is reasonable not only on the basis of minimum electrostatic repulsion but also is a necessary consequence if each donor atom in the complex is to be affected to essentially the same degree by the bound protons.

A diagrammatic structural model for the protonated metal complexes is given in Fig. 4. Only one-half of the model is depicted in order to make visual presentation and interpretation easier; the undepicted set of ligands and accompanying proton if shown would complete the octahedral-like disposition of donor atoms about iron.

The question as to how the protons are bound remains to be answered. It seems unlikely that any significant bonding occurs between the proton and the donor atoms in the metal complex.[5] One is led therefore to speculate that the protons are attracted and bound to the central metal ion by electron pairs in normally non-bonding orbitals. This seems less speculative than to suggest that two hypothetical metal-ligand π bonds can each be protonated; however the question is a moot one.

The successive shifts in wave lengths of maximum absorption to lower values on successive protonation of the metal complexes, illustrated in Figs. 2 and 3, are consistent with the probable nature of the excitation process[6] and give evidence in support of a model wherein significant interaction occurs between protons and the non-bonding d-orbitals of the central metal ion.[1,7]

With regard to the proton affinity of related complexes it is pertinent to note that hexacyanoferrate(II) behaves as a moderately weak dibasic ion[8] and that some evidence has been found concerning the existence of protonated species of the tris-(2,2-bipyridine)-iron(II) ion and of the 1,10-phenanthroline analog.[9] In the former there is the question of how significant the large negative charge is in determining the proton affinity, hence comparisons are not readily made between it and the neutral mixed ligand complexes of this study. The latter cases remain to be substantiated by more direct evidence.

Finally it may be noted that $HCo(CO)_4$ and $H_2Fe(CO)_4$ resemble in some respects the protonated species of the present study; structures for these have been proposed wherein the hydrogen atom interacts with both the metal ion and adjacent carbonyl ligands.[10]

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[5] Infrared spectra of the solid protonated species show no sign of significant interaction, *i.e.*, the $C\equiv N$ stretching frequency is unchanged and the over-all character of the spectra differs only very slightly from those of the unprotonated complexes.

[6] R. J. P. Williams, *J. Chem. Soc.*, 137 (1955).

[7] G. J. Brealey and M. Kasha, THIS JOURNAL, **77**, 4462 (1955).

[8] B. V. Nekrasov and G. V. Zotov, *J. Appl. Chem.* (*U.S.S.R*), **14**, 264 (1941); *C. A.*, **36**, 1834 (1942).

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Covalency of Metal–Ligand Bonds in Potassium Hexahaloplatinates(IV) Studied by the Pure Quadrupole Resonance of Halogens

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The pure quadrupole resonances of halogens in potassium hexahaloplatinates(IV) were determined at liquid nitrogen, Dry Ice and room temperatures. Potassium hexachloroplatinate(IV) showed only one resonance line, indicating that all chlorine atoms are crystallographically equivalent in agreement with the results of X-ray analysis. The same was true for potassium hexabromoplatinate(IV) above a transition point lying between the liquid nitrogen and Dry Ice temperatures, below which two resonance lines were observed. Three resonance lines observed for potassium hexaiodoplatinate(IV) along with X-ray powder patterns suggested the presence of crystallographically nonequivalent iodine atoms in the crystals. The ionic character of platinum–halogen bonds calculated from the quadrupole coupling constant ranges from 0.30 to 0.53, the net charge on a platinic ion being reduced to a fraction of an electronic charge. The electronegativity of platinum was estimated at 1.9.

Introduction

The nature of metal–ligand bonds in metal complex compounds has been discussed by Pauling[1] on the basis of the atomic orbital theory. In contrast to the crystalline field theory,[2–7] this theory puts too much emphasis on the covalency of metal–ligand bonds in some complexes. Based on the so-called "magnetic criterion for bond types," Pauling classified metal complexes into two groups, namely "essentially covalent" complexes and "essentially ionic" ones. His concept is in harmony with a general feeling among chemists that, for example, $[Ni(H_2O)_6]^{++}$ and $[Co(NH_3)_6]^{+++}$ represent different types of chemical bonding. This simple concept might suggest that no ionic contribution is involved in the bonds of diamagnetic complexes,[8,9] although this contradicts the results of electronegativity considerations that the covalency of metal–ligand bonds amounts to only about 45% even in a

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[1] L. Pauling, "The Nature of the Chemical Bond," Cornell Univ. Press, Ithaca, New York, 1948.

