The infrared and Raman spectra of potassium azidopentacyanocobaltate(III) dihydrate: $K_3[Co(CN)_5N_3] \cdot 2H_2O$

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Abstract

Infrared spectra of potassium azidopentacyanocobaltate(III) dihydrate (PACDH) were obtained from the polycrystalline substance, both normal and deuterated, and from the monocrystal using in this case a polarization analyzer. Raman spectra of the normal powder were also obtained. The observed bands were assigned either to the internal vibrational modes of the azidopentacyanocobaltate(III) ion (AC) or to the internal and librational modes of the hydration water.

Introduction

As a further contribution to the understanding of the IR spectra of water in crystalline hydrates (Varetti and Aymonino, 1973; Della Védova *et al.*,

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1981) this paper reports the spectra of potassium azidopentacyanocobaltate-(III) dihydrate (PACDH) both in the form of polycrystalline powder (normal and deuterated) and as the monocrystal. In the later case the polarization of the light transmitted through oriented plates was measured.

Results are interpreted in the light of a previous crystallographic work (Castellano *et al.*, 1982) which showed that PACDH belongs to the triclinic $P\bar{1}$-C_i^1 (No. 2) space group with $Z = 2$, $a = 8.514(2)$, $b = 8.943(1)$, $c = 9.397(2)$ Å, $\alpha = 81.47(2)$, $\beta = 76.32(2)$, $\gamma = 75.95(1)°$. The complex ion is located in sites of C_1 symmetry and the water molecules are distributed between two sets of nonequivalent C_1 sites.

The infrared spectrum of PACDH had been studied previously (Gutterman and Gray, 1971; Nazarenko *et al.*, 1978) although the published reports were limited to bands due to water were not considered. The findings reported for the anion are not in complete agreement with our results. In the earliest work (Gutterman and Gray, 1971) only one band for the non-degenerate NNN deformation modes was reported while we found the two expected bands (see below). Fewer components were also reported for the CN and CoC stretchings for which we found four and five peaks respectively (see below). Concerning the CoN stretching, three bands were assigned to this single mode whereas we were able to see only one band. The assignments made for the CoC stretching modes and for the CoCN bendings followed those made by Jones for the $[M(CN)_6]^{n-}$ anions (Swanson and Jones, 1971, 1974), where $\delta MCN > \nu MC$.

In the latest paper (Nazarenko *et al.*, 1978) only two bands were found for the CN stretchings, and the assignment made for the axial CN stretching differs from ours (see below). Assignments followed in this case Shimanouchi's criterion ($\nu CoC > \delta CoCN$) (Nakagawa and Shimanouchi, 1962).

Experimental

PACDH was prepared as a polycrystalline powder by the reaction in aqueous solution of $[Co(NH_3)_5N_3]Cl_2$ (prepared by the method of Linhard and Flygare, 1950) with KCN in the presence of added $CoCl_2 \cdot 6H_2O$ as a catalyst (Barca *et al.*, 1967). Ethanol was added to the resultant solution, and the yellow powder obtained was separated by filtration. The product was recrystallized from water. Single crystals in the form of small plates with the largest faces parallel to the (001) plane were obtained by slow evaporation of water solutions in the ice-box. For the IR work the plates were ground and polished to the desired thickness using CsI plates as supports, to which they were glued with paraffin wax. Partial deuteration of the substance was

accomplished by dissolving it in D_2O (Fluka 99.7%, nominal) and evaporating the solution to dryness over fresh $CaCl_2$ in a desiccator. A higher degree of deuteration was obtained by dissolving the anhydrous substance in D_2O. The anhydrous solid was obtained by heating PACDH at 100°C in an air oven and handled in a glove-bag under dry nitrogen. Powder spectra were run as mulls in Nujol and halocarbon oils between CsI plates, both at room and at low (boiling nitrogen) temperature.

Instrumentation

The IR spectra were recorded with Perkin-Elmer 457 and 580 B spectrophotometers. A dry-air purge system was used with the 580 B when measuring samples at room temperature. When running polarized spectra the a axis of the crystal was positioned at 45° with respect to the entrance slit of the monochromator, and the polarizer was oriented alternatively parallel and perpendicular to that axis. The spectrophotometers were calibrated using water, carbon monoxide, ammonia, and polyethylene absorption bands. Wavenumber accuracy was estimated to be ± 1 cm^{-1} for sharp bands and ± 2 cm^{-1} for poorly defined bands or shoulders. Low-temperature spectra were obtained at liquid-nitrogen temperature with an RIIC variable temperature cell (model VLT-2).

The Raman spectrum was recorded (at room temperature) with a Spex-Ramalog instrument provided with a Scamp microprocessor and a Spectra Physics Ar$^+$ laser tuned at the 514.5 nm line. The instrument was calibrated using the band at 459 cm^{-1} of carbon tetrachloride. Wavenumber accuracy was $\pm$ 1 cm^{-1}.

