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 $Hg[Co_xZn_{1-x}](NCS)_4$ 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 $Hg[Cu_xZn_{1-x}](NCS)_4$ 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

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TABLE II
UNIT CELL DIMENSIONS

Compound	a, A	c, A	Unit cell vol., A^3	Ref
HgMn(NCS)$_4$	11.29_3	4.25_7	542.9	This work
HgFe(NCS)$_4$	11.20_5	4.28_0	537.3	This work
HgZn(NCS)$_4$	11.09_7	4.40_5	542.4	This work, 5[a]
HgCo(NCS)$_4$	11.10_9	4.37_4	539.8	5
Hg[Mn$_{0.115}$Zn$_{0.885}$](NCS)$_4$	11.07_1	4.41_2	540.8	This work
Hg[Fe$_{0.111}$Zn$_{0.889}$](NCS)$_4$	11.11_0	4.37_0	539.4	This work
Hg[Co$_{0.166}$Zn$_{0.834}$](NCS)$_4$	11.08_5	4.43_5	545.0	5[b]
Hg[Ni$_{0.024}$Zn$_{0.976}$](NCS)$_4$	11.07_3	4.42_3	542.2	This work[c]
	11.07_1	4.43_3	543.3	
Hg[Cu$_{0.083}$Zn$_{0.917}$](NCS)$_4$	11.07_0	4.43_3	543.2	This work, 7[c]
	11.06_8	4.43_3	542.9	

[a] Reference 5 gives $a = 11.084$, $c = 4.438$, $V = 545.2$. [b] a, c, and V interpolated from data in ref 5. [c] Duplicate determinations on different specimens of the same samples.

solutions more concentrated in Cu than required to give $x = 0.4$, the green salt HgCu(NCS)$_4$ also precipitates.

The precipitation of Hg[M$_x$Zn$_{1-x}$](NCS)$_4$, for M = Mn(II), Fe(II), and Ni(II), occurs only when the concentration of M in the solution is high. The compositions in Table II were formed from solutions 1 M in Mn, Fe, and Ni sulfates and were stable to repeated washing by decantation in boiling water. As shown in Table II, the lattice constants for these compositions are practically unchanged from those of the pure Zn salt.

In none of these cases is any trace of superstructure observed, so the foreign ions are distributed randomly in the Zn sites.

The diffuse reflectance spectra of these compounds have been measured with a Beckman DK2A spectroreflectometer, using a cell described previously for measurements at room temperature and 77°K.[8] The spectra of the pure Mn, Fe, Co, Ni, and Cu compounds agree with those reported previously. From the spectrum of the Co salt, the parameters $\Delta = 4830$ cm^{-1} and $B = 694$ cm^{-1} were calculated from the centers of gravity of the two highest energy spin-allowed bands, agreeing well with values calculated by Cotton, *et al.*[3] The predicted energy of the $^4A_2 \rightarrow {}^4T_2$ transition is 4830 cm^{-1}. A previously unreported weak band (designated ν_1) is observed at 4560 cm^{-1} and is believed to belong to this transition. The weakness of this band is in agreement with the fact that this transition is forbidden for electric dipole transitions in true T_d symmetry.