[2] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 753 (1954).

[3] Y. Tanabe and S. Sugano, *ibid.*, **9**, 766 (1954).

[4] Y. Tanabe and S. Sugano, *ibid.*, 11, 864 (1956).

[5] L. E. Orgel, *J. Chem. Soc.*, 4756 (1952); *Quart. Revs.* (*London*), **8**, 422 (1954); *J. Chem. Phys.*, **23**, 1004, 1819, 1958 (1955).

[6] L. E. Orgel, *J. Chem. Phys.*, **23**, 1824 (1955).

[7] C. K. Jørgensen, "Absorption Spectra of Complexes with Unfilled *d*-Shell," Xth Solvay Conference, Brussels, 1956; "Energy Levels of Complexes and Gaseous Ions," Jul. Gjillerups Vorlag, Copenhagen, 1956.

[8] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice-Hall, New York, N. Y., 1952.

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typical "covalent" complex, $[Co(NH_3)_6]^{+++}$ [10,11]

On the other hand, the electronic absorption spectra and the magnetic behaviors of complexes have been discussed on the basis of the crystalline field theory. The theory in its simple form emphasizes pure ionic bonding in complexes. Recently, however, it has been recognized that the covalency in metal–ligand bonds cannot be disregarded because of these points[12–16]: (i) the decrease in the spin–orbit coupling constants of central metal ions[12,16–18] as well as in the interelectronic repulsion integrals of complexes or Racah parameters[3,6,12,13,16,19] below the corresponding values in gaseous metal ions, (ii) considerations on the spectrochemical series as a function of ligands and also of metal ions,[14] (iii) the hyperfine structure of the paramagnetic resonance spectrum of $(NH_4)_2[IrCl_6]$,[20] (iv) the nonempirical calculation of the energy difference between two 3d sub-levels caused by the ligand field of O_h symmetry,[4] and (v) the energetic consideration on the ionization potentials of metal ions and ligands.[16]

In view of these facts, it is desirable to bring to light by experimental studies the covalent character of metal–ligand bonds. This paper presents the results of investigation on the halogen pure nuclear quadrupole resonance of solid K_2PtCl_6, K_2PtBr_6 and K_2PtI_6, which permits the evaluation of the covalent character of Pt–X bonds by Townes–Dailey procedure.[21] These compounds were chosen for the present study, since it is expected from (i) and (ii) mentioned above that the covalent character is fairly large in these complexes,[12,15] and the halogen pure quadrupole resonances of these compounds are observable in an experimentally accessible frequency region.

The present study has its significance also from the standpoint of pure quadrupole resonance, because no data are available as yet on metal complexes except for potassium tetraiodomercurate.[22]

Experimental

Apparatus.—A pure quadrupole resonance spectrometer used in this study consisted of an oscillator detector, an amplifier, a display unit and attachments.

A modified Dean type[23] self-quenching super-regenerative spectrometer was employed with frequency modulation for the observation of quadrupole signals of chlorine isotopes. By employing various coils in the resonance circuit of the oscillator detector, the frequency could be varied from 14 to 70 Mc. The absorption signals were displayed on an oscilloscope screen through a high pass filter and a simple two-stage low frequency amplifier equipped with pentodes, the frequency being modulated with a commercially supplied 60 c.p.s. sine wave. For pen recording display, a lock-in amplifier similar to that described by Watokins[24] was used, the frequency being modulated with a 140 c.p.s. sine wave generated by an audio oscillator.

For detecting the resonance frequency of bromine and ν_1 of iodine appearing in a high frequency region beyond 100 Mc., it was convenient to use a self-quenching parallel-line super-regenerative oscillator detector having 955 acorn triodes in place of a usual LC circuit. The parallel lines were made of brass pipes 8 mm. in diameter. The spectrometer was operated in the frequency range 95–260 Mc. in combination with the oscilloscope display unit described above. The frequency was varied by using various terminal coils fixed to the parallel line and also by displacing reflecting disks. The quench frequency was about 60 kc.

For the determination of ν_2 of iodine, an externally quenched parallel-line super-regenerative spectrometer equipped with 955 acorn triodes was used for oscilloscope display in the frequency range of 300–650 Mc. It was similar to that described by Kojima, *et al.*[25] The frequency was varied by using various terminal coils on the plate side of the parallel line and also by shifting reflecting disks. The parallel lines were made of brass pipes of 6 mm. diameter, which were rigidly fixed by means of Teflon plates. The quench frequency (about 300 kc.) and the quench voltage were regulated so as to attain maximum sensitivity of the detector.

