni(NCS)_2(NH_3)_4$ and $Ni(NCS)_2(acox)_4$, possibly because the N-coordinating thiocyanate stands comparatively close to acox and NH_3 in the spectrochemical series.

The complex $Ni(NCS)_2(acox)_4$ undergoes decomposition gradually. Infrared bands due to unidentate N-coordinating thiocyanate ions appear at 2090 and 820 cm^{-1}, but in addition to them another band, probably originating from the decomposition product, appears at 2020 cm^{-1}.

The complexes $Ni(NCS)_2L_2$, L being acox and bzox, are paramagnetic (Table 1) and show electronic absorption spectra typical of the six-coordinate nickel(II) complex (Table 4). They show infrared ν(C–N) and ν(C–S) vibrations at 2115 and 780 cm^{-1} for L=acox and at 2130 and 785 cm^{-1} for L=bzox. The values lie in the range expected for the bridging NCS group.[7] It is highly probable that $Ni(NCS)_2L_2$ are multinuclear with six-coordinate nickel(II) ions and bridging NCS ions, having a similar structure to that of $Ni(NCS)_2(py)_2$.[8]

All the nickel(II) complexes show hydrogen bonded OH stretching vibrations at about 3150—3200 cm^{-1}, except for $Ni(NCS)_2(acox)_2$ and $Ni(NCS)_2(bzox)_2$, which show a sharp band at a much higher frequency, indicative of the presence of the non-hydrogen-bonded NOH group (Table 6).

Cobalt(II) Complexes. The following types of cobalt(II) complexes were isolated, L being acox and bzox: (1) CoX_2L_4 (X=Cl, Br); (2) $Co(NCS)_2L_2$; (3) $CoSO_4(acox)_3 \cdot 3H_2O$. The dichloro- and dibromo-complexes were prepared previously.[1]

The complexes $CoX_2(acox)_4$ and $CoX_2(bzox)_4$ are paramagnetic with magnetic moments of 4.9—5.2 BM, which are in the range expected for six-coordinate cobalt(II) complexes. Their electronic absorption spectra (Table 5) are also typical of the six-coordinate cobalt(II) complexes. Conductivity measurements show that they are non-electrolytes in nitrobenzene. It is most likely that in these cobalt(II) complexes the six-coordination of the cobalt(II) ion is achieved by two halide ions and four oximes, which are unidentate ligands coordinating through the nitrogen atom. In agreement with this, their OH stretching vibrations appear at frequencies close to those of the dihalogeno-nickel(II) complexes, which have been concluded to have a *trans*-configuration. The powder X-ray diffraction patterns of the dichloro-cobalt(II) complexes are similar to those of the dibromo-cobalt(II) complexes. When dissolved in chloroform, the dichloro-cobalt(II) complexes retain the structure existing in the solid state, while the dibromo-cobalt(II) complexes tend to undergo decomposition gradually. Both the dichloro- and the dibromo-complexes are decomposed in methanol, ethanol, and water.

In $CoSO_4(acox)_3 \cdot 3H_2O$, the ν_1 stretching vibration due to the sulfate group appears at 940 cm^{-1} and ν_3 is split into three bands at 1030, 1080, and 1190 cm^{-1}. As discussed in the preceding section of the present paper,

TABLE 5. MAXIMA OF MAIN d-d ABSORPTION BANDS OF COBALT(II) COMPLEXES WITH ACETALDEHYDE OXIME AND BENZALDEHYDE OXIME

Compound	Medium	ν_1(log ε)	ν_2(log ε)	ν_3(log ε)
$CoCl_2(acox)_4$	Nujol	8.4	15.3 sh	18.4, 19.5
	$CHCl_3$	8.3 (0.33)	15.4 sh	18.1 (0.91), 19.3 (0.96)
$CoBr_2(acox)_4$	Nujol	8.4	15.1 sh	17.8, 18.9
$CoCl_2(bzox)_4$	Nujol	8.3	15.2 sh	18.3, 19.1
	$CHCl_3$	8.3 (0.52)	15.2 sh	18.1 (1.37), 19.0 (1.38)
$CoBr_2(bzox)_4$	Nujol	8.2	15.1 sh	17.8, 18.9
$CoSO_4(acox)_3 \cdot 3H_2O$	Nujol	8.8	16.3 sh	19.5, 20.9 sh
$Co(NCS)_2(acox)_2$	Nujol	9.6	15.8 sh	18.9
$Co(NCS)_2(bzox)_2$	Nujol	8.8	15.5 sh	19.1

ν_1 $^4T_{2g} \leftarrow {}^4T_{1g}$; ν_2 $^4A_{2g} \leftarrow {}^4T_{1g}$; ν_3 $^4T_{1g}(P) \leftarrow {}^4T_{1g}$ or components thereof. sh: shoulder.

