Chelate Chemistry. V. Metal Chelates Based on Tropolone and Its Derivatives

E. L. Muetterties, H. Roesky, and C. M. Wright

*Contribution No. 1215 from the Central Research Department,
Experimental Station, E. I. du Pont de Nemours and Company,
Wilmington, Delaware 19898.* *Received June 4, 1966*

Abstract: Rare earth tris chelates based on the γ-isopropyltropolone anion are associated and presumably contain seven- or eight-coordinate metal ions. The degree of association drops significantly in going from the large lanthanide cations to the smaller ions such as lutetium(III). Some of the smaller ions, such as erbium, tend to separate from aqueous solutions as monohydrated tris chelates. Monomolecular formulations were established for the solution state of $(chel)_2SnCl_2$, $(chel)_3SnCl$, and $(chel)_3NbO$ with the γ-isopropyltropolone anion ligand. On the other hand, bis(isopropyltropolono)nickel(II) (paramagnetic) is not very soluble in nonbasic solvents and must be significantly associated. Chelate chemistry based on the monothio analog of tropolone is similar to that of the tropolone ion. Eight-coordinate lead and thorium(IV) chelates from thiotropone were readily obtained. Attempts to prepare ten-coordinate pentakis chelates like the known $Th(tropolonate)_5^-$ anion were unsuccessful with the thiotropone anion. Further distinctions between tropolone and thiotropone chemistry arise in nickel(II) chelates where the thiotropone derivative is diamagnetic and square-planar. Tracer studies of basic hydrolyses of thiotropone cationic chelates identified ligand attack by hydroxyl ion as a significant, but not dominating, hydrolysis course.

The preceding papers[1-5] in this series presented a fairly detailed characterization of tropolone ion (T) chelates encompassing synthesis, structure, and chemistry. Similarly, the nonmetal chemistry of N,N-dimethylaminotroponeimine ion (A) has been elaborated;[1] transition metal chelates derived from this ligand have been extensively investigated.[6] For this general class of chelate chemistry, the major areas for exploration that remain are (1) precise geometrical parameters for the various structural classes, six through ten coordinate, (2) information regarding the solution state, particularly the question of molecularity and coordination number, and (3) the character of chelates obtained from sulfur analogs. The first aspect, the structural one, is being explored by Professor J. L. Hoard and co-workers. It is to the second two topics that this article is addressed.

The solubility of neutral tropolone metal chelates is sufficiently low that reliable molecular weight determinations have been precluded for the most part. We have found that isopropyl substitution at the γ position imparts much greater solubility to the tropolone chelates and have employed the γ-isopropyltropolone (γ-thujaplicin) ion (Figure 1) as a probe to establish molecularity for certain structural classes. Additionally, we have instituted a study of the chelate chemistry based on monothio derivatives of tropolone, 2-thiotropone, and of aminotroponeimine, aminothiotropone (Figure 1).

γ-Isopropyltropolone Chemistry. Molecularity of Tropolone Chelates. The extraordinary intractability of the neutral tristropolonates of the larger rare earth ions strongly implicated polymeric lattices through bridging oxygen atoms, *i.e.*, three-coordinate chelate oxygen atoms and seven- or eight-coordinate metal atoms.[3] Characterization of the analogous γ-isopropyltropolone chelates clearly vindicates this view. Despite the presence of the solubilizing isopropyl groups, the tris chelates of the metal ions lanthanum through terbium(III) are insoluble in all common solvents. The behavior of the smaller ions varies. Holmium and erbium(III) tris chelates separate from an aqueous triethylamine solution as monohydrates and may represent seven- or eight- (polymeric) coordinate structures. Vacuum drying at 80° of the erbium chelate obtained from an aqueous anionic solution gives an anhydrous phase, which is intractable and isomorphous with the lanthanum (through terbium) chelate as judged by comparison of X-ray powder patterns. The infrared spectra of all the insoluble tris chelates are very similar. A soluble, anhydrous form of the erbium tris chelate was also isolated. It is identical with the anhydrous tris chelate of lutetium(III) based on infrared and X-ray criteria. Molecular weight studies of the soluble erbium and lutetium chelates in nonpolar solvents indicate an association that approximates a trimer. The molecularity of the tris chelate based on α-isopropyltropolone and lutetium(III) is trimeric in a variety of solvents.

Like the anhydrous nickel(II) acetylacetonate which is trimeric, the nickel(II) derivative of γ-isopropyltropolone must also be associated; it has only slight solubility in organic solvents such as chloroform. Nuclear magnetic resonance studies clearly show that this nickel compound is paramagnetic. The isopropyl proton resonances are shifted to high field and are broad; the aromatic protons were not detected, presumably because of line broadening from electron-spin relaxation.

Tin halides react with tropolone to give T_2SnX_2 and further replacement of halide can be effected only by tropolone ion going in discrete steps to T_3SnX and finally to T_4Sn.[1,7] The chemistry of γ-isopropyltropolone is analogous. Cessation of exchange at the

---

(1) E. L. Muetterties and C. M. Wright, *J. Am. Chem. Soc.*, 86, 5132 (1964).

(2) E. L. Muetterties and C. M. Wright, *ibid.*, 87, 21 (1965).

(3) E. L. Muetterties and C. M. Wright, *ibid.*, 87, 4706 (1965).

(4) E. L. Muetterties, *ibid.*, 88, 305 (1966).

(5) E. L. Muetterties, *J. Pure Appl. Chem.*, 10, 54 (1965).

(6) D. R. Eaton, A. D. Josey, W. D. Phillips, and R. E. Benson, *J. Chem. Phys.*, 39, 3513 (1963), and references therein.

(7) We have now found that the reaction of tetraphenyltin and tropolone at elevated temperatures is the simplest and cleanest route to T_4Sn. This method is similar to that used by K. Ranaiah and D. F. Martin to prepare the tetrakis(8-hydroxyquinolide) derivative of tin: *Chem. Commun.*, 130 (1965).

bis-chelate stage with tropolone might be ascribed to a low reactivity of the halogen atom or to a sterically congested structure for the bis chelate due to dimerization through chlorine- or oxygen-bridging atoms. The latter alternative was eliminated as a possibility by molecular weight studies which established bis(γ-isopropyltropolono)tin dichloride as a monomer. The ligand proton nmr resonances comprise simple AB aromatic bands and typical isopropyl fine structure indicative of but not definitive for ligand equivalence. An identical situation prevails for $(TJ)_3SnCl$ with regard to molecularity and spectroscopic equivalence of ligands. Thus, the tris chelate derivative must have a seven-coordinate tin atom.

