

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF CALIFORNIA AT LOS ANGELES]

## The Preparation and Magnetic Properties of Some Complex Compounds of Divalent Chromium<sup>1</sup>

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Previous workers<sup>3</sup> have described the properties of a number of complex salts of divalent chromium. The literature has been briefly reviewed by Balthis and Bailar.<sup>4</sup> In the present investigation three new compounds, monopyridino chromous acetate, chromous anthranilate (*o*-aminobenzoate), and chromous 8-hydroxyquinolate were obtained, and the magnetic susceptibilities of the complexes between chromous ion and ammonia, ethylenediamine, cyanide, and thiocyanate were measured in aqueous solution.

**Apparatus and Technique.**—Due to the extreme sensitivity of most chromous compounds to oxidation by the air, it was necessary to do almost all the experimental work under anaerobic conditions. Usually, manipulations were made in a closed system filled with nitrogen or carbon dioxide which had been bubbled through chromous chloride solution to effect complete removal of oxygen. For some purposes, it was sufficient to protect the solutions in open vessels by covering them with a layer of toluene. Most of the synthetic work was done in an apparatus similar to that of Balthis and Bailar.<sup>4</sup> Titrations were made in an apparatus similar to that of Crowell and Baumbach.<sup>5</sup>

### Experimental

The starting material used in the preparation of the complexes described in this paper was either pure solid chromous acetate or a solution of pure chromous chloride in hydrochloric acid. These were prepared in the manner recommended by Balthis and Bailar,<sup>4,6</sup> with two important modifications: the reduction of the chromic chloride by means of a Jones reductor and the omission of the precipitation with gaseous hydrogen chloride.

**Chromous Acetate.**—A freshly made solution, 2 *M* in green chromic chloride (dichlorotetraquo chromic chloride dihydrate) and 0.1 *M* in hydrochloric acid was passed slowly through an upflow type Jones reductor<sup>7</sup> filled with

amalgamated zinc (0.2% mercury). In this manner, complete reduction was obtained quickly without the necessity of adding a large amount of hydrochloric acid to the solution. The reduced solution was passed directly into an excess of saturated sodium acetate solution. The supernatant liquid was drawn off and the precipitated chromous acetate was washed with oxygen-free water and sucked as dry as possible in a stream of nitrogen.

**Chromous Chloride.**—Chromous acetate prepared in the above manner was decomposed by the addition of ice-cold saturated hydrochloric acid. The red acetate was immediately transformed into pale blue crystals of hydrated chromous chloride. The addition of gaseous hydrogen chloride was found to be unnecessary, and in fact undesirable, as the yield was not appreciably increased by its addition and some oxidation invariably took place during the process. The liquid was filtered and the precipitate washed several times with portions of cold, saturated hydrochloric acid and finally sucked as dry as possible in a stream of nitrogen. Such preparations were free from zinc and acetic acid, but retained much hydrochloric acid. More than 99% of the chromium present was in the divalent state.

**Monopyridino Chromous Acetate.**—Chatelet and Chatelet<sup>3f</sup> reported the preparation of hemipyridino chromous acetate, Cr(ACO)<sub>2</sub>·1/2Py, by the solution of dry chromous acetate in pyridine and precipitation by the addition of ether. The writers, in following the published directions, obtained only traces of a product. It was found that chromous acetate is only slightly soluble in pyridine (even at the boiling point) and that addition of ether does not greatly diminish the solubility. The undissolved residue was, however, not unchanged chromous acetate but monopyridino chromous acetate, a compound hitherto unreported.

Ten millimoles of freshly prepared chromous acetate were washed with alcohol and dried in a current of carbon dioxide. Ten ml. of anhydrous pyridine was added, the mixture refluxed for fifteen minutes, cooled, and filtered in the absence of air. The residual red solid was washed with several portions of alcohol, until the washings had no odor of pyridine. The entire solid was dissolved in dilute sulfuric acid and aliquots analyzed for chromium, pyridine, and acetate. The results are expressed as the ratios of moles of each constituent found.

Preparation	Cr	Pyridine	AcO
1	1.00	1.07	2.07
2	1.00	1.04	2.04

The compound is a red crystalline solid, easily oxidized by air, nearly insoluble in water and alcohol, and greatly resembling the original chromous acetate in appearance. The same product was obtained by the addition of 5 ml. of pyridine to 10 millimoles of chromous acetate dissolved in 10 ml. of 1 *M* hydrochloric acid. The characteristic red

(1) Abstract of a thesis submitted by David N. Hume in partial fulfillment of the requirements for the degree of Master of Arts.

