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Stereochemistry and molecular rearrangements of some six-, seven-, and eight-coordinate chelates of early transition metals [1]

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Contents

Abstract

This article is a review of the stereochemistry and molecular rearrangements of selected six-, seven-, and eight-coordinate chelates of early transition metals: primarily, metal β-diketonates, dithiocarbamates, and monothiocarbamates. Dihalobis(β-diketonato)metal complexes $M(dik)_2X_2$ ($M = Ti$, Zr, or Hf) generally have an octahedral cis configuration, but $Ti(acac)_2I_2$ and $V(dik)_2X_2$ exist in solution as an equilibrium mixture of cis and trans isomers. Nuclear magnetic resonance (NMR) line-shape studies show that the dialkoxy complexes *cis*-$Ti(dik)_2(OR)_2$ rearrange by an intramolecular twisting mechanism whereas the closely related *O,O′*-dimethyl dithiophosphates *cis*-$Ti(Me_2dtp)_2(OR)_2$ undergo metal–ligand bond rupture. The seven-coordinate complexes $Zr(acac)_3Cl$, $Ti(S_2CNMe_2)_3Cl$, $Ti(SOCNEt_2)Cl$, and $CpM(S_2CNMe_2)_3$ ($M = Ti$, Zr, or Hf) have a pentagonal bipyramidal structure with the Cl or Cp ligand in an axial position. Eight-coordinate structures and stereoisomers are described

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[1] Dedicated to the memory of Joseph Chatt.

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for several Ti(IV), Zr(IV), Nb(V), and Ta(V) tetrakis chelates with β-diketonate, dithiocarbamate, or monothiocarbamate ligands. The factors that determine the choice of coordination polyhedron, ligand wrapping pattern, and donor atom site occupancies are discussed. The seven- and eight-coordinate complexes are of special interest because they are among the first examples of higher coordination complexes that become stereochemically rigid on the NMR time scale.

Keywords:

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1. Introduction

The contributions of Joseph Chatt to the field of inorganic chemistry are both numerous and very important. Chatt's organization of ligand and metal atoms into class (a) and class (b) donors and acceptors [1], his recognition of the importance of metal–ligand π bonding in accounting for the trans effect [2] and the relative stabilities of cis and trans isomers of square planar platinum(II) complexes [3–5], and his studies of dipole moments [3–5] and IR spectra [6,7] are among the contributions that have influenced my own work. As a 1970 sabbatical visitor in Professor Chatt's laboratory, I had the opportunity to make a small contribution in the field of dinitrogen chemistry [8], but, more importantly, I was able to experience firsthand the personal kindness, as well as the scientific prowess, of one of the giants of twentieth-century chemistry.

This paper is a review of the stereochemistry and molecular rearrangements of selected six-, seven-, and eight-coordinate chelates of early transition metals: primarily, metal β-diketonates, dithiocarbamates, and monothiocarbamates. Kinetic studies show that the six-coordinate dialkoxybis(β-diketonato) complexes $Ti(dik)_2(OR)_2$ rearrange by an intramolecular twisting mechanism whereas closely related *O,O'*-dialkyldithiophosphates undergo metal–ligand bond rupture. The seven- and eight-coordinate complexes are of special interest because they are among the first examples of higher coordination complexes that become stereochemically rigid on the nuclear magnetic resonance (NMR) time scale. Because of space limitations, this review focuses primarily on work from my own laboratory.

2. Metal β-diketonates

2.1. Six-coordinate dihalobis(β-diketonates) and related compounds

Titanium(IV), zirconium(IV), and hafnium(IV) halides react with acetylacetone in anhydrous dichloromethane, benzene, or diethyl ether to give dihalobis(acetylacetonato) complexes $M(acac)_2X_2$, where X = F, Cl, Br, or I when M = Ti, X = Cl or Br when M = Zr or Hf, and acac = MeCOCHCOMe [9–11] (Eq. (1)). Analogous dipseudohalobis(β-diketonato)titanium(IV) complexes $Ti(dik)_2(NCO)_2$ and

$Ti(dik)_2(NCS)_2$, where dik = acac or dpm (*tert*-BuCOCHCO-*tert*-Bu), can be prepared by reaction of $Ti(dik)_2Cl_2$ with AgNCO or NaSCN [12] (Eqs. (2) and (3)).

$$MX_4 + 2H(acac) \rightarrow M(acac)_2X_2 + 2HX \qquad (1)$$

$$Ti(dik)_2Cl_2 + 2AgNCO \rightarrow Ti(dik)_2(NCO)_2 + 2AgCl \qquad (2)$$

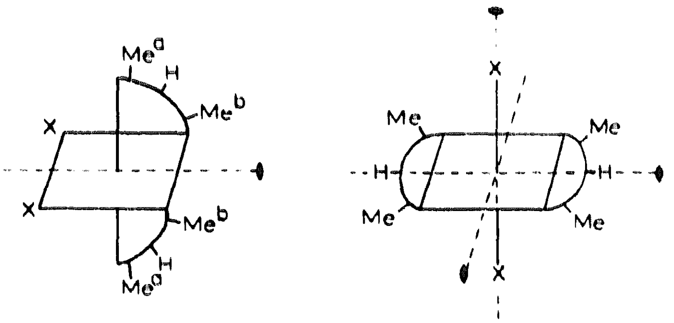
$$Ti(dik)_2Cl_2 + 2NaSCN \rightarrow Ti(dik)_2(NCS)_2 + 2NaCl \qquad (3)$$

All the $M(dik)_2X_2$ complexes are monomeric non-electrolytes in solution, and IR spectra indicate that all the β-diketonate carbonyl groups are coordinated to the metal. The following evidence demonstrates that the $M(dik)_2X_2$ (X = F, Cl, Br, NCO, or NCS) complexes have a cis octahedral configuration in solution (Fig. 1): (1) two methyl (or *tert*-butyl) resonances of equal intensity and one ring proton resonance in low-temperature ^1H NMR spectra of the Ti complexes [9,12]; (2) dipole moments of 6.4–8.3 D for the Ti, Zr, and Hf complexes [12,13]; (3) coincidence of ν(M–O) and ν(M–X) bands in IR and Raman spectra of the Zr and Hf complexes [14]; (4) two ν(CN), ν(Ti–NCS), and ν(Ti–NCO) bands in IR spectra of $Ti(dik)_2(NCS)_2$ and $Ti(dik)_2(NCO)_2$ [12].

The ν(CN), ν(CS), and ν(CO) frequencies and the integrated intensities of the ν(CN) bands in IR spectra of the $Ti(dik)_2(NCS)_2$ and $Ti(dik)_2(NCO)_2$ complexes [12] are in accord with the values expected for an N-bonded attachment of the pseudohalide ligands [15–18]. Ti–NCS bonding in the thiocyanate complexes is expected because titanium(IV) is a class (a) acceptor [1] (a hard acid [19]).

The behavior of $Ti(acac)_2I_2$ is strikingly different from that of the difluoro, dichloro and dibromo analogs. Conductance, electron spin resonance, and low temperature ^1H NMR studies indicate that $Ti(acac)_2I_2$ exists in dichloromethane solution as about 50% *cis*-$Ti(acac)_2I_2$, about 40% *trans*-$Ti(acac)_2I_2$, about 10% of an electrolytic dissociation product, presumably $[Ti(acac)_2I]^+I^-$, and 0.13% of a paramagnetic Ti(III) species [10].

Far-IR spectra and molar polarization measurements indicate that the



cis
2 Me and 1 ring H

trans
1 Me and 1 ring H

Fig. 1. $M(acac)_2X_2$ cis and trans isomers. The methyl groups in the a and b sites of the polar cis isomer (C_2 symmetry) are inequivalent. All methyl groups in the non-polar trans isomer (D_{2h} symmetry) are equivalent. (Reproduced with permission from Ref. [9].)

vanadium(IV) complexes V(dpm)$_2$Cl$_2$ and V(dpm)$_2$Br$_2$ also exist in solution as an equilibrium mixture of cis and trans isomers [20]. K = [cis]/[trans] for V(dpm)$_2$Cl$_2$ is about 0.33 in carbon tetrachloride and about 0.59 in benzene; $K = 0.18$ for V(dpm)$_2$Br$_2$ in benzene. Both complexes are trans in the solid state, and the fraction of *cis*-V(dpm)$_2$Cl$_2$ in solution increases as the solvent dielectric constant increases in the order $CCl_4 < C_6H_6 < CHCl_3 < CH_2Cl_2$. A decrease in the [cis]/[trans] ratio with increasing size of the halide and decreasing radius of the metal ion (0.68 Å for Ti(IV); 0.60 Å for V(IV)) suggests that steric effects play a role in destabilizing the cis isomer. The greater stability of the cis isomer in the absence of steric effects is probably due to the fact that the cis isomer is better able to maximize metal–ligand π bonding in a complex that contains two ligands with different π donor abilities [3]. In addition, the cis isomer is favored by increasing solvent polarity.

As mentioned previously, low temperature ^{1}H NMR spectra of the *cis*-Ti(dik)$_2$X$_2$ complexes exhibit two acac methyl (or dpm *tert*-butyl) resonances of equal intensity. These resonances coalesce to a single time-averaged resonance at higher temperatures owing to rapid exchange of β-diketonate Me or *tert*-Bu groups between the inequivalent a and b sites of the cis isomer (Fig. 1). Rate constants and activation parameters obtained by total line-shape analysis are listed in Table 1 [9,12]. In addition, rate constants at the coalescence temperatures were estimated for Ti(acac)$_2$I$_2$ ($k = 25$ s^{-1} at −64 °C) [10] and Ti(dpm)$_2$(NCS)$_2$ ($k = 23$ s^{-1} at −100 °C) [12]. These results indicate that (1) the rate of molecular rearrangement increases as the monodentate ligand varies in the order Cl < NCO < Br < F < I < NCS and (2) the dpm complexes rearrange about 5–10 times faster than the acac analogues.

Zr(acac)$_2$X$_2$ and Hf(acac)$_2$X$_2$ (X = Cl or Br) rearrange much faster than the corresponding Ti compounds [11]. These complexes exhibit a single sharp time-averaged methyl resonance at −108 °C in dichloromethane–1,1,2-trichloroethene, and Zr(acac)$_2$Cl$_2$ gives a single methyl resonance at −130 °C in dichloromethane–3-chloropropene; therefore, $k > 10$ s^{-1} at −130 °C.

