Spectroscopic studies of N-salicyl-N'-2-furanthiocarboxy hydrazine and its 3d metal complexes, new potential antitumour agents

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Abstract—A new ONS donor ligand, N-salicyl-N'-2-furanthiocarboxy hydrazine (H₂sfth) has been synthesized, characterized by i.r., ¹H, ¹³C NMR and mass spectral studies and its VO(IV), Mn(II), Fe(II), Co(II), Ni(II) and Zn(II) chelates of the types M(Hsfth)₂ and M(sfth) $\cdot nH_2O$, a new class of antitumour compounds, have been synthesized and authenticated by analytical data and by molar conductance, magnetic susceptibility and spectroscopic methods. Electronic, photoacoustic and Mössbauer spectra indicate high-spin octahedral geometry for all the complexes. Infrared and PMR spectral studies imply mononegative tridentate and dinegative tetradentate behaviour of the ligand in 1:2 and 1:1 (polymeric) deprotonated complexes, respectively, the bonding sites being thione sulphur, phenolate oxygen and hydrazinic nitrogen in the former type and thiolo sulphur, enolic oxygen and both of the hydrazinic nitrogens in the latter type. The X-band ESR spectral data are further suggestive of two nitrogen coordination with a d_{XY} ground state for vanadium in VO(sfth) · H₂O and octahedral geometry for Mn(Hsfth)₂. The ligand and its Cu(II) complex has been tested for antineoplastic activity, a full account of which together with the synthesis and characterization of the latter is to be published [1].

INTRODUCTION

The great expansion of research in complex chemistry of nitrogen-sulphur donor ligands such as substituted thiosemicarbazides, thiosemicarbazones and dithiocarbazates [2, 3] during the last three decades has been due to the remarkable antineoplastic activity displayed by them against a variety of tumours [4-7], in addition to their appreciable antifungal [8] and antibacterial [9] activities. In spite of very similar ligational behaviour, only recently have a few papers appeared on synthetic and structural aspects of 3d metal complexes of substituted thiohydrazides and thiohydrazones [10-13] and there is scant information regarding the antineoplastic activity of these complexes and the ligands. Therefore, interest in the chelating properties of thiohydrazides and a search for new antineoplastic metal complexes has led us to synthesize a series of metal chelates (as shown in Fig. 6) with the title ligand having nitrogen-sulphur donor groups.

EXPERIMENTAL

Ligand synthesis

All the chemicals used were of analytical reagent or equivalent grade. N-Salicyl-N'-2-furanthiocarboxy hydrazine, C₆H₄OHC(O)NHNHC(S)C₄H₃O (H₂sfth) was prepared by mixing 4.1 g of carboxymethyl-2-furadithioate and 3.0 g of salicylhydrazine, dissolved separately in one and two equivalents of aqueous solution of NaOH (2 N), respectively, and adding dilute acetic acid dropwise to the above reaction mixture, after allowing the solution to stand for ~ 2 h. The product thus obtained was suction filtered, washed with water and recrystallized from hot ethanol which yielded a straw coloured crystalline compound melting at 208°C, yield Salicylhydrazine [14] 90 %. and carboxymethyl-2furandithioate [15] required for the above purpose were prepared by reported literature procedures.

Analysis

Found: C = 54.45, H = 3.71, N = 10.49, S = 12.61; calcd: C = 54.95, H = 3.81, N = 10.69, S = 12.21 for $C_{12}H_{10}N_2O_3S$.

Synthesis and analysis of the complexes

VO(sfth) H_2O , Zn(sfth), Fe(Hsfth)₂, Co(Hsfth)₂ and Ni(Hsfth)₂ were prepared by mixing the methanolic solutions of the respective metal(II) acetate/vanadyl chloride/Mohr's salt (10 mmol) and the ligand (10 or 20 mmol), raising the pH of the reaction mixture by the addition of 1 g of sodium acetate and heating the reaction mixture for ~ 15 min in a water bath.

