

## Chemistry of Phenoxo Complexes. III. Preparation and Characterization of Some Bis(chelato)bis(phenoxo)titanium(IV) Complexes

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A large number of bis(chelato)bis(phenoxo)titanium(IV) complexes have been prepared by metathesis between a phenol and bis(chelato)bis(alkoxo)titanium(IV), where chelato = acetylacetonato, 8-oxoquinolinato, or 2-methyl-8-oxoquinolinato and alkoxo = *n*-butoxo or isopropoxo. In spite of the very wide range of electronic and steric properties of the phenoxo substituents, only complexes of *cis* stereochemistry were observed, and there seems little likelihood that complexes of this type can be induced to adopt a *trans* configuration. The dipole moments (*D*) and the relative chemical shifts ( $\Delta\delta$ ) of the methine protons for a number of acac complexes were measured. No systematic trends in the variation of  $\Delta\delta$  either with *D* or with the  $\sigma^-$  parameters of the phenoxy ligands were observed.

### Introduction

Attempts to synthesize high molecular weight polymers by cocondensation of a bifunctional phenol and a diacidobis(chelato)titanium(IV) complex yield only low molecular weight, apparently cyclic oligomers.<sup>1</sup> Since virtually all known titanium complexes of the latter kind have *cis* structures,<sup>2</sup> this is probably the reason that ring closure is strongly favored. A successful resolution of the problem of polymer synthesis seemed therefore dependent on the question of whether, or not, appropriate bis(chelato)titanium(IV) complexes could be induced to adopt a *trans* configuration.

In addition to its direct relevance to the synthesis of polymers, the phenoxo ligand lends itself to a systematic investigation of steric and electronic effects on the structure of complexes, arising from substitution in the benzene rings. At the present time it is not clear whether the observed existence of the *trans* isomers of diiodobis(acetylacetonato)titanium(IV)<sup>3</sup> and tetrafluorobis(2,6-dimethylpyridine *N*-oxide)titanium(IV)<sup>4</sup> is due to steric, or electronic effects, or a combination of both.

The present paper describes the synthesis, structural characterization, and some physical properties of a large number of bis(chelato)bis(substituted phenoxo)titanium(IV) complexes.

### Experimental Section

**Reagents and Solvents.** 8-Hydroxyquinoline and 8-hydroxyquinoline, from Fisher Chemical Co., were recrystallized twice, the former from ethanol and the latter from diethyl ether. Tetra-*n*-butyl titanate and tetraisopropyl titanate from Fisher Chemical were vacuum distilled immediately prior to use. Acetylacetone from Fisher was distilled at 40 Torr immediately before use, only the middle half being retained (bp 94–95°;  $n_D^{25}$  1.4480). All of the phenols used in this work were purchased from Aldrich Chemical Co. as reagent grade materials and were purified by either sublimation or recrystallization from benzene.

Reagent grade benzene, toluene, and *n*-hexane were refluxed over calcium hydride for 24 hr, distilled, and stored over molecular sieves.

**Synthesis of (chelato)<sub>2</sub>(OR)<sub>2</sub>Ti.** The synthetic procedure was essentially the same for four complexes: chelato = 8-hydroxyquinolinato (oxin) or 8-hydroxyquinolinate (quin) and R = *n*-butyl or isopropyl. Whereas the *n*-butyl reactions were run in pure benzene, the isopropyl complexes were formed in a benzene–hexane (3:1) mixture. A typical synthesis was as follows.

8-Hydroxyquinoline (0.20 mol) was dissolved in benzene (100 ml) in carefully dried glassware. A solution of *n*-butyl titanate (0.1 mol) in benzene (50 ml) was added slowly (5 ml/min) with vigorous stirring and exclusion of moisture. After stirring for 24 hr the precipitate of bright canary yellow crystals was filtered, washed with cold benzene, and recrystallized twice from toluene and dried *in vacuo*. The product was stored *in vacuo* and in the absence of light. Occasionally, in this synthesis, crystals are reluctant to form and it is necessary to induce crystallization by addition of a few milliliters of dry hexane.