Possible mechanisms for rearrangement of the M(dik)$_2$X$_2$ complexes include (1) complete dissociation of one diketonate ligand to give a four-coordinate intermediate, (2) dissociation of a halide or pseudohalide ligand to give a five-coordinate

Table 1
Kinetic data for methyl or *tert*-butyl group exchange in Ti(dik)$_2$X$_2$ complexes[a]

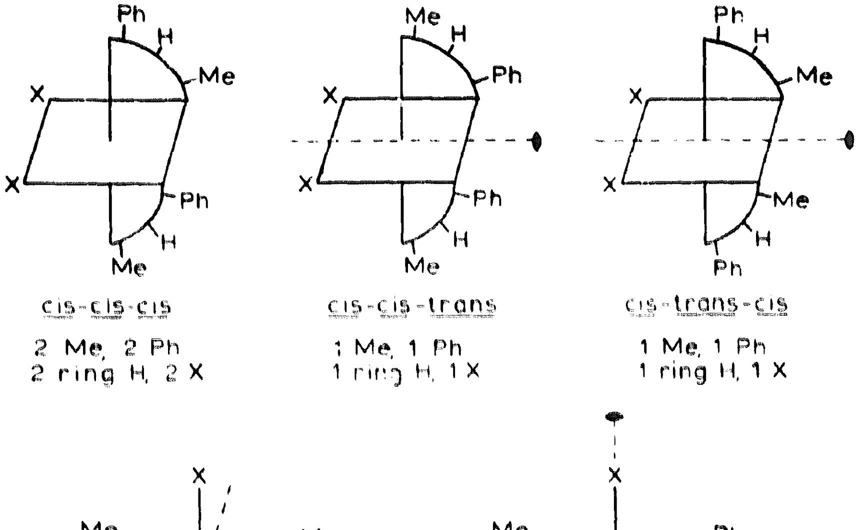
Compound	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ (J K^{-1} mol^{-1})	$\Delta G^\ddagger$(−43 °C) (kJ mol^{-1})	T_c[b] (°C)	k(−43 °C) (s^{-1})	k(25 °C) (s^{-1})
Ti(acac)$_2$(NCO)$_2$	43.9 ± 2.5	−39 ± 10	53.0 ± 0.2	−43	4.5	1.1×10^3
Ti(acac)$_2$F$_2$	46.4 ± 1.7	−9 ± 8	48.5 ± 0.2	−63	49	1.6×10^4
Ti(acac)$_2$Cl$_2$	44.8 ± 2.5	−41 ± 10	54.1 ± 0.3	−26	2.5	6.7×10^2
Ti(acac)$_2$Br$_2$	46.0 ± 2.1	−26 ± 8	52.1 ± 0.2	−34	7.2	2.3×10^3
Ti(dpm)$_2$(NCO)$_2$	39.3 ± 1.3	−40 ± 6	48.4 ± 0.2	−51	50	6.7×10^3
Ti(dpm)$_2$Cl$_2$	45.6 ± 1.7	−23 ± 6	51.1 ± 0.2	−34	12	3.5×10^3

[a] In dichloromethane solution. All errors are random errors estimated at the 95% confidence level.
[b] Coalescence temperature.

intermediate, (3) rupture of one M–O bond to give a five-coordinate intermediate containing one monodentate diketonate ligand, and (4) twisting mechanisms that effect rearrangement without metal–ligand bond rupture. Twisting mechanisms involve a 120° rotation of one triangular face of the octahedron with respect to the opposite face and proceed via a trigonal prismatic transition state. The twist can occur about any one of the four C_3 axes of the octahedral coordination polyhedron.

The intermolecular mechanisms 1 and 2 can be ruled out because intermolecular exchange of both dik and X ligands is slow compared with the rates of exchange of diketonate Me and *tert*-Bu groups [9,12,21]. The rearrangements are therefore intramolecular, but trends in the rates (Table 1) provide no basis for choosing between a one-bond rupture mechanism and a twist mechanism.

M(dik)$_2$X$_2$ complexes that contain unsymmetrical β-diketonate ligands can exist as five diastereoisomers, depicted in Fig. 2 for an M(bzac)$_2$X$_2$ complex, where bzac is the benzolylacetonate ligand (MeCOCHCOPh). The isomers are named by specifying first the orientation of the halogen atoms (cis or trans), then the orientation of the benzoyl groups, and finally the orientation of the acetyl groups. Low temperature NMR studies indicate that the Ti(bzac)$_2$X$_2$ complexes exist in dichloromethane solution as a near statistical equilibrium mixture of the three isomers that have the



cis-cis-cis
2 Me, 2 Ph
2 ring H, 2 X

cis-cis-trans
1 Me, 1 Ph
1 ring H, 1 X

cis-trans-cis
1 Me, 1 Ph
1 ring H, 1 X

trans-cis-cis
1 Me, 1 Ph
1 ring H, 1 X

trans-trans-trans
1 Me, 1 Ph
1 ring H, 1 X

Fig. 2. Possible diastereoisomers for an M(bzac)$_2$X$_2$ complex. The number of symmetry-inequivalent methyl groups, phenyl groups, ring protons, and halide ligands is indicated for each isomer. (Reproduced with permission from Ref. [22].)

halogen atoms in cis positions [22]. For example, low temperature ^{19}F NMR spectra of $Ti(bzac)_2F_2$ exhibit six resonance lines (Fig. 3), a four-line AB pattern due to the two inequivalent F atoms of the cis-cis-cis isomer and two lines that are best assigned to the equivalent F atoms of the other two isomers that have F atoms in cis positions (cis-cis-trans and cis-trans-cis). Consistent with this interpretation, low temperature ^{1}H NMR spectra exhibit four diketonate methyl resonances.

At higher temperatures, the six ^{19}F resonances of $Ti(bzac)_2F_2$ broaden simultaneously and coalesce into a single time-averaged resonance (Fig. 3). Similarly, the diketonate methyl proton resonances of $Ti(bzac)_2X_2$ (X = F, Cl, or Br) coalesce into a single time-averaged resonance. These spectra imply exchange of F atoms and diketonate Me groups among all four inequivalent sites of the three cis-dihalo isomers. A detailed mechanistic analysis [22,23] has shown that exchange of nuclei among all four inequivalent sites cannot be achieved by twisting about any one of the four C_3 axes of the octahedron. It was not possible, however, to distinguish between multistep twisting about different C_3 axes and a one-bond rupture mechanism.

Positive evidence for a twist mechanism comes from NMR studies [24–27] of chiral *cis*-$Ti(dik)_2(OR)_2$ complexes, where OR is an alkoxide ligand that contains diastereotopic groups. *cis*-$Ti(acac)_2(OCHMe_2)_2$, for example, exhibits two acac methyl resonances and two isopropoxide methyl doublets that coalesce in the same temperature range (Fig. 4), which indicates that acac methyl group exchange and inversion of configuration at the metal center occur at comparable rates. For all the compounds studied (Table 2) [27], the relative rates $R_k = k_{inv}/k_x$ of inversion and diketonate R group exchange lie in the range from about 1.0 to about 2.0, and the activation parameters for the two processes are essentially identical. The data indicate that inversion and diketonate R group exchange occur by a common, intramolecular mechanism.

Certain mechanisms may be ruled out as the sole rearrangement path on the basis of the observed R_k values. For example, rearrangement via trigonal bipyramidal-axial (TBP-axial) and TBP-equatorial five-coordinate intermediates with a monodentate dik ligand requires $R_k \geqslant 2.0$ and $R_k = 0$ respectively. Twists about a single octahedral C_3 axis predict $R_k = 1.0$ or $R_k = 2.0$, depending on the C_3 axis about which the twist occurs.

The variation in the rates with the steric bulk of the alkoxide ligand (Table 2) strongly supports a twist mechanism over a bond-rupture process. For the $Ti(dpm)_2(OR)_2$ complexes, for example, k(25 °C) decreases by a factor of about 10^3 and $\Delta H^{\dagger}$ increases by about 21 kJ mol^{-1} as OR varies from a primary alkoxide (OCH_2Ph) to a tertiary alkoxide ($OCMe_2Ph$). These steric effects are consistent with a twist mechanism because trigonal prismatic transition states are more congested than the octahedral ground state. In contrast, a bond-rupture process should be accelerated as the OR group becomes more bulky because steric strain is relieved on going to an intermediate of reduced coordination number. The fact that the R_k values vary monotonically from 2.0 to 1.0 with increasing steric bulk of the alkoxide ligand suggests a mixture of twists about the various octahedral C_3 axes, with the

