Synthesis & Structural Studies of Oxovanadium(IV), Chromium(III), Manganese(II), Cobalt(II & III), Nickel(II), Copper(II) & Zinc(II) Complexes of 2-Furanthiocarboxyhydrazide

N K SINGH, (MISS) SEEMA AGRAWAL & R C AGGARWAL
Department of Chemistry, Banaras Hindu University, Varanasi 221 005

Received 4 February 1982; revised and accepted 13 July 1982

2-Furanthiocarboxyhydrazide (Hfth) forms adducts and cationic-anionic and deprotonated types of complexes with oxovanadium(IV), Cr(III), Mn(II), Co(II & III), Ni(II), Cu(II) and Zn(II). Molar conductance measurements indicate that all deprotonated and dichloro complexes of Zn(II) and Cu(II) are non-electrolytes, complexes of oxovanadium(IV) and Cr(III) chlorides are 1:1 electrolytes and those of Ni(II) and Co(III) chlorides are 1:2 and 1:3 electrolytes respectively. Magnetic measurements and electronic spectral studies suggest square-planar geometry for Co(II), Ni(II) and Cu(II) deprotonated complexes and octahedral geometry for all the other complexes. Infrared spectral studies show neutral uninegative bidentate behaviour of Hfth, the bonding sites being terminal nitrogen and thionethiol sulphur.

Although transition metal complexes of acylhydrazines are well known1-4, comparatively much less work has been done on the transition metal complexes of thio analogues of acylhydrazines5-8. No previous work on transition metal complexes of 2-furanthiocarboxyhydrazide is reported except the synthesis and magnetic susceptibility measurements made on VO(Hfth)2SO4 (ref. 7). We report here the preparation and characterisation of oxovanadium(IV), Cr(III), Mn(II), Co(II & III), Ni(II), Cu(II) and Zn(II) complexes of 2-furanthiocarboxyhydrazide.

Materials and Methods

All the chemicals used were BDH or equivalent reagents. 2-Furanthiocarboxyhydrazide was prepared as described by Jensen and Pedersen9, m.p. 133 (lit.9 132-133').

The metal chloride complexes were prepared by mixing the ethanolic solution of the appropriate metal chloride and the ethanolic-ethereal solution of the ligand in ~ 1:2 molar ratio. All the complexes precipitated immediately or on stirring for sometime; the Co(III) chloride complex was, however, precipitated by the addition of dil. HCl. Pure Co(II) chloride complex could not be prepared because of its facile oxidation to the corresponding Co(III) complex.

VO(fth)2. H2O was prepared by refluxing for ~ 1 hr the ethanolic solutions of vanadyl chloride and the ligand and concentrating the reaction mixture to incipient crystallisation. The deprotonated complexes of Co(II), Ni(II), Cu(II) and Zn(II) were prepared by adding ethanolic solution of the ligand to the aqueous solution of respective metal(II) acetate in presence of sodium acetate in ~ 1:2 molar ratio and digesting the reaction mixture for ~ 30 min. The deprotonated complexes of Mn(II) and Cr(III) were prepared by adding the ligand dissolved in the minimum amount of ethanolic KOH to an aqueous solution of MnCl2.4 H2O/chrome alum keeping the metal-ligand ratios 1:2 and 1:3, respectively. All the deprotonated complexes thus obtained were suction-filtered, washed with water, ethanol and finally with ether and dried in vacuo. The deprotonated complexes of Cr(III) and Mn(II) were recrystallised from ethanol.

The complexes were analysed for their metal contents employing standard literature procedures after destroying the organic matter at first with a mixture of nitric and hydrochloric acids and then with conc. sulphuric acid. Sulphur and chloride were estimated as BaSO4 and AgCl, respectively. Nitrogen was determined by microanalysis.

Electrical conductances were measured on a WTW conductivity meter in MeOH/DMF. The magnetic susceptibilities of the complexes were determined by the Faraday method using Hg[Co(NCS)4] as the calibrant, and experimental magnetic susceptibilities were corrected for diamagnetism10. Analytical, molar conductance and magnetic moment data of the complexes are given in Table 1.

