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Sulfur Chelates. 30.[1] Crystal and Molecular Structures of Aryl Xanthates. Bis(*O*-4-*tert*-butylphenyl dithiocarbonato)nickel(II), $Ni(S_2COC_6H_4\text{-}4\text{-}t\text{-}Bu)_2$, Tris(*O*-2,4,6-trimethylphenyl dithiocarbonato)cobalt(III), $Co(S_2COC_6H_2\text{-}2,4,6\text{-}Me_3)_3$, and Bis(*O*-2,4,6-trimethylphenyl dithiocarbonato)palladium(II), $Pd(S_2COC_6H_2\text{-}2,4,6\text{-}Me_3)_2$

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The aryl xanthate complexes indicated in the title have been studied structurally by single-crystal x-ray crystallography. These are the first reported structures of *O*-aryl dithiocarbonates. The nickel complex crystallizes in the monoclinic space group $P2_1/c$, with $a = 16.826$ (8) Å, $b = 6.978$ (2) Å, $c = 28.282$ (7) Å, $\beta = 131.74$ (3)°, and $Z = 4$. The coordination about both the Ni(II) and Pd(II) complexes is planar with the phenyl ring approximately perpendicular to this plane. The Pd(II) complex crystallizes in the triclinic space group $P\bar{1}$ with $a = 8.661$ (5) Å, $b = 8.716$ (4) Å, $c = 7.938$ (3) Å, $\alpha = 78.99$ (4)°, $\beta = 99.27$ (4)°, $\gamma = 107.92$ (4)°, and $Z = 1$. The cobalt(III) complex crystallizes in $P2_1/c$ also and has cell constants $a = 8.781$ (3) Å, $b = 28.595$ (18) Å, $c = 17.458$ (7) Å, $\beta = 129.88$ (2)°, and $Z = 4$. The pseudooctahedral CoS_6 unit has a mean Co–S distance of 2.270 (6) Å. The structure is quite similar to the structure of the aliphatic analogue $Co(S_2COC_2H_5)_3$ reported by Merlino.[3]

Introduction

The synthesis of aryl xanthates has been reported.[1] In this paper we describe the results of single-crystal structural investigations. No structural data on aryl xanthates have been reported previously, although at least 18 structural reports have been presented for various metallic alkyl xanthates. For both the nickel(II) and cobalt(III) complexes presented here we have been able to compare the results with the results for the corresponding *O*-ethyl derivative.[2,3] Palladium(II) alkyl xanthate results have not appeared previously.

Experimental Section

The title compounds have been prepared as reported.[1]

Crystallographic Data

$Ni(S_2COPh\text{-}4\text{-}t\text{-}Bu)_2$. Space Group and Lattice Parameters. From preliminary film examinations of several crystals, the yellow-brown long flat needles recrystallized from carbon disulfide were found to be suitable for intensity data collection. Precession and Weissenberg photographs of a cut crystal exhibited systematic extinctions consistent with the space group $C_{2h}{}^5\text{-}P2_1/c$ (No. 14). The lattice parameters (Table I) were deduced (at room temperature) from the angular settings of 15 computer-centered reflections on a Syntex $P2_1$ diffractometer with graphite-monochromatized Mo Kα radiation.

Collection and Reduction of Intensity Data. Initial attempts to refine the structure with the data collected on a Picker diffractometer failed; the full-matrix isotropic refinement stopped at $R = 0.18$. However, all the atoms were found. The Syntex diffractometer then became available. The crystal, mounted on a glass fiber, was optically centered by telescope. A total of 4016 data to $2\theta = 50°$ (Mo Kα) were collected using a θ–2θ scan with three standards monitored every 50 reflections. A ±3% variation was observed in these standards throughout the data collection. Intensity and various correction factors are defined in Table II.

The Syntex-generated data tape was translated by a Fortran program into a suitably formated tape for the UNIVAV 1108 computer. A data reduction program system, CORR 6, modified from SYNCOR 2 of Wayne State University,[4] was used. The first reduction calculation determined the decay factors DCF to be ±3%. The data reduction process applied the usual Lorentz, polarization, and decay factor corrections. The electronic instability constant P was set at 0.02. There were 1189 corrected intensities for which $I/\sigma(I) \geq 3.0$ (Table II).

Solution and Refinement of the Structure. The heavy atom positions (x, y, z) were found from the three-dimensional Patterson function. They are $Ni_1(0, 0, 0)$ and $Ni_2(0, {}^1/_2, 0)$. Structure factors calculated based on the two Ni atoms yielded $R = 0.35$ for the largest 370 intensities of the Picker data set. Subsequent cycles of structure factor and Fourier calculations[5] led to the location of all nonhydrogen atoms. While the full-matrix isotropic refinement vs. the Picker data stopped at $R = 0.185$, refinement vs. the Syntex data stopped at $R_1 = 0.136$. At this stage disorder of the *tert*-butyl carbons was observed. Upon fixing the temperature factor of the disorder carbons at $B = 14$ Å^2, two cycles of anisotropic refinement reduced R to 0.095. The molecule has a pseudomirror plane; the temperature factors β_{12} and β_{23} of the atoms in the plane could not be refined successfully. The 120 reflections for which $(\sin\theta)/\lambda$ is below 0.205 were found[5] to have an R factor $= 0.1453$. With these 120 reflections excluded, two cycles of anisotropic refinement finally yielded $R = 0.073$ for 1069 reflections (Table II). Bond distances and angles were then calculated (Table III). The atomic scattering factors for neutral atoms were taken from Cromer and Waber.[6] The atomic position and thermal parameters are presented in Tables IV and A-I.[7]

