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Far Infrared and Raman Spectra of $K_3[Co(CN)_6]$ and $[Co(NH_3)_6][Co(CN)_6]$

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Far infrared spectra of $K_3[Co(CN)_6]$ and $[Co(NH_3)_6][Co(CN)_6]$ and a single crystal Raman spectrum of $K_3[Co(CN)_6]$ have been measured. Calculations of optically active crystal vibration frequencies have been made, on the basis of the crystal structure determined precisely. For these two types of established crystal structures (C_{2h}^5 for $K_3[Co(CN)_6]$ and C_{3i}^2 for $[Co(NH_3)_6]$) $[Co(CN)_6]$ of hexacyano-complex salts, lattice frequencies have been determined. For $[Co(NH_3)_6][Co(CN)_6]$ the mean amplitudes of two kinds of cobalt atoms have been calculated and compared with those obtained by Iwata and Saito assuming that both complex ions behave as a rigid body.

Many investigations have been done on the vibrational spectra of hexacyano-complex salts of transition metals and on the nature of the bonding in this complex ion.[1–11] Among them Jones *et al.* and we ourselves have made a thorough study on the basis of infrared and Raman spectra and a normal coordinate treatment including lattice modes. We have investigated far infrared spectra and lattice vibrations of $K_3[Fe(CN)_6]$, $K_3[Cr(CN)_6]$ and $Cs_3[Cr(CN)_6]$ which have the monoclinic structure with the space group C_{2h}^5.[7] Swanson and Jones have investigated infrared and single-crystal Raman spectra and lattice vibrations of $Cs_2Li[Co(CN)_6]$ which has the cubic structure and for which the Bravais primitive cell is composed of one formula unit.[10]

In the present study a measurement has been made for the far infrared and single-crystal Raman spectra of $K_3[Co(CN)_6]$ which is isomorphous with $K_3[Fe(CN)_6]$ and takes a monoclinic structure C_{2h}^5. A far infrared spectrum of $[Co(NH_3)_6][Co(CN)_6]$ has also been measured, since Iwata and Saito have recently performed a very detailed X-ray analysis for the crystal structure of this complex salt, according to which the space group of this crystal is C_{3i}^2 ($R\bar{3}$).[12] Optically active lattice frequencies of the crystal have been calculated for these two complex salts. For $[Co(NH_3)_6][Co(CN)_6]$, the mean amplitudes of the displacements for the two Cobalt atoms have been calculated, which may be compared with the data obtained by Iwata and Saito.[12]

Experimental

Infrared measurement: Samples dispersed homogeneously in polyethylene or Nujol mull were used for the measurement

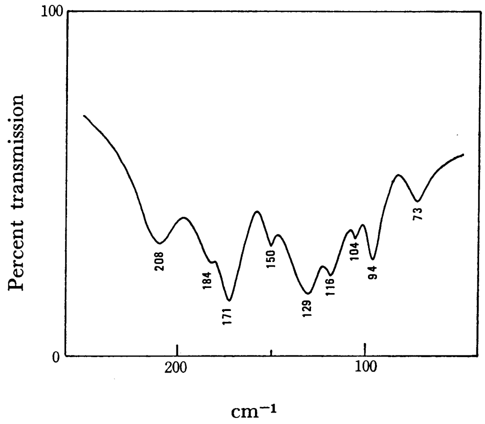

Fig. 1. Far infrared spectrum of $K_3[Co(CN)_6]$.

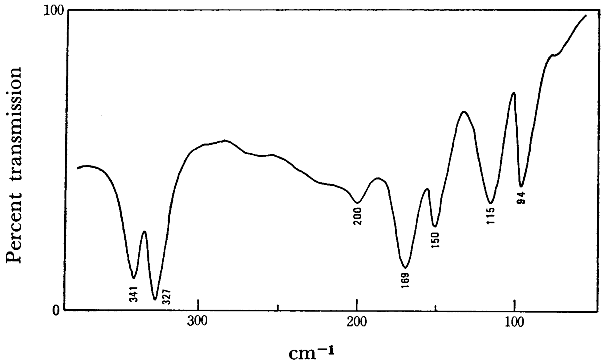

Fig. 2. Far infrared spectrum of $[Co(NH_3)_6][Co(CN)_6]$ (at liquid N_2 temperature).

