Sulfur Chelates. 31.[1] Synthesis and Characterization of Aryl Xanthogens, Xanthate Esters, and Esters of O-Aryl S-Alkyl Thiocarbonates. Synthesis and Single-Crystal X-Ray Structure of a Polymeric Xanthogen Complex of Copper(I), [CuCl(S₂COC₆H₄-4-CH₃)₂]ₙ

$[CuCl(S_2COC_6H_4\text{-}4\text{-}CH_3)_2]_n$

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Abstract: The synthesis and characterization of aryl xanthogens are reported in this paper. These materials are readily formed by oxidation of the metal aryl xanthates.[1,2] Attempts to prepare the analogous COS derivatives by a similar route failed, although esters of the O-aryl thiocarbonates were obtained by a less direct route. The reaction of the aryl xanthogens with CuCl leads to the formation of a copper(I) complex in which the thione sulfur atom of the xanthogen coordinates to the copper. Two such S atoms are bound to each Cu(I) atom. The overall structure is polymeric with the metallic portion containing discrete halide bridged $Cu_2Cl_2S_4$ units. A pseudotetrahedral coordination exists about each Cu(I) atom with a Cu–Cu distance of 2.872 Å. The Cu–Cl distances are 2.302 (6) and 2.430 (4) Å while the bonded Cu–S distances are 2.284 (5) and 2.330 (6) Å. The S–S distance in the disulfide portion of the structure is 2.070 (7) Å. The distance of the disulfide unit from Cu(I) is over 3.2 Å. The phenyl ring is tilted nearly perpendicular to the OCS_2 plane in each subunit. Anisotropic refinement of the heavy atoms with isotropic refinement of the carbon positions has produced agreement parameters $R = 0.063$, $R_w = 0.058$ for 906 data in an orthorhombic cell, $Z = 8$.

Introduction

Recently we reported[1,2] the first successful synthesis of a variety of metal aryl xanthates, derivatives of CS_2 with phenols. Oxidation of the metal xanthate (eq 1), where R = alkyl or aryl, to the xanthogen is readily accomplished. Aryl xanthogens have not been reported previously.

$$2M(S_2COR) \xrightarrow{\text{oxidn}} (ROC(S)S)_2 + 2M^+ + 2e^- \quad (1)$$
$$\text{xanthate} \qquad\qquad \text{xanthogen}$$
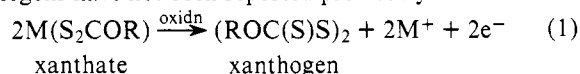
The reaction of organic disulfides with metal halides can produce a rupture of the S–S bond to give the mercaptide complex of the oxidized metal. Aryl xanthogens or thiuram disulfides, $(R_2NCS_2)_2$, oxidize metallic copper[2] to produce Cu(II) products, some of which are soluble in organic solvents. Beurskens et al.[3] also have isolated and characterized copper(III) dithiocarbamates, $CuX_2(S_2CNR_2)$, from the reaction of Cu(I) halides with thiuram disulfides. The reaction of Cu^ICl with the aryl xanthogen, R = *p*-methylphenyl, was found (eq 2) to produce a product with a stoichiometry that suggested possible formation of a copper(III) derivative, CuCl-(xanthate)₂. Subsequent structural analysis showed that the product contains the aryl xanthogen coordinated to copper(I). The structural details of this interesting polymeric copper(I) xanthogen complex are presented.

$$nCuCl(s) + n(ROCS_2)_2 \rightarrow [CuCl(S_2COR)_2]_n \quad (2)$$
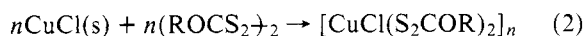
While the reaction of CS_2 with thallium(I) phenoxides leads to thallium(I) xanthates, COS did not give a successful insertion product with Tl(OAr). It had been hoped that the alkylation of the thallium(I) derivative thus obtained could be used to produce alkyl esters of the O-aryl thiocarbonates, RSC(S)OAr. It was possible to synthesize these esters by an alternative route, however.

Experimental Section

Aryl Xanthogens, (ArOCS₂)₂. A solution of 1.7 g of I_2 in 30 mL of pentane was slurried with 5.0 g of the thallium(I) salt for about 1 h. The mixture was filtered and the black solid washed with 2 × 10 mL of pentane. The filtrate was stirred with a small piece of clean sodium (0.5 g) or with excess aryl xanthate to remove excess I_2. The solution

was filtered again and the product obtained by slow evaporation.

The compounds prepared are reported in Table I. The yields are 85–96%.

Methyl Xanthates, CH₃SC(S)OAr. The method of McKay et al.[9] for the synthesis of S-methyl O-phenylxanthate was followed with slight modification. At room temperature 10 g of 2,6-dimethylphenol and 5.0 g of KOH in 80 mL of dimethylformamide (DMF) were stirred for 20 min. The solution was filtered and ~10 g of CS_2 was added slowly to the filtrate over 30 min at a water bath temperature of 20 °C. Methyl chloride was bubbled through the solution for 30 min at room temperature. Water (1500 mL) was added and the mixture extracted with ether (5 × 100 mL). The ether extracts were combined and washed with 5% NaOH, 5% HCl, and water. Evaporation and fractional distillation, bp 78–80 °C (0.1 mm), gave the desired S-methyl 2,6-dimethylphenylxanthate.

Anal.[10] Calcd for $C_{10}H_{12}OS_2$: C, 56.6; H, 5.7. Found: C, 56.7; H, 5.7.

