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Preparation of Copper(I) Carbonyl Complexes Derived from Sulfonic Acids. Crystal Structure of $Cu(CO)C_2H_5SO_3$

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A number of copper(I) carbonyl complexes derived from sulfonic acids have been synthesized by the reaction of Cu_2O with the acid in the presence of CO. In contrast to other copper carbonyl complexes derived from strong acids, the sulfonate complexes can be isolated in pure form and are reasonably stable. All the sulfonates are characterized by a CO stretching frequency greater than 2100 cm^{-1}. The ethanesulfonate complex was subjected to X-ray analysis. The Cu atom was found to be four-coordinate with a nearly tetrahedral geometry. The overall structure consists of infinite chains of eight-membered rings joined by sharing three-atom Cu–O–S groupings. The crystal data are as follows: space group $C2/c$, a = 20.630 (4) Å, b = 5.004 (1) Å, c = 13.410 (3) Å, β = 97.42 (2)°, V = 1372.7 Å^3, Z = 8. The final R factor was 0.045 for 802 observed reflections.

Introduction

Since the first disclosure of the interaction of carbon monoxide with Cu(I) compounds over a century ago,[1] a considerable number of copper(I) carbonyl complexes have been prepared and studied. In addition to the carbonyl group, most of the complexes also contain ligands of various types bound to the metal.[2] In the past decade, the detailed structures of a number of these complexes have been determined, mainly by the groups of Floriani[3] and Gagnê.[4] All the structures determined thus far contain di- or polyamine groups bound to the copper. The structures of copper carbonyl complexes not containing such ligands have yet to be determined.

The copper carbonyl complexes derived from strong acids, such as $Cu(CO)AsF_6$,[5] $Cu(CO)CF_3CO_2$,[6] $Cu(CO)CF_3SO_3$,[7] etc., form a particularly interesting class, since the anions are only weakly coordinating. All of these complexes are characterized by a relatively high CO stretching frequency in the infrared region, well above 2100 cm^{-1}, as compared to 2060–2090 cm^{-1} for the amine complexes. Many of these complexes reversibly complex CO and have been employed in separation processes for the separation of CO from gas mixtures.[8] Because the anions in these complexes are poor ligands and would be expected to be loosely bound and readily displaced by other incoming molecules, these materials seemed to be likely candidates for the study of the reactions of copper-bound CO. Since $Cu(CO)CF_3SO_3$ can be isolated as a stable crystalline solid, this material was chosen for our initial studies and eventually led to the preparation and characterization of a number of copper carbonyl salts of other sulfonic acids.

Table I. Selected Bond Lengths (Å)

Cu–O(2)	2.050 (4)	S–O(2)	1.445 (4)
Cu–O(3)	2.068 (3)	S–O(3)	1.452 (4)
Cu–O(4)	2.060 (3)	S–O(4)	1.462 (4)
Cu–C(1)	1.784 (8)	S–C(2)	1.765 (5)
C(1)–O(1)	1.116 (8)	C(2)–C(3)	1.486 (10)

Table II. Selected Bond Angles (deg)

Cu-C(1)-O(1)	178.36 (73)	Cu-O(4)-S	123.88 (21)
O(2)-Cu-O(3)	98.11 (16)	O(2)-S-O(3)	113.62 (23)
O(2)-Cu-O(4)	100.20 (14)	O(2)-S-O(4)	112.23 (23)
O(2)-Cu-C(1)	121.42 (25)	O(2)-S-C(2)	105.68 (25)
O(3)-Cu-O(4)	99.54 (13)	O(3)-S-O(4)	110.06 (20)
O(3)-Cu-C(1)	114.81 (24)	O(3)-S-C(2)	107.89 (26)
O(4)-Cu-C(1)	118.72 (27)	O(4)-S-C(2)	106.95 (25)
Cu-O(2)-S	132.03 (21)	S-C(2)-C(3)	112.22 (51)
Cu-O(3)-S	132.70 (22)		

