

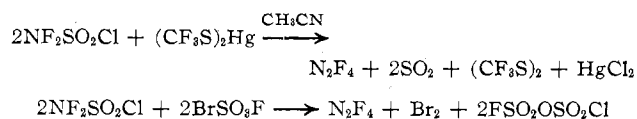
having boiling points in the range  $45.5 \pm 0.5^\circ$ . The temperature-pressure dependence for I may be expressed by the equation  $\log P_{\text{mm}} = 8.17 - 1683/T^\circ\text{K}$ . Vapor pressure data are as follows ( $T$ ,  $^\circ\text{K}$ ;  $P$ , mm): 257.5, 43.0; 273.0, 101.7; 280.5, 148.0; 287.0, 204.2; 292.3, 255.5; 296.5, 311.7; 300.5, 375.1; 303.5, 423.7; 309.2, 533.7; 311.8, 596.7; 314.8, 656.3; 320.3, 802.8. The molar heat of vaporization is 7.70 kcal and the Trouton constant is 24.2. The experimental molecular weight is 107.7 (calcd 106.5). I shows a single broad peak in the  $^{19}\text{F}$  nmr at  $\phi - 63.4$ . The infrared spectrum (22 mm pressure) is as follows: 2253 (m), 1560 (m, doublet), 1170 (s, doublet), 1138 (s, doublet), 990-962 (vs, complex), 680 (m, doublet), 541 (w, triplet), 500 (w, doublet), 408  $\text{cm}^{-1}$  (w). Peaks were attributed to the following species in the mass spectrum:  $\text{CN}^+$ ,  $\text{N}_2^+$ ,  $\text{CF}^+$ ,  $\text{Cl}^+$  (30%),  $\text{CCN}^+$ ,  $\text{CCl}^+$ ,  $(\text{CN})_2^+$ ,  $\text{N}=\text{CCl}^+$ ,  $\text{FN}=\text{CCN}^+$  (100%),  $\text{CICCN}^+$ ,  $\text{FNCCl}^+$ ,  $\text{CF}_2\text{Cl}^+$ ,  $\text{N}=\text{CClCN}^+$ ,  $\text{FN}=\text{CClCN}^+$  (93%). The parent,  $\text{FN}=\text{CCN}^+$ , and  $\text{Cl}^+$  were the three major peaks in the spectrum. All chlorine-containing fragments gave the correct isotopic peak ratios. Analysis of chlorine as  $\text{AgCl}$  and fluorine by specific ion electrode were run. *Anal.* Calcd for I: Cl, 33.3; F, 17.8. Found: Cl, 32.3; F, 18.4.

The temperature-pressure dependence for II can be expressed by the equation  $\log P_{\text{mm}} = 7.96 - 1621/T^\circ\text{K}$ . Vapor pressure data are as follows: ( $T$ ,  $^\circ\text{K}$ ;  $P$ , mm): 254.2, 38.3; 272.5, 100.2; 280.0, 149.7; 285, 184.4; 291, 253.7; 296.5, 312.0; 299.3, 352.0; 302.0, 397.0; 308.5, 511.5; 313.8, 625.5; 319.7, 779. The molar heat of vaporization is 7.42 kcal and the Trouton constant is 23.3. The experimental molecular weight is 105.0 (calcd 106.5). II shows a single broad peak in the  $^{19}\text{F}$  nmr at  $\phi - 69.0$ . The infrared spectrum (20 mm pressure) is as follows: 2249 (m), 1560 (w), 1200 (w), 1135 (s, doublet), 942 (s, triplet), 850 (w), 750  $\text{cm}^{-1}$  (w). The peaks in the mass spectrum were assigned to the following species:  $\text{CN}^+$ ,  $\text{N}_2^+$ ,  $\text{CF}^+$ ,  $\text{Cl}^+$  (16%),  $\text{CCN}^+$ ,  $\text{CCl}^+$ ,  $(\text{CN})_2^+$ ,  $\text{N}=\text{CCl}^+$ ,  $\text{FN}=\text{CCN}^+$  (100%),  $\text{CICCN}^+$ ,  $\text{FNCCl}^+$ ,  $\text{N}=\text{CClCN}^+$ ,  $\text{FN}=\text{CClCN}^+$  (47%). All isotopic fragments containing chlorine were found in the correct ratio. *Anal.* Calcd for II: Cl, 33.3; F, 17.8. Found: Cl, 33.2; F, 17.0.

