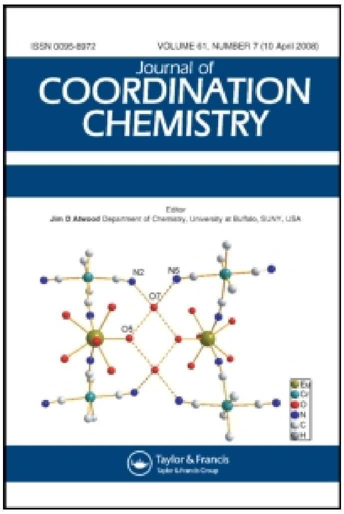

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COMPLEXES OF DITHIOBENZOIC ACIDS. II. PREPARATION OF SEVEN-COORDINATE DITHIOBENZOATO COMPLEXES OF TITANIUM(IV) INCLUDING OXO-BRIDGED EXAMPLES

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COMPLEXES OF DITHIOBENZOIC ACIDS.

II. PREPARATION OF SEVEN-COORDINATE DITHIOBENZOATO COMPLEXES OF TITANIUM(IV) INCLUDING OXO-BRIDGED EXAMPLES [1]

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The first complexes of titanium(IV) with dithiobenzoic acids, specifically $[Ti(dtb)_3Cl]$, $[Ti(mdtb)_3Cl]$ (where dtb = dithiobenzoate ion and mdtb = p-methoxydithiobenzoate ion) have been prepared and then hydrolyzed to produce the respective oxo-bridged species, $[Ti(dtb)_3]_2O$ and $[Ti(mdtb)_3]_2O$, which exhibit characteristic strong Ti–O–Ti absorptions in the IR at 750 and 745 cm^{-1}, respectively. The latter two compounds appear to be the first seven-coordinated oxo-bridged Ti(IV) species involving sulfur-donor ligands. The first tin(IV)-dithiobenzoato complex, $[Sn(dtb)_2Cl_2]$, was also prepared.

INTRODUCTION

During the course of the preparation of a number of complexes of molybdenum(IV) with a series of dithiobenzoic acids (dtbH),[1] attempts were made by us to try to prepare some analogous compounds with both titanium(IV) and tin(IV). It was anticipated that complexes of these respective d^0 and d^{10} electronic systems would prove useful in elaborating our study[1] of the series of d^2 dithiobenzoic acid complexes of Mo(IV). Unfortunately, neither the tin nor the titanium complexes turned out to be stoichiometrically analogous to the $Mo(dtb)_4$ compounds. However, we do report here the preparation and characterization of the first dithiobenzoic acid complexes of titanium in which the metal is seven-coordinate, and two examples of an unusual and apparently quite rare seven-coordinated oxo-bridged Ti(IV).

Earlier work on bidentate sulfur donor complexes of titanium has primarily been confined to dithiocarbamate compounds.[2] Those ligands have yielded not only six- but seven- and eight-coordinated complexes with titanium. However, we have found *no reports* of dithiobenzoic acid complexes.

There are few reports of oxo-bridged dinuclear titanium compounds. Of the fourteen oxo-bridged *compounds* (not all equally well characterized as such) only three appear to involve a seven-coordinated titanium and none contain sulfur-donor ligands. The reported compounds include: $K_2[Ti(O_2)dipic(H_2O)]_2O$,[3] (dipic = dipicolinato), $[TiCl(C_5H_7O_2)_2]_2$-$O{\cdot}CHCl_3$,[4] $[Cp_2TiX]_2O(X = F^-, Cl^-, Br^-, I^-, NO_3^-)$,[5] $[CpTiCl_2]_2O$,[6] $[Ti(CH_2C_6H_5)_3]_2O$,[7] $[TiX(8\text{-quinolinato})_2]_2O\ (X = Cl^-, Br^-)$,[8a] $[Ti(8\text{-quinolinato})_3]_2O$,[8b] $[TiCl_3(8\text{-quinolinol})]_2O$,[8a] and (possibly) $[Ti(tropolonato)_3]_2O$.[9]

EXPERIMENTAL

The dithiobenzoic acids were prepared and purified as previously described.[1]

Tetrachlorobis(propionitrile)titanium(IV) was prepared by a method similar to that of Emeléus and Rao.[10]

Carbon disulfide, dichloromethane, and petroleum ether (b.p. 30–60°C) were refluxed over phosphorous pentoxide for 24 hours before being distilled under nitrogen. Benzene was distilled under nitrogen from sodium-benzophenone.

