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,
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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.

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[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-

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[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).

mate (160°, 0.1 mm.) gave 2.7 g. (59% yield, based on cyclopentadienylvanadium tetracarbonyl) of brown-black crystals of $[C_5H_5V(CH_3S)_2]_2$, m.p. > 292° with decomposition beginning at 200°.

Anal.[4] Calcd. for $C_{14}H_{22}S_4V_2$: C, 40.0; H, 5.24; S, 30.5; V, 24.3; mol. wt., 420. Found: C, 40.2, 40.3; H, 4.9, 5.3; S, 30.3, 30.3; V, 24.1, 23.8; mol. wt. (isopiestic in dichloromethane at 30°), 423.

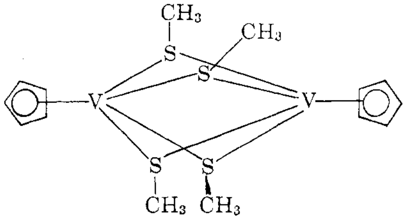
Infrared bands were observed at 2872 (m), 1294 (m), 1013 (m), and 795 (s) cm.$^{-1}$ (CS_2 solution) and at 1435 (m) cm.$^{-1}$ (C_2Cl_4 solution).

B. Preparation from Methyl Mercaptan.—A mixture of 2.3 g. (10.1 mmoles) of cyclopentadienylvanadium tetracarbonyl, 20 ml. of *n*-pentane, and 98.2 mmoles of methyl mercaptan was placed in a 150-ml. stainless steel bomb at −196°. The bomb was allowed to warm to room temperature and then was maintained at 110° for 12 hr. After cooling to room temperature, its contents were removed, the solvent evaporated, and the residue sublimed as above. A 0.42-g. (20%) yield of brown-black solid was obtained and analyzed after a second sublimation.

Anal. Found[4]: C, 41.0; H, 5.2; S, 30.2; V, 24.0. The infrared spectrum was identical with that above.

Discussion

The formation of the same product by reaction of $C_5H_5V(CO)_4$ with either methyl mercaptan or dimethyl disulfide is consistent with earlier results[5] which indicate the ready cleavage of S–S bonds by metal carbonyls, with the formation of monothio bridges and, often, of metal–metal bonds. Analogy with the iron and cobalt compounds mentioned above and with $[C_2H_5SFe(CO)_3]_2$[6] suggests structure I with four bridging CH_3S– groups for this new vanadium complex. If so this would represent the first example of a binuclear complex with four bridging groups. The configuration of groups around each vanadium might be similar to that suggested for $C_5H_5V(CO)_4$.[7] The electronic structure of the molecule is not particularly clear. One plausible explanation would be to regard each vanadium as formally V(0) and each sulfur atom as a three-electron donor to the pair of metal atoms.[3,8] Regardless of charge formulation, however, each vanadium will have two electrons less than the inert gas configuration if each sulfur retains one unshared electron pair. Each metal atom then possesses two electrons not directly involved in metal–ligand bonding. If these electrons are unpaired and do not interact appreciably with a similar set on the other vanadium, a magnetic moment of 2.8 B.M. per vanadium is expected. If, on the other hand, the electrons are locally paired, or by means of metal–metal interaction have their spins completely quenched through exchange forces, diamagnetism should result. Inspection of Table I reveals that the compound is weakly paramagnetic with increasing susceptibility as the temperature is raised. The susceptibilities, while very small, were reproducible to within ±5% on two different samples, and to ±2% on the same sample. The magnetic changes were entirely reversible with temperature, and the susceptibilities of a freshly prepared sample and one allowed to stand for about 8 months in contact with air were the same.



I

TABLE I

MAGNETIC DATA FOR $[C_5H_5V(CH_3S)_2]_2$[a]

T (°K.)	$10^6\chi_{\mathrm{cor}}^{M}$	μ_{eff} (B.M.)
195.1	308	0.70
280.1	340	.88
298.3	351	.92
313.3	366	.96
328.3	379	1.00
344.5	390	1.04

[a] Solid measured by the Gouy method, with results expressed per vanadium atom.