$\text{N}_2\text{F}_4$  + Perhalogenated Acetones.— $\text{N}_2\text{F}_4$  (10 mmol) and  $(\text{CF}_2\text{Cl})_2\text{CO}$  (excess) were photolyzed in the 2-l. vessel with a 450-W lamp using a Corex filter for 31 hr. The yield of  $\text{NF}_2\text{CFCl}_2$  after purification was 30%.  $\text{N}_2\text{F}_4$  (10 mmol) and  $\text{CF}_3\text{C}(\text{O})\text{CF}_2\text{Cl}$  (1.83 g, 10.0 mmol) were irradiated in the 2-l. vessel through Vycor for 1 hr. The yield of pure  $\text{NF}_2\text{CF}_2$  was 86 and 71% for  $\text{NF}_2\text{CF}_2\text{Cl}$ .<sup>6</sup>

## Results and Discussion

Tetrafluorohydrazine was found to react with sulfonyl chloride when irradiated in the gas phase with ultraviolet light of 2537 Å giving difluoramidosulfonyl chloride and chlorine as the main products. The chloride, however, lacks the thermal stability of the fluoride in that it slowly decomposes to  $\text{N}_2\text{F}_4$ ,  $\text{SO}_2$ , and  $\text{Cl}_2$  at ambient temperature. As expected,  $\text{NF}_2\text{SO}_2\text{Cl}$  reacts rapidly with mercury giving  $\text{N}_2\text{F}_4$  and  $\text{SO}_2$  as the volatile products. With bis(trifluoromethylthio)mercury,  $\text{N}_2\text{F}_4$  and  $\text{SO}_2$  are also obtained along with bis(trifluoromethyl) disulfide, while reaction with bromine fluorosulfate yields  $\text{N}_2\text{F}_4$ ,  $\text{Br}_2$ , and the mixed pyrosulfonyl derivative



It is interesting to compare the products of the latter

(5) R. K. Pearson and R. D. Dresner, *J. Amer. Chem. Soc.*, **84**, 4743 (1962).

(6) J. B. Hynes, B. C., Bishop and L. A. Bigelow, *Inorg. Chem.*, **6**, 417 (1967).

reaction with those between  $\text{CF}_3\text{SO}_2\text{Cl}$  and  $\text{BrOSO}_2\text{F}$ ,<sup>8</sup> where the Cl-S bond is severed and a sulfur-oxygen bond results ( $\text{CF}_3\text{SO}_2\text{OSO}_2\text{F} + \text{BrCl}$ ) while the  $\text{CF}_3$ -S bond remains essentially intact. With  $\text{NF}_2\text{SO}_2\text{Cl}$ , the nitrogen-sulfur bond is fissioned by the positive bromine because of the greater electronegativity of the  $\text{NF}_2$  group.  $\text{NF}_2\text{Br}$ , the  $\text{BrCl}$  analog, is unstable and decomposes to  $\text{Br}_2 + \text{N}_2\text{F}_4$ .

Dichlorocyanodifluoraminomethane was found to react slowly with mercury at room temperature to form roughly equal amounts of the fluorimino derivatives I and II. The assignment of configuration has been made on the basis of comparison of  $^{19}\text{F}$  data with similar known compounds.<sup>9</sup> The chemical shift of the  $=\text{N}-\text{F}$  fluorine was found to move successively downfield when chlorine or cyanide was substituted for the carbon fluorine, which is a result of the increasing paramagnetic contribution of these groups. A comparison of syn and anti isomers indicates that the greatest interaction is between anti groups. Thus, when fluorine is anti to fluorine, the shift is upfield relative to the syn configuration. The stronger interaction of anti groups is also exemplified by larger spin-spin coupling constants than those of the syn isomers. Based on the stronger anti interactions and the greater cyanide deshielding effect than the chlorine deshielding effect, the  $\text{NF}$  fluorine resonance in the isomer with the  $\text{CN}$  group anti to the fluorine was assigned to the resonance peak at  $\phi - 69.0$ .

