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CONTRIBUTION FROM THE LOS ALAMOS SCIENTIFIC LABORATORY,
UNIVERSITY OF CALIFORNIA, LOS ALAMOS, NEW MEXICO

Vibrational Spectra, Force Constants, and Bonding in Mixed Cyanide–Halide Complexes of Platinum[1]

BY LLEWELLYN H. JONES AND J. MICHAEL SMITH

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The infrared spectra of Solid $K_2Pt(CN)_4Cl_2$, $K_2Pt(CN)_4Br_2$, and $K_2Pt(CN)_4I_2$ are reported. The Raman spectrum of aqueous $K_2Pt(CN)_4Cl_2$ is also given. Many of the fundamental frequencies are assigned. The symmetry force constants for the A_{1g}, B_{1g}, A_{2u}, and E_u representations are calculated for a valence force potential function with neglect of off-diagonal interaction constants. The force constants (including interaction constants) for bond stretching are calculated. It is found that there is a remarkable similarity between the bonding in these Pt(IV) complexes and that in Au(III) cyanide complexes.

Introduction

Recently a study of the vibrational spectra of *trans*-dicyanodihalo complexes of gold(III) was reported.[2] It was shown that the substitution of halide ion for cyanide ion in the tetracyanoaurate(III) ion had only a small effect on the two remaining CN groups, which are *trans* to each other. An interesting group of compounds having similar bonding but a square-planar metal tetracyanide group is the tetracyanodihalo complexes of platinum(IV). A study of this group should add to our knowledge of bonding properties in metal cyanide complexes.

Experimental

Preparation.—The potassium salts of the tetracyanodihalo complexes of platinum were first reported by Blomstrand.[3] A slight modification of his procedure was used in this work. For the chloride, a slight excess of Cl_2 gas dissolved in methanol was added to aqueous $K_2Pt(CN)_4$, yielding $K_2Pt(CN)_4Cl_2$. The bromide and iodide salts were made by adding a slight excess of the free halogen directly to aqueous $K_2Pt(CN)_4$.

Thin, flat crystals were obtained by evaporating water solutions of the bromide and chloride and a 50–50 water–methanol solution of the iodide. The iodide is dark brown, the bromide yellow, and the chloride nearly colorless. The iodide solution partially decomposes on evaporation, yielding a mixture of the dark $K_2Pt(CN)_4I_2$ crystals and white $K_2Pt(CN)_4$ crystals. Once formed, however, the $K_2Pt(CN)_4I_2$ crystals are stable in dry air for at least several days. Over a period of weeks in room air they gradually lose I_2, forming $K_2Pt(CN)_4$. The bromide and chloride appear to be stable indefinitely at room temperature.

Recording of Spectra.—The Raman spectrum of aqueous $K_2Pt(CN)_4Cl_2$, as given in Table I, was recorded on a Cary Model 81 spectrometer. The bromide and iodide were too deeply colored to permit recording of Raman spectra with this spectrometer. Infrared spectra were recorded on a Perkin-Elmer 521 and 112 G. The observed infrared data are given in Table II. For the infrared studies both single crystals and dispersions in polyethylene melts were used. The Raman spectra and the high-frequency infrared spectra (above 200 cm.$^{-1}$) are not shown here as these are quite similar to those of the dicyanodihaloaurate[2] and tetracyanoaurate[4] ions. The middle frequency (300–550 cm.$^{-1}$) region of $Pt(CN)_4Cl_2^{-2}$ is shown in Figure 1.

TABLE I
RAMAN SPECTRUM OF AQUEOUS $K_2Pt(CN)_4Cl_2$ (CM.$^{-1}$)

2196	(60, P)[a]	455	(<10, sh, D)
2186	(33, D)	330	(100, P)
463	(10, P)	120	(25, D)

[a] Numbers in parentheses give intensities at maximum relative to 100 for strongest peak at 330 cm.$^{-1}$. P and D are polarized and depolarized, respectively.

