Table I

Vapor Pressures of Germylsilane

Temp., °C.	P_{mm}, obsd.	P_{mm}, calcd.	Temp., °C.	P_{mm}, obsd.	P_{mm}, calcd.
−83.4	4.6	4.5	−45.2	65.1	65.2
−79.1	6.6	6.5	−41.7	79.5	79.6
−78.1[a]	7.0	7.0	−39.9	87.7	87.7
−64.0	19.8	19.9	−39.3	90.9	90.6
52.6	41.7	41.9	−37.1	102.1	102.5
49.5	50.6	50.6	−36.3	106.2	106.7
−49.3[a]	51.1	51.0	−35.9	109.1	109.0
−49.3	51.3	51.0	−23.3	207.6	207.0
−46.3	61.3	61.2	−196[a]	0.0	0.0

[a] Values observed as the temperatures were decreased at the conclusion of the measurements. The infrared spectrum of the whole sample, after the measurements were completed, was identical with that of the starting materials.

fraction. Vapor pressures in the range −83.4 to −23.3° were determined by means of a mercury manometer and are represented by the equation: $\log P_{\text{mm}} = (-1307.06/T) + 7.54701$. The extrapolated boiling point is 7.0°. The molar heat of vaporization is 6.00 kcal. mole^{-1} and the Trouton constant is 21.3 cal. deg.$^{-1}$ mole^{-1}.

The reproducibility of the vapor pressures when the sample was cooled at the conclusion of the experiment, together with the fact that no hydrogen (which would exert a pressure at −196°) was formed during the determinations, indicates that no thermal decomposition of the compound had occurred. This conclusion is supported by the fact that the infrared spectrum of the sample was unchanged after the vapor pressures had been measured.

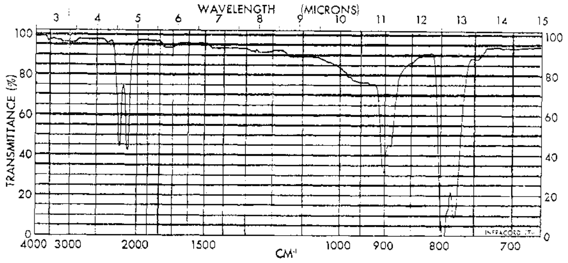


Figure 1.

The infrared spectrum of gaseous H_3GeSiH_3, observed at a pressure of 4.0 mm., is given in Fig. 1. The absorption maxima are: 2180 cm.$^{-1}$, m (Si–H); 2100 cm.$^{-1}$, m (Ge–H); 903 cm.$^{-1}$, m; 888 cm.$^{-1}$, sh, m; 796 cm.$^{-1}$, vs; 788 cm.$^{-1}$, sh, s; 778 cm.$^{-1}$, s.

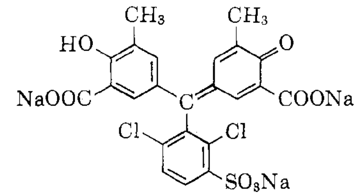
Contribution from the Chemical Laboratories,
University of Allahabad,
Allahabad, India

Composition and Stability of the Chelate between Uranium(VI) and Sulfodichlorohydroxydimethyl Fuchson Dicarboxylic Acid (Trisodium Salt)

By Suresh C. Srivastava* and Arun K. Dey

Received February 13, 1962

The trisodium salt of sulfodichlorohydroxydimethyl fuchson dicarboxylic acid (Chrome Azurol S)



forms colored complexes in aqueous solution with many metal ions and has widely been used in analytical chemistry,[1] though detailed data on the nature of the complexes produced are not available. In the present communication, detailed studies on the composition and stability of the uranyl Chrome Azurol S chelate are reported.

Experimental

Materials.—Standard solutions were prepared by dissolving uranyl sulfate (BDH L.R.) in double distilled water. Solutions of the trisodium salt of Chrome Azurol S (color index 723) in double distilled water were used and standardized by determining their sulfur content. In view of the strong complexing nature of carbonate with uranyl ions, care was taken to exclude carbon dioxide.

Instruments. Absorbance Measurements.—Measurements of absorbance were carried out with a Unicam SP 500 spectrophotometer, using matched glass cells (10-mm.) supplied with the instrument. At wave lengths of 625 mμ or below, the blue ultrasensitive phototube was used and above 625 mμ, the red sensitive phototube. The phototube circuit was kept at maximum sensitivity. The slit width corresponds to very nominal band widths and ranges between 0.030 and 0.080 mm. All absorbance readings were noted against distilled water blanks.

pH Measurements.—The hydrogen ion concentration of the solutions was measured with a Leeds and Northrup direct reading pH indicator, standardized by the buffer solution supplied with the instrument.