**Acknowledgments.**—Fluorine research at the University of Idaho is sponsored by the National Science Foundation and the Office of Naval Research. The HA-100 nmr spectrometer was funded in part by grants from the National Science Foundation and the Max C. Fleischmann Foundation. We thank Mr. Ron DeMarco and Mr. J. A. Johnson for mass spectra. Special thanks are due Dr. Kent Pullen, Boeing Co., for suggesting the  $\text{N}_2\text{F}_4-\text{SO}_2\text{Cl}_2$  reaction.

(7) R. E. Noftle, *ibid.*, **7**, 2167 (1968).

(8) D. D. DesMarteau, *ibid.*, **7**, 434 (1968).

(9) W. S. Brey, Jr., and J. B. Hynes, *Fluorine Chem. Rev.*, **2**, 111 (1968).

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## The Photochemical Preparation of Metal-Metal Bonds. II.<sup>1</sup> Some Tin-Manganese and Germanium-Manganese Systems

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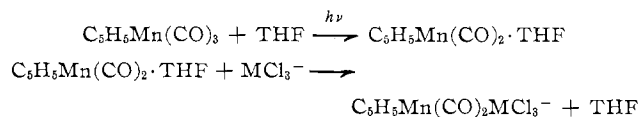
A large number of manganese carbonyl derivatives in which manganese is bonded to a group IV metal of the general type  $\text{R}_3\text{MMn}(\text{CO})_5$  have been prepared and

(1) Part I: J. K. Ruff, *Inorg. Chem.*, **6**, 1502 (1967).

(2) Alfred P. Sloan Foundation Fellow, 1969-1971.

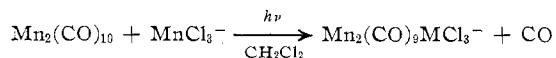
studied in recent years.<sup>3-8</sup> In general the preparation has involved either the nucleophilic displacement of a halide ion from  $R_3MX$  by the  $Mn(CO)_5^-$  ion or the reaction of  $R_3SiH$  with  $Mn_2(CO)_{10}$ . With the exception of the hydride  $\pi-C_5H_5Mn(CO)_2(H)SiCl_3$ , recently reported by Graham,<sup>9</sup> no other group IV metal derivatives containing a  $\pi$ -cyclopentadienylmanganese dicarbonyl moiety are known. This is perhaps due to the lack of simple anion formation by  $\pi$ -cyclopentadienylmanganese tricarbonyl. However, Lewis bases react readily with  $\pi$ -cyclopentadienylmanganese tricarbonyl, especially when the mixture is irradiated.<sup>10-13</sup> In general only monosubstitution occurs, except when certain ligands such as  $(C_6H_5)_3P$  were employed.<sup>14,15</sup> Since the anions  $SnCl_3^-$  and  $GeCl_3^-$  behave as Lewis bases toward the group VI metal carbonyls,<sup>1</sup> their interaction with  $\pi-C_5H_5Mn(CO)_3$  and  $\pi-CH_3C_5H_4Mn(CO)_3$  was investigated. Furthermore this reaction was extended to include  $Mn_2(CO)_{10}$  since it is known to undergo both mono- and disubstitution<sup>16,17</sup> when treated with Lewis bases.

Reaction of the  $SnCl_3^-$  and  $GeCl_3^-$  anions with both the  $\pi$ -cyclopentadienyl derivatives was accomplished photochemically in tetrahydrofuran solution (THF). Since the ligands are not stable in this solvent,<sup>1</sup> the unstable complex  $\pi-C_5H_5Mn(CO)_2 \cdot THF$ <sup>18</sup> was initially generated in the absence of the ligands. After completion of photolysis the ligands were allowed to displace the THF ( $M = Sn$  or  $Ge$ )



Only monosubstituted products were formed and they were isolated as the air-stable, yellow-orange tetraphenylarsonium salts.

Contrary to the results obtained in the above photolysis, mixtures of  $Mn_2(CO)_{10}$  and either the  $SnCl_3^-$  or  $GeCl_3^-$  ions in methylene chloride produced monosubstituted derivatives upon irradiation<sup>19</sup>



No evidence was found for the formation of a disubstituted product even in the presence of excess anion.

