lating discussions. Acknowledgment is made to the donors of the Petroleum Research Fund of the American Chemical Society for partial support of this research.

[CONTRIBUTION FROM THE WILLIAM ALBERT NOYES LABORATORY OF CHEMISTRY, UNIVERSITY OF ILLINOIS, URBANA, ILLINOIS]

Hexachlorometallates of Trivalent Chromium, Manganese and Iron

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Compounds containing hexachlorometallate ions of trivalent chromium, manganese, and iron have been prepared by stabilizing the anion in a crystal lattice with the tris-(1,2-propanediamine)-cobalt(III) cation. The existence of the complex anions has been proved by isomorphism with salts of known hexachlorometallate(III) ions and the same cation, and by X-ray data obtained from single crystals of $[Co(C_3H_{10}N_2)_3][FeCl_6]$. Magnetic data showed that the ground state of these compounds is the expected high-spin state. *Dq* values of 1318, 1754 and 920 cm.$^{-1}$ for $[CrCl_6]^{3-}$, $[MnCl_6]^{3-}$ and $[FeCl_6]^{3-}$, respectively, were determined from spectral data.

Introduction

Complex ions including those not found in appreciable concentrations in solution often can be stabilized in a crystal lattice providing that the energetics of formation of the complex ion from solvated species is not too unfavorable relative to the lattice energy. A good guide to a suitable counter ion is the rule that the lattice energy usually is largest for ions of equal and opposite charge. Furthermore, a counter ion of similar size is best since disparate sizes promote solvation.

This approach has been used recently by Gill and Nyholm,[1] who have isolated stable compounds containing such ions as the tetrahalonickellate(II) ion. Similarly, Mori[2] has prepared a number of chlorocuprates by stabilizing the complex anions in a lattice with the hexamminechromium(III) cation.

Although there are several references in the older literature to compounds having stoichiometries consistent with hexachlorometallate salts for trivalent first transition series elements, *e.g.*, Tl_3CrCl_6,[3] $Cs_3FeCl_6 \cdot H_2O$,[4] and $(NH_4)_3CrCl_6$,[5] the properties of the complex anions are unknown. In fact, evidence reported here casts doubt on the existence of any hexachlorometallate ions in these compounds. We now wish to report the preparation and some physical properties of compounds which do contain hexachlorometallate ions of trivalent chromium, manganese, and iron. Up to now the position of the chloride ion in the neuphelauxetic series has been based on spectral studies of anhydrous chromium(III) chloride and complexes of second and third transition series ions.[6] Studies on octahedral complexes of first transition series ions coordinated only by chloride should provide additional information concerning the ligand field of the chloride ion.

Experimental

Tris-(1,2-propanediamine)-cobalt(III) Hexachlorochromate(III).—A small amount of the pink compound crystallized from a concentrated hydrochloric acid solution (50 ml.) of chromium(III) chloride hexahydrate (5.4 g., 0.020 mole) and tris-(1,2-propanediamine)-cobalt(III) chloride (3.8 g., 0.010 mole) after standing for several days. The crystals were collected on a Büchner funnel, washed well with water, then with alcohol and ether, and dried in an oven at 110° for four days.

Anal. Calcd. for $CoC_9H_{30}N_6CrCl_6$: C, 19.80; H, 5.53; N, 15.40. Found: C, 19.87; H, 5.61; N, 15.09.

Tris-(1,2-propanediamine)-cobalt(III) Hexachloromanganate(III).—This compound was precipitated from a hot solution of manganese(II) sulfate monohydrate (3.4 g., 0.020 mole) and tris-(1,2-propanediamine)-cobalt(III) chloride (7.6 g., 0.020 mole) in a minimum amount of hydrochloric acid by the addition of small amounts of sodium chlorate. The dark brown compound was collected on a Büchner funnel, washed with alcohol, acetone, and ether, and dried in an evacuated desiccator over potassium hydroxide. The yield was 8.1 g. (75%).

Anal. Calcd. for $CoC_9H_{30}N_6MnCl_6$: C, 19.70; H, 5.50; N, 15.31; Cl, 38.72. Found: C, 20.18; H, 5.61; N, 15.24; Cl, 38.98.

The compound decomposed slowly upon standing presumably evolving chlorine. The magnetic moment of a sample that had been stored for three months was 0.3 B.M. higher than that of a freshly prepared sample.

Tris-(1,2-propanediamine)-cobalt(III) Hexachloroferrate(III).—A solution of iron(III) chloride hexahydrate (2.7 g., 0.010 mole) in 5 ml. of hot water was added to a solution of tris-(1,2-propanediamine)-cobalt(III) chloride (3.8 g., 0.010 mole) in 10 ml. of hot water. The solution was evaporated to about half the original volume. A few milliliters of concentrated hydrochloric acid was added; the yellow crystals formed were collected on a Büchner funnel, washed with alcohol, acetone, and ether, and air dried. The compound was recrystallized from hot water with the addition of hydrochloric acid. The yield was 1.8 g. (29%).