Fe(sfth) $2H_2O$, Co(sfth) $2H_2O$, Ni(sfth) $2H_2O$, Mn(Hsfth)₂ and Zn(Hsfth)₂ were obtained by digesting for 15 min a mixture of a methanolic solution of the respective hydrated metal(II) chloride/Mohr's salt (in the case of the Fe(II) complex) and 10 or 20 mmol solution of the ligand dissolved in 20 mmol methanolic solution of KOH. All the complexes thus obtained were filtered by suction, washed several times with water and hot ethanol and dried *in vacuo*.

The complexes were analysed for their metal content employing standard procedures after destroying the organic matter first with a mixture of nitric and hydrochloric acids and then with sulphuric acid. Sulphur was estimated as BaSO₄. Nitrogen, carbon and hydrogen were determined by microanalysis. The water content was determined by heating the complexes in the temperature range 120–190°C and determining the loss in weight.

Physical methods

Electrical conductance was measured at room temperature on a WTW conductivity meter in DMF. The room temperature magnetic susceptibility of the complexes was determined by the Faraday method using CoHg(SCN)₄ as calibrant and experimental magnetic susceptibilities were corrected for diamagnetism [16]. The ¹³C, ¹H NMR in DMSO(d_6) and mass spectra were recorded on a Jeol FX 90 Q multinuclear spectrometer equipped with a variable temperature controller and a Karotox-D S60 mass spectrometer, respectively. The electronic and i.r. spectra of the complexes and the ligand were recorded at room temperature on a Cary-14 spectrophotometer and a Perkin–Elmer spectrophotometer model 621, respectively, as solids in Nujol. ESR spectra of VO(sfth) H_2O and Mn(Hsfth)₂ recorded on a Varian E-11 X-band spectrophotometer using TCNE as a $\langle g \rangle$ marker in DMSO both at room temperature and liquid nitrogen temperature and are shown in Figs 3, 4 and 5. The room temperature Mössbauer spectrum of Fe(sfth) $2H_2O$ was obtained on a constant acceleration Mössbauer spectrometer using sodium nitroprusside as a calibrant. The spectrum was filted by least squares to the Lorentzian line shape by means of the Mösfit program. The photoacoustic spectra were recorded in the solid state on a Princeton Applied Research Instrument, Model 6001, in the 200–1500 nm range using carbon black as a reference.

RESULTS AND DISCUSSION

Characterization of the ligand

The i.r. spectrum of the ligand displays bands at 3340, 1640 and 910 cm⁻¹ which may be assigned to v(NH), v(C=O) and v(C=S) modes, respectively. v(OH) appears as a broad band at a lower frequency (3140 cm⁻¹) showing the presence of hydrogen bonding.

The PMR spectrum of the ligand exhibits resonances for the OH, NH and aromatic protons. The OH proton signal appears at $\delta 11.5$ ppm which disappears on D₂O exchange. NH proton signals are obscured by the aromatic protons which appear as multiplet between $\delta 6.1-8.1$ ppm [17].

The 13 C spectrum of the ligand shows 12 signals corresponding to the 12 carbon atoms present in the molecule as shown in Fig. 1. The assignments for these have been made by taking into account the chemical shift values of furan substituted compounds [18] and salicyloyl hydrazone [19]. The signals at $\delta 176.7$ and 164.19 ppm are due to CS and CO carbons. The chemical shifts for other carbons are as follows:

δ ppm C₁ 134.18, C₂ 157.80, C₃ 117.17, C₄ 115.55, C₅ 116.85, C₆ 129.63, C₇ 150.22, C₈ 119.56, C₉ 112.95, C₁₀ 145.99.

Mass spectrum

The spectrum of the ligand (Fig. 2) contains a peak due to the molecular ion M^+ at m/e 262. The other

peaks of appreciable intensity for the major fragments possible are shown in Scheme 1 [20].