The methyl ester of the phenyl xanthate was prepared, S-methyl phenylxanthate.

Anal.[10] Calcd for $C_8H_8OS_2$: C, 52.1; H, 4.4. Found: C, 51.2; 4.4.

Alkyl Esters of Aryl Thiocarbonates. It was thought that the synthesis of aryl thiocarbonates could be achieved by utilizing COS, paralleling the synthesis of the aryl xanthates. The resulting $TlSC(O)OC_6H_5$ product then could be reacted with alkyl iodide to produce the ester. Unfortunately the metal derivatives proved too unstable for the effective synthesis of the esters by this route. Instead, the following reactions were used.
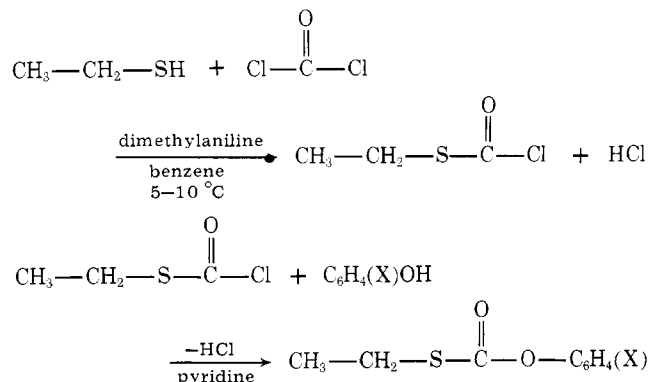
$$CH_3\text{—}CH_2\text{—}SH \;+\; Cl\overset{\displaystyle O}{\overset{\|}{\text{—}C\text{—}}}Cl$$

$$\xrightarrow[\substack{\text{benzene}\\ 5\text{–}10\ ^\circ C}]{\text{dimethylaniline}} CH_3\text{—}CH_2\text{—}S\overset{\displaystyle O}{\overset{\|}{\text{—}C\text{—}}}Cl \;+\; HCl$$

$$CH_3\text{—}CH_2\text{—}S\overset{\displaystyle O}{\overset{\|}{\text{—}C\text{—}}}Cl \;+\; C_6H_4(X)OH$$

$$\xrightarrow[\text{pyridine}]{-HCl} CH_3\text{—}CH_2\text{—}S\overset{\displaystyle O}{\overset{\|}{\text{—}C\text{—}}}O\text{—}C_6H_4(X)$$

Table I. Aryl Xanthogens[a]

Compd	Mp, °C	Anal. information[b,11]
$(S_2COC_6H_5)_2$	60-63	C, 49.7 (49.6); H, 3.19 (2.99); mol wt, 338 (320); ν(CO) 1220, 1170; ν(CS) 1020; δ_R ~7.25, ^{13}C, 206.1
$(S_2COC_6H_4$-4Me$)_2$	45-47	C, 52.4 (52.3); H, 3.84 (3.88); S, 35.0 (35.0); mol wt, 367 (327); ν(CO) 1230, 1172; ν(CS) 1050; δ_R 6.98, 7.23; δ(CH$_3$) 2.20, ^{13}C, 206.4
$(S_2COC_6H_4$-4-*t*-Bu$)_2$	25[c]	Mol wt, 451 (464); ν(CO) 1220, 1160; ν(CS) 1017, δ_{om} 7.03, 7.44; δ(CH$_3$) 1.33
$(S_2COC_6H_3$-3,5-Me$)_2$	101	Mol wt 395 (377); ν(CO) 1232; ν(CS) 1030
$(S_2COC_6H_3$-2,6-Me$)_2$)	122-124	C, 54.8 (54.6); H, 4.6 (4.6); δ_k 6.99; δ(CH$_3$) 2.08; ^{13}C 204.5
$(S_2COC_6H_2$-2,4,6 Me$)_2$	110-115	C, 56.8 (57.0); H, 5.2 (5.3); δ_r 6.78; δ(CH$_3$) 2.04, 2.26; ^{13}C, 205.3
$(S_2COC_6H_3$-2,6-*i*-Pr$)_2$	*c*	δ_R 7.10; δ(H) 2.85; δ(CH$_3$) 2.85, *J* = 7.0 Hz; ^{13}C, 206.7
$(S_2COC_6H_4$-2-*i*-Pr$)_2$	*c*	δ_R 6.92, 7.20; δ(CH$_3$) 1.14; δ(H) 2.97; *J* = 7.0 Hz; ^{13}C, 206.1

[a] For complete NMR data see ref 1b. [b] Results are presented in parentheses when compared with calculated. ^{13}C refers to carbon of CS$_2$ portion of molecule. [c] Liquid at room temperature.

The *S*-ethyl monothiochloroformate was prepared in a manner similar to the method described by Strain et al.[11] for other chloroformates. Phosgene was dried by passing it through concentrated sulfuric acid, and condensed in a three-necked, 250-mL round-bottom flask immersed in a dry ice/acetone bath. The flask was vented through a trap immersed in a dry ice/acetone bath. To 20 mL (0.28 mol) of the phosgene was added 75 mL of dry benzene. At this point, the dry ice/acetone bath used for the reaction flask was replaced with an ice bath. To the solid phosgene/benzene mixture was added a mixture of 15.5 mL (0.2 mol) of freshly distilled *N,N*-dimethylaniline and 14.8 mL (0.2 mol) of ethanethiol. During this addition, the temperature was held below 10 °C. The reaction mixture then was left to warm slowly overnight. To remove the *N,N*-dimethylaniline, the solution was washed with 3 × 100 mL of dilute hydrochloric acid followed by 2 × 100 mL of water. The benzene layer was dried over calcium chloride. Fractional distillation gave 19.8 g (80% yield) of the blue-green product which turned lime green on cooling. The NMR spectrum was consistent with the formation of *S*-ethyl monothiochloroformate. Also a parent ion mass spectrum was obtained with the three highest intensity lines at *m/e* values of 32, 89, and 124.

