

twice with 75% D<sub>2</sub>O and finally six times with 99.7% D<sub>2</sub>O. The deuterated I was again dissolved in 100 ml. of 99.7% D<sub>2</sub>O and cooled to 0°. Bromine was added dropwise with shaking until a faint yellow color persisted. The solution was then frozen and the deuterated water was removed by freeze-drying to give about 6 g. of product octahydroxycyclobutane-*d*<sub>8</sub>. The product was not analyzed, but spectral studies indicated it to be octahydroxycyclobutane with more than 97% of the hydrogen replaced by deuterium. It was free of carbonyl-containing impurities.

**Reduction of Octahydroxycyclobutane to I.**—In 5 ml. of water was dissolved 0.5 g. of octahydroxycyclobutane. A slow stream of sulfur dioxide was passed through the solution for 30 minutes. The solution was then evaporated to small volume, and the white crystals which formed were isolated and recrystallized from water. The product was identified as I by comparison of its ultraviolet and infrared spectra with those of an authentic sample.

**Ultraviolet Spectra of Octahydroxycyclobutane Solution.**—All spectra were determined using a Cary model 14 spectrophotometer. At 0.01 *M* in 1 *N* hydrochloric acid, IV showed no ultraviolet bands except for some end absorption below 2100 Å. A very weak band at about 2900 Å. became noticeable after several hours, and later a band with  $\lambda_{\max}$  2350 Å. appeared. The latter grew steadily and after 2 days had  $\epsilon_{\text{app}}$  100. A solution of IV at pH 1 was also initially transparent, but absorption developed somewhat more rapidly, leading to bands at about 2450 and 2750 Å. In pure water IV gave a weakly acidic solution which showed initially a band with  $\lambda_{\max}$  2450 Å.,  $\epsilon_{\text{app}}$  40.

A shoulder gradually appeared at about 2750 Å., and both peaks increased with time. Some of the maxima are close to those for diketocyclobutene in acid solution,<sup>13</sup> suggesting that compound I may be one of the decomposition products of IV. In a strongly basic solution of IV all of the ultraviolet bands disappeared except for very strong end absorption, and octahydroxycyclobutane was found not to be present when the solution was acidified.

**Infrared and Raman Spectra.**—Infrared spectra were determined on solid octahydroxycyclobutane and octahydroxycyclobutane-*d*<sub>8</sub> as mulls in Stanolind white petroleum oil and as pressed disks in KBr. A Baird model S spectrophotometer was used for the 650–4000 cm.<sup>-1</sup> and a Perkin–Elmer model 112 instrument with a cesium bromide prism was used for the 400–650 cm.<sup>-1</sup> region. For the Raman spectra, a 12% solution in 1 *N* hydrochloric acid was used for the protium compound, and a 15% solution in 1–2 *N* DCl in D<sub>2</sub>O was used for the octadeuterio compound. The spectra were determined on a Cary model 44 automatic recording Raman spectrometer at the Argonne National Laboratory.

**Acknowledgments.**—The authors are grateful to personnel of the Argonne National Laboratory for making the Raman spectrometer available for their use and to the National Science Foundation and the Wisconsin Alumni Research Foundation for financial support.

(13) H. Y. Niu, Thesis, University of Wisconsin, 1961.

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF WISCONSIN, MADISON 6, WIS.]

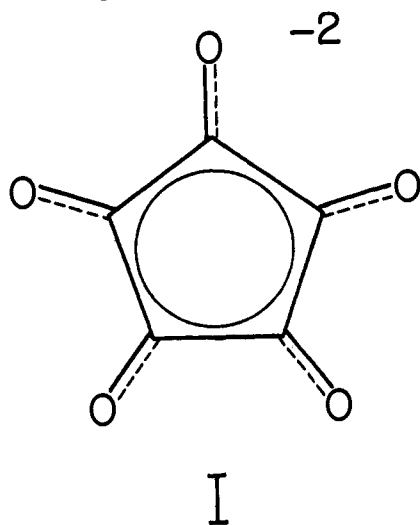
## New Aromatic Anions. VI. Complexes of Croconate Ion with Some Divalent and Trivalent Metals

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Complexes of croconate ion with the divalent metal ions Cu, Fe, Zn, Ni, Mn, Co, and Ca and trivalent Al, Fe, and Cr have been prepared and characterized by means of analysis, infrared spectroscopy, powder X-ray diffraction, and magnetic studies. All of the divalent metal complexes have the general formula  $\text{MC}_5\text{O}_5 \cdot 3\text{H}_2\text{O}$ . The divalent transition metal compounds are all high-spin complexes, and all have the same polymeric structure (Fig. 1), determined from a single-crystal X-ray analysis of the copper(II) compound. The trivalent metal complexes have more complicated formulas containing hydroxyl groups, and those of Fe(III) and Cr(III) show paramagnetism lower than that expected for high-spin complexes.