The electronic spectra of the complexes were recorded on a Cary-14 spectrophotometer in nujol. The various absorption bands, their assignments and the values of the ligand field parameters such as 10 Dq, B, β' and LFSE were calculated as described by Lever11.

The infrared spectra of the ligand and the complexes were recorded on a Perkin Elmer spectrophotometer model 621 in nujol.

Results and Discussion

Hfth has been found to form adducts (dichloro) cationic-anionic and deprotonated type of complexes.
Table I — Characterization Data of Hfth Complexes

<table>
<thead>
<tr>
<th>Compound</th>
<th>Colour (m.p., °C)</th>
<th>Found (Calc.), %</th>
<th>( \mu_{\text{eff.}} ) (B.M.)</th>
<th>( \Lambda_{\mu} ) (mosis cm² mol⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{VO(Hfth)}_2\text{Cl}]\text{Cl} )</td>
<td>Brown (&gt; 300)</td>
<td>12.84 (12.08)</td>
<td>13.80 (13.27)</td>
<td>17.30 (16.81)</td>
</tr>
<tr>
<td>([\text{Cr(Hfth)}_2\text{Cl}_2]\text{Cl}_2\text{H}_2\text{O} )</td>
<td>Dark-green (&gt; 300)</td>
<td>10.80 (11.29)</td>
<td>12.45 (12.16)</td>
<td>22.44 (23.09)</td>
</tr>
<tr>
<td>([\text{Mn(Hfth)}_2\text{Cl}_2] )</td>
<td>Yellow (198)</td>
<td>12.11 (13.41)</td>
<td>14.30 (13.61)</td>
<td>17.73 (17.30)</td>
</tr>
<tr>
<td>([\text{Ni(Hfth)}_2\text{Cl}_2] )</td>
<td>Pink (217)</td>
<td>10.37 (9.97)</td>
<td>14.94 (14.21)</td>
<td>17.64 (17.98)</td>
</tr>
<tr>
<td>([\text{Cu(Hfth)}_2\text{Cl}_2] )</td>
<td>Dirty-yellow (300)</td>
<td>10.73 (10.54)</td>
<td>15.48 (15.12)</td>
<td>12.18 (12.77)</td>
</tr>
<tr>
<td>([\text{Zn(Hfth)}_2\text{Cl}_2] )</td>
<td>Brown (260)</td>
<td>14.63 (14.95)</td>
<td>13.56 (13.32)</td>
<td>17.10 (16.94)</td>
</tr>
<tr>
<td>([\text{VO(fth)}_2\text{H}_2\text{O}] )</td>
<td>Brown (110)</td>
<td>14.14 (14.52)</td>
<td>15.68 (15.96)</td>
<td>— (—)</td>
</tr>
<tr>
<td>([\text{Cr(fth)}_2\text{OH})\text{H}_2\text{O} )</td>
<td>Brown (200)</td>
<td>13.68 (14.09)</td>
<td>15.10 (15.18)</td>
<td>— (—)</td>
</tr>
<tr>
<td>([\text{Mn(fth)}_2\text{2 H}_2\text{O}] )</td>
<td>Brown (300)</td>
<td>14.27 (14.73)</td>
<td>14.86 (15.02)</td>
<td>— (—)</td>
</tr>
<tr>
<td>([\text{Co(fth)}_2] )</td>
<td>Dark-brown (300)</td>
<td>16.80 (17.29)</td>
<td>16.80 (16.43)</td>
<td>16.70 (18.78)</td>
</tr>
<tr>
<td>([\text{Ni(fth)}_2] )</td>
<td>Brown (300)</td>
<td>16.72 (17.23)</td>
<td>16.27 (16.44)</td>
<td>— (—)</td>
</tr>
<tr>
<td>([\text{Cu(fth)}_2] )</td>
<td>Brown (163)</td>
<td>18.68 (18.10)</td>
<td>16.47 (16.21)</td>
<td>— (—)</td>
</tr>
<tr>
<td>([\text{Zn(fth)}_2\text{2 H}_2\text{O}] )</td>
<td>Yellow (173)</td>
<td>16.85 (17.06)</td>
<td>14.85 (14.61)</td>
<td>— (—)</td>
</tr>
</tbody>
</table>