In a preceding paper, we suggested that T_3NbO might be dimeric through NbONb bonds as in Cl_3NbO. However, characterization of the analogous γ-isopropyltropolone derivative destroyed this hypothesis. The $(TJ)_3NbO$ species is monomeric in chloroform solution and there is nmr spectroscopic equivalence of ligand α and of ligand β protons. Infrared absorption at 918 cm^{-1} is probably primarily associated with the NbO stretching frequency.

Maximum Coordination Numbers in Tropolone Chelates. The maximum coordination number that can be achieved in metal tropolonates is primarily a function of the size and charge of the metal ion; large size and high charge favor high coordination numbers. For trivalent or tetravalent metal ions, the break between six and higher coordination numbers occurs at about a metal ion radius of 0.68 A (ionic radius). Titanium(IV), which has an ionic radius of 0.68 A, achieves seven coordination in the compound T_3TiCl.[3] On the other hand, gallium(III) ion which has an ionic radius of 0.62 A consistently yields the octahedral tristropolonate; efforts to add tropolone ion or a unidentate donor molecule were unsuccessful. Eight coordination appears first at an ionic radius of 0.71 A in tin, SnT_4. These relationships suggested that higher coordination structures could be realized with Sb^{3+} and Bi^{3+}. Previously, we described the reaction products of these ions with tropolone as quasi-octahedral species, $:MT_2Cl$. Reaction of the chloro derivatives with sodium tropolonate has given SbT_3, BiT_3, and $NaBiT_4$. Attempts to force SbT_3 to the SbT_4^- anion were without success. The tristropolonates of these two metals bear no spectral or diffraction similarities to other tristropolonates, although $NaBiT_4$ may be isomorphous with the $NaMT_4$ series described in paper III.[3] We suggest that SbT_3 and BiT_3 are either six- or quasi-seven-coordinate structures and that BiT_4^- is either an eight-coordinate or a quasi-nine-coordinate species.

The general relationships for coordination number with ionic radius of the metals are summarized below for the tropolone derivatives of trivalent and tetravalent metal ions (see Table I). Nine coordination appears at thorium(IV) in the complexes of ThT_4 with donor molecules; the smaller zirconium and hafnium ions do not exhibit this acceptor property in their tetrakistropolono derivatives. Size relationships alone suggest that ten coordination is possible for the trivalent lanthanide ions, although all efforts to form an ion such as LaT_5^{2-} have failed. Coulombic repulsions may make the formation of a dinegative complex anion relatively unfavorable and provide the distinguishing factor in the behavior of the trivalent lanthanides relative to the tetravalent actinide ions toward tropolone ion.

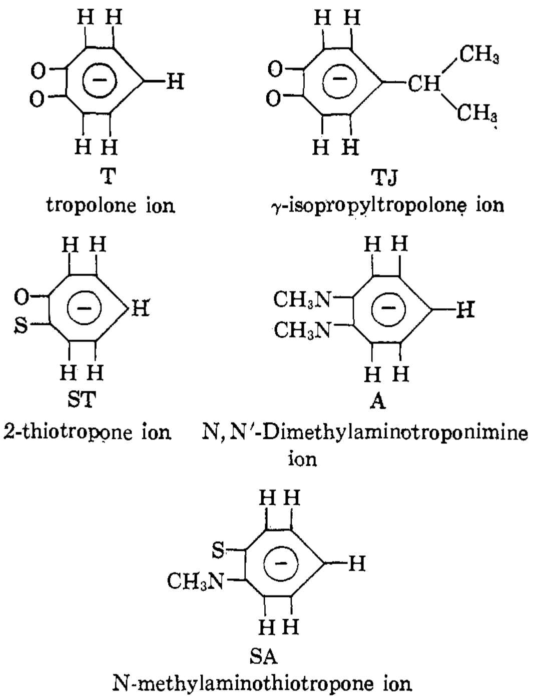

Figure 1. Ligands employed in this investigation.

Table I

Coordination no.	Metal ion	Ionic radius, A	Complex
6	Ge^{4+}	0.54	GeT_3^{+}[a]
6	Ga^{3+}	0.62	GaT_3[a]
7	Ti^{4+}	0.68	T_3TiCl
7	Sn^{4+}	0.71	T_3SnCl
6 or 7	Sb^{3+}	0.92(0.76)	$:SbT_3$
8	Sn^{4+}	0.71	SnT_4
8	In^{3+}	0.81	InT_4^-
8	Sc^{3+}	0.81	ScT_4^-
8	$Lanthanides^{3+}$	1.15–0.85	RT_4^-
8	Zr^{4+}	0.80	ZrT_4
8 or 9	Bi^{3+}	1.08	$:BiT_4^-$
9	Th^{4+}	1.02	$T_4Th\cdot OS(CH_3)_2$
10	Th^{4+}, U^{4+}	1.02, 0.97	MT_5^-

[a] A number of reactions with GeT_3^+ and GaT_3 with T^- and with neutral donor molecules like $(CH_3)_2SO$ were explored but there was no evidence of coordination numbers beyond six.

There are a number of quite large divalent metal ions which in principle could form high coordination structures with tropolone ions. These include Ca^{2+}, Ba^{2+}, Sr^{2+}, and many others. In all cases, divalent metal ions were found to form bistropolonates, although many initially separate from the aqueous reaction media with molecules of hydration, *e.g.*, $SrT_2\cdot 2H_2O$ and $BaT_2\cdot 2H_2O$. Anhydrous forms were obtained by vacuum dehydration. The tractability, volatility, and solution molecular weight studies strongly point toward monomolecular, four-coordinate species in BeT_2, CuT_2, and HgT_2. The first row transition metal bistropolonates from manganese through nickel are only slightly volatile, intractable, and display a more complex infrared pattern in the 1600–1500 cm^{-1} region. We propose that these bistropolonates are associated by sharing oxygen atoms between metal atoms to give structures in which the metal atom coordination numbers are greater than four. A similar phenomenon must be operative in the anhydrous bistropolonates of magnesium through barium; all of these are extremely intractable and are nonvolatile at 350° (0.01 μ). The analogous barium complex of γ-isopropyltropolone is insoluble in benzene and in chloroform; it must be significantly associated because the γ-isopropyl group confers benzene solubility to monomeric tropolone complexes. The lead(II) derivative of tropolone is a dimeric species in dichloromethane solution. Attempts to convert the heavy metal bistropolonates of d^0 and d^{10} configuration to anionic tris or tetrakistropolonates were unsuccessful with PbT_2, BaT_2, and $Ba(TJ)_2$. Such anion addition is a facile process for the neutral chelates of the large trivalent cations. Perhaps charge density, which is significantly lower in the divalent cations, is a limiting parameter in anion addition reactions.

