

## The Raman Studies of Trilithium Hexacyanocobaltate (III). $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$

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**Summary :** The Raman spectra of trilithium hexacyanocobaltate(III) have been studied in the solid state and aqueous solution. The Raman spectra are discussed from the point of view of possible lithium bonding present in solid  $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$ .

### Introduction.

The chemistry of cyano complexes of cobalt has been extensively studied<sup>1</sup>. The hexacyanocobaltate(III) ion,  $\text{Co}(\text{CN})_6^{3-}$  is a well established species and is a very stable ion. Sharpe<sup>1</sup> has made a very rough estimate of the formation constant of  $\text{Co}(\text{CN})_6^{3-}$  ion as  $10^{50}$ . Even with such large positive value, it is unlikely that an aqueous solution of  $\text{Li}_3\text{Co}(\text{CN})_6$  will be thermodynamically stable with respect to dissociation into say  $\text{Co}(\text{CN})_3$  and cyanide ions. Exchange of the  $\text{Co}(\text{CN})_6^{3-}$  ion with labelled cyanide is extremely slow<sup>2, 3</sup> though the process is accelerated by the action of light, under the influence of which the following aquation takes place.



Radiation of wavelength 254, 313 or 366 nm are reported<sup>4</sup> to give the same quantum yield. No photoaquation occurs with light of wavelength 436 nm<sup>5</sup>. All aqueous solutions of  $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$  used were stored in a dark cupboard.

The present paper is a study of Raman spectrum of solid and aqueous  $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$  and it also establishes whether the shift in wavenumber of the antisymmetric CN stretching vibration of  $\text{Co}(\text{CN})_6^{3-}$  with change of cation is paralleled by similar change in the two Raman active CN stretching vibrations.

### Experimental

It was proposed to prepare  $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$  from the interaction of  $\text{Ag}_3\text{Co}(\text{CN})_6$  and LiCl. Trisilver hexacyanocobaltate(III) was first prepared by interaction of tripotassium hexacyanocobaltate and silver nitrate.

#### 1. Preparation of trisilver hexacyanocobaltate(III). $\text{Ag}_3\text{Co}(\text{CN})_6$ .

$\text{AgNO}_3$  (B.D.H. Analar; 25.5g) was dissolved in the minimum amount of water (200 ml),  $\text{K}_3\text{Co}(\text{CN})_6$  (B.D.H. 16.6g), dissolved in the minimum amount of water (50ml), was added slowly from a burette with constant stirring of the mixture. The contents were stirred magnetically for 24 hours in the dark. After the digestion or ageing of 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 21.4g (79% yield based on  $\text{K}_3\text{Co}(\text{CN})_6$ ).

#### 2. Preparation of Trilithium hexacyanocobaltate(III) $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$ .

$\text{Ag}_3\text{Co}(\text{CN})_6$  (6.73g) was suspended in 35 ml of water and stirred magnetically. Anhydrous LiCl (B.D.H. 1.59g) dissolved in 10ml of water was added to the suspension. During the addition of LiCl the contents were magnetically stirred for ½ hour. The solution was filtered and the precipitate was washed with water. The washings and filtrate were combined together and the entire solution was evaporated to dryness in a rotary evaporator under vacuum.  $\text{Li}_3\text{Co}(\text{CN})_6$  was precipitated from the highly concentrated solution by adding 150ml of dioxan. Finally the precipitate was filtered and dried under vacuum. The weight of the product was 3.9g which (82% yield based on  $\text{Ag}_3\text{Co}(\text{CN})_6$ ).

#### 3. Raman Spectroscopy.

The Raman spectra of aqueous and solid

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$\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$  were obtained using 500 mW radiation at 488.0 nm from a Spectra-Physics argon ion laser. The spectrum under the polarised and depolarised conditions was recorded by the collection of all the Raman radiation at  $90^\circ$  from the plane polarised incident radiation, is reported in the Figs. 1 and 2. The spectrometer was calibrated using a neon lamp and the wavenumbers of bands and incompletely resolved features listed in Table 2 and 3 are accurated to  $\pm 1 \text{ cm}^{-1}$  and  $\pm 3 \text{ cm}^{-1}$  respectively. The aqueous  $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$  was a saturated solution.

