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

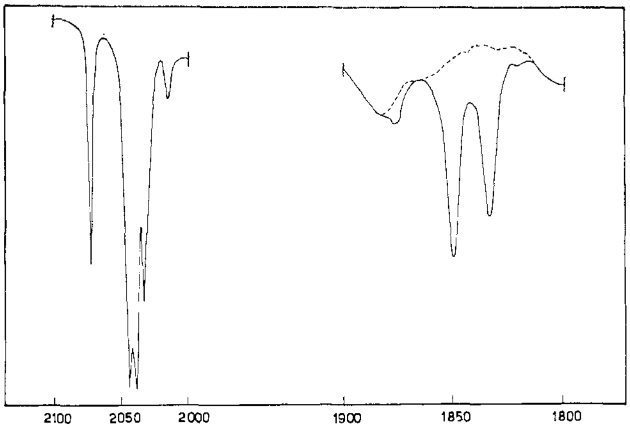

Figure 1.—Infrared spectrum of $Co_4(CO)_{11}P(C_6H_5)_3$ in *n*-heptane in the CO stretching region: ———, solution; – – – –, solvent.

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.

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Preparation and Characterization of μ-Hydroxo-μ-sulfato-octaaquodichromium(III)

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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).

column, and immediately below it was a 3-cm dark green band. The column was rinsed with water and the resin removed mechanically with an eye dropper. The material of the green band was placed on top of a 12.5-cm column of hydrogen-form resin in a glass column of 0.83-cm i.d. This second column was held at 0° by circulating ice water through an outer jacket. After rinsing with 0.1 *M* perchloric acid to remove any +1 species that might be present, displacement with 0.2 *M* cerous solution was continued at a flow rate of 15 sec/drop. After 60 ml of cerous solution had been added, the desired green band began to be eluted. A total of 40 ml of green solution was collected. A central cut of 20 ml was used for characterization studies.

The output of the ion-exchange column was about 0.2 *M* in chromium. A solution 1 *M* in chromium was prepared by removing water from the 0.2 *M* solution in a freeze-drying apparatus. The concentration procedure did not change the visible spectrum of the sample. Attempts to prepare a solid chloride salt by adding hydrogen chloride gas to the 1 *M* solution at −8° yielded only products containing coordinated chloride.

Characterization.—Characterization studies were conducted on solution obtained directly from the 0° ion-exchange separation. Purity of the sample was established initially by reabsorbing a fraction of the sample on another cooled ion-exchange column, displacing with cerous solution, and noting that only a single band could be observed. An analysis for chromium and sulfate gave a SO_4:Cr mole ratio of 0.498 ± 0.005. Measurement of the total charge concentration (normality) of the displacing solution together with the pH and chromium concentration of the green solution coming off the column allowed the average charge per chromium atom to be determined as 1.52 ± 0.02. The procedure is described elsewhere.[2]

Spectra.—Visible and ultraviolet spectral measurements were made on a solution of 0.03 *M* μ-hydroxo-μ-sulfato-octaaquodichromium(III) perchlorate in 0.1 *M* perchloric acid at 25° using a Cary Model 15 spectrophotometer. The positions and molar absorptivities of spectral peaks are as follows: 422 mμ, 21.0 cm^{-1} $mole^{-1}$ l.; 585 mμ, 19.5 cm^{-1} $mole^{-1}$ l.; shoulder at 672 mμ, 6.2 cm^{-1} $mole^{-1}$ l. The estimated error in the reported absorbancies is ±0.1 cm^{-1} $mole^{-1}$ l.

Infrared measurements were made on a 1 *M* solution of μ-hydroxo-μ-sulfato-octaaquodichromium(III) perchlorate in water using a Perkin-Elmer Model 521 spectrophotometer. The solution was held as a thin film between two silver chloride plates. The spectrum shows four peaks in the 900–1300-cm^{-1} region: 995 (m), 1035 (s), 1140 (s), and 1225 (s) cm^{-1}. The spectrum is shown in Figure 1.

