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Low-Frequency Infrared and Single-Crystal Raman Spectra of Dipotassium Tetracyanozincate(II)

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On the basis of far-infrared and single-crystal Raman experiments a definitive assignment is given for all the active and inactive modes of $K_2Zn(CN)_4$. A comparison is made with assignments for nickel tetracarbonyl.

Introduction

The vibrational assignment for the tetracyanozincate(II) anion has not been adequately proved. Although this may seem surprising, we note that detailed assignment of the vibrational spectrum of nickel tetracarbonyl has only recently been achieved, even though it has the same high symmetry and favorable selection rules.[1]

The ir spectrum of $K_2Zn(CN)_4$ was considered in detail by Jones.[2] Although he was unable to make direct observations below *ca.* 280 cm^{-1}, being then equipped with a CsBr prism instrument, lower frequency modes were assigned by means of an analysis of combination bands. Two polarized bands (2157, 347 cm^{-1}) have been found in the Raman spectrum of an aqueous solution, and the solid is reported to show further bands at 317, 125, and 92 cm^{-1}.[3] Both ir and Raman spectra are evidently incomplete, and no experimental distinction has been made, as yet, between the Raman-active E_g and T_{2g} modes. We have studied oriented single crystals to complete the Raman assignment but, as the material is isotropic, we restricted far-ir observations to mulls.

Experimental Section

The complex was prepared by mixing hot, saturated aqueous solutions of hydrated zinc nitrate and potassium cyanide in stoichiometric proportions. Upon cooling, a crop of fine crystals was obtained which were recrystallized from hot water. Slow evaporation of an aqueous solution of the purified material yielded small crystals which were used as seeds for the growth of larger specimens by a thermal convection method.[4] The large crystals were regular octahedra except that one vertex was absent where it had been attached to the support. For the Raman experiments faces were ground normal to axes running through the vertices giving a cube of form (100) of side approximately 4 mm. The optical quality was good.

Raman spectra were obtained using a Coderg PH1 spectrometer with 488.0-nm excitation. A "Cryocirc" cryostat was used. Frequencies are accurate to ±1.5 cm^{-1}. Ir spectra were recorded using an FS-720 Fourier spectrometer; frequencies are accurate to ±2 cm^{-1}.

Results

Selection Rules. $K_2Zn(CN)_4$ is cubic, $Fd3m$ (O_h^7) with $Z = 8$.[5] There are therefore two formula units in the primitive cell. Factor group analysis[6] yields the results

$$\Gamma\,(\text{internal modes}) = 2\,A_{1g} + 2\,E_g + T_{1g} + 4T_{2g} + 2\,A_{2u} + 2\,E_u + 4\,T_{1u} + T_{2u}$$

$$\Gamma\,(\text{anion rotatory}) = T_{1g} + T_{2u}$$

$$\Gamma\,(\text{translatory}) = T_{2g} + A_{2u} + E_u + 2\,T_{1u} + T_{2u}$$

Only T_{1u} modes are ir active and a simple six-band spectrum is therefore expected. T_{1g} and T_{2u} modes are inactive, ruling out observation of the rotatory modes. A_{1g}, E_g, and T_{2g} modes are Raman active by virtue of the tensor components shown on the correlation diagram in Table I. In this crystal both molecular and site symmetries are T_d; it therefore forms an excellent case for examination of the strength of the correlation field in a complex cyanide crystal since any frequency difference between T_{2g} and T_{1u} internal modes is entirely of this origin, if the possibility of interaction with lattice modes of these symmetry species is neglected.

