

#### 498. *Some Chlorouranate(v) and Chlorotungstate(v) Compounds.*

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Hexachlorouranate(v) compounds of the type  $M^I UCl_6$  ( $M^I = Cs^+$ ,  $Me_4N^+$ ,  $Me_2H_2N^+$ , and  $Ph_4As^+$ ), and some analogous tungsten(v) salts ( $M = Cs^+$ ,  $Me_4N^+$ , and  $Et_4N^+$ ), have been prepared from thionyl chloride solutions of uranium pentachloride and tungsten hexachloride, respectively. The octachlorouranate(v) compound  $(Me_4N)_3 UCl_8$  has also been isolated, and evidence for the heptachlorouranate(v) anion  $UCl_7^{2-}$ , in thionyl chloride solution, has been obtained by conductometric titration. The magnetic, crystallographic, and spectral properties of the compounds are reported.

COMPLEXES of uranium pentachloride with thionyl chloride<sup>1</sup> and phosphorus pentachloride<sup>2</sup> are well known, and a double salt, pyridinium oxochlorouranate(v),  $(pyH)_2 UOCl_5$ , is reported<sup>3</sup> to be formed by addition of pyridine to a solution of the uranium pentachloride–thionyl chloride complex,  $UCl_5 \cdot SOCl_2$ , in ethanol saturated with hydrogen chloride. Fully chlorinated double salts are not, however, known, although the double fluorides  $M^I UF_6$ ,  $(M^I)_2 UF_7$ , and  $(M^I)_3 UF_8$  ( $M^I = NH_4^+$ ,  $Na^+$ ,  $K^+$ ,  $Li^+$ ,  $Rb^+$ , and  $Cs^+$ ) have recently been reported.<sup>4</sup> Accordingly, it appeared of interest to determine how the uranium

<sup>1</sup> Hecht, Jander, and Schlapmann, *Z. anorg. Chem.*, 1947, **254**, 255.

<sup>2</sup> Panzer and Suttle, *J. Nuclear Inorg. Chem.*, 1961, **20**, 229.

<sup>3</sup> Bradley, Chakravarti, and Chatterjee, *J. Inorg. Nuclear Chem.*, 1957, **3**, 367.

<sup>4</sup> Penneman, Asprey, and Sturgeon, *J. Amer. Chem. Soc.*, 1962, **84**, 4608; *Inorg. Chem.*, 1964, **3**, 727.

pentachloride–thionyl chloride complex behaved with cationic species in non-aqueous media. The rapid disproportionation of uranium(v), into uranium(IV) and -(VI), in hydrochloric acid solution, in contrast to its stability in concentrated hydrofluoric acid,<sup>4</sup> precludes the preparation of double chlorides from aqueous solution. When this work began, the chemistry of tungsten(v) was in a similar position; only oxochlorotungstate(v) complexes were known,<sup>5</sup> and the preparation of the hexachlorotungstate(v) compounds

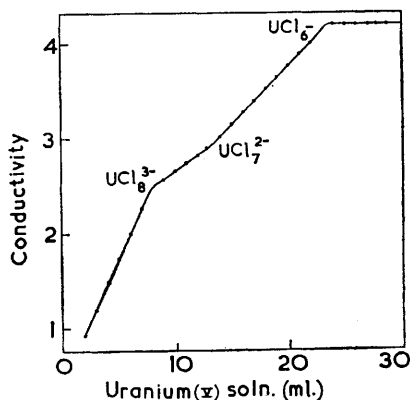


FIG. 1. Conductometric titration of a 0.1267M-solution of  $\text{UCl}_5 \cdot \text{SOCl}_2$  against pyridine, in thionyl chloride.

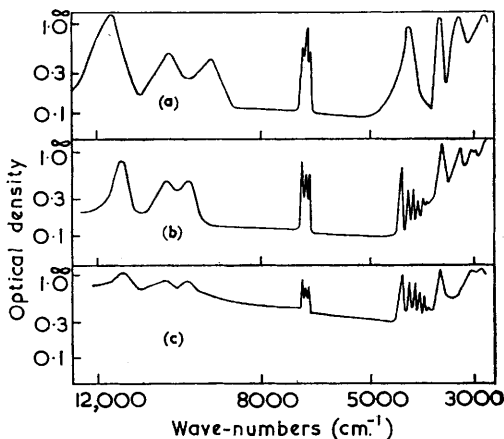


FIG. 2. Absorption spectra of 0.02M-solutions, in thionyl chloride, of (a)  $\text{UCl}_5$ , (b)  $\text{Me}_4\text{N}^+\text{UCl}_6^-$ , and (c)  $(\text{Me}_4\text{N}^+)_3\text{UCl}_8^-$ .

