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Perturbation of Intramolecular Vibrations by Strong Interionic Forces. Vibrational Spectra and Assignments for $Fe(CN)_6^{4-}$ and $Cs_2MgFe(CN)_6$

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Raman and infrared spectra have been observed for $Cs_2MgFe(CN)_6$ along with the Raman spectrum of $Fe(CN)_6^{4-}$ in aqueous solution. Vibrational assignments have been made for both species with the aid of Raman polarization data. The internal modes of the $Fe(CN)_6^{4-}$ moiety are observed to shift substantially in going from aqueous solution to the $Cs_2MgFe(CN)_6$ crystalline lattice. Surprisingly, the C–N and Fe–C stretching modes are all observed to increase by roughly 40 cm^{-1}. A_{1g} and E_g symmetry force constants have been estimated for $Fe(CN)_6^{4-}$ using ^{13}C and ^{15}N isotopic data. The above, in conjunction with a preliminary normal-mode calculation on $Cs_2MgFe(CN)_6$ including interionic potentials, show that the shifts observed in going from aqueous solution to $Cs_2MgFe(CN)_6$ can be reproduced without changing the intramolecular potential constants of the $Fe(CN)_6^{4-}$ ion, except for an increase in the valence C–N stretch force constant. The Mg–N interaction was found to be about twice as strong as the Li–N interaction in $Cs_2LiFe(CN)_6$ and $Cs_2LiCo(CN)_6$.

Introduction

Intermolecular forces in solids vary over a large dynamic range which extends from weak van der Waals forces in molecular crystals to the strong interactions present in polymeric species or ionic salts. Those workers who probe intramolecular forces in solids must be concerned with how the intermolecular forces perturb observations which are primarily attributed to internal bonding. Molecular vibrations in crystalline lattices provide a sensitive probe of intermolecular interactions and their perturbation of intramolecular forces. Studies of molecular crystals show little or no perturbation of the internal forces for a molecule in going from an isolated environment to a crystalline lattice.[1,2] Indeed, the internal modes of vibration show little change in going to the solid.

Perturbations of internal forces and modes of vibration are normally much greater for ionic salts. Vibrational shifts for $M(CN)_6^{3-}$ (M = Cr, Mn, Fe, Co, Ir) molecular vibrations in going from aqueous solution to the $Cs_2LiM(CN)_6$ crystalline lattice are substantial.[3] Siebert et al. have observed even greater shifts for the internal modes of $Pd(CN)_6^{2-}$ in going from aqueous solutions to the $MPd(CN)_6$ salts (M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, and Zn^{2+}).[4,5] For the $Cs_2LiM(CN)_6$ salts the C–M–C deformation modes are observed to increase as much as 80 cm^{-1}. Surprisingly, A_{1g} and E_g symmetry M–C and C–N stretching modes were shifted 10–20 cm^{-1}, even though there are no lattice modes of either A_{1g} or E_g symmetry. At first glance the observed shifts for high-frequency modes, such as C–N stretch, are inexplicable since they cannot result simply from mixing of internal and lattice modes. However, in a subsequent normal-mode calculation[6] the observed shifts were reproduced by including interionic potential constants. The normal-coordinate treatment based on a crystalline lattice model showed that the intramolecular potential function did not change in going from aqueous solution to the $Cs_2LiCo(CN)_6$ solid, except that the valence CN stretching force constant increased slightly.[6–8]

The recent studies of the $Cs_2LiM(CN)_6$ salts have shown the importance of including intermolecular interactions in modeling molecular vibrations in crystalline lattices.[6–8] The $Cs_2LiM(CN)_6$ salts are convenient for studying interionic interactions since their high crystallographic symmetry, *Fm*3*m*,[9,10] simplifies the observed vibrational spectra and allows one to make definitive assignments using single-crystal polarization data. Furthermore, the high symmetry reduces the number of interionic potentials needed in a general quadratic potential function. There is a need, however, to extend this study to systems which exhibit extremely strong interionic forces such as Prussian Blues.[11] Certainly, if we are ever to study bonding in Prussian Blue complexes using vibrational data, we need to know much more about strong interionic forces and how best to model them.

The highly insoluble $Cs_2MgFe(CN)_6$ is a useful model compound. As the salt is isostructural with the O_h^5 symmetry $Cs_2LiM(CN)_6$ complexes,[12] it will be possible to probe directly the difference in M'–N interaction when M' is changed from a univalent ion to a divalent ion. The dicesium magnesium complex should also provide an interesting comparison with Prussian Blue complexes as the structures are quite similar.[13] The primary difference between Prussian Blues and $Cs_2MgFe(CN)_6$ is that the M^{II}–N interaction in the former involves a transition metal while in the latter M^{II} is an alkaline earth. The nature of the unusual bonding in Prussian Blues and their ability to act as semipermeable membranes may be intimately tied to the M'–N interaction.

