Open Shell Hexamethyleneiminecarbodithioates of VO(IV), Cr(III), Mn(II & III), Fe(III), Co(II) & Cu(II)—Magnetic, Spectral & Antimicrobial Investigations

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The high spin complexes of sodium hexamethyleneiminecarbodithioate (NaHMICdt) with VO(IV), Cr(III), Mn(II and III), Fe(III), Co(II) and Cu(II) complexes have been prepared and characterized by elemental analyses, molar conductance and magnetic measurements (at 77 to 298 K) and electronic, IR, ESR and Mössbauer spectra. The Co(II) and Cu(II) complexes have square planar geometry and others octahedral except VO(IV), for which square pyramidal arrangement is indicated. The Mn(HMICdt)OH has antiferromagnetic interaction and probably hydroxy-bridged dimeric structure. The Fe(HMICdt) exhibits fast spin cross-over at room temperature. The ligand coordinates symmetrically through bisulphur fork. The Mn(II) complexes have been stabilised by the auxiliary ligands, viz. 1,10-phenanthroline and 2,2'-bipyridyl. The ligand and its complexes have been tested for their activity against bacteria and fungi. The ligand and the Mn(II) and Fe(III) complexes are shown to possess both antibacterial and antifungal activity.

The chemistry of metal dithiocarbamates has attracted the attention of many research workers due to their applications1-3 in diverse areas. The complexation of heterocyclic dithiocarbamates is less explored than that of N,N'-dialkyldithiocarbamates; however, it is found to be different in several respects4 because donor properties of CSS- group depend on the basicity of the parent amine. The behaviour of such a ligand having a seven-membered nonplanar saturated heterocyclic ring system linked to - CSS- group is expected to be different from that of planar heterocyclic dithiocarbamates. The seven-membered saturated ring system is expected to offer greater steric hindrance and thus can give metal complexes of unusual geometries. It is, therefore, thought worthwhile to examine the metal-hexamethyleneiminecarbodithioates and hence the title investigation.

Materials and Methods

Synthesis of ligand

Sodium hexamethyleneiminecarbodithioate (NaHMICdt.2H2O) was prepared as follows: Sodium hydroxide pellets (2 g) were dissolved in a minimum amount of ethanolic-water (4:1) mixture. Hexamethylenemine (5 mg) in diethyl ether was stirred with the NaOH slurry for 5 min and CS2 (4 g) in diethyl ether (100 ml) was slowly added to the mixture under vigorous stirring during 1.5 hr. The contents were further stirred for another 1.5 hr and the precipitate was filtered, washed with diethyl ether and dried in vacuo over anhydrous calcium chloride. The recrystallized product from acetonite-petroleum ether (m.p. 188-89°) yielded satisfactory elemental analyses, IR, PMR and mass spectra authenticating the purity of the compound. Thermogravimetric analysis confirmed the presence of 2 mol of water.

Synthesis of complexes

The complexes of VO(IV), Fe(II), Co(II) and Cu(II) were prepared respectively by reacting vanadyl sulphate, ferric ammonium sulphate, cobaltous nitrate and copper sulphate (0.25 g each), with 4-5 fold excess of NaHMICdt in aqueous solution. The compounds which precipitated out immediately were washed with cold water, filtered and dried in vacuo over anhydrous CaCl2. On reacting commercially available (BDH) manganous chloride in a similar way a compound having the composition Mn(HMICdt)OH was obtained instead of the expected Mn(HMICdt)2. The complexes of Mn(II) were prepared only as mixed ligand complexes with nitrogen donors, viz. 1,10-phenanthroline and 2,2'-bipyridyl by the following procedure.