Materials.—Commercial samples procured from Yokosawa Pure Chemicals Company were used. Potassium hexachloroplatinate(IV) and potassium hexabromoplatinate(IV) formed yellow and red powder crystals, respectively. The X-ray powder patterns agreed with those reported in the literature.[26,27] The preparation of potassium hexaiodoplatinate(IV) was black crystals having a metallic luster. The X-ray powder pattern was taken but no data were available in the literature for comparison.

Measurements and Results

Frequency measurements were made with a heterodyne frequency meter[28] calibrated with standard waves from JJY Wireless Station within the accuracy of about one part in 10^5. The signals of bromine and iodine (ν_1) were compared directly with that from the frequency meter on an oscilloscope screen. In order to avoid large disparities of intensities for comparison, the frequencies of chlorine and iodine (ν_2) were first determined by a frequency generator capable of changing its frequency over the range of 300 kc. to 30 Mc., which in turn was calibrated by means of the frequency meter mentioned above.

Measurements were made at liquid nitrogen, Dry Ice and room temperatures. The results are shown in Table I. All resonance lines decreased their frequencies with rising temperature. The data on less abundant isotopes, Cl^{37} and Br^{81}, are omitted from Table I, because the observed isotope ratios of resonance frequencies $\nu(Cl^{35})/\nu(Cl^{37}) = 1.269$ and $\nu(Br^{79})/\nu(Br^{81}) = 1.197$ agreed with those reported in the literature within experimental errors.

Potassium hexachloroplatinate(IV) showed only one resonance line at all temperatures studied. Potassium hexabromoplatinate(IV) absorbed a

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(10) L. Pauling, "Contrib. étude structure moléculaire," Vol. Commém. Victor Henri, 1 (1947/1948); Report of International Conference, Échanges isotopiques et structure moléculaire, 2 (1948).

(11) K. Ito, *Naturwissenschaften*, **46**, 445 (1959).

(12) J. Owen, *Proc. Roy. Soc. (London)*, **A227**, 183 (1955); *Discussions Faraday Soc.*, **19**, 127 (1955).

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(15) K. D. Bowers and J. Owen, *Repts. Progr. in Phys.*, **18**, 304 (1955).

(16) T. M. Dunn, *J. Chem. Soc.*, 623 (1959).

(17) T. Murao, *Progr. Theor. Phys. (Japan)*, **B21**, 657 (1959).

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(22) D. Nakamura, Y. Uehara, Y. Kurita and M. Kubo, *ibid.*, **31**, 1433 (1959).

(23) C. Dean, Thesis, Harvard Univ. (1952).

(24) G. D. Watokins, Thesis, Harvard Univ. (1952).

(25) S. Kojima, K. Tsukada, A. Shimauchi and Y. Hinaga, *J. Phys. Soc. Japan*, **9**, 795 (1954).

(26) ASTM Cards 7–199, American Society for Testing Materials (1957); NBS Circular 539, **5**, 49 (1955).

(27) R. W. G. Wyckoff, "Crystal Structures," Interscience Publishers, Inc., New York, N. Y., 1948.

(28) Model JM-133B, Japan Radio Co., Ltd., Tokyo, Japan.

single frequency at room and Dry Ice temperatures. This indicates that all atoms of chlorine or bromine in the crystals are crystallographically equivalent[29] in agreement with the results of X-ray analysis.[26,27] At liquid nitrogen temperature, potassium hexabromoplatinate(IV) showed two resonance lines, one of which was stronger than the other. Also the color changed from red at Dry Ice temperature to yellow at liquid nitrogen temperature. These facts suggest a phase change taking place between these two temperatures. The appearance of two resonance lines indicates that, in the crystals at this temperature, two kinds of crystallographically non-equivalent bromine atoms are present, those absorbing at a lower frequency being less abundant.