A detailed study of $Cs_2MgFe(CN)_6$ will also provide a probe of the bonding differences between tri- and divalent transition metal cyanides. X-Ray crystallographic studies of $Cs_2LiFe(CN)_6$[9] and $Cs_2MgFe(CN)_6$[12] have provided evidence for a large increase in $d\pi$–$p\pi^*$ bonding in going from Fe^{3+} to Fe^{2+}. Vibrational spectroscopy provides a useful comparative probe of bonding in these systems.

The present study is concerned with vibrational spectra and assignments for $Fe(CN)_6^{4-}$ in aqueous solution and the $Cs_2MgFe(CN)_6$ crystalline salt. Comparison of the $Fe(CN)_6^{4-}$ moieties' molecular vibrations in aqueous solutions and $Cs_2MgFe(CN)_6$ will provide evidence for the perturbations

Table I. Observed Fundamentals (cm^{-1}) and Assignments

$Fe(CN)_6{}^{3-}$ [a]	$Fe(CN)_6{}^{4-}$ [b]	$Cs_2LiFe(CN)_6$ [a]	$Cs_2MgFe(CN)_6$	Assignments
2132.3 ± 0.2	2093.6 ± 0.2	2142.1 ± 0.3	2129.6 ± 0.3	ν_1 (A_{1g}, CN)
388.0 ± 1.0	393.3 ± 3.0	411.9 ± 0.5		ν_2 (A_{1g}, FeC)
2124.7 ± 0.2	2058.0 ± 0.2	2137.1 ± 0.3	2090.6 ± 0.3	ν_3 (E_g, CN)
383.0 ± 2.0	410.0 ± 2.0	392.0 ± 10		ν_4 (E_g, FeC)
	508.7 ± 1.0	400.0 ± 10	512.2 ± 0.6	ν_{10} (F_{2g}, FeCN)
101.5 ± 1.0	93.0 ± 5.0	178.8 ± 1.0	230.7 ± 0.6	ν_{11} (F_{2g}, CFeC)
		40.4 ± 0.2	43.0 ± 0.3	ν_{17} (F_{2g}, CsN)
		2128.0 ± 0.2	2092.4 ± 1.0	ν_6 (F_{1u}, CN)
		522.0 ± 1.0	590.6 ± 1.0	ν_7 (F_{1u}, FeCN)
		405.0 ± 2.0	474.0 ± 5.0	ν_8 (F_{1u}, FeC)
		171.7 ± 1.0	224.5 ± 3.0	ν_9 (F_{1u}, CFeC)
		305.0 ± 3.0	298.6 ± 2.0	ν_{15} (F_{1u}, MN[c])
		58.0 ± 2.0	63.4 ± 2.0	ν_{16} (F_{1u}, CsN)

[a] Taken from ref 8. [b] Frequencies are from this work. [c] M = Li for $Cs_2LiFe(CN)_6$ and M = Mg for $Cs_2MgFe(CN)_6$.

of internal modes resulting from the strong Mg–N bond. A preliminary normal mode calculation will be used to discuss bonding changes in going from water solutions to the $Cs_2MgFe(CN)_6$ crystalline lattice.

Experimental Section

Single crystals of $Cs_2MgFe(CN)_6$ were grown by diffusion of Mg^{2+} and $Fe(CN)_6{}^{4-}$ ions through a CsCl-doped gel of sodium metasilicate. The detailed procedure has recently been reported.[12] KCN isotopically enriched with ^{13}C and ^{15}N was used to prepare the corresponding isotopes of $K_4Fe(CN)_6$ by treating iron(II) sulfate with excess cyanide.[14] Crystalline sodium metasilicate, $K_4Fe(CN)_6$, and $MgCl_2$ were obtained from Baker while CsCl was obtained from Matheson Coleman and Bell.