Phenanthroline or bipyridine (three-times over metal) dissolved in ethanol-water (2:1) was slowly added to an aqueous solution of the complex (2.7 g), stirred for 8 hr and filtered, washed with ethanol, and dried in vacuo over anhydrous CaCl2. To synthesize the Cr(III) chelate the ligand was added to a solution of CrCl3.6H2O in absolute ethanol in a 3:1 mol ratio. The resulting mixture was stirred, washed with absolute ethanol, and dried in vacuo over anhydrous CaCl2.
Analyses and spectral studies

The metals in the complexes after decomposing these with concentrated HNO₃ were estimated using a Pye-Unicam SP 191 atomic absorption spectrophotometer. The IR spectra of the samples were recorded in CsI discs in the range 4000-200 cm⁻¹ on Perkin-Elmer 580 B and Nicolet 5 DX FT-IR spectrophotometers. Electronic spectra in nujol and chloroform were recorded on 554 Perkin-Elmer and Hitachi 330 UV-Vis spectrophotometers. ESR spectra were recorded on Varian E-12 and E-112 EPR spectrometers. Mössbauer spectrum of iron complex was recorded on a wiesel drive coupled to Canberra multichannel analyzer operating in the multiscaling mode, using a 25 mCi ⁵⁷Co radioactive source embedded in Pd-matrix. Na₂[Fe(CN)₆NO]·2H₂O was employed as the calibrant. The programme of E. Von Meerwall was executed on an ICL 2960 computer to obtain the computer generated plot of the Mössbauer spectrum. The magnetic susceptibilities of the polycrystalline samples were measured on a PARC model 155 vibrating sample magnetometer at room temperature and low temperatures down to 77 K. The conductance measurements were made on a W.G. Pye conductance bridge.

Results and Discussion

The results of elemental analyses recorded in Table 1 authenticate the assigned stoichiometries. All the complexes were found to behave as non-electrolytes in nitrobenzene as expected.

The observed μ_eff = 1.65 B.M. of VO(HMICdth)₂ is close to the spin only value for one unpaired electron, ruling out the possibility of direct intermolecular V-V interaction. The bands at 16.447, 18.382 and 21.008 kK observed in its electronic spectrum in nujol, have been assigned to 2g → 1a, 2g → 1e and 2g → 1a transitions respectively, indicating square pyramidal arrangement of ligands with C₄ᵥ symmetry around vanadium. A band around 24 kK is believed to be ligand to metal charge transfer in origin. The electronic spectra in pyridine and DMSO exhibit a new band in the region 12.903-13.158 kK and a shoulder in 16.26-16.40 kK region, due to coordination of the solvent molecule with vanadium. Moreover, the 2g → 1e transition is found to decrease by 5 kK. These observations provide further support to square pyramidal structure. The ESR spectrum of the complex in DMF at room temperature was found to be isotropic containing eight lines. The g₁ and g₅ values (1.9004 and 2.0268 respectively) indicate substantial covalent character of V-S bond. The IR spectrum of the complex exhibits a band at 952 cm⁻¹ due to terminal ν(V=O), ruling out the presence of V—O—V—O chain. The nature and the extent of shift observed in ν(C—N), ν₁(C—S) and ν₃(C—S) modes on complexation are found to be of the same order as reported in literature, indicating symmetric bonding of the dithiocarbamate group. The IR spectrum of the complex also exhibits bands at 408 and 375 cm⁻¹ due ν(V=S).

The magnetic moment of Cr(HMICdt)₃ (3.8 B.M.) is slightly less than the spin only value as is generally the case with octahedral chromium(III) complexes due to very small spin-orbit coupling constant of Cr³⁺. Its electronic spectrum in chloroform displays two bands at 15.25 and 20.00 kK, assignable to 4A₂g → 4T₂g(F) and 4A₂g → 4T₁g(F) transitions respectively. The band at 33.50 kK is the charge transfer band masking the ν₁[4A₂g → 4T₁g(P)]. These observations agree well with an octahedral arrangement around chromium in the complex. The values of parameters B, β, z and CFSE are calculated to be 446 cm⁻¹, 0.49, 0.68 and 218.92 kJ mol⁻¹ respectively. The DT/DQ found to be lower than the limiting value (0.4226), supports the expected small trigonal distortion from the perfect cubic symmetry. The ESR spectrum of the powdered complex is isotropic at room temperature. The value of g (1.9742) and covalency parameter (γ, 0.60) suggest significant covalency of Cr-S bond. The ν(Cr=S) mode in the complex is observed at 378 cm⁻¹. A comparison of IR spectrum of the complex with that of ligand suggests symmetrical bonding of the bisulphur fork with chromium, as in the case of VO²⁺ complex.