Characterization of the complexes

The metal complexes which were isolated in the present study are presented in Table 1 together with some of their properties. Since deprotonation is very easy only 1:2 and 1:1 deprotonated complexes are formed by the loss of one and two protons, respectively, from the ligand. For steric considerations, the ligand acts either as uninegative ONS tridentate ligand, bonding through phenolate oxygen, hydrozinic nitrogen and thione sulphur atoms or as dinegative ONNS tetradentate ligand utilizing enolic oxygen, both the hydrazinic nitrogens and thiolo sulphur in a polymeric structure. The loss of weight between 160-190°C suggests the coordinated nature of the water molecules which is further supported by the i.r. spectral studies discussed later. All the complexes are insoluble in water; a few are slightly soluble in ethanol and methanol and are soluble in DMF and DMSO. The molar conductance values of the soluble com- 10^{-3} M concentration plexes at in DMF $(\sim 20 \text{ mhos cm}^2 \text{ mol}^{-1})$ demonstrate their non-ionic nature.

Magnetic properties

The magnetic moments of all the Fe(II) and Ni(II) complexes and Co(Hsfth)₂ are normal and suggest high-spin octahedral geometry for them. The anomalous magnetic moment displayed by Co(sfth) $2H_2O$ may be due to the spin equilibrium in the metal atom involving nearly equienergetic ${}^{4}T_1$ and ${}^{2}E$ terms [21]. VO(sfth) H_2O and Mn(Hsfth)₂ show normal magnetic moments corresponding to one and five unpaired electrons, respectively.

Electronic spectra

The electronic and photoacoustic spectral band positions and assignments thereof are indicated in Table 2. The visible spectrum of VO(sfth) H_2O yields



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Scheme 1.





Table 1. Analytical data and general behaviour of H₂sfth complexes

| | | | Fo | und (Calcd) (| %) | | Цeff | M.P. |
|------------------------------|--------|---------|----------|---------------|-----------------|----------|--------------------------|-------|
| Compound | Colour | Metal | Nitrogen | Sulphur | Carbon | Hydrogen | (B . M .) | (°C) |
| VO(sfth) · H ₂ O | Bottle | 14.62 | 7,92 | 9.42 | 41.54 | 2.75 | 1.70 | > 300 |
| | green | (14.77) | (8.12) | (9.27) | (41.66) | (2.80) | | |
| Fe(sfth) 2H ₂ O | Dark | 15.62 | 7.72 | 9.46 | 41.02 | 3.48 | 4,90 | > 300 |
| | brown | (15.82) | (7.93) | (9.06) | (40.83) | (3.40) | | |
| Co(sfth) · 2H ₂ O | Brown | 16.43 | 7.70 | 9.01 | 40.52 | 3.30 | 3.35 | > 300 |
| | | (16.56) | (7.86) | (8.99) | (40.47) | (3,37) | | |
| Ni(sfth) 2H ₂ O | Light | 16.34 | 7.92 | 9.10 | `40.68 ´ | 3.39 | 2.86 | > 300 |
| | green | (16.50) | (7.87) | (8.99) | (40.49) | (3.37) | | |
| Zn(sfth) | Light | 19.87 | 8.43 | 10.10 | 44.52 | 2.39 | Diamag. | > 300 |
| | yellow | (20.04) | (8.58) | (9.80) | (44.14) | (2.45) | | |
| Mn(Hsfth) ₂ | Light | 9.12 | 9.62 | 11.22 | `50.04 ´ | 3.08 | 5.95 | > 300 |
| | green | (9.49) | (9.71) | (11.08) | (49.83) | (3.11) | | |
| Fe(Hsfth) ₂ | Dark | 9.36 | 9.38 | 11.24 | 50.02 | 3.02 | 4.93 | > 300 |
| | brown | (9.64) | (9.67) | (11.06) | (49.76) | (3.11) | | |
| Co(Hsfth) ₂ | Dark | 10.43 | 9.48 | 11.34 | 49.68 | 3.12 | 5,40 | > 300 |
| | brown | (10.13) | (9.62) | (11.00) | (49.49) | (3.09) | | |
| Ni(Hsfth) ₂ | Dark | 10.24 | 9.48 | 11.23 | 49.70 | 2.99 | 3.38 | 248 |
| · · · - | yellow | (10.09) | (9.62) | (11.00) | (49.51) | (3.09) | | |
| Zn(Hsfth)2 | Yellow | 10.92 | 9.42 | 11.18 | 49.28 | 3.00 | Diamag. | 180 |
| · /- | | (11.11) | (9.51) | (10.89) | (49.05) | (3.06) | - | |

