of the O_2 comes from the inner, unexchanged coordination sphere of Co(III) as suggested by the previous study at 0.6 M Co(III) and 6 M $HClO_4$ (initial concentrations). This calculated value is the maximum expected assuming the same degree of polymerization and 100% decomposition. These results are clearly not consistent with the previous data[2] and suggest either that the coordination sphere of Co(III) is in complete equilibrium with the solvent before appreciable oxidation takes place or that the molecular oxygen comes entirely from the solvent.

Table II gives the results of one of two runs carried out to find a change in the ^{18}O content of O_2 as the reaction proceeded. The second run gave equivalent results. It had been previously observed[2] that the initial O_2 (0–8% reaction) was composed of nearly 50% of oxygen from the unexchanged Co(III) coordination sphere. Thus this type of experiment should be a much more sensitive test of oxygen holdback by polymeric Co(III) ions. The calculated values for $R_N(O_2/H_2O)$ are as follows: (a) O_2 completely from unexchanged Co(III) sphere, 0.27; (b) O_2 equally from the Co(III) sphere and the solvent, 0.63; (c) O_2 completely from the solvent, 1.00. These results show that the O_2 evolved has the same ^{18}O content as the final solvent and do not support the suggestion that Co(III) solutions in 1–5 M acid contain hydroxy polymers which give O_2 with the composition of the hydroxy groups when Co(III) is reduced in water. The last column in Table II gives the approximate maximum O_2 contamination from air as measured by the $^{28}N_2$ peak. Appreciable air contamination would lower the $R_N(O_2/H_2O)$ ratio and is not significant in this work. Runs 13, 15, and 16 show the results of purposely not flushing the O_3 out of the solution being electrolyzed. After transfer to the vacuum apparatus, however, it was degassed as usual. The effect was very small suggesting that the initial $[O_3]$ was very small or that its concentration is quite easily lowered to a small value by the degassing method employed. This result is in agreement with the measured O_3 concentration and suggests the presence of O_3 cannot account for the previous ^{18}O results.

TABLE II[a]

$$4Co(H_2O)_6^{3+} + 2H_2O^* \rightarrow O_2 + 4Co_{aq}^{2+} + 4H^+$$

Run no.[b]	% decompn[c]	$10^3 R_N(O_2)$	$R_N(O_2)/R_N(H_2O)$	% atm O_2 (max)
1	0–12	1.5550	1.0016	2.0
2	12–26	1.5565	1.0025	1.2
3	26–45	1.5600	1.0048	1.1
4	45–66	1.5585	1.0039	0.6
5	66–75	1.5610	1.0055	1.3
6	75–95	1.5590	1.0042	0.7

[a] Conditions: 10.00 ml of stock to 4.4 ml of H_2O enriched 8.4 times; stock solution $[Co^{3+}] = 0.929$ M, $[H^+] = 3.32$ M, % $Co^{3+} = 98$; after dilution $[Co^{3+}] = 0.645$ M, $[H^+] = 2.31$ M; $R_N(H_2O \text{ and } Co^{3+}) = 4.18 \times 10^{-3}$, $R_N(H_2O \text{ enriched}) = 3.48 \times 10^{-2}$, $R_N(\text{final } H_2O) = 1.5525 \times 10^{-2}$. [b] Some O_3 present. Degassed 4 times before H_2O was added; then degassed 3 times. [c] Decomposed at 20–25° in diffuse light. Determined spectrally (±1%).

It was noted by a referee that the final total $[Co^{3+}]$ was greater than that used previously and a reasonable explanation of the discrepancy between laboratories could be made on this basis. Thus a few measurements were made at high dilution and are reported in Table III. These results are consistent with the others reported in this paper.

TABLE III

^{18}O TRANSFER DURING H_2O OXIDATION BY Co(III)[a]

$[Co(III)]_i$, M	$[HClO_4]_i$, M	% Co(III)[b]	$R(O_2)/R(H_2O)$
0.32[c]	2.86	94	0.9901
0.74[c]	5.33	93	0.9936
0.62[c]	5.50	100	0.9982
0.62[d]	5.50	100	0.9816
0.73[e]	4.85	99	1.0026

[a] Conditions: 1 ml of Co(III) stock + 20 ml of H_2O of differing ^{18}O content. Complete decomposition. [b] As determined spectrophotometrically. [c] Co(III) in normal water; enriched water (3.49 times) added. [d] Co(III) in normal water; normal water added. [e] Co(III) in enriched water (4.54 times); normal water added.

