Synthesis, characterization and electrical conductivities of the complexes of oxovanadium(IV), iron(III), copper(II), zinc(II) and cadmium(II) with N-isonicotinoyl-N'-p-hydroxythiobenzhydrazine

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A new potential tetradentate ligand, N-isonicotinoyl-N'-p-hydroxythiobenzhydrazine (H₂INptbh) has been found to form complexes [M(INptbh)] (M = OV⁴⁺, Cu²⁺, Zn²⁺), [Fe(INptbh)(acac)] by loss of two protons from the ligand whereas, [Cd(HINptbh)]₂ is formed by loss of one proton. The complexes have been characterized by elemental analyses, magnetic susceptibility measurements UV-Vis, IR, ESR, ¹H and ¹³C NMR, Mössbauer and FAB mass spectral data. The room temperature ESR spectra of OV⁴⁺, Fe⁶⁺ and Cu⁹⁺ complexes yield <g> values characteristic of square pyramidal, octahedral and square planar complexes, respectively. The Mössbauer spectra of [Fe(INptbh)(acac)] at room temperature and 78 K suggest the presence of high spin Fe³⁺. The solid state electrical conductivity of the complexes are found to be low with σ, in the range of 10⁻¹-10⁻⁸ S cm⁻¹, however the conductivities of [Fe(INptbh)(acac)], [Cu(INptbh)], [Zn(INptbh)] and [Cd(HINptbh)] increase as the temperature increases from 307-397 K, with a band gap of 0.12 - 0.95 eV indicating their semiconducting behaviour. Other complexes are insulators.

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The chemistry of transition metal complexes derived from sulphur ligands has wide spectrum, ranging from synthesis to application in many diverse fields. Over the last more than one decade, there has been a dramatic growth of interest in inorganic complexes based materials that exhibit unusual solid-state properties. Some sulphur and nitrogen containing ligands and their complexes have been found to be important precursor for semiconducting materials¹ used as photosensitizer for conversion of light energy to electricity². Work has been reported on 3d metal complexes of p-hydroxy-thiobenzhydrazine³ and its N-aroyl derivatives⁴. In view of this we synthesized N-isonicotinoyl-N'-p-hydroxythiobenzhydrazine (Structure I) having oxygen, nitrogen and sulphur donors which is expected to form addition complexes without loss of a proton and deprotonated complexes by loss of one or both hydrazinic proton(s).

N-isonicotinic acid hydrazide was purchased from Sigma Chemical Company, USA. All other chemicals used were of analytical reagent or equivalent grade. Ammonium polysulphide⁵, bis(acetylacetonato)-oxovanadium(IV) and tris(acetylacetonato)iron(III) were prepared by reported procedures⁶. Sodium salt of p-hydroxydithiobenzoate was prepared by treating a solution of p-hydroxybenzaldehyde (25 g) in ethanol at 65 °C with the filtered ammonium polysulphide solution (135 mL), keeping the temperature at 65 °C. The reaction mixture was boiled to reflux for 30 min, immediately cooled in ice, acidified with conc HCl in the presence of ether. The dithio acid that separated as red oil was transferred into a separating funnel and the ethereal layer containing the dithio acid was separated and washed with cold distilled water. The red coloured sodium salt of dithio acid was extracted by shaking the dithio acid with aqueous 2N NaOH solution.

Synthesis of caboxymethyl-p-hydroxydithiobenzoate

To the sodium salt of p-hydroxydithiobenzoate was added a solution of chloroacetic acid (20 g) neutralized with sodium carbonate and pH of the mixture was adjusted to ~ 7. After standing the
reaction mixture overnight at room temperature, the dark solution was acidified with conc HCl and the ester, which separated on cooling, was filtered off, washed with cold water and recrystallized from hot ethanol in the presence of animal charcoal, m.p. 195°C (lit 194-197°C).

**Synthesis of H$_2$INptbh**

N-Isonicotinoyl-N'-p-hydroxythiobenzhydrazine (H$_2$INptbh) was prepared by reacting solutions of isonicotinic acid hydrazide (2.75 g, 20 mmol) and carboxymethyl-p-hydroxydithiobenzoate (4.56 g, 20 mmol) each dissolved separately in 40 mL of 0.5 N NaOH solution followed by dropwise addition of dilute acetic acid (20%) to the above reaction mixture, after letting the solution stand for 2 h. The product which precipitated was filtered, washed with water and recrystallized from ethanol m.p. 155°C, yield ~60%.

