CH$_3$-1,2-B$_{10}$C$_2$H$_{10}$, 32630-05-0; *cis*-(PPh$_3$)$_2$PtCl$_2$, 15604-36-1; *cis*-(P(*n*-Pr)$_3$)$_2$PtCl$_2$, 15977-21-6; 1-Li-2-C$_6$H$_5$-1,2-B$_{10}$C$_2$H$_{10}$, 41655-52-1; *trans*-(PEt$_3$)$_2$PtCl$_2$, 15692-07-6; 1-Li-7-CH$_3$-1,7-B$_{10}$C$_2$H$_{10}$, 32630-07-2; 1-Li-7-C$_6$H$_5$-1,7-B$_{10}$C$_2$H$_{10}$, 42012-25-9; *trans*-(P(*n*-Pr)$_3$)$_2$PtCl$_2$, 15977-22-7; *n*-butyllithium, 109-72-8; *trans*-(PEt$_3$)$_2$PdCl$_2$, 15642-19-0; HCl, 7647-01-0; HCN, 74-90-8; phosphorus-31, 7723-14-0.

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Vibrational Spectra and Bonding in Pentacyanohaloplatinate(IV) Complexes[1]

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The infrared and Raman spectra of solid complex species M$_2$Pt(CN)$_5$X (M = alkali metal; X = Cl, Br, I, CN) have been observed in the regions 2250–2000 and 540–35 cm^{-1}. Infrared intensities of C–N stretching vibrations and Raman polarization data have also been obtained for aqueous solutions of these complexes. The results have been combined to assign many of the fundamental frequencies. Replacement of a cyanide group by a halide results in a slight decrease of the M–C as well as the C–N stretching frequencies, iodide having the greatest effect and chloride, the least. Bonding implications are made on the basis of a mechanism in which the degree of σ interaction predominates over the extent of platinum–carbon π bonding.

Introduction

In contrast to the numerous vibrational studies concerning substituted metal carbonyls, relatively few studies have dealt with analogous metal cyanides. Because of the complexity of the spectra and the significant amount of mode mixing in the M–C stretching region, few detailed vibrational analyses have been made.[3] Several approximate normal-coordinate analyses have been undertaken for a number of regular hexacyanometalates from which additional information on the bonding has been derived.[4] Assignments made for these complexes are of great assistance in the interpretation of the spectra of substituted metal cyanides.

Platinum(IV) cyanide complexes are interesting in that the central metal is in a high oxidation state. The C–N and Pt–C stretching force constants of K$_2$Pt(CN)$_6$ have been found to be the largest yet determined for six-coordinate metal cyanide systems.[5] These results indicate strong metal–carbon σ bonding and weak metal–carbon π bonding. Infrared intensity studies furnish additional information concerning the extent of electron delocalization during a particular vibration.[6] For this reason we have measured the intensities of antisymmetric C–N stretching vibrations in order to compare the degree of π bonding with that found in other metal cyanides.

It is of interest to determine the changes in metal–ligand σ and π bonding which accompany partial replacement of cyanides with other ligands, such as the halides. For this purpose we have compared the fundamental M–C vibrations of the anions, Pt(CN)$_5$X^{2-} (X = Cl, Br, I), so that the effect of the halide on the Pt–C bond strengths could be estimated. At the same time, we have investigated the effect on other vibrations and have also compared the magnitude of counterion interaction effects to the intramolecular electronic effects of the substituent halides. The results of this study should contribute to the current knowledge of bonding properties of substituted metal cyanides and related compounds.

Experimental Section

Preparations. In general, simple salts and other common reagents were of analytical grade. Platinum-containing starting materials such as Na$_2$PtCl$_4$ and PtCl$_2$ were purchased from Englehard Industries. The precursor complex, sodium tetracyanoplatinate(II), was obtained as the trihydrate from the reaction of platinum(II) chloride (PtCl$_2$) with an excess of sodium cyanide in aqueous solution. Potassium tetracyanonickelate(II) and -palladate(II) were available from previous studies.[7]

Preparation of K$_2$Pt(CN)$_5$I involved the method of Babkov in which K$_2$Pt(CN)$_4$ is oxidized by cyanogen iodide.[8] The bromo and chloro species were prepared by *in situ* oxidations of the iodide by the respective halogen;[9] the hexacyano complex, by cyanide substitution of the iodo complex.[8] The sodium salts were obtained by analogous reactions with Na$_2$Pt(CN)$_4$ or by precipitating K$_2$SiF$_6$ from the appropriate potassium salt with fluosilicic acid and carefully neutralizing the filtrate with sodium bicarbonate. The cesium compounds were prepared by simple metathesis of the appropriate potassium salts using excess cesium sulfate, bromide, and chloride for the cesium–iodo, -bromo, and -chloro salts, respectively; the resulting salts were purified from potassium salts by recrystallizing from water. Analytical purity of the platinum(IV) complexes was verified by the Microanalytical Laboratory of the University of Illinois.

Instrumentation and Techniques. Infrared spectra of mineral oil mulls were recorded in the regions 2250–2000 and 540–250 cm^{-1} on a Perkin-Elmer Model 521 spectrometer. The mulls were supported by NaCl, CsBr, and CsI plates, the latter two being used in the low-frequency region. The pressed-disk technique was not employed as we wished to avoid the possibility of solid-state reactions. Low-temperature spectra were measured using an evacuated liquid nitrogen cell having CsBr windows. Spectra were run at a dispersion of 5 cm^{-1}/cm at a scan speed of approximately 5 cm^{-1}/min. Mull spectra on polyethylene plates were measured in the far-infrared region (33–350 cm^{-1}) by a Beckman IR-11 spectrometer at a dispersion of 7.5-

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[1] (a) Abstracted in part from the Ph.D. dissertation of M. N. M., University of Illinois, 1971. (b) Supported in part by the U. S. Atomic Energy Commission.

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10 cm^{-1}/in. Both ir spectrometers were purged of water vapor in the low-frequency regions by flushing with either dry nitrogen or dry air. All spectra were calibrated using CO vapor in the C–N stretching region and water vapor in the low-frequency regions.

Raman spectra of powders and aqueous solutions were determined in the regions 2100–2250 and 30–540 cm^{-1} on a Cary Model 81 spectrometer using a Spectra-Physics 125 helium-neon laser (exciting line 6328 Å) or a Carson krypton laser (exciting line 5682 Å). All spectra were run at a dispersion of 10 cm^{-1}/in. at a scan speed of 3 cm^{-1}/min and were calibrated by a neon lamp. Polarization studies were performed on saturated solutions using a 5-ml Raman tube.

Infrared intensity studies of aqueous solutions of potassium salts (~0.2 *M* for Pt(IV) cyanides; 0.05 *M* for Pt(II), Pd(II), and Ni(II) cyanides) were conducted in the C–N stretching region on a Perkin-Elmer 521 spectrometer using a fixed-thickness cell with a 2-mil tantalum spacer and calcium fluoride windows. Slit width was set at 750 μ and an identical cell containing water only was placed in the reference beam. From the spacing between interference peaks in the empty cells, the path length was found to be 0.0064 cm for both sample and reference cells. Transmittance spectra were recorded on a log scale and replotted on linear paper to obtain an absorbance band shape. Integrated absorption coefficients were determined by the weight method.

Symmetry Considerations and Selection Rules. As an isolated anion, the complex $Pt(CN)_5X^{2-}$ possesses the molecular symmetry of point group C_{4v}. A factor group analysis indicates that the 30 fundamental modes arising from this halo-substituted cyano complex fall into the following species: 7 A_1 + A_2 + 4 B_1 + 2 B_2 + 8 E. A further classification may be made according to the type of vibration: C–N stretch, 2 A_1 + B_1 + E; Pt–C stretch, 2 A_1 + B_1 + E; Pt–X stretch, A_1; Pt–C–N bend, A_1 + A_2 + B_1 + B_2 + 3 E; C–Pt–C bend, A_1 + B_1 + B_2 + 2 E; C–Pt–X bend, E. The A_1 and E modes are both infrared and Raman active. The B_1 and B_2 modes are Raman active only. The A_2 mode is inactive altogether. The symmetry coordinates for the $Pt(CN)_5X^{2-}$ anion are listed in Table I; the internal coordinates are defined in Figure 1.