Table 6. Main infrared bands of nickel(II) and cobalt(II) complexes with acetaldehyde oxime and bezaldehyde oxime

Compound	ν(OH)	ν(NO)
$NiCl_2(acox)_4$	3210	939, 953
$NiBr_2(acox)_4$	3215	939, 953
$Ni(NCS)_2(acox)_4$	3210	938
$Ni(NCS)_2(acox)_2$	3450	940
$Ni(NO_3)_2(acox)_2$	3210	940, 960
$NiSO_4(acox)_3 \cdot 3H_2O$	3250	935, 950
$NiCl_2(bzox)_4$	3200	940, 967
$NiBr_2(bzox)_4$	3235	938, 962
$NiI_2(bzox)_4 \cdot H_2O$	3203	936, 955
$Ni(NCS)_2(bzox)_2$	3415	940
$CoCl_2(acox)_4$	3215	945, 950
$CoBr_2(acox)_4$	3210	935, 950
$CoCl_2(bzox)_4$	3205	938, 950
$CoBr_2(bzox)_4$	3205	938, 957
$Co(NCS)_2(acox)_2$	3450	940
$Co(NCS)_2(bzox)_2$	3425	942
$CoSO_4(acox)_3 \cdot 3H_2O$	3270	945

ν: cm^{-1}.

Table 7. Maxima of main d-d absorption bands and of some infrared bands of copper(II) complexes with acetaldehyde oxime and benzaldehyde oxime

Compound	d-d band, 10^3 cm^{-1}	Infrared bands, cm^{-1}	
		ν(M-X)	ν(M-L)
$CuCl_2(acox)_2$	14.8	296, 235	272
$CuBr_2(acox)_2$	14.8	243, 208	259
$CuCl_2(bzox)_2$	14.3	295, 224	267
$CuBr_2(bzox)_2$	14.2	235, 210	261
$CuCl_2(acox)_4$	16.5	285	272
$CuBr_2(acox)_4$	16.6	238	271
$CuCl_2(py)_2$*	14.5	294, 235	268
$CuBr_2(py)_2$*	14.6	255, 202	269

* Multinuclear. The data are taken from references 9 and 10 in the text.

these results indicate that the sulfate group in this complex is coordinated as a bidentate ligand to the cobalt(II) ion. Its electronic spectrum (Table 5) is typical of the six-coordinate cobalt(II) complex, and its magnetic moment (5.15 BM) lies in the range expected for the six-coordinate cobalt(II) complex. The powder X-ray diffraction pattern is very similar to that of the corresponding nickel(II) complex, indicating that these cobalt(II) and nickel(II) complexes have a similar structure.

The complexes $Co(NCS)_2L_2$, L being acox and bzox, are paramagnetic with magnetic moments of 4.86 and 4.93 BM, which are in the range expected for the octahedral cobalt(II) complexes. Their electronic absorption spectra are also typical of the six-coordinate cobalt(II) complexes. They show infrared ν(C–N) and ν(C–S) vibrations at 2100 and 785 cm^{-1} for L=acox and at 2110 and 780 cm^{-1} for L=bzox. In the same way as in $Ni(NCS)_2(bzox)_2$, the infrared data indicate that the NCS groups function as bridging ligands. It is thus most likely that the complexes $Co(NCS)_2L_2$ have a similar multinuclear structure to that of $Ni(NCS)_2L_2$. The powder X-ray diffraction patterns of $Co(NCS)_2L_2$ are almost identical with those of $Ni(NCS)_2L_2$. Exactly like the corresponding nickel(II) compounds, they exhibit a sharp OH band at 3450 and 3425 cm^{-1} typical for the NOH group, which is not involved in hydrogen bonding.

The other cobalt(II) complexes show OH stretching vibrations at about 3150—3200 cm^{-1}.

Copper(II) Complexes. The copper(II) complexes obtained are of the following three types, X being Cl and Br: (1) $CuX_2(acox)_4$; (2) $CuX_2(acox)_2$ and $CuX_2(bzox)_2$; (3) $CuSO_4(acox)_4 \cdot H_2O$. The complexes $CuCl_2(acox)_2$ and $CuCl_2(bzox)_2$ were prepared previously.[1]

Since $CuCl_2(acox)_4$ shows a powder X-ray diffraction pattern similar to that of *trans*-$NiCl_2(acox)_4$, it also has a six-ccordinate *trans*-dichloro-structure, in which the molecules of acox are bound to the copper(II) ion through the nitrogen atom. The electronic absorption spectrum of $CuBr_2(acox)_4$ is very similar to that of $CuCl_2(acox)_4$. Their d-d band maxima lie at almost equal frequencies (Table 7). It is, therefore, very likely that $CuBr_2(acox)_4$ has a structure similar to that of $CuCl_2(acox)_4$, namely a six-coordinate *trans*-dihalogeno-structure.