Description of $Ni(S_2COPh\text{-}4\text{-}t\text{-}Bu)_2$. The crystal structure consists of two crystallographically independent molecules in which each nickel atom is coordinated by two aryl xanthate groups, each group behaving as a bidentate ligand through two sulfur atoms. The nickel atoms are on the *bc* plane and form three chains along the *b* axis (see Figure 1). The internickel atom distance is 3.489 (1) Å. The Ni–S distances are not significantly different: 2.219 (4), 2.213 (6) Å and 2.222 (7), 2.205 (5) Å. The $NiS_4C_2O_2$ unit forms a plane parallel to the *c* axis and perpendicular to the *b* axis, and the phenyl ring is perpendicular to this plane (Figure 2). The C–O–Ph angles are 116.7 and 120.5°.

$Co(S_2COPh\text{-}2,4,6\text{-}Me_3)_3$. Space Group and Lattice Parameters. The dark green crystals were recrystallized from 1:1 acetone–CS_2 solution. Most of the crystals were thin plates. A good quality long thin plate, cut to approximately oblong box shape, was selected for data collection. Seven axial photographs on the Syntex $P2_1$ diffractometer showed it to be a good crystal. The systematic extinctions were consistent with the space group $C_{2h}{}^5\text{-}P2_1/c$ (No. 14) (Table I).

Collection and Reduction of Intensity Data. The data were collected and reduced as described above. A total of 6139 reflections were measured within 10 days. The decay factors, less than ±1%, indicated no crystal deterioration. There were 2106 reflections for which $I/\sigma(I) \geq 3$. Data were indexed for the nonstandard space group $P2_1/n$. After a cell transformation (I) the systematic extinctions were consistent

$$\begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ -1 & 0 & 1 \end{pmatrix} \begin{pmatrix} h \\ k \\ l \end{pmatrix}_{P2_1/n} = \begin{pmatrix} h \\ k \\ l \end{pmatrix}_{P2_1/c} \qquad \text{(I)}$$

with the space group $C_{2h}{}^5\text{-}P2_1/c$ (No. 14).

Solution and Refinement of Structure. The density, measured by flotation in CCl_4–$CHBr_3$ mixture, is 1.41 (1) g/cm^3 (calcd $Z = 4$). This suggests that the Co atoms occupy general positions in $P2_1/c$. The structure was solved by direct methods (MULTAN). The overall temperature factor and absolute scale were estimated from a WILSON

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Table I. Summary of Crystal Data

	$Ni(S_2COC_6H_4\text{-}4\text{-}t\text{Bu})_2$	$Co(S_2COC_6H_2\text{-}2,4,6\text{-}Me_3)_3$	$Pd(S_2COC_6H_2\text{-}2,4,6\text{-}Me_3)_2$
Formula wt	509.41	692.908	529.050
d(calcd), g/cm^3	1.388	1.377	1.579
d(obsd), g/cm^3	1.38 (2)	1.41 (1)	1.58 (1)
Z, formula units/cell	4	4	1
Linear absorption coeff, μ, cm^{-1}	28.52	10.88	11.9
λ(Mo Kα), A	0.71069	0.71069	0.71069
Crystal dimensions, mm^3	0.15 × 0.40 × 0.25[b]	0.05 × 0.2 × 0.25[b]	0.30 × 0.20 × 0.10
Systematic absences	$h0l$, $l = 2n + 1$ $0k0$, $k = 2n + 1$ hkl, $k + l = 2n + 1$	$h0l$, $l = 2n + 1$ $0k0$, $k = 2n + 1$	None
Space group	$C_{2h}{}^5\text{-}P2_1/c$ (No. 14) Monoclinic	$C_{2h}{}^5\text{-}P2_1/c$ (No. 14) Monoclinic	$C_i{}^1\text{-}P\bar{1}$ (No. 2) Triclinic
Cell constants[a]			
a, A	16.826 (8)[c]	8.781 (3)[d]	8.661 (5)[e] $\alpha = 78.99$ (4)
b, A	6.978 (2)	28.595 (18)	8.714 (4) $\beta = 99.27$ (4)
c, A	28.282 (7)	17.458 (7)	7.938 (3) $\gamma = 107.92$ (4)
β, deg	131.74 (3)	129.88 (2)	
$\cos\beta$	−0.66575	−0.64118	
V, A^3	2477.74 (172)	3363.91 (378)	556.25 (50)
$F(000)$	1064	1440	268

[a] Ambient temperature, 25 °C, least-squares fit of 15 high 2θ reflections obtained after data collection. [b] Cut to an oblong box. [c] $2\theta = 20.00°$ (av). [d] $2\theta = 20.30°$ (av). [e] $2\theta = 20.96°$ (av).