Some properties of the (chelato)<sub>2</sub>(OR)<sub>2</sub>Ti complexes are sum-

marized in Table I. Yields were normally in the range of 80–90% based on titanate ester.

**Synthesis of (chelato)<sub>2</sub>(OAr)<sub>2</sub>Ti.** The synthetic procedure was essentially the same for all complexes: chelato = 8-hydroxyquinolinato, 8-hydroxyquinolinate, or acetylacetonate (acac), and OAr is phenoxide, substituted or unsubstituted.

(acac)<sub>2</sub>(O-*i*-Pr)<sub>2</sub>Ti was prepared according to the method of Yamamoto and Kambara.<sup>5</sup>

A solution of a phenol (0.10 mol) in benzene (250 ml) was added slowly, with constant stirring to a solution of (chelato)<sub>2</sub>(OR)<sub>2</sub>Ti (0.05 mol) in benzene. The benzene–alcohol azeotrope was slowly distilled off under reduced pressure (ca. 400 Torr) over a period of 24 hr to give a final solution volume of ca. 50 ml. Crystals of product usually appeared during reaction or on subsequent cooling. In cases where crystallization did not occur, precipitation was effected by slow addition of hexane to the stirred solution. Products were collected by filtration, recrystallized several times from benzene–hexane mixtures, and dried and stored *in vacuo* in the absence of light.

Some properties of (chelato)<sub>2</sub>(OAr)<sub>2</sub>Ti complexes are summarized in Table I.

**NMR Spectra.** The proton NMR spectra of all new compounds were recorded using a Varian A-60 spectrometer with a probe temperature of 37°. Chemical shifts were measured relative to an internal standard of tetramethylsilane. The magnetic field sweep width was calibrated with a 2% (by volume) solution of benzene in CCl<sub>4</sub>. All chemical shift data reported in Figure 1 were measured in CHCl<sub>3</sub>.

Solvent effects on the chemical shift were negligible in CHCl<sub>3</sub>, CH<sub>2</sub>Cl<sub>2</sub>, CDCl<sub>3</sub>, and CCl<sub>4</sub>. However, slight downfield effects were observed in C<sub>5</sub>H<sub>5</sub>N and C<sub>6</sub>H<sub>5</sub>NO<sub>2</sub>, while large upfield shifts were observed in C<sub>6</sub>H<sub>6</sub>.

Concentration effects on chemical shifts were found to be negligible at the concentrations used in the NMR work. At very high concentrations, slight upfield shifts were observed.

$\Delta\delta$  is the difference between the chemical shifts measured for the M(acac)<sub>2</sub>X<sub>2</sub> compounds and average values for a series of neutral nonpolar M(acac)<sub>n</sub> complexes. The latter reference values were the same as those previously used by Fay and Serpone, namely, –5.47 ppm for the methine proton and –2.02 ppm for the methyl protons.<sup>6</sup>

**Uv-Visible Spectra.** Uv-visible spectra were recorded on a Unicam SP800 spectrometer at 25°. Extinction coefficients were determined from measurements at six concentrations and all compounds obeyed the Beer–Lambert law.

**Conductivity Measurements.** The equivalent conductance of a representative series of complexes was determined using a standard conductivity cell in a Wheatstone conductivity bridge. The cell was calibrated with a 0.02 M aqueous KCl solution; all other measurements were conducted on nitrobenzene solutions at 25°.

**Dipole Moment Measurements.** The dipole moments reported in this work were calculated from measured dielectric constants and refractive indices, using the procedure of Guggenheim and Smith.<sup>7</sup>

Dielectric constants were measured with a Wissenschaftlich-Technische-Werkstätten Model DMOI dipole meter and a modified measuring cell, Type DFLI.<sup>8</sup> The instrument was calibrated at 25° using benzene,<sup>9</sup> cyclohexane,<sup>10</sup> and carbon tetrachloride.<sup>11</sup>

Refractive indices were measured with a Phoenix Model BP-2000V differential refractometer. Both the refractometer and the dipole meter cell were maintained at a constant and equal temperature to within