Assignment of Frequencies

The $Pt(CN)_4X_2^{-2}$ ion is treated as having D_{4h} symmetry. The fact that we observe for the chloride two Raman-active CN stretching frequencies and only one infrared-active CN stretching frequency, different from the two Raman frequencies, establishes that the halides are *trans* to each other. This is also borne out by observation of one Pt–Cl Raman frequency and one (different) Pt–Cl infrared frequency. Thus the spectra of the dichloride are consistent with D_{4h} symmetry and not consistent with the *cis* structure of C_{2v} symmetry,

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(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) L. H. Jones, *Inorg. Chem.*, **3**, 1581 (1964); (b) *ibid.*, **4**, 1472 (1965).

(3) C. W. Blomstrand, *Ber.*, **2**, 202 (1869). Reported in "Gmelin's Handbuch der Anorganischen Chemie," No. 68, Auflage (Pt), p. 207.

(4) L. H. Jones and J. M. Smith, *J. Chem. Phys.*, **41**, 2507 (1964).

TABLE II

INFRARED ABSORPTION PEAKS OF $K_2Pt(CN)_4X_2$

$K_2Pt(CN)_4Cl_2$		$K_2Pt(CN)_4Br_2$		$K_2Pt(CN)_4I_2$		Assignment
ν, cm.$^{-1}$	I^a	ν, cm.$^{-1}$	I^a	ν, cm.$^{-1}$	I^a	
4368	1	4361	2	4342	3	$\nu_1 + \nu_{16}$
4345	1	4335	1.5	4316	4	$\nu_5 + \nu_{16}$
3582	35	3610		3595		H_2O
3422	40	3410		3425		H_2O
3216		3225				H_2O
2642	4	2642	4	2631	7	$\nu_2 + \nu_{16}$
				2622	6	$\nu_6 + \nu_{16}$
2608	4	2603	3	2589	9	$\nu_1 + \nu_{18}$
		2193	3	2181	3	ν_1
				2170	sh	ν_5
2176	100	2172	100	2161	100	ν_{16}
2151	3	2141	17			$C^{15}N$
				2137		$K_2Pt(CN)_4$
2135	8	2132	16	2121	15	^{13}CN
496	50	494	40	490	80	ν_{12}
473	25	476	30	476	70	ν_{18}
460	5 sh	458	5			
422	5 sh	421	sh	415	sh	
412	100	412	100	407	100	ν_{17}
349	90	247	65	199	50	ν_{11}

[a] Intensities are relative on an optical density scale based on 100 for the most intense band in the spectrum for each compound. They are very approximate as the weaker bands were determined from single crystals and the intense bands were determined from dispersions in a polyethylene melt.

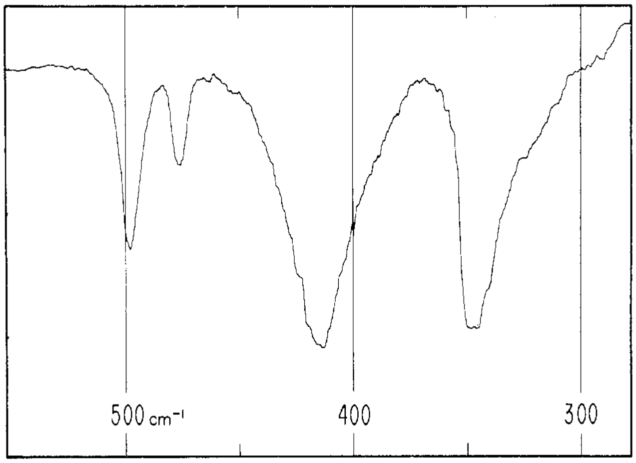

Figure 1.—Infrared spectrum from 300 to 550 cm.$^{-1}$ of a dispersion of $K_2Pt(CN)_4Cl_2 \cdot xH_2O$ in polyethylene. The concentration of salt is about 3 mg./cm.^{2}.

which would have two Pt–Cl and four CN stretching frequencies, all of which may be active in both the Raman and infrared. There is no indication of strong lattice interactions which would negate the approximation of D_{4h} symmetry. The spectrum of the bromide resembles that of the chloride and is also treated under D_{4h}. The iodide shows a few bands forbidden by D_{4h} selection rules, similar to the case of $KAu(CN)_2I_2$.[2] However, the observed fundamentals are analogous to those of the chloride and therefore it is also treated under the D_{4h} point group.

