ligand levels. This gives the bonding orbitals such appreciable central metal character that the calculated charge on the central metal is much less than the assumed starting charge and self-consistency is not achieved. Therefore, *appreciable covalency is an automatic consequence of the assumptions of the method.* Whether this conforms to physical reality is highly debatable.

For the same reasons, the method will always indicate that π-bonding is significant; that is, the π-bonding orbitals will have appreciable central metal character. In terms of relative separations, the 3d metal orbitals are closer to the π-ligand orbitals than to the σ-orbitals. Hence the 3d$_\pi$–π-bonding orbitals will be responsible for a large part of the charge reduction on the central metal necessary to achieve self-consistency.

Conclusion

It is apparent from the foregoing discussion that the semiempirical method presently employed for the determination of the electronic energy levels in transition metal complexes should not be accepted without strong reservations. It is to be hoped that continued investigations, both theoretical and experimental, will eventually result in an approach having a comparable simplicity without the uncertainty of the present method.

Acknowledgment.—The author wishes to express his thanks to Miss Carol C. Sweeney for her assistance in the computer calculations and to Professor L. F. Dahl for illuminating discussions. This work was partially supported by a grant from the National Science Foundation.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY, ILLINOIS INSTITUTE OF TECHNOLOGY,
TECHNOLOGY CENTER, CHICAGO, ILLINOIS 60616

Infrared Studies of Ligand–Ligand Interaction in Dihalogenodiammineplatinum(II) Complexes[1]

BY KAZUO NAKAMOTO, PAUL J. MCCARTHY, JUNNOSUKE FUJITA,
ROBERT A. CONDRATE, AND GEORGE T. BEHNKE

Received March 24, 1964

The infrared spectra of *cis*- and *trans*-$[\mathrm{Pt(NH_3)_2X_2}]$ (X = Cl, Br, I) and $[\mathrm{Pt(ND_3)_2Cl_2}]$ have been measured from 4000 to 200 cm.$^{-1}$. It has been shown that the infrared spectra of these complexes can better be explained if ligand–ligand interaction through a filled d-orbital of the platinum atom is considered. The results of a normal coordinate analysis of *trans*-$[\mathrm{Pt(NH_3)_2Cl_2}]$ support the postulated ligand–ligand interaction. The influence of *cis–trans* isomerism and of halogen substitution on the spectra has also been discussed.

I. Introduction

Chatt and co-workers[2] were the first to postulate the existence of intramolecular interaction between the ammine hydrogen atoms and the nonbonding d-electrons of the metal in a platinum ammine complex. They based this assumption on infrared studies (the N–H stretching region) of compounds of the type *trans*-$[\mathrm{Pt(am)LCl_2}]$, where am is a primary or secondary amine and L is a varied series of ligands. It is reasonable to expect that such an intramolecular interaction may operate in other platinum complexes, and that in them the ligands around the metal may interact electronically through the d-electrons of the platinum atom. Even though this interaction is electronic in origin, its effects will be observed more clearly in the vibrational spectra than in the electronic spectra, because of the rather small magnitude of the interaction.

The main purpose of this investigation was to investigate the possible presence of ligand–ligand interaction by a careful experimental and theoretical analysis of the vibrational spectra of dihalogenodiammineplatinum(II) complexes. The second purpose was to study the influence of *cis–trans* isomerism and of halogen substitution on the infrared spectra of these compounds.

II. Experimental

The compounds *cis*- and *trans*-$[\mathrm{Pt(NH_3)_2X_2}]$ (X = Cl, Br, I) have long been known, but it is only rather recently that their infrared spectra have been determined. Babaeva and Evstaf'eva[3] have reported the spectra of all these compounds in the NaCl region. Powell and Sheppard[4] have also reported the spectrum of *trans*-$[\mathrm{Pt(NH_3)_2Cl_2}]$ and Powell[5] that of the corresponding *cis* isomer, both in the range 4000 to 450 cm.$^{-1}$. Barrow, Krueger, and Basolo[6] have measured the spectra of *cis*- and *trans*-$[\mathrm{Pt(NH_3)_2Cl_2}]$ and their deuterated analogs from 4000 to 300 cm.$^{-1}$. Mizushima, *et al.*,[7] have also reported the infrared spectra of *cis*- and *trans*-$[\mathrm{Pt(NH_3)_2Cl_2}]$ and their palladium analogs in the NaCl region. Finally, the far-infrared spectra (460–170 cm.$^{-1}$) of *cis*- and *trans*-$[\mathrm{Pt(NH_3)_2X_2}]$ (X = Cl, Br) have recently been

---

(1) This work was partly supported by a research grant, GM-10072-01, from the National Institutes of Health, Public Health Service.

(2) (a) J. Chatt, L. Duncanson, and L. Venanzi, *J. Chem. Soc.*, 4461 (1955); L. Duncanson and L. Venanzi, *ibid.*, 3841 (1960); (b) J. Chatt, L. Duncanson, B. Shaw, and L. Venanzi, *Discussions Faraday Soc.*, **26**, 131 (1958); J. Chatt, L. Duncanson, and R. Guy, *Nature*, **184**, 526 (1959).

(3) A. V. Babaeva and O. N. Evstaf'eva, *Zh. Neorgan. Khim.*, **6**, 61 (1961).

(4) D. B. Powell and N. Sheppard, *J. Chem. Soc.*, 3108 (1956).

(5) D. B. Powell, *ibid.*, 4495 (1956).

(6) G. Barrow, R. Krueger, and F. Basolo, *J. Inorg. Nucl. Chem.*, **2**, 340 (1956).

(7) S. Mizushima, I. Nakagawa, M. Schmelz, C. Curran, and J. V. Quagliano, *Spectrochim. Acta*, **13**, 31 (1958).