TABLE I

PURE QUADRUPOLE RESONANCE FREQUENCIES OF POTASSIUM HEXAHALOPLATINATES(IV)

Compound		Temp., °C.	Freq., Mc./sec.	S/N ratio
K_2PtCl_6 (8 g.)		23.5 ± 0.2	25.813 ± 0.001	3
		−75.0 ± 2.0	25.910 ± .001	3
		Liquid N_2	26.021 ± .001	3
K_2PtBr_6 (6 g.)		26.3 ± 0.2	200.18 ± .07	15
		−72.0 ± 3.0	200.74 ± .07	15
		Liquid N_2	204.11 ± .07	15
			202.25 ± .15	3
K_2PtI_6 (4 g.)	ν_1	26.5 ± 0.2	202.20 ± .07	10
			201.99 ± .07	10
			198.90 ± .10	2
		−73.5 ± 3.0	203.65 ± .08	15
			203.04 ± .08	15
			200.93 ± .15	2
		Liquid N_2	204.68 ± .08	20
			203.70 ± .08	20
			202.60 ± .15	3
	ν_2	26.1 ± 0.2	403.80 ± .03	6
			403.56 ± .03	6
			397.68 ± .15	2
		−72.0 ± 3.0	406.47 ± .05	10
			405.70 ± .05	10
			401.80 ± .20	2
		Liquid N_2	408.28 ± .05	25
			407.18 ± .05	25
			405.02 ± .02	4

Three resonance lines of potassium hexaiodoplatinate(IV) were observed at all temperatures studied, one line being much weaker than two others. Although no data on the crystal structure of this compound were available in the literature, the X-ray powder pattern indicated that the structure was different from that of potassium hexachloroplatinate(IV). A preliminary examination showed that the powder patterns could be interpreted fairly well by assuming a body-centered tetragonal lattice with $c/a = 1.05$ and $a = 7.73$ Å. for potassium hexaiodoplatinate(IV), whereas potassium hexachloroplatinate(IV) and hexabromoplatinate(IV) are known to crystallize as cubic lattices. However, a possibility of symmetry lower than the tetragonal symmetry was by no means ruled out by the powder pattern method. The multiple resonance lines of potassium hexaiodoplatinate(IV) suggesting the presence of at least three kinds of crystallographically non-equivalent iodine atoms in the crystals can be interpreted only in terms of the structure of low symmetry.

Discussion

The pure quadrupole resonance frequency of a nucleus having a spin $I = 3/2$ and those of a nucleus having $I = 5/2$ are given by these equations[30-33]

$$\nu = \frac{1}{2}\,|eQq|(1+\eta^2/3)^{1/2} \text{ for } I = 3/2 \tag{1}$$

$$\left.\begin{aligned} \nu_1 &= \frac{3}{20}\,|eQq|(1 + 1.0926\eta^2 - 0.634\eta^4 + \ldots) \\ \nu_2 &= \frac{3}{10}\,|eQq|(1 - 0.2037\eta^2 + 0.162\eta^4 - \ldots) \end{aligned}\right\} \text{for } I = 5/2 \tag{2}$$

where eQq denotes the quadrupole coupling constant and η the asymmetry parameter, which is assumed to be small in equations 2. Two frequencies, ν_1 and ν_2, correspond to transitions $m = \pm 1/2 \leftrightarrow \pm 3/2$ and $m = \pm 3/2 \leftrightarrow \pm 5/2$, respectively.

By use of equations 2, the quadrupole coupling constant and the asymmetry parameter of potassium hexaiodoplatinate(IV) were evaluated as shown in Table II. The latter was finite and temperature dependent. This parameter is often interpreted[34] in terms of the π-character of a bond between a halogen atom in question and an atom bonded to it.

TABLE II

QUADRUPOLE COUPLING CONSTANTS AND ASYMMETRY PARAMETERS OF Cl^{35}, Br^{79} AND I^{127} IN POTASSIUM HEXAHALOPLATINATES(IV)

Compound	Temp., °C.	eQq, Mc./sec.	η
K_2PtCl_6	Liquid N_2	52.04	0
K_2PtBr_6	Liquid N_2	408.2	0 assumed
		404.5	0
K_2PtI_6	26	1346.32 ± 0.05	0.034 ± 0.004
		1345.43 ± .05	.029 ± .005
		1325.7 ± .5	.02
	−72	1355.31 ± .05	.038 ± .004
		1352.51 ± .05	.025 ± .005
		1339.3 ± .8	.01
	Liquid N_2	1361.50 ± .05	.045 ± .004
		1357.38 ± .05	.020 ± .007
		1350.2 ± .8	.02

However, the finite asymmetry parameter of potassium hexaiodoplatinate(IV) must be attributed partly to other causes such as the low symmetry of the crystal, because, if only the π-bond character is responsible for the asymmetry parameter, the parameter should be temperature independent in contradiction with the experimental results. For simplicity, the π-character of Pt-X bonds is assumed to be zero in the following discussion. The coupling constants of potassium hexachloroplatinate(IV) and hexabromoplatinate(IV) were calculated by

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[29] For the definitions of the chemical effect and crystal effects on frequency shifts, see C. D. Cornwell and R. S. Yamasaki, *J. Chem. Phys.*, **27**, 1060 (1957).