was undertaken for comparison with those of uranium(v). However, while the work was in progress, the preparation of tetraethylammonium hexachlorotungstate(v),  $\text{Et}_4\text{N}^+\text{WCl}_6^-$ , was reported.<sup>6</sup>

Conductometric titration (Fig. 1) of the uranium pentachloride–thionyl chloride complex against pyridine in thionyl chloride indicates the existence of the anionic species  $\text{UCl}_6^-$ ,  $\text{UCl}_7^{2-}$  (a weak inflexion only), and  $\text{UCl}_8^{3-}$ . Absorption spectra of thionyl chloride solutions containing 1:1 and 3:1 ratios of tetraethylammonium chloride and uranium pentachloride do not differ markedly (Fig. 2; Table 1), the solutions being, respectively,

TABLE 1.

Absorption spectra ( $\text{cm}^{-1}$ ) of uranium(v) chloro-species in thionyl chloride.

$\text{UCl}_5 \cdot \text{SOCl}_2$ .....	11,710	10,360	9325	6850, 6765vs, 6675	4195	3270
$\text{Me}_4\text{N}^+\text{UCl}_6^-$ .....	11,480	10,420	9900	6905vs, 6805, 6710	—	3275
$(\text{Me}_4\text{N}^+)_3\text{UCl}_8^-$ .....	11,480	10,450	9935	6910, 6810, 6717	—	—

orange-yellow and bright yellow. The peak at  $3275 \text{ cm}^{-1}$  in the uranium pentachloride and hexachlorouranate(v) spectra, probably due to co-ordinate thionyl chloride, and its absence in the octachlorouranate(v) spectrum, indicate that the hexachloro-anion is solvated, probably again by the uranium becoming octacovalent. The spectra of the sodium, lithium, and caesium hexafluorouranates(v)<sup>4</sup> show a group of three peaks between  $7200$  and  $7500 \text{ cm}^{-1}$ , similar to those which we observe at  $6700$ – $6900 \text{ cm}^{-1}$ , but, unfortunately, spectra of the corresponding octafluorouranates are not available.

With tetramethylammonium chloride we have isolated the deep yellow hexachloro-compound,  $\text{Me}_4\text{N}^+\text{UCl}_6^-$ , and the lighter yellow octachloro-salt  $(\text{Me}_4\text{N}^+)_3\text{UCl}_8^-$ ; both are soluble in thionyl chloride and are precipitated therefrom by carbon disulphide. They are

<sup>5</sup> Collenberg, *Z. anorg. Chem.*, 1918, **102**, 247.

<sup>6</sup> Adams, Chatt, Davidson, and Gerratt, *J.*, 1963, 2189.

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soluble in acetone, methyl cyanide, nitromethane, diethyl ether, and phosphorus oxytrichloride; in fact, the difference in the solubilities of the octachlorouranate(v) compound and tetramethylammonium chloride in methyl cyanide (23.0 and 2.6 g./l.) is a strong indication that the uranium(v) compound is not a mixture of the hexachlorouranate(v) and tetramethylammonium chloride. With dimethylammonium chloride, tetraphenylarsonium chloride, and caesium chloride, the deep yellow hexachlorouranates(v) have been prepared. Attempts to isolate an octachlorouranate(v) by means of the tetraphenylarsonium cation produced the hexachlorouranate(v) contaminated with 0.8—1.5 molecules of tetraphenylarsonium chloride. Apart from the caesium salt, which is only slightly soluble in hot or cold thionyl chloride, the solubilities of the salts are similar to those of the tetramethylammonium chlorouranates(v). All the compounds are extremely sensitive to moisture, rapidly hydrolysing and disproportionating to a mixture of uranium-(iv) and -(vi) chlorides; the tetraphenylarsonium salt is rather less rapidly attacked than the others. They are, however, relatively stable to heat; the tetraphenylarsonium hexachlorouranate(v) melts sharply at 224°, and the caesium salt (m. p. ~360°) sublimes with partial decomposition at 320°/1 mm., but the tetramethylammonium octachlorouranate(v) and the hexachlorouranate(v) decompose at 245°/1 mm. and 345°/1 mm., respectively, the former giving a white sublimate of the alkylammonium chloride. All the compounds change from yellow to dark red when heated, and revert to the original colour on cooling provided that the decomposition temperature has not been reached.

