Five and Six Coordinated Complexes of Di and Trivalent Iron with Ligands Derived from Acidhydrazides and Acetylacetone

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Picolinic acid hydrazide (PH) and isonicotinic acidhydrazide (INH) react with acetylacetone in the presence of iron(II) and iron (III) salts and give complexes of open chain tetradentate ligands through a template effect. The complexes are isolated and characterised as five and six-coordinated by the help of analyses, conductance, molecular weight, magnetic, Mössbauer, electronic and infrared spectral studies. Two molecules of PH or INH condense with a single acetylacetone moiety giving open chain tetradentate ligands. Attempts to isolate the ligand in the free state are, however, unsuccessful. The Ac(PH)$_2$ coordinates through azomethine and pyridine nitrogens, while Ac(INH)$_2$ does so through azomethine nitrogens and amide oxygen. Mössbauer spectra are consistent with their proposed geometries and reveal that iron is in the high-spin state. Various ligand field parameters are calculated using normalised spherical harmonic Hamiltonian theory and the amount of distortion is calculated in terms of $DT/DQ$. Metal-ligand vibrations in the far IR region are discussed.

The transition metal chemistry of iron(II) and iron(III) complexes with phosphines and arsines is very extensive; however, relatively few reports are available concerning compounds of pyridine based ligands. Interestingly, a few iron(III) complexes exist as five coordinate monomers and bridged binuclear species and among multidentate ligands, such complexes have recently been synthesised with pentadentate ligands. In general, Mössbauer spectra of iron compounds containing two or more metal atoms can provide evidence for the occurrence of structurally non-equivalent metal atoms and there have been several valuable applications of this technique. Although complexes of hydrazides and their hydrazones have been widely studied, no work appears to have been done on the complexes obtained by the condensation of hydrazides and acetylacetone in the presence of various metal ions. The present paper deals with magnetic, Mössbauer, electronic and IR spectral studies of five and six coordinated complexes of iron(II) and iron(III) with Ac(PH)$_2$ and Ac(INH)$_2$.

**EXPERIMENTAL**

Ethyl-2-picolinate and isonicotinic acid hydrazides were obtained from Koch-Light and acetylacetone from BDH, England. All other reagents used were of reagent grade.

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Synthesis of Picolinic acid Hydrazide

The picolinic acid hydrazide (PH) was synthesised by refluxing ethyl-2-picolinate (0.10 mol) and hydrazine hydrate (99%) (0.10 mol) in a water bath for 4 h. The product obtained was recrystallised from ethanol m.p. ≈ 99.5 °C.

The acetylacetone picolinoyl (AcPH) and acetylacetone isonicotinyl (AcINH) monohydrazones were synthesised by refluxing methanolic solutions of picolinic (PH) or isonicotinic (INH) acid hydrazide (1.4 g) and acetylacetone (1.0 g) for 4 h in a water bath. The white solid obtained was recrystallised from methanol. The yield for acetylacetone picolinoyl monohydrazone (m.p. ≈ 230 °C) was poor (30%) while a 60% yield for acetylacetone isonicotinoyl monohydrazone (m.p. ≈ 255 °C) was obtained. For both compounds, elemental analyses and IR spectra show that acac is condensed to the NH$_2$ group of single hydrazide molecule and thus confirm the formation of acetylacetone monohydrazones of PH and INH.

Preparation of Complexes

Iron(II) sulphate or nitrate (10 mmol) dissolved in minimum quantity of water was diluted by 50 cm$^3$ of methanol. Metal salt solution was added dropwise with constant stirring to the mixture of PH or INH (20 mmol) and acetylacetone (10 mmol). The reaction mixture was refluxed for 4 h and cooled. The crystalline precipitate was filtered, washed with ethanol, acetone, and ether and dried at 110 °C in an oven. Yield ≈ 30–40%.

Methanolic solutions of PH or INH (20 mmol), acetylacetone (10 mmol) and iron(III) salt (10 mmol) were mixed with constant stirring. The reaction mixture was refluxed for 5 h, when a syrupy liquid was obtained. It was kept in a refrigerator for 48 h, brown red crystals separated, were filtered off, washed with acetone, methanol, and ether and dried in a oven at 110 °C. Yield ≈ 30%/.