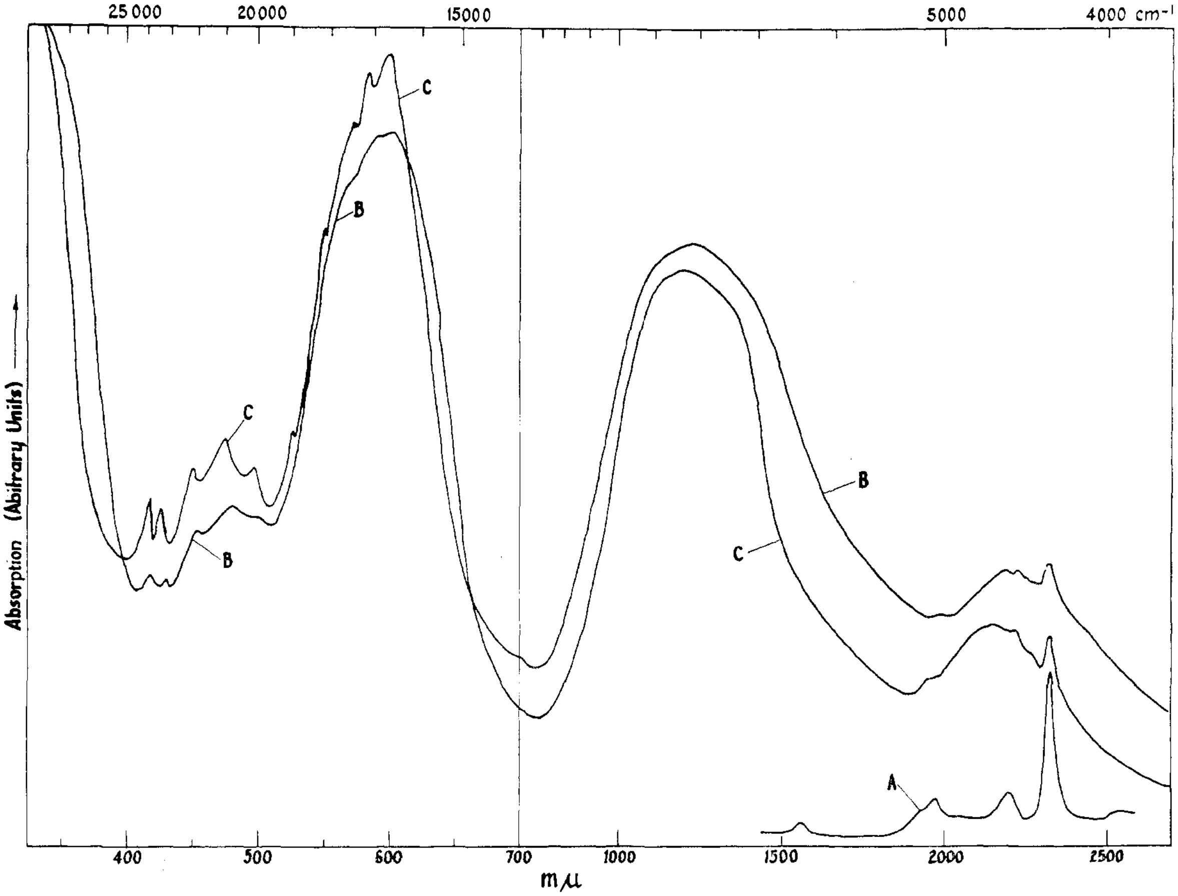

Figure 1.—Diffuse reflectance spectra of (A) HgZn(NCS)$_4$, (B) Hg[Co$_{0.166}$Zn$_{0.834}$](NCS)$_4$ (room temp), (C) Hg[Co$_{0.166}$Zn$_{0.834}$](NCS)$_4$ (77°K).

The compound Hg[Co$_{0.166}$Zn$_{0.834}$](NCS)$_4$ has a room-temperature spectrum (Figure 1) almost identical with that of HgCo(NCS)$_4$ but with $\Delta = 4730$ cm^{-1},

[8] D. E. Scaife, *J. Sci. Instr.*, **43**, 484 (1966).