Dark green tetraethylammonium and tetramethylammonium <sup>6</sup> hexachlorotungstates(v) are produced when freshly sublimed tungsten hexachloride reacts with the alkylammonium chloride in thionyl chloride. The hexachloride, which is only slightly soluble in thionyl chloride, dissolves readily as it is reduced, the hexachlorotungstate(v) compounds being, like, their uranium counterparts, extremely soluble. The high solubility has been utilised in the preparation of the dark blue caesium hexachlorotungstate(v) which is precipitated when caesium chloride in iodine monochloride is added to the alkylammonium compounds in thionyl chloride. The reduction of tungsten hexachloride in iodine monochloride-thionyl chloride mixtures is very slow in the presence of caesium chloride, and the yield of caesium hexachlorotungstate(v) is low even after several weeks with intermittent refluxing. A recent report,<sup>7</sup> however, describes the preparation of hexachlorotungstate(iv) salts from the reaction between tungsten hexachloride and alkali-metal chlorides in iodine monochloride, at high temperatures in sealed tubes. The reduction of the hexachloride by alkylammonium chlorides is probably due to impurities in them, or to decomposition products formed from them in thionyl chloride; similar behaviour has also been observed <sup>8</sup> with rhenium oxytetrachloride, ReOCl<sub>4</sub>, in which case hexachlororhenates(iv) are produced. Attempts to prepare the tetramethylammonium octachlorotungstate were inconclusive.

The hexachlorotungstate(v) compounds are more stable to hydrolysis than their uranium analogues; the caesium salt slowly turns dark red in moist air, and the X-ray powder pattern then shows the presence of caesium oxychlorotungstate(v), Cs<sub>2</sub>WOCl<sub>5</sub>.<sup>9</sup> The compounds dissolve in acetone, methyl cyanide, and nitromethane, to give bright yellow, unstable solutions. The tetralkylammonium salts start to decompose at 180° whereas the caesium salt is stable up to 360°.

The magnetic behaviour of all the compounds has been examined. Curie-Weiss dependence is observed for the hexachlorouranates(v) (Fig. 3; Table 2) from 310°K to temperatures varying between 140 and 205°K; below this temperature marked deviations occur (Fig. 3). The moments at the higher temperatures are 1.62, 1.71, 2.09, and 2.14 B.M., for the tetramethylammonium, caesium, dimethylammonium, and tetraphenylarsonium salts, respectively, but the large values of the Weiss constant,  $\theta$ , namely -189,

<sup>7</sup> Kennedy and Peacock, *J.*, 1963, 3392.

<sup>8</sup> Bagnall, Brown, and Colton, *J.*, 1964, in the press.

<sup>9</sup> Brown, *J.*, 1964, in the press.

TABLE 2.

Magnetic data for uranium(v) chloro-complexes.

CsUCl <sub>6</sub>		(Me <sub>2</sub> H <sub>2</sub> N)UCl <sub>6</sub>		Me <sub>4</sub> NUCl <sub>6</sub>		Ph <sub>4</sub> AsUCl <sub>6</sub>		(Me <sub>4</sub> N) <sub>3</sub> UCl <sub>6</sub>	
T (°K)	χ <sub>m</sub>	T (°K)	χ <sub>m</sub>	T (°K)	χ <sub>m</sub>	T (°K)	χ <sub>m</sub>	T (°K)	χ <sub>m</sub>
308	775.5	288	803.6	291	659	285	1005	301	1105
287	816.6	266	812.7	275	704	265	1104	289	1105
263	864.7	251	840.0	252	738	240	1153	281	1105
233	921.5	226	867.4	236	765	219	1172	258	1106
203	977.8	211	903.5	190	868	196	1241	247	1119
173	1084	181	976.8	173	910	162	1349	207	1150
141	1205	156	1094	148	1035	143	1467	178	1210
113	1391	136	1176	129	1153	116	1653	149	1290
100	1521	111	1647	94	1397	91	2075	121	1570
83	1805			87	1518			99	1780
								86	2110

−161, −388, and −280°, indicate that these values of the moments have little significance. Tetramethylammonium octachlorouranate(v) exhibits temperature-independent paramagnetism from 310 to 250°K (molar susceptibility, χ<sub>m</sub> = 1100 × 10<sup>−6</sup> c.g.s. units), below which temperature the susceptibility shows temperature-dependence similar to that of the hexachlorouranates(v). Mixtures of tetramethylammonium hexa-

TABLE 3.