Results and Discussion

The customary synthesis of $Cu(CO)CF_3SO_3$ by the reaction of CO with the benzene complex $(CuCF_3SO_3)_2C_6H_6$[7] works quite well. However, we sought an even more simplified procedure that would avoid the intermediate formation of the benzene complex and would also be applicable to the formation of other sulfonate derivatives. We found that $Cu(CO)CF_3SO_3$ can be prepared directly from Cu_2O and CF_3SO_3H in the presence of CO in diethyl ether (eq 1). The complex is

$$Cu_2O + 2CF_3SO_3H + 2CO \rightarrow 2Cu(CO)CF_3SO_3 + H_2O \quad (1)$$

isolated as a white microcrystalline solid, which often contains some water. The water can be eliminated by carrying out the reaction in the presence of a molecular sieve drying agent. Other sulfonate derivatives can be prepared in the same manner by use of the appropriate acid. There appears to be no obvious limitation on the sulfonate complexes that can be formed, although the number of acids tried was quite limited. All the complexes prepared are stable indefinitely under a CO atmosphere, but some will slowly lose CO if stored under nitrogen for extended periods. They have limited stability in air, most likely due to a combination of hydration and oxidation along with the loss of CO.

Each of the copper carbonyl sulfonate complexes thus far prepared displays an intense, single, sharp CO stretching band in its infrared spectrum. In all cases, the observed frequency of the band falls in the narrow range from 2113 and 2130 cm^{-1}, even for the CF_3SO_3 complex that had previously been reported at 2143 cm^{-1} by Dines.[9] These relatively high CO stretching frequencies are indicative of a high positive charge or low electron density on the copper and are consistent with a weak metal–ligand interaction between the copper and the sulfonate groups. An examination of the infrared bands due to the sulfonate groups gave little information as to the structure of the complexes. For the CH_3SO_3 and the CF_3SO_3

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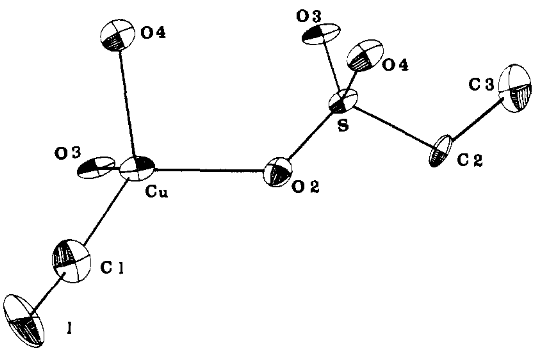

Figure 1. Geometry about the Cu atom in $\mathrm{Cu(CO)C_2H_5SO_3}$.

complexes, the spectra resembled those of the sodium salts[10] and no clues as to the degree or the mode of coordination, if indeed the sulfonate groups were coordinated at all, could be obtained.

In order to determine the nature of the coordination about the copper, a single-crystal X-ray study was undertaken. Neither the $\mathrm{CH_3SO_3}$, the $\mathrm{CF_3SO_3}$, nor the *p*-$\mathrm{CH_3C_6H_4SO_3}$ complex yielded suitable crystals, but the $\mathrm{C_2H_5SO_3}$ complex proved satisfactory and the structure was solved.

The geometry about the copper atom as shown in Figure 1 is essentially tetrahedral, consisting of the carbonyl group and three sulfonate oxygen atoms bound to the metal. The Cu–C–O angle (Table II) is very nearly linear as expected, and the Cu–C and C–O bond distances (Table I) are consistent with the few copper carbonyl complexes whose structures have previously been determined.[11] All previously reported structures were for molecules with relatively strongly bound polyamine ligands coordinated to the copper. A comparison of the infrared spectra of the amine complexes with the spectra of complexes containing the poorly coordinating sulfonate groups would suggest a somewhat higher CO bond order and a lower Cu–C bond order for the sulfonate complexes. A decrease in the CO distance and an increase in the Cu–C bond distance might have been expected in the $\mathrm{Cu(CO)(C_2H_5SO_3)}$ complex, but this was not observed.

