Synthesis and characterization of iron(III) complexes of N-(2-thienylidene)-N'-isonicotinoylhydrazine, N-(2-furylidene)-N'-salicyloylhydrazine and N-(2-thienylidene)-N'-salicyloylhydrazine

M Alaudeen & C P Prabhakaran*
Department of Chemistry, University of Kerala, Kariyavattom, Trivandrum 695 581
Received 26 October 1995; revised 18 January 1996

A few complexes of iron(III) with Schiff bases N-(2-thienylidene)-N'-isonicotinoylhydrazine, N-(2-furylidene)-N'-salicyloylhydrazine and N-(2-thienylidene)-N'-salicyloylhydrazine have been isolated and characterised by elemental analysis, IR, electronic and Mössbauer spectral studies and molar conductance and magnetic measurements. The antibacterial properties of a few complexes are also reported.

Iron(III) complexes of aryl and heteroarylhydrazones are known for their antibacterial activities. These and many other Schiff base complexes of iron(III) have been the subject of detailed investigations as they also show interesting magnetic properties. This note deals with the synthesis and spectral, magnetic and antibacterial studies of some iron(III) complexes of Schiff bases, viz., N-(2-thienylidene)-N'-isonicotinoylhydrazine (TINH₂), N-(2-furylidene)-N'-salicyloylhydrazine (FSAH₂) and N-(2-thienylidene)-N'-salicyloylhydrazine (TSAH₂).

Experimental
The hydrazones were prepared by refluxing for 1 h, a mixture of isonicotinic or salicylic acid hydrazide (0.1 mol) and furfural or thiophene-2-aldehyde (0.1 mol) in 200 ml ethanol. On cooling, the hydrazones were obtained as solids, yield 80%.

The chloro complexes were prepared by stirring a hot solution of appropriate ligand (0.02 mol) with required amount of FeCl₃ in 100 ml ethanol when the precipitation of the complexes occurred. The nitrato, acetato, benzoato and thiocyanato complexes were prepared by refluxing a mixture of TINH₂ (0.02 mol) with Fe(NO₃)₃ (0.02 mol), Fe(CH₃COO)₃ (0.02 mol), Fe(C₆H₅COO)₃ (0.01 mol) and Fe(CNS)₃ (0.02 mol) respectively in 100 ml ethanol for 2 h. The solid complexes which separated out were filtered, washed with ethanol and dried over P₂O₅, yield 68%.

Iron was estimated by direct pyrolysis of the complexes to its oxide. The elemental analyses were carried out by the usual methods. Molar conductance values were measured in methanol, acetonitrile and nitrobenzene using direct reading Elico conductivity meter. Molecular mass of four complexes were determined by cryoscopic method. Magnetic moments at room temperature were determined using a Gouy type magnetic balance calibrated with Hg[Co(CNS)₄]. IR spectra were recorded as KBr discs on a Perkin-Elmer 397 spectrophotometer and electronic spectra were obtained for nujol mulls using a Schimadzu spectrophotometer. Mössbauer spectra of the solid complexes at room temperature were recorded on a drive system supplied by Sissel Electronics, Germany with a data acquisition system based on a dynalog microprocessor learning kit. The source used was⁵⁷ Co in a Rh matrix and calibration was carried out using Fe foil, CG = 235.5109 and 1 channel = 0.04359 mms⁻¹, Na₂[Fe(CN)₅NÖ] was used as the reference absorber. The curves were fitted to Lorentian curves by least square method.

Results and discussion
The analytical data are in agreement with the molecular formulae of the complexes shown in Table 1. The molar conductance data reveal that [Fe(TINH₂)₂Cl₂]Cl is a 1:1 electrolyte and all the other complexes are non-electrolytes in the solvents studied. Molecular mass determination showed that the complexes [Fe₂(FSAH)₂Cl₄] and [Fe(TSAH)₂Cl₄] are dimeric. All these complexes are found to decompose before melting.

The IR spectra of [Fe(TINH₂)₂Cl₂]Cl and [Fe(TINH₂)[NO₃]₃] reveal that TINH₂ is coordinated to the metal atom in its keto form. The ν(C=O) mode which appears at 1660 cm⁻¹ in the spectrum of the free Schiff base is shifted by 30 cm⁻¹ in the complexes, suggesting carbonyl oxygen coordination. This is supported by the negative shift of 25 cm⁻¹ for the amide-II band and positive shift of 20 cm⁻¹ for the amide-III band upon complexation. The free Schiff base bands at 1600 cm⁻¹ for ν(C=O) and 1000 cm⁻¹ for ν(N–N) show downward and upward shifts of 25 and 20 cm⁻¹ respectively in the complexes due to
In the thiocyanato complex, NCS is probably N-coordinated, as suggested by the presence of bands at 820 for $\nu(C-S)$ and 490 cm$^{-1}$ for NCS bend. The acetate group of acetato complex is apparently unidentate, as the complex shows bands at 1580 and 1350 cm$^{-1}$ assignable to $\nu(OCO)$ and $\nu_{s}(OCO)$ respectively. The benzoato complex has two strong bands at 1545 and 1480 cm$^{-1}$ characteristic of either ionic or bridge coordination of the imine nitrogen. In $\text{Fe}([\text{TINH})_2\text{Cl}_2]\text{Cl}$, the ring stretching and out-of-plane ring deformation of the thiophene group show negative and positive shifts, both ~20 cm$^{-1}$, suggesting participation of the ring sulphur in coordination. The medium intensity band at 345 cm$^{-1}$ in the spectrum of the nitrato complex can be assigned to $\nu(Fe-S)$.