Thiotropone and Aminothiotropone Chemistry. Nickel(II) acetate reacts with an aqueous methanol solution of 2-thiotropone to give deep purple crystals of bis(thiotropono)nickel which can be sublimed *in vacuo*. The chelate is monomeric and diamagnetic; hence, unlike the tropolonates this analog is four-coordinate, square-planar. The deep color of the chelate probably arises from a charge-transfer band.

Tropolone ion is a unique ligand in the ease with which high-coordinate structures are generated from it in reactions with many metal ions. Much of this character is retained in the thiotropone ion. Eight-coordinate chelates were obtained with lead(IV) and thorium(IV). However, unlike tropolone ion in its conversion of ThT_4 to ThT_5^-, thiotropone ion gave no indication of reaction with $Th(ST)_4$. Nevertheless, acceptor activity is still evident in $Th(ST)_4$, and an apparent nine-coordinate adduct was obtained with dimethyl sulfoxide.

Boron tribromide and thiotropone yield the cationic $B(ST)_2^+$ chelate which is very similar to the tropolone derivative. The cation is stable to aqueous acid but is degraded by aqueous base (*vide infra*). N-Methylaminothiotropone behaved in an analogous fashion to yield $B(SA)_2^+$, a cation stable to acidic conditions and only slowly degraded by strong aqueous alkali. The stability to base is similar to, but not as striking as, that of BA_2^+, and apparently the sulfur function appreciably quenches the acid instability associated with the nitrogen function since BA_2^+ itself is degraded by strong acid.

Thiotropone and germanium tetrachloride react to give the molecular bis complex $(ST)_2GeCl_2$. Reaction of the sodium salt of thiotropone with the bis complex yields the salt $(ST)_3Ge^+Cl^-$ which was converted to PF_6^-, I^-, and $B_{12}Cl_{12}^{2-}$ salts by metathetical reactions. Phenyltin trichloride and tin tetrachloride react with thiotropone to give $(ST)_2SnCl_2$ which is converted to $(ST)_3SnCl$ with the sodium salt of thiotropone. The tris complex $(ST)_3SnCl$ does not display any ionic properties; it does not undergo metathetical reactions with salts of large anions. This behavior parallels that of the tropolone system and, like T_3SnCl, $(ST)_3SnCl$ is probably a seven-coordinate tin structure.

Hydrolysis Mechanism for $B(ST)_2^+$ and $B(SA)_2^+$. Characterization of the alkaline hydrolysis of metal tropolonates has established ligand attack at the carbon atom α to the oxygen atom as the dominating hydrolysis path provided the metal chelate bears a formal charge, and it was of interest to compare the hydrolysis path of the sulfur derivatives with that of the tropolone systems.

Alkaline hydrolysis of the bis(thiotropono)boron cation, $B(ST)_2^+$, gives the thiotropone anion in essentially quantitative yield. Examination of this hydrolysis in water enriched in O^{18} showed that introduction of O^{18} into the chelate did in fact occur. The degree of enrichment was about 10% compared with the theoretical value of 50% if the sole operable mechanism in removal of the first ligand were attack at the carbon atom α to the chelate oxygen atom as observed experimentally for the bis(tropolono)boron cation. Clearly another hydrolysis mechanism (or mechanisms) is quite effectively competing in the case of the thiotropone derivative.

The rate of hydrolysis of the bis(N-methylaminothiotropono)boron cation, $B(SA)_2^+$, is relatively low in strongly acidic or basic media which places this cation intermediate in hydrolytic character with respect to the bis(tropolono)boron cation which resists acid degradation and the bis(aminotroponeimine)boron cation which is not attacked by strong base. The alkaline hydrolysis products of the aminothiotropone derivatives are N-methylaminothiotropone and N-methylaminotropone in approximately equimolar quantities. However, many side reactions occur under basic conditions and a materials balance for the basic hydrolysis was not realized. The yield of hydrolyzed ligand was only about 12%.

Experimental Section

Preparation of $La(C_{10}H_{11}O_2)_3$. γ-Isopropyltropolone (2.5 g, 0.015 mole) was added to a solution of lanthanum chloride heptahydrate (1.9 g, 0.005 mole) in 100 ml of water and 70 ml of methanol. The clear solution was slowly evaporated on a steam bath to give a pale yellow precipitate. The precipitate was collected and then slurried in a hot mixture of methanol, water, and acetonitrile. The slurry was warmed on a steam bath for 0.5 hr and then filtered hot. The solid was collected by filtration and then vacuum dried at 60°, mp >410°. *Anal.* Calcd for $La(C_{10}H_{11}O_2)_3$: La, 22.1; C, 57.3; H, 5.30. Found: La, 21.8; C, 57.2; H, 5.29. The tris chelate was essentially insoluble in acetonitrile, benzene, chloroform, ethanol, and methanol.

Preparation of $Eu(C_{10}H_{11}O_2)_3$ and $Gd(C_{10}H_{11}O_2)_3$. γ-Isopropyltropolone (1.2 g, 0.0073 mole) was added to a solution of europium nitrate hexahydrate (0.98 g, 0.0022 mole) in 50 ml of water and 30 ml of methanol to give a clear yellow solution. A yellow solid began to separate several minutes later. After 24 hr the solid was isolated by filtration and slurried in a methanol–water mixture on a steam bath for 0.5 hr. This slurry was then filtered, and the solid was vacuum dried at 60°, mp >400°. *Anal.* Calcd for $Eu(C_{10}H_{11}O_2)_3$: Eu, 23.7; C, 56.2; H, 5.15. Found: Eu, 24.0; C, 56.1; H, 5.19. This tris chelate was insoluble in all common organic solvents. The infrared spectrum is identical with that of the lanthanum derivative.

A similar procedure was followed with gadolinium nitrate hexahydrate. The solid was insoluble in CH_3CN, $CHCl_3$, and CH_3OH. *Anal.* Calcd for $Gd(C_{10}H_{11}O_2)_3$: Gd, 24.3; C, 55.7; H, 5.10. Found: Gd, 23.3; C, 55.5, 55.8; H, 5.14, 5.22.

Preparation of $Tb(C_{10}H_{11}O_2)_3$. A solution of terbium nitrate hexahydrate (0.45 g, 0.0011 mole) in 50 ml of water was added to a solution of γ-isopropyltropolone (0.61 g, 0.0037 mole) in 20 ml of methanol. During the addition, the solution turned yellow and than a yellow solid separated. The slurry was stirred for 6 hr, and during this time, 50 ml of water was added to complete the precipitation. The solid was collected, washed with water, and dried at

25° (1 μ) for 8 hr. The solid was soluble in methanol and chloroform but insoluble in acetone. *Anal.* Calcd for $Tb(C_{10}H_{11}O_2)_3$: Tb, 24.1; C, 55.6; H, 5.10. Found: Tb, 24.1; C, 56.0; H, 5.30.