Although copper(II) and silver derivatives of croconate ion ( $\text{C}_5\text{O}_5^{-2}$ , I) have been known for over a hundred years,<sup>1,2</sup> no general study of transition metal cro-



conates has been reported. The present investigation was initiated because it seemed likely that the planar, symmetrical croconate ion<sup>2,3</sup> (I) might show unusual

properties as a complexing agent. In particular, sandwich complexes with ring-bonding to transition metal ions were thought to be possible. Such  $\pi$ -complexes of the sandwich type were not found; instead, the croconate ion bonds to metals through oxygen, serving both as a monodentate and bidentate ligand toward divalent transition metals. The resulting metal complexes form an interesting new class of inorganic coordination polymers.

**Divalent Transition Metal Croconates.**—The croconate derivatives of Mn(II), Fe(II), Cu(II), Ni(II), Co(II), Ca(II), and Zn(II) were all prepared from aqueous solutions of salts of the divalent cations and of dipotassium croconate. All of the compounds were trihydrates with general formula  $\text{MC}_5\text{O}_5 \cdot 3\text{H}_2\text{O}$ , and all of the divalent transition metal croconates had closely similar powder X-ray diffraction patterns, differing only slightly in interplanar *d*-spacing. Representative data are shown in Table I. The croconate derivative of the nontransition metal calcium is also a trihydrate, but it has a quite different X-ray pattern and hence probably a different structure.

Preliminary single-crystal X-ray work on copper croconate trihydrate was carried out previously by Takehara and Yokoi,<sup>4</sup> who found that the crystals are orthorhombic with eight molecules per unit cell. The lattice parameters reported were  $a = 15.1 \text{ \AA}$ ,  $b = 11.4 \text{ \AA}$ , and  $c = 7.83 \text{ \AA}$ . Redetermination of the lattice

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(2) K. Yamada, N. Mizuno, and Y. Hirata, *Bull. Chem. Soc. Japan*, **31**, 543 (1958).

(3) M. Ito and R. West, *J. Am. Chem. Soc.*, **85**, 2580 (1963); R. West, H. Y. Niu, D. L. Powell, and M. V. Evans, *ibid.*, **82**, 6204 (1960).

(4) A. Takehara and M. Yokoi, *Shinshu Daigaku Sen Igakubu Kenkyu Hokoku*, **8**, 108 (1958).

TABLE I  
LATTICE SPACINGS OF METAL CROCONATES, IN Å.

