Synthesis, spectral and magnetic studies of some polynuclear, mixed-ligand complexes of iron and cobalt with 3-mercaptopropionic acid

B P Baranwal*, Tarakeshwar Gupta & Atresh K Singh
Department of Chemistry, DDU Gorakhpur University, Gorakhpur 273 009, India

Received 30 July 2002; revised 20 February 2003

Some mixed-ligand, trinuclear complexes of mixed-valence iron (III, II) and dinuclear cobalt(II) have been synthesize by enforced substitution of acetate ions from their respective acetato complexes. The isolated products of the types [Fe₂O(OOCR)₃(OOCR'SH)]₂⁺ and [Co(OOCR)(OOCR'SH)]₃⁺ (where R = C₆H₅, C₃H₇ or C₁₅H₃₁ and R' = -CH₂CH₂-) are mixed (carboxylato)(mercaptocarboxylato) complexes. These have been characterised by microanalytical data and infrared, UV-visible and Mössbauer spectra. Non-electrolytic behaviour and polynuclear nature of the complexes have been assessed from their low conductance and high molecular weight data. The octahedral environment around both the metals has been suggested on the basis of UV-visible and magnetic moment data. Mössbauer studies reveal two resolved quadrupole doublets due to Fe(II) and Fe(III) confirming the valence-localised classification of the iron compounds.

Transition metal complexes containing sulphur ligands are active catalysts in a number of homogeneous reactions. Apart from this, these complexes show significant biological activity and possess medicinal properties. Mercaptocarboxylic acids (HOOC-R'-SH) display very interesting structural and bonding properties as they contain both a ‘soft’ sulphur and ‘hard’ oxygen donor sites which may lead to aggregation of hard and soft or intermediate class of metal(s). On the other hand, the mixed-ligand complexes of transition metals are also interesting due to their novel structural feature, unusual magnetic properties, catalytic activities and as synthetic models for explaining the biochemical reactions. A perusal of literature reveals that very little work has been reported on mixed-ligand complexes of iron and cobalt with sulphur containing ligands.

In the present note we report the synthesis and characterization of some novel mixed-ligand iron(III, II) and cobalt(II) complexes with higher carboxylic acids and 3-mercaptopropionic acid.

Experimental

Glass apparatus with interchangeable joints were used throughout. The organic solvents (Qualigens) were purified by standard procedures before use. 3-Mercaptopropionic acid (Aldrich) was used after distillation (b.p. 110°C at 15 mm). Infrared spectra were recorded on a Perkin-Elmer model 125 spectrophotometer using KBr discs. Microanalyses (C and H) in each sample were done on Heraeus Carlo Erba 1108 analyser. Electronic spectra were recorded on Shimadzu (model-UVmini-1240) UV-visible spectrophotometer in toluene (spectroscopic grade) solution. Mössbauer spectra were recorded from IIC, IIT Roorkee. Metals, sulphur and liberated acetic acid in the azetropne were determined by the standard methods. Magnetic susceptibility measurements of the complexes were carried out by Gouy method using Hg[Co(SCN)₄] as a calibrant. The molar conductance was measured on a Century CC-601 digital conductivity meter with a dip type cell using 10⁻²⁻¹⁻⁴ molal solution of the complexes in nitrobenzene. Molecular weights of the complexes were determined by cryoscopic method using benzene as a solvent (cryoscopic constant, K₁ = 5.12 K Kg mol⁻¹).

