Inorganica Chimica Acta, 126 (1987) 99–106

^{27}Al, ^{13}C and ^{1}H NMR Spectral Studies of β-Diketone and β-Ketoester Derivatives of Zirconium Diisopropoxide Bis(tetraisopropoxyaluminate)

RAMA JAIN, A. K. RAI and R. C. MEHROTRA*

Department of Chemistry, University of Rajasthan, Jaipur-302004, India

(Received April 10, 1986; revised August 11, 1986)

Abstract

Synthesis of β-diketone and β-ketoester derivatives of zirconium diisopropoxide bis(tetraisopropoxyaluminate), of the type, $ZrAl_2(OPr^i)_{10-x}L_x$ (where L = acetylacetone, benzoylacetone, dibenzoylmethane, methylacetoacetate or ethylacetoacetate; $x = 1$, 2, 4 or 6) have been reported. Structural aspects of these derivatives have been discussed on the basis of elemental analyses, molecular weight determinations and IR, NMR (^{1}H, ^{13}C and ^{27}Al) spectral studies. NMR spectral data demonstrate that these compounds exist in non-aqueous solution as geometrical isomers, having isopropoxy groups in both the *cis* and *trans* positions.

Introduction

The β-diketone and β-ketoester derivatives of a number of metals have been investigated extensively during the last two decades [1]. The stereochemistry and configurational rearrangement of these compounds are the subject of considerable interest. With the exception of $Ti(acac)_2I_2$ [2], which exists as an equilibrium mixture of *cis* and *trans* isomers, most of the Sn(IV) [3,4], Ti(IV) [5], Zr(IV) [6,7] and Hf(IV) [6,7] complexes adopt a *cis* octahedral configuration in solution. The dihalo bis(β-diketonato) germanium(IV) complexes [8] have been shown to exist as both *cis* and *trans* isomers. The stereochemistry of the simple zirconium derivatives are comparatively much more explored than those of the corresponding bimetallic complexes.

In the present communication, the synthesis and characterization of some β-diketonate and β-ketoester derivatives of $(OPr^i)_2Zr[Al(OPr^i)_4]_2$ are reported and attempts have been made to establish the existence of *cis* and *trans* isomeric forms on the basis of available spectroscopic data.

Experimental

Stringent precautions have been taken to exclude moisture from all the experimental procedures to avoid hydrolysis.

Acetylacetone, methylacetoacetate and ethylacetoacetate were dried by refluxing over aluminium isopropoxide and distillation (boiling point (b.p.) 135–137, 168–170 and 180 °C respectively). Benzoylacetone and dibenzoylmethane were used after distillation under reduced pressure.

Aluminium [10], zirconium isopropoxides [11] and $ZrAl_2(OPr^i)_{10}$ [12] were prepared according to the literature methods.

Zirconium and aluminium were estimated [13] as ZrO_2 and $(C_9H_6NO)_3Al$ respectively. Alcohol in azeotrope was determined by the oxidimetric method [14].

Molecular weights were determined ebullioscopically in benzene. IR spectra were recorded as neat, KBr or Nujol mulls in the range of 4000–200 cm^{-1} on a Perkin-Elmer 577 grating spectrophotometer using cesium iodide plates. ^{1}H and ^{13}C NMR spectra were recorded in CCl_4 or $CDCl_3$ solution on a Jeol FX 90Q NMR spectrometer using TMS as the internal standard. The ^{27}Al NMR were taken on a Brucker 360 MHz spectrometer using aluminium isopropoxide as reference.

Synthesis

β-Diketone and β-ketoester derivatives were synthesized during the course of the present investigations by the reactions of $ZrAl_2(OPr^i)_{10}$ with ligand moieties in different ratios (Table I). The details of only one representative reaction have been given.

Reaction of $ZrAl_2(OPr^i)_{10}$ with Acetylacetone in 1:4 Molar Ratio

On addition of acetylacetone (1.10 g, 11 mmol) to $ZrAl_2(OPr^i)_{10}$ (1.95 g, 2.65 mmol) in benzene (~40 ml); an exothermic reaction occurred. The reaction mixture was refluxed for ~3 h with the continuous

---

*Author to whom correspondence should be addressed.

TABLE I. Synthetic and Analytical Data of β-Diketone and β-Ketoester Derivatives of $(OPr^i)_2Zr[Al(OPr^i)_4]_2$