Results and discussion

According to the X-ray study (Castellano *et al.*, 1982) and to the results reported below, the azidopentacyanocobaltate(III) (AC) ion in PACDH was approximately C_s symmetry; therefore its 36 normal vibrational modes can be classified as $21\,A' + 15\,A''$ which are all IR and Raman active. In fact, the AC ions occupy sites of C_1 symmetry in the crystal lattice. This site group correlates with the C_s point group and the C_i factor group as described in Table 1. No additional bands are expected, therefore, for the vibrational modes in the IR and Raman spectra of AC in the crystal as compared with the

Table 1. Correlation table for $[Co(CN)_5N_3]^{3-}$ and H_2O fundamentals in
$K_3[Co(CN)_5N_3] \cdot 2H_2O^a$

	Point group	Site group	Factor group
Anion			
	C_s	C_1	C_i
ν_1 to ν_{21}, T_x, T_y, R_z	A' (IR, R)	A (IR, R)	A_g (R)
ν_{22} to ν_{36}, T_z, R_x, R_y	A'' (IR, R)		A_u (IR)
H_2O			
	C_{2v}	C_1	C_i
ν_1, ν_2, T_z	A_1 (IR, R)		A_g (R)
R_z (twist)	A_2 (R)	A (IR, R)	
ν_3, T_x, R_y (rock)	B_1 (IR, R)		A_u (IR)
T_y, R_x (wag)	B_2 (IR, R)		

^{a}IR, infrared active; R, raman active.

isolated ion. Signs of dynamical coupling between the anions in the unit cell are found only in the antisymmetric stretching of the azido group which band shows a significant wavenumber shift when compared in the IR and Raman spectra (see below). This shift could be due to the proximity and anti-parallelism of the azido groups in the crystal (Castellano *et al.*, 1982). The assignment of the IR-active bands of the anion can be facilitated by considering first that the ion $[Co(CN)_6]^{3-}$ is of O_h symmetry and then admitting a C_{4v} pseudosymmetry for the $[Co(CN)_5N_3]^{3-}$ ion, as an inter-mediate step between O_h and C_s symmetries.

Polarized spectra and optical properties

The crystallographic axes were located in the single crystals of PACDH by standard X-ray methods. It is to be noted that the NNN axis of the azido group makes an angle of about 7.3° with the (a,b) plane and is nearly perpendicular to the a axis (89.6°). Using a polarizing microscope it was found that the a axis is a dielectric axis. Taking into account these facts, the following dichroic behavior can be predicted for the vibrational modes of the AC ion. The vibrational modes A' with transition moments in the σ plane which contains the azido group and makes an angle of 45° with the equatorial CN groups should appear in the spectra of the (a,b) section when the light is analyzed perpendicular to the a axis, and the modes with transition moments normal to this plane (A'') should be active when the light is analyzed parallel to the a axis. The dichroism of the water bands cannot be predicted because only one hydrogen atom could be positioned from X-ray data.

The assignment of bands due to the azidopentacyanocobaltate(III) (AC) ion

CN stretching bands

In the $[Co(CN)_6]^{3-}$ (O_h) ion the CN stretching bands belong to the A_{1g} (R), E_g (R), and F_{1u} (IR) species. When lowering the symmetry of the ion to the C_{4v} and C_s point groups by changing adequately the sixth ligand, the correlation of Table 2 can be established. The following assignments based in the C_s point group are only tentative.

An intense band at 2125 cm^{-1} with a shoulder at 2131 cm^{-1} and a weak band at 2147 cm^{-1} are observed in the CN stretching region in the Nujol-mull spectrum at room temperature. In the low-temperature spectrum shown also in Fig. 1 these bands appear respectively at 2124 and 2148 cm^{-1}, the shoulder is resolved as a peak at 2131 cm^{-1}, and a new band is seen at 2138 cm^{-1}. In the Raman spectrum of a powdered sample at room temperature, bands are observed (Fig. 1) at 2144 cm^{-1} (very strong), 2135 cm^{-1} (medium), and 2125 cm^{-1} (very weak). The most intense bands in the low-temperature IR spectrum, those at 2124 and 2131 cm^{-1}, are assigned respectively to the A' (eq) and A'' (eq) modes which should result from the splitting on the degenerate E (C_{4v}) and $F_{1u}(O_h)$ stretching modes. The small difference in intensities noted between these two bands could be explained by the existence of another band not resolved in our spectra which could be assigned to the axial stretching mode A'. The band which appears in the IR spetrum at 2138 cm^{-1} and in the Raman spectrum at 2135 cm^{-1} is assigned to the A'' (eq) mode. In the $[Co(CN)_6]^{3-}$ ion the corresponding E_g mode appears at about the same wavenumber (2137 cm^{-1}). The medium intense IR band at 2148 cm^{-1} is assigned to the equatorial A' stretching (cf. Nazarenko et al., 1978). In the Raman spectrum it appears at 2144 cm^{-1} as a very strong band, as expected for a highly symmetric mode.

