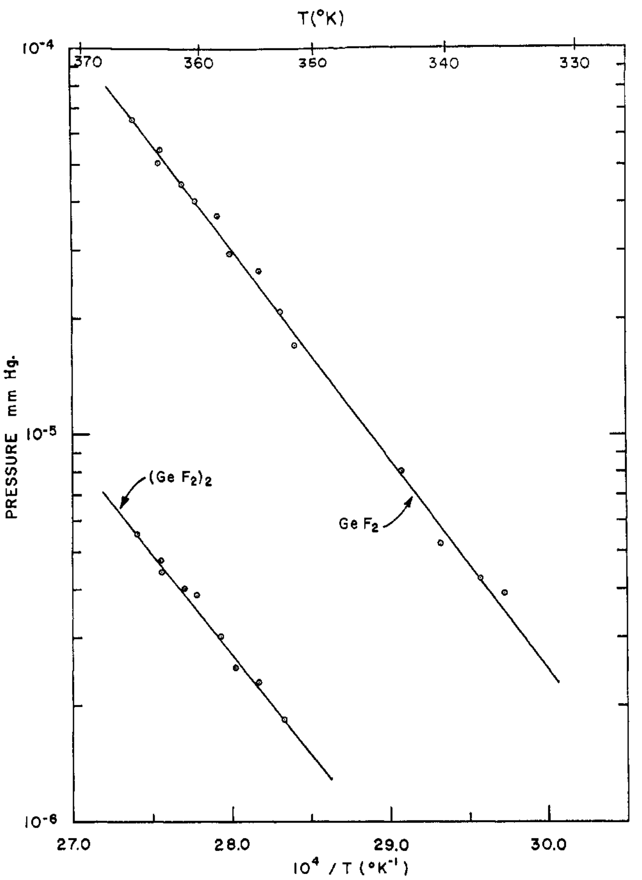

Figure 1.—Variation of GeF_2 monomer and dimer pressures as a function of temperature.

Table I

Thermodynamic Data for Reactions of $(GeF_2)_n$

Reaction	$\Delta H°_{861}$, kcal/mole	$\Delta G°_{861}$, kcal/mole	$\Delta S°_{861}$, eu
1. $GeF_2(s) \rightarrow GeF_2(g)$	27.0 ± 1	10.4 ± 0.5	46 ± 3
2. $2GeF_2(s) \rightarrow (GeF_2)_2(g)$	27.0 ± 1	12.1 ± 0.6	41 ± 3
3. $2GeF_2(g) \rightarrow (GeF_2)_2(g)$	-27.0 ± 1	-8.6 ± 1	-51 ± 2
4. $GeF_2(g) + (GeF_2)_2(g) \rightarrow (GeF_2)_3(g)$	-24 ± 3	-9.7 ± 1.5	-40 ± 5

possibility seems to be unlikely as a Ge–Ge bond is reported to be stronger than an Sn–Sn bond[7] but the stabilities of the dimers are found to be the reverse. The structure of the solid,[4] for which the unit cell is $(GeF_2)_4$, is also thought to involve a pseudo-tetrahedral arrangement about Ge with a tendency to form chains. Thus the latter type of structure seems very feasible.

If the decreasing stability trend from $(SnF_2)_2$ to $(GeF_2)_2$ continues to $(SiF_2)_2$ one can understand more readily the current lack of conclusive evidence for $(SiF_2)_n$ polymers in the vapor phase, particularly at higher temperatures.[3]

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(7) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p 348.

Contribution from the Institute of Chemistry,
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Monosubstituted Derivatives of Tetracobalt Dodecacarbonyl

By G. Cetini, O. Gambino, R. Rossetti,
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Tetracobalt dodecacarbonyl has both bridge and terminal CO groups.[1] Substitution of two bridging carbonyls by a bidentate ligand, such as an acetylenic compound, has been reported by Krüerke and Hübel;[2] the general formula of these compounds is $Co_4(CO)_{10}(RC_2R')$.

We wish to report the preparation of some new derivatives of $Co_4(CO)_{12}$ by the reaction

$$Co_4(CO)_{12} + L \rightleftharpoons Co_4(CO)_{11}L + CO \qquad (1)$$

where L [$= P(C_6H_5)_3$, $As(C_6H_5)_3$, or $Sb(C_6H_5)_3$] can displace one of the terminal CO groups.

The same reaction had already been carried out by Hieber and Breu.[3] Using more drastic experimental conditions than ours, they obtained the compound $[Co(CO)_3P(C_6H_5)_3]_2$ from $Co_4(CO)_{12}$ and $P(C_6H_5)_3$.