Anal. Calcd. for $CoC_9H_{30}N_6FeCl_6$: C, 19.66; H, 5.50; N, 15.28; Cl, 38.69. Found: C, 19.88; H, 5.14; N, 15.46; Cl, 38.69, 38.61.

Tris-(1,2-propanediamine)-cobalt(III) Hexachloroindate(III).—This compound was prepared as was the corresponding iron compound. The yield was 87%.

Anal. Calcd. for $CoC_9H_{30}N_6InCl_6$: C, 17.76; H, 4.96; N, 13.81; Cl, 34.96. Found: C, 17.68; H, 5.00; N, 13.08; Cl, 35.00.

Tris-(1,2-propanediamine)-rhodium(III) Hexachlorometallates(III).—Compounds with the tris-(1,2-propanediamine)-rhodium(III) cation were prepared by the methods described above. The analytical data for the new compounds are given in Table I.

Hexaamminecobalt(III) Hexachloroferrate(III).—A solution of ferric chloride hexahydrate (1.4 g., 0.005 mole) in 10 ml. of hot water was added to a hot solution of hexaamminecobalt(III) chloride (0.43 g., 0.0016 mole) in 70 ml. of 3.4 *N* hydrochloric acid. The resulting solution was heated for a few minutes until an orange product crystallized. The crystals were collected on a Büchner funnel, washed with alcohol and ether and dried in an evacuated desiccator over potassium hydroxide. The yield was 0.5 g. (72%).

Anal. Calcd. for $CoN_6H_{18}FeCl_6$: N, 19.54; H, 4.18; Cl, 49.55. Found: N, 19.52; H, 4.13; Cl, 48.42.

The preparation could not be made at room temperature because of the insolubility of hexaamminecobalt(III) chloride in a solution with a chloride ion concentration high enough to facilitate the formation of the hexachloroferrate(III) ion. Detailed studies of this compound were not undertaken because we experienced difficulties in preparing the corresponding manganese compound.

Experiments with Other Cations and Anions.—Proper conditions could not be found for the preparation of hexachloroferrate(III) salts of the tris-(2,3-butanediamine)-cobalt(III) or tris-(1,2-cyclohexanediamine)-cobalt(III) cation. An orange product crystallized from a solution of tris-(ethylenediamine)-cobalt(III) chloride and ferric chloride after a few days. The crystals were collected on a Büchner funnel, washed with alcohol and ether, and dried in air.

Anal. Calcd. for $CoC_6H_{24}N_6FeCl_6 \cdot 1.5H_2O$: C, 13.48; H, 5.08; N, 15.74. Found: C, 13.21; H, 4.68; N, 15.92.

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[1] N. S. Gill and R. S. Nyholm, *J. Chem. Soc.*, 3997 (1959).

[2] M. Mori, *Bull. Chem. Soc. Japan*, **33**, 985 (1960).

[3] G. Neuman, *Ann.*, **244**, 329 (1888).

[4] P. T. Walden, *Am. J. Sci.*, [3] **148**, 283 (1894); *Z. anorg. u. allgem. Chem.*, **7**, 332 (1894).

[5] H. I. Schlesinger, *J. Am. Chem. Soc.*, **51**, 3520 (1929).

[6] C. E. Schäffer and C. K. Jørgensen, *J. Inorg. Nuclear Chem.*, **8**, 143 (1958).

TABLE I

ANALYTICAL DATA FOR $[Rh(C_3H_{10}N_2)_3][MCl_6]$

Compound	Color	Calculated, % C	Calculated, % H	Calculated, % N	Found, % C	Found, % H	Found, % N
$[Rh(C_3H_{10}N_2)_3][CrCl_6]$	Bluish-pink	18.32	5.12	14.41	18.61	5.09	14.22
$[Rh(C_3H_{10}N_2)_3][MnCl_6]$	Brown	18.23	5.10	14.17	18.00	4.98	13.91
$[Rh(C_3H_{10}N_2)_3][FeCl_6]$	Yellow	18.20	5.09	14.15	18.22	5.18	14.00
$[Rh(C_3H_{10}N_2)_3][RhCl_6]\cdot 4.5H_2O$	Pink	14.97	5.44	11.64	14.98	4.81	11.88

TABLE II

MAGNETIC DATA

Compound	$\chi_g \times 10^6$, c.g.s. units	$\chi_m^{corr} \times 10^6$, c.g.s. units	T, °K.	θ, °K.	μ_{eff}, B.M.
$[Co(pn)_3][CrCl_6]$[a]	11.03 ± 0.08	6,353 ± 34	294.7	+2	3.87
	17.25 ± .02	9,740 ± 11	195.7		(3.87)[b]
	43.76 ± .13	24,170 ± 72	80.6		
$[Co(pn)_3][MnCl_6]$	17.68 ± .28	10,130 ± 160	294.5	+1	4.91
	27.80 ± .13	15,660 ± 71	195.7		(4.90)[b]
	68.40 ± .07	37,810 ± 38	80.7		
$[Co(pn)_3][FeCl_6]$	25.94 ± .42	14,620 ± 230	294.8	0	5.86
	39.50 ± .09	22,060 ± 49	195.8		(5.91)[b]
	93.30 ± .20	51,600 ± 110	83.0		

[a] pn is an abbreviation for 1,2-propanediamine. [b] Spin-only magnetic moment.