In view of the results on the corresponding cobalt(II) and nickel(II) complexes, it may be reasonable to assume that acox and bzox are coordinated through their nitrogen atom in the complexes of the types $CuX_2(acox)_2$ and $CuX_2(bzox)_2$. In agreement with this, they show OH-stretching vibrations at about 3150—3200 cm^{-1}, which lie close to those of $MX_2(acox)_4$ and $MX_2(bzox)_4$. Since acox and bzox lie close to pyridine in the spectrochemical series, it may be pertinent to remember previous studies on the copper(II) pyridine complexes of a similar composition. Billing and Underhill[9] examined correlation between electronic spectra and stereochemistries of complexes of the type CuX_2L_2, L being pyridine and its derivatives. They obtained two types of the complexes. The complexes of one type have a multinuclear structure, in which the copper(II) ion is in a six-coordinate, tetragonally distorted pseudo-octahedral environment, showing a broad d-d band with a maximum at 14—15×10^3 cm^{-1}. The d-d band maxima vary considerably, depending upon the extent of the tetragonal distortion. The complexes of the other type have a binuclear structure with square-pyramidal coordination about the copper(II) ion with bridging apical chloride ions and basal pyridine or substituted pyridine molecules. The spectra of the latter complexes have a d-d band at 16—19×10^3 cm^{-1} with a shoulder at 13.5×10^3 cm^{-1}. The uninuclear square-pyramidal copper(II) complex would show the corresponding d-d band at a higher frequency.

The complexes $CuX_2(acox)_2$ and $CuX_2(bzox)_2$ obtained in the present work show a broad d-d band at about 14.2—14.8×10^3 cm^{-1} (Table 7). According to the criteria derived previously,[9] these copper(II) complexes probably have a multinuclear structure similar to that of $CuX_2(py)_2$; $CuCl_2(py)_2$ and $CuBr_2(py)_2$ show a d-d band at about 14.5 and 14.6×10^3 cm^{-1}, respectively.

Their infrared ν(M-X) and ν(M-L) bands also seem to correspond well to those of multinuclear $CuCl_2(py)_2$ and $CuBr_2(py)_2$ (Table 7).[9,10]

When left in a desiccator for a long period, the blue form of $CuCl_2(acox)_2$ transformed into the green form of the same composition. The green form shows almost the same infrared spectrum as that of the blue form of $CuCl_2(acox)_2$ in the range from 200 to 3500 cm^{-1}. The electronic spectrum of the green substance is similar to that of the blue form, although the green form shows a d-d band at a slightly lower frequency than the blue form (Table 7). From the spectral criteria proposed previously,[9] both the two modifications probably have a similar multinuclear structure. The slight difference in the band maximum between the two may arise from the different extent of the tetragonal distortion.

In $CuSO_4(acox)_4 \cdot H_2O$, the ν_3 stretching vibration due to the sulfate group is split into two bands at 1035 and 1195 cm^{-1}, indicating that the sulfate group in this complex is coordinated as a unidentate ligand to the copper(II) ion.[5] The copper(II) ion probably takes five-coordination with four molecules of acetaldehyde oxime and a unidentate sulfate group.

Its electronic absorption spectrum has a broad d-d band with a maximum at 16.5×10^3 cm^{-1}, being in accordance with the five-coordinate structure.[11] A six-coordinate model with a water molecule as an additional ligand may not be eliminated.

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References

1) W. Hieber and F. Leutert, *Ber.*, **60**, 2296 (1927).

2) M. E. Stone and K. E. Johnson, *Can. J. Chem.*, **51**, 1260 (1973).

3) M. E. Stone, B. E. Robertson, and E. Stanley, *J. Chem. Soc. A*, **1971**, 3632.

4) (a) A. B. P. Lever, *Coord. Chem. Rev.*, **3**, 119 (1968); (b) C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, **40**, 788 (1964).

5) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," Wiley-Interscience, New York (1970).

6) C. R. Hare and C. J. Ballhausen, *J. Chem. Phys.*, **40**, 792 (1964).

7) S. M. Nelson and T. M. Shepherd, *J. Inorg. Nucl. Chem.*, **27**, 2123 (1965); R. A. Bailey, S. L. Kozak, T. W. Michelsen, and W. N. Mills, *Coord. Chem. Rev.*, **6**, 407 (1971).

8) M. A. Porai-Koshits and G. N. Tishchenko, *Kristallografiya* **4**, 239 (1959); *Chem. Abstr.*, **55**, 12990a (1961).

9) D. E. Billing and A. E. Underhill, *J. Inorg. Nucl. Chem.*, **30**, 2147 (1968).

10) R. J. H. Clark and C. S. Williams, *Inorg. Chem.*, **4**, 350 (1965).

11) B. J. Hathaway and A. A, G. Tomlinson, *Coord. Chem. Rev.*, **5**, 1 (1970).