When the crystal spectra are analyzed parallel to the a axis the intensity of the broad antisymmetric stretching band of the axido group at 2063 cm^{-1} is greatly reduced and a set of weak but sharp bands appears clearly (Fig. 2). In addition, there are two shoulders at 2104 and 2089 cm^{-1} which are not reproduced in Fig. 2 but which are clearly seen in the spectra of a thicker plate. These features could be assigned to the stretching vibrations of naturally occurring $^{13}C^{14}N$ and $^{12}C^{15}N$ groups. Due to the known abundances of the different isotopic CN groups ($^{13}C^{14}N$: 1.10%; $^{12}C^{15}N$: 0.38%; $^{13}C^{15}N$: 0.004%) (Holzbecher et al., 1971), the species $^{13}C^{14}N$ should dominate the spectrum in the region located immediately below the $^{12}C^{14}N$ stretching bands. The stretching band of $^{12}C^{15}N$ should be only one-third as intense, and those of $^{13}C^{15}N$ will be too weak to appear in the spectrum. The ratios between the stretching wavenumbers for normal and isotopic groups are theoretically (in the diatomic approximation) the following (cf. Holzbecher et al., 1971):

Table 2. Spectral correlations and assignments for the $[Co(CN)_5N_3]^{3-}$ ion in $K_3[Co(CN)_5N_3] \cdot 2H_2O^{a,b}$

			Raman, R.t.	IR R.t	IR L.t	IR Single crystal, L.t	IR Anhydrous, L.t
$[Co(CN)_6]^{3-c}$	$[Co(CN)_5X]^{3-d}$	$[Co(CN)_5N_3]^{3-}$					
ν (CN)							
A_{1g} (R) 2150 ——	A_1 (eq) (IR, R) ——	A' (eq)	2144(vs)	2147(w)	2148(m)	2147	2150(w)
E_g (R) 2137 ——	B_1 (eq) (R) ——	A'' (eq)	2135(m)		2138(s)		
F_{1u} (IR, R) 2129 ——	E' (eq) (IR, R) ——	A'' (eq)		2131(sh)	2131(vvs)	f	2134(vvs)
		A' (eq)	2125(w)	2125(vvs)	2124(vvs)		2129(vvs)
	A_1 (ax) (IR, R) ——	A' (ax)	2125 ?	2125 ?	2124 ?^{e}		2129 ?
ν (CN) (isotopic species)							
$^{12}C^{15}N + {}^{13}C^{14}N$						$\Big\{$ 2109^e, 2104(sh)^e, 2103^e, 2095^e, 2089(sh)^e, 2088^e, 2081^e $\Big\}$	
δ (CoCN)^g							
F_{1u} (IR) 564 ——	E (IR, R) ——	A'			555(vw)	555	553(vw)
		A''			555(vw)	555	
	A_1 (IR, R) ——	A''	549(w)	548(vvw)	549(vvw)	550	545(sh)

ν (CoC)

Free ion	Correlation	Sub-group					
F_{1g} (i) 358	E (IR, R)	A'	354(s)	357(m)	359(s)	365	362(w)
		A''					
A_2 (i)		A''					
F_{2g} (R) 482	B_2 (R)	A'		500(sh)	487(vw)	485	472(vw)
	E (IR, R)	A''	462(w)	465(w)	474(w)	470	458(vvw)
		A'	379(w)		467(w)	465	
F_{2u} (i) 402	B_1 (R)	A''			383(sh)	378	376(vw)

ν (CoC)

Free ion	Correlation	Sub-group					
F_{1u} (IR) 416	A_1 (ax) (IR, R)	A' (ax)	429(m)	428(vs)	432(vs)	430	433(s)
	E (eq) (IR, R)	A'' (eq)	422(w)	420(vs)	423(vs)	425	422(vs)
		A' (eq)		410(s)	417(vs)	418	415(sh)
A_{1g} (R) 408	A_1 (eq) (IR, R)	A' (eq)			414(s)	412	413(s)
E_g (R) 391	B_1 (eq) (R)	A'' (eq)	398(m)	395(vvw)	397(vvw)	395	395(sh)

δ (CCoC)^g

			142(vvw)				

ν (NNN)^h

N_3^- ‖ [Co(CN)$_5$N$_3$]$^{3-}$

Free ion	Correlation						
Σ_u^+ (IR) 2041	A' (asym) ^{14}N^{15}N^{14}N	2035(vvw)	2060(vvs)	2063(vvs)	2060 / 2015 / 2003	$\begin{cases}2071(\text{vvs})\\2050(\text{vvs})\end{cases}$
Σ_g^+ (R) 1344	A' (sym) ^{14}N^{14}N^{15}N	1297(vvw)	1296(s)	1300(s)	1302 / 1278	1318(vs)

Table 2. Spectral correlations and assignments for the $[Co(CN)_5N_3]^{3-}$ ion in $K_3[Co(CN)_5N_3] \cdot 2H_2O$ [a,b]

$[Co(CN)_6]^{3-}$ [c]	$[Co(CN)_5X]^{3-}$ [d]	$[Co(CN)_5N_3]^{3-}$	Raman, R.t	IR			
				R.t	L.t	Single crystal, L.t	Anhydrous, L.t
δ (NNN) [h]							
(π_u (IR) 645	A'		675(vvw)	670(vw)	678(vw)	675	675(w)
	A''			600(w)	602(m)	605	599(vw)
ν (CoN)		A'	378(vw)	375(m)	378(m)	370	376(vw)
δ (CoNN)		A'	195(m)				