Using a procedure similar to that described by Joshi et al.,[12] the aryl monothiocarbonates were easily prepared. To 1.24 g (0.01 mol) of *S*-ethyl monothiochloroformate in 10 mL of pyridine was added (with stirring) 1.5 g (0.01 mol) of the phenol. No heating was necessary. After 1 h, ethyl ether was added to the reaction mixture to assure complete precipitation of the white pyridine hydrochloride which was then suction filtered. The yellow, oily product (~65% yield) was recovered by evaporating the excess pyridine with a stream of nitrogen. To remove any unreacted starting material, the product was passed through a 25-cm alumina-packed column using 50 mL of methylene chloride as the solvent. The compounds were characterized by NMR and IR with the principal mass spectral peaks listed below. Strong parent ion peaks were observed in each case.

S-Ethyl *O*-4-*tert*-butylphenylthiocarbonate: mol wt calcd 238. Strongest five lines observed *m/e* 163, 135, 210, 238, 185.

S-Ethyl *O*-4-chlorophenylthiocarbonate: mol wt calcd 216. Strongest six lines observed *m/e* 128, 89, 216, 188, 156, 130 (the last four lines have approximately equal intensity).

S-Ethyl *O*-3-chlorophenylthiocarbonate: mol wt calcd 216. Strongest four lines observed *m/e* 128, 216, 89, 32.

S-Ethyl *O*-3,4-dichlorophenylthiocarbonate: mol wt calcd 250. The eight strongest lines observed *m/e* 90, 79, 152, 122, 52, 150, 154, 250.

[CuCl(S$_2$COC$_6$H$_4$-4-CH$_3$)$_2$]$_n$. This complex was synthesized by mixing a 1:1 ratio of freshly prepared CuCl[13] with the xanthogen in CS$_2$ until the solution changed color from yellow to brown-orange. In a few days some long, yellow-orange needles were obtained which

Table II. Summary of Crystal Data for [Cu(Cl)(xanthogen)]$_n$

Molecular formula	[Cu(Cl)(S$_2$COC$_6$H$_4$CH$_3$)$_2$]$_n$
Formula weight	465.535
d calcd, g/cm^3	1.562
d obsd, g/cm^3	1.53 (1)
Z, formula units/cell	8
Linear absorption coeff μ, cm^{-1}	17.2
λ (Mo Kα), Å	0.71069
Crystal dimensions	0.12 × 0.25 × 0.15 mm
Systematic absences	0*kl*: *k* = 2*n*
	h0l: *l* = 2*n*
	*hk*0: *h* = 2*n*
Space group	D_{2h}^{15}-*Pbca* (no. 61), orthorhombic
Cell constants[a]	
a, Å	21.536 (4)
b, Å	16.956 (4)
c, Å	10.839 (1)
Volume, Å^3	3958.1 (15)
F (000)	1812

[a] The data were obtained at ~25 °C. The refined cell constants were obtained with 15 reflections having $2\theta_{av}$ = 15.47°.

Table III. Summary of Final Refinement Results for [Cu(Cl)(xanthogen)]$_n$[a]

Data used	$I/\sigma(I) \geq 3.0$
No. of reflections (not corrected for absorption)	906
No. of varied parameters (nonhydrogen)/cycle	127
No. of reflections/no. of varied parameters	7.1
Final R [$R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$]	0.063
R_w [$R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$]	0.058
Final weighting scheme	$w_i = 1/\sigma_i^2(F)$

[a] With 1296 data, $I/\sigma(I) \geq 1.2$, $R = 0.09$, $R_w = 0.067$.

were removed by evaporation of the solvent, mp 150 ° dec.

Crystallographic Data. Space Group, Lattice Parameters, Data Collection, and Reduction. A long (needle) crystal was cut to suitable size (see Table II) for data collection. The systematic absences are consistent with the orthorhombic space group D_{2h}^{15}-*Pbca* (no. 61). The lattice parameters were deduced (at ambient temperature, 25 °C) from the angular settings of 15 centered reflections, average 2θ = 15.47° (using graphite crystal monochromatic Mo Kα radiation). A total of 4118 (of which 1978 were independent *hkl* reflections) with $0° \leq 2\theta \leq 50°$ were collected on a Syntex P2$_1$ diffractometer, using θ–2θ scan technique with variable scan rates from 2.0° to 29.30°/min and a scan range from 2θ = (Mo Kα_1) − 1.0° to 2θ (Mo Kα_2) + 1.0°. During data collection two standard reflections were monitored every 50 reflections. The maximum variation of the standard reflections was ±5% throughout data collection. The data reduction process incorporated the usual Lorentz, polarization, and decay factor corrections. The number of reduced data with $I/\sigma(I) \geq 0.0$, 1.2, and 3.0 are 1513, 1296, and 906. Only 906 data were used in the final refinement.

Solution and Refinement of the Structure. The heavy atom positions were found both from a direct-methods (MULTAN) solution and from a Patterson synthesis.

