increasing as the interatomic distances decrease, hence, as the density increases. The coulombic energies between nonclosest neighbors would be expected to be fairly large in substances such as the borates. They are both attractions and repulsions, and both types increase as the density increases. It seems impossible to evaluate the net effect in any simple way and it will not now be attempted.

Neglecting the possible effect of differences in the density dependence of the nonclosest-neighbor coulombic energy, increasing pressure should favor class C structures, with higher coordination numbers and higher densities, over class A structures of the same chemical composition. This is in line with the fact that the stable structure for boric oxide at normal pressures is class A, while a high-pressure phase has a class C structure.

Conclusion

The types of structons in known structures of anhydrous boric oxide and borates have been listed and compared. Certain regularities have been noted and related to stability factors. It has been found that the arrangements of boron and oxygen atoms almost invariably conform to a few "minimum sets" of structon types. The relative stabilities of different sets, as affected by overall composition and by the cation–oxygen arrangements, have been discussed in some detail. Factors affecting the stability of nonbridging oxygens (O′) and oxygens with three boron neighbors (O‴) have been especially considered. It is hoped that this paper will serve as a basis for prediction of the structon types (and relative numbers of each) in crystals that have not yet been analyzed and in borate glasses.

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Metal Isotope Effect on Metal–Ligand Vibrations. VI. Metal Complexes of 8-Hydroxyquinoline[1]

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Low-frequency infrared spectra (650–100 cm^{-1}) have been obtained for isotopic pairs of some first-row transition metal oxinates (8-hydroxyquinolinates) of the types MQ_2 (M = ^{58,62}Ni, ^{63,65}Cu, and ^{64,68}Zn), $MQ_2 \cdot 2H_2O$ (M = ^{54,57}Fe, ^{58,62}Ni, and ^{64,68}Zn), $CuQ_2 \cdot 2H_2O$–$CuQ_2 \cdot 2D_2O$, and MQ_3 (M = ^{54,57}Fe) where Q denotes an oxinate anion. Based on the observed isotopic shifts, the metal–oxygen and metal–nitrogen stretching bands have been assigned in the regions of 332–210 and 300–190 cm^{-1}, respectively. Structures of several metal oxinates have been elucidated from the number of isotope-sensitive bands and the general pattern of the spectra. The spectra of CoQ_2 and its dihydrated derivative have been studied. The spectra of α and β forms of anhydrous CuQ_2 have been compared and discussed.

Introduction

The importance of metal oxinates (8-hydroxyquinolinates) in analytical chemistry is well known.[2] The oxine ligand plays an important role in some biological systems, and its function is related at least in part to its chelating ability with metals.[3] Thus far, metal oxinates have been a subject of various physicochemical investigations including X-ray diffraction,[4–10] ir,[11–15] uv–visible,[16–18] nmr,[19] magnetic susceptibility,[20] mass spectrometry,[21] esr,[22] ENDOR (electron nuclear double resonance),[23] and potentiometric studies.[24]

X-Ray diffraction studies have been made on a series of compounds of the type $MQ_2 \cdot 2H_2O$, where M is Zn, Cu, Ni, Co, Cd, or Pb, and Q is an oxinate anion. The results of these investigations[4–6] show that two chelating oxinate anions coordinate to the metal by forming a trans-planar structure, and two water molecules occupy the axial positions to complete a six-coordinate

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structure. Recently, the crystal structures of some anhydrous oxinates (CuQ_2[7-9] and PdQ_2[10]) have also been determined. Anhydrous copper oxinate has been isolated as two crystal forms, *i.e.*, α form[7] and β form.[8,9] They are different in color, density, infrared spectra, and magnetic moments.[25] The α form has a six-coordinate structure; the central copper atom is bound to two oxinate anions through the ring nitrogen and the hydroxyl oxygen in a trans-planar arrangement and also to the oxygen atoms of adjacent molecules to complete a distorted octahedral structure.[7] On the other hand, the copper atom in the β form is five-coordinate; it is bound to the two oxinate ions to form a trans-planar structure, and only the fifth position is occupied by an oxygen atom of a neighboring molecule to form a dimeric structure.[9] This last oxygen atom is only weakly bound to the copper atom since its copper-oxygen bond length (2.83 Å) is much longer than those of the chelate ring (1.93 Å).[9] Crystal structures of other anhydrous metal oxinates are not known.

Previous infrared studies[11-15] are limited to the high-frequency region where the vibrations due to the oxinate ligand appear. In order to obtain information about the structure of the complex and the strength of the metal-ligand bond, it is necessary to study the metal-ligand vibrations in the low-frequency region. However, these metal-ligand vibrations are difficult to assign by the conventional methods due to the complexity of the spectra in the low-frequency region.[26] Previously,[26-31] we have demonstrated that the metal isotope technique provides a valuable means of assigning metal-ligand vibrations of a variety of coordination compounds. In this paper, we have applied this method to interpret the spectra of metal oxinates in the low-frequency region.

Experimental Section

Preparation of the Metal Oxinates.—The metal oxinates were prepared by mixing an aqueous solution of each metal chloride with an ethanol solution of oxine in a 1:1.05 molar ratio. The pH of each solution was adjusted to 6.4–7.0 by adding a 2 *N* ammonium hydroxide solution. The precipitates were filtered and washed with 95% ethanol to remove excess oxine. These products were dried according to the standard procedure.[2b]

α- and β-copper oxinates were prepared by mixing copper acetate with oxine in absolute methanol.[25] The α form was isolated as bronze-colored crystals which were dried at 110°. The β form was obtained as black crystals which were also dried at 110°. The purity of each compound was checked by comparing its infrared spectrum with that reported in literature.[12,25]

Hydration of anhydrous copper oxinate by D_2O was performed by dissolving the anhydrous salt (α form) in dry tetrahydrofuran and then adding an excess amount of D_2O into the solution. Upon addition of D_2O, the color of the solution changed from dark green to bright greenish blue. The precipitate formed was collected on a filter paper and dried carefully in air by gentle suction with an aspirator for 0.5 hr. The presence of D_2O in the complex was confirmed by the appearance of a broad and strong infrared band at about 2430 cm^{-1} (O–D stretching vibration).

