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Crystal Structure of Thallous Tetracarbonylcobaltate and the Relation of Its Chemistry and Solution State

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Yellow air-sensitive crystals of thallous tetracarbonylcobaltate, prepared by the reactions of thallous nitrate with sodium tetracarbonylcobaltate, of thallium metal with bis(tetracarbonylcobalt)mercury, or of metallic thallium with dicobalt octacarbonyl, crystallized in the cubic space group $P2_13$ with $a = 8.869$ (3) Å determined by powder diffraction techniques. An observed density of 3.55 (2) g/cm^3 indicated the presence of 4 formula units per unit cell ($\rho_{\text{calcd}} = 3.58$ g/cm^3). Using a data set of 135 observed reflections ($I > \sigma(I)$) collected by counter methods from a spherical crystal, the structure was solved by Patterson and Fourier techniques and refined to a final unweighted and weighted residual of 0.083 and 0.044, respectively. The structure consists of discrete Tl^+ and $Co(CO)_4^-$ ions arranged in an NaCl-like structure with the closest approach of Tl and Co atoms being 3.55 (1) Å which is about 0.35 Å longer than the sum of their covalent radii. Although essentially ionic in the solid state, in solvents of low dielectric constant $TlCo(CO)_4$ exists as a tight ion pair with some degree of Tl–Co covalent bonding. The reactions of $TlCo(CO)_4$ with Lewis bases in dichloromethane and its reaction with $In[Co(CO)_4]_3$ compared with that of $NaCo(CO)_4$ with $In[Co(CO)_4]_3$ reflected this interaction. With excess $Co(CO)_4^-$, the Tl(I) complex $Tl[Co(CO)_4]_2^-$ was observed. In solvents of high dielectric constant the reactions of $TlCo(CO)_4$ were consistent with the presence of free ions.

Introduction

Although the reaction of thallium metal, cobalt metal, and carbon monoxide was first reported in 1942 as giving $TlCo(CO)_4$, a volatile yellow solid soluble in benzene,[1] little subsequent information about the chemistry and structure of thallium(I)–metal carbonyl derivatives is available. Only passing references to $Tl[(C_5H_4CHPh_2)Cr(CO)_3]$[2] and $Tl[(C_5H_5)M(CO)_3]$ (M = Mo,[3] W[4]) appear in the literature. Attempts to prepare other thallous compounds such as $Tl[Mn(CO)_5]$[5] or $Tl[Co(CO)_3P(C_6H_5)_3]$[6] have resulted in formation of the corresponding thallium(III) compounds.

During the course of our studies of the chemistry of $Tl[Co(CO)_4]_3$,[6] we observed that this compound disproportionated in tetrahydrofuran and dichloromethane as reported by Graham.[7] The process occurring in solution was that indicated by eq 1, although the infrared spectra of these solutions were not those of the free, tetrahedral $Co(CO)_4^-$ ion.[8,9]

$$Tl[Co(CO)_4]_3 \rightleftarrows TlCo(CO)_4 + Co_2(CO)_8 \qquad (1)$$

A detailed spectral study with pure $TlCo(CO)_4$ has elucidated the solution site character for this compound in selected solvents and will be reported elsewhere.[10] In solvents of high dielectric constant and good coordinating ability (water, dimethyl sulfoxide, and dimethylformamide) the spectra are consistent with the presence of Tl^+ and $Co(CO)_4^-$ as free ions or solvent-separated ion pairs. In solvents of low dielectric constant and weak coordinating ability (tetrahydrofuran and dichloromethane), spectra consistent with tight ion pairs and triple ions with significant amounts of thallium–cobalt bonding are observed. In order to determine the effect of the solution state of $TlCo(CO)_4$ on its chemical reactivity and to determine if the covalent interaction observed in some solvents is retained in the solid state, we have undertaken the studies reported in this work.

Experimental Section

All operations were conducted under nitrogen using Schlenk-type equipment. The solvents used were thoroughly deoxygenated. Tetrahydrofuran was distilled over calcium hydride, but all other materials were used without further purification.

Preparation of $TlCo(CO)_4$. Thallous tetracarbonylcobaltate was prepared by three methods.

A. A solution of 2 g of $Co_2(CO)_8$ dissolved in 15 ml of toluene and a piece of thallium metal of approximately 3 g were stirred at room temperature. A red solution which turned yellow-brown after 2 hr was produced. The solution was filtered, an equal volume of pentane was added, and the solution was cooled to −78°. Yellow crystals were filtered from the solution and washed in several portions of pentane. The yield was about 95%. Under similar conditions no reaction was observed with $[(C_5H_5)Fe(CO)_2]_2$, $Mn_2(CO)_{10}$, or $[(C_5H_5)Mo(CO)_3]_2$.

B. Stirring 1 g of $Hg[Co(CO)_4]_2$ in 15 ml of toluene over a 3-g piece of thallium metal produced $TlCo(CO)_4$ after approximately 2 hr. The isolation and purification was performed as indicated in method A.

C. $Co_2(CO)_8$ (3 g) was converted to $NaCo(CO)_4$ by stirring in 20 ml of tetrahydrofuran over an excess of solid NaOH.[11] The solution was filtered into a solution of 3.39 g (12.3 mmol) of $TlNO_3$ in 30 ml of H_2O. The tetrahydrofuran was removed *in vacuo* and the yellow product was filtered. It was then washed with 5 ml of water, two 5-ml portions of dichloromethane, and two 10-ml portions of pentane. The yield was 48% based on $Co_2(CO)_8$.

Thallium was analyzed as TlI by addition of $TlCo(CO)_4$ to an aqueous potassium iodide solution and filtering, drying, and weighing the TlI produced. Carbon was determined by the Purdue Microanalytical Laboratory. *Anal.* Calcd for $TlCo(CO)_4$: C, 12.8; Tl, 54.7. Found: C, 12.6; Tl, 54.6.