The manganese complex Mn(HMICdth)₂ could not be isolated. This may be due to the tendency of Mn(II) to form an octahedral complex. The octahedral Mn(HMICdth)(H₂O)₂ is not stable and, therefore stabilization through relatively stronger auxiliary ligands is needed. The steric factor due to non-planarity of the ring, perhaps prevents the formation of a polymeric structure with composition Mn(HMICdt)₂ as is observed for diethylidithiocarbamate. The isolation of Mn(II) as well as Mn(III) complex of HMICdth (later in low yield) was possible from the commercially available manganese dichloride, without involving any additional oxidising agent. The presence of (MnOH)Cl₂ in commercial MnCl₂ seems to be responsible for the formation of Mn(III) complex, which contains an OH group.

The magnetic moments of [Mn(HMICdth)phen] and [Mn(HMICdth)bipy] in the range of 5.76-5.97 B.M., indicate these to be high spin octahedral complexes. The low temperature magnetic susceptibility measurements (upto 77 K) indicate that the complexes follow Curie-Weiss law. The bands observed in their electronic spectra at 16.67, 21.05-21.74, 27.78-28.57 and 36.10-37.04 kK are assigned to 6A₁g → 4T₁g(G), 6A₂g → 4T₂g(G), 6A₂g → 4T₅g(D) and charge transfer transitions respectively.
Fe(II) complex at room temperature consists of quadrupole-split, well-resolved doublet with $b = 0.4 \text{ mm s}^{-1}$ and $\Delta E_q = 0.53 \text{ mm s}^{-1}$. This implies that time of spin cross over is shorter than life-time of $^{57}\text{Fe}$ excited state ($1.45 \times 10^{-7}\text{s}$). The $b$-value is closer to the weak ligand field and supports electron donation from the ligand $\alpha$-orbitals to metal $d$-orbitals. The electronic spectrum of $\text{Fe(HMICdt)}_3$ has the charge transfer and intraligand transition bands in the range 25.64-37.74 kK. The band at 16.95 kK may be attributed to $^2T_z \rightarrow ^2T_g$ transition. These observations support an octahedral geometry for the complex. The $\nu(\text{Fe-S})$ mode appears at 368 cm$^{-1}$. The difference between IR spectrum of HMICdt Na and its Fe(III)-complex is of the type observed in other complexes described above. Therefore, the ligand seems to be symmetrically bonded in the iron complex too.

The Co(HMICdt)$_2$ has the room temperature magnetic moment value of 2.51 B.M., as expected for a square planar complex. Its electronic spectrum in chloroform exhibits peaks at 15.75 $^2A_g \rightarrow ^2B_2$), 20.83 ($^2A_g \rightarrow ^2E$) and 25 kK ($^2A_g \rightarrow ^2B_1$) compatible with a square planar geometry. The ESR spectrum of Fe(III) complex at room temperature consists of quadrupole-split, well-resolved doublet with $\delta = 0.4 \text{ mm s}^{-1}$ and $\Delta E_q = 0.53 \text{ mm s}^{-1}$. This implies that time of spin cross over is shorter than life-time of $^{57}\text{Fe}$ excited state ($1.45 \times 10^{-7}\text{s}$). The $\delta$-value is closer to the weak ligand field and supports electron donation from the ligand $\sigma$-orbitals to metal $d$-orbitals. The electronic spectrum of $\text{Fe(HMICdt)}_3$ has the charge transfer and intraligand transition bands in the range 25.64-37.74 kK. The band at 16.95 kK may be attributed to $^2T_z \rightarrow ^2T_g$ transition. These observations support an octahedral geometry for the complex. The $\nu(\text{Fe-S})$ mode appears at 368 cm$^{-1}$. The difference between IR spectrum of HMICdt Na and its Fe(III)-complex is of the type observed in other complexes described above. Therefore, the ligand seems to be symmetrically bonded in the iron complex too.