Since the monochlorotitanium complexes are very susceptible to hydrolysis, especially in solution, the preparation and subsequent handling of these complexes were conducted in a dry box under dry, oxygen-free nitrogen. Samples and solutions for UV, IR and NMR spectroscopy studies were likewise prepared in a dry box.

The preparation and handling of the oxo-bridged species, on the other hand, were conducted outside the dry box. These complexes were found to be relatively air stable in the solid state, with some decomposition occurring only after prolonged exposure (weeks) to the air. Their solutions, however, did decompose within one or two days after being exposed to the air.

Solutions of the tin complex did not seem to be susceptible to hydrolysis, therefore, solutions and samples for spectroscopy studies were prepared outside the dry box.

IR measurements were made on a Perkin-Elmer 621 on Nujol mulls (4000–700 cm^{-1}, NaCl; 700–200 cm^{-1}, CsI). Ultraviolet and visible spectra were recorded on a Cary Model 14 in dichloromethane solutions (10^{-5}-10^{-6} M). Proton magnetic resonance spectra were recorded in $CDCl_3$ at 32°C on a Varian A-60 spectrometer. Melting and/or decomposition points were obtained from a thermogram recorded on a Dupont Model 900 Thermal Analyzer. These melting and/or decomposition points were corrected for the nonlinearity of the thermocouples.

Ti, S, C and H analysis were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Chlorotris(dithiobenzoato)titanium(IV)

A solution of 3.00 g (1.94×10^{-2} mol) of dithiobenzoic acid in 20 ml of benzene was added to a solution of 1.25 g (4.17×10^{-3} mol) of tetrachlorobis(propionitrile)titanium(IV) in 10 ml of benzene. The resulting reddish-brown solution was heated to boiling for two to three minutes and was then set aside to cool to room temperature. After four hours, reddish-brown crystals were collected by filtration and were recrystallized from CS_2 to yield brick-red needle-like crystals. These were dried under vacuum at room temperature for six hours prior to analysis. m.p. 204°C (decomp.) yield 1.62 g (71.6%). *Anal.* Calcd. for $Ti(C_7H_5S_2)_3Cl$: C, 46.44; H, 2.79. Found: C, 46.30; H, 2.93.

Chlorotris(p-methoxydithiobenzoato)titanium(IV)

A solution of 2.50 g (1.36×10^{-2} mol) of *p*-methoxydithiobenzoic acid in 20 ml of dichloromethane was added to a solution of 1.10 g (3.68×10^{-3} mol) of tetrachlorobis(propionitrile)titanium(IV) in 15 ml of dichloromethane. The dark reddish-brown solution was then heated to boiling while being vigorously stirred. After two or three minutes, a maroon precipitate formed. The resulting slurry was heated for an additional two minutes before being allowed to cool to room temperature. The precipitate was then collected by filtration and was recrystallized from dichloromethane. The dark maroon prisms, which have a tendency to fall apart very easily, were dried under vacuum at room temperature for six hours. m.p. 261°C (decomp.) yield 1.95 g (83.7%). *Anal.* Calcd. for $Ti(C_8H_7S_2O)_3Cl$: C, 45.52; H, 3.35. Found: C, 45.01; H, 3.53.