Preparation of Hydrated Chelates of Ho^{3+} and Er^{3+}. The holmium and erbium chelates were prepared by adding a solution of holmium nitrate hexahydrate or erbium nitrate hexahydrate (0.0011 mole) in 25 ml of water to a solution of γ-isopropyltropolone (0.5 g, 0.003 mole) in 30 ml of methanol. Triethylamine was added to the reaction mixture until the pH was about 6. The mixture was stirred for 3 hr and during this time 60 ml of water was added to cause precipitation. The collected solids were vacuum dried at 25° (1 μ). The infrared spectra displayed strong water bands. *Anal.* Calcd for $Ho(C_{10}H_{11}O_2)_3H_2O$: Ho, 24.4; C, 53.4; H, 5.20. Found: Ho, 23.3; C, 53.2; H, 5.67. Calcd for $Er(C_{10}H_{11}O_2)_3\cdot 2H_2O$: Er, 24.2; C, 52.0; H, 5.35. Found: Er, 24.1; C, 51.7; H, 5.50.

Preparation of Anhydrous Chelates of Holmium, Erbium, and Lutetium. A solution of γ-isopropyltropolone (1.2 g, 0.0073 mole) in 20 ml of methanol was added to a solution of holmium nitrate hexahydrate (1.0 g, 0.0022 mole) in 40 ml of water. The reaction mixture was warmed on a steam bath and then 50 ml of acetonitrile and 30 ml of methanol were added. Ammonium hydroxide was added to the reaction mixture until the pH was about 6. Addition of the ammonium hydroxide gave a somewhat gummy precipitate. The reaction slurry was further heated on a steam bath for 1 hr and then filtered. The collected solid was vacuum dried at 80°. *Anal.* Calcd for $Ho(C_{10}H_{11}O_2)_3$: C, 55.1; H, 4.94. Found: C, 55.0; H, 5.19. The infrared spectrum was identical with that of the europium and lanthanum chelates.

In a similar fashion, erbium nitrate hexahydrate was treated with γ-isopropyltropolone. The crude product was added to a hot mixture of 30% cyclohexane and 70% chloroform. The slurry was filtered. The insoluble material after vacuum drying at 80° had an infrared spectrum identical with those of the tris chelates of lanthanum, europium, and holmium, mp 380–386° dec. *Anal.* Calcd for $Er(C_{10}H_{11}O_2)_3$: C, 54.8; H, 4.92. Found: C, 53.8; H, 5.04. The cyclohexane–chloroform filtrate was concentrated to yield a crystalline solid, mp 380–389° dec. The infrared spectrum of this solid was identical with that of $Lu(C_{10}H_{11}O_2)_3$. *Anal.* Calcd for $Er(C_{10}H_{11}O_2)_3$: C, 54.8; H, 4.92; mol wt, 1312 (dimer), 1968 (trimer). Found: C, 55.1; H, 5.35; mol wt, 1686, 1663 ($CHCl_3$, vapor pressure osmometry).

The same procedure was followed with lutetium nitrate hexahydrate. The crude product obtained was completely soluble in chloroform. It was recrystallized from a hot mixture of chloroform–methanol. The recrystallized product was vacuum dried at 80° for 40 hr, mp 375–385° dec. *Anal.* Calcd for $Lu(C_{10}H_{11}O_2)_3$: C, 54.3; H, 4.87; mol wt, 1328 (dimer), 1992 (trimer). Found: C, 54.5; H, 5.33. The molecular weight in $CHCl_3$ (vapor pressure osmometry) was 1475 and 1521. The tris(α-isotropolono) lutetium chelate was similarily made. For this isomer, the molecular weight in benzene (ebullioscopic) was 1813, in $CHCl_3$ and CH_2Cl_2 1806 and 1750, respectively (vapor pressure osmometry), and in benzene (cryoscopic) 2100.

Preparation of $Ba(C_{10}H_{11}O_2)_2$. Barium chloride dihydrate (0.49 g, 0.002 mole) and γ-thujaplicin (0.65 g, 0.004 mole) were dissolved in 50 ml of water and 50 ml of methanol. Ammonium hydroxide was added to a pH of 7.5 to give a yellow precipitate. The slurry was heated to reflux and methanol was added until a clear solution was achieved. The solution was filtered hot and cooled. On cooling, a yellow solid separated. This was recovered by filtration and vacuum dried at 100° for 4 hr. The compound did not sublime under vacuum at elevated temperatures and it was insoluble in hot benzene, mp 372–375°. *Anal.* Calcd for $Ba(C_{10}H_{11}O_2)_2$: C, 51.8; H, 4.75. Found: C, 50.1; H, 5.57.

Preparation of $(C_{10}H_{11}O_2)_3NbO$. A solution of γ-isopropyltropolone (7.3 g, 0.045 mole) in 70 ml of methanol was added to 5.4 g of niobium pentachloride (0.02 mole) in 5 ml of concentrated hydrochloric acid. The solution became red immediately upon mixing. After heating over steam for 20 min, the solution was cooled to room temperature and neutralized to pH 6 with aqueous sodium hydroxide during which time a yellow solid separated. The solid was isolated by filtration and recrystallized from a water–methanol mixture, mp 295–296° dec. *Anal.* Calcd for $(C_{10}H_{11}O_2)_3NbO$: C, 60.4; H, 5.52; Nb, 15.5; mol wt, 599. Found: C, 60.8; H, 5.79; Nb, 15.4; mol wt, 613 ($CHCl_3$, vapor pressure osmometry).

Preparation of $Ni(C_{10}H_{11}O_2)_2$. A solution of nickel acetate tetrahydrate (0.83 g, 0.0033 mole) in 100 ml of water was mixed with a solution of γ-isopropyltropolone (0.99 g, 0.0067 mole) in 30 ml of warm methanol. A chartreuse precipitate appeared on mixing. The reaction slurry was warmed on a steam bath for 2 hr and then filtered. The solid was vacuum dried at 100° for a period of 2 hr. At this point the solid was an orange-yellow material. The compound was purified by sublimation at 310° (0.01 mm); mp 365–370° dec. *Anal.* Calcd for $Ni(C_{10}H_{11}O_2)_2$: Ni, 15.3; C, 62.5; H, 5.72. Found: Ni, 15.1; C, 61.2; H, 5.91. There was no evidence of water bands in the infrared spectrum.