Observed Spectra. Infrared spectra of the solids at room temperature have been summarized in Table II. Those obtained at liquid nitrogen temperature are very similar except that absorption peaks are generally sharper (with some splitting) and shifted to higher energies; these data have not been reported. The Raman data for the solids are included in Table III; polarization data for solutions, in Table IV. Vibrational frequency data for the $Pt(CN)_6^{2-}$ complexes are reported separately in Table V. A further description of these spectra in regions of particular interest is noted in the following sections.

(a) **Cyanide Stretching Region.** Although three infrared bands are expected in this region for these complexes, only two well-resolved bands generally appear. [It should be mentioned that two very weak absorption bands are generally found at ~25 and ~40 cm^{-1} toward lower energy from the most intense infrared band. These are due to species containing naturally abundant $C^{15}N$ and ^{13}CN, respectively.] Likewise, the aqueous solution spectra of the three halo-substituted cyanides also exhibit only two peaks (*vide infra*). For this reason, infrared mull spectra were run at liquid nitrogen temperature as well as room temperature in an attempt to resolve overlapping bands.

The potassium salts exhibit only two well-resolved infrared peaks; the position of the shoulder reported on the intense E mode of the chloro complex is uncertain. Extensive broadening of absorption bands, particularly that of the E mode, occurs in the sodium salts. On the other hand, the cesium salts of the chloro and iodo species exhibit three resolved peaks in this region. At low temperature, broadening effects are reduced and a number of peaks are sharpened and/or split.

Likewise, the Raman spectra (Figure 2) for the C–N region are quite disappointing because only two (rather than four) peaks generally appear. At least three peaks are observed for the iodo complexes, the cesium salt being the only compound to exhibit the four expected peaks. When only two peaks are found, the one at lower energy appears to be skewed unsymmetrically to lower energies.

(b) **Low-Frequency Region.** Because of the complexity of spectra in the region 540–250 cm^{-1}, it is very difficult, if not impossible, to determine the relative intensities of vibrational bands in this region with any certainty. Curve-resolving techniques were employed but reproducible results could not be obtained. For this reason, the relative intensities of these peaks could be judged only by inspection. Nevertheless, positions of peaks which appear to correspond are shifted to lower energies in the order Cl > Br > I.

Throughout the low-frequency regions, the spectra of the sodium and potassium salts exhibit similar features; *e.g.*, both ir spectra exhibit two medium-strong peaks in the range 140–100 cm^{-1} and a strong, broad band centered near 180 cm^{-1}. These bands must arise from the CMC and CMX bends coupled with one or more lattice modes. The considerable difference between the spectra of the cesium salts and those of the others probably arises from shifting of the lattice modes and different amounts of coupling of the internal and external modes. In the CMC bending region, the Raman spectra exhibit only one broad depolarized band near 105 cm^{-1} for aqueous solutions of the three halo species (*cf.* Table IV).

Table I. Symmetry Coordinates of $Pt(CN)_5X^{2-}$

A_1	S_1(planar C–N str)	$(1/2)(r_1 + r_2 + r_3 + r_4)$
	S_2(apical C–N str)	r_0
	S_3(planar Pt–C str)	$(1/2)(d_1 + d_2 + d_3 + d_4)$
	S_4(apical Pt–C str)	d_0
	S_5(Pt–X str)	Δ
	S_6(planar Pt–C–N def)	$(1/2)(\gamma_1 + \gamma_2 + \gamma_3 + \gamma_4)$
	S_7(apical C–Pt–C def)	$(1/2\sqrt{2})[(\psi_1 + \psi_2 + \psi_3 + \psi_4) - (\delta_1 + \delta_2 + \delta_3 + \delta_4)]$
A_2	S_8(Pt–C–N def)	$(1/2)(\beta_1 + \beta_2 + \beta_3 + \beta_4)$
B_1	S_9(planar C–N str)	$(1/2)(r_1 - r_2 + r_3 - r_4)$
	S_{10}(planar Pt–C str)	$(1/2)(d_1 - d_2 + d_3 - d_4)$
	S_{11}(planar Pt–C–N def)	$(1/2)(\gamma_1 - \gamma_2 + \gamma_3 - \gamma_4)$
	S_{12}(apical C–Pt–C def)	$(1/2\sqrt{2})[(\psi_1 - \psi_2 + \psi_3 - \psi_4) - (\delta_1 - \delta_2 + \delta_3 - \delta_4)]$
B_2	S_{13}(planar Pt–C–N def)	$(1/2)(\beta_1 - \beta_2 + \beta_3 - \beta_4)$
	S_{14}(planar C–Pt–C def)	$(1/2)(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4)$
E	S_{15}(planar C–N str)	$(1/2)^{1/2}(r_1 - r_3)$
	S_{16}(planar Pt–C str)	$(1/2)^{1/2}(d_1 - d_3)$
	S_{17}(planar Pt–C–N def)	$(1/2)^{1/2}(\beta_1 - \beta_3)$
	S_{18}(planar Pt–C–N def)	$(1/2)^{1/2}(\gamma_1 - \gamma_3)$
	S_{19}(apical Pt–C–N def)	$(1/2)^{1/2}(\phi_1 - \phi_3)$
	S_{20}(planar C–Pt–C def)	$(1/2)(\alpha_1 - \alpha_2 - \alpha_3 + \alpha_4)$
	S_{21}(apical C–Pt–C def)	$(1/2)^{1/2}(\psi_1 - \psi_3)$
	S_{22}(apical C–Pt–X def)	$(1/2)^{1/2}(\delta_1 - \delta_3)$

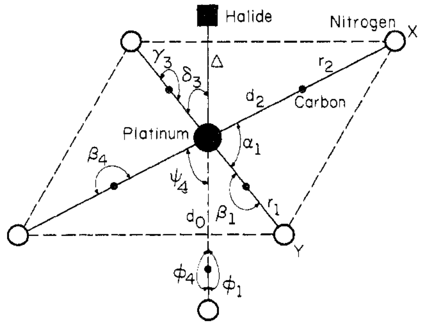

Figure 1. Internal coordinates for the $Pt(CN)_5X$ anion: γ_{1-4}, Pt-C-N angle above *xy* plane; β_{1-4}, Pt-C-N angle in *xy* plane; ϕ_1, Pt-C-N angle in the same plane as d_1 and d_0; δ_{1-4}, C-Pt-X angle; ψ_{1-4}, C-Pt-C angle below *xy* plane; α_{1-4}, C-Pt-C angle in *xy* plane.

Results and Discussion

Assignments. Since crystal structure data are unavailable for any of these monosubstituted complexes, solid-state assignments and characterizations will be made assuming the site symmetry is not significantly different from C_{4v}. Assignments are reported in Table VI; those for A_1 and E modes represent an average of Raman and infrared data whenever definite correspondence occurs.