Reactants (g) (mmol)		Molar ratio	Product yield (%)[a]	PriOH (g) found (calc.)	Physical state volatility Melting point (°C/mm Hg)	Analysis (%) found (calc.)		Molecular weight found (calc.)
$ZrAl_2(OPr^i)_{10}$	$RCOCH_2COR'$ R, R' =					Zr	Al	
2.25 (3.06)	CH_3, CH_3 0.31 (3.11)	1:1	$ZrAl_2(OPr^i)_9(RCOCHCOR')$ 70*	0.18 (0.18)	Yellow viscous liquid 132/0.12	11.89 (11.76)	6.90 (6.97)	760 (775)
1.16 (1.57)	CH_3, CH_3 0.32 (3.20)	1:2	$ZrAl_2(OPr^i)_8(RCOCHCOR')_2$ 60*	0.18 (0.19)	Yellow viscous liquid 134/0.1	11.31 (11.18)	6.65 (6.62)	802 (815)
1.95 (2.65)	CH_3, CH_3 1.10 (11.0)	1:4	$ZrAl_2(OPr^i)_6(RCOCHCOR')_4$ 56*	0.62 (0.63)	Yellow viscous liquid 138/0.05	10.33 (10.19)	6.11 (6.03)	846 (895)
1.26 (1.71)	CH_3, CH_3 1.02 (10.20)	1:6	$ZrAl_2(OPr^i)_4(RCOCHCOR')_6$ 95	0.61 (0.61)	Light yellow solid 200–204	9.48 (9.35)	5.68 (5.53)	879 (975)
1.80 (2.44)	C_6H_5, CH_3 0.80 (4.93)	1:2	$ZrAl_2(OPr^i)_8(RCOCHCOR')_2$ 40*	0.26 (0.29)	Brown viscous liquid 142–145/0.2	10.10 (9.71)	5.72 (5.74)	–
1.74 (2.36)	C_6H_5, CH_3 1.54 (9.50)	1:4	$ZrAl_2(OPr^i)_6(RCOCHCOR')_4$ 97	0.57 (0.57)	Yellow foamy solid 105	8.00 (7.97)	4.80 (4.72)	1081 (1143)
1.19 (1.62)	C_6H_5, CH_3 1.58 (9.75)	1:6	$ZrAl_2(OPr^i)_4(RCOCHCOR')_6$ 97	0.56 (0.57)	Yellow foamy solid 225	6.88 (6.77)	3.94 (4.00)	–
1.81 (2.46)	C_6H_5, C_6H_5 1.10 (4.91)	1:2	$ZrAl_2(OPr^i)_8(RCOCHCOR')_2$ 98	0.30 (0.32)	Yellow sticky solid	9.70 (8.57)	4.92 (5.07)	–
1.18 (1.60)	C_6H_5, C_6H_5 1.45 (6.47)	1:4	$ZrAl_2(OPr^i)_6(RCOCHCOR')_4$ 98	0.38 (0.39)	Yellow solid 268–272	6.65 (6.55)	3.87 (4.03)	–
1.33 (1.81)	C_6H_5, C_6H_5 2.45 (10.94)	1:6	$ZrAl_2(OPr^i)_4(RCOCHCOR')_6$ 97	0.63 (0.65)	Yellow solid 280–285	5.45 (5.31)	3.12 (3.13)	–
1.77 (2.41)	CH_3, CH_3 0.58 (5.00)	1:2	$ZrAl_2(OPr^i)_8(RCOCHCOOR')_2$ 90*	0.28 (0.29)	Colourless viscous liquid 126/0.05	10.90 (10.76)	6.24 (6.37)	–
2.38 (3.24)	CH_3, CH_3 1.54 (13.27)	1:4	$ZrAl_2(OPr^i)_6(RCOCHCOOR')_4$ 86*	0.75 (0.77)	White solid 136–138/0.05	9.55 (9.47)	5.68 (5.60)	912 (963)
1.65 (2.24)	CH_3, CH_3 1.56 (13.44)	1:6	$ZrAl_2(OPr^i)_4(RCOCHCOOR')_6$ 84*	0.81 (0.80)	White solid 138–140/0.05	8.65 (8.51)	4.96 (5.04)	1006 (1065)
2.32 (3.15)	CH_3, C_2H_5 0.84 (6.46)	1:2	$ZrAl_2(OPr^i)_8(RCOCHCOOR')_2$ 90*	0.39 (0.39)	Colourless viscous liquid 133–136/0.20	10.64 (10.42)	6.10 (6.16)	–
1.55 (2.11)	CH_3, C_2H_5 1.13 (8.69)	1:4	$ZrAl_2(OPr^i)_6(RCOCHCOOR')_4$ 84*	0.51 (0.51)	White solid 145/0.10	9.04 (8.98)	5.24 (5.32)	957 (1015)
1.65 (2.24)	CH_3, C_2H_5 1.78 (13.69)	1:6	$ZrAl_2(OPr^i)_4(RCOCHCOOR')_6$ 82*	0.79 (0.80)	White solid 145–152/0.10	8.00 (7.89)	4.87 (4.67)	1097 (1155)

[a] Asterisk indicates distilled yield.

fractionation of isopropanol, liberated during the reaction between 72 and 80 °C. Removal of the solvent under reduced pressure yielded a yellow pasty mass which was distilled at 138 °C/0.05 mm to give a highly viscous yellow liquid which gradually solidified. (The azeotrope collected between 72–80 °C was found to contain 0.62 g isopropanol; calc. for 4 moles, 0.63 g.) *Anal.* Calc. for $ZrAl_2(OPr^i)_6(acac)_4$: Zr, 10.19; Al, 6.03. Found: Zr, 10.33; Al, 6.11%.