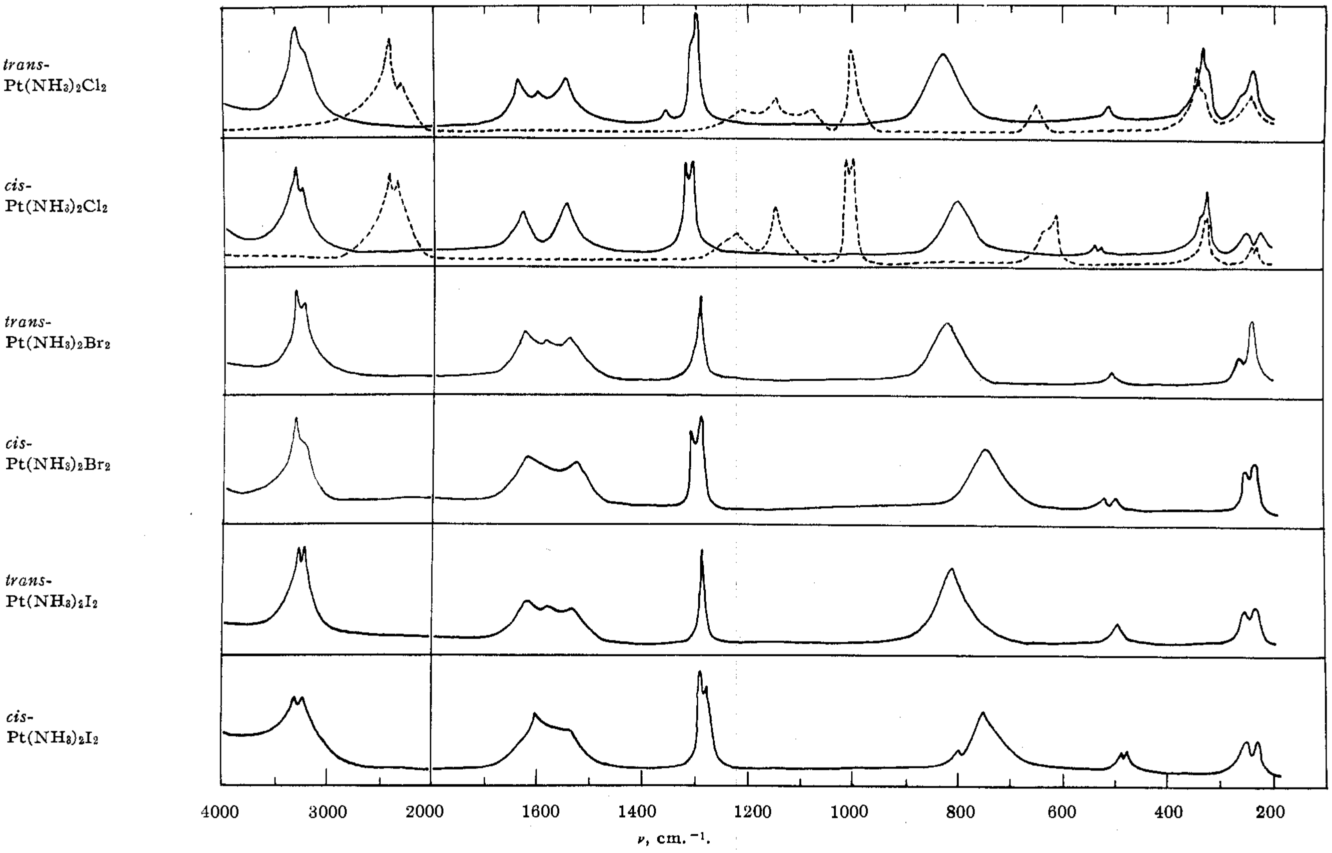


Figure 1.—Infrared spectra of dihalogenodiammineplatinum(II) complexes (dotted lines are for the corresponding deuterated compounds).

published by Adams and co-workers.[8] In order to confirm previous results and to supplement the data in the low-frequency region, we have prepared *cis*- and *trans*-$[Pt(NH_3)_2X_2]$ (X = Cl, Br, I) and $[Pt(ND_3)_2Cl_2]$ and have obtained their infrared spectra from 4000 to 200 cm.$^{-1}$.

Preparation of the Compounds. (1) ***cis*-Dichlorodiammineplatinum(II).**—$K_2[PtCl_4]$ (0.826 g., 0.0020 mole) was dissolved in 15 ml. of an aqueous solution containing 0.5 ml. of concentrated HCl and 0.6 g. of NH_4Cl. While the solution was maintained at 0° it was neutralized with NH_4OH, and 0.004 mole of additional NH_4OH was added. The solution was then kept at 0° for 48 hr. The yellow precipitate which slowly formed was removed, washed with ice–water, then dissolved in boiling water, reprecipitated by cooling, and finally recrystallized from hot 0.01 *M* HCl.

(2) **Deuterated *cis*-Dichlorodiammineplatinum(II).**—Compound **1** (0.1 g.) was dissolved in 15 ml. of D_2O at 80°. The solution was allowed to cool slowly and was left standing for 3 days. The product which separated was removed by filtration.

(3) ***cis*-Dibromodiammineplatinum(II).**—A portion of compound **1** was dissolved in a saturated aqueous solution of KBr and was then kept at 60° for 30 min. The yellow product which separated on cooling was removed and recrystallized from dilute HBr.

(4) ***cis*-Diiododiammineplatinum(II).**—Compound **1** was dissolved in 3 ml. of a saturated aqueous solution of KI at 80° and was shaken for 10 min. The desired product separated as a yellow precipitate upon cooling.

(5) ***trans*-Dichlorodiammineplatinum(II).**—$K_2[PtCl_4]$ (2.68 g., 0.0056 mole) was dissolved in 48 ml. of an aqueous solution containing 1.8 ml. of concentrated HCl. It was brought to boiling, 6.5 ml. of concentrated NH_4OH was added, and the solution was evaporated nearly to dryness; 260 ml. of 6.0 *M* HCl was added and the solution was evaporated to a volume of 20 ml. The yellow product was removed by filtration and recrystallized from boiling 0.1 *M* HCl.[9]

(6) **Deuterated *trans*-Dichlorodiammineplatinum(II).**—Compound **5** (0.1 g.) was refluxed with 20 ml. of D_2O for 18 hr. The deuterated compound precipitated on cooling.

(7) ***trans*-Dibromodiammineplatinum(II).**—This compound was prepared in the same way as compound **3**; the starting material was *trans*-$[Pt(NH_3)_2Cl_2]$.

(8) ***trans*-Diiododiammineplatinum(II)** was prepared in the same way as compound **4** with *trans*-$[Pt(NH_3)_2Cl_2]$ as the starting material.

Determination of the Spectra.—A Perkin-Elmer Model 21 double-beam infrared spectrophotometer, equipped with NaCl and KBr optics, was used to obtain the spectra from 4000 to 400 cm.$^{-1}$. The KBr disk method was employed in this region. The spectra between 700 and 200 cm.$^{-1}$ were measured with a Beckman Model IR-7 infrared spectrophotometer equipped with CsI optics. For these spectra the Nujol mull technique and CsI plates were used. Calibration of frequency readings was made with polystyrene film, 1,2,4-trichlorobenzene, indene, and water vapor.

III. Ligand–Ligand Interaction (Experimental Evidence)

Figure 1 shows the infrared spectra of *cis*- and *trans*-$[Pt(NH_3)_2X_2]$ (X = Cl, Br, I) from 4000 to 200 cm.$^{-1}$, and the frequencies are listed in Table I. Special attention should be focused on the bands around 1580 cm.$^{-1}$, which are usually classified as the degenerate deformation vibration of the NH_3 group.[10] This band splits into two or three peaks in these compounds. The magnitude of the splitting is between 140 and 65 cm.$^{-1}$ for all the compounds, including the deuterated analogs.