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(3) Notably: (a) Traube and Passarge, *Ber.*, **46**, 1505 (1913); (b) Traube and Lange, *ibid.*, **58**, 2773 (1925); (c) Traube, Burmeister and Stahn, *Z. anorg. allgem. Chem.*, **147**, 50 (1925); (d) Christiansen, *J. prakt. Chem.*, **31**, 169 (1885); (e) Chatelet, *Compt. rend.*, **199**, 290 (1934); (f) Chatelet and Chatelet, *ibid.*, **198**, 833 (1934); (g) Barbieri and Tettamanzi, *Atti Accad. Lincei*, **15**, 877 (1932); (h) Sand and Burger, *Ber.*, **39**, 1771 (1906); and (i) Schlesinger and Hammond, *THIS JOURNAL*, **55**, 3971 (1933).

(4) Balthis and Bailar, *ibid.*, **58**, 1474 (1936).

(5) Crowell and Baumbach, *ibid.*, **57**, 2607 (1935).

(6) Balthis and Bailar, "Inorganic Synthesis," Vol. I, McGraw-Hill Book Co., Inc., New York, N. Y., 1939, p. 125.

(7) Stone and Beeson, *Ind. Eng. Chem., Anal. Ed.*, **8**, 190 (1936); and Stone and Hume, *ibid.*, **11**, 598 (1939).

precipitate was washed with water, alcohol, and ether before analysis.

**Chromous Anthranilate.**—It was found that alkali metal salts of anthranilic acid gave an orange precipitate of the normal inner complex salt, chromous *o*-aminobenzoate, on addition to nearly neutral (*pH* 5) chromous chloride solutions. If the chromous chloride were present in excess, it could easily be washed out of the precipitate. The use of acidified chromous chloride or an excess of the organic salt resulted in the formation of a precipitate contaminated with anthranilic acid. Chromic chloride gives no precipitate under these conditions.

In the absence of air, 50 ml. of chromous chloride solution 0.14 *M* in chromous ion and 0.30 *M* in hydrogen ion, were neutralized to *pH* 5.0 with 0.5 *M* potassium hydroxide. To the resulting solution was added slowly and with stirring 10 ml. of 1.0 *M* potassium anthranilate. The resulting orange precipitate was stirred with the mother liquor for thirty minutes and drawn off into centrifuge tubes under toluene. The precipitate was centrifuged and washed repeatedly with water until the washings showed only traces of chloride to be present. The precipitate was then dissolved in 1 *M* perchloric acid and analyzed for chromium, anthranilic acid and chloride. The results are reported as the ratio of moles of chromium to moles of anthranilic acid found. Chloride was present in scarcely detectable traces.

Preparation	Chromium	Anthranilic acid
1	1.00	1.96
2	1.00	1.94

The product is an orange solid, insoluble in water and organic solvents but easily decomposed by dilute mineral acids.

**Determination of Anthranilic Acid.**—It was found that anthranilic acid may be determined to within an accuracy of about 1% by bromination if the conditions of reaction are carefully controlled. A 10-ml. sample of solution containing about 2.5 millimoles of anthranilic acid and 2 millimoles of hydrochloric acid was cooled to 0° in a glass-stoppered flask. Ten ml. of ice-cold bromine water (0.1 *M* in bromine and 0.5 *M* in sodium bromide) was added by means of a pipet, and the mixture swirled for fifteen seconds. One gram of sodium iodide dissolved in 5 ml. of water was added quickly and the liberated iodine was titrated to a starch end-point with standard thio-sulfate solution. A blank was run on the bromine water, and the difference in the number of equivalents of thio-sulfate required was found to be equal to the number of equivalents of anthranilic acid present, or four times the number of moles, since dibromoanthranilic acid was formed.

**Chromous 8-Hydroxyquinolate.**—Addition of chromous chloride solution (0.2 *M*) to an excess of 5% 8-hydroxyquinoline in 2 *M* acetic acid resulted in the quantitative precipitation of the chromium as a voluminous orange-yellow precipitate. The product is insoluble in water, dilute acids and bases, and most organic solvents. It is soluble in pyridine, from which it may be obtained pure in yellow crystals. The compound does not seem to be affected by air. One would expect the normal salt, with two hydroxyquinolate radicals per chromium, but the analyses of the purified product (10.24% Cr and 7.80% N) do not

correspond with this or any other simple formula which has suggested itself to the writers.

