

Physical Sciences Section

Pakistan J. Sci. Ind. Res., Vol.25 No.4, August 1982

THE RAMAN STUDIES OF TRIHYDROGEN HEXACYANOCOBALTATE(III) $H_3Co(CN)_6$

S.U. Qureshi, B.M. Chadwick, D.A. Long

*Institute of Chemistry, University of Sind,
Jamshoro (Sind), Pakistan*

(Received October 27, 1980 ; revised August 4, 1982)

The Raman spectra of Trihydrogen hexacyanocobaltate(III) has been studied in the solid state and aqueous solution. Solid trihydrogen hexacyanocobaltate(III) $H_3Co(CN)_6$ is unusual in possessing abnormality high value for the wavenumber of the antisymmetric CN stretching vibration and a NHN distance in $H_3Co(CN)_6$ which indicates the shortest N-H-N hydrogen bond yet discovered.

INTRODUCTION

The chemistry of cyano complexes of cobalt has been extensively studied [1]. The hexacyanocobaltate(III) ion, $Co(CN)_6^{3-}$, is a well established species and is a very stable ion. Sharpe [1] has made a "very rough estimate" of the formation constant of $Co(CN)_6^{3-}$ ion as 10^{50} . Even with a large positive value, it is unlikely that an aqueous solution of $H_3Co(CN)_6$, will be thermodynamically stable with respect to dissociation into say $Co(CN)_3$ and cyanide ions. $H_3Co(CN)_6$, a strong tribasic acid, is almost certainly kinetically inert to dissociation of $Co(CN)_6^{3-}$ ion. Exchange of the $Co(CN)_6^{3-}$ ion with labelled cyanide is extremely slow [2,3] though the process is accelerated by the action of light, under the influence of which the following equation takes place:



Radiations of wave length 254,313 or 366 nm are reported [4] to give the same quantum yield. No photoaquation occurs with light of wave length 436 nm [5]. All aqueous solutions of $H_3Co(CN)_6$ used were stored in dark cupboard.

Evaporation to crystallisation of an aqueous solution of $H_3Co(CN)_6$ followed by drying over P_2O_5 or at 100° yields the anhydrous solid acid $H_3Co(CN)_6$. The IR spectrum of solid $H_3Co(CN)_6$ shows a single relatively sharp CN stretching band at 2202 cm^{-1} and a broad absorption, without pronounced structure and little affected by deuteration, between 1900 and 600 cm^{-1} . It was argued [6,7,8] before $H_3Co(CN)_6$ was investigated by X-ray or

neutron diffraction that this broad absorption indicated that symmetrical N-H-N bonds are present. It has also been argued [1] that the fact that the antisymmetric CN stretching vibration is some 70 cm^{-1} higher than in the free ion, indicates that the cyanide ion takes part in bridging [9] and that the near identity of the electronic spectra of $H_3Co(CN)_6$ and $K_3Co(CN)_6$ [10] indicates that this bridging only slightly affects the $Co(CN)_6^{3-}$ ion. It should be noted however that appreciable shifts can occur in the antisymmetric CN stretching wave number for reason other than CN bridging. Thus Armstrong and Chadwick [11] have established that this wave number varies from 2106 cm^{-1} in $Li_3Co(CN)_6 \cdot 8H_2O$. A neutron diffraction study of $H_3Co(CN)_6$ and $D_3Co(CN)_6$ has established the solid structure. The $Co(CN)_6^{3-}$ ions are centred at the corners of a rhombohedral unit cell with $a=6.43$, $C=5.69\text{ \AA}$, $Z=1$. Each H^+ ion is linearly coordinated by two nitrogen atoms of different $Co(CN)_6^{3-}$ ions. The NHN distance is 2.60 \AA , the shortest N-H-N hydrogen bond yet formed. It is not clear whether it is a symmetric hydrogen bond. The objectives of this work is to obtain the Raman spectrum of solid and aqueous $H_3Co(CN)_6$, and to establish whether the Raman spectrum provides evidence for strong hydrogen bonding $H_3Co(CN)_6$ was prepared by the interaction of $Ag_3Co(CN)_6$ and HCl.