Results and Discussion

The reactions of zirconium diisopropoxide bis(tetraisopropoxyaluminate) with β-diketones and β-ketoesters were carried out in refluxing benzene solution in different stoichiometric ratios and can be represented by the following equations

$$(OPr^i)_2Zr[(\mu\text{-}OPr^i)_2Al(OPr^i)_2]_2 + Hacac \xrightarrow{C_6H_6} (OPr^i)_2Zr(\mu\text{-}OPr^i)_4Al_2(OPr^i)_3(acac) + Pr^iOH \qquad (1)$$

$$(OPr^i)_2Zr[(\mu\text{-}OPr^i)_2Al(OPr^i)_2]_2 + 2\beta\text{-}dk'H \xrightarrow{C_6H_6} (OPr^i)_2Zr[(\mu\text{-}OPr^i)_2Al(OPr^i)(\beta\text{-}dk')]_2 + 2Pr^iOH \qquad (2)$$

$$(OPr^i)_2Zr[(\mu\text{-}OPr^i)_2Al(OPr^i)_2]_2 + 4\beta\text{-}dk'H$$
$$C_6H_6 \begin{cases} \rightarrow (OPr^i)_2Zr[(\mu\text{-}OPr^i)_2Al(\beta\text{-}dk')_2]_2 \\ \rightarrow (\beta\text{-}dk')_2Zr[(\mu\text{-}OPr^i)_2Al(OPr^i)(\beta\text{-}dk')]_2 + 4Pr^iOH \end{cases} \qquad (3)$$

$$(OPr^i)_2Zr[(\mu\text{-}OPr^i)_2Al(OPr^i)_2]_2 + 6\beta\text{-}dk'H \xrightarrow{C_6H_6} (\beta\text{-}dk')_2Zr[(\mu\text{-}OPr^i)_2Al(\beta\text{-}dk')_2]_2 + 6Pr^iOH \qquad (4)$$

where β-dk′ = acetylacetone, benzoylacetone, dibenzoylmethane, methylacetoacetate and ethylacetoacetate.

All these compounds are either colourless or light yellow viscous liquids or white solids, soluble in common organic solvents like C_6H_6, CCl_4, $CHCl_3$ etc. except dibenzoylmethane derivatives which are found to be insoluble yellow powders. They all exhibit monomeric behaviour in refluxing benzene solution. In the case of β-diketone derivatives only $ZrAl_2(OPr^i)_9(acac)$, $ZrAl_2(OPr^i)_8(acac)_2$, $ZrAl_2(OPr^i)_6(acac)_4$ and $ZrAl_2(OPr^i)_8(bzac)_2$ could be volatilized whereas the remaining derivatives tend to decompose when heated even under reduced pressure. However, the corresponding β-ketoester derivatives show a volatile nature and undergo distillation in quantitative yields without any decomposition under reduced pressure.

IR Spectra

Infrared absorption frequences for the β-diketonate and β-ketoester derivatives of $ZrAl_2(OPr^i)_{10}$ were observed in the range 4000–200 cm^{-1} and are summarized in Table II. The bands due to ν(Al–O), ν(Zr–O) and isopropoxy groups were identified in the spectra of all these derivatives and assigned [15, 16]. The IR spectra of all these derivatives also exhibit two bands of strong intensity at 1600 ± 30 and 1530 ± 20 cm^{-1} due to ν(C···O) and ν(C···C) vibrations respectively. No bands were observed in the region 1650–1750 cm^{-1}, where ketonic carbonyl modes have been reported [17] for the keto form of the ligand, indicating the coordination of all the carbonyl groups to the metal atoms. In addition to the above, one more band at 1605 ± 5 cm^{-1} for ν(C=C) vibration has been observed in the case of benzylacetone and dibenzoylmethane derivatives.

NMR (^1H, ^{27}Al and ^{13}C) Spectra

The ^1H NMR spectrum of $ZrAl_2(OPr^i)_{10}$ exhibits three types of doublets for isopropoxy groups as reported previously [18].

^{27}Al NMR of $ZrAl_2(OPr^i)_{10}$ at 297 K in d_8-toluene gave a single broad peak at δ 61.94 ppm. At higher temperatures, 353 K, the peak is somewhat narrowed and observed at δ 59.75 ppm. The value of chemical shift is very similar to that of AlO_4^- resonance (δ 62.5 ppm) suggesting a tetrahedral environment for aluminium [19, 20].

The ^{13}C NMR spectrum of $ZrAl_2(OPr^i)_{10}$ also shows three signals having an intensity ratio of 2:1:2 for methyl and methine carbons of the isopropoxy groups, confirming the presence of three types of isopropoxy groups as observed in the ^1H NMR spectra. These may be assigned to methyl and methine carbons respectively for four bridging (δ 28.00, 72.06 ppm), two terminal (δ 26.54, 69.60 ppm) on zirconium and four terminal (δ 25.51, 63.00 ppm) isopropoxy groups on aluminium atoms.

$ZrAl_2(OPr^i)_9(acac)$

The spectrum of $ZrAl_2(OPr^i)_9(acac)$ exhibits three signals for $-CH_3$ and a multiplet for $-CH$ protons of the acetylacetone moiety alongwith a multiplet (δ 0.90–1.40 ppm) for methyl protons of the isopropoxy groups. Two signals of equal intensity at δ 1.90 and 1.80 ppm may be consistent [2, 8] with the presence of the *cis* isomer while the other signal at 1.90 ppm may be attributed to the *trans* isomer.