The three oxygen atoms bound to the copper are derived from three different ethanesulfonate groups, which results in an interesting polymeric structure shown in Figure 2. The overall structure can best be described as consisting of infinite chains of fused eight-membered rings. Each ring contains two Cu, four O, and two S atoms, with a Cu, an O, and a S atom being common to each adjacent ring. None of the bond distances or angles involving the sulfonate rings seem unusual when compared to those of other sulfonate salts[12] or the few metal complexes whose structures are known.[13] Overall, the mode of coordination of the sulfonate group and the formation of the infinite chains of eight-membered rings is very reminiscent of the structure of $\mathrm{(CuCF_3SO_3)_2C_6H_6}$.[14] In other complexes, coordinated sulfonate groups behave as rather conventional mono-[33] or bidentate[15] ligands in contrast to the tridentate bridging behavior determined for $\mathrm{Cu(CO)C_2H_5SO_3}$ and $\mathrm{(CuCF_3SO_3)_2C_6H_6}$. Because of the lack of sufficient data, it cannot be certain whether this type of coordination is present in the other $\mathrm{Cu(CO)RSO_3}$ complexes prepared.

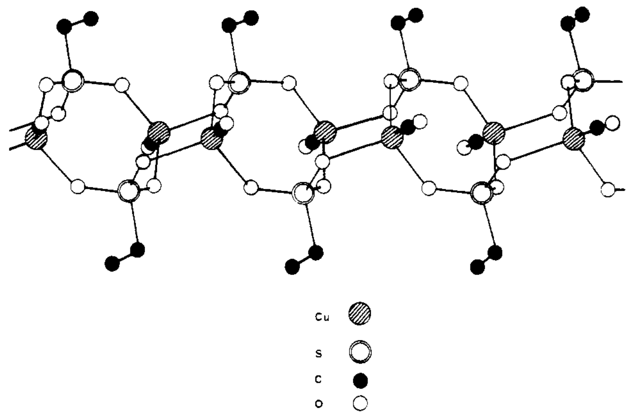

Figure 2. View of $\mathrm{Cu(CO)C_2H_5SO_3}$ showing a portion of the infinite chain.

The reaction of the $\mathrm{Cu(CO)SO_3R}$ complexes with Lewis basees such as amines or phosphines is interesting. One might expect that Lewis base adducts would form quite readily since the sulfonate groups, which are very weak bases, should be quite easily displaced, either partially or completely. A partial displacement in which a ligand replaces one or two of the coordinated sulfonate oxygens would still leave a sulfonate group coordinated to the copper, while a complete displacement would result in ionic derivatives of the type $\mathrm{Cu(CO)L^+SO_3R^-}$. In some cases such adducts are formed and can be isolated; however, this type of reaction is only observed for a rather narrow class of ligands, namely chelating amines. When treated with 1 equiv of 2,2′-bipyridyl or 1,10-phenanthroline, $\mathrm{Cu(CO)CF_3SO_3}$ forms 1:1 adducts, which can be isolated as white crystalline solids. These materials have CO stretching frequencies at 2115 and 2110 $\mathrm{cm^{-1}}$, respectively. Amines such as *N,N,N′,N′*-tetramethylethylenediamine (tmed) also react in a manner similar to that of bipyridyl, forming adducts with the composition $\mathrm{(diamine)Cu(CO)SO_3R}$. In these complexes, ν(CO) is at considerably lower frequencies, generally 2080 $\mathrm{cm^{-1}}$ or less. Bipyridyl and phenanthroline might be expected to be poorer donors than the alkyldiamines, and this is reflected in the much smaller decrease in ν(CO). Complexes of this type can also be prepared by the reaction of the thallium(I) or silver sulfonates with the (diamine)copper(I) halides in the presence of CO as shown in

