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Vibrational Spectra of Some Acetylenic Derivatives of the Pentacyanocobaltate(II) Ion*

P. S. SANTOS, K. KAWAI** and O. SALA
Instituto de Química, Universidade de São Paulo, C.P. 20780, São Paulo, Brazil

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The Raman and IR spectra of complexes of the general formula $K_6[Co_2(CN)_{10}C_2X_2]\cdot nH_2O$ *(X = H, COOMe or COOEt) were obtained and, based on a* trans-*configuration, a tentative assignment of some characteristic group frequencies was made.*

Introduction

Griffith and Wilkinson [1] isolated the salt $K_6[Co_2(CN)_{10}C_2H_2]\cdot 4H_2O$ (hereafter referred to as I) from the reaction of $[Co(CN)_5]^{3-}$ ion in aqueous solution with acetylene, in the absence of oxygen. Based on NMR and IR spectra, they proposed a *trans*-configuration. However, they assigned some IR bands to vibrational modes expected to be inactive in this centrosymmetric structure, assuming a possible distortion from a strictly *trans*-configuration and deviation from planarity around the C=C bond. To determine more reliably the structure of this complex, it would be desirable also to obtain the Raman spectrum.

The potassium salts of the ions $[Co_2(CN)_{10}C_2(COOCH_3)_2]^{6-}$ (II) and $[Co_2(CN)_{10}C_2(COOC_2H_5)_2]^{6-}$ (III) were reported by Kimball *et al.* [2] and were not yet subjected to any structure determination using spectroscopic methods. Due to the similarity of these compounds to I, we decided to investigate the Raman and IR spectra of these three complexes in both the anhydrous and hydrated forms and to check the previous assignment for I [1].

Experimental

Complex I was prepared according to Griffith and Wilkinson [1] and the analytical results were: Found: Co, 16.5; C, 20.1; N, 20.1; H, 1.8%. Calcd. for $C_{12}H_{10}O_4N_{10}Co_2K_6$: Co, 16.6; C, 20.3; N, 20.1, H, 1.7%.

The anhydrous compound was obtained by heating the hydrate at 50 °C under vacuum. In the presence of water vapour the anhydrous sample yielded the hydrate, as determined by its IR spectrum. The potassium salt of the deuterated ion $[Co_2(CN)_{10}C_2D_2]^{6-}$ was also prepared to check the assignment of the out-of-plane C–H bending frequencies.

The complexes II and III were prepared according to Kimball *et al.* [2] and the analytical results for II and III were, respectively: Found: C, 22.55; N, 16.61; H, 2.13%. Calcd. for $C_{16}H_{16}O_9N_{10}Co_2K_6$: C, 22.70; N, 16.58; H, 1.91%; and Found: C, 24.42; N, 15.80; H, 2.33%. Calcd. for $C_{18}H_{20}O_9N_{10}Co_2K_6$: C, 24.77; N, 16.05; H, 2.31%.

The anhydrous compounds were obtained as for I. Kimball *et al.* [2] reported II as dihydrated. Our analytical results were more consistent with a pentahydrate. However, the hygroscopic nature of the compound introduces large error in the determination of the H content.

The Raman spectra were recorded on a Jarrell–Ash 25-300 spectrometer using the 514.5 nm exciting line of an Ar^+ laser. The rotatory cell technique [3] was employed. The IR absorption spectra were recorded on a Perkin–Elmer 180 spectrophotometer using Nujol and hexachlorobutadiene mulls.

Results and Discussion

The Raman and IR spectra of I are reproduced in Figure 1. The observed frequencies are listed in Tables I and II. The tentative assignments are based on the comparison with those available for similar compounds.

A strong dependence of the intensities and frequency values of the C–H stretching vibrations on the degree of hydration was observed for all of the three compounds.

A very important point to be discussed is that concerning the assignment of the C=C stretching vibration, which is expected to be only Raman-active for the *trans*-configuration. Griffith and Wilkinson [1] assigned an IR band at 1615 cm^{-1} to the C=C stretching vibration, claiming that the presence of this band was due to a distortion of the centro-

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*Part from the Thesis for Master Degree of P.S.S., University of São Paulo, 1974.

