mediately on either side of it, but, in general, more to whichever is closer in energy to it. Our results can be explained if the primary products of the oxidation–reduction processes are "intermediates" like $Co(NH_3)_5^{2+}$. This entity has to be in a low spin state and to be tetragonally pyramidal in shape, with the cobalt atom lying in the square face (which we will suppose contains the x and y axes). Lying in the z axis in place of a sixth ligand there must be a localized orbital containing a single electron. In order to achieve satisfactory localization a considerable admixing with the $3d_{z^2}$ orbital by the $4p_z$ is necessary. The $Co(NH_3)_5^{2+}$ "intermediate" will almost certainly have a high energy relative to the reactants, and therefore a similarity in geometry between it and the transition state would be expected. It would be interesting if the "intermediate" were a metastable entity corresponding to a minimum in the potential energy surface, although it need, from the point of view of our argument, to have no more physical significance than that associated with the region on the slope leading downward once the transition state saddle has been crossed.

The single electron associated with the hybrid orbital is one of those involved in the oxidation–reduction process. How it ultimately reaches the cobalt atom cannot be said, but it leaves the oxygen through a σ orbital.

The nitrogen fractionation in NH_3 is greater in the $Co(en)_2NH_3OH^{2+}$ complexes than in the pentaammine analog. This effect suggests that what slight changes do occur in the Co–N links tend to be restricted to those involving ammonia rather than ethylenediamine, which is reasonable as it is probably harder to distort a chelated structure than the bond to a monodentate ligand.

The fractionation factors for the hydroxo complexes are significantly greater than for the chloro. It is possible that there is a difference in the fundamental process of electron transfer in the two cases. Chlorine, but not oxygen, has vacant low-lying orbitals and these may well play an important role for they would facilitate a synergic process in which one electron was transferred to the crucial bridging atom at the same time as another left it.

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Hydrogen Bonding in Ferrocyanic, Ruthenocyanic, and Osmocyanic Acids

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The infrared spectra of the anhydrous metallocyanic acids $H_4M(CN)_6$ and $D_4M(CN)_6$ (M = Fe, Ru, and Os) were measured in the solid state from 10,000 to 300 cm.$^{-1}$ at room temperature and at 80°K. The results indicate that these compounds consist of $H_4M(CN)_6$ units, with the *trans* arrangement of the hydrogen atoms, which are linked together by asymmetrical $N–H\cdots N$ hydrogen bonds into a three-dimensional network. *All four* hydrogen atoms per $H_4M(CN)_6$ unit are involved in hydrogen bonding, but two of them are more strongly hydrogen-bonded than the other two. Assignments are given for most of the bands in the spectra.

Introduction

The protonation of transition metal cyanide complexes has been the subject of several recent papers.[1,2] This work demonstrated that strong acids reversibly diprotonate the complexes dicyanobis(1,10-phenanthroline)iron(II), dicyanobis(2,2′-bipyridine)iron(II), -ruthenium(II), and -osmium(II). It was at first suggested that the protons are directly bound to the metal atom as in various protonated transition metal carbonyl complexes and carbonyl hydrides. However, later work[2-4] indicated that this is incorrect and that the protons are linked to the nitrogen of the cyanide groups, *e.g.*, $[(phen)_2Fe(CNH)_2]^{2+}$. Surprisingly though, there appears to be no evidence of NH stretching or bending absorptions in the infrared spectra of the solid protonated complexes.[2]

The results outlined above prompted us to investigate the infrared spectra of the metallocyanic acids $H_4M(CN)_6$ and $D_4M(CN)_6$, M = Fe, Ru, and Os. Although $H_4Fe(CN)_6$ was first reported in 1820[5] there was until recently no direct evidence bearing on the arrangement or bonding of the protons. The spectra of these compounds are not simple, but they yield interesting information about the arrangement of the protons as well as their bonding. While this work was in

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[1] A. A. Schilt, *J. Am. Chem. Soc.*, **82**, 3000, 5779 (1960).

[2] A. A. Schilt, *ibid.*, **85**, 904 (1963).

[3] N. K. Hamer and L. E. Orgel, *Nature*, **190**, 439 (1961).

[4] G. Wilkinson in "Advances in the Chemistry of the Coordination Compounds," The Macmillan Co., New York, N. Y., 1961, p. 56.

[5] J. J. Berzelius, *Schweigger's J.*, **30**, 44 (1820).

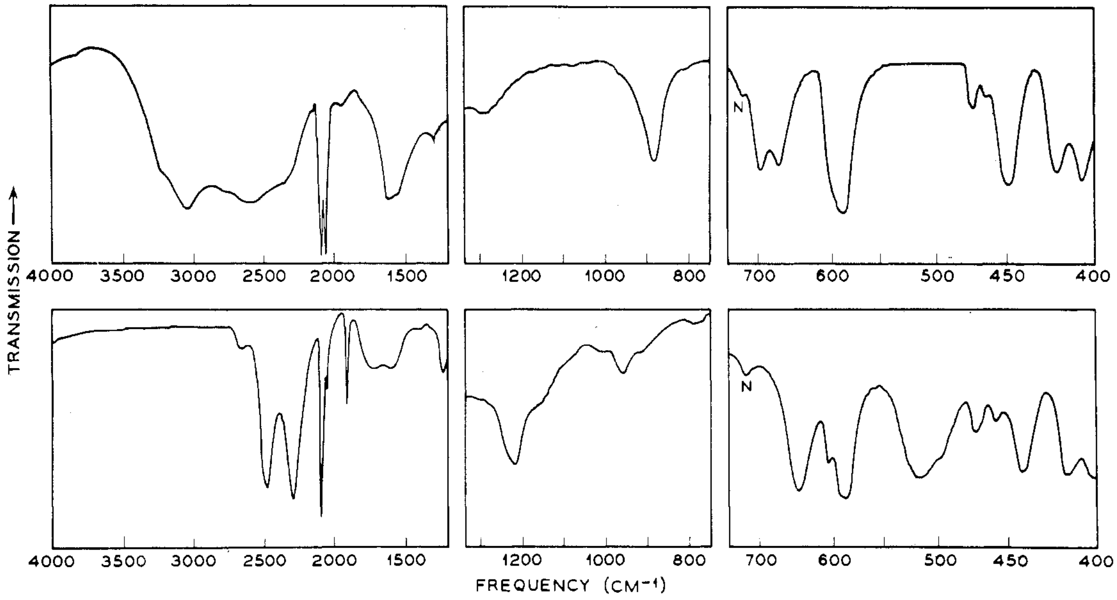

Figure 1.—Infrared spectra of $H_4Fe(CN)_6$ (upper) and $D_4Fe(CN)_6$ (lower) from 4000 to 400 cm.$^{-1}$ at room temperature.

progress there appeared a preliminary note[6] followed by a paper[7] in which the room temperature infrared spectra (4000–400 cm.$^{-1}$) of the $H_4M(CN)_6$ acids and their deuterio analogs were reported. However, these authors do not attempt as detailed an interpretation of the spectra as we do here, and conclude only that there is evidence for the presence of unsymmetrical N–H···N bonds. Furthermore, the measurements we report are more extensive (10,000–300 cm.$^{-1}$ at room temperature and at 80°K.) and differ in several important respects from the results of Evans, *et al.* There has also recently appeared a note[8] reporting the space group and number of molecules per unit cell of $H_4Fe(CN)_6$. This information greatly facilitated interpretation of the spectra.