TABLE III

X-RAY DIFFRACTION DATA FOR $[M(C_3H_{10}N_2)_3][MCl_6]$

$[Co(pn)_3][MCl_6]$				$[Rh(pn)_3][MCl_6]$			
M = Fe	M = Mn	M = Cr	M = In	M = Rh	M = Cr	M = Mn	M = Fe
9.24^a $(10)^b$	9.28^a $(10)^b$	9.14^a $(10)^b$	9.40^a $(10)^b$	9.28^a $(10)^b$	9.35^a $(10)^b$	9.28^a $(10)^b$	9.48^a $(10)^b$
....	....	....	7.22 (1)	....	....	7.14 (1)	....
5.36 (8)	5.42 (7)	5.33 (6)	5.46 (8)	5.35 (7)	5.39 (8)	5.38 (8)	5.33 (7)
4.63 (5)	4.64 (3)	4.70 (4)	4.73 (4)	4.62 (3)	4.64 (4)	4.66 (4)	4.68 (2)
4.23 (1)	4.27 (2)	4.22 (1)	4.34 (3)	4.20 (1)	....	....	....
3.80 (4)	3.81 (4)	3.78 (2)	3.88 (6)	3.83 (4)	3.80 (4)	3.83 (3)	3.82 (3)
3.52 (1)	3.53 (1)	3.49 (1)	3.58 (4)	3.49 (1)	3.42 (1)	3.54 (1)	3.60 (1)
3.33 (3)	3.36 (2)	3.29 (2)	3.38 (1)	3.34 (1)	3.34 (4)	3.35 (3)	3.36 (4)
2.93 (7)	2.95 (6)	2.90 (5)	3.03 (7)	2.92 (4)	2.94 (6)	2.94 (4)	2.97 (4)
2.69 (1)	2.71 (1)	2.68 (1)	2.72 (3)	2.66 (2)	2.68 (2)	2.66 (1)	2.71 (1)
2.51 (1)	....	2.49 (1)	2.55 (2)	....	....	2.53 (1)	....
2.40 (2)	....	2.37 (1)	2.44 (2)	2.38 (2)	2.40 (2)	2.45 (1)	2.43 (1)
2.31 (2)	2.31 (1)	2.29 (3)	2.35 (2)	2.30 (2)	2.31 (2)	2.33 (2)	2.35 (1)
2.14 (1)	....	2.13 (1)	....	2.12 (2)	2.13 (1)	....	2.09 (1)
2.03 (2)	2.03 (1)	2.02 (1)	2.06 (2)	2.01 (2)	2.03 (2)	2.03 (2)	2.05 (1)
1.94 (1)	....	1.95 (1)	....	....	1.90 (3)	1.92 (1)	1.92 (1)
1.91 (2)	1.92 (1)	1.89 (1)	1.92 (2)	....	....	....	....

[a] d_{hkl}. [b] Visually estimated intensity.

Deep red crystals were obtained from a solution of tris-(1,10-phenanthroline)-cobalt(III) bromide and ferric bromide. The visible absorption spectrum of the compound was very similar to that reported by Gill[7] for the tetrabromoferrate(III) anion. The analytical results support formulation of the compound as $[Co(C_{12}H_8N_2)_3][FeBr_4]_3$.

Anal. Calcd. for $CoC_{36}H_{24}N_6Fe_3Br_{12}$: C, 25.05; H, 1.39; N, 4.86. Found: C, 26.67; H, 1.34; N, 5.86.

We have been unable to isolate a pure compound from tris-(1,2-propanediamine)-rhodium(III) or -cobalt(III) nitrate, ferric nitrate, and hydrobromic acid. However, we are continuing our work with these compounds and will report the results in a later publication.

Ammonium Pentachloroaquoferrate(III).—Large well-formed crystals were grown from a concentrated aqueous solution of ammonium chloride and ferric chloride as described by Lindqvist.[8]

Magnetic Susceptibility Determinations.—Equipment for the determination of magnetic susceptibilities by the Faraday method was assembled. Since the apparatus was extremely convenient to use and yielded exceptionally precise results, it will be described briefly. The merits of the Faraday method as compared to the Gouy method are not generally appreciated. Now that a device for measuring the small forces involved is commercially available, the construction of a Faraday balance is straightforward. The advantages include (1) small sample (*ca.* 1–10 mg.), (2) avoidance of packing errors characteristic of the Gouy method, (3) ease of thermostating since the region to be thermostated is considerably smaller and (4) rapidity with which measurements may be made.