The ^{27}Al NMR chemical shift appears at δ −0.413 ppm and may be assigned to the penta-coordinated [9] aluminium atom because the band due to the tetrahedral aluminium atom has been observed at δ 61.94 ppm in the spectrum of $ZrAl_2(OPr^i)_{10}$. How-

TABLE II. Some Characteristic IR Absorption Frequencies (cm^{-1}) for β-Diketone and β-Ketoester Derivatives of $(OPr^i)_2Zr[Al(OPr^i)_4]_2$

Compound	ν(Zr–O)	ν(Al–O)	ν(O–Pr^i)	ν(C$\cdots$C) (C$^+$=C)	ν(C$\cdots$O)
$ZrAl_2(OPr^i)_9(CH_3COCHCOCH_3)$	559s 500–480brw	690m 670m 650w	1155vs, 1130vs, 1015vs, 945vs	1510vs	1580vs
$ZrAl_2(OPr^i)_8(CH_3COCHCOCH_3)_2$	495w 420w	690m 650m 600w	1190vs, 1170vs 1010s, 1950s	1520vs	1585vs
$ZrAl_2(OPr^i)_6(CH_3COCHCOCH_3)_4$	490s 415w	685m 660s	1170vs, 1020vs, 935vs	1525vs	1580vs
$ZrAl_2(OPr^i)_4(CH_3COCHCOCH_3)_6$	495vs 425s	695s 665s	1195vs, 1030vs, 940vs	1550vs	1600vs
$ZrAl_2(OPr^i)_8(C_6H_5COCHCOCH_3)_2$	515w 470s	710s 680s	1160vs, 1130vs, 1005bs, 955s	1520vs 1590vs	1560vs
$ZrAl_2(OPr^i)_6(C_6H_5COCHCOCH_3)_4$	570w 475s	720vs 700m 605w	1190m, 1120m 1035s, 975s	1540vs 1605vs	1575vs
$ZrAl_2(OPr^i)_4(C_6H_5COCHCOCH_3)_6$	520w 480m	720vs 700m 600w	1115m, 1035s, 1015s, 970s	1535vs 1605vs	1575vs
$ZrAl_2(OPr^i)_6(C_6H_5COCHCOC_6H_5)_4$	540m 480m	730vs 700vs 640s	1190m, 1145w, 1035vs, 1010m, 955s	1540vs 1610vs	1560vs
$ZrAl_2(OPr^i)_4(C_6H_5COCHCOC_6H_5)_6$	540m 475m	730vs 695vs 640s	1190m, 1150m, 1035vs, 1010m, 955s	1540vs 1610vs	1565vs
$ZrAl_2(OPr^i)_8(CH_3COCHCOOCH_3)_2$	530s 490m	720vs 695s 625m	1190vs, 1170vs, 1055vs, 1010vs, 950vs	1545vs	1640vs
$ZrAl_2(OPr^i)_6(CH_3COCHCOOCH_3)_4$	510s 480w	740s 630s 600w	1180vs, 1070vs, 1020vs, 960s	1540vs	1630vs
$ZrAl_2(OPr^i)_4(CH_3COCHCOOCH_3)_6$	500m 440w	725m 705m 610m	1180m, 1160vs 1050vs, 1010vs	1520vs	1610vs
$ZrAl_2(OPr^i)_8(CH_3COCHCOOC_2H_5)_2$	570s 460m	710s 635m 620m	1180vs, 1140m 1025vs, 985m	1540vs	1625vs
$ZrAl_2(OPr^i)_6(CH_3COCHCOOC_2H_5)_4$	530s 470m	645s 610m	1195vs, 1070s, 1090vs, 1035vs, 935s	1545vs	1630vs
$ZrAl_2(OPr^i)_4(CH_3COCHCOOC_2H_5)_6$	500br.m 465m	635s 605m	1185vs, 1075vs 1025vs, 925s	1535vs	1630vs

ever, the presence of only one signal indicates that the ligand moiety is in a dynamic equilibrium between the two aluminium atoms (Fig. 1).

$ZrAl_2(OPr^i)_8(acac)_2$ and $ZrAl_2(OPr^i)_8(CH_3COCHCOOCH_3)_2$

The spectrum of $ZrAl_2(OPr^i)_8(CH_3COCHCOOCH_3)_2$ shows a prominent doublet (δ 1.84–1.87

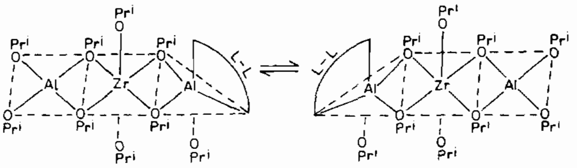


Fig. 1. Structure of $ZrAl_2(OPr^i)_9(acac)$ (L-L = $CH_3COCHCOCH_3$).