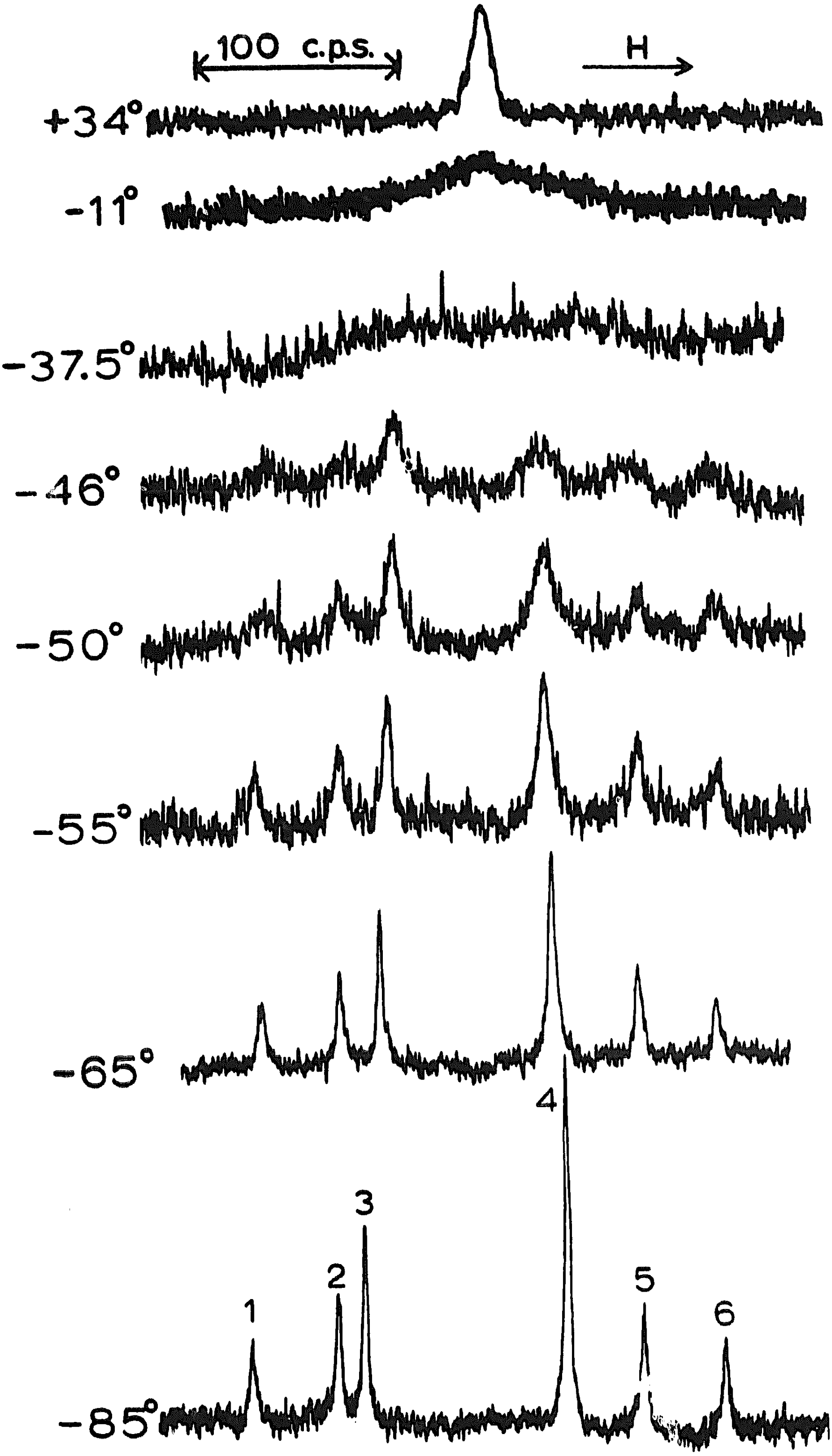


Fig. 3. ^{19}F NMR spectra of $Ti(bzac)_2F_2$ in dichloromethane solution. (Reproduced with permission from Ref. [22].)

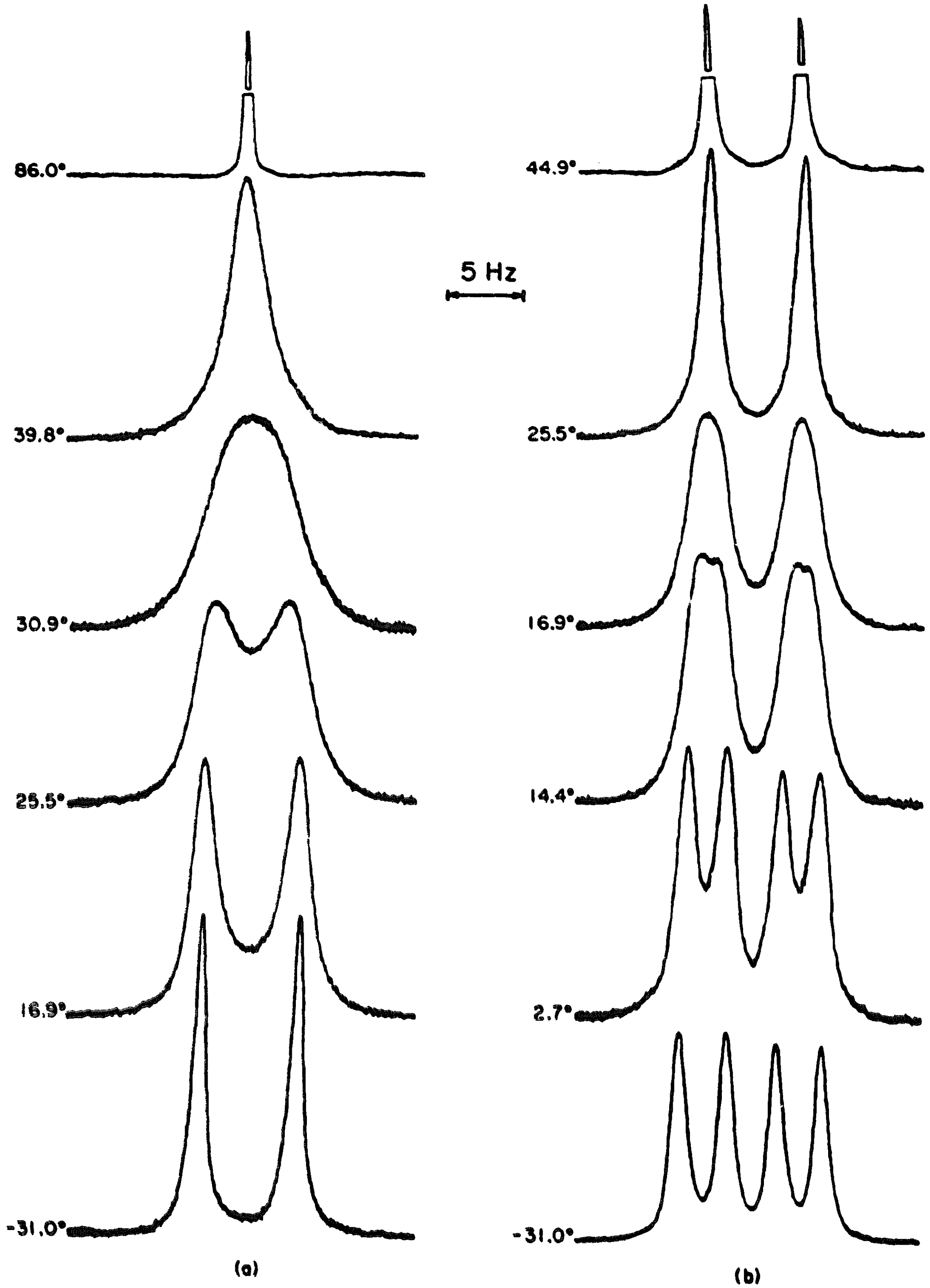


Fig. 4. ^1H NMR spectra of $Ti(acac)_2(OCHMe_2)_2$ in $CDCl_3$ solution: (a) acac methyl resonances; (b) isopropoxide methyl resonances. (Reproduced with permission from Ref. [27a].)

relative amount of twisting about the different axes depending on the amount of steric crowding.

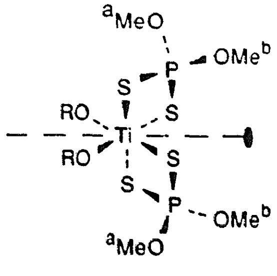
It is interesting to compare the kinetic results for the $Ti(dik)_2(OR)_2$ complexes

Table 2
Kinetic data for inversion and diketonate R group exchange in $Ti(dik)_2(OR)_2$ complexes[a]

Compound	Process	$\Delta H^\dagger$ (kJ mol^{-1})	$\Delta S^\dagger$ (J K^{-1} mol^{-1})	k(25 °C) (s^{-1})	$\Delta G^\dagger$ (kJ mol) (T_c^b (°C))	k (s^{-1}) (about T_c (°C))	$R_k = k_{inv}/k_{ex}$ at about T_c
Ti $(acac)_2(OCH_2Ph)_2$[c]	Exchange	48.5±2.1	−49±7	47.1	63.0±0.3 (15)	23.2±2.6 (15)	
Ti $(acac)_2(OCH_2CHMe_2)_2$	Inversion	49.4±2.1	−48±8	41.3	63.6±0.3 (20)	26.9±3.2 (19)	2.09±0.4
	Exchange	48.5±2.9	−58±10	19.6	65.3±0.3 (19)	12.9±1.7 (19)	
Ti $(acac)_2(OCHMe_2)_2$	Inversion	58.6±2.9	−26±10	15.8	65.9±0.3 (15)	12.3±1.5 (22)	1.78±0.3
	Exchange	59.0±1.3	−28±5	8.9	67.7±0.3 (29)	6.9±0.6 (22)	
Ti $(acac)_2(OCMe_2Ph)_2$[d]	Inversion	64.0±1.7	−30±5	1.01	73.6±0.3 (45)	12.7±1.2 (56)	1.41±0.2
	Exchange	63.6±1.7	−35±5	0.73	75.3±0.2 (67)	9.0±0.7 (56)	
Ti $(dpm)_2(OCH_2Ph)_2$	Inversion	49.0±1.7	−51±6	32.5	64.1±0.2 (20)	45.9±3.8 (30)	1.64±0.2
	Exchange	50.6±1.3	−51±5	19.7	66.1±0.3 (34)	28.0±2.6 (30)	
Ti $(dpm)_2(OCH_2CHMe_2)_2$	Inversion	58.2±3.3	−27±11	17.4	66.0±0.2 (28)	26.0±2.7 (30)	1.37±0.2
	Exchange	56.5±1.3	−34±4	12.8	67.0±0.2 (33)	19.0±1.6 (30)	
Ti $(dpm)_2(OCMe_2Ph)_2$[d]	Inversion	70.7±3.8	−39±10	0.023	84.5±0.3 (82)	9.2±1.0 (100)	1.06±0.2
	Exchange	71.5±2.1	−37±5	0.020	86.1±0.3 (119)	8.7±0.9 (100)	

[a] In $CDCl_3$ unless indicated otherwise. All errors are estimated at the 95% confidence level.
[b] Coaelescence temperature.
[c] In 1,2-dichloroethane.
[d] In 1,1,2,2-tetrachloroethane.

with results [28] for the analogous dialkoxybis(*O*,*O'*-dimethyl dithiophosphato)titanium(IV) complexes, *cis*-Ti($Me_2dtp)_2(OR)_2$ ($Me_2dtp = S_2P(OMe)_2$; R = CH_2Ph, $CHMe_2$, or CMe_2Et) (1).



(1)

For the Me_2dtp complexes, inversion of configuration and exchange of dithiophosphate methyl groups occur at the same rate by a common intramolecular mechanism; in the coalescence region (−35 °C), where the rate constants are most accurately determined, $R_k = k_{inv}/k_{ex} = 1.0 \pm 0.3$ (Table 3). Activation parameters for the two processes are nearly identical. Because the dtp methyl groups lie above and below the plane of the chelate rings, rather than in the plane of the rings as in the $Ti(dik)_2(OR)_2$ complexes, the various rearrangement mechanisms predict different R_k values for the two sets of complexes. The R_k values for the $Ti(Me_2dtp)_2(OR)_2$ complexes rule out intramolecular twist mechanisms and all the common bond-rupture mechanisms except rupture of a Ti–S bond trans to an alkoxide ligand to give a TBP intermediate that has the dangling ligand in an axial position. In accord with a bond-rupture mechanism, the rates increase with increasing steric bulk of the alkoxide ligand (Table 3).