Raman spectra were observed using a Cary Model 82 and the 5682- and 6407-Å lines of a Kr^+ ion laser, Spectra Physics 165. Cary's standard multipass cell was employed in gathering spectra of the $Fe(CN)_6{}^{4-}$ ion in aqueous solution. $Li_4Fe(CN)_6$ was used to observe the F_{2g} C–Fe–C deformation of the ferrocyanide ion. $Li_4Fe(CN)_6$ was prepared from the potassium salt by ion exchange (hydrogen-form resin, Bio-Rad, AG50W-X16 with H replaced by Li). The Raman spectra for $Cs_2MgFe(CN)_6$ were observed using a polycrystalline sample since crystals large enough for a single crystal experiment could not be obtained. The infrared spectra were observed using the Beckman IR9 and IR11. Mineral oil mulls were used for the infrared spectra and standard gases were used to calibrate both infrared instruments.[15,16]

Assignments

The Raman modes for the ferrocyanide ion have been reported.[17] However, the E_g Fe–C stretch mode was not observed in solution and the assignment for this mode was made using solid-state data. This band was reported to be at 376 cm^{-1}. We have observed two bands in solution in the Fe–C stretch region (see Figure 1). The depolarized band at 410.0 cm^{-1} shifts to 404.5 cm^{-1} upon ^{15}N isotopic substitution. Because of the consistency of this shift with shifts for M–C stretch modes in other metal hexacyanides, and the rapid convergence of the E_g symmetry block, we assign the band at 410 cm^{-1} to be ν_4. The observed Raman modes and their assignments for $Fe(CN)_6{}^{4-}$(aq) are compared with those for the ferricyanide ion in Table I.

The selection rules for the $Fe(CN)_6{}^{4-}$ internal vibrations in the $Cs_2MgFe(CN)_6$ lattice are the same as those of the isolated $Fe(CN)_6{}^{4-}$ ion since the ferrocyanide group occupies a site of O_h symmetry. In addition to the internal $Fe(CN)_6{}^{4-}$ modes we expect one inactive librational mode (ν_{14}, F_{1g}) and three translational modes (ν_{15} and ν_{16}, F_{1u} infrared active, and ν_{17}, F_{2g} Raman active). An approximate description of the expected normal modes and their selection rules are given in ref 3.

As we were unable to obtain crystals of suitable size for single-crystal Raman polarization studies, the Raman-active modes for $Cs_2MgFe(CN)_6$ have been assigned by comparison with $Fe(CN)_6{}^{4-}$ and the $Cs_2LiM(CN)_6$ salts.[3] The Raman spectrum for $Cs_2MgFe(CN)_6$ is shown in Figures 1 and 2.

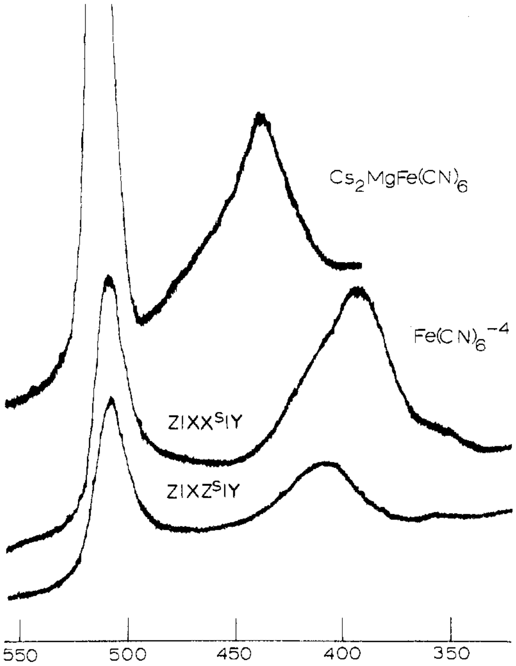

Figure 1. Raman spectra of solid $Cs_2MgFe(CN)_6$ and aqueous $Fe(CN)_6{}^{4-}$ ion in the metal–carbon stretch region. The relative intensity of the weak band at 354 cm^{-1} decreased on recrystallization. We attribute this band to an impurity present in commercial $K_4Fe(CN)_6$.

The observed bands and their assignments are given in Table I.

The two-high energy bands observed at 2129.6 and 2090.6 cm^{-1} in the Raman effect are assigned to ν_1 and ν_3, respectively. This assignment maintains the relative frequency positions of ν_1 and ν_3 observed for the ferrocyanide ion in aqueous solution (see above). For the trivalent hexacyanides, where definitive assignments could be made using single-crystal polarization data, the relative orders of ν_1 and ν_3 did not change in going from aqueous solutions to the $Cs_2LiM(CN)_6$ crystalline lattices.[3]

Only two bands are observed in the Fe–C–N deformation and Fe–C stretch regions rather than the expected three. The strong band at 512.2 cm^{-1} can be assigned to the Fe–C–N deformation mode since this mode was observed at 508.7 cm^{-1} for the ferrocyanide ion in aqueous solution. By analogy with the trivalent hexacyanides we do not expect this mode to shift in going from aqueous solution to the $Cs_2MgFe(CN)_6$ lattice. The rather broad band observed at 437 cm^{-1} can be attributed to unresolved components of ν_2 and ν_4. A similar broad feature is observed for ν_2 and ν_4 for the $Fe(CN)_6{}^{4-}$ ion in aqueous solution and the two bands can only be resolved using polarization data (see Figure 1). This gives the expected increase