$$\mathrm{(diamine)CuX + TlO_3SR + CO \rightarrow (diamine)Cu(CO)O_3SR + TlX}$$

No mixed-ligand complexes containing CO have been isolated or even detected in solution as a result of the reaction of phosphines, arsines, or phosphites with any of several $\mathrm{Cu(CO)RSO_3}$ compounds. When a phosphine, arsine, or phosphite is added, CO is liberated and $\mathrm{Cu(L)O_3SR}$ complexes are isolated where L is the phosphine, arsine, or phosphite. These complexes are similar to those previously reported by Dines.[16] This reaction occurs even when a large excess of the carbonyl complex is maintained. Although ligands such as phosphines would be expected to be more competitive with the CO than the diamines, it is somewhat difficult to see why a mixed-ligand complex containing both a phosphorus donor ligand and CO cannot be formed, since the diamine CO complexes are quite stable. The displacement of CO by a phosphine seems to be a general phenomenon, since there appears to be no other literature reports of copper carbonyl complexes with a soft donor ligand also coordinated to the metal.

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Table III. Elemental Analyses for Copper(I) Sulfonate Derivatives

	anal., % calcd (found)				
compd	carbon	hydrogen	sulfur	copper	nitrogen
$Cu(CO)CF_3SO_3$	9.98 (9.84)	0.00 (0.34)	13.32 (12.78)	26.40 (25.82)	
$Cu(CO)C_2H_5SO_3$	17.95 (17.22)	2.51 (2.25)	15.98 (15.71)	31.66 (31.31)	
$Cu(CO)CH_3SO_3$	12.87 (12.64)	1.61 (2.13)	17.18 (17.04)		
$Cu(CO)CH_3C_6H_4SO_3$	36.57 (36.32)	2.69 (2.65)	12.20 (11.76)		
$Cu(bpy)(CO)CF_3SO_3$	36.27 (36.05)	2.01 (2.12)	8.06 (8.29)	15.12 (16.01)	7.05 (6.95)
$Cu(tmed)(CO)CH_3SO_3$	31.69 (31.14)	6.60 (7.10)	10.57 (11.26)		9.24 (9.13)
$Cu(phen)(CO)CF_3SO_3$	39.95 (39.73)	1.90 (2.04)	7.61 (7.47)	15.10 (14.80)	6.66 (6.80)
$Cu(C_2H_4)CH_3SO_3$	19.30 (18.82)	3.78 (3.89)	17.18 (18.18)	34.04 (34.73)	
$Cu(C_7H_{10})CH_3SO_3$	38.01 (37.29)	5.18 (4.99)	12.68 (12.92)	25.13 (24.94)	
$Cu_2(PhC{\equiv}CPh)_3(CH_3SO_3)_2$	62.03 (61.75)	4.26 (4.35)	7.53 (7.07)	14.92 (15.52)	
$Cu_2(COD)_3(CF_3SO_3)_2$	28.23 (27.83)	4.26 (4.17)	15.07 (16.76)	29.87 (29.63)	
$Cu_2(COD)_3(CH_3SO_3)_2$	48.64 (49.09)	6.60 (6.54)	9.99 (9.64)	19.80 (20.59)	
$Cu_2(C_3H_7C{\equiv}CCH_3)(CH_3SO_3)_2$	24.05 (23.81)	4.04 (3.03)	16.06 (16.41)	31.81 (31.69)	
$Cu_2(C_7H_8)(CH_3SO_3)_2$	26.40 (26.50)	3.45 (3.53)	15.66 (15.83)	31.04 (30.03)	

Salomon and Kochi[17] described the preparation of a variety of olefin and diolefin complexes of the type $Cu(olefin)CF_3SO_3$, some of which were surprisingly stable. It seemed likely that other sulfonate derivatives could also form reasonably stable complexes with unsaturates, and a few experiments were carried out in order to demonstrate this and to get a rough order of stability between the CO, alkene, and perhaps alkyne complexes.