A summary of the kinetic results for the $Ti(dik)_2(OR)_2$ and $Ti(Me_2dtp)_2(OR)_2$ complexes is presented in Table 4. Rearrangement rates are about 10^4 times slower for the diketonates; $\Delta H^{\dagger}$ is somewhat higher, and $\Delta S^{\dagger}$ is negative. The following factors may contribute to the change in mechanism for the two sets of complexes: (1) the oxophilic, class (a) Ti atom should form stronger bonds to dik O atoms than to dtp S atoms, thus suppressing a bond-rupture mechanism in the dik complexes; (2) dtp ligands are somewhat more versatile than diketonates. Dithiophosphate ligands often adopt a monodentate or unsymmetrical bidentate attachment to metal atoms, suggesting that rupture of a bond to a dtp ligand may be a rather facile process.

2.2. *Seven-coordinate halotris(β-diketonates)*

Zirconium(IV) and hafnium(IV) halides react with acetylacetone in benzene, carbon tetrachloride, or tetrahydrofuran, yielding the halotris(acetylacetonato) complexes $M(acac)_3X$ (M = Zr or Hf, X = Cl or Br; M = Zr, X = I) (Eq. (4)). The choice of solvent and reaction conditions is crucial to the success of these syntheses [11].

$$MX_4 + 3H(acac) \rightarrow M(acac)_3X + 3HX \qquad (4)$$

IR spectra of the $M(acac)_3X$ complexes exhibit metal–halogen stretching bands in

Table 3
Kinetic data for inversion and dithiophosphate methyl group exchange in $Ti(Me_2dtp)_2(OR)_2$ complexes[a]

OR	Process	$\Delta H^\ddagger$ (kJ mol^{-1})	$\Delta S^\ddagger$ (J K^{-1} mol^{-1})	k(25 °C) (s^{-1})	T_c[b] (°C)	$\Delta G^\ddagger$(−35 °C) (kJ mol^{-1})	k(−35 °C) (s^{-1})	$R_k = k_{inv}/k_{ex}$ at −35 °C
OCH_2Ph	Inversion	56.3 ± 3.1	24 ± 12	$(1.4 \pm 0.3) \times 10^4$	−27	50.7 ± 0.4	40 ± 8	0.9 ± 0.2
	Exchange	51.6 ± 0.8	6 ± 3	$(1.1 \pm 0.2) \times 10^4$	−21	50.3 ± 0.3	46 ± 8	
$OCHMe_2$	Inversion	47.0 ± 2.9	−2 ± 13	$(2.8 \pm 1.0) \times 10^4$	−50	47.5 ± 0.5	186 ± 42	0.9 ± 0.3
	Exchange	45.2 ± 1.0	−9 ± 5	$(2.5 \pm 0.4) \times 10^4$	−42	47.4 ± 0.4	202 ± 33	
$OCMe_2Et$	Inversion	52.6 ± 3.7	26 ± 16	$(8.3 \pm 4.1) \times 10^4$	−53	46.5 ± 0.4	315 ± 79	1.0 ± 0.3
	Exchange	49.4 ± 1.6	12 ± 7	$(6.5 \pm 1.1) \times 10^4$	−44	46.6 ± 0.4	302 ± 66	

[a] In toluene-d_8. All errors are estimated at the 95% confidence level.

[b] Coalescence temperature.

Table 4
Comparison of kinetic results for $Ti(dik)_2(OR)_2$ and $Ti(Me_2dtp)_2(OR)_2$

	$Ti(dik)_2(OR)_2$	$Ti(Me_2dtp)_2(OR)_2$
k(25 °C) (s^{-1})	10^{-2}–10^{2}	10^{4}–10^{5}
$\Delta H^{\ddagger}$ (kJ mol^{-1})	48–72	45–56
$\Delta S^{\ddagger}$ (J K^{-1} mol^{-1})	−58 to −26	−9 to +24
Mechanism (based on R_k)	Twist (mixture of C_3 axes)	Bond rupture (TBP-axial)
Variation in k[a]	Decrease (50–1000 ×)	Increase (7 ×)

[a] Variation as steric bulk increases from a primary to a tertiary alkoxide.

the range 314–93 cm^{-1} and indicate that all the carbonyl groups are coordinated [14]. Dipole moments of about 5–6 D in benzene solution are in good agreement with the values expected for a seven-coordinate structure [13]. The chloro and bromo complexes are monomeric nonelectrolytes in ionizing solvents [11,29], but $Zr(acac)_3I$ is about 10% dissociated in 1,2-dichloroethane and about 26% dissociated in nitrobenzene [11]. The dissociated species of $Zr(acac)_3I$ in 1,2-dichloroethane are markedly stabilized by tetrahydrofuran, probably because of coordination by the THF (Eq. (5)).

$$Zr(acac)_3I + THF \rightleftharpoons Zr(acac)_3(THF)^+ + I^- \qquad (5)$$

A seven-coordinate structure has been confirmed for $Zr(acac)_3Cl$ by X-ray diffraction [30]. The molecule has a distorted pentagonal bipyramidal (PBP) geometry (Fig. 5) with the Cl atom in an axial position (Zr–Cl, 2.472(6) Å). The other axial position and one equatorial position are spanned by acac ligand a, while the remain-

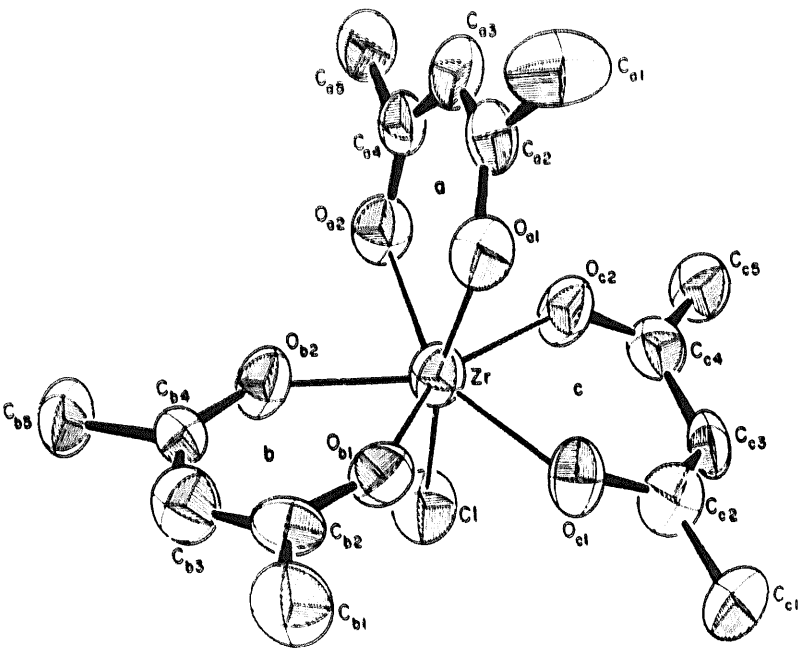


Fig. 5. Pentagonal bipyramidal structure of the $Zr(acac)_3Cl$ molecule. (Reproduced with permission from Ref. [30].)

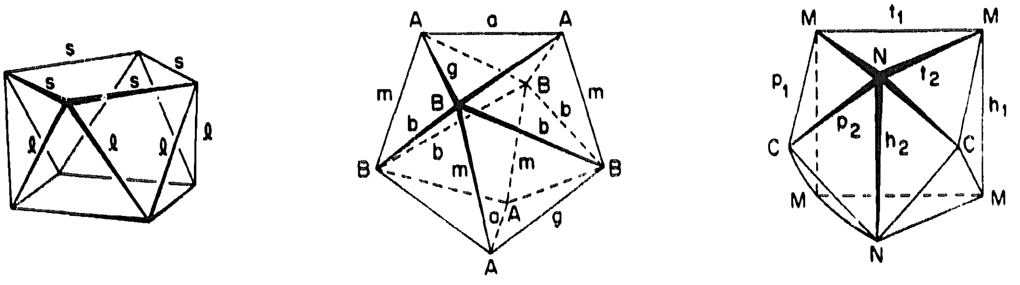
ing equatorial positions are occupied by acac ligands b and c. A PBP structure appears to be the preferred configuration for M(chelate)$_3$X complexes when X is a ligand that forms a relatively strong, covalent M–X bond. The axial Zr–O bond is about 0.06 Å shorter than the averaged length (2.14 Å) for the five, quite uniform, equatorial Zr–O bonds. Because of extremely close O···O contacts in the equatorial plane, the pentagonal girdle of O atoms is appreciably puckered. In solution, Zr(acac)$_3$Cl is stereochemically non-rigid on the NMR time scale at temperatures down to −130 °C [11].

IR and Raman spectra of six-coordinate M(acac)$_2$X$_2$, seven-coordinate M(acac)$_3$X, and eight-coordinate M(acac)$_4$ complexes (M = Zr or Hf) exhibit two M–O stretching bands in the 400–500 cm^{-1} region that are sensitive to coordination number [14]. The ν_{as}(M–O) frequency decreases from about 448 to 432 to 422 cm^{-1} and the ν_s(M–O) frequency decreases from about 460 to 451 to 444 cm^{-1} as the coordination number increases from 6 to 7 to 8. A parallel increase is observed in the acac carbonyl frequencies: from about 1337 to 1383 to 1397 cm^{-1} for ν_{as}(CO). These frequency shifts can be rationalized in terms of an increase in the M–O bond lengths as the coordination number increases from 6 to 7 to 8.