Reaction of $TlCo(CO)_4$ with $Co_2(CO)_8$. A solution of 2.19 g (5.84 mmol) of $TlCo(CO)_4$ and 2.2 g (10% excess) of $Co_2(CO)_8$ in 20 ml of dichloromethane was stirred for 1 hr. The solution turned dark red. A 10-ml amount of heptane was added and the dichloromethane was removed *in vacuo*. The heptane solution was cooled to −80°, and the $Tl[Co(CO)_4]_3$ was filtered from the solution and washed with 10 ml of cold pentane. The yield of black crystals was 84% based on thallium. The product was identified by its melting point (60–61°; lit.[7] 61–65°) and its infrared spectrum in dichloromethane.[7]

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[3] R. B. King, *Inorg. Chem.*, **9**, 1936 (1970).

[4] British Patent No. 827,374 (1968); *Chem. Abstr.*, **55**, 3612*g* (1961).

[5] A. T. T. Hsieh and M. J. Mays, *J. Organometal. Chem.*, **38**, 243 (1972).

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[10] W. F. Edgell, W. R. Robinson, A. Barbetta, and D. P. Schussler, unreported observations.

[11] W. F. Edgell and J. Lyford, IV, *Inorg. Chem.*, **9**, 1932 (1970).

Under similar conditions no reaction was observed with $[(C_5H_5)Fe(CO)_2]_2$, $Mn_2(CO)_{10}$, or $[(C_5H_5)Mo(CO)_3]_2$.

Preparation of $[(C_6H_5)_3(C_6H_5CH_2)P][Co(CO)_4]$. To a solution of about 11 mmol of $NaCo(CO)_4$ which was prepared by stirring 3.0 g of $Co_2(CO)_8$ in 20 ml of THF over solid NaOH[11] was added an equivalent amount of benzyltriphenylphosphonium chloride. A 20-ml amount of water was added to the solution and the THF was removed under reduced pressure. The resulting pale yellow air-stable solid was filtered from the aqueous mother liquor, washed with water, and dried. Although no elemental analysis was determined, the sample contained no chloride and the only carbonyl peak present in an infrared spectrum was due to $Co(CO)_4^-$.

Reaction of $TlCo(CO)_4$ with $[(C_6H_5)_3(C_6H_5CH_2)P]Co(CO)_4$. To 0.31 g (0.83 mmol) of $TlCo(CO)_4$ in 10 ml of dichloromethane was added 0.42 g (0.81 mmol) of $[(C_6H_5)_3(C_6H_5CH_2)P]Co(CO)_4$. The solution was covered with 40 ml of heptane and the heptane was allowed to diffuse slowly into the solution over a period of 12 hr. Black crystals were deposited which were exceedingly air sensitive. A 57% yield of product was obtained by filtering the compound and washing it with heptane. *Anal.* Calcd for $[(C_6H_5)_3(C_6H_5CH_2)P][Tl(Co(CO)_4)_2]$: Tl, 22.7; C, 44.0; H, 2.47. Found: Tl, 22.3; C, 44.3; H, 2.70.

Reaction of $NaCo(CO)_4$ and $TlCo(CO)_4$ with $In[Co(CO)_4]_3$. Mixtures of a 1:1 mole ratio of $NaCo(CO)_4$ with $In[Co(CO)_4]_3$ and $TlCo(CO)_4$ with $In[Co(CO)_4]_3$ were dissolved in a minimum amount of both dichloromethane and tetrahydrofuran. The infrared spectra of the four solutions were recorded promptly and showed a reaction forming $In[Co(CO)_4]_4^-$ only with $NaCo(CO)_4$. Spectra after 0.5 hr showed no change in the results.

Reaction of $TlCo(CO)_4$ with $P(C_6H_5)_3$. A solution of 1.62 g (4.32 mmol) of $TlCo(CO)_4$ and 2.1 g (8 mmol) of $P(C_6H_5)_3$ in 15 ml of dichloromethane was stirred for 3 hr. Gas evolution was observed and a metallic mirror formed. This mirror was soluble in dilute nitric acid, and the nitric acid solution gave a white precipitate upon addition of NaCl. Addition of 40 ml of heptane to the filtered solution gave a 55% yield of crystalline $Tl[Co(CO)_3P(C_6H_5)_3]_3 \cdot 2CH_2Cl_2$, mp 195-196°. *Anal.* Calcd for $Tl[Co(CO)_3P(C_6H_5)_3]_3 \cdot 2CH_2Cl_2$: C, 49.2; H, 3.08; P, 5.85; Cl, 8.93. Found: C, 49.6; H, 3.47; P, 5.90; Cl, 8.66.

Reaction of $Tl[Co(CO)_4]_3$ with $P(C_6H_5)_3$. A solution of 1.72 g (2.4 mmol) of $Tl[Co(CO)_4]_3$ and 2.2 g (8.4 mmol) of $P(C_6H_5)_3$ was stirred in 15 ml of dichloromethane for 10 hr. The solution was filtered and 10 ml of heptane was added. Removal of the dichloromethane under vacuum produced a 75% yield of black crystals which were filtered off, washed with pentane, and dried under vacuum; mp 195-196°. *Anal.* Calcd for $Tl[Co(CO)_3P(C_6H_5)_3]_3 \cdot 2CH_2Cl$: C, 49.2; H, 3.08. Found: C, 49.4; H, 3.23.