two bands at 17 390 and 25 000 cm⁻¹ assigned to ${}^{2}B_{2} \rightarrow {}^{2}B_{1}$ and ${}^{2}B_{2} \rightarrow {}^{2}A_{1}$ transitions, respectively, in an octahedral geometry of the complex [22].

electronic spectra of Fe(sfth) $2H_2O$ and Fe(Hsfth)₂, respectively, may be attributed to a ${}^5T_{2g} \rightarrow {}^5E_g(D)$ transition in an octahedral geometry around Fe(II) [23]. The spectra of Co(II) complexes display a

The bands at $13\,330\,\mathrm{cm}^{-1}$ and $9340\,\mathrm{cm}^{-1}$ in the

| Complex | Band maxima (cm ⁻¹) | Assignments |
|------------------------------|---------------------------------|--|
| VO(sfth)·H ₂ O | 17390 | $^2B_2 \rightarrow ^2B_1$ |
| | 25 000 | ${}^{2}B_{1} \rightarrow {}^{2}A_{1}$ |
| Fe(sfth) · 2H ₂ O | 13 300 | ${}^{5}T_{2a} \rightarrow {}^{5}E_{a}(D)$ |
| Fe(Hsfth) ₂ | 9340 | ${}^{2}T_{2a} \rightarrow {}^{5}E_{a}(D)$ |
| Co(sfth) 2H ₂ O | (9710) | ${}^{4}T_{1a}^{0}(F) \rightarrow {}^{4}T_{2a}(v_{1})$ |
| | (12 990) | ${}^{4}T_{1a}(F) \rightarrow {}^{4}A_{2a}(v_{2})$ |
| | 21 050 (20 000) | ${}^{4}T_{1,c}(F) \rightarrow {}^{4}T_{1,c}(P)(v_{2})$ |
| Co(Hsfth)2 | 22 000 | ${}^{4}T_{1a}^{(\mu)}(F) \rightarrow {}^{4}T_{1a}^{(\mu)}(P)(v_{1})$ |
| Ni(sfth) · 2H ₂ O | 9340 (9260) | ${}^{3}A_{2a}(F) \rightarrow {}^{3}T_{2a}(F)(y_{1})$ |
| · · - | (14080) | ${}^{3}A_{2a}(F) \rightarrow {}^{3}T_{1a}(F)(v_{2})$ |
| | 22 220 (23 810) | ${}^{3}A_{2a}(F) \rightarrow {}^{3}T_{1a}(P)(v_{2})$ |
| Ni(Hsfth) ₂ | 11 110 | ${}^{3}A_{2a}(F) \rightarrow {}^{3}T_{2a}(F)(v_{1})$ |
| | 18 180 | ${}^{3}A_{2g}^{2g}(F) \rightarrow {}^{3}T_{1g}^{2g}(F) (v_{2})$ |

Table 2. Electronic and photoacoustic spectral bands and their assignments

Photoacoustic spectral bands are given in parentheses.



Fig. 3. ESR spectrum of VO(sfth) H₂O at room temperature.

band in the 21 050-22 000 cm⁻¹ region characteristic of octahedral Co(II) complexes [24] and may be assigned to a ${}^{4}T_{1g}(F) \rightarrow {}^{4}T_{1g}(P)(v_{3})$ transition.

The occurrence of v_1 and v_2 bands at 11110 and 18180 cm⁻¹ in Ni(Hsfth)₂, v_1 and v_3 bands at 9340 and 22220 cm⁻¹ in Ni(sfth) $2H_2O$ are suggestive of their octahedral geometry [25].