Table I. Some Properties of (chelato)<sub>2</sub>X<sub>2</sub>Ti Complexes

Compd no.	Chelate	X	Analysis			Mp, °C	Mol wt	
			Element	% calcd	% found		Calcd	Found
1	acac	Phenoxy	C	61.1	61.2	127-128	432	450 <sup>a</sup>
			H	5.58	5.73			
			Ti	11.1	11.1			
2	acac	4-Methylphenoxy	C	62.6	62.3	157-158	460	458 <sup>a</sup>
			H	6.13	6.33			
			Ti	10.4	10.8			
3	acac	2-Methylphenoxy				84-85		
4	acac	2,6-Dimethylphenoxy	C	63.9	63.0	128-130	488	475 <sup>b</sup>
			H	6.61	6.01			
			Ti	9.83	9.12			
5	acac	2-Methyl-6- <i>tert</i> -butylphenoxy	C	67.1	67.3	207-208		
			H	7.74	7.92			
			Ti	8.39	8.56			
6	acac	2,6-Diisopropylphenoxy	C	68.0	68.1	128-139	600	595 <sup>a</sup>
			H	8.06	8.10			
			Ti	8.00	8.22			
7	acac	2,6-Dichlorophenoxy	C	46.3	45.8	570	550 <sup>b</sup>	
			H	3.50	3.91			
			Cl	24.6	23.1			
			Ti	8.50	8.10			
8	acac	2,4,6-Trichlorophenoxy				110-112	639	630 <sup>b</sup>
9	acac	2,3,5,6-Tetrachlorophenoxy				155-156		
10	acac	Pentachlorophenoxy				215-216	777	660 <sup>b</sup>
11	acac	2-Iodophenoxy				145-146		
11a <sup>c</sup>	acac	2-Chlorophenoxy						
12	acac	2,4,6-Triiodophenoxy	C	22.2	22.8	237-238	1188	1150 <sup>a</sup>
			H	1.60	2.05			
			Ti	4.04	4.35			
			I	64.1	63.1			
13	acac	2,4,6-Tribromophenoxy	C	29.1	28.7	199-200		
			Br	2.00	1.52			
			Ti	5.30	5.11			
			Br	53.0	51.0			
14	acac	2,4,6-Trinitrophenoxy				168-169		
15	acac	2,3,4,5,6-Pentafluorophenoxy	C	43.2	43.0	153-154	612	605 <sup>a</sup>
			H	2.29	2.48			
			Ti	7.84	7.74			
			F	31.0	31.4			
16	acac	2-Nitrophenoxy	C	50.5	50.0	139-141		
			H	4.22	4.57			
			N	5.36	4.90			
			Ti	9.20	10.7			
17	acac	2-Isopropylphenoxy				106-107		
18	acac	2-Methyl-6-methoxyphenoxy				110-111		
19	acac	3-Aminophenoxy				140-141		
20	acac	3-Dimethylaminophenoxy						
21 <sup>c</sup>	acac	2,6-Dimethoxyphenoxy						
22	acac	4-Acetoxyphenoxy	C	60.5	60.9	516	501 <sup>a</sup>	
			H	5.43	4.92			
			Ti	9.30	9.85			
23	acac	4-Chlorophenoxy				124-125		
24 <sup>c</sup>	acac	4-Carbomethoxyphenoxy						
25 <sup>c</sup>	acac	4-Methoxyphenoxy						
26 <sup>c</sup>	acac	4-Aminophenoxy						
27 <sup>c</sup>	acac	4-Tritylphenoxy						
28 <sup>c</sup>	acac	4-Nitrophenoxy						
29	ox	<i>n</i> -Butoxy	C	64.7	65.0	155-156	482	480 <sup>a</sup>
			H	6.27	6.53			
			N	5.85	6.04			
			Ti	10.0	10.0			
30	ox	Isopropoxy				182-183	454	460 <sup>a</sup>
31	ox	Phenoxy				200-205		
32	ox	2-Isopropylphenoxy				233-234		
33	ox	4-Methylphenoxy	C	69.7	69.6	172-173	550	565 <sup>a</sup>
			H	4.76	5.23			
			N	5.09	4.49			
			Ti	8.72	8.04			
34	ox	2-Methylphenoxy				179-180	550	560 <sup>a</sup>
35	ox	2,6-Diisopropylphenoxy	C	73.0	73.2	259-260	691	700 <sup>a</sup>
			H	6.72	6.99			
			N	4.06	4.18			
			Ti	6.95	7.14			
36	ox	2,6-Dimethylphenoxy	C	70.5	70.8	208-210	578	565 <sup>a</sup>
			H	5.24	5.52			
			N	4.84	4.78			
			Ti	8.30	8.00			