**The Reaction of Chromous Chloride with Ethylenediamine.**—Balthis and Bailar<sup>4</sup> noted the formation of a transient blue precipitate on the addition of ethylenediamine to chromous chloride solutions. They were unable to isolate the substance, but suggested that it was a complex. The writers found that the blue precipitate could easily be isolated if an excess of amine were avoided. Analysis showed it to contain only a trace of ethylenediamine, being basic chromous chloride, the properties of which are being described in another communication. The solubility of the precipitate in excess ethylenediamine with the formation of an unstable chromous complex, as reported by Balthis and Bailar, was confirmed. The solution rapidly evolved hydrogen, being oxidized to chromic complexes, but was stable enough to permit magnetic measurements to be made.

**Chromous Ammonia Complex.**—A series of anhydrous chromous amines is known,<sup>51</sup> but these complexes decompose in aqueous solution. Addition of concentrated ammonia solution to a chromous chloride solution resulted in the precipitation of basic chromous chloride, followed by a partial solution in excess reagent with formation of a deep blue complex. Such a solution, about 8 *M* in ammonia, was found to be about 0.03 *M* in chromium. These solutions were quite unstable, precipitating chromic oxide within two hours, but were sufficiently stable to be used for magnetic measurements.

**Potassium Chromocyanide.**—Solutions of potassium chromocyanide were prepared by the addition of excess potassium cyanide to chromous chloride solutions. An initial dark brown precipitate (probably basic salts or chromous hydroxide) dissolved readily in excess of cyanide with formation of the reddish-orange complex. If the original chromous chloride solution contained free acid, the complex rapidly decomposed, yielding the potassium chromicyanide. If the complex were prepared from a chromous chloride solution which had been neutralized to *pH* 5 or 6 by addition of sodium hydroxide, the solution formed was quite stable. This would indicate either that hydrogen cyanide is the oxidizing agent or that the reaction is acid catalyzed. According to Traube,<sup>5b</sup> methylamine is formed in the reaction. Heating accelerates the decomposition, while the presence of platinum results in catalytic decomposition of the chromous compound with rapid evolution of hydrogen. Magnetic measurements were made on both the chromocyanide and chromicyanide solutions.

**Chromous Thiocyanate Complex.**—The addition of excess potassium thiocyanate to chromous chloride solutions resulted in the formation of a deep blue, unstable complex. No solids were isolated, but magnetic measurements were made on the solutions.

**Magnetic Measurements.**—The magnetic susceptibilities per ml. of dilute solutions of chromous chloride and its complexes with cyanide, thiocyanate, ammonia, and ethylenediamine, and of potassium chromicyanide were measured at 25° by the Gouy method. The apparatus and the technique employed were similar to those of Coryell, Stitt and Pauling.<sup>8</sup> Samples of 25.00 ml. of the solu-

(8) C. D. Coryell, F. Stitt and L. Pauling, *THIS JOURNAL*, **59**, 633 (1937).

TABLE I  
 PARAMAGNETIC SUSCEPTIBILITY AND MOMENT OF CHROMIUM IN VARIOUS COMPOUNDS

Compound	$M$ of Cr	$M$ of other constituent	$\kappa_{\text{obsd.}} \times 10^6$	$\chi_{\text{molal}} \times 10^6$	$\mu_{\text{obsd.}}$	$\mu_{\text{theoret.}}$
Chromous chloride	0.1358	...	+0.679	10,400	5.00	4.90
Ammonia complex	.0281	8.38	-.418	10,000	4.90	4.90
Ethylenediamine complex	.0370	1.44	-.303	8,000 to 8500	4.4 to 4.5	4.90
Thiocyanate complex	.0680	2.50	-.076	9,970	4.90	4.90
Chromocyanide	.0442	0.664	-.537	4,130	3.15	2.83
Chromicyanide	.0453	1.00	-.416	6,320	3.90	3.88

tions to be examined were placed in the upper compartment of the cylindrical tube, the lower part being filled with water. The solutions were protected from the air by a layer of toluene, the effect of which on the susceptibility was found to be negligible. In the cases where the chromous solutions were undergoing spontaneous oxidation by hydrogen ion, the susceptibilities measured were plotted against time and extrapolated back to the time of mixing of the solutions.