Preparation of $(C_{10}H_{11}O_2)_2SnCl_2$. Tin tetrachloride (2.60 g, 0.01 mole) was added to a solution of γ-isopropyltropolone (3.28 g, 0.02 mole) in 80 ml of benzene to give a pale yellow precipitate. Methanol was added until a clear solution was obtained. The reaction slurry was then warmed on a steam bath for 0.5 hr during which time a white solid separated. The solid was collected and recrystallized from a mixture of benzene and chloroform and then dried at 80° (0.01 mm) for 12 hr; mp 392–395°. *Anal.* Calcd for $(C_{10}H_{11}O_2)_2SnCl_2$: C, 46.6; H, 4.30; Sn, 23.0; Cl, 13.7; mol wt, 515.9. Found: C, 46.7; H, 4.33; Sn, 22.6; Cl, 13.7; mol wt, 545 ($CHCl_3$, vapor pressure osmometry).

Preparation of $(C_{10}H_{11}O_2)_3SnCl$. A slurry of $(C_{10}H_{11}O_2)_2SnCl_2$ (1.87 g, 0.0036 mole) and the sodium salt of γ-isopropyltropolone (0.58 g, 0.003 mole) in 60 ml of acetonitrile and 30 ml of methanol was warmed on a steam bath. Essentially all solids went into solution after about 5 min at reflux temperature. After 10 min, a small amount of water was added and all of the solids dissolved. Water was added to the point of incipient precipitation, and the reaction mixture was allowed to cool while stirring. On cooling, a gummy solid separated; this was collected and recrystallized from a hot mixture of chloroform and cyclohexane. The solid was vacuum dried at 80° (0.01 mm) for 12 hr; mp 241–244°. *Anal.* Calcd for $(C_{10}H_{11}O_2)_3SnCl$: C, 56.1; H, 5.17; Sn, 18.4; Cl, 5.52; mol wt, 643.5. Found: C, 56.5; H, 5.21; Sn, 17.4; Cl, 4.90; mol wt, 613 ($CHCl_3$, vapor pressure osmometry).

Preparation of $NaBi(C_7H_5O_2)_4$. A mixture of sodium tropolonate (1.4 g, 0.01 mole) and $(C_7H_5O_2)_2BiCl$ (2.43 g, 0.005 mole) in 200 ml of methanol and 50 ml of water was warmed to mild reflux whereupon a yellow precipitate formed. The slurry was held at reflux conditions for 1 hr and then filtered. The filtrate was recrystallized from a mixture of methanol, acetonitrile, and water to give an ivory solid which was dried under vacuum at 90° for 4 hr, mp >400°. *Anal.* Calcd for $NaBi(C_7H_5O_2)_4$: Na, 3.21; C, 46.9; H, 2.81. Found: Na, 2.96; C, 47.0; H, 2.97.

Preparation of $Bi(C_7H_5O_2)_3$. The procedure described above was followed but with 0.005 mole of sodium tropolonate. The crude product was recrystallized from a mixture of chloroform and acetonitrile. The product was dried under vacuum at 90° for 4 hr, mp 323–326° dec. *Anal.* Calcd for $Bi(C_7H_5O_2)_3$: Bi, 36.5; C, 44.1; H, 2.62. Found: Bi, 38.6; C, 44.1; H, 2.63.

Preparation of $Sb(C_7H_5O_2)_3$. The procedure described for the preparation of $Bi(C_7H_5O_2)_3$ was employed. The crude product was recrystallized from a hot mixture of water, methanol, and acetonitrile, and the yellow solid was vacuum dried at 90° for 4 hr, mp 335–337° dec. *Anal.* Calcd for $Sb(C_7H_5O_2)_3$: Sb, 25.1; C, 52.0; H, 3.10. Found: Sb, 26.2; C, 52.1; H, 3.17. The same product was obtained employing excess sodium tropolonate. There was no evidence for the formation of $NaSb(C_7H_5O_2)_4$.

Synthesis of Alkaline Earth Metal Tropolonates. Calcium chloride (0.55 g, 0.005 mole) and tropolone (1.2 g, 0.01 mole) were dissolved in 60 ml of water and 20 ml of methanol. Triethylamine was added to the solution to give a yellow precipitate. The reaction slurry was heated to reflux for 0.5 hr and then filtered to give a yellow solid. The solid was recrystallized from a large volume of hot acetonitrile–ethanol–water to give pale yellow crystals, mp >400°. *Anal.* Calcd for $Ca(C_7H_5O_2)_2$: Ca, 14.2. Found: Ca, 14.2.

The same procedure was followed with barium chloride. The crude product analyzed roughly for a dehydrated bistropolonate. This product was dried under vacuum at 180° for 12 hr to give the bistropolonate, mp >400°. *Anal.* Calcd for $Ba(C_7H_5O_2)_2$: Ba, 36.2; C, 44.3; H, 2.64. Found: Ba, 37.1; C, 42.5; H, 2.90.

The same procedure was followed with strontium nitrate. The crude product was recrystallized from a hot mixture of acetonitrile, methanol, and water. *Anal.* Calcd for $Sr(C_7H_5O_2)_2\cdot 2H_2O$: Sr, 24.0; C, 46.0; H, 3.85. Found: Sr, 24.6; C, 46.1; H, 3.56. The dihydrate was dried at 130° under vacuum for 12 hr. *Anal.* Calcd for $Sr(C_7H_5O_2)_2$: Sr, 26.6; C, 51.0; H, 3.04. Found: Sr, 26.0; C, 50.4; H, 3.41.

The same procedure was followed with magnesium. The crude product was recrystallized from a hot mixture of acetonitrile, ethanol, and water. *Anal.* Calcd for $Mg(C_7H_5O_2)_2\cdot 2H_2O$: Mg, 8.02; C, 55.7; H, 4.63. Found: Mg, 8.48; C, 56.2; H, 4.47. The dihydrate was dried under vacuum at 35° for 16 hr, mp >310°. *Anal.* Calcd for $Mg(C_7H_5O_2)_2$: Mg, 9.10; C, 63.0; H, 3.75. Found: Mg, 9.25; C, 62.9; H, 3.94.

The infrared spectra of the anhydrous magnesium, calcium, strontium, and barium bistropolonates were virtually identical. These tropolonates were essentially insoluble in all common solvents and showed no evidence of volatility below 350–400°.

The same procedure as described above was employed with beryllium chloride. *Anal.* Calcd for $Be(C_7H_5O_2)_2$: Be, 3.59; C, 66.9; H, 3.98. Found: Be, 3.46; C, 66.9; H, 4.62. The bistropolonate of beryllium was sublimed at 100° (0.1 μ), mp 178–210° dec.