Magnetic data for tungsten(v) chloro-complexes.

CsWCl <sub>6</sub>				Me <sub>4</sub> NWCl <sub>6</sub>				Et <sub>4</sub> NWCl <sub>6</sub>			
T (°K)	χ <sub>m</sub>	T (°K)	χ <sub>m</sub>	T (°K)	χ <sub>m</sub>	T (°K)	χ <sub>m</sub>	T (°K)	χ <sub>m</sub>	T (°K)	χ <sub>m</sub>
304	360.3	116	400.2	297	626.8	161	678.5	302	168.4	158	180.0
264	360.3	97	402.3	271	633.6	140	676.5	271	168.4	139	187.3
234	360.3	88	381.2	254	626.8	113	706.5	251	168.4	115	161.5
206	364.4	84	376.9	230	633.6	97	721	230	168.4	91	124.7
177	376.9	81	364.4	208	636	84	664.2	204	164	82	87.8
145	385.5			185	652	76	596.1	183	175.6		

chlorouranate(v) and tetramethylammonium chloride show the same magnetic behaviour as the hexachlorouranate(v) alone, indicating that the octachlorouranate(v) is a true compound. Magnetic results are available for only one other uranium(v) compound, the octafluoro-salt Na<sub>3</sub>UF<sub>8</sub>, for which Curie-Weiss dependence has been reported;<sup>10</sup> the magnetic moment is 2.29 B.M. with θ = −150°, and it is assumed that the U<sup>5+</sup> ion in the compound has the 5f<sup>1</sup> configuration.

In contrast to the chlorouranates(v), the hexachlorotungstates(v) all exhibit anti-ferromagnetism similar to that observed<sup>11</sup> for the hexafluorotungstates(v). The Néel points for the caesium, tetraethylammonium, and tetramethylammonium salts are approximately 105, 100, and 140°K, respectively (Table 3; Fig. 4).

The metal-chlorine vibrational frequencies in the far-infrared have been measured (Table 4); the peaks were generally rather broad, and the slight indications of splitting in those of the tungsten compounds have been attributed to instrumental aberrations. Our figures for the chlorouranates(v) are about 50 cm.<sup>−1</sup> higher than those reported for tetraethylammonium hexachlorouranate(IV); this may be expected for such a change in valency.<sup>12</sup> The value for tetraethylammonium hexachlorotungstate(v), however, is much lower than the value (329 cm.<sup>−1</sup>) obtained by others.<sup>6</sup> (The octachlorouranate(v) appears to decompose to some extent in Nujol.)

All the compounds give poor X-ray powder photographs; these have not been indexed, but the caesium salts are clearly isostructural with the caesium and ammonium hexachloro-niobates(v) and -tantallates(v), on which single-crystal studies are at present being

<sup>10</sup> Rüdorff and Leutner, *Annalen*, 1960, **632**, 1.<sup>11</sup> Hargreaves and Peacock, *J.*, 1958, **3776**.<sup>12</sup> Adams, Gebbie, and Peacock, *Nature*, 1963, **199**, 278.

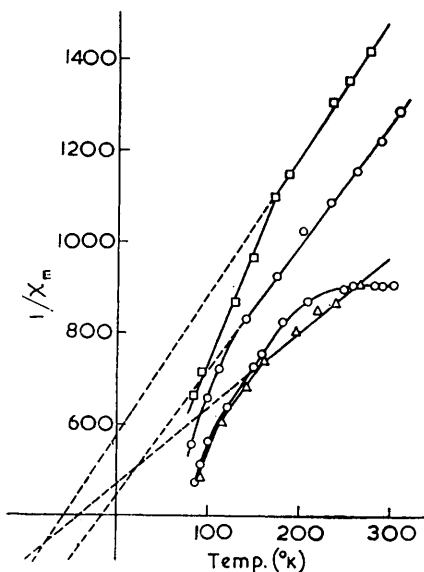


FIG. 3. Magnetic properties.

- ,  $\text{Me}_4\text{NUCl}_6$  ( $\theta = -189^\circ$ ).  
 ○ (upper curve),  $\text{CsUCl}_6$  ( $\theta = -161^\circ$ )  
 ○ (lower curve),  $(\text{Me}_4\text{N})_3\text{UCl}_6$ .  
 △,  $\text{Ph}_4\text{AsUCl}_6$  ( $\theta = -280^\circ$ ).