---

(8) D. M. Adams, J. Chatt, J. Gerratt, and A. D. Westland, *J. Chem. Soc.*, 734 (1964).

(9) G. B. Kauffman and D. O. Cowan, *Inorg. Syn.*, **7**, 239 (1963).

(10) S. Mizushima, I. Nakagawa, and J. V. Quagliano, *J. Chem. Phys.*, **23**, 1367 (1955).

TABLE I

OBSERVED FREQUENCIES OF DIHALOGENODIAMMINEPLATINUM(II)[a]

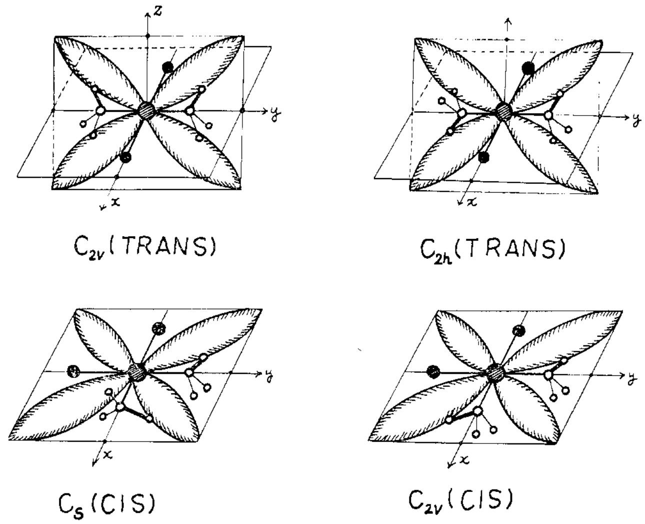
trans-[Pt(NH$_3$)$_2$X$_2$]			*cis*-[Pt(NH$_3$)$_2$X$_2$]			[Pt(ND$_3$)$_2$Cl$_2$][b]		Band assignment[c]
X = Cl	X = Br	X = I	X = Cl	X = Br	X = I	*trans*	*cis*	
3300	3284	3268	3297	3275	3294	2455	2465	ν(NH)
3220	3210	3200	3232	(3180)	3230	2318	2341	
1635	1627	1620	1625	1623	1604	1210	1212	δ(NH$_3$)
1597	1587	1579	...	...	...	1145	...	
1538	1537	1534	1544	1523	1532	1072	1147	
(1307)	...	...	1316	1307	1293	...	1013	δ(NH$_3$)
1294	1289	1290	1301	1288	1278	997	1003	
					806			
819	813	806	795	774	752	637	630	ρ_r(NH$_3$)
							604	
509	502	498	517	513	491	474	477[d]	ν(Pt–N)
...	...	...	508	499	477	...	470[d]	
330	...	...	(324)	...	...	337	(327)	ν(Pt–Cl)
(322)	...	...	317	...	...	(326)	319	
(253)	263	263	256	251	254	230	237	Skeletal bend
238	237[e]	230	222	226[e]	235	...	...	
...	237[e]	...	...	226[e]	...	...	...	ν(Pt–Br)[e]

[a] Values in parentheses indicate shoulders. [b] All the ammine bands are shifted to lower frequencies on deuteration by a factor of 1.29 to 1.43 (over-all average 1.34). [c] Band assignments are given for the nondeuterated compounds. [d] Extremely weak bands. [e] Overlapping of the bands assumed.

A compilation of all pertinent data on square-planar palladium(II) and platinum(II) ammine complexes is shown in Table II. It is clear from this table that the palladium complexes and the monoammine platinum complexes show no splitting of the NH$_3$ deformation band, whereas all others show from two to four bands in this region. Therefore, this splitting seems to be a characteristic feature of square-planar platinum complexes containing at least two ammine groups. There is no evident correlation, however, between the number of bands and the structure of the complex or nature of the ligands involved. Similar splittings, although much smaller in magnitude, occur in the spectra of *cis*-[Pt(NH$_3$)$_2$X$_2$] (X = Cl, Br, I) in the bands near 1300 cm.$^{-1}$ (classified as the NH$_3$ symmetric deformation vibration[10]) and in those near 500 cm.$^{-1}$ (assigned to the Pt–N stretching vibration[4,7]).

As will be shown later, the highest symmetry possible in *trans*-[Pt(NH$_3$)$_2$X$_2$] is only C$_{2v}$ or C$_{2h}$. Therefore, these splittings cannot be attributed to the removal of vibrational degeneracies by the crystal field. Furthermore, the splittings cannot be attributed to hydrogen bonding between an ammine group and the halogen of a neighboring molecule; such splittings would be expected to depend on the strength of the hydrogen bond formed and would accordingly be at most very slight for the iodo compounds. The data shown in Tables I and II clearly indicate that this is not the case. The possibility of Fermi resonance between the NH$_3$ deformation (*ca.* 1580 cm.$^{-1}$) and NH$_3$ rocking (*ca.* 800 cm.$^{-1}$) vibrations can be ruled out, since the splittings cannot be seen in monoammine complexes.

The splitting of the band around 1580 cm.$^{-1}$ can be explained if we assume that one hydrogen of each ammonia interacts with one of the filled platinum d-orbitals, as shown in Figure 2. If we assume C$_{2v}$ symmetry with the PtN$_2$Cl$_2$ skeleton lying in the *xy* plane and one hydrogen of each ammonia in the *yz* plane, these two hydrogen atoms could conceivably interact with the filled d$_{yz}$ orbital of the platinum. Any bending of one H–N–H angle would result in a slight weakening or strengthing of this hydrogen–electron interaction, which might in turn cause some local variation in electron density within the d-orbital. This effect could be transmitted through the orbital to the other side of the molecule, where the strength of the other hydrogen–electron interaction might undergo some slight variation. One can show through normal coordinate analysis that such an interaction results in two different frequencies for the NH$_3$ deformation vibration. The fact that analogous palladium ammine complexes show no splitting of the NH$_3$ deformation bands provides additional evidence for the hydrogen–electron interaction, since the 4d-orbitals of the palladium atom are spatially less extensive than the 5d-orbitals of the platinum atom.



C$_{2v}$(TRANS)

C$_{2h}$(TRANS)

C$_s$(CIS)

C$_{2v}$(CIS)

Figure 2.—Probable structures of *cis*- and *trans*-dihalogenodiammineplatinum(II) complexes.