(a) in methanol, (b) in DMF

The first two types of complexes are in general formed in neutral solution while the formation of the latter type results at pH 6-7 on the addition of requisite amount of sodium acetate or potassium hydroxide solution. All the complexes are insoluble in water but soluble in DMF, DMSO and, with a few exceptions, in EtOH and MeOH. The molar conductance values in MeOH/DMF show that all deprotonated complexes and adducts of 

\[
\text{Cu(II)} \text{ and } \text{Zn(II)} \text{ chlorides are } \text{non-electrolytes whereas the other metal chloride complexes are ionic, being } 1:1, 1:2 \text{ or } 1:3 \text{ electrolytes.}
\]

The magnetic moment data given in Table I suggest high-spin tetrahedral/octahedral geometry for Mn(II) and Cr(III) complexes, high-spin octahedral geometry for Ni(II(Hfth))Cl₂, low-spin octahedral geometry for Co(Hfth)₃Cl₃ and square-planar geometry for Co(fth)₂ (ref. 13) and Ni(fth)₂. The magnetic moments of Cu(II) and oxovanadium(IV) complexes are normal and correspond to one unpaired electron giving no specific information about their stereochemistry.

The visible spectra of VO(Hfth)₂Cl₃ and VO(fth)₂H₂O show two bands in the regions 13090-13330 and 16800-16950 cm⁻¹ assigned to \( 2B₂ \rightarrow 2E \) and \( 2B₂ \rightarrow 2B₁ \) transitions, respectively on the basis of octahedral geometry. The Cr(Hfth)₂Cl₃, H₂O shows three bands at 16900, 19050 and 23530 cm⁻¹. The first two bands, arising from a splitting of \( \nu₁ \) mode in \( D₄h \) symmetry, may be assigned to \( 4A₂ \rightarrow 4Eₗ \) and \( 4B₁ \rightarrow 4B₂ \) transitions, respectively in \( D₄h \) symmetry. The third band may be assigned to the envelope of \( 4B₁ \rightarrow 4B₂ \) and \( 4B₁ \rightarrow 4Eₗ \) transitions in \( D₄h \) symmetry. The \( \nu₃ \) band could not be located because of its occurrence in the same region as the intra-ligand transition. Due to the non-splitting of the \( \nu₂ \) band, it has not been possible to calculate the ligand field parameters for the above complex.

The spectrum of Cr(fth)₂(OH)(H₂O), however, gives four \( d-d \) transitions at 12000, 17540, 24100 and 37040 cm⁻¹. The first band of weak intensity may be assigned to the spin-forbidden transition \( 4A₂ \rightarrow 4Eₗ \) (ref. 17) while the other three may be attributed to \( 4A₂ \rightarrow 4Eₗ \) transitions.
transitions, respectively on the basis of octahedral geometry. The values of $Dq$, LFSE, $B_{3g}$ and $B_{3g}$ calculated from the first two spin-allowed transitions came out to be 17540 em$^{-1}$, 251 kJ mol$^{-1}$, 642 em$^{-1}$ and 0.70, respectively.

Co(Hfth)$_2$Cl$_2$ shows bands at 18500, 25600 and 34500 cm$^{-1}$ of which the first two bands may be assigned to $^3A_1g$ and $^3T_2g$ transitions, respectively in octahedral geometry of Co(III)$^{17}$ and the third may be attributed to a charge-transfer transition.

The spectrum of Co(CN)$_2$ shows a sharp band at 10260 cm$^{-1}$ and another band at 22200 cm$^{-1}$ assigned to $^2B_2g$ and $^2A_1g$ transitions, respectively in square-planar environment of Co(II)$^{18}$. Taking the energy of the first band to be equal to 15 $\epsilon_B$, the value of $B$ works out to be 645 cm$^{-1}$.

The bands occurring at 11430, 17390 and 26700 cm$^{-1}$ in Ni(Hfth)$_2$Cl$_2$ may be assigned to $^3A_1g$ and $^3T_1g$ transitions, respectively in octahedral geometry$^{19}$. These bands occur in the same regions as reported for square-planar complexes of Ni(II) with sulphur containing ligands$^{19}$. The single electron parameter $\Delta_1$ and $\Delta_2$ have been calculated from the observed $d$-$d$ transitions as suggested by Gray et al.$^{20}$ assuming after Shupack et al.$^{21}$ that $F_2/10 F_2$ = 800 cm$^{-1}$; the calculated values are 20040 and 4770 cm$^{-1}$, respectively.