EXPERIMENTAL

1. *Preparation of Trisilver Hexacyanocobaltate(III).*
 $Ag_3Co(CN)_6 \cdot AgNO_3$ (B.D.H. AnalaR, 25.5 g) was dissolved in the minimum amount of water (200 ml);

$K_3Co(CN)_6$ (B.D.H. 16.6 g) dissolved in the minimum amount of water (50 ml); was added slowly from a burette with constant stirring of the mixture. The contents were stirred magnetically for 24 hr in the dark. After this digestion or ageing of the precipitate it was filtered at the suction pump and washed liberally with hot water, followed by absolute alcohol and sodium-dried ether. The weight of the product was 21.4 g which is a yield of 79 % based on $K_3Co(CN)_6$.

2. *Preparation of Trihydrogen Hexacyanocobaltate(III) $H_3Co(CN)_6$.* To $Ag_3Co(CN)_6$ (2.5 g) a large excess amount of concentrated HCl (15 ml; B.D.H. AnalaR) was added drop by drop and the slurry was magnetically stirred for 30 min. It was then filtered and the filtrate was evaporated to dryness at the room temperature.

3. *Raman Spectroscopy.* The Raman spectra of aqueous and solid $H_3Co(CN)_6$ were obtained using 500 mW of 488.0 nm excitation from a spectra-physics argon ion laser. The spectra under the polarised and depolarised conditions, recorded by involving the collection of all the Raman radiation at 90° from the plane polarised incident radiation, is reported in Figs. 1 and 2. The spectrometer was calibrated using Neon lamp and the wavenumbers of bands and incompletely resolved features listed Tables 2 and 3 are accurate to $\pm 1 \text{ cm}^{-1}$ and $\pm 3 \text{ cm}^{-1}$ respectively. The aqueous $H_3Co(CN)_6$ was 0.3M.

RESULT AND DISCUSSION

(i) *Introduction:* The 33 degrees of vibrational freedom of an octahedral $Co(CN)_6^{3-}$ ion lead to an expected 13 fundamental vibrational wave numbers; six of which are Raman active (Table 1). The experimental results and assignments for aqueous $H_3Co(CN)_6$ are listed in Table 2 where it is compared with the corresponding values for aqueous $K_3Co(CN)_6$ and are illustrated in Figs. 1 and 2. The experimental results and assignments for solid $H_3Co(CN)_6$ are listed in Table 3 where they are compared with the corresponding values for solid $K_3Co(CN)_6$ and are illustrated in Figs. 3 and 4.

(ii) *Trihydrogen Hexacyanocobaltate in Aqueous Solution.* The results obtained are very similar to those for aqueous $K_3Co(CN)_6$. Only three fundamentals can be observed with certainty, the two CN stretching vibrations and the totally symmetric CoC stretching vibration. The wavenumbers of each fundamental are identical within experimental error for aqueous $H_3Co(CN)_6$ and are larger than the corresponding wavenumbers for aqueous $K_3Co(CN)_6$. This increase is largest for ν_3 , the a_{1g} CN stretching vibration (8 cm^{-1}) Another interesting observa-