For synthesising bromo and thiocyanato complexes, iron(II) sulphate and iron(II) nitrate were first treated with an excess of lithium bromide and ammonium thiocyanate, in order to generate the corresponding bromide and thiocyanate salts of iron(II) in solution.

The complexes are soluble in water and DMF but insoluble in other common organic solvents. They are stable up to 300 °C.

Magnetic and Spectral Measurements

The magnetic susceptibilities at room temperature were measured with a Gouy’s balance using [HgCo(CNS)$_2$] (γ = 51.65 × 10$^{-12}$ at 293 K) as calibrant. IR spectra in the range (4000–250) cm$^{-1}$ were recorded on a Perkin-Elmer-337 spectrophotometer. Far IR spectra (650–200) cm$^{-1}$ were recorded in nujol-mull on a Beckmann IR-12 spectrophotometer. Iron-57 Mössbauer spectra were obtained using a 400 channel constant acceleration Mössbauer spectrophotometer equipped with a $^{57}$Co source in a copper matrix. All the spectra were recorded at room temperature over a narrow range of ±3 mm s$^{-1}$ and the instrument was calibrated with sodium nitroprusside. Molar conductance was measured with a Toshniwal type CL01/01 conductivity bridge using a dip type cell. The molecular weights of the complexes were determined by Beckmann’s cryoscopic method.

Iron was estimated with EDTA titrations using sulphasalicylic acid as indicator. The results were confirmed by titration with KMnO$_4$ after reducing Fe(III) to Fe(II) with stannous chloride. The microanalyses of C, H, and N were performed by Micro-analytical Division, C.D.R.I., Lucknow.

RESULTS AND DISCUSSION

The analytical data reported in Table I reveal the molecular formulae for the complexes to be [Fe$^{II}$(L)X] and [Fe$^{III}$(L)X$_2$], where L = Ac(PH)$_2$ or Ac(INH)$_2$, and X = Cl, Br, NO$_3$, or NCS. The conductance data show their non-electrolytic nature and the molecular weights (determined cryoscopically) are consistent with their proposed formulae. Tests for anions were positive only after decomposition of the complexes showing their presence in the coordination sphere.
<table>
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<th>Found %</th>
<th>Calculated %</th>
<th>Halogen</th>
<th>B.M. (μ eff)</th>
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<td>12.00 48.50 3.55 22.03 --- 12.41 47.89 3.77 21.73 --- 5.17</td>
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<td>10.00 --- --- 15.80 28.20 10.12 36.88 3.07 15.19 28.93 5.93</td>
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<td>Black</td>
<td>10.98 45.20 3.52 21.20 --- 11.00 44.79 3.34 22.00 --- 5.89</td>
<td>521</td>
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The magnetic moments of iron(II) complexes are in the range of \((44.5 \ldots 48.2) \times 10^{-24} \text{ m}^2/\text{mol}\). These values approach the range \((46.4 \ldots 51.0) \times 10^{-24} \text{ m}^2/\text{mol}\) observed for the five coordinate complexes reported earlier\(^5\). The magnetic moments observed for iron(III) complexes, \((51.0 \ldots 57.5) \times 10^{-24} \text{ m}^2/\text{mol}\) are well within the range reported for high-spin six coordinate iron(III) complexes\(^7\).

