line)LW(CO)$_5$ with triphenylphosphine in toluene at 35.4° was studied for several ratios of [A] to [L].[7] The resulting plots of $(\log x)(A_t - A_{\text{blank}})$ *vs.* t, exhibited in Figure 1, indicate reaction 2, M = W(CO)$_5$, to be markedly inhibited by added amine.[8] In the presence of 10-20-fold excesses of amine the reactions *fail to attain equilibrium over the time allowed for equilibration by A-I* (2 days).[1] The activation parameters are readily explicable on this basis: the reactions proceed further toward equilibrium at higher temperature, resulting in the previously discussed temperature sensitivity of "K_{eq}."

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Registry No. (Aniline)W(CO)$_5$, 16969-72-5; triphenylphosphine, 603-35-0.

Supplementary Material Available. A table of all rate observations 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, 24× 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-74-1790.

[7] Specific ratios of [A] to [L] were not given in ref 1. However, from the concentration ranges of amine and L employed in that study ([amine], (100-1600) × 10^{-4} *M*; [L], (2-100) × 10^{-4} *M*) and from the magnitudes of the reported values of K_{eq}, it can be inferred that 10-20-fold exesses of amine relative to triphenylphosphine conservatively represent conditions employed in those studies.

[8] For triphenylstibine at an [A] to [L] ratio of 9.90, $t_{1/2}$ was observed to be 22.2 (2) hr.

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Crystal and Molecular Structure of Tris(ethyl thioxanthato)cobalt(III). A Reinvestigation

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Sir:

There has been considerable interest in transition metal 1,1-dithiolate complexes, especially tris-chelate compounds.[1-3] Attention has focused on iron(III) complexes of the kind Fe(S$_2$CY)$_3$ (Y = NR$_2$, OR, SR) largely because of temperature- and pressure-dependent magnetic studies that have been interpreted[4,5] in terms of a spin equilibrium between two energetically similar ground states of symmetries ^{6}A and ^{2}T.[6] There is, morever, firm structural evidence correlating the Fe-S bond lengths in these compounds with their magnetic moments,[3] both of which depend not only upon temperature and pressure but also upon the substituent Y.[5] The mean Fe-S distance in Fe(S$_2$CY)$_3$ compounds can vary from ~2.29 to 2.42 Å depending upon the magnetic moment. Low-spin ($\mu_{250°} \approx 2.4$-3.0 BM) compounds with bond lengths of 2.297-2.316 Å occur for Y = SR,[7] OR,[8] and NMePh[9] whereas high-spin ($\mu_{250°} \approx 6$ BM) molecules having Fe-S distances of 2.40 Å or larger occur for Y = N(CH$_2$)$_4$[9] and N(*t*-Bu)$_2$.[10] The analogous cobalt(III) complexes, Co(S$_2$CY)$_3$, which are all spin paired (^{1}A ground state), have metal-sulfur bond lengths of ~2.26-2.27 Å,[11] slightly shorter than low-spin iron(III) compounds. It was therefore surprising when the structure of "Co(S$_2$CSEt)$_3$" was reported to have a mean Co-S bond length of 2.398 (1) Å.[12] This distance is nearly 0.1 Å larger than the value found for Fe(S$_2$CS-*t*-Bu)$_3$,[7] which has an isomorphous cobalt(III) analog with nearly identical unit cell parameters (Table I), raising the possibility that a substantial metal-ligand bond length change might occur without a concomitant change in spin state. Since this possiblity seemed most unlikely to us, and in view of our previous work on Co(S$_2$CSR)$_3$ and related compounds,[13] we have reinvestigated the structure of tris(ethyl thioxanthato)cobalt(III).

Dark green-black crystals of Co(S$_2$CSEt)$_3$ were prepared as described earlier[13] and examined by precession photography. The triclinic lattice[12] was confirmed. Using several high-angle reflections centered about the Kα_1 line on a Picker FACS-I-DOS diffractometer, the lattice parameters were refined by a least-squares method. The discrepancy (Table I) between our results and those reported previously[12] encouraged us to collect a full set of intensity data with Mo Kα radiation. The data were obtained and reduced in the usual manner[14] except that the diffractometer was newly equipped with a highly oriented single-crystal graphite monochromator. Using the atomic parameters published originally,[12] the structure was refined by full-matrix anisotropic least-squares methods.[14] Hydrogen atoms were assigned isotropic thermal parameters. The final agreement factors are $R_1 = 0.037$ and $R_2 = 0.044$ based on 6514 observed ($F^2 > 3\sigma(F^2)$) reflections. Tables of the final atomic parameters, selected bond lengths and angles, and a list of observed and calculated structure factor amplitudes are available.[15]