For D_{4h} symmetry the $Pt(CN)_4X_2^{-2}$ ion will have twenty fundamental vibrations ($3A_{1g}$, $1A_{2g}$, $2B_{1g}$, $2B_{2g}$, $2E_g$, $3A_{2u}$, $2B_{2u}$, and $5E_u$). Of these A_{2u} and E_u are infrared-active only, while A_{1g}, B_{1g}, B_{2g}, and E_g are Raman-active only. The A_{2g} and B_{2u} vibrations are inactive. An approximate characterization of the vibrations is given in Table III, along with the assignments, which are discussed below.

$Pt(CN)_4Cl_2^{-2}$ Vibrations. **A_{1g}.**—In the Raman spectrum of the chloride we see three polarized bands at 2196, 463, and 330 cm.$^{-1}$. These are readily assigned as the totally symmetric (A_{1g}) CN stretching, Pt–C stretching, and Pt–Cl stretching vibrations, respectively. The band at 330 cm.$^{-1}$ is definitely from the Cl stretching vibration as 463 cm.$^{-1}$ is too high and also the infrared-active Pt–Cl stretch is at 349 cm.$^{-1}$.

A_{2g}.—The A_{2g} vibration is inactive and not observed, even in a combination band. Due to the nature of the interactions it is a low-frequency MCN bending vibration—probably in the region 350–400 cm.$^{-1}$.[5]

B_{1g}.—The B_{1g} CN stretching vibration is observed at 2186 cm.$^{-1}$ as a depolarized Raman frequency. The B_{1g} MC stretching vibration is obscured by the A_{1g} MC stretching at 463 cm.$^{-1}$. However, when the 463 cm.$^{-1}$ band is reduced by polarization of the incident light parallel to the sample tube axis, it is apparent that there is a depolarized Raman band at about 455 cm.$^{-1}$ which we assign as ν_6 (B_{1g}). This is analogous to the case of $Au(CN)_4^-$,[4] with Raman shifts at 461 (P) and 452 (D) cm.$^{-1}$.

B_{2g}.—We have no information about the B_{2g} vibrations. The MCN bending, ν_7, is probably in the region 400–450 cm.$^{-1}$,[4] while the CMC bending, ν_8, will be around 110 cm.$^{-1}$.[4] There is a Raman shift at 120 cm.$^{-1}$, but this we believe arises from the CMCl bending vibration of E_g symmetry, by analogy[2] with $Au(CN)_2Cl_2^-$.

E_g.—The MCN bending frequency (ν_9) of E_g symmetry was not observed. It involves bending of MCN against an MCl bond and is probably in the region 350–400 cm.$^{-1}$ by analogy with $Au(CN)_2Cl_2^-$.[2] The CMCl bending vibration, ν_{10}, is assigned at 120 cm.$^{-1}$ as mentioned under the B_{2g} discussion.

A_{2u}.—There are three infrared-active bands in the region 400–500 at 496, 473, and 412 cm.$^{-1}$. There appears to be no conclusive way to assign these; however, the most satisfactory force constant solution, by analogy[2] with $Au(CN)_2Cl_2^-$, is obtained by assigning 496 cm.$^{-1}$ as the MCN bending vibration, ν_{12}, of A_{2u} symmetry. The band at 349 cm.$^{-1}$ is obviously the MCl stretching vibration, ν_{11}, as it shifts to 247 cm.$^{-1}$ for the bromide and 199 cm.$^{-1}$ for the iodide. The frequency for the CMCl bending vibration, ν_{13}, was not observed but is expected to be slightly above 100 cm.$^{-1}$.[2]

B_{2u}.—The inactive B_{2u} frequencies are not known. The MCN bending frequency, ν_{14}, should be close to ν_{12} as it involves the same coordinates with slightly different interactions. Similarly ν_{15} should be near ν_{13}.