The electronic spectra of iron(II) complexes exhibit the spectral bands \(\approx 5400 \ldots 5550, \approx 8500 \ldots 8950, \approx 11200 \ldots 11900\) and \(\approx 15900 \ldots 16350\) cm\(^{-1}\). The spectral bands do not resemble those of four or six-coordinate, but are well within the range reported for five-coordinate complexes\(^8\). The bands above 15000 cm\(^{-1}\) arise from energy transfer which may be due to metal to ligand or ligand to metal transitions\(^9\). It is, however, difficult to differentiate between trigonal-bipyramidal or square pyramidal geometry, although the band \(\approx 11000\) cm\(^{-1}\) may be taken as evidence of square pyramidal stereochemistry\(^9\). A five-coordinate field splits into \(^5\text{E}, ^5\text{B}_2, ^5\text{A}_1\) and \(^5\text{B}_1\) in \(C_{3v}\) symmetry thus, the bands \(\approx 5500\) and \(11000\) cm\(^{-1}\) may be assigned to \(^5\text{E} \rightarrow ^5\text{A}_1\) and \(^5\text{E} \rightarrow ^5\text{B}_1\), respectively\(^11,12\). The values of \(Dq\) have been calculated using the equation: \(A = f(\text{ligand}) \times g(\text{metal ion})\). The values of \(f\) are calculated from values measured for chromium(III) complexes\(^14\) of the same ligands, using a value for \(g\) of 10.0\(^14\). In view of the tetragonal nature of the complexes, as expected due to the presence of donor atoms of unequal size and strength, the values of \(\Delta D\) are derived by splitting the first band which is equivalent to \(35/4 \Delta D\). The values of \(\Delta D\) and \(Dq\) are also calculated (Table II). These values are used to determine the 'NSH' ligand field parameters\(^16\). The amount of distortion in terms of \(\Delta D/\Delta Q\) reveals that the complexes of Ac(INH)\(_2\) are more distorted than those of Ac(PH)\(_2\).

The Mössbauer spectra of Fe\(^{II}\)Ac(PH)\(_2\)Cl and Fe\(^{II}\)Ac(INH)\(_2\)Cl at room temperature exhibit isomer shift values (Table III) of 1.50 and 1.45 mm s\(^{-1}\), respectively. These values are consistent with high-spin iron(II) with \(S = 2\). However, the possibility of magnetic crossover is ruled out because of the isomer shift is above the range suggested for these systems\(^19\).

The Mössbauer spectra of Fe\(^{II}\)Ac(PH)\(_2\)Cl and Fe\(^{II}\)Ac(INH)\(_2\)Cl at room temperature exhibit isomer shift values (Table III) of 1.50 and 1.45 mm s\(^{-1}\), respectively. These values are consistent with high-spin iron(II) with \(S = 2\). However, the possibility of magnetic crossover is ruled out because of the isomer shift is above the range suggested for these systems\(^19\). The value of \(\Delta EQ\) for iron(II) complexes of Ac(PH)\(_2\) and Ac(INH)\(_2\) are 2.90 and 2.72 mm s\(^{-1}\); these values are greater than 2.7 mm s\(^{-1}\) at room temperature, suggesting ground state splitting\(^29\) in accordance with the results arrived at by the interpretation of their electronic spectra. The values of FWHM for Ac(PH)\(_2\) and Ac(INH)\(_2\) complexes of Fe(II) are 0.4582 and 0.3792 mm s\(^{-1}\) for left hand peaks.
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<th>Complex</th>
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<th>Dq'</th>
<th>Dq'</th>
<th>Dt</th>
<th>DT</th>
<th>DQ</th>
<th>DQ₂</th>
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and 0.4108 and 0.3634 mm s\(^{-1}\) for right hand peaks, respectively. These values again show that in \([\text{II} \text{Fe} \text{II} \text{Ac}(\text{PH})_2 \text{Cl}]\), pyridine-nitrogen coordinates with the metal atom, while in \([\text{II} \text{Fe} \text{II} \text{Ac}(\text{INH})_2 \text{Cl}]\) complexes, it does not do so\(^{21}\).

