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Raman Spectra of Bis-Diphosphate Metal Complexes in Aqueous Solution[1]

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Infrared spectra of diphosphate complexes show splittings of the antisymmetric PO_3 vibration to a widely varying degree, depending upon the nature of the cation.[3] In some of the bis-diphosphate complexes, e.g., in those of Cu(II), Zn(II), and Be(II), the components of the antisymmetric vibration are split by as much as 60–70 cm^{-1}, whereas in other bis complexes, like those of Ni(II), Co(II), or Mg(II), only a broadening of the corresponding infrared band at 1120 cm^{-1} is observed, which sets an upper limit of *ca.* 30 cm^{-1} for the splitting of the components of this vibration.

To find out which differences in chemical bonding in these complexes cause the drastic differences in splitting of the ligand vibrations and to establish the assignments of the observed vibrations, we have undertaken a study of the corresponding Raman spectra. This study concerns the bis-diphosphate complexes of Be(II) and Zn(II). These two are the only ones of those previously studied which are sufficiently soluble and transparent to give Raman spectra with the 4358-A exciting line. All measurements were made with a Cary 81 Raman spectrophotometer.[4] Polarization measurements were made with calibrated Polaroid sheets to surround the 7-ml sample tubes.[5]

The Raman spectrum of free diphosphate has a strong, polarized line at 1020 cm^{-1}. In solutions of 1 *M* Zn(II) and 2 *M* diphosphate, this line is shifted to 1030 cm^{-1} and its intensity is decreased by about 10%, remaining polarized. In addition a new Raman line appears at 1135 cm^{-1}, which is broad and has a depolarization ratio of 0.52 ± 0.07 (Figure 1). At 1080 cm^{-1} an extremely weak additional line is observed, the polarization of which is difficult to assess because the band is situated in the trough between the two stronger bands at 1030 and at 1135 cm^{-1}.

For a solution of 0.5 *M* Be(II) and 1 *M* diphosphate, the polarized main line of diphosphate is shifted to 1040 cm^{-1}. For this less concentrated solution, the new lines found with Zn could not be detected. Judging from the intensity in the Zn case, the lines in the more dilute Be solution might lie below the limit of detection. For neither system were there marked changes in the lower frequency P–O bending region. Of some sig-
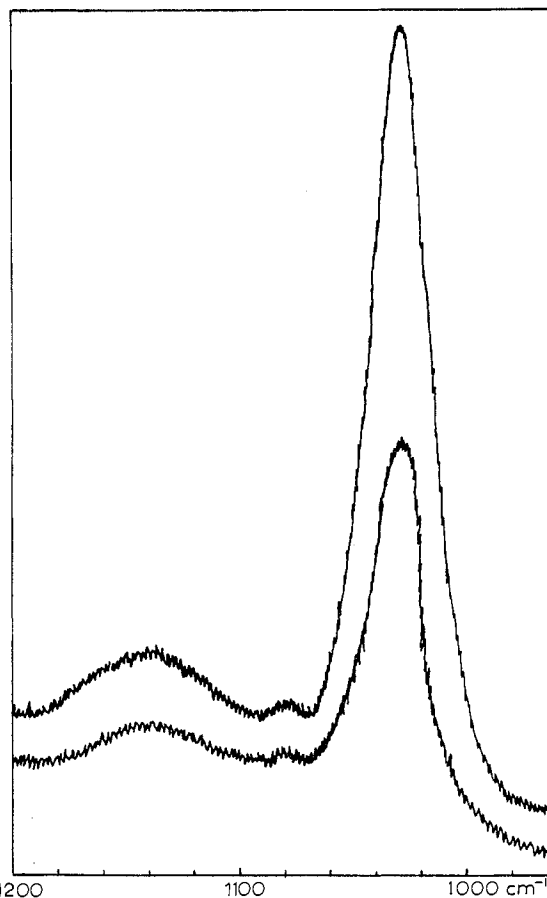
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(2) On leave from The University of Basel.

(3) H. Brintzinger, *Helv. Chim. Acta*, **48**, 47 (1965).

(4) Preliminary spectra were obtained by the kind mediation of Dr. R. C. Taylor, Department of Chemistry, University of Michigan, with a Gaertner F3.5 spectrograph. The rather weak lines of the phosphate spectra were better discernible from the background when measured with the photoelectric instrument.

(5) D. H. Rank and R. E. Kangarise, *J. Opt. Soc. Am.*, **40**, 89 (1950).

