Synthesis, Reactivity, Magnetic & Spectral Studies of Some Bimetallic Alkoxides of Iron(III) with Zirconium

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A novel bimetallic alkoxide of iron(III) with zirconium, $\text{[Fe\{Zr}_3\text{OPr}\}$_9$\text{]}$ has been synthesized and its alcohol interchange reactions have been studied. Structures of these new alkoxide derivatives have been elucidated by magnetic and spectral (UV, IR and ESR) studies.

The bimetallic alkoxides of iron have not received as much attention as the simple alkoxides of iron$^1$. The formation of a bimetallic 'ate' complex of the type $\text{Na\{Fe(OEt)4\}}$ was first suggested$^2$ during the titration of $\text{Fe(OEt)3}$ with $\text{NaOEt}$ using thymolphthalein as indicator. Later two siloxides of the types $\text{Na\{Fe(OSiMe3)4\}}$ (ref. 3) and $\text{[SbMe4\{Fe(OSiMe3)4\}}$ (ref. 4) and a bimetallic alkoxide, $\text{K}_3\text{Fe(OEt)6}$ (ref. 5) of iron were also reported. The first X-ray crystal structural elucidation of a bimetallic alkoxide of iron(III), $\text{Li\{Fe(OCHBu)4\}}\cdot\text{BuCHOH}$ has been recently made by Wilkinson and coworkers$^6$. Recently a few tetraalkoxylaluminates of iron have been synthesized in our laboratories$^7$. In continuation of our earlier investigations on the bimetallic alkoxide chemistry$^1,8$ especially of later 3d transition metals$^9-11$, we have now synthesized and characterized a number of new and interesting iron(III) tris-dizirconium enneaalkoxides and some other new bimetallic iron-zirconium isopropoxides.

Materials and Methods

Infrared spectra were recorded on a Perkin-Elmer model 557 instrument, reflectance spectra, (in nujol) on a Beckman DK 2 spectrophotometer and ESR spectrum on a X-band JEOL instrument. The variable temperature magnetic data were recorded on a magnetic balance at TIFR, Bombay, and the room temperature data on a Brucker magnetic balance. Zirconium was estimated as oxide after precipitation as mandelate. Iron was estimated colorimetrically as ferric thiocyanate on a Bausch and Lomb Spectronic 21. Alkoxy groups were estimated by dichromate oxidation$^{12}$.

**Synthesis of compounds**

For brevity, one typical reaction of each type is given and further details for other derivatives are presented in Table 1.

(a) **Preparation of iron(III) tris (dizirconium enneaalkoxide) (I)**

To a solution of freshly sublimed ferric chloride (0.29 g, 1.79 mmol) in benzene, potassium dizirconium