The Mössbauer spectra of \([\text{II} \text{Fe} \text{II} \text{Ac}(\text{PH})_2 \text{Cl}]\) and \([\text{II} \text{Fe} \text{II} \text{Ac}(\text{INH})_2 \text{Cl}]\) at room temperature give values (Table III) for the isomer shifts (\(\delta\)) of 0.60 and 0.58 mm s\(^{-1}\), which are comparable with high-spin (\(S = \frac{5}{2}\)) iron complexes having a configuration\(^{22}\) of \(t_2^g e_g^2\). The values for quadrupole splitting (\(\Delta EQ\)) are found to be 0.79 and 0.82 mm s\(^{-1}\), which are in conformity with a high-spin (\(S = \frac{5}{2}\)) nature for these complexes with a ground state\(^{23}\) \(6\Delta 1\). The positive value of \(\Delta EQ\) suggests that \(D_{eq} > 0\), wherein the equatorial field strength of the ligand is greater than the axial one\(^{24}\) and is in conformity with the results arrived at by interpretation of the electronic spectra. The values of FWHM are 0.8532 and 0.5372 mm s\(^{-1}\) for left hand peaks and 0.7052 and 0.3952 mm s\(^{-1}\) for right hand peaks in \([\text{II} \text{Fe} \text{II} \text{Ac}(\text{PH})_2 \text{Cl}]\) and \([\text{II} \text{Fe} \text{II} \text{Ac}(\text{INH})_2 \text{Cl}]\) complexes, respectively and are in accordance with the results arrived at by i.r. studies (vide infra), in the sense that in Ac(PH)\(_2\) complexes pyridine nitrogen coordinates to the metal atom, giving rise to a larger value of FWHM compared with Ac(INH) complexes, wherein pyridine nitrogen does not take part in coordination.\(^{21}\)

### Infrared Spectra

A comparison of the spectra of the free ligands with those of the Ac(PH)\(_2\) complexes shows changes in the pyridine ring vibrations. The band \(I \approx 1580\) cm\(^{-1}\) shows an upward shift of 15 cm\(^{-1}\), while the other two bands II and III, appearing at \( \approx 1470\) cm\(^{-1}\) show a downward shift of about 15 cm\(^{-1}\). The ring breathing mode at \( \approx 990\) cm\(^{-1}\) increases in frequency and appears at \( \approx 1005\) cm\(^{-1}\).\(^{25}\) All these changes in pyridine ring vibrations point towards pyridine nitrogen coordination. The strong band \( \approx 730\) cm\(^{-1}\), assignable to \(q_4 (C-C)\) disappears in the spectra of Ac(PH)\(_2\) complexes, and new bands appear at \( \approx 720\) and 760 cm\(^{-1}\). The \(C-C\) deformation vibrations designated as 6a and 16b modes at 610 and 410 cm\(^{-1}\) show an upward shift of 35–40 and 10–15 cm\(^{-1}\), respectively. These changes also suggest that the pyridine nitrogen coordinates with the metal atom\(^{26}\) in these complexes. However, the spectra of Ac(INH)\(_2\) complexes do not exhibit such changes, ruling out any possibility of pyridine nitrogen coordination\(^{26}\).

In the spectra of Ac(INH)\(_2\) complexes, the amide I band appears at \( \approx 1640\) cm\(^{-1}\) showing a downward shift, the amide II band at 1340 cm\(^{-1}\) showing an upward shift, while the amide III band splits into two bands appearing at \( \approx 1200\) and 1380 cm\(^{-1}\), respectively. The VI band shows an upward shift and
appears at \( \approx 500\ \text{cm}^{-1} \). All these changes are consistent with amide-oxygen coordination with the metal atom in these complexes\(^{37}\). Similar changes are, however, not observed in the spectra of Ac(PH)\(_2\) complexes, indicating that amide oxygen does not coordinate in Ac(PH)\(_2\) complexes.

The bands at \( \approx 1630\) and 840 cm\(^{-1}\) may be assigned to NH deformation coupled with OCN antisymmetric vibrations and NH out-of-plane bending, respectively. These bands disappear in the spectra of the complexes and new bands appear at \( \approx 1330\) and 1280 cm\(^{-1}\), respectively. These bands may be assigned to the amide group coupled with OCN stretching vibrations. The new sharp bands which appear in the spectra of the complexes show a downward shift of 10–20 cm\(^{-1}\), which indicates that azomethine nitrogen takes part in coordination. Thus, it appears that each acac molecule has reacted with the amino group of two hydrazide molecules. This is analogous to the fact that one acac or even one acetone molecule reacts with the two available amino groups, forming ring closure, and giving rise to macrocyclic molecules\(^{36}\). This contention finds support in the presence of new bands in the spectra of the complexes at \( \approx 2920, \approx 1265, \approx 1190\) and 680 cm\(^{-1}\), characteristic of the acac moiety, and assignable to \( \nu (\text{CH}_3) , \delta (\text{Sym.CH}) , \nu (\text{C-CH}_3) , \delta (\text{CH}) + \nu (\text{C-CH}_2) \) and ring deformations, respectively. The absence of a strong band at \( \approx 1530\) cm\(^{-1}\), characteristic of bonded carbonyl, further shows that both oxygen atoms of acac have reacted with two molecules of PH or INH, thus forming Ac(PH)\(_2\) or Ac(INH)\(_2\) species in the form of their metal complexes. Coordination with similar donor atoms in both sides of the molecules is indicated, since in the absence of such a coordination, the number of bands assigned to the various groups would have been doubled. It is clear from IR studies that though the isolation of the free tetradeionate ligand is not feasible, its metal complexes are obtained by the reaction of hydrazides and acac in the presence of these metal salts.

