



Fig. 1.—The equivalent conductivity of $[\text{Co}(\text{NH}_3)_5\text{NO}][\text{NO}_3]_2 \cdot 0.5\text{H}_2\text{O}$, Δ ; of $\text{K}_4\text{Fe}(\text{CN})_6$, \circ ; and of $(\text{Co}(\text{NH}_3)_5\text{NO}_2)\text{Cl}_2$, \square .

The infrared frequencies are: 3300 (s), 1630 (m), 1490 (w), 1350 (vs), 1135 (m), 1050 (m), 930 (m), 850 (m), 820 (m), and 720 (w). The infrared spectrum of the compound was measured in Nujol and halocarbon mulls on a Beckman IR-9 spectrophotometer. The conductivity of the compound was measured as a function of concentration in nitrogen-purged distilled water using an Industrial Instruments, Inc., Model 16B2 conductivity bridge.

Results

The conductivity of the red cobalt nitrosopentaammine compound, along with that of $\text{K}_4\text{Fe}(\text{CN})_6$ ⁷ and $\text{Co}(\text{NH}_3)_5\text{NO}_2\text{Cl}_2$,⁸ is shown in Fig. 1. This graphical method for presenting the conductivity data has been found to be most advantageous.⁹ It consists of extrapolating the conductivity to infinite dilution to obtain Λ_0 , and then plotting the data as a function of $\Lambda_0 - \Lambda$. In this way a large variety of ion types can be compared on a single graph.

The slope, $\Lambda_0 - \Lambda/\sqrt{C}$, is a function of the electrolyte type and, as can be seen from Fig. 1, clearly distinguishes between 2:1 and 4:1 electrolytes. The fact that the slope of the red isomer is identical with that of $\text{K}_4\text{Fe}(\text{CN})_6$ unequivocally establishes the red isomer as a 4:1 electrolyte.

Discussion

The fact that the red isomer is a 4:1 electrolyte iden-

tifies it as the dimer, as was originally postulated by Werner.⁵ These results are in agreement with the ionic weight of the red isomer measured by Brintzinger.¹⁰ He found an ionic weight of 380 (vs. 348 calcd. for the dimer) for the red cobalt pentaammine. These results were also confirmed by recent ion-exchange measurements.¹¹

The way in which the complex dimerizes cannot be decided on the basis of the conductivity measurements. The polarographic measurements indicate that the cobalt atom in the red isomer is similar to complexes of the type $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$, and should be formulated as a dimeric $\text{Co}(\text{III})$ pentaammine complex. The absorption at 1050 cm^{-1} in the infrared spectrum occurs in the same region in which the hyponitrite ion absorbs.¹² It is therefore concluded that the red isomer is the cobalt(III) pentaammine hyponitrite, $[(\text{NH}_3)_5\text{CoON}=\text{NOC}(\text{NH}_3)_5]^{4+}$.

It was not possible to measure the conductivity of the black isomer because of its instability. However, it must be the monomeric nitrosyl. This agrees with the conclusion of Bertin³ that the black isomer is a nitrosyl with the nitrosyl frequency at 1620 cm^{-1} . Although not pointed out by the authors in ref. 3, this frequency is in good agreement with the nitrosyl frequency found for $[(\text{CH}_3)_2\text{NCS}_2]_2\text{NOCO}$.¹³

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(11) M. Ardon, *Bull. Res. Council Israel*, **11A**, 182 (1962).

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N-Methylpyridinium Triiodotetracarbonylmetallates of Molybdenum and Tungsten

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Received January 20, 1964

The anion $[\text{Cr}(\text{CO})_5\text{I}]^-$ has been oxidized to neutral $\text{Cr}(\text{CO})_5\text{I}$ by treatment with certain oxidizing agents such as triiodide ion, ferric ion, and aqueous hydrogen peroxide.¹ It seemed of interest to investigate oxidation of the analogous molybdenum and tungsten derivatives $[\text{M}(\text{CO})_5\text{I}]^-$,² readily available as their N-methylpyridinium salts, in order to prepare neutral carbonyl iodide derivatives of these metals.

Studies on the iodine oxidation of the salts $[\text{C}_5\text{H}_5\text{NCH}_3][\text{M}(\text{CO})_5\text{I}]$ (M = Mo or W) have instead led to the unexpected discovery of the interesting derivatives $[\text{C}_5\text{H}_5\text{NCH}_3][\text{M}(\text{CO})_4\text{I}_3]$ described in this note.