## Results and Discussion

### i.) Introduction:

The 33 degrees of vibrational freedom of an

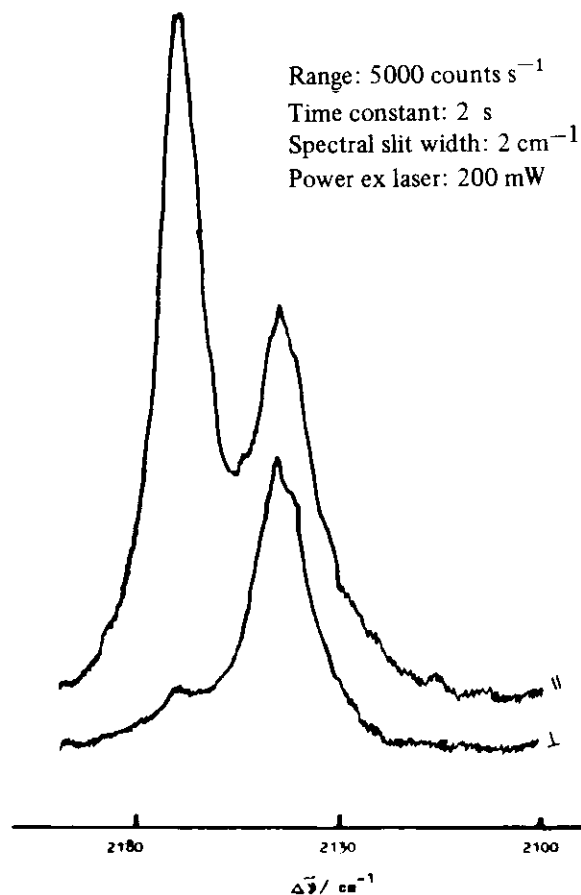


Fig. 1: The Raman spectra of  $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$  in aqueous solution in the CN stretching ( $2180\text{--}2100 \text{ cm}^{-1}$ ) region, recorded under polarised and depolarised conditions, with  $\lambda_{\text{exc}} = 488.0 \text{ nm}$ .

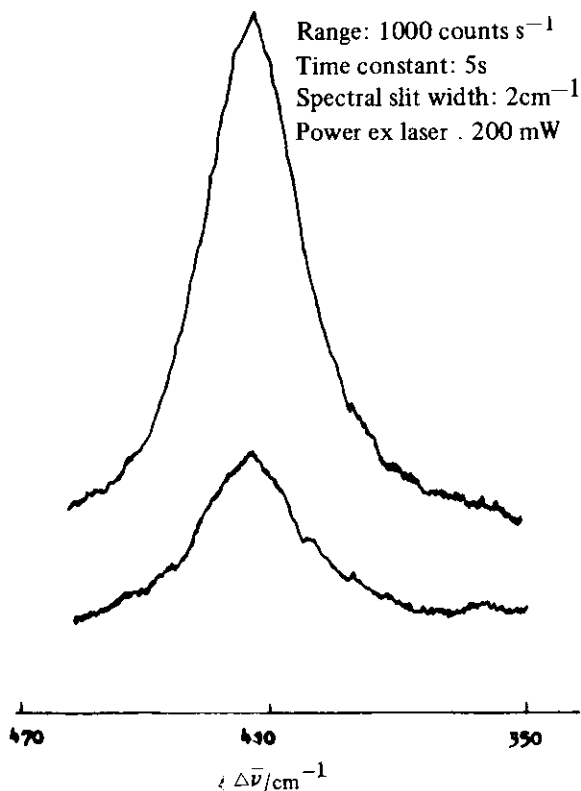


Fig. 2: The Raman spectra of  $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$  solution in the CoC stretching ( $470\text{--}350 \text{ cm}^{-1}$ ) region, recorded under the polarised and depolarised conditions with  $\lambda_{\text{exc}} = 488.0 \text{ nm}$ .

