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STEREOCHEMICALLY RIGID 7-COORDINATE, TRIS(N-PHENYL,N-METHYLDITHIOCARBAMATO) COMPLEXES OF Ti(IV), Zr(IV) AND Hf(IV)

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Abstract—Tris(N-phenyl,N-methyldithiocarbamato) complexes of the type η^5-$C_5H_5M[S_2CN(C_6H_5)(CH_3)]_3$ and η^5-$CH_3C_5H_4M$-$[S_2CN(C_6H_5)(CH_3)]_3$ (where M = Ti, Zr or Hf) have been prepared by the reaction of $(C_5H_5)_2MCl_2$ or $(MeC_5H_4)_2MCl_2$ with anhydrous $Na[S_2CN(C_6H_5)(CH_3)]$ in refluxing CH_2Cl_2 or THF. Conductivity measurements and molecular weight determinations indicate that these complexes are monomeric and nonelectrolytic. IR spectra indicate that these complexes are seven coordinate in which all the dithiocarbamate ligands are bidentate. ^1H NMR spectra indicate that in these complexes the metal centered rearrangement and $S_2C{=}N$ bond rotation both are slow on NMR time scale at ambient temperature. A capped octahedron configuration, a rare geometry is assigned to η^5-$C_5H_5Hf[S_2CN(C_6H_5)(CH_3)]_3$.

INTRODUCTION

Stereochemically rigid 7-coordinate tris(N,N-dialkyldithiocarbamato) chelates of the type η^5-$C_5H_5M(S_2CNR_2)_3$ or η^5-$MeC_5H_4M(S_2CNR_2)_3$ (R = Me, Et and M = Ti or Zr) have been reported[1–6], which assume pentagonal bipyramidal structure. We report herein tris(N-phenyl,N-methyldithiocarbamato) chelates of the type η^5-$C_5H_5M[S_2CN(C_6H_5)(CH_3)]_3$ and η^5-$MeC_5H_4M[S_2CN(C_6H_5)(CH_3)]_3$ (M = Ti, Zr or Hf). η^5-$C_5H_5Hf[S_2CN(C_6H_5)(CH_3)]_3$, reported herein, is the first 7-coordinate dithiocarbamate complex which assumes capped octahedron structure.

EXPERIMENTAL

Reagent and techniques. $Na[S_2CN(C_6H_5)(CH_3)]$ was prepared by the usual method[7] and dried *in vacuo* over P_2O_5, first at room temperature and then at 110°. $C_5H_5MCl_2$ (M = Zr or Hf)[8] and $(MeC_5H_4)_2MCl_2$ (M = Ti or Zr)[9] were prepared by the reaction of C_5H_5Na or MeC_5H_4Na on MCl_4 in THF as described in the literature. Nitrobenzene for conductivity measurements was purified as described by Fay and Lowry[10]. Other organic solvents used were predried and well purified.

Preparation of η^5-$CH_3C_5H_4Ti[S_2CN(C_6H_5)(CH_3)]_3$. $(MeC_5H_4)_2TiCl_2$(0.227 g, 0.001 mol) was refluxed with anhydrous $Na[S_2CN(C_6H_5)(CH_3)]$ (0.615 g, 0.003 mol) in CH_2Cl_2 or THF (50 cm³) for 10–12 hr. The reaction mixuure was cooled and filtered. The filtrate was concentrated by distilling off the solvent *in vacuo* and petroleum ether (60–80°) was added to it. The precipitate obtained was collected and dried *in vacuo* and recrystallized from CH_2Cl_2 to give >80% yield of η^5-$CH_3C_5H_4Ti[S_2CN(C_6H_5)(CH_3)]_3$.

Preparation of other complexes. η^5-$C_5H_5Zr[S_2CN(C_6H_5)(CH_3)]_3$, η^5-$MeC_5H_4Zr[S_2CN(C_6H_5)(CH_3)]_3$ and η^5-$C_5H_5Hf[S_2CN(C_6H_5)(CH_3)]_3 \cdot CH_2Cl_2$ have been prepared by method A using (0.2922 g, 0.001 mol) $(C_5H_5)_2ZrCl_2$, (0.3202 g, 0.001 mol) $(MeC_5H_4)_2ZrCl_2$ or (0.3795 g, 0.001 mol) $C_5H_5HfCl_2$ respectively and (0.615 g, 0.003 mol) anhydrous $Na[(S_2CN(C_6H_5)(CH_3)]$. The yield of each complex was >80%.