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Alcohol taken</th>
<th>Product (Yield. ° in distilled product)</th>
<th>Found (Calc)%</th>
<th>Temp. °C/mm</th>
<th>$\mu_{eff}$ at 295 K</th>
<th>Colour &amp; appearance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>$\text{Fe{Zr}_3\text{OPr}}$_9$\text{]}$ (IIIa)</td>
<td>58.0 (58.1) 38.2 (38.0) 4.2 (3.9) 5.12</td>
<td>Yellow brown solid</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.</td>
<td>MeOH (excess)</td>
<td>$\text{[Fe{Zr}_3\text{OMe}}$_9$\text{]}$ (IIIa)</td>
<td>67.3 (67.3) 29.9 (29.7) 3.2 (3.0)</td>
<td>160/0.2</td>
<td>5.02 Brown solid</td>
<td></td>
</tr>
<tr>
<td>2.</td>
<td>EtOH (excess)</td>
<td>$\text{[Fe{Zr}_3\text{OEt}}$_9$\text{]}$ (IIib)</td>
<td>67.3 (67.3) 29.9 (29.7) 3.2 (3.0)</td>
<td>160/0.2</td>
<td>5.06 Brown solid</td>
<td></td>
</tr>
<tr>
<td>3.</td>
<td>Pr$^3$OH (excess)</td>
<td>$\text{[Fe{Zr}_3\text{OPr}$$_3$}$_9$\text{]}$ (IIIC)</td>
<td>67.3 (67.3) 29.9 (29.7) 3.2 (3.0)</td>
<td>160/0.2</td>
<td>5.06 Brown solid</td>
<td></td>
</tr>
<tr>
<td>4.</td>
<td>Bu$^3$OH (excess)</td>
<td>$\text{[Fe{Zr}_3\text{OBu}$$_3$}$_9$\text{]}$ (IIID)</td>
<td>67.3 (67.3) 29.9 (29.7) 3.2 (3.0)</td>
<td>160/0.2</td>
<td>5.06 Brown solid</td>
<td></td>
</tr>
<tr>
<td>5.</td>
<td>Bu$^3$OH (excess)</td>
<td>$\text{[Fe{Zr}_3\text{OBu}$$_3$}$_9$\text{]}$ (IIIE)</td>
<td>67.3 (67.3) 29.9 (29.7) 3.2 (3.0)</td>
<td>160/0.2</td>
<td>5.06 Brown solid</td>
<td></td>
</tr>
<tr>
<td>6.</td>
<td>Bu$^3$OH (excess)</td>
<td>$\text{[Fe{Zr}_3\text{OPr}$$_3$}$_9$\text{]}$ (IIIF)</td>
<td>67.3 (67.3) 29.9 (29.7) 3.2 (3.0)</td>
<td>160/0.2</td>
<td>5.06 Brown solid</td>
<td></td>
</tr>
<tr>
<td>7.</td>
<td>Am$^3$OH (excess)</td>
<td>$\text{[Fe{Zr}_3\text{OPr}$$_3$}$_9$\text{]}$ (IIIG)</td>
<td>67.3 (67.3) 29.9 (29.7) 3.2 (3.0)</td>
<td>160/0.2</td>
<td>5.06 Brown solid</td>
<td></td>
</tr>
</tbody>
</table>

The synthesis of iron-zirconium bimetallic alkoxides is an expanding field of research, and the present communication reports the synthesis and characterization of a novel tris-dizirconium enneaalkoxide of iron(III).
enneaaisopropoxide [prepared from potassium (0.21 g, 5.38 mmol) and zirconium isopropoxide isopropanolate (4.14 g, 10.68 mmol)] was added and the reaction mixture, refluxed. A quantitative amount of KCl (0.40 g, 5.37 mmol) which separated out was filtered off, the filtrate concentrated under reduced pressure and the product distilled at 165°/0.2 mm to afford the title compound as a brown solid (Found: PrDH, 72.4; Zr, 25.1; Fe, 2.8. Reqd.: PriOH, 72.6; Zr, 24.9; Fe, 2.5%).

(b) Preparation of \([\text{Fe} (\text{OPr})_4]_2 \cdot 2(\text{Zr(OPr)}_2)\)

To a solution of freshly distilled ferric isopropoxide (2.51 g, 10.77 mmol) in benzene, zirconium isopropoxide isopropanolate (2.10 g, 5.42 mmol) was added in (2:1) stoichiometric ratio and the clear solution obtained was refluxed for 6-8 hr. The solvent was stripped off under reduced pressure; the residual mass, dried and distilled at 155°/0.2 mm to afford the desired compound as a dark brown viscous liquid, yield 65% (2.48 g) (Found: PrOH, 74.5; Zr, 11.8; Fe, 14.6. Reqd.: PrOH, 74.4; Zr, 11.5; Fe, 14.1%); \(\mu_{\text{eff}}\) 5.14 B.M., IR: 425, 370 (\(\nu\text{Fe-O}\)), 560 (\(\nu\text{Zr-O}\)); and 955, 1020 cm \(^{-1}\) (\(\nu\text{M(O-C)}\)).

Alcohol interchange reactions
(a) Preparation of \([\text{Fe} (\text{Zr}(\text{OPr})_2(\text{OBu})_6)]\) (Va) (under refluxing conditions)

Interaction of I (1.08 g) with excess of n-butanol under refluxing condition resulted in a mixed alkoxide complex (1.21 g). The solvent was stripped off under reduced pressure; the product was finally dried and distilled at 168°/0.2 mm.

(b) Preparation of \([\text{Fe} (\text{Zr}(\text{OBu})_4)]\) (IIIe) (with continuous azeotropic fractionation)

A benzene solution of I (2.18 g) was refluxed with excess of s-butanol (~40 ml) with continuous azeotropic removal of liberated isopropanol with benzene. The solvent was stripped off under reduced pressure, the product (2.47 g) dried under reduced pressure and distilled at 172°/0.2 mm.