The structure of Co(S$_2$CSC$_2$H$_5$)$_3$ is very similar to that reported previously[12] with two major differences. The cobalt-sulfur distances range from 2.257 (1) to 2.276 (1) Å with a mean (σ mean) of 2.266 (7) Å, and the mean S-Co-S angle is 76.2 (1)°. These results are in close agreement with structural parameters for other tris(1,1-dithiolato)cobalt(III) complexes[11] but differ significantly from the mean

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Table I. Lattice Parameters for Several Triclinic ($P\bar{1}$) $M(S_2CSR)_3$ Complexes[a]

	M = Fe R = t-C_4H_9	M = Co R = t-C_4H_9	M = Co R = C_2H_5	M = unknown R = C_2H_5	M = Cr R = C_2H_5
a	19.44 (1)	19.408 (5)	10.134 (2)	10.23 (1)	10.228 (2)
b	5.917 (4)	5.915 (1)	17.328 (9)	17.56 (1)	17.562 (4)
c	11.016 (6)	11.000 (3)	11.613 (2)	11.71 (1)	11.711 (2)
α	100.36 (1)	100.35 (2)	90.99 (3)	91.1 (1)	91.08 (2)
β	86.30 (1)	86.33 (2)	115.09 (9)	115.5 (1)	115.51 (3)
γ	90.84 (2)	90.77 (2)	94.42 (3)	94.6 (1)	94.59 (2)
Z	2	2	4	4	4
Ref	*b*	*c*	*c*	*d*	*c*

[a] Cell edges are in angstrom units and cell angles in degrees. [b] Reference 7. [c] This work. [d] Reference 12.

values of Co-S = 2.398 (1) Å and S-Co-S = 74.1 (2)° reported by Villa, *et al.*[12] Apart from these discrepancies, the bond distances and angles agree with their findings. Minor differences exist in the geometry of the ligands, and these can be attributed to the lengthening of the M-S bonds. The results strongly suggest that Villa, *et al.*,[12] have solved the structure of a $M(S_2CSC_2H_5)_3$ complex in which M is not cobalt(III).

Table II summarizes M-S distances for several tris(1,1-dithiolato)metal(III) complexes of the first-row transition elements. From this compilation it may be seen that both chromium(III) and high-spin iron(III) have metal-sulfur bond lengths of ~2.4 Å. Magnetic studies[16] have shown $Fe(S_2CSC_2H_5)_3$ to be a low-spin complex. We therefore determined the lattice parameters of $Cr(S_2CSC_2H_5)_3$, previously prepared as green-black crystals in our laboratory.[13] Table I shows that the unit cell dimensions are essentially identical with those of the compound assumed to be $Co(S_2CSC_2H_5)_3$ by Villa, *et al.*, and we suggest that the structure determined by them was actually that of tris(ethyl thioxanthato)chromium(III). With this assignment, the results of these authors are in very nice agreement with other chromium(III) 1,1-dithiolate compounds, as can be seen from Table II. And, with this assignment, it is possible to explain essentially all the discrepancies pointed out by these authors in their original paper.

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Table II. Summary of Metal-Sulfur Distances in $M(S_2CY)_3$ Complexes

M	Y	Bond dist, Å	Ref
Cr	Ph	2.38 (1)	*a*
	OEt	2.393 (8)	*b*
Fe (low spin)	S-*t*-Bu	2.297 (7)	7
	NEt_2	2.306 (4)	3
	NMePh	2.312 (19)	9
	OEt	2.316 (10)	8
Fe (high spin)	NEt_2	2.357 (5)	3
	$N(CH_2)_4$	2.41 (3)	9
	$N(t\text{-}Bu)_2$	2.418 (6)	10
Co	SEt	2.266 (7)	*c*
	NEt_2	2.267 (3)	11a
		2.258 (2)	11b
	OEt	2.277 (1)	11c

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Registry No. $Co(S_2CSC_2H_5)_3$, 15277-79-9.

Supplementary Material Available. Tables III and IV showing nonhydrogen and hydrogen atomic positional and thermal parameters, Table V showing bond distances and angles, and Table VI giving structure factor amplitudes for $Co(S_2CSEt)_3$ 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, 24× 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 $7.00 for photocopy or $2.00 for microfiche, referring to code number INORG-74-1791.

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