**Synthesis of [VO(INptbh)], [M(INptbh)] (M = Cu$^{II}$, Zn$^{II}$), [Cd(INptbh)]**

These complexes were prepared by refluxing together methanolic/chloroform solution (25 mL) each of the respective [M(OAc)$_2$·(H$_2$O)] (1 mmol) or [VO(acac)$_2$] (0.26 g, 1 mmol) and H$_2$INptbh (0.27 g, 1 mmol or 0.54 g, 2 mmol) for 1 h. The precipitated complexes were filtered, washed with methanol except [VO(INptbh)] which was washed with chloroform and dried *in vacuo*.

**Synthesis of [Fe(INptbh)(acac)]**

This was prepared by refluxing methanolic solution (25 mL) each of [Fe(acac)$_3$] (0.35 g, 1 mmol) and H$_2$INptbh (0.27 g, 1 mmol) for 3 h. The precipitated complex was removed by filtration, washed with methanol and dried *in vacuo*.

The complexes were analyzed for their metal content following the standard procedure$^8$, after decomposition with a mixture of HNO$_3$ and HCl followed by H$_2$SO$_4$. Sulphur was determined as BaSO$_4$. Carbon, hydrogen and nitrogen were determined on an EA 1108 CHN elemental analyzer. Magnetic susceptibility measurements were made at room temperature on a Cahn-Faraday balance using [Co(NCS)$_4$Hg] as calibrant. Analytical data and physical properties of the complexes are given in Table 1. Electronic spectra were recorded on a Cary-2390 UV-vis spectrophotometer as Nujol mulls$^9$. IR spectra were recorded in the 4000-400 cm$^{-1}$ region in KBr discs on a JASCO FT/IR-5300
obtain ed on a shapes u sing a Normos V spectrometer using DPPH as a $<g>$ marker. The Mössbauer spectra were recorded on a Cryophysics MS-1 microprocessor-controlled spectrometer. The source was a 25 mCi, 925 MBq $^{57}$Co that was mounted on an MVT-1000 transducer. The laser velocity was calibrated with an MVC-450 driving triangle waveform generated by an MD4-1200 driver unit and a DFG-1000 digital function generator. Data collection utilized a PC driven CMCA-550 MCA/PHA card from Wissel GmbH, Germany. The collected data was then fitted to Lorentzian line shapes using a Normos V 9.0 program. 78 K spectra were recorded as above using a custom-made cryostat (Prototech Ltd.). The FAB mass spectra were obtained on a JEOL SX 102, DA-600 mass spectrometer using m-nitrobenzyl alcohol (NBA) as a matrix. The solid-state electrical conductivity of pressed pellets of the complexes was measured by a conventional two-probe method in the 307-397 K range with contact made on the pellet surfaces. A Keithley 236 source measure unit was used to measure the resistance. The pellets were prepared at a loading of 15 Kilo-Newton's and contact on the pellet surfaces was made with silver paint. A sequence of increasing voltage in the +10 to -10V range with an increase of 5V in each step was applied and the current was measured. The resistance was calculated from the slope of the I vs V curve. The specific resistance was calculated from the resistance measurement using the known dimensions of the sample disc and converted into the specific conductance.

Results and discussion

The presence of a peak at m/z = 274 for [MH]$^+$ shows the monomeric nature of H$_2$INptbh. The ligand has also been characterized by IR and NMR ($^1$H and $^{13}$C) discussed in the respective sections. All compounds are air stable, [VO(INptbh)] and [Cd(HINptbh)$_2$] melt at 185 and 140°C, respectively. Other complexes do not decompose or melt up to 360°C. The ligands N-aroyl-N'-thioarylhydrazines generally act as binegative tetradeinate with hard metal ions forming 1:1 metal-ligand complexes but yield 1:2 complexes with soft metal ions (Cd$^{II}$, Pd$^{II}$) via deprotonation only through thiol sulphur$^{10}$. All complexes having a 1:1 metal-ligand stoichiometry, are formed by loss of two protons from the ligand generating a conjugated system, R'-C(S)=N=N-C(O)R. Because of steric consideration, all four potential sites cannot be attached to a single metal and, therefore, the ligand binds in a polymeric fashion. [Zn(INptbh)] is somewhat soluble in coordinating solvents such as DMSO and DMF. All the complexes are insoluble in water, ethanol, methanol, DMF and DMSO. The following equations represent the formation of the ligand and the complexes:

\[
\begin{align*}
(OH)C_6H_4CSSCH_2COOH+6H_2NCONH_2N_2H_2 & \xrightarrow{NaOH} (OH)C_6H_4CSSCH_2COOH+5H_2NCONH_2N_2H_2 \\
(OH)C_6H_4CSSCH_2COOH+6H_2NCONH_2N_2H_2 & \xrightarrow{AcOH} (OH)C_6H_4CSSCH_2COOH+5H_2NCONH_2N_2H_2
\end{align*}
\]

\[
[VO(acac)$_2$] + H$_2$INptbh \xrightarrow{CHCl_3} [VO(INptbh)] + 2Hacac
\]

\[
[Fe(acac)$_3$] + H$_2$INptbh \xrightarrow{MeOH} [Fe(INptbh)(acac)] + 2Hacac
\]

\[
[M(OAc)$_2n$H$_2$O] + H$_2$INptbh \xrightarrow{MeOH} [M(INptbh)] + 2AcOH + nH$_2$O
\]

\[
[CD(OAc)$_22$H$_2$O] + 2H$_2$INptbh \xrightarrow{MeOH} [Cd(HINptbh)$_2$] + 2AcOH + 2H$_2$O
\]