TABLE III. ^1H NMR Spectral Data for β-Diketone Derivatives of $(Pr^iO)_2Zr[Al(OPr^i)_4]_2$

Compound	$-C(CH_3)_2$	Chemical shifts δ (ppm)			
		$-CH_3$	$-OCH$	$=CH$	$-C_6H_5$
$ZrAl_2(OPr^i)_9(CH_3COCHCOCH_3)$	0.90–1.40m(54H)	1.80 1.90 (6H) 1.95	3.70–4.50m(9H)	5.20–5.50m(1H)	–
$ZrAl_2(OPr^i)_8(CH_3COCHCOCH_3)_2$	1.08–1.40m(48H)	1.87–1.91d 1.99s(12H)	4.02–4.48m (8H)	5.32–5.58m (2H)	–
$ZrAl_2(OPr^i)_6(CH_3COCHCOCH_3)_4$	0.85–1.10m(36H)	1.65, 1.70 1.75, 1.85 (24H)	3.75–4.30m (6H)	5.10–5.40m (4H)	–
$ZrAl_2(OPr^i)_4(CH_3COCHCOCH_3)_6$	1.06–1.16d(24H)	1.85s(36H)	3.66–4.20m (4H)	5.36s(6H)	–
$ZrAl_2(OPr^i)_8(C_6H_5COCHCOCH_3)_2$	1.08–1.39m(48H)	2.15s(6H)	4.08–4.28m (8H)	6.10s(2H)	7.23–7.34m (10H)
$ZrAl_2(OPr^i)_6(C_6H_5COCHCOCH_3)_4$	0.93–1.06d(36H)	2.03s(12H)	3.66–4.06m (6H)	6.06s(4H)	7.06–7.81m (20H)
$ZrAl_2(OPr^i)_4(C_6H_5COCHCOCH_3)_6$	1.00–1.12d(24H)	2.01s(18H)	3.61–4.06m (4H)	6.06s(6H)	7.09–7.83m (30H)

ppm) along with other poorly resolved signals (δ 1.89, 1.93, 1.95 ppm) for $-CH_3$ protons, whereas six signals (δ 3.59, 3.64, 3.68, 3.72, 3.77 and 3.81 ppm) for $-OCH_3$ and six signals (δ 4.87, 4.89, 4.90, 4.94, 4.98 and 5.01 ppm) for $-CH$ protons of the ligand moieties have been observed.

In view of the assymetry of the ligand, a *cis* diisopropoxy configuration should give rise to three geometric isomers [1, 8]; two of the isomers have C_2 symmetry and the third has C_1 symmetry while *trans* diisopropoxy configuration gives two isomers with point group symmetries of C_{2h} and C_{2v}. If all the five isomers are present in an equilibrium mixture then the $-CH_3$, $-OCH_3$ and $=CH$ regions of the NMR spectrum [8] should contain six resonance lines. However, the presence of only five signals for $-CH_3$ protons may be due to coalescence of two signals into one.

The proton NMR spectrum of $ZrAl_2(OPr^i)_8(acac)_2$ in $CDCl_3$ shows a doublet and a singlet for $-CH_3$ protons of the ligand moiety (Table III). The doublet may be assigned to the *cis* configuration [8] while the remaining singlet strongly suggests the presence of a *trans* isomer.

The ^{27}Al NMR spectrum of $ZrAl_2(OPr^i)_8(acac)_2$ exhibits a narrow signal (Fig. 2) of high intensity with a chemical shift of δ +3.16 ppm, corresponding to the octahedrally coordinated aluminium [19–21].

^{13}C NMR spectra of these compounds exhibit the signals due to methyl carbons of the isopropoxy groups as well as those of the ligand moieties in the region δ 23.73–27.98 ppm as a complex multiplet [23–25]. The same complexity has also been observed in the signals due to $-OCH$ and $=CH$ carbons.

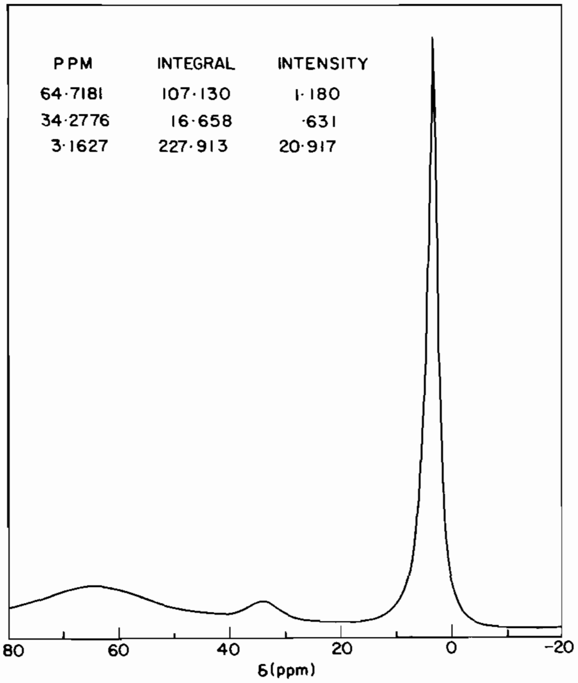


Fig. 2. ^{27}Al NMR spectrum of $ZrAl_2(OPr^i)_8(acac)_2$.