E_u.—The strong CN stretch at 2176 cm.$^{-1}$ is obviously ν_{16} of E_u symmetry. After assigning 496 cm.$^{-1}$ as an A_{2u} frequency we are left with 473 and 412 cm.$^{-1}$ for the MCN bend and MC stretch of E_u symmetry (ν_{17} and ν_{18}). By analogy with $Au(CN)_2Cl_2^-$ (ref. 2b),

(5) L. H. Jones, *J. Chem. Phys.*, **41**, 856 (1964).

the lower, more intense, frequency at 412 cm.$^{-1}$ is assigned to MC stretching, ν_{17}. The CMC and CMCl bends, ν_{19} and ν_{20}, are not known but must be in the neighborhood of 100 cm.$^{-1}$.

$Pt(CN)_4Br_2^{-2}$.—For the infrared-active vibrations, of A_{2u} and E_u symmetry, the assignments, as given in Table III, are based on the same arguments as given above for the chloride.

TABLE III

FUNDAMENTAL FREQUENCIES OF THE IONS $Pt(CN)_4X_2^{-2}$ (CM.$^{-1}$)

Representation	Type	$Pt(CN)_4Cl_2^-$	$Pt(CN)_4Br_2^-$	$Pt(CN)_4I_2^-$
A_{1g}	$\nu_1(\nu_{CN})$	2196	2193	2181
	$\nu_2(\nu_{MC})$	463	(467)^a	(467)^a
	$\nu_3(\nu_{MX})$	330	(200)^b	(141)^b
A_{2g}	$\nu_4(\delta_{MCN})$			
B_{1g}	$\nu_5(\nu_{CN})$	2186	(2178)^c	2170
	$\nu_6(\nu_{MC})$	455	(455)^d	(455)^d
B_{2g}	$\nu_7(\delta_{MCN})$			
	$\nu_8(\delta_{CMC})$			
E_g	$\nu_9(\delta_{MCN})$			
	$\nu_{10}(\delta_{CMX})$	120		
A_{2u}	$\nu_{11}(\nu_{MX})$	349	247	199
	$\nu_{12}(\delta_{MCN})$	496	494	490
	$\nu_{13}(\delta_{CMX})$	(105)^e	(97)^e	(90)^e
B_{2u}	$\nu_{14}(\delta_{MCN})$			
	$\nu_{15}(\delta_{CMX})$			
E_u	$\nu_{16}(\nu_{CN})$	2176	2172	2161
	$\nu_{17}(\nu_{MC})$	412	412	407
	$\nu_{18}(\delta_{MCN})$	473	476	476
	$\nu_{19}(\delta_{CMC})$	(93)^f	(103)^f	(100)^f
	$\nu_{20}(\delta_{CMX})$	(120)^g	(76)^h	(63)^h

[a] From combinations. [b] Calculated assuming $F_{MX,MX'}$ is proportional to F_{MX}. [c] Calculated assuming anharmonicity corrections for the bromide are an average of those for the iodide and chloride. [d] Not observed. Assumed the same as for the chloride for calculation. [e] Assumed by comparison with ν_{10} and analogy with ν_{15} of $Au(CN)_2X_2^{-2}$, which is a similar mode of vibration. [f] Assumed to have the same force constant (0.50 mdyne Å. radian^{-2}) as the analogous vibration in $Au(CN)_4^-$.[4] [g] Assumed the same as ν_{10} by analogy with $Au(CN)_2Cl_2^-$.[2] [h] Same force constants assumed for bending of CPtBr and CPtI as for CPtCl.