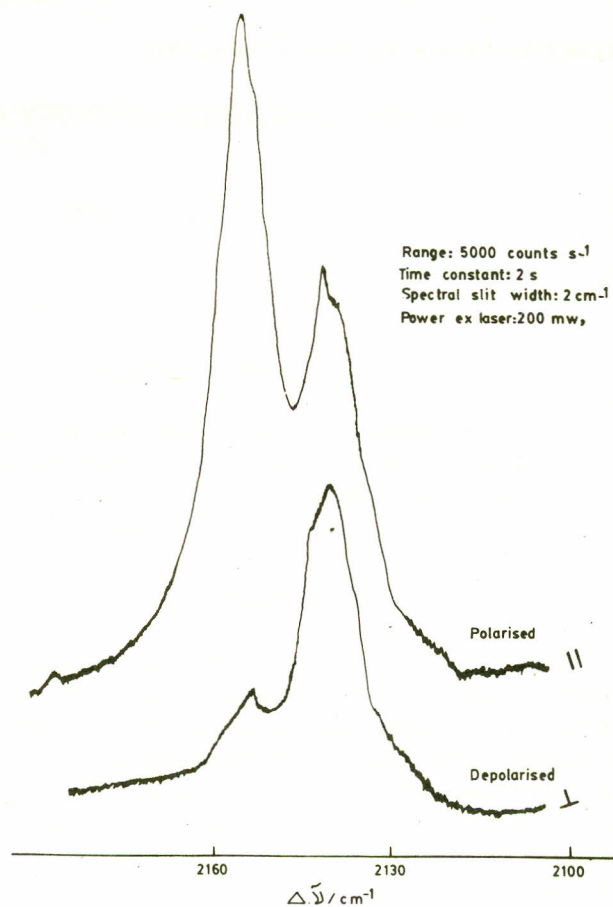


Fig. 1. The Raman spectra of $H_3Co(CN)_6$ in aqueous solution in the CN stretching ($2200\text{--}2100 \text{ cm}^{-1}$) region, recorded under polarised and depolarised conditions with $\lambda_{exc} = 488.0 \text{ nm}$.

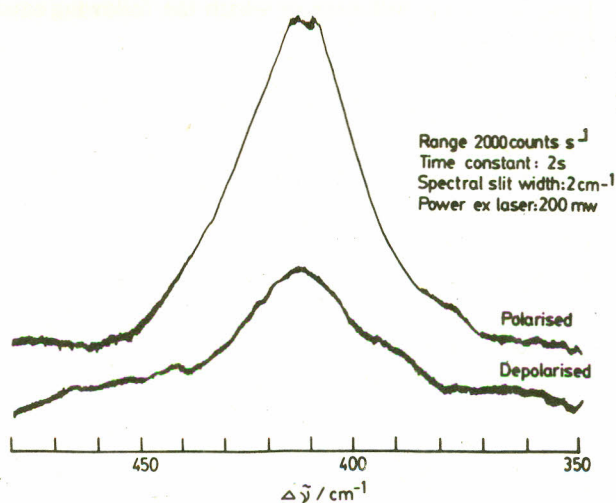


Fig. 2. The Raman spectra of $H_3Co(CN)_6$ in aqueous solution in CoC stretching ($480\text{--}350 \text{ cm}^{-1}$) region, recorded under polarised and depolarised conditions with $\lambda_{exc} = 488.0 \text{ nm}$.

tion is that the half-widths of ν_2 , the totally symmetric CoC stretching vibration are appreciable larger for aqueous

Table 1. Normal modes of vibration of a $\text{Co}(\text{CN})_6^{3-}$ ion of O_h symmetry.

Fundamentals	Symmetry species	Activity	Approximate description
ν_1	a_{1g}	R	ν (CN)
ν_2	a_{1g}	R	ν (CoC)
ν_3	e_g	R	ν (CN)
ν_4	e_g	R	ν (CoC)
ν_5	f_{1g}	Inactive	δ (CoCN)
ν_6	f_{1u}	IR	ν (CN)
ν_7	f_{1u}	IR	δ (CoCN)
ν_8	f_{1u}	IR	ν (CoC)
ν_9	f_{1u}	IR	δ (CCoC)
ν_{10}	f_{2g}	R	δ (CoCN)
ν_{11}	f_{2g}	R	δ (CCoC)
ν_{12}	f_{2g}	Inactive	δ (CoCN)
ν_{13}	f_{2g}	Inactive	δ (CCoC)

R = Raman; IR = Infra-red.

Table 2. Wavenumbers (cm^{-1}) of Raman-active fundamentals of $\text{Co}(\text{CN})_6^{3-}$ for aqueous $\text{H}_3\text{Co}(\text{CN})_6$ compared to those for $\text{K}_3\text{Co}(\text{CN})_6$.

Fundamental	Symmetry species	Wavenumbers/ cm^{-1}	
		$\text{K}_3\text{Co}(\text{CN})_6$ (a)	$\text{H}_3\text{Co}(\text{CN})_6$ (b)
ν_1	a_{1g}	2149	2154 (vs,pol)
ν_3	e_g	2137	2139(s,dep)
ν_{10}	f_{2g}	485	—
ν_2	a_{1g}	406	414 (pol)
ν_4	e_g	—	—

(a) Ref.11; (b) Present work.