Table I (Continued)

Compd no.	Chelate	X	Analysis			Mp, °C	Mol wt	
			Element	% calcd	% found		Calcd	Found
37	ox	2-Methyl-6- <i>tert</i> -butylphenoxy	C	72.5	71.3	260-261		
			H	6.39	6.64			
			N	4.23	4.29			
			Ti	7.25	7.14			
38	quin	<i>n</i> -Butoxy	C	64.7	64.8	145-147	482	490 <sup>a</sup>
			H	6.26	6.26			
			N	5.81	6.15			
			Ti	9.95	9.67			
39	quin	Isopropoxy	C	71.0	71.6	155-156		
			H	5.61	6.40			
			N	4.62	4.69			
			Ti	8.00	8.40			
40	quin	2-Isopropylphenoxy	C	73.5	73.01	258-259	718	701 <sup>a</sup>
			H	7.02	7.00			
			N	3.90	4.13			
			Ti	6.68	6.83			

<sup>a</sup> Solvent used for molecular weight measurements was benzene.  
<sup>c</sup> Prepared but not characterized.

<sup>b</sup> Solvent used for molecular weight measurements was chloroform.

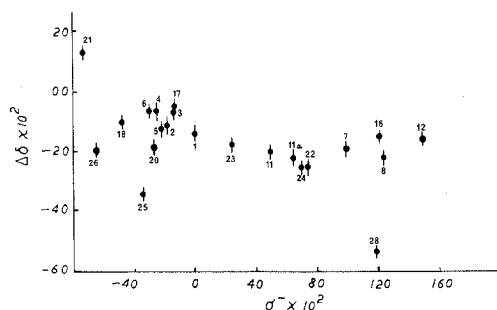


Figure 1. Correlation between the relative chemical shifts of the methine protons of acac and the  $\sigma^-$  parameters for some  $(\text{acac})_2\text{Ti}^{\text{IV}}$  complexes.

$\pm 0.1^\circ$ . At least five measurements were made on each complex in solution in benzene with a range of solute weight fraction from 0.007 to 0.10.

A check of the precision of the method, using nitrobenzene, gave values of 4.006 and 4.011 D for two independent measurements. These values may be compared to literature values of 4.01,<sup>10</sup> 3.967,<sup>7</sup> 4.220,<sup>12</sup> 4.14,<sup>13</sup> and 3.85-4.11.<sup>14</sup> Errors in dipole moment data, when estimated at the 95% confidence level, did not exceed 0.2 D.

## Results

**Synthesis of  $(\text{chelato})_2(\text{OAr})_2\text{Ti}$  Complexes.** The synthetic method described above proved to be quite general for the synthesis of a large range of bis(chelato)bis(phenoxo)titanium(IV) complexes. The proton NMR spectra, chemical analyses, molecular weights, and sharp melting points supported the fact that all of the products obtained were monomeric six-coordinate complexes of the expected composition. Assay of the distillate alcohol by NMR indicated a virtually quantitative stoichiometry for the reaction as indicated in (1).  
 $(\text{chelato})_2(\text{OR})_2\text{Ti} + 2\text{ArOH} \rightarrow (\text{chelato})_2(\text{OAr})_2\text{Ti} + 2\text{ROH}$  (1)