Preparation of $Mn(C_7H_5O_2)_2$. A solution of tropolone (1.22 g, 0.01 mole) in 40 ml of methanol was added to a solution of manganeous acetate tetrahydrate (1.23 g, 0.005 mole) in 30 ml of water to give a pale yellow precipitate. The reaction slurry was digested on a steam bath for 2 hr. The product was collected by filtration and vacuum dried. The crude product was sublimed at 320° (0.01 μ), mp >400°. *Anal.* Calcd for $Mn(C_7H_5O_2)_2$: C, 56.6; H, 3.37. Found: C, 56.7; H, 3.42.

Preparation of $Fe(C_7H_5O_2)_2$. Ferrous sulfate heptahydrate (1.4 g, 0.005 mole) was dissolved in 100 ml of water containing 3 drops of concentrated sulfuric acid and 20 ml of methanol. Tropolone (1.2 g, 0.01 mole) was added to the solution while a nitrogen atmosphere was maintained in the reaction flask. The reagents on mixing yielded a dark solution. On warming on a steam bath, dark red-brown crystals separated out, mp 395–400° dec. *Anal.* Calcd for $Fe(C_7H_5O_2)_2$: Fe, 18.8; C, 56.5; H, 3.36. Found: Fe, 18.1; C, 56.1; H, 3.32. The crude product was sublimed at 260° (0.01 μ) to give a product that melted at 395–397°. However, the iron content of the sublimate was consistently lower than theory and ran about 15% Fe. Apparently in the sublimation process some of the iron was oxidized to the 3+ state and the product must have contained a significant amount of the iron(III) tropolonate.

Preparation of $Cu(C_7H_5O_2)_2$, $Ni(C_7H_5O_2)_2$, $Co(C_7H_5O_2)_2$. A solution of tropolone (2.69 g, 0.022 mole) in 40 ml of methanol was added to a solution of $Cu(C_2H_3O_2)_2\cdot H_2O$ (2.0 g, 0.01 mole) in 300 ml of water and 50 ml of methanol. The olive precipitate was collected and washed with water. The solid was recrystallized from hot acetonitrile, mp 323.5–327°. Another sample was sublimed at 260° (0.1 μ), mp 323–327°. *Anal.* Calcd for $Cu(C_7H_5O_2)_2$: Cu, 20.8; C, 55.0; H, 3.28. Found: Cu, 20.9; C, 55.2; H, 3.49.

The same procedure was followed with cobalt and nickel acetates. The crude products in these cases were not susceptible to recrystallization because of very low solubility. They were sublimed at 310° (0.1 μ). Neither of the two sublimed products melted below 400°. *Anal.* Calcd for $Ni(C_7H_5O_2)_2$: Ni, 19.5; C, 55.8; H, 3.32. Found: Ni, 19.5; C, 56.0; H, 3.39. Calcd for $Co(C_7H_5O_2)_2$: Co, 19.6; C, 55.7; H, 3.32. Found: Co, 19.5; C, 55.8; H, 3.51. There were similarities in the X-ray powder patterns of the sublimed cobalt and nickel tropolonates, but there were no similarities between the pattern of these two and that of the copper tropolonate.

Preparation of $Pd(C_7H_5O_2)_2$. A solution of K_2PdCl_4 (1.6 g, 0.005 mole) in 60 ml of water was added to a solution of tropolone (1.2 g, 0.01 mole) in 30 ml of ethanol to give an orange precipitate. The crude product was recrystallized from a mixture of acetonitrile, dichloromethane, and chloroform. The orange crystals were vacuum dried at 70° for 24 hr, mp 330–370° dec. *Anal.* Calcd for $Pd(C_7H_5O_2)_2$: Pd, 30.6; C, 48.2; H, 2.87. Found: Pd, 30.7; C, 48.2; H, 2.82.

Preparation of $Zn(C_7H_5O_2)_2$. Zinc chloride (1.4 g, 0.01 mole), dissolved in a minimum of a 50:50 mixture of ethanol and water, was added to a solution of tropolone (3.7 g, 0.03 mole) in 100 ml of methanol to give a clear solution. The solution was evaporated and the solid residue was recrystallized from a hot ethanol–water mixture. *Anal.* Calcd for $Zn(C_7H_5O_2)_2$: Zn, 21.2; C, 54.7; H, 3.25. Found: Zn, 21.7; C, 55.2; H, 3.30.

Preparation of $Pb(C_7H_5O_2)_2$. Tropolone (1.2 g, 0.01 mole) and lead acetate trihydrate (7.6 g, 0.02 mole) were added to 30 ml of water and 40 ml of methanol. The mixture was heated to reflux and ethanol was added to give a clear solution. On cooling, orange-yellow crystals were obtained. These were recrystallized from a hot mixture of methanol and water, mp 230–232°. *Anal.* Calcd for $Pb(C_7H_5O_2)_2$: Pb, 46.2; C, 37.5; H, 2.23; mol wt, 449.2. Found: Pb, 46.3; C, 37.5; H, 2.25; mol wt, 841 (vapor pressure osmometer in dichloromethane, extrapolated to infinite dilution).

Preparation of $Hg(C_7H_5O_2)_2$. The procedure described above for lead tropolonate was followed with mercuric acetate as the reagent. *Anal.* Calcd for $Hg(C_7H_5O_2)_2$: Hg, 46.5; C, 38.0; H, 2.16. Found: Hg, 44.3; C, 37.9; H, 2.13. Hydrolysis of the mercuric tropolonate in deuterium oxide led to no introduction of deuterium into the aromatic C–H positions of the tropolone hydrolysate. Thus, there was no evidence for mercury–carbon bonding in this tropolone derivative.

Preparation of $Ni(C_7H_5OS)_2$. A slurry of thiotropone (1.05 g, 0.0076 mole) in 200 ml of methanol was added to a solution of nickel acetate tetrahydrate (0.95 g, 0.0038 mole) in 75 ml of water and 50 ml of methanol; a black solid immediately separated. The slurry was stirred for a period of 1 hr and then filtered. The solid was recrystallized twice from a mixture of acetonitrile and chloroform and then dried at 100° (0.01 mm). The deep violet crystals melted at 276–280° with decomposition. *Anal.* Calcd for $Ni(C_7H_5OS)_2$: C, 50.5; H, 3.02; S, 19.2. Found: C, 50.5; H, 3.02; S, 19.3. The bis chelate sublimed with some degradation under vacuum above 200°.