[VO(INptbh)] shows a magnetic moment of 1.80 BM which indicates the presence of one unpaired electron. It shows two absorptions at 14285 and 11900 cm$^{-1}$ corresponding to the $^2$B$_2 \rightarrow ^2E$, $^2A_1$, transitions, respectively, in the square pyramidal geometry. [Fe(INptbh)(acac)] shows a magnetic moment of 5.80 BM indicating the presence of high spin state of iron(III). It exhibits a d-d transition band at 12500 cm$^{-1}$ characteristic of an octahedral iron(III) complex. [Cu(INptbh)] shows a magnetic moment of 2.01 BM as expected for the presence of one unpaired electron and it exhibits a d-d band at 12500 cm$^{-1}$ due to the envelope of $^2$B$_{1g} \rightarrow ^2A_{1g}$, $^2$B$_{2g}$, $^2$E, transitions, usually observed for square planar Cu(II) complexes$^{11}$. [Cd(HINptbh)$_2$] exhibits two charge-transfer absorptions at 24100 and 21050 cm$^{-1}$. 

The room temperature EPR spectrum of [VO(Nptbh)] is typical of oxovanadium(IV) complexes with a well resolved sixteen line hyperfine structure (-100 atom % $^{51}$V, $I = 7/2$). The measured parameters are: $g_1 = 1.950$, $g_2 = 1.968$, $A_z = 180.000 \times 10^{-4}$ cm$^{-1}$ and $A_y = 80.000 \times 10^{-4}$ cm$^{-1}$ (ref.12). The observed order in the spin Hamiltonian parameters ($g_2 > g_1$ and $A_y > A_z$) suggest that the unpaired electron is largely in the $d_{xy}$ orbital with a square pyramidal structure around oxovanadium(IV). The room temperature solid state ESR spectrum of [Fe(INptbh)(acac)] yields two absorptions with $g_1$ and $g_2$ values of 4.140 and 2.005, respectively, for an octahedral iron(III). The spectrum of [Cu(INptbh)] shows a broad signal with $g_{av} = 2.248$ for a square planar Cu(II). The IR spectrum of H$_2$INptbh in KBr shows bands at 3170 and 3110 cm$^{-1}$ due to the presence of two NH groups. Other bands at 1659, 1440, 1320, 1005 and 903 cm$^{-1}$ are assigned to $v$(C=O), thioamide I [$\beta$(NH) + $v$(CN)], thioamide II [$v$(CN) + $\gamma$(NH)], $v$(N-N) and $v$(C=S) modes, respectively. In the KBr spectra of the complexes [M(INptbh)] (M = OV$^IV$, Cu$^II$, Zn$^{II}$ ) and [Fe(INptbh)(acac)] bands due to $v$(NH), $v$(C=O) and $v$(C=S) modes are absent, but new bands appear at ca. 1605-1620 and 750-760 cm$^{-1}$ due to $v$(N=C) and $v$(C=S) modes, respectively, suggesting removal of both the -NH- protons via enolisation and thioenolisation and bonding of the resulting enolic oxygen and thiolato sulphur takes place with the metal ion. Furthermore, positive shifts in thioamide I, thioamide II and $v$(N-N) bands in the complexes suggest involvement of these groups as bonding sites. These observations show the involvement of thiolato sulphur and both the hydrazinic nitrogens in addition to enolic oxygen in bonding. Thus, H$_2$INptbh acts as a binegative tetradeionate ligand. In addition, the spectrum of [Fe(INptbh)(acac)] shows bands at 2920, 1470 and 1330 cm$^{-1}$, assigned to $v$(CH$_3$), $v$(CH) + $v$(C-C) and $v$(CH$_2$) modes, respectively, which are very close to the bands reported for a chelated acetylenicato group. The IR spectrum of [Cd(HINptbh)$_2$] in KBr shows a band at 3165 due to $v$(NH) suggesting loss of one -NH- proton via thioenolisation. Furthermore, $v$(C=S) band is absent and $v$(N-N) band shows a positive shift of 40 cm$^{-1}$, suggesting bonding through thiolato sulphur and one hydrazinic nitrogen. The $v$(C=O) band shows a negative shift of 39 cm$^{-1}$ suggesting an additional bonding through the carbonyl oxygen.

