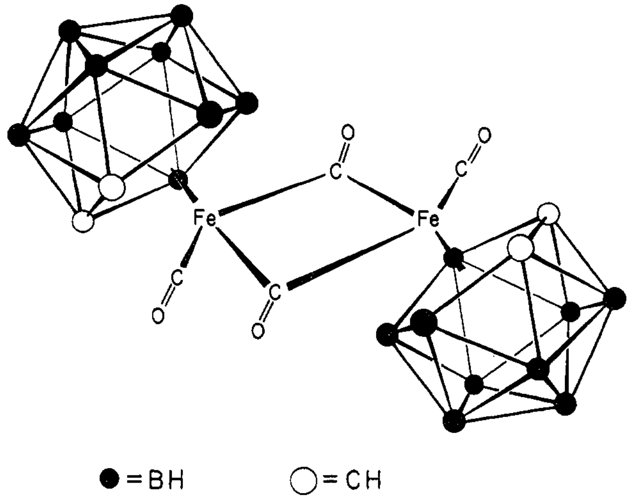

Figure 1.—Schematic structure proposed for the *trans*-[(3)-1,2-$B_9C_2H_{11}]_2Fe_2(CO)_4^{2-}$ ion.

suggests a species containing only terminal carbonyl groups, possibly the [π-(3)-1,2-$B_9C_2H_{11}$]$Fe(CO)_2^{2-}$ ion. No attempts were made to isolate the latter mononuclear ion.

If iron pentacarbonyl and (3)-1,2-$B_9C_2H_{11}^{2-}$ are used in a molecular ratio of 1:1, [π-(3)-1,2-$B_9C_2H_{11}]_2Fe^{2-}$ is formed in addition to the carbonyl complex.

Dicobalt octacarbonyl treated for 1 hr with a tetrahydrofuran solution of the (3)-1,2-dicarbollide ion at the reflux temperature gives a green solution. Precipitation with tetramethylammonium chloride, chromatography on polyamide, and recrystallization from ethanol gives yellow crystals of [$(CH_3)_4N$][π-(3)-1,2-$B_9C_2H_{11}$]$Co(CO)_2$. In both the solid state and solution the complex exhibits extreme air sensitivity, which makes purification very difficult. Even when kept under nitrogen, the solid complex partially decomposes within days.

The complex (Nujol mull) exhibits three strong carbonyl bands in the infrared spectrum at 2010, 1949, and 1924 cm^{-1}. In ethanol solution only the first two bands appear, which is more in agreement with two carbonyl groups. The pattern in the region of 1200–900 cm^{-1} indicates the presence of the (3)-1,2-$B_9C_2H_{11}$ group. The ^{11}B nmr spectrum again shows two doublets with a relative intensity of approximately 1:2 and resembles that of the chromium carbonyl complex.

So far, similar reactions with nickel tetracarbonyl were unsuccessful, owing to purification problems. Although a brown tetramethylammonium salt of an ion displaying both B–H (2520 cm^{-1}) and CO bands (1870 and 1820 cm^{-1}) in the infrared spectrum has been isolated, analytical data and ^{11}B nmr spectra indicate the presence of impurities.

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Sodium 6-Niobo(ethylenediamine)cobaltate(III) and Its Chromate(III) Analog

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In the course of investigating some transition metal heteropolyniobates,[1] compounds of chromium(III) and cobalt(III) with ethylenediamine (en) have been obtained. To our knowledge, these are the first heteropoly complexes reported in which a polydentate ligand, as well as a heavy oxometalate group, is bound to the heteroion.

Experimental Section

Starting Materials.—All materials used were commercially available reagents. Niobium(V) oxide (99.9+%) was obtained through Gallard-Schlesinger Chemical Mfg. Co.

Potassium 6-Niobate.—Niobium(V) oxide was fused with excess KOH in a nickel crucible, and the product was extracted with a minimum amount of water to remove most of the excess KOH. After the crude niobate was washed with an ethanol–water mixture, it was dissolved in water, and the solution was heated and filtered and made about 1 *M* in niobium. The product was precipitated with ethanol,[2] filtered, and washed successively with 1:1 v/v ethanol–water, 95% ethanol, and diethyl ether, and then air dried.