| $K_2C_2O_4$ | $NiC_2O_4 \cdot 3H_2O$ |        | $CoC_2O_4 \cdot 3H_2O$ |        | $CuC_2O_4 \cdot 3H_2O$ |        | $CaC_2O_4 \cdot 3H_2O$ |  | M(III) <sup>a</sup><br>cpd. |
|-------------|------------------------|--------|------------------------|--------|------------------------|--------|------------------------|--|-----------------------------|
|             | $H_2O$                 | $H_2O$ | $H_2O$                 | $H_2O$ | $H_2O$                 | $H_2O$ | $H_2O$                 |  |                             |
| 6.36        | 7.72                   | 7.67   | 7.80                   | 8.31   | 9.36                   |        |                        |  |                             |
| 3.60        | 6.48                   | 6.52   | 6.52                   | 7.46   | 8.31                   |        |                        |  |                             |
| 3.18        | 4.82                   | 4.84   | 4.95                   | 5.53   | 6.20                   |        |                        |  |                             |
| 3.13        | 4.61                   | 4.62   | 4.55                   | 5.06   | 5.89                   |        |                        |  |                             |
| 3.07        | 4.08                   | 4.10   | 4.09                   | 4.70   | 5.19                   |        |                        |  |                             |
| 2.97        | 3.95                   | 3.93   | 3.91                   | 4.43   | 5.01                   |        |                        |  |                             |
| 2.84        | 3.74                   | 3.70   | 3.70                   | 4.22   | 4.68                   |        |                        |  |                             |
| 2.71        | 3.34                   | 3.35   | 3.36                   | 3.63   | 4.47                   |        |                        |  |                             |
| 2.63        | 3.19                   | 3.19   | 3.19                   | 3.46   | 4.17                   |        |                        |  |                             |
| 2.57        | 3.08                   | 3.08   | 3.09                   | 3.15   | 3.99                   |        |                        |  |                             |
| 2.49        | 3.00                   | 3.00   | 2.95                   | 3.07   | 3.49                   |        |                        |  |                             |
| 2.41        | 2.81                   |        |                        | 2.96   | 3.31                   |        |                        |  |                             |
| 2.37        | 2.72                   | 2.73   | 2.72                   | 2.84   | 3.14                   |        |                        |  |                             |
| 2.33        | 2.60                   | 2.59   | 2.60                   | 2.79   | 3.07                   |        |                        |  |                             |
| 2.23        | 2.46                   | 2.46   | 2.47                   | 2.71   | 2.94                   |        |                        |  |                             |
| 2.16        | 2.40                   | 2.41   | 2.41                   | 2.64   | 2.77                   |        |                        |  |                             |
| 2.09        | 2.36                   | 2.35   | 2.38                   | 2.58   | 2.70                   |        |                        |  |                             |
| 1.968       | 2.29                   |        |                        | 2.52   | 2.59                   |        |                        |  |                             |
| 1.897       | 2.18                   | 2.18   | 2.18                   | 2.46   | 2.49                   |        |                        |  |                             |
| 1.803       | 2.09                   | 2.09   | 2.09                   | 2.41   | 2.45                   |        |                        |  |                             |
| 1.781       | 2.00                   | 2.01   | 2.02                   | 2.35   | 2.37                   |        |                        |  |                             |
| 1.765       | 1.974                  |        |                        | 2.31   | 2.31                   |        |                        |  |                             |
| 1.737       | 1.944                  | 1.937  | 1.949                  | 2.26   | 2.26                   |        |                        |  |                             |
| 1.682       | 1.878                  | 1.878  | 1.895                  | 2.16   | 2.19                   |        |                        |  |                             |
| 1.652       | 1.851                  |        | 1.849                  | 2.17   | 2.15                   |        |                        |  |                             |
| 1.602       | 1.785                  |        |                        | 2.10   | 2.11                   |        |                        |  |                             |
| 1.570       | 1.745                  | 1.743  |                        | 2.08   | 2.07                   |        |                        |  |                             |
| 1.490       |                        | 1.696  | 1.704                  | 2.04   | 2.03                   |        |                        |  |                             |
| 1.469       |                        |        |                        | 1.974  | 1.992                  |        |                        |  |                             |
| 1.384       |                        |        |                        | 1.916  | 1.912                  |        |                        |  |                             |
| 1.367       |                        |        |                        |        | 1.875                  |        |                        |  |                             |

<sup>a</sup> M = Al, Fe, Cr; data from  $AlOHC_4O_4 \cdot 3H_2O$ .

parameters gave  $a = 15.56$  Å,  $b = 11.77$  Å, and  $c = 8.09$  Å.<sup>5</sup> The density of 2.31 calculated from the X-ray data is in good agreement with the experimental value of 2.30.

A complete three-dimensional X-ray diffraction study has shown that copper(II) croconate has an infinite chain polymeric structure (Fig. 1).<sup>5</sup> The copper ions are surrounded by six oxygen atoms at the corners of a distorted octahedron. Each croconate ion is chelated through oxygen to one copper ion and singly-coordinated to another, leaving two of its five oxygen atoms uncoordinated. The similarity of the powder diffraction patterns (Table I) indicates that the croconates of divalent Fe, Zn, Ni, Mn, and Co must have the same polymeric structure, although the degree of tetragonal distortion around the metal ion may vary among these compounds.

The infrared spectra of the metal complexes show a band at  $1725$   $cm^{-1}$ , probably due to the noncoordinated C=O groups which could have considerable double bond character. A broad, very strong band from  $1300$  to  $1700$   $cm^{-1}$  may be assigned to vibrational modes representing a mixture of C=O and C-C stretching motions. Weak bands are found near  $1230$ ,  $1100$ ,  $900$ , and  $800$   $cm^{-1}$ ; their position and intensity remain nearly constant among all of the divalent transition metal croconates. The magnetic data show that all of these compounds are high-spin complexes (Table II).

The preparations of cobalt(II) croconate trihydrate led at first to a mixture of solid products. The mixtures were treated with hot water to dissolve the trihydrate complexes, which separated in pure form from the

(5) L. F. Dahl, M. Glick, and G. Downs, unpublished studies. We are greatly indebted to these authors for permission to report their findings in advance of publication.