The Wilson plot[14] and the distribution of the |*E*|'s were in good agreement with the theoretical values for a centric space group. The normalized structure factors (270 data with *E* ≥ 1.0) were generated. The phases of the (11,1,1), (6,7,0), and (0,6,5) reflections were chosen in MULTAN to fix the origin. Three other reflections, (10,0,0), (10,6,5), and (5,6,1), also were used in the starting set. Eight sets of phases were generated for 204 *E*'s. The eighth solution had the highest ABS FORM = 2.305 and the lowest RESID = 30.28. The *E* map generated by this solution revealed once copper, one chlorine atom, and four S atom positions. A structure factor calculation using these six positions yielded $R = 0.26$, $R_w = 0.34$ for 906 data. Subsequent Fourier synthesis revealed all the nonhydrogen atoms. Two cycles of full matrix isotropic refinement gave $R = 0.087$, $R_w = 0.080$ (with a statistical weighting scheme). Two cycles of full matrix anisotropic refinement of Cu, one Cl, and four S atoms and isotropic refinement of 18 C atoms gave the final values (Table III). Analysis of agreement factors as functions of fixed *h*, *k*, *l*, sin θ/λ, and F_o revealed no unac-

Table IV. Positional and Thermal Parameters with Estimated Standard Deviations for [Cu(Cl)(xanthogen)]$_n$

	x	y	z	B
Cu	0.4529 (1)	0.4481 (1)	0.4534 (2)	
S(1)	0.3632 (2)	0.3984 (3)	0.5347 (6)	
S(2)	0.4530 (3)	0.2951 (3)	0.6484 (5)	
S(3)	0.4283 (3)	0.4662 (8)	0.2460 (5)	
S(4)	0.4488 (3)	0.2987 (3)	0.2703 (5)	
Cl	0.5539 (2)	0.4127 (2)	0.4952 (4)	
C(1)	0.3787 (10)	0.3245 (11)	0.6236 (18)	3.9 (5)
O(1)	0.3336 (6)	0.2801 (7)	0.6805 (12)	4.6 (3)
CB(1)	0.2689 (9)	0.2926 (11)	0.6517 (19)	3.8 (5)
CB(2)	0.2451 (8)	0.2570 (10)	0.5501 (19)	3.8 (4)
CB(3)	0.1804 (8)	0.2669 (10)	0.5283 (18)	3.8 (4)
CB(4)	0.1463 (10)	0.3124 (12)	0.6139 (20)	5.0 (5)
CB(5)	0.1735 (10)	0.3489 (11)	0.7089 (19)	4.3 (5)
CB(6)	0.2371 (9)	0.3417 (11)	0.7355 (19)	4.2 (5)
CME(1)	0.0751 (10)	0.3217 (12)	0.5780 (19)	6.2 (6)
C(2)	0.4256 (8)	0.3796 (10)	0.1858 (16)	2.9 (4)
O(2)	0.4107 (5)	0.3630 (6)	0.06660 (12)	4.0 (3)
CB(7)	0.3855 (9)	0.4271 (10)	−0.0112 (16)	3.3 (5)
CB(8)	0.4241 (19)	0.4496 (11)	−0.1018 (17)	3.9 (5)
CB(9)	0.3991 (10)	0.5095 (12)	−0.1769 (19)	5.2 (6)
CB(10)	0.3373 (10)	0.5378 (12)	−0.1595 (20)	4.8 (5)
CB(11)	0.3005 (9)	0.5066 (11)	−0.0616 (20)	4.9 (5)
CB(12)	0.3260 (10)	0.4494 (11)	−0.0148 (18)	4.5 (5)
CMe(2)	0.3089 (10)	0.5997 (11)	−0.2495 (24)	6.1 (5)

	β_{11}[a]	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cu	0.0024 (1)	0.0028 (1)	0.0097 (3)	−0.0005 (1)	−0.0008 (2)	−0.0001 (2)
S(1)	0.0018 (1)	0.0029 (2)	0.0138 (8)	−0.0002 (2)	−0.0002 (3)	0.0024 (4)
S(2)	0.0018 (2)	0.0029 (2)	0.0115 (7)	−0.0002 (2)	−0.0011 (4)	0.0017 (3)
S(3)	0.0033 (2)	0.0019 (2)	0.0083 (6)	0.0000 (2)	−0.0013 (3)	−0.0003 (3)
S(4)	0.0030 (2)	0.0025 (2)	0.0083 (6)	0.0002 (2)	−0.0022 (3)	−0.0006 (3)
Cl	0.0020 (1)	0.0021 (2)	0.0087 (6)	−0.0002 (1)	−0.0004 (3)	−0.0001 (2)

[a] The form of the thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.
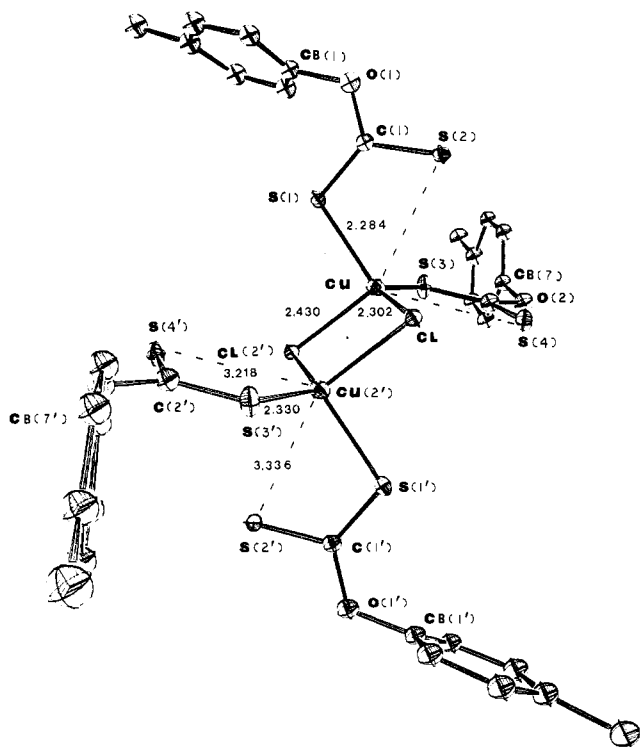