The Raman spectrum was not observed because of the deep yellow color of the material. Therefore, the A_{1g} vibrations are assigned by indirect methods. A weak peak observed at 2193 cm.$^{-1}$ is assigned as ν_1, the symmetric CN stretch, made active by decrease of symmetry below D_{4h} in the crystal. The combination band at 2642 cm.$^{-1}$, assigned as $\nu_2 + \nu_{16}$, places ν_2 at about 466 cm.$^{-1}$ by comparison with the analogous $Pt(CN)_4Cl_2^{-2}$ combination.

The B_{1g} CN stretch, ν_5, is assigned as 2178 cm.$^{-1}$ from the combination band at 4335 cm.$^{-1}$, which is definitely $\nu_5 + \nu_{16}$. The anharmonicity applied was -16 cm.$^{-1}$, the average of the values for the chloride (-17) and iodide (-15). There is no concrete evidence for ν_6 so it is chosen to be about the same as for the chloride.

$Pt(CN)_4I_2^{-2}$.—The A_{2u} and E_u assignments follow in the same manner as for the chloride and bromide.

The iodide is very deeply colored (almost black) and thus Raman data were not obtained. However, the A_{1g} and B_{1g} CN stretches were observed in the infrared, at about 2181 and 2170 cm.$^{-1}$, respectively. This is a result of breakdown of the isolated ion selection rules in the crystal. The same breakdown was observed[2] for $Au(CN)_2I_2^-$.

The A_{1g} and B_{1g} Pt–C stretches are assigned in the same manner as those of the bromide.

Calculation of Force Constants

In order to calculate force constants F and G matrices were set up by the method of Wilson, Decius, and Cross.[6] The symmetric coordinates used are given in Table IV. The internal coordinates are defined in Figure 2. Force constant solutions were obtained for the A_{1g}, B_{1g}, A_{2u}, and E_u matrices using the frequencies of Table III. They are listed in Table V.

TABLE IV

A_{1g}	$S_1 = 2^{-1}(r_1 + r_2 + r_3 + r_4)$
	$S_2 = 2^{-1}(R_1 + R_2 + R_3 + R_4)$
	$S_3 = \sqrt{2}^{-1}(d_1 + d_2)$
A_{2g}	$S_4 = 2^{-1}(\beta_1 + \beta_2 + \beta_3 + \beta_4)$
B_{1g}	$S_5 = 2^{-1}(r_1 - r_2 + r_3 - r_4)$
	$S_6 = 2^{-1}(R_1 - R_2 + R_3 - R_4)$
B_{2g}	$S_7 = 2^{-1}(\beta_1 - \beta_2 + \beta_3 - \beta_4)$
	$S_8 = 2^{-1}(\alpha_1 - \alpha_2 + \alpha_3 - \alpha_4)$
E_g	$S_9 = \sqrt{2}^{-1}(\beta_6 - \beta_8)$
	$S_{10} = 2^{-1}(\gamma_1 - \gamma_2 + \gamma_3 - \gamma_4)$
A_{2u}	$S_{11} = \sqrt{2}^{-1}(d_1 - d_2)$
	$S_{12} = 2^{-1}(\beta_5 + \beta_6 + \beta_7 + \beta_8)$
	$S_{13} = \sqrt{8}^{-1}(\gamma_1 + \gamma_2 - \gamma_3 - \gamma_4 + \gamma_5 + \gamma_6 - \gamma_7 - \gamma_8)$
B_{2u}	$S_{14} = 2^{-1}(\beta_5 - \beta_6 + \beta_7 - \beta_8)$
	$S_{15} = \sqrt{8}^{-1}(\gamma_1 + \gamma_2 - \gamma_3 - \gamma_4 - \gamma_5 - \gamma_6 + \gamma_7 + \gamma_8)$
E_u	$S_{16} = \sqrt{2}^{-1}(r_2 - r_4)$
	$S_{17} = \sqrt{2}^{-1}(R_2 - R_4)$
	$S_{18} = \sqrt{2}^{-1}(\beta_1 - \beta_3)$
	$S_{19} = 2^{-1}(\alpha_1 - \alpha_2 - \alpha_3 + \alpha_4)$
	$S_{20} = 2^{-1}(\gamma_1 - \gamma_2 - \gamma_3 + \gamma_4)$