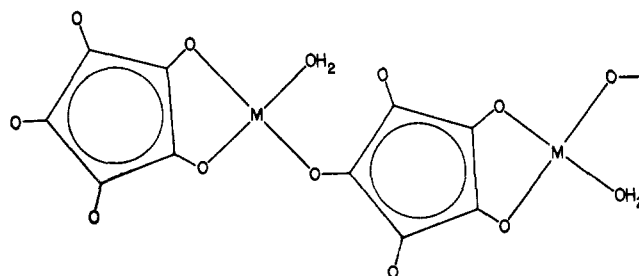


Fig. 1.—The structure of the divalent transition metal croconates. Coordinated water molecules above and below the metal atoms have been omitted.

aqueous solution. The other components of the solid mixtures were left as insoluble residues which could be purified only by washing with water. These insoluble solids, which had metal:croconate ratios of about 2:1, may possibly be coordination polymers cross linked through oxygen atoms.

TABLE II  
MAGNETIC MOMENTS OF CROCONATE COMPLEXES

| Croconate | Temp., °K. | $\mu$ , Bohr magnetons | $e^a$ |
|-----------|------------|------------------------|-------|
| Cu(II)    | 295        | 1.98                   | 1     |
| Ni(II)    | 298        | 3.26                   | 2     |
| Co(II)    | 298        | 5.11                   | 3     |
| Fe(II)    | 296        | 5.41                   | 4     |
| Mn(II)    | 296        | 5.84                   | 5     |
| Cr(III)   | 298        | 3.11                   | 3     |
| Fe(III)   | 298        | 4.89                   | 5     |

<sup>a</sup> No. of unpaired electrons for maximum multiplicity.

**Trivalent Metal Croconates.**—These substances were also prepared by the addition of croconate ion to aqueous solutions of Al(III), Fe(III), and Cr(III) compounds. However, the complexes of trivalent metals have a much more complicated constitution, including hydroxyl groups as well as water molecules and croconate ions. The three substances have identical X-ray powder patterns (Table I) and so must have the same over-all structure.

The aluminum complex gave analyses indicating an Al:croconate ratio of about 6:5. The chromium compound has approximately the same metal:croconate ratio, but there is apparently less water of crystallization in the chromium than in the aluminum compound. All of these substances showed some variability in composition in different preparations, and this variability was particularly marked in the iron(III) complex. However, all of the samples of the iron(III) compound gave a much lower metal:croconate ratio, averaging about 10:11.<sup>6</sup> A preliminary single crystal X-ray study of the Cr(III) complex by L. F. Dahl and M. A. Neuman provides evidence for the nature of the repeating unit in the structures of these compounds. The weight of the unit cell calculated from the experimentally observed density of  $1.89$  g./ml. is  $2548 \pm 100$ , and there are 2 repeating units (or molecules) per unit cell. The unit cell weight is consistent with the empirical formula  $Cr_6(C_6O_8)_4(OH)_7(H_2O)_{16}$  (formula wt. 1227), which agrees roughly with the analytical data.

The magnetic moments of 3.11 and 4.89 Bohr magnetons determined for the Cr(III) and Fe(III) complexes, respectively, are slightly low for high-spin complexes of these metals. A possible explanation is that antiferromagnetic spin-pairing may take place between the metal atoms, reducing the paramagnetism. This effect has been shown to lower paramagnetism in

(6) The compounds cannot readily be purified, and it is possible that a persistent contaminant is present in the iron compound.

other hydroxoiron(III) complexes such as carboxylic acid derivatives and in related complexes of Cr(III).<sup>7</sup> However, the temperature dependence of the paramagnetism has not yet been measured to check on this possibility, and alternative explanations for the low magnetic moments must be considered.<sup>8</sup>

The infrared spectra of the three compounds are quite similar and indicate the probable presence of both coordinated and noncoordinated carbonyl groups. Bands are found at 3250(s, OH stretch), 1800 (C=O), 1615(s), 1550–1400(vs), 1150(w), 1105(m), 1090(m), 1040(s), and 900(s) cm.<sup>-1</sup>. The evidence suggests that the trivalent croconate complexes are coordination polymers, perhaps linked both through croconate ions and hydroxyl groups, having similar crystal structures but slightly variable composition. Detailed knowledge of the structure will require complete X-ray crystallographic studies.