Figure 1. An ORTEP thermal ellipsoid (50% probability) view of one dimeric unit in [Cu(Cl)(xanthogen)]$_n$. One-half of each xanthogen ligand is not shown.

countable trends. Atomic scattering factors for neutral atoms were taken from Cromer and Waber.[15] The final refinement is summarized in Table III with coordinates and thermal parameters presented in

Table V. Significant Intramolecular Bond Lengths and Angles for [Cu(Cl)(xanthogen)]$_n$

Bond	Length, Å	Angle	Deg
		Cl–Cu–Cl(2′)	105.3 (2)
Cu–Cu*(2)	2.872 (3)	Cl–Cu–S(1)	128.8 (3)
Cu–Cl	2.302 (6)	Cl–Cu–S(3)	116.0 (3)
Cu–Cl*(2)	2.430 (4)	Cl(2)–Cu–S(1)	102.6 (3)
Cu–S(1)	2.284 (5)	Cl(2)–Cu–S(3)	94.6 (3)
Cu–S(3)	2.330 (6)	S(1)–Cu–S(3)	103.2 (3)
S(1)–C(1)	1.611 (20)	Cu–Cl–Cu(2)	74.7 (2)
S(2)–C(1)	1.698 (21)	Cu–S(1)–C(1)	109.9 (8)
S(3)–C(2)	1.608 (17)	Cu–S(3)–C(2)	106.2 (7)
S(4)–C(2)	1.722 (18)	S(1)–C(1)–C(2)	121.4 (12)
C(1)–O(1)	1.378 (24)	S(3)–C(2)–S(4)	120.1 (10)
C(2)–O(2)	1.361 (22)	S(1)–C(1)–O(1)	123.2 (12)
O(1)–CB(1)	1.444 (24)	S(2)–C(1)–O(1)	115.4 (12)
O(2)–CB(7)	1.478 (21)	S(3)–C(2)–O(2)	125.6 (11)
S–S	2.070 (7)	S(4)–C(2)–O(2)	114.1 (11)
		C(1)–O(1)–CB(1)	120.2 (12)
		C(2)–O(2)–CB(7)	118.5 (11)
		Av S–S–C	106.7 (8)

Table IV, and Table V contains the significant bond lengths and angles.

Description of the Structure. The structure of [CuCl(xanthogen)]$_n$ displaying one dimeric unit containing half of the four xanthogen ligands is presented in Figure 1. Each dimeric unit is connected with four other dimeric units through four different xanthogen ligands, as shown in Figure 2. One dimeric unit is located on the bc plant at $a \simeq 0.5$. This dimer at the unit cell center (0.5, 0.5, 0.5) connects with dimeric units which are located at the four edges of the unit cell. On the bc plane with $a = 0$, the dimeric units are centered at the edges of the unit cell.
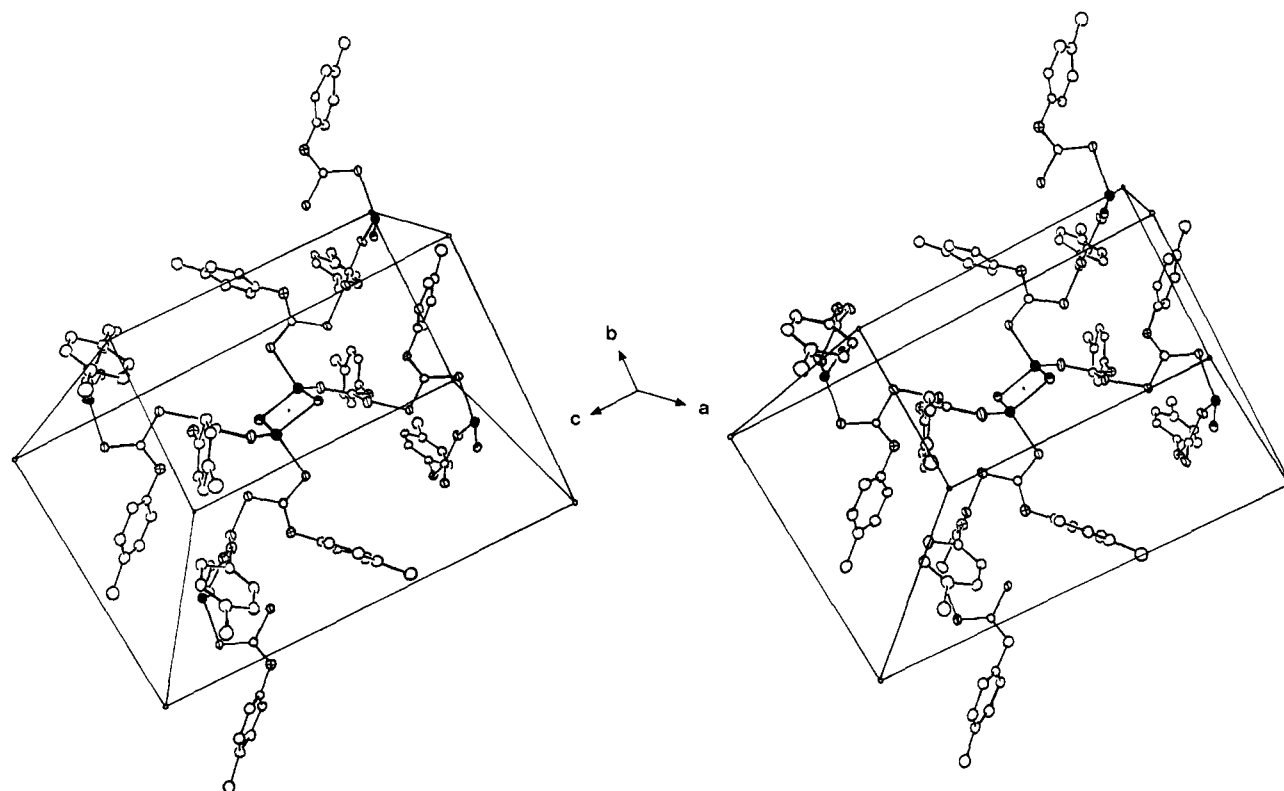
Figure 2. A stereoview (ORTEP) of the [Cu(Cl)(xanthogen)]$_n$ cell. ● = Cu; ◖ = Cl; ⊕ = S; ⊕ = O; ○ = C.