Table II. Summary of Final Refinement[a]

	Xanthate		
	Ni	Co	Pd
Data used, $I/\sigma(I) \geq 3$	1069[b]	2106	1248
No. varied non-H parameters	107	226	124
Reflections:parameters	9.9	9.3	10.0
R[c]	0.073[b]	0.072	0.059
R_w,[c] $w_i = 1/\sigma_i{}^2(F)$	0.080[b]	0.084	0.064

[a] $I = [Ig -$ (sum of background counts)/(background time to scan time ratio)] × scan rate; $\sigma_c = [Ig +$ (sum of background counts)/(background time to scan time ratio)$^2]^{1/2}$ × scan rate; $\sigma^2 = \sigma_c{}^2 + (I{\cdot}P)^2 + (I{\cdot}\sigma(\text{DCF})/\text{DCF})^2$; $\sigma(I) = (\sigma^2)^{1/2}$; $\sigma(F) = {}^1/_2\sigma(I)(1/LP{\cdot}I)^{1/2}$; I = net count; Ig = total scan count; background time to scan time ratio = 0.5; DCF = decay factor; LP = Lorentz and polarization corrections; P = electronic instability usually is 0.02. [b] Data $(\sin\theta)/\lambda \geq 0.205$ cut. Full data, 1189. Reflections, $R = 0.095$, $R_w = 0.130$. [c] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$; $R_w = \{\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2\}^{1/2}$.

Table III. Significant Lengths (Å) and Angles (deg) for $Ni(S_2COC_6H_4\text{-}4\text{-}t\text{-}Bu)_2$

Bond Lengths			
Molecule 1		Molecule 2	
Ni-S(1)	2.219 (4)	Ni(2)-S(21)	2.222 (7)
Ni-S(11)	2.213 (6)	Ni(2)-S(22)	2.205 (5)
Mean	2.216 (5)	Mean	2.214 (6)
S(1)-C(1)	1.670 (27)	S(21)-C(2)	1.676 (21)
S(11)-C(1)	1.699 (19)	S(22)-C(2)	1.687 (30)
Mean	1.685 (23)	Mean	1.682 (26)
C(1)-O(1)	1.318 (19)	C(2)-O(2)	1.323 (18)
O(1)-C(B1)	1.438 (22)	O(2)-C(B7)	1.444 (29)
$(C\text{-}C)_{AR}$(av)	1.38	$(C\text{-}C)_{AR}$(av)	1.40
Bite Distances			
S(1)-S(11)	2.822 (9)	S(21)-S(22)	2.827 (11)
Angles			
Ni-S(1)-C(1)	83.8 (7)	Ni(2)-S(21)-C(2)	82.9 (7)
Ni-S(11)-C(1)	83.4 (7)	Ni(2)-S(22)-C(2)	83.3 (7)
S(1)-Ni-S(11)	79.1 (2)	S(21)-Ni(2)-S(22)	79.4 (2)
S(1)-C(1)-S(11)	113.7 (10)	S(21)-C(2)-S(22)	114.4 (11)
S(1)-C(1)-O(1)	127.1 (11)	S(21)-C(2)-O(2)	127.4 (12)
S(11)-C(1)-O(1)	119.2 (11)	S(22)-C(2)-O(2)	118.2 (12)
C(1)-O(1)-C(B1)	116.7 (10)	C(2)-O(2)-C(B7)	120.5 (10)

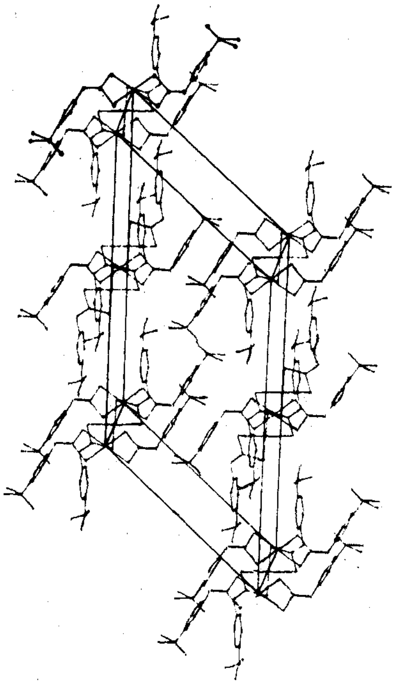


Figure 1. An ORTEP cell projected drawing of the $Ni(S_2COC_6H_4\text{-}4\text{-}t\text{-}Bu)_2$ cell.

