

Studies on salicylaldehyde-2-aminobenzophenone-2-thenoylhydrazone complexes with 3d metal ions

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MS received 14 August 1990; revised 22 March 1991

Abstract. Salicylaldehyde-2-aminobenzophenone-2-thenoylhydrazone (Hsabth) complexes of $QV(IV)$, $Mn(II)$, $Co(II)$, $Ni(II)$, $Cu(II)$ and $Zn(II)$ having 1:2 metal–ligand stoichiometry have been prepared and characterized by elemental analyses, molar conductance, magnetic susceptibility, electronic, ESR, infrared, NMR (1H and ^{13}C) and X-ray powder diffraction studies. Square pyramidal geometry around oxovanadium(IV) and octahedral geometry around the rest of the metal ions have been proposed on the basis of magnetic and spectral studies.

Keywords. Salicylaldehyde-2-aminobenzophenone-2-thenoylhydrazone; transition metal complexes; square pyramidal geometry; octahedral geometry.

1. Introduction

Complexes of 2-aminobenzophenone- (Singh *et al* 1988) and 2-aminoacetophenone-2-thenoylhydrazones (Singh and Srivastav 1989) with 3d metal ions have been reported. These papers deal with different modes of bonding of the hydrazones and stereochemistry of the complexes.

This work has now been extended to synthesis and structural studies of salicylaldehyde-2-aminobenzophenone-2-thenoylhydrazone (Hsabth) (figure 1) complexes of $OV(IV)$, $Mn(II)$, $Co(II)$, $Ni(II)$, $Cu(II)$ and $Zn(II)$ in order to study the effect of additional bonding on the stereochemistry of the complexes. The results are described in the present paper.

2. Experimental

2.1 Materials

All the chemicals used were of BDH reagent grade. Salicylaldehyde (Sarabhai Chemicals, India), 2-aminobenzophenone and 2-thenoylhydrazine (Aldrich, Germany) were used as obtained. 2-Aminobenzophenone-2-thenoylhydrazone (Habth) was prepared as reported earlier (Singh *et al* 1988).

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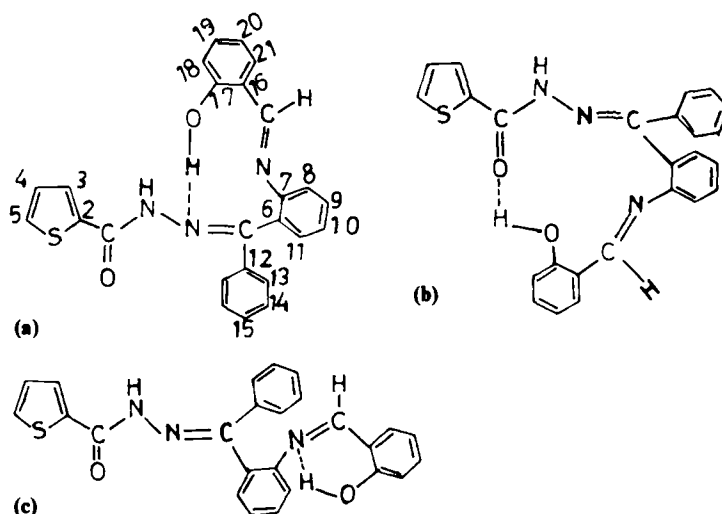


Figure 1. Different isomeric forms of H₂sabth.

2.2 Preparation of salicylaldehyde-2-aminobenzophenone-2-thenoylhydrazone

The compound was prepared by refluxing salicylaldehyde (2.4 cm³) and an ethanolic solution (20 cm³) of 2-aminobenzophenone-2-thenoylhydrazone (6.4 g, 1 mmol) for ~4 h. After cooling, the product was filtered and recrystallized from ethanol. Yield, 52.5%, m.p. 98–100°C (Found: C = 70.4, H = 4.4, N = 9.8, N₂H₄ = 7.5, C₂₅H₁₉N₃O₂S, Calcd.: C = 70.6, H = 4.5, N = 9.9, N₂H₄ = 7.5%). The hydrazone was also characterized by IR, ¹H and ¹³C NMR spectra.