Preparation of $(C_7H_5OS)_2B^+PF_6^-$. Boron tribromide (2.5 g, 0.01 mole) was slowly added from a hypodermic syringe through a serum cap to a flask containing thiotropone (2.7 g, 0.02 mole) in 200 ml of dichloromethane. Triethylamine (4 ml) was added, and the reaction mixture was taken to dryness by vacuum evaporation. The residue was dissolved in chloroform, carbon black was added, and the slurry was refluxed, filtered, and then diluted with benzene. On concentration the yellow filtrate yielded yellow crystals, which were collected and dissolved in a water–methanol mixture. To this solution was added a concentrated solution of ammonium hexafluorophosphate to give a yellow solid. The solid was recrystallized from acetonitrile and then recrystallized again from a mixture of acetonitrile and toluene. The crystalline material was dried at 80° (0.01 mm) for 1 hr, mp 163–165°. *Anal.* Calcd for $(C_7H_5OS)_2B^+PF_6^-$: C, 39.1; H, 2.35; S, 14.9; F, 26.5. Found: C, 38.0, 39.6; H, 2.81, 2.91; S, 14.5; F, 26.2.

Preparation of Salts of $Ge(C_7H_5OS)_3^+$. Thiotropone (4.14 g, 0.030 mole) was slurried in 150 ml of acetonitrile and germanium tetrachloride (2.1 g, 0.01 mole) was added to give a yellow precipitate. The slurry was warmed until mild reflux conditions were achieved, then 25 ml of chloroform was added. The slurry was then filtered while hot to give a yellow solid, mp 290° (dec). *Anal.* Calcd for $(C_7H_5OS)_2GeCl_2$: C, 40.3; H, 2.40; S, 15.4; Ge, 17.4; Cl, 17.0. Found: C, 41.1; H, 2.61; S, 15.6; Ge, 16.6; Cl, 17.0.

Triethylamine (4 ml) was added to a slurry of $(C_7H_5OS)_2GeCl_2$ (4.0 g) and thiotropone (1.4 g) in 250 ml of acetonitrile. To the reaction slurry was added 35 ml of chloroform and then the slurry was warmed to reflux for 3 hr. After cooling to room temperature, 30 ml of dimethyl sulfoxide was added and the slurry was stirred for about 16 hr. The solution was filtered, and the solid was added to a refluxing mixture of 70 ml of methanol, 70 ml of ethanol, and 70 ml of water. The slurry was filtered while hot and to the filtrate was added ammonium hexafluorophosphate to give a yellow-brown solid. *Anal.* Calcd for $(C_7H_5OS)_3Ge^+PF_6^-$: C, 40.1; H, 2.39; S, 15.3; F, 18.1. Found: C, 41.7; H, 2.86; S, 15.1; F, 18.2.

Preparation of $(C_7H_5OS)_3SnCl$. Thiotropone (5.5 g, 0.04 mole) was added to a solution of tin tetrachloride (2.6 g. 0.01 mole) in 350 ml of acetonitrile. A yellow precipitate formed on addition of the thiotropone. The solid was collected by filtration, washed with acetonitrile, and vacuum dried (5.04 g yield). This product, $(C_7H_5OS)_2SnCl_2$, was identical with that obtained from thiotropone and trichlorophenyltin. The crude tin complex was slurried in a mixture of 350 ml of acetonitrile and 50 ml of ethanol. Thiotropone (1.6 g) was added to the slurry followed by 3 ml of triethylamine to yield a deep red-brown slurry. The slurry was stirred for 16 hr and then concentrated to about three-fourths volume. The solid was collected by filtration and vacuum dried, mp 195° (dec). *Anal.* Calcd for $(C_7H_5OS)_3SnCl$: C, 44.5; H, 2.66; S, 17.0; Sn, 20.9; Cl, 6.28. Found: C, 43.0; H, 2.68; S, 17.4; Sn, 20.3; Cl, 5.90.

Preparation of $Sn(C_7H_5OS)_2Cl_2$. A solution of trichlorophenyltin (3.02 g, 0.010 mole) in 50 ml of chloroform was added to a solution of thiotropone (4.14 g, 0.030 mole) in 60 ml of chloroform. A small amount of yellow precipitate appeared. Approximately 160 ml of acetonitrile was added to the reaction slurry which was then warmed to reflux for 1 hr. During this time a considerable amount of solid separated from solution. Then 50 ml of dioxane was added and the solution was warmed to reflux and filtered while hot. The greenish solid was added to 2 l. of a solution containing approximately 60% acetonitrile, 30% methanol, 8% ethanol, and 2% dimethyl sulfoxide. The slurry was heated to reflux and filtered while hot. The filtrate on concentration gave a yellow solid which was dried at 80° (0.01 mm), mp 375–377° dec. *Anal.* Calcd for $Sn(C_7H_5OS)_2Cl_2$: C, 36.3; H, 2.16; S, 13.8; Cl, 15.3. Found: C, 36.5; H, 2.31; S, 14.1; Cl, 14.8.

Preparation of $Pb(C_7H_5OS)_4$. A slurry of lead tetraacetate (1.6 g, 0.0036 mole) in 200 ml of benzene was added to a solution of thiotropone (2.3 g, 0.016 mole) in 150 ml of benzene. An orange precipitate immediately appeared. The reaction slurry was warmed to 60° for a period of 10 min, cooled, and then filtered. The orange solid was dried at 80° (0.01 mm), mp 202.5° dec. *Anal.* Calcd for $Pb(C_7H_5OS)_4$: Pb, 27.4; C, 44.5; H, 2.65; S, 16.9. Found: Pb, 27.8; C, 43.8; H, 2.88; S, 17.1.

Attempted recrystallization of the tetrakis chelate from dimethyl sulfoxide led to degradation to the lead(II) chelate. Dissolution of the tetrakis chelate in dimethyl sulfoxide at about 40° yielded a dark solution. This was filtered into toluene, and petroleum ether was added to give two phases. After several minutes an orange solid separated out at the interface. This was collected and dried at 80° (0.01 mm), mp 255–257°. *Anal.* Calcd for $Pb(C_7H_5OS)_2$: Pb, 43.0; C, 35.0; H, 2.18; S, 13.3. Found: Pb, 43.0; C, 35.2; H, 2.26; S, 14.0.

Preparation of $Th(C_7H_5OS)_4$. Thiotropone (2.6 g, 0.019 mole) was added to a solution of thorium nitrate tetrahydrate (2.76 g, 0.005 mole) in 40 ml of water and 80 ml of methanol. An orange precipitate separated and the slurry was stirred for a period of 1 hr. The solid was collected by filtration and vacuum dried. Attempts to sublime part of the crude product under vacuum were unsuccessful. Decomposition occurred at approximately 290° under vacuum. The remaining crude product was dissolved in warm dimethyl sulfoxide and filtered while hot. The filtrate was diluted with methanol and water to yield an orange solid which was dried at 80° (0.01 mm); discoloration begins about 235°, no evidence of melting below 400°. *Anal.* Calcd for $Th(C_7H_5OS)_4 \cdot OS(CH_3)_2$: Th, 27.0; C, 42.0; H, 3.03; S, 18.7. Found: Th, 27.4; C, 42.6; H, 3.37; S, 18.7.