We employed petroleum ether (bp 40–70°) as solvent at room temperature and found that, with $P(C_6H_5)_3$, (1) was shifted completely to the right whereas with $As(C_6H_5)_3$ and $Sb(C_6H_5)_3$ equilibrium was soon reached with 70–80% of the start carbonyl still present. As a proof of this, gaseous CO was bubbled through solutions of $Co_4(CO)_{11}L$. With $L = As(C_6H_5)_3$ or $Sb(C_6H_5)_3$, $Co_4(CO)_{12}$ formed but not with $L = P(C_6H_5)_3$. In no case, however, did other carbonyl derivatives form, in particular, polysubstituted derivatives of $Co_4(CO)_{12}$.

Separation of the derivatives from unreacted $Co_4(CO)_{12}$ was accomplished by thin layer chromatography and by further crystallization from *n*-heptane. All of the compounds were obtained as dark brown crystals, relatively stable to air, insoluble in water but soluble in organic solvents such as *n*-heptane, benzene, CCl_4, etc. The brown solutions were found to be as air sensitive as those of $Co_4(CO)_{12}$. The infrared spectra (Table I) show bands in the CO stretching region at 2000–2100 cm^{-1} (terminal CO) and 1800–1900 cm^{-1} (bridging CO) and in the phenyl CH bending out of the plane region at 600–800 cm^{-1}. Figure 1 shows the spectrum of $Co_4(CO)_{11}P(C_6H_5)_3$ in *n*-heptane. The molecular weight determinations carried out in benzene (Mechrolab osmometer) on these compounds are in agreement with the $Co_4(CO)_{11}L$ formulation.

The compounds obtained would appear to be the first known $Co_4(CO)_{12}$ derivatives in which a monodentate ligand replaces a terminal CO group and, in all

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(1) P. Corradini, *Ric. Sci.*, **36**, 188 (1966); C. H. Wei and L. F. Dahl, *J. Am. Chem. Soc.*, **88**, 1821 (1966); D. L. Smith, *J. Chem. Phys.*, **42**, 1460 (1965); P. Corradini, *ibid.*, **31**, 1676 (1959).

(2) H. Krüerke and W. Hübel, *Ber.*, **94**, 2829 (1961).

(3) W. Hieber and R. Breu, *ibid.*, **90**, 1259 (1957).

TABLE I

ANALYTICAL DATA FOR MONOSUBSTITUTED DERIVATIVES OF $Co_4(CO)_{12}$

Compound	% C		% H		% Co		% O		% X[a]		Mol wt	
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
$Co_4(CO)_{11}P(C_6H_5)_3$	43.20	43.21	1.98	1.88	29.1	29.24	21.89	21.83	3.78	3.84	780	806
$Co_4(CO)_{11}As(C_6H_5)_3$	39.75	40.97	2.00	1.78	27.9	27.73	20.18	20.70	8.85	8.81	827	850
$Co_4(CO)_{11}Sb(C_6H_5)_3$	38.39	38.83	1.94	1.69	26.7	26.28	19.44	19.62	13.4	13.57	865	897

[a] X = P, As, or Sb.

TABLE II

INFRARED FREQUENCIES IN THE CO STRETCHING REGION OF MONOSUBSTITUTED DERIVATIVES OF $Co_4(CO)_{12}$

Compound	Medium	ν_{CO}, cm^{-1}					
$Co_4(CO)_{11}P(C_6H_5)_3$	*n*-Heptane	2084	2045	2039	2030	1854.5	1837.5
$Co_4(CO)_{11}As(C_6H_5)_3$	*n*-Heptane	2085	2045	2040	2031	1855	1837
$Co_4(CO)_{11}Sb(C_6H_5)_3$	*n*-Heptane	2085	2047	2041	2031	1855	1832

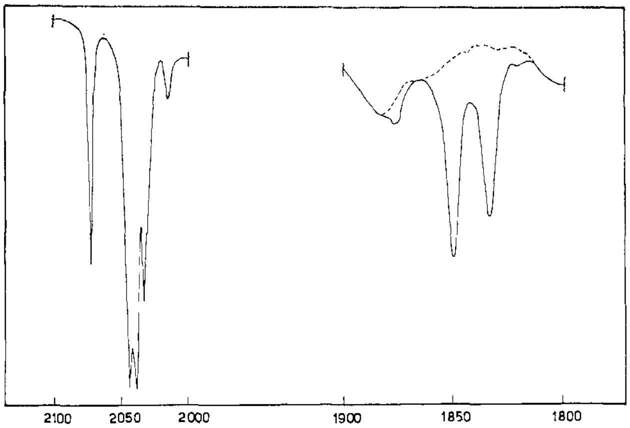

Figure 1.—Infrared spectrum of $Co_4(CO)_{11}P(C_6H_5)_3$ in *n*-heptane in the CO stretching region: ———, solution; – – – –, solvent.