Infrared Spectra. All spectra were recorded on a Perkin-Elmer 221 spectrometer with NaCl optics. The spectra were calibrated in the carbonyl region using polystyrene and $Hg[Co(CO)_4]_2$ in heptane. The CO frequencies of this solution were taken from Adams.[12]

Space Group and Unit Cell. From precession and Weissenberg photographs of several crystals in different orentations $TlCo(CO)_4$ was found to exhibit $m3$ diffraction symmetry. From the systematic absences observed on $hk0$, $hk1$, and $0kl$-$2kl$ photographs ($h00$, $h = 2n + 1$; $0k0$, $k = 2n + 1$; $00l$, $l = 2n + 1$), the cubic space group was found to be $P2_13$ (No. 198). The unit cell parameter was determined from powder photographs using NaCl as an internal calibrant ($a = 5.640$ Å) and refined to 8.869 (3) Å using 44 2θ values in the least-squares program of Williams.[13] This parameter was determined at 23° using 1.5418 Å as the wavelength of Cu Kα radiation. The density of a sample measured by displacement of heptane was 3.55 (2) g/cm^3, while that calculated assuming four formula units per unit cell is 3.58 g/cm^3. Since $P2_13$ is a space group with 12 general positions, the thallium, cobalt, and one CO group must lie on a threefold axis in the special position 4a.

Data Collection and Reduction. In order to minimize the error in the absorption correction, crystals for data collection were ground to spheres using an Enraf-Nonius Inc. crystal grinder. A spherical crystal of 0.225 (2)-mm diameter was mounted in a random orentation under nitrogen in a Lindemann capillary. The data set was collected using an automated Enraf-Nonius CAD-4 diffractometer with Mo radiation (λ 0.71069) filtered through 2 mils of Zr foil. An incident beam collimator of 0.8-mm diameter at a takeoff angle of 4.0° was used with a receiving aperture located 173 mm from the crystal. The pulse height analyzer used with the scintillation counter was set to admit approximately 95% of the diffracted intensity. Following optical centering of the crystal, 18 reflections were located by a systematic search. These reflections were widely separated in the reciprocal lattice and were located at as high a 2θ value as possible consistent with obtaining reasonable intensity. Accurate values of 2θ, ω, κ, and ϕ were determined by scanning ω, κ, and 2θ and locating the peak at the average positions of the half-heights. Both the search and alignment procedures were under the control of the computer using programs supplied by Enraf-Nonius. Following X-ray centering of the crystal, the reflection centering procedure was repeated, and the reflections were indexed from the known cell constants and the relative positions of the reflections. The orentation matrix was determined from these reflections using a least-squares program provided with the instrument.

A data set of 778 reflections from an octant of reciprocal space was collected in the range $4° < 2\theta < 50°$. It was evident from the film data that there were very few reflections with significant intensities above $2\theta = 50°$. The θ-2θ scanning technique with a variable scanning speed was used with a 2θ range of $1.6 + \tan\theta$ degrees centered about the average peak position. The aperture was set at 3 mm wide by 4 mm high. Each reflection was first scanned at a rate of 20.1° min^{-1} to determine its approximate intensity. If this intensity was not sufficient to accumulate a minimum of 100 counts above background with a slow scan of 180 sec (a net intensity to background ratio of about 1:1), the reflection was considered unobserved, the results of the fast scan were recorded, and the next reflection was processed. The observed reflections were scanned twice at a slower rate necessary to accumulate the desired net count. The maximum rate for the slower scan was set at 6.7° min^{-1} with the majority of reflections counted at this rate. The intensities of 85% of these reflections were well above the minimum net count required, although the counting rates were such that no coincidence corrections were required. For no strong reflections were the results of the two scans statistically different. Background counts were made for one-fourth of the scan time at each end of both scans. The 600, 031, and 006 reflections were monitored alternately every 20 min and did not change significantly during the course of the data collection period.

Integrated intensities, I, were obtained using the expression $I = C - 2B$ where C is the sum of the counts collected during the two slower scans and B is the sum of the background counts during these scans. A standard deviation was assigned to each measured intensity using the expression $\sigma(I) = [C + 4B]^{1/2}$. The data were corrected for absorption using the correction for a spherical crystal and for the Lorentz-polarization effect.[14] The crystal was measured in a variety of positions using a microscope with a micrometer eyepiece. The diameter of the crystal in all positions did not differ from 0.225 (2) mm. For a linear absorption coefficient of 256.8 cm^{-1} $\mu R = 2.89$ and A^* varies from 34.7 to 21.0.[15]

Crystals of $TlCo(CO)_4$ gave sharp but relatively weak diffraction effects. The relatively weak peaks coupled with the scattering from the capillary tube resulted in a large number of unobserved reflections. Of the 778 reflections measured, only 402 were observed with $I > \sigma(I)$. The equivalent reflections were averaged giving 135 observed reflections. All reflections of a symmetry-related set were within 1.5σ of the average value of that set.

Solution and Refinement of Structure. The atomic coordinates of the Tl and Co atoms were derived from a Patterson map.[16] Both atoms occupy the fourfold special positions on the threefold axes in the unit cell. Following two cycles of least-squares refinement[17] of the scale factor, the positional parameters for Tl and for Co, and isotropic temperature factors, a Fourier map located the CO groups. Four subsequent weighted refinement cycles of the scale factor, all variable atomic parameters, and isotropic temperature factors reduced R_1 ($R_1 = \Sigma |F_o - F_c| / |F_o|$) to 0.083 and R_2 ($R_2 = [\Sigma w |F_o - F_c|^2]^{1/2} / [\Sigma w |F_o|^2]^{1/2}$) to 0.044. Weights were assigned as $w = 1/\sigma^2(F) =$

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(12) D. M. Adams, "Metal-Ligand and Related Vibrations," St. Martin's Press, New York, N. Y., 1968.

(13) D. E. Williams, "LCR-2, a Fortran Lattice Constant Refinement Program," IS-1052, Iowa State University, Ames, Iowa, 1966.

