Solution and Single-Crystal Raman Spectra of Potassium Hexacyanoferrate(III)

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All the Raman-active modes of [Fe(CN$_6$)]$^{3-}$ have been observed in aqueous solution. For single-crystals (ambient and *ca.* 160 K) the predictions of factor-group analysis are largely borne out by experiment, as is most of the Raman spectrum calculated by Nakagawa and Shimanouchi. Bonding in the crystal is discussed.

MANY i.r. studies have been made of the hexacyanoferrate(III) ion,[1] including recent single-crystal work,[2] but the Raman spectra in both solution and solid phases [3] are not yet adequately established. We wished to determine the extent to which factor-group predictions are borne out in a complex cyanide, as a natural extension of our studies on metal carbonyl complexes,[4] and to see whether a recent theoretical prediction of the Raman-active modes of the unit cell of the crystal was substantiated in practice.[5]

Theory.—$K_3Fe(CN)_6$ has a monoclinic form isostructural with $K_3Co(CN)_6$ for which the full structure has been determined.[6] The space-group is $P2_1/c$ (C_{2h}^5) with $Z = 2$. Selection rules both for the complex anion and the unit cell have been published before.[2,3,5] In Table 1 we summarise the predictions for the Raman spectrum. All gerade modes in O_h mix *via* C_i site-symmetry yielding $A_g + B_g$ pairs.

TABLE 1

Raman-active species for $K_3Fe(CN)_6$

		Complex ion O_h	Factor group C_{2h} (2 molecules)
ν(CN)	ν_1	a_{1g}	$3A_g + 3B_g$
	ν_3	e_g	
ν(Fe–C)	ν_2	a_{1g}	$3A_g + 3B_g$
	ν_4	e_g	
δ(FeCN)	ν_5	t_{1g} [a]	$6A_g + 6B_g$
	ν_{10}	t_{2g}	
δ(CFeC)	ν_{11}	t_{2g}	$3A_g + 3B_g$
External Modes:	rotatory		$3A_g + 3B_g$
	translatory		$3A_g + 3B_g$

[a] Inactive in O_h.

EXPERIMENTAL

Crystals were grown by slow evaporation of aqueous solutions of AnalaR grade material and were oriented by *X*-ray diffraction techniques. The determined orientation and morphology agreed with that reported by Dunsmuir and Lane.[2] Raman data were collected using a Coderg PH 1 spectrometer with 632·8 nm excitation and a ' Cryocirc ' cold cell. Experiments were conducted using the *b*- and *c*-axis directions with a third member, *a**, making an orthogonal set *a**, *b*, *c*. These axes are re-labelled so that the unique axis *b* corresponds to *z*, *a** to *x*, and *c* to *y*.

RESULTS AND DISCUSSION

The data for $[Fe(CN)_6]^{3-}$ in aqueous solution are shown in Table 2. They are an improvement upon previous work in that all three bands expected at *ca.* 400 cm^{-1} have been observed, as has ν_{11} at 102 cm^{-1}. The values are in reasonable agreement with those calculated by Nakagawa and Shimanouchi.[5] The only ambiguity in the assignment concerns ν_4 and ν_{10}. Since both are depolarised in solution there is no experimental means of distinguishing them, although the calculations clearly require the order $\nu_{10} > \nu_4$.

TABLE 2

Raman data for aqueous solutions of $K_3Fe(CN)_6$

Calc.[a]	Obs.	Assignment
2130	2131s, pol ($\rho \approx 0$)	ν_1
2121	2124m, dpol	ν_3
450	417vw, dpol	ν_{10} [b]
394	388w, pol ($\rho \approx \frac{1}{3}$)	ν_2
353	363vw, dpol	ν_4 [b]
119	102wm, dpol	ν_{11}

[a] Ref. 5. [b] See text. s = Strong, m = medium, w = weak, v = very, pol = polarised, depol = depolarised.

The crystal spectrum shows a multiplicity of lines, considerably more than reported by Devéze and Krauzman.[3] On cooling the crystal to *ca.* 160 K a few more weak bands were detected, and some changes of intensity (Tables 3 and 4).