### Table 1—Physical Properties and Analytical Data of Metal-Hexamethyleniminecarbodithioates

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>m.p. (°C)</th>
<th>ΔM (Ω$^{-1}$ cm$^2$.mol$^{-1}$)</th>
<th>Calc (Found)%</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO(HMICdt)$_2$</td>
<td>yellow</td>
<td>81-83</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>Cr(HMICdt)$_3$</td>
<td>bluish-grey</td>
<td>&gt; 250</td>
<td>0.44</td>
<td></td>
</tr>
<tr>
<td>[Mn(HMICdt)$_2$phen]</td>
<td>saffron</td>
<td>210</td>
<td>0.80</td>
<td></td>
</tr>
<tr>
<td>[Mn(HMICdt)$_2$bipy]</td>
<td>brick red</td>
<td>120</td>
<td>0.90</td>
<td></td>
</tr>
<tr>
<td>[Mn(HMICdt)$_2$OH]</td>
<td>violet red</td>
<td>98</td>
<td>1.43</td>
<td></td>
</tr>
<tr>
<td>Fe(HMICdt)$_3$</td>
<td>dark brown</td>
<td>247</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>Co(HMICdt)$_2$</td>
<td>dark green</td>
<td>&gt; 250</td>
<td>0.46</td>
<td></td>
</tr>
<tr>
<td>Cu(HMICdt)$_2$</td>
<td>chocolate</td>
<td>145</td>
<td>0.40</td>
<td></td>
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</tbody>
</table>

Three bands provide further support to octahedral geometry of the complexes. The value of $\beta (0.723)$ indicates appreciable covalent character of Mn-S bond.

The magnetic moment of Mn(HMICdt)$_2$OH in the range of 4.35-4.9 B.M., is lower than the spin-only value. The low temperature magnetic measurements reveal that Curie-Weiss law is not followed and complex has a bi- or poly-nuclear structure having antiferromagnetic interactions. The electronic spectrum of this complex displays a shoulder at 16.5 kK assignable to $^2E_g \rightarrow ^2T_{2g}$ transition as expected for octahedral geometry, and charge-transfer bands at 19.50, 27.50 and 36.78 kK. The ESR spectrum of the polycrystalline Mn(III)-complex exhibits a broad signal whereas that in chloroform solution, the spectrum exhibits a four-line signal. The $g_\parallel$ and $g_\perp$ are found to be 2.3314 and 1.9534 respectively (from spectrum of polycrystalline sample), indicating that metal-ligand bond does not have much covalency. The IR spectrum of this complex displays a band at 962 cm$^{-1}$ which seems to arise from the bending mode of bridging OH group and therefore, structure (A) seems logical for this Mn(III) complex. However, $\nu_{\text{Mn-O}}$ could not be unequivocally assigned in the far IR region. The IR spectra of Mn(II) complexes exhibit bands around 1300 cm$^{-1}$ which seem to arise from the coordinated phen or bipy as reported in the literature. In view of the above facts structure (B) seems more appropriate for the Mn(II) complexes.

The room temperature magnetic moment of 4.65 B.M. of the Fe(HMICdt)$_3$ complex indicates the mixed ground state in octahedral geometry around Fe(III). The variation of $\mu_{\text{eff}}$ with temperature (77 to 293 K) suggests the existence of a spin state equilibrium ($^5A_g \leftrightarrow ^3T_2$). The Mössbauer spectrum of the Fe(III) complex at room temperature consists of quadrupole-split, well-resolved doublet with $\delta = 0.4 \text{ mm s}^{-1}$ and $\Delta E_q = 0.53 \text{ mm s}^{-1}$. This implies that time of spin cross over is shorter than life-time of $^{57}\text{Fe}$ excited state ($1.45 \times 10^{-7}\text{s}$). The $\delta$-value is closer to the weak ligand field and supports electron donation from the ligand $\sigma$-orbitals to metal $d$-orbitals. The electronic spectrum of $\text{Fe(HMICdt)}_3$ has the charge transfer and intraligand transition bands in the range 25.64-37.74 kK. The band at 16.95 kK may be attributed to $^2E \rightarrow ^2T_{2g}$ transition. These observations support an octahedral geometry for the complex. The $\nu(\text{Fe-S})$ mode appears at 368 cm$^{-1}$. The difference between IR spectrum of HMICdt Na and its Fe(III)-complex is of the type observed in other complexes described above. Therefore, the ligand seems to be symmetrically bonded in the iron complex too.