A small hemispherical sample bucket was suspended between the constant gradient pole pieces[9] of a Varian V4004 electromagnet by a quartz fiber from the beam of a Cahn Model G Gram Electrobalance. The forces observed at room temperature for *ca.* 5 mg. samples of the iron compound were 200 micrograms (HdH/dx = 1.7 × 10^7 gauss^2/cm., pole gap = 1.5 inches). The forces could be read to 0.1 μg. with the electrobalance. Replicate determinations usually agreed within 1.0 μg. Mercury(II) tetrathiocyanatocobaltate(II) was used as a magnetic susceptibility standard.[10]

The magnetic susceptibility data are listed in Table II. A plot of the reciprocal of the corrected molar susceptibility *versus* temperature for each of the compounds yielded a straight line from which the Weiss constant and C (the slope) were determined graphically. The magnetic moments were calculated using the equation $\mu_{eff} = 2.84C^{1/2}$.

Spectrophotometric Measurements.—Spectra of finely powdered solid samples were obtained with a Beckman DU Spectrophotometer equipped with the standard Beckman reflectance attachment. Reagent grade magnesium oxide was used as a standard.

Spectra of the compounds at *ca.* 77°K. were obtained with a Cary Model 14 recording spectrophotometer. Powder pressings of the finely powdered solid samples in cesium chloride matrices were suspended in a dewar flask fitted with optical windows.

X-Ray Powder Patterns.—X-Ray powder patterns were obtained with nickel filtered copper Kα radiation using a Debye–Scherrer camera of 14.01 cm. diameter. The samples were contained in 0.5 mm. glass capillary tubes with 0.01 mm. wall thickness. The d-spacings and visually estimated intensities for the salts with the tris-(1,2-propanediamine)-cobalt(III) or -rhodium(III) cation are presented in Table III. The data for hexaamminecobalt(III) hexachloroferrate(III), which have been indexed assuming an isometric space group, are presented in Table IV, along with the data for hexaamminecobalt(III) hexachlorothallate(III). Watanabe, Atoji and Okazaki[11] have determined the structure of hexaamminecobalt(III) hexachlorothallate(III) and found the space group to be Pa3. The similarity in the powder patterns for these two compounds suggests that they are isomorphous. The unit cell dimension of hexaamminecobalt(III) hexachloroferrate(III) was found to be 11.22 ± 0.04 A.

X-Ray Single Crystal Study.—Very small (*ca.* 0.02 mm.) acicular crystals were chosen for the X-ray investigation as it was

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[7] N. S. Gill, *J. Chem. Soc.*, 3512 (1961).

[8] I. Lindqvist, *Arkiv Kemi, Mineral. Geol.*, **24A**, No. 1 (1947).

[9] R. D. Heyding, J. D. Taylor and M. L. Hair, *Rev. Sci. Instruments*, **32**, 161 (1960).

[10] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

[11] T. Watanabe, M. Atoji and C. Okazaki, *Acta Cryst.*, **3**, 405 (1950).

TABLE IV

X-RAY DIFFRACTION DATA FOR $[Co(NH_3)_6][MCl_6]$

$[Co(NH_3)_6][FeCl_6]$			$[Co(NH_3)_6][TlCl_6]$		
d_{hkl}	I/I_0	hkl	d_{hkl}	I/I_0	hkl
..	..	..	6.61	4	111
5.56	10	200	5.69	10	200
3.95	5	220	4.04	7	220
3.73	1	221, 330	..	..	..
3.37	1	311	3.45	1	311
3.24	2	222	3.30	3	222
3.00	7	321	3.06	2	321
2.82	1	400	..	..	..
2.65	5	411	2.70	1	411
..	..	..	2.62	3	331
2.52	1	420	2.56	4	420
2.40	6	332	2.44	1	332
2.30	6	422	2.34	7	422
2.21	2	431	2.21	2	431
2.00	5	440	2.03	4	440
..	..	..	1.94	2	531
1.88	4	600, 442	1.91	5	600, 442
1.78	2	620	1.81	3	620
1.77	1	621	..	..	..

noticed that the larger crystals appeared under the microscope to be badly striated along the needle axis. That this observed striation was due to twinning was clearly shown by Weissenberg photographs. Whereas the reflections of *c*-axis rotation photographs were sharp and showed no streaking, reflections of Weissenberg photographs of the same crystals showed extensive streaking, the amount of which varied from crystal to crystal. This suggests that a large number of very small needle-like crystallites make up the macrocrystals, and these crystallites while ordered in the *c* direction are slightly disordered perpendicular to the needle axis, thereby accounting for the observed continuous diffraction over large Bragg angles (observed range, 5 to 15°θ).