probability, leaves the structure of the start molecule unchanged. It is thus possible that these compounds may throw new light on the still-debated problem of the structure of tetracobalt dodecacarbonyl. The two structures so far proposed[1] provide for the formation of one or two isomers of $Co_4(CO)_{11}L$ derivatives. In our case, subsequent crystallizations or thin layer chromatography separations with different solvents (*n*-heptane, CCl_4, CS_2, etc.) did not alter the characteristics of the compounds. It is, however, likely that two proposed isomers have very similar chemical and physical properties, and, for this reason, we do not feel that final conclusions can be drawn from the present series of experiments.

Experimental Section

Preparation of $Co_4(CO)_{11}P(C_6H_5)_3$.—A two-neck flask with a refluxing condenser, an He inlet, and an Hg valve was purged by He for 15 min. Then a solution of 2.40 g of $Co_4(CO)_{12}$ (4.2 mmol) in petroleum ether (100 ml) was introduced and treated with 50 ml of 0.10 *M* triphenylphosphine in ether solution.

The mixture was stirred at room temperature for 10 min, then separated by thin layer chromatography (Kieselgel G adsorbent, mixture CS_2–petroleum ether 1:1 developer). The solvent was removed *in vacuo* and the residue was dissolved in *n*-heptane and cooled at −20° to obtain $Co_4(CO)_{11}P(C_6H_5)_3$ in microcrystalline powder; yield, 1.62 g (48% with respect $Co_4(CO)_{12}$).

Preparation of $Co_4(CO)_{11}As(C_6H_5)_3$.—The reaction between $Co_4(CO)_{12}$ (3.15 g) and $As(C_6H_5)_3$ (1.80 g) was carried out for 1 hr in the same way as we have described before; yield, 0.75 g (16%) of $Co_4(CO)_{11}As(C_6H_5)_3$.

Preparation of $Co_4(CO)_{11}Sb(C_6H_5)_3$.—By a procedure similar to that described above 0.65 g of $Co_4(CO)_{11}Sb(C_6H_5)_3$ (yield 14%) was obtained from 2.95 g of $Co_4(CO)_{12}$ and 2.00 g of $Sb(C_6H_5)_3$.

Elemental analyses and molecular weights are reported in Table II.

CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY,
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Preparation and Characterization of μ-Hydroxo-μ-sulfato-octaaquodichromium(III)

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KEITH KIMBALL, AND ELLIOT UHLENHOPP

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Recently in this laboratory a mixture of sulfatochromium(III) species was separated using cation-exchange resin. It was observed that a dark green band was displaced just before the violet hexaaquochromium(III) band. The material in this band proved to be a new sulfatochromium(III) species, and this paper describes its synthesis and characterization.

Experimental Section

Reagents.—Dowex AG 50W-X8, 200–400 mesh ion-exchange resin in the hydrogen form, was used in all experiments. All other reagents were analytical reagent grade. Ordinary distilled water was used for all solutions.

Analytical Methods.—The procedures used to determine chromium and sulfate have been described previously.[1]

Preparation of $(H_2O)_4Cr(OH)(SO_4)Cr(H_2O)_4^{3+}$.—A starting solution was prepared by dissolving 120 g of $Cr_2(SO_4)_3 \cdot xH_2O$ into 300 ml of water and then adding 150 ml of 2 *M* NaOH solution over a 15-min period. The solution was then refluxed for 24 hr in a system protected from carbon dioxide by an Ascarite trap. A glass column of 2.2-cm i.d. was packed to a height of 32 cm with ion-exchange resin, rinsed with several column volumes of water, and loaded with 70 ml of reflux solution. After a water rinse, displacement was begun with a 0.2 *M* cerous perchlorate solution at a flow rate of 12 sec/drop. Displacement was halted after 190 ml of cerous solution had been added to the column. At this point a 4-cm purple band was observed halfway down the

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[1] J. Finholt, R. Anderson, J. Fyfe, and K. Caulton, *Inorg. Chem.*, **4**, 43 (1965).