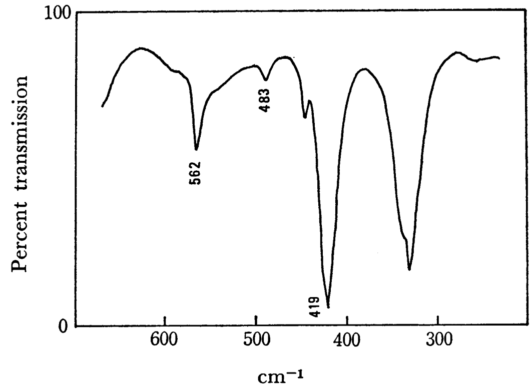

Fig. 3. Infrared spectrum of $[Co(NH_3)_6][Co(CN)_6]$ in the region 700~300 cm⁻¹ (at room temperature).

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1) L. H. Jones, *J. Chem. Phys.*, **36** 1209 (1962).
2) L. H. Jones, *Inorg. Chem.*, **2**, 777 (1963).
3) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **18**, 101 (1962).
4) V. Lorenzelli and P. Delorme, *ibid.*, **19**, 2033 (1963).
5) D. Bloor, *J. Chem. Phys.*, **41**, 2573 (1964).
6) L. H. Jones, *Inorg. Chem.*, **4**, 1472 (1965).
7) I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **26A**, 131 (1970).
8) B. I. Swanson and L. H. Jones, *J. Chem. Phys.*, **53**, 3761 (1970).
9) L. H. Jones, M. N. Memering and B. I. Swanson, *ibid.*, **54**, 4666 (1971).
10) B. I. Swanson and L. H. Jones, *ibid.*, **55**. 4174 (1971).
11) D. M. Adams and M. A. Hooper, *J. Chem. Soc., Dalton*, **1972**, 160.
12) M. Iwata and Y. Saito, *Acta Crystallogr.*, **29B**, 822 (1973).

of far infrared spectrum. A Hitachi EPI-L double beam spectrometer flushed by dry air (700—300 cm^{-1}) and a Hitachi FIS-1 vacuum double beam far infrared spectrometer (500—60 cm^{-1}) were used. The observed spectra are reproduced in Figs. 1~3.

Raman measurement: Raman spectra of a single-crystal sample of $K_3[Co(CN)_6]$ were observed using a JEOL JRS-U1 Raman spectrometer equipped with an Ar ion laser and a Spex 1401 double monochromator equipped with a He–Ne laser. The observed spectrum is reproduced in Fig. 4. Polarization measurements for this monoclinic crystal do not supply sufficient data to determine the a_g and b_g species vibrations.

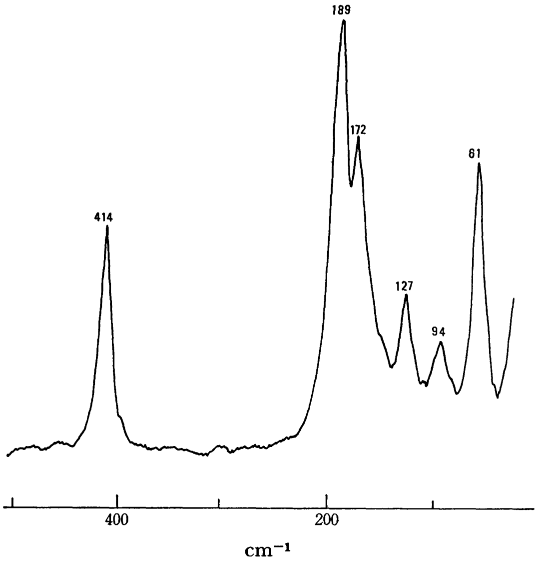

Fig. 4. Single crystal Raman spectrum of $K_3[Co(CN)_6]$.