Iron(II) oxinate was prepared in the same manner as other divalent metal oxinates, except that the reaction was carried out in a nitrogen atmosphere. Iron powder was obtained by passing hydrogen gas over ferric oxide at 450°. The ferrous chloride solution was prepared *in situ* under nitrogen by dissolving iron powder in 2 *N* HCl solution. The precipitate of $FeQ_2 \cdot 2H_2O$ was collected on a filter paper and dried over $CaCl_2$ at room temperature. The complex $FeQ_2 \cdot 2H_2O$ is reddish brown in contrast to the black color of FeQ_3.

All complexes containing metal isotopes were prepared on a milligram scale using metal isotopes purchased from Oak Ridge National Laboratory. The purity of each metal isotope is the same as that reported in previous investigations of this series.[27-31]

Spectral Measurements.—Infrared spectra were measured on a Beckman IR-12 (4000–200 cm^{-1}) and Hitachi Perkin-Elmer FIS-3 (410–33 cm^{-1}) infrared spectrophotometer. The Nujol mull technique with CsI plates (4000–200 cm^{-1}) or polyethylene plates (410–33 cm^{-1}) was employed for all complexes. The spectra were run on an expanded scale with a scanning speed of 2–4 cm^{-1}/min. The low-frequency spectra (410–33 cm^{-1}) were obtained under vacuum except those of $CuQ_2 \cdot 2H_2O$–$CuQ_2 \cdot 2D_2O$ which were run in dry nitrogen atmosphere to prevent any dissociation of coordinated water under vacuum. Reproducibility of the spectra was checked by multiple scans of several samples over the desired frequency range. Calibration of the frequency reading was made by recording the spectra of polystyrene, 1,3,5-trichlorobenzene, and water vapor.

Results and Discussion

1. MQ_2-Type Complexes (M = Cu, Ni, Zn, and Co).—Figure 1 shows the actual tracing of the infrared spectra (410–100 cm^{-1}) of potassium oxinate and the α and the β forms of $^{63,65}CuQ_2$, $^{58,62}NiQ_2$, and $^{64,68}ZnQ_2$.

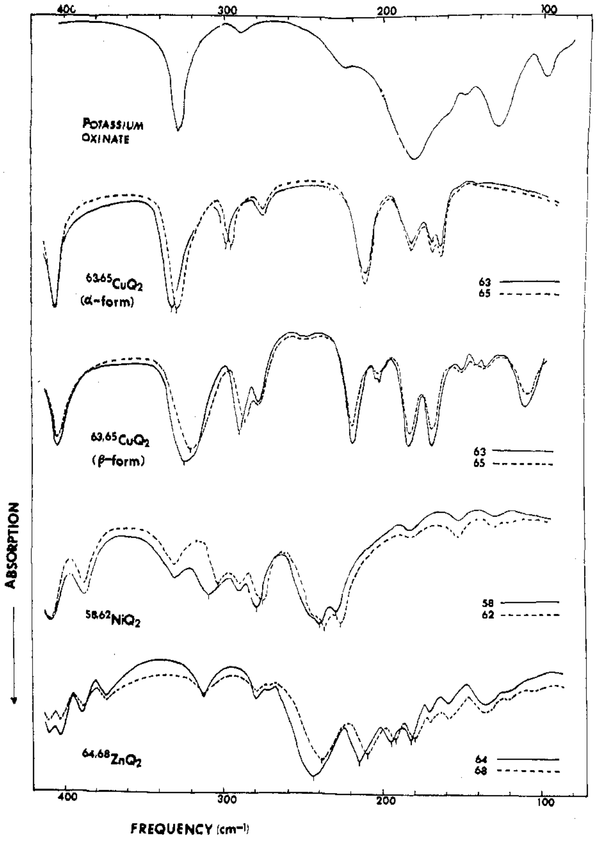

Figure 1.—Infrared spectra of KQ, CuQ_2, NiQ_2, and ZnQ_2.

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TABLE I

OBSERVED FREQUENCIES, ISOTOPIC SHIFTS, AND BAND ASSIGNMENTS FOR MQ_2-TYPE METAL OXINATES AND POTASSIUM OXINATE (CM^{-1})

	$^{63}CuO_2$									
Potassium oxinate	α		β		$^{58}NiQ_2$		$^{64}ZnQ_2$		CoQ_2	
	Freq	Δν[c]	Freq	Δν[c]	Freq	Δν[c]	Freq	Δν[c]	Freq	Assignment[a]
642 s	645.7 m	0.0	646.0 m	0.0	649.8 s	0.2	650.5 vs	0.0	649 s	δ(ligand)[b]
583 s	634.3 s	0.5	633.0 s	0.9	627.5 m	0.5	606.0 vs	0.0	616 s	δ(ligand)[b]
					613.5 sh	0.3	591.0 sh	0.0	602 s	
					606.0 sh	0.0			594 sh	
					598.0 s	0.0				
553 m	585.3 m	0.0	583.0 m	0.0	574.0 m	0.0	561.8 m	0.0	571 m	δ(ligand)[b]
488 m	524.0 vs	0.0	522.5 vs	0.0	519.0 sh	0.6	503.5 vs	0.0	504 vs	δ(C–O)[b]
481 m					506.3 vs	0.0				
...	406.0 vs	0.0	404.0 s	0.5	414.5 s	0.3	409.5 s	0.0	406 vs	Chelate ring def
					409.2 s	0.0	403.0 s	0.0		
					388.5 s	0.5	389.0 m	0.0	382 m	
							374.0 w	0.0		
327 m	(overlapped)[d]		(overlapped)[d]		330.0 m	−0.6	312.5 w	0.0	326 w	Ligand vib
288 w	274.5 w	0.0	277.0 w	0.0	290.0 m	0.4	279.5 w	0.0	(278)	Ligand vib
...	*332.1 s*[e]	*3.0*	*324.0 vs*	*3.5*	*309.6 s*	*6.0*	*243.0 vs*	*5.0*	278 vs	ν_a(M–O)
...	...	...	...	...	*280.8 s*	*4.8*	*214.4 s*	*4.2*	263 s	ν_s(M–O)
224 sh	210.5 s	0.3	218.0 s	−0.4	246.0 vs	0.0	(overlapped)[d]		228 vs, b	Ligand vib
			202.4 w	0.0						
...	*297.3 m*	*2.8*	*289.7 m*	*3.2*	*242.0 vs*	*3.8*	*195.5 m*	*2.5*	(228)	ν_a(M–N)
...	...	...	...	...	*231.0 s*	*3.2*	*182.4 m*	*2.0*	(228)	ν_s(M–N)
180 vs, vb	181.5 m	0.1	182.0 m	0.0	184.0 w	0.1	180.4 m	0.0		Ligand vib
	168.4	0.6	168.2 m	0.0	...		170.0 w	0.2		Ligand vib
159 w	163.2	0.4	...	...	...		158.5 w	0.0	156 vw	Ligand vib
149 w	153.0 vw	0.0	151.0 vw	0.0	153.8 vw	0.3	...	...		Ligand vib
128 m, b	...	...	141 vw	−0.3	131 w, b	0	138 w, b	0	138 w	Ligand vib
							131 w, b	0		
97 m	91 w	...	110 m	...	...		...			