[a] Data in cm^{-1}. Powder spectra unless otherwise stated. IR, infrared-active bands; R, Raman-active bands; i, inactive bands; vvw, very very weak; vw, very weak; w, weak; m, medium; s, strong; sh, shoulder; vs, very strong; vvs, very very strong. R.t, room temperature; L.t, low temperature (liquid-nitrogen temperature).
[b] The spectral data of the anhydrous compound are included for the sake of comparison.
[c] See Swanson and Jones (1971, 1974).
[d] X = monatomic ligand.
[e] See text.
[f] Absorption was too intense. This fact did not allow the estimation of the relative intensities of the other bands.
[g] No detailed assignment has been attempted for the $Co(CN)_5$ deformation modes.
[h] See Basolo and Hammaker (1960, 1962).
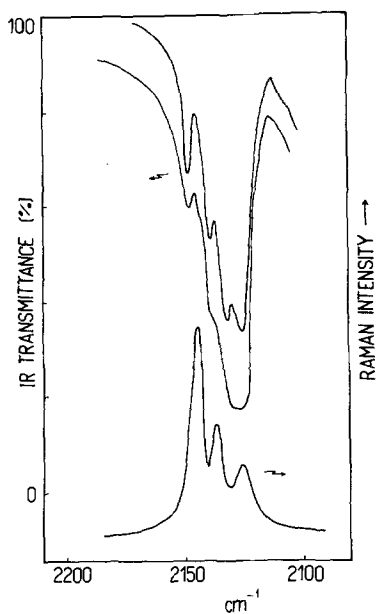
Fig. 1. Infrared and Raman spectra in the CN stretching region. The uppermost spectrum was recorded at liquid-nitrogen temperature.
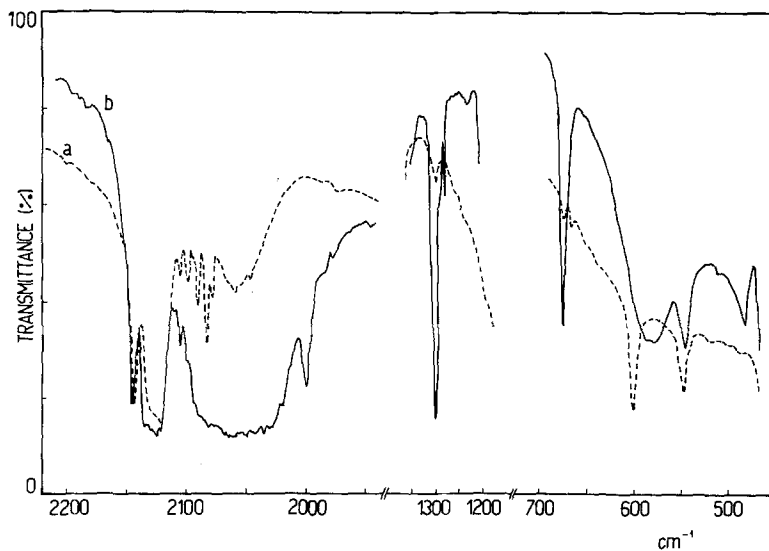
Fig. 2. Single-crystal IR spectra in the stretching and bending regions of the azide ligand. (a) $E \parallel a$; (b) $E \perp a$.

$$\nu(^{12}C^{15}N)/\nu(^{12}C^{14}N) = 0.984;$$
$$\nu(^{13}C^{14}N)/\nu(^{12}C^{14}N) = 0.979;$$
$$\nu(^{13}C^{15}N)/\nu(^{12}C^{14}N) = 0.963$$

This means that $\nu(^{12}C^{14}N) > \nu(^{12}C^{15}N) > \nu(^{13}C^{14}N) > \nu(^{13}C^{15}N)$ for the stretchings of any isolated CN group.

Four of the five bands mentioned above should be assigned therefore to isolated equatorial $^{13}C^{14}N$ groups (an axial group should be inactive when one analyzes the light in a direction parallel to the a axis). The two shoulders should be assigned to equatorial species of the less abundant $^{12}C^{15}N$. The other two features expected from the same group are perhaps buried under the most intense peaks. The fifth band should have therefore a different origin than a CN stretching. Present information is not enough to attempt a detailed assignment of all these features, an isotopic enrichment being required for this purpose.

The assignments discussed above as well as the assignment to follow are gathered together in Table 2.

NNN and CoN stretching bands

The strong and broad band at 2063 cm^{-1} in the low-temperature IR spectrum of polycrystalline PACDH is due to the NNN antisymmetric stretching. In the Raman spectrum this mode is observed at 2035 cm^{-1}. The difference between these wave numbers could be due to the interaction between the azido groups mentioned above. The NNN symmetric mode was found at 1300 cm^{-1} in the low-temperature IR spectrum and at 1297 cm^{-1} in Raman. Both IR bands show the dichroic behavior expected for A' modes. The very very weak band observed at 2015 in the single crystal spectrum is assigned to the antisymmetric stretching of the isotopic froms $^{14}N^{15}N^{14}N$, and the also very very weak band at 1278 cm^{-1}, to the symmetric stretching of the isotopic species $^{14}N^{14}N^{15}N$. The wave number ratios calculated for the isotopic forms relative to the normal form on the basis of the three-atoms model are the following:

$$\nu_3(^{14}N^{15}N^{14}N)/\nu_3(^{14}N^{14}N^{14}N) = 0.977;$$
$$\nu_1(^{14}N^{14}N^{15}N)/\nu_1(^{14}N^{14}N^{14}N) = 0.983;$$

Observed wavenumbers are in agreement with such ratios.

The NNN deformations are assigned to the bands which appear at 675 and 599 cm^{-1} in the IR spectrum of the anhydrous compound and at 678 and 602 cm^{-1} in the hydrated sample. Because of its dichroic behavior, the band at 678 cm^{-1} is assigned to an A' mode (in-plane deformation) and the band at 602 cm^{-1} to and A'' mode (out-of-plane deformation) (see Fig. 2).