Figure 1.—Raman spectrum of a 1 *M* aqueous solution of $Zn(P_2O_7)_2^{6-}$ (1 *M* in $ZnCl_2$ and 2 *M* in $K_4P_2O_7$): top spectrum, light polarized perpendicular to Wood's tube axis; bottom spectrum, light polarized parallel to axis.

nificance is the fact that in neither case are metal–oxygen stretching frequencies observed. Raman spectral characteristics of the complexes, along with those of free diphosphate, dihydrogen diphosphate, and the diphosphate dimethyl ester are given in Table I.

Discussion

Comparison of the spectra in the tables shows that the complexes do not involve merely local hydrolysis of ligand and hydrated metal ion, which might be expected to occur between acidic metal ions and basic ligands. Instead, the changed P–O stretching frequencies must stem from complexes involving direct coordination. The absence of free diphosphate spectral lines in the metal ion containing solutions studied indicates that association with Zn(II) or Be(II) is complete at the concentrations used. The absence of observable M–O lines indicates an essentially ionic association.

A most interesting question, however, concerns the identity of the two components of the split antisymmetric vibration, since such an identification should allow a distinction between monodentate and bidentate coordination of the PO_3 groups of the diphosphate ligand.

If only one of the oxygen atoms of a PO_3 group is coordinated to a metal ion (Figure 2 (I)), the antisymmetric stretching vibration will split in such a way that

TABLE I

RAMAN AND INFRARED LINES OF DIPHOSPHATE DERIVATIVES IN AQUEOUS SOLUTION[a]

$P_2O_7^{4-}$	$Zn(P_2O_7)_2^{6-}$	$H_2P_2O_7^{2-}$	$(CH_3)_2P_2O_7^{2-}$	
		Raman Lines		
	1135 m, br, p	1100 s, p?	1110 s, p	"ν_{as}"PO$_3$ (A')
	1080 vw			"ν_{as}"PO$_3$ (A'')
1015 s, p	1030 s, p	950 w	1050 w, dp	ν_sPO$_3$ + ?
			820 w, dp	
710 m, p	715 m, p	715 m, p	700 m, p	ν_sPOP
510 w, dp	500?			
455 w, dp?	460? w, br	490 w, br, dp	450 w, dp	δPO$_3$
330 m, dp	340 m, dp	320 m, dp	320 m, dp	ρPO$_3$?
		Infrared Lines[3]		
	1080 s	1200 s	1215 s	"ν_{as}"PO$_3$ (A'')
1110 s	1135 s	1100 m	1110 m	"ν_{as}"PO$_3$ (A')
1015 w	1020 m	1080 s	1075 s	$\{\nu_s$PO$_3$ + νCO +
975	990 w	990 s	1050 sh	ν_{as}POP
915 s	915 m	950 w	975 s	ν_{as}POP + ?

[a] s, strong; m, medium; w, weak; vw, very weak; sh, shoulder; br, broad; p, polarized; dp, depolarized; δ, deformation; ρ, torsion.
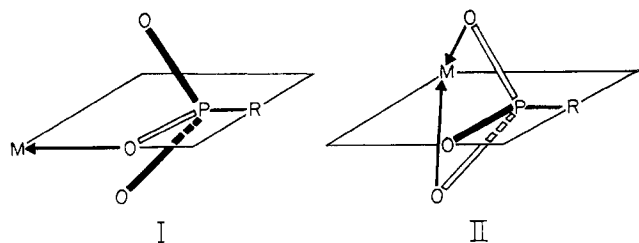

Figure 2.—Monodentate and bidentate coordination of metal M to a PO$_3^{2-}$ group (solid PO bonds strengthened by polarization of the anion; open PO bonds weakened).

its A' component (symmetric with respect to the symmetry plane in Figure 2) moves to lower frequencies and its A'' component (antisymmetric to the same plane) moves to higher frequencies than the original vibration.[6,7] If, however, two oxygen atoms of a PO$_3$ group become attached to a metal ion, either in a bidentate chelate (Figure 2 (II)) or in a bridged coordination structure, then it is to be expected, as it is known for the corresponding nitrate complexes,[8,9] that it is now the symmetric component which moves to higher frequencies, whereas the antisymmetric component is lowered in frequency. That bidentate coordination lowers the frequency of the antisymmetric component A'' of ν_{as} not only in planar anions[8] but also in nonplanar anions like R–PO$_3^{2-}$ can be qualitatively derived from a consideration of the bond-weakening and -strengthening effects of coordination. Since A'' in structure II of Figure 2 involves a stretching of weakened PO bonds only (the strengthened PO bond lies in the symmetry plane which cannot contain a displacement vector for the antisymmetric mode), it must occur at lower frequencies than in the free anion. This is in contrast to

(6) H. Brintzinger and R. E. Hester, *Inorg. Chem.*, **5**, 980 (1966).