Rotation, Weissenberg and precession photographs (Co and Mo Kα radiation) showed the crystals to be hexagonal based on a hexagonal lattice and to have the cell dimensions: $a = 18.33 \pm 0.03$ Å.; $c_0 = 10.81 \pm 0.02$ Å. The observed density, determined by flotation, was found to be 1.707 g./cm.^{3}. The density for a unit cell containing six molecules was calculated to be 1.742 g./cm.^{3}.

Extinctions of reflection observed from Weissenberg and precession photographs were; *hkil*, none; $0.00l$–$l = 2n$, thus placing the crystal into the space groups $P6_3$–C_6^6 or $P6_3/m$–$C6h^2$. The latter requires the molecular symmetry to be *m* which is ruled out for this molecule, except in the case of disorder.

The best disposition of the complex ions from the point of view of electrostatics would place the cations near the $0, {}^1/_3, z$, etc., positions and the anions near the $0, {}^2/_3, z$, etc., positions. This arrangement, particularly with disorder of the cation orientation, would confer pseudodihedral axes. This supposition is partly confirmed by the intensity relation $h\bar{h}0l$ intense when $l = 2n$.

Results and Discussion

The powder patterns of all the compounds with the tris-(1,2-propanediamine)-cobalt(III) or -rhodium(III) cations were recorded and compared. The great similarity in the *d*-spacings and relative intensities indicate that all the compounds are isomorphous.

Two of the compounds ($[Rh(C_3H_{10}N_2)_3][RhCl_6]$ and $[Co(C_3H_{10}N_2)_3][InCl_6]$) contain well-known hexachlorometallate(III) ions. Furthermore, the reflectance spectrum of $[Rh(C_3H_{10}N_2)_3][RhCl_6]$ is identical with the spectrum of the $[RhCl_6]^{3-}$ ion that was reported by Jørgensen.[12] Therefore the isomorphisms strongly indicate that the first row transition metal ions Cr(III), Mn(III) and Fe(III) do form hexachlorometallate ions in these compounds. The magnetic data confirm that the ground state is the expected high-spin state.

We have not attempted to establish the existence of hexachlorometallate ions in any of the previously reported compounds partly because of the difficulties in working with these hygroscopic and excessively soluble compounds. On the basis of color alone it is doubtful that they do contain such ions. The best characterized is $(NH_4)_3CrCl_6$, which is reported to be red-violet.[5] We find that $[CrCl_6]^{3-}$ is pink; there is the possibility of polymeric species in this case. The salt $Cs_3FeCl_6 \cdot H_2O$ is reported[4] to be the color of $Na_2Cr_2O_7$. Since this is the same color as $(NH_4)_2[FeCl_5OH_2]$[8] and quite different from the pale yellow of $[FeCl_6]^{3-}$, we suggest that the Cs salt contains hydrated species.

Stabilization of Unstable Ions in the Solid State.—It is not surprising that hexachlorometallate(III) anions of first transition series elements have been thought to be unstable. The cation to anion radius ratio is less than the value 0.414 at which anion–anion contact begins to occur in octahedral coördination. Moreover, a simple ionic model calculation for the chloroferrate complexes, considering only metal–ligand attraction and ligand–ligand repulsion and using an iron–chlorine distance of 2.38 Å.[13] reveals that in the gas phase the $[FeCl_6]^{3-}$ ion is less stable than the $[FeCl_5]^{2-}$ ion by 71 kcal. and is less stable than the $[FeCl_4]^-$ ion by 43 kcal. Gill and Nyholm[1] imply that the instability of the $[FeCl_6]^{3-}$ ion is due to the polarizability of the chloride ion. These authors point out that, although iron achieves coördination number six when surrounded by fluoride ions, near electroneutrality is achieved with coördination number four when chloride is the ligand. Gill[7] has reported that chloride ions have little or no effect on the spectrum of $[FeCl_4]^-$ in dimethylformamide.

Despite these objections and the lack of evidence for the existence of the $[FeCl_6]^{3-}$ ion in solution, it is clear that this ion as well as other hexachlorometallate(III) ions of first row transition elements can be stabilized in the solid state. Stabilization of these ions must be attributed to the large crystal lattice energy of their salts with trivalent cations of appropriate size.