Observed Results and Analysis

$K_3[Co(CN)_6]$. The crystal structure is monoclinic with the space group $C_{2h}{}^5$. The Bravais primitive cell contains two formula units and the factor group analysis shows that the 21 a_g and 21 b_g vibrations are Raman active and the 26 a_u and 25 b_u vibrations are infrared active. The 21 modes in each of the a_g and b_g species are composed of 15 inner modes and 3 rotational and 3 translational lattice modes. The 26 a_u modes are composed of 18 inner and 8 translational lattice modes, while the 25 b_u modes of 18 inner and 7 translational lattice modes. A vibrational analysis and a normal coordinate treatment of optically active crystal vibrations are made just in the same way as in the case of $K_3[Fe(CN)_6]$ described in the previous paper.[7] The detailed structure of $K_3[Co(CN)_6]$ was determined by neutron diffraction study.[13] Potential constants (intramolecular and interionic force constants) used in this calculation are taken the same values as those in $K_3[Fe(CN)_6]$ except for the Co–C and C≡N stretching force constants, *K*(Co–C) and *K*(C≡N) (see Table 3 of Ref. 7). The values of *K*(Co–C) and *K*(C≡N) are taken 2.6 mdyn/Å and 16.5 mdyn/Å, respectively. The results of the calculations are listed

TABLE 1. OBSERVED AND CALCULATED FREQUENCIES IN cm^{-1} OF $K_3[Co(CN)_6]$

Obsd (IR)	Calcd (b_u)	Calcd (a_u)	Calcd $[Co(CN)_6]^{3-}$	Mode
2118	2105, 2105, 2104	2105, 2105, 2104	2103 (f_{1u})	CN str.
565	565, 564, 562	565, 564, 562	561 (f_{1u})	CoC str.
414	412, 407, 404	412, 407, 404	402 (f_{1u})	CoCN bend.
	388, 385, 381	388, 385, 381	380 (f_{2u})	
208	205	206		lattice
184	193	193		
171	163	165		
150	143	143		
129	127, 123	130, 123	128 (f_{1u})	CCoC def.
116	112	116		
104	102	95	100 (f_{2u})	CCoC def.
94	89	86		lattice
73	74, 68	79, 62		
	50, 24	49, 22, 14		
Obsd (Raman)	Calcd (a_g)	Calcd (b_g)	Calcd $[Co(CN)_6]^{3-}$	Mode
	2110, 2101, 2100	2110, 2101, 2100	2109 (a_{1g}) 2099 (e_g)	CN str.
	458, 454, 451	458, 454, 451	450 (f_{2g})	CoCN bend.
414	438	438	431 (a_{1g})	CoC str.
	405, 399	405, 399	394 (e_g)	
	318, 313, 305	318, 313, 305	303 (f_{1g})	CoCN bend.
189	197	191		lattice
172	174	181		
129	143, 112	138, 118	119 (f_{2g})	CCoC def.
94	91, 87	93, 84		lattice
61	62	56		
	41, 9	41, 27		

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[13] N. A. Curry and W. A. Runciman, *ibid.*, **12**, 674 (1959).

in Table 1, together with the observed frequencies. The calculated frequencies, for which the interionic force constants were neglected (as an isolated complex ion), are also included in this table.

In Table 1 the observed infrared bands as a whole correspond well with the calculated frequencies as in the case of isomorphous $K_3[Fe(CN)_6]$. Furthermore it is noted that the Raman frequencies are also in good agreement with the calculated values using the same values of potential constants without any modification. Now that the vibrational analysis of this type of complex salts, $K_3[M(CN)_6]$, with the monoclinic structure C_{2h}^5, has been established rather fully, some discussions will be given below. The lattice frequencies due to the interaction between the complex ions and outer cations may be classified into two groups for both infrared and Raman spectra. One is located above 150 cm^{-1} and the other below 100 cm^{-1}. In the former the displacements of the K^+ ions are predominant while in the latter those of the complex ions are appreciable. The rotaional lattice frequencies in the a_g and b_g vibrations correspond with the lower group of vibrations and some of them may not be observed. Adams and Hooper argued that the high frequencies of the lattice modes in contrast with those of complex halides K_2MCl_6 indicate a higher degree of covalent bonding between anions and cations than in complex halides.[11] In fact the nearest distance between K^+ ion and N atom is about 2.5 Å. Anyhow the lattice dynamical treatment of optically active crystal vibrations, where the interionic potential constants for the atom pairs with distances shorter than 4.0 Å are taken into account and they are vaired according to the distances, is a plausible analysis to interpret both the lattice vibrations and the inner vibrations for the complex salts. The calculated frequencies as an isolated complex ion show that the outer ion affects very little upon the metal-ligand stretching frequencies in both the gerade and ungerade species though the low-frequency CCoC deformation modes are more or less coupled with the lattice modes.