The values in Tables I and III using normal water are slightly low. The reason for this observation is uncertain since many factors could contribute including experimental problems and cobalt(III) water holdback with the O_2 having the composition of the resulting solvent.

For future comparisons an analysis of the stock cobalt(II) perchlorate solution (from $CoCl_2$) was made by arc spectra: Mn, Ca, Mg, Pb, Sn, Ag, Ti, Mo, V, Cr, Al < 10 ppm, Zn < 300 ppm, Cu < 20 ppm, Fe < 1 ppm, Ni (flame photometry) 3000 ppm based on cobalt. This represents a relatively pure cobalt with the nickel content unmodified by the purification procedure.[11]

Summary

On the basis of these measurements, the molecular oxygen obtained from the oxidation of water by Co(III) has the composition of the solvent. No evidence was found for oxygen "holdback" by 3–6 M Co(III) in 1.5–6 M $HClO_4$, when diluted with ^{18}O-labeled water, in the time necessitated by the rate of water oxidation (~5 min). The ozone often present in Co(III) solutions prepared electrochemically cannot account for the differences observed in the two studies. The much higher ^{18}O enrichment used in the first study seems to be the only experimental change, but it is difficult to explain the differing results on this basis. An additional study of this reaction is indicated.

Acknowledgment.—The arc-spectra analysis was the courtesy of E. E. Pickett and R. Koirtyohann and is appreciated.

[11] NOTE ADDED IN PROOF.—A highly purified $Co(ClO_4)_2$ solution with the observable impurities being Cu, Fe, Mg, and Ni (all below 10 ppm) gave essentially the same results as in Table I.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
GENEVA COLLEGE, BEAVER FALLS, PENNSYLVANIA 15010

Dimethyl Sulfide–Borane as a Borane Carrier

BY JOHN BERES, ALAN DODDS, ALFRED J. MORABITO,
AND ROY M. ADAMS*

Received August 6, 1970

Since diborane is not stable at room temperature, the preparation of borane adducts of Lewis bases has generally involved *in situ* preparation of borane or diborane. Solutions of borane in tetrahydrofuran are commercially available but in only 1.5 wt % concentration, and they require refrigeration for extended storage. It seemed to us that dimethyl sulfide–borane (I), a liquid which is 18 wt % borane, might offer advantages as a borane carrier, particularly in laboratories like our own which hesitate to have undergraduates manipulate highly flammable gaseous diborane. Compound I was first reported by Burg and Wagner[1] and studied by Stone and coworkers,[2] who concluded that it was more strongly associated than other sulfide–boranes. The preparation of I in more than millimolar quantities had not been studied to our knowledge nor had its utility for the preparation of other borane adducts.

Through the courtesy of Callery Chemical Co. a mole-scale sample of I was prepared from commercial diborane in their laboratories. Dimethyl sulfide (1 mol, 62 g) in a 500-ml round-bottom flask containing a magnetic stirrer was connected through a vacuum stopcock to a vacuum line. Diborane was introduced to the capacity of the line (approximately 4000 cm^3) and condensed in a liquid nitrogen trap. The line was evacuated to remove any noncondensables. The diborane was then allowed to vaporize and slowly introduced into the stirred dimethyl sulfide at 0° over a period of approximately 1 hr. Two more fillings of the line with diborane were necessary to introduce slightly over 0.5 mol of diborane. The product was then pumped on to remove any excess reactants which were flushed out of the vacuum line into a scrubbing system with nitrogen.

The product flask was then removed to a drybox and the contents transferred to screw cap bottles. These were transported to our laboratories in a nitrogen-filled glove bag which was stored at room temperature in a hood. An exactly 25.0-ml sample was introduced into a volumetric flask and weighed at 23° to give a density of 0.801 g/ml.