Synthesis of iron complexes

μ₃-Oxohexakis(acetato)tri(aqua)iron(II)diiron(III), [Fe₆O(OOCCH₃)₆(H₂O)₃], prepared by the method reported in the literature. Three acetate ions from this compound were substituted by three carboxylate anions of higher fatty acids as reported in an earlier communication. The products were soluble in toluene in which [Fe₆O(OOCCH₃)₆(H₂O)₃] was insoluble. They were isolated with the general formula [Fe₆O(OOCCH₃)₆(OOCR)₃(C₃H₇OH)₃], by reprecipitation with an excess of ethanol. A toluene solution of 3-mercaptopropionic acid (0.61 g; 5.75 mmol) was added to the toluene solution of μ₃-oxo tri(acetato)tri(ethanol)tri(palmitato)iron(II) diiron(III) (2.41 g; 1.90 mmol) with constant stirring. The reaction mixture was refluxed for 34 h with slow and continuous azetotropic fractionation of acetic acid, ethanol and toluene to enforce the reaction. After
completion of the reaction (known by estimation of acetic acid content in the collected azeotrope), the resulting solution was concentrated by distillation of excess solvent. A blackish brown non-volatile solid of the formula \([\text{Fe}_2\text{O}(\text{OOCCH}_3\text{H}_3)_2][\text{OOCCH}_2\text{CH}_2\text{SH}]_3\) was obtained after drying the contents under reduced pressure (1.5 mm/60°C). Other complexes of iron were synthesized following the same procedure and the analytical results are summarized in Table 1. All the complexes were obtained as microcrystalline/powdery colored solid.

**Synthesis of cobalt complexes**

Cobalt acetate was treated with higher fatty acids in toluene (equimolar ratio) to yield mono(acetato)-, mono(carboxylato) complexes of cobalt(II)\(^9\). A toluene solution of 3-mercaptopropionic acid was introduced to a toluene solution of mono(acetato)-mono(palmitato)cobalt(II) in equimolar ratio. The contents were refluxed for 14 h with slow and continuous fractionation of acetic acid-toluene azeotrope, which could be fractionated out at lower temperature (below 110 °C, b.p. of toluene). All the complexes were synthesized following the same procedure and the analytical results are summarized in Table 1. All the complexes were obtained as microcrystalline/powdery colored solid.

**Results and discussion**

Some mixed-ligand complexes of cobalt(II) and mixed-valence iron(III, III, II) have been prepared by the reactions:

\[
\begin{align*}
\text{[Fe}_2\text{O(OOCCH}_3\text{H}_3)_2][\text{OOCCH}_2\text{CH}_2\text{SH}]_3 + 3 \text{HOOC(CH}_2\text{)SH} & \rightarrow \text{[Fe}_2\text{O(OOCCH}_3\text{H}_3)_2][\text{OOCCH}_2\text{CH}_2\text{SH}]_3 + 3 \text{CH}_3\text{COOH} + 3 \text{C}_2\text{H}_4\text{OH} & \rightarrow \text{(1)} \\
\text{[Co(OOCC}_2\text{H}_3\text{H}_3][\text{OOC(CH}_2\text{)SH}]_2 + \text{HOOC(CH}_2\text{)SH} & \rightarrow \text{[Co(OOCC}_2\text{H}_3\text{H}_3][\text{OOC(CH}_2\text{)SH}]_2 + \text{CH}_3\text{COOH} & \rightarrow \text{(2)} \\
\end{align*}
\]

(where R = C\(_7\)H\(_{15}\), C\(_8\)H\(_{17}\) or C\(_{11}\)H\(_{23}\))

The use of toluene as a solvent was a very suitable choice in these substitutions because it pushed the reactions in the forward direction after removal of the liberated ethanol and acetic acid in the form of azeotrope, which could be fractionated out at lower temperature (below 110°C, b.p. of toluene). All the (carboxylato)(mercaptocarboxylato) complexes were soluble in organic solvents like toluene, benzene or nitrobenzene. Determination of molar conductances of all the complexes in nitrobenzene at 10\(^{-2}\)-10\(^{-4}\) molar concentrations (Table 1) indicated them to be non-electrolytes.