Experimental

Preparation of Compounds.—The acids were all obtained by essentially the same procedure, as described in the literature ($H_4Fe(CN)_6$,[9] $H_4Ru(CN)_6$,[10] and $H_4Os(CN)_6$[11]). Briefly, the potassium salt of the hexacyanide was dissolved in dilute hydrochloric acid and the solution was shaken with excess ether to precipitate an "etherate" of the acid contaminated with KCl. The "etherate" was purified by reprecipitating twice from an ethanol solution by addition of excess ether. Ether-free $H_4Os(CN)_6$ and $H_4Ru(CN)_6$ were obtained as white solids by pumping the "etherates" for several hours at 80°. Ether-free $H_4Fe(CN)_6$ resulted from pumping on the "etherate" for about 3 hr. at 50°.

The compounds were characterized by a potentiometric titration with standard base and by analysis for carbon and nitrogen (Schwarzkopf Microanalytical Laboratory, Woodside, N. Y.). In the case of ferrocyanic acid the residue weight from the carbon determination gave the iron content. *Anal.* Calcd. for $H_4Fe(CN)_6$: C, 33.36; N, 38.91; Fe, 25.86; equiv. wt., 54.00. Found: C, 33.6; N, 39.15; Fe, 26.3; equiv. wt., 54.8. Calcd. for $H_4Ru(CN)_6$: C, 27.52; N, 32.10; equiv. wt., 65.46. Found: C, 28.1; N, 30.8; equiv. wt., 66.3. Calcd. for $H_4Os(CN)_6$: C, 20.57; N, 23.99; equiv. wt., 87.57. Found: C, 20.75; N, 23.6; equiv. wt., 86.0.

The deuterio acids were obtained by carrying out the preparations with D_2O and DCl and reprecipitating the product from C_2H_5OD. All manipulations with the deuterio compounds were carried out in an argon-filled drybox.

Infrared Spectra.—Spectra were measured from 10,000 to 300 cm.$^{-1}$ at room temperature and at 80°K. using various instruments: from 10,000 to 4000 cm.$^{-1}$ on a Cary Model 14 spectrophotometer, from 4000 to 800 cm.$^{-1}$ on a Perkin-Elmer Model 337 grating spectrophotometer and also on a Perkin-Elmer Model 21 spectrophotometer with sodium chloride optics, from 800 to 400 cm.$^{-1}$ on a Perkin-Elmer KBr Model 137 spectrophotometer, and from 400 to 300 cm.$^{-1}$ on a Perkin-Elmer Model 421 dual grating spectrophotometer. In addition, the Model 421 was used to obtain high-resolution spectra in the 2200–2000 cm.$^{-1}$ range (CN stretching region). Samples were measured as fluorocarbon oil or Nujol oil mulls and also as KBr disks. The mull and disk spectra are essentially the same, except for the presence of an OH stretching band in the disk spectra due to a trace of moisture in the KBr. Measurements at ~80°K. were made on KBr disks only.

Results

The spectra of the Fe, Ru, and Os acids are very similar. In Table I are listed all of the observed frequencies. The estimates of relative intensity given in Table I are very rough. Figure 1 presents the room temperature spectra of $H_4Fe(CN)_6$ and $D_4Fe(CN)_6$ from 4000 to 400 cm.$^{-1}$. The region from 400 to 300 cm.$^{-1}$, not illustrated, contains only two very weak bands in the case of $H_4Fe(CN)_6$, but with the Ru and Os acids the medium intensity bands corresponding to 419 and 406 cm.$^{-1}$ in $H_4Fe(CN)_6$ occur below 400 cm.$^{-1}$. From 10,000 to 4000 cm.$^{-1}$ only very weak absorptions are found; spectra could be recorded only with extremely concentrated KBr disks (~1:1 sample:KBr, ~2 mm. thick; such a sample is completely opaque in the 4000–300 cm.$^{-1}$ region). Cooling to 80°K. causes a very marked increase in the intensity of these bands; this is illustrated in Figure 2, which shows the

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(6) D. Jones and D. F. Evans, *Nature*, **199**, 277 (1963).

(7) D. F. Evans, D. Jones, and G. Wilkinson, *J. Chem. Soc.*, 3164 (1964).

(8) R. Kern, *Acta Cryst.*, **17**, 1612 (1964).

(9) "Handbuch der Preparativen Anorganischen Chemie," Brauer, Ed., 2nd Ed., Vol. 2, Ferdinand Enke, Stuttgart, 1962, p. 1315.

(10) F. Krauss and G. Schrader, *Z. anorg. allgem. Chem.*, **165**, 59 (1927).

(11) A. Martius, *Ann.*, **117**, 356 (1861).

TABLE I

INFRARED ABSORPTION FREQUENCIES (CM.$^{-1}$) OF $H_4M(CN)_6$ AND $D_4M(CN)_6$ ACIDS[a]