(14) PDD, a local Fortran program for diffractometer data reduction on the CDC 6400 computer at Purdue University.

(15) W. L. Bond in "International Tables for X-Ray Crystallography," Vol. II, Kynoch Press, Birmingham, England, 1967, p 302.

(16) M. G. Rossman, "FOUR, a General Three Dimensional Fourier Program," Department of Biological Sciences, Purdue University, West Lafayette, Ind. 47907.

(17) S. J. S. Helms, "PMIALS, Purdue Mixed Isotropic-Anisotropic Least-Squares," a local version of W. R. Busing, K. O. Martin, and H. A. Levy's "ORFLS, Fortran Crystallographic Least-Squares Program," Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1963.

$4F_o^2/\sigma^2(F_o^2)$ except for the three reflections for which F_c was greater than 200. These reflections were assigned a weight of zero in order to reduce the effects of extinction. The scattering factors for Tl^+, Co^0, O^0, and C^0 were those of Ibers[18] with real and imaginary anomalous scattering corrections[19] applied for Tl and Co. Refinement with the reflections indexed as their Friedel opposites gave higher R values indicating that the reflections were correctly indexed with respect to Friedel inversion.

Final shifts in parameters were less than 0.2 times their respective standard deviations. With the exception of the three strongest reflections, the final F_o and F_c values all agreed within $1.5\sigma(F_o)$ and 80% of these values agreed within $1.0\sigma(F_o)$. The distribution of $F_o - F_c$ and the value of 0.72 for the final standard deviation of an observation of unit weight probably reflect an overestimation of $\sigma(F^2)$. During the course of averaging a set of equivalent reflections, the larger value of the average of the esd's of all equivalent reflections or the root-mean-square deviation was taken as the error in a deliberate attempt to avoid underestimation of the error. No peaks larger than about 1.5 e $Å^{-1}$ were found in the final difference map, and these peaks were found along the threefold axis near the thallium atom. Refinement with anisotropic temperature factors produced no improvement in either R_1 or R_2.

The final atomic parameters are listed in Table I while bond distances and angles may be found in Table II. A table of structure factor amplitudes may be found in the microfilm edition.[20] A diagram of the top half of the unit cell is presented in Figure 1 while Figure 2 is a stereodrawing of the entire unit cell.

Results

Preparation, Characterization, and Reactions. Most of the common synthetic routes to transition metal derivatives of the main-group elements[21,22] have been applied successfully for the preparation of $TlCo(CO)_4$. All of these reactions require careful deoxygenation of solvents and reaction vessels in order to avoid the formation of $Tl[Co(CO)_4]_3$. The common metathetical reaction is represented by the reaction of $NaCo(CO)_4$ with $TlNO_3$ according to eq 2. Although this

$$NaCo(CO)_4 + TlNO_3 \xrightarrow[H_2O]{THF} NaNO_3 + TlCo(CO)_4 \qquad (2)$$

procedure may be used successfully, it involves several steps and produces a lower yield than the following methods.

Metal-exchange reactions have been exploited for the preparation of a variety of zinc- and cadmium-metal carbonyl derivatives,[23] $In[Co(CO)_4]_3$,[6] $In[Mn(CO)_5]_3$,[24] and $(THF)_4Er[Co(CO)_4]_3$.[25] The exchange reaction of $Hg[Co(CO)_4]_2$ with elemental thallium produces $TlCo(CO)_4$ by reaction 3.

$$Hg[Co(CO)_4]_2 + 2Tl \xrightarrow{toluene} Hg + 2TlCo(CO)_4 \qquad (3)$$

$Tl[Co(CO)_4]_3$ forms only upon exposure of the solution to air. The similar reaction using indium leads to the formation of $In[Co(CO)_4]_3$ as comparison of the In(I)-In(III) and Tl(I)-Tl(III) potentials in water would lead one to expect.

Like other active metals,[21,22] elemental thallium will reduce $Co_2(CO)_8$ according to reaction 4. The simplicity of this

$$2Tl + Co_2(CO)_8 \xrightarrow{toluene} 2TlCo(CO)_4 \qquad (4)$$

method and its high yield make it the preferred route for the preparation of $TlCo(CO)_4$. We have unsuccessfully attempted the same reaction at room temperature with $[Fe(\pi\text{-}C_5H_5)(CO)_2]_2$, $Mn_2(CO)_{10}$, and $[Mo(\pi\text{-}C_5H_5)(CO)_3]_2$, demonstrating the relatively easy cleavage of the Co-Co bond of $Co_2(CO)_8$.

Table I. Atomic Positional and Isotropic Thermal Parameters for $TlCo(CO)_4$[a]

	x	y	z	B, $Å^2$
Tl^b	0.1843 (3)			3.41 (8)
Co^b	0.6982 (8)			2.7 (3)
C_1	0.629 (4)	0.679 (7)	0.896 (3)	0.1 (7)
O_1	0.631 (4)	0.698 (4)	1.027 (4)	3.8 (9)
$C_2{}^b$	0.584 (9)			7 (4)
$O_2{}^b$	0.501 (6)			5 (2)

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Atom is located at the special position x, x, x.

Table II. Interatomic Distances (Å) and Bond Angles (deg) for $TlCo(CO)_4$[a]

Tl'-Co'	3.551 (9)	Tl'-C_2'	3.27 (9)
Tl-O_{1A}'	3.03 (4)	Co-C_1	1.89 (3)
Tl'-O_{1C}'	3.87 (5)	Co-C_2	1.76 (9)
Tl'-O_{1A}'	4.29 (4)	C_1-O_1	1.17 (5)
Tl'-O_2'	3.63 (5)	C_2-O_2	1.29 (10)
Tl'-C_{1B}'	3.35 (7)	O_2-O_{1A}'	2.97 (7)
Tl'-C_{1C}'	3.55 (4)		
C_1-Co-C_{1B}	112 (4)	Co-C_1-O_1	155 (6)
C_1-Co-C_2	107 (3)	Co-C_2-O_2	180

[a] Labels correspond to atoms in Figure 1.