Electrical Conductance Measurements.—The measurements of electrical conductance were performed with a Leeds and Northrup Kohlrausch slidewire with an audiofrequency oscillator in the circuit using a dip type measuring cell having a cell constant of 0.580.

All experiments were performed at 30°. The total volume of all the mixtures prepared for the measurements was kept at 50 ml. The individual solutions and mixtures were adjusted to pH 5.0 by addition of HCl or NaOH and stored at 30 ± 0.01°, for about 1 hr. before use. Added electrolytes in the solution produced coagulation of the lake, hence constant ionic strength could not be attained.

Procedure.—Three different methods: (i) the method of continuous variations[2] (using absorbance as well as electrical conductance measurements), (ii) the mole ratio method,[3] and (iii) the slope ratio method[4] (both using absorbance measurements) were employed to establish the composition of the chelate.

A series of mixtures is prepared for the mole ratio method, containing a constant amount of the metallic ion but with increasing ratios of the metal to the reagent (or *vice versa*). When

---

* Department of Chemistry, Louisiana State University in New Orleans, New Orleans, 22, La.

(1) (a) H. H. Willard and C. A. Horton, *Anal. Chem.*, **22**, 1190 (1950); (b) M. Theis, *Z. anal. Chem.*, **144**, 106, 192, 275 (1955); (c) A. Musil and M. Theis, *ibid.*, **144**, 427 (1955); (d) J. S. Fritz and M. O. Fulda, *Anal. Chem.*, **26**, 1206 (1954); (e) M. Malát and M. Tenerova, *Chem. Listy*, **51** (11), 2135 (1957); (f) T. Matsuo, *Bunseki Kagaku*, **7**, 557 (1958); (g) S. P. Sangal and A. K. Dey, *Z. anal. Chem.*, **178**, 415 (1961); (h) D. Ravinson and J. H. Harley, *Anal. Chem.*, **25**, 794 (1953); (i) B. J. MacNulty and L. D. Woolard, *Anal. Chim. Acta*, **14**, 452 (1956); (j) L. Silverman and M. E. Shideler, U. S. At. Energy Comm. NAA-SR 2686, 1958; *Anal. Chem.*, **31**, 152 (1959).

(2) P. Job, *Compt. rend.*, **180**, 928 (1925); *Ann. Chim.*, (10) **9, 113 (1928)**.

(3) J. H. Yoe and A. L. Jones, *Ind. Eng. Chem., Anal. Ed.*, **16**, 111 (1944).

(4) A. E. Harvey and D. L. Manning, *J. Am. Chem. Soc.*, **72**, 4488 (1950).

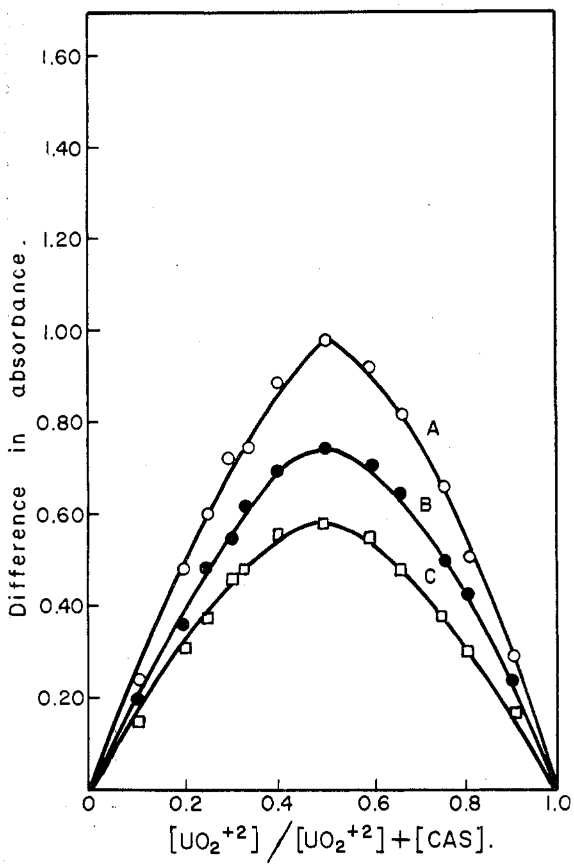


Fig. 1.—Determination of the composition from absorption spectra studies of equimolecular solutions, at 585 mμ, $p = 1$, pH 5.0 ± 0.2: curve A, $c = 1.25 \times 10^{-4}\ M$; curve B, $c = 1.00 \times 10^{-4}\ M$; curve C, $c = 0.83 \times 10^{-4}\ M$.

the absorbances of the mixtures are measured and plotted against the concentration ratios, the curves rise from the origin as a straight line when both the interactants are colorless, and break sharply to a constant absorbance at the molar ratio of the components in the complex.