Table No. I: Normal modes of vibration of a  $\text{Co}(\text{CN})_6^{3-}$  ion of  $O_h$  symmetry.

Fundamentals	Symmetry species	Activity	approximate description.
$\nu_1$	$a_{1g}$	R	$\nu(\text{CN})$
$\nu_2$	$a_{1g}$	R	$\nu(\text{CoC})$
$\nu_3$	$e_g$	R	$\nu(\text{CN})$
$\nu_4$	$e_g$	R	$\nu(\text{CoC})$
$\nu_5$	$f_{1g}$	inactive	$\xi_{\infty}(\text{CoCN})$
$\nu_6$	$f_{1u}$	IR	$\nu(\text{CN})$
$\nu_7$	$f_{1u}$	IR	$\xi(\text{CoCN})$
$\nu_8$	$f_{1u}$	IR	$\nu(\text{CoC})$
$\nu_9$	$f_{1u}$	IR	$\xi(\text{CCoC})$
$\nu_{10}$	$f_{2g}$	R	$\xi(\text{CoCN})$
$\nu_{11}$	$f_{2g}$	R	$\xi(\text{CCoC})$
$\nu_{12}$	$f_{2g}$	inactive	$\xi(\text{CoCN})$
$\nu_{13}$	$f_{2g}$	inactive	$\xi(\text{CCoC})$

R = Raman IR = Infra-red.

Table No. 2: Wavenumbers ( $\text{cm}^{-1}$ ) of Raman-active fundamentals of  $\text{Co}(\text{CN})_6^{3-}$  for aqueous  $\text{Li}_3\text{Co}(\text{CN})_6$  and compared to those for  $\text{K}_3\text{Co}(\text{CN})_6$ .

Fundamental	Symmetry species	Wavenumbers $\text{cm}^{-1}$	
		(a) $\text{K}_3\text{Co}(\text{CN})_6$	(b) $\text{LiCo}(\text{CN})_6$
$\nu_1$	$a_{1g}$	2149	2154(vs.pol)
$\nu_3$	$e_g$	2137	2138(s, dep)
$\nu_{10}$	$f_{2g}$	485	—
$\nu_2$	$a_{1g}$	406	414 (s,pol)
$\nu_4$	$e_g$	—	—

(a) Ref. 6 (b) Present work.

octahedral  $\text{Co}(\text{CN})_6^{3-}$  ion lead to an expected 13 fundamental vibrational wavenumbers, six of which are Raman active (Table 1). The experimental results and assignments for aqueous  $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$  are listed in Table 2, where they are compared with the corresponding value for aqueous  $\text{K}_3\text{Co}(\text{CN})_6$  and are illustrated in Fig. 1 and 2. The experimental results and assignments for solid  $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$  are listed in Table 3 where they are compared with the corresponding value for solid  $\text{K}_3\text{Co}(\text{CN})_6$  and are illustrated in Figs. 3 and 4.

### ii) Aqueous Trilithium hexacyanocobaltate(III).

The results obtained are very similar to those

Table 3: Wavenumber ( $\text{cm}^{-1}$ ) of fundamentals of the  $\text{Co}(\text{CN})_6^{3-}$  ion in solid  $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$  and observed in their Raman Spectra.

