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.

Acknowledgment.—This work was supported in part by ARPA Grant SD-131.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
UNIVERSITY OF GEORGIA, ATHENS, GEORGIA 30601

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

BY J. K. RUFF AND R. B. KING[2]

Received August 30, 1968

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-

---

(1) Part IV: J. K. Ruff, *Inorg. Chem.*, **8**, 86 (1969). For related papers on organosulfur derivatives of metal carbonyls see R. B. King and C. A. Eggers, *ibid.*, **7**, 1214 (1968), and earlier papers of that series.

(2) Fellow of the Alfred P. Sloan Foundation, 1967–1969.

(3) J. K. Ruff, *Inorg. Chem.*, **7**, 1821 (1968).

(4) R. G. Hayter, *J. Am. Chem. Soc.*, **88**, 4376 (1966).

(5) R. Appel and A. Hauss, *Z. Anorg. Allgem. Chem.*, **311**, 290 (1961).

(6) E. W. Abel and D. B. Brady, *J. Chem. Soc.*, 1192 (1965).

(7) J. K. Ruff, *Inorg. Chem.*, **2**, 813 (1963).

(8) See E. W. Abel and B. C. Crosse, *Organometal. Rev.*, **2**, 443 (1967), for a recent review.

TABLE I

ANALYTICAL DATA FOR THE BIS(TRIPHENYLPHOSPHINE)IMINIUM ALKYLTHIODECACARBONYLDIMETALATES PREPARED IN THIS WORK

				Analyses, %									
				Calcd					Found				
Anion	Mp, °C	Yield, %	Color	C	H	N	S	M	C	H	N	S	M
$Cr_2(CO)_{10}SCH_3^-$	96–98	76	Orange	58.3	3.41	1.44	3.30	10.7	57.8	2.99	1.46	3.10	11.1
$Cr_2(CO)_{10}SCH_2C_6H_5^-$	111–112	16	Yellow-orange	60.9	3.54	1.34	3.06	9.95	59.7	3.16	1.40	2.71	10.1
$Cr_2(CO)_{10}SC_6H_5^-$	117–119	26	Yellow-orange	60.9	3.39	1.36	3.10	10.1	59.9	3.40	1.33	2.89	9.7
$W_2(CO)_{10}SCH_3^-$	103–105	80	Yellow-orange	45.8	2.68	1.14	2.60	29.8	45.5	2.68	1.23	2.44	29.4
$W_2(CO)_{10}SCH_2C_6H_5^-$	105–107	15	Yellow	48.6	2.83	1.07	2.44	28.4	48.4	2.85	1.02	2.41	27.8
$W_2(CO)_0SC_6H_5^-$	115–117	15	Yellow	48.2	2.70	1.08	2.47	28.5	48.4	2.80	1.10	2.30	28.0
$Mo_2(CO)_{10}SCH_3^-$	98–100	26	Yellow	53.4	3.12	1.33	3.02	18.2	52.7	3.29	1.32	2.85	18.6

TABLE II

INFRARED STRETCHING FREQUENCIES OF THE COMPOUNDS PREPARED IN THE ν(CO) REGION (CM^{-1})

$Cr_2(CO)_{10}SCH_3^-$	2055 w, 2035 m, 1972 w, sh, 1942 vs, 1911 m, 1878 s
$Cr_2(CO)_{10}SCH_2C_6H_5^-$	2048 w, 2031 m, 1967 w, sh, 1934 vs, 1908 m, 1874 s
$Cr_2(CO)_{10}SC_6H_5^-$	2051 w, 2036 m, 1972 w, sh, 1941 vs, 1906 m, 1864 s
$W_2(CO)_{10}SCH_3^-$	2060 w, 2047 m, 1968 w, sh, 1936 vs, 1907 m, 1874 s
$W_2(CO)_{10}SCH_2C_6H_5^-$	2058 w, 2046 m, 1967 w, sh, 1936 vs, 1905 m, 1866 s
$W_2(CO)_{10}SC_6H_5^-$	2055 w, 2040 m, 1973 w, sh, 1926 vs, 1908 m, 1869 s
$Mo_2(CO)_{10}SCH_3^-$	2059 w, 2045 m, 1974 w, sh, 1942 vs, 1916 m, 1874 s