The purity was determined by methanolysis. Samples of 0.20 ml (2.0 mmol) each were taken with a 1-ml hypodermic syringe in the glove bag and introduced into a 25-ml two-necked flask containing 5 ml of benzene and stirred magnetically. The flask was equipped with a rubber septum in one neck and connected through the other neck to a mercury bubbler and in turn to a gas-measuring tube over water. Three samples evolved an average of 67 cm^3 of hydrogen (corrected to STP) which indicated a pure product within the precision of the method: $(CH_3)_2S\cdot BH_3 + 3CH_3OH \rightarrow (CH_3)_2S + B(OCH_3)_3 + 3H_2$.

Young, McAchran, and Shore[3] reported the ^{11}B nuclear magnetic resonance to be 38.4 ppm upfield from methyl borate and the B–H coupling constant to be 104 Hz. Coyle and Stone found the methyl proton signal to be 3.12 ppm upfield from methylene chloride. No mention was made of the boron-attached proton signal.[2c] Since their spectrum was not referred to tetramethylsilane and since the chemical shifts are slightly different, we are reporting our data on the neat liquid. The methyl peak was found at δ 1.89 (lit.[2c] δ 2.01 in CH_2Cl_2) and the ^{11}B-coupled proton peaks at δ −1.30, 0.40, and 3.99. The peak at δ 2.01 is swamped by the methyl signal. This places the B-bonded proton chemical shift at δ 1.30 and confirms the reported B–H coupling constant.

Borane-transfer reactions of I on a 2-mmol-scale were studied with a number of Lewis bases. In each case the reagents were measured in a 1-cm^3 hypodermic syringe and were introduced through a septum into a 25-ml flask containing 5 ml of benzene and connected through a mercury bubbler to a gas-measuring tube. With chlorodiphenylphosphine (II), triphenylphosphine, methyl, ethyl, and butyl phosphites, *tert*-butylamine, and triethylamine, no hydrogen was evolved upon addition of methanol to the products, indicating complete transfer of the borane to the other Lewis base. Evaporation of the solvent left the borane adduct in each case (identified by its ir spectrum) except for the reaction with II.

The product with II was methoxydiphenylphosphine–borane, mp 70.5°. *Anal.* Calcd for $BC_{12}H_{16}OP$: B, 4.71; C, 67.9; H, 6.96; P, 13.5. Found: B, 5.01; C, 67.7; H, 6.62; P, 13.4. The product has symmetric and asymmetric B–H stretching bands at 2330 and 2380 cm^{-1} and C–H aromatic and aliphatic stretching bands at 3070 and 2920 cm^{-1}, respectively, and is otherwise compatible with the assigned structure. The proton nmr spectrum shows a doublet at δ 3.915 with J_{PH} = 12 Hz assigned to the methyl protons and an aromatic singlet at δ 7.25. Any B–H signal was lost in the background. We were surprised to find that the Cl on P is more susceptible to solvolysis than the hydrogen on boron: $Cl(C_6H_5)_2P\cdot BH_3 + CH_3OH \rightarrow CH_3O(C_6H_5)_2P\cdot BH_3 + HCl$.

With aniline, *N*-methylaniline, and dichloro(phenyl)phosphine hydrogen was evolved upon the addition of methanol. We did not attempt to isolate these adducts.

Since the utility of I as a borane-transfer agent had been demonstrated, we used it to attempt the preparation of ammonia–borane by slowly introducing gaseous ammonia into a magnetically stirred flask containing I. Temperatures from −78 to +70° were tried. Under these conditions −20° was found to be optimum. The reaction rate was slower at lower temperatures and at higher temperatures excessive amounts of "diborane diammoniate,"[4] $(NH_3)_2BH_2^+BH_4^-$, were formed. This by-product was removed by recrystallization of the ammonia–borane in ethyl ether. The product was identified by comparison of its infrared spectrum with a sample prepared by the method of Shore and Parry.[5] In contrast to the report of slight instability of ammonia–borane at room temperature,[5] it was found to be stable for 5 days at 70° and sublimable with partial decomposition at 80° and 0.1 Torr. The melting range of the sublimed product was found to be 121–124°. Sorokin, Vesnina, and Klimova[6] reported start of decomposition at 50° and a melting point of 104.5 ± 0.5°. The conversion of the "diammoniate" by-product to ammonia–borane by reaction with ammonium chloride in ether was confirmed.[4,5]

Conclusions.—Dimethyl sulfide–borane is a con-

---

(1) A. B. Burg and R. I. Wagner, *J. Amer. Chem. Soc.*, **76**, 3307 (1954).