(7) This holds true if the splitting pattern is dominated by the changes in bond orders of the P–O bonds associated with the coordination of the metal ion and not by the effects of the oxygen–metal bond. This condition is fulfilled with the disphosphate complexes under consideration here (*cf.* ref 6).

(8) R. E. Hester and W. E. L. Grossman, *Inorg. Chem.*, **5**, 1308 (1966).

(9) J. R. Ferraro, A. Walkers, and C. Cristallini, *Inorg. Nucl. Chem. Letters*, **1**, 25 (1966).

monodentate coordination (structure I) which shifts A'' to higher frequencies, since here the weakened PO bond lies in the symmetry plane and only strengthened PO bonds are involved in the antisymmetric mode.

In the infrared spectrum of zinc(II) bis(diphosphate) the two components of the antisymmetric stretch appear at 1080 and at 1135 cm^{-1}. It is the higher one of these frequencies which coincides with the stronger polarized Raman line (Figure 1), and we are therefore inclined to assign this line at 1135 cm^{-1} to the symmetric component of the split vibration. The observed degree of polarization alone makes it improbable that this line corresponds to an antisymmetric A'' mode. Furthermore, the intuitive idea that the symmetric component A' should have a higher Raman intensity than A'' can be substantiated as follows. In the free anion, where the effective symmetry of each PO$_3^{2-}$ group is C$_{3v}$, both of the modes are contained in the E representation which requires them to be Raman active from symmetry considerations. Since there is no detectable Raman emission present in the 1130-cm^{-1} region in the free anion, however, this can be taken to mean that the (appropriate) components of the polarizability tensor connected with this mode are too small, quantitatively, to induce significant Raman intensity. The A'' mode in the reduced C$_s$ symmetry of the coordinated anion contains these same tensor components, and it is most likely, therefore, that A'' in C$_s$ has equally low Raman intensity as has E in C$_{3v}$. The A' representation on the other hand contains—as does A$_1$ in C$_{3v}$—the mean of the elements of the polarizability tensor and should therefore have an intensity more comparable to that of the A$_1$ mode of the free anion.

The preceding considerations suggest that the diphosphate ligand in zinc(II) bis(diphosphate) is coordinated to zinc *via* two oxygen atoms of the PO$_3$ group. If both PO$_3$ groups of a diphosphate ion were coordinated to a single Zn(II) ion, it would thus be a quadridentate ligand. However, steric considerations

seem to indicate that it is difficult for diphosphate ion to achieve more than tridentate coordination. Although the spectra are not complete enough to indicate the state of both ends of the diphosphate, it seems clear that at least one PO_3 end must be coordinated through two O atoms. Since bidentate coordination of an oxyanion group is known to produce a stronger splitting than monodentate coordination,[6,8] this could explain why Zn(II) and probably also Cu(II) and Be(II) are so effective in splitting the antisymmetric stretching vibration of phosphate ligands, whereas the lower efficiency of cations like Ni(II) and Co(II) might be connected with a monodentate coordination of these cations to each of the PO_3 groups. The latter question could be further investigated if Raman spectra of these colored complexes could be obtained with a suitable exciting source.

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Structural and Spectral Relationships in Some Mercury Thiocyanate Complexes

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Complexes of the type $HgM(NCS)_4$ with $M^{2+} = Mn^{2+}$, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} have been known for some time, and their reflectance spectra have recently been described.[1-3] This note reports studies of the reflectance spectra and X-ray powder patterns of the solid solutions of Mn(II), Fe(II), Co(II), Ni(II), and Cu(II) in the zinc salt and some powder photograph data for the Mn and Fe salts.