Fundamental	Symmetry species	Approximate Description	$\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$ Wavenumber/ $\text{cm}^{-1}$
$\nu_1$	$a_{1g}$	$\nu(\text{CN})$	2179
$\nu_3$	$e_g$	$\nu(\text{CN})$	2164
$\nu_{10}$	$f_{2g}$	$\zeta(\text{CoCN})$	485
$\nu_2$	$a_{1g}$	$\nu(\text{CoC})$	457
$\nu_4$	$e_g$	$\nu(\text{CoC})$	430
$\nu_5$	$f_{1g}$	$\zeta(\text{CoCN})$	323

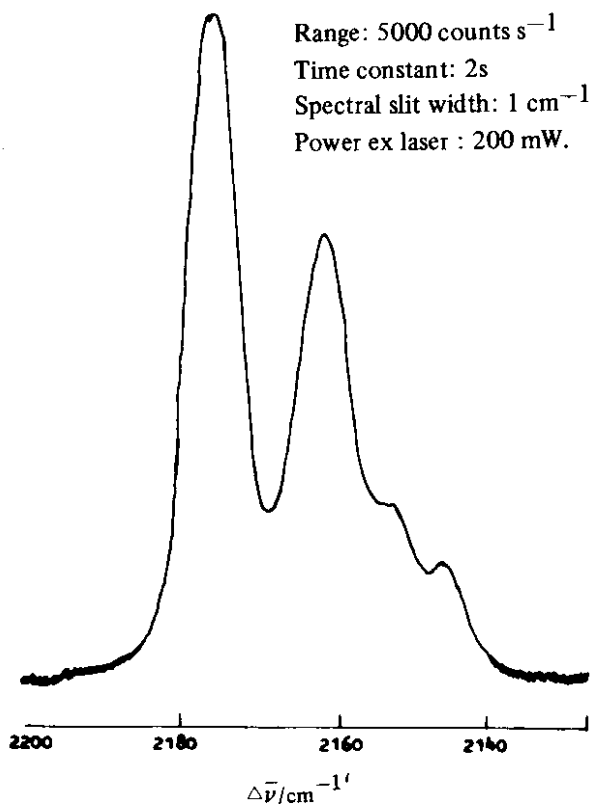


Fig. 3: The Raman spectrum of solid  $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$  at room temperature in the CN stretching ( $2200-2120 \text{ cm}^{-1}$ ) region, with  $\lambda_{\text{exc}} = 488.0 \text{ nm}$ .

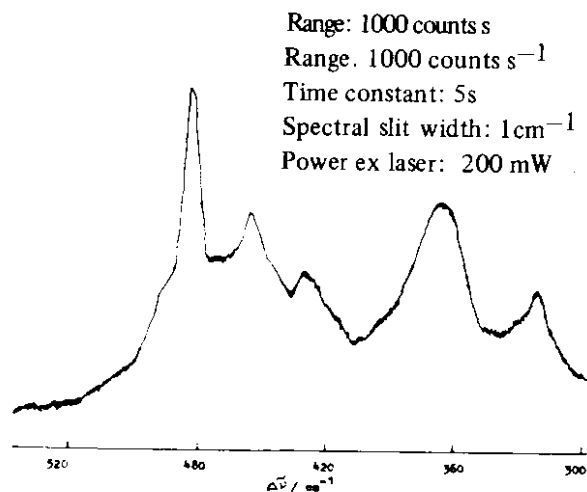


Fig. 4: The Raman spectrum of solid  $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$  at room temperature in the  $520-300 \text{ cm}^{-1}$  region with  $\lambda_{\text{exc}} = 488.0 \text{ nm}$ .

for aqueous  $\text{K}_3\text{Co}(\text{CN})_6$ . Only three fundamentals can be observed with certainty—the two CN stretching vibration. The wavenumbers of each funda-

mental are identical within experimental error for aqueous  $\text{Li}_3\text{Co}(\text{CN})_6$  and are larger than the corresponding wavenumbers for aqueous  $\text{K}_3\text{Co}(\text{CN})_6$ . This increase is largest for  $\nu_3$ , the  $a_{1g}$  CN stretching vibration ( $8 \text{ cm}^{-1}$ ). Another interesting observation is that the half widths of  $\nu_2$ , the totally symmetric CoC stretching vibration are appreciably larger for aqueous  $\text{Li}_3\text{Co}(\text{CN})_6$  than for aqueous  $\text{K}_3\text{Co}(\text{CN})_6$  and is slightly larger than that of  $\text{Li}_3\text{Co}(\text{CN})_6$  ( $22.8 \text{ cm}^{-1}$ ).