Discussion

The charge per chromium atom result of +1.5 indicates that the total charge per species must be +3, +6, or some higher multiple of 3. Since the green species was displaced before the +3 hexaaquochromium(III) species, the charge per species must be +3. This means that each ion must contain two chromium atoms. The SO_4:Cr ratio of 0.5 shows that in addition to the two chromium atoms each ion contains one sulfate group. The proposed formula, $(H_2O)_4Cr(OH)(SO_4)Cr(H_2O)_4{}^{3+}$, is consistent with these observations.

The appearance of four bands in the 900–1300-cm^{-1} region of the infrared spectrum is evidence that the sulfate has C_{2v} symmetry and is acting as a bidentate ligand.[1,3] All of these peaks are due to sulfate group vibrations. The lines at 1225, 1140, and 1035 cm^{-1} are ν_3 and the line at 995 cm^{-1} is ν_1. Previous work has shown that sulfate is a monodentate ligand in monosulfatopentaaquochromium(III) chloride and it was suggested that the O–O distance in sulfate was too small for the sulfate to occupy two coordination positions on the chromium atom.[1] In the case of the dimer reported here, the sulfate can act as a bidentate by bridging the two chromium atoms in the dimer. The sulfate O–O distance should not be very critical for a bridging sulfate. The dimer must also contain a hydroxide bridging group. If the hydroxide ligand were not a bridging group it would be basic enough to acquire a proton in the pH 2 solution in which the charge per chromium atom was determined.

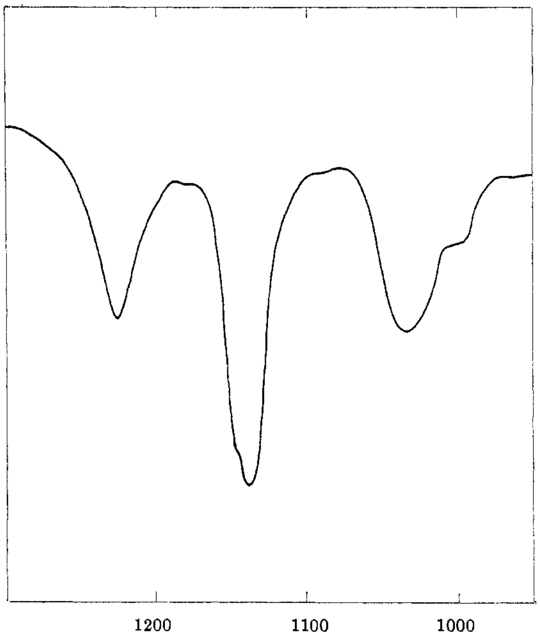

Figure 1.—Infrared spectrum of μ-hydroxo-μ-sulfato-octaaquodichromium(III) chloride in aqueous solution between silver chloride plates.

Although no chromium(III) species containing bidentate sulfate ligand has previously been characterized, some cobalt(III) species have been shown to contain bidentate sulfate. The compound $[(NH_3)_4Co(SO_4)(NH_2)Co(NH_3)_4](NO_3)_3$ contains a bidentate, bridging sulfate group. Its infrared spectrum in the 900–1300-cm^{-1} region contains four peaks—995 (m), 1060 (s), 1105 (s), and 1170 (s) cm^{-1}— and is very similar to the infrared spectrum of the μ-hydroxo-μ-sulfato-octaaquodichromium(III) ion reported here.[3] A mononuclear species $[Co(SO_4)(en)_2]Br$ has also been shown to contain a bidentate sulfate ligand.[4] Unlike the dimeric species, this species is quite unstable in aqueous solution; the sulfate is converted to a monodentate ligand and an additional water molecule enters the inner coordination sphere.

Acknowledgments—We wish to thank the National Science Foundation, Undergraduate Research Participation Program, for partial financial support of this work.

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(2) J. E. Finholt, Lawrence Radiation Laboratory Report UCRL 8879, University of California, Berkeley, Calif., 1960, pp 23–24; H. W. Cady and R. E. Connick, *J. Am. Chem. Soc.*, **80**, 2646 (1958).

(3) K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *ibid.*, **79**, 4904 (1957).

(4) C. G. Barraclough and M. L. Tobe, *J. Chem. Soc.*, 1993 (1961).