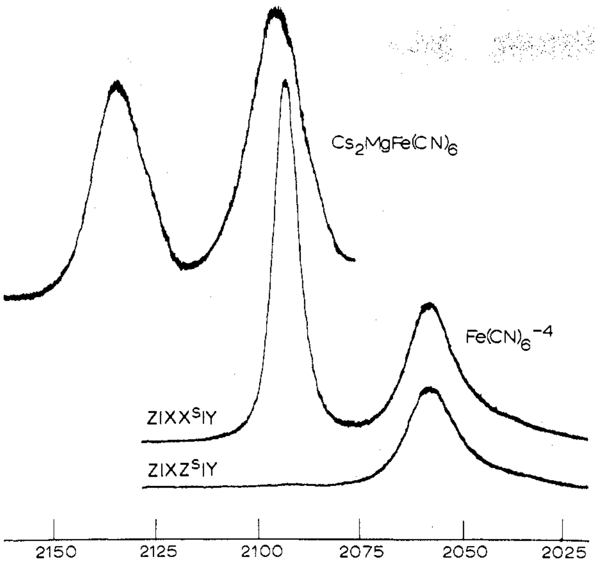

Figure 2. Raman spectra of solid $Cs_2MgFe(CN)_6$ and aqueous $Fe(CN)_6^{4-}$ ion in the cyanide stretch region.

of ν_2 and ν_4 in going from aqueous solution to the $Cs_2MgFe(CN)_6$ salt.

The two remaining bands at 230.7 and 43.0 cm^{-1} can be assigned to ν_{11} (δ(C–M–C)) and ν_{17} (Cs lattice mode), respectively. This agrees well with the previous assignments for the $Cs_2LiM(CN)_6$ salts.

Six infrared bands have been observed for the $Cs_2MgFe(CN)_6$ salt. The three highest frequency bands at 2082.4, 590.6, and 474.0 cm^{-1} can be assigned to ν_6 (C–N stretch), ν_7 (δ(Fe–C–N)), and ν_8 (Fe–C stretch) by comparison to the trivalent salts.[3] The two lattice modes and the C–Fe–C deformation are expected at lower energy. The band at 63.4 cm^{-1} is too low for the C–Fe–C deformation and can therefore be assigned to a lattice mode involving primarily Cs atom motion. For the $Cs_2LiM(CN)_6$ salts this mode was observed at ca. 55 cm^{-1}. The band at 224.5 cm^{-1} can be assigned to F_{1u} C–Fe–C deformation in agreement with the observed position for the F_{2g} C–Fe–C deformation. The remaining band at ca. 298.6 cm^{-1} can be assigned to the lattice mode involving Mg atom movement, ν_{15}. The relative intensitites of ν_9 and ν_{15} for the $Cs_2MgFe(CN)_6$ salt agree well with those observed for the $Cs_2LiM(CN)_6$ salts.

Discussion

Comparison of observed Raman modes of $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ (Table I) shows several significant differences. The CN stretching modes are found ca. 60 cm^{-1} lower for the ferrocyanide than for the ferrihexacyanide. On the other hand, the M–C stretching modes do not shift appreciably. The latter fact is consistent with structural data for $Cs_2LiFe(CN)_6$[9] and $Cs_2MgFe(CN)_6$[12] where the Fe–C bond length for the ferrocyanide was observed to be slightly shorter than that of the ferricyanide. Thus, the Fe–C bond strength does not appear to change appreciably in going from Fe^{III} to Fe^{II}, indicating that any decrease in Fe–C bond order resulting from a decrease in σ overlap is offset by an increase in the $d\pi$–$p\pi^*$ overlap.

This apparent increase in $d\pi$–$p\pi^*$ overlap in going from Fe^{III} to Fe^{II} indicated by the Fe–C bond lengths is also manifest in the significant decrease in C–N stretching modes. That is, added electron density in the CN π^* level reduces the CN bond order.

The spectrum of $Fe(CN)_6^{4-}$ differs from those of the trivalent hexacyanides in two respects. There is a suprising change in the relative frequencies of the A_{1g} and E_g modes. For the trivalent hexacyanides the A_{1g} M–C stretch is always found at higher frequency than the E_g mode while for $Fe(CN)_6^{4-}$ $\nu_4 > \nu_2$.[18] The F_{2g} MCN deformation was also observed to be much more intense than those for any of the trivalent hexacyanides.

