

Table I. Analyses of *o*-Aminobenzenethiol Complexes

Compound ^a	% metal		% C		% H		% N		% O	
	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found	Calcd
VO(SC ₆ H ₄ NH ₂) ₂	16.11	16.15	45.82	45.71	3.91	3.84	8.76	8.88	4.93	5.07
Cr(SC ₆ H ₄ NH ₂) ₂	48.14	48.00	3.95	4.03	9.35	9.33
Mn(SC ₆ H ₄ NH ₂) ₂	18.04	18.12	47.51	47.54	4.11	3.99	8.99	9.24
Fe(SC ₆ H ₄ NH ₂) ₂	18.35	18.35	47.19	47.39	4.12	3.98	9.04	9.21
Co(SC ₆ H ₄ NH ₂) ₂ ^b	19.18	19.19	46.84	46.92	4.03	3.94	9.06	9.12
	18.91	...	46.87	...	3.85	...	9.28
Co(SC ₆ H ₄ NH ₂) ₃	13.59	13.66	50.04	50.13	4.17	4.20	9.68	9.74
"Co(SC ₆ H ₄ NH ₂) ₂ OH" ^b	17.88	18.18	44.26	44.46	4.02	4.04	8.63	8.64	4.87	4.94
	17.96	...	44.66	...	3.99	...	8.56	...	5.40	...
Ni(SC ₆ H ₄ NH ₂) ₂	19.12	19.13	45.93	46.96	3.72	3.94	9.53	9.13
	47.16 ^c	...	3.91 ^c
Ni(SC ₆ H ₄ NH) ₂ ^d			47.23		3.51				1.12	
	19.16	19.25	47.70 ^e	47.26	2.97 ^e	3.30	8.78	9.18	0.78 ^e	0
			47.50 ^e		3.14 ^e		8.39 ^e		0.69 ^e	
Cu(SC ₆ H ₄ NH ₂) ₂	33.86	33.86	38.52	38.39	3.21	3.22	7.27	7.46
Zn(SC ₆ H ₄ NH ₂) ₂	20.77	20.84

^a O, C, H, and N microanalyses were performed by A. Bernhardt, Max Planck Institut, Mulheim, Germany. ^b Analyses are from different preparations. ^c Duplicate analyses. ^d Sample was recrystallized from benzene. The other compounds could not be recrystallized because of poor solubility; nevertheless, the analytical figures are satisfactory throughout. ^e Unrecrystallized sample, different preparation from *d*.

peared when the ligand was added to cobalt acetate in hot aqueous alcohol. We have found that the orange-brown compound, prepared in the absence of air, is the true cobalt(II) complex Co(SC₆H₄NH₂)₂. It has a room temperature magnetic moment of 4.1 BM, *i.e.*, is high spin, and the moment is in the range expected for tetrahedral cobalt(II). However, the plot of reciprocal susceptibility *vs.* temperature shows departures from linearity at the lower temperatures, and extrapolation of the linear, higher temperature, part of the curve gives a large value of 53° for θ , the Curie-Weiss constant. Since this antiferromagnetic behavior could be due to interactions between the metal atoms in a sulfur-bridged structure, the magnetic moment is not immediately diagnostic of stereochemistry. The iron(II) compound is antiferromagnetic with a Neel point at 138°K. The original cobalt results suggested that *o*-aminobenzenethiol should be classified as a high-field ligand. However, in all complexes where states of different multiplicity are possible, high-spin complexes are formed, except with nickel(II).

As shown in Table I reproducible analytical data, including oxygen analyses, indicate empirical formulation of the blue substance as Co(SC₆H₄NH₂)₂OH or Co(SC₆H₄NH₂)₂O, although its color and magnetic moment ($\mu_{\text{eff}} = 2.7$ BM, $\theta = 16^\circ$) are consistent with formulation analogous to I. Similar moments and θ values have been reported before.^{3,4} The blue substance and the compounds listed above show composite infrared absorptions arising from the NH₂ stretching modes, whereas with the blue nickel compound, and with the similar blue compound Ni(NHC₆H₄NH)₂, a single, sharp and strong NH absorption is found.⁷ In addition, the blue substance has a broad absorption at 3500 cm⁻¹ which would seem to indicate a hydroxo species.

However, aerial oxidation in other conditions, *e.g.*, acetone or aqueous alkali at room temperature, gave paramagnetic blue materials with unreproducible analyses. Furthermore, aerial oxidation in aqueous ammoniacal solution gave the dark green compound Co(SC₆H₄NH₂)₃. This has previously been reported² but could not be obtained by the published method.

(7) D. J. Phillips, unpublished work.

Analytical data are given in Table I; only metal analyses were previously reported. The compound is essentially diamagnetic. Its infrared spectrum, except for the absence of an OH absorption, and its reflectance spectrum are identical with those of the blue compound. Their X-ray powder photographs are almost identical. Thus we believe that the so-called blue cobalt(II) complex is not a true compound, but a mixture of the cobalt(III) compound Co(SC₆H₄NH₂)₃ and some black, paramagnetic, and very finely divided cobalt oxide or hydroxide species. The aerial oxidation in boiling acetone is apparently accompanied by ligand transfer to produce the tris complex Co(SC₆H₄NH₂)₃ and the cobalt oxide or hydroxide species in the appropriate proportions to account for the analytical data.

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Synthesis and Optical Properties of Bis(toluene-3,4-dithiolato)silicon(IV), -germanium(IV), -tin(IV), and -lead(IV)

Sir:

In this communication are reported the synthesis and partial resolution of a new series of optically active compounds containing as the central atom silicon, germanium, tin, and lead. By reaction of a group IV-A tetrachloride (in the case of lead, the tetracetate) with toluene-3,4-dithiol in an appropriate solvent, a racemic mixture of the enantiomers was prepared.