- (3) R. D. Gorsich, *J. Amer. Chem. Soc.*, **84**, 2486 (1962).  
 (4) J. A. J. Thompson and W. A. G. Graham, *Inorg. Chem.*, **6**, 1365 (1967).  
 (5) W. Jetz, P. B. Simons, J. A. J. Thompson, and W. A. G. Graham, *ibid.*, **5**, 2217 (1966).  
 (6) J. A. J. Thompson and W. A. G. Graham, *ibid.*, **6**, 1875 (1967).  
 (7) H. C. Clark and J. H. Tsai, *ibid.*, **5**, 1407 (1966).  
 (8) H. C. Clark, J. D. Cotton, and J. H. Tsai, *ibid.*, **5**, 1528 (1966).  
 (9) W. Jetz and W. A. G. Graham, *J. Amer. Chem. Soc.*, **91**, 3375 (1969).  
 (10) W. Strohmeier and J. F. Guttenberger, *Ber.*, **97**, 1256 (1964).  
 (11) W. Strohmeier and J. F. Guttenberger, *ibid.*, **97**, 1871 (1964).  
 (12) R. S. Nyholm, S. S. Sandhur, and M. H. B. Stiddard, *J. Chem. Soc.*, 5916 (1963).  
 (13) W. Strohmeier and K. Gerlach, *Z. Naturforsch. B*, **19**, 353 (1964).  
 (14) W. Strohmeier, C. Barbeau, and D. von Hobe, *Ber.*, **96**, 3254 (1963).  
 (15) C. Barbeau, *Can. J. Chem.*, **45**, 161 (1967).  
 (16) A. G. Osborne and M. H. B. Stiddard, *J. Chem. Soc.*, 634 (1964).  
 (17) H. Wawersik and F. Basolo, *Chem. Commun.*, 366 (1966).  
 (18) E. O. Fischer and M. Herberhold, *Experientia, Suppl.*, **9**, 259 (1964).  
 (19) Photolysis of  $\pi-C_5H_5Mn(CO)_3$  in  $CH_2Cl_2$  resulted in rapid decomposition of the manganese compound and no complexes could be isolated even when the Lewis base was present.

This is in contrast to the photochemical reaction of  $Mn_2(CO)_{10}$  with excess triphenylphosphine<sup>15</sup> and is perhaps due to repulsion of like-charged ions. However the thermal reaction produced the monoaxial-substituted compound  $Mn_2(CO)_9(C_6H_5)_3P$ .<sup>17</sup> As in the case of the  $\pi$ -cyclopentadienyl derivatives the anions were isolated as air-stable, yellow-orange tetraphenylarsonium salts.

The yield of complexes in both types of reactions was quite low and attempts to optimize it by varying the ratio of reactants or solvent were not successful. The complexes obtained were characterized by analysis, infrared, and conductivity studies. In every case only 1:1 electrolytes were formed indicating that disubstitution by  $MCl_3^-$  ligands did not occur. Thus an average value of the equivalent conductance of approximately 70  $cm^2/(ohm\ equiv)$  was obtained, which is within the expected range.<sup>20</sup>

The infrared spectra of the  $\pi$ -cyclopentadienyl derivatives are completely compatible with monosubstitution. The decrease in the  $\nu_{CO}$  frequencies over those in the starting material has been observed for a large number of monosubstituted compounds,  $\pi-C_5H_5Mn(CO)_2L$ . In fact for compounds in which L is an oxygen, nitrogen, sulfur ligand or  $(C_6H_5)_3E$  (where  $E = P, As, or Sb$ ) the observed  $\nu_{CO}$  frequencies lie in a relatively narrow range (1930–1938 and 1850–1866  $cm^{-1}$ ) indicating a lack of sensitivity of these frequencies to the nature of the ligand.<sup>21</sup> The observed  $\nu_{CO}$  frequencies of the complexes prepared in this study are close to the above ranges except that the high-frequency band falls below 1930  $cm^{-1}$ . This may in part be attributable to the presence of a negative charge on the complex. The slight differences found in the  $\nu_{CO}$  frequencies for the tin and germanium derivatives does not allow a distinction between the  $\pi$ -acceptor ability of the ligands. This was also found to be true for complexes formed with the group VI carbonyls.<sup>1</sup>