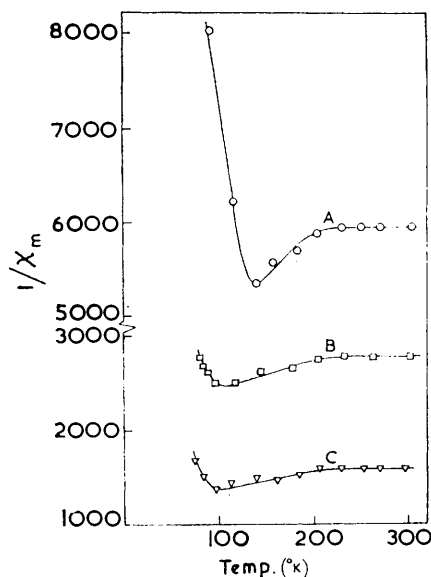
FIG. 4. Magnetic properties. A,  $\text{Et}_4\text{NWCl}_6$ .  
B,  $\text{CsWCl}_6$ . C,  $\text{Me}_4\text{NWCl}_6$ .

TABLE 4.

Far-infrared metal-chlorine vibrational frequencies ( $\text{cm}^{-1}$ ).

$\text{CsUCl}_6$ .....	$\nu_3$	$(\text{Me}_4\text{N})_3\text{UCl}_6$ .....	$\nu_3$	$\text{Me}_4\text{NUCl}_6$ .....	$\nu_3$	$\text{Me}_4\text{NWCl}_6$ .....	$\nu_3$
$\text{Ph}_4\text{AsUCl}_6$ .....	303	$\text{CsWCl}_6$ .....	310	$(\text{Me}_2\text{NH}_2)\text{UCl}_6$ ...	310	$\text{Et}_4\text{NWCl}_6$ .....	315
			317		308		305

TABLE 5.

X-Ray diffraction data.

$\text{CsWCl}_6$						$\text{CsUCl}_6$			
$\text{Sin}^2 \theta_{\text{obs}}$	$I_{\text{obs}}$	$\text{Sin}^2 \theta_{\text{obs}}$	$I_{\text{obs}}$	$\text{Sin}^2 \theta_{\text{obs}}$	$I_{\text{obs}}$	$\text{Sin}^2 \theta_{\text{obs}}$	$I_{\text{obs}}$	$\text{Sin}^2 \theta_{\text{obs}}$	$I_{\text{obs}}$
0.0186	10	0.0656	5	0.1274	1	0.0150	5	0.0808	10
0.0210	30	0.0674	5	0.1289	40	0.0198	20	0.1181	10
0.0247	100	0.0736	5	0.1304	20	0.0228	100	0.1213	50
0.0261	100	0.0762	40	0.1420	5	0.0256	70	0.1340	10
0.0315	5	0.0774	40	0.1436	1	0.0361	50	0.1450	10
0.0387	5	0.0796	40	0.1470	5	0.0475	80	0.1548	5
0.0402	50	0.0834	1	0.1570	5	0.0608	20	0.1708	30
0.0506	50	0.0850	5	0.1613	1	0.0725	50	0.1840	5
0.0514	60	0.1243	1						

made. The observed  $\text{sin}^2 \theta$  values for caesium hexachlorotungstate(v) and hexachlorouranate(v) are listed in Table 5, with visually estimated intensities.

## EXPERIMENTAL

The moisture-sensitive solids were handled in a dry-box after isolation, although preparation in the open laboratory was possible because of the protection from moisture afforded by the thionyl chloride. Solutions of uranium pentachloride in thionyl chloride were prepared by the published method.<sup>3</sup> Commercial tungsten hexachloride was freshly sublimed in dry argon ( $250^\circ$ ) after removal of tungsten oxychloride,  $\text{WOCl}_4$ , at lower temperatures.

*Preparative.*—(a) *Caesium hexachlorouranate(v)*. Caesium chloride (2.8 g.), dissolved in

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iodine monochloride–thionyl chloride (12 ml.; 23% w/v), was added to uranium pentachloride in thionyl chloride (30 ml.; 0.13M). The precipitate was washed with thionyl chloride (10 ml.) and vacuum-dried. The *product* was also obtained by adding a solution of uranium pentachloride in thionyl chloride to solid caesium chloride; it could be separated from residual caesium chloride by flotation and decantation because of the much higher density of the latter [Found: U(v), 41.1; Cl<sup>-</sup>, 36.5; Cs<sup>+</sup>, 22.7. CsUCl<sub>6</sub> requires U(v), 40.8; Cl<sup>-</sup>, 36.45; Cs<sup>+</sup>, 22.75%].