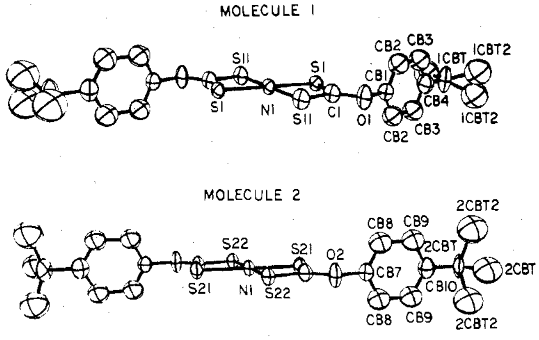


Figure 2. An ORTEP thermal ellipsoid projected view (50% probability) of $Ni(S_2COC_6H_4\text{-}4\text{-}t\text{-}Bu)_2$, molecules 1 and 2.

plot. The normalized structure factors were computed for the reflections which have E larger than or equal to 1.5. A total of 177 data ($E \geq 1.5$) were generated by the WILSON program. The distribution of the E's is in good agreement with the theoretical centrosymmetric values. Using MULTAN, the (400) reflection is the only one which has a probability larger than 98% to have correct phasing.

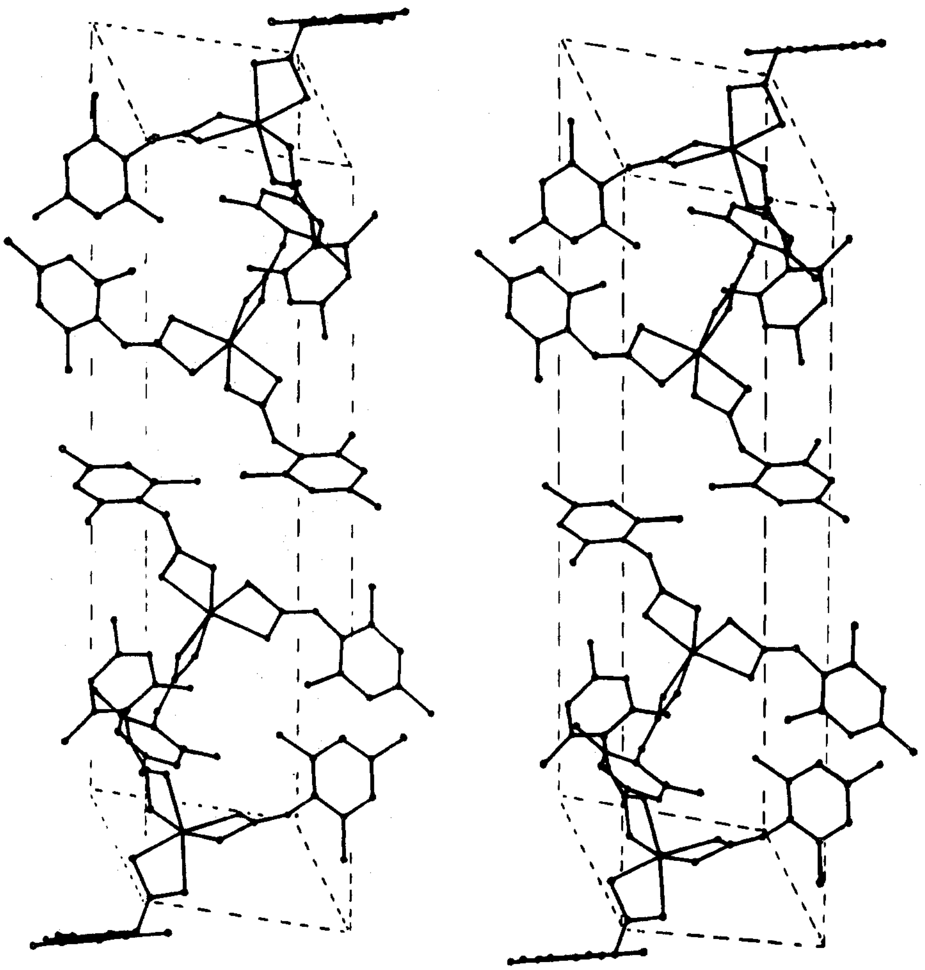


Figure 3. An ORTEP stereodrawing of the Co(S$_2$COC$_6$H$_2$-2,4,6-Me$_3$)$_3$ cell.

Table IV. Positional Parameters and Estimated Standard Deviations of Ni(S$_2$COC$_6$H$_4$-4-*t*-Bu)$_2$

	x	*y*	*z*
Ni(1)	0.0000	0.5000	0.5000
Ni(2)	0.0000	0.5000	0.0000
S(1)	0.1235 (3)	0.5000	0.6051 (2)
S(11)	0.1471 (3)	0.5000	0.5152 (2)
S(21)	0.0057 (4)	0.5000	0.0808 (2)
S(22)	0.1736 (4)	0.5000	0.0807 (2)
C(1)	0.2081 (13)	0.5000	0.5930 (7)
C(2)	0.1376 (14)	0.5000	0.1239 (8)
O(1)	0.3130 (9)	0.5000	0.6365 (4)
O(2)	0.2138 (9)	0.5000	0.1864 (4)
CB(1)	0.3601 (12)	0.5000	0.7015 (7)
CB(2)	0.3853 (12)	0.6678 (25)	0.7303 (7)
CB(3)	0.4376 (12)	0.6714 (27)	0.7963 (8)
CB(4)	0.4617 (14)	0.5000	0.8281 (8)
1CBT	0.5184 (14)	0.5000	0.8972 (8)
1CBT(1)	0.4557 (42)	0.5000	0.9056 (13)
1CBT(2)	0.6268 (20)	0.5778 (30)	0.9354 (12)
CB(7)	0.1876 (12)	0.5000	0.2257 (6)
CB(8)	0.1849 (11)	0.6686 (25)	0.2451 (7)
CB(9)	0.1720 (11)	0.6719 (25)	0.2925 (7)
CB(10)	0.1659 (12)	0.5000	0.3143 (7)
2CBT	0.1603 (16)	0.5000	0.3646 (6)
2CBT(1)	0.2571 (26)	0.5000	0.4219 (15)
2CBT(2)	0.1628 (22)	0.2766 (36)	0.3838 (13)