The contributions to the observed susceptibilities due to the diamagnetism of the water and other ions in the solution were calculated from the susceptibility data in the "International Critical Tables" and the "Landolt-Börnstein Tabellen." Corrections were applied for the probable diamagnetism of all atoms in the complexes, and the corrected molal paramagnetic susceptibilities ( $\chi_{\text{molal}}$ ) of the chromium in the complexes were calculated. The corresponding paramagnetic moments  $\mu$  (in Bohr magnetons) were calculated from the relation  $\mu = 2.84 \sqrt{\chi_{\text{molal}} T_1}$  assuming the validity of Curie's law, and are compared in Table I with the moments calculated for predicted bond structures.<sup>9</sup> The molar concentrations of chromium and of the complex-forming constituents are given in columns two and three. The observed susceptibilities per ml. of the solutions,  $\kappa_{\text{obsd.}}$  are given in column four, and the calculated values of  $\chi_{\text{molal}}$  are given in column five. The  $\kappa_{\text{obsd.}}$  values are reliable to 0.1% while the  $\chi_{\text{molal}}$  values may be considered to have uncertainties up to about 5%, leading to uncertainties up to 3% for the values of  $\mu_{\text{obsd.}}$  in column six.

Chromous ion has four  $3d$  electrons, all unpaired, leading to an expected spin magnetic moment of 4.90 for the ion and ionically bounded complexes, with a small orbital contribution. Octahedral covalent bond formation ( $d^2sp^3$ ) results in the pairing of two of these electrons, reducing the spin moment to 2.83.

The chromic ion is expected to have a spin moment of 3.88 (for three unpaired  $3d$  electrons) and the formation of  $d^2sp^3$  octahedral covalent

bonds will not change this. In column seven of Table I the theoretical spin moments,  $\mu_{\text{theoret.}}$  in best accord with the observations of column six are recorded.

It is seen that the cyanide complex is the only one in which divalent chromium forms octahedral covalent bonds. The magnetic criterion does not distinguish in this case between ionic bonds and covalent bonds other than octahedral, but it is unlikely that these complexes (aside from the cyanide) should be anything but predominantly ionic.

Two old values for  $10^6 \chi_{\text{molal}}$  for chromous ion in solution average 10,000.<sup>10</sup> This is in good agreement with the above determinations. Lips<sup>11</sup> has studied solid chromous sulfate hexahydrate and anhydrous chromous chloride over a large temperature range. The former obeys Curie's law and has a moment,  $\mu$ , of 4.82; the latter shows abnormal behavior, but at higher temperatures exhibits the same moment. Serres<sup>12</sup> obtained an average value for the moment of the chromous ion in solid chromous chloride of 4.79 at room temperature.

The magnetic moment of chromium in the chromicyanide ion has been reported as 3.74 and 3.92 by Welo<sup>13</sup> and Biltz,<sup>14</sup> respectively. The data of Rây and Bhar<sup>15</sup> when corrected for the diamagnetism of the complex lead to a value of 3.53 and Szegö and Ostinelli<sup>16</sup> gave a value of 3.79 in aqueous solution.

These workers found the chromocyanide too unstable to be measured accurately, but estimated a probable moment greater than 3.9. The data of Rây and Dhar (corrected for diamagnetism) lead to a moment of 3.4 in accord with predictions and in agreement with the present

(10) "Int. Crit. Tables," Vol. VI, McGraw-Hill Book Co., Inc., New York, N. Y., 1929, p. 359.

(11) E. Lips, *Helv. Phys. Acta*, **7**, 537 (1934).

(12) A. Serres, *Ann. phys.*, **17**, 5 (1932).

(13) L. A. Welo, *Phil. Mag.*, [7] **6**, 481 (1928).

(14) W. Biltz, *Z. anorg. allgem. Chem.*, **170**, 161 (1928).

(15) P. Rây and H. Bhar, *J. Indian Chem. Soc.*, **5**, 497 (1928).

(16) L. Szegö and P. Ostinelli, *Gazz. chim. ital.*, **60**, 946 (1930).

(9) L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1939.

work. No previous magnetic work seems to have been done on other chromous complexes.