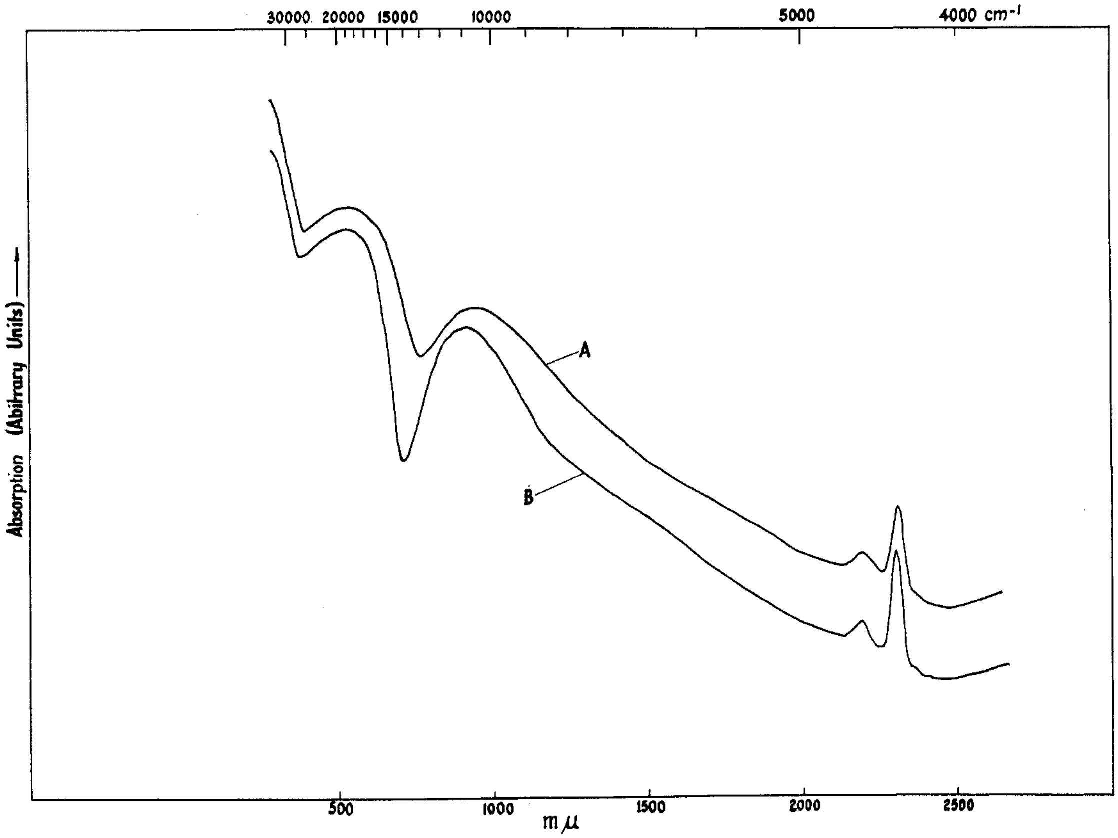

Figure 2.—Diffuse reflectance spectra of $Hg[Cu_{0.083}Zn_{0.917}](NCS)_4$ (A) at room temperature and (B) at 77°K.