(30) H. G. Dehmelt and H. Krüger, *Z. Physik*, **129**, 401 (1951).

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(32) T. P. Das and E. L. Hahn, "Solid State Physics," Supplement 1, Academic Press, Inc., New York, N. Y., 1958.

(33) H. Robinson, H. G. Dehmelt and W. Gordy, *J. Chem. Phys.*, **22**, 511 (1954).

(34) R. Bersohn, *ibid.*, **22**, 2078 (1954).

means of eq. 1, assuming $\eta = 0$. These assumptions do not alter the essential conclusions derived below.

Townes and Dailey[21] have shown that the measured quadrupole coupling constant of a halogen atom is related to the ionic character i of the bond beween the halogen atom and an atom bonded to it.

$$eQq = (1 - i)(1 - s)(eQq)_{\text{atom}} \tag{3}$$

where $(eQq)_{\text{atom}}$ denotes the atomic quadrupole coupling constant and s the extent of s-character in the bonding orbital of the halogen. Potassium ions more than 3 Å. distant from the nearest halogen atom are much too far to affect the electric field gradient at the halogen atom in an appreciable manner. Gordy[35] has assumed that $s = 0$, while Dailey and Townes[36] that the atomic orbital of halogen has 15% s-character when the halogen atom is bonded to an atom more electropositive than the halogen by as much as 0.25 unit. Therefore, assuming $s = 0$ or 0.15, the ionic character of Pt–X bonds was evaluated as shown in Table III. The net charge ρ_{Pt} on the central metal ion can be calculated by

$$\rho_{\text{Pt}} = 4 - 6(1 - i) \tag{4}$$

because the platinum ion is formally tetrapositive but is surrounded by six halogen ions, from which charges migrate toward the central metal ion through coördination bonds.

TABLE III

THE IONIC CHARACTER OF Pt–X BONDS IN POTASSIUM HEXAHALOPLATINATES(IV) AND THE NET CHARGE ON A PLATINUM ATOM AT LIQUID NITROGEN TEMPERATURE

Compound	Ionic character $s = 0$	Ionic character $s = 0.15$	Net charge $s = 0$	Net charge $s = 0.15$	β^2 $s = 0.15$
K_2PtCl_6	0.53	0.44	1.18	0.64	0.28
K_2PtBr_6	.47	.38	0.82	.28	.31
K_2PtI_6	.41	.30	0.46	− .20	.35

The values calculated for the ionic character of Pt–X bonds range from 0.30 to 0.53. This shows definitely that the assumption of pure ionic bonding in metal–ligand bonds, as is often presumed in a simple form of the crystalline field theory, is far from true insofar as the present complexes are concerned. On the other hand, the result shows also that too much emphasis should not be laid on covalency in metal–ligand bonds in general, since the compounds under investigation are expected, as mentioned above, to have a rather large covalent character in comparison with complexes having a 3d group metal ion or a dipositive or tripositive ion. For the theoretical calculation of electronic states of complexes, both electrostatic and exchange interactions between a metal ion and the ligands must not be disregarded for the present compounds.

As shown in Table II, the ionic character increases with increasing electronegativity of halogens. In fact, Gordy[37] and also Dailey and Townes[36] have plotted the ionic character of a bond against the electronegativity difference between atoms forming the bond and found the same tendency. By means of this curve, the electronegativity of platinum is estimated at about 1.9, because, by assuming this value, the data of the present investigation can be fitted most closely to the ionic character *versus* electronegativity difference curve.