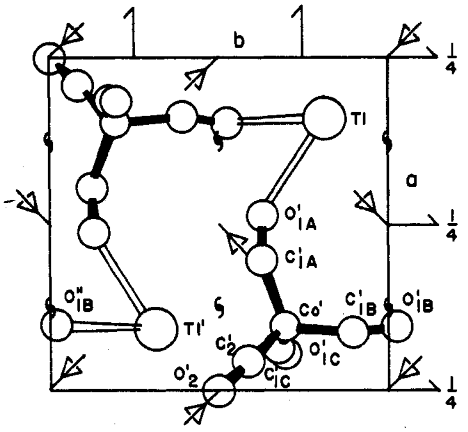

Figure 1. A drawing of the top half of the $TlCo(CO)_4$ unit cell. The origin is in the upper right-hand corner. Tl' is at $1 - x$, $^1/_2 + x$, $^1/_2 - x$. Co', C_{1C}', O_{1C}', C_2', and O_2' are related to Co, C_1, O_1, C_2, and O_2 (Table I), respectively, by the twofold screw axis at $^3/_4$, $^1/_2$, z. C_{1A}', O_{1A}', C_{1B}', and O_{1B}' are generated by the threefold axis through C_2', O_2', and Co'. Open lines indicate relative positions, not covalent bonds.

The pale yellow crystalline $TlCo(CO)_4$ produced by any of the routes described above may be handled in air for brief periods (about 2 min) without significant decomposition. $TlCo(CO)_4$ sublimes readily at pressures of about 10^{-2} Torr and a temperature of about 80°. It dissolves to a limited extent in water and is soluble in polar organic solvents such as methanol, dimethyl sulfoxide, dichloromethane, and nitromethane. The compound is very soluble in toluene and benzene but insoluble in alkanes. Solutions of $TlCo(CO)_4$ are quite air sensitive. As shown,[10] the infrared spectra of $TlCo(CO)_4$ vary markedly with solvent. In solvents of high dielectric constant and good coordinating ability (water, dimethyl sulfoxide, and dimethylformamide) the spectra are consistent with the presence of Tl^+ and $Co(CO)_4{}^-$ as free ions or solvent-separated ion pairs. In solvents of low dielectric constant and weak coordinating ability (tetrahydrofuran and dichloromethane), spectra consistent with tight

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(18) J. A. Ibers in "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1968, pp 202-212.

(19) D. H. Templeton, ref 18, p 215.

(20) See paragraph at end of paper regarding supplementary material.

(21) R. B. King, *Advan. Organometal. Chem.*, 2, 157 (1964).

(22) R. B. King, *Accounts Chem. Res.*, 3, 417 (1970).

(23) J. M. Burlitch and A. Ferrari, *Inorg. Chem.*, 9, 563 (1970).

(24) A. T. T. Hsieh and M. J. Mays, *J. Organometal. Chem.*, 22, 29 (1970).

(25) R. S. Marianelli and M. T. Durney, *J. Organometal. Chem.*, 32, C41 (1971).

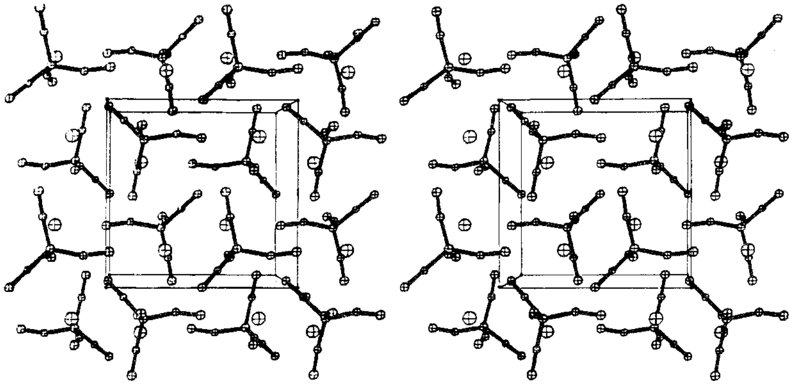

Figure 2. A stereoscopic view of the unit cell. The unit cell axes are oriented as in Figure 1.

ion pairs or triple ions with significant amounts of covalent Tl-Co bonding are observed.

The reaction of $TlCo(CO)_4$ with triphenylphosphine varied with solvent as do the infrared spectra. In dimethyl sulfoxide no reaction was observed, even at elevated temperatures. In dichloromethane, however, thallous tetracarbonylcobaltate and triphenylphosphine reacted at room temperature under carefully deoxygenated conditions with evolution of a colorless gas and precipitation of metallic thallium. $Tl[Co(CO)_3P(C_6H_5)_3]_3 \cdot 2CH_2Cl_2$ was isolated from the reaction mixture in 55% yield. The product was identical with that isolated from the reaction of $Tl[Co(CO)_4]_3$ with triphenylphosphine in dichloromethane.

The association of thallous tetracarbonylcobaltate in solvents of low dielectric constant was also reflected in the reaction of this compound with $In[Co(CO)_4]_3$. In both tetrahydrofuran and dichloromethane, $NaCo(CO)_4$, a compound which forms only weak ion pairs with no covalent interaction,[8] reacted with $In[Co(CO)_4]_3$ giving the complex indium(III) anion $In[Co(CO)_4]_4^-$. The reaction in dichloromethane was heterogeneous since $NaCo(CO)_4$ is not soluble in this material. In the same solvents, $TlCo(CO)_4$ did not react with $In[Co(CO)_4]_3$ even upon standing. The identification of $In[Co(CO)_4]_4^-$ was obtained by comparison of the infrared spectra of the reactant and reaction solutions and that of $[As(C_6H_5)_4]In[Co(CO)_4]_4$[26] in the respective solvents.

