

Magnetic and spectral studies of transition metal complexes of salicylaldehyde-2-aminoacetophenone-2-thenoylhydrazone

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Abstract. Salicylaldehyde-2-aminoacetophenone-2-thenoylhydrazone (H_2 saath) has been found to react with the transition metal salts to form the complexes $VO(H_2saath)_2SO_4$, $M(H_2saath)_2Cl_2$ and $M(Hsaath)_2$ [$M=OV(IV)$, $Mn(II)$, $Co(II)$, $Ni(II)$, $Cu(II)$ and $Zn(II)$]. The complexes have been characterized by elemental analyses, molar conductance, magnetic susceptibility, electronic and photoacoustic, ESR, IR, 1H and ^{13}C NMR studies. X-ray diffraction study suggests a tetragonal unit lattice for zinc(II) and an orthorhombic one for copper(II) complexes.

Keywords. Aroylhydrazone complexes; transition metal complexes; tetragonal unit lattice; orthorhombic lattice.

1. Introduction

We have been studying the coordination properties of aroylhydrazones. In continuation of our previous work (Singh *et al* 1988; Singh and Srivastav 1989), we describe the results of our investigations on the synthesis and structural studies of $OV(IV)$, $Mn(II)$, $Co(II)$, $Ni(II)$, $Cu(II)$ and $Zn(II)$ complexes of salicylaldehyde-2-aminoacetophenone-2-thenoylhydrazone, hereafter abbreviated as H_2 saath (figure 1).

2. Experimental

2.1 Materials

The chemicals used were of BDH reagent grade. Salicylaldehyde (Sarabhai Chemicals) and 2-aminoacetophenone and 2-thenoylhydrazone (Aldrich, W Germany) were used

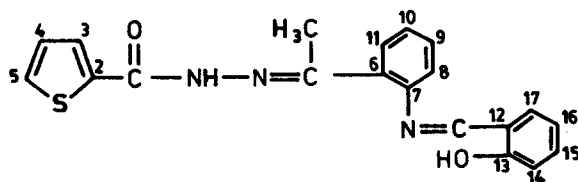


Figure 1. Structure of salicylaldehyde-2-aminoacetophenone-2-thenoylhydrazone (H_2 saath).

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as obtained. 2-Aminoacetophenone-2-thenoylhydrazone (Haath) was prepared as reported earlier (Singh and Srivastav 1989).

2.2 Preparation of ligand

H₂saath was prepared by refluxing salicylaldehyde (3 ml) and an ethanolic solution (20 ml) of 2-aminoacetophenone-2-thenoylhydrazone (7.5 g) for ~ 4 h. After cooling, the product was filtered and recrystallized from ethanol. Yield, 65%; m.p. 238–240°C (Found: C = 66.0, H = 4.6, N = 11.4, N₂H₄ = 8.7, C₂₀H₁₇N₃O₂S, Calcd: C = 66.1, H = 4.7, N = 11.6, N₂H₄ = 8.8%). The hydrazone was also characterized by IR, ¹H and ¹³C NMR spectra. The PMR spectrum of the hydrazone at 24°C in DMSO-*d*₆ shows signals at 2.49, 8.61, 11.11, 12.08 and 6.52–8.19 ppm which are assigned to CH₃, –NCH, –NH, OH and aromatic protons, respectively. The ¹³C NMR spectrum of the hydrazone shows signals at 198.01, 154.95, 148.66 and 12.47 ppm which are assigned to the carbonyl, azomethine, NCH and CH₃ carbons, respectively (Silverstein *et al* 1981). The signals for the aromatic carbons are assigned as C₂ = 151.91, C₃ = 139.99, C₄ = 134.20, C₅ = 133.87, C₆ = 126.94, C₇ = 136.63, C₈ = 124.91, C₉ = 116.97, C₁₀ = 130.84, C₁₁ = 116.54, C₁₂ = 120.82, C₁₃ = 128.13, C₁₄ = 114.21, C₁₅ = 128.56, C₁₆ = 115.18 and C₁₇ = 129.01 ppm, respectively.