The dimethyl sulfoxide complex of $Th(C_7H_5OS)_4$ (1.0 g, 0.0012 mole) was added to a solution of lithium hydroxide (0.1 g, 0.04 mole) and thiotropone (0.6 g, 0.004 mole) in 50 ml of water, 75 ml of methanol, and 50 ml of acetonitrile. The reaction slurry was heated to reflux for a period of 1.5 hr. The slurry was filtered while hot and a yellow insoluble material was vacuum dried at 80° (0.01 mm). *Anal.* Calcd for $Th(C_7H_5OS)_4$: Th, 29.7; C, 43.1; H, 2.58. Found: Th, 29.8; C, 43.0; H, 2.52; Li, <10 ppm.

Preparation of $(C_7H_5O_2)_4Sn$. A microdistillation apparatus was set up and the pot was heated to 300°. Tetraphenyltin (1.28 g, 0.003 mole) and tropolone (1.47 g, 0.012 mole) were mixed and added to the preheated pot. A liquid, which was identified as benzene, began to distil off immediately. The heating was continued (~0.5 hr) until the benzene evolution ceased. The black-brown solid remaining in the pot was slurried with a hot 10% water–90% acetonitrile solution and filtered. The yellow solution was evaporated to dryness and the cream-colored solid vacuum dried. *Anal.* Calcd for $Sn(C_7H_5O_2)_4$: Sn, 19.7; C, 55.7; H, 2.65. Found: Sn, 19.4; C, 55.5; H, 3.56.

Preparation of $(CH_3)_2Sn(C_7H_5O_2)Cl$. A solution of $(CH_3)_2SnCl_2$ (4 g, 0.02 mole) in 35 ml of ether was slowly added to tropolone (5 g, 0.04 mole) in 100 ml of ether. A creamy precipitate appeared. Then 100 ml of dimethoxyethane was added. The reaction was warmed to mild reflux for 0.5 hr whereupon most of the solids went into solution. The ether was removed under reduced pressure, and benzene was added. A solid separated and was removed by filtration. Toluene was added to the filtrate and the solution was concentrated under reduced pressure to give a crystalline solid. This solid was recrystallized from a hot toluene–cyclohexane mixture to give colorless crystals, mp 111.5–112.5°. *Anal.* Calcd for $(CH_3)_2Sn(C_7H_5O_2)Cl$: C, 35.4; H, 3.61; Sn, 38.8; Cl, 11.6; mol wt, 305.2. Found: C, 35.8; H, 3.90; Sn, 37.3; Cl, 11.1; mol wt (freezing point, benzene), 320.

Preparation of $(CH_3)_2Si(C_7H_5O_2)_2$. A solution of dimethyldichlorosilane (5 g, 0.04 mole) in 20 ml of toluene was added to a solution of tropolone (10 g, 0.08 mole) in 200 ml of toluene. On standing the solution turned slightly yellow and slowly became opaque. The reaction mixture was warmed to 65° for about 15 min and then cooled to room temperature. About half of the solvent was removed under reduced pressure and then the reaction slurry was filtered. The solid was recrystallized from hot toluene containing about 10% carbon tetrachloride to give yellow crystals, mp 205–216°. *Anal.* Calcd for $(CH_3)_2Si(C_7H_5O_2)_2$: C, 64.0; H, 5.34; Si, 9.33; Cl, 0.00. Found: C, 63.3; H, 5.56; Si, 8.97; Cl, 0.00.

Preparation of $C_6H_5SiCl(C_7H_5O_2)_2$. Phenyltrichlorosilane (4.2 g, 0.02 mole) was added to a solution of tropolone (5.1 g, 0.042 mole) in 100 ml of benzene. Initially a yellow gum separated, which was then followed by a fine white solid. Acetonitrile was added until a nearly clear solution was obtained. Then about 50 ml of toluene was added and the reaction solution was concentrated under reduced pressure to give a crystalline solid, which was recrystallized from an acetonitrile–toluene mixture, mp 280° dec. *Anal.* Calcd for $C_6H_5SiCl(C_7H_5O_2)_2$: C, 62.7; H, 3.92; Cl, 9.27. Found: C, 62.2; H, 4.42; Cl, 8.85.

Hydrolysis of $(C_7H_5OS)_2B^+PF_6^-$. Sodium hydroxide (0.17 g, 0.004 mole) was dissolved in water (1.1775 g) containing 10.60 atom % O^{18} and methanol (2 ml) and $(C_7H_5OS)_2B^+PF_6^-$ (0.110 g, 0.0002 mole) was added to the solution. The mixture was stirred 9 min, then neutralized to pH 6 by litmus with 85% phosphoric acid. Benzene (20 ml) was added and the mixture was stirred 15 min. The benzene layer was extracted and then evaporated to dryness under reduced pressure. The red solid was sublimed at 40° (1 μ) to give 4×10^{-4} mole of C_7H_5SOH. The O^{18} content of the ligand was determined by mass spectral analysis. The spectrometer used was a Consolidated Engineering Corporation Model 103-C and samples of the 2-thiotropone were introduced into the spectrometer from an inlet heated to 150°. The *m/e* 138 is the parent ion and the most abundant in the cracking pattern. The increase in the *m/e* 140 ion represents the increase in O^{18} content. The observed O^{18} content corrected for natural abundance was 0.94 and 1.21 %, giving a per cent enrichment of 8.9 and 11.4%.

Hydrolysis of $(C_8H_8NS)_2B^+I^-$. Sodium hydroxide (3 g) was dissolved in 60 ml of water, and the solution was added to a slurry of $(C_8H_8NS)_2B^+I^-$ (2 g, 0.0069 mole) in 80 ml of methanol. The solution was stirred 3 days at room temperature, neutralized to pH 6 with 6 *N* sulfuric acid, and then filtered. The filtrate was evaporated to dryness under reduced pressure. The gummy residue was dissolved in a minimum of chloroform and chromatographed on a grade I neutral aluminum oxide eluting with benzene–chloroform mixtures and finally with chloroform. The N-methylaminothiotropone and the N-methylaminotropone fractions were recrystallized and identified by infrared and melting point data; these purified fractions amounted to 0.12 g (0.0008 mole) and 0.11 g (0.0008 mole), respectively. There were a number of unidentified fractions; none contained the starting material.