$Cu(CO)CH_3SO_3$ reacts with 1,5-cyclooctadiene in a rather unusual manner. When 1 equiv of the diene is added to a solution containing the carbonyl complex, the CO is displaced, forming a solid precipitate that analyzes for $(CuCH_3SO_3)_2$-COD. The precipitate contained only half of the copper in the starting $Cu(CO)CH_3SO_3$ complex. The remaining soluble copper can be recovered as a white crystalline solid complex with the composition $(CuCH_3SO_3)_2(COD)_3$. Diphenylacetylene (DPA) reacts in a very similar manner, again forming an insoluble complex with the composition $(CuCH_3SO_3)_2L$, whereas monoolefins such as norbornylene and ethylene yield complexes with the composition $CuCH_3SO_3L$. The reaction of olefins with $Cu(CO)CH_3SO_3$ contrasts somewhat with their reaction with $CuCF_3SO_3$. $CuCF_3SO_3$ appears to form 1:1 complexes with monoolefins but may form complexes with 2 mol of a diene bound to the copper.[17] Solely on the basis of the ease of interconversion of ligands, there appears to be no large difference in stability between the CO, olefin, diolefin, or acetylene complexes formed from $CuCH_3SO_3$.

Experimental Section

Reagents. All reagents and solvents were high-purity materials obtained from commercial sources and were used without further purification.

Analyses. Elemental analyses were carried out by either Galbraith Analytical Laboratories or by the Analytical and Information Division, Exxon Research and Engineering Co. All complexes reported gave satisfactory elemental analyses. The data are summarized in Table III.

Infrared spectra were recorded in solution or as Nujol mulls and were calibrated by comparison with the spectrum of polystyrene film. A Perkin-Elmer Model 283 spectrophotometer was used.

Preparation of the Complexes. Unless otherwise stated, all reactions were carried out under a nitrogen atmosphere in a glovebox or in conventional glassware under a nitrogen blanket.

$Cu(CO)CF_3SO_3$. A solution containing 6.12 g (0.04 mol) of HCF_3SO_3 in 50 mL of diethyl ether was added dropwise over 20 min to a suspension of 2.86 g (0.0204 mol) of Cu_2O in 75 mL of diethyl ether while a steady stream of CO was passed through the solution. After being stirred for 1 h at room temperature, the solution was filtered to remove the excess Cu_2O and the filtrate was slowly evaporated under vacuum. A pale pink solid, formed as a residue, was washed several times with pentane and dried. $Cu(CO)CF_3SO_3$ was obtained in nearly quantitative yields. The IR spectrum of the solid displayed a band at 2128 cm^{-1}.

$Cu(CO)CH_3SO_3$, $Cu(CO)C_2H_5SO_3$, and $Cu(CO)$-*p*-$CH_3C_6H_4SO_3$. These compounds were prepared in exactly the same manner as the $CF_3SO_3^-$ salts by substituting the appropriate acid. The infrared spectra of these materials displayed bands at 2130, 2117, and 2113 cm^{-1} for the methanesulfonate, ethanesulfonate, and *p*-toluenesulfonate, respectively.

$Cu(CO)(bpy)CF_3SO_3$. A solution of 1.25 g (8.0 mmol) of 2,2′-bipyridine in 50 mL of diethyl ether was slowly added to a mixture of 2.0 g (8.3 mmol) of $Cu(CO)CF_3SO_3$ in 100 mL of diethyl ether at room temperature while a steady stream of CO was passed through the mixture. After the addition, the mixture was stirred at room temperature for an additional 30 min. The purple solid that precipitated was then filtered off and dried under vacuum. The yield of $Cu(CO)(bpy)CF_3SO_3$ was quantitative.

$Cu(CO)(phen)CF_3SO_3$. This compound was prepared from 1.64 g (8.3 mmol) of 1,10-phenanthroline hydrate and 2.0 g (8.3 mmol) of $Cu(CO)CF_3SO_3$ in exactly the same manner as the bipyridyl complex.