(1) H. Behrens and H. Zizlsperger, *Z. Naturforsch.*, **16b**, 349 (1961).

(2) M refers to molybdenum and tungsten.

(7) The International Critical Tables, Vol. 6, The Maple Press Co., York, Pa., 1929, p. 253.

(8) N. R. Dhar, *Z. anorg. Chem.*, **84**, 225 (1914).

(9) R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, in press.

TABLE I
 INFRARED AND PROTON N.M.R. SPECTRA

	(A) Infrared spectra, cm^{-1}	
	Metal carbonyl bands ^a	Other bands ^b
$[\text{C}_5\text{H}_5\text{NCH}_3][\text{Mo}(\text{CO})_4\text{I}_3]$	2065 (s), 2003 (s), 1994 (s), 1961 (s), 1941 (s)	1630 (w), 1580 (vww), 1495 (sh), 1485 (vw), 1304 (vww), 1280 (vw), 1185 (vw), 764 (w), 758 (w)
$[\text{C}_5\text{H}_5\text{NCH}_3][\text{W}(\text{CO})_4\text{I}_3]$	2067 (s), 1995–1983 (s, br), 1949 (s), 1930 (s)	1626 (w), 1574 (vww), 1485 (w), 1300 (vww), 1280 (w), 1183 (w), 763 (w), 756 (w)

(B) Proton n.m.r. spectra of some N-methylpyridinium derivatives, τ

	Ring protons ^c			Methyl protons
	ortho ^d	para ^e	meta	
$[\text{C}_5\text{H}_5\text{NCH}_3]\text{I}^f$	0.72	1.34	1.76	5.33
$[\text{C}_5\text{H}_5\text{NCH}_3][\text{Mo}(\text{CO})_5\text{I}]^f$	0.91	1.35	1.70	5.38
$[\text{C}_5\text{H}_5\text{NCH}_3][\text{W}(\text{CO})_4\text{I}_3]^f$	0.90	1.33	1.72	5.37
$[\text{C}_5\text{H}_5\text{NCH}_3][\text{Mo}(\text{CO})_4\text{I}_3]^g$	0.91	1.37	1.77	5.37

^a Beckman IR-9 spectrometer, halocarbon oil mull. ^b Perkin-Elmer Model 21 with NaCl optics, KBr pellet. ^c Assignment of the ring protons made by comparison with the spectrum of pyridine given by the Varian Associates N.M.R. Spectra Catalog, 1962, spectrum 96. ^d Apparent doublets, separation ~ 5 c.p.s. ^e Apparent doublets, separation 8–10 c.p.s. ^f Acetone solution. ^g Hexa-deuterioacetone solution.

Experimental

Microanalyses were performed by Pascher Mikroanalytisches Laboratorium, Bonn, Germany. Infrared spectra were taken in potassium bromide pellets and recorded on a Perkin-Elmer Model 21 spectrometer. In addition, the metal carbonyl regions of the new compounds were investigated in greater detail in halocarbon oil mulls and recorded on a Beckman IR-9 grating spectrometer. Proton n.m.r. spectra were recorded on a Varian A-60 spectrometer.

The salts $[\text{C}_5\text{H}_5\text{NCH}_3][\text{M}(\text{CO})_5\text{I}]^2$ were prepared from the corresponding hexacarbonyls and N-methylpyridinium iodide by published procedures or minor modifications thereof.^{3,4}

Preparation of the Derivatives $[\text{C}_5\text{H}_5\text{NCH}_3][\text{M}(\text{CO})_4\text{I}_3]$.²—A 0.8–1.2-mmol sample of $[\text{C}_5\text{H}_5\text{NCH}_3][\text{M}(\text{CO})_5\text{I}]^2$ was partially dissolved in ~ 50 ml. of chloroform. The resulting yellow solution was titrated immediately⁵ with a 0.06–0.07 *M* chloroform solution of iodine of predetermined normality. Initially the purple color of the iodine solution was discharged immediately upon contact with the $[\text{C}_5\text{H}_5\text{NCH}_3][\text{M}(\text{CO})_5\text{I}]^2$. The rather unclear end point of the titration was reached when the reaction mixture assumed a noticeably darker brown color due to persistence of the purple color of excess iodine mixed with the yellow solution. In several experiments with either the molybdenum or the tungsten derivative iodine consumption ranged from 0.89 to 1.08 moles of I_2 for each mole of $[\text{M}(\text{CO})_5\text{I}]^2$.