The magnetic moments, calculated from the Curie law, are considerably less than that expected for even one unpaired electron. These results are suggestive of a strong exchange interaction between the metal atoms whereby a ground state singlet is produced. The multiplicity of the lowest paramagnetic state is presumably triplet, but the data are insufficiently extensive to allow a test with theory and an evaluation of the exchange energy.[9] A molecular triplet state could arise by formation of a strong vanadium–vanadium bond, leaving a single electron on each metal which then could couple through a weaker exchange mechanism. The latter effect is now well established in binuclear complexes such as the cupric alkanoates[10] and $[Fe(phen)_4(OH)_2]Cl_4$.[9,11]

The susceptibility value at 195° and, especially, that (422 × 10^{-6}, 0.48 B.M.) obtained at 78° on one sample are too large to be compatible with a thermal distribution model and likely are due to traces of paramagnetic impurity. The behavior at higher temperatures, however, is not that expected from the presence of only dilute paramagnetic impurities.[12]

This vanadium complex appears to represent the

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[4] Analyses by A. Bernhardt, Max-Planck-Institut, Mülheim, Germany.

[5] W. Hieber and W. Beck, *Z. anorg. allgem. Chem.*, **305**, 265 (1960).

[6] In an X-ray structural investigation of this compound, L. F. Dahl (private communication) has found the $Fe(CO)_3$ groups to be bridged by two C_2H_5S groups and additionally joined by a metal–metal bond.

[7] F. A. Cotton, A. D. Liehr, and G. Wilkinson, *J. Inorg. Nucl. Chem.*, **1**, 175 (1955).

[8] S. F. A. Kettle and L. E. Orgel, *J. Chem. Soc.*, 3890 (1960).

[9] See, for example, A. Earnshaw and J. Lewis, *ibid.*, 296 (1961).

[10] (a) B. N. Figgis and R. L. Martin, *ibid.*, 3837 (1956); (b) R. L. Martin and H. Waterman, *ibid.*, 1359, 2690 (1959).

[11] N. Elliott, *J. Chem. Phys.*, **35**, 1273 (1961).

[12] While we believe impurities must be present, we have no knowledge of their exact nature. The vanadium trichloride used in the preparation of $C_5H_5V(CO)_4$ was obtained from an assayed lot (Union Carbide Metals Co.) containing less than 0.5% metallic chloride impurity which most likely contains iron. It appears likely in the synthesis of starting material that iron chloride impurities would be converted to diamagnetic organo-iron compounds. We believe it reasonable to assume the impurity to be a dilute paramagnetic. If it then is assumed that the entire susceptibility at 78°K. arises from this impurity, from the Curie law no more than 31% of the value at 298°K. and 25% of the value at 344°K. can be due to impurity. Otherwise, the impurity has a most peculiar temperature dependence.

first example of a binuclear organometallic in which a paramagnetic state is within thermal range. It has been estimated that in diamagnetic polynuclear carbonyls wherein the strong metal–metal exchange interaction is formalized by metal–metal bonds (*e.g.*, $Fe_2(CO)_9$), the singlet–triplet separation is of the order of $\sim$700 cm.$^{-1}$. The strong exchange interaction in I presumably is effected by the tetra-bridged structure in which the V–S–V angle probably is near the tetrahedral value. Finally, it appears likely that the magnetic behavior described above can occur only in bridged vanadium (or titanium) complexes of this type since with other transition metals the inert gas configuration can be attained with (or without) the formation of metal–metal bonds. Other paramagnetic V(0) complexes are $[(C_6H_5)_3P]_2V(CO)_4$[13] and the mononuclear $V(CO)_6$,[14] which have the expected moments of 1.8 B.M. for one unpaired electron.

Acknowledgment.—We thank the National Science Foundation for financial support and Dr. P. M. Treichel for valuable experimental assistance.

[13] R. P. M. Werner, *Z. Naturforsch.*, **16b**, 477 (1961).

[14] F. Calderazzo, R. Cini, and R. Ercoli, *Chem. Ind.* (London), 934 (1960)

CONTRIBUTION FROM THE
ESSO RESEARCH AND ENGINEERING COMPANY,
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Reactions of the Borohydride Group with the Proton Donors Hydroxylammonium, Methoxyammonium, and Hydraziniummagnesium Ions[1]

BY FRANK C. GUNDERLOY, JR.[2]

Received December 15, 1961

Ammonia and amines, coördinated either to a proton as ammonium ion or to metal cations, have sufficient acidity to react with the borohydride group yielding amine boranes or borohydrides of low stability that degrade to amine boranes.[3] This reaction has now been applied to the ions $Mg(N_2H_4)_x^{++}$, $CH_3ONH_3^+$, and $HONH_3^+$.