[a] ν, stretching; δ, in-plane bending. [b] These assignments were made according to ref 13. [c] Δν indicates metal isotope effects: ν(^{63}Cu) − ν(^{65}Cu), ν(^{58}Ni) − ν(^{62}Ni), or ν(^{64}Zn) − ν(^{68}Zn). [d] Overlapped with ν(M–O). [e] Italic entries in this and succeeding tables indicate metal isotope sensitive bands.

Table I lists the observed frequencies, isotopic shifts, and band assignments for the MQ_2-type complexes. There are three possible structures for the MQ_2-type complex: trans planar (C_{2h}), cis planar (C_{2v}), and tetrahedral (C_{2v}). According to group theory, the number of infrared-active metal–ligand stretching bands is 2 for C_{2h} symmetry (2 B_u) and 4 for C_{2v} symmetry (2 A_1 + 2 B_1 for cis planar and 2 A_1 + B_1 + B_2 for tetrahedral).

The α and β Forms of CuQ_2.—As is seen in Table I and Figure 1, the α and β forms of CuQ_2 exhibit spectra which are similar to each other. Originally, Fanning and Jonassen[25] proposed a tetrahedral and a square-planar structure for the α and β forms, respectively. On the other hand, Tackett and Sawyer[13] suggested a cis-planar structure for the α form and a trans-planar structure for the β form. As is seen in Table I, both forms exhibit two bands (332.1 and 297.3 cm^{-1} for the α form and 324.0 and 289.7 cm^{-1} for the β form) which give relatively large isotopic shifts by the ^{63}Cu–^{65}Cu substitution. Thus the structures of both forms must be trans planar (C_{2h}). The present results are in good agreement with those of previous X-ray studies.[7-9]

In general, the metal–oxygen stretching band is more intense than the metal–nitrogen stretching band in the infrared spectrum. Therefore, the stronger bands (332.1 cm^{-1} (α) and 324.0 cm^{-1} (β)) with higher frequencies may be assigned to the Cu–O stretching modes, whereas the weaker ones (297.3 cm^{-1} (α) and 289.7 cm^{-1} (β)) with lower frequencies may be assigned to the Cu–N stretching modes. The Cu–O stretching band at 324.0 cm^{-1} of the β form is broader than the corresponding band at 332.1 cm^{-1} of the α form. This may originate in the difference in crystal structure between these two forms. According to X-ray analysis,[7] the two Cu–O bonds of the chelate rings are identical in the α form, whereas they are slightly different in the β form.[9] In the latter, the oxygen atom which serves as the fifth ligand for the adjacent copper atom in the dimeric structure is displaced from the plane of the quinoline ring whereas the other oxygen of the chelate ring is coplanar with it.[9] Thus the β form lacks a center of symmetry. This may result in an overlap of two Cu–O stretching bands which have slightly different frequencies in the β form. One might expect an additional Cu–O stretching band due to the Cu–O bond (2.83 Å) between the central copper atom and the oxygen atom of the adjacent molecule. However, this Cu–O stretching band was not located from our isotopic studies probably because its frequency is too low.

The Cu–N stretching bands of six-coordinate Cu-X_2L_2-type complexes (L = pyridine, alkyl-substituted pyridines, and quinoline; X = Cl and Br) have been assigned in the region of 269–241 cm^{-1}.[32] These frequencies are somewhat lower than those of the copper

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oxinates. The bands at 406.0 cm^{-1} (α) and 404.0 cm^{-1} (β) may be assigned to the chelate ring deformation modes, since they are absent in the potassium oxinate and no appreciable isotopic shifts were observed for these bands. Four bands between 650 and 500 cm^{-1} have been assigned to the ligand vibrations (Table I),[13] since their isotopic shifts are negligibly small and their frequencies correspond to those of the oxinate ligand.

NiQ$_2$.—As is seen in Figure 1 and Table I, four bands at 309.6, 280.8, 242.0, and 231.0 cm^{-1} show large isotopic shifts relative to other bands by the ^{58}Ni–^{62}Ni substitution. NiQ$_2$ is also known to have a magnetic moment of 3.24 BM.[20] Combining these results, it may be concluded that NiQ$_2$ is tetrahedral (C_{2v}). Generally, the asymmetric stretching mode appears at a higher frequency and is expected to give a larger isotopic shift by the ^{58}Ni–^{62}Ni substitution than the symmetric one. Considering this trend with their relative intensities and frequencies, we have assigned two bands at 309.6 and 280.8 cm^{-1} to the asymmetric (B$_1$) and symmetric (A$_1$) Ni–O stretching modes, respectively, and two bands at 242.0 and 231.0 cm^{-1} to the asymmetric (B$_2$) and symmetric (A$_1$) Ni–N stretching modes, respectively. It should be noted in Figure 1 that the intensities of the Ni–N stretching bands (242.0 and 231.0 cm^{-1}) are increased because they are overlapped on the strong ligand band at around 246 cm^{-1}. The Ni–N stretching bands of monomeric tetrahedral NiX$_2$L$_2$-type complexes (L = pyridine, α- or β-picoline, and quinoline; X = halogen) have been assigned around 243–212 cm^{-1}.[33]

In the 600-cm^{-1} region, NiQ$_2$ (C_{2v}) shows four medium to strong bands (627.5, 613.5, 606.0, and 598.0 cm^{-1}), whereas CuQ$_2$ (C_{2h}) shows only one band (634.3 cm^{-1} of the α form and 633.0 cm^{-1} of the β form). Similarly, NiQ$_2$ exhibits three bands whereas CuQ$_2$ shows only one band in the 400-cm^{-1} region. These spectral differences clearly indicate the difference in structure between NiQ$_2$ (tetrahedral) and CuQ$_2$ (trans planar).