In the slope ratio method, the stoichiometry is arrived at by comparing the slopes of the two straight line plots obtained by varying one component in the presence of a large excess of the other.

Evaluation of the Stability Constant.—A convenient method for the evaluation of the apparent stability constant is the method of Anderson and co-workers[5] based on the comparison of the composition of mixtures having identity of color, *i.e.*, the same absorbance value. The method has been adapted[6] for use of a colored ligand and colorless cation instead of a colorless ligand and colored cation.

A corroboration of the stability constant calculated by the above mentioned method also has been sought by the mole ratio method through a calculation of the degree of dissociation as suggested by Harvey and Manning.[4]

Results and Discussion

Behavior of the Reagent as a Colloidal Electrolyte.—As reported earlier,[7] it was found that the reagent behaves as a colloidal electrolyte and therefore very dilute solutions of the order $\backsimeq 10^{-4}$ and $10^{-5}\ M$ were employed in these investigations, as it has been emphasized by Dey[8] that in the case of colloidal solutions, the characteristics of a true solution often are displayed when extremely dilute solutions are used.

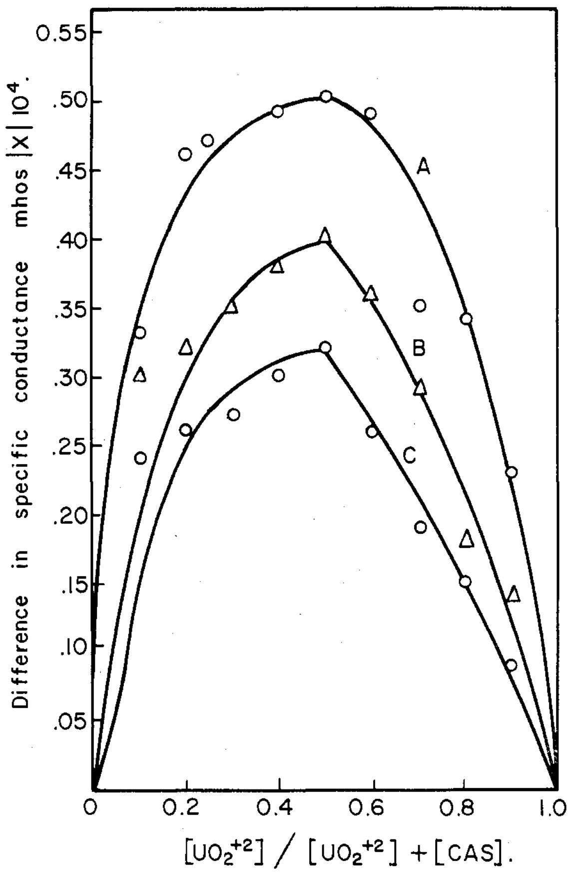


Fig. 2.—Determination of the composition from electrical conductance studies of equimolecular solutions ($p = 1$): curve A, $c = 6.66 \times 10^{-4}\ M$; curve B, $c = 5.00 \times 10^{-4}\ M$; curve C, $c = 3.33 \times 10^{-4}\ M$.

Effect of Time on the Color of the Chelate.—Color formation was observed to be immediate and the absorbance values remained constant at least up to 72 hr. Order of reagent addition was not a significant variable. However, all the mixtures were kept for an hour to attain equilibrium.

Nature of the Complex in Solution.—For the determination of the nature of the complex formed in solution, the method of Vosburgh and co-workers[9] was followed. Mixtures containing uranyl sulfate and Chrome Azurol S in different stoichiometric ratios (*e.g.*, 0:1, 1:1, 1:2, 1:3, etc.) were prepared and the absorbance of each of them was measured at suitable wave length intervals between a range from 355 to 750 mμ. The results show that the reagent has its maximum absorption at 465 mμ at pH 5.0, whereas in the mixtures the wave length of maximum absorbance shifts to 585 mμ, indicating the formation of only one chelate having $\lambda_{\max}$ at 585 mμ under the conditions of study.