$H_4Fe(CN)_6$	$H_4Ru(CN)_6$	$H_4Os(CN)_6$	$D_4Fe(CN)_6$	$D_4Ru(CN)_6$	$D_4Os(CN)_6$	Assignment[b]
5848^c vw	5882^c vw	5865^c vw				$\nu_1 + \nu'_{22}$, $\nu'_1 + \nu_{22}$
5634^c sh	5634^c vw	5634^c vw				$\nu_1 + \nu_{23}$, $\nu_2 + \nu_{22}$
5089^c vw	5102^c vw	5102^c vw				$\nu_1 + \nu_{16b}$, $\nu_7 + \nu_{22}$
$\sim 5050^c$ sh	...	...				Ternary combination
4854^c sh	$\sim 4831^c$	...				$\nu_7 + \nu'_{22}$, $\nu'_1 + \nu_{16b}$
$\sim 4739^c$ sh	. .	. .	Not examined	Not examined	Not examined	$\nu'_2 + \nu'_{23}$
$\sim 4612^c$ sh	$\sim 4630^c$ sh	...				$\nu_2 + \nu_{16b}$, $\nu_7 + \nu_{23}$
4562^c <vvw	4568^c <vvw	$\sim 4520^c$ <vvw				Ternary combination
...	$\sim 4494^c$ <vvw	...				$\nu'_2 + \nu_{28}$, $\nu_8 + \nu'_{23}$
4444^c vvw	4444^c vvw	4434^c vvw				$\nu'_1 + \nu_{24}$, $\nu_3 + \nu'_{22}$, $\nu'_2 + \nu_{16b}$, $\nu_7 + \nu'_{23}$
4210^c w	4224^c w	4224^c w				$\nu_2 + \nu_{24}$, $\nu_3 + \nu_{23}$, $\nu_8 + \nu_{28}$, $\nu_8 + \nu_{16a}$
4167^c w	4167^c w	4163^c w				$\nu_{12} + \nu_{16b}$, $\nu_7 + \nu_{16a}$
$\sim 4115^c$ sh	4154^c sh	4144^c sh				$\nu_7 + \nu_{16b}$
$\sim 3200^c$ sh, wm	$\sim 3200^c$ sh, w	~ 3200 sh, w	2630 w	2640 w	~ 2630 w	$\nu_1 + L,^e$ $\nu_{22} + L^e$
3040^c vs	3050^c vs	3060^c vs	2460 vs	2470 vs	2460 vs	ν_{22}
$\sim 2770^c$ ms	$\sim 2790^c$ ms	$\sim 2780^c$ ms	...	...	...	$\nu'_{22} = \nu_{24} + \nu_4$, $\nu_3 + \nu_{26}$ res. with ν_{22} in H acids
$\sim 2630^c$ sh	$\sim 2650^c$ sh	...	...	...	...	$\nu_4 + \nu_{26}$
2570^c s	2580^c s	2580^c s	2280 vs	2290 vs	2280 vs	ν_{23}
2370^c ms	2370^c ms	2350^c ms	1905 wm	1905 wm	1905 wm	$\nu'_{23} = \nu_{24} + \nu_5$, $\nu_3 + \nu_{25}$ res. with ν_{23} in H acids
2300^c sh, vw	...	...	...	...	...	?
2134 w	2145 w	2149 w	...	...	...	$\nu_8 + L,^f$ $\nu_{28} + L^f$
2125 sh, w	2135 sh, w	2134 w	...	...	. .	$\nu_{12} + L,^f$ $\nu_{16a} + L^f$
~ 2106 sh	2110 s	2108 s	2100 s^d	2100 s^d	2100 s^d	ν_{28}
2096 s	2104 sh	2097 sh	~ 1720 s	~ 1710 s	~ 1710 s	$\left.\begin{matrix}\nu_{16a}\\ \nu_{16b}\end{matrix}\right\}\nu_{16}$
2072 s	2078 s	2072 s	~ 1610 ms	~ 1610 s	~ 1590 s	
~ 2060 sh, vw?	~ 2062 sh, vw?	~ 2058 sh, vw?	2061 vw	~ 2064 vw	~ 2058 sh, vw	$\nu(^{13}CN)$
~ 2040 sh, vw?	~ 2045 sh, vw?	~ 2045 sh, vw?	...	...	...	$\nu(^{13}CN)$
1960 w	1950 w	1920 w	~ 1400 w	~ 1410 w	~ 1400 w	$\nu_6 + \nu_{26}$ and $\nu_4 + \nu_{27}$
$\sim 1775^c$ sh, w	. .	...	~ 1300 sh, w	...	~ 1275 sh, w	$\nu_5 + \nu_{25}$
1650^c ms	$\sim 1650^c$ ms	$\sim 1650^c$ ms	1215 ms	1235 ms	$\left.\begin{matrix}\text{1220 ms}\\ \text{...}\end{matrix}\right\}$	ν_{24}
1620^c sh	...	...	...	...		
1590^c sh	$\sim 1600^c$ sh	$\sim 1600^c$ sh	~ 1150 sh	~ 1175 sh, m	~ 1150 sh	$\nu_6 + \nu_{25}$ and $\nu_5 + \nu_{27}$
$\sim 1475^c$ sh, w	$\sim 1450^c$ sh, w	$\sim 1450^c$ sh	~ 1100 sh	~ 1100 sh	...	?
1380^c vw	1380^c vw	...	~ 1020 sh	...	~ 1000 sh	$\nu_6 + \nu_{27}$
1290^c w	1300^c wm	~ 1280 wm	960 wm	965 wm	$\left.\begin{matrix}\text{950 w}\\ \sim\text{930 sh, w}\end{matrix}\right\}$	ν_{26}
1270^c sh, w	$\sim 1275^c$ sh	...	~ 920 sh, w	...		
~ 960 sh	...	~ 960 sh	...	...	...	?
887 m	895 m	890 m	640 m	647 m	644 m	ν_{25}
~ 815 sh, vw	~ 835 sh, vw	~ 835 sh, vw	~ 790 vw	~ 825 vw	~ 825 vw	?
692 m	~ 690 sh	~ 680 sh	515 m	515 m	$\left.\begin{matrix}\text{502 m}\\ \text{485 sh}\end{matrix}\right\}$	ν_{27}
668 m	670 m	660 m	500 sh	...		
~ 600 sh	~ 550 sh	...	602 sh	~ 555 sh	$\left.\begin{matrix}\text{...}\\ \text{544 ms}\end{matrix}\right\}$	ν_{29} and ν_{18} or ν_{19}
588 ms	543 ms	544 ms	588 ms	543 ms		
473 w	475 sh	496 sh	472 w	476 w	...	?
463 sh, vw	450 sh	470 sh	457 vw	462 vw	~ 470 sh	ν_{32}
448 m	459 m	484 m	441 m	414 m	430 m	ν_{19} or ν_{18}
...	...	~ 446 sh	...	...	~ 446 vw	?
419 m	~ 367 sh	376 sh	415 m	~ 363 sh	$\left.\begin{matrix}\text{370 m}\\ \text{360 m}\end{matrix}\right\}$	ν_{17} and ν_{29}
406 m	362 m	371 m	400 m	355 m		
342 vw	332 vw	348 vw	...	...	...	?
300 vw	...	302 vw	...	...	...	?

[a] m, medium; s, strong; v, very; w, weak; sh, shoulder; ?, questionable band or assignment; ~, indicates an absorption, the position of which was difficult to estimate because it was imperfectly resolved from adjoining bands or because it was very broad. In the case of bands *not* prefixed by a ~ sign, the estimated accuracy of the quoted frequencies is ±5 cm.$^{-1}$ from 10,000 to 4000 cm.$^{-1}$, ±20 cm.$^{-1}$ from 4000 to 2200 cm.$^{-1}$, ±2 cm.$^{-1}$ from 2200 to 2000 cm.$^{-1}$, ±20 cm.$^{-1}$ from 2000 to 1300 cm.$^{-1}$ and ±5 cm.$^{-1}$ from 1300 to 300 cm.$^{-1}$. [b] Alternate assignments are possible for the NH bending modes and the combination tones arising from them. We emphasize that there is no very strong reason to favor the set of assignments of these bands chosen for this table. [c] From spectrum of sample cooled to 80°K. [d] Very asymmetrical band. [e] L is presumed to be a lattice frequency of ~170 cm.$^{-1}$. [f] L is taken to be a lattice frequency of ~30 cm.$^{-1}$.

6500–4000 cm.$^{-1}$ region. From 6500 to 10,000 cm.$^{-1}$ the absorption increases steadily without reaching a maximum. In the 4000–300 cm.$^{-1}$ range cooling the proton acids to 80°K. results in a sharpening of many of the bands with a consequent improvement in the resolution of overlapping absorptions. Figure 3 exhibits the parts of the low-temperature spectrum of $H_4Fe(CN)_6$ that are most effected—the dashed lines are considered to represent the envelopes of the individual bands which contribute to the over-all absorption. The spectra of the deuterio acids are practically unchanged by cooling to 80°K.; this indicates the absence of any phase change between room temperature and 80°K. In Figure 4 is shown a room temperature high-resolution spectrum of $H_4Os(CN)_6$ from 2200 to 2000 cm.$^{-1}$. Table II summarizes the frequency shift factors (ν_H/ν_D) observed on deuteration.

Interpretation of the Spectra

The main objective of our study of the $H_4M(CN)_6$ acids was to obtain information about the arrangement and bonding of the protons in the solid. In presenting the interpretation we first discuss each region of the spectrum, making empirical identifications of the absorptions (*e.g.*, as CN stretching fundamentals, combination tones, etc.). This leads to definite conclusions about the bonding of the protons and their arrangement. It is not possible to deduce unambiguously from the spectra the site symmetry of M, but the X-ray space group of $H_4Fe(CN)_6$ supplies this. In the last section

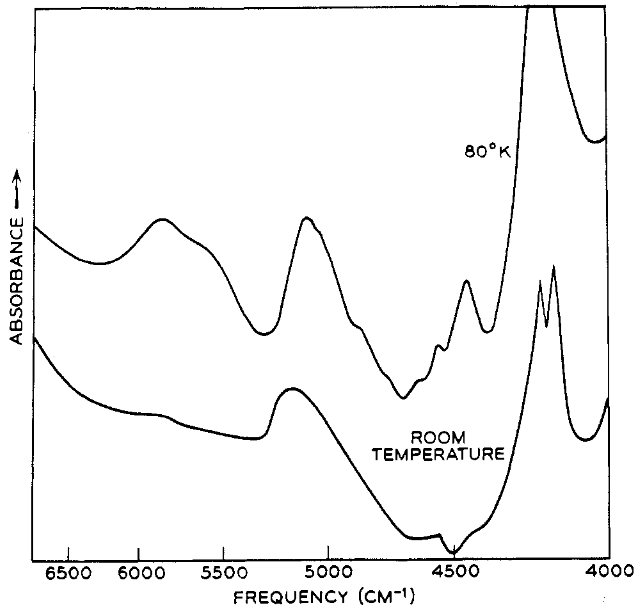

Figure 2.—Infrared spectrum of $H_4Fe(CN)_6$ from 6500 to 4000 cm.$^{-1}$ at room temperature and at 80°K.