2.3 Preparation of the complexes

M(H₂saath)₂Cl₂ complexes [M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)] were prepared by mixing together the ethanolic solutions of the hydrazone (2 mmol in 20 ml) and the appropriate metal chloride (1 mmol in 10 ml). The complexes, which precipitated after reducing the volume and adding ether, were filtered, washed with ethanol and dried at room temperature. VO(H₂saath)₂SO₄ was prepared by a similar method using a methanolic solution of vanadyl sulphate.

M(H saath)₂ complexes [M = OV(IV), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II)] were prepared by adding an ethanolic solution of H₂saath (2 mmol in 20 ml) to the aqueous solution of the appropriate metal salt (1 mmol in 10 ml). The complexes precipitated out on raising the pH of the solution to ~ 7 by adding NaOH solution. The complexes were digested on a water bath for ~ ½ h, then they were filtered, washed with water first and then with ethanol and ether, and dried over fused calcium chloride in a dessiccator under vacuum at room temperature.

2.4 Analysis

The complexes were analysed for their metal content after decomposing the organic moiety by aqua regia followed by conc. H₂SO₄, employing standard literature procedure (Vogel 1969). Chloride and sulphate were estimated gravimetrically as AgCl and BaSO₄, respectively. Hydrazine was determined volumetrically using KIO₃ after hydrolysing the complexes with dilute HCl. The complexes give satisfactory results of carbon, hydrogen and nitrogen analyses.

2.5 Physical measurements

The C, H and N have been microanalysed on a Perkin–Elmer CHN analyser 240C.

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

Compound	Colour	Found (Calc.)%						μ_{eff} (B.M.)	Molar conduc- tance in DMF (ohm ⁻¹ cm ² mol ⁻¹)	m.p. (°C)
		Metal	N ₂ H ₄	Nitrogen	Cl/SO ₄	Carbon	Hydrogen			
VO(H ₂ saath) ₂ SO ₄	Black	5.2 (5.7)	—	9.4 (9.5)	10.6 (10.8)	53.8 (54.0)	3.7 (3.8)	1.78	2.5	> 350
Mn(H ₂ saath) ₂ Cl ₂	Whitish yellow	6.1 (6.5)	7.2 (7.5)	9.7 (9.9)	8.1 (8.3)	56.1 (56.3)	3.9 (4.0)	5.97	10.2	> 350
Co(H ₂ saath) ₂ Cl ₂	Brown	6.4 (6.9)	7.0 (7.5)	9.6 (9.8)	7.8 (8.3)	55.8 (56.1)	4.0 (4.0)	4.82	15.8	> 350
Ni(H ₂ saath) ₂ Cl ₂	Dirty brown	6.8 (6.9)	7.3 (7.5)	9.7 (9.8)	8.1 (8.3)	55.8 (56.1)	3.8 (4.0)	3.18	18.1	188–89 ^d
Cu(H ₂ saath) ₂ Cl ₂	Dirty brown	6.8 (7.4)	—	9.6 (9.8)	7.9 (8.3)	55.5 (55.8)	3.9 (4.0)	2.11	19.1	185–87 ^d
Zn(H ₂ saath) ₂ Cl ₂	Dirty yellow	7.2 (7.6)	7.3 (7.4)	9.5 (9.7)	7.9 (8.2)	55.4 (55.7)	3.9 (3.9)	diamag- netic	2.6	> 350
VO(Hsaath) ₂	Brown	5.9 (6.4)	—	10.4 (10.6)	—	60.5 (60.7)	4.1 (4.3)	1.73	2.4	216–18 ^d
Mn(Hsaath) ₂	Dirty yellow	6.8 (7.1)	7.9 (8.2)	10.4 (10.8)	—	61.4 (61.6)	4.2 (4.4)	5.93	2.4	212–14 ^d
Co(Hsaath) ₂	Brown	6.8 (7.5)	7.8 (8.2)	10.3 (10.7)	—	61.0 (61.2)	4.2 (4.3)	4.91	2.8	> 350
Ni(Hsaath) ₂	Dirty yellow	7.1 (7.5)	8.1 (8.2)	10.3 (10.7)	—	61.1 (61.2)	4.1 (4.3)	2.82	4.2	> 350
Cu(Hsaath) ₂	Dirty green	7.9 (8.1)	—	10.4 (10.7)	—	60.7 (61.0)	4.2 (4.3)	2.12	10.2	> 350
Zn(Hsaath) ₂	Yellow	8.1 (8.3)	7.8 (8.1)	10.3 (10.6)	—	60.5 (60.8)	4.1 (4.3)	diamag- netic	5.7	> 350