2.3 Preparation of the complexes

M(Hsabth)₂Cl₂ [M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)] complexes were prepared by adding an ethanolic solution (20 cm³) of Hsabth (2 mmol) and the appropriate metal chloride (1 mmol) in the same solvent (10 cm³). The complexes were precipitated after reducing the volume and adding ether. VO(Hsabth)₂SO₄ was prepared by adding a methanolic solution (10 cm³) of vanadyl sulphate (1 mmol) to an ethanolic solution (20 cm³) of the ligand (2 mmol).

M(sabth)₂ [M = OV(IV), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)] was prepared by mixing an ethanolic solution (20 cm³) of Hsabth (2 mmol) and an aqueous solution (10 cm³) of appropriate metal salt (1 mmol) and then precipitating the complexes by adding N NaOH solution to raise the pH to ~7. The complexes were digested on a water bath for ~0.5 h.

The addition compounds were filtered, washed with ethanol, followed by ether and then dried in vacuo. The deprotonated complexes were filtered, washed first with water and then with ethanol and ether and finally dried in vacuo.

2.4 Analysis

The complexes were analysed for their metal contents using literature procedures (Vogel 1969). Chloride and sulphate were estimated gravimetrically as AgCl and

BaSO₄, respectively (Vogel 1969). C, H and N were analysed microanalytically. Hydrazine was estimated (Vogel 1969) volumetrically by titrating against KIO₃ after hydrolysing the complexes in dilute HCl for ~ 4 h. The analytical data are given in table 1.

2.5 Physical measurements

C, H and N microanalyses were done on a Perkin Elmer C H N analyser 240 C. The equipment and methods employed for recording molar conductance, magnetic susceptibility, electronic, ESR, IR, NMR (¹H and ¹³C) and X-ray powder diffraction were the same as described in our previous papers (Singh *et al* 1988; Singh and Srivastav 1989). Pertinent data are given in tables 2-5.

3. Results and discussion

Hsabth reacts with metal salts yielding two types of complexes possessing neutral (Hsabth) and deprotonated (sabth) hydrazone as indicated by analytical data (table 1).

Table 1. Analytical data and general behaviour of the complexes.

Compound	Colour	Found (calcd.) %						μ_{eff} (B.M.)	m.p. (°C)
		M	N ₂ H ₄	N	Cl/SO ₄	C	H		
VO(Hsabth) ₂ SO ₄	Dark brown	8.5 (8.7)	—	7.0 (7.1)	16.4 (16.3)	50.8 (51.0)	3.2 (3.2)	1.91	160-62 ^d
Mn(Hsabth) ₂ Cl ₂	Light brown	5.4 (5.6)	6.2 (6.2)	8.5 (8.6)	6.9 (7.3)	61.4 (61.5)	3.8 (3.9)	5.89	155-57 ^d
CO(Hsabth) ₂ Cl ₂	Orange yellow	5.9 (6.0)	6.3 (6.5)	8.5 (8.6)	7.1 (7.3)	60.9 (61.2)	3.9 (3.9)	4.91	> 350
Ni(Hsabth) ₂ Cl ₂	Yellow	5.8 (6.0)	6.3 (6.5)	8.4 (8.6)	7.2 (7.3)	61.1 (61.2)	3.9 (3.9)	3.20	> 350
Cu(Hsabth) ₂ Cl ₂	Dark green	6.2 (6.5)	—	8.4 (8.5)	7.0 (7.2)	61.0 (60.9)	4.0 (3.9)	2.24	117-18 ^d
Zn(Hsabth) ₂ Cl ₂	Pale yellow	6.3 (6.6)	6.4 (6.5)	8.3 (8.5)	7.1 (7.2)	60.6 (60.8)	3.9 (3.9)	diamagnetic	191-93 ^d
VO(sabth) ₂	Dark green	5.3 (5.6)	—	9.0 (9.2)	—	65.5 (65.6)	3.8 (3.9)	1.83	155-57 ^d
Mn(sabth) ₂	Dirty brown	6.0 (6.1)	6.9 (7.1)	9.2 (9.3)	—	66.3 (66.5)	4.1 (4.0)	5.93	187-88 ^d
Co(sabth) ₂	Dirty yellow	6.2 (6.5)	7.0 (7.1)	9.1 (9.3)	—	66.1 (66.2)	3.9 (4.0)	4.89	250-52 ^d
Ni(sabth) ₂	Yellow	6.3 (6.5)	7.1 (7.1)	9.4 (9.3)	—	66.0 (66.2)	4.0 (4.0)	2.87	260-61 ^d
Cu(sabth) ₂	Shining green	6.8 (7.0)	—	9.1 (9.2)	—	66.6 (66.8)	3.9 (4.0)	1.95	255-57 ^d
Zn(sabth) ₂	Yellow	6.9 (7.2)	6.8 (7.0)	9.0 (9.2)	—	65.8 (65.7)	4.0 (3.9)	dimagnetic	179-81 ^d