The CoN stretching mode appears at 378 cm^{-1} and its assignment was made by comparison with the spectra of other compounds containing the azido group (Forster and Harrocks, 1966; Druding *et al.*, 1973).

CoC stretchings and CoCN deformations

The bands originated by these vibrations appear between 555 and 365 cm^{-1}, in a region of considerable complexity due to the librational bands of water. In $[Co(CN)_6]^{3-}$ the CoC stretching and CoCN deformation modes belong to the A_{1g} (R), E_g (R), and F_{1u} (IR) species and to the F_{1g} (i), F_{1u} (IR), F_{2g} (R), and F_{2u} (i) species, respectively. For the CoC stretching modes the correlation between the O_h, C_{4v}, and C_s point groups is the same as discussed for the CN stretchings (see above), while for the CoN deformations the correlation is as in Table 2, where again tentative assignments of the observed bands to the expected modes for C_s symmetry are included.

The criterion of Jones (Swanson and Jones, 1971, 1974) for the assignment of these modes is adopted in the following discussion. Relative wavenumbers and intensities, and the behavior of the bands in the polarized spectra, when possible, have been used as criteria for assignments.

In the region between 500 and 450 cm^{-1}, the features at ca. 500 (sh) and 465 cm^{-1} (room temperature) and at 487, 474, and 467 cm^{-1} (low temperature) are all apparently related to internal vibrational modes of the anion because they appear in the same places in the normal and deuterated spectra. In the anhydrous sample only two bands are seen in this region at 472 and 458 cm^{-1} and therefore the splitting and shifts observed in the spectra of the hydrate should be traced to a structural change of the salt when passing from the anhydrous to the hydrated form. It is interesting to note that the powder X-ray diffraction patterns of the hydrated and the anhydrous salt differ from each other (Olabe and Aymonino, 1980). Bands at 553, 545, 472, 384, and 362 cm^{-1} (low temperature) in the anhydrous compound and at 555, 549, 487, 474, 467, 383, and 359 cm^{-1} (low temperature) in the hydrate are assigned to CoCN deformation modes. Bands observed at 433, 422, 413, and 395 cm^{-1} (low temperature) in the anhydrous compound and at 432, 423, 417, 414, and 397 cm^{-1} (low temperature) in the hydrate are assigned to the CoC stretchings (see Table 2).

CoNN, CCoC, and CCoN deformations

These modes should absorb in the following order $\delta_{CoNN} > \delta_{CCoC} > \delta_{CCoN}$ (Forster and Harrocks, 1966) below the useful limit of our IR instruments (see above). In the Raman spectrum only two bands are clearly seen at 195 and 142 cm^{-1} which could be assigned to these deformation modes, the band of higher wavenumber corresponding perhaps to the CoNN deformation by comparison with the assignment reported for the tetraazidozincate(III)

complex, $[Zn(N_3)_4]^{2-}$ (Forster and Harrocks, 1966). The other band at 142 cm^{-1} could be due to the CCoC deformation. Other deformation bands should be hidden by the strong Rayleigh scattering which puts a useful limit to our spectra at 130 cm^{-1}.

Bands due to water

The relevant features due to the water molecules in the spectrum at room temperature are: a) a broad band in the OH stretching region, characterized by the presence of well-defined peaks at 3616 and 3536 cm^{-1}, b) a single band in the bending region at 1605 cm^{-1}, and c) four features in the librational region at 563, 530(sh), 340, and 327 cm^{-1}. The intensities of the latter bands are greatly enhanced by lowering the sample temperature, in which case the shoulder resolves into a band at 537 cm^{-1}. All these bands disappear upon dehydration of the sample. More information about the spectral behavior of water molecules in PACDH was obtained through deuteration.