The magnitude of the lattice energy was calculated assuming the structure suggested above and that the trivalent ions may be represented by point charges. The Madelung constant of this lattice has not previously been calculated. The coulomb contribution to the lattice energy may be expressed as $Nq_i\Sigma q_j/r_{ij}$ where q_i is the charge of a reference cation or anion, i; q_j is the charge on the other ions in the lattice, j; r_{ij} is the distance between the ions i and j, and N is Avogadro's number. For the hexagonal structure under consideration we may utilize the known c/a ratio and express the coulomb contribution as NAq^2/R_a where q is the magnitude of the charge on the ions, R_a is distance between nearest neighbors in the $(000l)$ planes, and A is a Madelung constant. In order to evaluate the Madelung constant, the summation was made over neutral aggregates of ions as suggested by Evjen.[14] The aggregates of ions which were chosen were hexagonal rings containing three cations and three anions. These rings were considered in order of increasing distance from the reference ion. The contributions to the Madelung constant from the various rings are listed in Table V. In a given column of the table, contributions from rings in a given $(000l)$ plane are considered; the three nearest neighbor rings are labeled A, the three next nearest neighbor rings B, etc. In the rows, contributions from rings in different $(000l)$ planes are considered. The terms considered yield -1.67 for the constant A. It is unlikely that the sum of an infinite number of terms differs from this value by more than ± 0.02. The coulomb contribution to the lattice energy was calculated to be 817 kcal. If the Born repulsion energy is about

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[12] C. K. Jørgensen, *Acta Chem. Scand.*, **10**, 500 (1956).

[13] This is the iron–chlorine distance in anhydrous iron(III) chloride in which the iron is octahedrally coördinated: N. Wooster, *Z. Krist.*, **83**, 35 (1932).

[14] H. M. Evjen, *Phys. Rev.*, **39**, 675 (1932).

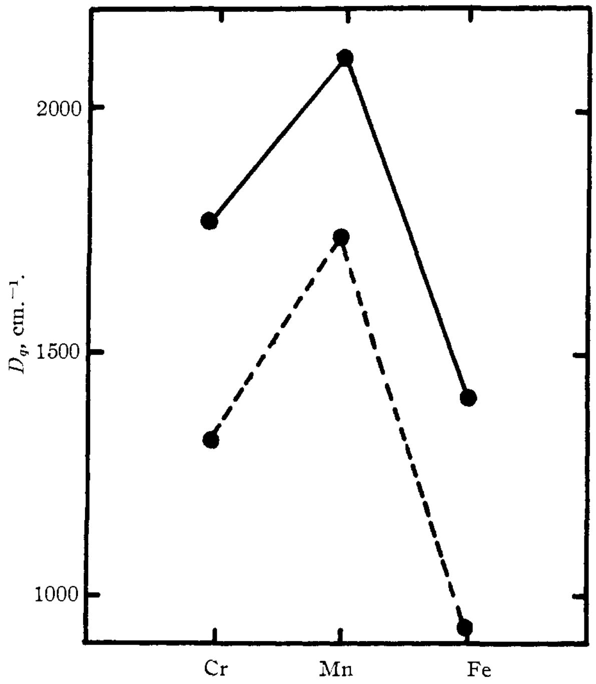

Fig. 1.—Comparison of Dq values: ---- $[MCl_6]^{3-}$, ——— $[M(H_2O)_6]^{3+}$ (M for Cr^{3+}, Mn^{3+} and Fe^{3+}).

10% of this value, we obtain 735 kcal. for the lattice energy.

It is obvious that the high lattice energy is due primarily to the large charge on the ions. The relative sizes of the ions, however, are also extremely important. Our experiments indicate that smaller cations than $[Co(pn)_3]^{3+}$ form excessively soluble compounds.

Table V

Contributions to the Madelung Constant

	Number of (000*l*) planes from reference ion				
	0	1	2	3	Total
A	−1.3453	−0.2035	+0.0144	−0.0018	−1.5362
B	−0.2679	+ .1170	− .0254	......	−0.1763
C	+ .0881	− .0570	+ .0207	......	+ .0518
D	− .0343	+ .0274	− .0152	......	− .0221
E	+ .0151	......	......	......	+ .0151

Electronic Spectra.—The spectral data with band assignments are collected in Table VI. The rhodium cation was used because it is colorless.

Table VI

Observed Spectral Data

Compound	Maxima, cm.$^{-1}$	Assignment
$[Rh(C_3H_{10}N_2)_3][CrCl_6]$[a]	13,180	$^4A_2 \rightarrow {}^4T_2$
	18,700	$^4A_2 \rightarrow {}^4T_1(F)$
$[Rh(C_3H_{10}N_2)_3][MnCl_6]$[b]	17,540	$^5E \rightarrow {}^5T_2$
	22,400	Charge transfer
$[Rh(C_3H_{10}N_2)_3][FeCl_6]$[b]	18,730	$^6A_1 \rightarrow {}^4T_2$
	22,080	$^6A_1 \rightarrow {}^4A_1, {}^4E$
$[Rh(C_3H_{10}N_2)_3][RhCl_6]\cdot 4.5H_2O$[a]	19,400	$^1A_1 \rightarrow {}^1T_1$
	24,400	$^1A_1 \rightarrow {}^1T_2$

[a] Reflectance. [b] Pressing in CsCl at 77°K.