The infrared spectra of the  $Mn_2(CO)_9MCl_3^-$  anions are more interesting. They confirm monosubstitution and furthermore suggest that substitution occurs in an axial position since all five of the predicted bands ( $3A' + 2E$ ) are observed. Also the spectra of these anions are in good agreement with that of the known monoaxial-substituted  $Mn_2(CO)_9P(C_6H_5)_3$  (e.g.,  $\nu_{CO}$  2098 (s), 2015 (s), 1997 (s), 1969 (w), 1937  $cm^{-1}$ ),<sup>17</sup> except that some of the  $\nu_{CO}$  frequencies of the anions are shifted to slightly higher frequencies. This is unexpected in view of the negative charge on these complexes and suggests that the  $SnCl_3^-$  and  $GeCl_3^-$  ions are much better  $\pi$  acceptors than  $(C_6H_5)_3P$ . No such difference was noted with the group VI metal carbonyl complexes.<sup>1</sup>

#### Experimental Section

**Materials.**—The tetraphenylarsonium salts of the  $SnCl_3^-$  and  $GeCl_3^-$  anions were prepared by the literature method.<sup>22</sup> The

- (20) R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).  
 (21) W. Strohmeier, J. F. Guttenberger, and H. Hellmann, *Z. Naturforsch. B*, **19**, 353 (1964).  
 (22) M. P. Johnson, D. F. Shriver, and S. A. Shriver, *J. Amer. Chem. Soc.*, **88**, 1588 (1966).

TABLE I  
 PREPARATIVE DATA ON THE NEW COMPOUNDS

Anion	Mp, °C	Yield, %	Calcd				Analyses, %			
			C	H	Mn	Cl	C	H	Mn	Cl
$C_5H_5Mn(CO)_2SnCl_3^-$	163-164	30	47.4	3.2	7.0	13.6	47.2	3.3	6.5	13.7
$C_5H_5Mn(CO)_2GeCl_3^-$	141-142	18	50.4	3.4	7.5	14.4	50.6	3.2	7.9	14.0
$CH_3C_5H_4Mn(CO)_2SnCl_3^-$	149-150	27	48.1	3.4	6.9	13.3	48.3	3.5	6.2	13.0
$CH_3C_5H_4Mn(CO)_2GeCl_3^-$	133-135	25	51.1	3.6	7.3	14.2	50.8	3.8	7.6	14.6
$Mn_2(CO)_9SnCl_3^-$	117-119	27	40.8	2.1	11.3	11.0	40.5	2.4	10.8	11.5
$Mn_2(CO)_9GeCl_3^-$	107-109	22	42.9	2.2	11.9	11.5	43.3	1.9	12.3	11.8

samples of  $C_5H_5Mn(CO)_3$  and  $CH_3C_5H_4Mn(CO)_3$  were generously donated by Ethyl Corp. Dimanganese decacarbonyl was obtained from Strem Chemical Co.

**Preparation of  $(C_5H_5)_4AsC_5H_5Mn(CO)_2MCl_3$ .**—Since both the tin and germanium derivatives were prepared in the same manner, only one preparation will be described. A 0.70-g sample of  $\pi-C_5H_5Mn(CO)_3$  dissolved in 100 ml of THF was irradiated under an inert atmosphere for 2 hr with a GE AH4 floodlamp. To the red solution a 0.6-g sample of  $(C_5H_5)_4AsSnCl_3$  was added. The mixture was stirred for 15 min and the solvent was removed under vacuum. The residue was extracted with a mixture containing 20 ml of  $CH_2Cl_2$  and 100 ml of diethyl ether. The extract was filtered and pentane was slowly added to the filtrate. An orange-yellow solid, 0.21 g, was obtained.

This same procedure was used to prepare the corresponding methyl- $\pi$ -cyclopentadienyl derivatives. See Table I for details.

**Preparation of  $(C_5H_5)_4AsMn_2(CO)_9MCl_3$ .**—Since the preparations of both the tin and the germanium compounds were identical, only one will be described. A mixture containing 0.63 g of  $(C_5H_5)_4AsSnCl_3$  and 0.69 g of  $Mn_2(CO)_{10}$  in 50 ml of  $CH_2Cl_2$  was irradiated under an inert atmosphere with the same lamp described above. After approximately 0.5 hr some solid had formed in the reactor. This was removed by filtration and the irradiation continued for 1 hr more. The solvent was removed under vacuum and the residue was dissolved in 10 ml of  $CH_2Cl_2$ . Diethyl ether, 60 ml, was added and the mixture was filtered. Pentane was added slowly to the filtrate (too rapid addition results in oiling) and a 0.28-g sample of product was obtained. See Table I for details.

**Infrared Spectra.**—The infrared spectra were taken on  $CH_2Cl_2$  solutions (concentrations about 10 mg/ml) using a Perkin-Elmer Model 621 spectrometer which had been calibrated with indene. See Table II.