Physical measurements. The molecular weights of the complexes were determined ebullioscopically in benzene whereas conductivity of each complex was determined in nitrobenzene using Backman RC-18A conductivity bridge. IR spectra were recorded on Perkin-Elmer 621 grating spectrometer using KBr pellets whereas ^1H NMR spectra in $CDCl_3$ at a sweep width of 500 Hz were recorded on Varian A-60 spectrometer using TMS as an internal standard.

RESULTS AND DISCUSSION

These complexes have been prepared in high yield by the following reaction

$$L_2MCl_2 + 3Na[S_2CN(C_6H_5)(CH_3)] \xrightarrow[\text{reflux}]{\substack{CH_2Cl_2\\ \text{or}\\ \text{THF}}} LM[S_2CN(C_6H_5)(CH_3)]_3 + 2NaCl + LNa$$

(M = Ti, Zr or Hf and L = C_5H_5 or MeC_5H_4).

In case of hafnium complex η^5-$C_5H_5[S_2CN(C_6H_5)(CH_3)]_3CH_2Cl_2$ is recrystallized from CH_2Cl_2. These complexes are orange yellow to white and are soluble in solvents like CH_2Cl_2, $CHCl_3$, CS_2, C_6H_6 and THF. These complexes are thermally stable in inert dry atmosphere, however hydrolyse slowly on exposure to air. Moreover solutions hydrolyse relatively rapidly. These complexes are monomeric in benzene and the conductivity measurements in nitrobenzene solution indicate these complexes to be nonelectrolytic. Physical data for these complexes are indicated in Table 1.

IR spectra

The complexes having both monodentate and bidentate dithiocarbamate ligands, such as $Ru(NO)(S_2CNR_2)_3$ (R = Me or Et)[11, 12], $Rh(PPh_3)(S_2CNMe_2)_3$[13, 14], exhibit additional IR bands not found for the complexes having only bidentate dithiocarbamate ligands such as $Mo(NO)(S_2CNR_2)_3$ (R = Me or Bu)[11, 13, 15]. The more

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Table 1. Elemental analysis and physical data

Complexes	Conductivity $ohm^{-1}cm^{2}mole^{-1}$	Molarity in mM	Found (calcd.) % C	H	N	(Ti or Zr or Hf)	M. W. Found (calcd.)	M. P.	Colour
1. η^5-$CH_3C_5H_4Ti$-$[S_2CN(C_6H_5)(CH_3)]_3$	0.25	0.05	54.2 (53.49)	4.5 (4.60)	6.5 (6.24)	7.3 (7.13)	690 (673.0)	90°	Orange yellow
2. η^5-C_5H_5Zr-$[S_2CN(C_6H_5)(CH_3)]_3$	0.22	0.06	49.2 (49.60)	4.0 (4.10)	6.1 (6.0)	12.8 (13.0)	679 (702.2)	236°(d)	White
3. η^5-$CH_3C_5H_4Zr$-$[S_2CN(C_6H_5)(CH_3)]_3$	0.24	0.05	50.9 (50.26)	4.4 (4.32)	5.9 (5.86)	12.9 (12.73)	730 (716.2)	215°	White
4. η^5-C_5H_5Hf-$[S_2CN(C_6H_5)(CH_3)]_3$-CH_2Cl_2	0.22	0.04	41.5 (41.17)	3.4 (3.50)	4.7 (4.80)	20.9 (20.41)	890 (874.5)	205°(d)	White

significant of these extra bands are a second $\nu_{C\stackrel{...}{-}N}$ band near 1470 cm^{-1}[12, 14] and a second $\nu_{C\stackrel{...}{-}S}$ band near 1000 cm^{-1}[16]. The IR spectra of these complexes exhibit only one $\nu_{C\stackrel{...}{-}N}$ band ~ 1510 cm^{-1} and only one $\nu_{C\stackrel{...}{-}S}$ band ~ 1000 cm^{-1}. Therefore all the dithiocarbamate ligands are bidentate in these complexes.

Pentahapto cyclopentadienyl or methylcyclopentadienyl ring in these complexes is identified by the characteristic IR bands viz., ν_{C-H} ~ 2960 cm^{-1}, ν_{C-C} ~ 1430 cm^{-1}, symmetric ring breathing ~ 1140 cm^{-1}, C-H asymmetrical in plane deformation ~ 1060 cm^{-1}, C-H asymmetrical out of plane deformation ~ 845 cm^{-1} and symmetrical out of plane deformation ~ 820 cm^{-1}[17].