$Cu(CO)(tmed)CH_3SO_3$. A solution of 1.0 g (8.6 mmol) of *N*,*N*,*N*′,*N*′-tetramethylethylenediamine in 25 mL of THF was added to a solution of 0.81 g (4.3 mmol) of $Cu(CO)CH_3SO_3$ in 50 mL of THF under a CO atmosphere. After being stirred for 1 h, the solution was evaporated to dryness on a rotary evaporator, giving a white solid. This was washed with several portions of pentane and dried. The yield was 1.8 g.

$Cu_2(C_6H_5C{\equiv}CC_6H_5)_3(CH_3SO_3)_2$. A mixture of 1.0 g (5.4 mmol) of $Cu(CO)CH_3SO_3$ and 0.95 g (5.3 mmol) of diphenylacetylene in 70 mL of THF was stirred for 12 h at room temperature and then rfluxed for 15 min. The mixture was then filtered to remove 0.6 g of white solids. The clear yellow filtrate was evaporated to dryness, and the residue was washed several times with pentane. A 1.20-g yield of yellow $Cu_2(C_6H_5C{\equiv}CC_6H_5)_3(CH_3SO_3)_2$ was obtained.

$Cu_2(C_7H_8)(CH_3SO_3)_2$. A mixture of 1.0 g (5.4 mmol) of $Cu(CO)CH_3SO_3$ and 0.5 g (5.4 mmol) of norbornadiene in 75 mL of THF was stirred for several hours until no evidence of the CO complex could be detected by infrared spectroscopy. The white solids that formed were collected on a frit and washed with 20 mL of THF followed by several small portions of pentane. A 1.13-g yield of product was obtained.

$Cu(C_7H_{10})CH_3SO_3$. A solution of 1 g (5.4 mmol) of $Cu(CO)CH_3SO_3$ and 0.5 g (5.4 mmol) of norbornene in 75 mL of THF was stirred for 8 h and then brought to reflux for 10 min. The hot solution was filtered, and after cooling, the clear filtrate was evaporated, giving a solid yellow residue. This was washed with pentane and vacuum dried, giving 0.96 g of product.

$Cu_2(C_3H_7C{\equiv}CCH_3)(CH_3SO_3)_2$. A solution containing 1.5 g (8.0 mmol) of $Cu(CO)CH_3SO_3$ and 0.66 g (8.0 mmol) of 2-hexyne in 70 mL of THF was refluxed for 30 min and then filtered to remove a small amount of solid material. The clear filtrate was evaporated to dryness, and the solid residue was extracted several times with small portions of pentane. The resulting white solid was dried in vacuum. The yield was 1.42 g.

$Cu(C_2H_4)CH_3SO_3$. Ethylene was bubbled through a solution containing 1.0 g (5.4 mmol) of $Cu(CO)CH_3SO_3$ in 75 mL of THF

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Table IV. Positional Parameters

atom	*x*	*y*	*z*
Cu	0.8443 (1)	0.0390 (2)	0.5323 (1)
C(1)	0.9250 (4)	−0.0611 (17)	0.5823 (7)
O(1)	0.9760 (3)	−0.1182 (22)	0.6129 (8)
S	0.7037 (1)	−0.0533 (3)	0.6036 (1)
O(2)	0.7699 (2)	0.0471 (9)	0.6198 (3)
O(3)	0.6635 (3)	0.0716 (8)	0.5194 (3)
O(4)	0.7015 (2)	−0.3441 (9)	0.5927 (3)
C(2)	0.6694 (4)	0.0243 (13)	0.7141 (5)
C(3)	0.6021 (4)	−0.0828 (19)	0.7118 (7)
H(1)	0.679 (3)	0.245 (15)	0.723 (5)
H(2)	0.706 (3)	−0.062 (14)	0.764 (5)
H(3)	0.568 (4)	−0.029 (16)	0.675 (6)
H(4)	0.609 (4)	−0.291 (17)	0.701 (5)
H(5)	0.590 (4)	−0.027 (16)	0.775 (6)

for several hours. When there was no evidence of the CO complex remaining, the white solid that had formed was isolated by filtration. After the solid was washed with additional THF and pentane and then dried, 0.6 g of product was obtained.