### iii) Solid $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$

Two unambiguous assignments can be made for the bands observed in the Raman spectrum of solid  $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$ . In the CN stretching region two strong bands are observed (Fig. 3) The higher wavenumber, band at  $2179 \text{ cm}^{-1}$  is stronger and sharper and is assigned to  $\nu_1 (a_{1g})$ , the totally symmetric CN stretching vibration. The other band at  $2164 \text{ cm}^{-1}$  is assigned to  $\nu_3(\text{eg})$ . It should also be noted that there are two shoulders on the low wavenumber side of  $\nu_3(\text{eg})$  at  $2154 \text{ cm}^{-1}$ . It is possible that the shoulder at  $2148 \text{ cm}^{-1}$  is a genuine coincidence with  $\nu_6 (f_{1u})$  which has been observed in the infra-red spectrum. The assignments of  $\nu_1 (a_{1g})$  and  $\nu_3(\text{eg})$  mean that these two fundamentals, each shift upwards by  $25 \text{ cm}^{-1}$  and  $26 \text{ cm}^{-1}$  respectively on going from the aqueous solution phase to solid phase. These assignments of  $\nu_1 (a_{1g})$  and  $\nu_3(\text{eg})$  also mean that these two fundamentals shift upwards by  $18 \text{ cm}^{-1}$  and  $14 \text{ cm}^{-1}$  respectively in going from solid  $\text{Cs}_2\text{LiCo}(\text{CN})_6$  to  $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$ . These latter shifts are perhaps even more surprising because in the  $\text{Cs}_2\text{LiCo}(\text{CN})_6$  structure every CN group forms part of a CN..... $\text{Li}^+$ .....NC bridge.

While the spectrum of the CN stretching region is characteristic of transition metal hexacyanides in general the spectrum of the CoC stretching and CoCN bending regions is not.

First, there appears to be a very broad band centred at  $470 + 5 \text{ cm} \pm$  with three bands superimposed on it. This very broad band could possibly be a water liberation.

Secondly, of the remaining band, the sharpest and most intense is that at  $485 \text{ cm}^{-1}$ . Because of its intensity and profile the most obvious assignment is to  $\nu_2 (a_{1g})$ . However this assignment has at least two serious drawbacks. It would mean a shift in  $\nu_2$

( $a_{1g}$ ) on going from the aqueous solution phase to the solid phase of  $71 \text{ cm}^{-1}$ . It would also mean a shift in  $\nu_2 (a_{1g})$  on going from solid  $\text{Cs}_2\text{LiCo}(\text{CN})_6$  to solid  $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$  of  $53 \text{ cm}^{-1}$ . There is an alternative assignment. Armstrong and Chadwick have shown that the wavenumber of the  $\nu_{10}(f_{2g})$  fundamental is not at all sensitive to change in cation. Thus it varies from  $479 \text{ cm}^{-1}$  in  $\text{Ti}_3\text{Co}(\text{CN})_6$  through  $\text{Cs}_3\text{Co}(\text{CN})_6$  and  $\text{K}_3\text{Co}(\text{CN})_6$  to only  $485 \text{ cm}^{-1}$  in  $\text{Cs}_2\text{LiCo}(\text{CN})_6$ . Thus the band at  $485 \text{ cm}^{-1}$  in  $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$  could well be  $\nu_{10}(f_{2g})$ . The difficulty presented by this alternative assignment is that there is no obvious explanation of why the intensity of  $\nu_{10}(f_{2g})$  when compared to that of  $\nu_2(a_{1g})$  and  $\nu_4(\text{eg})$  should be weakest in  $\text{Cs}_2\text{LiCo}(\text{CN})_6$  and strongest in  $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$ . Thus, at this stage it is not clear whether the band at  $485 \text{ cm}^{-1}$  is  $\nu_2(\text{eg})$  or  $\nu_{10}(f_{2g})$ .