As predicted by Graham,[7] a soluble Tl(I) species (in this case, $TlCo(CO)_4$) inserted into the Co-Co bond of $Co_2(CO)_8$ according to reaction 5. The reaction proceeded rapidly at

$$TlCo(CO)_4 + Co_2(CO)_8 \overset{CH_2Cl_2}{\rightleftarrows} Tl[Co(CO)_4]_3 \qquad (5)$$

room temperature and proved to be the most convenient preparative route to $Tl[Co(CO)_4]_3$. Since the reaction is reversible, an excess of $Co_2(CO)_8$ was required for the quantitative preparation of $Tl[Co(CO)_4]_3$. No problem was encountered in removing the excess $Co_2(CO)_8$ since it is very soluble in saturated hydrocarbons and easily sublimes. $TlCo(CO)_4$ did not, under similar conditions, react with either $[Fe(\pi\text{-}C_5H_5)(CO)_2]_2$, $Mn_2(CO)_{10}$, or $[Mo(\pi\text{-}C_5H_5)(CO)_3]_2$.

$TlCo(CO)_4$ also exhibited Lewis acid properties. A mixture of $TlCo(CO)_4$ and $[(C_6H_5CH_2)(C_6H_5)_3P][Co(CO)_4]$ in dichloromethane in a 1:1 stoichiometry produced a red solution from which a black very air-sensitive crystalline solid with the composition $[(C_6H_5CH_2)(C_6H_5)_3P][Tl(Co(CO)_4)_2]$ was isolated. The infrared spectrum of this compound in dichloromethane is complex. It is dominated by the strong bands associated with $TlCo(CO)_4$ in this solvent and the strong band of the $Co(CO)_4^-$ in a loose ion pair. While overlapping makes it hard to fix the bands for the $Tl[Co(CO)_4]_2^-$ anion, they are consistent with those obtained from the resolution of the $TlCo(CO)_4$ in tetrahydrofuran spectrum, namely, 2020 (m), 1937 (m), and 1904 (s) cm^{-1}.[10] A comparison of the 2039-cm^{-1} band of $TlCo(CO)_4$ with the 2020-cm^{-1} band of $Tl[Co(CO)_4]_2^-$ indicates the two are present in comparable amounts in the dichloromethane solution of $[(C_6H_5CH_2)(C_6H_5)_3P][Tl(Co(CO)_4)_2]$. Addition of either $TlCo(CO)_4$ or $[(C_6H_5CH_2)(C_6H_5)_3P][Co(CO)_4]$ to solutions of $Tl[Co(CO)_4]_2^-$ shifted the relative intensities of the CO stretching frequencies in a manner consistent with equilibrium shown in reaction 6.

$$Tl[Co(CO)_4]_2^- \rightleftarrows TlCo(CO)_4 + Co(CO)_4^- \qquad (6)$$

Structure of $TlCo(CO)_4$ in the Solid State. The crystal structure of $TlCo(CO)_4$ is analogous to that of sodium chloride. If the thallium atoms in the x, x, x positions in eight adjacent unit cells are taken as defining a cube, other thallium atoms are located roughly in the centers of the faces of the cube. Cobalt tetracarbonyl groups are located at approximately $^1/_2$, 0, 0; 0, $^1/_2$, 0; 0, 0, $^1/_2$; and $^1/_2$, $^1/_2$, $^1/_2$ in this cube.

Within the crystal there are chains of alternate Tl^+ and $Co(CO)_4^-$ ions parallel to the unit cell edges (Figures 1 and 2). Within each chain the Tl^+ ions are coordinated on one side by a single $Co(CO)_4^-$ oxygen and on the other side by three CO groups of a second $Co(CO)_4^-$ moiety so that the Tl^+ sits in a tripod or cup formed by these three CO groups. Since each Tl^+ is located on a threefold axis, it is located at the intersection of three mutually perpendicular chains. As in the sodium chloride structure, each cation is surrounded by six anions, two anions in each of the three chains. Three of these $Co(CO)_4^-$ groups, which are related by the threefold axis, direct a single CO at the Tl with resulting Tl-O distances of 3.03 (4) Å. Each of the remaining three $Co(CO)_4^-$ moieties directs three CO groups toward the Tl^+. The Tl-O distances in this second geometry are 3.63 (5), 3.87 (5), and 4.29 (4) Å while the Tl-C distances are 3.27 (9), 3.35 (7), and 3.55 (4) Å, respectively. The distance of the Tl from the Co in this second $Co(CO)_4^-$ is 3.551 (9) Å. This is the closest approach of Tl and Co in the unit cell.

Each $Co(CO)_4^-$ group in the chain of alternate Tl-$Co(CO)_4$-Tl units also is located at the intersection of three mutually perpendicular chains with the Co on a threefold axis. The $Co(CO)_4^-$ groups are six-coordinate as are the anions in a sodium chloride type structure. A given $Co(CO)_4^-$ directs the oxygen atoms of its threefold related CO groups to three

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[26] W. R. Robinson and D. P. Schussler, *J. Organometal. Chem.*, 30, C5 (1971).

Tl^+ ions. Three other Tl^+ ions are located in the threefold-related cups of the $Co(CO)_4^-$. The nearest approach of $Co(CO)_4^-$ anions is 2.97 (7) Å between oxygen atoms of CO groups.