a. The stretching modes

The changes brought about by deuteration were rather simple. In the OD stretching region only three bands appear clearly at 2655, 2639, and 2616 cm^{-1} in the low-temperature spectra of samples with a small degree of deuteration as seen in Fig. 3 (the weak features at 2687 and 2587 cm^{-1} are also found in the spectrum of the normal hydrate and in the anhydrous substance). As the deuterium content increases, two new bands appear at 2689 and 2592 cm^{-1} (Fig. 3). The first three bands should be due to the uncoupled OD stretchings of the HOD molecules, although four such bands should be expected from the four crystallographically different OH bonds. However, it is possible to assign a weak band at 2600 cm^{-1} as the fourth expected but there is some ambiguity in this assignment because the compound shows combination bands and overtones precisely in this zone (see below). As the deuterium content increases, this weak feature is buried in the more intense bands due to the D_2O stretchings (although a shoulder at ca. 2606 cm^{-1} can still be observed). The bands at 2689 cm^{-1} and 2592 cm^{-1} (with shoulders at 2670 cm^{-1} and 2587 cm^{-1}), which increase in intensity with the deuterium content and become the strongest at the highest deuterium concentration attained, can be assigned to the stretching vibrations of one type of D_2O molecules while the shoulders could be due to the other type. The three distinct OD stretching bands assigned to the HOD molecules and the weak band of the same probable origin confirm the existence of two different kinds of water molecules in the lattice and the predicted nonequivalence of their OD (OH) bonds (as stated above, the water molecules were found located in sites of C_1 symmetry (Castellano et al., 1982). Counterparts of the OD stretchings were located at 3602, 3588, and 3551 cm^{-1} for the uncoupled OH and at 3618 and 3534 cm^{-1} for
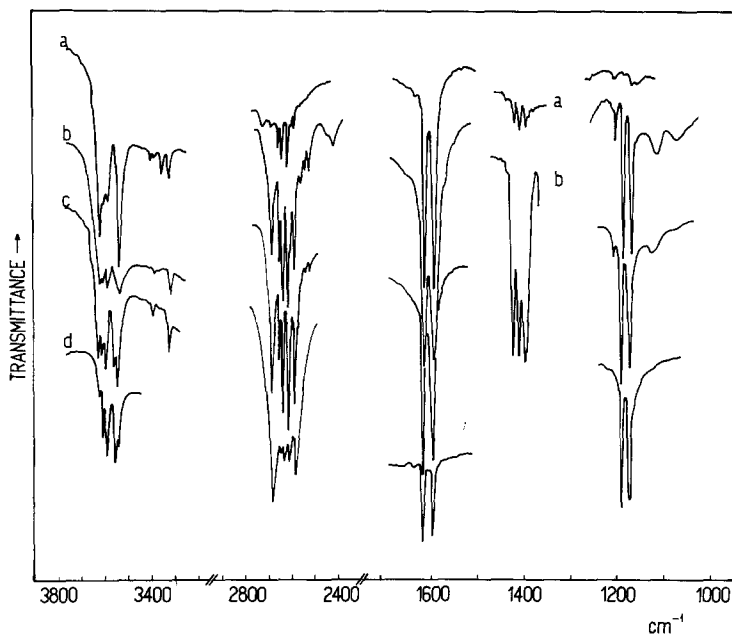
Fig. 3. IR water bands (due to internal vibrations) in partially deuterated samples of K$_3$[Co(CN)$_5$N$_3$] · 2H$_2$O at liquid-nitrogen temperature: (a) 5% D; (b) 45% D; (c) 54% D; (d) 75% D.

the H$_2$O stretching modes. The eventual counterpart of the weak OD band at 2600 cm^{-1} could not be found, but it should be located at ca. 3540 cm^{-1}, in which case it is probably buried in the more intense band at 3534 cm^{-1}. No features corresponding to the D$_2$O stretchings at 2670 and 2587 cm^{-1} could be seen in the H$_2$O region. The corresponding ratios ν(OH/ν(OD) for the uncoupled stretchings, $3602/2655 = 1.357$; $3588/2639 = 1.360$, and $3551/2616 = 1.357$, are similar to values previously reported (cf. Varetti and Aymonino, 1973; Holzbecher et al., 1971).

b. The bending modes

The corresponding bands for H$_2$O, HOD, and D$_2$O appear as broad singlets at room temperature, but each of them splits respectively into two, four, and two components at low temperature (in the last case, a third band is also seen, but it is assigned to an overtone, as mentioned below; see Fig. 3 and Table 3). The magnitude of the splittings does not depend on the degree of deuteration (21 cm^{-1} for H$_2$O and 17 cm^{-1} for D$_2$O). This confirms that the dynamic coupling of water vibration is not appreciable. The double peaks observed for the bending fundamentals of H$_2$O and D$_2$O are again explained as arising from two nonequivalent types of water molecules in the lattice. For

Table 3. Bands due to the hydration water in $K_3[Co(CN)_5N_3] \cdot 2H_2O$ (Nujol mulls)[a]

Vibration	Room temperature	Low temperature[b]	Assignment
Stretchings	3616	3618	H_2O (W1 + W2)
		3602	HOD (isolated OH) (W1)
		3588	HOD (isolated OH) (W2)
		3551	HOD (isolated OH) (W2)
			HOD (isolated OH) (W1)[c]
	3536	3534	H_2O (W1 + W2)
	2681	2689	D_2O (W2)
		2670 (sh)	D_2O (W1)
		2655	HOD (isolated OD) (W1)
	2646	2639	HOD (isolated OD) (W2)
	2624	2616	HOD (isolated OD) (W2)
		ca. 2600	HOD (isolated OD) (W1)
	2591	2592	D_2O (W2)
		2587 (sh)	D_2O (W1)
Bendings		1614	HOH (W1)
	1605	1593	HOH (W2)
		1423[d]	
			HOD (W1)
		1412[d]	
	1415[d]		
		1400 (sh)[d]	
			HOD (W2)
		1397[d]	
		1187	DOD (W1)
	1186		
		1170	DOD (W2)
Librations	563	588	H_2O (rocking) (W1)
	530(sh)	537	H_2O (rocking) (W2)
	420	420	D_2O (rocking) (W1 + W2)[c]
	340	343	H_2O (wagging) (W1)
	327	328	H_2O (wagging) (W2)
		276	D_2O (wagging) (W1)?