ν(CN) *Region*.—Factor-group splitting is small, resulting in only three lines, although each has A_g and B_g components which are coincident within 0·5 cm^{-1}, thereby accounting for all six predicted modes. In contrast, hexacarbonyls show very pronounced correlation splitting.[4b]

ν(Fe–C) *and* δ(FeCN) *Region*.—The group of lines extending from 317 to 423 cm^{-1} is clearly associated with these internal co-ordinates. Six $A_g + B_g$ pairs are observed in contrast to the nine predicted (Table 1). Two alternative interpretations can be advanced. (i) The lines at 359, 391, and 423 cm^{-1} are to be correlated with ν_4, ν_2, and ν_{10} because these frequencies are close to those found in aqueous solution. [The ν(CN) frequencies were little shifted upon change of state.] If this is correct then the 359 and 423 cm^{-1} lines should

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[1] L. H. Jones, *J. Chem. Phys.*, 1962, **36**, 1209; D. Bloor, *ibid.*, 1964, **41**, 2573; W. A. McAllister, *ibid.*, 1970, **52**, 2786; V. Lorenzelli and P. Delorme, *Spectrochim. Acta*, 1963, **19**, 2033; J. P. Mathieu and H. Poulet, *ibid.*, 1963, **19**, 1966; L. H. Jones, *Inorg. Chem.*, 1963, **2**, 777; M. Krauzman, *Compt. rend.*, 1966, **162**, *B*, 765.

[2] J. T. R. Dunsmuir and A. P. Lane, *J. Chem. Soc.* (*A*), 1971, 776.

[3] J. Devéze and M. Krauzman, *Compt. rend.*, 1966, **263**, *B*, 864.

[4] (*a*) D. M. Adams, M. A. Hooper, and A. Squire, *J. Chem. Soc.* (*A*), 1971, 71; (*b*) D. M. Adams, W. S. Fernando, and M. A. Hooper, unpublished work.

[5] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, 1970, **26**, *A*, 131.

[6] N. A. Curry and W. A. Runciman, *Acta Cryst.*, 1959, **12**, 674.

show more structure than was observed: however these lines are broader than most and we consider that what we have seen is the unresolved envelope of at least two components in each case. The lines at 340, 331, and 317 cm^{-1} must then be assigned as the six components predicted for the O_h-inactive t_{1g} mode in the crystal.

(ii) Since all gerade modes mix *via* site-symmetry C_i the group of lines from 317 to 423 cm^{-1} is the result of nearly complete correlation splitting which has resulted in complete mixing, *i.e.* it is meaningless to attempt a correlation to complex ion modes classified under O_h.

TABLE 3

Single-crystal Raman frequencies (cm^{-1}) and intensities (arbitrary units) [a] at ambient temperature for $K_3Fe(CN)_6$

	$x(yy)z$	$x(zz)y$	$x(yx)y$	$x(zx)y$	$x(zy)y$	
2131	81	100		12		$A_g + B_g$
2126	81	5		18		$A_g + B_g$
2123			36		14	$A_g + B_g$
422	9	10	<1	5	1	$A_g + B_g$
389	90	100	37	18	24	$A_g + B_g$
360	15	16	18	8	16	$A_g + B_g$
337	<1	<1	9	4	3	$A_g + B_g$
315	<1	<1	1	3	6	$A_g + B_g$
177	11	25				A_g
174				20		B_g
156	42	35	5	9	75	$A_g + B_g$
147					21	B_g
140			11			A_g
124	13	6				A_g
106					18	B_g
100	16	2				A_g
83			46			A_g
73			12			A_g
55		3	1	100	1	B_g
46		1				A_g

[a] Peak heights (cm^{-1}), slits (cm^{-1}), and photomultiplier voltage: (i) 2100—2150, 2, 1000; (ii) 300—500, 6, 1100 (×35); and (iii) 0—200, 4, 1000 (×5).

We note that whichever explanation we adopt it follows from the number of lines observed that the O_h-inactive ν_5 has become active in the crystal, a result which is not to be expected on the basis of the 'oriented gas' model.

It is interesting to consider these results in connection with a recent calculation of the modes of the whole unit cell of $K_3Fe(CN)_6$.[5] Although normal-co-ordinate analyses can be notoriously misleading the authors in question have carried out several calculations on complete unit cells of complex ionic crystals with results in impressive harmony with experimental evidence. For $K_3Fe(CN)_6$, in the ν(CN) region, their predictions fit our observations very closely. In the ν(Fe–C), δ(FeCN) region their model predicts that ν_5 should be below ν_2, ν_4, and ν_{10} and that it should be resolved into a triplet. The exact frequencies and the splittings are slightly different from those observed but sufficiently close to suggest that explanation (i) is to be preferred to (ii). The closely spaced multiplets associated with ν_{10} and ν_4 in the calculations support our observation that the lines in these vicinities are broad.