In order to study bonding modes of 3-mercaptopropionic acid and carboxylic acid to the metal in the complexes, IR spectra of the free ligands were compared with the spectra of the metal complexes. In IR spectra of all the complexes, no band was observed in the region 3400-3250 cm\(^{-1}\). This indicated the absence of O-H stretching vibration of free carboxylic acid or 3-mercaptopropionic acid. The bands at 1710 cm\(^{-1}\) (CO stretch) and at 935 (OH deformation) of free carboxylic acids were also found absent in spectra of the complexes in which two strong bands were observed at \(-1600\) cm\(^{-1}\) (\(\nu_{\text{sym}}\text{OCO}\)) and \(-1440\) cm\(^{-1}\) (\(\nu_{\text{asym}}\text{OCO}\)) stretching vibrations. The coordination mode of the carboxylate ligand can be assigned on the basis of the difference (\(\Delta \nu = -160\)) of these two frequencies\(^10\), which indicated the presence of bridging mode of coordination of the carboxylate and mercaptocarboxylic ions in the complexes. The bands observed at \(-665\) cm\(^{-1}\) could be assigned to \(\delta\text{(OCO)}\) vibration of the bridging carboxylate ligands and at \(-600\) cm\(^{-1}\) to the O-C-O out-of-plane deformation mode \([\pi\text{(COO})]\)\(^1\). A weak absorption band at \(-530\) cm\(^{-1}\) could be assigned to asymmetric stretching of the Fe\(_2\)O core\(^7\). The lowering in \(\nu\text{(O-H)}\) from 2570 to \(-2550\) cm\(^{-1}\) and \(\nu\text{(C-S)}\) from 740 to 722 cm\(^{-1}\) indicated the coordination of -SH group in all the complexes. The bands observed at \(-415\) and \(-490\) cm\(^{-1}\) may be due to M-S and M-O vibrations, respectively\(^10\).

Electronic spectra of the complexes were recorded in the range 8000-33000 cm\(^{-1}\) at 300 K. The electronic spectra of iron complexes display weak absorption bands in the region 18560-29620 cm\(^{-1}\) characteristics of octahedral geometry\(^12\). These bands may be assigned to \(6\text{A}_{1g}\rightarrow 4\text{T}_{1g}\) \((\nu_1), (-18667); 6\text{A}_{1g}\rightarrow 4\text{T}_{2g}(\text{G})\) \((\nu_2), (-22870); 6\text{A}_{1g}\rightarrow 4\text{E}_{g}(\text{G})\) \((\nu_3), (-25190); 6\text{A}_{1g}\rightarrow 4\text{T}_{2g}(\text{D})\) \((\nu_4), (-27503)\) and \(6\text{A}_{1g}\rightarrow 4\text{E}_{g}(\text{D})\) \((\nu_5), (-29550)\) transitions. A broad absorption observed at 13840 cm\(^{-1}\) has been assigned to an intervalence-transfer band \((\nu_{\text{a}})\) which has not been observed in singly valent iron compounds\(^7\). The electronic spectra of cobalt complexes exhibited a broad band and two shoulders in the range 8600-20800 cm\(^{-1}\). These bands may be assigned to \(4\text{T}_{1g}\rightarrow 4\text{T}_{2g}\) \((\nu_1), (-8318); 4\text{T}_{1g}\rightarrow 4\text{A}_{2g}\) \((\nu_2), (-16580)\) and \(4\text{T}_{1g}\rightarrow 4\text{T}_{1g}\) \((\nu_3), (-19957)\) transitions. The value of \(\nu_{\text{a}}/\nu_{\text{b}}\) (-2) indicated the octahedral geometry around cobalt(II)\(^12,13\). Li-
### Table 1—Analytical, magnetic and conductance results for the complexes