Owing to the charge migration from ligands, the net charge on a platinic ion is reduced significantly, as shown in Table III. It is as small as a fraction of an electronic charge for $s = 0.15$, which is presumably a better approximation than the alternative assumption, $s = 0$. This is in good agreement with the neutrality principle of Pauling.[38] In the case of potassium hexaiodoplatinate(IV), however, the net charge is negative provided that $s = 0.15$. This result is unlikely, because the atomic state of a metal ion is expected to become rapidly unstable with increasing negative net charge on the ion. The s-character of 15% may be somewhat too large at least for this molecule. If approximately the same amount of neutralization as in Table III is assumed for other complexes, the covalency in hexacoördinated complexes of tripositive and dipositive metal ions is expected to be about 30–45% and 15–30%, respectively. It would be worth noting that, as pointed out by Murao,[17] the neutralization of charges taking place more or less on a central metal ion in a majority of complexes affects the values of Racah parameters and spin-coupling constants significantly.

The net charge ρ on Pt^{IV} of diamagnetic octahedral complexes can be related to the probability β_i^2 of finding an electron in the ith bonding molecular orbital in the vicinity of Pt^{IV} by

$$\rho_{\text{Pt}} = 4 - 2\sum_{i}\beta_i^2 \tag{5}$$

where the summation is taken over one a_{1g} bonding orbital, two bonding e_g orbitals and three bonding f_{2g} orbitals. Substituting eq. 4 in eq. 5, one has

$$\sum_{i}\beta_i^2 = 3(1 - i) \tag{6}$$

If one assumes the d^2sp^3 hybridization for Pt^{IV} as proposed by Pauling, one has

$$\beta_i^2 \equiv \beta^2 = \frac{1}{2}(1 - i) \tag{7}$$

This gives the values of β^2 shown in Table III. On the other hand, β_i^2 for the bonding e_g orbitals is correlated to the probability α^2 of finding an anti-bonding d_σ ($d\gamma$) orbital electron on a central metal ion by the relation

$$\beta(e_g)^2 = 1 - \alpha^2 \tag{8}$$

Since the value of α^2 has been estimated[12,15] at about 0.5 for $[M^{IV}Cl_6]^=$ and $[M^{IV}Br_6]^=$ type ions involving 5d group metals, eq. 8 gives $\beta(e_g)^2 = 0.5$ for the bonding e_g orbitals. A comparison between the two sets of values of β^2 obtained by eqs. 7 and 8 suggests that the amount of d-character must be larger than can be expected from the d^2sp^3 hybridization, although the value of α^2 used here may be subject to some change if the neutralization of formal charges is taken into account.

The energy separation between a d_π ($d\epsilon$) level and an anti-bonding d_σ ($d\gamma$) level in octahedral complexes presents an important problem in the chemistry of coördination compounds. According to the spectrochemical series[39] established mainly for Co^{III} complexes, the ligand-field absorption

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(35) W. Gordy, *J. Chem. Phys.*, **19**, 792 (1951).

(36) B. P. Dailey and C. H. Townes, *ibid.*, **23**, 118 (1955).

(37) W. Gordy, *Discussions Faraday Soc.*, **19**, 14 (1955).

(38) L. Pauling, *J. Chem. Soc.*, 1461 (1948).

(39) R. Tsuchida, *Bull. Chem. Soc. Japan*, **13**, 395 (1938).

bands of a complex shift toward lower wave numbers, when Cl^- coördinated on a metal atom is replaced by Br^- and also when Br^- is substituted with I^-. This rule seems to hold[40] also for the present compounds. Accordingly, the energy separation between d_π and anti-bonding d_σ levels decreases with decreasing ionic character in the order of hexachloroplatinate(IV), hexabromoplatinate(IV) and hexaiodoplatinate(IV). Conceivable causes for the energy separation are electrostatic effect and covalent bonding effect, the effect of π-bonding being disregarded. One is tempted to presume from the parallelism between the energy separation and the ionic character that the electrostatic effect is mainly responsible for the energy separation. However, this presumption can be made only with reservations, since the parallelism shows only the balance between the changes in the electrostatic effect and the covalent bonding effect accompanying the replacement of halogen ions with heavier ones.

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(40) C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 518 (1956).