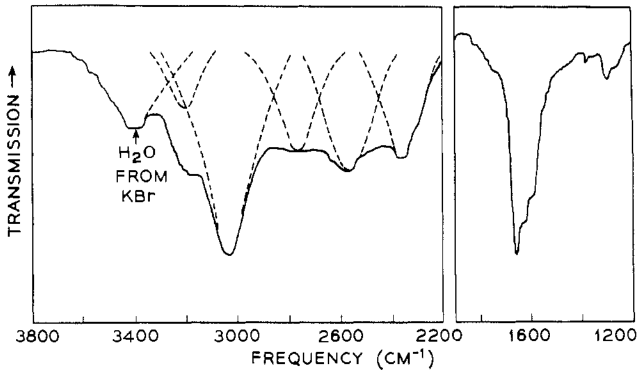

Figure 3.—Infrared spectrum of $H_4Fe(CN)_6$ at 80°K. in the regions 3800–2200 and 1900–1200 cm.$^{-1}$ The sample used for this spectrum was less concentrated than that which gave Figure 1.

TABLE II

SHIFTS OF VIBRATIONAL FREQUENCIES ON DEUTERATION OF $H_4M(CN)_6$ ACIDS

$H_4Fe(CN)_6$		$H_4Ru(CN)_6$		$H_4Os(CN)_6$	
ν_H[a]	ν_H/ν_D[a]	ν_H[a]	ν_H/ν_D[a]	ν_H[a]	ν_H/ν_D[a]
~3200	1.22	~3200	1.21	~3200	1.22
3040	1.24	3050	1.23	3060	1.24
2570	1.13	2580	1.13	2580	1.13
2370	1.24	2370	1.24	2350	1.23
2096	1.22	2104	1.23	2097	1.23
2072	1.29	2078	1.29	2072	1.30
1960	1.40	1950	1.38	1920	1.37
~1775	1.36	. . .	. . .	. . .	. . .
1650	1.36	~1650	1.34	~1650	1.35
1590	1.38	~1600	1.36	~1600	1.39
~1475	1.34	~1450	1.32	~1450	. . .
1380	1.35	1380	. . .	. . .	. . .
1290	1.34	1300	1.35	~1280	1.35
1270	1.38	1275	. . .	. . .	. . .
887	1.38	895	1.38	890	1.38
692	1.34	690	1.34	~680	1.35
668	1.34	670	. . .	660	1.36

[a] ν_H = frequency in ^1H acid; ν_D = frequency in ^2H acid.

we make assignments of the infrared bands to normal vibrational modes.

In the ensuing discussion the frequencies quoted are for ferrocyanic acid unless otherwise indicated. The corresponding frequencies for ruthenocyanic and osmocyanic acid may be found in Table I.

NH Stretching Frequencies.—The $H_4M(CN)_6$ acids absorb very strongly from 3500 to 2200 cm.$^{-1}$. At room temperature the over-all absorption envelope in this region appears as two partially resolved bands with one shoulder on the higher and two shoulders on the lower energy band. On cooling to 80°K. these features are much better resolved (Figure 3) so that the over-all absorption envelope is seen to be made up of five rather broad overlapping bands (~3200, 3040, ~2770, 2570, and 2370 cm.$^{-1}$) some of which have weak shoulders. Each of these bands either shifts or disappears on deuteration.

In the spectrum of deuterioferrocyanic acid there is no absorption between 2700 and 3500 cm.$^{-1}$, demonstrating that the sample is completely deuterated. The bands at 2630, 2460, 2280, 1905, ~1720, and ~1610 cm.$^{-1}$ are clearly related to the proton acid absorptions just discussed.[12] Cooling to 80°K. has little effect on them. At room temperature they are considerably narrower than the related proton acid bands. The correspondence between these deuterio acid absorptions and the proton acid absorptions in the 3500–2200 cm.$^{-1}$ region is not straightforward; we defer discussion of this until the section on CN stretching frequencies.

The NH stretching frequency in HNC (probably linear) has recently been assigned as 3583 cm.$^{-1}$ from observations on HNC in an argon matrix.[13] In HNCO (HNC angle = 125.5°), the NH stretching vibration is reported[14] to be at 3531 cm.$^{-1}$. It is well known that hydrogen bonding lowers AH stretching frequencies and makes the absorption bands very broad and intense.[15] In view of these facts we assign the strong proton acid bands at 3040, ~2770, 2570, and 2370 cm.$^{-1}$, at least in part, to NH stretching vibrations lowered in energy by hydrogen bonding. The weak shoulders (~3200 and ~2630 cm.$^{-1}$) may be attributed to combination tones. Comparison with stretching frequencies for hydrogen-bonded OH, where correlations have been made[16] with the O–H···O bond type, suggest that the hydrogen bonding is of the unsym-

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(12) Since the sample is completely deuterated we reject the possibility that either the ~1720 or ~1610 cm.$^{-1}$ band is a residue of the absorption, observed to shift on deuteration, which occurs in this region in $H_4Fe(CN)_6$. The possibility of an underlying unshifted absorption is also rejected because a plausible assignment could not be made for it. In ref. 7 a broad strong absorption at 1600 cm.$^{-1}$ in both $D_4Fe(CN)_6$ and $D_4Os(CN)_6$ ($D_4Ru(CN)_6$ was not examined) is attributed to residual H in the partially deuterated (90–95%) samples. We have checked this point carefully and have obtained spectra of all three deuterio acids which show practically no absorption between 2700 and 3500 cm.$^{-1}$ and still have strong absorptions at ~1610 and ~1720 cm.$^{-1}$. This is a conclusive argument against the interpretation of ref. 7.

(13) D. E. Milligan and M. E. Jacox, *J. Chem. Phys.*, **39**, 712 (1963).

(14) C. Reid, *ibid.*, **18**, 1544 (1950).

(15) See, for example, G. C. Pimentel and A. L. McClellan, "The Hydrogen Bond," W. H. Freeman and Company, San Francisco, Calif., 1960, Chapter 3.

(16) R. Blinc, D. Hadzi, and A. Novak, *Z. Elektrochem.*, **64**, 567 (1960).

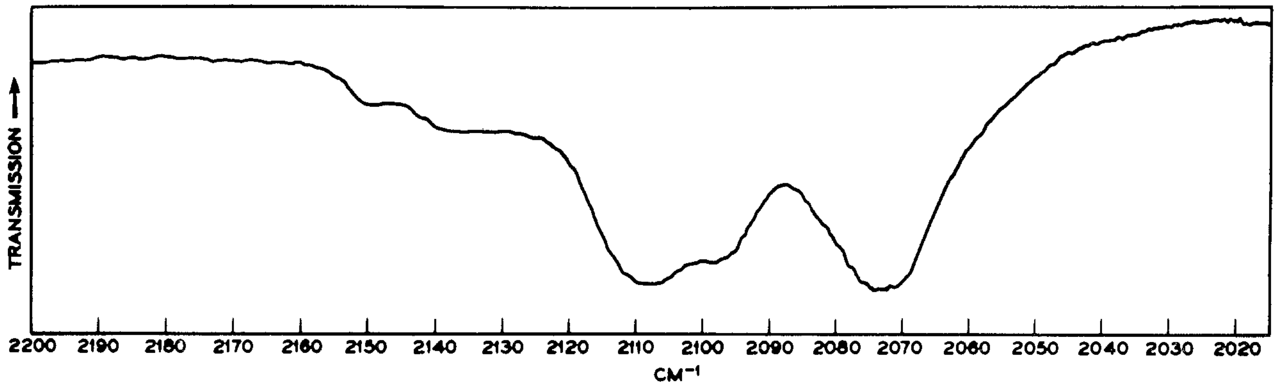


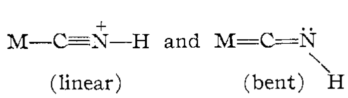
Figure 4.—High-resolution infrared spectrum of $H_4Os(CN)_6$ from 2200 to 2000 cm.$^{-1}$.

metrical N–H···N type (this description includes bonds which become effectively symmetrical because of tunneling of the proton between two potential energy minima).