Table V. Significant Lengths (Å) and Angles (deg) for Co(S$_2$C$_6$H$_2$-2,4,6-Me$_3$)$_3$

	Bond Lengths		
Co–S(1)	2.258 (7)	C(1)–O(1)	1.365 (21)
Co–S(2)	2.277 (7)	C(2)–O(2)	1.324 (15)
Co–S(3)	2.292 (5)	C(3)–O(3)	1.330 (22)
Co–S(4)	2.269 (5)	Mean C–O	1.340 (19)
Co–S(5)	2.288 (5)		
Co–S(6)	2.261 (7)	O(1)–C(B1)	1.439 (29)
Mean Co–S	2.274 (6)	O(2)–C(B2)	1.429 (26)
		O(3)–C(B3)	1.464 (29)
S(1)–C(1)	1.680 (22)	Mean O–C	1.444 (28)
S(2)–C(1)	1.648 (24)		
S(3)–C(2)	1.689 (20)	Mean C–C(aromatic)	1.403 (31)
S(4)–C(2)	1.694 (24)	A	1.410 (28)
S(5)–C(3)	1.675 (24)	B	1.402 (30)
S(6)–C(3)	1.711 (19)	C	1.396 (35)
Mean S–C	1.683 (22)		
	Bite Distances		
S(1)–S(2)	2.814 (9)	S(5)–S(6)	2.822 (8)
S(3)–S(4)	2.835 (9)	Mean S–S	2.823 (9)
	Average Angles		
Co–S–C	84.4 (9)	S–C–S(internal)	114.1 (11)
S–Co–S(internal)	76.8 (3)	C–O–C	117.8 (12)

It was used as a known phase 0° (+) by the program. The phases of reflections (056), (14$\bar{9}$), and (16$\bar{8}$) were chosen to fix the origin and three other reflections, (5,1,$\overline{13}$), (2,14,0), and (025), were used in the starting set.

The *E* map computed with the chosen MULTAN solution (ABS FORM = 1.4969, RESID = 18.31), showed a chemically reasonable structural fragment consisting of one Co and six S atoms. The *R* factor calculated with these seven atoms was 0.40 for 2106 data. Subsequent Fourier and structure factor calculations led to the location of all nonhydrogen atoms. The full-matrix isotropic refinement brought the *R* factor to 0.11. In order to save computer time, only the Co atom, six sulfurs, three carbons, and three oxygens were allowed anisotropic refinement. Three more cycles of anisotropic refinement of 13 atoms and isotropic refinement of 27 atoms lowered the *R* factor to 0.072 and R_w to 0.084 (Table II). The important bond distances and angles are summarized in Table V.

Table VI. Positional Parameters and Estimated Standard Deviation of $Co(S_2COC_6H_2\text{-}2,4,6\text{-}Me_3)_3$