$Cu_2(COD)(CH_3SO_3)_2$ and $Cu_2(COD)_3(CH_3SO_3)_2$. A solution of 1 g (9.24 mmol) of 1,5-cyclooctadiene in 25 mL of methylene chloride was added dropwise to a suspension of 1.72 g (9.22 mmol) of $Cu(CO)CH_3SO_3$ in 50 mL of methylene chloride, and the mixture was stirred at room temperature overnight. The white solid that resulted was filtered off, washed with methylene chloride, and dried. A 1.0-g yield of product identified as $Cu_2(COD)(CH_3SO_3)_2$ was obtained. The filtrate was evaporated to dryness and the white solid residue washed several times with pentane and dried. The yield of $Cu_2(COD)_3(CH_3SO_3)_2$ was 1.3 g.

X-ray Diffraction Data. A pale green crystal of $Cu(CO)C_2H_5SO_3$ with approximate dimensions of 0.20 × 0.25 × 0.30 mm was selected for the experiment and was mounted in a thin-walled glass capillary. Initially, 25 reflections were automatically located and centered on an Enraf-Nonius CAD4 diffractometer using Mo Kα (λ = 0.71073 Å) radiation. A least-squares fit of the 2θ values of these reflections gave a monoclinic unit cell with dimensions of a = 20.630 (4) Å, b = 5.004 (1) Å, c = 13.410 (3) Å, and β = 97.42 (2)°.[18]

Data were collected in the range $2\theta \leq 50°$ by utilizing the diffractometer in an ω–2θ scan mode with a variable scan rate of 2–13° in 2θ/min. The scan of each intensity was begun 1.0° below the $K\alpha_1$ angle and terminated 1.0° above the $K\alpha_2$ angle, with a total background counting time equal to half the total scan time and evenly divided on each side of the reflection peak. A total of 1202 unique diffraction maxima were measured, of which 802 were considered to be observed ($I \geq 2\sigma(I)$). Three reflections were monitored at periodic intervals throughout the data collection to ensure that the crystal was not deteriorating and no significant intensity changes were observed.

A calculated density of 1.94 g/cm^3 was obtained for $Z = 8$ with a unit cell volume of 1372.7 Å^3 and a formula weight of 200.7 for $CuC_3H_5SO_3$. The systematic extinctions ($h0l$, $l = 2n$; hkl, $h + k = 2n$) and the density considerations were consistent with the monoclinic space group $C2/c$ and one $Cu(CO)C_2H_5SO_3$ group per asymmetric unit. Absorption corrections were not applied to the data since inspection of the φ-scan data revealed the effect to be negligible.

The positions of the copper and sulfur atoms in the complex were located by interpretation of a three-dimensional Patterson synthesis. The remaining atoms were located in subsequent difference Fourier maps. Full-matrix least-squares refinement of atomic parameters with anisotropic thermal parameters for all non-hydrogen atoms and fixed isotropic temperature factors for the hydrogen atoms converged to the standard crystallographic residuals of R = 4.5% and R_w = 5.7%. The quantity minimized in the least-squares refinement was $\sum w(|F_o| - |F_c|)^2$ where $w = \sigma(F_o)^{-2}$ and $\sigma(F_o) = \sigma(I)/2|F_o|Lp$, where L and p are the Lorentz and polarization corrections. The largest peak in the final difference Fourier synthesis had an electron density equal to 0.7 e/Å^3. Table IV gives a list of the atomic coordinates.