An important observation is that no absorption maxima are found between 3200 and 3600 cm.$^{-1}$, where nonhydrogen-bonded NH would be expected to absorb. This indicates that *all* of the protons in the $H_4M(CN)_6$ acids are engaged in hydrogen bonding.

Room temperature spectra of all three proton acids show a moderately broad and strong absorption at 1625 cm.$^{-1}$ with an indistinct shoulder at ~1560 cm.$^{-1}$. On cooling to 80°K. this absorption is sharpened and better resolved into a band at 1650 cm.$^{-1}$ with a shoulder at 1590 cm.$^{-1}$ (the resolution of these bands was best in the case of ferrocyanic acid, where a shoulder at 1620 cm.$^{-1}$ also appeared). Both bands have deuteration shifts in the range $\nu_H/\nu_D = 1.37 \pm 0.03$, and they are probably NH bending modes or a bending mode plus a combination tone. However, we must also consider the possibility that one or both of the 1650, 1590 cm.$^{-1}$ bands is due to a very strongly hydrogen-bonded NH stretching frequency. A symmetrical collinear N–H–N hydrogen bond would be expected to give rise to a broad and intense absorption in the 1500–1800 cm.$^{-1}$ range.[16,17] A symmetrical noncollinear N–H–N bond might also give rise to an absorption in this region.

There is nothing in the infrared spectra to tell us whether the hydrogen bonding in the $H_4M(CN)_6$ acids is intramolecular or intermolecular. However, we note that intramolecular hydrogen bonding requires a very highly bent C–N–H arrangement: for a linear internal N–H···N bond a C–N–H angle of 45° would be required. A decrease in the C–N–H angle below 180° is to be expected because of resonance between the canonical forms[18]



$$\underset{\text{(linear)}}{M{-}C{\equiv}\overset{+}{N}{-}H} \quad \text{and} \quad \underset{\text{(bent)}}{M{=}C{=}\ddot{N}{\setminus}H}$$

This should lead to a C–N–H angle intermediate between 180° and 114°. The methyl derivatives of $H_4Fe(CN)_6$, $Fe(CNCH_3)_6Cl_2$, and *trans*-$Fe(CNCH_3)_4(CN)_2$ are reported to have C–N–C angles of 173 and 167°, respectively.[19] The Fe–C distances in these compounds correspond to a bond order of 1.5.[19] Furthermore, for a linear Fe–C–N arrangement the intramolecular N–N distance should be about 4.25 Å., which is far too great for hydrogen bonding. Hence intramolecular hydrogen bonding would also require that the Fe–C–N angle be considerably less than 180°. In view of these facts it seems safe to assume that the hydrogen bonding is intermolecular.

The space group of $H_4Fe(CN)_6$ is reported[8] to be $P2_1/a$ (C_{2h}^5) with two molecules per unit cell. The iron atoms must therefore have site symmetry C_i. The great similarity of the spectra of $H_4Ru(CN)_6$ and $H_4Os(CN)_6$ to that of $H_4Fe(CN)_6$ indicates that the ruthenium and osmium atoms also have C_i site symmetry.

If the acids contain symmetrical N–H–N bonds, there should be six hydrogen atoms associated with each $Fe(CN)_6$ unit. Four of the hydrogen atoms will be shared with neighboring $Fe(CN)_6$ units through N–H–N bonds while the remaining two will be connected to neighboring units only *via* weak asymmetrical hydrogen bonds. Under the site symmetry C_i such a system must give rise to *three* infrared-active N–H stretching modes ($3\ A_u$). Of these, two should be in the 1500–1800 cm.$^{-1}$ range and might be assigned as the 1650 and 1590 cm.$^{-1}$ bands. The third band is expected in the region where we observe four strong bands attributable to N–H stretching. For the model with symmetrical N–H–N bonds to be acceptable we would therefore have to account for all four of these bands as somehow arising from one N–H stretching fundamental. It does not appear possible to do this in a reasonable manner: at least two of the bands in the 2300–3200 cm.$^{-1}$ region must be due to *different* N–H stretching fundamentals.

We conclude that the spectra indicate all of the hydrogen bonds to be of the asymmetrical N–H···N type. Since the site symmetry is C_i the four hydrogens must have the *trans* arrangement (in a later section this fact is deduced independently from the spectra). For linear C–N–H this geometry has D_{4h} symmetry. The site symmetry is reduced to C_i by the hydrogen

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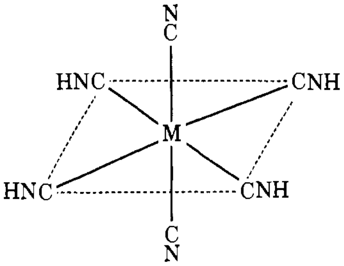
[17] R. G. Snyder and J. A. Ibers, *J. Chem. Phys.*, **36**, 1356 (1962).

[18] L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, pp. 336–338.

[19] H. M. Powell and G. W. R. Bartindale, *J. Chem. Soc.*, 799 (1945); R. Hulme and H. M. Powell, *ibid.*, 719 (1957).

bonding and possibly also by nonlinearity of the C–N–H. The expected number of infrared-active N–H stretching modes for this model is two (2 A_u), and each of these might be split into two bands by interaction between the two molecules in the unit cell (unit cell group splitting) to give a total of four bands as observed. Although unit cell group splitting might be appreciable in a hydrogen-bonded lattice, the separation between the observed bands (>200 cm.$^{-1}$) is probably much too large to be explained in this way, and it seems necessary to account for the two "extra" bands in another manner. This is discussed in the last section.



CN Stretching Frequencies.—Between 2000 and 2200 cm.$^{-1}$ two main bands are found in $H_4Fe(CN)_6$, at 2072 and 2096 cm.$^{-1}$. Under high resolution the 2096 cm.$^{-1}$ band exhibits a shoulder at ~2106 cm.$^{-1}$. For the ruthenium and osmium compounds the situation is slightly different in that the shoulder on the higher-energy main band appears on its low-energy side (Figure 4). The high-resolution spectra also show the presence of two weak absorptions, at 2125 and 2134 cm.$^{-1}$, and the probable presence of very weak shoulders at ~2060 and ~2040 cm.$^{-1}$.

Under C_i site symmetry three ν(CN) fundamentals are expected to be active in the infrared (3 A_u). The observed spectrum is in good agreement with this: the 2072, 2096, and ~2106 cm.$^{-1}$ bands must be the three fundamentals. The remaining weak and very weak absorptions are assigned as combination tones and as $\nu(^{13}CN)$.

In the deuterio acids ν(ND) should occur close to ν(CN). Since four CN groups per $D_4M(CN)_6$ are directly bound to deuterium, and since ν(CN) and ν(ND) belong to the same symmetry species, we may expect that the two ν(ND) fundamentals will interact strongly with two of the ν(CN) frequencies, while the third CN stretching frequency should be relatively unaffected. The spectra are consistent with this expectation. A band is observed at 2100 cm.$^{-1}$ which even under high resolution remains single, although it is asymmetric. This must be the ν(CN) fundamental due to stretching of the undeuterated cyanide groups. The bands at ~1720 and ~1610 cm.$^{-1}$ may then be identified as resulting from a very strong interaction between the remaining two ν(CN) frequencies and the two ND stretching vibrations. The strong absorptions at 2460 and 2280 cm.$^{-1}$ are the other two bands which result from this interaction. In Tables I and II it is assumed that the 2460 and 2280 cm.$^{-1}$ absorptions correspond to the ν(NH) at 3040 and 2570 cm.$^{-1}$, while the ~1720 and ~1610 cm.$^{-1}$ bands are taken to correspond to the ν(CN) at 2096 and 2072 cm.$^{-1}$, respectively. The nature of these corresponding vibrations is, however, quite different in the proton acids and the deuterio acids.