The C–S–S–C torsion angle on the xanthogen ligands produces a helical twist of the polymer away from the center of symmetry located within the Cu$_2$Cl$_2$ rhombus, Figure 2. The Cu–Cu and Cl–Cl distances in the dimeric unit are 2.872 (2) and 3.763 (6) Å, respectively.

The Cu(I) has a distorted tetrahedral coordination. The Cu–Cl bond lengths are 2.302 (6) and 2.430 (4) Å with Cu–S bond lengths of 2.284 (5) and 2.330 (6) Å. The bond angles also show distortions, 128.8 (3), 116.0 (3), and 102.6 (3)° for the Cl–Cu–S angles and 105.3 (2)° for the Cl–Cu–Cl angle.

There are two different S–C bond distances in the xanthogen ligand. S(1)–C(1) and S(3)–C(2) retain substantial double bond character with lengths of 1.611 (20) and 1.608 (17) Å, respectively. The S(2)–C(1) and S(4)–C(2) bonds are 1.698 (21) and 1.722 (18) Å, respectively. Each xanthogen ligand is coordinated to two different copper(I) atoms (see figures). The bonded S–S atoms are not coordinated with the copper(I) atoms, since they are 3.346 (5) and 3.218 (5) Å away. The S–S bond distance is 2.070 (7) Å, in good agreement with other reported values. These C–O distances are 1.378 (24), 1.361 (22) Å for C(1)–O(1) and C(2)–O(2) and 1.444 (24), 1.478 (21) Å for O(1)–CB(1) and O(2)–CB(7). The C–C bond distances in the phenyl are normal, ~1.39 Å.

The phenyl group is tilted and perpendicular to the OCS$_2$ plane. This tilt is also observed in other aryl xanthate structures.[2] The two C(1)–O(1)–CB(1) and C(2)–O(2)–CB(7) angles are 120.2 (12) and 118.5 (11)°, respectively, a normal angle for an ether structure. The torsion angle (dihedral angle[50]) of C–S–S–C is 77.0 (7)°.

Results and Discussion

The synthesis of aryl xanthogens and their esters follows readily the synthesis of the metal complexes. Chemical oxidation of the metal salts with iodine gives good yields of xanthogens. Both liquids and solids were obtained.

The synthesis of the methyl ester of phenyl xanthate was reported in 1960 by McKay et al.[9] We have found this procedure to be quite satisfactory. No attempts were made to synthesize the esters directly from the metal salts with alkylating agents.

Since xanthates have received considerable attention by industries interested in agricultural chemicals, an attempt was

made to produce the *O*-aryl thiocarbonates. We assumed that an insertion of COS into a thallium(I) phenoxide would produce the desired metal complex from which xanthogens and esters could be obtained. Unfortunately these attempts failed. However, it was found that the esters could be synthesized by procedures similar to the reactions reported by Joshi et al.[12] and Strain et al.[11] as outlined in the Experimental Section. Biological testing[16] of these compounds suggested that insufficient activity existed to prompt additional work.

The reaction on Cu^{I}Br with tetramethylthiuram disulfide, [(CH$_3$)$_2$NC(S)S]$_2$, has been reported by Steggerda and co-workers[3] to produce an oxidized copper species, Cu$_2$(S$_2$CNMe$_2$)$_3$Br$_2$, which contains both copper(II) and copper(III). The reaction of the aryl xanthogens with CuCl also produces a species with a stoichiometry that would suggest the formation of a copper(III) product, CuCl(xanthate)$_2$. However, structural data reveal the formation of a polymeric copper(I) xanthogen complex. Xanthogens and thiuram disulfides react with metallic copper to rupture the S–S bonds and produce Cu(I) and Cu(II) products. It is also well known that organic disulfides can be cleaved easily by common reducing agents.[3-8] Aqueous HgCl$_2$, for example, will cleave the disulfide to form RSHgCl and RSCl. On the other hand, copper(II) salts react with mercaptides to be reduced to copper(I), forming the disulfides.