**NMR Spectra.** Many of the acac complexes prepared in the present work showed a pair of nonequivalent acac methyl resonances due to a *cis* configuration of the bis(chelato) unit.<sup>2,15,16</sup> Some of the compounds, although undoubtedly of *cis* geometry, showed only a single acac methyl resonance, presumably because the coalescence temperature was below the lowest temperature available in the cavity (ca.  $-80^\circ$ ).<sup>16</sup>

The spectra of the quinaldinate complexes showed only a sharp singlet for the chelate methyl resonance in the temperature range  $-80$  to  $+120^\circ$  in a number of solvents. The complexes 32, 35, 40, and 41 all gave spectra in which the isopropyl methyl resonances appeared as two doublets of equal intensity.<sup>16</sup> Since the most obvious explanation of the latter

Table II. Dipole Moments of Some  $(\text{chelato})_2\text{Ti}$  Complexes in Benzene

Compd	Dipole moment		Compd	Dipole moment	
	( $\pm 0.2$ ), D	Temp, °C		( $\pm 0.2$ ), D	Temp, °C
$(\text{acac})_2$ - $(\text{isopro-}$ $\text{poxy})_2\text{Ti}$	3.15	25	14	8.77	25
			15	7.68	25
			16	5.51	25
$(\text{acac})_2$ - $(\text{isopro-}$ $\text{poxy})_2\text{Ti}$	3.17	60	17	4.59	25
			29	4.85	25
			30	4.58	25
1	4.65	25	30	4.53	50
1	4.65	60	30	4.44	70
3	4.45	25	32	6.84	25
4	4.78	25	33	6.49	25
5	5.33	25	34	6.48	25
5	5.34	60	35	6.95	25
6	5.16	25	35	6.97	60
6	5.31	60	36	6.47	25
23	4.4	25	36	6.36	60
7	6.26	25	39	3.86	25
8	6.17	25	40	6.45	25
9	7.16	25	41	5.97	25
10	7.89	25			
11	5.13	25			
12	6.56	25			
13	6.39	25			

observation is that the splitting arises from diastereotopic inequivalence, it is most likely that the four complexes have a *cis* structure in solution.

In the course of measuring the proton nmr spectra discussed above, a large amount of chemical shift data was collected. Some of these data are summarized in Figure 1.

**Dipole Moments.** The dipole moments of a selection of phenoxotitanium(IV) and alkoxotitanium(IV) complexes are listed in Table II. In all cases a substantial permanent dipole was observed.

Temperature dependence of polarization was measured for several complexes. These results are also given in Table II. The invariability of dipole moment with temperature in the range  $27$ - $70^\circ$  is indicative of a negligible contribution from atomic polarization in these complexes. Nelson arrived at the same conclusion for a series of bis(acetylacetonato)tin(IV) complexes.<sup>17</sup>

The dipole moments listed in Table II suggest that all of the complexes studied exist primarily as the *cis* isomers in solution. Although severely distorted *trans* isomers may possess a finite permanent dipole, the magnitudes of the dipoles reported here, along with the other physical evidence, leave little

Table III. Uv-Visible Spectral Parameters for Some (chelato)<sub>2</sub>Ti Complexes

Compd	$\lambda_1$ , nm	$\lambda_2$ , nm	$10^3 \epsilon(\lambda_2)$	Solvent
(acac) <sub>2</sub> (isopropoxy) <sub>2</sub> Ti	275	327	8.65	CHCl <sub>3</sub>
2	342	390	14.4	CHCl <sub>3</sub>
6	341	380	13.2	CHCl <sub>3</sub>
6	334	376	13.4	C <sub>6</sub> H <sub>14</sub>
8	295	325	8.4	CHCl <sub>3</sub>
30	304	383	6.5	CHCl <sub>3</sub>
31	305	384	7.1	CHCl <sub>3</sub>
34	316	384	7.1	CHCl <sub>3</sub>
34	325	384	7.1	C <sub>6</sub> H <sub>14</sub>
39	317	370	6.7	CHCl <sub>3</sub>
41	317	370	5.8	CHCl <sub>3</sub>
41	320	372	16.4	C <sub>6</sub> H <sub>14</sub>

doubt that we are dealing with *cis* isomers.