We have accounted for all of the bands in the 4000–1500 cm.$^{-1}$ region of the deuterio acids with the exception of the weak band at 2630 cm.$^{-1}$ and the rather narrow band at 1905 cm.$^{-1}$. The former is clearly the deuterio analog of the weak ~3200 cm.$^{-1}$ band, but the origin of the latter is not certain. We tentatively assume that it corresponds to the 2370 cm.$^{-1}$ band in the proton acid spectra. There appears to be no deuterio analog of the 2770 cm.$^{-1}$ proton acid absorption.

The CN stretching frequencies in the acids are greater than those in the corresponding potassium salts. Bonino and Fabbri[20] have made a careful study of $K_4Fe(CN)_6 \cdot 3H_2O$ and anhydrous $K_4(CN)_6$ in the CN stretching region. They found nine bands at nearly the same frequencies in both the trihydrate and the anhydrous compound. The spectrum of the anhydrous salt is well resolved, consisting of two very strong doublets and one strong doublet as well as one medium intensity and two weak bands. High-resolution spectra[21] of anhydrous $K_4Ru(CN)_6$ and $K_4Os(CN)_6$ in the CN stretching region are nearly identical with that of $K_4Fe(CN)_6$. Crystal structure determinations[22] have shown that $K_4Fe(CN)_6 \cdot 3H_2O$ exists in monoclinic and tetragonal forms while $K_4Ru(CN)_6 \cdot 3H_2O$ forms only monoclinic crystals isomorphous with the iron salt. For the monoclinic structure the space group is C2/c (C_{2h}^6) with four molecules in a unit cell. The metal atoms must therefore be at sites with C_i symmetry. Bonino[23] assigns the three strong doublets in $K_4Fe(CN)_6$ to the 3 A_u ν(CN) expected under C_i site symmetry, and he assumes that each band is doubled by the unit cell group splitting. If we accept this we may compare the average of each doublet frequency in the potassium salts with the corresponding ν(CN) in the acid, to get the increase in ν(CN) on protonation. The results are given in Table III.

TABLE III

CN STRETCHING FREQUENCIES IN $K_4Fe(CN)_6$, $K_4Ru(CN)_6$, AND $K_4Os(CN)_6$ AND THEIR SHIFTS ON PROTONATION

ν(CN), cm.$^{-1}$						$\nu(CN)_{acid} - \nu(CN)_{salts}$, cm.$^{-1}$		
$K_4Fe(CN)_6$		$K_4Ru(CN)_6$		$K_4Os(CN)_6$		$H_4Fe(CN)_6$	$H_4Ru(CN)_6$	$H_4Os(CN)_6$
2073 2062	2068	2085 2076	2080	2082 2069	2076	38	30	32
2050 2044	2047	2060 2055	2058	2053 2045	2049	49	46	48
2031 2026	2028	2042 2036	2039	2029 2022	2026	44	39	46

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(20) G. B. Bonino and G. Fabbri, *Atti accad. nazl. Lincei, Rend. Classe Sci. fis. mat. nat.*, **20**, 414 (1956).

(21) A. P. Ginsberg and K. Koubek, unpublished results.

(22) V. A. Pospelov and G. S. Ždanov, *Z. Fiz. Khim.*, **21**, 405, 521, 879 (1947).

(23) G. B. Bonino, *Atti accad. nazl. Lincei, Rend. Classe Sci. fis. mat. nat.*, **20**, 418 (1956).

There is considerable evidence indicating that ν(CN) always increases when an atom is attached to the nitrogen of a cyanide group already bound in a molecule *via* its carbon atom.[24,25] The possibility that this effect is due to a genuine increase in the CN force constant has been suggested, but it has been shown[25] that in many cases the observed increase in ν(CN) may be accounted for by mechanical interaction between the CN stretch and the stretching motion of the atom linked to the CN nitrogen (the latter occurs at *lower* frequencies than ν(CN)). In the $H_4M(CN)_6$ acids we have a somewhat different situation: ν(NH) is at higher energy than ν(CN) and so mechanical interaction with the NH stretch should *lower* ν(CN). However, mechanical interaction with the hydrogen-bond stretching frequency $\nu(N\cdots H)$ might raise ν(CN). We do not have a satisfactory explanation for these results.

NH Bending Frequencies.—In HNC the NH bending frequency has been observed[13] at 535 cm.$^{-1}$, and in HNCO it has been assigned[14] as 798 cm.$^{-1}$. Hydrogen bonding is known to shift AH bending modes to higher energy.[15] It may be expected that a hydrogen bond which is not collinear with the AH bond, and which has an appreciable component in the direction of the AH bending motion, would be especially effective in raising the AH bending frequency.

Under site symmetry C_i $H_4M(CN)_6$ should give rise to four infrared-active NH bending modes (4 A_u). Unit cell group splitting might split some or all of these into two closely spaced bands.

We have already discussed the 1650 and 1590 cm.$^{-1}$ bands. Since their assignment as symmetrical N–H–N stretching frequencies is not satisfactory, they must be a split NH bending fundamental or, more likely, a bending fundamental (1650 cm.$^{-1}$) and a combination tone. The second component of the 1650 cm.$^{-1}$ fundamental might be the 1620 cm.$^{-1}$ band, observed only in $H_4Fe(CN)_6$, for which we have no other assignment (*cf.* the last section).[26]

In addition to the 1590, 1620, and 1650 cm.$^{-1}$ bands there are between 650 and 1800 cm.$^{-1}$ eight other absorptions for which ν_H/ν_D is in the range 1.35 ± 0.03. Of these the rather indistinct shoulders at $\sim$1775 and $\sim$1475 cm.$^{-1}$ and the very weak band at 1380 cm.$^{-1}$ are undoubtedly combination tones. The pair of bands at 1290 and 1270 cm.$^{-1}$ (only the 1290 cm.$^{-1}$ component can be seen at room temperature) are the least intense of the remaining five bands. One possibility is to assign the 1290, 1270 cm.$^{-1}$ pair as an NH bending fundamental split by the unit cell group interaction. The third and fourth NH bending modes must then be the 887 cm.$^{-1}$ band and the doublet at 692, 668 cm.$^{-1}$. An alternative is to assign the 1290, 1270 cm.$^{-1}$ pair as combination tones. The bands at 887, 692, and 668 cm.$^{-1}$ are then the three remaining NH bending fundamentals.[27]

MC Stretching and MCN Bending Modes.—In the 300–650 cm.$^{-1}$ region $K_4Fe(CN)_6$ in aqueous solution exhibits strong bands at 583 and 416 cm.$^{-1}$.[28] According to Jones[28] these are, respectively, the F_{1u} δ(MCN) bending vibration and the F_{1u} ν(MC) stretching vibration. Jones[29] has also identified δ(MCN) as being at higher energy than ν(MC) in $K_3Co(CN)_6$, $K_3Rh(CN)_6$, and $K_3Ir(CN)_6$.