C–N Stretching Vibrations. The vibrational spectroscopy of metal cyanides exemplifies a fundamental difference in the bonding from that of metal carbonyls. Though CO and CN^- are isoelectronic, the cyanide ion has the better σ-bonding properties because it is a stronger base on the other hand, perhaps by virtue of its negative charge, metal–carbon π bonding is apparently less important for cyanide complexes. The infrared intensities of ν_{CN} are generally at least an order of magnitude smaller than those of ν_{CO} in analogous metal

Table II. Observed Infrared Absorption Frequencies[a] for Mineral Oil Mulls of $M_2Pt(CN)_5X$

$M_2Pt(CN)_5Cl$			$M_2Pt(CN)_5Br$			$M_2Pt(CN)_5I$		
M = Na	M = K	M = Cs	M = Na	M = K	M = Cs	M = Na	M = K	M = Cs
2216.0 w[b]	2210.1 w	2197.3 vw	2213.7 m	2208.6 w	2195.1 w	2209.0 mw	2203.9 w	2193.4 w
2192.3 s, br	2194.7 sh	2182.4 m	2189.4 s, br	2186.0 s	2172.3 ms	2185.7 s	2181.4 vs	2184.3 w
	2186.9 s	2174.8 s				2178.7 sh		2169.5 s
494.2 vw	493.7 vw	490.3 mw	492.3 m	491.3 w	487.2 w	488.4 s	492.1 m	484.4 m
		476.7 sh			474.5 sh			
472.7 m	473.9 m	471.2 ms	472.5 ms	473.1 m	469.8 ms	472.4 m	470.8 m	471.4 mw
460.3 s	454.9 m	453.0 vs	456.2 s	449.9 s	447.3 vs	443.3 s		
	438.9 sh	430.5 s			426.8 s	428.3 sh	433.5 vs	434.9 sh
420.0 vbr	417.7 vs	416.5 vs	423.9 vbr	421.3 sh	415.9 vs	418.4 vs	426.1 sh	419.2 vs
		406.3 vs		418.1 vs	405.6 vs		415.1 s	407.8 s
348.0 ms	348.6 m	348.1 s	345.5 s	346.6 m	344.1 m	342.2 s	344.8 m	341.4 m
329.3 vs	328.3 s	324.8 vs	328.4 w		323.5 w			338.0 m
		318.5 sh		245.8 vw	317.8 sh			
			227.8 vs	224.7 vs	222.4 vs			
183.7 vbr	183.1 s		181.8 vbr	181.8 s, br		181.2 vbr	184.5 s, br	179.8 s
136.3 s			139.2 s	155.3 w	139.3 sh	140.6 m	135.1 s	134.9 sh
	126.8 m	123.9 s, br		131.5 s	122.2 s, br		123.2 vw	123.6 s, br
115.2 s	102.7 m		110.9 s	101.8 s		107.4 w	104.5 s	
			77.9 w				86.9 w	
		65.9 s, br			63.1 s, br		68.0 w	63.2 vbr

[a] Frequencies are given in cm^{-1}. [b] Intensity symbols: s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad.

Table III. Observed Raman Shifts[a] for Powders of $M_2Pt(CN)_5X$

$M_2Pt(CN)_5Cl$			$M_2Pt(CN)_5Br$			$M_2Pt(CN)_5I$		
M = Na	M = K	M = Cs	M = Na	M = K	M = Cs	M = Na	M = K	M = Cs
2215.9 s[b]	2209.7 s	2198.1 s	2213.5 s	2208.5 s	2194.3 s	2208.4 s	2202.5 s	2195.5 s
2202.8 m	2197.9 ms	2187.2 m	2201.1 ms	2196.1 ms	2184.0 m	2196.1 m	2192.2 m	2184.7 m
						2187.6 mw	2181.0 m	2177.0 w
								2170.8 w
512.9 w	494.7 m	492.4 w	512.3 mw			511.3 w	491.1 w	487.2 w
484.8 s	473.1 vs	478.7 ms	481.9 s	474.1 s	475.8 m	484.9 s	471.8 s	479.2 m
		468.0 s		469.7 s	466.8 vs		468.4 sh	461.2 s
462.2 s	455.4 s	453.8 s	457.1 s	451.9 s	447.1 vs	445.4 vs	436.5 s	437.1 vs
434.1 w	435.2 w	431.4 mw	428.0 m	429.0 m	425.0 m		426.5 m	427.3 sh
416.6 w	426.2 m	421.9 mw				418.4 ms		421.2 s
	409.7 w			405.8 w	407.6 vw		409.7 w	408.3 w
390.4 mw			390.4 w			389.8 vw		388.3 vw
	343.5 w	348.2 mw	345.1 w	350.3 w	346.5 vw	339.8 vw	349.0 vw	341.4 vw
329.3 vs	328.0 s	324.6 vs	326.5 w	323.5 w	322.7 w	318.0 w		
297.7 w		298.5 vw	271.8 vw	293.4 w	271.6 vw	273.1 w	273.0 vw	
			226.4 vs	225.1 vs	221.9 vs	182.2 vs	178.3 vs	182.0 vs
146.3 s	158.0 w	150.3 s	142.3 s	163.1 vw	146.0 m	144.5 ms		142.9 m
	131.8 s	135.5 vs		129.2 s	132.2 s		132.0 s	129.0 ms
					110.7 m		115.8 m	114.4 m
	90.0 vw				80.4 w		89.1 vw	
	79.4 w						68.4 w	

[a] Frequencies are given in cm^{-1}. [b] Intensity symbols: s, strong; m, medium; w, weak; v, very; sh, shoulder; br, broad.

carbonyls.[6,10] This implies that metal-ligand π bonding and changes in π bonding during the vibrational cycle are less significant for the cyanides.

In addition, a problem of resolving C-N stretching frequencies is commonly encountered in the vibrational spectroscopy of metal cyanides. The symmetric and antisymmetric C-N stretching frequencies of individual cyanide complexes lie fairly close together, whereas the corresponding carbonyl complexes exhibit C-O stretching frequencies in a much broader range. For example, for $Cr(CO)_6$ the C-O frequencies range from 2119 to 2000 cm^{-1};[11] whereas, for $Co(CN)_6^{3-}$, C-N frequencies range from 2151 to 2128 cm^{-1}.[4d] This slight separation of C-N stretching frequencies results from relatively small CN-CN interactions.[12] The carbonyls, on the other hand, exhibit considerable CO-CO interaction, apparently due to dipole-dipole coupling.[11]

Absorptions in the high-frequency region (above 2000 cm^{-1}) are denoted as C-N stretching frequencies though normal mode calculations show that, for metal cyanides as well as metal carbonyls, these modes involve considerable M-C stretching. Overtone and combination spectra were not observed and therefore no anharmonic corrections were attempted in this work.

The assignment of the radial A_1 and E vibrations is fairly straightforward and utilizes rationale developed for monosubstituted metal carbonyls. The weak infrared band located at highest energy is obviously due to the planar A_1 stretching or "breathing" mode (ν_1). This weak band corresponds to an intense, highly polarized Raman peak in solution (Table IV).

The antisymmetric E mode (ν_{15}) should exhibit the most intense infrared absorption by virtue of the fact that a large change in dipole moment of the complex accompanies this vibration. Thus, the E mode is confidently assigned to the

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(11) L. H. Jones, R. S. McDowell, and M. Goldblatt, *Inorg. Chem.*, 8, 2349 (1969).

(12) L. H. Jones, "Advances in the Chemistry of Coordination Compounds," S. Kirschner, Ed., Macmillan, New York, N. Y., 1961, p 398.

Table IV. Polarization Data for Aqueous Platinum(IV) Cyanide Complexes[a]

$Pt(CN)_6{}^{2-}$ [b]	$Pt(CN)_5Cl^{2-}$	$Pt(CN)_5Br^{2-}$	$Pt(CN)_5I^{2-}$	$Pt(CN)_4Br_2{}^{2-}$ [c]
2211 (p)[d]	2204.9 (p)	2203.0 (p)	2199.5 (p)	2194.0 (p)
2200 (d)	2192.7 (d)	2191.5 (d)	2187.7 (d)	2184.8 (d)
			2179.5 (d)	
469 (p)	462.9 (p)	465.8 (p)	467.0 (p)	465.8 (p)
464 (d)		452.5 (p)	432.9 (p)	431.1 (d)
431 (d)				
	329.5 (p)	226.0 (p)	180.6 (p)	201.9 (p)
109 (d)	109.1 (d)	105.2 (d)	107.4 (d)	100.2 (d)

[a] Frequencies are expressed in cm^{-1}. [b] Data taken from ref 5 for solution of $Na_2Pt(CN)_6$; all other data from this work, for saturated solutions of the potassium salts. [c] These results are included for comparison purposes and to supplement the results of a previous study of mixed cyanohalides of platinum(IV): L. H. Jones and J. M. Smith, *Inorg. Chem.*, 4, 1677 (1965). [d] p = polarized; d = depolarized.