Figure 2 shows that the hydrogen–electron interaction described above could take place equally well in

TABLE II

NH_3 DEFORMATION FREQUENCIES OF Pt(II) AND Pd(II) AMMINE COMPLEXES

Compound	Frequency, cm.$^{-1}$			
Platinum				
Monoammines				
trans-$[Pt(NH_3)Cl_2((C_2H_5)_2S)]$				1631^a
trans-$[Pt(NH_3)Cl_2(C_2H_4)]$				1610^a
cis-$[Pt(NH_3)Cl_2(C_2H_5CN)]$				1647^b
Diammines—*trans*				
$[Pt(NH_3)_2Cl_2]$		1540	1594	1645^c
		1540	1596	1643^d
		1538		$1638^{a,e}$
				1632^f
$[Pt(NH_3)_2Br_2]$		1541	1594	1639^d
$[Pt(NH_3)_2I_2]$		1536		1630^d
$[Pt(NH_3)_2(SCN)_2]$		1526	1542	1659^d
$[Pt(NH_3)_2(NO_2)_2]$		1549		1646^g
		1560		1659^d
$[Pt(NH_3)_2(NO_2)Cl]$		1551	1607	1662^g
		1549	1616	1658^d
$[Pt(NH_3)_2(NO_2)Br]$		1546		$\sim 1627^g$
		1545		1653^d
$[Pt(NH_3)_2(NO_2)(SCN)]$		1563		$\sim 1643^g$
$Na_2[Pt(NH_3)_2(SO_3)_2]$		1571	1606	1636^h
Diammines—*cis*				
$[Pt(NH_3)_2Cl_2]$		1546		1626^f
		1538		1646^d
		1536		$1630^{a,e}$
		1544		1628^c
$[Pt(NH_3)_2Br_2]$		1530		1630^d
$[Pt(NH_3)_2I_2]$		1525		1620^d
$[Pt(NH_3)_2(NO_2)_2]$		1565		1639^g
		1554		1651^d
$[Pt(NH_3)_2(SCN)_2]$	1522	1541	1560	1644^d
Triammines				
$[Pt(NH_3)_3SO_3]$		1584		1617^h
Tetraammines				
$[Pt(NH_3)_4]Cl_2$		1570		1630^c
		1562		1630^d
		1587		$\ldots^e$
$[Pt(NH_3)_4]I_2$		1556	1631	1650^d
Palladium				
trans compounds				
$[Pd(NH_3)_2Cl_2]$			1605^e	
			1615^c	
$[Pd(NH_3)_2(NO_2)_2]$			1620^g	
$[Pd(NH_3)_4]Cl_2$			1620^c	
$[Pd(NH_3)_4]Cl_2 \cdot H_2O$			1595^e	
cis compounds				
$[Pd(NH_3)_2Cl_2]$			1605^c	

[a] Reference 5. [b] Y. Y. Kharitonov, N. Chia-chien, and A. V. Babaeva, *Zh. Neorgan. Khim.*, **7,** 997 (1962). [c] Reference 7. [d] Reference 3. [e] Reference 4. [f] Reference 6. [g] A. V. Babaeva, O. N. Evstaf'eva, and Y. Y. Kharitonov, *Zh. Neorgan. Khim.*, **7,** 34 (1962). [h] A. V. Babaeva, Y. Y. Kharitonov, and Z. M. Novozhenyuk, *ibid.*, **6,** 2281 (1961).

the C_{2h} model, in which the two ammonia groups are staggered. Furthermore, the same hydrogen–electron interactions would occur through the d_{xy} orbital if one hydrogen of each ammonia were in the xy plane. Again the symmetry of the molecule is C_{2v} or C_{2h} depending upon whether the hydrogens of the two ammine groups are eclipsed or staggered. Although a similar hydrogen–electron interaction would also occur in the *cis* compounds, it can occur only through the d_{xy} orbital as is shown in Figure 2. The resulting symmetry may be C_s or C_{2v}.

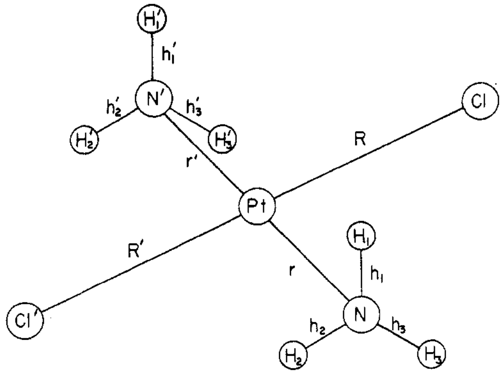


Figure 3.—Molecular model and internal coordinates for *trans*-$[Pt(NH_3)_2Cl_2]$ (C_{2v} symmetry).

In any case, the NH_3 deformation frequencies of these rotational isomers are expected to be very similar to each other. Therefore, the rather large splittings observed cannot be ascribed to the mixing of rotational isomers. Although the present study cannot tell which isomer is most probable in the crystalline state, the observed splittings should be attributed to the hydrogen–electron interaction which occurs in one particular rotational isomer, whichever that may be.

IV. Ligand–Ligand Interaction (Theoretical)

We have carried out a normal coordinate analysis of *trans*-$[Pt(NH_3)_2Cl_2]$ and its deuterated analog with all the hydrogen atoms of the ammine groups included. All the normal coordinate analyses of ammine complexes thus far reported have made use of some simplification, such as a 1:1 metal:ligand model, or the assumption that the ammine group can be treated as an atom of mass 17.[11,12] Such an approximation could not be employed in the present case, since we wished to investigate possible vibrational interaction of the two NH_3 groups in the molecule.

Molecular Model.—Figure 2 shows two of four probable configurations for *trans*-$[Pt(NH_3)_2Cl_2]$. The symmetry of the molecule depends upon whether the hydrogens of the two ammine groups are eclipsed (C_{2v}) or staggered (C_{2h}). The final results of our analysis do not depend upon which of these models is chosen, since neither accounts for the observed splitting of the NH_3 deformation band unless the ligand–ligand interaction described above is considered. In this research we adopted the molecular model of C_{2v} symmetry shown in Figure 2; the internal coordinates of this model are shown in Figure 3.

Procedure of Calculation.—The *trans*-$[Pt(NH_3)_2Cl_2]$ molecule consists of eleven atoms, and its 27 normal vibrations are classified under C_{2v} symmetry as follows: $9A_1 + 5A_2 + 6B_1 + 7B_2$. The two NH_3 twisting modes (A_2 and B_1) and two out-of-plane skeletal bending modes ($2A_1$) were omitted from the calculation. Since the frequencies of these vibrations are expected to be

---

(11) T. Shimanouchi and I. Nakagawa, *Spectrochim. Acta*, **18,** 89 (1962).

(12) L. Gribov, A. Gel'man, F. Zakharova, and M. Orlova, *Zh. Neorgan. Khim.*, **5,** 987 (1960).