In the case of $ZrAl_2(OPr^i)_8(acac)_2$ four resonances due to $C{\cdot\cdot}O$ groups have been observed in the region δ 189.18–192.69 ppm indicating the coordination of the keto groups of the ligand moieties with the metal atom [23–25]. In the case of $ZrAl_2(OPr^i)_8(CH_3COCHCOOCH_3)_2$, two types of signals were observed for $C\overset{\cdots}{-}O$ and $O-C\overset{\cdots}{-}O$ at δ 186.76 and 174.82 ppm, respectively. The multiplicity of the signals in

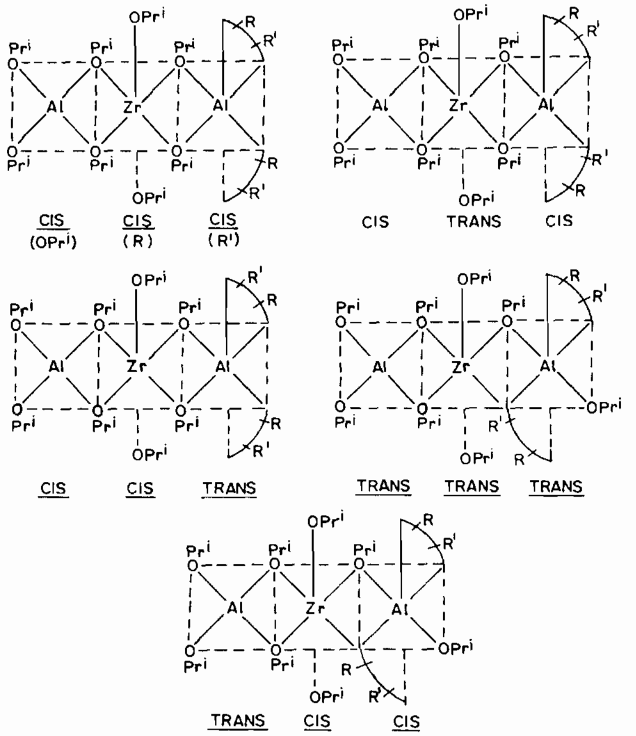


Fig. 3. Structure of $ZrAl_2(OPr^i)_8(RCOCHCOR')$ where R = CH_3, R' = CH_3, OCH_3, OC_2H_5.

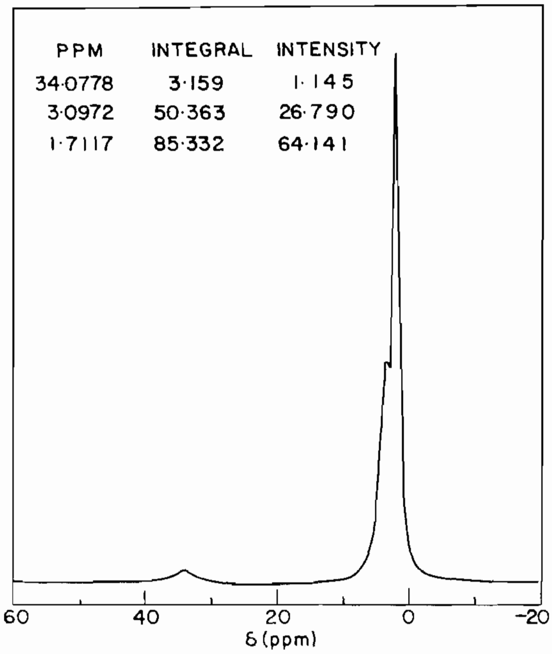
^{13}C NMR spectra also reveals the presence of different geometric isomers, showing their identity at room temperature. Thus different geometrical isomers may be postulated for $ZrAl_2(OPr^i)_8(\beta\text{-dik})_2$ and $ZrAl_2(OPr^i)_8(\beta\text{-ketoester})_2$ derivatives (Fig. 3).

$ZrAl_2(OPr^i)_6(acac)_4$, $ZrAl_2(OPr^i)_6(CH_3COCHCOOCH_3)_4$ and $ZrAl_2(OPr^i)_6(CH_3COCHCOOC_2H_5)_4$

The spectra show four resonance lines each due to $-CH_3$, $-OCH_3$ and $=CH$ protons of the ligand moieties which can also be explained on the basis of the existence of both *cis* and *trans* isomers. The replacement of the isopropoxy groups may take place on both of the metals.

The ^{27}Al NMR spectrum recorded for $ZrAl_2(OPr^i)_6(acac)_4$ shows two signals at δ 1.71 and 3.09 ppm (Fig. 4). The signal with a chemical shift of δ +3.09 ppm suggests an octahedral coordination for aluminium [19–22]. The second signal with a chemical shift of δ +1.71 ppm may be assigned to the penta-coordinated aluminium. Thus, in the compound $ZrAl_2(OPr^i)_6(acac)_4$, an equilibrium appears to exist between these two forms (Fig. 5).

^{13}C NMR spectra of these derivatives show all the characteristic signals due to $-CH_3$, $-OCH_3$, $-OCH_2$, O–CH, =CH, C$\overset{\cdot\cdot}{-}$O and $-O-C\overset{\cdot\cdot}{-}O$ carbons and are summarized in Table IV. However the splitting to the signals is greatly reduced here in comparison to the derivatives like $ZrAl_2(OPr^i)_8(acac)_2$ etc. described earlier.