[a] Wavenumbers are in cm^{-1}.
[b] Liquid-nitrogen temperature.
[c] See text.
[d] Measured in halocarbon mull.

the HOD bendings the peaks found at 1423 and 1412 cm^{-1} are of similar intensity while the third band at 1397 cm^{-1} is the more intense and shows a shoulder at 1400 cm^{-1}, which completes the set of four bands expected from the two different types of asymmetric sites occupied by the water molecules.

c. The librational modes

The features which appear at 563, ca. 530 (sh), 340, and 327 cm^{-1} at room temperature and at 588, 537, 343, and 328 cm^{-1} at low temperature are assigned respectively to the rocking modes (the two with the highest wavenumbers) and to the wagging modes (the two with the lowest) of the different water
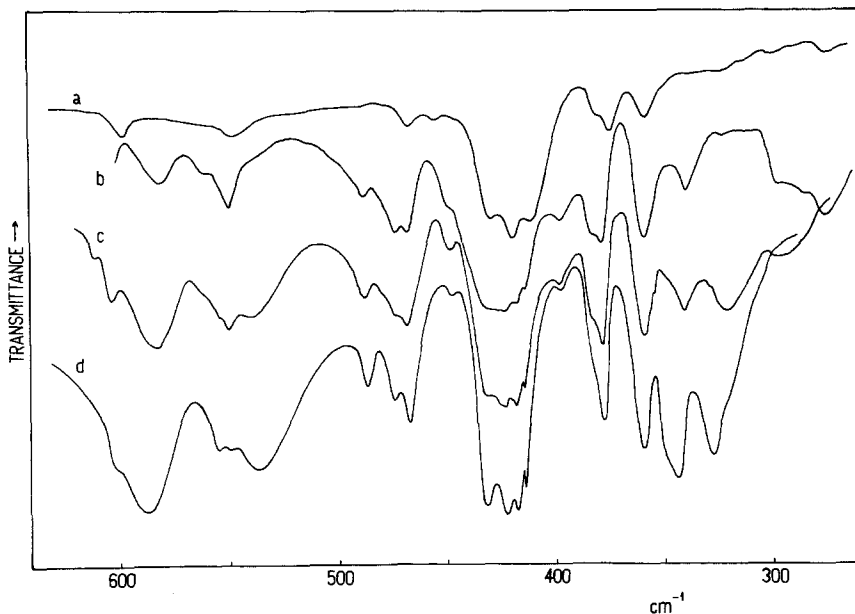
Fig. 4. Low-frequency IR spectra (liquid-nitrogen temperature) for $K_3[Co(CN)_5N_3]$ (a) and
$K_3[Co(CN)_5N_3] \cdot 2(H_2O + D_2O)$: 75% D (b); 54% D (c); 0% D (d).

molecules (Brun, 1968). Figure 4 reproduces the low-temperature infrared
spectra between 600 and 250 cm^{-1} of the normal hydrate and of two deuterated
samples with different deuterium concentrations together with the spectrum
of the anhydrous substance for the sake of comparison. Band shifts are noted
as expected when passing from the normal to the deuterated spectum. Bands
of the deuterated waters corresponding to the features found at 588 and 537
cm^{-1} for the normal waters should be buried under the broad band centered at
420 cm^{-1}, whereas the bands at 343 and 328 cm^{-1} find their counterparts in the
complex band extending from about 350 to 250 cm^{-1}.

d. The possible hydrogen bonds

Both kinds of hydration waters are coordinated at the same potassium
ions (K1 and K3) with distances $d(K1-OW1) = 2.72$ Å, $d(K3-OW1) = 2.98$
Å, $d(K1-OW2) = 2.73$ Å, and $d(K3-OW2) = 2.97$ Å (Castellano *et al.*,
1982). The atoms in the neighborhood of OW1 which could be involved in
H bonding are the following: a) N1 at 3.02 Å from OW1, forming a
K3-OW1-N1 angle of 103.6° and b) N4' at 3.59 Å from OW1 and forming
a K1-OW1-N4' angle of 106.9°. For W2 the more probable acceptors are:
a) N1 at 3.07 Å apart from OW2, forming a K3-OW2-N1 angle of 100.6°,
and b) N4 at 3.5 Å from OW2 and forming a K1-OW2-N4 angle of 109.6°.

The single hydrogen atom which could be located in the X-ray diffraction study (Castellano *et al.*, 1982) belongs to W1, and this fact and the favorable geometrical bonding parameters [d(OW1-H) = 1.03 Å, d(H $\cdots$ N1) = 2.02 Å, d(OW1$\cdots$N1) = 3.034 Å, angle OW1-H-N1) = 166.2° (Castellano *et al.*, 1978)] (cf. Falk and Knop, 1973; Berglund *et al.*, 1978) seem to indicate that this water (W1) originates the strongest hydrogen bond. Taking into account the correlations established between donor–acceptor distance and the OH stretching wavenumber (Falk and Knop, 1973; Berglund *et al.*, 1978) corrected for the 0.1 Å difference existing between the van der Waals radii of N and O (Rigotti *et al.*, to be published), the weak band at ca. 2600 cm^{-1} could be assigned to this bond. In the same way, we are assigning tentatively the band at 2655 cm^{-1} to the stretching of the other OD bond of the W1 water, and the shoulders at 2670 and 2587 cm^{-1} to the corresponding D_2O stretching modes. It should be pointed out that the wavenumber of the band assigned to the stretching of the least-bonded OD group of W1 equals the highest wavenumber reported for such a stretching in $Na_2[Fe(CN)_5NO] \cdot 2(H_2O + D_2O)$ (2654 cm^{-1}) (Holzbecher *et al.*, 1971), a value which was considered as the highest ever found in crystalline hydrates. Similar values have been found also in the highest hydrates of the alkaline-earth nitroprussides (2658 cm^{-1} in $Ca[Fe(CN)_5NO] \cdot 4H_2O$ (Rigotti *et al.*, to be published; Varetti and Aymonino, 1982), 2650 cm^{-1} in $Sr[Fe(CN)_5NO] \cdot 2H_2O$ (Della Védova *et al.*, 1981), and in $Ba[Fe(CN)_5NO] \cdot 2H_2O$ (Varetti and Aymonino, 1973). In fact an even higher wavenumber (2686 cm^{-1}) has been assigned to an OD stretching in $Ca[Fe(CN)_5NO] \cdot 4H_2O$ (Rigotti *et al.*, to be published; Varetti and Aymonino, 1982). This latter value is quite near to the wavenumber reported for the OD stretching in gaseous HOD (2727 cm^{21}) (Nakamoto, 1978) where no hydrogen bonding exists. The bonding of the OD groups responsible for the bans around 2650 cm^{-1} should be therefore very weak, if it exists at all. The assignment of the corresponding OH and H_2O stretchings follows immediately from the isotopic shifts (see paragraph a above).