Photoacoustic spectra

With the help of this technique, which is very similar to electronic spectroscopy, the optical absorption spectra of almost any type of material, irrespective of whether the sample is crystalline, amorphous, powder or a gel can be obtained in the range $5000-50\ 000\ \text{cm}^{-1}$ [26]. The bands at 9710, 12 990 and 20 000 cm⁻¹ in the spectra of Co(sfth) · 2H₂O and at 9260, 14 080 and 23 810 cm⁻¹ in the case of Ni(sfth) · 2H₂O (Table 2) are due to *d*-*d* transitions and are quite comparable to the bands observed in their electronic spectra. These bands are in good agreement with the proposed stereochemistries (high-spin octahedral) based on the electronic spectral data [27].

ESR spectra

The room temperature ESR spectra of VO (sfth) H₂O (Fig. 3) and Mn(Hsfth)₂ (Fig. 4) are typical of VO(IV) and Mn(II) chelates consisting of well resolved signals at $q \approx 2$. A six line spectrum of Mn(Hsfth)₂ arising due to hyperfine interaction between the unpaired electrons with the ⁵⁵Mn nucleus (I = 5/2) is suggestive of symmetrical coordination of the metal ion and near octahedral geometry of the complex [28, 29]. The spectrum of VO(sfth) H₂O is nearly axially symmetric at 77 K. The room temperature spectrum of the VO(IV) complex consists of ligand hyperfine splitting lines (although not well resolved) indicating the interaction of unpaired spin of vanadium with two coordinated ¹⁴N nuclei. The magnetic ESR parameters for calculated VO(sfth) \cdot H₂O are as follows:

$$g_{\rm iso} = 1.98; g_{\parallel} = 1.93; g_{\parallel} = 1.98$$

$$A_{\rm iso}({\rm G}) = 114; A_{\parallel} = 190; A_{\parallel} = 71$$

The trend $g_{\parallel} < g_{\perp} < 2$ (free electron value) observed for the complex suggests that the unpaired electron is present in the d_{xy} orbital of the metal ion [30].



Fig. 4. ESR spectrum of VO(sfth) H_2O at liquid nitrogen temperature.



Fig. 5. ESR spectra of MnL·H₂O at liquid nitrogen temperature. (A) Solid state, (B) chloroform solution.

Mössbauer spectrum

The isomer shift $\delta(0.69 \pm 0.005 \text{ mm s}^{-1})$ and quadrupole splitting ($\Delta Eq = 1.10 \pm 0.01 \text{ mm s}^{-1}$) values for Fe(sfth)·2H₂O are typical of a high-spin Fe(II) complex in an octahedral environment [31]. The large quadrupole splitting is suggestive of the distorted octahedral structure expected for metal chelates having metal ions bonded to non-identical donor atoms.

Infrared spectra (Table 3)

The bands due to v(NH), v(C=O) and v(C=S) modes of the ligand disappear in the spectra of the 1:1 deprotonated complexes and two new bands appear at ~ 1530 and ~ 725 cm⁻¹ due to v(NCO) and v(C-S) modes, respectively, suggesting the removal of both the NH protons via enolization and thioenolization and bonding of the resulting thiolo sulphur and enolic oxygen with the metal ion [32]. The thioamide bands at 1510, 1290 and 1080 cm⁻¹ in the spectrum of the ligand due to vNH + β CN (mainly vNH), vCN + β NH and v(N-N) suffer a positive shift of ~ 40 cm⁻¹ in the spectra of the 1:1 complexes [33-35]. The magnitude of the positive shift in these modes supports the bonding sites indicated above and also suggests the involvement of both the hydrazinic nitrogens in coordination. The band due to v(OH) in the spectrum of the



 $M(\Pi) = Fe, Co, Ni$



M(II) = Mn, Fe, Co, Zn

Fig. 6.