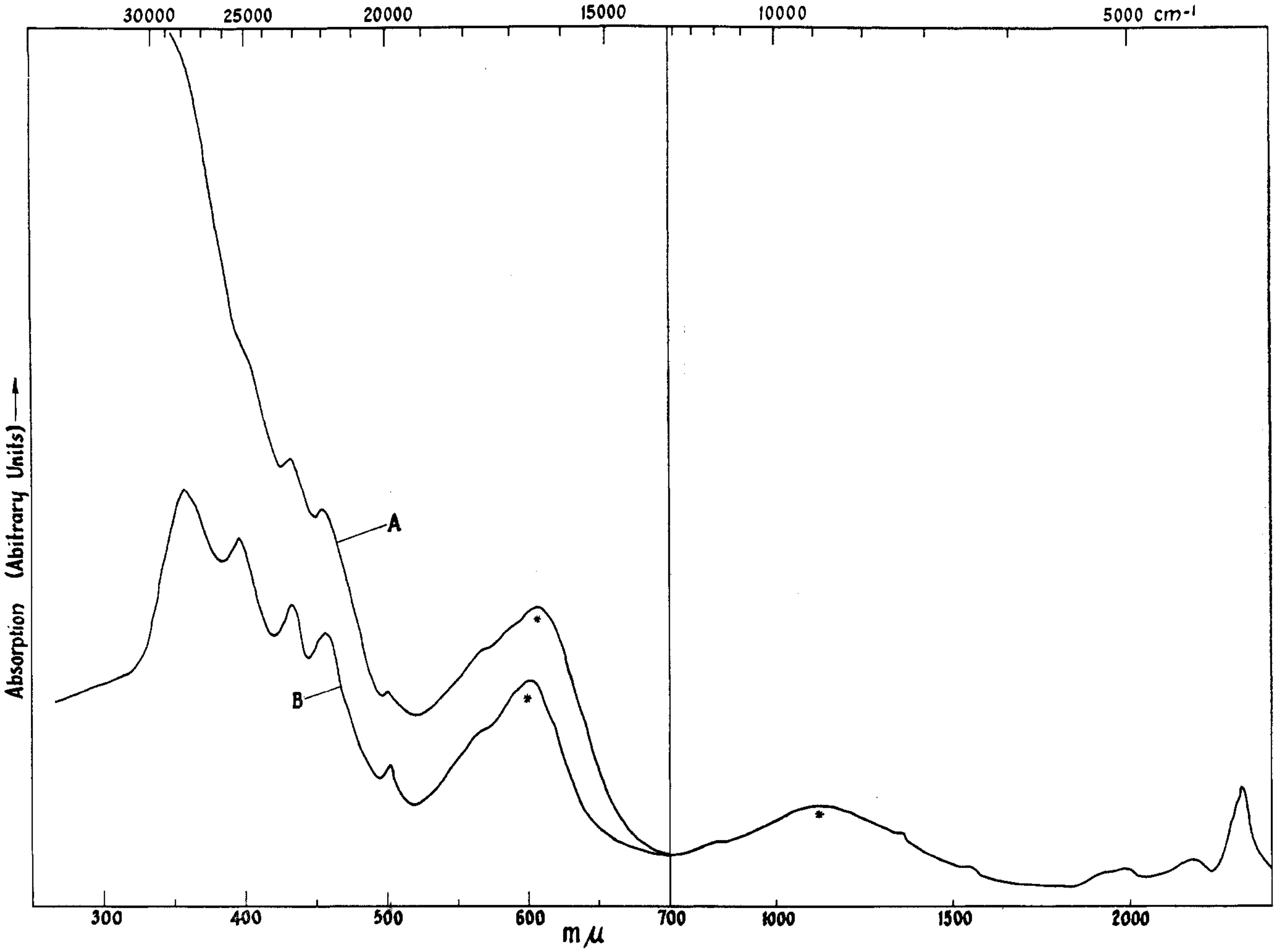

Figure 3.—Diffuse reflectance spectra of $Hg[Mn_{0.115}Zn_{0.885}](NCS)_4$: A, MgO ref; B, $HgZn(NCS)_4$ ref; *, due to Co(II) in sample.