Single-Crystal Spectra. The crystals were of good optical quality; consequently good extinctions were obtained between spectra associated with diagonal and off-diagonal tensor components, respectively. Details are shown in Tables II and III and in Figures 1 and 2. Better resolved spectra were obtained at liquid nitrogen temperature but the assignment was quite clear even from data collected at ambient temperature, although the 357-cm^{-1} band was only seen clearly at low temperature. We did not observe a band at 92 cm^{-1}, but in other respects there is no disagreement with the earlier Raman work.[3]

Discussion

Assignment of Raman and Infrared Data. Assignment of T_{2g} modes is unequivocal since only this species is associated with off-diagonal tensor components. Experimental distinction between A_{1g} and E_g modes is not possible on the basis of single-crystal spectra; however, the two a_1 (in T_d) modes are clearly identified by their solution polarization property. This leaves the E_g modes clearly assigned.

Three of the six T_{1u} modes were identified in his ir spectra by Jones,[2] *viz.*, 2151.5, 358.5, and 315 cm^{-1}. To these we add our observation of two low-frequency vibrations at 155 and 128 cm^{-1}, Table IV. There should be *three* low-frequency ir bands. That at 155 cm^{-1} (ir, T_{1u}) together with the 156-cm^{-1} (Raman, T_{2g}) band is clearly a correlation pair. In contrast, the equally close 128- (ir) and 129-cm^{-1} (Raman) bands *cannot* be a correlation doublet because (i) the Raman band is of E_g symmetry and (ii) all possible T_{1u}-T_{2g} doublets have already been located. Hence, both the 128-cm^{-1} (ir) band and the missing ir band are due to lattice modes.

In the crystal, splitting in the ν(CN) region is very slight. The molecular a_1 and t_2 modes are very close together, while the T_{2g}-T_{1u} split due to the correlation field is 2.5 cm^{-1}. (It is not clear from Jones' paper whether the frequencies he listed are from the ambient or low-temperature runs; we

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[2] L. H. Jones, *Spectrochim. Acta*, **17**, 188 (1961).

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[4] T. G. Petrov, E. G. Treivius, and A. P. Kasatkin, "Growing Crystals from Solution," Consultants Bureau, New York, N. Y., 1969.

[5] A. Sequeira and R. Chidambaram, *Acta Crystallogr.*, **20**, 910 (1966).

[6] D. M. Adams and D. C. Newton, "Tables for Factor Group and Point Group Analysis," Beckman-RIIC Ltd., Croydon, England, 1970.

Table I. Correlation Table for $K_2Zn(CN)_4$

Anion and site symmetry (T_d)	Factor group symmetry (O_h)
ν_1, ν_2 2 A_1 (R)	2 A_{1g} (R; $x^2 + y^2 + z^2$)
	2 A_{2u}
ν_3, ν_4 2 E (R)	2 E_g (R; $2z^2 - x^2 - y^2; x^2 - y^2$)
	2 E_u
ν_9 T_1	T_{1g}
	T_{2u} (ν_9)
ν_5–ν_8 4 T_2 (R, ir)	4 T_{2g} (R; xy, yz, zx)
	4 T_{1u} (ir)

Table II. Single-Crystal Raman Spectra of $K_2Zn(CN)_4$ at 100°K (Intensities in Arbitrary Units)

cm^{-1}	$x(zz)y^a$	$x(yz)y^b$	Assignment
61	5	18	ν_L, T_{2g}
137	430	49	ν_4, E_g
161	11	43	ν_8, T_{2g}
320	82	23	ν_3, E_g; ν_7, T_{2g}
346	25	4	ν_2, A_{1g}
357	1	4	ν_6, T_{2g}
464	1	0.2	2 × 230 (T_{1g} or T_{2u}) = 460
548	0.2	0.8	228 (T_{1g}) + 320 = 548
635	0.9	0.1	2 × 320 = 640
2109	1	0.3	$\nu(^{13}CN)$
2127	0.3	0.1	
2156		25	ν_5, T_{2g} component of anion ν_5
2157.5	83		ν_1, A_{1g}

[a] $y(xx)z$ and $x(yy)z$ spectra are virtually identical with that of $x(zz)y$. [b] $x(yx)y$ and $x(zx)y$ spectra are virtually identical with that of $x(yz)y$.