The $^1$H NMR spectrum of the ligand shows three signals at $\delta$ 9.63, 10.39 and 11.53 ppm due to the presence of -NHC(S)-, -NHC(O)- and -OH protons, respectively, which disappear on D$_2$O exchange. Phenyl ring protons appear at $\delta$ 6.89 (t, 2H) and 7.26 (d, 2H) ppm and the pyridine ring protons appear at $\delta$ 8.03 (d, 2H) and 9.03 (d, 2H) ppm. The assignments for the pyridine ring protons have been made by comparing the $^1$H NMR spectrum of H$_2$INptbh with that of isonicotinic acid hydrazide, INH. The NH signals are absent from the $^1$H NMR spectrum of [Zn(INptbh)], suggesting loss of both NH protons via enolisation and thioenolisation. The phenyl ring protons appear at 6.86 (s, 2H) and 7.66 (s, 2H) ppm and pyridine ring protons are observed at $\delta$ 8.13 (m, 2H) and 8.73 (m, 2H) ppm. The $^{13}$C NMR spectrum of H$_2$INptbh shows thirteen signals of which two signals at $\delta$ 196.93 and 163.45 ppm are due to the C=S and C=O carbons, respectively. On comparing the spectrum of H$_2$INptbh with that of INH, the chemical shift for the ring carbons in H$_2$INptbh are: (\$ ppm) 150.44 (C$_{26}$); 121.35 (C$_{33}$); 139.56 (C$_4$); 115.12 (C$_1$); 160.79 (C$_2$); 114.74 (C$_{43}$); 129.21 (C$_{22}$). The signals at $\delta$ 200.47 and 164.95 ppm in [Zn(INptbh)] show downfield shift of 3.54 and 1.50 ppm, respectively, as compared to the ligand suggesting the formation of C-S and C-O groups from the ligand on thioenolisation and enolisation, respectively. A signal at 159.44 ppm for C$_2$ shows that the OH group of the ligand is present in the complex. Due to the paramagnetic nature of oxovanadium(IV), Fe(III) and Cu(II) complexes and insolvency of [Cd(HINptbh)$_2$], their NMR spectral studies could not be made.

H$_2$INptbh is identified by the FAB mass spectrum, which shows many peaks due to various fragments. The spectrum shows molecular ion peak at $m/z = 274$ [MH]$^+$. Other peaks at $m/z = 256$ [(OH)$_2$C$_2$H$_5$CN$_2$CSC$_3$H$_7$N]$^+$, 240 [(OH)$_2$C$_2$H$_5$CN$_2$CO$_2$C$_3$H$_7$N]$^+$ and 195[(OH)$_2$C$_2$H$_5$CSC$_3$H$_7$CO] $^+$ are formed by release of H$_2$O, H$_2$S and C$_2$H$_4$N, respectively, from the ligand. The FAB mass spectra of the complexes could not be obtained either due to their insolubility or high melting nature.

The Mössbauer spectra of [Fe(INptbh)(acac)] at room temperature and at liquid nitrogen temperatures have been studied. The spectra show a doublet at both temperatures. The $\delta$ and $\Delta E$ values are 0.328 and 0.660 mm s$^{-1}$, respectively, at room temperature, while these values at liquid nitrogen temperature are
0.425 and 0.645 mm s⁻¹, respectively, which are indicative of a high-spin, S = 5/2 state of iron(III) with a distorted octahedral geometry.

Compressed pellet molecular electrical conductivities of the complexes were measured over 307-397 K range using two-probe technique. The values of the solid state electrical conductivities of the complexes were found to be in the range of 10⁻¹⁰⁻⁻¹⁰⁻⁹ S cm⁻¹ and they are semiconductors because their conductivities increase with increase in temperature and decrease upon cooling over the above temperature range. The ln(σ) of the complexes decreases with 1/T, indicating that the complexes show typical semiconducting behaviour. The plot is almost linear. The band gaps evaluated from the plots using the relationship: 2.303 × 8.314 × 10⁻⁵ x slope were found to be 0.44, 0.95, 0.12, 0.25 for [Fe(INptbh)(acac)], [Cu(INptbh)], [Zn(INptbh)] and [Cd(HINptbh)], respectively, which indicate their potential to be used as sensitizer for wide band-gap semiconductor electrode such as ZnO, TiO₂, SnO₂ etc., a component of dye sensitized photoelectrochemical cells for practical applications such as solar cells etc. Furthermore, the lower conductivity of the complexes as compared to transition metal complexes of dithio ligands¹⁷ show weaker intermolecular contact and less extended delocalization and rules out any possibility of partial oxidation of the central metal producing higher conductivity.

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References