Thiuram disulfides have been reported to coordinate metal ions,[17,18] MX$_n$ + R$_4$tds → MX$_n$(R$_4$tds), M = Hg, Co, Ni, Cr. The crystal structure of HgI$_2$(Me$_4$tds) was reported by Cras and his co-workers.[19,20] A similar thiuram disulfide structure is known for the ethyl compounds. These structures show thiocarbonyl coordination to the metal ion with no bonding interaction between the disulfide units and the metal.[20b] Several studies have reported[21-33] organic disulfide coordination to metal ions. In particular, Seff and co-workers[24] have noted that the structure of a dipyridyl disulfide complex of copper(I) with ClO$_4^-$ as the anion contains both coordinated and noncoordinated S–S linkages. They have pointed out a possible

Table VI. Summary of Cu–S and S–S Bond Distances (Å) and CSSC Torsion Angles of Disulfide Compounds or Complexes

Compd	Cu–S[a] (disulfide)	S–S	Torsion angle, deg C–S–S–C	Ref
[Cu(Cl)(xanthogen)]$_n$	3.218 (5)	2.070 (7)	77.0 (7)	This work
	3.346 (5)			
[CuCl·(C$_2$H$_5$)$_2$-S$_2$]$_n$	2.34 (1)	2.04 (2)	97.7	22
	2.40 (1)			
[Cu(RSSR)$_2$]$_2$-(BF$_4$)$_2$	2.288 (6)	2.084 (9)	105.9 (13)	23
	2.302 (7)	2.068 (8)	106.7 (13)	
	2.283 (7)			
	2.326 (6)			
[Cu(RSSR)]$_n$-(ClO$_4$)$_n$	2.318 (1)	2.081 (1)	59.73 (13)	23
	2.325 (1)			
[Cu^{II}-D-PDS]$_2$·9H$_2$O	3.057 (10)	2.03 (1)	103 (1)	21
	3.138 (9)	2.05 (1)	101 (1)	
[Cu(C$_{10}$H$_8$N$_2$-S$_2$)$_2$]^b	2.418^c	2.032 (4)	81.1.–93.3	24
		2.047 (5)		
		2.025 (4)		
		2.026 (4)		
Me$_4$tds		2.00 (1)	88	34
Et$_4$tds		2.00	90.2	35
CuTDP·2py·H$_2$O	5.443	2.0 (1)	81.6 (9)	53

^{a} The oxidation state of Cu is +1 or +2. ^{b} The reported Cu–S bond distance is in the range of 2.19–2.472 Å. Other examples are Cu(SCN$_2$H$_4$)$_3$Cl, 2.313–2.424;[36] Cu(SCMeNH$_2$)$_4$Cl, 2.343 (5);[37] Cu$_4$[SC(NH$_2$)$_2$]$_9$(NO$_3$)$_4$, 2.291–2.372;[38] [Cu[SC(NH$_2$)$_2$]$_2$Cl, 2.240–2.310;[39] [Cu(SPMe$_3$)$_3$]ClO$_4$, 2.253–2.264;[40] [Cu(SPMe$_3$)Cl]$_3$, 2.264–2.267;[41] [Cu(S$_2$CN(Et)$_2$)]$_4$, 2.246–2.290;[42] [(C$_3$H$_7$)$_2$-NCOSCu]$_6$, 2.20–2.25;[43] Cu$_8$(i-MNT)$^{4-}$, 2.237–2.266;[44] (Ph$_4$P)$_4$Cu$_8$DTS$_6$, 2.229–2.268;[45] CuI(C$_4$H$_5$NOS$_2$), 2.301 (3);[46] Cu$_4$[SC(NH$_2$)$_2$]$_6$(NO$_3$)$_4$·4H$_2$O, 2.19–2.31;[47] Cu$_4$[SC(NH$_2$)$_2$]$_9$-(NO$_3$)$_4$·4H$_2$O, 2.24–2.42;[47] (Me$_4$N)$_2$Cu$_4$(SPh$_6$)], 2.29 (1);[48] [Cu(etu)$_3$]$_2$SO$_4$, 2.27–2.28;[49] [Cu(tmtu)$_3$]BF$_4$, 2.236–2.257 Å.[49] Some important S–S bond distances are listed in ref 50, 51, and 25–33. ^{c} Average bond distance.

similarity to the ESR-inactive copper site in ceruloplasmin.[53] Recently Thich et al.[52] have published a structure showing that dithiodipropionate will link CuN$_2$O$_3$ units. This polymer, unlike ours, contains copper(II). Thus there appears to be a delicate balance in these systems between oxidized or reduced disulfide linkages and reduced or oxidized metal centers. Of course, the L$_4$Cu$^I_2$Cl$_2$ dimeric unit also is capable of undergoing a two-electron oxidation to L$_4$Cu$^{II}_2$Cl$_2$.[54] Literature values of the Cu–S bond distances, S–S bond distances, and C–S–S–C torsion angles are listed in Table VI.

A geometric relationship between the C–S–S–C torsion angle and the S–S bond length in the *uncomplexed disulfides* has been suggested by Hordvik.[50] A torsion angle of about 90° has a bond length of about 2.03 Å, but that of ~0° a length of 2.10 Å. This trend is also suggested in Table VI. However, this relationship does not appear to be valid generally for coordination compounds containing disulfides. In the [CuCl(xanthogen)]$_n$ reported here, the S–S distance is 0.02–0.03 Å longer than calculated assuming a torsion angle of 77°. For the tetraethylthiuram disulfide complex with HgI$_2$ reported by Chieh,[20b] the S–S distance is actually below 2.00 Å, although the torsion angle is 88°. In the sulfur-rich dithioarylate complexes,[55] the torsion angle is less than 10° but the S–S distance is around 2.02 Å. However, in these complexes and the HgI$_2$ adduct of Chieh, the S–S linkages are part of a chelate ring.

