in a neutral or slightly alkaline medium (pH 6.0–10.2), the λ_{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).

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The Exchange of Ammonia between Aqueous Ammonia and Co(NH₃)₆Cl₃[1]

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

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(NH₃)₆Cl₃–N¹⁵H₄OH EXCHANGE AT 35°

Time (days)	Complexed NH₃ % N¹⁵	Uncomplexed NH₃ % N¹⁵
0	0.44	82.2
16	2.24	77.8
51	3.84	73.7
98	5.34	69.9
∞		23.48 (calcd.)

(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).

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

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

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

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

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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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]

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).