TABLE V

SYMMETRY FORCE CONSTANTS OF $Pt(CN)_4X_2^{-2}$ [a,b]

		X = Cl	X = Br	X = I
A_{1g}	F_{11}	17.296	17.265	17.052
	F_{22}	3.485	3.546	3.548
	F_{33}	2.277	1.89	1.49
B_{1g}	F_{55}	17.170	17.036	16.903
	F_{66}	3.360	3.362	3.363
A_{2u}	$F_{11,11}$	1.892	1.567	1.236
	$F_{12,12}$	0.569	0.58	0.58
	$F_{13,13}$	0.51	0.51	0.51
E_u	$F_{16,16}$	17.373	17.307	17.143
	$F_{17,17}$	2.158	2.157	2.102
	$F_{18,18}$	0.52	0.53	0.53
	$F_{19,19}$	0.50	0.50	0.50
	$F_{20,20}$	0.60	0.60	0.60

[a] The stretching force constants (F_{11}, F_{22}, F_{33}, F_{55}, F_{66}, $F_{11,11}$, $F_{16,16}$, and $F_{17,17}$) are in units of mdynes/Å. The bending force constants ($F_{12,12}$, $F_{13,13}$, $F_{18,18}$, $F_{19,19}$, and $F_{20,20}$) are in units of mdynes Å. radian^{-2}. [b] Distances used are CN = 1.15, PtC = 1.99, PtCl = 2.32, PtBr = 2.47, and PtI = 2.66 Å.

Discussion of Force Constants

The bending force constants listed in Table V are quite approximate, as can be seen from the assumptions

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(6) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill Book Co., New York, N. Y., 1955.