**Permanent address: Faculty of Literature and Science, Toyama University, Toyama, Japan.

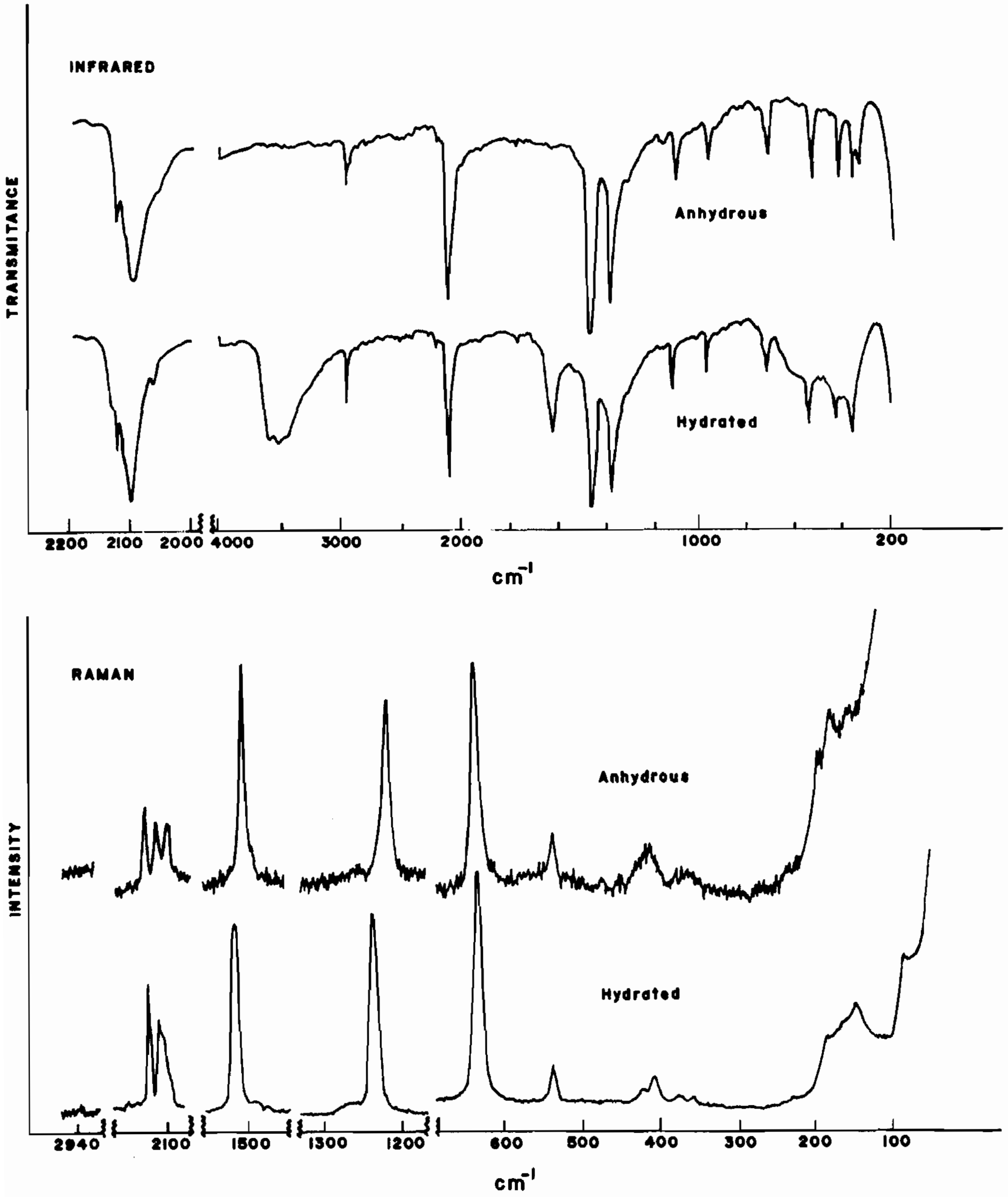

Figure 1. Infrared and Raman spectra of anhydrous and hydrated $K_6[Co_2(CN)_{10}C_2H_2]$.

symmetric structure of the complex ion. These authors also prepared the compound with D_2O to confirm their assignment. However, the band at 1621 cm^{-1} (1615 of ref. 1) seems to be too strong for one with expected inactivity and the frequency values too high for a double bond linked to $Co(CN)_5$ groups. In describing the preparation of the D_2O hydrated compound, they gave no details about the isolation and analysis of this complex.

In the present work, the IR band at 1621 cm^{-1} was attributed to the deformation mode of water, based mainly on the decrease of its intensity during dehydration and its absence in the IR spectrum of the anhydrous compound. Another important point for the assignment of the C=C stretching mode is given by the Raman spectrum. If the 1621 cm^{-1} band was due to the C=C stretching vibration it should appear in the Raman spectrum with reasonable intensity. However, no Raman band was detected in this region. On the other hand, the Raman spectra show a very intense band at 1516 cm^{-1} for the hydrate and 1505 cm^{-1} for the anhydrous compound.