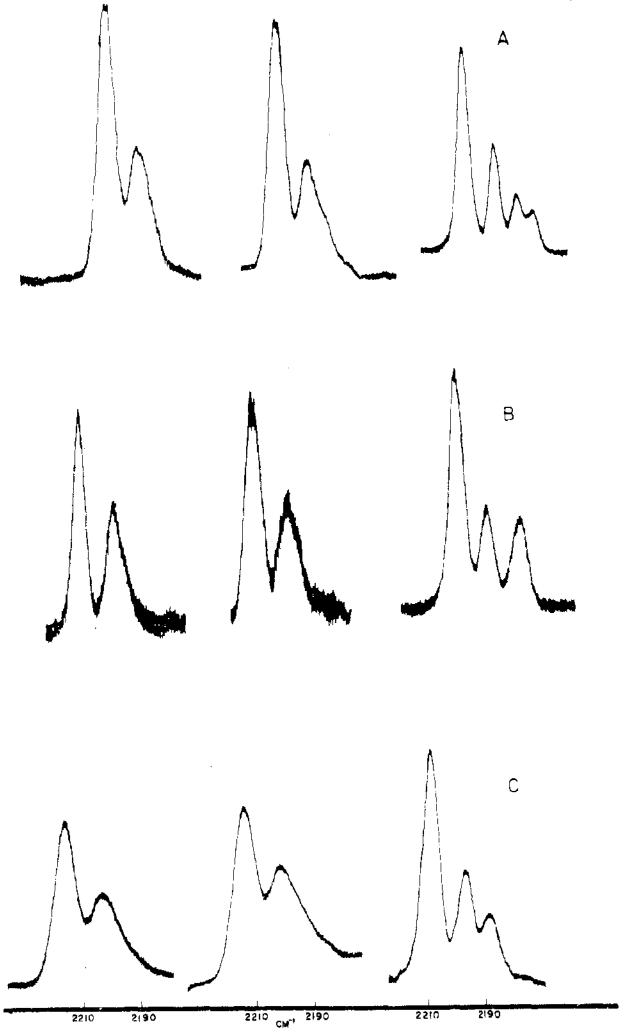

Figure 2. Raman spectra of $M_2Pt(CN)_5X$ in the C-N stretching region. The spectra depicted from left to right are the chloro, bromo, and iodo complexes, respectively; the labels are designated as follows: A, M = Cs; B, M = K; C, M = Na.

strong band found in all the infrared spectra of these complexes. This fundamental is too weak to be observed in the Raman spectra (except for the cesium iodo complex). This absence has also been noted in the case of analogous metal carbonyl halides.[13]

The B_1 mode (ν_9) is Raman active only and appears with medium to strong intensity in all species. A very weak shoulder sometimes is found in the infrared spectra at very nearly the same value.

The exact position of the apical C-N stretching band (ν_2) is difficult to establish because of overlapping by other bands. The iodo complexes do exhibit three Raman peaks in this region, the lowest of which may be assigned to this A_1 mode. No doubt each of the two A_1 CN stretches involve both radial and axial CN groups to some extent. We are not in a position to estimate the amount of such coupling at this time. In the infrared spectra, this peak is apparently obscured by the intense E mode for the bromo and chloro complexes. Likewise, the Raman peak arising from the A_1 apical vibration is nearly coincident with that of the B_1 mode. The pattern is definitely established by the cesium-iodo salt, for which four Raman peaks and three infrared peaks are observed. It is apparent that $\nu_1 > \nu_9 > \nu_2 > \nu_{15}$.

Pt-X Stretching Vibrations. The platinum-halide stretching vibrations transform as A_1 species and therefore are active in both the infrared and Raman spectra. These peaks are generally intense and can be easily detected by the traditional method of noting the characteristic shift when one halide is replaced by another in a series of analogous complexes. Furthermore, these vibrations give rise to peaks that are highly polarized in the Raman spectra. The Pt-X frequencies obtained from solid-state infrared and Raman data correspond very closely, except for a fairly large discrepancy for the potassium salt of the iodo complex. The ir spectrum for this species exhibits a very broad band, the breadth of which may arise from lattice effects such as combinations with acoustical modes.

The Pt-Cl frequencies exhibit unsymmetrical band shapes at room temperature; indeed, a splitting is observed in the ir spectrum of the cesium salt (*cf.* Table VII). At low temperature a splitting is clearly resolved (except for the sodium salt where lattice broadening is too extensive). This phenomenon is undoubtedly due to an isotopic splitting of the nondegenerate Pt-Cl vibration similar to that noted by Bennett and Clark in chloro-substituted metal carbonyls.[13] The shift of 7 cm^{-1} agrees with that calculated for $Pt\text{-}^{35}Cl \rightarrow Pt\text{-}^{37}Cl$.

Pt-C Stretching Vibrations. Since the Pt-C stretching vibrations transform similarly to the C-N stretches, they may be assigned according to the same criteria. Furthermore, since assignments have been made for the more symmetrical unsubstituted (the O_h system)[5] and trans-disubstituted platinum(IV) cyanides (the D_{4h} system),[14] the problem of assigning frequencies to Pt-C and other low-energy vibrations is greatly simplified because several of the vibrations in these systems are mechanically similar. There are two strong Raman peaks in this region which we believe to arise from ν_3 and ν_4.

The planar A_1 Pt-C stretching (breathing) mode (ν_3) is readily assigned to a very intense Raman peak observed near 470 cm^{-1} for the solid potassium salts. This band is polarized in solution, though slightly displaced toward lower energies. As expected, for most of these compounds, this vibration is absent from the infrared spectra. The mechanically analogous vibration is found in the O_h system for $K_2Pt(CN)_6$ at 471 cm^{-1} and in the D_{4h} system for $K_2Pt(CN)_4Cl_2$ at 463 cm^{-1}. The assignments for the sodium and cesium salts follow similar arguments except that they are shifted by the different cationic interactions.

An intense band appearing in both the infrared and Raman

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(13) M. A. Bennett and R. J. H. Clark, *J. Chem. Soc.*, 5560 (1964).

(14) L. H. Jones and J. M. Smith, *Inorg. Chem.*, 4, 1677 (1965).

Table V. Vibrational Spectral Data[a] for Solid $M_2Pt(CN)_6$

Infrared					Raman		
M = Na	M = K		M = Cs	Assignment[b]	M = K		Assignment[b]
2195.3 vs[c]	2191 vs	2190.0 s	2179.4 vs	$\nu_{CN}(F_{1u})$	2216 (10)[d]	2214.9 vs	$\nu_{CN}(A_{1g})$
	2165 vw	2164.7 vw		$\nu_{CN}(^{15}N)$[e]	2203 (9)	2201.9 vs	$\nu_{CN}(E_g)$
	2148 w	2147.2 w		$\nu_{CN}(^{13}C)$[e]			
488.4 s	486 s	485.4 s	485.3 s	$\delta_{PtCN}(F_{1u})$	471 (6)	472.7 vs	$\nu_{PtC}(A_{1g})$
482.0 sh	482 m	481.3 sh	482.3 sh				
443.7 w	439 w	439.7 w	448.8 s	$\delta_{PtCN}(F_{2g})$?	464 sh (4)	463.2 s	$\nu_{PtC}(E_g)$
423.9 s, br	419 s, br	417.8 vs	414.6 s	$\nu_{PtC}(F_{1u})$	428 (1)	426.8 m	$\delta_{PtCN}(F_{2g})$
			399.6 s			409.3 vw	
		175.5 s, br				180.0 w	
		132.6 s, br				156.0 m	
	(102)[f]	97.5 s		$\delta_{CPtC}(F_{1u})$		90.5 vw	
		49.0 w, br			52 (1)	53.1 w	Lattice

[a] Frequencies are reported in cm^{-1}. [b] First column of data for $K_2Pt(CN)_6$ refers to results of Siebert and Siebert;[5] second column refers to this work; assignments taken from ref 5. [c] Intensities are designated as follows: s, strong; m, medium; w, weak; br, broad; sh, shoulder; v, very. [d] Numbers in parentheses designate intensity relative to the most intense band in the spectrum. [e] CN stretch for monosubstituted species. [f] Calculated value.