TABLE III

SYMMETRY COORDINATES[a]

A_1	$S_1 = 1/\sqrt{6}[h_1 + h_2 + h_3 + h_1' + h_2' + h_3']$	ν(NH)
	$S_2 = 1/\sqrt{12}[2h_1 - h_2 - h_3 + 2h_1' - h_2' - h_3']$	ν(NH)
	$S_3 = 1/\sqrt{2}[r + r']$	ν(Pt–N)
	$S_4 = 1/\sqrt{2}[R + R']$	ν(Pt–Cl)
	$S_5 = 1/\sqrt{12}[rh_1 + rh_2 + rh_3 + r'h_1' + r'h_2' + r'h_3' - h_1h_2 - h_1h_3 - h_2h_3 - h_1'h_2' - h_1'h_3' - h_2'h_3']$	$\delta(NH_3)$
	$S_6 = 1/\sqrt{12}[2rh_1 - rh_2 - rh_3 + 2r'h_1' - r'h_2' - r'h_3']$	$\rho_r(NH_3)$
	$S_7 = 1/\sqrt{12}[-h_1h_2 - h_1h_3 + 2h_2h_3 - h_1'h_2' - h_1'h_3' + 2h_2'h_3']$	$\delta(NH_3)$
	$*S_8 = 1/\sqrt{12}[rh_1 + rh_2 + rh_3 + r'h_1' + r'h_2' + r'h_3' + h_1h_2 + h_1h_3 + h_2h_3 + h_1'h_2' + h_1'h_3' + h_2'h_3']$	
	$*S_9 = 1/2[rR' + rR + r'R' + r'R]$	
A_2	$S_{10} = 1/2[h_2 - h_3 - h_2' + h_3']$	ν(NH)
	$S_{11} = 1/2[rh_2 - rh_3 - r'h_2' + r'h_3']$	$\rho_r(NH_3)$
	$S_{12} = 1/2[h_1h_2 - h_1h_3 - h_1'h_2' + h_1'h_3']$	$\delta(NH_3)$
	$S_{13} = 1/2[-rR' + rR + r'R' - r'R]$	δ(N–Pt–Cl)
B_1	$S_{14} = 1/2[h_2 - h_3 + h_2' - h_3']$	ν(NH)
	$S_{15} = 1/\sqrt{2}[R - R']$	ν(Pt–Cl)
	$S_{16} = 1/2[rh_2 - rh_3 + r'h_2' - r'h_3']$	$\rho_r(NH_3)$
	$S_{17} = 1/2[h_1h_2 - h_1h_3 + h_1'h_2' - h_1'h_3']$	$\delta(NH_3)$
	$S_{18} = 1/2[-rR' + rR - r'R' + r'R]$	δ(N–Pt–Cl)
B_2	$S_{19} = 1/\sqrt{6}[h_1 + h_2 + h_3 - h_1' - h_2' - h_3']$	ν(NH)
	$S_{20} = 1/\sqrt{12}[2h_1 - h_2 - h_3 - 2h_1' + h_2' + h_3']$	ν(NH)
	$S_{21} = 1/\sqrt{2}[r - r']$	ν(Pt–N)
	$S_{22} = 1/\sqrt{12}[rh_1 + rh_2 + rh_3 - r'h_1' - r'h_2' - r'h_3' - h_1h_2 - h_1h_3 - h_2h_3 + h_1'h_2' + h_1'h_3' + h_2'h_3']$	$\delta(NH_3)$
	$S_{23} = 1/\sqrt{12}[2rh_1 - rh_2 - rh_3 - 2r'h_1' + r'h_2' + r'h_3']$	$\rho_r(NH_3)$
	$S_{24} = 1/\sqrt{12}[-h_1h_2 - h_1h_3 + 2h_2h_3 + h_1'h_2' + h_1'h_3' - 2h_2'h_3']$	$\delta(NH_3)$
	$S_{25} = 1/2[rR' + rR - r'R' - r'R]$	δ(N–Pt–Cl)
	$*S_{26} = 1/\sqrt{12}[rh_1 + rh_2 + rh_3 - r'h_1' - r'h_2' - r'h_3' + h_1h_2 + h_1h_3 + h_2h_3 - h_1'h_2' - h_1'h_3' - h_2'h_3']$	

[a] An asterisk indicates a redundant coordinate; ν, stretching; δ, bending; ρ_r, rocking mode.

extremely low (below 200 cm.$^{-1}$), it was assumed that they couple very little with other modes.

The G- and F-matrix elements were calculated using the symmetry coordinates listed in Table III. The molecular parameters used in the calculation of the G-elements were taken from the results of the X-ray analysis reported by Porai-Koshits[13]; they are Pt–N = 2.17 Å. and Pt–Cl = 2.30 Å. The N–H distance was taken as 1.01 Å. All the angles around the nitrogens were assumed to be tetrahedral, and those around the platinum to be 90°. The F-elements were expressed in terms of the modified Urey–Bradley force (UBF) field.[14] The reason for the modifications and the procedure in making them are discussed below. Finally, the matrix secular equations of the form $|GF - E\lambda| = 0$ were solved for each species to obtain the eigenvalues and the eigenvectors for each normal vibration.

Force Constants and Modification of Potential Field.—In carrying out a normal coordinate analysis of *trans*-$[Pt(NH_3)_2Cl_2]$, it was found that both the simple UBF field[15] and the generalized valence force (GVF) field fail to explain the observed splitting of the NH_3 deformation band; both these fields yield the same frequency for all the four modes belonging to different species. Secondly, these force fields yield two Pt–N stretching frequencies separated by about 45 cm.$^{-1}$, although only one Pt–N stretching band was observed at 509 cm.$^{-1}$. Thirdly, they yield two Pt–Cl stretching frequencies separated by about 40 cm.$^{-1}$, whereas two Pt–Cl stretching bands were observed at 330 and 322 cm.$^{-1}$.

Shimanouchi[14] recently suggested that molecules having a central atom with d-orbitals require that interaction force constants between two stretching or two bending vibrations be added to the simple UBF field. Therefore, in the present case it is reasonable to introduce additional force constants, and, as a matter of fact, the difficulties mentioned above can be overcome, if the simple UBF field is modified to take the following long-range interactions into consideration. Table IV includes three new interaction constants in addition to the simple UBF constants. H'(H–N–H) is the over-all interaction constant between angles HNH and H'N'H',[16] and takes a value of 0.038 × 10^5 dynes/cm., which is about 7% of the HNH bending force constant. K'(Pt–N) is the interaction constant between two Pt–N stretching vibrations and takes a value of 0.190 × 10^5 dynes/cm., which is about 9% of the Pt–N stretching force constant. The need for this interaction constant is a reasonable consequence of the interaction between two NH_3 bending modes. K'(Pt–Cl) denotes

---

(13) M. Porai-Koshits, *Tr. Inst. Krist., Akad. Nauk SSSR*, **9**, 229 (1954).