**Conductivity Measurements.** Construction of molecular models indicated that most of the complexes prepared in the present work suffer severe steric encumbrance. It was not unlikely therefore that some, particularly those with weakly basic phenoxo ligands, might undergo ionization to relieve steric strain. However, conductivity measurements showed all of the complexes to be nonelectrolytes. The highest observed molar conductance was exhibited by compound **13** in nitrobenzene (0.14 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> at 25°).

**Uv-Visible Spectra.** All of the compounds examined exhibited two broad absorption bands in the range 35–25 kK. The higher energy band ( $\lambda_1$ ) is probably due to internal ligand transitions, and a similar band is observed in the analogous bis(chelato)dialkyl- and bis(chelato)diaryltin(IV) complexes.<sup>18–21</sup> The lower energy band ( $\lambda_2$ ), not observed in analogous tin(IV) complexes, is probably due to ligand-to-metal charge-transfer transitions and is responsible for the bright yellow or orange colors of these complexes.

Some values for the absorption maxima and extinction coefficients for a selection of complexes are listed in Table III.

## Discussion

**Stereochemistry of the Complexes.** The weight of evidence in the present and previous studies leads to the conclusion that all bis(chelato)bis(phenoxo)- or bis(chelato)bis(alkoxo)titanium(IV) complexes prepared to date have a *cis* geometry in solution. Crystal structures on several of these complexes indicate that the same is true in the solid state.<sup>22</sup> In view of the very wide range of steric and electronic effects represented within the group of complexes prepared for the present study, it seems most unlikely that bis(phenoxo)titanium(IV) chelates can be induced to adopt a *trans* geometry. That the steric limit was reached with the 2-methyl-6-*tert*-butylphenoxo complexes reported in Table I was indicated by the complete failure of 2,6-di-*tert*-butylphenol to undergo reaction with any of the bis(chelato)bis(alkoxo)titanium(IV) reactants.

**Dipole Moments.** A quantitative evaluation of dipole moment data for the compounds under discussion is precluded by lack of detailed knowledge of the molecular structures. What information is available from crystallographic structure determinations on phenoxo complexes<sup>22–24</sup> indicates that Ar–O–M (M = metal) angles and the spatial orientation of the phenoxo ligands are very variable. The latter parameters can have a major effect on the magnitudes of dipole moments. Despite the above limitations it is quite evident that certain qualitative trends are identifiable from the data in Table III.

The systematic increase in dipole moment for the acac complexes on passing from the unsubstituted phenoxo derivative to derivatives where the phenoxo ligand is increasingly loaded with electron-withdrawing substituents clearly indicates that the negative end of the dipole is located in the hemisphere occupied by the phenoxo ligands. That this should be so for halo- or nitro-substituted complexes is perhaps not surprising, but the localization of negative charge toward alkoxo, un-

substituted phenoxo, or alkyl-substituted phenoxo ligands is less expected. Such an effect is probably due to the localization of the formal negative charge of the monodentate ligands in the O<sub>P</sub>–Ti–O<sub>P</sub> plane (O<sub>P</sub> = oxygen of phenoxo ligand) while the formal charge of the acac ligands has a substantial component perpendicular to that plane. Even if the delocalization of charge in the acac ligand were symmetrical, the latter effect would diminish the ability of the O<sub>acac</sub> trans to O<sub>P</sub> to cancel the bond dipole of Ti–O<sub>P</sub>. However, the detailed molecular structure of the complex **6**<sup>22</sup> reveals that the axial O<sub>acac</sub> bond lengths are slightly shorter than the equatorial O<sub>acac</sub> bond lengths (ca. 0.05 Å), suggesting a concentration of the ligand charge at the axial positions and further diminishing the cancellation of the Ti–O<sub>P</sub> bond moments. The charge delocalization effect will be slightly offset by the observed<sup>22</sup> displacement of the axial O<sub>acac</sub> atoms away from the plane of the hemisphere containing the phenoxo ligands.