At about the midpoint of each titration yellow crystals of $[\text{C}_5\text{H}_5\text{NCH}_3][\text{M}(\text{CO})_4\text{I}_3]$ began to separate from the solution. After filtration fairly pure samples of $[\text{C}_5\text{H}_5\text{NCH}_3][\text{M}(\text{CO})_4\text{I}_3]$ were obtained in $\sim 80\%$ yield. The analytical samples were purified further by recrystallization from dichloromethane-hexane mixtures.

Anal. (A) $[\text{C}_5\text{H}_5\text{NCH}_3][\text{Mo}(\text{CO})_4\text{I}_3]$: Calcd. for $\text{C}_{10}\text{H}_5\text{I}_3\text{NO}_4\text{Mo}$: C, 17.6; H, 1.2; N, 2.1; I, 55.8; Mo, 14.0; O, 9.4. Found: C, 17.8; H, 1.4; N, 2.1; I, 54.9; Mo, 14.0; O, 9.8. (B) $[\text{C}_5\text{H}_5\text{NCH}_3][\text{W}(\text{CO})_4\text{I}_3]$: Calcd. for $\text{C}_{10}\text{H}_5\text{I}_3\text{NO}_4\text{W}$: C, 15.6; H, 1.0; N, 1.8; I, 49.4; W, 23.9; O, 8.3. Found: C, 16.1; H, 1.4; N, 1.9; I, 49.6; W, 24.6; O, 8.4.

Conductivity. (A) $[\text{C}_5\text{H}_5\text{NCH}_3][\text{Mo}(\text{CO})_4\text{I}_3]$: The molar conductances of acetone solutions ranged from 211 $\text{ohm}^{-1} \text{cm}^2$.

mole⁻¹ in a 1.232×10^{-3} *M* solution to 188 $\text{ohm}^{-1} \text{cm}^2$ mole⁻¹ in a 2.93×10^{-3} *M* solution. (B) $[\text{C}_5\text{H}_5\text{NCH}_3][\text{W}(\text{CO})_4\text{I}_3]$: The molar conductances of acetone solutions ranged from 200 $\text{ohm}^{-1} \text{cm}^2$ mole⁻¹ in a 9.95×10^{-4} *M* solution to 181 $\text{ohm}^{-1} \text{cm}^2$ mole⁻¹ in a 3.41×10^{-3} *M* solution. (C) $[\text{C}_5\text{H}_5\text{NCH}_3][\text{W}(\text{CO})_5\text{I}]$: The molar conductances of acetone solutions ranged from 208 $\text{ohm}^{-1} \text{cm}^2$ mole⁻¹ in a 1.42×10^{-3} *M* solution to 179 $\text{ohm}^{-1} \text{cm}^2$ mole⁻¹ in a 7.06×10^{-3} *M* solution.

Discussion

The proton n.m.r. spectra of the compounds $[\text{C}_5\text{H}_5\text{NCH}_3][\text{M}(\text{CO})_4\text{I}_3]$ (Table I), besides indicating diamagnetism, correspond entirely to those of the two well-established N-methylpyridinium derivatives $[\text{C}_5\text{H}_5\text{NCH}_3]\text{I}$ and $[\text{C}_5\text{H}_5\text{NCH}_3][\text{Mo}(\text{CO})_5\text{I}]$. These data and the high conductivity of acetone solutions of the $[\text{C}_5\text{H}_5\text{NCH}_3][\text{M}(\text{CO})_4\text{I}_3]$ compounds clearly indicate them to be salts containing the N-methylpyridinium cation and the previously unreported diamagnetic heptacoordinate $[\text{M}(\text{CO})_4\text{I}_3]$ anions.² These anions are isoelectronic with the previously reported heptacoordinate compounds of the type $\text{L}_2\text{M}(\text{CO})_3\text{I}_2$ ($\text{L}_2 = \text{C}_6\text{H}_4\text{-As}(\text{CH}_3)_2$)⁶ or $\text{CH}_3\text{SCH}_2\text{CH}_2\text{SCH}_3$.^{2,7}