^d Decomposes

Table 2. Electronic spectral bands (cm^{-1}) and their assignments.

Compound	Bands (cm^{-1})	Assignments
VO(Hsabth) ₂ SO ₄	10595, 15530, 23255	$d_{xy} \rightarrow d_{yz}, d_{zx}, d_{x^2-y^2}$
VO(sabth) ₂	12195, 16420, 25510	$d_{xy} \rightarrow d_{yz}, d_{zx}, d_{x^2-y^2}$
Co(Hsabth) ₂ Cl ₂	9440, 18590(15015), 24040	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F), {}^4A_{2g}(F), {}^4T_{1g}(P)$
Co(sabth) ₂	9425(10235), 19610, 24875	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F), {}^4A_{2g}(F), {}^4T_{1g}(P)$
Ni(Hsabth) ₂ Cl ₂	10990, 17855	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F), {}^3T_{1g}(F)$
Ni(sabth) ₂	11015(11430), 22370	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F), {}^3T_{1g}(P)$
Cu(Hsabth) ₂ Cl ₂	13090	${}^2E_g \rightarrow {}^2T_{2g}$
Cu(sabth) ₂	15890	${}^2E_g \rightarrow {}^2T_{2g}$

Table 3. ESR magnetic and bonding parameters.

Compound	g_{\parallel}/g_{zz}	g_{xx}	g_{\perp}	g_{yy}	g_{zz}	A_{\parallel}/A_{zz}	A_{xx} (G)	A_{\perp} (G)	A_{yy} (G)	A_{zz} (G)	α^2/β_2^2
VO(Hsabth) ₂ SO ₄	1.9363	—	1.9767	—	1.9632	194.28	—	72.14	—	114.85	0.93
VO(sabth) ₂	1.9136	—	1.9812	—	1.9587	160.00	—	68.57	—	99.05	0.80
Cu(Hsabth) ₂ Cl ₂	2.2529	2.0670	—	2.0280	2.1290	168.33	13.33	—	16.67	65.00	0.75
Cu(sabth) ₂	2.3073	2.0473	—	2.0067	2.1340	176.70	15.00	—	14.17	68.90	0.80

Table 4. ¹³C NMR spectral data (ppm) of Hsabth and Zn(Hsabth)₂Cl₂.