	x	y	z
Co	0.7599 (3)	0.0707 (1)	0.7931 (2)
S(1)	1.0046 (6)	0.0300 (2)	0.8140 (3)
S(2)	0.7644 (6)	0.0019 (2)	0.8601 (3)
S(3)	0.4658 (6)	0.0983 (2)	0.7463 (3)
S(4)	0.5338 (6)	0.0459 (2)	0.6329 (3)
S(5)	0.9546 (7)	0.1133 (2)	0.9374 (3)
S(6)	0.8248 (7)	0.1365 (2)	0.7466 (3)
C(1)	0.9325 (22)	−0.0129 (6)	0.8503 (11)
C(2)	0.3686 (24)	0.0760 (6)	0.6336 (12)
C(3)	0.9540 (25)	0.1538 (7)	0.8678 (12)
O(1)	0.9988 (15)	−0.0580 (4)	0.8669 (7)
O(2)	0.1830 (15)	0.0807 (4)	0.5501 (7)
O(3)	1.0489 (18)	0.1944 (4)	0.9042 (8)
CB(1)	1.1190 (23)	−0.0697 (6)	0.8403 (11)
CB(2)	1.3220 (22)	−0.0694 (6)	0.9145 (11)
CB(3)	1.4423 (24)	−0.0827 (6)	0.8893 (12)
CB(4)	1.3426 (25)	−0.0955 (6)	0.7869 (13)
CB(5)	1.1372 (25)	−0.0950 (6)	0.7149 (12)
CB(6)	1.0190 (24)	−0.0821 (6)	0.7401 (12)
CME(1)	1.4187 (24)	−0.0565 (6)	1.0223 (12)
CME(2)	1.4707 (26)	−0.1090 (6)	0.7576 (13)
CME(3)	0.7900 (25)	−0.0812 (6)	0.6608 (13)
CB(7)	0.0486 (23)	0.1099 (6)	0.5482 (11)
CB(8)	0.0564 (25)	0.1581 (6)	0.5363 (12)
CB(9)	−0.0912 (25)	0.1867 (6)	0.5255 (12)
CB(10)	−0.2342 (24)	0.1659 (6)	0.5229 (12)
CB(11)	−0.2392 (25)	0.1173 (6)	0.5336 (12)
CB(12)	−0.0930 (23)	0.0881 (6)	0.5483 (11)
CME(4)	0.2172 (26)	0.1803 (6)	0.5341 (13)
CME(5)	−0.3966 (27)	0.1973 (7)	0.5069 (13)
CME(6)	−0.0913 (26)	0.0352 (7)	0.5628 (13)
CB(13)	1.0484 (27)	0.2242 (7)	0.8358 (13)
CB(14)	1.2001 (26)	0.2167 (7)	0.8340 (13)
CB(15)	1.2000 (30)	0.2469 (7)	0.7692 (15)
CB(16)	1.0518 (29)	0.2801 (7)	0.7146 (14)
CB(17)	0.9020 (28)	0.2859 (7)	0.7187 (14)
CB(18)	0.8909 (28)	0.2566 (7)	0.7804 (14)
CME(7)	1.3583 (28)	0.1801 (7)	0.8932 (14)
CME(8)	1.0510 (32)	0.3133 (8)	0.6422 (17)
CME(9)	0.7226 (29)	0.2584 (7)	0.7839 (15)

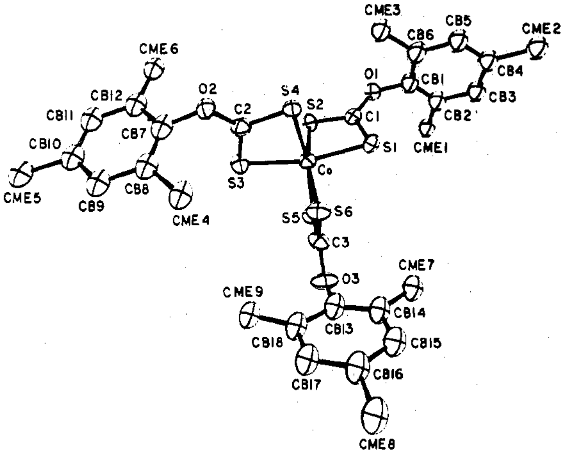


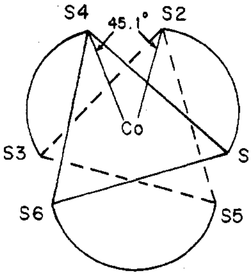
Figure 4. An ORTEP thermal ellipsoid projected view (50% probability) of $Co(S_2COC_6H_2\text{-}2,4,6\text{-}Me_3)_3$.

Table VII. Significant Intramolecular Distances (Å) and Angles (deg) for $Pd(S_2COC_6H_2\text{-}2,4,6\text{-}Me_3)_2$

	Bond Lengths		
Pd–S(1)	2.333 (4)	C(1)–O(1)	1.330 (12)
Pd–S(2)	2.328 (3)	O(1)–CB(1)	1.439 (16)
S(1)–C(1)	1.663 (12)	Mean C-C(aromatic)	1.396
S(2)–C(1)	1.687 (13)		
	Nonbond Lengths		
S(1)–S(2)	2.844 (5)	Pd–C(1)	2.730 (10)
	Angles		
S(1)–Pd–S(2)	75.2 (2)	S(1)–Pd–S(2)	104.8 (2)
S(1)–Pd–S(1)	180.0 (2)		

The atomic scattering factors for neutral atoms were taken from Cromer and Waber.[6] Anomalous dispersion corrections[8] (real and imaginary) were used for the Co and six S atoms. The atomic positions and thermal parameters are summarized in Tables VI and A-II.[7]

Description of $Co(S_2COC_6H_2\text{-}2,4,6\text{-}Me_3)_3$. The crystal is composed of four discrete molecules with all atoms in general positions (see Figures 3 and 4). The cobalt atom is surrounded by three aryl xanthate ligands. The six sulfur atoms are at distances ranging from 2.258 to 2.292 Å (mean 2.274 Å). There are two nonequivalent Co–S bonds. Six sulfur atoms are situated at the corners of two parallel triangles, 2.39 Å apart, where one triangle is rotated with respect to the other by 45.1°, as shown below (II). The upper triangle has shorter Co–S(1,4,6) bonds than the lower triangle Co–S(2,3,5).