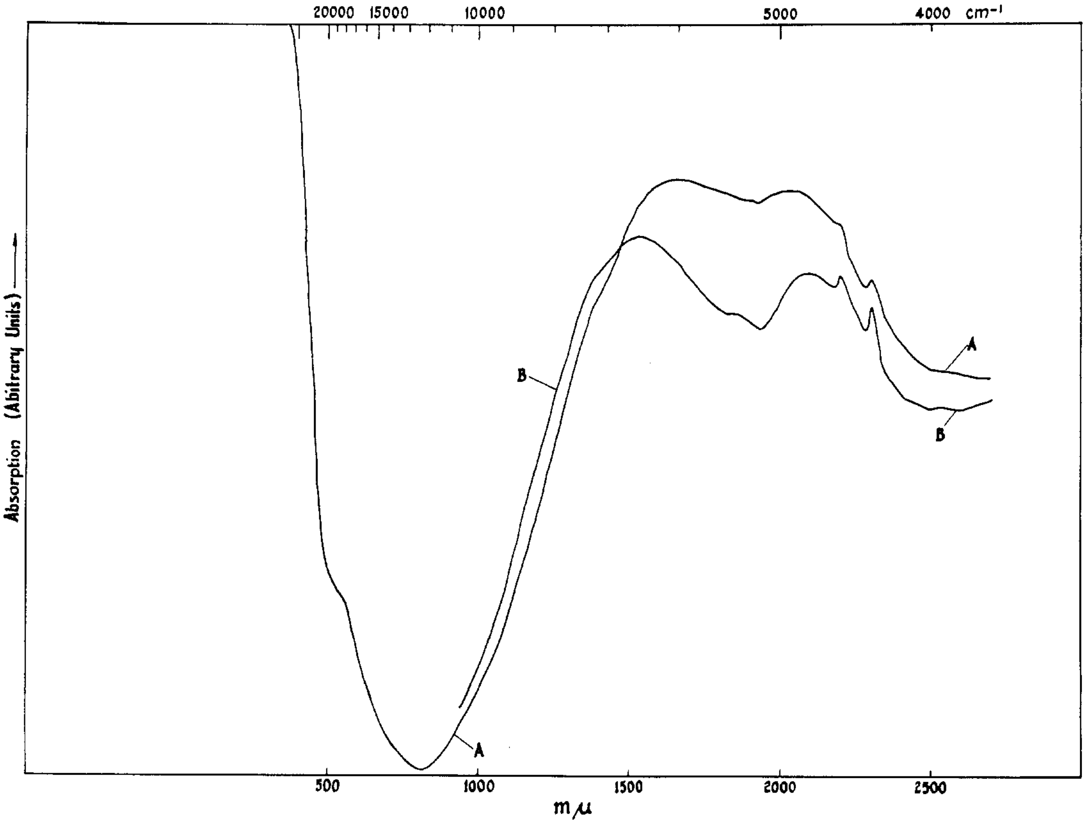

Figure 4.—Diffuse reflectance spectra of Hg[$Fe_{0.111}Zn_{0.889}$]$(NCS)_4$ (A) at room temperature and (B) at 77°K.