Table VI. Assigned Frequencies[a] for Solid $M_2Pt(CN)_5X$

		$M_2Pt(CN)_5Cl$			$M_2Pt(CN)_5Br$			$M_2Pt(CN)_5I$		
Species	Mode	M = Na	M = K	M = Cs	M = Na	M = K	M = Cs	M = Na	M = K	M = Cs
A_1	1	2216	2210	2197	2214	2209	2195	2208	2203	2194
	2		2195	2182	2196	2194		2186	2181	2177
	3	485	473	468	482	474	467	485	472	461
	4	461	455	453	457	451	447	444	435	437
	5	329	328	325	227	225	222	182	178	182
	6	494	494	490	492	491	487	488	492	484
	7									
A_2	8									
B_1	9	2203	2198	2187	2201	2196	2184	2196	2192	2185
	10	473?[b]			473?	469?		471?	468?	
	11			478?			476?			479?
	12									
B_2	13	435	426	422	428	429	425		427	421
	14									
E	15	2192	2187	2175	2189	2186	2172	2182	2182	2170
	16	420	417	410	424	418	410	418	415	413
	17	473	474	471	472	473	470	472	471	471
	18		435	430			427			428
	19	348	348	348	346	347	345	342	345	341
	20									
	21									
	22									

[a] Frequencies are expressed in cm^{-1}. [b] Question mark indicates that the assignment is uncertain.

Table VII. Platinum-Halide Stretching Frequencies for $M_2Pt(CN)_5X$ Complexes[a]

		M = Na		M = K		M = Cs	
X	Temp, °K	Ir	Raman	Ir	Raman	Ir	Raman
Cl	300	329.3	329.3	328.3	328.0	324.8 318.5	324.6
	100[b]	332.0		333.9 326.9		324.9 317.9	
Br	300	227.8	226.4	224.7	225.1	222.4	221.9
I	300	181.2	182.2	184.5	178.3	179.8	182.0

[a] Frequencies are expressed in cm^{-1}. [b] Approximately liquid nitrogen temperature.

spectra in the C_{4v} system is assigned to the apical A_1 stretching mode (ν_4). This band is completely absent from the spectra of the O_h and D_{4h} systems. The solid-state Raman and infrared peak positions nearly coincide; the aqueous solution Raman spectra exhibit polarized bands at 453 and 433 cm^{-1} for the pentacyanobromo and -iodo complexes, respectively. For the chloro complex, this peak is apparently coincident with ν_3 in solution.

The B_1 vibration (ν_{10}) may be correlated with the B_{1g} mode in the D_{4h} system to which a peak found at 455 cm^{-1} in $K_2Pt(CN)_4Cl_2$ was attributed. The assignments of this mode are based on the observation of a weak ill-defined shoulder on the low-energy side of the symmetric A_1 stretching peak. A number of other modes may fall in this region, so this assignment is quite uncertain.

The assignment of the antisymmetric E mode (ν_{16}) at 410-420 cm^{-1} is straightforward. This vibration has the same form as the platinum-carbon vibration of T_{1u} symmetry in $K_2Pt(CN)_6$ (419 cm^{-1}) and the similar vibration of E_u symmetry in the D_{4h} system (412, 412, and 407 cm^{-1} for the chloro, bromo, and iodo species, respectively). The C_{4v} vibration appears very intense in the infrared spectra but is very weak or not observed in the Raman spectra. The ir spectra of the cesium species exhibit a splitting of this mode.

Pt-C-N Deformation Vibrations. The A_1 planar deformation mode (ν_6) has the same form as an A_{2u} mode in the D_{4h} system[14] which has been assigned at 496, 494, and 490 cm^{-1} for the chloro, bromo, and iodo species, respectively. The peak attributed to this mode is rather weak in the infrared spectra except for the iodo complex. It is also weak in the Raman spectra.

Assignments made for the B_1 deformation mode (ν_{11}) are tenuous. They are based on the appearance of a Raman peak in the spectra of the cesium salts slightly above ν_3.

This mode involves the same coordinates as the A_1 mode (ν_6) and should lie near it in energy.

The B_2 planar deformation has exactly the same form as the inactive F_{2g} mode in the O_h system.[5] Siebert[5] has assigned a weak ir band found for $K_2Pt(CN)_6$ at 428 cm^{-1} to this mode. A Raman shift appears in this region for nearly all the C_{4v} salts; a corresponding peak is not observed in the infrared spectra.

Since the planar E vibration (ν_{17}) is mechanically analogous to an E_u mode in the D_{4h} system, it should appear at nearly the same energy. The D_{4h} ir absorptions appear at 473, 476, and 476 cm^{-1} for the chloro, bromo, and iodo salts, respectively. Peaks roughly correspond in this region in the infrared and Raman spectra, but this may be due to an accidental degeneracy of this E mode with other fundamentals (A_1 and B_1 Pt-C stretches and the B_1 deformation). A splitting is observed in the low-temperature ir spectra of a number of C_{4v} complexes which seems to suggest further the degenerate nature of this absorption.

We feel that the remaining planar deformation (ν_{18}) should absorb at lower energy than ν_{17} since the former vibration does not involve two MCN groups bending into each other. We therefore tentatively assign some peaks in the 430-cm^{-1} region to ν_{18}.

The peak which appears in all the salts at around 345 cm^{-1} is assigned to the apical Pt-C-N deformation (ν_{19}). There is no hint of a band in this region for the O_h and D_{4h} complexes. Furthermore, the infrared absorption splits into a symmetrical doublet at liquid nitrogen temperature. The corresponding Raman peak is relatively weak. We should point out that this band could also arise from the inactive A_2 mode, made active by reduction in symmetry in the crystal lattice.

C-Pt-C Deformation Vibrations. The low-frequency (C-Pt-C and C-Pt-X) modes are impossible to assign with any confidence at this time. In the solution Raman spectrum we see only one band (depolarized) from 105 to 109 cm^{-1}. For C-Pt-C and C-Pt-X bending modes, the selection rules predict one polarized band and five depolarized bands in this region. In the solid state, we can expect significant shifts from the solution frequency due to coupling with lattice modes.[4e,15,16] Several peaks are observed in the infrared and Raman spectra between 60 and 190 cm^{-1} which no doubt arise from mixed modes, involving both internal and external coordinates. It would be presumptuous to attempt an assignment at this time, especially without knowing the crystal structure. Suffice it to point out that these frequencies appear to be particularly sensitive to the cation mass.

Infrared Intensity Data. While the nature of σ and π bonding in metal cyanides can be elucidated by determining M-C and C-N force constants from their vibrational spectra, further insight into the nature of equilibrium electronic configurations can be obtained from the measurement of intensities of infrared absorption bands. Intensity studies have been shown to be particularly useful in describing the mode of bonding in metal cyanides.[6] These studies indicate that the intensity of antisymmetric vibrations may be used as a measure of the extent of π bonding in cyanide complexes.

