borate by external replacement. The samples of 1,2-dichlorodecaborane(14), 2,4-dichlorodecaborane(14), and 1,3-dichlorodecaborane(14) were prepared by addition of 2 equiv of chlorine to 1 equiv of decaborane(14) in methylene chloride in the presence of aluminum chloride. The resulting mixture was then separated by preparative thin-layer chromatography over silica gel.[4] The samples of 1-chloro-9-bromodecaborane(14) and 2-chloro-6-bromodecaborane(14) were prepared by addition of anhydrous hydrogen bromide to a refluxing benzene solution of 1-chloro-6,9-bis(dimethyl sulfide)decaborane and 2-chloro-6,9-bis(methyl sulfide) decaborane, respectively. Both products were also purified by preparative thin-layer chromatography. The samples of 2,4-diiododecaborane(14) and 1,2-diiododecaborane(14) were prepared by heating decaborane in a sealed bulb with 2 equiv of iodine at 115° for 2 days. The products were separated by recrystallization from benzene and preparative thin-layer chromatography over silica gel.

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Registry No. Decaborane(14), 17702-41-9; 2,4-dichlorodecaborane(14), 51933-38-1; 1,2-dichlorodecaborane(14), 51933-39-2; 1,3-dichlorodecaborane(14), 51933-40-5; 2-chloro-9-bromodecaborane(14), 51933-41-6; 1-chloro-6-bromodecaborane(14), 52022-16-9; 2,4-diiododecaborane(14), 23835-60-1; 1,2-diiododecaborane-(14), 51933-42-7; ^{11}B, 14798-13-1.

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Vibrational Spectra of $K_2Zn(CN)_4$, $K_2Cd(CN)_4$, and $K_2Hg(CN)_4$

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Recently Adams and Christopher[1] reported infrared and Raman studies of $K_2Zn(CN)_4$ along with frequency assignments for the vibrational modes. Similar studies have been made in this laboratory for the three isostructural crystals $K_2Zn(CN)_4$, $K_2Cd(CN)_4$, and $K_2Hg(CN)_4$. Most of the vibrational modes have been assigned with certainty from polarized Raman spectra of single crystals or from infrared studies of the powder. This report includes $K_2Zn(CN)_4$ as the frequencies found are slightly different from those reported in ref 1.

Experimental Section

$K_2Zn(CN)_4$ and $K_2Cd(CN)_4$ are readily prepared from the nitrates by first precipitating the dicyanides, washing, and adding a stoichiometric amount of KCN. $K_2Hg(CN)_4$ is prepared from stock $Hg(CN)_2$ and KCN. Single crystals of 1-2 mm size were grown by slow evaporation of aqueous solutions. The crystals grew as rather irregular octahedra. The faces were imperfect; however, they gave good polarized Raman spectra. The spectra were improved by immersing the crystal in chlorobenzene as a medium for matching the refractive index of the crystal to minimize reflection defects.

The Raman spectra were observed on a Cary 82 and the infrared spectra on a Perkin-Elmer 521, a Beckman IR-11, and a Cary 14.

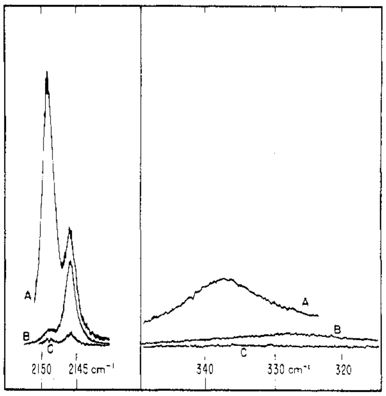

Figure 1. Raman spectrum of a single crystal of $K_2Hg(CN)_4$ immersed in chlorobenzene: A, $[110]\ [[1\bar{1}0]\ [1\bar{1}0]^{s}]\ [001]$, A_{1g}, F_{2g}; B, $[110]\ [[1\bar{1}0]\ [110]^{s}]\ [001]$, E_g; C, $[110]\ [[001]\ [1\bar{1}0]^{s}]\ [001]$, F_{2g}. Slit: 1 cm^{-1} for 2100-cm^{-1} region; 2 cm^{-1} for 300-cm^{-1} region. Gain: 20,000 counts/sec (except as noted in figure).

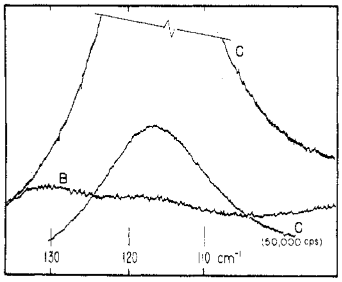

Figure 2. Raman spectrum of a single crystal of $K_2Hg(CN)_4$ immersed in chlorobenzene. Slit: 2 cm^{-1}; see Figure 1 for gain and polarization.