Partial resolution of the enantiomers was accomplished on a column of activated *d*-quartz. The quartz crystals were activated by boiling in concentrated nitric acid, rinsing with distilled water, and heating in an oven at 110° for at least 3 hr. A column was prepared by placing the dry quartz crystals in a standard 50-ml buret to a height of 30 cm. A saturated solution of each of the compounds in acetonitrile was passed through separate columns and collected in 5-ml increments. These solutions were diluted to a concentration

Table I. Chemical Analysis of the Prepared Compounds

Compound	% C		% H		% S		% metal	
	Exptl	Theor	Exptl	Theor	Exptl	Theor	Exptl	Theor
Si(IV)	...	49.96	...	3.59	...	38.10	8.51	8.36
Ge(IV)	44.48	44.12	3.07	3.15	32.90	33.66	18.85	19.05
Sn(IV)	33.38	30.81	2.39	2.22	24.88	23.52	43.02	43.51
Pb(IV)	...	32.60	...	2.35	...	24.87	40.00	40.18

Table II

Metal Compd	λ_0 , $m\mu$	β ($^1B_{ab}$), $m\mu$
Si(IV)	242.5	232
Ge(IV)	233.5	231
Sn(IV)	237.5	234
Pb(IV)	238.0	237

Optical rotatory dispersion data was obtained by use of the Cary 14 recording spectrophotometer equipped with the optical rotatory dispersion attachment. Data are contained in the Table II.

Infrared absorption measurements were made by use of the Beckman IR-8. All compounds prepared except that of tin, plus the ligand, were measured. The data are shown compiled in Table III.

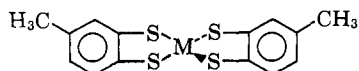
Table III. Infrared Absorptions of Toluene-3,4-dithiol and IV-A Complexes (cm^{-1})

Toluene-3,4-dithiol (in $CHCl_3$)	720-810	867	1050	1130	1285	1392	1470	1600	2570	2900-3100	3670
Si complex	792	856	(1012-1080)		1250						
Ge complex	680	801	860	1025	1099	1251					
Pb complex	680, 741	804	860	1030	1105	1250					

of approximately 10^{-5} M, and ultraviolet and optical rotatory dispersion spectra were obtained.

Although rotation was too slight to be measured in the visible portion of the spectrum, it was dramatic in the ultraviolet region. The point at which the sign of rotation changed was in excellent agreement with the $^1B_{ab}$ transition of the ultraviolet absorption spectrum. Molecular rotations up to a magnitude of 10^8 were observed in the ultraviolet region (the ORD attachment to our Cary spectrophotometer was checked vs. *d*-camphor). To our knowledge, no previously reported series of optically active compounds have molecular rotations of this magnitude.

The presence of optical activity, chemical analyses, infrared spectra, proton nuclear magnetic resonance spectra, and molecular weight determinations support the model depicted below.



Whereas the aromatic rings are probably too far apart to experience perturbation by the ring substituents which would lead to a coupled oscillator model, another model is then required. It is postulated that the electron cloud around the central atom is asymmetrically distorted and that in the solid state, there is a possibility one could observe four nonequivalent metal to sulfur bonds.

A full paper with experimental detail and discussion will follow shortly.¹ A brief summary of the pertinent data is given in Table I.

The germanium compound was the only one having sufficient solubility for the determination of molecular weight on our Mechrolab osmometer; it was observed at 373 vs. a theoretical value of 381. The range of concentrations we could obtain limited our accuracy.

(1) The syntheses and optical activity were announced at the combined Southeast-Southwest Regional Meeting of the American Chemical Society, Memphis, Tenn., Dec 2, 1965, paper no. 81.

The germanium compound was the only compound possessing sufficient solubility to give proton nuclear magnetic resonance data. Hydrogen absorptions were split into four peaks at 7.25, 7.12, 6.84, and 6.71 ppm in a ratio of 1:3:1:1, respectively.

Ultraviolet absorption data were obtained by use of the Cary 14. All compounds were in acetonitrile; spectra were obtained for solvent, ligand, tetraethyllead, and the four IV-A compounds. Table II shows the correlation of sign of optical rotation inversion with the ultraviolet absorption data.

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The Crystal Structure of $CH_3CO^+SbF_6^-$

Sir:

The existence of oxocarbenium ions is of interest in Friedel-Crafts acylations,¹ and has been established²⁻⁶ by infrared studies in the solid state and nmr methods in solution. An X-ray structure determination has not hitherto been reported for an oxocarbenium ion, although the structure of an acyl halide-metal halide complex was recently published.⁷ Methyloxocarbenium ion (CH_3CO^+) has previously² been isolated as the crystalline hexafluoroantimonate salt, and is now shown to have linear geometry. The carbon-methyl bond distance is unusually short and is attributed on the basis of

(1) For a review of this subject see G. Olah, "Friedel-Crafts and Related Reactions," Vol. 1, Interscience Publishers, Inc., New York, N. Y., 1963, pp 91-95, 665-680, and 790-812.

(2) G. A. Olah, S. J. Kuhn, W. S. Tolgyesi, and E. B. Baker, *J. Am. Chem. Soc.*, **84**, 2733 (1962).

(3) G. A. Olah, *Rev. Chim.*, **7**, 1139 (1962).

(4) B. P. Susz and J. Wuhrmann, *Helv. Chim. Acta*, **40**, 722 (1957).

(5) B. P. Susz and J. Wuhrmann, *ibid.*, **40**, 971 (1957).

(6) D. Cook, *Can. J. Chem.*, **37**, 48 (1959).

(7) S. E. Rasmussen and N. C. Broch, *Chem. Commun.*, 289 (1965).