Anal. Calcd for $K_7HNb_6O_{19} \cdot 13H_2O$: Nb, 40.7; H_2O, 17.1. Found: Nb, 40.2; H_2O, 17.5.

Sodium 6-Niobate.—An aqueous solution of potassium 6-niobate, about 1 *M* in niobium, was heated, and sodium acetate was added to an excess concentration of 0.3 *M*. After cooling to 0–5°, the precipitated product was redissolved in a minimum amount of boiling water, and sodium acetate was added to a concentration of 0.3 *M*. After recooling to 0–5°, the recrystallized product was filtered, washed successively with 1:4 v/v ethanol–water, 95% ethanol, and ether, and air dried.

Anal. Calcd for $Na_7HNb_6O_{19} \cdot 15H_2O$: Nb, 43.1; H_2O, 20.8; Na, 12.4. Found: Nb, 42.6; H_2O, 21.6; Na, 11.9.

Tris(ethylenediamine)chromium(III) Iodide Hydrate and *trans*-Dichlorobis(ethylenediamine)cobalt(III) Chloride.—These were prepared according to published procedures.[3,4] Analyses were satisfactory.

Sodium 6-Niobo(ethylenediamine)cobaltate(III) Hydrate.[5]—A solution of sodium 6-niobate (2.6 g, 12 mg-atoms of Nb) in 60 ml of boiling water was treated with a fresh solution of 0.57 g (2 mmol) of *trans*-[$Co(en)_2Cl_2$]Cl in 20 ml of water. The resultant rose-purple mixture was boiled down to about half its initial volume, and 6 ml of 1 *M* NaOH was added. On continued boiling, the reddish purple solution turned blue-gray and then dark bluish green. The solution was centrifuged to remove a little light-colored fine precipitate. On cooling, a dusty greenish blue solid separated, leaving a red solution. This solid was recrystallized four times from hot 0.2 *M* sodium acetate. The product was finally collected, washed with 1:4 v/v ethanol–water followed by 95% ethanol, and air dried. The yield of greenish tinged blue powder was 0.7 g, about 25%.

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[3] J. C. Bailar, Jr., and C. L. Rollinson, *Inorg. Syn.*, **2**, 199 (1946).

[4] J. C. Bailar, Jr., *ibid.*, **2**, 222 (1946).

[5] Nomenclature follows that for heteropolymolybdates and -tungstates. The prefix "niobo" is used similarly to the prefixes "molybdo" and "tungsto."

Anal. Calcd for $Na_5Co(C_2H_8N_2)Nb_6O_{19}\cdot 18H_2O$ (mol wt, 1419.68): Na, 8.10; Co, 4.15; C, 1.69; H, 3.13; N, 1.97; Nb, 39.26; O, 41.70. Found: Na, 7.96; Co, 4.10; C, 1.79; H, 3.11; N, 2.01; Nb, 39.90; O, 41.13 (by difference) [$Na_{4.98}Co_{1.0}(en)_{1.05}Nb_{6.17}O_{18.90}(H_2O)_{18.05}$].

In larger scale syntheses, it was apparent that $Co(en)_3^{3+}$ was also a product of the reaction. The fine precipitate removed initially was yellow-pink. In addition, evaporation of the red solution left after obtaining the blue product led to the formation of brownish red crystals. These appeared to be the double salt $2Co(en)_3Cl_3\cdot NaCl\cdot 6H_2O$ by comparison with an authentic sample. In a separate experiment, $Co(en)_3^{3+}$ was found to give a pinkish yellow precipitate on reaction with sodium 6-niobate solution. This precipitate was unreactive under the conditions used for the above preparation of the niobate complex.