Selection Rules

Adams and Christopher[1] have given the factor group analysis for these crystals which are cubic, F_{d3m} $(O_h{}^7)$, $Z = 8$. There are two formula units per primitive unit cell. The correlation table has been given before[1,2] and is not shown here. There are three Raman-active symmetries: A_{1g} $(x^2 + y^2 + z^2)$, E_g $(x^2 + y^2 - 2z^2; x^2 - y^2)$, and F_{2g} (xy, yz, zx). These three symmetries can be distinguished with one crystal orientation. For example the crystal can be mounted with its [110] axis along the incoming laser beam and its [001] axis along the exiting Raman beam. The incoming laser beam polarization can be rotated through 90° with a polarization rotator to give orientation of $[1\bar{1}0]$ or [001] for the polarization of the incoming beam. The exiting Raman beam passed through a polarization analyzer and a scrambler. We then have the following selection rules, using Swanson's notation[3] for the polarizations

$[110]\ [[1\bar{1}0]\ [1\bar{1}0]^{s}]\ [001]$ A_{1g}, F_{2g}
$[110]\ [[1\bar{1}0]\ [110]^{s}]\ [001]$ E_g
$[110]\ [[001]\ [110]^{s}]\ [001]$ F_{2g}

Results and Discussion

As an example of the Raman spectra, in Figures 1 and 2 are shown part of the spectra for a crystal of $K_2Hg(CN)_4$ mounted with [110] along the incoming beam and [001] along the exiting Raman beam. This crystal was immersed in chlorobenzene to reduce scattering from imperfections and tilted faces. In Figure 1 it is readily apparent that there

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[1] D. M. Adams and R. E. Christopher, *Inorg. Chem.*, **12**, 1609 (1973).

[2] L. H. Jones, *Spectrochim. Acta*, **17**, 188 (1961).

[3] B. I. Swanson, *Appl. Spectrosc.*, **27**, 382 (1973).

Table I. Frequency Assignments[a] for Solid $K_2M(CN)_4$

		M		
		Zn	Cd	Hg
A_{1g}	ν_{1a} (r_{CN})	2154.8 ± 0.2	2146.4 ± 0.2	2149.1 ± 0.2
	ν_{2a} (r_{MC})	340.5 ± 0.5	322.7 ± 0.5	336.9 ± 0.5
E_g	ν_{3a} (δ_{MCN})	315.9 ± 1.0	255.7 ± 0.5	275.4 ± 0.5
	ν_{4a} (δ_{CMC})	126.4 ± 0.5	114.3 ± 0.5	116.4 ± 0.5
F_{2g}	ν_{5a} (r_{CN})	2153.2 ± 0.2	2145.9 ± 0.2	2145.9 ± 0.2
	ν_{6a} (r_{MC})	348.4 ± 1.0	318.0 ± 2.0	326.9 ± 1.0
	ν_{7a} (δ_{MCN})	316 ± 2	254.5 ± 1.0	237.6 ± 1.0
	ν_{8a} (δ_{CMC})	152.5 ± 1.0	137.8 ± 1.0	130.6 ± 1.0
	ν_{12} (T)	59.4 ± 0.2	45.9 ± 0.2	35.0 ± 0.2
F_{1g}	ν_{9a} (δ_{MCN})	(230)[b]	(194)[b]	(180)[b]
	ν_{10} (rot.)			
A_{2u}	ν_{1b} (r_{CN})			
	ν_{2b} (r_{MC})			
	ν_{13} (T)			
E_u	ν_{3b} (δ_{MCN})			
	ν_{4b} (δ_{CMC})			
	ν_{14} (T)			
F_{1u}	ν_{5b} (r_{CN})	2152.9 ± 0.2	2145.5 ± 0.2	2145.8 ± 0.2
	ν_{6b} (r_{MC})	355.7 ± 1.0	321 ± 1	330 ± 2
	ν_{7b} (δ_{MCN})	314.4 ± 1.0	249 ± 1	232 ± 2
	ν_{8b} (δ_{CMC})	150 ± 2	133[c]	140 ± 10
	ν_{15} (T)	126 ± 2		117 ± 2
	ν_{16} (T)	84?	71 ± 2	69 ± 2?
F_{1u}	$\nu_{1a} + \nu_{5b}$ $\nu_{5a} + \nu_{5b}$	4281.0 ± 0.5	4267.5 ± 0.5	4268.8 ± 0.5
F_{2u}	ν_{9b} (δ_{MCN})			
	ν_{11} (rot.)			
	ν_{17} (T)			

[a] Units are cm^{-1}. [b] From ref 2 as estimated from combination bands. [c] This band was observed to split into two, at 147 and 124 cm^{-1}, when cooled to ~100° K.