---

(5) R. T. Foley and R. C. Anderson, *J. Am. Chem. Soc.*, **70**, 1195 (1948); **71**, 909 (1949); S. E. Turner and R. C. Anderson, *ibid.*, **71**, 912 (1949).

(6) A. K. Mukherji and A. K. Dey, *J. Inorg. Nucl. Chem.*, **6**, 314 (1958); *Anal. Chim. Acta*, **18**, 324 (1958); S. K. Banerji and A. K. Dey, *Proc. Symp. Chem. Co-ord. Compounds, Agra, 1959*, **2**, 198 (1960).

(7) S. C. Srivastava, R. L. Seth, and A. K. Dey, *J. Colloid Sci.*, **17**, 86 (1962).

(8) A. K. Dey, *ibid.*, **3**, 473 (1948).

(9) W. C. Vosburgh and co-workers, *J. Am. Chem. Soc.*, **63**, 437 (1941); **64**, 1630 (1942).

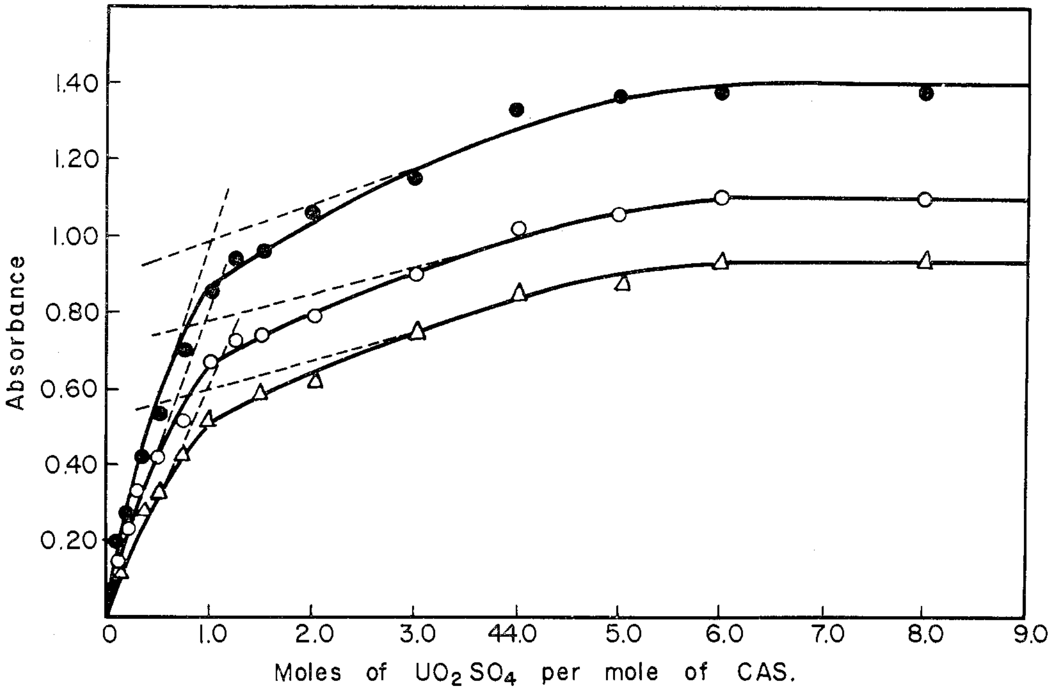


Fig. 3.—Determination of the composition from absorbance studies using the mole ratio method at 585 mμ; pH 5.0 ± 0.2, concentration of CAS: ●, 5.0 × 10^{-5} *M*; ○, 4.0 × 10^{-5} *M*; △, 3.33 × 10^{-5} *M*.

Stoichiometry of the Components.—Continuous variation curves at 570 and 585 mμ confirmed the stoichiometry as one UO$_2$(II) to one Chrome Azurol S. Some of the observations are represented in Fig. 1.

The results from the continuous variations method using electrical conductance measurements, shown in Fig. 2, confirm the above stoichiometry, as do the mole ratio method (Fig. 3) and the slope ratio method (Fig. 4).