ZnQ$_2$.—In accordance with the expected tetrahedral structure of ZnQ$_2$, we have observed four bands which give large isotopic shifts relative to other bands (Table I and Figure 1). From the intensity and frequency considerations, these four bands at 243.0, 214.4, 195.5, and 182.4 cm^{-1} may be assigned to the asymmetric Zn–O (B$_1$), symmetric Zn–O (A$_1$), asymmetric Zn–N (B$_2$), and symmetric Zn–N (A$_1$) stretching modes, respectively. The asymmetric Zn–N stretching frequency of ZnQ$_2$ is in the same region as that reported for the tetrahedral Zn(II) complexes (220–200 cm^{-1}) such as ZnCl$_2$(py)$_2$,[33] [Zn(py$_4$](ClO$_4$)$_2$, and [Zn(α-pic)$_4$] (ClO$_4$)$_2$.[34] As expected, the general pattern of the far-infrared spectrum of ZnQ$_2$ is similar to that of NiQ$_2$ but is rather different from that of CuQ$_2$ (trans planar) especially in the 400- and 600-cm^{-1} regions (Table I).

CoQ$_2$.—The infrared spectrum of CoQ$_2$ was obtained only for the oxinate containing the metal of natural abundance since no stable isotopic pair was available for cobalt. CoQ$_2$ shows three bands in the 640–590-cm^{-1} region, two bands in the 420–370-cm^{-1} region, and three bands in the 280–200-cm^{-1} region. Since this spectral pattern is very similar to those of NiQ$_2$ and ZnQ$_2$, the structure of CoQ$_2$ is probably tetrahedral. Two strong bands at 278 and 263 cm^{-1} can be assigned to the asymmetric and symmetric Co–O stretching modes, respectively. The Co–N stretching modes may be assigned at about 228 cm^{-1} where a very strong and broad band is observed.

Summary of MQ$_2$-Type Complexes.—As stated above, the structure of the Cu complex (α and β forms) is trans planar whereas those of the Ni, Zn, and Co complexes are tetrahedral. In spite of these structural differences, the observed M–O stretching frequencies give a straight line when plotted against the atomic number of the metal from Co to Cu (Figure 2.) The observed M–N stretching frequencies also show a trend similar to that of the M–O stretching frequencies. It is interesting to note that this order of metals is the same as the Irving–Williams stability order[24]

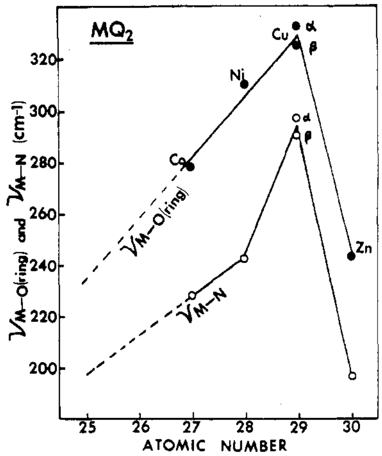

Figure 2.—A plot of M–O and M–N stretching frequencies *vs.* atomic number for MQ$_2$-type complexes.

	Co	<	N	<	Cu	≫	Zn
M–O asym str, cm^{-1}	278	<	310	<	332 (α) 324 (β)	≫	243
M–N asym str, cm^{-1}	228	<	242	<	297 (α) 290 (β)	≫	196

For a series of divalent metal oxinates, Charles, *et al.*,[12] have shown previously that a plot of the C–O stretching frequency *vs.* the atomic weight of the metal yields two straight lines with different slopes: Mn, Co, Ni, and Cu on one line and Mg, Ca, Zn, Cd, and Pb on the other. Two possible explanations were given to account for the difference between these two groups of metals.[12] One was the possible participation of the 3d orbitals in metal–ligand bonding in the former group, and the other was a difference in crystal structure between two groups of metal chelates. Recently, Tackett and Sawyer[13] postulated that crystal structures of metal oxinates with available 3d orbitals for metal–ligand bonding are different from those with no available 3d orbitals; one group (Cu, Ni, Co, and Mn) forms square-

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(34) D. H. Brown, R. H. Nuttal, J. McAvoy, and D. W. A. Sharp, *J. Chem. Soc. A*, 892 (1966).

planar complexes with oxine by using the dsp^2 hybrid orbitals, whereas the other group (Zn, Cd, Pb, and the alkaline earths) with no available 3d orbitals forms tetrahedral complexes by using the sp^3 hybrid orbitals. The present study shows, however, that CuQ_2 is trans planar whereas NiQ_2 is tetrahedral although both metals have 3d orbitals available for metal–ligand bonding and that the M–O (and the C–O) stretching frequencies of these two oxinates fall on the same line even though their structures are different.

2. $MQ_2 \cdot 2H_2O$-Type Complexes (M = Mn, Fe, Co, Ni, Cu, and Zn).—According to X-ray diffraction studies[4-6] on the $MQ_2 \cdot 2H_2O$ (M = Co, Ni, Cu, and Zn) type compounds, two oxinate anions coordinate to the metal by forming a trans-planar structure, and two water molecules occupy the axial positions (C_{2h} symmetry). Group theory then predicts three infrared-active metal–ligand stretching bands ($A_u + 2\ B_u$), *i.e.*, one metal–oxygen, one metal–nitrogen, and one metal–OH_2 stretching vibration.

Figure 3 shows an actual tracing of the far-infrared spectra (410–100 cm^{-1}) for pairs of complexes $CuQ_2 \cdot 2H_2O$–$CuQ_2 \cdot 2D_2O$, $^{58,62}NiQ_2 \cdot 2H_2O$, $^{54,57}FeQ_2 \cdot 2H_2O$, and $^{64,68}ZnQ_2 \cdot 2H_2O$. Tables II and III list the observed frequencies, isotopic shifts, and band assignments for these complexes. The far-infrared spectra of $CoQ_2 \cdot 2H_2O$ and $MnQ_2 \cdot 2H_2O$ have also been obtained, and the observed frequencies are listed in Table III with probable band assignments.