2.3. *Eight-coordinate tetrakis(β-diketonates) and related compounds*

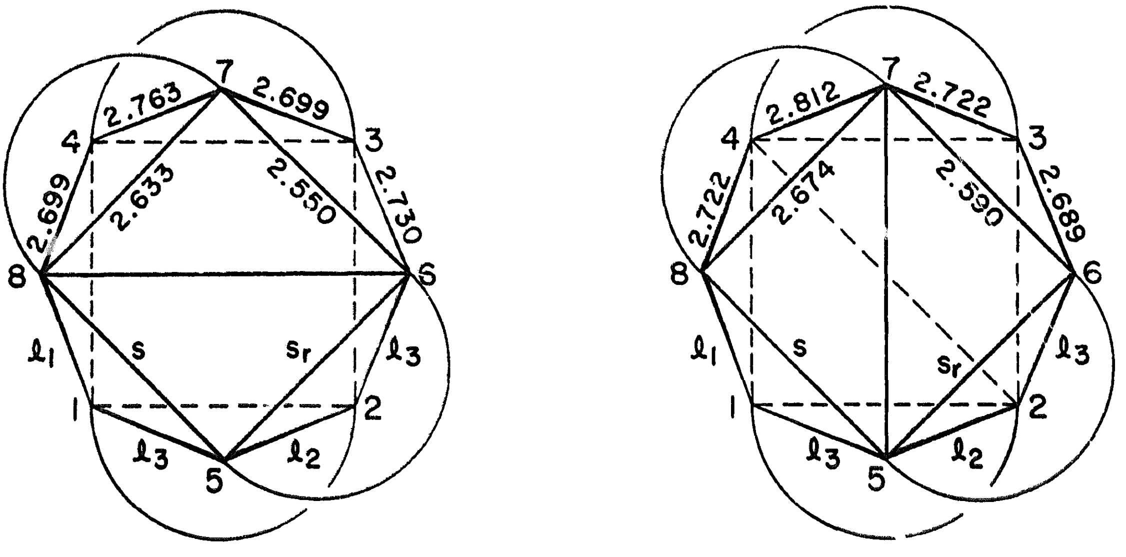
The three most common coordination polyhedra for coordination number 8, the D_{4d} square antiprism (SAP), the D_{2d} dodecahedron (DD), and the C_{2v} bicapped trigonal prism (BTP), are shown in Fig. 6. Polyhedral edges are labeled according to the nomenclature of Hoard and Silverton [31] and Porai-Koshits and Aslanov [32]. The eight vertices of the SAP are equivalent, whereas the D_{2d} DD has two sets of vertices (A and B) and the C_{2v} BTP has three sets of vertices (M, N, and the capping sites, C). Stereoisomers of tetrakis chelate complexes are named by specifying the point group symmetry and the polyhedral edges spanned by the bidentate ligands. Thus, Zr(acac)$_4$ has a structure in which the acac ligands span *s* edges of an SAP to give the D_2-*ssss* stereoisomer [33]. The same stereoisomer has been found for the tetrakis(dibenzoylmethanato) complex Zr(bzbz)$_4$ (bzbz = PhCOCHCOPh) [34]. In both complexes, the SAP is slightly distorted: in the direction of a C_{2v} BTP in the case of Zr(bzbz)$_4$, and in the direction of a D_{2d} DD in the case of Zr(acac)$_4$ (Fig. 7).

Because the more common eight-coordination polyhedra are of comparable ener-



(a) (b) (c)

Fig. 6. Perspective views of (a) the D_{4d} SAP, (b) the D_{2d} DD, and (c) the C_{2v} BTP.



(a) (b)

Fig. 7. Structures of (a) $Zr(bzbz)_4$ and (b) $Zr(acac)_4$. Dimensions of the coordination polyhedra are averaged in accord with approximate D_2 symmetry. Distortions of the square antiprism involve slight folding of the quadrilateral faces about the indicated face diagonals. (Reproduced with permission from Ref. [34].)

gies [31,35–40], crystal packing can affect the choice of coordination polyhedron and ligand wrapping pattern. For example, the α and β crystalline forms of $M(acac)_4$ contain different stereoisomers. The β form, found for M = Zr, Ce, U, or Np, contains the SAP D_2-*ssss* stereoisomer, whereas the α form, found for M = Ce or Th, contains molecules that are best described as the BTP $h_1h_1p_2p_2$ stereoisomer [41].

A more important determinant of coordination polyhedron and ligand wrapping pattern is the matching of ligand bite with polyhedral edge lengths [31,37]. For example, the bidentate nitrate ligand has a short bite of about 2.1 Å and is not well suited for spanning the relatively long edges of the SAP. Thus, in the mixed-ligand complex $Zr(acac)_2(NO_3)_2$, the nitrate (and acac) ligands span the relatively short *m* edges of the D_{2d} DD [42]. The observed stereoisomer (Fig. 8) is the C_2-*mmmm* isomer, which has one acac ligand and one nitrate ligand on each of the dodecahedral BAAB trapezoids (Fig. 6). Averaged Zr–O bond lengths are as follows: Zr–O(acac), 2.096 Å; Zr–O(nitrate), 2.295 Å. Within each chelate ring, the Zr–O bonds to the A sites are longer than the Zr–O bonds to the B sites by 0.015–0.051 Å (5σ–17σ), and these differences are propagated in the N–O and C–O bonds in the ligands, $N-O_A$ and $C-O_A$ being longer than $N-O_B$ and $C-O_B$ (by 3σ–6σ).

$Zr(acac)_3(NO_3)$ has an eight-coordinate structure in which the bidentate nitrate ligand spans an *a* edge and the three acac ligand span *b*, *m*, and *g* edges of a distorted D_{2d} DD (Fig. 9) [43]. This unprecedented C_1-*abmg* ligand wrapping pattern (Fig. 10) is preferred over the commonly observed *mmmm* wrapping pattern because the bite of the acac ligand is too large to permit two acac ligands to be located on the same trapezoid of a ZrO_8 DD. The acac ligand bite exhibits significant variation with the type of polyhedral edge it spans: *m* (2.618(2) Å) < *g* (2.689(2) Å) < *b* (2.786(2) Å).

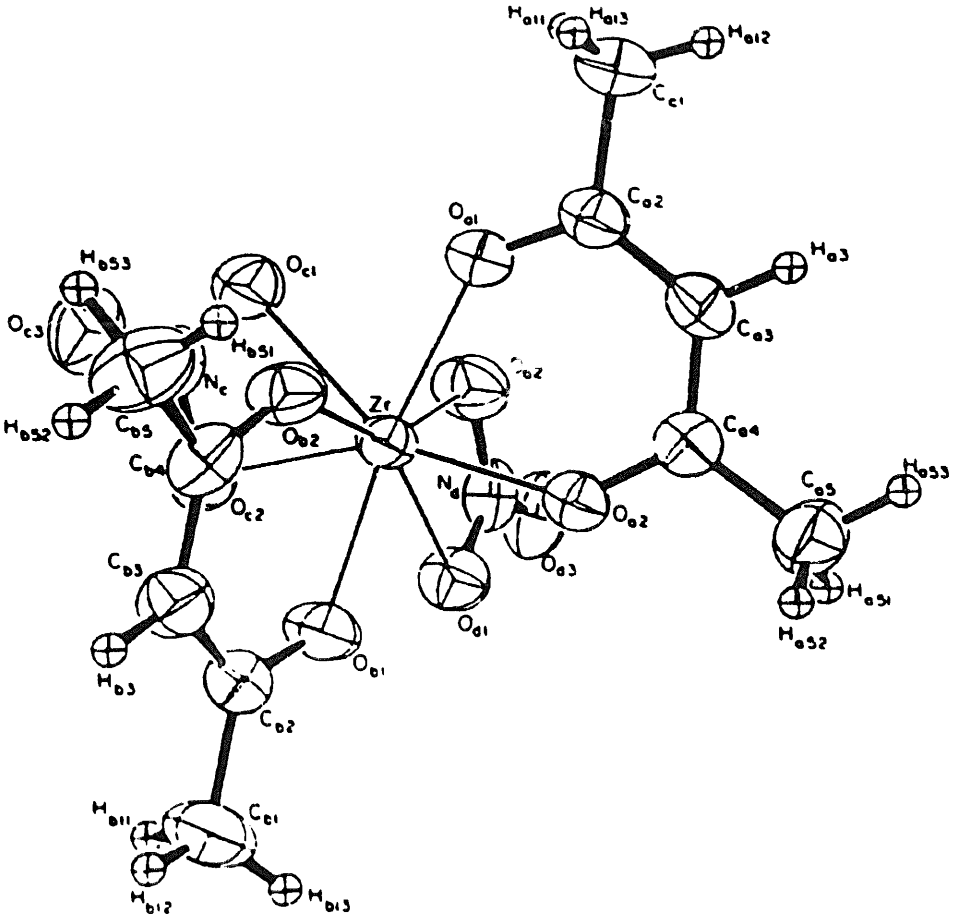
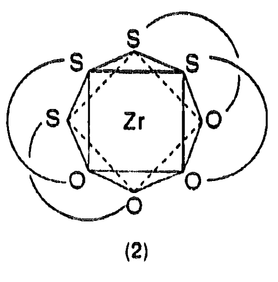


Fig. 8. Dodecahedral structure of the $Zr(acac)_2(NO_3)_2$ molecule. The BAAB trapezoids of Fig. 6 are defined by atoms O_{a2}, O_{a1}, O_{c1}, and O_{c2} and by atoms O_{b2}, O_{b1}, O_{d1}, O_{d2}. The quasi-twofold axis passes midway between atoms O_{a2} and O_{b2} and atoms O_{c2} and O_{d2}. (Reproduced with permission from Ref. [42].)

Zr–O bonds to the acac ligands are systematically shorter than those to the nitrate ligand, averaging 2.141(1) Å and 2.366(2) Å respectively. The averaged length for all eight Zr–O bonds is 2.196 Å, essentially identical to averaged Zr–O bond lengths in $Zr(acac)_2(NO_3)_2$ (2.195 Å) [42] and $Zr(acac)_4$ (2.198 Å) [33].

Tetrakis(thioacetylacetonato)zirconium(IV), $Zr(Sacac)_4$ (Sacac = MeCSCHC-OMe), has an SAP structure (**2**) in which the Sacac ligands span the *s* polyhedral edges in such a way as to cluster the four S atoms in all-cis positions [44].



(2)

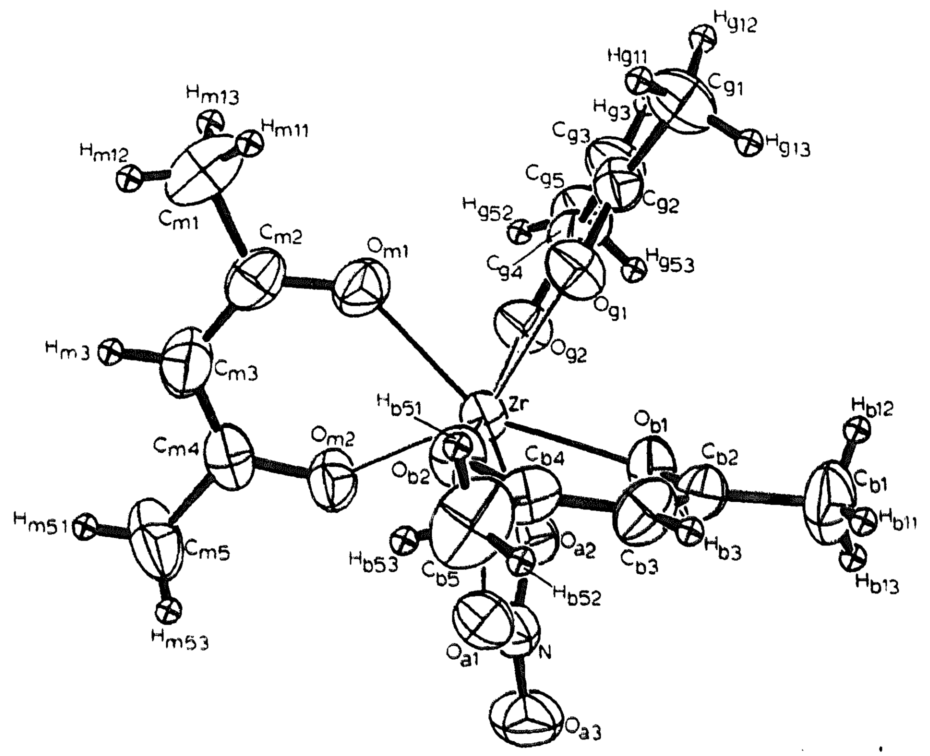


Fig. 9. Dodecahedral structure of the Zr(acac)$_3$(NO$_3$) molecule. The ligands are labeled *a*, *b*, *m*, or *g* according to the dodecahedral edge that the ligand spans. (Reproduced with permission from Ref. [43].)