The electronic spectrum of tris-(1,2-propanediamine)-rhodium(III) hexachloroferrate(III) was obtained from a 20% powder pressing in a cesium chloride matrix at 77°K. The spectrum consisted of a band at 18,730 cm.$^{-1}$ and a broader more intense band with a maximum intensity at 22,080 cm.$^{-1}$. The bands are assigned to the $^6A_1 \rightarrow {}^4T_2$ (^4G) and $^6A_1 \rightarrow {}^4E$, $^4A_1$ (^4G) transitions, respectively. The higher energy band was unsymmetrical with the band envelope trailing off toward the ultraviolet. Even though much of this asymmetry is due to scattering of the incident light beam by the pellet, there remains the distinct possibility that the $^6A_1 \rightarrow {}^4T_2(^4D)$ transition is in this region.

The $^6A_1 \rightarrow {}^4T_1$ transition could not be found, presumably because of the low intensity. The spectrum at 77°K. of a single crystal of $(NH_4)_2[FeCl_5(H_2O)]$ did exhibit a band at 13,920 cm.$^{-1}$. The ligand field of five chloride ions and one water molecule should not differ much from the field of six chloride ions, so this is probably a good approximation to the $^6A_1 \rightarrow {}^4T_1$ transition of $[FeCl_6]^{3-}$. For an estimation of Dq, these three pieces of data were fitted to the parameters Dq, B and C. Dq was found to be 1000 cm.$^{-1}$.

A second approach was used for the estimation of Dq for $[FeCl_6]^{3-}$. The free ion ratio of B and C was assumed for the complex, and B was calculated from the relation $10B + 5C = {}^4G$. Since the energy of the ^4E, ^4A component of ^4G is independent of the ligand field strength, the energy of the transition to this level was used in the calculation of B yielding a value of 655 cm.$^{-1}$. The secular equation for d^5 then was solved directly for Dq yielding a value of 920 cm.$^{-1}$.

Tris-(1,2-propanediamine)-rhodium(III) hexachloromanganate(III) is a dark brown compound at room temperature but the color changes to a deep red at 77°K. The electronic spectrum of a 2% powder pressing in a cesium chloride matrix at 77°K. exhibited bands at 17,540 and 22,400 cm.$^{-1}$. The latter band is probably a charge transfer transition. The low energy of the transition is in accord with the large oxidizing power of Mn(III).

The band at 17,540 cm.$^{-1}$ is assigned to $^5E \rightarrow {}^5T_2$. This gives a Dq for the hexachloromanganate(III) ion of 1754 cm.$^{-1}$. The value is in reasonable agreement with the Dq values for the hexachloroferrate(III) and hexachlorochromate(III) ions in view of the trend observed for the hexaaquometal(III) ions.[15] In Fig. 1, the Dq's found for the hexachlorometallate(III) ions are compared graphically with the values previously found for the hexaaquometal(III) ions. Piper and Carlin[16] have pointed out that the Dq for $[Mn(H_2O)_6]^{3+}$ is too high in view of the expected splitting of the ^5E ground state by a Jahn-Teller distortion. In the absence of experimental data for $[MnCl_6]^{3-}$ bearing on this point, it is sufficient to note that the observed trends lend credence to these assignments.

The $^5E \rightarrow {}^3T_1$ transition could not be found. From the Tanabe and Sugano diagram, it may be seen that the assignment of the band at 17,540 cm.$^{-1}$ to this transition would require an especially low Dq. Since we have established Dq for $[CrCl_6]^{3-}$ to be 1320 cm.$^{-1}$ (see below), this possibility can be ruled out with confidence.

Ibers and Davidson[17] reported the absorption spectrum of Mn(III) in 10 F hydrochloric acid. The position of the high energy band in their spectrum agrees well with the energy of the $^5E \rightarrow {}^5T_2$ transition which we observed for the $[MnCl_6]^{3-}$ ion. There also appears to be a broad low intensity band centered at about 12,000 cm.$^{-1}$ in their spectrum. This is the order of magnitude expected for the energy of the $^5E \rightarrow {}^3T_1$ transition. It is possible that one of the species contributing to the absorption spectrum which they observed was the $[MnCl_6]^{3-}$ ion.