TABLE II

OBSERVED FREQUENCIES, ISOTOPIC SHIFTS, AND BAND ASSIGNMENTS FOR $CuQ_2 \cdot 2H_2O$–$CuO_2 \cdot 2D_2O$[a] (CM^{-1})

$CuQ_2 \cdot 2H_2O$	$CuQ_2 \cdot 2D_2O$	$\Delta\nu$	Assignment[c]
642.0 s	642.4 s	−0.4	δ(ligand)[b]
~630 s, vb		. . .	$\delta_r(H_2O)$ or $\rho_w(H_2O)$
(631.0 m)[d]	631.0 m		δ(ligand)[b]
590.5 m	590.5 m	0.0	δ(ligand)[b]
579.5 sh	579.5 sh	0.0	δ(ligand)[b]
519.0 vs	519.5 sh	−0.5	δ(C–O)[b]
680 b	523.5 s	. . .	$\delta_r(D_2O)$ or $\delta_w(D_2O)$
404.0 s	404.0 s	0.0	Chelate ring def
. . .	~390 s, vb	. . .	$\rho_r(D_2O)$ or $\rho_w(D_2O)$
310.5 s	310.2 s	0.3	ν_a(Cu–O)
289 sh	288 sh	1.0	ν_a(Cu–N)
269.0 w	268.4 w	0.6	Ligand
207.0 vs	207.0 vs	0.0	Ligand
193.0 m	188.0 m	5.0	$\nu_a(Cu–OH_2)$ or $\nu_a(Cu–OD_2)$
181.8 sh	181.6 sh	0.2	Ligand
169.0 vw	169.0 vw	0.0	Ligand
155.5 m	154.8 m	0.7	Ligand
109.0 m	109.0 m	0.0	Ligand

[a] Cu in natural abundance. [b] See footnotes in Table I. [c] ρ_r, rocking; ρ_w, wagging (see ref 35). [d] Overlapped with the 630-cm^{-1} band.

$CuQ_2 \cdot 2H_2O$–$CuQ_2 \cdot 2D_2O$.—The general pattern of the spectrum of $CuQ_2 \cdot 2H_2O$ is very similar to that of anhydrous CuQ_2. This may indicate that the arrangement of the two chelate rings around the Cu atom does not change on hydration, as expected from the results of X-ray diffraction studies.[4,5] By comparing the spectrum of $CuQ_2 \cdot 2H_2O$ with that of the anhydrous CuQ_2, two bands at 310.5 and 289 cm^{-1} can be assigned to the Cu–O and Cu–N stretching modes of $CuQ_2 \cdot 2H_2O$, respectively. Some differences are noted, however, below 650 cm^{-1} due to the presence of water. In the hydrated complex there appear two new bands, one around 630 cm^{-1} (b) and another at 193.0 cm^{-1} (sp). Upon deuteration, the former band becomes one sharp band at 631 cm^{-1} with a new band appearing around 390 cm^{-1}, and the latter band at 193.0 cm^{-1} is shifted to 188.0 cm^{-1}. The former may be attributed to a rocking or wagging mode of coordinated water[35] overlapped with a ligand band, and the latter, to the Cu–OH_2 stretching mode. The magnitude of the shift of the latter (5 cm^{-1}) is in good agreement with that predicted from the diatomic model calculation of the Cu–OH_2 vibration.

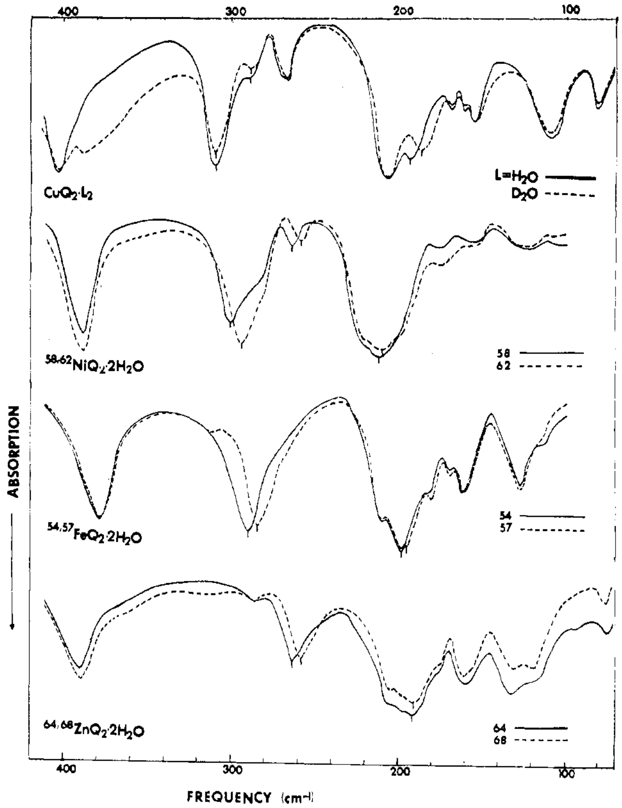

Figure 3.—Infrared spectra of $CuQ_2 \cdot 2H_2O$, $NiQ_2 \cdot 2H_2O$, $FeQ_2 \cdot 2H_2O$, and $ZnQ_2 \cdot 2H_2O$.

It is interesting to note that the Cu–O stretching frequency decreases almost linearly as the Cu–O distance increases. Thus the Cu–O stretching frequencies of CuQ_2 (Cu–O distance 1.93 Å) and $CuQ_2 \cdot 2H_2O$ (Cu–O distance 2.0 Å) are 324 and 310 cm^{-1}, respectively, and the Cu–OH_2 stretching frequency of $CuQ_2 \cdot 2H_2O$ (Cu–O distance 2.3 Å) is 193 cm^{-1}.