Within the error of the determination, each CoC_4 unit is tetrahedral although the threefold-related carbonyl groups have Co-C-O angles which are just significantly different (4σ) from 180°. The nonlinearity of these groups may reflect packing effects since each oxygen atom in these Co-C-O groups is bent toward a Tl^+ ion at a distance of 3.03 Å. The Co-C distances average 1.82 Å, and the C-O distances, 1.23 Å. The large standard deviations associated with the C and O positions reflect the limited data set, the relatively low values of $I/\sigma(I)$ for the observed reflections, and the difficulties associated with locating light atoms in the presence of very heavy atoms. The Tl and Co atoms in this structure contain 66% of the electron density of the structure, and the nonweighted residual based only on Tl and Co was 0.121. This value was reduced only by 0.038 to 0.083 when the C and O atoms were included in the refinement.

Discussion

The solid-state structure of thallous tetracarbonylcobaltate is that of an essentially ionic solid composed of Tl^+ and $Co(CO)_4^-$ ions. There are no discrete $TlCo(CO)_4$ moieties in the solid state, nor are there any particularly close distances between thallium and other atoms which are consistent with the existence of strong covalent bonds. No unique single-bond radius is available for Tl(I), but a number of structural observations place this radius at less than 1.9 Å. If one accepts the Tl-I distance[27] in gaseous TlI as resulting from a single Tl-I covalent bond, a covalent radius of 1.54 Å (2.87 − 1.33 Å where 1.33 Å is the covalent radius of iodine[28]) may be obtained. From the Tl-O distances in thallous acetylacetonate[29] an average covalent radius of 1.83 Å is obtained. The Tl-O distances are 2.43 and 2.54 Å while the covalent radius of oxygen may be taken as 0.66 Å.[28] The Tl-S distances of 2.88 and 2.91 Å in thallous dipropyldithiocarbamate[30] suggest a covalent radius of 1.85 Å (2.89 − 1.04 Å where 1.04 Å is the sulfur radius[28]). The covalent radius of cobalt in $RCo(CO)_4$ may be taken as 1.33 Å.[31] Thus the observed Tl-Co distance of 3.55 Å is appreciably longer than the maximum of 3.2 Å calculated for a single Tl-Co bond. Similarly, the closest Tl-O distance of 3.03 Å is clearly longer than that (2.5 Å) expected for a single Tl-O bond.

Although $TlCo(CO)_4$ is an ionic compound in the solid state, the behavior of $TlCo(CO)_4$ in solution varies with solvent. Infrared spectral studies[10] have shown the kinds of solution sites occupied by $TlCo(CO)_4$ in representative solvents. In solvents of high donor ability and high dielectric constant (water, DMSO, DMF), the solvent-surrounded anion characteristic of the solvent-separated ion pair or free ion was found. In dichloromethane, only a tight ion pair to which some metal-metal covalent bonding was ascribed was seen. Tetrahydrofuran solutions show a mixture of ion sites. In this solvent again a tight ion-pair site with less covalent bonding than in dichloromethane predominates with small amounts of a solvent-separated ion pair and of the complex ion $Tl[Co(CO)_4]_2^-$. Similar site mixtures were also found for $TlCo(CO)_4$ in acetonitrile and nitromethane. It is noteworthy that solutions with these two solvents are red as are solutions of the $Tl[Co(CO)_4]_2^-$ ion in contrast to the yellow-brown color found with dichloromethane and tetrahydrofuran.

Solutions of $NaCo(CO)_4$ also involve a variety of ion sites.[8,9,32] In particular, the tetrahydrofuran solution contains a tight ion pair in the largest amount with a moderate amount of a solvent-separated ion pair and small amounts of a third site which may be the $Na[Co(CO)_4]_2^-$. In contrast to the $TlCo(CO)_4$ case, the tight ion pair for the sodium salt involves association through an oxygen atom and involves little covalent character.

It has been postulated[33] that differences would be found in the way the same chemical species reacts when it is at different ion sites in solution. Such differences are demonstrated here in two types of reactions. The first reaction involves the formation of the complex indium(III) anion $In[Co(CO)_4]_4^-$ from $In[Co(CO)_4]_3$ and a source of the $Co(CO)_4^-$ ion. The reaction proceeds readily between $NaCo(CO)_4$ and $In[Co(CO)_4]_3$ in tetrahydrofuran but does not take place between $TlCo(CO)_4$ and $In[Co(CO)_4]_3$ in the same solvent even on standing. The same results were obtained when dichloromethane was the reaction solvent. In the kind of tight ion pair formed by $TlCo(CO)_4$ in these solvents, the additional stability conferred by the covalent interaction between Tl and Co is sufficient to prevent the reaction.

The second reaction involves the displacement of CO by Lewis bases. In dimethyl sulfoxide, where the $Co(CO)_4$ moiety is present as the solvent-surrounded anion, no reaction with triphenylphosphine was observed even at elevated temperatures. In contrast, $TlCo(CO)_4$ and triphenylphosphine react in dichloromethane. In dimethyl sulfoxide the $Co(CO)_4$ moiety has a full negative charge which, as is well known, results in substantial multiple-bond character in the Co-CO bond which stabilizes the ion to ligand substitution. On the other hand, the Tl-Co covalent interaction in the tight ion pair which exists in dichloromethane reduces the electron density on the $Co(CO)_4$ moiety with a concomitant reduction of the Co-CO multiple bonding and hence its stability to ligand substitution. This explanation is consistent with known chemistry. Covalently bonded post transition metal-transition metal carbonyl derivatives react readily with phosphines and arsines with the evolution of CO and formation of a substituted metal carbonyl.[34] In contrast, ionic $Co(CO)_4^-$ salts do not undergo substitution.[21]

In dichloromethane, $TlCo(CO)_4$ and triphenylphosphine reacted giving $Tl[Co(CO)_3P(C_6H_5)_3]_3 \cdot 2CH_2Cl_2$. This product was identical with that isolated from the reaction of $Tl[Co(CO)_4]_3$ with triphenylphosphine in dichloromethane. Similar reactions have been observed with triphenylarsine, triphenylstibine, and tributylphosphine while triphenyl phosphite gave the thallium(I) derivative $TlCo(CO)_3P(OC_6H_5)_3$.[35] A detailed study of the reactions of $TlCo(CO)_4$ with Lewis bases is in progress and will be reported in a subsequent communication.