 TABLE II  
 INFRARED STRETCHING FREQUENCIES FOR THE NEW COMPOUNDS

Anion	Freq, $cm^{-1}$
$C_5H_5Mn(CO)_2SnCl_3^-$	1926 s, 1863 s
$C_5H_5Mn(CO)_2GeCl_3^-$	1924 s, 1858 s
$CH_3C_5H_4Mn(CO)_2SnCl_3^-$	1924 s, 1859 s
$CH_3C_5H_4Mn(CO)_2GeCl_3^-$	1922 s, 1855 s
$Mn_2(CO)_9SnCl_3^-$	2102 m, 2062 m, 2016 s, 1974 sh, 1934 m
$Mn_2(CO)_9GeCl_3^-$	2091 mw, 1062 m, 2015 s, 1982 sh, 1932 m

**Conductivity Measurements.**—The conductivities of the salts were determined in nitromethane solutions using a Yellow Springs Instrument Co. Ind. Model 31 conductivity bridge. The cell constant of the cell employed was 0.1792 and the specific conductivity of the nitromethane was  $5.70 \times 10^{-7} \text{ ohm}^{-1} \text{ cm}^{-1}$ . The anion, concentration ( $M$ ), and equivalent conductance ( $cm^2/\text{ohm equiv}$ ) for the material prepared are as follows:  $C_5H_5Mn(CO)_2SnCl_3^-$ ,  $1.052 \times 10^{-3}$ , 70.2;  $C_5H_5Mn(CO)_2GeCl_3^-$ ,  $1.117 \times 10^{-3}$ , 73.1;  $CH_3C_5H_4Mn(CO)_2SnCl_3^-$ ,  $0.989 \times 10^{-3}$ , 65.8;  $CH_3C_5H_4Mn(CO)_2GeCl_3^-$ ,  $1.20 \times 10^{-3}$ , 75.7;  $Mn_2(CO)_9SnCl_3^-$ ,  $1.002 \times 10^{-3}$ , 67.1;  $Mn_2(CO)_9GeCl_3^-$ ,  $1.071 \times 10^{-3}$ , 71.0.

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## Magnetochemical Investigation of Stereochemical Change for the Cobalt(II) Ion in Solution

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In the crystalline state or in solution, the cobalt(II) ion is found most frequently in one of two ligand environments: four-coordinate tetrahedral or six-coordinate octahedral. In the former, the ion possesses an orbitally nondegenerate electronic ground state,  $^4A_2$ , while in the latter (weak-field limit), it possesses a threefold degenerate ground state,  $^4T_{1g}$ . The magnetic moment would therefore be expected to contain a larger orbital contribution for the ion in the octahedral field than in the tetrahedral field. A considerable amount of work has verified this correlation of the magnetic moment with the geometrical structure for crystalline cobalt(II) compounds.<sup>3-6</sup> However, with the exception of some early work, prior to the development of the ligand field theory and a few recent measurements in single solvents, the authors are unaware of any systematic magnetochemical study of stereochemical change for the cobalt(II) ion in solution. In the present investigation, the magnetic moment of this ion has been determined in water as a function of added chloride or thiocyanate ion and in water-dimethylformamide solutions as a function of solvent composition.

### Experimental Section

The magnetic moments, determined by the Gouy method at  $25.0 \pm 0.5^\circ$  in a Pyrex tube (25.00 ml) calibrated with nickel chloride solutions,<sup>7</sup> are reproducible to better than  $\pm 0.02$  BM. The diamagnetic gram-susceptibilities of methanol and dimethylformamide (DMF) were determined to be  $-0.640 \times 10^{-6}$

(1) This work is based in part on the honors thesis of J. M., 1968.

(2) To whom correspondence should be directed.

(3) F. A. Cotton, D. M. L. Goodgame, M. Goodgame, and A. Sacco, *J. Amer. Chem. Soc.*, **83**, 4157 (1961), and previous papers in the series.

(4) F. A. Cotton and R. H. Holm, *ibid.*, **82**, 2983 (1960).

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

(6) B. Chiswell and S. E. Livingstone, *ibid.*, 97 (1960).

(7) H. R. Nettleton and S. Sugden, *Proc. Roy. Soc., London*, **173**, 313 (1939).