(14) T. Shimanouchi, *Pure Appl. Chem.*, **7**, 131 (1963).

(15) T. Shimanouchi, *J. Chem. Phys.*, **17**, 245 (1949).

(16) We have assumed that the angle H_1'–N'–H_2' interacts with the angle H_1–N–H_2, its mirror image, and also with angles H_1–N–H_3 and H_2–N–H_3 (see Figure 2). The latter two interactions will be equal. If we label the force constant for the first interaction x, and that for the other two y, the over-all interaction force constant is $x + 2y$. The interactions between angles H_1'–N'–H_3' or H_2'–N'–H_3' and the H–N–H angles can be expressed in exactly the same manner. The force constants, x and y, however, must satisfy the relation $x + 2y = 0$, since this expression appears in some G elements which correspond to redundancies and which accordingly must vanish. In the F matrix the term $y - x$ occurs as part of some nonzero elements. It was found that the calculated NH_3 deformation frequencies are in good agreement with those observed if $y - x$ is taken as 0.038 × 10^5 dynes/cm.

TABLE IV

FORCE CONSTANTS OF *trans*-$[Pt(NH_3)_2Cl_2]$ (10^5 DYNES/CM.)

Stretching	Bending	Repulsive	Interaction
$K(N-H) = 5.900$	$H(H-N-H) = 0.525$	$F(H\cdots H) = 0.060$	$K'(Pt-N) = 0.190$
$K(Pt-N) = 2.090$	$H(H-N-Pt) = 0.180$	$F(H\cdots Pt) = 0.100$	$K'(Pt-Cl) = 0.230$
$K(Pt-Cl) = 1.820$	$H(N-Pt-Cl) = 0.220$	$F(N\cdots Cl) = 0.100$	$H'(H-N-H) = 0.038$
	$\kappa = -0.060$[a]		

[a] κ has the dimension 10^{-11} dyne/cm. (see ref. 15).

TABLE V

COMPARISON OF CALCULATED AND OBSERVED FREQUENCIES AND THEORETICAL BAND ASSIGNMENTS FOR *trans*-$[Pt(NH_3)_2Cl_2]$

	trans-$[Pt(NH_3)_2Cl_2]$		*trans*-$[Pt(ND_3)_2Cl_2]$		Theoretical
	Obsd.	Calcd.	Obsd.	Calcd.	band assignment[a]
A_1	3300	3320	2455	2451	$\nu(NH)$ or $\nu(ND)$
	(3220)[b]	3242	2318	2322	$\nu(NH)$ or $\nu(ND)$
	1538	1537	1072	1104	$\delta(NH_3)$ or $\delta(ND_3)$
	1294	1330	997	1030	$\delta(NH_3)$ or $\delta(ND_3)$
	819	830	638	616	$\rho_r(NH_3)$ or $\rho_r(ND_3)$
	509	509	474	460	$\nu(Pt-N)$
	(322)[b]	320	(326)[b]	320	$\tau(Pt-Cl)$
A_2[c]	...	3321	...	2455	$\nu(NH)$ or $\nu(ND)$
	...	1641	...	1181	$\delta(NH_3)$ or $\delta(ND_3)$
	...	839	...	628	$\rho_r(NH_3)$ or $\rho_r(ND_3)$
	...	279	...	257	$\delta(N-Pt-Cl)$
B_1	3300	3321	2455	2454	$\nu(NH)$ or $\nu(ND)$
	1538	1538	1072	1106	$\delta(NH_3)$ or $\delta(ND_3)$
	819	836	637	628	$\rho_r(NH_3)$ or $\rho_r(ND_3)$
	330	331	337	330	$\nu(Pt-Cl)$
	(253)[b]	244	230	219	$\delta(N-Pt-Cl)$
	238				
B_2	3300	3320	2455	2453	$\nu(NH)$ or $\nu(ND)$
	(3220)[b]	3242	2318	2322	$\nu(NH)$ or $\nu(ND)$
	1635	1640	1210	1180	$\delta(NH_3)$ or $\delta(ND_3)$
	1294	1327	997	1017	$\delta(NH_3)$ or $\delta(ND_3)$
	819	834	637	617	$\rho_r(NH_3)$ or $\rho_r(ND_3)$
	509	509	474	468	$\nu(Pt-N)$
	...	181	...	180	$\delta(N-Pt-Cl)$

[a] Based on the calculation of potential energy distribution. [b] Parentheses indicate a shoulder band. [c] A_2 vibrations are infrared inactive under C_{2v} symmetry.

the interaction constant between two Pt–Cl stretching vibrations and takes a value of 0.230×10^5 dynes/cm., which is about 13% of the Pt–Cl stretching force constant. This interaction may be attributed to the tendency of the chlorine atom to form a partial double bond with the platinum atom. The fact that $K'(Pt-Cl)$ is greater than $K'(Pt-N)$ seems to suggest that the ligand–ligand interaction is greater between two chlorine atoms than between two ammine groups in the *trans* position.

Results.—Table V compares the observed frequencies of *trans*-$[Pt(NH_3)_2Cl_2]$ and its deuterated analog with those calculated by using the set of force constants listed in Table IV. It is seen that the agreement is quite satisfactory for both compounds; the maximum deviation is only 3.5%. The calculations show that the NH_3 deformation band splits into two peaks (1640 and 1538 cm.$^{-1}$), that the Pt–N stretching mode does not split, and that the Pt–Cl stretching modes split by 11 cm.$^{-1}$, in agreement with the observed spectrum. The good agreement obtained for the deuterated analog also confirms the results of the calculation. Clearly the calculations do not explain the whole spectrum perfectly, for no frequency is calculated which corresponds to the observed weak band at 1597 cm.$^{-1}$. However, Table II shows that all *cis* and *trans* Pt(II) diammine complexes exhibit bands at about 1540 and 1640 cm.$^{-1}$, while only five of the *trans* compounds show a third band between these two. Although the exact nature of this band is at present unknown, it does not seem to correspond to any fundamental vibration of the $Pt(NH_3)_2$ group.

TABLE VI

POTENTIAL ENERGY DISTRIBUTION[a]

A_1, cm.$^{-1}$	S_1	S_2	S_3	S_4	S_5	S_6	S_7
3300	0.00	*1.00*	0.00	0.00	0.00	0.00	0.00
3220	*1.00*	0.00	0.00	0.00	0.00	0.00	0.00
1538	0.00	0.00	0.00	0.00	0.00	0.06	*1.00*
1294	0.00	0.00	0.03	0.00	*1.00*	0.00	0.00
819	0.00	0.00	0.00	0.00	0.00	*1.00*	0.09
509	0.00	0.00	*1.00*	0.00	0.01	0.00	0.00
322	0.00	0.00	0.00	*1.00*	0.00	0.00	0.00

[a] Numbers indicate relative contribution from each symmetry coordinate.