$^{58,62}NiQ_2 \cdot 2H_2O$.—As is seen in Figure 3, the spectrum of $NiQ_2 \cdot 2H_2O$ is similar to that of $CuQ_2 \cdot 2H_2O$. Since the two chelate rings of $NiQ_2 \cdot 2H_2O$ are in a trans-planar configuration,[4] three metal–ligand stretching bands are expected to be infrared active. Indeed, three isotope-sensitive bands were observed at 301.2, 264.0, and 212.5 cm^{-1}. From frequency and intensity con-

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(35) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **20**, 429 (1964).

TABLE III

OBSERVED FREQUENCIES, ISOTOPIC SHIFTS, AND BAND ASSIGNMENTS FOR $MQ_2 \cdot 2H_2O$-TYPE METAL OXINATES (cm^{-1})

$^{58}NiQ_2 \cdot 2H_2O$		$^{54}FeQ_2 \cdot 2H_2O$		$^{64}ZnQ_2 \cdot 2H_2O$		$CoQ_2 \cdot 2H_2O$	$MnQ_2 \cdot 2H_2O$	
Freq	$\Delta\nu$	Freq	$\Delta\nu$	Freq	$\Delta\nu$	Freq	Freq	Assignment
646.5 vs	0.0	645.5 s	0.3[c]	645.5 vs	0.0	646 vs	647 vs	δ(ligand)
630 m, b		630 m, b		630 m, b		630 s, b	630 m, b	$\rho_r(H_2O)$ or $\rho_w(H_2O)$ + δ (ligand)
						609 s	604 s	
594.2 sh	0.0	589.8 sh	0.3	591.0 sh	0.0	590 s	587 sh	δ(ligand)
573.3 s	0.0	566.0 s	0.8	570.0 s	0.0	571 s	563 sh	δ(ligand)
507.0 vs	0.0	506.2 vs	0.0	504.9 s	0.0	507 vs	501 vs	δ(C–O)
389.0 s	0.0	378.8 s	0.8	390.5	0.5	386 s	373 s	Chelate ring def
301.2 s	*6.2*	*289.5 s*	*5.0*	*264.0 s*	*5.0*	295 s	279 s	ν_a(M–O)
284.0 sh	0	(280–290)[a]		286.8 m	0.0	(280–290)[a]	(280–290)[a]	Ligand vib
264.0 w	*4.0*	(212–199)[b]		(207–192)[b]		240 sh	(200–190)[b]	ν_a(M–N)
223 s, sh	0	212 s, sh		207 vs, b	0	217 s, sh	200 vs	Ligand vib
200 s, sh	0	199.0 vs		199 vs, vb		203 vs	190	Ligand vib
212.5 vs, b	*2.5*	(*199.0*	*2.1*)[b]	*192 vs, b*	*1.0*	(217–203)[b]	(190–200)[b]	$\nu_a(M–OH_2)$
183.8 m, sh	0	181.4 m	0.4	177 sh	0	184 sh	178 m, sh	Ligand vib
173.0 w	0.0	170.0 w	0.0			172 sh	170 sh	Ligand vib
162.0 w	0.0	161.4 m	0.7	162.0 w	0.3	164 m	157 m	Ligand vib
. . .		128.4 w	0.4	139, 132	. . .	132 m, b	130 m, b	Ligand vib
				120 m			124 m	

[a] Overlapped with the strong M–O (ring) stretching band. [b] Overlapped with the strong ligand band. [c] $\Delta\nu = \nu(^{54}Fe) - \nu(^{57}Fe)$; also see footnotes in Table I.

siderations, these three bands have been assigned to the Ni–O, Ni–N, and $Ni–OH_2$ stretching modes, respectively.

In contrast to the case of copper oxinate dihydrate, the Ni–N stretching frequency increased by *ca.* 20 cm^{-1} while the Ni–O stretching frequency decreased by 8 cm^{-1} upon hydration. This may be attributed to the increased Ni–N π-bonding character in the six-coordinate $NiQ_2 \cdot 2H_2O$ relative to the tetrahedral NiQ_2 complex. Such metal-to-ligand π bonding has been postulated for the Ni(II) complexes of the type NiX_2L_4 (X = NCO, NCS, NCSe, or N_3; L = pyridine, 3- or 4-methylpyridine, or quinoline).[36]

$^{54,57}FeQ_2 \cdot 2H_2O$.—Although the crystal structure of this complex is not known, its far-infrared spectrum resembles those of analogous Cu and Ni complexes. Hence, it may be concluded that the two chelate rings of this complex are also trans planar. We have observed two bands at 289.5 and 199.0 cm^{-1} for $^{54}FeQ_2 \cdot 2H_2O$ which show isotopic shifts of 5.0 and 2.1 cm^{-1}, respectively. The higher frequency band at 289.5 cm^{-1} has been assigned to the Fe–O stretching mode. The band at 199.0 cm^{-1} may be due to the $Fe–OH_2$ stretching band overlapped on a strong ligand band at 199.0 cm^{-1} because $^{57}FeQ_2 \cdot 2H_2O$ exhibits a new band at 196.9 cm^{-1} ($Fe–OH_2$ stretching) in addition to a band at 199.0 cm^{-1}. The isotopic shift of the Fe–N stretching band was not observed probably because it is weak and overlapped by the strong ligand band at 212 cm^{-1}.

$^{64,68}ZnQ \cdot 2H_2O$.—The spectrum of this complex is similar to that of the corresponding Ni complex. A metal isotope sensitive band was observed at 264.0 cm^{-1} which has been assigned to the Zn–O stretching mode. The Zn–N stretching band is expected to appear around 200 cm^{-1}.[34] Three strong bands were observed at 207 (b), 199 (b), and 192.0 cm^{-1}. However, the exact Zn–N stretching frequencies were not determined because of the same reason as that given for the Fe–N stretching band of $FeQ_2 \cdot 2H_2O$. The band at 192.0 cm^{-1} shows a small isotopic shift of 1.0 cm^{-1}. This band may be due to the $Zn–OH_2$ stretching mode.