Results and Discussion
Freshly sublimed ferric chloride reacts with potassium dizirconium enneaaisopropoxide in 1:3 stoichiometric ratio in benzene to afford \([\text{Fe} (\text{Zr}(\text{OPr})_3)]\) (I) in accordance with Eq. (1):

\[
\text{FeCl}_3 + 3\text{K}[\text{Zr}_2(\text{OPr})_6] \rightarrow \text{[Fe} (\text{Zr}(\text{OPr})_3)] + 3\text{KCl} \quad (1)
\]

In our attempts to synthesize bimetallic isopropoxides of iron and zirconium by heating the isopropoxides of the individual metals in different molar ratios, we have isolated another type of bimetallic isopropoxide having the composition, \([\text{Fe}_2\text{Zr}(\text{OPr})_3]_2\) (II) by the interaction of ferric isopropoxide with zirconium isopropoxide isopropanolate in 2:1 molar ratio in benzene (Eq. 2):

\[
2\text{Fe(OPr)}_3 + \text{Zr(OPr)}_3 \cdot \text{PriOH} \rightarrow \text{Fe}_2\text{Zr(OPr)}_3 \cdot 2\text{PriOH} \quad (2)
\]

Both the above bimetallic alkoxides (I and II) are volatile, soluble in common organic solvents and are monomeric.

However, when reaction (I) was carried out in isopropanol instead of benzene, \([\text{Fe} (\text{Zr}(\text{OPr})_3)]\) appeared to disproportionate in accordance with Eq. (3), into ferric isopropoxide and zirconium isopropoxide isopropanolate which crystallized out of the solution probably because of its lower solubility in isopropanol in contrast to that of I:

\[
\text{FeCl}_3 + 3\text{K}[\text{Zr}_2(\text{OPr})_6] \rightarrow \text{Fe(OPr)}_3 + \text{Zr(OPr)}_3 \cdot \text{PriOH} + 3\text{KCl} \quad (3)
\]

Further confirmation of the lower solubility of Zr(OPr)_3· PriOH was provided by the fact that it crystallized out when I was dissolved in a minimum quantity of isopropanol and refluxed.

Alcohol interchange reactions
The reactions of I with different alcohols have been carried out and are illustrated by the following equations:

(i) Reactions with primary and secondary alcohols (Eq. 4): The interaction of I with methanol in benzene was facile (stirring for 12-14 hr) and resulted in an insoluble methoxy derivative (IIa) at room temperature. Under refluxing conditions, the reaction was faster:

\[
\text{I} + 27\text{MeOH} \rightarrow \text{[Fe} (\text{Zr}(\text{OR})_3)] + 27\text{PriOH} \quad (4)
\]

Similar reaction with ethanol under reflux led to the product IIIb.

In contrast, the reactions with normal and secondary butanols at room temperature (12-14 hr stirring) resulted in mixed alkoxy derivatives IVa and IVb (Eq. 5):

\[
\text{I} + 9\text{ROH} \rightarrow \text{[Fe} (\text{Zr}(\text{OR})_3)] + 9\text{PriOH} \quad (5)
\]

Refluxing the above reaction mixture for about 12 hr yielded products Va (R = n-butyl) and Vb (R = s-butyl) in accordance with Eq. (6):

\[
\text{I} \rightarrow \text{[Fe} (\text{Zr}(\text{OPr})_3)] + 21\text{PriOH} \quad (6)
\]
The reaction of I with n-propyl, n-butyl and s-butyl in refluxing benzene with azeotropic fractionation of the liberated isopropanol led to a total replacement of the isopropoxy groups to give products IIIc-e [(c), R = n-Pr, (d), R = n-Bu; and (e), R = s-Bu].

(ii) Reactions with tertiary alcohols: The alcohol interchange reactions of \([\text{Fe}\{\text{Zr}_2\text{(OPr)}_9\}_3]\) (I) with tertiary alcohols such as \(t\)-butanol and \(t\)-amyl alcohol were much less facile; even continuous azeotropic removal of the liberated isopropanol from the reaction mixtures resulted in mixed alkoxide derivatives \(\text{Vc}(R = t-Bu)\) and \(\text{Vd}(R = t-Am)\) having the composition, \([\text{Fe}\{\text{Zr}_2\text{(OPr)}_2\text{(OR)}_7\}_3]\). However, the reaction with \(t\)-amyl alcohol, was even slower (~ 32 hr for completion) than with \(t\)-butanol (~ 26 hr for completion).