(2) (a) W. A. G. Graham and F. G. A. Stone, *J. Inorg. Nucl. Chem.*, **3**, 1964 (1956); (b) T. D. Coyle, H. G. Kaez, and F. G. A. Stone, *J. Amer. Chem. Soc.*, **81**, 2989 (1959); (c) T. D. Coyle and F. G. A. Stone, *ibid.*, **83**, 4138 (1961).

(3) D. E. Young, G. E. McAchran, and S. G. Shore, *ibid.*, **88**, 4390 (1966).

(4) D. R. Schultz and R. W. Parry, *ibid.*, **80**, 4 (1958).

(5) S. R. Shore and R. W. Parry, *ibid.*, **80**, 8 (1958).

(6) V. P. Sorokin, B. I. Vesnina, and N. S. Klimova, *Zh. Neorg. Khim.*, **8**, 66 (1963).

venient means for handling diborane for chemical applications and can be used to prepare high-purity borane adducts.

Acknowledgments.—We thank Callery Chemical Co. for providing materials and facilities for some of this work and the Air Force Office of Scientific Research (Grant AFOSR872-65) and the National Science Foundation (Undergraduate Research Grant GY7375) for partial support of this work.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF NORTH CAROLINA,
CHAPEL HILL, NORTH CAROLINA 27514

Magnetic Properties of Hexaamminechromium(III) Pentachlorocadmate(II)

BY WILLIAM E. ESTES,[1a] DAVID Y. JETER,[1b]
JUDITH C. HEMPEL, AND WILLIAM E. HATFIELD*

Received September 21, 1970

Recent structural investigations[2,3] have revealed interesting variances in the equatorial *vs.* axial metal–ligand bond distances in the trigonal-bipyramidal anions $CuCl_5^{3-}$ and $CdCl_5^{3-}$. In the copper compound the axial and equatorial bond distances are 2.295 and 2.392 Å, respectively, while in the cadmium compound $(Cd–Cl)_{ax}$ = 2.527 Å and $(Cd–Cl)_{eq}$ = 2.564 Å. These unique five-coordinate complexes may be stabilized in the solid state by hexaammine cations of cobalt(III), chromium(III), and rhodium(III). It has been suggested that the electronic structure of the copper ion is responsible for the inequivalences of the bond distances. This question remains as an interesting problem to be considered elsewhere. Recently, it was shown that the pentachlorocuprate ions in $[Co(NH_3)_6][CuCl_5]$ are antiferromagnetically coupled with a transition near 8°K.[4] It was of interest to determine whether comparable interactions occurred between hexaamminechromium(III) cations in the analogous compound $[Cr(NH_3)_6][CdCl_5]$. The results of our studies are reported in this note.

Experimental Section

Preparation of Hexaamminechromium(III) Pentachlorocadmate(II).—Hexaamminechromium(III) chloride (0.8 g, 4.6 mmol) and cadmium chloride dihydrate (2.0 g, 91 mmol) were dissolved in water (60 ml), and the resulting solution was filtered and heated to 60°. Concentrated hydrochloric acid (20 ml) was added to the warm solution and the resulting mixture was cooled in an ice bath for 30 min. The bright yellow crystals which precipitated were collected on a Büchner funnel, washed with ethanol (95%, 10 ml) and then with diethyl ether (10 ml), and were allowed to air dry on the filter frit for 20 minutes. The large well-formed crystals (0.35 g) were stored in the absence of light. *Anal.* Calcd for $[Cr(NH_3)_6][CdCl_5]$: N, 18.94; H, 4.09; Cl, 39.93. Found: N, 18.73; H, 4.05; Cl, 39.81.

Characterization.—The X-ray powder photograph obtained using a Philips X-ray generator and a Debye–Scherrer (114.6 mm) camera was substantially identical with the powder photographs of $[Cr(NH_3)_6][CuCl_5]$ and $[Co(NH_3)_6][CuCl_5]$. This similarity is considered to be good evidence that the $CdCl_5^{3-}$ ion has the trigonal-bipyramidal structure in $[Cr(NH_3)_6][CdCl_5]$. However, we must call attention to the difference in solubilities of the compound prepared here and the cobalt analog reported previously by Long, *et al.*[3] In the latter case it was necessary to use diffusion techniques in order to grow even the microcrystals necessary for X-ray diffraction studies.