tion of preparative techniques of Abel, Crosse, and Brady[9,10] utilizing reactions of the chloropentacarbonylmetalates with trialkyl(alkylthio)tin derivatives according to the equation

$$2M(CO)_5Cl^- + R'_3SnSR \longrightarrow M_2(CO)_{10}SR^- + R'_3SnCl + Cl^-$$

where R = CH_3, $CH_2C_6H_5$, or C_6H_5; R′ = CH_3 or C_4H_9; M = Cr, Mo, or W. No evidence was obtained in the above systems for the presence of a mononuclear alkylthio derivative $M(CO)_5SR^-$ even when a large excess of the trialkyltin mercaptide was employed. Apparently the mononuclear anion, $M(CO)_5SR^-$, is a sufficiently strong nucleophile to displace rapidly Cl^- from the $M(CO)_5Cl^-$ anion.

All of the $M_2(CO)_{10}SR^-$ anions were isolated as their bis(triphenylphosphine)iminium salts which were orange to yellow solids varying in stability according to the following sequences: M = W (most stable) > Cr ≫ Mo (least stable); R′ = CH_3 (most stable) > C_6H_5 > $C_6H_5CH_2$ (least stable). The lowest stability of the molybdenum complexes is in accord with previous studies on anionic bridged derivatives. The only molybdenum complex which could be isolated in this work was [PPN][$Mo_2(CO)_{10}SCH_3$]. This complex was not very stable and decomposed within 1 week at ambient temperatures. The other complexes containing chromium or tungsten were more stable in the solid state. However, in either dichloromethane or nitromethane solutions the stabilities of even these complexes were greatly reduced. This instability in solution prevented reliable measurements of the conductivity and proton nmr spectra of the benzyl derivatives.

The proton nmr and conductivity measurements supported the proposed formulas. Thus the proton nmr spectra of the methylthio derivatives [PPN][$M_2(CO)_{10}SCH_3$] showed only single peaks in the methyl region (M = Cr, τ 8.07; M = W, τ 8.32) and complex split resonances in the phenyl region. The integrated area ratios of the phenyl resonances to the methyl resonances in these two compounds were 10.2:1 (M = Cr) and 10.1:1 (M = W), respectively. This indicates the presence of only one SCH_3 group for each cation. The proton nmr spectra of the phenylthio derivatives [PPN][$M_2(CO)_{10}SC_6H_5$] exhibited only resonances in the phenyl region. These resonances were slightly more complex than those found in the nmr spectrum of the bis(triphenylphosphine)iminium cation alone. No hydridic hydrogen or paramagnetic impurities were found. The conductivity data on approximately 0.001 *M* solutions in nitromethane were consistent with the formulation of the salts as 1:1 electrolytes[11] (see Experimental Section).

The infrared spectra in the ν(CO) region of the new $M_2(CO)_{10}SR^-$ anions resemble closely those of the halodecacarbonyldimetalate anions $M_2(CO)_{10}X^-$ (X = Cl, Br, or I) with respect to the number, relative intensities, and spacings of the observed bands. One of the halodecacarbonyldimetalate anions, $Cr_2(CO)_{10}I^-$, has been shown by X-ray crystallography to have a bent iodine bridge.[12] This suggests that the new $M_2(CO)_{10}SR^-$ complexes with one SR bridge described in this publication likewise have bent SR bridges similar to those in the numerous known neutral metal carbonyl derivatives with two, three, and four SR bridges.

---

[9] E. W. Abel and B. C. Crosse, *J. Chem. Soc., A*, 1141 (1966).

[10] E. W. Abel, B. C. Crosse, and D. B. Brady, *J. Am. Chem. Soc.*, **87**, 4397 (1965).

[11] R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

[12] The Cr–I–Cr angle in the $Cr_2(CO)_{10}I^-$ ion is 118° and the Cr–I distance is 2.79 Å: L. Handy, J. K. Ruff, and L. F. Dahl, to be submitted for publication.