**Electronic spectral studies**

The reflectance spectra exhibited \(d-d\) transitions in the region 4-14 \(\times 10^3\) cm\(^{-1}\). The bands in the region 4-8 \(\times 10^3\) cm\(^{-1}\) may be due to infrared overtones. The bands at 9,300 and 13,100 cm\(^{-1}\) could be assigned to the spin forbidden \(d-d\) transitions, \(^6A_1 \rightarrow 4^2T_1\) and \(^6A_1 \rightarrow 4^4T_2\), respectively in an octahedral environment of iron\(^{15-17}\).

**ESR spectral studies**

In a weak octahedral field, the lowest state \(^6A_1\) of Fe\(^{3+}\) splits into one four-fold \((T_8)\) and one two-fold \((T_2)\) levels. If an axial field is also present, an additional splitting of the four-fold \(T_8\) level occurs. Thus the \(^6A_1\) level is finally resolved into three Kramers' doublets. The ESR spectrum of Fe\(^{3+}\) \((d^6)\) in an octahedral geometry such as \(\text{Fe(H}_2\text{O})_6^{3+}\) has been characterized by an intense signal\(^{18}\) with \(g \approx 4.3\). The intense band with \(g = 4.18\) observed in the ESR spectrum of complex(I) may be associated with an octahedral geometry around Fe(III).

### Table 2—Variable Temperature Magnetic Studies of \([\text{Fe}\{\text{Zr}_2\text{(OPr)}_9\}_3]\) (I)

<table>
<thead>
<tr>
<th>Sl. No.</th>
<th>Temp. (K)</th>
<th>(\chi_s \times 10^6)</th>
<th>(\chi_m \times 10^6)</th>
<th>(\chi_{\text{M.S.}} \times 10^6)</th>
<th>(\mu_{\text{eff.}}) (B.M.)</th>
</tr>
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<tbody>
<tr>
<td>1</td>
<td>14.6</td>
<td>58.871</td>
<td>125051</td>
<td>126725</td>
<td>3.62</td>
</tr>
<tr>
<td>2</td>
<td>15.0</td>
<td>53.079</td>
<td>116715</td>
<td>117399</td>
<td>3.66</td>
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<tr>
<td>3</td>
<td>20.0</td>
<td>40.368</td>
<td>89203</td>
<td>90427</td>
<td>3.66</td>
</tr>
<tr>
<td>4</td>
<td>22.2</td>
<td>34.009</td>
<td>74781</td>
<td>76005</td>
<td>3.67</td>
</tr>
<tr>
<td>5</td>
<td>25.6</td>
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<td>65834</td>
<td>3.67</td>
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<td>6</td>
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<td>25.781</td>
<td>56690</td>
<td>57914</td>
<td>3.70</td>
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<td>49673</td>
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<td>8</td>
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<td>42001</td>
<td>3.69</td>
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<tr>
<td>9</td>
<td>40.9</td>
<td>18.604</td>
<td>32924</td>
<td>34149</td>
<td>3.69</td>
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<tr>
<td>10</td>
<td>45.9</td>
<td>16.511</td>
<td>25208</td>
<td>16432</td>
<td>4.22</td>
</tr>
<tr>
<td>11</td>
<td>52.0</td>
<td>5.231</td>
<td>10913</td>
<td>12137</td>
<td>4.63</td>
</tr>
<tr>
<td>12</td>
<td>295.0</td>
<td>4.322</td>
<td>9508.9</td>
<td>10728</td>
<td>5.03</td>
</tr>
</tbody>
</table>