Table II. Expressions for the A_{1g} and E_g Symmetry Force Constants in $Cs_2MgFe(CN)_6$[a]

$$F_{11}, F_{33} = F^{\nu}{}_{CN,CN}{}^{b} + F^{\nu}{}_{MgN,MgN} - 2F^{\nu}{}_{CN,MgN}$$

$$F_{22}, F_{44} = F^{\nu}{}_{FeC,FeC} + F^{\nu}{}_{MgN,MgN} - 2F^{\nu}{}_{FeC,MgN}$$

$$F_{12}, F_{34} = F^{\nu}{}_{FeC,CN} + F^{\nu}{}_{MgN,MgN} - F^{\nu}{}_{CN,MgN} - F^{\nu}{}_{FeC,MgN}$$

[a] The terms involving the redundant CsN coordinate $S^{A_{1g}}{}_{R_2}$ and $S^{E_g}{}_{R_2}$ have been neglected. [b] $\nu = A_{1g}$ for F_{11}, F_{22}, and F_{12}, $\nu = E_g$ for F_{33}, F_{44}, and F_{34}. $F^{A_{1g}}{}_{ij} = F_{ij} + 4F^{cis}{}_{ij} + F^{trans}{}_{ij}$. $F^{E_g}{}_{ij} = F_{ij} - 2F^{cis}{}_{ij} + F^{trans}{}_{ij}$.

The observed shifts for the $Fe(CN)_6^{4-}$ modes in going from aqueous solution to the $Cs_2MgFe(CN)_6$ lattice are much greater than those observed for the trivalent salts (Table I). The shifts observed for the M–C and C–N A_{1g} and E_g stretch modes for all of the trivalent salts were in the range 10–20 cm^{-1} with the M–C modes generally exhibiting larger perturbations. All of the Fe–C and C–N A_{1g} and E_g modes in the case of ferrocyanide shift up ca. 40 cm^{-1}. These large shifts occur in spite of the fact that there are no external modes of A_{1g} or E_g symmetry. This simply indicates that the large perturbations are not a result of mixing of internal and external modes. It is also somewhat suprising that the high-energy CN stretching modes should be so strongly perturbed, since we normally observe little interaction between energy-factored vibrations.[19]

The M–C stretch shifts observed for $Co(CN)_6^{3-}$ in going from aqueous solution to $Cs_2LiCo(CN)_6$ could be reproduced by including a Li–N interaction of ca. 0.25 mdyn/Å in the A_{1g} and E_g force constant expressions. The force constant for the A_{1g} and E_g redundant coordinates involving Li–N stretch enters into the A_{1g} and E_g symmetry force constants for Co–C and C–N stretch linearly (Table II). Essentially, this means that stretching either M–C or C–N bonds in $Cs_2LiM(CN)_6$ lattices results in the compression of the Li–N coordinates. Thus, more force is required to stretch M–C and C–N bonds in the $Cs_2LiM(CN)_6$ salts than for "isolated" $M(CN)_6^{3-}$ ions in aqueous solution.

In order to reproduce the observed shifts in C–N stretch modes it was necessary to allow the valence C–N stretch force constant to increase ca. 0.1 mdyn/Å. The increase in f_{CN} is reasonable since the Li–N interaction withdraws electron density from the lone pair on the N end of the CN^- moiety which is slightly antibonding. The above explanation of the $Co(CN)_6^{3-}$ frequency shifts[6] was later substantiated by a complete treatment of $Fe(CN)_6^{3-}$ and $Cs_2LiFe(CN)_6$ where isotopic data were used to refine a more general quadratic potential function.[8] Thus it seemed possible that the more significant Fe–C and C–N shifts observed for $Fe(CN)_6^{4-}$ could be reproduced in the same manner. The treatment of the A_{1g} and E_g symmetry blocks is discussed below.