Using the same criteria as above, the bands at 2639 and 2616 cm^{-1} are tentatively assigned to the isolated OD bonds of the water W2, and those at 2689 and 2592 cm^{-1} to the D_2O stretchings of this molecule. This assignment seems to be in accordance with the observations made in the HOD bending zone which suggest that the water molecule W1 is more asymmetric than W2, showing therefore the greatest wavenumber difference for the isolated OD stretchings (see above).

In the same way, the bending band at 1593 cm^{-1} is assigned to the more weakly hydrogen-bonded molecules (W2), and that at 1614 cm^{-1} to the W1 water molecules. The corresponding librational bands could be those located at 588 and 343 cm^{-1} for W1 and at 537 and 328 cm^{-1} for W2 molecules, respectively.

As a conclusion, the existence of two different types of waters seems to be

Table 4. Combinations and overtones from the infrared spectrum of
K$_3$[Co(CN)$_5$N$_3$] · nH$_2$O (n = 0,2)

Normal hydrate	Anhydrous	Polarized		Assignments	
		A'	A''		
3910(vvw)		3910^a	3910	3602 + 328	
	3501(vw)				?
	3419(vw)				?
3400(vvw)	3403(vvw)			2053 + 2 × 678	
3388(vvw)		3390			?
3348(vvw)				2053 + 1300	
3321(vvw)		3325			?
3224(vvw)		3224		2 × 1614	
3195(vw)			3197	2 × 1300 + 602	
3155(vvw)		3155	3155		?
		2710			?
			2700	2148 + 555	
		2697		2148 + 549	
	2688(vvw)		2689	2138 + 555	
2642(vvw)	2657(vw)	2643		2053 + 602, 1300 + 2 × 678	
			2635		?
2616(vvw)		2617	2618	2149 + 474, 2149 + 468	
2587(vw)	2600(vw)	2587		2 × 1300	
2570(vvw)			2572	2148 + 423	
2561(vvw)	2565(vw)	2562		2138 + 423, 2148 + 417, 2148 + 414	
2555(vvw)			2554	2138 + 414, 2138 + 417	
2540(vvw)		2541	2542	2124 + 423, 2124 + 417, 2145 + 414	
2521(vvw)		2521	2522		?
2509(vvw)		2511	2510^a	1300 + 2 × 602	
		2420	2420^a		?
		2400			?
			2240		?
		2230			?
		2210			?
			2180		?
1961(w)	1963(w)	1962		1300 + 678	
			1955	1614 + 343	
		1942^a	1940	1614 + 328	
		1922^a	1922	1593 + 328	
			1909	1300 + 602	
		1900			?
			1894		?
		1882			?
	1358(vw)	1365		2 × 678	
		1285			?
1205(vvw)		1205		2 × 602	
		943		2 × 474	
		936	939	588 + 350, 2 × 468	
		928		588 + 343	
		920		549 + 378	
			909	487 + 423	
		900		487 + 418	
		872			?

^{a}Weak band.

proved beyond doubt, although the vibrational differences are not always fully displayed. The clearest evidence is provided by the HOD bending bands.

The assignment of overtones and combination bands

In addition to the bands assigned to fundamentals of the anion and of the water molecules, we have observed many weak absorption bands which may be assigned to overtones and combinations. The symmetry species and activity of the combinations of fundamental modes can be obtained easily by group theory (Cotton, 1967). In this way, any binary combination of modes of A species (either A' or A'') is predicted as infrared active. In the region of high wavenumbers one of the components of the combinations should be a mode such as a CN stretching or the NNN antisymmetric stretching, and the other, a mode of far lower wavenumber such as a CoX (X = C, N) stretching or a Co-ligand bending. The first overtone of the symmetric stretching band of the azido group should appear also in this region, as it commonly occurs in azido compounds (Bryant, 1963). In the low-wavenumber spectral region overtone and combination bands should involve either CoX stretchings and Co-ligand bendings or water librational vibrations. The features assigned to overtones and combination bands are gathered together in Table 4, which also includes the symmetry assignments as deduced from the dichroism of the bands and the proper combinations of the symmetry species of fundamentals in accordance with the multiplication table for the A' and A'' species (Cotton, 1967).

Acknowledgments

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