Table III. Single-Crystal Raman Spectra of $K_2Zn(CN)_4$ at Ambient Temperature (Intensities in Arbitrary Units)

cm^{-1}	$x(zz)y^a$	$x(yz)y^a$	Assignment
60	5	27	T_{2g}
129	300	15	E_g
156	10	36	T_{2g}
318	67	13	E_g, T_{2g}
344^b	18	3	A_{1g}
463	1.3	0.1	2 × 230 (T_{1g} or T_{2u}) = 460
546	0.2	0.5	228 (T_{1g}) + 318 = 546
630	0.6	0.2	2 × 318 = 636
2107	1	0.3	$\nu(^{13}CN)$
2124	0.3	0.1	
2154.5		23	T_{2g}
2156	85		A_{1g}

[a] Footnotes as in Table II. [b] At ambient temperature the T_{2g} band is overlaid by the tail of the A_{1g} band. They are resolved at 100°K, Table II.

Table IV. Infrared Spectra (Mulls) of $K_2Zn(CN)_4$[a]

Ambient temp	*Ca.* 100°K	Assignment
128	131	ν_L (translational)
155	160	δ(CZnC), ν_8
315	319	ν(Zn–C) and δ(ZnCN), ν_6 and ν_7
359	363	
2152		ν(CN), ν_5

[a] All modes, cm^{-1}, are of T_{1u} symmetry.

take them to be at ambient temperature.) The T_{2g}-T_{1u} correlation splitting is therefore within experimental error. Similarly, in the ν(Zn-C)-δ(ZnCN) region *ca.* 350 cm^{-1}, the T_{2g}-T_{1u} split is only 6 cm^{-1} for the 357- and 363-cm^{-1} bands. It is clear, therefore, that the correlation field is very weak.

In the ν(CN) and δ(CZnC)-lattice mode regions of the Raman spectra predictions and observations agree exactly. However, at first sight the situation for the ν(Zn-C)-δ(ZnCN) region is less obvious. Since the group of bands *ca.* 350 cm^{-1} is strong relative to those at 463, 546, and 630 cm^{-1}, we take the former to be fundamentals. Assignment of the 346- (A_{1g}) and 357-cm^{-1} (T_{2g}) bands is unambiguous and that at 320 cm^{-1} is evidently E_g from its high zz intensity (A_{1g} being ruled out by the solution depolarization ratio). Where is the second T_{2g} mode predicted for this region?

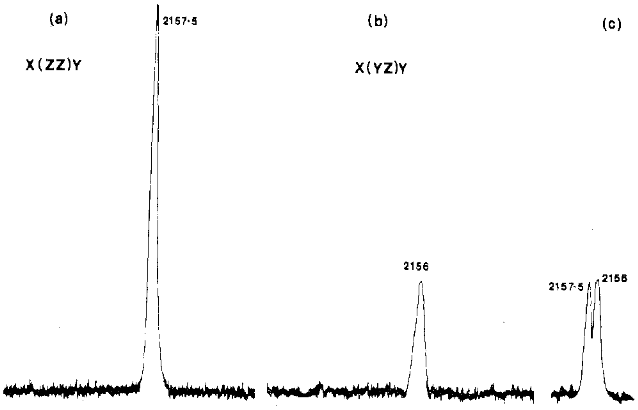

Figure 1. Raman spectra of $K_2Zn(CN)_4$ in the ν(CN) region at 100°K. (a) and (b) show zz and yz spectra from a high-quality oriented single crystal; (c) shows the spectrum of a misaligned crystal sample. Spectral slit width 0.25 cm^{-1}; 488.0-nm excitation; *ca.* 700 mW at the sample.