Additional information can be obtained about the bonding in metal cyanides by studying the effect of replacing one or more cyanide groups by other ligands. The changes in the intensities of the C-N stretching frequencies indicate changes in metal-carbon π bonding which accompany the replacement of cyanides by these ligands. For this reason the intensities of the antisymmetric C-N stretching modes were measured for various platinum cyanides. Intensities are listed in Table VIII for a variety of metal cyanides. The integrated absorption coefficients are reported as integral multiples of k per linear N-C-M-C-N unit, the integers indicating the degree of degeneracy of a particular antisymmetric mode.

Because of the high kernel charge of platinum(IV), strong Pt-C σ bonding and little π bonding are expected for cyanoplatinum(IV) complexes. Intensity measurements verify this expected minimal amount of π bonding. The integrated absorption coefficient for the $Pt(CN)_6{}^{2-}$ ion is lower than that of any of the other hexacyanometalates with the exception of the $Cr(CN)_6{}^{3-}$ ion which possesses only three dπ electrons and, as a result, exhibits little π bonding. The isoelectronic cobalt(III)-, rhodium(III)-, iridium(III)-, and iron(II)-cyano complexes have considerably higher intensities, primarily because of the lower effective nuclear charge of the central metal. The high-frequency band position of $Pt(CN)_6{}^{2-}$ gives further indication that σ bonding predominates since strong M-C σ bonding leads to relatively high F_{CN} while π bonding depresses this constant.[6,17] It can also be seen that the C-N band position is gradually shifted to lower energies in the order CN > Cl > Br > I, *i.e.*, in the order of increasing electron-releasing ability which results in increased M-CN π^* bonding.

The mono- and disubstituted platinum(IV) cyanides each contain a square-planar array of four cyanides around the central metal and each therefore has an ir-active C-N mode of E symmetry. Since this vibration is mechanically analogous to the triply degenerate mode of the parent complex, the effect on metal-cyanide bonding by halide substitution can be determined by comparing the absorption per linear N-C-Pt-C-N unit of the unsubstituted and substituted complexes. The reported intensities for the monosubstituted species are actually sums of the intensities of the axial A_1 mode and the antisymmetric E mode since these modes are not resolved. However, we expect the A_1 mode to be much weaker than the E mode because it does not involve the interaction of two collinear MCN π systems. There is a significant increase in intensity of the measured C-N stretching band in the order Cl < Br < I which suggests an increase in Pt-C-N π bonding in the same order, similar to the $Au(CN)_2X_2{}^-$ and $Pt(CN)_4X_2{}^{2-}$ systems.

The intensity per linear unit is greatly enhanced in the dihalo complexes relative to the hexacyano and the pentacyano complexes. It appears that the extent of Pt-CN π bonding increases in the order CN < Cl < Br < I and in the order $Pt(CN)_5X^{2-} < Pt(CN)_4X_2{}^{2-}$. Such a result is not surprising since the effect of replacing a π acid group (*viz.*, CN) by σ donors such as the halides should be to increase the electron density around the platinum atom. The added negative charge on platinum raises the energies of its d orbitals which in turn facilitates the extent of back-bonding with the π^* orbitals of the cyanide groups. The further depression of the C-N stretching frequency with additional replacement of cyanides by halides is also consistent with this argument. Jones noted the same intensity trends for the halo-substituted cyanoaurates(III).[18] The intensity measurements of Abel

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(15) B. I. Swanson and L. H. Jones, *J. Chem. Phys.*, **53**, 3761 (1970).

(16) B. I. Swanson and L. H. Jones, *J. Chem. Phys.*, **55**, 4174 (1971).

(17) R. F. Fenske and R. L. DeKock, *Inorg. Chem.*, **11**, 437 (1972).

(18) L. H. Jones, *Proc. Symp. Coord. Chem., 1964*, 349 (1965).

Table VIII. Vibrational Frequency and Intensity Data for Various Metal Cyanides

Solute	ν_{max}, cm^{-1}	ϵ_{max}, l. mol^{-1} cm^{-1}	k,[a] l. mol^{-1} cm^{-2}	Ref
$KCu(CN)_2$	2125	165		*b*
$KAg(CN)_2$	2135	264	3100	*c, d*
$KAu(CN)_2$	2147	477	4980	*c, d*
$Hg(CN)_2$	2190	0	71	*c, e*
$K_3Cr(CN)_6$	2128	232	3 × 700	*c*
$K_3Mn(CN)_6$	2112	584	3 × 3735	*c*
$K_3Fe(CN)_6$	2118	1062	3 × 4100	*c*
$K_3Co(CN)_6$	2129	1748	3 × 6100	*c*
$K_3Rh(CN)_6$	2133	1600	3 × 5735	*c*
$K_3Ir(CN)_6$	2130	1920	3 × 7370	*c*
$K_4Fe(CN)_6$	2044	4600	3 × 30,670	*c*
$KAu(CN)_4$	2189	34	2 × 160	*f*
$KAu(CN)_2Cl_2$	2181	19	180	*f*
$KAu(CN)_2Br_2$	2177	48	425	*f*
$KAu(CN)_2I_2$	2171	94	1180	*f*
$K_2Pt(CN)_6$	2185	205	3 × 802	*g*
$K_2Pt(CN)_5Cl$	2180	143	2 × 824[h]	*g*
$K_2Pt(CN)_5Br$	2179	180	2 × 950[h]	*g*
$K_2Pt(CN)_5I$	2176	243	2 × 1270[h]	*g*
trans-$K_2Pt(CN)_4Cl_2$	2174	187	2 × 1134	*g*
trans-$K_2Pt(CN)_4Br_2$	2171	268	2 × 1486	*g*
$K_2Pt(CN)_4$	2134	1265	2 × 5080	*g*
$K_2Ni(CN)_4$	2124	870	2 × 3325	*g*
$K_2Pd(CN)_4$	2136	855	2 × 3170	*g*

[a] Integrated absorption coefficients obtained by the weight method; these are broken up into integral multiples of linear N-C-M-C-N groups. [b] R. A. Penneman and L. H. Jones, *J. Chem. Phys.*, **24**, 293 (1956). [c] Reference 6. [d] L. H. Jones and R. A. Penneman, *J. Chem. Phys.*, **22**, 965 (1954). [e] R. A. Penneman and L. H. Jones, *J. Inorg. Nucl. Chem.*, **20**, 19 (1961). [f] L. H. Jones, *Proc. Symp. Coord. Chem., 1964*, 349 (1965). [g] This work. [h] The apical CN stretch contributes to this intensity; however, we believe this contribution is relatively small.

and Butler on the complexes $M(CO)_5X^-$ and $M'(CO)_5X$ ($M =$ Cr, Mo, W; $M' =$ Mn, Re; $X =$ Cl, Br, I) also indicate the same trend of increased intensity with increasing mass of the halogen substituent, with the exception of $W(CO)_5X^-$ and $Re(CO)_5X$ which exhibit the opposite trend.[19] The latter anomaly may be resolved by considering the fact that greater orbital overlap is expected between the large central metal and the iodide when compared to the smaller halides. This "direct donation" mechanism has been invoked to explain anomalies in trends observed for cis C-O force constants in substituted metal carbonyls.[20]

It is of interest to compare the three species $Ni(CN)_4^{2-}$, $Pd(CN)_4^{2-}$, and $Pt(CN)_4^{2-}$, each having eight d electrons and about the same effective nuclear charge on the central metal. From intensity data and peak positions, it is seen that there is a marked enhancement of the degree of π bonding relative to that in the Pt(IV) system. The extent of π bonding as monitored by intensity decreases in the irregular order Pt > Ni > Pd. Similar results were obtained for the hexacyano complexes of tripositive cobalt, rhodium, and iridium.[6] It should be emphasized at this time that small changes in C-N band positions cannot be used as the sole criterion for measuring changes in π bonding in cyano complexes. If the intensity of the antisymmetric E modes had not been determined, the amount of π bonding in the nickel-palladium-platinum series would appear to be greatest for $Ni(CN)_4^{2-}$ on the basis of frequency data alone.