The authors wish to acknowledge the kind assistance of Dr. Charles D. Coryell, whose generous cooperation has made the magnetic measurements possible.

### Summary

Three new complex compounds of divalent chromium have been prepared: monopyridino

chromous acetate, chromous anthranilate, and chromous 8-hydroxyquinolate. The magnetic properties of a number of other chromous complexes have been studied. The free ion and the ammonia, ethylenediamine, and thiocyanate complexes contain four unpaired electrons with presumably ionic bonds being formed. The chromocyanide complex has two unpaired electrons, indicating octahedral covalent bond formation.

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## Radioactive Determination of the Relative Abundance of the Isotope $K^{40}$ in Terrestrial and Meteoritic Potassium<sup>1</sup>

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The use of radioactive substances in determining ages of rocks and other geological formations is well known. In the present work, the age of the potassium atoms in the Pultusk meteorite in relation to the age of potassium atoms in the earth has been determined by the use of the long-lived beta emitter, potassium, *viz.*,  $K^{40}$ . This was accomplished by the separation and comparative study of the specific activity of potassium chloride obtained from the meteorite and from a pure terrestrial sample.

The Pultusk meteorite is listed in von Niessl and Hoffmeister's<sup>2</sup> catalog of fireballs as having an hyperbolic orbit. More recent work, however,<sup>3</sup> has led to the opposite opinion, indicating that the meteoritic fragment used is of solar system origin and not extra-solar as previously supposed.

This work is based on the assumption that the abundance ratios of the isotopes of each element are the same at the time of their formation, no matter where in the universe the formation occurred. A number of investigations of isotopic abundance ratios have been made on meteorites<sup>4</sup> and in no case has the ratio obtained differed from that found for the corresponding element in terrestrial material. In the case of the Pultusk meteorite, the isotopic abundance ratio of  $O^{16}$  to

$O^{18}$  has been determined<sup>5</sup> and is reported as the same as that found for terrestrial oxygen; and the same is true<sup>4</sup> for the ratio of  $U^{238}$ : $U^{235}$ .

The chemical separation of potassium is based on the low solubility of potassium perchlorate in alcohol as compared with other perchlorates. The only hindering feature is the even lower solubility of rubidium perchlorate in alcohol. The presence of an appreciable amount of rubidium would make this method inoperative, because of the radioactivity of the rubidium isotope,  $Rb^{87}$ , but when the amount of rubidium is 1% or less of the potassium present, the method should be applicable.

The Geiger-Müller counter used in the radioactivity measurement was of the "bell" type (Fig. 1). Except for minor changes, the amplifier circuit, power supplies, and drum camera-galvanometer recorder used in this work are the same as those developed by Evans and Alder.<sup>6</sup> The finely ground potassium chloride was placed in a cylindrical well in a small brass disk (D in Fig. 1) and leveled by shaking and rocking. This is brought into close proximity to the thin (21 micron) mica window of the counter. Nearly all of the salt used in such a determination can be recovered effectively and used again. In this manner, one-half gram of salt can be used in dozens of measurements.

**Chemical Method.**—The procedure used in the separation of the potassium from the meteorite was an adaptation of a method given by Morgan<sup>7</sup> and later by Green.<sup>8</sup>

After the meteoritic sample of about 10 g. had been thoroughly disintegrated by treatment with 47% hydrofluoric acid and the excess hydrogen fluoride removed, the large iron and magnesium content was precipitated by

(1) From a thesis submitted by W. M. Leaders in partial fulfillment of the requirements for the degree of Doctor of Philosophy, Massachusetts Institute of Technology, June, 1940.

(2) Von Niessl and Hoffmeister; *Denkschr. d. Akad. Wiss. Wien, Math. natw. Kl.*, **100**, 1-70 (1926).

(3) C. C. Wylie, *Science*, **9**, 264 (1939).

(4) Cf. Schumb, Evans and Hastings, *THIS JOURNAL*, **61**, 3451 (1939), and other references given therein.

(5) Manian, Urey and Bleakney, *ibid.*, **56**, 2601 (1934).

(6) Evans and Alder, *Rev. Sci. Instruments*, **10**, 332 (1939).

(7) J. J. Morgan, *Ind. Eng. Chem.*, **13**, 225 (1921).

(8) M. M. Green, *ibid.*, **15**, 163 (1923).