The formation of the $[\text{M}(\text{CO})_4\text{I}_3]^-$ anions from the $[\text{M}(\text{CO})_5\text{I}]^-$ anions and iodine is exactly analogous to the formation of $\text{L}_2\text{M}(\text{CO})_3\text{I}_2$ from $\text{L}_2\text{M}(\text{CO})_4\text{I}^2$ and iodine and^{6,7} to the formation of $\text{Fe}(\text{CO})_4\text{I}_2$ from iron pentacarbonyl and iodine.⁸ Attempts to prepare $\text{W}(\text{CO})_4\text{I}$ analogous to $\text{Cr}(\text{CO})_5\text{I}^1$ by treatment of a chloroform solution of $[\text{C}_5\text{H}_5\text{NCH}_3][\text{W}(\text{CO})_5\text{I}]$ with iodine in the mole ratio 0.5 mole of $\text{I}_2/1.0$ mole of $[\text{W}(\text{CO})_5\text{I}]^-$ led instead only to the production of $[\text{W}(\text{CO})_4\text{I}_3]^-$ in lesser quantity. On the other hand, treatment of $[\text{C}_5\text{H}_5\text{NCH}_3][\text{Cr}(\text{CO})_5\text{I}]$ in chloroform solution with iodine led to blue-green $\text{Cr}(\text{CO})_5\text{I}^1$ rather than to $[\text{C}_5\text{H}_5\text{NCH}_3][\text{Cr}(\text{CO})_4\text{I}_3]$. It is thus apparent that the stable iodination products of $[\text{Cr}(\text{CO})_5\text{I}]^-$

(3) B. Moore and G. Wilkinson, *Proc. Chem. Soc.*, 61 (1959), described this method of preparation of $[\text{C}_5\text{H}_5\text{NCH}_3][\text{Mo}(\text{CO})_5\text{I}]$ but incorrectly formulated the product. This formulation was corrected by Fischer and Fele.⁴

(4) E. O. Fischer and K. Öfele, *Ber.*, **93**, 1156 (1960).

(5) If the chloroform solution of $[\text{C}_5\text{H}_5\text{NCH}_3][\text{M}(\text{CO})_5\text{I}]^2$ is allowed to stand at room temperature, decomposition occurs with carbon monoxide evolution.

(6) H. L. Nigam, R. S. Nyholm, and M. H. B. Stiddard, *J. Chem. Soc.*, 1806 (1960).

(7) H. C. E. Mannerskantz and G. Wilkinson, *ibid.*, 4454 (1962).

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and its molybdenum and tungsten analogs are entirely different, apparently due to the reluctance for the 3d-transition metal chromium, unlike the 4d- and 5d-transition metals molybdenum and tungsten, to attain a coordination number greater than six, at least with monodentate ligands.

Acknowledgment.—The author is indebted to Mr. M. B. Bisnette for experimental assistance.

CONTRIBUTION FROM PENNSALT CHEMICALS CORPORATION,
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High Temperature, High Pressure Synthesis of a New Bismuth Sulfide

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Received December 18, 1963

The preparation of a new bismuth sulfide of empirical formula BiS_2 has recently been carried out in our laboratory. To our knowledge, this is the first bismuth sulfide reported with a S:Bi ratio greater than 3:2. The product, consisting of soft, gray, needle-like crystals, resulted when a 4:11 atomic mixture of Bi and S, each of greater than 99% purity, was subjected to a pressure of 50 kbars and a temperature of 1250° for 5–10 min. The tetrahedral anvil apparatus¹ and procedure² have been described previously in detail. The only addition was a boron nitride insulating sleeve placed between the sample pellet and the graphite heating sleeve. Excess sulfur present in the product was removed by several CS_2 washings followed by ethanol rinsing and vacuum drying.

Anal. Calcd. for BiS_2 : Bi, 76.5; S, 23.5. Found: Bi, 74.0, 73.4; S, 23.0, 23.2. These results were supported by determination of weight losses on oxidation of two samples in pure O_2 . Loss calculated for BiS_2 converted to Bi_2O_3 : 14.7; found: 14.7, 15.0. The results of analysis of the residue were as follows. *Anal.* Calcd. for Bi_2O_3 : Bi, 89.7; S, 0.0. Found: Bi, 90.0; S, <0.1. When heated *in vacuo* to 300°, the product decomposed to Bi_2S_3 , as evidenced by the X-ray diffraction pattern of the residue.