<table>
<thead>
<tr>
<th>Reactants* (g; mmol)</th>
<th>Product (Colour), Reaction time(h)</th>
<th>CH₃COOH in Azeotrope (g)</th>
<th>Found (Calcd)</th>
<th>Mol. wt.</th>
<th>Magnetic moment (μ₀)</th>
<th>Molar conductance (Ohm⁻¹ cm² mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fe₃O(L₁)(L₂)(L₃) + HL₄</td>
<td>Fe₂O(L₂)(L₄) (Brownish black) (29)</td>
<td>0.39</td>
<td>18.13</td>
<td>42.59</td>
<td>6.46</td>
<td>10.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.41)</td>
<td>(42.68)</td>
<td>(6.53)</td>
<td>(10.36)</td>
</tr>
<tr>
<td>Fe₂O(L₁)(L₂)(L₃) + HL₄</td>
<td>Fe₂O(L₃)(L₄) (Blackish gray) (32)</td>
<td>0.36</td>
<td>15.20</td>
<td>49.43</td>
<td>7.38</td>
<td>8.66</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.35)</td>
<td>(49.27)</td>
<td>(7.73)</td>
<td>(8.77)</td>
</tr>
<tr>
<td>Fe₂O(L₁)(L₂)(L₃) + HL₄</td>
<td>Fe₂O(L₄)(L₄) (Blackish brown) (34)</td>
<td>0.31</td>
<td>13.14</td>
<td>54.00</td>
<td>8.62</td>
<td>7.93</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.34)</td>
<td>(54.11)</td>
<td>(8.62)</td>
<td>(7.60)</td>
</tr>
<tr>
<td>Co(L₁)(L₂) + HL₄</td>
<td>Co(L₂)(L₄) (Reddish brown) (10)</td>
<td>0.40</td>
<td>19.21</td>
<td>42.73</td>
<td>6.56</td>
<td>9.98</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.43)</td>
<td>(43.00)</td>
<td>(6.57)</td>
<td>(10.44)</td>
</tr>
<tr>
<td>Co(L₁)(L₃) + HL₄</td>
<td>Co(L₃)(L₄) (Reddish brown) (12)</td>
<td>0.39</td>
<td>16.29</td>
<td>49.54</td>
<td>7.77</td>
<td>8.68</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.40)</td>
<td>(49.58)</td>
<td>(7.78)</td>
<td>(8.83)</td>
</tr>
<tr>
<td>Co(L₄)(L₄) + HL₄</td>
<td>Co(L₄)(L₄) (Violet red) (14)</td>
<td>0.33</td>
<td>14.56</td>
<td>54.28</td>
<td>8.66</td>
<td>7.36</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td>(0.37)</td>
<td>(54.40)</td>
<td>(8.67)</td>
<td>(7.64)</td>
</tr>
</tbody>
</table>

*L₁ = CH₃COO ; L₂ = C₂H₅COO ; L₃ = C₃H₇COO ; L₄ = C₄H₉COO ; L₅ = C₅H₁₁COO ; L₆ = C₆H₁₅OH ; L₇ = OOCCH₂CH₂SH

### Table 2—Mössbauer parameters (mm/s)* for [Fe₃O(OOC₃H₇)(OOCCH₂CH₂SH)]

<table>
<thead>
<tr>
<th>Temperature (K)</th>
<th>Isomeric shift (δ)</th>
<th>Quadrupole splitting (ΔE₀)</th>
<th>Line width (Γ)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Fe²⁺</td>
<td>Fe³⁺</td>
<td>Fe²⁺</td>
</tr>
<tr>
<td>80</td>
<td>1.22 (2)</td>
<td>0.56 (2)</td>
<td>2.00</td>
</tr>
<tr>
<td>200</td>
<td>1.06 (3)</td>
<td>0.53 (1)</td>
<td>2.28 (2)</td>
</tr>
<tr>
<td>250</td>
<td>0.91 (1)</td>
<td>0.52 (2)</td>
<td>2.03 (1)</td>
</tr>
<tr>
<td>295</td>
<td>0.81 (2)</td>
<td>0.54 (1)</td>
<td>1.98 (1)</td>
</tr>
</tbody>
</table>

*The isomeric shift (δ) is reported relative to iron metal at room temperature. The error in the last significant figure is given in parentheses.
The gand field splitting energy (10 Dq) and interelectronic repulsion parameter (B) have been calculated using the secular equations given by Underhill and Billing. The nephelauxetic parameter (β) is readily obtained using the relationship β = B (complex)/B (free ion). The values of 10 Dq, B and β for the complexes were found in the range 8750-9013, 872-890 cm⁻¹ and 0.78-0.80, respectively. The observed lowering of the B values from 1120 cm⁻¹ (for free Co(II) ion) indicated an appreciable covalent nature of the metal-ligand bond in the complexes.