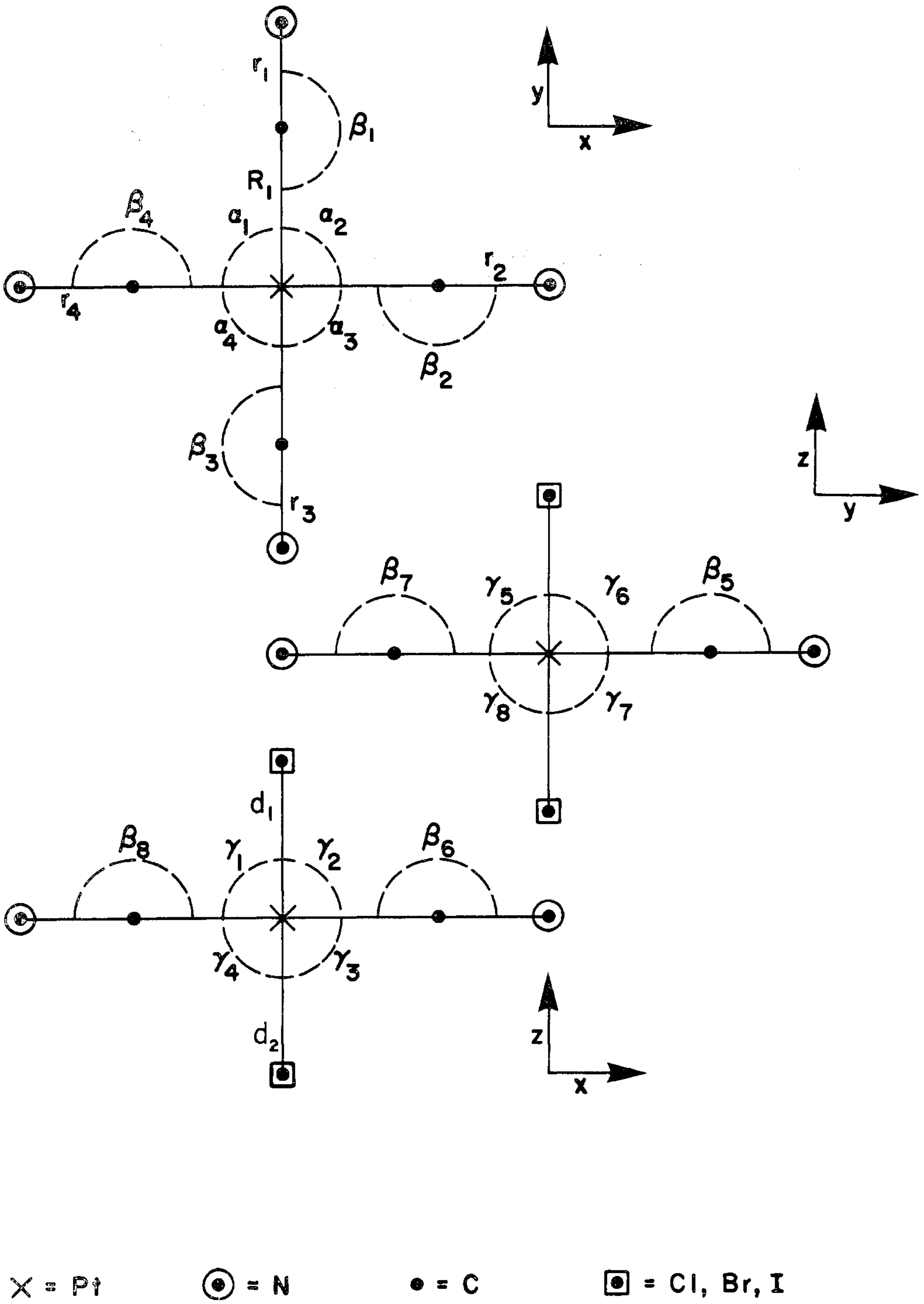

Figure 2.—Internal coordinates of $Pt(CN)_4X_2^{-2}$.

involved in selecting the fundamental bending frequencies. These assumptions are listed at the bottom of Table III. Nevertheless, the calculated stretching force constants do not change significantly with changes of several wave numbers for assignments of bending frequencies. Therefore the stretching force constants can be considered as reliable insofar as the potential function is reliable. This potential function is a general quadratic force field with neglect of off-diagonal interaction constants.[7] The bend–stretch interaction constants have only a small effect on the stretching force constants; thus, their neglect is not serious. In the past[2] we have neglected the CN, MC interaction constants. For comparison we shall neglect them here also. The effect of including them will be considered. The MX, MC and MX, CN interactions have only a small effect on the other calculated force constants as the bonds are perpendicular to each other. Detailed calculations show this to be true. Furthermore, since they are perpendicular their interactions will be small by analogy with the perpendicular MC, MC″ interactions.[4] Their neglect is therefore not serious.

Stretching Force Constants.—From the results of

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(7) By off-diagonal interaction constants we mean the elements not on the diagonal in the symmetry force constant matrix. They represent interaction between two different symmetry coordinates of the same symmetry.

Table V we arrive at the bond stretching force constants of Table VI. The CN stretching force constant is slightly lower than for $Au(CN)_2X_2^-$, probably because of the higher effective kernel charge on the Au atom than on the Pt atom. This leads to stronger σ bonding for the gold compound which is evidenced also by the slightly higher MC force constant for $Au(CN)_2X_2^-$ than for $Pt(CN)_4X_2^{-2}$. The MX force constant (and $F_{MX,MX'}$) is also slightly lower for the Pt compounds than for the Au compounds, except possibly for the iodide. However, the results for the iodide, and possibly the bromide, must be considered in doubt as the symmetric stretching vibration, ν_3, was not observed.