$CoQ_2 \cdot 2H_2O$ and $MnQ_2 \cdot 2H_2O$.—The observed frequencies of these complexes are given in Table III. According to X-ray analysis,[4] the structure of $CoQ_2 \cdot 2H_2O$ is trans planar. The structure of $MnQ_2 \cdot 2H_2O$ is not known. However, the latter seems to take the same trans-planar structure, since there is a close resemblance in infrared spectra between these complexes. Two bands at 295 cm^{-1} (Co) and 279 cm^{-1} (Mn) are assigned to the Co–O and Mn–O stretching modes, respectively. A weak band at 240 cm^{-1} of the Co complex is probably due to the Co–N stretching mode. In the 200-cm^{-1} region, $CoQ_2 \cdot 2H_2O$ shows two bands at 217 and 203 cm^{-1}. One of these may be due to the $Co–OH_2$ stretching mode. In the same region, $MnQ_2 \cdot 2H_2O$ exhibits two strong bands at 200 and 190 cm^{-1}. The higher frequency band may be assigned to the Mn–N and the lower one to the $Mn–OH_2$ stretching mode, or *vice versa*. The Mn–N stretching band of the complexes $Mn(quinoline)_2X_2$ (X = ClO_4 or BF_4) has been assigned at 200 cm^{-1}.[34]

Summary of $MQ_2 \cdot 2H_2O$-Type Complexes.—If the observed M–O stretching frequency is plotted against the atomic number of each metal in the series of $MQ_2 \cdot 2H_2O$-type complexes, a straight line such as shown in Figure 4 is obtained. However, its slope is different from that of the line corresponding to anhydrous compounds. The order of the frequencies is given below.

	Mn		Fe		Co		Ni		Cu		Zn
		<		<		<		<		≫	
M–O str, cm^{-1}	279	<	289	<	295	<	301	<	310	≫	264
M–N str, cm^{-1}	200–190	<	212–199	<	240	<	264	<	289	≫	207–192

Since these complexes have the same structure and the masses of the metals do not differ appreciably, the pres-

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(36) S. M. Nelson and T. M. Shephard, *Inorg. Chem.*, 4, 813 (1965).

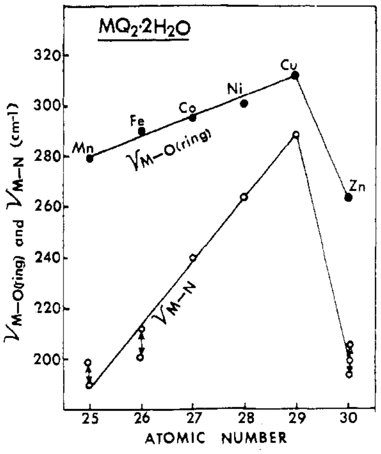

Figure 4.—A plot of M–O and M–N stretching frequencies *vs.* atomic number for $MQ_2 \cdot 2H_2O$-type complexes.

ent result may be taken as indicating that the M–O bond strength increases in the same order of metals. Although the exact frequencies of the Mn–N, Fe–N, and Zn–N stretching bands were not determined, their approximate frequencies follow the same trend as shown above. The $M-OH_2$ stretching bands seem to appear in the 220–190-cm⁻¹ region. It is interesting to note that the $Cu-OH_2$ stretching frequency is lower than the $Ni-OH_2$ stretching frequency although the Cu–O (310 cm⁻¹) and Cu–N (289 cm⁻¹) stretching frequencies are higher than the Ni–O (301 cm⁻¹) and Ni–N (264 cm⁻¹) stretching frequencies. This indicates that the $Cu-OH_2$ bond is weaker than the $Ni-OH_2$ bonds in this type of complex.

Previously, Magee and Gordon[14] assigned a band around 850–870 cm⁻¹ to the M–O (ring) stretching mode of the divalent metal oxinates (M = Ca, Mg, Mn, Cu, Zn), based on their observation that the band is metal sensitive. However, the present study reveals that their assignments are erroneous since these high-frequency bands are not metal isotope sensitive.

All the $MQ_2 \cdot 2H_2O$ type compounds studied exhibit one intense band at 410–370 cm⁻¹. Magee and Gordon[14] previously assigned this band to the water of crystallization. However, we have assigned it to the chelate ring deformation mode characteristic of the trans-planar structure because of the following reasons: (i) there is no corresponding band in the infrared spectrum of the oxinate ligand, (ii) anhydrous CuQ_2 (trans planar) shows one strong band in this region which does not shift much upon hydration, and (iii) this band gives only a small isotopic shift. Again, the frequency of this chelate ring deformation mode increases with increasing atomic number of the metal from Mn to Cu.

$$\begin{array}{ccccccccccccc} \text{Mn} & < & \text{Fe} & < & \text{Co} & < & \text{Ni} & < & \text{Cu} & > & \text{Zn} & & \\ 373 & < & 379 & < & 386 & < & 389 & < & 404 & > & 391 & & (\text{cm}^{-1}) \end{array}$$

3. $^{54,57}FeQ_3$.—There are two probable structures for the octahedral FeQ_3 molecule: one is the cis-cis structure, and the other is the trans-cis structure. The former is of C_3 symmetry, whereas the latter is of C_1 symmetry. In C_3 symmetry, one expects four infrared-active metal–ligand stretching bands (2 A + 2 E), whereas six bands are expected for C_1 symmetry. As is seen in Figure 5, we have observed four metal isotope sensitive bands at 314.9, 280.5, 259.5, and 201.5 cm⁻¹ with the isotopic shifts of 5.1, 2.5, 3.4, and 1.3 cm⁻¹, respectively. Since the number of isotope-sensitive bands is the same as that predicted for the C_3 symmetry, the structure of FeQ_3 may be concluded to be cis-cis.

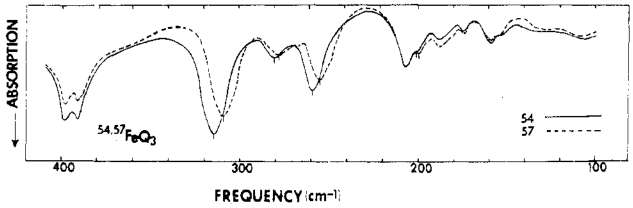

Figure 5.—Infrared spectra of $^{54}FeQ_3$ and its ^{57}Fe analog.