In the spectra of the nitrate complexes, the various bands observed at \( \approx 1260, 1050\) and 830 cm\(^{-1}\) are consistent with the presence and monodentate nature of the nitrate group\(^{31}\). Various \( \nu (\text{M-ONO}) \) bands observed in the far IR support this coordination. The spectra of the thiocyanato complexes show various bands at \( \approx 2130\) cm\(^{-1}\) \( \nu (\text{CN}) \), 820 cm\(^{-1}\) \( \nu (\text{CS}) \) and 480 cm\(^{-1}\) NCS bending, respectively. These bands are characteristic of a monodentate N-bonded thio­cyanate group\(^{32}\).

**Far IR Spectra**

Far IR spectra of complexes of Ac(INH)\(_2\) exhibit new bands at \( \approx 415–420\) cm\(^{-1}\). These bands may be assigned to \( \nu (\text{Fe}^{III}-\text{O}) \) and \( \nu (\text{Fe}^{II}-\text{O}) \), respectively. The absence of these bands in the corresponding complexes of Ac(PH)\(_2\) further indicates that the amido-oxygen does not take part in coordination. The bands observed in the regions \( \approx 285–270\) cm\(^{-1}\) for Fe(II) and 255–260 cm\(^{-1}\) for Fe(III) complexes of Ac(PH)\(_2\), may be assigned to the metalpyridine stretching vibrations\(^{33}\). All the complexes of iron(II) and iron(III) exhibit strong bands in the regions 385–390 and 370–375 cm\(^{-1}\) and may be assigned to metal-nitrogen (azomethine) stretching frequencies, respectively. The vibrational modes observed in the regions 330–335 and 305 cm\(^{-1}\) may be assigned to \( \nu (\text{Fe}^{II}-\text{Cl}) \) and \( \nu (\text{Fe}^{III}-\text{Cl}) \), respectively. In the thiocyanato complexes of
Ac(PH)$_2$, the $\nu$(Fe$^{\text{II}}$–NCS) vibrations are observed at comparatively higher energy ($\approx 365$ cm$^{-1}$). The $\nu$(Fe$^{\text{III}}$–NCS) vibrations observable at $\approx 275$ cm$^{-1}$ with a shoulder on either side are consistent with the range reported for distorted octahedral thiocyanato complexes$^{36}$.

Based on magnetic, electronic Mössbauer and IR studies, the following structures may be proposed for these complexes:

\[
\begin{align*}
\text{where } M &= \text{Fe}^{\text{II}} \text{ or Fe}^{\text{III}}, \text{ and } X = \text{Cl, Br, NO}_3 \text{ or NCS.}
\end{align*}
\]

REFERENCES


**SAZETAK**

5- i 6-koordinirani kompleksi dvo- i trovaljanog željeza s ligandima izvedenim iz kiselinskih hidrazida i acetilacetona

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Hidrazidi pikolinske kiseline (PH) i izonikotinske kiseline (INH) reagiraju s acetilacetonom u nazočnosti željeza(II) i željeza (III) dajući kompleksne novoga lančanog kvadridentnog liganda u kojima je koordinacijski broj željeza pet ili šest. Ti su kompleksi bili izolirani i proučeni različitim tehnikama (elementna analiza, konduktometrija, određivanje molne mase, određivanje magnetskih susceptibilnosti, elektrokska i infracrvena spektroskopija te Mossbauerova spektroskopija).

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