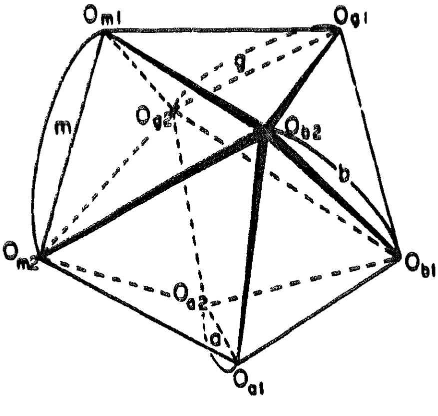


Fig. 10. Ligand wrapping pattern in Zr(acac)$_3$(NO$_3$). The ligands are labeled *a*, *b*, *m*, or *g* according to the dodecahedral edge that the ligand spans. (Reproduced with permission from Ref. [43].)

The observed C_2-*ssss* stereoisomer is distorted in the direction of the DD C_1-*mmgg* and BTP C_1-$t_1t_1p_2p_2$ stereoisomers. Consistent with the former distortion, the averaged Zr–O and Zr–S bond lengths fall into two classes (Zr–O$_A$, 2.185 Å; Zr–O$_B$, 2.132 Å; Zr–S$_A$, 2.734 Å; Zr–S$_B$, 2.665 Å). An all-cis arrangement of S atoms has also been observed in square planar bis- and octahedral tris(thio-β-diketonate) complexes [45–53] and is probably due to a trans influence arising from differences in the donor properties of sulfur and oxygen.

The more common eight-coordination polyhedra are of comparable energy and are easily interconverted by small angular deformations [31,35–40]. Consequently, most eight-coordinate complexes are highly fluxional. Nevertheless, ^1H and ^{19}F NMR studies of eight-coordinate β-diketonates in $CHClF_2$ solution at temperatures down to −170 °C have identified several complexes that become stereochemically rigid on the NMR time scale at temperatures in the range from −115 to −170 °C [54]. $Zr(acac)_4$ and $Hf(acac)_4$ in the slow-exchange limit exhibit two methyl proton resonances of equal intensity, consistent with the SAP D_2-*ssss* stereoisomer found in the solid state. Low temperature spectra of the unsymmetrical-ligand complex $Zr(dmh)_4$ (dmh = *tert*-BuCOCHCOMe) display just two Me and two *tert*-Bu resonances, which indicates that the alkyl resonances do not probe the overall symmetry of the expected mixture of SAP stereoisomers, only the local symmetry of the alkyl groups. The ^{19}F NMR spectrum of $Zr(tfac)_4$ (tfac = $CF_3COCHCOMe$) at −160 °C, however, exhibits four resonances of relative intensities about 1:3:3:2, consistent with a mixture of stereoisomers. $Zr(acac)_2(NO_3)_2$ exhibits two methyl resonances of equal intensity below the coalescence temperature T_c of −144 °C, in accord with the DD C_2-*mmmm* structure found in the solid state, but $Zr(acac)_3(NO_3)$ is stereochemically non-rigid at even lower temperatures.

Kinetic data for intramolecular rearrangement of several of the Zr(IV) complexes have been obtained by NMR line-shape analysis (Table 5) [54]. These complexes are highly fluxional; for $Zr(acac)_4$, for example, the extrapolated rate constant at 25 °C for exchange of methyl groups between the two inequivalent sites of the D_2-*ssss* stereoisomer is 4.7×10^5 s^{-1}, and the rearrangement barrier $\Delta H^{\dagger}$ is only 17 kJ mol^{-1}. Th(IV) and U(IV) β-diketonates are even more fluxional. $Th(acac)_4$ exhibits a single time-averaged methyl resonance at −169 °C [54b], and $U(acac)_4$ has a rate constant of 2.8×10^5 s^{-1} at −106 °C [54a]. The rearrangement mechanism in the Zr(IV) complexes has been discussed in terms of a polytopal rearrangement that interconverts SAP and DD stereoisomers [54b]. Zr(IV) β-diketonates also undergo intermolecular ligand exchange, but that process is much slower than intramolecular rearrangement [55–57].

Table 5
Kinetic data for methyl or *tert*-butyl group exchange in zirconium(IV) β-diketonate complexes[a]

	$Zr(acac)_4$[b]	$Zr(dmh)_4$[c]	$Zr(acac)_2(NO_3)_2$[b]
T_c[d] (°C)	−145	−116	−144
k(25 °C) (s^{-1})	4.7×10^5	1.7×10^5	1.4×10^6
k(−125 °C) (s^{-1})	2.0×10^2	6.8	2.9×10^2
$\Delta G^{\dagger}$(−125 °C) (kJ mol^{-1})	28.9 ± 0.3	33.1 ± 0.1	28.5 ± 0.2
$\Delta H^{\dagger}$ (kJ mol^{-1})	17.2 ± 1.3	23.0 ± 2.1	18.8 ± 1.3
$\Delta S^{\dagger}$ (J K^{-1} mol^{-1})	−78 ± 10	−68 ± 12	−64 ± 10

[a] In $CHClF_2$ solution. All errors are random errors estimated at the 95% confidence level.

[b] Methyl group exchange.

[c] *tert*-Butyl group exchange.

[d] Coalescence temperature.

3. Metal dithiocarbamates and monothiocarbamates

3.1. Seven-coordinate chlorotris(dithiocarbamates) and -(monothiocarbamates)

Chlorotris(dithiocarbamato)- and chlorotris(monothiocarbamato)titanium(IV) complexes, $Ti(S_2CNR_2)_3Cl$ and $Ti(SOCNR_2)_3Cl$ ($R=Me$, Et, $CHMe_2$, or CH_2CHMe_2), have been prepared by reaction of $TiCl_4$ with stoichiometric amounts of anhydrous sodium salts of the ligands in dichloromethane or benzene [58,59]. X-ray studies of $Ti(S_2CNMe_2)_3Cl$ [60] and $Ti(SOCNEt_2)_3Cl$ [59] indicate that both complexes have a seven-coordinate PBP structure with the Cl atom in an axial position. In the monothiocarbamate (mtc) complex, the ligands are oriented so as to cluster the three S atoms in all-cis positions on one triangular face of the PBP (Fig. 11).

^1H NMR spectra indicate that $Ti(S_2CNMe_2)_3Cl$ is stereochemically non-rigid on the NMR time scale at temperatures down to −90 °C, but $Ti(SOCNMe_2)_3Cl$ is rigid below a T_c of approximately −58 °C. The low temperature spectra exhibit four methyl resonances of relative intensities 1:2:2:1 (Fig. 12), consistent with the PBP structure found in the solid state. At higher temperatures, the NMR line shape changes indicate the existence of two distinct kinetic processes: (1) a low temperature intramolecular metal-centered rearrangement process that exchanges the unique and the equatorial mtc ligands ($\Delta G^{\dagger}(-58.2\,^{\circ}C)=45.1\pm0.4$ kJ mol^{-1}, $\Delta H^{\dagger}=$

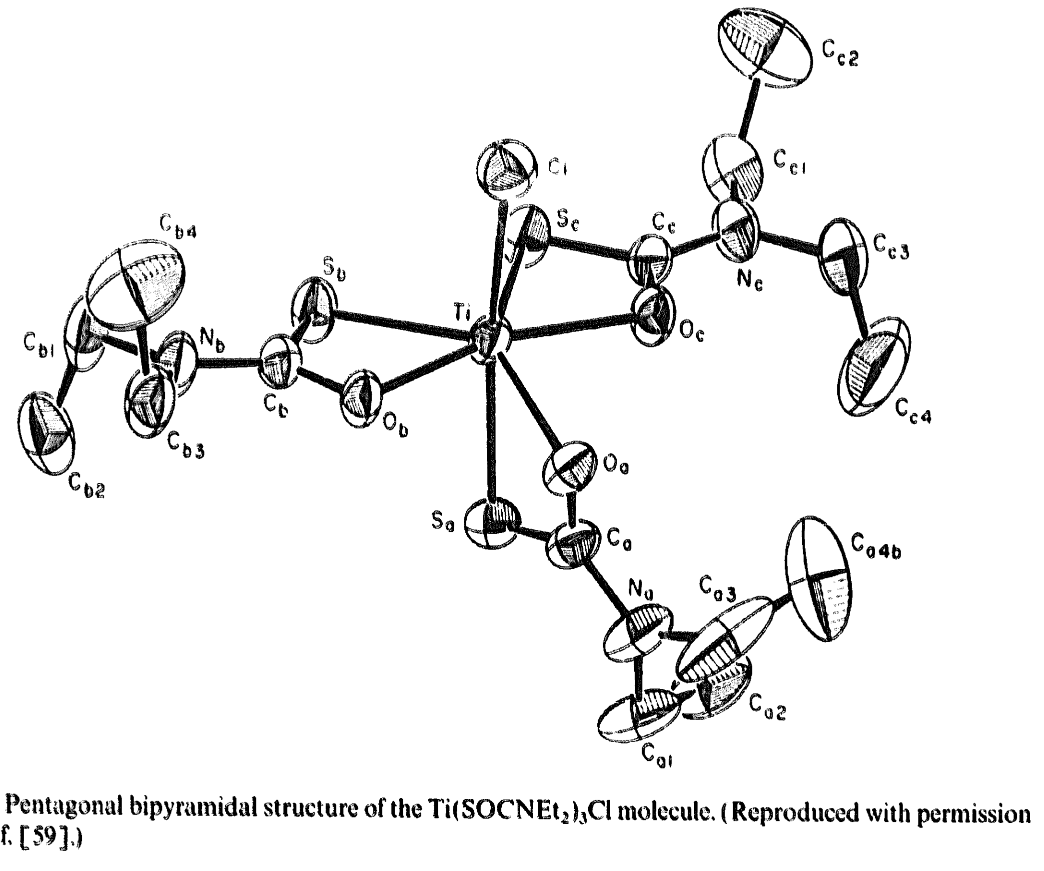


Fig. 11. Pentagonal bipyramidal structure of the $Ti(SOCNEt_2)_3Cl$ molecule. (Reproduced with permission from Ref. [59].)