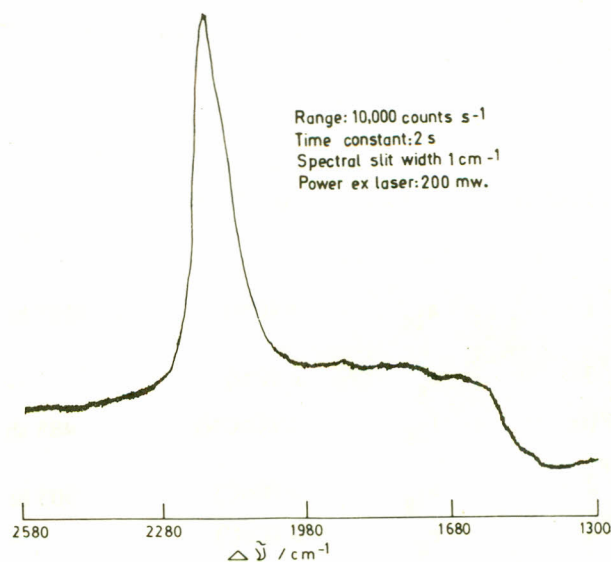


Fig. 3. The Raman spectra of solid $\text{H}_3\text{Co}(\text{CN})_6$ in the CN stretching $2500\text{-}1380\text{ cm}^{-1}$ region with $\lambda_{\text{exc}} = 488.0\text{ nm}$.

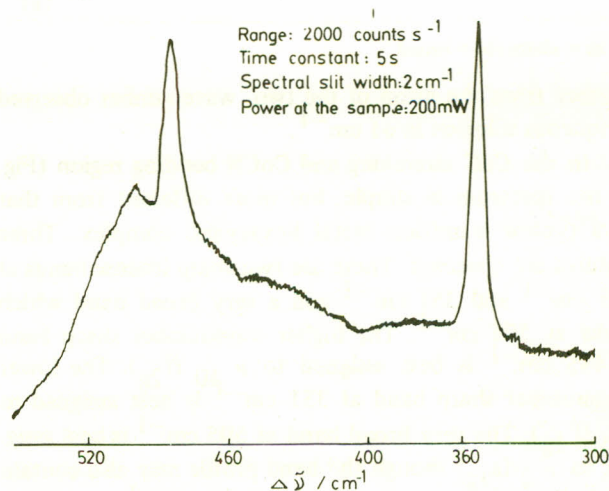


Fig. 4. The Raman spectrum of solid $\text{H}_3\text{Co}(\text{CN})_6$ in the $520\text{-}300\text{ cm}^{-1}$ region at room temperature, with the $\lambda_{\text{exc}} = 488.0\text{ nm}$.

$\text{H}_3\text{Co}(\text{CN})_6$ than for aqueous $\text{K}_3\text{Co}(\text{CN})_6$.

(iii) $\text{H}_3\text{Co}(\text{CN})_6$ in Solid State. The Raman spectrum of solid $\text{H}_3\text{Co}(\text{CN})_6$ is completely different to that of aqueous $\text{H}_3\text{Co}(\text{CN})_6$. In the CN stretching region (Fig.3) only one very strong broad band at 2207 cm^{-1} is obtained. This feature must represent ν_1 (a_{1g}) and ν_3 (e_g). This is the first solid hexacyanocobaltate(III) complex where it has not been possible to observe the two Raman CN stretching vibrations. In other solid salts the wavenumber separation between these two modes is never large with minimum separation being 11 cm^{-1} for $\text{Cs}_2\text{LiCo}(\text{CN})_6$. The failure to observe both modes for solid $\text{H}_3\text{Co}(\text{CN})_6$ must be a consequence of broadening either one or both modes. It should be noted that the upward shift in wave-

Table 3. Wavenumber (cm^{-1}) of fundamentals of the $\text{Co}(\text{CN})_6^{3-}$ ion in solid $\text{H}_3\text{Co}(\text{CN})_6$ observed in their Raman spectra.