From the above consideration M(IV) in these complexes may be assigned a coordination number 11 and the MS_6C_5 coordination polyhedron may be considered as a distorted icosahedron with one vertex suppressed. Due to relative small size of C_5H_5 or MeC_5H_4 ring, it is considered to occupy a single coordination site. Therefore coordination number seven is assigned to Ti(IV), Zr(IV) or Hf(IV) in these complexes.

NMR spectra

Three kinetic processes affect NMR spectral line shapes of metal dithiocarbamato complexes (i) metal centered rearrangement[18] (ii) $S_2C\stackrel{...}{-}N$ bond rotation[19] and (iii) hindred rotation about the C–N single bonds in the NR_2 portion of the S_2CNR_2 ligand[20]. The expected number and relative intensities of $-CH_3$ and $-C_6H_5$ group resonances in these complexes are indicated in Table 2, for the four idealized structures of seven coordinate complexes.

$S_2C\stackrel{...}{-}N$ bond rotation in methyl esters MeS_2CNR_2 (R = Me, Et[21]; i-pr, i-Bu[22]), exhibiting $\nu_{C\stackrel{...}{-}N}$ at 1477–1498 cm^{-1}, is reported to be slow at −30°. These complexes exhibit $\nu_{C\stackrel{...}{-}N}$ at 1500–1515 cm^{-1}. Therefore the $S_2C\stackrel{...}{-}N$ bond rotation should be still slower in these complexes. This is further substantiated by the fact that in all the 7-coordinate complexes[1–6] exhibiting $\nu_{C\stackrel{...}{-}N}$ at ~ 1500 cm^{-1}, for which metal centered rearrangement is slow, the $S_2C\stackrel{...}{-}N$ bond rotation is also found to be slow.

Interpretation of ^1H NMR spectra

^1H NMR spectra of η^5-$CH_3C_5H_4Ti[S_2CN(C_6H_5)(CH_3)]_3$ and η^5-$CH_3C_5H_4Zr[S_2CN(C_6H_5)(CH_3)]_3$ at −30° show four different resonances. (i) Two signals of relative intensity 2 : 1 due to $-C_6H_5$ protons (ii) Two multiplets due to $CH_3C_5H_4$ ring protons (iii) two signals of relative intensity 2 : 1 due to $-CH_3$ protons attached to N atom and (iv) a sharp signal due to $-CH_3$ protons of $CH_3C_5H_4$. The overall integrals of these resonances are in the ratio (15 : 4 : 9 : 3). The ^1H NMR spectra of η^5-$CH_3C_5H_4Ti[S_2CN(C_6H_5)(CH_3)]_3$ is shown in Fig. 1, the ^1H NMR spectrum of η^5-$C_5H_5Zr[S_2CN(C_6H_5)(CH_3)]_3$ exhibits the same pattern except for C_5H_5 ring protons, a sharp signal is obtained. Considering the slow $S_2C\stackrel{...}{-}N$ bond rotation and the ^1H NMR spectra of these complexes which indicate a slow metal centered rearrangement, it is clear that these complexes may conform to pentagonal bipyramid or monocapped trigonal prism or tetragonal base-trigonal base (possibility A of Table 2).

The ^1H NMR spectra of η^5-$C_5H_5Hf[S_2CN(C_6H_5)(CH_3)]_3 \cdot CH_2Cl_2$ exhibits a different pattern. It shows single sharp signal due to $-C_6H_5$, C_5H_5 ring, CH_2Cl_2 and $-CH_3$ protons respectively[Fig. 1]. The over all integrals of these signals are in the ratio (15 : 5 : 2 : 9).

Considering the slow S_2C—N bond rotation (as already discussed in IR spectra), and slow metal centered

Table 2. Predicted number and relative intensities for $-CH_3$ or $-C_6H_5$ groups resonances for various rearrangement possibilities in η^5-$C_5H_5M[S_2CN(C_6H_5)(CH_3)]_3$ or η^5-$CH_3C_5H_4M$-$[S_2CN(C_6H_5)(CH_3)]_3$ (where M = Ti, Zr or Hf)

Geometry	Symmetry	A	B	C
Pentagonal bipyramid	D_{5h}	2 (2:1)	2 (2:1)	1 —
Capped octahedron	C_{3v}	1 —	1 —	1 —
Monocapped trigonal prism	C_{2v}	2 (2:1)	2 (2:1)	1 —
Tetragonal base-trigonal base	C_s	2 (2:1)	2 (2:1)	1 —

A = Metal centered rearrangement and $S_2C\stackrel{...}{-}N$ bond rotation are both slow on the n.m.r. time scale at ambient temperature

B = $S_2C\stackrel{...}{-}N$ bond rotation is fast but metal centered rearrangement is slow.