μ-oxo-hexakis(dithiobenzoato)dititanium(IV)

1.0 g (1.84×10^{-3} mol) of chlorotris(dithiobenzoato)titanium(IV) was added to 100 ml of CS_2. The CS_2 was heated carefully until all of the titanium complex had dissolved (more CS_2 may be added if necessary). The beaker was then removed from the heat and left in the fume hood until all of the CS_2 had evaporated. Thirty milliliters of hot benzene was then added to the residue (which consisted of red crystals, TiO_2, and a black decomposition product), and the mixture was stirred vigorously for a few minutes before being filtered. This procedure was repeated until no black material remained behind on the filter. The red product was then separated from TiO_2 by recrystallization from CS_2. The bright red crystals were vacuum dried for three hours at room temperature. m.p. 269°C (decomp.), yield ca. 10% (variable). *Anal.* Calcd. for $[(C_7H_5S_2)_3Ti]_2O$: C, 48.91; H, 2.94; Ti, 9.29; S, 37.31. Found: C, 48.71; H, 3.02; Ti, 9.04; S, 37.51.

μ-oxo-hexakis(p-methoxydithiobenzoato)-dititanium(IV)

A solution of 1.0 g (1.58×10^{-3} mol) of chlorotris-(*p*-methoxydithiobenzoato)titanium(IV) in 100 ml of dichloromethane was added to 75 ml of water in a 250 ml separatory funnel. The funnel and its contents were then shaken vigorously for about two minutes. During this period, the color of the dichloromethane solution changed from reddish-brown to a deep greenish-black. After the two layers had separated, the lower layer was filtered to collect the suspended brownish-red precipitate. The precipitate was washed first with 20 ml of acetone and then with 30 ml portions of dichloromethane until all of the brownish-red color had been washed away, leaving a red-orange powder remaining on the filter. This powder was first dried under vacuum at room temperature for four hours, and was then recrystallized from dichloromethane in the dry box. Small bright-red crystals were collected and were dried under vacuum at room temperature for twelve hours. m.p. ca. 265°C (decomp.), yield 0.575 g (59.5%). Calcd. for $[(C_8H_7OS_2)_3Ti]_2O$: C, 47.59; H, 3.50;

O, 9.24; Ti, 7.91; S, 31.76. Found: C, 47.76; H, 3.81; O, 9.02; Ti, 8.09; S, 31.32.

Dichlorobis(dithiobenzoato)tin(IV)

The complex was prepared by a procedure similar to that used in the preparation of the chlorotris(dithiobenzoato)titanium(IV) complex. A dark yellow solution was obtained from the reaction of 1.0 g (2.51×10^{-3} mol) of tetrachlorobis(butyronitrile)tin(IV)[11] with 1.56 g (1.01×10^{-2} mol) of dithiobenzoic acid. After the solution had cooled to room temperature, petroleum ether was added dropwise until the yellow precipitate (which forms during the addition of pet. ether) just redissolves. The flask was again stoppered and was allowed to sit undisturbed for four hours. Bright yellow needles were then collected by filtration. After being washed with thirty milliliters of pet. ether, the crystals were dried under vacuum at room temperature for eight hours. m.p. 202°C, yield 0.86 g (68.9%). Calcd. for $Sn(C_7H_5S_2)_2Cl_2$: C, 33.89; H, 2.04. Found: C, 33.90; H, 2.14.

RESULTS AND DISCUSSION

Efforts to prepare tetrakisdithiobenzoato complexes of either Sn(IV) or Ti(IV), analogous to $Mo(dtb)_4$, were not successful, In the case of tin, the product of the reaction between either $SnCl_4$ or $SnCl_4 \cdot 2CH_3CH_2CH_2CN$ and dtbH in benzene was $[Sn(dtb)_2Cl_2]$ (see Experimental section), and efforts to force an additional dithio ligand to replace chloride failed. Although we did not thoroughly characterize the tin compound, its chemical analysis, melting point and IR spectrum leave no doubt that this new tin complex has been prepared.

With titanium, the product of the reaction of dtbH with either $TiCl_4$ or $TiCl_4 \cdot 2CH_3CH_2CN$ turned out to be $[Ti(dtb)_3Cl]$. Analogously, the reaction using mdtbH yielded $[Ti(mdtb)_3Cl]$. Efforts to force an additional dithio ligand to replace the chloride, such as (a) adding excess ligand, or (b) heating the reaction mixture for longer time periods,[12] or (c) treating the chloro complex with the sodium salt of the ligand anion, all failed to yield the tetrakis complex.