If solutions are chilled and concentrations kept low, $MgCl_2 \cdot 6H_2O$ may be dissolved in hydrazine without $Mg(OH)_2$ forming. The addition of $NaBH_4$ to such solutions results in the precipitation of NaCl, but no gas is evolved. While this indicates that an intermediate magnesium borohydride is stable in the solution, it is not isolated, since removing the solvent yields a solid that evolves hydrogen, and $N_2H_4 \cdot BH_3$[4] appears as a product.

The original $MgCl_2 \cdot 6H_2O$ solution may be evaporated carefully and vacuum dried to yield a solid magnesium chloride hydrazinate. Hydrogen evolves when this hydrazinate is allowed to react with $NaBH_4$ in tetrahydrofuran suspension, and $N_2H_4 \cdot BH_3$ is again a product.

Methoxyammonium chloride and $NaBH_4$ as a tetrahydrofuran suspension also give the corresponding $CH_3ONH_2 \cdot BH_3$.[5]

Hydroxylammonium salts do not give $HONH_2 \cdot BH_3$ under similar conditions. While the evolved hydrogen : borohydride mole ratio in the first two cases approaches 1:1, it is 1:3 with the $HONH_3^+$ salts, unless the reaction is conducted well below room temperature. The product is a solid formulated as $(HONBH)_x$, although secondary reactions with the solvent have prevented a truly definitive characterization.

$(HONBH)_x$ may be the borazine ($x = 3$), but this has not been definitely established in the present work. Molecular weight values have been erratic, and the infrared spectrum shows broad and ill-defined absorptions beyond 6.5 μ.

In reactions conducted at $-80°$, H_2 evolution does slow near 1:1 $H_2 : BH_4^-$ when ethers of high base strength are the reaction media. However, products isolated in the cold evolve additional hydrogen when warmed to room temperature, paralleling the direct reaction of B_2H_6 and $HONH_2$.[6] Once, using trimethylene oxide, the final solid had a hydrolyzable hydrogen content greater than theory for $(HONBH)_x$ but still well below that expected for the hydroxylamino- or hydroxylamine borane. In all other cases, only $(HONBH)_x$ remained after gas evolution ceased.

It should be noted that $(HONBH)_x$ is *extremely hazardous*. It explodes with high brisance under conditions of mild friction or impact. One sample, isolated by evaporating a tetrahydrofuran solution, exploded when simply pierced with a spatula.

Experimental

All reactions were carried out under nitrogen atmospheres and at room temperature except where specified. Ethers were dried over CaH_2. Hydrazine was a 96+% commercial product.

Hydrogen was measured in a closed system with a mercury filled gas buret, on a scale calculated not to exceed the capacity of the buret. Reactions were initiated by injection of a measured volume of solvent through a serum cap, and the pressure adjusted during measurements to compensate for the vapor pressure of the solvent.

Larger preparative reactions, described below, were conducted in magnetically stirred erlenmeyer flasks.

(1) **$N_2H_4 \cdot BH_3$—Method 1.**—$MgCl_2 \cdot 6H_2O$ (0.41 g., 2 mmoles) and $NaBH_4$ (0.15 g., 4 mmoles) were mixed in 20 ml. of iced hydrazine. A small amount of NaCl (X-ray identification) precipitated and was filtered off; no gas evolved. The hydrazine was evaporated under a N_2 stream and the resulting solid vacuum-dried. NaCl was present in this material, and hydrogen evolution could now be detected. The solid was allowed to stand under hexane for 1 week, and then extracted with tetra-

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[1] This work was carried out under Contract DA-30-069-ORD-2487 for the Advanced Research Projects Agency.

[2] Rocketdyne, A Division of North American Aviation, Canoga Park, California.

[3] R. W. Parry, D. R. Schultz, and P. R. Giradot, *J. Am. Chem. Soc.*, **80**, 1 (1958).

[4] J. Goubeau and E. Ricker, *Z. anorg. allgem. Chem.*, **310**, 123 (1961).

[5] T. C. Bissot, D. H. Campbell, and R. W. Parry, *ibid.*, **80**, 1868 (1958).

[6] D. H. Campbell, T. C. Bissot, and R. W. Parry, *ibid.*, **80**, 1549 (1958).