In the 300–650 cm.$^{-1}$ region of the $H_4Fe(CN)_6$ spectrum there are bands of appreciable intensity at 406, 419, 448, and 588 cm.$^{-1}$ with a shoulder at $\sim$600 cm.$^{-1}$.[30] These bands are either unshifted or shifted by very small amounts on deuteration.[31] Under C_i site symmetry three infrared-active MC stretching vibrations (3 A_u) and six infrared-active MCN bending vibrations (6 A_u) are expected. Under the unperturbed D_{4h} symmetry of $H_4M(CN)_6$ there should be two MC stretching ($A_{2u} + E_u$) and three MCN bending ($A_{2u} + 2\ E_u$) modes active in the infrared. The observed spectrum is in poor agreement with the prediction of nine fundamentals for the C_i site symmetry, but it is in good agreement with the prediction of five fundamentals for D_{4h} symmetry. Following Jones we may assign 406 and 419 cm.$^{-1}$ as the MC stretching frequencies and 448, 588, and $\sim$600 cm.$^{-1}$ as the MCN bending frequencies. Evidently the site symmetry perturbation, which is presumably due mainly to the hydrogen bonding, does not observably split the E_u MC stretching and MCN bending vibrations. The very weak shoulder at 463 cm.$^{-1}$ may be a B_{2u} MCN bending mode which is not infrared-active under D_{4h} but becomes active under the site group.

If the $H_4M(CN)_6$ acids have the *cis* arrangement of the protons their maximum unperturbed symmetry would be C_{2v}, for which six MC stretching and nine MCN bending vibrations should be active in the infrared. This is in complete disagreement with the spectrum and, coupled with the very good agreement for D_{4h} symmetry, indicates that the protons have the *trans* geometry. This conclusion is independent of our knowledge of the space group, from which the same result is reached.

The MC stretching vibrations in $H_4Fe(CN)_6$ are at practically the same frequencies as in the potassium salt. This suggests that protonation of the CN groups has little effect on the MC bonding.

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(24) H. J. Coerver and C. Curran, *J. Am. Chem. Soc.*, **80**, 3522 (1958); W. Gerrard, M. F. Lappert, H. Pyszora, and J. W. Wallis, *J. Chem. Soc.*, 2182 (1960); D. F. Shriver, *J. Am. Chem. Soc.*, **85**, 1405 (1963).

(25) D. A. Dows, A. Haim, and W. K. Wilmarth, *J. Inorg. Nucl. Chem.*, **21**, 33 (1961); J. H. Enemark and R. H. Holm, *Inorg. Chem.*, **3**, 1516 (1964).

(26) The possibility that the 1650 cm.$^{-1}$ band is due to alcohol or water in the sample is rejected because there is no indication in the spectra of an OH stretching band (except in KBr disk spectra where it is due to water in the KBr), and also because the 1650 cm.$^{-1}$ band is intense and the analytical results show the samples to be essentially solvent-free.

(27) Reference 7 reports only three bands in the 650–1800 cm.$^{-1}$ region. These are at *ca.* 1600, 880, and 680 cm.$^{-1}$. The 1600 and 880 cm.$^{-1}$ bands are reported to have ν_H/ν_D of about 1.45 and 1.38, respectively. Only the 1600 and 880 cm.$^{-1}$ bands were considered to be NH bending modes.

(28) L. H. Jones, *Inorg. Chem.*, **2**, 777 (1963).

(29) L. H. Jones, *J. Chem. Phys.*, **36**, 1209 (1962); **41**, 856 (1964).

(30) Reference 7 reports only the 448 and 588 cm.$^{-1}$ bands.

(31) The 459 cm.$^{-1}$ band of $H_4Ru(CN)_6$ shifts by 45 cm.$^{-1}$ while the 484 cm.$^{-1}$ band of $H_4Os(CN)_6$ shifts by 54 cm.$^{-1}$. These absorptions correspond to the 448 cm.$^{-1}$ band of $H_4Fe(CN)_6$, which shifts by only 7 cm.$^{-1}$. The reason for this difference is not apparent.

Nature of the Hydrogen Bonding in $H_4M(CN)_6$ Acids

We have seen that the solid acids consist of $H_4M(CN)_6$ units, with *trans* arrangement of the hydrogen atoms, which are linked together by asymmetrical N–H···N hydrogen bonds. *All* of the hydrogen atoms are involved in hydrogen bonding. This means that there must be four hydrogen-bond acceptors per $H_4M(CN)_6$ unit; two of these are obviously the lone pairs on the two unprotonated cyanide groups. Possibilities for the other two acceptors are: (1) the additional lone pairs on the unprotonated cyanide groups made available by resonance with the double-bonded canonical form, (2) the lone pairs on the protonated cyanide groups also made available by resonance with the double-bonded form, and (3) the π electrons in the C≡N bond.

It does not appear to be possible to decide upon a definite structure for the $H_4M(CN)_6$ acids on the basis of the information we have. Several plausible three-dimensional networks of $H_4M(CN)_6$ units linked together by hydrogen bonds may be imagined.

Assignment of Frequencies

While the hydrogen-bonding perturbation on the NH stretching and bending vibrations is very great, the effect on the CN stretching frequencies is small and on the MC stretching modes very small. In view of this the normal CN stretching, MC stretching, MCN bending, and CMC bending modes are probably best described by the representations of the molecular symmetry group (D_{4h}), while the selection rules which govern the infrared activity of these normal modes will be determined by the site group (C_i). Hence, for all but the NH stretching and bending modes, we will assign the activity of the site group representation to the representation of the molecular group with which it is correlated and then assign the observed frequencies to the appropriate representation of the molecular group. The NH stretching and bending frequencies, however, will be assigned to representations of the site group, bearing in mind the possibility that each of these frequencies may be split by interaction between the two molecules in a unit cell.

Table IV shows the correlation between the molecular symmetry group, the site group, and the unit cell group. Table V lists the representation, activity, and an approximate description for each normal mode of vibration of an $H_4M(CN)_6$ unit. Our assignments of the observed frequencies to the normal modes are given in the last column of Table I.

TABLE IV

CORRELATION TABLE FOR REPRESENTATIONS OF $H_4M(CN)_6$ IN THE SPACE GROUP C_{2h}^5

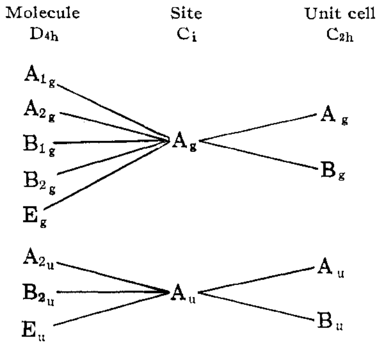

TABLE V

NORMAL MODES OF VIBRATION OF $H_4M(CN)_6$

Representation[a]	Approximate description[b]	Frequency and activity[c] D_{4h}	C_i
A_g	ν(NH)	...	ν_1 R
	ν(NH)	...	ν_2 R
	δ(NH)	...	ν_3 R
	δ(NH)	...	ν_4 R
	π(NH)	...	ν_5 R
	π(NH)	...	ν_6 R
A_{1g}	ν(CN)	ν_7 R	R
	ν'(CN)	ν_8 R	R
	ν(MC)	ν_9 R	R
	ν'(MC)	ν_{10} R	R
A_{2g}	δ(MCN)	ν_{11} In	R
B_{1g}	ν(CN)	ν_{12} R	R
	ν(MC)	ν_{13} R	R
B_{2g}	δ(MCN)	ν_{14} R	R
	δ(CMC)	ν_{15} R	R
E_u	ν(CN)	ν_{16} IR	IR
	ν(MC)	ν_{17} IR	IR
	δ(MCN)	ν_{18} IR	IR
	δ'(MCN)	ν_{19} IR	IR
	δ(CMC)	ν_{20} IR	IR
	δ'(CMC)	ν_{21} IR	IR
A_u	ν(NH)	...	ν_{22} IR
	ν(NH)	...	ν_{23} IR
	δ(NH)	...	ν_{24} IR
	δ(NH)	...	ν_{25} IR
	π(NH)	...	ν_{26} IR
	π(NH)	...	ν_{27} IR
A_{2u}	ν'(CN)	ν_{28} IR	IR
	ν'(MC)	ν_{29} IR	IR
	π(MCN)	ν_{30} IR	IR
	π(CMC)	ν_{31} IR	IR
B_{2u}	π(MCN)	ν_{32} In	IR
	π(CMC)	ν_{33} In	IR
E_g	π(MCN)	ν_{34} R	R
	δ'(MCN)	ν_{35} R	R
	δ'(CMC)	ν_{36} R	R

[a] Under C_i symmetry for NH modes; under D_{4h} symmetry for all other modes. [b] The symbols ν, ν', δ, δ', and π are, respectively, in-plane stretching, axial stretching, in-plane bending, axial bending, and out-of-plane bending. [c] R = Raman active, IR = infrared active, In = inactive.