The Region below 200 *cm*$^{-1}$.—In contrast to the higher-frequency regions all but one of the lines observed below 200 cm^{-1} carries only one symmetry label. This behaviour is often associated with external modes. We have observed $7A_g + 9B_g$ modes whereas $9A_g + 9B_g$ are predicted (Table 1). The two missing A_g modes can be located approximately, as follows. Because A_g and B_g components are close to each other in this crystal we can pair them off, looking for regions short of A_g lines. The 157 cm^{-1} line is an $A_g + B_g$ pair; there is evidently a missing A_g mode between 160 and 190 cm^{-1}, probably at the higher end. Similarly, since the 102, 105 cm^{-1} lines are a pair it is probable that the final A_g is *ca.* 135 cm^{-1}.

Since the full number of lines predicted has now been accounted for it is clear that the O_h ν_{11} (t_{2g}) has split considerably, giving at least five separate (observed) components. In doing so its nature must have changed because it is inextricably embedded in a complex series of lattice vibrations with which it must be considerably mixed. It is probable that δ(CFeC) motion contributes to most of the lines from 75 up to 149 cm^{-1}.

Having accounted for all of the predicted modes, the lowest observed being at 51 cm^{-1}, it is evident that the detail of the calculations by Nakagawa and Shimanouchi is not fully borne out by our observations. However, only minor adjustments to their force field would bring their predictions close to the experimental results.

TABLE 4

Single-crystal Raman frequencies (cm^{-1}) and intensities (arbitrary units) [a] at *ca.* 160 K

	$x(zz)y$	$x(yx)y$	$x(zx)y$	$x(yz)y$	
2134	100	3	8		$A_g + B_g$
2128	9	1	20		$A_g + B_g$
2126		37	0·5	11	$A_g + B_g$
423	18	4	11	9	$A_g + B_g$
391	100	15	14	11	$A_g + B_g$
359	58	67	12	31	$A_g + B_g$
340		50	33	57	$A_g + B_g$
331	18	18	11		$A_g + B_g$
317		18	9	15	$A_g + B_g$
185			4		B_g
182	48	1			A_g
177			25		B_g
157	50	12	16	88	$A_g + B$
149			12	22	B_g
143		13			A_g
138			4		B_g
127				4	B_g
124	10				A_g
105			3	30	B_g
102	4	6			A_g
83	1	32			A_g
75		15	2		A_g
58		3	16		B_g
51	6		100		B_g

[a] Peak heights (cm^{-1}), slits (cm^{-1}), and photomultiplier voltage: (i) 2100—2150, 2, 890; (ii) 300—750, 6, 1050 (×28); and (iii) 0—250, 4, 995 (×8).

Conclusions.—Single-crystal Raman observations on $K_3Fe(CN)_6$ are in close agreement with the predictions of factor-group analysis and the calculations of Nakagawa and Shimanouchi and together with recent i.r. work on single crystals [2] establish the spectrum of this compound rather fully.

These results cast a rather interesting side-light on the bonding in this crystal. In particular we are intrigued by two pieces of evidence: the very high frequencies of the lattice modes (up to **185** cm^{-1}) in contrast with those typical of complex halides K_2MCl_6,[7] and the increase in intensity of the **360** and **337** cm^{-1} lines (Table **3**) upon cooling the crystal (Table 4).

We consider that the high lattice modes indicate a higher degree of covalent bonding between anions and cations than in complex halides. This is tantamount to saying that it is possible to consider the crystal in terms of a partially delocalised bonding scheme. Upon cooling the small contraction will increase orbital overlap leading to increase in the strength of bonding and hence to changes in electron distribution. Whilst the changes in frequency upon cooling are small, it is evident that the alteration of electron distribution is sufficient to affect intensities and in particular those associated with the O_h-inactive ν_5 which probably tends towards more complete interaction with the neighbouring ν_4 as a delocalised (rather than a quasi-molecular) description becomes more appropriate.

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[7] See D. M. Adams, ' Metal–Ligand and Related Vibrations,' Arnold, London, 1967; ' Spectroscopic Properties of Inorganic Compounds,' vols. I, II, and III, ed. N. N. Greenwood, Chem. Soc., London.