The X-ray structure[4] shows that the blue salt $HgCo(NCS)_4$ contains Co(II) in almost regular tetrahedral sites surrounded by four nitrogen atoms (angles N–Co–N 117.6 and 105.6°), while there is essentially tetrahedral coordination of the mercury atom by four sulfur atoms. The corresponding zinc salt is isomorphous with the cobalt salt.[5] In the green salt $HgCu(NCS)_4$, the Cu atom is surrounded by an approximate square plane of nitrogen atoms, with bridging sulfur atoms above and below the plane.[6] The reflectance spectrum of the anhydrous nickel salt,[2] which is obtained by dehydration of $HgNi(NCS)_4 \cdot 2H_2O$, shows that the Ni atom must be six-coordinate in roughly the same way as the Cu atom in $HgCu(NCS)_4$, although the powder

patterns show that the nickel and copper salts are not isomorphous.

The powder patterns of the Mn and Fe salts are identical but for spacing, but differ significantly from those of the Co and Zn salts. However, the patterns can be indexed fully on the basis of tetragonal unit cells of similar dimensions to those of the Co and Zn salts, but with slightly larger a dimensions and smaller c dimensions. The indexing is shown in Table I. The unit cell volumes, shown in Table II, are almost the same as those of the Co and Zn salts, and, for the Fe salt, the measured density, 3.00 ± 0.05 g/cc, and the calculated density, 3.021 g/cc, are very close to those of the Co and Zn salts. The Mn and Fe salts are thus isomorphous with the Co and Zn salts, but not isostructural, differing in space group. The Co and Zn salts have space group $I\bar{4}$, while the Mn and Fe salts have additional mirror planes.

TABLE I

X-RAY POWDER PHOTOGRAPH DATA

$HgMn(NCS)_4$ $a = 11.29_3$ $c = 4.26_7$				$HgFe(NCS)_4$ $a = 11.20_5$ $c = 4.28_0$			
Intensity	d(obs.)	d(calc.)	hkl	Intensity	d(obs.)	d(calc.)	hkl
m	7.85	7.99	110	m	7.76	7.92	110
s	5.59	5.65	200	s	5.53	5.60	200
s	3.955	3.991 / 3.984	220 / 101	s	3.969	3.999 / 3.962	101 / 220
vw	3.564	3.571	310	vw	3.520	3.544	310
s	3.243	3.255	211	s	3.236	3.254	211
s	2.810	2.823 / 2.820	400 / 301	s	2.805	2.814 / 2.801	301 / 400
w	2.656	2.662	330	w	2.635	2.641	330
s	2.518	2.525 / 2.523	420 / 321	s	2.505	2.513 / 2.506	321 / 420
m	2.301	2.304	411	m	2.289	2.295	411
vvw	2.216	2.215	510	vvw	2.194	2.198	510
vw	2.055	2.057	112	vw	2.064	2.066	112
m	1.994	1.996 / 1.995 / 1.992	440 / 431,501 / 202	vvw	1.999	1.999	202
				m	1.983	1.985 / 1.981	431,501 / 440
vvw	1.936	1.937	530	vvw	1.922	1.922	530
w	1.880	1.882 / 1.881 / 1.878	600 / 521 / 222	w	1.877	1.884 / 1.871	222 / 521
m	1.829	1.828	312	m	1.832	1.832	312
vw	1.786	1.786	620	vw	1.772	1.772	620
vw	1.701	1.702 / 1.700	611 / 402	vw	1.696	1.701 / 1.692	402 / 611
vvw	1.665	1.662	332	vvw	1.665	1.663	332
vw	1.629	1.629 / 1.627	541 / 422	vw	1.623	1.620	541
vw	1.598	1.597	550,710	vw	1.586	1.585	550,710
vw	1.566	1.566 / 1.565	640 / 631	vw	1.557	1.556 / 1.554	631 / 640
w	1.535	1.535	512	w	1.535	1.533	512
vw	1.459	1.458 / 1.456	721 / 442	vw	1.449	1.448	721
				vw	1.432	1.435 / 1.430	650 / 532

The precipitation of salts of composition $Hg[Co_x\text{-}Zn_{1-x}](NCS)_4$ from solutions containing both Co(II) and Zn(II) is well known, and the small variation in lattice parameters in the solid solution range $x = 0\text{-}1$ has been studied.[5] Similar salts of the type $Hg[Cu_x\text{-}Zn_{1-x}](NCS)_4$ have also been studied, and the lattice constants were found to vary only slightly from $x = 0$ to $x = 0.4$, the apparent maximum value.[7] From

(1) D. Forster and D. M. L. Goodgame, *J. Chem. Soc.*, 268 (1965).
(2) D. Forster and D. M. L. Goodgame, *Inorg. Chem.*, **4**, 823 (1965).
(3) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Am. Chem. Soc.*, **83**, 4157 (1961).
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