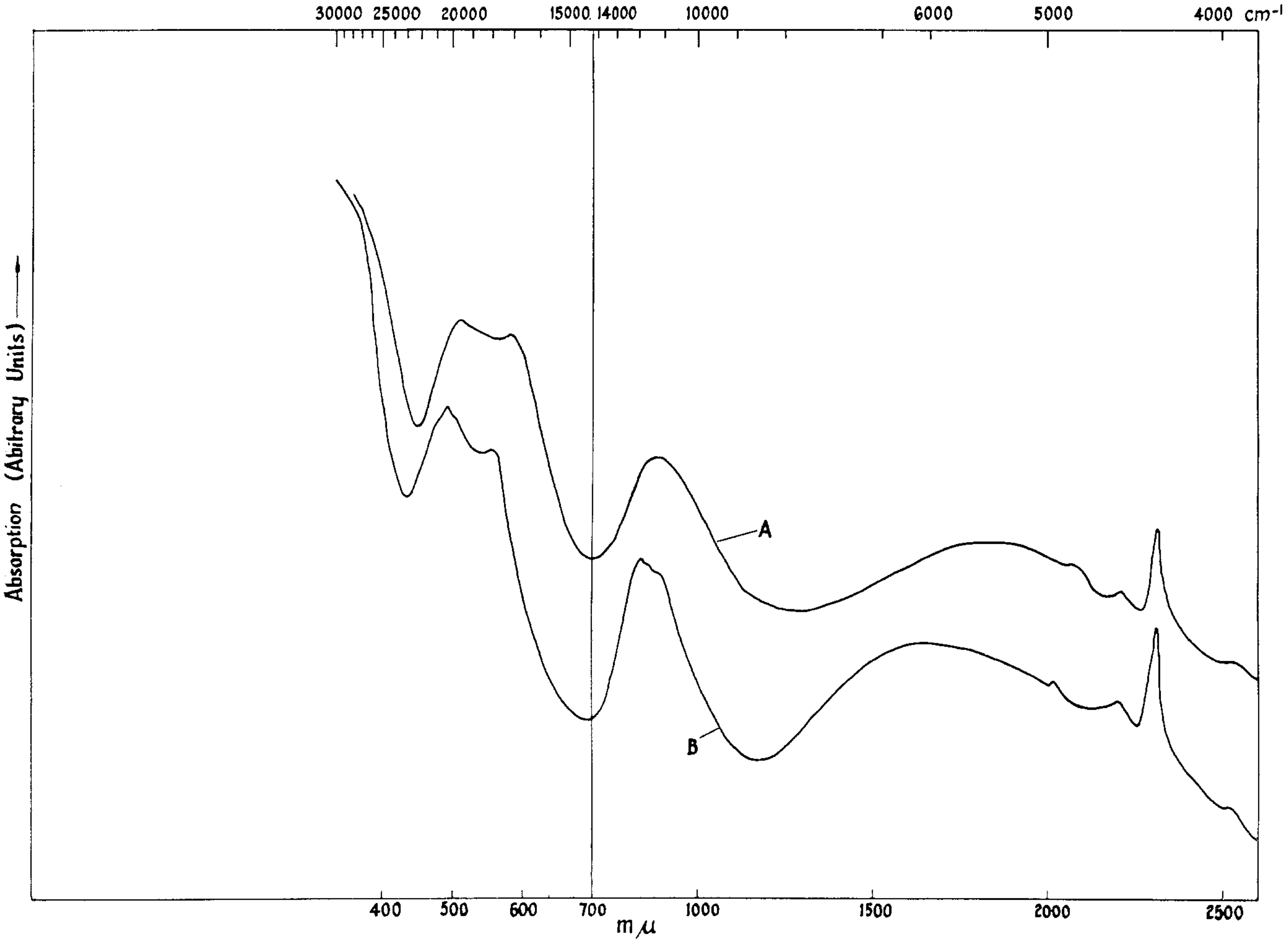

Figure 5.—Diffuse reflectance spectra of Hg[$Ni_{0.024}Zn_{0.976}$]$(NCS)_4$ (A) at room temperature and (B) at 77°K.

$B = 717$ cm^{-1}, while ν_1 is at 4530 cm^{-1}. At 77°K, $\Delta = 4890$ cm^{-1}, $B = 719$ cm^{-1}, and ν_1 is at 4740 cm^{-1}. The slight reduction in Δ for the room-temperature spectrum of the mixed salt in comparison with the value for $HgCo(NCS)_4$ is consistent with the slightly larger lattice constant of $HgZn(NCS)_4$. There is an increase in Δ at 77°K for the mixed salt, and if the thermal expansion coefficients found by Straumanis[5] for $HgCo(NCS)_4$ can be applied here, it appears that a unit cell volume contraction on cooling of about 0.3% increases Δ by about 3.3%. No large departure from tetrahedral symmetry for the Co ion can be detected for the Co or mixed Co–Zn salts.

It will be noted that the energies of ν_1 in the Co(II) spectra are always 150–270 cm^{-1} less than the values of Δ calculated from the other two bands. In fact, it is not possible to fit all three bands in the spectra accurately on the basis of simple first-order perturbation theory. There are several possible reasons for these discrepancies. First, it is not possible to determine accurately the centers of gravity of the two high-energy bands without detailed knowledge of their structure; the work of Ferguson[9] shows the difficulty of complete assignments for these bands. Second, it is likely that the band system in the region of ν_1 has a great deal of structure which is not revealed at 77°K, as found for Co(II) in ZnO[10] and CdS[11] crystals. This structure is partly of spin–orbit origin and partly of vibronic origin, and it is not certain that the center of the $^4T_2$ multiplet will be at the same energy as the intensity maximum we have taken as ν_1. Third, if the discrepancy is real, it may be caused by covalent bonding which will lead to, among other things, differential expansion of the e and t_2 orbitals.