Compound	Hsabth	Zn(Hsabth) ₂ Cl ₂	Compound	Hsabth	Zn(Hsabth) ₂ Cl ₂
C=O	198.82	—	C ₁₁	117.56	117.18
C=N	163.93	164.29	C ₁₂	130.94	130.83
-NCH-	158.73	158.86	C ₁₃	149.58	149.58
C ₂	162.63	162.79	C ₁₄	119.07	119.34
C ₃	161.33	161.49	C ₁₅	129.26	—
C ₄	141.02	—	C ₁₆	129.75	129.91
C ₅	138.80	—	C ₁₇	131.86	131.04
C ₆	131.37	—	C ₁₈	114.80	—
C ₇	152.88	149.96	C ₁₉	132.46	—
C ₈	128.72	128.82	C ₂₀	117.07	—
C ₉	119.83	119.99	C ₂₁	134.57	132.08
C ₁₀	134.68	132.73			

M(Hsabth)₂Cl₂ [M = Co(II) and Ni(II)] does not melt or decompose below 350°C while the remaining complexes decompose in the 117–261°C temperature range. The complexes are insoluble in common organic solvents but are slightly or fairly soluble in acetonitrile, DMF and DMSO. The complexes are non-electrolytes (Geary 1971) in 0.001 M acetonitrile solution as indicated by their molar conductance values (6.8–27.5 ohm⁻¹ cm² mol⁻¹).

3.1 Magnetic and electronic spectral studies

The magnetic moments (Figgis and Lewis 1964) of cobalt(II) and nickel(II) complexes lie in the range expected for an octahedral ligand field. Octahedral coordination around metal ions is also supported by the number and position of electronic spectral

Table 5. Observed and calculated d and hkl values for copper(II) complexes.

Cu(Hsabth) ₂ Cl ₂			Cu(sabth) ₂		
2θ	d	hkl	2θ	d	hkl
7.255	12.1845	100	8.134	10.8697	100
7.494	11.7975	010	12.078	7.3276	010
8.682	10.1849	001	12.430	7.1210	001
10.429	8.4824	020	15.319	5.7837	101
12.071	7.3321	002	16.287	5.4422	400
13.040	6.7889	030	17.740	4.9996	002
15.722	5.6364	202	21.798	4.0771	700
17.647	5.0256	600	22.762	3.9066	130
19.805	4.4826	601	24.540	3.6274	900
21.958	4.0478	900	25.054	3.5542	004
26.117	3.4118	009	26.002	3.4529	104
26.652	3.3446	940, 903	26.063	3.4188	801
27.719	3.2182	950, 913	28.239	3.1602	150
28.605	3.1205	705	29.826	2.9955	060
29.615	3.0164	725	30.328	2.9461	033
31.447	2.8447	745, 708	32.424	2.7612	070
31.840	2.8105	981	32.944	2.7188	550
34.289	2.6152	983	33.625	2.6652	840
39.866	2.2612	898	34.047	2.6332	460
40.406	2.2322	998	37.238	2.4146	760
—	—	—	40.520	2.2262	137
—	—	—	43.987	2.0585	537
—	—	—	44.593	2.0319	664
—	—	—	56.168	1.6375	897

bands (Mathews and Walton 1971; Lever 1968; Sacconi 1969) and their assignments. The electronic spectra of oxovanadium(IV) and copper(II) complexes are in accord with square pyramidal (Ballhausen and Gray 1962; Farmer and Urbach 1974; Stoklosa *et al* 1974) and octahedral (Mathews and Walton 1971) ligand fields, respectively. The μ_{eff} (Cotton and Wilkinson 1976) values are indicative of the presence of one unpaired electron. The magnetic moments of manganese(II) complexes are indicative of five unpaired electrons and indicate that these complexes may have either octahedrally or tetrahedrally coordinated metal ions.

3.2 ESR spectra

The DMF glass spectra of oxovanadium(IV) complexes give two sets of eight lines arising from interaction of the unpaired electron with the ^{51}V nucleus yielding $g_{\parallel} < g_{\perp} < g^e$ (2.0023). The trend in g values indicates the presence of unpaired electrons in the $d_{xy}(b_{2g}^*)$ orbital (Kon and Sharpless 1965; Hathaway and Billing 1970).

In DMF glass ESR spectra of copper(II) complexes, the spectra are consistent with rhombic symmetry (Hathaway and Billing 1970). The σ -bonding parameter (α^2) indicates the presence of an appreciable amount of covalent character in the metal-ligand bond (Goodman and Raynor 1970).