TABLE VI

VALENCE STRETCHING FORCE CONSTANTS FOR $Pt(CN)_4X_2^{-2}$ [a]

	$Pt(CN)_4Cl_2^{-2}$	$Pt(CN)_4Br_2^{-2}$ [b]	$Pt(CN)_4I_2^{-2}$ [b]
F_{CN}	17.30	17.23	17.06
F_{MC}	2.79	2.81	2.78
F_{MX}	2.09	1.73	1.37
$F_{CN,C'N'}$ [c,d]	−0.07	−0.08	−0.08
$F_{CN,C''N''}$ [d]	0.03	0.06	0.04
$F_{MC,MC'}$ [c]	0.63	0.65	0.68
$F_{MC,MC''}$ [d]	0.06	0.09	0.05
$F_{MX,MX'}$	0.19	0.16	0.13

[a] Units are mdynes/Å. Force constants are calculated with neglect of CN, MC interactions. [b] The values for the bromide and iodide are less reliable than those for the chloride because of the assumptions made about ν_8 and ν_6 (see Table III). [c] The single prime refers to opposite bonds; the double prime refers to adjacent bonds (at 90°). [d] These values, less than 0.1, are essentially zero within the accuracy of the calculations because of the approximations involved.

The trend with halide is similar to that for $Au(CN)_2X_2^-$; thus, F_{CN} decreases slightly with increasing mass of the halide atom. The MX force constant decreases considerably with the mass of the halide which is certainly to be expected as a strong M–I σ bond is much longer than a strong M–Cl σ bond.

Perhaps the most interesting feature is the large constant for interaction of opposite MC bonds (0.63–0.68 mdyne/Å.). This is appreciably larger than for $Au(CN)_2X_2^-$,[2b] and almost as large as the analogous constant for $K_3Ir(CN)_6$ (0.69) and $K_3Rh(CN)_6$ (0.75).[5] For the Ir and Rh compounds it was previously[5] thought that the strong metal–cyanide π bonding led to the high MC, MC′ interaction constant. However, in $Pt(CN)_4X_2^{-2}$ we expect only slight metal–cyanide π bonding and thus the strong MC, MC′ interaction must have another explanation, as discussed in ref. 2b. In the latter paper it was pointed out that perhaps it is best explained as a removal of electrons from the metal when one MC bond is stretched, causing a stronger attraction of the metal for the other carbon atom.

The MC, CN Interactions.—Some recent work[8] indicates that for $Au(CN)_2^-$ the interaction of a CN bond with a nonadjacent MC′ bond is negligible, but that the adjacent CN, MC interaction constant is about 0.3 mdyne/Å. It is not yet known whether this interaction constant is transferable from one metal–cyanide complex to another. If we include a value of 0.3 mdyne/Å. for $F_{CN,MC'}$ in the normal coordinate analyses for the $Pt(CN)_4X_2^{-2}$ ions, it has the effect of raising the CN force constant and lowering the MC force constant, each by about 2%.

Alternative Solution.—There is another reasonable solution which interchanges the assignments ν_{12} (δ_{MCN}) and ν_{18} (δ_{MCN}). This leads to a value of 0.52 mdyne Å. radian^{-2} for $F_{12,12}$ and to 0.58 for $F_{18,18}$. At present there is little from which to choose between the two solutions.

Summary

From the infrared spectra of the complex ions $Pt(CN)_4Cl_2^{-2}$, $Pt(CN)_4Br_2^{-2}$, and $Pt(CN)_4I_2^{-2}$ and the Raman spectrum of $Pt(CN)_4Cl_2^{-2}$ many of the fundamental vibrational frequencies have been assigned. Force constants have been calculated. There is a remarkable similarity of the bonding in $Pt(CN)_4X_2^{-2}$ with that in $Au(CN)_2X_2^-$,[2] and $Au(CN)_4^-$,[4] showing that the Pt–C bonds have strong σ character and little π character as expected from the high positive charge.

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(8) L. H. Jones, *J. Chem. Phys.*, **43**, 594 (1965).