In order to make theoretical band assignments, we have calculated the potential energy distribution[17] in each symmetry coordinate (Table III) for each normal vibration. Table VI shows the results obtained for the A_1 species; similar results were obtained for the B_1 and

---

(17) Y. Morino and K. Kuchitsu, *J. Chem. Phys.*, **20**, 1809 (1952).

B_2 species. It is clear that almost no coupling exists between various vibrational modes. This result, therefore, justifies the assumption that the ammine group can be treated as a single atom having the mass of NH_3.[7] It is obvious, however, that such a simplification fails to explain the observed splitting of the NH_3 deformation band. The last column of Table V summarizes the theoretical band assignments based on the potential energy distribution.

The bands at 330 and 322 cm.$^{-1}$ of *trans*-[Pt$(NH_3)_2Cl_2$] are definitely due to the Pt–Cl stretching modes. This agrees with Adams and Gebbie,[18] who assigned a band at 320 cm.$^{-1}$ in the infrared spectrum of $K_2[PtCl_4]$ to the Pt–Cl stretching mode, and with Stammreich and Forneris,[19] who have given the following assignments for Raman lines of the $[PtCl_4]^{2-}$ ion; ν_5 (antisymmetric stretch), 304 cm.$^{-1}$; ν_1 (symmetric stretch), 335 cm.$^{-1}$. Coates and Parkin[20] also point out that for several *trans* platinum complexes they have investigated, the Pt–Cl stretching frequency falls between 326 and 339 cm.$^{-1}$.

According to the results of our calculation, the unresolved doublet at 253 and 238 cm.$^{-1}$ is assigned to the in-plane bending vibration of the PtN_2Cl_2 skeleton. The average frequency of this doublet (245 cm.$^{-1}$) is between those of the corresponding modes of the $[Pt(NH_3)_4]^{2+}$ ion (270 cm.$^{-1}$)[7] and of the $[PtCl_4]^{2-}$ ion (183 cm.$^{-1}$).[18] It is possible that the origin of this doublet may be Fermi resonance between the skeletal vibration and some overtone of a lattice vibration.

V. Spectra of Bromo and Iodo Compounds

As is seen in Figure 1, the features of the infrared spectra of the bromo and iodo compounds are similar to those of the chloro compounds. Therefore, the band assignments obtained for the latter should in general be applicable to the former. Substantial changes in the spectra occur only in the low-frequency region where the Pt–Br and Pt–I stretching bands appear. It is known that the platinum–halogen stretching frequency decreases markedly as the halogen is changed from Cl to Br to I.[19,21] For example, the Pt–Br stretching frequencies of the $[PtBr_4]^{2-}$ and $[PtBr_6]^{2-}$ ions are 233 and 240 cm.$^{-1}$, respectively, and the Pt–I stretching frequency of the $[PtI_6]^{2-}$ ion is only 186 cm.$^{-1}$.[18] It is, therefore, reasonable to expect the Pt–Br stretching modes to be around 240 cm.$^{-1}$ for *cis*- and *trans*-[Pt$(NH_3)_2Br_2$]. Table I indicates that both the bromo and iodo compounds exhibit two bands at *ca.* 265–250 and 240–220 cm.$^{-1}$. In analogy with the chloro compounds we tentatively assign these bands to the in-plane bending mode of the PtN_2X_2 skeleton, but it is quite probable that the Pt–Br stretching bands overlap the lower frequency band of this doublet.

VI. Effect of *cis–trans* Isomerism on Spectra

A comparison of the infrared spectra of the corresponding *cis* and *trans* isomers permits several generalizations to be made: (1) The NH_3 deformation bands (about 1580 cm.$^{-1}$) are split into three in the *trans* and into two in the *cis* isomers. A comparison of the bands of the highest frequency in these multiplets indicates that each *trans* isomer absorbs at a higher frequency than its corresponding *cis* isomer. (2) The NH_3 deformation bands (about 1300 cm.$^{-1}$) are split into two distinct peaks in the *cis* isomer, but are only very slightly, if at all, split in the *trans* isomer. Here the frequencies are higher in the *cis* than in the corresponding *trans* isomer. (3) The NH_3 rocking frequency (about 800 cm.$^{-1}$) is always higher in the *trans* than in the *cis* isomer. Furthermore, the difference in frequency between the *cis* and *trans* isomers increases as the halogen is changed in the order $Cl < Br < I$. In this and the previous generalizations our data agree quite well with those of Babaeva and Evstaf'eva.[3] They, however, observed a splitting of the NH_3 rocking band in the *cis* isomers, but added that in the iodo compound the splitting is barely perceptible. We observed such a splitting only in the ND_3 rocking band of *cis*-[Pt$(ND_3)_2Cl_2$]. (4) The Pt–N stretching band (about 500 cm.$^{-1}$) appears as a singlet in the *trans* and as a doublet in the *cis* isomers. (5) The Pt–Cl stretching frequency is slightly lower in the *cis* than in the *trans* isomers.

It is usually stated[22,23] that a *cis* isomer, because of its lower symmetry, exhibits more bands than the corresponding *trans* isomer. The above data indicate that this is true for the compounds here investigated. The fact that this trend is reversed in the NH_3 deformation bands (1550–1650 cm.$^{-1}$) may indicate that the third band observed near 1585 cm.$^{-1}$ for the *trans* compounds is not due to a fundamental vibration.

VII. Effect of Halogen Substitution on Spectra

Figure 1 and Table I show that in the compounds *trans*- and *cis*-[Pt$(NH_3)_2X_2$] (X = Cl, Br, I), all the ammine bands are in general shifted to lower frequencies as the halogen is changed from Cl to Br to I. Furthermore, the frequency shifts are larger in the *cis* series than in the *trans* series (see especially the NH_3 rocking band). This result is in good agreement with the theory of the *trans* effect,[24] since in the *cis* series the halogens exert a *trans* effect on the ammine groups, and this effect increases in the order $Cl < Br < I$.

The Pt–N stretching band (about 500 cm.$^{-1}$) in both *cis* and *trans* series is also shifted to a lower frequency as the halogen is changed from Cl to Br to I. Here again the effect is somewhat larger in the *cis* series, probably for the same reason as given for the ammine bands. This is in agreement with Powell's earlier observation[5] that the Pt–N stretching frequency is shifted to a lower frequency as a ligand of stronger *trans* effect is introduced *trans* to the Pt–N bond.