The Co(HMICdt)$_2$ has the room temperature magnetic moment value of 2.51 B.M., as expected for a square planar complex. Its electronic spectrum in chloroform exhibits peaks at 15.75 ($^2A_g \rightarrow ^2B_2$), 20.83 ($^2A_g \rightarrow ^2E$) and 25 kK ($^2A_g \rightarrow ^2B_1$) compatible with a square planar geometry. The ESR spectrum of
the polycrystalline sample is anisotropic at room temperature as well as liquid N\textsubscript{2} temperature. The small difference in the g values may be due to the formation of a weak axial Co-S bond at liquid N\textsubscript{2} temperature. The low value of g\textsubscript{1} (1.5262) arises from admixture of 4s and 3d\textsubscript{z} orbitals, and intermolecular cobalt-sulphur interaction. The absence of s.h.f.s. in the spectrum indicates that the unpaired electron most probably resides in d\textsubscript{z} orbital. The v (Co-S) mode in the IR spectrum is observed at 360 cm\textsuperscript{-1}. The symmetric bonding of HMICdt is indicated by its IR spectrum. The low value of g\textsubscript{1} (1.5262) arises from admixture of 4s and 3d\textsubscript{z} orbitals, and intermolecular cobalt-sulphur interaction. The absence of s.h.f.s. in the spectrum indicates that the unpaired electron most probably resides in d\textsubscript{z} orbital. The v (Co-S) mode in the IR spectrum is observed at 360 cm\textsuperscript{-1}. The symmetric bonding of HMICdt is indicated by its IR spectrum. The magnetic moment of Cu(HMICdt\textsubscript{2})\textsubscript{2} (1.73 B.M.) is close to the spin-only value and \mu\textsubscript{eff} is independent of temperature. Its electronic spectrum in chloroform displays a broad shoulder at 16.39 kK and an intense band at 22.99 kK due to 2B\textsubscript{1g} \rightarrow 2A\textsubscript{g} and 2B\textsubscript{1g} \rightarrow 2E\textsubscript{g} transitions, respectively, indicating the square planar geometry. The ESR spectrum of polycrystalline copper complex is anisotropic. The ESR spectrum of frozen chloroform solution of the complex is very similar, probably due to weak Cu-S axial interactions. The g\textsubscript{1} and g\textsubscript{2} values (\sim 2.1292 and \sim 1.9764 respectively) are lower than those expected for an octahedral complex, and suggest that unpaired electron lies in d\textsubscript{z} orbital and Cu-S bond has considerable covalent character. The vCu-S mode in its IR spectrum appears at 368 cm\textsuperscript{-1}. The other IR frequencies are in favour of symmetrical bonding of bisulphur fork.

Antimicrobial screening

The HMICdtNa as well as its complexes have been tested for antibacterial activities against Streptococcus faecalis (I), Klebsiella pneunomiae (II), Escherichia coli (III), Pseudomonas aeruginosa (IV) and Staphylococcus aureus penicillin-resistant (V) and for the antifungal activities against Candida albicans (VI), Cryptococcus neoformans (VII), Sporotrichum schenckii (VIII), Trichophyton mentagrophytes (IX) and Aspergillus fumigatus (X). The antibacterial tests were carried out in peptone broth and antifungal tests in Sabouraud's broth. The 12.5 to 25 \mu g cm\textsuperscript{-3} of HMICdtNa was found to inhibit the growth of all fungi and bacteria except IV and VIII. For [Mn(HMICdt\textsubscript{2}) \textsubscript{2}phen] and [Mn(HMICdt\textsubscript{2},bipy] minimum inhibitor concentrations were in the range of 6.25 to 25 \mu g cm\textsuperscript{-3}. The 2,2'-bipyridyl derivative of Mn(II) was not active against III, IV, VI and IX whereas the 1,10-phenanthroline derivative was active against I, II, III, V and X only. The 12.5 to 25 \mu g cm\textsuperscript{-3} of Fe(HMICdt\textsubscript{2}) inhibited the growth of I, V, VII and IX. The other complexes have not been found active against these bacteria and fungi.

References