Magnetic Measurements.—Magnetic susceptibilities of a powdered sample of the complex were determined at 294 and 77°K using a Faraday balance.[5] At several temperatures below 25°K, measurements were made with a Foner-type vibrating sample magnetometer,[6] with temperatures being measured with a calibrated germanium resistance thermometer. Both systems were calibrated using the magnetic susceptibility standard $HgCo(NCS)_4$.[7] Corrections were made for the diamagnetism of the constituent atoms using Pascal's constants[8] and for that of the sample holder assemblies.

Epr Measurements.—A sample of $[Cr(NH_3)_6][CdCl_5]$ diluted in the diamagnetic host $[Co(NH_3)_6][CdCl_5]$ was prepared by the method described above for the chromium compound except a 1:10 mole ratio of $[Cr(NH_3)_6]Cl_3$ to $[Co(NH_3)_6]Cl_3$ was used. The epr spectrum of a powdered sample of the diluted material was obtained at room temperature using a Varian Model 4502 X-band spectrometer with 100-kHz modulation at a frequency of 9.480 GHz. Magnetic field strengths were calibrated with an nmr probe. Cylindrical quartz sample tubes were used with the standard Varian E-4531 cavity.

Results

The magnetic susceptibility data for $[Cr(NH_3)_6][CdCl_5]$ are presented in Table I. The data obey the Curie–Weiss law over the entire temperature range with an intercept on the temperature axis at $\chi^{-1} = 0$ of −1.4°; thus θ = 1.4°K. From the relationship $\mu_{eff} = 2.828C^{1/2}$, with C = 1.813, we calculate a magnetic moment of 3.81 BM.

TABLE I

MAGNETIC SUSCEPTIBILITY DATA FOR HEXAAMMINECHROMIUM(III) PENTACHLOROCADMATE(II)

Temp, °K	$10^{-6}\chi_m^{cor}$, cgsu	Temp, °K	$10^{-6}\chi_m^{cor}$, cgsu	Temp, °K	$10^{-6}\chi_m^{cor}$, cgsu
4.2	307,800	6.2	238,900	14.0	119,500
4.9	288,300	7.0	219,400	22.0	73,690
5.2	276,800	8.3	193,000	77.0	24,200
5.7	255,400	10.4	158,000	293.8	6,080

The epr spectrum of a powdered sample of $[Cr(NH_3)_6][CdCl_5]$ diluted in the corresponding cobalt matrix is shown in Figure 1. The spectrum was analyzed by the method described recently by Mohrman, Garrett, and Lewis[9] using the axial spin Hamiltonian

$$\mathcal{H} = \beta\vec{H}\cdot g\cdot\vec{S} + D(S_z^2 - {}^5/_4) \qquad (1)$$

The energies of the components of the $^4A_2$ ground state manifold are given by[10]

$$H = H_z$$

$$E({}^3/_2, -{}^1/_2) = g_{||}\beta H/2 \pm (D + g_{||}\beta H) \qquad (2)$$

$$E(-{}^3/_2, +{}^1/_2) = -g_{||}\beta H/2 \pm (D - g_{||}\beta H)$$

---

[1] (a) NSF Undergraduate Research Participant, Summer 1970. (b) NSF Trainee, 1968–1971.

[2] K. N. Raymond, D. W. Meek, and J. A. Ibers, *Inorg. Chem.*, **7**, 1111 (1968).

[3] T. V. Long, A. W. Herlinger, E. F. Epstein, and I. Bernal, *ibid.*, **9**, 459 (1970).

[4] W. E. Hatfield and E. R. Jones, *ibid.*, **9**, 1502 (1970).

[5] W. E. Hatfield, C. S. Fountain, and R. Whyman, *ibid.*, **5**, 1855 (1966).

[6] S. Foner, *Rev. Sci. Instrum.*, **30**, 548 (1959).

[7] B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 4190 (1958).

[8] E. Konig, "Magnetic Properties of Transition Metal Compounds," Springer-Verlag, Berlin, 1966.

[9] L. E. Mohrmann, B. B. Garrett, and W. B. Lewis, *J. Chem. Phys.*, **52**, 535 (1970).

[10] B. R. McGarvey, *Transition Metal Chem.*, **3**, 89 (1967).