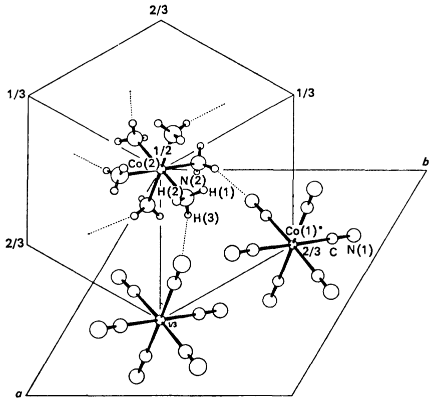

Fig. 5. Crystal structure of $[Co(NH_3)_6][Co(CN)_6]$. (Reproduced from Fig. 1 of Ref. 12 with the courtesy of Prof. Saito).

$[Co(NH_3)_6][Co(CN)_6]$. Figure 5 (the reproduction of the figure (Fig. 1) in Ref. 12) shows the crystal structure determined by Iwata and Saito.[12] This crystal is trigonal with the space group C_{3i}^2 ($R\bar{3}$) and as shown in Fig. 5 the Bravais primitive cell contains one formula unit, in other words, one $[Co(NH_3)_6]^{3+}$ ion and one $[Co(CN)_6]^{3-}$ ion (38 atoms). It can be shown from the factor group analysis that the 19 a_u and 19 e_u vibrations are infrared active, of which only 1 a_u and 1 e_u vibrations correspond to the interionic lattice modes. The 18 a_g and 18 e_g vibartions are Raman active. However, the displacements of cobalt atoms occur only for the infrared active ungerade modes.

A normal coordinate analysis of optically active crystal vibrations has been done based on the geometry[14] determined by X-ray analysis,[12] using the potential constants listed in Table 2. The values of the intramolecular force constants were at first obtained from our previous study on ammine complexes[15] and $K_3[Co(CN)_6]$ described above and then modified slightly so that the calculated frequencies may ex-

TABLE 2. POTENTIAL CONSTANTS USED IN THE CALCULATION OF $[Co(NH_3)_6][Co(CN)_6]$

Intramolecular force constants of $[Co(NH_3)_6]^{3+}$ and $[Co(CN)_6]^{3-}$					
K(Co-N)	1.05 mdyn/Å	H(NCoN)	0.40 mdyn/Å	F(N···N)	0.05 mdyn/Å
K(N-H)	5.60 mdyn/Å	H(HNH)	0.53 mdyn/Å	F(H···H)	0.06 mdyn/Å
K(Co-C)	2.30 mdyn/Å	H(CoNH)	0.15 mdyn/Å	F(Co···H)	0.10 mdyn/Å
K(C≡N)	16.5 mdyn/Å	H(CCoC)	0.14 mdyn/Å	F(C···C)	0.15 mdyn/Å
Y(NH_3)	0.01 mdyn·Å	H(CoCN)	0.25 mdyn/Å		

Interaction potential constants		
f(N···H)	0.15 mdyn/Å	(for 2.17 Å)
f(N···H)	0.03 mdyn/Å	(for 2.50 Å)
f(N···H)	0.03 mdyn/Å	(for 2.52 Å)
f(C···H)	0.022 mdyn/Å	(for 2.68 Å)
f(C···H)	0.018 mdyn/Å	(for 2.75 Å)

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[14] CoC_6 and CoN_6 are taken as regular octahedra and Co–C–N is taken as linear, which is not exactly the same as the geometry determined by X-ray analysis.

[15] I. Nakagawa and T. Shimanouchi, *Spectrochim. Acta*, **22**, 759 (1966).

TABLE 3. OBSERVED INFRARED AND CALCULATED FREQUENCIES IN cm^{-1} OF $[Co(NH_3)_6][Co(CN_6)]$

Obsd	Calcd (a_u)	Calcd (e_u)	Mode	Calcd[a)] (isolated)
3275	3258, 3245	3258, 3245	NH_3 asym. str.	3237, 3229
3126	3181	3181	NH_3 sym. str.	3167
2122	2132	2132	CN str.	2131
1570	1591, 1576	1591, 1576	NH_3 deg. def.	1583, 1574
1367	1434	1434	NH_3 sym. def.	1434
843	843, 831	849, 819	NH_3 rock.	848, 834, 831, 816
562	560	560	CoC str.	556
483	509	509	CoN str.	507
419	411	412	CoCN bend.	407
	389	391	CoCN bend.	388
341	348	339	NCoN def.	330
327	294	304	NCoN def.	278
200				
169	181	172	CCoC def.	132
150	146	141	CCoC def.	102
115	117	124	NH_3 torsion	92
94	66	79	lattice mode	

a) Calculated value where interaction potential constants were neglected.