Registry No. $Cu(CO)CF_3SO_3$, 81967-72-8; $Cu(CO)C_2H_5SO_3$, 86689-38-5; $Cu(CO)CH_3SO_3$, 86689-26-1; $Cu(CO)CH_3C_6H_4SO_3$, 81967-73-9; $Cu(bpy)(CO)CF_3SO_3$, 86689-27-2; $Cu(tmed)(CO)CH_3SO_3$, 86689-28-3; $Cu(phen)(CO)CF_3SO_3$, 86689-29-4; $Cu(C_2H_4)CH_3SO_3$, 86689-30-7; $Cu(C_7H_{10})CH_3SO_3$, 86689-31-8; $Cu_2(PhC{\equiv}CPh)_3(CH_3SO_3)_2$, 86689-32-9; $Cu_2(COD)_3(CF_3SO_3)_2$, 86689-33-0; $Cu_2(COD)_3(CH_3SO_3)_2$, 86689-34-1; $Cu_2(C_3H_7C{\equiv}CCH_3)(CH_3SO_3)_2$, 86689-35-2; $Cu_2(C_7H_8)(CH_3SO_3)_2$, 86689-36-3; Cu_2O, 1317-39-1.

Supplementary Material Available: Tables of thermal parameters and observed and calculated structure factors (5 pages). Ordering information is given on any current masthead page.

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(18) All calculations were performed with use of the Enraf-Nonius structure determination package, an integrated set of crystallographics computer programs for PDP II series computers.

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Syntheses and Crystal and Molecular Structures of $M_6(Ph_2PCH_2CH_2CO_2)_{12}$ (M = Ni(II), Co(II))

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The isostructural complexes $M_6(Ph_2PCH_2CH_2CO_2)_{12}$ (M = Ni(II), Co(II)) have been prepared by the interfacial reaction of solutions of $Ph_2PCH_2CH_2CO_2H$ in CH_2Cl_2 and $M(NO_3)_2$ in aqueous $NaHCO_3$. Satisfactory crystals of the Ni(II) and Co(II) complexes were obtained from CH_2Cl_2/C_6H_{14} and acetone, respectively. The complexes crystallize in space group $R\bar{3}$ with $Z = 3$. For M = Ni(II): $a = b$ = 27.559 (5) Å, c = 21.607 (4) Å, V = 14212 (8) Å^3, ρ(calcd) = 1.205 g cm^{-3} with mol wt 3439.3. For M = Co(II): $a = b$ = 27.597 (4) Å, c = 21.425 (4) Å, V = 14131 (7) Å^3, ρ(calcd) = 1.213 g cm^{-3} with mol wt 3440.6. The common structure is based on a M_6O_6 ring with a nearly octahedral field of five oxygen atoms and one phosphorus atom about each M. Half of the $Ph_2PCH_2CH_2CO_2^-$ is coordinated through the carboxylato oxygens to two M sites (average M–O = 2.04 ± 0.03 Å) in a conventional syn–syn manner, with the phosphorus donor site remaining uncoordinated. The other $Ph_2PCH_2CH_2CO_2^-$ ligands chelate the metal sites through P and O2 with M–O2 = 2.128 (3) and 2.169 (5) Å for Ni(II) and Co(II), respectively. The carboxylato oxygen O2 also bridges to a second metal site with M′–O2 = 2.069 (3) and 2.116 (5) Å for Ni(II) and Co(II), respectively. The second carboxylato oxygen atom (O1) bridges to still a third metal atom (M–O1 = 2.034 (3) and 2.037 (5) Å for Ni(II) and Co(II), respectively) to complete a η^3 bonding scheme. The M–M distances of 3.510 (1) Å for Ni(II) and 3.557 (1) Å for Co(II) preclude any type of direct metal–metal bonding.

Introduction

Individually, tertiary phosphines and carboxylate anions constitute two important and well-studied classes of ligands. Frequently, both types of ligands are incorporated into the same complex,[1-3] and in recent years ligands containing both functions have gained attention.[4-26] The bifunctional ligands

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(1) Marko, L. *Pure Appl. Chem.* **1979**, *51*, 2211.

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