### Table 3—Infrared Spectral Data of Bimetallic Alkoxides of Iron(II)

<table>
<thead>
<tr>
<th>Compounds</th>
<th>(\nu\text{Fe-O})</th>
<th>(\nu\text{Zr-O})</th>
<th>(\nu(\text{C-O}))</th>
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</thead>
<tbody>
<tr>
<td>I</td>
<td>445,415</td>
<td>560</td>
<td>1012,1120,1160</td>
</tr>
<tr>
<td>IIa</td>
<td>455,395</td>
<td>585</td>
<td>975,940,1063</td>
</tr>
<tr>
<td>IIb</td>
<td>465,410</td>
<td>560,590</td>
<td>965,1010</td>
</tr>
<tr>
<td>IIIc</td>
<td>435,395</td>
<td>565,540</td>
<td>965,1000</td>
</tr>
<tr>
<td>IIId</td>
<td>445,385</td>
<td>555,495</td>
<td>955,1035,1095</td>
</tr>
<tr>
<td>IIIe</td>
<td>460,365</td>
<td>585</td>
<td>990,1010,1155</td>
</tr>
<tr>
<td>Va</td>
<td>425,360</td>
<td>550,500</td>
<td>980,1125,1130,1195</td>
</tr>
<tr>
<td>Vb</td>
<td>455,355</td>
<td>515,560,610</td>
<td>950,1010,1030, 1070,1165,1185</td>
</tr>
</tbody>
</table>

**Magnetic studies**

Theoretically, iron(III) can exist in two possible spin states: (i) low spin, with a magnetic moment of 1.73 B.M. and (ii) high spin (octahedral and tetrahedral) with a magnetic moment of 5.92 B.M. (S=5/2 state). The room temperature magnetic moments of the present complexes are in the range of 5.02-5.14 B.M. as against the spin only value of 5.92 B.M., indicating a high spin nature of the present bimetallic alkoxide complexes. The variable temperature magnetic susceptibility studies of I showed a significant temperature-dependent behaviour (Table 2). At 295 K the observed \(\mu_{\text{eff.}}\) is 5.03 B.M., which is lowered with decrease in temperature and at 14.6 K, it reaches a value of 3.62 B.M., which is almost the value expected for the \(S = 3/2\) state of Fe\(^{3+}\). The above data appear to indicate an equilibrium of the type \(^6A_{1g} \leftrightarrow 4^2T_{2g}\) with spin cross-over between the two states\(^{19}\). Such an equilibrium has been observed in other cases of iron also in octahedral geometry. Alternatively, the lowering in the magnetic moment with decrease in temperature may be associated with the internuclear antiferromagnetic interactions in the solid state in a magnetically concentrated system. Although the former possibility appears to be more plausible, yet attempts to rule out the latter by magnetic studies in solution have been inconclusive so far.

On the basis of the above studies, it appears that \([\text{Zr}_2\text{(OPr)}_9]\) anion behaves as a bidentate ligand giving rise to an octahedral environment around iron atom, as shown in structure (A):
The room temperature magnetic moment of Fe₂Zr(OPr)₁₀ (II) has been found to be 5.15 B.M., as against the spin only value of 5.92 B.M., which could be ascribed either to the intermolecular antiferromagnetic interaction in the solid state or to some long range coupling between the two paramagnetic iron centers separated by the diamagnetic zirconium atom.

In contrast to the octahedral nature of Fe(III) in [Fe{Zr₂(OR)₉}₆] (I), Fe(III) is expected to be in tetrahedral environment in [[{Zr(OPr)₉}]{Fe(OPr)₄}₂]. This is corroborated to some extent by the tetrahedral nature of aluminium [atomic radii of Fe(III) and Al(III) are almost equal, i.e. 1.26 Å and 1.22 Å, respectively] in the analogous aluminium derivative, [[{Zr(OPr)₉}]{Al(OPr)₄}₂], in which case tetrahedral nature of Al(III) has been established by NMR (¹H, ¹³C and ²⁷Al) spectral studies. Fe₂Zr(OPr)₁₀ (II) can therefore, be represented by the structure (B) similar to that proposed for the aluminium analogue:

![Diagram of structure B]

**Infrared spectral studies**

Structurally significant IR bands for these new heterobimetallic alkoxides are observed in the regions 355-455 (νFe-O), 495-610 (νZr-O), 940-1063 (νC-O for primary alcohol derivatives), 990-1160 (νC-O for secondary alcohol derivatives) and 950-1195 cm⁻¹ (for mixed tertiary and isopropoxy derivatives). The characteristic alkyl group frequencies get masked by the nujol band. Details are given in Table 3.

**Acknowledgements**

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**References**