Table II. Frequency Assignments (cm^{-1}) for Aqueous $M(CN)_4{}^{2-}$

		M		
		Zn	Cd	Hg
A_{1g}	ν_1	2151.2 ± 0.5	2144.0 ± 0.5	2147.3 ± 0.5
	ν_2	341 ± 2	322 ± 1	334.2 ± 1
E_g	ν_3	317 ± 1	260 ± 2	280 ± 2
F_2	ν_5	2149.2 ± 0.5	2142.0 ± 0.5	2143.0 ± 0.5
	ν_7	317 ± 1	260 ± 2	232 ± 2

are A_{1g} modes at 2149 and 337 cm^{-1} active only in A and there are F_{2g} modes at 2146 and 327 cm^{-1} active in A and B. In Figure 2 the C orientation which should be active for only E_g modes shows that the strong peak at 166 cm^{-1} is an E_g mode. It follows that the weak peak at 131 cm^{-1} is F_{2g}. Residuals of strong peaks remain in "forbidden" orientations because of imperfections and misorientation. In a similar manner a weak and broad E_g mode was found at 275 cm^{-1}, a weak and broad F_{2g} mode at 238 cm^{-1}, and a fairly strong and sharp F_{2g} mode at 35 cm^{-1}.

Infrared frequencies were observed in mineral oil mulls of the powders. Aqueous Raman frequencies are presented also for comparison. The results for all three compounds are presented in Tables I and II.

There are several points of interest. As noted by Adams and Christopher for $K_2Zn(CN)_4$, except for the translatory lattice modes the F_{2g}-F_{1u} correlation field splitting is quite small. The low-frequency F_{2g} mode shows an unexpectedly large decrease in the series Zn-Cd-Hg. The motion involved is primarily a translation of the complex ions against the potassium atoms, which do not move. One would expect the frequency to be proportional to $m^{-1/2}$ where m is the total mass of the $M(CN)_4{}^{2-}$ group. This would lead to a decrease from 59 to 52 to 44 cm^{-1} for Zn → Cd → Hg. The significantly greater decrease observed suggests that the N-K force constant decreases in the same order $[F_{NK}(Zn) > F_{NK}(Cd) > F_{NK}(Hg)]$. Though we do not know the NK distance for these three compounds, we would expect them to be about the same. However, it is possible that the effective charge on the nitrogen atoms varies with the metal atom causing changes in the N-K interaction. Another possibility is that variation of coupling of ν_{12} with the other F_{2g} coordinates leads to the discrepancy. It is unfortunate that we have been unable to observe the low-frequency F_{1u} lattice mode. It would be interesting to know if it follows a similar trend.

From the correlation table we expect the inactive A_{2u} modes, ν_{1b} and ν_{2b}, to have about the same frequencies as the A_{1g} modes. The E_u modes ν_{3b} and ν_{4b} may be shifted significantly from the corresponding E_g modes by coupling the E_u translatory coordinate. We can say nothing about the F_{2u} and F_{1g} modes except for the previous assignment of ν_{9a} from combination bands,[2] as verified by Adams and Christopher[1] for $K_2Zn(CN)_4$.

We plan to observe isotope shifts for the completely substituted ^{13}C and ^{15}N species in order to estimate the force fields of these crystals. The result should help to explain the trends observed in the present work.

In order to estimate anharmonic corrections for the CN stretching modes the combinations $\nu_{1a} + \nu_{5b}$ and $\nu_{5a} + \nu_{5b}$ were searched for in single crystals on the Cary 14 spectrometer. For each species only one band was observed in this region (see Table I). From the nickel carbonyl spectrum[4] one expects comparable intensities for these two combination transitions. Perhaps this is an example of the loss of intensity of one band in a Fermi resonance doublet as discussed by El Sayed.[5] The calculated anharmonicity correction is either $X_{1a,5b}$ or $X_{5a,5b} \approx 25$ cm^{-1} and must be viewed with some uncertainty in light of the possibility of Fermi resonance.[5]

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Registry No. $K_2Zn(CN)_4$, 14244-62-3; $K_2Cd(CN)_4$, 14402-75-6; $K_2Hg(CN)_4$, 591-89-9.

(4) L. H. Jones, *J. Chem. Phys.*, 28, 1215 (1958).
(5) M. El Sayed, *J. Chem. Phys.*, 37, 680 (1962).

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Stereochemistry of β-Diketone Complexes of Cobalt(III). XIII. Linkage and Geometrical Isomers of Thiocyanatopyridinebis(acetylacetonato)cobalt(III)

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The stereochemistry of several complexes of the type $[Co(acac)_2(X)py]$ ($X^- = CN^-, N_3^-, NCO^-, NO_2^-$) has been studied and the marked influence of the monodentate anion on the reactivity of the complexes noted.[1] As an extension of that work we have examined the complexes of the anion NCS^-. We wish to report here the synthesis and characterization of several isomers of the new compound $[Co(acac)_2(NCS)py]$.[2]

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(1) D. R. Herrington and L. J. Boucher, *Inorg. Chem.*, 12, 2378 (1973).
(2) Abbreviations used in this paper: $acac^-$, 2,4-pentanedionato (acetylacetonato); py, pyridine; DMSO, dimethyl sulfoxide.