Acknowledgment.—We wish to express our sincere thanks to Professor Fred Basolo and his co-workers for

---

(18) D. Adams and H. Gebbie, *Spectrochim. Acta*, **19**, 925 (1963).

(19) H. Stammreich and R. Forneris, *ibid.*, **16**, 363 (1960).

(20) G. Coates and C. Parkin, *J. Chem. Soc.*, 421 (1963).

(21) L. Woodward and J. Creighton, *Spectrochim. Acta*, **17**, 594 (1961).

(22) J. Faust and J. V. Quagliano, *J. Am. Chem. Soc.*, **76**, 5346 (1954).

(23) P. Merritt and S. Wiberley, *J. Phys. Chem.*, **59**, 55 (1955).

(24) For example, see F. Basolo and R. Pearson, *Progr. Inorg. Chem.*, **4**, 385 (1962).

giving us very pure samples of several compounds. These afforded us a valuable check on the purity of our own preparations. We are also grateful to the personnel of the Argonne National Laboratory who permitted us to use their Beckman 1R-7 infrared spectrophotometer.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
CARLETON COLLEGE, NORTHFIELD, MINNESOTA

An Infrared Study of Monosulfatopentaaquochromium(III) Chloride

BY JAMES E. FINHOLT, ROGER W. ANDERSON, JAMES A. FYFE, AND KENNETH G. CAULTON

Received August 31, 1964

Solid monosulfatopentaaquochromium(III) chloride was prepared and the infrared spectrum of a Nujol mull obtained. From an analysis of the spectrum in the region from 900 to 1300 cm.$^{-1}$ the sulfate was found to be a monodentate ligand.

Introduction

The isolation of an aqueous solution of monosulfatochromium(III) ion was recently reported by Fogel and co-workers.[1] On the basis of entropy arguments and other considerations it was suggested that sulfate might be a bidentate ligand in this species. The question of whether or not the sulfate is a bidentate ligand is of considerable interest. Kinetic studies might be expected to show that aquation of the monosulfato ion proceeds in two steps if the sulfate is bidentate, since two Cr–O bonds would have to be broken. If the sulfate is monodentate, its aquation mechanism might be expected to resemble that of the monohalochromium(III) species. A knowledge of the way sulfate bonds to the chromium in this species will certainly be important in any attempt to interpret the visible and ultraviolet spectra of the species.

We were able to establish that sulfate is a monodentate ligand in the monosulfatochromium(III) ion by examining the infrared spectrum of its chloride salt. For this purpose we prepared and characterized solid monosulfatopentaaquochromium(III) chloride. It is believed that this is the first reported preparation of a solid containing the $Cr(OH_2)_5SO_4^+$ ion. The method used to analyze the infrared data was developed by Nakamoto and co-workers[2] in a study of sulfatoamminecobalt(III) compounds.

Experimental

Materials.—Dowex AG 50W X8 200–400 mesh resin in the hydrogen form was used in all experiments. The resin was obtained from the Bio Rad Laboratories, Richmond, Calif. All other materials were analytical reagent quality. Ordinary distilled water was used throughout.

Analytical Methods.—Chromium was determined spectrophotometrically after oxidation to chromate by alkaline peroxide. Chloride was determined by adding excess silver nitrate and carrying out a potentiometric back titration with potassium chloride solution using an Ag–AgCl electrode *vs.* a glass electrode. Sulfate was determined as barium sulfate after first oxidizing the chromium(III) to chromium(VI) to destroy the complex and then reducing the chromium(VI) to chromium(III) in the presence of acetic acid.[3]

Preparation of $[Cr(OH_2)_6]Cl_3$.—This compound was prepared by precipitation from a chromic nitrate solution at 0° upon treatment with hydrogen chloride gas.[4] The visible spectrum of a sample dissolved in 0.1 *M* perchloric acid agreed with that[5] reported for $Cr(OH_2)_6^{3+}$. When an aqueous solution of the solid was passed into an ion-exchange column in the hydrogen form only one band could be observed. This band was the violet color characteristic of $Cr(OH_2)_6^{3+}$.

Anal. Calcd. for $[Cr(OH_2)_6]Cl_3$: Cr, 19.5; Cl, 40.0. Found: Cr, 19.3; Cl, 39.9.

Preparation of $[Cr(OH_2)_5SO_4]Cl \cdot 0.5H_2O$.—A 2 *M* chromium(VI) and 0.02 *M* perchloric acid solution was prepared by mixing chromium trioxide, water, and perchloric acid. This solution was cooled to −10° and sulfur dioxide gas was bubbled into the solution. Care was taken to keep the temperature of the solution below 5°. The sulfur dioxide was oxidized to sulfate and the chromium(VI) was reduced to a mixture of chromium(III) species. When the reaction was complete, as evidenced by the cessation of heat evolution, more chromium(VI) solution was added to destroy any excess sulfite. The amount of chromium(VI) added was equal to about 10% of the original chromium(VI). This method was suggested by the work of Colson.[6]

The monosulfato species was isolated by an ion-exchange procedure. A glass column of 2.2 cm. i.d. and 40 cm. long with a sintered glass bottom was packed with hydrogen-form ion-exchange resin to a height of 27 cm. A 55-ml. portion of the solution obtained by the reduction of chromium(VI) was passed into the column. The column was then rinsed with 50 ml. of 0.0005 *M* perchloric acid. At this point the top 2 cm. of the column was violet and the rest of the column was green. The green monosulfato ion was eluted with 2 *M* hydrochloric acid. About 45 ml. of monosulfato solution was obtained.

The 45 ml. of monosulfato solution was concentrated by placing it on a vacuum line and removing about 20 ml. of water. Five-ml. portions of the concentrated solution were placed in 9-ml. test tubes, cooled to −10°, and treated with hydrogen chloride gas. Care must be taken to keep the temperature below 0° during the treatment with hydrogen chloride gas. A dark green precipitate formed and was separated by filtration. The product was immediately placed in a vacuum desiccator and dried for 6 hr. A weight change of only 0.1% took place during the last 3 hr. About 5 g. of product can be obtained from 45 ml. of

---

(1) N. Fogel, J. Tai, and J. Yarborough, *J. Am. Chem. Soc.*, **84**, 1145 (1962).

(2) K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *ibid.*, **79**, 4904 (1957).

(3) H. Willard and R. Schneidewind, *Trans. Am. Electrochem. Soc.*, **56**, 333 (1929).

(4) N. Bjerrum, *Z. physik. Chem.*, **59**, 336 (1907).

(5) R. Plane and J. Hunt, *J. Am. Chem. Soc.*, **79**, 3342 (1957).

(6) A. Colson, *Compt. rend.*, **142**, 402 (1906).