(b) *Dimethylammonium, tetramethylammonium, and tetraphenylarsonium salts.* The calculated quantities of the chlorides and a thionyl chloride solution of uranium pentachloride (1 : 1 or 3 : 1) were mixed; the *product* was precipitated by addition of half the volume of freshly purified carbon disulphide, and vacuum-dried.

(Me<sub>2</sub>NH<sub>2</sub>)UCl<sub>6</sub> [Found: U(v), 48.0; Cl<sup>-</sup>, 42.55. Required: U(v), 47.9; Cl<sup>-</sup>, 42.8%].

Me<sub>4</sub>NUCl<sub>6</sub> [Found: U(v), 45.5; Cl<sup>-</sup>, 40.6. Required: U(v), 45.3; Cl<sup>-</sup>, 49.5%].

(Me<sub>4</sub>N)<sub>3</sub>UCl<sub>6</sub> [Found: U(v), 32.2; Cl<sup>-</sup>, 38.0. Required: U(v), 32.0; Cl<sup>-</sup>, 38.1%].

Ph<sub>4</sub>AsUCl<sub>6</sub> [Found: U(v), 28.7; Cl<sup>-</sup>, 25.6. Required: U(v), 28.55; Cl<sup>-</sup>, 25.5%].

(c) *Tetraalkylammonium hexachlorotungstates(v).* A two-fold excess of tetraethyl or tetramethylammonium chloride in thionyl chloride was added to freshly sublimed tungsten hexachloride, and the resulting solution cooled to -10°. The *crystals* were washed with a little cooled thionyl chloride, and vacuum-dried.

Me<sub>4</sub>NWCl<sub>6</sub> (Found: W, 39.5; Cl<sup>-</sup>, 44.9. Required: W, 39.1; Cl<sup>-</sup>, 45.1%).

Et<sub>4</sub>NWCl<sub>6</sub> (Found: W, 34.2; Cl<sup>-</sup>, 39.3. Required: W, 34.3; Cl<sup>-</sup>, 39.6%).

(d) *Caesium hexachlorotungstate(v).* A solution of caesium chloride in iodine monochloride–thionyl chloride was added to tetramethylammonium hexachlorotungstate(v) in thionyl chloride; the *precipitate* was washed repeatedly with thionyl chloride and vacuum-dried (Found: W, 34.3; Cl<sup>-</sup>, 40.05. CsWCl<sub>6</sub> requires W, 34.7; Cl<sup>-</sup>, 40.15).

*Analysis.*—Uranium(v) was determined by direct titration to uranium(vi) with dichromate; the valency was confirmed by reduction to uranium(iv) on a lead column in 3M-hydrochloric acid, and titration to uranium(vi) as before.<sup>13</sup> Tungsten was weighed as barium tungstate,<sup>14</sup> precipitated from neutral solution after dissolving the salt in acetone, or, alternatively, by titration with dichromate as for uranium(v). Caesium was weighed as the hexachlorostannate<sup>15</sup> after removal of uranium by precipitation as hydroxide with calcium hydroxide. Chloride was determined potentiometrically against standard silver nitrate solution.

*Physical Properties.*—Magnetic susceptibilities were measured by the Gouy method, over the temperature range 80 to 310°K, on a balance described elsewhere.<sup>16</sup> Previously calibrated tubes were packed in a dry-box, and stoppered with Polythene bungs. Infrared spectra were taken, for mulls in Nujol, on a Hilger H800 spectrometer. X-Ray powder photographs were taken with 19-cm. Unicam Debye–Scherrer and Guinier focusing cameras, with filtered Cu K<sub>α</sub> radiation (λ = 1.54051 Å).

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<sup>13</sup> Sill and Peterson, *Analyt. Chem.*, 1952, **24**, 1175.

<sup>14</sup> Vogel, "A Text-book of Quantitative Inorganic Analysis," Longmans, London, 2nd edn., 1951, p. 491.

<sup>15</sup> Treadwell and Hall, "Analytical Chemistry," Wiley, New York, 1945, Vol. II, p. 286.

<sup>16</sup> Brown and Colton, *J.*, 1964, 714.