C = Metal centered rearrangement is fast ($S_2C\stackrel{...}{-}N$ bond rotation is fast or slow).

Table 3. Proton chemical shifts (in Hz) at 30° in $CDCl_3$

Complexes	$-C_6H_5$ protons	C_5H_5 ring protons	$CH_3C_5H_4$ ring protons	CH_2Cl_2 protons	$-CH_3$ protons of $[S_2CN(C_6H_5)(CH_3)]$	CH_3 protons of $CH_3C_5H_4$
1. η^5-$CH_3C_5H_4Ti$-$[S_2CN(C_6H_5)(CH_3)]_3$	-429; -424	-	-350; -327 (m) (m)	-	-211; -208	-129
2. η^5-C_5H_5Zr-$[S_2CN(C_6H_5)(CH_3)]_3$	-435; -430	-361	-	-	-213; -210	-
3. η^5-$CH_3C_5H_4Zr$-$[S_2CN(C_6H_5)(CH_3)]_3$	-433; -428	-	-355; -328 (m) (m)	-	-214; -211	-130
4. η^5-C_5H_5Hf-$[S_2CN(C_6H_5)(CH_3)]_3$-CH_2Cl_2	-438	-358	-	-314	-212	-

m = multiplet

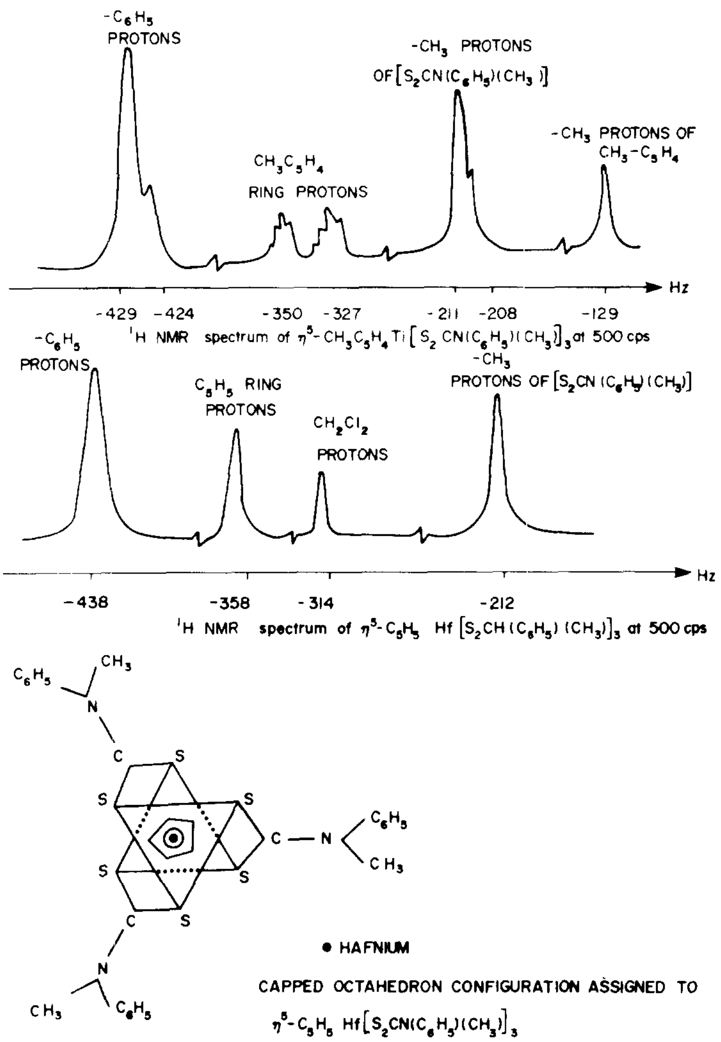

Fig. 1.

rearrangement (shown slow in similar complexes of the type η^5-$C_5H_5Hf[S_2CNR_2]_3$ (where R = Me or Et[23] or i-pr[6]), η^5-$C_5H_5Hf[S_2CN(C_6H_5)(CH_3)]_3\cdot CH_2Cl_2$ conforms to a capped octahedron configuration (possibility A of Table 2).

Thus η^5-$C_5H_5Hf[S_2CN(C_6H_5)(CH_3)]_3\cdot CH_2Cl_2$ is the first 7-coordinate dithiocarbamato complex, which assumes a capped octahedron geometry as shown in Fig. 1.

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