[Contribution from the Department of Chemistry, Cornell University, Ithaca, New York]

The Association of Trisethylenediamineplatinum(IV) with Various Anions[1a]

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From measurements of absorption spectra in the region 255 to 270 mμ the extent of association of $Pt(en)_3^{+4}$ with Cl^-, Br^-, $SO_4^=$, NO_3^- and ClO_4^- were determined. Of these anions all but the last were found to form a 1 to 1 outer-sphere ion-pair. An extended Debye–Hückel activity coefficient equation was used to determine values of association constants at infinite dilution. The values thus found were 11 for Cl^-, 8 for Br^-, 3.3×10^3 for $SO_4^=$ and ca. 0.8 for NO_3^-. The lack of increased absorption when ClO_4^- is added to solutions of $Pt(en)_3^{+4}$ and the fact that ClO_4^- does not lower the association of Cl^- with $Pt(en)_3^{+4}$ at constant ionic strength are taken to indicate that the association of even a +4 complex cation with ClO_4^- is negligible.

In recent years a number of articles have appeared on the stability of outer-sphere complexes formed by complex metal cations with various anions. The results of these investigations have been summarized by Basolo and Pearson[1c] and include some widely quoted values of Evans and Nancollas.[2] These later authors have reported sets of stability constants and thermodynamic properties for complexes of $Co(NH_3)_6^{+3}$ and $Co(en)_3^{+3}$ with various anions. Recently, King, Espensen and Visco[3] have shown that the stability constant for the $Co(NH_3)_6^{+3}$–Cl^- ion pair is actually much smaller than the value 74 reported by Evans and Nancollas that the proper value of K_1^0 was less than 5. Although King and co-workers were able to set an upper limit on the constant, they could not set a lower limit. In view of this discrepancy, the present work was undertaken to establish the magnitude of the association constants for outer-sphere complexes of complex cations and also to determine the effect of size and charge of the anion on the magnitude of the stability constant of the ion pairs. The trisethylenediamineplatinum(IV), $Pt(en)_3^{+4}$, cation was chosen because complexes of this cation should be somewhat more stable than those of cobalt(III) by reason of its higher charge. Thus ion-pairs would be easier to detect at the low concentrations of complexing anion corresponding to low ionic strengths, and hence activity coefficient problems should be minimal. Furthermore, the high-charge of the cation increases the possibility of finding a case of ClO_4^- association.

Experimental

Chemicals.—$[Pt(en)_3]Cl_4$ was prepared starting with scrap platinum which was purified by the barium carbonate procedure of Wichers.[4] The Pt thus purified was converted to H_2PtCl_6 by dissolution in aqua regia, and the nitric acid removed by three evaporations almost to dryness with concentrated hydrochloric acid. Platinum then was precipitated as $(NH_4)_2PtCl_6$ and converted back to the metal by thermal decomposition. This process was repeated three times to insure purity.[5] The last preparation of $H_2PtCl_6 \cdot xH_2O$ was dissolved in absolute ethanol and converted to $[Pt(en)_3]Cl_4$.[6] Excess of 98% ethylenediamine was added dropwise to the cold solution with stirring, and subsequently the mixture was heated to 75° for one hour also with constant stirring. The crude product was recrystallized several times by the following procedure. Ten grams of crude $[Pt(en)_3]Cl_4$ was dissolved in 20 ml. of water at the boiling point; 20 ml. of concentrated hydrochloric acid was added and a precipitate immediately formed. Sufficient water (approximately 80 ml.) then was added until the precipitate just redissolved completely. The sample was filtered rapidly and allowed to stand for several hours so that slow crystallization occurred. The colorless product was collected on a Hirsch funnel and washed twice with 10 ml. portions of cold 1:1 HCl to H_2O, and finally with a minimum amount of cold water. After drying for 3 hours at 125° in an oven, 8.8 g. of purified product was obtained.

After a second recrystallization, a typical analysis and that of the sample used in the investigation was: Pt: Found, 37.67%. Theoretical for $[Pt(en)_3]Cl_4$, 37.73%. Cl: Found, 27.43%. Theoretical for $[Pt(en)_3]Cl_4$, 27.41%.

$NaClO_4$ was prepared by the neutralization of reagent grade NaOH and $HClO_4$ solutions and crystallizing. The other sodium salts (which were dried at 110°) and the acids were reagent grade, used without further purification.

Water employed in the spectrophotometric studies was redistilled from alkaline permanganate in a Barnstead still, and was of the quality of "Conductivity Water."

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(1) (a) This research was supported by the United States Air Force through the Air Force Office of Scientific Research of the Air Research and Development Command, under Contract No. AF 49(638)-279. Reproduction in whole or in part is permitted for any purpose of the United States Government. (b) On sabbatical leave from the Department of Chemistry, Washington State University. (c) F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, New York, 1958, p. 380.

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