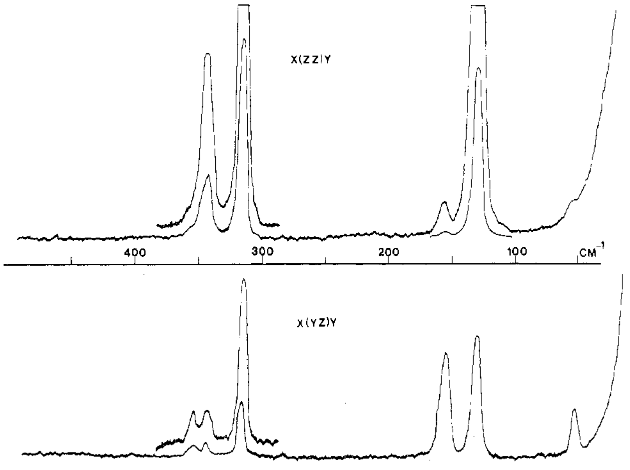

Figure 2. Single-crystal Raman spectra of $K_2Zn(CN)_4$ at 100°K. Spectral slit width 2 cm^{-1}; 488.0-nm excitation; *ca.* 200 mW at the sample.

Two pieces of evidence show that it is coincident with the E_g mode at 320 cm^{-1}. (i) Extinctions are good throughout the Raman experiments; observation of high intensity in both zz and yz spectra at 320 cm^{-1} clearly suggests coincidence of E_g and T_{2g} bands. (ii) We showed above that correlation splitting causes only slight differences between T_{2g}-T_{1u} pairs. In the region *ca.* 350 cm^{-1} two T_{1u} (ir) modes are expected and were found by Jones at 315 and 358.5 cm^{-1}. We look for Raman bands at similar positions: the T_{2g} nature of the 357-cm^{-1} band has already been demonstrated. We therefore confidently attribute the 318-cm^{-1} band to the T_{2g} mode as well as to E_g.

In the E_g spectrum the 318-cm^{-1} band is intense; it is almost pure δ(ZnCN) motion. In contrast, in metal carbonyls δ(MCO) modes are extremely weak in the Raman effect. We note that E_g modes are due to *internal* modes only.

Modes of the δ(CZnC) type are the most temperature sensitive. Raman bands at 129 and 156 cm^{-1} rise by 8 and 5 cm^{-1}, respectively, on cooling to 100°K, and the corresponding ir ν_8 also rises by 5 cm^{-1}. In contrast, lattice modes shift by about half this amount.

Following again the argument that correlation splitting is slight, it is reasonable to assume that the inactive A_{2u} and E_u modes will be close in frequency to the known A_{1g} and E_g modes. This is important in that restrictions are then placed upon interpretation of the combination bands at 464, 548, and 635 cm^{-1}. The only modes for which we now have absolutely no *direct* experimental evidence are the sole T_{1g}-T_{2u} pair associated with δ(ZnCN) motion. Jones placed this mode, ν_9, at 230 cm^{-1} on the basis of combination-band evidence. Such arguments can be very misleading, but we support this one mainly because it is difficult to find plausible alternatives to our assignment (Table II) for the 548-cm^{-1} band. This can arise from either or both of the combinations 320 cm^{-1} (E_g or T_{2g}) + 228 cm^{-1} (T_{1g}) although we are inclined to favor the T_{2g} label because of the observed *zz* component. Likewise, the 635-cm^{-1} band is most probably an overtone of that at 320 cm^{-1} with either or both symmetry species involved (since the products $E_g \times E_g$ and $T_{2g} \times T_{2g}$ both contain E_g).

The provenance of the 464-cm^{-1} band is less readily settled. Combinations 346 + 137 = 483 cm^{-1} and 320 + 161 = 481 cm^{-1} are improbable for two reasons: (i) they suggest an improbably high anharmonicity; (ii) the 464-cm^{-1} combination is not temperature sensitive but both the 137- and 161-cm^{-1} fundamentals are. We consider that it is the first overtone of the inactive T_{1g}-T_{2u} mode. Alternatively, it could be the first overtone of the T_{1g} part of this correlation doublet (but *not* their combination as $T_{1g} \times T_{2u}$ is not Raman active).

General Comments

Although he saw only three fundamentals directly, Jones located others from combinations. On this basis he conducted a normal-coordinate analysis. The difficulty with CZnC bending force constants is readily understood as our assignments for these modes are rather different from those which he had deduced.