3.3 IR spectra

The hydrazone sites involved in bonding have been established by comparing its IR spectrum with the spectra of the complexes. The bands appearing in the metal-free hydrazone at 1660, 1620(1615 *sh*) and 1035 cm^{-1} are due to $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{N})$ hydrazine (amine) and $\nu(\text{N}-\text{N})$ modes, respectively. In the Hsabth complexes, $\nu(\text{C}=\text{O})$ shifts to lower frequencies, suggesting coordination through the carbonyl oxygen. The shifting to lower frequencies, and the broadening and decrease in the intensity of the $\nu(\text{C}=\text{N})$ band in all the complexes except $\text{VO}(\text{Hsabth})_2\text{SO}_4$, suggest bonding through one of the $\text{>C}=\text{N}$ nitrogens. However, $\nu(\text{N}-\text{N})$ (Aggarwal and Narang 1973) is observed at higher frequencies in comparison to its position in the free hydrazone, which is commensurate with involvement of azomethine nitrogen in bonding. The $\nu(\text{OH})$ observed at 3460 cm^{-1} in the hydrazone is localized in the 3340–3480 cm^{-1} region in the Hsabth complexes indicating noninvolvement in bonding.

In the sabth complexes, $\nu(\text{C}=\text{O})$ does not show any shift, indicating that the carbonyl oxygen is not involved in bonding. Weakening, splitting and shifting of $\nu(\text{C}=\text{N})$ to lower frequencies and the shifting of $\nu(\text{N}-\text{N})$ to higher frequencies are observed. $\nu(\text{OH})$ disappears and new bands due to $\nu_{\text{asym}}(\text{C}-\text{O})$ appear in conjunction with shifting of $\nu_{\text{sym}}(\text{C}-\text{O})$ to higher frequencies (Sinn and Harris 1969). These observations are indicative of uninegative tridentate bonding through both the $\text{>C}=\text{N}$ nitrogens and phenolate oxygen. The square pyramidal geometry for $\text{VO}(\text{sabth})_2$ as inferred from electronic and ESR studies suggest that only one of the $\text{>C}=\text{N}$ nitrogens is involved in bonding. The chelating bidentate nature of SO_4^{2-} in the VOSO_4 complex is inferred (Nakamoto 1978) from the appearance of bands at 1245, 1150, 1020 and 975 cm^{-1} . However the band at 970 cm^{-1} may be attributed to $\nu(\text{V}=\text{O})$ and thus the ν_1 band of SO_4^{2-} makes the assignment (Selbin *et al* 1963) of $\nu(\text{V}=\text{O})$ rather uncertain though the band at 970 cm^{-1} in $\text{VO}(\text{sabth})$ may be unequivocally assigned to $\nu(\text{V}=\text{O})$. The bands observed in the 420–450, 320–345 and 285–300 cm^{-1} regions, which are absent from the spectrum of the free hydrazone, may tentatively be assigned to $\nu(\text{M}-\text{O})$ (Noboru and Nakamoto 1975), $\nu(\text{M}-\text{N})$ (Noboru and Nakamoto 1975) and $\nu(\text{M}-\text{Cl})$ (Clark 1963) modes, respectively.

3.4 NMR spectra

In order to confirm further the bonding site of the Hsabth involved in the complexes, the ^1H NMR spectrum of $\text{Zn}(\text{Hsabth})_2\text{Cl}_2$ in $\text{DMF}-d_7$ is compared with that of the Schiff base in the same solvent. The Schiff base may exist in different isomeric forms (figure 1). The ^1H and ^{13}C NMR spectra of Hsabth are characteristic of the existence of only one isomeric form as these show normal spectra. If Hsabth exists in more than one isomeric form, doubling of the signals are expected (Lewin *et al* 1975). In view of the steric factors and H-bonding, the more favourable structure of the ligand may be proposed as shown in figure 1b. The ^1H and ^{13}C NMR spectra of $\text{Zn}(\text{Hsabth})_2\text{Cl}_2$ are also characteristic of the presence of the compound in only one isomeric form. On the basis of steric factors, H-bonding, size of the chelate ring and strain in the chelate ring, the most favourable structure (figure 2) may be proposed for the complexes.