Effect of pH.—The absorbances of various mixtures containing uranyl sulfate and Chrome Azurol S in their stoichiometric ratio, *i.e.*, 1:1 (each 6.66 × 10^{-5} *M*) at different pH values were measured at different wave lengths and it was found that the λ_{max} of the chelate, which is 585 mμ, remains the same between pH 4.0 and 6.0, indicating that the uranyl Chrome Azurol S chelate is stable over this range of pH. The maximum extinction lies at pH 5.0 ± 0.3.

Stability Constant of the Chelate.—The value of the apparent stability constant for the 1:1 chelate at a pH of 5.0 and temperature of 30° is 4.5 ± 0.1 as determined by the modified method of Anderson and co-workers[5] and 4.9 ± 0.1 as determined by the mole ratio method. The corresponding free energy change of formation works out to be −6.2 ± 0.1 and −6.8 ± 0.1 kcal., respectively, at 30°.

Suggestions on the Structure of the Chelate.—It is not possible to derive any definite information on the basis of the experimental results mentioned in the present paper about the structure of the chelate. There are evidently two alternative positions where chelation might occur. The metal ion may be coördinated between the phenolic oxygen and the adjacent carboxylic oxygen or between the quinoid oxygen and the adjacent oxygen of the carboxylic group. It is interesting to note that in a strongly alkaline medium (pH 11.6 and above), where the structure suggests the removal of phenolic hydrogen by ionization, the region of maximum absorbance of Chrome Azurol S lies at 595 mμ, whereas

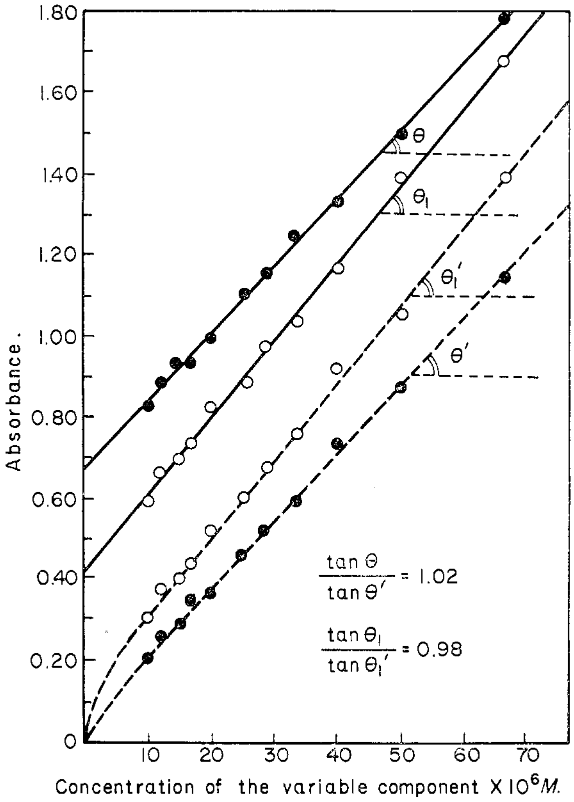


Fig. 4.—Determination of the composition from absorbance studies by the slope ratio method: pH 5.0 ± 0.2; concentration of excess component 2.0 × 10^{-4} *M*; ——— UO$_2$SO$_4$ varying, -------- CAS varying; ● 570 mμ, ○ 585 mμ.

in a neutral or slightly alkaline medium (pH 6.0–10.2), the $\lambda_{\max}$ is found to be at 425 mμ and shifts to 465 mμ in an acidic medium (below pH 6.0). Thus it seems possible that as a result of chelation, the phenolic hydrogen is replaced by the metal ion and hence, the wave length of maximum absorbance of the chelate is 585 mμ. This would lead to the formation of an anionic complex, which has further been confirmed by the complete adsorption of the color of the chelate by ion-exchange resin Amberlite IR-45 (OH) (BDH AnalaR).

Acknowledgment.—The authors are thankful to the Council of Scientific and Industrial Research, India, for supporting the work and for the award of a research fellowship to S. C. S.

CONTRIBUTION FROM THE CHEMISTRY DIVISION,
OAK RIDGE NATIONAL LABORATORY,
OAK RIDGE, TENNESSEE

The Exchange of Ammonia between Aqueous Ammonia and $Co(NH_3)_6Cl_3$[1]

BY A. C. RUTENBERG AND J. S. DRURY

Received June 25, 1962

The rate of exchange of NH_3 in an aqueous solution of $Co(NH_3)_6Cl_3$ and NH_4OH was investigated in conjunction with a study of isotopic equilibrium constants involving solutions of metal–ammonia complexes. The $Co(NH_3)_6Cl_3$ was prepared by the method of Bjerrum and McReynolds.[2] The $N^{15}H_4OH$ was prepared by the reduction of $N^{15}O_3^-$ with Dvarda's alloy (45% Al, 50% Cu, 5% Zn).