Fundamentals	Symmetry species	Approximate description.	$\text{H}_3\text{Co}(\text{CN})_6$ wavenumbers/ cm^{-1}
ν_1	a_{1g}	ν (CN)	2207 br
ν_3	e_g	ν (CN)	—
ν_{10}	f_{2g}	δ (CoCN)	485 sh
ν_2	a_{1g}	ν (CoC)	505 br
ν_4	e_g	ν (CoC)	—
ν_5	f_{1g}	δ (CoCN)	331 sh

(a)

(a) sh = sharp; br = broad.

number from the mean of the two wavenumber observed in aqueous solution in 61 cm^{-1} .

In the CoC stretching and CoCN bending region (Fig. 4) the spectrum is simple, but more different from that of a typical transition metal hexacyano complex. Three features are observed. There are two sharp intense bands at 485 cm^{-1} and 351 cm^{-1} and a very broad band which peaks at 505 cm^{-1} . The higher wavenumber sharp band at 485 cm^{-1} is best assigned to ν_{10} (f_{2g}). The lower wavenumber sharp band at 351 cm^{-1} is best assigned to ν_5 (f_{1g}). The very broad band at 505 cm^{-1} is best assigned to ν_2 (a_{1g}) though the band profile may also contain ν_4 (e_g). Assignment of ν_2 (a_{1g}) at 505 cm^{-1} means that this fundamental has under gone an upward shift in wavenumbers of 91 cm^{-1} .

CONCLUSION

The Raman spectrum of solid $\text{H}_3\text{Co}(\text{CN})_6$ is drastically different from that of aqueous $\text{H}_3\text{Co}(\text{CN})_6$. There are appreciable upward wavenumber shifts in ν_1 (a_{1g}), ν_3 (e_g) and ν_2 (a_{1g}). There is also the remarkable broadening of ν_1 (a_{1g}), and or ν_3 (e_g) and of ν_2 (a_{1g}) and possible

also ν_4 (e_g). Finally there is the large intensification of ν_{10} (f_{2g}) and specially of ν_5 (f_{1g}). It is included that the Raman spectrum of $\text{H}_3\text{Co}(\text{CN})_6$ provides substantial empirical evidence of strong hydrogen bonding and to a greater extent than does the IR spectrum. This evidence is the upward wavenumber shifts and broadening of the CN and CoC stretching vibrations, the intensification of the formally f_{2g} CoCN bending vibration and perhaps the most noteworthy the intensification of the formally f_{1g} CoCN bending vibration. No evidence was found of bands assignable to NH stretching and NHN bending models.

Acknowledgement. We are thankful to Ministry of Education, Government of Pakistan for providing financial assistance to one of us (S.U.Q).

REFERENCES

1. A. G. Sharpe, *The Chemistry of Cyano Complexes of the Transition Metals* (Academic Press, London, 1976).
2. A.W. Adamson, J.P. Walker and M. Volpe, *J. Am. Chem. Soc.*, **72**, 4030 (1950).
3. A.G. Macdiarmid and N.F. Hall, *J. Am. Chem. Soc.*, **76**, 4222 (1954).
4. L. Moggi, F. Bolletta, V. Balzani and F.J. Scandola, *J. Inorg. Nucl. Chem.*, **28**, 2589 (1966).
5. R. Matsushima, *Chem Lett. Japan*, 115 (1973).
6. D.F. Evans, D. Jones and G. Wilkinson, *J. Chem. Soc.*, 3164 (1964).
7. W. Beck and H.S. Smedal, *Z Naturforsch.*, **20b**, 109 (1965).
8. A. Luddi, H. U. Gudel and V. Dvorak, *Helv. Chim. Acta.*, **50**, 2035 (1967).
9. D.A. Dows, A Haim and W.K. Wilmarth, *J. Inorg. Nucl. Chem.*, **21**, 33 (1961).
10. H. U. Gudel, A Luddi and H. Burki, *Helv. Chim. Acta.*, **51**, 1383 (1963).
11. J.R. Armstrong and B.M. Chadwick. Unpublished observations (J.R. Armstrong Ph.D Thesis, Bradford University, 1974).