The spectrum of $Hg[Cu_{0.083}Zn_{0.917}](NCS)_4$ found here, Figure 2, agrees with that found by Forster and Goodgame[2] for $Hg[Cu_{0.16}Zn_{0.84}](NCS)_4$. The broad band at 10,600 cm^{-1} at room temperature is shifted to 11,000 cm^{-1} at 77°K, while a weak band at about 6000 cm^{-1} becomes evident, particularly in plots against wavenumber. The exact assignment of these bands must await single-crystal work, but similar work[12] on $CuCl_4^{2-}$ suggests that they are ligand field transitions in tetrahedrally coordinated Cu with moderate tetragonal distortion. This distortion is occurring here without changing the lattice constants.

The spectrum of $HgMn(NCS)_4$ indicates tetrahedral coordination of the Mn ion. The spectrum, Figure 3, of $Hg[Mn_{0.115}Zn_{0.885}](NCS)_4$ is almost identical, and the better resolved spectrum obtained by comparing the Mn–Zn salt against the Zn salt indicates tetrahedral coordination of the Mn, while being rather insensitive to small distortions.

The spectrum of $HgFe(NCS)_4$ shows a broad, double-peaked band at 4800 and 6000 cm^{-1}. The almost identical room-temperature spectrum of $Hg[Fe_{0.111}Zn_{0.889}](NCS)_4$, Figure 4, shows a similar poorly resolved band system, with maxima at 4930 and 6050 cm^{-1}. On cooling to 77°K, this spectrum is more clearly resolved into two bands at 4810 and 6490 cm^{-1}. The low-energy band therefore remains almost unaltered but the splitting increases from 1120 cm^{-1} at room temperature to 1520 cm^{-1} at 77°K. This splitting is also observed[1] in solution spectra of the tetrahedral ion $Fe(NCS)_4^{2-}$ and, being too large for spin–orbit splitting, probably results from a static Jahn–Teller distortion. In the Fe–Zn mixed crystal, it is not possible to determine if the distortion is inherent in the lattice or is a static Jahn–Teller type. Both are probably of tetragonal type, and a further ligand field band would be expected at lower frequencies. No such band was observed for either $HgFe(NCS)_4$ or $Hg[Fe_{0.111}Zn_{0.889}](NCS)_4$ in the region 4000–650 cm^{-1}.

The reflectance spectrum of the salt $Hg[Ni_{0.024}Zn_{0.976}](NCS)_4$, Figure 5, differs considerably from that of $HgNi(NCS)_4$[2] and from the spectra of systems containing the tetrahedral ion $Ni(NCS)_4^{2-}$.[2] It cannot be fitted well on the basis of either regular octahedral or regular tetrahedral symmetry. It has the over-all appearance of a tetrahedral spectrum but is shifted to higher energies throughout and is considerably split. The shifting to higher energies suggests that the Ni(II) atom is under considerable compression in the lattice, while the splitting suggests distortion, most probably of a tetragonal nature. The lattice constants do not reflect the compression and distortion, but it may be significant that 2.4 mole % seems to be the maximum Ni content which can be incorporated in the $HgZn(NCS)_4$ lattice.

It is significant that only in the cases of Fe, Ni, and Cu, which have degenerate ground states (excluding spin–orbit coupling), are significant distortions present about the M^{2+} ion in $Hg[M_xZn_{1-x}](NCS)_4$. These distortions are therefore likely to be of Jahn–Teller or pseudo-Jahn–Teller[13] type. The distortions have little effect on the relatively "soft" lattice of the $HgZn(NCS)_4$ crystal. The size of the M^{2+} ion is seen as playing little part in the distortions, as shown by the similar unit cell volumes in the pure and mixed salts, and by the near identity of the spectra of the Mn, Fe, and Co salts with those of a series of analogous compounds $(Cat^+)_2M(NCS)_4$ in which the M–N distances are relatively free to adjust themselves.

Experimental Section

The X-ray data were obtained with an 11.46-cm diameter Philips Debye–Scherrer camera using filtered Cu Kα radiation. Line positions on some films were calibrated by incorporation of thorium oxide of accurately known lattice parameters. Line positions were determined with an accurate traveling microscope. Cell dimensions were obtained by least-squares fitting of the data.

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