TABLE IV

OBSERVED FREQUENCIES, ISOTOPIC SHIFTS, AND BAND ASSIGNMENTS FOR FeQ_3 (CM⁻¹)

^{54}Fe	$\Delta\nu$[a]	Assignment
646.9 m	0.0	δ(ligand)
628.3 s	0.7	δ(ligand)
619.9 s	−0.8	δ(ligand)
594.0 w	0.0	δ(ligand)
567.0 m	0.0	δ(ligand)
525.5 vs	0.5	δ(C–O)
496.8 s	0.0	δ(ligand)
{398.4 s	0.4	Chelate ring def
{391.4 s	0·2	
314.9 vs	*5.1*	ν(Fe–O) (E)
280.5 w	*2.5*	ν(Fe–O) (A)
259.5 m	*3.4*	ν(Fe–N) (E)
208.5 m	0.5	Ligand
201.5[b]	*1.3*	ν(Fe–N) (A)
188.5	0.0	Ligand
175.0 w	0.0	Ligand
160.0 w	0.0	Ligand
...	...	...

[a] See footnotes in Table III. [b] Overlapped with a ligand band.

Generally, the M–O stretching band is stronger than the M–N stretching band. Furthermore, the E vibration is stronger and gives a larger metal isotopic shift than the A vibration. Thus these four bands at 314.9, 280.5, 259.5, and 201.5 cm⁻¹ may be assigned to the Fe–O (E), Fe–O (A), Fe–N (E), and Fe–N (A) stretching modes, respectively. The Fe–O stretching bands at 314.9 and 280.5 cm⁻¹ seem to correspond to the two bands at 308 and 297 cm⁻¹ observed in chloroform solution by Larsson and Eskilsson.[15] In agreement with our assignments, they have assigned these bands to the Fe–O stretching modes of the cis-cis complex. Larsson and Eskilsson[15] also observed several bands at 390–360 cm⁻¹ and attributed some of these bands to the presence of the trans-cis isomer. We have observed two strong bands at 398.4 and 391.4 cm⁻¹ in the crystalline state and assigned them to the chelate ring deformation modes of the cis-cis complex. Since their spectrum was obtained in a phase different from ours (Nujol mull), an exact comparison cannot be made. (See Table IV.)

It is interesting to compare the Fe–O and Fe–N stretching frequencies of FeQ_3 to those of $FeQ_2 \cdot 2H_2O$. The Fe–O and Fe–N stretching bands of FeQ_3 are higher by 36 and 60 cm^{-1}, respectively, than those of $FeQ_2 \cdot 2H_2O$. Thus the higher the oxidation state, the higher the Fe–O and Fe–N stretching frequencies. The same trend seems to hold between CoQ_3[15] and $CoQ_2 \cdot 2H_2O$.

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Bridged Binuclear Bis-Dithiolene Complexes of Iron and Cobalt

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An extensive series of bridged binuclear bis-dithiolene complexes of iron and cobalt, $(R_4C_4S_4)M{-}(L\text{-}L){-}M(S_4C_4R_4)^z$, with $z = 2-$, R = CN, CF_3, and $z = 0$, R = CF_3, have been prepared by reaction of the bidentate bridging ligand L-L with the appropriate dimeric dithiolene. The bridging ligands contain nitrogen or phosphorus donor atoms. Magnetic moments of the binuclear complexes are consistent with those of analogous mononuclear five-coordinate adducts reported earlier. Cobalt complexes with R = CF_3, $z = 0$, $2-$, and L-L = 1,4-bis(diphenylphosphino)benzene, bis(diphenylphosphino)acetylene (DPPA), or *trans*-1,2-bis(diphenylphosphino)ethylene (DPPE) were studied in the most detail. Polarography in dichloromethane reveals a three-member electron-transfer series ($z = 2-$, $1-$, 0). Half-wave potentials for the two redox processes of the bridged complexes and the $1- \rightleftharpoons 0$ process of the mononuclear triphenylphosphine analog occur in a range of only 0.2 V, indicating that in the former the cobalt–dithiolene units behave as essentially independent sites in electron-transfer reactions. Mononuclear adducts of L-L formed in the presence of excess bridging ligand were detected by polarography and epr. Solutions containing equimolar amounts of neutral and dianionic complexes with L = DPPA and DPPE were found to exhibit electronic absorption bands at 6850 and 7350 cm^{-1}, respectively, which are attributed to intramolecular electron transfer in the monoanion.

Introduction

The chemistry of bis-dithiolene complexes of transition metals is characterized by the existence of electron-transfer series, which in several cases include members with overall charge z of $2-$, $1-$, and 0.[2] Although in a number of instances the monomeric species have been shown to have a planar four-coordinate structure, some metal dithiolene systems, particularly those of iron and cobalt, readily form five-coordinate dimers,[2-4] five-[2,3-10] and six-coordinate[2,5,8,11,12] base adducts, and tris complexes.[13] Of particular interest in the present study are the species containing five-coordinate base adducts, for which the available structural data reveal a square-pyramidal coordination unit.[9]

In the course of investigating the syntheses and properties of transition metal complexes in which the metals are linked by an unsaturated bridge L-L, we have prepared a series of dithiolene complexes of the general type $(R_4C_4S_4)M{-}(L\text{-}L){-}M(S_4C_4R_4)^z$ with M = Fe, Co, R = CF_3, CN,[14] and $z = 2-$, 0. The following bidentate bridging groups have been employed: pyrazine (pyz), 4,4′-bipyridyl (4,4′-bipy), 4,4′-dipyridyl disulfide (pySSpy), *trans*-1,2-di(4-pyridyl)ethylene (pyC_2H_2py), 1,2-di(4-pyridyl)ethane (pyC_2H_4py), 1,4-bis(diphenylphosphino)benzene (DPPB), *trans*-1,2-bis-(diphenylphosphino)ethylene (DPPE), and bis(diphenylphosphino)acetylene (DPPA). These groups have been selected according to their potential or demonstrated ability to bridge two metal centers in discrete dimers or polymers and because certain of their monodentate analogs (*e.g.*, pyridine, triphenylphosphine) have been shown to form five-coordinate adducts with iron and cobalt dithiolenes.[2,5-9] A number of bi- and polynuclear pyz complexes have been prepared,[15,16] and X-ray diffraction[17] has confirmed the ability of pyrazine ligands to function as a bridge. The known 4,4′-bipy complexes are polymeric.[18] Bridged struc-

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[14] The following abbreviations are used throughout: tfd, $(CF_3)_2C_2S_2$; mnt, $(CN)_2C_2S_2$.

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