Since under the site group only modes of u symmetry are allowed in the infrared, the first overtones and binary combinations of infrared-active fundamentals will not be infrared-active. However, binary combinations of infrared fundamentals with Raman fundamentals will be infrared-active; assignment of such bands enables the frequency of several Raman-active fundamentals to be predicted. The fact that the combination tone absorptions do not decrease in intensity on cooling to 80°K. demonstrates that they are not difference bands.

A_u Vibrations.—These comprise the infrared-active NH stretching and bending modes. For the stretching vibrations we have, as already discussed, the problem of accounting for two "extra" bands. In Table I we have labeled the 3040 and 2570 cm.$^{-1}$ bands as the fundamentals ν_{22} and ν_{23} and designated the "extra" bands as ν'_{22} and ν'_{23}. The "extra" bands are most readily explained as being combination tones of NH bending modes in Fermi resonance with ν_{22} and ν_{23}. Suitable binary combinations occur, and this is the interpretation we favor (the assignment of combination tones is discussed in the section on A_g vibrations). The absence of a deuterio analog of ν'_{22}, and the weakness of the deuterio analog of ν'_{23}, may be attributed to the combination tones going out of resonance with ν_{22} and ν_{23} on deuteration.

We have also considered the possibility that the ν(NH) fundamentals are doubled because of tunneling of the protons between two symmetric potential energy minima (it has been shown[32] that the observation of a doublet which can be ascribed to an *asymmetric* double minimum potential is very unlikely). This mechanism has been invoked[17,33] in a number of instances to account for splittings of hydrogen-bonded AH stretching modes of the order of magnitude which we observe (270 and 200 cm.$^{-1}$). In the present case the behavior of ν'_{22} and ν'_{23} on deuteration shows that they do not arise because of proton tunneling.

The assignment of the NH bending modes in Table I is as discussed earlier; the alternative in which the 1290, 1270 cm.$^{-1}$ pair is assigned as a fundamental was chosen because this allows the combination tones at 2630 and 1960 cm.$^{-1}$ to be assigned as binary sums. An assignment of the bending frequencies according to the second alternative, in which the 1290, 1270 cm.$^{-1}$ bands are considered to be combination tones, is also possible, but the combination bands at 2630 and 1960 cm.$^{-1}$ must then be expressed as ternary sums.

A_g Vibrations.—The thirteen weak absorptions above 4000 cm.$^{-1}$ are undoubtedly due to combinations of NH stretching, NH bending, and CN stretching fundamentals. Eleven of these bands agree reasonably well with binary sums of infrared frequencies. Of the remaining two bands one is found only in $H_4Fe(CN)_6$ (~5050 cm.$^{-1}$) and the other is exceedingly weak (4562 cm.$^{-1}$); several ternary sums of infrared frequencies fall near these bands. These facts suggest that there are no Raman-active NH stretching, NH bending, or CN stretching fundamentals with frequencies greatly different from the corresponding infrared-active fundamental, for if there were we would expect to see combination tones that did not correspond to a sum of infrared frequencies. This is a reasonable conclusion since in a $H_4M(CN)_6$ molecule the vibrations of the NH groups should be independent, as should also the stretching motions of the CN groups.[34] Hence corresponding u and g vibrations will have nearly the same energy. To be explicit, we assume that $\nu_1 \sim 3050$ cm.$^{-1}$, $\nu'_1 \sim 2780$ cm.$^{-1}$, $\nu_2 \sim 2580$ cm.$^{-1}$, $\nu'_2 \sim 2370$ cm.$^{-1}$, $\nu_3 \sim 1650$ cm.$^{-1}$, $\nu_4 \sim 1290$ cm.$^{-1}$, $\nu_5 \sim 890$ cm.$^{-1}$, and $\nu_6 \sim 680$ cm.$^{-1}$, and that on deuteration these bands shift by the same amounts as the corresponding infrared bands. ν'_1 and ν'_2 are the Raman analogs of ν'_{22} and ν'_{23}. With these assumptions the assignment of the combination tones above 4000 cm.$^{-1}$, and most of those below 4000 cm.$^{-1}$ (including ν'_{22} and ν'_{23}), are as given in Table I. We do not think it is justified to write down more exact predictions of the frequencies of the A_g vibrations than those just given.

E_u, A_{2u}, and B_{2u} Vibrations.—With our earlier discussion in mind it is clear that the 2100 cm.$^{-1}$ band in the deuterio acid spectra must be assigned as ν_{28}. It seems likely that deuteration will cause ν_{28} to shift slightly to lower energy because of decreased interaction with the hydrogen-bond stretching frequency $\nu(N\cdots H)$. We therefore assign the ~2106 cm.$^{-1}$ proton acid band as ν_{28}. The absorptions at 2096 and 2072 cm.$^{-1}$ must then be assigned as ν_{16} split by the site symmetry (ν_{16a} and ν_{16b}).

Again on the basis of the earlier discussion the bands at 419 and 406 cm.$^{-1}$ are attributed to ν_{17} and ν_{29}, but we cannot say which is which. This leaves the ~600, 588, 473, 463, and 448 cm.$^{-1}$ bands as possibilities for assignment to ν_{18}, ν_{19}, ν_{30}, and ν_{32}. If we consider the $Fe(CN)_6^{4-}$ ion in $H_4Fe(CN)_6$ as having O_h symmetry with a D_{4h} perturbation, the 588 and ~600 cm.$^{-1}$ absorptions would be assigned as the F_{1u} MCN bend split into its A_{2u} and E_u components, and the 448 cm.$^{-1}$ band would have to be the E_u components of the F_{2u} MCN bend. Hence the 588 and 600 cm.$^{-1}$ bands are ν_{29} and ν_{18} or ν_{19} while 448 cm.$^{-1}$ must be ν_{19} or ν_{18}. The very weak shoulder at 463 cm.$^{-1}$ is reasonably assigned as ν_{32}, the B_{2u} π(MCN) mode, which is not allowed under D_{4h} but becomes infrared-active under C_i and should therefore have only little intensity.

A_{1g} Vibrations.—For the purpose of assigning combination tones we have assumed that $\nu_7 \sim 2070$ cm.$^{-1}$, $\nu_8 \sim 2110$ cm.$^{-1}$, and $\nu_{12} \sim 2090$ cm.$^{-1}$.

Acknowledgment.—We thank Mr. C. R. Sprinkle for assistance with the experimental work.

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[32] R. L. Somorjai and D. F. Hornig, *J. Chem. Phys.*, **36**, 1980 (1962).

[33] R. Blinc and D. Hadzi, *Mol. Phys.*, **1**, 391 (1958); C. L. Bell and G. M. Barrow, *J. Chem. Phys.*, **31**, 1158 (1959).

[34] See, for example, L. H. Jones, *J. Mol. Spectry.*, **8**, 105 (1962). There is considerable MC, MC interaction.