The molecular structures of the oxinate complex **35** and the quinaldinate complex **41** both reveal a *cis* arrangement of the nitrogen atoms and of the O<sub>P</sub> atoms.<sup>22</sup> The axial Ti–O bond lengths are shorter than in the analogous acac complex, and the considerably shortened Ti–O<sub>P</sub> and long Ti–N bonds indicate that the nitrogen atoms are carrying relatively little of the burden of neutralizing the metal charge. Again, concentration of the chelate charge at the axial oxygen atoms would explain the rather large dipole moments observed for these complexes.

**NMR Chemical Shifts.** At the present time, both through-bond and through-space interactions are believed to contribute to the downfield shifts of the methyl and ring proton resonances in diacidobis(acetylacetonato) complexes, relative to the neutral nonpolar complexes of the type M(acac)<sub>3</sub>. Smith and Wilkins<sup>25</sup> argued that, in *cis* complexes, the molecular dipole field gradient should cause a substantial downfield shift of the acac protons, whereas negligible shifts would be observed for nonpolar *trans* complexes. Serpone and Fay<sup>13</sup> have studied the relative influence of various parameters on the chemical shifts of dihalobis(acetylacetonato) complexes and have shown that the electric field model may account for the sign of  $\Delta\delta$  and also for the fact that  $\Delta\delta$  is larger for the methine than for the methyl protons of the acac ligand. Although the electric field model accounted for the total methine proton shift in tin(IV) complexes, the calculated values for transition complexes of group IV were only about half of the observed values. Better agreement could not be expected on the basis of the crudeness of the model and on the limited range of chemical shifts and dipole moments for isostructural compounds.

In the course of the present work, the nmr spectra of a large number of bis(phenoxo)bis(acetylacetonato)titanium(IV) complexes were measured. The fact that the complexes exhibited a relatively wide range of dipole moments (4.4–7.9 D) and the phenoxo ligands a wide range of electronic properties seemed to offer a possibility of further testing the relative importance of molecular polarity and bonding effects on the proton chemical shifts of the acac ligand.

A plot of the relative chemical shift for the acac proton *vs.* the  $\sigma^-$  parameter<sup>26</sup> for the parent phenol for **22** complexes is shown in Figure 1, and there is no evident relationship between the two parameters.<sup>27</sup>

Figure 2 shows a plot of  $\Delta\delta$  *vs.* dipole moment for a number of complexes. Again, the correlation between the two parameters is too poor for any conclusion to be drawn. This correlation is not expected to be linear, or particularly good, since the dominant term for field-induced chemical shift is the component of the field along the C–H bond.<sup>28,29</sup> It is unlikely that the molecular moments measured in the present study all have the same spatial relationship to the acac C–H bonds.

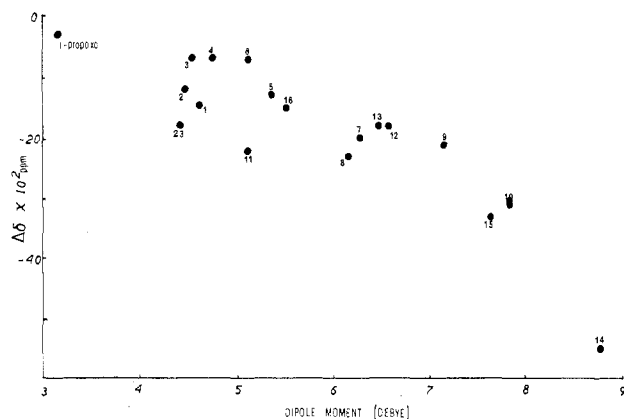


Figure 2. Correlation between the relative chemical shifts of the methine protons of acac and the dipole moments for some  $(acac)_2-(OAr)_2Ti^{IV}$  complexes.

In addition, localized field effects, due to steric encroachment of polar groups and ring current effects due to the phenoxo ligands, are probably far from negligible in these highly congested molecules.