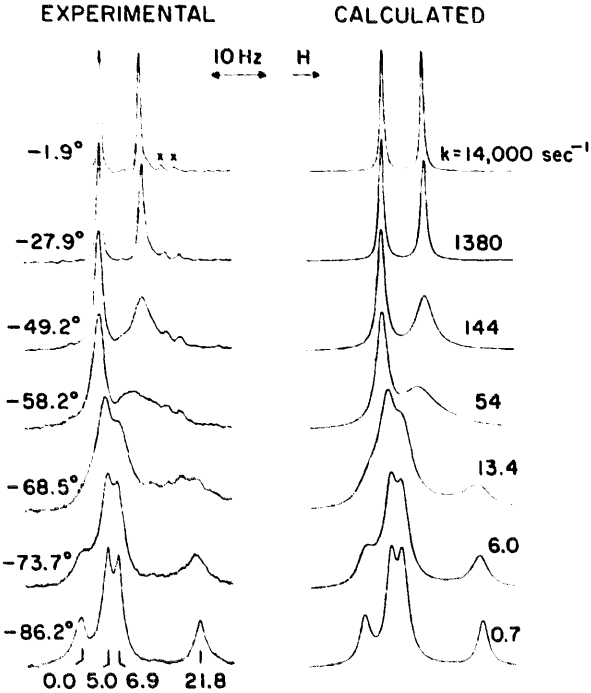


Fig. 12. Observed and calculated NMR line shapes for the methyl proton resonances of $Ti(SOCNMe_2)_3Cl$ in CD_2Cl_2 solution. (Reproduced with permission from Ref. [59].)

46.9 ± 1.3 kJ mol^{-1}, $\Delta S^{\dagger} = 8 \pm 7$ J K^{-1} mol^{-1}, $k(25\,^{\circ}C) = 9.8 \times 10^4$ s^{-1}) and (2) a high temperature process that involves rotation about the $C \overset{...}{=} N$ bond in the ligands ($\Delta G^{\dagger}(110\,^{\circ}C) = 84$ kJ mol^{-1}). A polytopal rearrangement mechanism involving a monocapped octahedral transition state that maintains the all-cis arrangement of the S atoms has been suggested for the metal-centered rearrangement [59].

3.2. Cyclopentadienyltris(dithiocarbamates)

The cyclopentadienyltris(dithiocarbamate) complexes $CpM(S_2CNMe_2)_3$ (M = Ti, Zr, or Hf) also have a PBP structure, with the η^5-Cp ligand in an axial position (Fig. 13) [61–63]. The cyclopentadienyl complexes are of special interest because of extreme crowding in the MS_6C_5 coordination group and because, unlike $Ti(S_2CNMe_2)_3Cl$, they are stereochemically rigid on the NMR time scale. Low temperature ^1H NMR spectra exhibit four dithiocarbamate dtc methyl resonances of relative intensities 2:1:2:1, consistent with the PBP structure found in the solid state.

For $CpTi(S_2CNMe_2)_3$, the two Me resonances of relative intensity 2 coalesce at −17 °C (Fig. 14) to give a three-line pattern (4:1:1) that persists until about 27 °C. Above 27 °C (Fig. 15), the two lines of relative intensity 1 coalesce with each other and with the time-averaged line of relative intensity 4 to give a single time-averaged line above $T_c \approx 57\,^{\circ}C$. For $CpM(S_2CNMe_2)_3$ (M = Zr or Hf), all four Me resonances broaden simultaneously and coalesce into a single resonance at $T_c = 74$–$89\,^{\circ}C$. NMR line-shape analysis [63] indicates the presence of three kinetic processes: (1) exchange

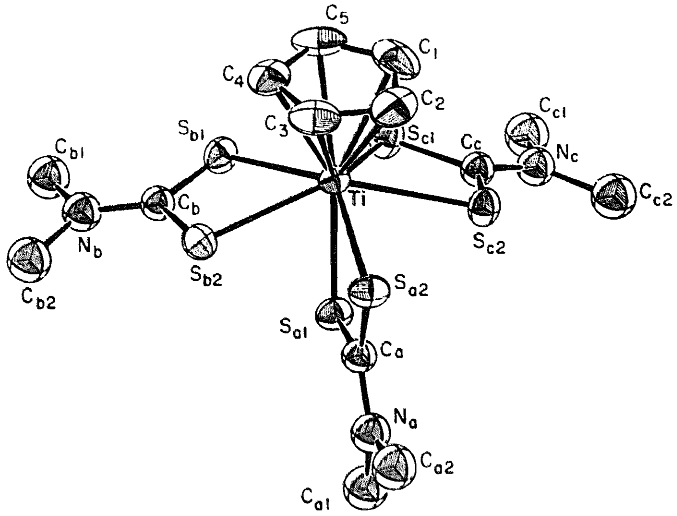


Fig. 13. Pentagonal bipyramidal structure of the $CpTi(S_2CNMe_2)_3$ molecule. (Reproduced with permission from Ref. [62].)

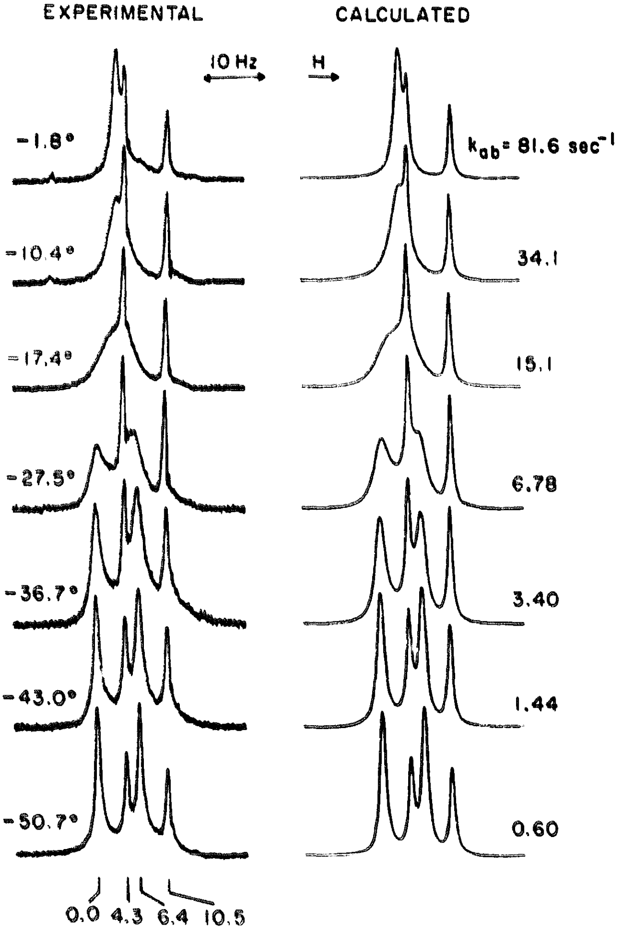


Fig. 14. Observed and calculated NMR line shapes (low temperature region) for the methyl proton resonances of $CpTi(S_2CNMe_2)_3$ in CH_2Cl_2 solution. (Reproduced with permission from Ref. [63].)

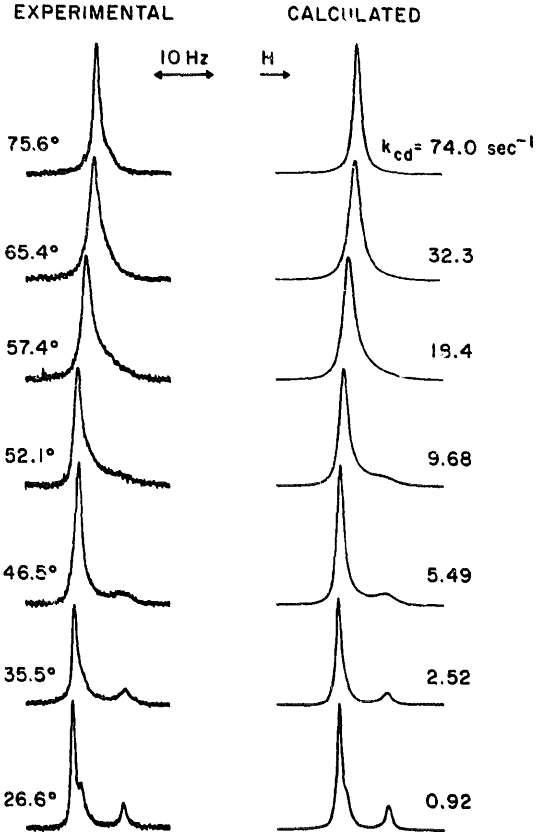


Fig. 15. Observed and calculated NMR line shapes (high temperature region) for the methyl proton resonances of $CpTi(S_2CNMe_2)_3$ in CH_2Cl_2 solution. (Reproduced with permission from Ref. [63].)

of dtc methyl groups within the equatorial ligands (process le, the low temperature process for M = Ti); (2) exchange of Me groups within the unique ligand (process lu); (3) exchange of the equatorial and the unique ligands (process ll).

Process le in $CpTi(S_2CNMe_2)_3$ ($\Delta G^{\dagger}(70\,^{\circ}C) \approx 59$ kJ mol^{-1}) is about 10^2–10^3 times faster than process lu and about 10^3 times faster than process le in $CpM(S_2CNMe_2)_3$ (M = Zr or Hf) ($\Delta G^{\dagger}(70\,^{\circ}C) \approx 79$–$82$ kJ mol^{-1}). The rates of processes le and lu in $CpM(S_2CNMe_2)_3$ (M = Zr or Hf) are the same within a factor of 2. The barrier $\Delta G^{\dagger}(70\,^{\circ}C)$ for process ll in $CpTi(S_2CNMe_2)_3$ is 78–79 kJ mol^{-1}, $\Delta S^{\dagger} \approx 0$ J K^{-1} mol^{-1}, and the rates and activation parameters are relatively independent of the nature and polarity of the solvent. Processes le and lu are believed to involve rotation about the $C \overset{\ldots}{=} N$ bond in the dtc ligands, perhaps preceded by rupture of an equatorial M–S bond. The faster rate of process le in $CpTi(S_2CNMe_2)_3$ appears to be related to the unusually long Ti–S bonds to the equatorial ligands in this compound. These Ti–S bonds (2.609–2.666 Å, average 2.633 Å) are significantly longer than the bonds to the unique ligand (2.565 and 2.570 Å), whereas, in $CpZr(S_2CNMe_2)_3$, the bonds to the equatorial ligands (2.683–2.717 Å, average 2.701 Å) exceed the lengths of the bonds to the unique ligand (2.681 and 2.655 Å) by a much smaller amount.