### Experimental

**Copper(II) Croconate Trihydrate.**—One gram (0.0046 mole) of dipotassium croconate dissolved in 10 ml. of water was added to a solution of 0.85 g. (0.005 mole) of copper(II) chloride dihydrate in 10 ml. of water. The resulting solution was filtered and evaporated on a steam-bath to a volume of about 5 ml. Brown crystals formed during the evaporation. The solution was cooled and the crystals were removed by filtration, washed successively with cold water, acetone, and ether, and finally dried under vacuum at room temperature for 48 hr.

*Anal.* Calcd. for  $\text{CuC}_5\text{O}_5 \cdot 3\text{H}_2\text{O}$ : Cu, 24.7; C, 23.31; H, 2.35. Found: Cu, 25.2; C, 23.50; H, 2.41.

The density of copper(II) croconate trihydrate was determined by flotation. A mixture of methylene iodide and carbon tetrachloride, adjusted so that crystals of copper(II) croconate trihydrate would just float, was found to have a density of 2.30 using a pycnometer.

**Calcium, Manganese(II), Iron(II), and Zinc(II) Croconate Trihydrates.**—All of these compounds were prepared in the same manner as copper(II) croconate trihydrate. Chlorides were used as starting materials except for iron(II), in which case the sulfate was employed. Manganese(II) croconate trihydrate formed as dark green crystals, the calcium and zinc complexes were yellow, and the iron(II) complex was dark purple. The products were obtained in essentially quantitative yield except for iron(II) croconate, which was obtained in about 75% yield. Two attempts were made to prepare the magnesium complex, but in neither case was a pure product obtained.

*Anal.* Calcd. for  $\text{CaC}_5\text{O}_5 \cdot 3\text{H}_2\text{O}$ : C, 25.56; H, 2.58. Found: C, 25.05; H, 2.46. Calcd. for  $\text{FeC}_5\text{O}_5 \cdot 3\text{H}_2\text{O}$ : C, 24.03; H, 2.42. Found: C, 24.22; H, 2.51. Calcd. for  $\text{MnC}_5\text{O}_5 \cdot 3\text{H}_2\text{O}$ : C, 24.13; H, 2.43. Found: C, 24.29; H, 2.53. Calcd. for  $\text{ZnC}_5\text{O}_5 \cdot 3\text{H}_2\text{O}$ : C, 23.14; H, 2.33. Found: C, 23.24; H, 2.24.

**Cobalt Croconate Trihydrate.**—Two grams (0.009 mole) of dipotassium croconate in 10 ml. of water was added to a solution of 2.38 g. (0.01 mole) of cobalt chloride hexahydrate in 10 ml. of water. As water was evaporated away, some pink powder and purple crystals appeared. The two solids were then separated by boiling with hot water which dissolved the purple crystals, leaving a small amount of pink powder as a residue. The pink powder was filtered off, washed several times with hot water, acetone, ether, and finally dried at 100°. Analysis gave 31.19% of cobalt, 12.97% of carbon, and 2.52% of hydrogen. The filtrate was evaporated to small volume, and purple crystals of cobalt(II) croconate reappeared. These were recrystallized from water and dried at room temperature and 0.05 mm. pressure for 48 hr. The yield was 90%.

*Anal.* Calcd. for  $\text{CoC}_5\text{O}_5 \cdot 3\text{H}_2\text{O}$ : C, 23.73; H, 2.39. Found: C, 23.72; H, 2.42.

**Nickel(II) Croconate Trihydrate.**—The reaction of dipotassium croconate with nickel chloride solution gave results similar to

those obtained with cobalt(II) chloride. With nickel(II) chloride, a mixture of green solids precipitated. On boiling with water, most of the solid material slowly dissolved. The insoluble portion was then filtered off, washed with hot water, acetone, and ether, and dried at 100°. Analysis of the solid gave 28.31% of nickel, 14.20% of carbon, and 2.45% of hydrogen.

The filtrate was evaporated to small volume and nickel(II) croconate reappeared as a green powder. This was recrystallized from water and dried under vacuum at room temperature and 0.05 mm. pressure for 48 hr. The yield was about 90%.

*Anal.* Calcd. for  $\text{NiC}_5\text{O}_5 \cdot 3\text{H}_2\text{O}$ : C, 23.75; H, 2.39. Found: C, 23.81; H, 2.46.