PPM	INTEGRAL	INTENSITY
34·0778	3·159	1·145
3·0972	50·363	26·790
1·7117	85·332	64·141

Fig. 4. ^{27}Al NMR spectrum of $ZrAl_2(OPr^i)_6(acac)_4$.

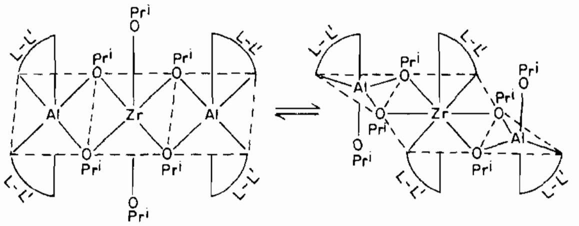


Fig. 5. Structure of $ZrAl_2(OPr^i)_6(acac)_4$; L-L = $CH_3COCHCOCH_3$.

$ZrAl_2(OPr^i)_4(acac)_6$, $ZrAl_2(OPr^i)_4(CH_3COCHCOOCH_3)_6$ and $ZrAl_2(OPr^i)_4(CH_3COCHCOOC_2H_5)_6$

A doublet for bridging isopropoxy groups in the range δ 1.14–1.20 ppm has been observed in the spectra of these derivatives. The other proton signals due to β-diketone and β-ketoester moieties are observed at their usual positions and are summarized in Tables III and V respectively. The β-ketoester protons attached to aluminium and zirconium appear separately as the NMR spectrum of $ZrAl_2(OPr^i)_4(CH_3COCHCOOCH_3)_6$ shows two doublets for $-CH_3$ protons of the ligand moieties at (δ 1.83–1.87 ppm) and (δ 1.93–1.96 ppm) respectively with the intensity ratio of 1:2.5. Thus, the low intensity doublet may be assigned to the methyl protons of the ligand moieties attached to the zirconium atom. Similarly two doublets each for $-OCH_3$ and $=CH$ protons have been observed. The presence of a

TABLE IV. ^{13}C NMR Spectral Data (δ ppm) of some β-Diketone and β-Ketoester Derivatives of $(OPr^i)_2Zr[Al(OPr^i)_4]_2$

Compound	$(CH_3)_2C-$, $-CH_3$,	$-OCH_3$ or $-OCH_2$	$-OCH$	$=CH$	$\underset{\substack{\vert \\ O}}{C}\cdots O$	$C\cdots O$
$ZrAl_2(OPr^i)_{10}$	25.51		63.08 69.60 72.26			
$ZrAl_2(OPr^i)_8(acac)_2$	23.73–27.98m		62.57–71.80m	100.30– 103.01m		189.18 190.21 191.30 192.69
$ZrAl_2(OPr^i)_6(acac)_4$	26.32, 26.48		63.18 70.26	100.21 100.43		189.98
$ZrAl_2(OPr^i)_8(CH_3COCHCOOCH_3)_2$	24.27–27.92m	51.51 52.53	62.87–71.95m	84.25 85.50 87.62 89.23	173.57 173.89	184.71 186.76
$ZrAl_2(OPr^i)_6(CH_3COCHCOOCH_3)_4$	23.73–27.76m	51.50	63.67 65.94 66.67 70.63	84.04 84.84 85.06 87.48	173.94	187.65
$ZrAl_2(OPr^i)_4(CH_3COCHCOOCH_3)_6$	25.19 25.73 26.28	50.33 50.55	69.83	83.38 83.70 84.03 80.46	173.20 173.41	186.31 186.74
$ZrAl_2(OPr^i)_6(CH_3COCHCOOC_2H_5)_4$	14.51, 23.72 25.62, 26.00 26.48	51.02	59.47 63.38 66.46 70.47	84.29 84.36 88.08	172.43 173.40	184.78 184.96
$ZrAl_2(OPr^i)_4(CH_3COCHCOOC_2H_5)_6$	14.35, 21.88 26.00, 26.54	51.08	59.91	84.39 84.77	173.62 173.89	187.00 187.38

TABLE V. ^{1}H NMR Spectral Data of β-Ketoester Derivatives of $(Pr^iO)_2Zr[Al(OPr^i)_4]_2$

Compound	Chemical shift δ (ppm)				
	$-C(CH_3)_2$	$-CH_3$	$-OCH_3$ or $-CH_2$	$-OCH$	$=CH$
$ZrAl_2(OPr^i)_8(CH_3COCHCOOCH_3)_2$	1.08–1.40m (48H)	1.84–1.87d 1.89, 1.93 1.95 (6H)	3.59, 3.64 3.68, 3.72 3.77, 3.81 (6H)	4.02–4.55m (8H)	4.84, 4.89, 4.89, 4.90 4.98, 5.01 (2H)
$ZrAl_2(OPr^i)_6(CH_3COCHCOOCH_3)_4$	1.09–1.22m (36H)	1.83, 1.86 1.93, 1.96 (12H)	3.64, 3.67 3.76, 3.80 (12H)	4.04–4.32 (6H)	4.84–4.92m (4H)
$ZrAl_2(OPr^i)_4(CH_3COCHCOOCH_3)_6$	1.14–1.20d (24H)	1.83–1.87d 1.93–1.96d (18H)	3.62, 3.64, 3.67, 3.70 (18H)	4.08–4.34m (4H)	4.89–4.96d 4.99–5.00d (6H)
$ZrAl_2(OPr^i)_8(CH_3COCHCOOC_2H_5)_2$	1.09–1.36m (54H)	1.80, 1.84 1.87, 1.89 1.93, 1.96 (6H)	3.59, 3.64 3.68, 3.72 3.77, 3.82 (4H)	4.02–4.45m (8H)	4.83, 4.88 4.94, 4.96 5.01, 5.05 (2H)