It is important to point out that, though our intensity studies indicate considerable variations in the extent of metal-ligand π bonding among metal-cyanide complexes, the degree of such back-bonding is probably an order of magnitude greater in metal carbonyls. This is evidenced by the increased infrared absorption intensity and lowering in CO force constant for metal carbonyls.

Lattice Effects. In general, a shift to higher energies is observed for the C-N stretching frequencies of all the complexes in the solid state as the size of the alkali metal ion decreases. This is expected, since a smaller cation interacts more strongly with the complex anion. Such interaction can be expected to lead to an increase in the C-N frequency.[16] Although no definite trend can be observed for the deformations, the Pt-C and Pt-X stretches also shift to lower energy with increasing size of the counterion. A strong lattice interaction apparently restricts all the internal vibrations, though this is not so pronounced for the deformation modes. Extensive broadening observed as the cation size decreases is also indicative of strong lattice interaction. Perhaps the most striking aspect of the intermolecular lattice effect is its magnitude relative to the intramolecular effect of the halide substituent. For example, the position of the C-N stretching frequencies shifts from 5 to 8 cm^{-1} within a halide series, whereas a variation of cation from sodium to cesium results in almost a 20-cm^{-1} shift. The magnitude of the shift due to the nature of the halide is also slightly dependent on the nature of the cation; the range of cyanide frequencies for the halide series is largest for the sodium salts and smallest for the cesium salts.

The unit cells of the cesium salts apparently involve a lower site symmetry than the sodium and potassium analogs since the antisymmetric degenerate Pt-C stretching modes are split (see Figures 3 and 4) and the intensities of a number of absorptions are enhanced. Even at low temperature, the potassium salts still exhibit only one strong absorption for the E mode when the cyanide groups are replaced by halides. The $Cs_2Pt(CN)_6$ complex exhibits a more complex spectrum than the analogous potassium salt. The doublet nature of the antisymmetric Pt-C stretch is retained throughout the halide series which implies that the manner of distortion is similar for all the cesium salts.

Substituent Effects. The halides have a small effect on all the internal vibrations of these species, but the effect on the Pt-C stretching modes is particularly interesting. The iodo complexes exhibit a different absorption pattern than the others primarily because the apical Pt-C stretching mode is shifted toward lower energies (*cf.* Figures 3 and 4). The positions of all the Pt-C vibrational bands are almost invariably shifted to lower energies in the order Cl > Br > I. Bennett and Clark have noted the opposite trend for halo-substituted metal carbonyls.[13] A substantial increase in π bonding per carbonyl is expected in this system since a π-accepting carbonyl group is replaced by a σ-donating halide group. The increase in M-C stretching frequencies is due to an increase in the M-C bond strengths of the remaining M-C bonds as a result of the enhanced amount of π bonding in this system. Since the iodide is more electron releasing than the chloride or bromide, a greater amount of π bonding is anticipated in the iodo complex.

It would appear that the same arguments should apply to the analogous cyanide complexes. The intensity data indicate increased M-CN π bonding in the order Cl < Br < I. But since π bonding is relatively unimportant in metal cyanides, the opposite trend observed for the Pt-C stretching frequencies may be explained by inductive effects because of a predominance of σ interaction of platinum(IV) with ligands in

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(19) E. W. Abel and I. S. Butler, *Trans. Faraday Soc.*, **63**, 45 (1967).

(20) R. A. Brown and G. R. Dobson, *Inorg. Chim. Acta*, **6**, 65 (1972).

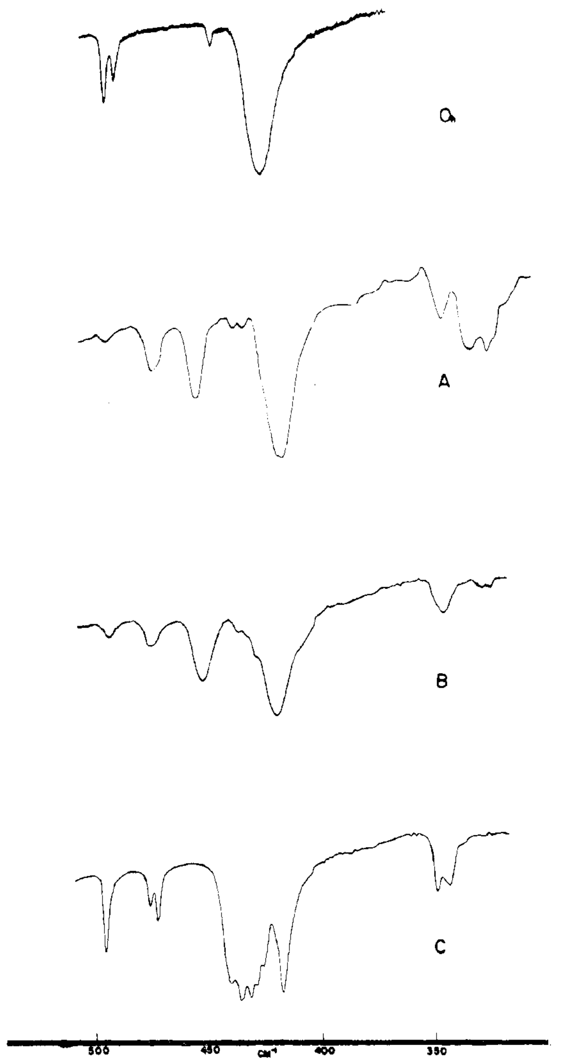

Figure 3. Infrared mull spectra of $K_2Pt(CN)_5X$ at liquid nitrogen temperature in the medium-frequency region; the labels are designated as follows: O_h, X = CN; A, X = Cl; B, X = Br; C, X = I.

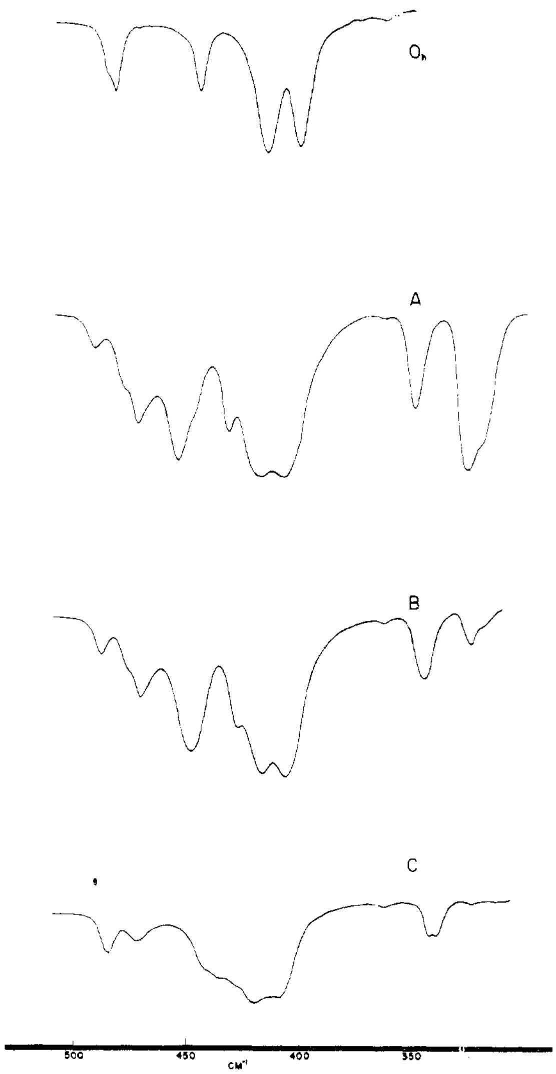

Figure 4. Infrared mull spectra of $Cs_2Pt(CN)_5X$ at room temperature in the medium-frequency region; the labels are designated as follows: O_h, X = CN; A, X = Cl; B, X = Br; C, X = I.

the coordination sphere. Hence, this trend must be due to the fact that the Pt-C σ-bond strength in the pentacyanohaloplatinate(IV) series decreases in the order $(\sigma_{\text{Pt-C}})_{\text{Cl}} > (\sigma_{\text{Pt-C}})_{\text{Br}} > (\sigma_{\text{Pt-C}})_{\text{I}}$. The bonding mechanism proposed for the halo-substituted carbonyls should of course be operative to some extent in the platinum series, but changes in σ bonding must be dominant in order to explain the observed trend in the Pt-C stretching frequencies. This same conclusion was reached for the cyanohalides of gold(III), which, like platinum(IV) complexes, involve a highly charged central metal atom.