**Aluminum(III) Croconate.**—Dipotassium croconate (0.65 g., 0.0032 mole) in 10 ml. of water was added to a solution of 1.00 g. (0.0032 mole) of aluminum nitrate hexahydrate in 10 ml. of water. The resulting solution was filtered through sintered glass and evaporated to a volume of 5 ml. and then cooled. The yellow crystals of aluminum croconate which precipitated were removed by filtration, washed with water, acetone, and ether, and dried *in vacuo*. The yield was about 70%.

*Anal.* Calcd. for  $\text{Al}_3(\text{C}_5\text{O}_5)_3(\text{OH})_3 \cdot 22\text{H}_2\text{O}$ : Al, 11.69; C, 21.69; H, 3.78; for  $\text{Al}_3(\text{C}_5\text{O}_5)_3(\text{OH})_3 \cdot 18\text{H}_2\text{O}$ : Al, 11.85; C, 21.10; H, 3.81. Found: Al, 11.60, 11.73; C, 21.10, 21.60; H, 4.08; 4.00.

**Chromium(III) and Iron(III) Croconates.**—These two compounds were prepared in the same way as aluminum croconate, from the corresponding nitrates and dipotassium croconate. Crystalline products were obtained in about 80% yield. Chromium(III) croconate is brown and iron(III) croconate is purple.

*Anal.* Calcd. for  $\text{Cr}_3(\text{C}_5\text{O}_5)_3(\text{OH})_3 \cdot 16\text{H}_2\text{O}$ : Cr, 21.18; C, 19.56; H, 3.20. Found: Cr, 21.10; C, 20.22, 20.47; H, 3.67, 3.17. Found for Fe(III) croconate: Fe, 21.48; C, 23.90, 24.46, 25.25, 26.27; H, 2.51, 2.24, 3.02, 2.85.

**Powder X-Ray Diffraction Patterns.**—Cobalt K $\alpha$  radiation was used for all of the compounds. Ilford industrial type X-ray film was used in a camera with a 5.73 cm.<sup>-1</sup> radius. In studying the chromium complex, a piece of aluminum foil the same size as the film was placed in front of the film to eliminate fluorescence, and the exposure time was increased to 18 hr. from the normal 12 hr.

**Magnetic Properties.**—Magnetic susceptibilities were determined by the Gouy method using a Mettler type B balance mounted over a Varian Associates V-4004 4-in. electromagnet. Measurements were made at three different magnet currents. All calculations were referred to mercury(II) tetrathiocyanatocobaltate as a standard.<sup>9</sup> Diamagnetic corrections were made for transition metal ions, water, and hydroxyl groups using published tables.<sup>10</sup> The diamagnetic correction for croconate ion was established by measuring the magnetic susceptibility of dipotassium croconate, and subtracting the diamagnetic contribution of two potassium ions. Croconate ion was found to have a diamagnetic susceptibility of  $35.1 \times 10^{-6}$  g.-atom n at 25°.

Paramagnetic susceptibilities of the divalent transition metals were calculated in the usual way using the ideal formulas for the croconate trihydrates. For iron(III) and chromium(III) croconates this was not possible because the formulas were not established. Accordingly, the paramagnetic susceptibilities of these metals are based on the metal content as determined by analysis.

**Infrared Spectra.**—Infrared spectra were taken as mulls in Stanolind white petroleum oil and also for most compounds as pressed disks in KBr. A Baird model S spectrophotometer was employed.

**Acknowledgments.**—The authors are grateful for support from the Air Force Office of Scientific Research of the Air Research and Development Command.<sup>11</sup> They also thank Dr. Mitsuo Ito for assistance in obtaining the infrared spectra and Dr. Lawrence Dahl for helpful discussions.

(9) J. Lewis and R. G. Wilkins, "Modern Coordination Chemistry," Interscience Publishers, Inc., New York, N. Y., 1960, p. 403;  $\text{HgCo}(\text{CNS})_4$  has a magnetic susceptibility of 16.44 g.-atom at 20° (B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958)). Correction was made to the temperature of the apparatus.

(10) P. W. Selwood, "Magnetochemistry," 2nd Edition, Interscience Publishers, Inc., New York, N. Y., 1956, p. 78; ref. 8, p. 403.

(11) Under Contract No. AF49(638)-285. Reproduction in whole or part is permitted for any purpose of the United States Government.

(7) B. Tsai and J. Wucher, *J. phys. radium*, **13**, 485 (1952); A. Abragam, J. Horowitz, and J. Yvon, *ibid.*, **13**, 489 (1952); A. Earnshaw and J. Lewis, *Nature*, **181**, 1262 (1958); K. Kambe, *J. Phys. Soc. Japan*, **5**, 48 (1950).

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