Sodium 6-Niobo(ethylenediamine)chromate(III) Hydrate.—Sodium niobate (2.6 g, 12 mg-atoms of Nb) was dissolved in 60 ml of boiling water. To this solution was added a warm solution of 1.26 g (2 mmol) of $Cr(en)_3I_3\cdot H_2O$ in 20 ml of water. A light pink-yellow to light orange milky precipitate formed immediately. The solution was boiled down to about half its initial volume, by which time the mixture had become purplish tinged. If the precipitate was allowed to settle, the solution was seen to be dull purple-violet. A 1 *M* NaOH solution (6 ml) was added and the evaporation was continued to a volume of about 20 ml, at which point the initial precipitate was all dissolved. The solution was centrifuged to remove a little light gray-green fine precipitate. Sodium acetate was added to the grayish violet solution to a concentration of about 0.3 *M*. On cooling, the solution became violet-purple, and a purplish pink product separated on standing at 0–5°. The product was recrystallized three or four times from hot 0.3 *M* sodium acetate by cooling to 0.5°. It was finally isolated by washing successively with cold 0.2 *M* sodium acetate, 1:4 v/v ethanol–water, and 95% ethanol and air dried at room temperature. About 1.7 g (roughly 60% yield) of purplish pink powder was obtained.

Anal. Calcd for $Na_5Cr(C_2H_8N_2)Nb_6O_{19}\cdot 18H_2O$ (mol wt, 1412.75): Na, 8.14; Cr, 3.68; C, 1.70; H, 3.14; N, 1.98; Nb, 39.46; O, 41.90. Found: Na, 7.96; Cr, 3.71; C, 1.74; H, 3.17; N, 1.92; Nb, 39.85; O, 41.75 (by difference) [$Na_{4.87}Cr_{1.0}(en)_{0.99}Nb_{6.03}O_{18.54}(H_2O)_{18.13}$].

Chemical Analyses.—Microanalyses were performed by J. Nemeth of the microanalytical laboratory of the chemistry department of the University of Illinois and by V. Mossotti and coworkers of the Materials Research Laboratory, University of Illinois. The procedure followed for the niobium analysis in the heteropolyniobates was that of Freund and Levitt.[6] A standard was prepared from 49.5 mg of high-purity niobium kindly supplied by Professor C. J. Altstetter of the metallurgy department of the University of Illinois. The samples were prepared by fusing approximately 55 mg with 2 g of $KHSO_4$ and 2 ml of H_2SO_4. The resulting solid was dissolved in 0.5 *M* tartaric acid and diluted to 250 ml. This method tended to give niobium concentrations up to 2.5% (error in the per cent composition) too high when carried out on known polyniobate compounds. An alternative method was also used in which the sample was fused with $KHSO_4$ and $K_2S_2O_8$, extracted with water, and then boiled to decompose excess $K_2S_2O_8$. Dilute HCl and HNO_3 were then added and the resulting precipitate was filtered, ignited, and weighed as Nb_2O_5. This method gave results which were up to 2.5% too low on known polyniobate compounds.

The cobalt concentration was determined by first fusing the heteropolyniobate complex with KOH and then extracting with water. HF was added followed by $NaNO_2$ to reduce any Co(III) to Co(II). The solution was boiled to expel nitrogen oxides and the Co(II) was determined with EDTA. The chromium concentration was determined by first fusing the sample with $KHSO_4$ and $K_2S_2O_8$. The fusion product was extracted with water and boiled. HF was then added and the chromium concentration was determined iodometrically. Sodium was determined by flame emission.

Electronic Absorption Spectra.—Aqueous solutions of the complexes were examined on a Cary 14 recording spectrophotometer from 1000 to 350 mμ.

Infrared Spectra.—Samples were pressed in KBr and the spectra were recorded from 500 to 4000 cm^{-1} on a Perkin-Elmer 521 instrument.

X-Ray Powder Patterns.—A 114.6-mm diameter Debye–Scherrer camera was used with Cu Kα radiation (λ 1.5418 Å, Ni filter). The temperature was about 25°.