Although the final products of the substitution reactions

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with the phosphines, triphenylarsine, and triphenylstibine are thallium(III) derivatives and thallium metal, the reaction probably involves the initial formation of the substituted thallous cobalt carbonyl followed by disproportionation as indicated in eq 7 and 8. At 0°, the reaction of $TlCo(CO)_4$

$$TlCo(CO)_4 + L \rightarrow TlCo(CO)_3L + CO \qquad (7)$$

$$3TlCo(CO)_3L \rightarrow 2Tl(s) + Tl[Co(CO)_3L]_3 \qquad (8)$$

with triphenyl phosphite proceeds only through reaction 7 giving the thallium(I) derivative. At higher temperatures some conversion to the thallium(III) derivative by reaction 8 is observed. Since thallous tetracarbonylcobaltate does not disproportionate, even at elevated temperatures,[35] the reaction of the other Lewis bases probably proceeds by the initial formation of a thallium(I) derivative followed by disproportionation. In addition, the reaction of thallous nitrate and $NaCo(CO)_3P(C_6H_5)_3$ also forms $Tl[Co(CO)_3P(C_6H_5)_3]_3$[6] and almost certainly involves the initial formation of $TlCo(CO)_3P(C_6H_5)_3$.

The weakness of the Tl–Co interaction in solutions of $TlCo(CO)_4$ in dichloromethane, benzene, and tetrahydrofuran is reflected in its reactions with covalent metal halides. Thallous tetracarbonylcobaltate is an excellent source of the $Co(CO)_4$ group.[36] It reacts with triphenyltin chloride in benzene, with bromomanganese pentacarbonyl in dichloromethane, and with indium(III) chloride in tetrahydrofuran giving high yields of $(C_6H_5)_3SnCo(CO)_4$, $(CO)_4CoMn(CO)_5$, and $In[Co(CO)_4]_3$, respectively.

Like the Hg(II),[37] In(III),[26] and Tl(III)[26] derivatives of $Co(CO)_4^-$, $TlCo(CO)_4$ will add 1 additional equiv of $Co(CO)_4^-$. A weak complex, $Tl[Co(CO)_4]_2^-$, is formed which is extensively dissociated in solution in dichloromethane. This complex is similar in its stability to the dihalothallate(I) complexes,[38] TlX_2^-, and the thallium(I) complex with pentacyanocobaltate(II),[39] $Tl[Co(CN)_5]_2^{5-}$. The complex probably contains two Tl–Co bonds rather than Tl–O coordination since no CO stretching frequencies lower than that of free $Co(CO)_4^-$ are observed in the infrared spectrum. Bonding of the oxygen of a metal carbonyl group to a second metal has been observed to reduce the stretching frequency of the CO involved.[40,41] As with the anions $Hg[Co(CO)_4]_3^-$,[37] $In[Co(CO)_4]_4^-$,[26] and $Tl[Co(CO)_4]_4^-$,[26] the CO stretching frequencies of the anion $Tl[Co(CO)_4]_2^-$ are of lower energy than respective frequencies of the neutral parent compound. This reduction in frequency from $TlCo(CO)_4$ to $Tl[Co(CO)_4]_2^-$ reflects the correspondingly greater electron density in the antibonding orbitals of the CO groups resulting from the negative charge on the anion.

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Registry No. $TlCo(CO)_4$, 38991-21-8; $Co_2(CO)_8$, 10210-68-1; $[(C_6H_5)_3(C_6H_5CH_2)P][Co(CO)_4]$, 42535-64-8; $[(C_6H_5)_3(C_6H_5CH_2)P][Tl[Co(CO)_4]_2]$, 39433-90-4; $Tl[Co(CO)_3P(C_6H_5)_3]_3$, 42535-65-9; $Tl[Co(CO)_4]_3$, 42535-66-0; $Hg[Co(CO)_4]_2$, 13964-88-0.

Supplementary Material Available. A listing of structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-74-153.

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Coordination Chemistry of Scandium. VI.[1] Crystal and Molecular Structure of Tris(tropolonato)scandium(III). Stereochemistry of Some Six-Coordinate Complexes

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The crystal and molecular structure of tris(tropolonato)scandium(III), $Sc(C_7H_5O_2)_3$, has been determined by a single-crystal X-ray diffraction technique. The compound crystallizes in the space group $R\bar{3}c$, with cell constants $a = 10.455$ (2) and $c = 32.595$ (1) Å in the hexagonal setting. Least-squares refinement of the counter data gave a final R factor of 0.033 for 783 significant reflections. The complex has D_3 imposed molecular symmetry. The coordination environment is intermediate between trigonal antiprismatic and trigonal prismatic as determined from a value of 33° for the projected twist angle Φ. The significance of Φ and its relationship to both metal ion and ligand restrictions is discussed.

Introduction

Studies of complexes exhibiting six-coordination have recently attracted considerable attention because of the characterization of octahedral (or trigonal-antiprismatic (TAP)), trigonal-prismatic (TP), and intermediate stereochemistries. For complexes where the ligands do not control stereochemistry, Wentworth[2] has shown that for most metal ions the ligand field stabilization energy (LFSE) of a trigonal-pris-

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