The molar susceptibility (χ_m) measurements of all the complexes were carried out at 295 K and effective magnetic moments (μ_eff) per molecule (Table 1) were calculated by the expression, μ_eff = 2.83(χ_m,T)^1/2. The magnetic moments were corrected for the magnetism of the sample holder and a diamagnetic correction, calculated from Pascal’s constants, was applied. For iron complexes, the ground state of a molecule with two high-spin Fe(III) (S = 5/2) and one high-spin Fe(II) (S = 2) centers can have total spin (S_T) values ranging from 0 to 7. The obtained magnetic moment values for iron complexes are in the range 3.18-3.23 μ_B indicating the presence of octahedral geometry around iron in mixed-valence state and a net antiferromagnetic exchange coupling. Cobalt(II) complexes, in an octahedral field is orbitally degenerate, this causes an orbital angular momentum contribution to the magnetic moment, therefore, the experimental magnetic moment values lie between μ_S0 = [4S(S+1)]^1/2 = 3.88 μ_B and μ_S±L = [4S(S+1)+L(L+1)]^1/2 = 5.2 μ_B values. The obtained magnetic moment values (Table 1) for the complexes are in the range reported for cobalt(II) compounds in an octahedral geometry.

Molecular weights of all the complexes were determined cryoscopically in benzene at room temperature using Beckmann thermometer and the results (Table 1) indicated the iron complexes are trinuclear while cobalt complexes are dinuclear. The proposed structures (Structures 1 and 2) appear to be most plausible for trinuclear iron and dinuclear cobalt complexes, respectively.

Mössbauer spectra of [Fe₃O(OOCC₆H₄SH₂)]₃ (OOCH₂CH₂SH₃) at 80-295 K temperature range revealed the presence of Fe(III) and Fe(II) sites with an intensity ratio ~ 2 : 1. The Mössbauer parameters obtained from least-squares fits of the experimental data of Lorentzian lines are presented in Table 2. The values at 80 K are typical for high-spin ferric (S = 5/2) and high-spin ferrous (S = 2) ions. The proposed structure revealed two similar Fe(III) sites which has been confirmed by Mössbauer spectra as no separate quadrupole doublets could be observed for two Fe(III) ions.

The quadrupole splitting of the high-spin ferric component of the spectrum shows a pronounced and unusual temperature dependence, while the temperature-dependent quadrupole splitting exhibited by the ferrous subsite is consistent with that expected for high-spin Fe(II). On the other hand, the variation of the isomeric shift of the ferrous site is much greater than anticipated from the second order Doppler shift which arises from thermal excitations of vibronic states. In contrast, the isomer shift of the ferric site is independent of temperature.

The pronounced lowering in the isomer shift of the Fe(II) center in complex with increasing temperature
and the consistency of the isomer shifts of Fe(III) sites with temperature indicated a shift in electron density from Fe(II) to Fe(III). Such an electronic redistribution, which probably occurs via the Fe-(µ-oxo) bonds, is responsible for the observed temperature dependence of the quadrupole splitting parameter. The observation of resolved quadrupole doublets, one for the ferric and the other for the ferrous site, confirmed the complexes of iron were having localized mixed-valence species which belong to class 1 of the Robin and Day scheme.

Acknowledgement
The authors express their sincere thanks to the UGC, New Delhi [Grant No. F. 12-59/2001 (SR-I)] for financial support. One of us (TG) thanks to CSIR, New Delhi for the award of a senior research fellowship. Further, we are thankful to RSIC, CDRI, Lucknow for doing microanalyses.

References
8 Baranwal B P, Das S S, Gupta T & Singh A K, J crys growth & mater Charact (Accepted for publication) 2002.