Cu(Hfth)$_2$Cl$_2$ and Cu(CN)$_2$ yield one broad band at 14815 and 20000 cm$^{-1}$, respectively. The former complex gives an additional well-defined shoulder at 13 330 cm$^{-1}$ on the low energy side. The above spectral features together with the composition of the complexes indicate distorted octahedral geometry for the former complex$^{25}$ and a square-planar geometry for the latter$^{26}$.

The low values of $B$ and $\beta$ as found for Cr(III) and Ni(II) complexes suggest high degree of covalency in the metal-ligand bond and pronounced nephelauxetic effect of sulphur in these complexes having some $\pi$-character in the M-S bond$^{22}$. The $10Dq$ values of Ni(II), Cu(II) and Cr(III) complexes suggest that the ligand field produced by Hfth is stronger than those for xanthates$^{17}$ and dithiocarbamates$^{22}$ but weaker than that for ethylenediamine$^{28,29}$. However, the splitting energies are very close to those reported for the complexes of S-alkyl dithiocarbazates$^{26}$, thiosemicarbazide and thiocarbohydrazide$^{30}$ in which the ligands are coordinated through hydrazidic nitrogen and sulphur atoms as in the present case.

The nujol spectrum of the ligand shows $\nu$NH at 3240, 3180 and 3140 cm$^{-1}$; the bands shift in the chloroform solution spectrum to 3410, 3310 and 3245 cm$^{-1}$ respectively presumably due to breaking of hydrogen bonding present in the solid state. The first band in each case may be assigned to NH stretching of the imino group while the other two bands may be attributed to NH of the primary amine$^{31}$. The highest energy band due to NH group remains practically unchanged in the adducts and cationic-anionic complexes but disappears in the deprotonated complexes indicating that nitrogen of the imino group is not involved in bonding in the former case, and proton of this group is involved in the formation of deprotonated complexes via thioenolisation. The other two bands due to NH$_2$ group of the ligand show negative shifts in all types of complexes indicating coordination through thiohydrazidic nitrogen. $\beta$NH$_2$ and $\nu$N-N bands occurring in the ligand at 1630 and 995 cm$^{-1}$ respectively show positive shifts of 10-20 and 20-30 cm$^{-1}$ respectively in the complexes indicating that the nitrogen of the amino group is involved in bonding$^{30}$. Thioamide band-I ($\beta$NH + $\nu$CN) and thioamide band-II ($\nu$CN + $\beta$NH) occurring at 1530 and 1300 cm$^{-1}$ respectively in the ligand undergo positive shifts of 20-40 cm$^{-1}$ in adducts as well as cationic-anionic complexes and of 70-100 cm$^{-1}$ in deprotonated complexes indicating that the sulphur of the thioamide group is involved in bonding$^{30,31}$. The positive shifts in these bands in the case of adducts and cationic-anionic complexes are due to coordination through sulphur which decreases the C=S bond order and increases the C-N bond order due to inductive effect while the pronounced positive shifts in these bands in the case of deprotonated complexes are due to reduction of C=S bond order from two to one and increase in C-N bond order from one to two as a result of thioenolisation.

The thioamide band IV ($\nu$CN + $\beta$NH) occurring at 810 cm$^{-1}$ in the ligand is shifted to 765-780 cm$^{-1}$ in the adducts and cationic-anionic complexes. This band, however, disappears in the deprotonated complexes and a new band due to $\nu$C=S appears around 720 cm$^{-1}$ in the deprotonated complexes$^{32}$. These observations are consistent with bonding through
'thione' sulphur in the case of adducts and cationic-anionic complexes and through thiolato sulphur in the case of deprotonated complexes. The non-ligand bands occurring in 260-380, 285-350 and 250-300 cm⁻¹ regions are tentatively assigned to νM-N, νM-S and νM-Cl modes respectively. 

Acknowledgement
The authors thank the Head of the Department of Chemistry, Banaras Hindu University, Varanasi for providing the laboratory facilities.

References