TABLE I. Raman and Infrared Frequencies (cm^{-1}) for $K_6[Co_2(CN)_{10}C_2H_2]$.[a]

Approximate Description	Anhydrous		Hydrated		
	Raman	Infrared	Raman		Infrared
			solid	solution	
			84(0.5)		
$\delta(C-Co-C)$	141(2)		145(3)		
	167(3)		165(2)		
	184(2)		184(2)		
	230(0.5)		231(0.5)		
		345wm			
$\delta(Co-C-N)$, $\nu(Co-CN)$, $\delta(Co-C-H)$, $\nu(CO-C=)$	360(1)		360(0.5)	368(0.5)	360m
		370m	376(0.5)		
	410(2)		410(2)	415(2)P	
	424sh		424(1)		
		430m			428m
	535(2)		539(2)	536(2)P	
		540m			540m
					545sh
$\delta_s(C=C-H)_{o.p.}$	634(10)		634(10)	627(10)	
$\delta_{as}(C=C-H)_{o.p.}$		970m			970m
$\delta_{as}(C=C-H)_{i.p.}$		1110m			1125m
$\delta_s(C=C-H)_{i.p.}$	1220(8.5)		1233(7)	1222(7)P	
				1300(1)P	
		1305vw			1305vw
$\nu(C=C)$	1505(10)		1516(7)	1515(4)P	
$\delta(H_2O)$					1621s
					1640sh
		2060w			2060w
$\nu(CN)$	2100(3)	2098vs	2097(0.5)		2099vs
			2105(2)	2103sh	2104sh
	2113(2)	2112sh	2110(3)	2112(1)P	2110sh
	2127(4)	2125m	2124(4)	2132(2)P	2123m
					2130sh
$\nu(CH)$		2930wm	2938(0)		2940m
		2955m			
$\nu(H_2O)$					3440sh
					3510s
					3590s

[a] vs, very strong; s, strong; m, medium; w, weak; sh, shoulder; ν, stretch; δ, bend; o.p., out-of-plane; i.p., in-plane.

This band is polarized in solution and IR inactive, and therefore readily assigned to the C=C stretching vibration. These frequencies are lower by about 110 cm^{-1} than the C=C stretching frequency of ethylene, and this pronounced decrease in the frequencies may be due mainly to the charge, which is donated from the cobalt atoms, on the π^* orbital of the bond.

Griffith and Wilkinson [1] assigned the band at 1120 cm^{-1} to the in-plane C=C–H deformation vibration and considered its IR activity as another evidence for a distortion in the complex ion. However, two bands are expected for this in-plane vibration, one Raman active (*g* type) and another IR active (*u* type). In the present paper, the Raman band at 1233 cm^{-1} (1220 cm^{-1} anhydrous) and the IR band at 1125 cm^{-1} (1110 cm^{-1} anhydrous) are assigned to these in-plane C=C–H deformation vibrations.

The IR band at 970 cm^{-1} is assigned to the antisymmetric C=C–H out-of-plane deformation, which is in agreement with that observed for *trans*-alkenes [4]. Rasumussen *et al.* [5] have also shown that the IR band at 970 cm^{-1} is characteristic of the *trans*-form of alkenes. The very strong band at 634 cm^{-1} may be attributed to the corresponding Raman-active symmetric mode. For alkyl substituted ethylenes this vibration usually appears as a weak or very weak band [6]. To check the assignment of this out-of-plane C–H bending, the vibrational spectrum of the deuterated compound and a normal coordinate

TABLE II. Raman and Infrared Frequencies (cm^{-1}) for $K_6[Co_2(CN)_{10}C_2(COOMe)_2]$ and $K_6[Co_2(CN)_{10}C_2(COOEt)_2]$.