The effect of halide on the Pt-C bond is most apparent when considering the apical A_1 stretching vibration. Strictly speaking, the two A_1 M-C stretching modes of $Pt(CN)_5X^{2-}$ are actually mixtures of radial and axial stretches. Evidence on other systems indicates that M-C frequencies cannot always be assigned uniquely to axial or radial stretches because of extensive coupling between these two types of coordinates. However, the radial Pt-C stretching mode in the C_{4v} complexes, which is mechanically analogous to a symmetric stretching mode in the O_h system, is shifted very slightly relative to the unsubstituted case (*cf.* Tables V and VI). On the other hand, the apical A_1 mode is shifted considerably to lower energies. Such a separation of A_1 modes could be explained by in-phase and out-of-phase coupling. However, the fact that the radial stretch is unshifted while the apical stretch shows a shift dependent on the halide ligand indicates that the halides appear to have a weakening effect on the trans Pt-C bond but an insignificant effect on the cis Pt-C bond. In other words, the trans influence of the halide substituents is greater than their cis influence. (By convention, the larger the trans (cis) influence, the greater the trans (cis) platinum-carbon bond weakening.)

A corollary of the preceding discussion is the fact that the trans influence of the halides is greater than that of the cyanide ion. Thus, the trans-influence series may be described as follows: I > Br > Cl > CN. It is interesting to note that the position of the apical A_1 stretching frequency is directly related to the electronegativity of the halogen substituent. A plot (not shown) of Pt-C stretching frequencies *vs.* the Allred-Rochow electronegativities of the halogen is found to be linear for the apical mode; whereas, for the radial mode, a definite trend is difficult to establish because of the small differences in frequencies. The position of cyanide in the series can be rationalized by comparing the relative electron-withdrawing abilities of the cyanide and halide groups. Since the cyanide can be a π acid, it has additional capacity to withdraw electrons from the central metal. For this reason, the extent of Pt-C σ interaction should be greatest and accordingly Pt-C bond strengths should be largest in the unsubstituted hexacyanoplatinate(IV).

Similar arguments may be applied to the trends observed in the C-N stretching region. The shift of all C-N stretching modes to lower energies in the order $Cl > Br > I$ is consistent both with σ- and π-bonding arguments. However, the shift of the apical A_1 stretching mode to lower energy than the radial mode (which remains essentially unshifted from the analogous peak of the parent complex) indicates that σ bonding must predominate when one considers the trans influence discussed above for the M-C bonds.

The observations made for the nitroprusside ion are entirely consistent with the above arguments. The apical Fe-C stretching frequency is found at a higher energy than the radial stretching frequency; likewise, the apical C-N stretching frequency appears at a higher energy than the radial C-N frequency.[21] This, of course, is due to the fact that the positively charged nitrosyl ligand, formally designated as NO^+, has a greater capacity for electron withdrawal than the isoelectronic cyanide ion. It exhibits a larger "inductive effect" than the cyanide ion and a greater σ interaction is observed, particularly for the trans cyanide.

An inherent uncertainty is involved in the previous discussions. Strictly speaking, in order to make deductions about bond strengths, stretching force constants rather than stretching frequencies should have been used as the criterion. However, the normal-coordinate analysis has not yet been attempted for the pentacyanohaloplatinates(IV). There may be considerable mode mixing or other interactions which complicate the interpretation of data. Nevertheless, in a series of closely related compounds, these effects will be nearly constant, and the suggested conclusions and trends should be substantially correct even if one argues from frequencies alone. Hopefully, the results of the present work will stimulate further interest in the vibrational spectra of substituted cyanides, particularly in the metal-carbon stretching region.

Summary

Many of the fundamental frequencies have been assigned for the complex ions $Pt(CN)_5Cl^{2-}$, $Pt(CN)_5Br^{2-}$, and $Pt(CN)_5I^{2-}$. The symmetric radial Pt-C and C-N stretching frequencies of these complexes remain essentially unshifted from the unsubstituted complex. However, the apical Pt-C and C-N frequencies are shifted to lower energies in the order $Cl > Br > I$.

Because of the high degree of σ bonding exhibited in these complexes, a number of interesting phenomena are observed: (1) the extent of π bonding, as measured by infrared intensities, is minimal; (2) the positions of C-N absorptions occur at rather high energies; (3) the halide substituents have a greater trans influence than cis influence, though this influence is relatively small in both cases; (4) the trans-influence series is found to be $I > Br > Cl > CN$; (5) by comparison with the effect of halides on the vibrational spectra and bonding in these complexes, intermolecular lattice interactions are sometimes dominant.

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Registry No. $Na_2Pt(CN)_5Cl$, 41523-78-8; $K_2Pt(CN)_5Cl$, 19536-96-0; $Cs_2Pt(CN)_5Cl$, 19536-95-9; $Na_2Pt(CN)_5Br$, 41523-79-9; $K_2Pt(CN)_5Br$, 19536-94-8; $Cs_2Pt(CN)_5Br$, 12071-37-3; $Na_2Pt(CN)_5I$, 41523-81-3; $K_2Pt(CN)_5I$, 18972-63-9; $Cs_2Pt(CN)_5I$, 19537-43-0; $Na_2Pt(CN)_6$, 18988-11-9; $K_2Pt(CN)_6$, 16920-94-8; $Cs_2Pt(CN)_6$, 41523-83-5; *trans*-$K_2Pt(CN)_4Cl_2$, 12072-77-4; *trans*-$K_2Pt(CN)_4Br_2$, 12072-67-2; $K_2Pt(CN)_4$, 562-76-5; $K_2Ni(CN)_4$, 14220-17-8; $K_2Pd(CN)_4$, 14516-46-2.

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Cobalt-59 Nuclear Magnetic Resonance Studies of Stereoisomerism in Tris(bidentate)cobalt(III) Complexes[1]

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Cobalt-59 nmr spectra of stereoisomers of several tris(bidentate)cobalt(III) complexes, where the ligands are (*S*)-1,2-propanediamine and several chiral and achiral β-diketones, have been examined. Chemical shift and line width differences were found among stereoisomers of most of the complexes. Chemical shifts appear to be unrelated in any general way to absolute configuration of the complexes; however, line widths are generally larger for isomers of lower symmetry. Relative chemical shifts and relative energies of the low-energy ligand-field electronic transition, as determined from absorption or circular dichroism spectra, are compared among the different complexes and also among the individual stereoisomers of a given complex. Relative chemical shifts among cobalt(III) complexes of a series of achiral β-diketonate ligands can be explained qualitatively in terms of relative contributions from temperature-independent paramagnetism to the ^{59}Co shielding constant. However, the observed chemical shift differences among diastereomers of complexes having chiral ligands cannot be explained in a similar fashion.

The extremely wide range of chemical shifts occurring in ^{59}Co nmr is well documented; in fact, the ^{59}Co nucleus was one of the first for which the chemical shift phenomenon was observed.[2] Previous work has shown that for a large number of six-coordinate cobalt(III) complexes a fairly linear

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