Hsabth exhibits signals at δ 12.40, 11.66, 8.70 and 8.27–6.40 which are assigned to $-\text{OH}$, $-\text{NH}$, $-\text{CH}$ and aromatic protons, respectively. The downfield shift of the $-\text{NH}$

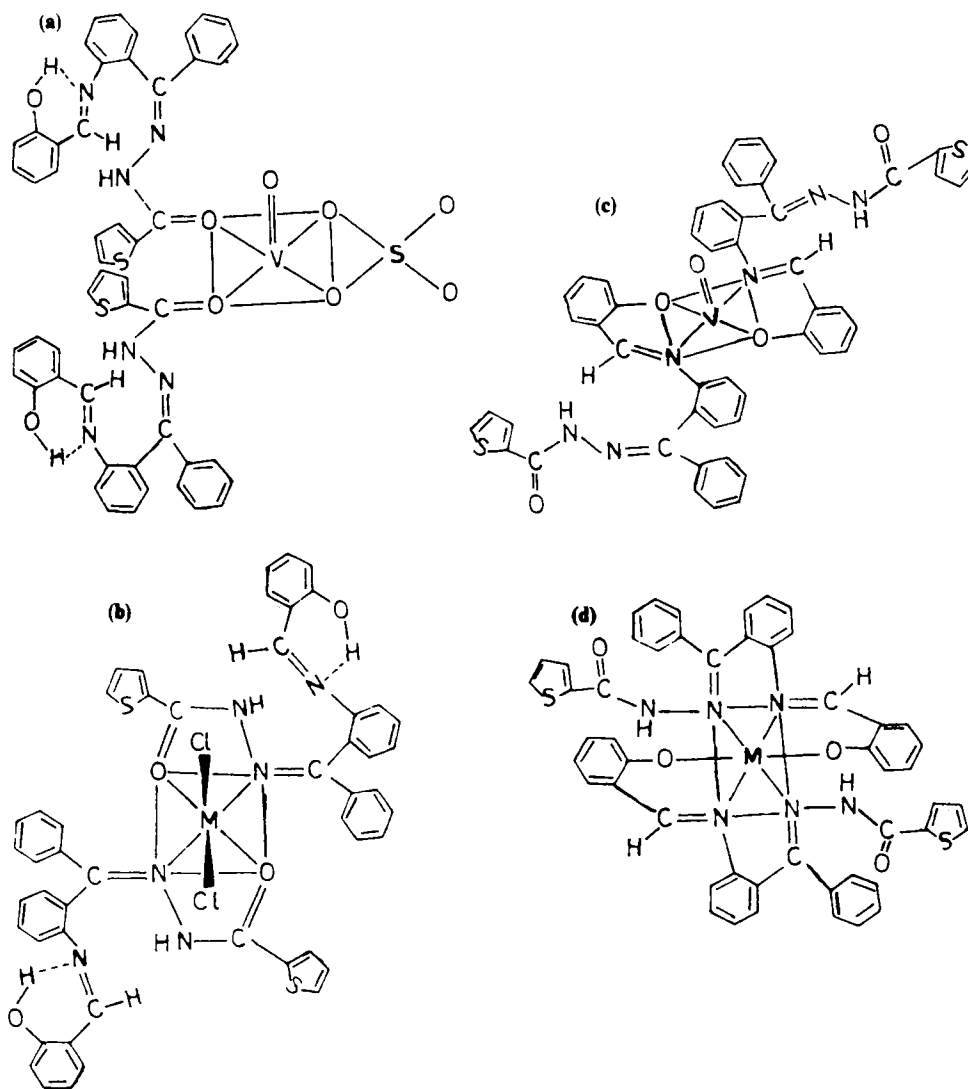


Figure 2. Proposed structures of the complexes; (a) $\text{VO}(\text{Hsabth})_2\text{SO}_4$, (b) $\text{M}(\text{Hsabth})_2\text{Cl}$ [$\text{M} = \text{Mn}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$]; (c) $\text{VO}(\text{sabth})_2$; (d) $\text{M}(\text{sabth})_2$ [$\text{Mn} = \text{Mn}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II})$ and $\text{Zn}(\text{II})$].