Magnetic Susceptibilities.—Measurements were made on a Faraday balance at 23°. The balance was calibrated with $HgCo(SCN)_4$, $\chi = 16.44 \times 10^{-6}$ cgsu. All samples and the standard were enclosed in gelatin capsules. Diamagnetic corrections were taken from Mulay[7] for H_2O, C, H, N, Nb^{5+}, O^{2-}, Cr^{3+}, Co^{3+}, and Na^+. Measurements were taken over a range of five different magnetic field strengths. For the chromium complex, the values of Mulay gave a diamagnetic correction of -5.96×10^{-14} esu/mol. The bulk susceptibility was found to be 6.06×10^{-3} esu/mol. This gives a paramagnetic susceptibility of 6.66×10^{-3} esu/mol. For the cobalt sample, a small net negative deflection in the magnetic field was observed which led to a negative bulk susceptibility slightly greater (0.7×10^{-4}) in magnitude than the diamagnetic correction.

Ion-Exchange Experiments.—Strong-acid cationite (IR-120), weak-base anionite (IR-45), and strong-base anionite (IRA-401S) Mallinckrodt Amberlite resins were used. Strong-acid cationite in the K^+ form did not absorb the cobalt-containing species. Both weak-base and strong-base anionite in the Cl^- form adsorbed the cobalt complex strongly. Dilute KOH eluted the complex from the weak-base anionite; however, it was necessary to use HCl containing HF to decompose the complex in order to free it from the strong-base anionite. The charge on the adsorbed anion was determined by titrating the Cl^- liberated from the strong-base anionite. In two separate runs, the equivalent weights of the complex were indicated to be 288.1 and 292.5. This gives 4.93 and 4.85 equiv/mol for a formula weight of 1419.68, $Na_5Co(en)Nb_6O_{19}\cdot 18H_2O$.

Results and Discussion

These chromium and cobalt compounds appear stable indefinitely in the solid state and in aqueous solution. Treatment of the solutions with dilute acids gives gelatinous precipitates from which the original complexes are re-formed by addition of dilute sodium hydroxide. Their infrared spectra are nearly identical, being characterized by absorptions in the region 500–1000 cm^{-1}, attributed to metal–oxygen vibrations, and in the regions 1600–1650 and 2500–4000 cm^{-1}, assigned to water of crystallization.[8] These spectra are similar to that of sodium 6-niobate; indeed the close similarity in the 500–1000-cm^{-1} region suggests that the $Nb_6O_{19}^{8-}$ group[9] is present in these consistent with the stoichiometry. The X-ray powder patterns of the two compounds show that they are isostructural.

The absorption spectra of these complexes are typical of six-coordinate chromium(III) and low-spin cobalt(III) complexes.[10,11] For the chromium complex, the absorption maxima are λ_1 561 mμ, E_1 17.8

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kK, ϵ_1 39 and λ_2 409 mμ, E_2 24.4 kK, ϵ_2 26. For the cobalt complex, the maxima are λ_1 600 mμ, E_1 16.7 kK, ϵ_1 64 and λ_2 408 mμ, E_2 24.5 kK, ϵ_2 51.

Assuming that the simple Curie law is obeyed, the value of μ_{eff} for the chromium complex is estimated to be 3.98 ± 0.20 BM, and, for the cobalt complex, the effective magnetic moment is zero within the experimental error. Although it appears that the diamagnetic contributions may be somewhat underestimated, these values strongly suggest the presence of Cr(III) and Co(III), respectively. The ion-exchange experiment unequivocally favors an anion containing Co and Nb as opposed to a double salt containing a Co complex cation and isopolyniobate anion. In addition, the charge of 4.9 found for the anion agrees well with the charge of −5 expected for the $Co(en)Nb_6O_{19}^{5-}$ group.

From the method of synthesis and from the general behavior of ethylenediamine toward these metal ions, the ethylenediamine is most likely bidentate. The most reasonable way for the 6-niobate group to coordinate to form a stable complex is through three niobium-bridging oxygen atoms common to one face of the octahedron about the hetero atom. The sodium salts would then be formulated $Na_5[M^{III}(en)(Nb_6O_{19})(H_2O)]\cdot 17H_2O$. The proposed coordination of the 6-niobate group has actually been found in a hydrated sodium 12-niobomanganate(IV), whose structure will be described in a subsequent publication.