Compared with $Ni(CO)_4$ there are major differences of intensity, as well as of interaction force constants (*e.g.*, separation of ν(CN) and ν(M-CN) modes is negligible compared with the analogous ν(CO) and ν(M-CO) modes). δ(MCO) modes are weak in the Raman effect: it was the extreme feebleness of ν_3(e)-δ(MCO) which long delayed completion of the assignment for $Ni(CO)_4$. In contrast, δ(ZnCN) appears to be quite intense. CMC bending modes are much higher for $[Zn(CN)_4]^{2-}$ than for $Ni(CO)_4$, although this may well be due to the constraints provided by interaction with potassium cations.

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Kinetic Studies of Oxygen Exchange between Oxocyanorhenate(V) Complex Ions and Solvent Water[1]

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The rates of oxygen exchange between *trans*-dioxotetracyanorhenate(V) and water have been determined in both acidic and basic media. At unit ionic strength the rate law is given by $R = k_1[ReO(OH)(CN)_4{}^{2-}] + k_b[ReO_2(CN)_4{}^{3-}]$. In the presence of added cyanide ions, $k_b = k_2[CN^-]^{-0.90}$ and in the absence of added cyanide ions $k_b = k_3[OH^-]^{0.22}$. The value for k_1 at 35.0° is $(3.42 \pm 0.05) \times 10^{-2}$ sec^{-1}. The value for k_2 at 89.7° is $(4.16 \pm 0.23) \times 10^{-7}$ *M* sec^{-1} and the value for k_3 at 70.3° is $(4.23 \pm 0.04) \times 10^{-3}$ sec^{-1}. The Arrhenius activation energies for k_1 and k_3 are 23.3 ± 0.3 and 20.3 ± 0.1 kcal/mol, respectively. In acidic media a mechanism is proposed in which exchange of an oxo ligand is facilitated by protonation. The mechanism for exchange in basic media is proposed to involve solvent replacement of an equatorial cyano ligand with consequent axial oxo ligand labilization. The rates of oxygen exchange of the dimeric anion μ-oxo-bis[oxotetracyanorhenate(V)] have also been determined. At unit ionic strength the rate law for the terminal oxygens is given by $R = k_1[Re_2O_3(CN)_8{}^{4-}] + k_2[Re_2O_3(CN)_8{}^{4-}][H^+]$. At 50.0°, the values of k_1 and k_2 are $(1.11 \pm 0.07) \times 10^{-4}$ sec^{-1} and $(3.46 \pm 0.24) \times 10^{-2}$ *M* sec^{-1}, respectively. The Arrhenius activation energy for terminal oxo ligand exchange is 30.3 ± 0.9 kcal/mol. At 70.3° and $[H^+] = 2.0 \times 10^{-4}$ *M*, the rate of terminal oxo ligand exchange is 40 times faster than the rate of bridging oxo ligand exchange. A mechanism is proposed in which exchange of terminal oxo ligands is facilitated by association with $H_{aq}{}^+$.

Introduction

The existence of *trans*-dioxotetraligand(metal ion) complexes of second and third-row transition elements has been recognized for some time.[2] It is becoming increasingly clear that such complexes are of fundamental importance in the aqueous solution chemistry of $4d^2$ and $5d^2$ metal ions such as molybdenum(IV), ruthenium(VI), tungsten(IV), rhenium(V), and osmium(VI). It is only recently, however, that kinetic studies of ligand substitution reactions of these complex ions have been undertaken. In a survey study of several such rhenium(V) complexes Beard, *et al.*, reported[3] preliminary results of kinetic studies of oxo and equatorial ligand exchange of $ReO_2L_4{}^{n+}$ where $L = CN^-$, pyridine, or $^1/_2$ ethylenediamine (en). More recently Kriege and Murmann[4]

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[1] Taken in part from the Ph.D. dissertation of D. L. Toppen, University of Missouri, 1971.

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