Approximate Description	$K_6[Co_2(CN)_{10}C_2(COOMe)_2]$					$K_6[Co_2(CN)_{10}C_2(COOEt)_2]$				
	Anhydrous		Hydrated			Anhydrous		Hydrated		
	Raman	Infrared	Raman		Infrared	Raman	Infrared	Raman		Infrared
			solid	solution				solid	solution	
δ(C–Co–C)	150(6)		145(5)	140(2)P		150(8)		152(10)	130(8)P	
			170sh							
δ(Co–C–N), ν(Co–CN), δ(C–O–C), ν(Co–C=)	295(2)		300(2)	297(2)P		274(2)		276(2)	268(2)P	
		365wm	372(0)		375wm		368wm	370(0)	368(1)	368w
	400(2)		400(1)	407(2)P		398(2)		403(2)	400(2)P	
		415wm	414(0)		425wm		425wm			
			485(0)			480(0)		482(0)	480(0)	
	542(2)	540wm	540(1)	545(2)P	545wm	545(2)	540m	545(2)	542(3)P	540wm
	580(0.5)		598(0.5)	574(1)P		576(0.5)		580(0.5)	574(1)	
δ(C=C–C), δ(O=C–O)	640(0.5)		640(2)	645(0.5)		641(1)		645(2)	640(2)P	
	670(7)		667(7)	677(8)P		671(7)		678(9)	670(10)P	
		680w			685w	690sh	685w	692(0)	688(2)	685w
		790w			790w		790w			790w
	802(4)		804(4)	804(6)						
ν_s(C–O–C), CH_3 rock, ν_{as}(C–O–C)						825(4)	827(5)	823(7)P		
		885w	873(1)		890w	870(1)	870vw	875(0.5)	870(1)	870vw
	908(10)		907(10)	910(10)P						
						963(10)	965w	967(10)	964(10)P	967wm
		970w	966(0)	952(0.5)	975vw					
	1004(5)		996(5)	1008(8)P						
		1020m	1021(1)	1028sh	1020wm					
						1032(2)	1032m	1032(1)	1032(2)P	1030m
		1155sh			1150sh	1160sh				1160w
	1182(0 5)		1190(1)	1188(0.5)P						
		1215wm			1215m		1215m	1220(0)		1215m,b
δ(CH_3), δ(CH_2)					1230m					
		1360w			1365w		1365wm			1365m
							1390w			1390wm
		1415w	1425(0)	1430(0.5)P	1425m					
		1450w			1455w		1450sh			1450sh
							1470w			1470wm
ν(C=C)	1545(7)		1558(4)	1545(7)P		1548(7)		1550(8)	1546(5)P	1550w
	1587sh		1589(4)	1587(0.5)						
δ(H_2O)					1620m					1640m
					1660s					1660ms
ν(C=O)	1678(0.5)	1670m	1678(1)	1680(0.5)	1670s		1665ms			1670ms
ν(CN)	2102sh	2102vs	2104(0.5)		2106vs		2104vs			2108vs
	2114(3)		2113(1)	2114(3)		2115(3)		2112(3)	2114(2)	
								2120(3)		
	2130(3)	2126s	2129(1)	2132(5)P	2129s	2132(3)	2126ms	2132(5)	2132(5)P	2130ms
ν(CH_2), ν(CH_3)		2925w			2925sh					
						2940(0)	2930w	2940(0)		2940w
		2950wm	2962(0)		2955wm					
							2980w	2985(0)		2990w
					3005vw					
								3070(0)		
ν(H_2O)					3500s,b		3400w,b			3450s,b

calculation for the skeleton have been obtained for both isotopic species. There was good agreement between the calculated and observed values for the in-plane C–H deformations and the antisymmetric out-of-plane C–H bending (a_u species), but for the symmetric out-of-plane C–H bending (b_g species), the calculated value for the deuterated compound was about 540 cm^{-1} and the observed value 585 cm^{-1}. Since no coupling is expected in this species, it is difficult to explain this deviation. A noticeable decrease in the relative intensities of this vibration and that of C=C stretching was observed for the deuterated compound.

It is difficult to make definitive assignments of bands to the Co–CN stretching and Co–C–N bending vibrations. Only their expected frequency region is indicated in the Tables, where the assignment of characteristic frequencies is given.

For hydrated II and III, the Raman bands at 1558 cm^{-1} (1545 cm^{-1} anhydrous) and 1550 cm^{-1} (1548 cm^{-1} anhydrous) are assigned to the C=C stretching vibration. These frequencies are higher by about 40 cm^{-1} than that assigned to the C=C stretching vibration of I, suggesting that the C=C bond of II or III increases in the strength because the electrons, which are donated from the cobalt atoms, distribute partly on the $-CO_2R$ groups of the esters.

In the IR spectra of hydrated II and III there is a partial overlap of the bands assigned to the C=O stretching vibration (1678 and 1670 cm^{-1}, respectively) with the bands assigned to the H_2O bending vibrations (1620 and 1660 cm^{-1} for II and 1640 and 1660 cm^{-1} for III).

Contrary to a previous report, the present results provide no spectroscopic evidence consistent with distortions of a *trans*-configuration for any of the three compounds investigated.

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