plain the observed frequencies as a whole. The value of NH_3 torsional force constant is somewhat arbitrary, since a definite observed frequency is not determined for this mode. As for the interaction potential constants, several kinds of the bent type hydrogen bonding N–H···N and N–H···C should be taken into account. From the crystal structure shown in Fig. 5, there are 3 kinds of N···H atom-pairs whose distances are about 2.17 Å, 2.50 Å and 2.52 Å, respectively, and 2 kinds of C···H atom-pairs of about 2.68 Å and 2.75 Å. The interatomic force constants are taken for these atom pairs. The values of f(C···H) were determined according to Harada-Shimanouchi's potential,[16)] while those of f(N···H) were determined on referring to the data of the hydrogen-bonded dimers such as adenine and uracil crystals studied by Harada and Lord.[17)] The results of the calculations are listed in Table 3, together with the infrared observed frequencies. The frequencies are well interpreted based on the trigonal structure determined by X-ray analysis.

Then mean amplitudes of displacements of two kinds of cobalt atoms in $[Co(NH_3)_6][Co(CN)_6]$ were calculated, using the value of potential constants in Table 2. The Cartesian displacement of i-th atom is expressed as:

$$\Delta x_i = \sum_a (L_X)^a_{x_i} Q_a$$

where Q_a denotes a-th normal coordinate. Therefore one obtains

$$\langle \Delta \mathrm{x}_i^2 \rangle = \sum_a [(L_\mathrm{X})^a_{\mathrm{x}i}]^2 \langle Q_a^2 \rangle$$

$$\langle \Delta x_i \Delta y_i \rangle = \sum_a [(L_\mathrm{X})^a_{\mathrm{x}i} (L_\mathrm{X})^a_{\mathrm{y}i}] \langle Q_a^2 \rangle$$

where ⟨ ⟩ denotes mean values. $\langle Q_a{}^2 \rangle$ is expressed as

$$\langle \mathrm{Q}_a^2 \rangle = (\mathrm{h}/8\pi^2 c\nu_\mathrm{a}) \coth\ (hc\nu_\mathrm{a}/2kT)$$

TABLE 4. MEAN AMPLITUDES OF DISPLACEMENTS OF Co ATOMS IN $[Co(NH_3)_6][Co(CN)_6]$

	Co (in $[Co(NH_3)_6]^{3+}$)	Co (in $[Co(CN)_6]^{3-}$)
$2\sqrt{\langle \Delta z_i^2 \rangle}$	0.151 Å	0.131 Å
$2\sqrt{\langle \Delta x_i^2 \rangle}$ $(2\sqrt{\langle \Delta y_i^2 \rangle})$	0.133 Å	0.122 Å

Taking the principal axes as x, y and z axes, $\langle \Delta x_1 \Delta y_1 \rangle$ naturally disappears. Mean amplitudes of displacements of cobalt atoms were calculated at 300 K, the vibrations of the ungerade species being only taken into consideration for the displacements of cobalt atoms. The result is shown in Table 4. Iwata and Saito[12)] made the calculations of thermal parameters assuming that both complex ions behave as a rigid body. They obtained tensors to describe the translational vibration and libration of the rigid body and showed that rigid-body motions are similar in both complex ions and are strikingly isotropic (the mean amplitude of translational motion is 0.12∼0.13 Å). It should be noted that the result in Table 4 is in good agreement with that by Iwata and Saito.

In conclusion both $K_3[Co(CN)_6]$ and $[Co(NH_3)_6]$-$[Co(CN)_6]$ are well-established typical cyano-complex salts from the crystal-structural point of view. Vibrational spectra are interpreted satisfactorily on the basis of the crystal structure determined by neutron and X-ray analyses. Mean amplitudes calculated using the potential constants based on the spectroscopic data may supply thermal parameters in the X-ray analysis.

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16) I. Harada and T. Shimanouchi, *J. Chem. Phys.*, **46**, 2708 (1967).

17) I. Harada and R. C. Lord, *Spectrochim. Acta*, **26A**, 2305 (1970).