II

Co–S(1)	2.258 (7) Å	Co–S(2)	2.277 (7) Å
Co–S(4)	2.269 (5) Å	Co–S(3)	2.292 (5) Å
Co–S(6)	2.261 (7) Å	Co–S(5)	2.288 (5) Å
Mean	2.263 (6) Å	Mean	2.286 (6) Å

The difference is about 0.02 Å between each pair. The three angles are significantly different in each triangle.

S(1)–Co–S(6)	93.2°	S(2)–Co–S(3)	97.1°
S(1)–Co–S(4)	91.6°	S(2)–Co–S(5)	98.0°
S(4)–Co–S(6)	92.4°	S(3)–Co–S(5)	94.9°
Mean	92.6°	Mean	96.7°

The nonbonded S–S distances in the upper triangle are 0.15 Å longer than the lower triangle distances. The two carbon–oxygen bonds in each ligand have average bond lengths of 1.340 and 1.444 Å. The shorter bond has considerable double bond character (Table V).

The phenyl group is tilted and perpendicular to the O–CS_2 plane, as observed in $Ni(S_2COC_6H_4\text{-}4\text{-}t\text{-}Bu)_2$. The C–C bonds in the phenyl group are normal. Considerable strain within the four-membered 1,1-dithiolato chelates is evidenced by a significant deviation from ideal octahedral coordination. The intraligand angles differ considerably from 90°. The opposing S–Co–S angles (which, in O_h, would be 180°) vary between 165.9 and 167.9°.

$Pd(S_2COPh\text{-}2,4,6\text{-}Me_3)_2$. Space Group and Lattice Parameters. The orange crystals recrystallized from CS_2 or $CHCl_3$ were found to be suitable for data collection. Most of the crystals were thin plates. The lack of systematic extinctions indicated the space group to be $P1$ or $P\bar{1}$. The structure was refined satisfactorily in C_i^1-$P\bar{1}$ (No. 2) (Table I).

Collection and Reduction of Intensity Data. Details of instrumentation, data collection, and data reduction were as above, except two more octants (four total) were collected. A total of 2031 data were collected in 3 days. There were 1248 reflections, for which $I/\sigma(I) \geq 3.0$. No systematic extinctions of the reduced data were found.

Solution and Refinement of Structure. Given a triclinic space group with $Z = 1$, the Pd atom position was chosen to be (0, 0, 0). The R factor calculated with the Pd atom only was 0.30 for the strongest 682 reflections. Subsequent Fouriers led to the location of all the nonhydrogen atoms. Full-matrix isotropic refinement brought the R factor down to 0.115 for the 1248 strongest reflections. Two more cycles of anisotropic refinement of 14 atoms yielded $R = 0.059$ and $R_w = 0.064$. A statistic weighting scheme was used in the final refinement. The atomic scattering factors for the neutral atoms were taken from Cromer and Waber.[6] Anomalous dispersion corrections[8] (real and imaginary) were used for the Pd atom in the final refinement. The atomic positions, thermal parameters, bond distances, and bond

Table VIII. Positional Parameters and Estimated Standard Deviations of $Pd(S_2COC_6H_2\text{-}2,4,6\text{-}Me_3)_2$

Atom	*x*	*y*	*z*
Pd	0.0000	0.0000	0.0000
S(1)	0.1910 (4)	−0.1454 (4)	0.0317 (4)
S(2)	0.0482 (3)	−0.0766 (4)	0.2967 (4)
O(1)	0.2426 (8)	−0.2615 (8)	0.3646 (9)
C(1)	0.1707 (11)	−0.1721 (12)	0.2410 (14)
CB(1)	0.3286 (13)	−0.3593 (13)	0.3130 (12)
CB(2)	0.2433 (13)	−0.5122 (14)	0.2791 (13)
CB(3)	0.3272 (14)	−0.6100 (14)	0.2376 (14)
CB(4)	0.5005 (15)	−0.5485 (14)	0.2370 (14)
CB(5)	0.5811 (14)	−0.3944 (14)	0.2711 (14)
CB(6)	0.5004 (13)	−0.2918 (13)	0.3131 (13)
CME(1)	0.0568 (13)	−0.5794 (15)	0.2876 (17)
CME(2)	0.5932 (15)	−0.6609 (16)	0.1937 (15)
CME(3)	0.5883 (14)	−0.1237 (14)	0.3534 (16)

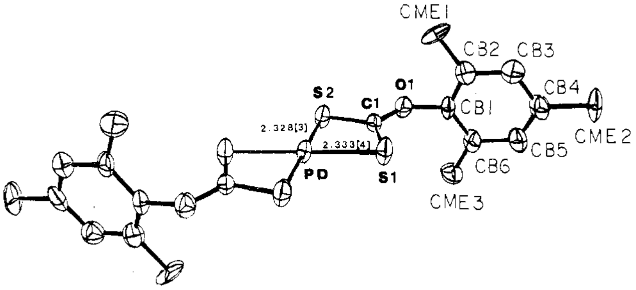


Figure 5. An ORTEP thermal ellipsoid projected view (50% probability) of $Pd(S_2COC_6H_2\text{-}2,4,6\text{-}Me_3)_2$.