Approximately 120 ml. of a solution containing 62.1 mequiv. of $Co(NH_3)_6Cl_3$ and 48.6 mequiv. of NH_4OH (82.59% N^{15}) was thermostated at 35° and sampled periodically. The samples were placed in a vacuum system and the uncomplexed NH_3 was distilled at room temperature and collected. The NH_3 from the complex was isolated, using the usual Kjeldahl procedure for nitrogen. All samples of NH_3 were oxidized with NaOBr and the resulting N_2 was analyzed in a mass spectrometer.

The isotopic compositions of the samples as a function of time are shown in Table I.

TABLE I

$Co(NH_3)_6Cl_3$–$N^{15}H_4OH$ EXCHANGE AT 35°

Time (days)	Complexed NH_3 % N^{15}	Uncomplexed NH_3 % N^{15}
0	0.44	82.2
16	2.24	77.8
51	3.84	73.7
98	5.34	69.9
∞		23.48 (calcd.)

Plots were made of the logarithm of the difference between the N^{15} content at time (t) and the time for complete exchange (t_∞) as a function of time. With the exception of the initial sample, the data for the complexed NH_3 fit well the least squares line

$$\log (\%N_{t\infty}{}^{15} - \%N_t{}^{15} = 1.339 - 0.000830t \qquad (1)$$

where t is time in days. Similarly, the data for the uncomplexed NH_3 were given by

$$\log (\%N_t{}^{15} - \%N_{t\infty}{}^{15}) = 1.746 - 0.000827t \qquad (2)$$

The data for the zero time samples were not used in the least squares computations. These points fell above the lines given by eq. 1 and 2. This anomaly was attributed to a faster than normal rate of exchange which occurred during the initial period of the equilibration. The agent responsible for this catalysis was not identified.

From eq. 1 and 2, the half-time for the exchange of NH_3 in the observed system was computed to be 363 ± 1 days.

---

[1] This paper is based on work performed for the U. S. Atomic Energy Commission by Union Carbide Nuclear Company.

[2] J. Bejerrum and J. P. McReynolds, *Inorg. Syn.*, **2**, 217 (1946).

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY
HARVARD UNIVERSITY, CAMBRIDGE, MASSACHUSETTS

Chemistry of the Metal Carbonyls. XX. Nature of the Reaction Product from Cyclopentadienylvanadium Tetracarbonyl and Dimethyl Disulfide[1]

BY R. H. HOLM, R. B. KING, AND F. G. A. STONE[2]

Received March 12, 1962

Recently the thio-bridged complexes $[C_5H_5Fe(CO)SCH_3]_2$ and $[C_5H_5CoSCH_3]_2$ were prepared by the reaction of dimethyl disulfide with cyclopentadienyliron dicarbonyl dimer and cyclopentadienylcobalt dicarbonyl, respectively.[3] This prompted an investigation of reactions of other cyclopentadienyl metal carbonyls with dimethyl disulfide. In connection with this work, we have isolated a compound of molecular formula $[C_5H_5V(CH_3S)_2]_2$ from the reaction between cyclopentadienylvanadium tetracarbonyl and dimethyldisulfide or methylmercaptan.

Experimental

A. Preparation from Dimethyl Disulfide.—A mixture of 5.0 g. (22 mmoles) of cyclopentadienylvanadium tetracarbonyl, 35 ml. of dimethyl disulfide, and 200 ml. of 2,2,4-trimethylpentane was refluxed for 42 hr. under nitrogen, the reaction mixture becoming brown-black. The mixture then was allowed to cool to room temperature and the solvent removed at 20 mm. to leave a brown-black residue. The product was isolated by sublimation (160°, 0.1 mm.), discarding the small quantities of oily material and cyclopentadienylvanadium tetracarbonyl which first appeared. Resublimation of the brown-black subli-

---

[1] Previous article in this series, R. A. Plowman and F. G. A. Stone, *Z. Naturforsch.*, **17b**, 575 (1962).

[2] Queen Mary College, University of London, London, E1.

[3] R. B. King, P. M. Treichel, and F. G. A. Stone, *J. Am. Chem. Soc.*, **83**, 3600 (1961).