For the trivalent salts large solid-state shifts were also observed for the C–M–C deformation modes (ca. 50–80 cm^{-1}). The frequency shifts in going from $Fe(CN)_6^{4-}$(aq) to $Cs_2MgFe(CN)_6$ appear to be even larger as both F_{1u} and F_{2g} C–Fe–C deformations are observed at abnormally high energy, ca. 224.5 and 230.7 cm^{-1}, respectively. In the case of the trivalent salts the increase in ν_9 and ν_{11} results in part from the additional Cs–N coordinates in the $Cs_2LiM(CN)_6$ crystalline lattice; the Cs–N coordinates compress as the CMC angles are deformed. That is, more force is required to deform the C–M–C angles in $Cs_2LiM(CN)_6$ than is required for the $M(CN)_6^{3-}$ ion in aqueous solution. Thus the large C–M–C shifts could be reproduced without changing the intramolecular potential constants.[6-8]

One possible explanation for the larger apparent shifts for $Fe(CN)_6^{4-}$ is that the Cs–N interactions are larger in

Table III. Raman Frequencies and A_{1g} and E_g Symmetry Force Constants for Aqueous $Fe(^kC^lN)_6{}^{4-}$ [a]

	k, *l*		
	12, 14	13, 14	12, 15
ν_1	2093.6 (0.0)[b]	2047.9 (0.2)	2063.1 (0.2)
ν_2	393.3 (0.1)		385.4 (−0.1)
ν_3	2058.0 (0.4)	2011.8 (−0.2)	2027.7 (−0.2)
ν_4	410.0 (−0.9)		404.5 (1.1)

A_{1g}	F_{11}	16.55 (5)[c]	E_g	F_{33}	15.86 (12)
	F_{22}	2.40 (3)		F_{44}	2.65 (8)
	F_{13}	0.53 (5)		F_{34}	0.49 (11)

[a] Frequencies are in cm^{-1} and the force constants are in mdyn $Å^{-1}$. [b] The values in parentheses are $\nu_{obsd} - \nu_{calcd}$. [c] Numbers in parentheses are least-squares standard deviations in units of the last digit.

$Cs_2MgFe(CN)_6$ than in $Cs_2LiM(CN)_6$. This suggestion is reasonable since the Cs hole size in $Cs_2MgFe(CN)_6$ is slightly smaller than that observed for the $Cs_2LiM(CN)_6$ salts.[9,10,12] The slightly higher observed frequencies for the Cs lattice modes in $Cs_2MgFe(CN)_6$ also indicate that the Cs atoms are more tightly bound.

Finally, the observed frequency for the Mg lattice mode (ν_{15} = 298.6 cm^{-1}) is about the same as that found for the Li mode in $Cs_2LiCo(CN)_6$ and $Cs_2LiFe(CN)_6$. In these two trivalent complexes the Li lattice mode was found to be relatively pure; the mode at ca. 305.0 cm^{-1} was found to be made up almost entirely of Li–N stretch. The above indicates that the Mg–N interaction is substantially greater than the Li–N interaction found for the trivalent salts. Certainly, this was no surprise as we expect the M'–N interaction to increase significantly as the formal charge on M' is increased. The exact value of the Mg–N force constant must await a more detailed study where isotopic data can be used to help to define a general quadratic potential function. However, the Mg–N interaction can be conveniently estimated by a careful treatment of the A_{1g} and E_g symmetry blocks where $F^{A_{1g}}_{MgN,MgN}$ and $F^{E_g}_{MgN,MgN}$ enter into the force constant expressions for FeC and CN stretch (Table II).

A_{1g} and E_g Symmetry Force Constants

In order to estimate the Mg–N interaction using the A_{1g} and E_g M–C and C–N stretching modes in $Cs_2MgFe(CN)_6$, we must first evaluate the A_{1g} and E_g symmetry force constants for $Fe(CN)_6{}^{4-}$ in aqueous solutions. The A_{1g} and E_g blocks are two-dimensional and have only three unique symmetry force constants each. By using ^{13}C and ^{15}N isotopic data both blocks are overdetermined. Schachtschneider's[20] force constant perturbation program was used and the individual observed frequencies were weighted as $\nu_i{}^{-2}\sigma(\nu_i)^{-2}$ where $\sigma(\nu_i)$ is the estimated error for observed frequency ν_i. As we are interested only in the change in the intramolecular potentials in going from $Fe(CN)_6{}^{4-}$(aq) to the $Cs_2MgFe(CN)_6$ lattice, no corrections have been made for anharmonicity. Harmonic force constants will be reported later. Both A_{1g} and E_g blocks converge readily and the final force constants and errors between observed and calculated frequencies are presented in Table III. Symmetry coordinates and expressions for the symmetry force constants for $Cs_2MgFe(CN)_6$ are the same as those reported earlier for $Cs_2LiM(CN)_6$.[6,8] In order to reproduce the observed $Fe(CN)_6{}^{4-}(aq) \rightarrow Cs_2MgFe(CN)_6$ frequency shifts the following assumptions were used. (a) The intramolecular A_{1g} and E_g symmetry force constants were augmented by $F^{A_{1g}}_{MgN,MgN}$ and $F^{E_g}_{MgN,MgN}$. (b) The symmetry force constants $F^{A_{1g}}_{MgN,MgN}$ and $F^{E_g}_{MgN,MgN}$ were assumed to be the same as was found for the ferricyanide system.[8] (As can be seen by the force constant expressions, $F^{A_{1g}}_{MgN,MgN}$ and $F^{E_g}_{MgN,MgN}$ differ by $6F^{cis}_{MgN,MgN}$. Since we expect the cis interaction to be negligible, then $F^{A_{1g}}_{MgN,MgN} \simeq F^{E_g}_{MgN,MgN}$.) (c) The valence C–N stretch constant is allowed to change by refining F_{11} and F_{33} to fit the observed C–N stretching modes.