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**Registry No.** 1, 54548-77-5; 2, 54548-78-6; 3, 54548-79-7; 4, 54517-18-9; 5, 54517-03-2; 6, 38781-11-2; 7, 54548-73-1; 8, 54548-74-2; 9, 54566-74-4; 10, 54517-04-3; 11, 54548-75-3; 11a, 54548-76-4; 12, 54575-94-9; 13, 54517-05-4; 14, 54516-96-0; 15, 54548-70-8; 16, 54516-97-1; 17, 54548-71-9; 18, 54516-98-2; 19, 54516-99-3; 20, 54517-00-9; 21, 54517-01-0; 22, 54517-02-1; 23, 54548-72-0; 24, 54548-68-4; 25, 54516-93-7; 26, 54516-94-8; 27, 54516-95-9; 28, 54548-69-5; 29, 17034-82-1; 30, 23329-69-3; 31, 54516-91-5; 32, 33939-16-1; 33, 54516-92-6; 34, 54516-88-0; 35, 38781-12-3; 36, 54516-89-1; 37, 54516-90-4; 38, 54516-87-9; 39,

33888-32-3; 40, 33888-31-2; 41, 38781-13-4;  $(acac)_2(isopropoxy)_2Ti$ , 23072-32-4; *n*-butyl titanate, 5593-70-4.

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## Synthesis of the Carbamato(carbonyl)manganese(I) Complexes $Mn(CO)_4(XYCNMe_2)$ ( $XY = SS, SSe, \text{ and } SeSe$ ) and $Mn(CO)_5(XC(O)NMe_2)$ ( $X = S \text{ and } Se$ ) and Their Thermal Dimerization Reactions in the Solid State

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The reaction of  $BrMn(CO)_5$  with  $XYCNMe_2^-$  ( $XY = SS, SSe, \text{ and } SeSe$ ) gives  $Mn(CO)_4(XYCNMe_2)$ , where the carbamato ligands act in a bidentate manner, while  $BrMn(CO)_5$  reacts with  $XC(O)NMe_2^-$  ( $X = S, Se$ ) to give  $Mn(CO)_5(XC(O)NMe_2)$ . The former three complexes on heating in the solid state under dry nitrogen evolve one molecule of carbon monoxide to give the dimanganese complexes  $[Mn(CO)_3(XYCNMe_2)]_2$ , and the latter two under similar conditions yield analogous dinuclear complexes via  $Mn(CO)_4(XC(O)NMe_2)$ . A comparison of  $\sigma$ -donor and/or  $\pi$ -acceptor capacities among the carbamato anions is discussed on the basis of Graham's  $\sigma$ - $\pi$  parameters or the carbonyl stretch-stretch interaction constants in the mononuclear complex, and configurations of the dinuclear complexes are proposed from the appearance of  $\nu(C\equiv O)$  bands. Thermochemical and kinetic parameters were also obtained by a differential scanning calorimeter to discuss the mechanism of the dimerization reactions.

### Introduction

Metal complexes of dithio- and diselenocarbamate have been extensively studied, and the thioselenocarbamate analogs were reported by two groups of investigators.<sup>1,2</sup> These carbamato ligands usually act in a bidentate manner, while in certain circumstances the dithiocarbamate anion is known to behave as a monodentate ligand.<sup>3</sup> On the other hand, considerable attention has been paid to metal complexes of monothiocarbamate.<sup>4,5</sup> The analogous monoselenocarbamate complexes were prepared by us for the first time, although they are limited

to  $Sn(IV)$ ,<sup>6</sup>  $Ni(II)$ ,<sup>7</sup>  $Pd(II)$ ,<sup>8</sup> and  $Pt(II)$ <sup>8</sup> complexes. Monothio- and monoselenocarbamates act as monodentate or bidentate ligands depending on the circumstances in which the ligand is placed, such as the nature of metal ions coordinated and the concentration of the complex in solution.<sup>9</sup>

Recently, Abel and Dunster reported the preparation and configuration of bis(*N,N*-dimethylmonothiocarbamato)-hexacarbonyldimanganese(I),  $[Mn(CO)_3SC(O)NMe_2]_2$ , by reaction of  $Mn(CO)_5Br$  with  $Me_3SnSC(O)NMe_2$ .<sup>10</sup> The only other carbamato complex of manganese(I) carbonyl reported