<table>
<thead>
<tr>
<th>Complex colour</th>
<th>Molecular mass</th>
<th>Found (Calc),%</th>
<th>$\mu_{eff}$ at 303 K (BM)</th>
<th>Mössbauer parameter</th>
<th>Percentage inhibition</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Fe(TINH)$_2$Cl$_2$]Cl</td>
<td>393.3</td>
<td>(8.9) (42.0) (2.8) (13.4) (10.2) (17.0)</td>
<td>1.02</td>
<td>0.322</td>
<td>0.609</td>
</tr>
<tr>
<td>[Fe(TINH)$_2$(NO$_3$)$_2$]</td>
<td>464.2</td>
<td>(11.8) (27.9) (1.9) (17.7) (6.8)</td>
<td>1.02</td>
<td>0.304</td>
<td>0.678</td>
</tr>
<tr>
<td>[Fe(TINH)$_2$C$_6$H$_5$COO]</td>
<td>8.7</td>
<td>(54.6) (3.9) (13.2) (10.0)</td>
<td>1.02</td>
<td>0.340</td>
<td>0.783</td>
</tr>
<tr>
<td>[Fe(TINH)$_2$(CH$_3$COO)$_2$]</td>
<td>13.7</td>
<td>(44.6) (3.5) (10.4) (7.9)</td>
<td>1.02</td>
<td>0.284</td>
<td>0.617</td>
</tr>
<tr>
<td>[Fe$_2$(FSA)$_2$Cl$_4$]</td>
<td>605.3</td>
<td>15.6</td>
<td>10.3</td>
<td>7.9</td>
<td>1.02</td>
</tr>
<tr>
<td>[Fe$_2$(TSA)$_2$Cl$_4$]</td>
<td>839.9</td>
<td>15.0</td>
<td>39.0</td>
<td>2.7</td>
<td>18.9</td>
</tr>
</tbody>
</table>

In the thiocyanato complex, NCS is probably coordinated, as suggested by the presence of bands at 820 for $\nu(C-S)$ and 490 cm$^{-1}$ for NCS bend. The acetate group of acetato complex is apparently unidentate, as the complex shows bands at 1580 and 1350 cm$^{-1}$ assignable to $\nu(OCO)$ and $\nu_{s}(OCO)$ respectively. The benzoato complex has two strong bands at 1545 and 1480 cm$^{-1}$ characteristic of either ionic or bridg-
ing benzoate. Since the electrical conductance data rule out the presence of ionic benzoate, it is likely that it functions as a bridging unit.

The v(O – H) (hydrogen bonded) mode observed at 3120 cm$^{-1}$ for FSAH$_2$ and TSAH$_2$ is absent in the spectra of their complexes, suggesting coordination of the deprotonated phenolic oxygen to metal atom. This is supported by the negative shift in v(C-O) (phenolic) by 25 cm$^{-1}$ (ref. 14). The v(C=O) and v(C=N) frequencies of the free Schiff bases observed at 1640 and 1610 cm$^{-1}$ show downward shifts in the spectra of the complexes as a result of coordination of the carbonyl oxygen and azomethine nitrogen to the metal atom. Thus, both FSAH and TSAH act as uninegative tridentate ligands (structure Ic). All the complexes show medium intensity bands at 580 and 530 cm$^{-1}$ which can be assigned to v(Fe-N) and v(Fe-O) frequencies respectively.

The electronic spectra of the complexes show broad absorption bands in the region 25000-27000 cm$^{-1}$ which are attributed to charge-transfer transitions.

The room temperature magnetic moments of [Fe(TINH$_2$)$_2$Cl$_2$]Cl, [Fe(TINH$_2$)(NO$_3$)$_3$] and [Fe(TINH)(CH$_3$COO)$_2$] are 5.9 BM, which corresponds to five unpaired electrons as expected for iron(III) complexes having no metal-metal interaction. The slightly low values shown by the other complexes suggest weak interaction between the iron atoms, either directly or through bridging unit.

The Mössbauer spectra of the complexes at room temperature show isomer shift ($\delta$) values in the range 0.284–0.340 mm s$^{-1}$, less than the values reported (0.40–0.70 mm s$^{-1}$) for high spin iron(III) octahedral complexes. This indicates higher s-electron density at iron, possibly due to higher covalent character for the bonds to iron and/or reduced $d$-electron density at iron(III) resulting in deshielding of the $s$-electrons.

The quadrupole splitting values ($\Delta$E$_Q$) of the complexes range from 0.609 to 0.784 mm s$^{-1}$, slightly above the average of value reported (0.60 mm s$^{-1}$) for octahedral complexes. This may be due to rather unsymmetric ligand field around the iron atom.

**Antibacterial activity**

The iron(III) complexes of TINH$_2$ were tested for their antistaphylococcal activity by administering them separately into culture media containing *S. aureus* and estimating the bacterial growth by turbidimetric assay. Each complex was tested at concentrations ranging from 0.01 to 0.05 mg ml$^{-1}$; statistically relevant antibacterial activity was exhibited only at 0.05 mg ml$^{-1}$. The percentage inhibition against *S. aureus* growth by the complexes are given in Table 1. Under identical condition, free TINH$_2$ showed 26% inhibition.

**References**