Using the above model it has been possible to reproduce the observed frequency shifts to less than 1 cm^{-1}. We found $F^{A_{1g}}_{MgN,MgN} = F^{E_g}_{MgN,MgN} = 0.55$ mdyn/Å and $\Delta F^{A_{1g}}_{CN,CN} = 0.54$ while $\Delta F^{E_g}_{CN,CN} = 0.46$ mdyn/Å. Here $\Delta F^{\nu}_{CN,CN}$ ($\nu = A_{1g}$ or E_g) refers to the additional change in F_{11} and F_{33} required to fit the observed frequency shift after correction for $F^{\nu}_{MgN,MgN}$.

The value of 0.55 mdyn/Å for $F^{\nu}_{MgN,MgN}$ is more than twice than that found for $F^{\nu}_{LiN,LiN}$ for the $Cs_2LiCo(CN)_6$ and $Cs_2LiFe(CN)_6$ salts. This indicates that the valence Mg–N interaction is roughly twice that found for the Li–N interaction. This increase is consistent with the formal charge difference. As is the case for the $Cs_2LiM(CN)_6$ salts and the Prussian Blues, the strong Mg–N interaction dominates crystal packing and is probably the primary cause for the high insolubility of $Cs_2MgFe(CN)_6$.

The necessary increase in f_{CN} required to reproduce the frequency shifts (0.54 and 0.46 for A_{1g} and E_g, respectively) is suprisingly large. The approximate change in f_{CN} required for the trivalent salts, ca. 0.12 mdyn/Å for both A_{1g} and E_g, is much less. The origin of the large increase in f_{CN} is again presumably due to electron withdrawal from the antibonding σ^* MO on the CN^- moiety by the Mg^{2+} ion. While we expect this increase to be greater for the magnesium salt since $F^{\nu}_{MgN,MgN} > F^{\nu}_{LiN,LiN}$, it is not clear why f_{CN} increases nearly four times as much for $Cs_2MgFe(CN)_6$ compared with $Cs_2LiM(CN)_6$.

The rather substantial shifts observed for the internal modes of the ferrocyanide ion in going from aqueous solution to the $Cs_2MgFe(CN)_6$ lattice provide a striking example of how internal modes of vibration may be perturbed by strong interionic forces in a crystalline lattice. Certainly, one must be cautious in using solid-state vibrational data to discuss internal forces in a complex ion. Fortunately, it is often possible to treat the molecular vibrational problem by using a crystalline lattice model where interionic potentials are included. In the present case, the large shifts observed for the A_{1g} and E_g symmetry $Fe(CN)_6{}^{4-}$ vibrations could be reproduced by inclusion of a Mg–N interaction (ca. 0.55 mdyn/Å) and an increase in the valence C–N stretch constant. The present work and earlier studies of $Cs_2LiCo(CN)_6$[6] and $Cs_2LiFe(CN)_6$[8] show that detailed vibrational analysis including interionic potentials is feasible for high-symmetry systems. In the following article, this effect is extended to the pseudo Prussian Blue $Mn_3[Co(CN)_6]_2 \cdot xH_2O$ where interionic potentials approach the magnitude of the interionic forces in the complex ion.

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Registry No. $Cs_2MgFe(CN)_6$, 19496-94-7; $Fe(CN)_6{}^{4-}$, 13408-63-4; $Fe(^{13}CN)_6{}^{4-}$, 57325-46-9; $Fe(C^{15}N)_6{}^{4-}$, 57345-98-9.