(continued)

TABLE V. *(continued)*

Compound	Chemical shift δ (ppm)				
	$-C(CH_3)_2$	$-CH_3$	$-OCH_3$ or $-CH_2$	$-OCH$	$=CH$
$ZrAl_2(OPr^i)_6(CH_3COCHCOOC_2H_5)_4$	1.09–1.21m (48H)	1.83, 1.87 1.94, 1.96 (12H)	3.64, 3.67 3.70, 3.77 (8H)	4.06–4.34m (6H)	4.87, 4.89 4.94, 4.96 (4H)
$ZrAl_2(OPr^i)_4(CH_3COCHCOOC_2H_5)_6$	1.14–1.20d (42H)	1.83–1.87d 1.93–1.96d (18H)	3.62, 3.64 3.67, 3.70 (12H)	4.02–4.36m (4H)	4.92, 4.89 4.96, 5.00 (6H)

doublet may be associated with the *cis* arrangement [4–6] of the ligand species to the metal atom.

The ^{27}Al NMR spectrum of $ZrAl_2(OPr^i)_4(CH_3COCHCOOCH_3)_6$ shows only one signal at δ +4.58 ppm which indicates that the aluminium atoms achieve a hexa-coordination.

Acknowledgements

One of the authors (R.J.) is grateful to the University Grants Commission, New Delhi for providing financial assistance.

References

1 R. C. Mehrotra, R. Bohra and D. P. Gaur, 'Metal β-Diketonates and Allied Derivatives', Academic Press, London, 1978.
2 R. C. Fay and R. N. Lowry, *Inorg. Chem., 9,* 2048 (1970).
3 J. A. S. Smith and E. J. Wilkins, *J. Chem. Soc. A,* 1749 (1966).
4 J. W. Faller and A. Davison, *Inorg. Chem., 6,* 182 (1967).
5 R. C. Fay and R. N. Lowry, *Inorg. Chem., 6,* 1512 (1967).
6 T. J. Pinnavaia and R. C. Fay, *Inorg. Chem., 7,* 502 (1968).
7 R. C. Fay and T. J. Pinnavaia, *Inorg. Chem., 7,* 508 (1968).
8 T. J. Pinnavaia, B. J. Matienzo and Y. A. Peters, *Inorg. Chem., 9,* 993 (1970).
9 R. Jain, A. K. Rai and R. C. Mehrotra, *Polyhedron, 5,* 1017 (1986).
10 H. Adkins, *J. Am. Chem. Soc., 44,* 2178 (1922).
11 D. C. Bradley, R. C. Mehrotra and W. Wardlaw, *J. Chem. Soc.,* 2027 (1952).
12 D. C. Bradley, R. C. Mehrotra and D. P. Gaur, 'Metal Alkoxides', Academic Press, London, 1978.
13 A. I. Vogel, 'A Text Book of Quantitative Inorganic Analysis', ELBS and Longmans, 1973.
14 R. C. Mehrotra, *J. Ind. Chem. Soc., 30,* 585 (1953).
15 D. C. Bradley and A. H. Westlake, 'Proc. Symp. Coord. Chem., Tihany, Hungary', Hungarian Acad. Sci., Budapest, 1965.
16 C. G. Barraclough, D. C. Bradley, J. Lewis and I. M. Thomas, *J. Chem. Soc.,* 2601 (1961).
17 J. Lewis, R. F. Long and C. Oldham, *J. Chem. Soc.,* 6740 (1965).
18 R. Jain, A. K. Rai and R. C. Mehrotra, *Synth. React. Inorg. Met.-Org. Chem., 15,* 789 (1985).
19 J. W. Akitt and A. Farthing, *J. Chem. Soc., Dalton Trans.,* 1624 (1981).
20 J. W. Akitt and G. Gessner, *J. Chem. Soc., Dalton Trans.,* 147 (1984).
21 J. W. Akitt and A. Farthing, *J. Chem. Soc., Dalton Trans.,* 1615 (1981).
22 S. J. Karlik, E. Tarien, G. A. Elgavish and G. L. Eichhorn, *Inorg. Chem., 22,* 525 (1983).
23 J. C. Hamwel and J. A. S. Smith, *J. Chem. Soc. A,* 2883 (1969).
24 D. T. Haworth and C. A. Wilkie, *Inorg. Nucl. Chem. Lett., 13,* 485 (1977).
25 C. A. Wilkie, G. Y. Lin and D. T. Haworth, *J. Inorg. Nucl. Chem., 40,* 1009 (1978).