There were two well-resolved bands in the reflectance spectrum of tris-(1,2-propanediamine)-rhodium(III) hexachlorochromate(III). These were at 13,180 and

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18,700 cm.$^{-1}$, and are readily assigned to be the $^4A_2 \rightarrow$ $^4T_2$ and $^4A_2 \rightarrow$ $^4T_1$ transitions, respectively; thus Dq for the hexachlorochromate(III) ion is 1,318 cm.$^{-1}$. Using the experimental Dq and the energy of the $^4A_2 \rightarrow$ $^4T_1(F)$, the Racah parameter, B', was calculated to be 575 cm.$^{-1}$ from the secular equation for d^3 in the weak field formalism. From this value β, the ratio of the Racah parameter for the complex to that of the free ion, was found to be 0.625. The magnitude of β is indicative of covalent bonding[6] and determines the position of the chloride ion in the neuphelauxetic series.

In conclusion, we compare the ligand field of the hexachlorochromate(III) ion to those of chromium(III) chloride,[18] in which the chromium ion is also six coordinate,[19] and of the corresponding fluorides[20] in Table VII.

From Table VII, it can be seen that the ligand field parameters of the chloride ion in $CrCl_3$ and $[CrCl_6]^{3-}$ ion are not much different. However, the small differences which do exist have just the opposite trend expected and observed for the corresponding fluorides[20]; one would expect that, if the halide ion were exposed to the full polarizing effect of a single tripositive ion in a hexahalide ion, the ligand field strength would increase and β would decrease.

TABLE VII

SPECTRAL DATA FOR SOME CHROMIUM(III) COMPLEXES

Ligand	Dq, cm.$^{-1}$	β
$Cl^-(CrCl_6^{3-})^a$	1318	0.62
$Cl^-(CrCl_3)^b$	1380	.56
$F^-(CrF_3)^c$	1460	.81
$F^-(CrF_6^{3-})^c$	1650	.74
H_2O^b	1740	.79

[a] This work. [b] Ref. 6. [c] Ref. 20.

We have already pointed out that the chlorine-chlorine distance in the $[MCl_6]^{3-}$ ion is within the contact radius. Perhaps the large net negative charge on the $[CrCl_6]^{3-}$ ion and the larger size of the chloride ion enhance repulsion effects and hence decrease the ligand field as well as delocalized metal electron density onto the ligand.

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Free Radicals by Mass Spectrometry. XXIX. Ionization Potentials of Substituted Cyclopentadienyl Radicals

BY R. F. POTTIE[1] AND F. P. LOSSING

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The vertical ionization potentials of a number of substituted cyclopentadienyl radicals have been measured by electron impact. In order of decreasing ionization potential, the substituents are: CN, Br, F, Cl, H, CH_3, C_2H_3, C_4H_4 (indenyl radical), NH_2 and $(C_4H_4)_2$ (fluorenyl radical). A qualitative relationship between the ionization potential and substituent constants of the σ- and σ^+-type is found. Some modes of thermal decomposition of the radicals, and of their precursors the substituted phenoxyl radicals, are described.

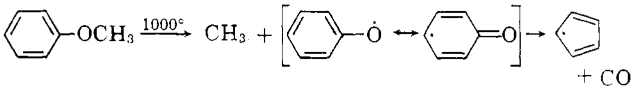
Introduction

It recently has been shown[2] that the vertical ionization potentials of benzyl radicals substituted in the *p*- and *m*-positions by characteristic groups exhibit large differences which are generally in accord with the electron-releasing or electron-attracting powers of the substituents. A plot of the ionization potentials of the substituted benzyl radicals against σ^+-values showed a close correspondence from $\sigma^+ = -0.8$ to $\sigma^+ = +0.6$. In the present work the effect of substitution on a non-aromatic nucleus has been examined by measuring the vertical ionization potentials of a number of substituted cyclopentadienyl radicals.

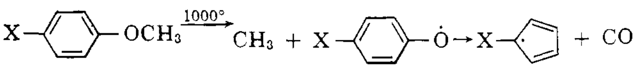
Experimental

The radicals were produced by the thermal decomposition of suitable compounds in a fused-silica capillary reactor leading into the ionization chamber of a mass spectrometer.[3] The decomposition of the parent substance and the formation of stable products were followed by their mass spectra using 50-v. electrons. Observations on the production of radicals were made using electrons of energy sufficient to ionize the radical, but insufficient to form the radical ion by dissociative ionization of the parent substance. The method used for comparing the ionization efficiency curves for a radical and the standard gas, usually xenon or krypton, has been described.[4,5] In some cases the net 50-v. peak for the radical could not be determined, since the spectra of one or more products of greater mass were unknown. The ionization efficiency curves were in these cases compared by matching the slopes of logarithmic plots by vertical displacement.[6,7]

Production of the Radicals.—The pyrolysis of anisole in a fused-silica capillary furnace at 950° was found in earlier[3] work to proceed by formation of methyl and phenoxyl radicals, followed by decomposition of the latter into CO and a cyclopentadienyl radical.



In the present work the substituted cyclopentadienyl radicals were produced by similar reactions, starting with the corresponding substituted anisole



In addition to these final products, however, the reaction of a small fraction of the substituted phenoxyl radicals with hydro-

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