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Aspects of the Structure and Bonding in Prussian Blues. A Single-Crystal Raman Study of $Mn_3[Co(CN)_6]_2 \cdot xH_2O$ and $Cd_3[Co(CN)_6]_2 \cdot xH_2O$

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Single-crystal polarized Raman spectra have been obtained for the Prussian Blue analogs $Mn_3[Co(CN)_6]_2 \cdot xH_2O$ and $Cd_3[Co(CN)_6]_2 \cdot xH_2O$ and their Raman-active fundamentals have been assigned. Raman spectra have also been obtained for both salts following dehydration and after substitution of ammonia for water. Large shifts are observed for the $Co(CN)_6{}^{3-}$ modes in going from aqueous solution to the Prussian Blue lattices; the Co–C stretching modes increase by 65–75 cm^{-1}. The observed shifts for the Co–C and C–N stretching modes can be reproduced by inclusion of M–N (M = Mn or Cd) interactions without changing the intramolecular potentials except for an increase in the valence C–N stretching constant. The high value estimated for the Mn–N force constant and the calculated change in f_{CN} provide evidence for an unusually strong Mn–N interaction and for a $d\pi-p\pi^*$ overlap between the manganese and the nitrogen end of the cyanide. Results obtained for the dehydrated samples show that the M–N bond strength increases as water is removed. Also, both salts undergo a phase change to a low-symmetry space group as water is removed. Raman data show that substitution of ammonia for water in the cadmium salts destroys the strong Prussian Blue lattice generating a double salt of the type $[Cd(NH_3)_n][Co(CN)_6]_2 \cdot yNH_3$.

Introduction

There has been considerable interest over the years in the series of transition metal cyanides, referred to as Prussian Blues. These salts are highly insoluble, indicating the presence of unusually strong interionic forces. More importantly, these cyano complexes, notably cupric ferrocyanide, act as semipermeable membranes.

While a great deal of work has been done on these simple cyanides, their structures have remained a mystery until very recently. Early structural work was based on powder samples as single crystals could not be obtained. Ludi's recent success in obtaining single crystals of manganous cobalticyanide,[1] $Mn_3[Co(CN)_6]_2 \cdot xH_2O$, and other Prussian Blue analogues[2] has provided a consistent structural model for these cyano complexes. Ludi's structural work, and the availability of single crystals, now make it possible to carry out detailed vibrational spectroscopic studies which were not possible with powder samples.

The molecular vibrations of Prussian Blues are interesting from two standpoints. First, the structural simplicity of the Prussian Blues makes them ideal model systems for studying molecular transport through membranes. Similar studies on noncrystalline membranes are difficult since the local guest molecule environment is either unknown or variable. With a crystalline membrane it should be possible to probe directly the interactions between the membrane lattice and the guest molecule using vibrational spectroscopy. Perturbations of the host membrane molecular vibrations as water is removed and replaced by other small molecules provide direct information concerning the membrane bonding as a function of the guest molecule. Similarly, shifts in the guest molecule's molecular vibrations in going from an isolated envionment to the membrane lattice will tell us something of the bonding changes in the guest molecule.

Prussian Blues are intriguing model systems for studying membranes for several reasons. There are only three discrete types of sites for the guest molecule, and each has high symmetry.[1,2] Thus, the guest–host interactions are few and relatively simple. The high space group symmetry of the Prussian Blues, *Fm*3*m*, and the high site symmetry of the hexacyanide moieties, O_h, simplifies both vibrational assignments and the interionic interactions. Also, the abundance of information on related cyano complexes provides adequate basis for comparative studies. The principal ingredient of the Prussian Blues, the transition metal hexacyanide, has been probed by vibrational spectroscopy,[3,4] electronic spectra,[5] and MO calculations.[5,6] The cubic $Cs_2LiM(CN)_6$ salts, which are structurally similar to the Prussian Blues, have been studied in detail using vibrational spectroscopy[7,8] and x-ray crystallography.[9,10] The effort spent on the dicesium lithium salts and the recent emergence of related cyanides[11,12] should simplify our present effort.

The bonding in Prussian Blues is also interesting from the standpoint of their unusually strong interionic potentials. In ionic species, external forces often perturb the internal modes of vibration in a dramatic way. The frequency shifts observed for $M(CN)_6{}^{3-}$ internal modes in going from aqueous solution to the $Cs_2LiM(CN)_6$ lattices are substantial.[7,8] Surprisingly, even the high-frequency C–N stretching modes were observed to shift. Normal-mode calculations for $Cs_2LiCo(CN)_6$ and $Cs_2LiFe(CN)_6$,[7] where interionic potentials were included, have shown that these large frequency shifts could be reproduced without changing the intramolecular potential function; except for a slight increase in the valence C–N force constant.

For the dicesium lithium salts the large frequency shifts result primarily from the strong Li–N interaction.[4b,7] Since the structures of the $Cs_2LiM(CN)_6$ salts closely parallel those of Prussian Blues and since in place of a Li–N interaction there is now a much stronger M–N interaction (where M is a di-