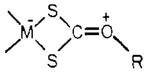
angles are summarized in Tables VII, VIII, and A-III.[7]

Description of $Pd(S_2COC_6H_2\text{-}2,4,6\text{-}Me_3)_2$. The structure is similar to the structure of $Ni(S_2COC_6H_4\text{-}4\text{-}t\text{-}Bu)_2$, except there is only one molecule in the unit cell. Interpalladium distances range from 8.716 to 6.938 Å, indicating no significant Pd–Pd interactions. The nearest Pd–S intermolecular distance is 5.843 Å. The intramolecular Pd–S bond distances are identical within 1 standard deviation, 2.333 (4) and 2.328 (3) Å. The two S–C bond distances have the usual lengths, 1.663 (12) and 1.687 (13) Å. Two kinds of C–O bonds in the ligand C(1)–O(1) and O(1)–CB(1) are 1.330 (12) and 1.439 (16) Å, respectively. The bite distance S(1)–S(2) is 2.844 (5) Å, significantly larger than the bite distances in the Ni and Co structures. The C–C phenyl bond distances are normal. The average C–C(CH_3–phenyl) bond length is 1.534 Å (Figure 5).

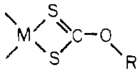
The PdS_4 atoms form a plane to which the phenyl ring plane is perpendicular. The C(1)–O(1)–CB(1) angle is 117.8 (6)°. The S–Pd–S angle [75.2 (2)°] is significantly smaller than the S–Ni–S and S–Co–S angles, while the S–C–S angle is comparable with those found in the Ni and Co structures.

Discussion

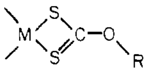
A compilation of structures for xanthate complexes reveals C–S bond distances of 1.675 (35) Å and S_2C–O distances of 1.336 (30) Å. In particular, the latter distance is some 12 pm shorter than the second O–C distance (1.46 Å) found in xanthates. This result shows up quite clearly in the aryl xanthates reported here and suggests that resonance structure III contributes significantly to a description of the bonding.



III



IV



V

Using a Pauling bond order–bond length relationship[9] (VI)

$$r_x = r_1 - [3x(r_1 - r_2)/(2x + 1)] \qquad \text{(VI)}$$

to estimate the percentage of double bond character (III) and hence the percentages of III, IV, and V, values around 20% are obtained for III.

The structural data[3] for $Co(S_2COEt)_3$ when compared with the data reported here for the aryl complex suggests a slight shortening (1.337 Å vs. 1.359 Å) of the S_2C–O bond in the aryl derivative. Since the phenyl ring is tilted 90° to the MS_2C plane, π contributions must be minimal. For the nickel(II) complexes, however, there is a much larger reported difference. The $Ni(S_2COEt)_2$ is said[2] to have a S_2C–O distance of 1.38 Å. We believe that this distance is suspect and simply may reflect crystallographic difficulties.

The vibrational spectra in the C–O region for the complexes reported here suggest that slight increases in the S_2C–O bond order occur in going from Co(III) to Ni(II) to Pd(II). A somewhat more substantial increase in the C–O stretch occurs with the Pt(II) complexes. Presumably this result reflects an increasing affinity for sulfur as a donor atom in this series of metal complexes.

Packing forces appear to produce the nonequivalent Co–S distances found in the cobalt complex. Comparing twist angle data with data for $Co(S_2COEt)_3$ and $Fe(S_2COEt)_3$ suggests that our average values are in good agreement even though individual parameters for each ligand are not. From the packing diagram it is noticed that only one of the ligands interacts substantially with a symmetry-related ligand from another molecule, thus producing the nonequivalence of Co–S distances.

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Registry No. $Ni(S_2COC_6H_4\text{-}4\text{-}t\text{-}Bu)_2$ (complex form), 64314-93-8; $Ni(S_2COC_6H_4\text{-}4\text{-}t\text{-}Bu)_2$ (salt form), 64314-75-6; $Co(S_2COC_6H_2\text{-}2,4,6\text{-}Me_3)_3$ (complex form), 64314-92-7; $Co(S_2COC_6H_2\text{-}2,4,6\text{-}Me_3)_3$ (salt form), 64314-76-7; $Pd(S_2COC_6H_2\text{-}2,4,6\text{-}Me_3)_2$ (complex form), 64314-91-6; $Pd(S_2COC_6H_2\text{-}2,4,6\text{-}Me_3)_2$ (salt form), 64314-77-8.

Supplementary Material Available: Listings of anisotropic thermal parameters (Tables A-I–A-III) and structure factor amplitudes (Tables A-IV–A-VI) (10 pages). Ordering information is given on any current masthead page.

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(5) Programs used: GENFR, a local Fourier program written by S. T. Rao; ORFLS, W. R. Busing, H. A. Levy, and K. O. Martin, Oak Ridge National Laboratory (ORNL-TM-305) full-matrix least squares; the local version is ORFL 90 and STRFAC as modified by A. Avdeef. Our agreement analysis program AGREE was produced locally: C. K. Johnson, ORTEP/II; data statistics, WILSON, locally written; direct methods, MULTAN, as modified at Indiana University.
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