The *d* spacings (Å) and relative intensities of the strongest lines of the X-ray diffraction powder pattern obtained from the new sulfide were: 3.11, 100; 2.91, 60; 2.62, 65; 2.27, 60; 1.88, 70; 1.81, 70; and 1.504, 60.

No conclusions can as yet be drawn about the structure of this sulfide. Nevertheless, the possibility exists that bismuth is present in both +3 and +5 oxidation states, as, e.g., if the compound were Bi^{+3} .

(1) E. C. Lloyd, U. O. Hutton, and D. P. Johnson, *J. Res. Natl. Bur. Std.*, **63C**, 59 (1959).

(2) J. R. Soulen and M. S. Silverman, *J. Polymer Sci.*, **1**, 823 (1963).

$(\text{BiS}_4)^{-3}$. We hope to carry out single crystal X-ray studies to determine the structure of the compound.

Acknowledgments.—This investigation was supported in part by the Office of Naval Research. The author is indebted to Dr. J. R. Soulen for helpful discussions and to our analytical and shop groups for their assistance.

CONTRIBUTION FROM THE UNIVERSITY OF CALIFORNIA,
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The System Beryllium Oxide–Water at Moderate Temperatures and Pressures¹

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Received October 7, 1963

The successful synthesis of BeO crystals by hydrothermal techniques and the design of nuclear reactor components containing BeO for higher ambient service temperatures and pressures requires some knowledge of compound stability regions. This paper reports, in the absence of suitable data,^{1–9} the phase relationships which exist at moderate temperatures and pressures in the system $\text{BeO-H}_2\text{O}$.

Experimental

The impurities in the $\beta\text{-Be(OH)}_2$ powder used in the studies, determined by emission spectrographic analysis, were: Cr, 25 p.p.m.; Cu, 60 p.p.m.; Sn, 12 p.p.m.; Pt, 20 p.p.m.; Si, 60 p.p.m.; Ni, 60 p.p.m.; Al, 12 p.p.m.; Fe, 20 p.p.m.; Mg, 5 p.p.m.; Mn, 7 p.p.m.; Zr, 100 p.p.m.; B, 4 p.p.m.; S, 16,000 p.p.m.

The loss in weight on igniting the $\beta\text{-Be(OH)}_2$ at 1200° was 43.78% and probably represents losses due to the volatilization of water (41.87% theoretical) and the decomposition of anion impurities such as fluorides, sulfates, phosphates, or carbonates. The surface area, measured by nitrogen absorption, was determined to be 45 m^2/g . Observations using the petrographic and electron microscope showed the material to consist mainly of spherical aggregates 0.5–1.0 μ in diameter. Some bladed crystals, 14–23 μ in length, were occasionally observed. The refractive index of these crystals was 1.585 ± 0.015 . The optical sign was uniaxial negative and the birefringence was low.

Studies were conducted by wrapping samples of the $\beta\text{-Be(OH)}_2$ powder in platinum envelopes and inserting the envelopes in pressure vessels. The vessels were connected to calibrated Bourdon tube gages and a source of high pressure water by a system of valves and fittings. The vessels were heated at the chosen

(1) Work performed under the auspices of the U. S. Atomic Energy Commission.

(2) (a) M. G. Berkman and S. L. Simon, Argonne National Laboratory Report ANL-4177, July 15, 1948 (unclassified); (b) C. A. Hutchison, Jr., and J. G. Malm, *J. Am. Chem. Soc.*, **71**, 1338 (1949).

(3) H. V. Wartenberg, *Z. Elektrochem.*, **55**, 445 (1951).

(4) L. I. Grossweiner and R. L. Seifert, *J. Am. Chem. Soc.*, **74**, 2701 (1952).

(5) G. R. B. Elliott, "Gaseous Hydrated Oxides, Hydroxides, and Other Hydrated Molecules," University of California Lawrence Radiation Laboratory (Berkeley) Rept. UCRL-1831, June, 1952 (unclassified).

(6) D. T. Livey and P. Murray, *J. Nucl. Energy*, **2**, 202 (1956).

(7) R. L. McKisson, *J. Nucl. Mater.*, **2**, 196 (1959).

(8) W. A. Young, *J. Phys. Chem.*, **64**, 1003 (1960).

(9) J. E. Antill, "The Volatilization of Beryllia in a High Temperature Gas Cooled Reactor," AERE-M-917, 1961 (official use only).