proton from 11.66 in Hsabth to 11.73 δ in $\text{Zn}(\text{Hsabth})_2\text{Cl}_2$ suggests the coordination of the carbonyl oxygen to the metal ion. The observed lower value of the downfield shift may be due to the solvent effect because of the strong acceptor properties of DMF towards the acidic-hydrogens of the solute molecules (Bell and Mortimore 1975). There is no change in position of signals due to $-\text{OH}$, $-\text{CH}$ and aromatic protons suggesting the non-involvement of phenolic oxygen and azomethine nitrogen (salicylaldehyde moiety) in bonding.

The 22.49 MHz proton noise decoupled ^{13}C NMR spectral data of Hsabth and $\text{Zn}(\text{Hsabth})_2\text{Cl}_2$ are given in table 4. The ^{13}C assignments for Hsabth have been

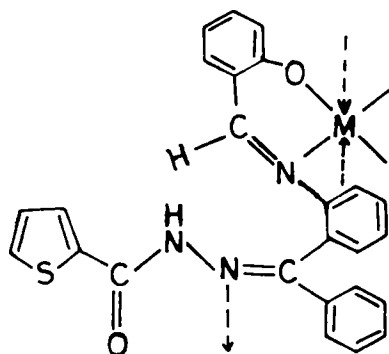


Figure 3. Proposed polymeric structure of $M(\text{sabth})_2$ complexes; $M = \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Cu(II)}$ and Zn(II) .

made on the basis of thiophene-2-carboxaldehyde and benzaldehyde (Silverstein *et al* 1981). In $\text{Zn}(\text{Hsabth})_2\text{Cl}_2$, $\nu(\text{C}=\text{O})$ is not observed due to high excitation energy. The deshielding of the azomethine carbon of the hydrazone moiety is observed (Howorth *et al* 1981) suggesting the bonding of the azomethine nitrogen to the metal ion. The azomethine carbon (salicylaldehyde moiety) does not show any change suggesting the non-involvement of the $-\text{NCH}$ nitrogen in bonding to the metal ion.

3.5 X-ray powder diffraction

The X-ray powder lines observed in copper(II) complexes have been successfully indexed on the basis of an orthorhombic unit lattice (Azaroff and Buerger 1958). The indexing yields the lattice constants as $a = 12.18$, $b = 11.80$, $c = 10.18 \text{ \AA}$ for $\text{Cu}(\text{Hsabth})_2\text{Cl}_2$ and $a = 10.87$, $b = 7.33$ and $c = 7.12 \text{ \AA}$ for $\text{Cu}(\text{sabth})_2$.

Based on chemical compositions and physico-chemical studies, square pyramidal geometry for the vanadyl complexes and octahedral geometry for the $M(\text{Hsabth})_2\text{Cl}_2$ and $M(\text{sabth})_2$ have been proposed, as shown in figure 2. However, a polymeric structure without involving any lowering in μ_{eff} may also be proposed (figure 3) for $M(\text{sabth})_2$ which shows high decomposition temperature as compared to the addition compounds.

Acknowledgements

The authors thank Prof. P Chandra for encouragement. One of us (AKS) is thankful to the Council of Scientific & Industrial Research, New Delhi, for the award of a fellowship. The X-ray powder diffraction data obtained from the Physics Department are gratefully acknowledged. Thanks are also due to the Regional Sophisticated Instrumentation Centre, Indian Institute of Technology, Bombay, for recording the ESR spectra.

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