A double-facial twist mechanism involving a capped trigonal prismatic transition state of C_s symmetry has been proposed for process II [63]. Consistent with this mechanism, the rate of process II in the more crowded $(\eta^5\text{-}C_5Me_5)Zr(S_2CNMe_2)_3$ ($T_c > 138$ °C; $\Delta G^\ddagger(122.6\ ^\circ C) = 98$ kJ mol^{-1}) is about 10 times slower than the rate of process II in $CpZr(S_2CNMe_2)_3$ [64]. A polytopal rearrangement mechanism has also been suggested for exchange of dtc methyl groups in the PBP aryldiazenido complexes $Mo(N_2C_6H_4X)(S_2CNMe_2)_3$ (X = *p*-OMe, *p*-Me, H, *p*-Cl, *m*-NO_2, or *p*-NO_2) [65].

3.3. Eight-coordinate tetrakis(dithiocarbamates) and -(monothiocarbamates)

Eight-coordinate tetrakis(dithiocarbamates) and tetrakis(monothiocarbamates) have structures in which the bidentate chelating ligands span the *m* edges of a D_{2d} DD. X-ray crystal structures are available for the following Ti, Nb, and Ta compounds: $Ti(S_2CNEt_2)_4$ [66], $[Nb(S_2CNEt_2)_4]Br$ [67], $[Ta(S_2CNMe_2)_4]Cl\cdot CH_2Cl_2$ [68,69], $[Ta(S_2CNMe_2)_4][TaCl_6]\cdot 0.5CH_2Cl_2$ [68,69], $Ti(SOCNEt_2)_4$ [70,71], and $Zr(SOCNEt_2)_4$ [71].

In the mtc complexes, the S and O atoms do not sort between the DD A and B sites, as suggested by Orgel's rule [72–77]. Instead, two of the S atoms occupy A sites and the other two occupy B sites so as to give the C_{2v}-*mmmm* stereoisomer in which the four S atoms are clustered in all-cis positions on one side of the coordination polyhedron. This isomer is the most polar of the six possible stereoisomers that have an *mmmm* ligand wrapping pattern (Fig. 16). Dipole moments for $Ti(SOCNEt_2)_4$ (4.49 ± 0.11 D) and $Zr(SOCNEt_2)_4$ (3.61 ± 0.16 D) are relatively large, indicating that the C_{2v} isomer is the predominant solution species as well [78]. The clustering of S atoms in these complexes is similar to that noted previously for

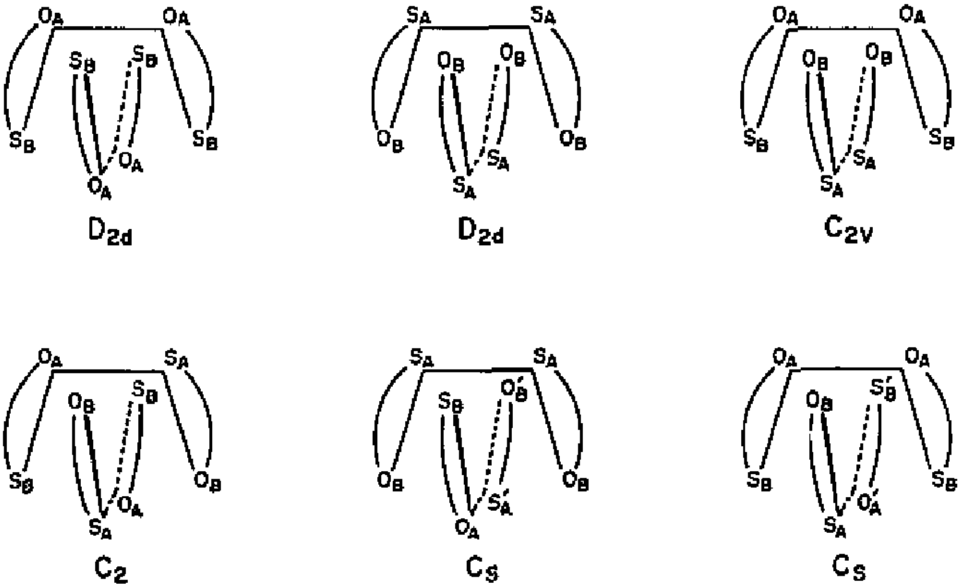


Fig. 16. Schematic representation of the six possible dodecahedral *mmmm* stereoisomers of an $M(SOCNR_2)_4$ complex. The two mutually perpendicular BAAB trapezoids are outlined, and the A and B site occupancy of the S and O atoms is shown. (Reproduced with permission from Ref. [78].)

Table 6
Kinetic data for metal dithiocarbamate and monothiocarbamate complexes[a]

Compound	T_c[b] (°C)	$\Delta G^\dagger(T_c)$ (kJ mol^{-1})	$\Delta H^\dagger$ (kJ mol^{-1})	$\Delta S^\dagger$ (J K^{-1} mol^{-1})	k(25°C) (s^{-1})
Metal-centered rearrangement:					
$[Nb(S_2CNMe_2)_4]Cl$[e]	-76.0	42.5 ± 0.2	29.1 ± 1.0	-69 ± 5	1.2×10^4
$[Ta(S_2CNMe_2)_4][TaCl_6]$[d]	-62.0	46.2 ± 0.3	43.7 ± 1.8	-13 ± 8	3.0 ± 10^4
$[Ta(S_2CN(Me)CHMe_2)_4][TaCl_6]$	-55.0	47.2 ± 0.4	46.3 ± 2.0	-4 ± 9	2.9 ± 10^4
$[Ta(S_2CN(Me)Ch)_4][TaCl_6]$	-51.5	48.1 ± 0.2	44.7 ± 1.4	-15 ± 6	1.4×10^4
$Ti(S_2CNEt_2)_4$[c]	<-140				
$Zr(S_2CNEt_2)_4$[c]	<-140				
$[Nb(SOCNMe_2)_4][NbCl_6]$	-15.2	61.5 ± 0.7	67.5 ± 7.9	22 ± 31	1.4×10^2
$[Ta(SOCNMe_2)_4][TaCl_6]$	-2.0	59.0 ± 0.3	60.9 ± 1.2	7 ± 5	3.2×10^2
$Ti(SOCNMe_2)_4$	-84.2	41.3 ± 0.3	44.9 ± 1.3	19 ± 7	7.6×10^5
$Zr(SOCNMe_2)_4$	-53.5	47.1 ± 0.2	39.6 ± 1.1	-34 ± 5	1.1×10^4
C=N bond rotation:					
$Ti(SOCNMe_2)_4$	29.9	70.1 ± 0.5	66.7 ± 2.7	-11 ± 9	3.4
$Zr(SOCNMe_2)_4$	78.2	82.7 ± 0.5	99.3 ± 5.2	47 ± 15	7.1×10^{-3}

[a] In CH_2Cl_2 or CD_2Cl_2 unless indicated otherwise. All errors are estimated at the 95% confidence level.
[b] Coalescence temperature.
[c] In *cis*-1,2-dichloroethene.
[d] In CH_2Cl_2–CD_3CN (10%–15% CD_3CN by weight).
[e] In $CHClF_2$–CD_2Cl_2.

$Zr(Sacac)_4$ and $Ti(SOCNEt_2)_3Cl$ and probably arises from a trans influence of the S atoms. A comparison of non-bonded contacts in the Ti and Zr compounds indicates that the clustering of S atoms cannot be attributed to attractive S···S interactions [71].

The $[Ta(S_2CNMe_2)_4]^+$ cation was the first reported example of an eight-coordinate tetrakis chelate that becomes stereochemically rigid on the NMR time scale [68]. It exhibits two equally intense methyl proton resonances below $T_c = -62$ °C, consistent with the D_{2d}-*mmmm* stereoisomer found in the solid state [69]. Similarly, $[Nb(S_2CNMe_2)_4]^+$ becomes rigid below $T_c = -76$ °C [79]. Low temperature spectra of the unsymmetrical dtc complexes $[Ta(S_2CNRMe)_4]^+$ (R = Ch, $CHMe_2$, or Bz) suggest the presence of an equilibrium mixture of *mmmm* stereoisomers that differ in the distribution of Me groups between the dodecahedral A and B sites [79]. Analogous Ti and Zr tetrakis(dithiocarbamates), however, give only time-averaged spectra at temperatures down to −140 °C, thus affording no evidence for stereoisomers or inequivalent A and B site *N*-alkyl groups [58,80,81]. Because the dimensions of the $[Ta(S_2CNMe_2)_4]^+$ and $Ti(S_2CNEt_2)_4$ coordination polyhedra are nearly identical, the charge on the Nb(V) and Ta(V) complexes must play a dominant role in slowing the rate of rearrangement.

Low temperature ^1H NMR spectra of the mtc complexes $Ti(SOCNMe_2)_4$, $Zr(SOCNMe_2)_4$, and $[Ta(SOCNMe_2)_4]^+$ exhibit four methyl resonances of approximately equal intensities [78,79,82], consistent with the C_{2v}-*mmmm* stereoisomer found in the solid state for the Ti and Zr compounds [71]. The relative intensities

(3:1:3:1) of the resonances for $[Nb(SOCNMe_2)_4]^+$, however, point to one of the C_s stereoisomers (Fig. 16). The variable temperature spectra indicate the presence of two distinct kinetic processes: (1) a low temperature process (LTP) that involves metal-centered rearrangement and (2) a high temperature process (HTP) that involves rotation about the C–N bond in the mtc ligand. For the cationic Nb and Ta complexes, the LTP is slower than for the Ti and Zr complexes (by a factor of about 10^2–10^4), and the HTP is too slow to be observed at 70 °C, the limit of our measurements. Kinetic data are summarized in Table 6.

The most important result in Table 6 is the greater stereochemical rigidity of the mtc complexes in comparison with the dtc analogues, which is evidence for a polytopal rearrangement mechanism [79,82]. Because the energy difference between the DD *mmmm* ground state and an SAP *llll* transition state increases with decreasing normalized bite of the ligand [37], a polytopal rearrangement predicts greater rigidity for the mtc complexes. In contrast, a bond-rupture mechanism predicts little difference in rearrangement rates for the mtc and dtc complexes because the mean Ti–S bond lengths in $Ti(SOCNEt)_4$ [71] and $Ti(S_2CNEt)_4$ [66] are nearly identical.

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