Thirdly, there is a moderately intense band at  $367 \text{ cm}^{-1}$ . If it is an internal fundamental of  $\text{Co}(\text{CN})_6^{3-}$  the most plausible assignment would be to  $\nu_5(f_{1g})$ , which is Raman inactive under  $\text{O}_h$ . However Armstrong and Chadwick<sup>6</sup> have shown that the wavenumber of this fundamental like that of  $\nu_{10}(f_{2g})$  is not at all sensitive to variation in cation, changing only from  $335 \text{ cm}^{-1}$  to  $344 \text{ cm}^{-1}$  in the four salts previously mentioned. Also when it is observed in the Raman spectrum it is only a very weak feature. Perhaps the least unsatisfactory assignment is that the moderately intense band at  $367 \text{ cm}^{-1}$  is another librational mode of water.

Fourthly, the next most intense band is at  $457 \text{ cm}^{-1}$ . Perhaps the best assignment here is that of  $\nu_2(a_{1g})$ . This would mean an upward shift in wavenumber of  $43 \text{ cm}^{-1}$  on going from the aqueous solution to the solid phase, and of  $25 \text{ cm}^{-1}$  on going from solid  $\text{Cs}_2\text{LiCo}(\text{CN})_6$  to solid  $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$ . Another factor is favour of this assignment is that  $\nu_8(f_{1u})$  is known to be at  $455 \text{ cm}^{-1}$  from the infra-red spectrum; and  $\nu_2(a_{1g})$  and  $\nu_8(f_{1u})$  always have a similar wavenumbers in salts of  $\text{Co}(\text{CN})_6^{3-}$ . Armstrong and Chadwick in the four salts previously mentioned observed a maximum deviation for ( $\nu_8 - \nu_2$ ) of  $11.5 \text{ cm}^{-1}$  in  $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$  the deviation is so small,  $-2 \text{ cm}^{-1}$ , that it raises the question of whether the Raman band at  $457 \text{ cm}^{-1}$  and the infra-red band at  $455 \text{ cm}^{-1}$  are a genuine coincidence. This possibility cannot be

completely excluded but it is rejected on the grounds that formally active infra-red bands only occur weakly, if at all, in the Raman spectra of transition metal hexacyano-complexes.

Fifthly, there are two relatively weak bands at  $430\text{ cm}^{-1}$  and  $330\text{ cm}^{-1}$ . Given the assignments of  $\nu_2(a_{1g})$  at  $457\text{ cm}^{-1}$  then the band at  $430\text{ cm}^{-1}$  is plausibly assigned to  $\nu_4(eg)$ . Perhaps the least unsatisfactory assignment of the band at  $323\text{ cm}^{-1}$  is to  $\nu_5(f_{1g})$ .

### Conclusion

i. The Raman spectrum of solid  $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$  is significantly different from that of aqueous  $\text{Li}_3\text{Co}(\text{CN})_6$ . There are appreciable upward wave-number shifts in  $\nu_1(a_{1g})$ ,  $\nu_3(eg)$  and  $\nu_2(a_{1g})$ . There is also the remarkable intensification of  $\nu_{10}(f_{2g})$  which is unobserved in solution but is the strongest band in  $500\text{--}300\text{ cm}^{-1}$  region in the solid state.

ii. It is concluded that the Raman spectrum of solid  $\text{Li}_3\text{Co}(\text{CN})_6 \cdot 8\text{H}_2\text{O}$  provides sufficient empirical evidence of "Lithium" bonding and stronger "Lithium" bonding than is present in  $\text{Cs}_2\text{LiCo}(\text{CN})_6$ . This evidence is upward shifts of the CN and CoC

stretching vibrations, and the intensification of the formally  $f_{2g}$ -CoCN bending vibration.

### Acknowledgement

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