ligand remains practically unchanged in the spectra of the 1:1 complexes indicating the non-involvement of phenolic oxygen in bonding. The absence of the v(OH) band and the presence of a v(C=O) band in the spectra of the 1:2 deprotonated complexes is suggestive of the destruction of the OH group and involvement of the phenolic oxygen and non-participation of carbonyl oxygen in bonding with metal ions [35]. The negative shifts of 30-40 cm⁻¹ in v(NH) and v(C=S)and positive shifts of ~ 20 cm⁻¹ in vNH + β CN and $vCN + \beta NH$ modes may be explained as arising from the coordination of one of the hydrazinic nitrogens and thione sulphur in these complexes. Thus the i.r. results show that H₂sfth behaves as an uninegative tridentate ligand in 1:2 complexes and as a dinegative tetradentate ligand in 1:1 complexes. The preferential bonding in 1:1 complexes through enolic oxygen and thiolo sulphur may be due to the extended conjugation S – 0

(-C=N-N=C-) formed during complex formation. Since all the four bonding sites indicated above cannot be bonded to a single metal ion due to steric consider-

| | | Table . | 3. Important infra | tred spectral by | ands (cm ⁻¹) a | nd their assignme | nts | | | |
|----------------------------|--------|----------|--------------------|------------------|----------------------------|-------------------|--------|--------|----------------|------------|
| Compound | (H-N)v | v(OH) | v(C=0/v(NCO) | BNH + vCN | $vCN + \beta CN$ | v(C=S)/v(C-S) | v(N-N) | v(M-O) | v(M-S) | v(M-N) |
| H,sfth (DMSO) | 3310 | 3040(br) | 1640 | 1510 | 1290 | 068 | 1080 | | ł | ł |
| H _s fth (Nujol) | 3340 | 3070(br) | 1630 | 1520 | 1300 | 910 | 1090 | | ļ | 1 |
| VÔ(sfth) · H, Ô | ł | 3410 | 1520 | 1550 | 1320 | 730 | 1150 | 310 | 9 6 | <u> 96</u> |
| Fe(sfth) 2H,O | 1 | 3415 | 1520 | 1550 | 1325 | 725 | 1155 | 340 | 370 | 90£ |
| Co(sfth) 2H,O | Ì | 3400 | 1520 | 1550 | 1330 | 725 | 1160 | 335 | 375 | 295 |
| Ni(sfth) 2H, O | 1 | 3420 | 1530 | 1550 | 1320 | 720 | 1155 | 325 | 380 | 290 |
| Zn(sfth) | ١ | 3400 | 1510 | 1535 | 1330 | 725 | 1150 | 315 | <u>3</u> 80 | 285 |
| Mn(Hsfth), | 3295 | | 1645 | 1540 | 1330 | 865 | 1120 | 320 | 380 | 275 |
| Fe(Hsfth) | 3290 | ł | 1645 | 1540 | 1315 | 860 | 1110 | 320 | 370 | 290 |
| Co(Hsfth), | 3280 | Į | 1645 | 1545 | 1310 | 860 | 1120 | 320 | 360 | 290 |
| Ni(Hsfth), | 3290 | l | 1640 | 1550 | 1330 | 850 | 0111 | 325 | 365 | <u>8</u> |
| Zn(Hsfth) ₂ | 3300 | ļ | 1630 | 1535 | 1330 | 870 | 1115 | 320 | 360 | 290 |

ations, a polymeric structure is proposed for the 1:1 complexes. The appearence of new bonds in the 3400 and 740–760 cm⁻¹ regions due to ν (OH) and ρ_r (H₂O) modes in the spectra of the hydrated complexes is suggestive of the coordinated nature of the water molecules.

¹H NMR spectra

The OH proton signal is not observed in the spectrum of $Zn(Hsfth)_2$ but is present in Zn(sfth) suggesting phenolate oxygen as the bonding site in the former complex [17]. In the spectra of both the complexes, a marked deshielding is observed for all the aromatic and NH protons as a result of the ligand involved in coordination.

No information could be drawn from the ${}^{13}C$ spectra of these complexes because of the poor spectra obtained due to the lack of solubility in DMSO (d_6).

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