It was found that if the chloro complex were exposed to humid air it would slowly react to produce an oxo compound and release HCl. This reaction was more rapid in wet solvents. After exposure of solutions of the chloro complexes to humid air, we were able to isolate pure compounds which proved to be devoid of chlorine and to contain oxo-bridged species which we formulate as $[(dtb)_3Ti\text{-}O\text{-}Ti(dtb)_3]$ and $[(mdtb)_3Ti\text{-}O\text{-}Ti(mdtb)_3]$. The formulation is based upon chemical analysis and upon infrared spectral interpretation. Thus the titanium seems to be seven-coordinated in these oxo-bridged compounds.

In Table I are listed some of the pertinent IR

TABLE I
Infrared frequencies (cm^{-1}) and assignments of some pertinent absorptions[a]

	$\bar{\nu}$(phenyl-C)	$\bar{\nu}_{as}$(CSS)	$\bar{\nu}_s$(CSS)	$\bar{\nu}$(Ti–O–Ti)	$\bar{\nu}$(Ti–Cl)	$\bar{\nu}$(TiSS)
$Ti(dtb)_3Cl$	1255(vs) (1248) (1235)	995(vs) (987)	(945) 940(vs) (938)	–	400(ms)	355(ms)
$Ti(mdtb)_3Cl$	1260(vs)	1025(ms) 1000(m)	940(s)	–	382(m)	342(m)
$[Ti(dtb)_3]_2O$	1255(vs) 1243(s) 1248(ms)	1005(s) (995) (900)	942(ms) 935(ms) 928(m)	750(vs)		351(m)
$[Ti(mdtb)_3]_2O$	1260(vs)	1029(s) 1010(m)	939(s)	745(vs)		342(m)
$[Sn(dtb)_2Cl_2]$	1247(vs) 1223(m)	989(s)	922	–	(Sn–S and Sn–Cl bands overlap producing broad band)	

[a] Abbreviations: vs = very strong; s = strong; ms = medium strong; m = medium; dtb = dithiobenzoate; mdtb = *p*-methoxydithiobenzoate. Values in parenthesis are shoulders.

bands for the new titanium compounds. Ligand vibrations have been assigned in agreement with earlier work on the ligands and compounds with other metals.[13] We have additionally assigned Ti–Cl bands for the two chloro complexes and Ti–O–Ti bands for the two oxo-bridged species. It is the appearance of the very strong and somewhat broadened absorption band in the otherwise clear region around 750 cm^{-1} which clearly signals the presence of the oxo-bridging. For only eight of the thirteen previously reported oxo-bridged compounds (*vide supra*) were there IR bands reported, and for these the Ti–O–Ti vibrations show up as strong bands in the region 720 ± 10 cm^{-1}, except for the complex $[cpTiCl_2]_2O$, where the vibration is reported to be at 770 cm^{-1}.[14] In our two new oxo-bridged complexes, the first to contain Ti–S bonds, the bridging vibrations appear at 750 and 745 cm^{-1}, for $[Ti(dtb)_3]_2O$ and $[Ti(mdtb)_3]_2O$, respectively.

In addition to the characterizing data reported in the experimental section (elemental analyses, melting or decomposition points and crystal colors), we have obtained nmr data for the ligands and the chloro complexes in $CDCl_3$ (Table II). There are no surprises in the data and the chemical shifts are easily rationalized. The oxo-bridged species were not soluble enough in inert solvents to yield good data and they unfortunately decomposed in stronger solvents which dissolved them.

TABLE II
Chemical shifts (ppm from TMS) of the tin and titanium complexes and of the parent ligands in $CDCl_3$

	ortho[a]	meta, para[a]	CH_3
$[Ti(dtb)_3Cl]$	8.25	7.53	–
dtbH	8.03	7.33	–
$[Ti(mdtb)_3Cl]$	8.24	6.95	3.87
mdtbH	8.11	6.87	3.86
$[Sn(dtb)_2Cl_2]$	8.26	7.57	–

[a] Centers of multiplets.

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