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The Chemistry of the Dinuclear Carbonyl Anions. V.[1] Sulfur-Bridged Derivatives

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A series of metal carbonyl anions of the type $M_2(CO)_{10}L^-$ (where L = H, I, Br, Cl, SCN, or CN and M = Cr or W) have recently been prepared[1,3,4] in which the ligand L bridges the two metal atoms. This series has now been extended to include anionic alkylthio and arylthio derivatives of chromium, molybdenum, and tungsten.

Experimental Section

All manipulations, except the weighing of starting materials and products, were carried out in an inert (N_2) atmosphere.

Materials.—The salts $[(C_6H_5)_3P]_2N[M(CO)_5Cl]$ (M = Cr, Mo, or W) were prepared photochemically using the metal hexacarbonyl and $[(C_6H_5)_3P]_2NCl$.[5] The cation employed in this study will hereafter be abbreviated as PPN.

The trialkyl(alkylthio)tin derivatives were prepared by the reaction of the trialkyltin chloride with an equimolar amount of mercaptan in diethyl ether in the presence of 1 equiv of triethylamine at ambient temperature. After removal of the precipitated triethylammonium chloride by filtration, the solvent was removed from the filtrate under vacuum and the residue was vacuum distilled. The properties of the products $(C_4H_9)_3SnSR$ (R = CH_3 and C_6H_5) were identical with those in the literature.[6] The benzylthio derivative $(CH_3)_3SnSCH_2C_6H_5$ had a boiling point of 52° (0.4 mm) and was used without further characterization.

Preparations of [PPN][$M_2(CO)_{10}SR$] Derivatives.—The preparations of all of the compounds were performed in an analogous manner. The analytical data and yields are presented in Table I.

In a typical reaction, 1.42 g of [PPN][$Cr(CO)_5Cl$] and 1.0 g of $(C_4H_9)_3SnSCH_3$ were stirred at ambient temperature in 50 ml of dichloromethane for 1 hr. The mixture was filtered and the solvent was removed from the filtrate under vacuum. The solid residue was extracted two times with 25-ml portions of diethyl ether. Pentane was added to the ether extract. A 0.71-g sample of product was obtained. It was recrystallized from ether and pentane.

Infrared Spectra.—The infrared spectra of the new compounds were obtained on solutions of approximately 0.005 g/ml in tetrahydrofuran in a 0.2-mm cell. The instrument, a Perkin-Elmer Model 621 spectrometer, was calibrated with indene. Table II tabulates the bands observed in the carbonyl stretching region.

Conductance Measurements.—The equipment employed has already been described.[7] The specific conductivity of the nitromethane used was 4.39×10^{-7}. The anion, concentration (M), and molar conductance (cm²/ohm mol) are: $Cr_2(CO)_{10}SCH_3^-$, 0.995×10^{-3}, 69.9; $W_2(CO)_{10}SCH_3^-$, 1.022×10^{-3}, 64.3; $Cr_2(CO)_{10}SC_6H_5^-$, 0.908×10^{-3}, 67.6; $W_2(CO)_{10}SC_6H_5^-$, 1.090×10^{-3}, 62.8. The chromium and tungsten derivatives containing the benzylthio group were too unstable in nitromethane solution for determination of their conductivities.

Nmr Measurements.—The ^1H nmr spectra of the methylthio and phenylthio derivatives were run in CH_2Cl_2 solutions using a Varian Model A-60 spectrometer and a Varian Model 4300 B spectrometer. The benzylthio derivatives were not sufficiently stable in the concentrated dichloromethane solutions to enable their spectra to be recorded.

Results and Discussion

A large number of metal carbonyl derivatives containing bridging alkylthio groups have been prepared.[8] However, until this work neither metal carbonyl derivatives with singly bridged alkylthio groups nor anionic metal carbonyl alkylthio derivatives had been reported. The previous observation that the metal hexacarbonyls $M(CO)_6$ (M = Cr, Mo, or W) react photochemically with certain anions to produce singly bridged anionic derivatives suggested that these metal hexacarbonyls might also react similarly with mercaptide ions as exemplified by

$$2Cr(CO)_6 + SCH_3^- \xrightarrow[THF]{uv} Cr_2(CO)_{10}SCH_3^- + 2CO$$

This reaction was found to take place but the yields were low. Higher yields were obtained by an adapta-

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