Supplementary Material Available: Tables of observed and calculated structure factors (4 pages). Ordering information is given on any current masthead page.

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Structural Effects of Cross-Linking in Polymer-Bound Bromotris(triphenylphosphine)rhodium(I) Catalyst by X-Ray Absorption Studies

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Abstract: The influence of cross-linking by divinylbenzene (DVB) in styrene polymer-bound bromotris(triphenylphosphine)-rhodium(I) catalyst has been studied by extended x-ray absorption fine structure (EXAFS) spectroscopy. We report here that the 2% DVB cross-linked polymer-bound rhodium catalyst has two phosphorus atoms at 2.16 (1) and 2.32 (1) Å and two bromine atoms at 2.49 (1) Å as nearest neighbors to the rhodium atom thereby consistent with a dimeric structure. On the other hand, the 20% DVB cross-linked polymer-bound catalyst is found to be a four-coordinate polymer-attached monomer with three phosphorus atoms, one at 2.14 (1) Å and two at 2.26 (1) Å, and one bromine atom at 2.50 (1) Å from the rhodium atom. This study suggests that there is probably some degree of cross-linking between 2 and 20% which is optimum in catalytic activity, and that not all the phosphorus atoms are polymer bound.

Introduction

In a recent communication,[1] we demonstrated that extended x-ray absorption fine structure (EXAFS) could be used to determine the interatomic distances and coordination of Wilkinson's catalyst, $RhCl(PPh_3)_3$,[2-4] and polymer-bound Wilkinson's catalyst.[5] It was reported that polymer-bound Wilkinson's catalyst was a chloro-bridged dimer. This polymer-bound catalytic dimer was supported on a polystyrene cross-linked with 2% divinylbenzene (DVB) skeleton.

One of the major catalytic influences in polymer-bound catalyst is the degree of cross-linking of styrene by divinylbenzene.[6] Our previous results suggest that cross-linking of 1–2% produces dimeric structures inside the swellable insoluble polymer gel where the polymer molecule is mobile enough to form chelates resulting in dimers of the rhodium complex attached to the phosphinated resin support. However, it has been proposed that higher cross-linking in the 20% range renders the ligands attached to this polymer resin less mobile and more brittle.

The catalytic activity generally decreases when the homogeneous catalytic analogue is bound to the polymer framework.[6] We suggested[1] that one of the reasons for the slower rate of hydrogenation could be the formation of the catalytically less active halogen-bridged dimer.[7] In contrast, it has been shown that a high degree of cross-linking could help break up any aggregates formed.[6]

We report a study of the structural changes found in 2% DVB–styrene and 20% DVB–styrene polymer-bound $RhBr(PPh_3)_3$ catalyst[25] by the technique of extended x-ray absorption fine structure (EXAFS). The polymer-bound bromotris(triphenylphosphine)rhodium(I) was chosen both because its structure was unknown and because measurements can be done on both Rh and Br as absorbers to give indepen-

dent measurements for the Rh–Br bond distance. This x-ray absorption technique for the determination of interatomic distances has been used previously to determine bond distances in iron-sulfur proteins,[8] copper salts in aqueous solutions,[9] and in polymer-bound rhodium(I) catalysts.[1]

Experimental Section

The 2% and 20% DVB–styrene polymer-bound $RhBr(PPh_3)_3$ catalyst was purchased from Strem Chemicals. It was prepared by a method similar to that in ref 5 which involved refluxing benzene containing $RhBr(PPh_3)_3$ and the particular cross-linked phosphinated polystyrene resin. The analyses of the polymer-bound resin were the following: 2% cross-linked catalyst, 17.5% P and 2.28% Rh; 20% cross-linked catalyst, 6.5% P an 1.47% Rh.

The photoabsorption K edges of Rh and of Br in 2% and 20% DVB–styrene polymer-bound bromotris(triphenylphosphine)rhodium(I) catalyst were measured using the tunable x-ray synchrotron source at the Stanford Synchrotron Radiation Project, Stanford University. The instrumentation has been previously described.[10,11]

The relationship $\mu x = \ln (I_0/I)$, where μ is the linear absorption coefficient and x is the thickness, is obtained by measuring the intensity of the incident x-ray radiation I_0 passing through an ionization chamber (He + N₂), then transmitted through the sample, and finally monitoring I, the transmitted intensity, by a second ionization chamber (N₂). The absorption is then plotted against the photon energy.

As early as 1931, Kronig proposed the first theory of EXAFS in solids.[12] The current theoretical basis for the EXAFS effect has been advanced by several groups.[13-17] Various methods of data analysis have been published.[16,18-20]

It has been shown[14,16,18,21] that the modulation $\Delta\mu$ of the x-ray absorption coefficient of an atom is given by

$$\frac{\Delta\mu}{\mu} = \sum_j \frac{-N_j |f_j(k,\pi)|}{R_j^2 k} e^{-2\sigma_j^2 k^2} \sin (2kR_j + \phi_j(k)) \qquad (1)$$

where N_j is the number of scattering atoms j at a distance R_j from the absorbing atom with a Debye–Waller-like factor $e^{-2\sigma_j^2 k^2}$. The

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