^d Decomposes

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

Complex	Bands (cm^{-1})	Assignments
$\text{VO}(\text{H}_2\text{Saath})_2\text{SO}_4$	11110, 15385, 23530	$d_{xy} \rightarrow d_{yz}, d_{xz}, d_{x^2-y^2}$
$\text{VO}(\text{Hsaath})_2$	12500, 15875, 20835	$d_{xy} \rightarrow d_{yz}, d_{xz}, d_{x^2-y^2}$
$\text{Co}(\text{H}_2\text{saath})_2\text{Cl}_2$	9300, 14390(14925), 19415	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F), {}^4A_{2g}(F), {}^4T_{1g}(P)$
$\text{Co}(\text{Hsaath})_2$	9435, 15385, 22470	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F), {}^4A_{2g}(F), {}^4T_{1g}(P)$
$\text{Ni}(\text{H}_2\text{saath})_2\text{Cl}_2$	11110, 23530(20620)	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F), {}^3T_{1g}(P)$
$\text{Ni}(\text{Hsaath})_2$	10930, 16130, 23530	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F), {}^3T_{1g}(F), {}^3T_{1g}(P)$
$\text{Cu}(\text{H}_2\text{saath})_2\text{Cl}_2$	13795	${}^2E_g \rightarrow {}^2T_{2g}$
$\text{Cu}(\text{Hsaath})_2$	14285	${}^2E_g \rightarrow {}^2T_{2g}$

The other experimental details pertaining to the molar conductance, magnetic susceptibility, electronic and photoacoustic, ESR, IR, NMR and X-ray diffraction studies were the same as described in our previous papers (Singh *et al* 1988; Singh and Srivastav 1989). Pertinent data are given in tables 1–6.

3. Results and discussion

H_2saath reacts with the metal salts yielding two types of complexes possessing the neutral (H_2saath) and the deprotonated (Hsaath) forms as indicated by analytical data (table 1). The complexes are insoluble in organic solvents but are slightly or fairly soluble in DMF and DMSO. $\text{Ni}(\text{H}_2\text{saath})_2\text{Cl}_2$, $\text{Cu}(\text{H}_2\text{saath})_2\text{Cl}_2$, $\text{VO}(\text{Hsaath})_2$ and $\text{Mn}(\text{Hsaath})_2$ decompose at 185–218°C while the remaining complexes do not melt or decompose below 350°C. The values of molar conductance of the complexes in DMF at 0.001 M concentration lie in the range 2.38–19.24 $\text{ohm}^{-1}\text{cm}^2\text{mol}^{-1}$ suggesting that they are nonionic in nature (Geary 1971).

3.1 Magnetic moments

The μ_{eff} values of cobalt(II) and nickel(II) complexes are consistent with octahedral geometry (Figgis and Lewis 1964). The magnetic moments of oxovanadium(IV) and copper(II) complexes indicate the presence of one unpaired electron giving no definite information about their stereochemistries (Cotton and Wilkinson 1976). The manganese(II) complexes are high-spin as is evident from the magnetic moments which correspond to five unpaired electrons (table 1).

3.2 Electronic spectra

The electronic spectra of OV(IV) complexes show three bands which may be assigned to $d-d$ transitions assuming square pyramidal geometry (Ballhausen and Gray 1962; Farmer and Urbach 1974; Stoklosa *et al* 1974). The number, position and assignments of the bands observed in the spectra of cobalt(II) and nickel(II) complexes are consistent with octahedral geometry (Lever 1968; Sacconi 1969; Mathews and Walton 1971). The electronic spectra suggest distorted octahedral coordination of the ligand around copper(II).

Table 3. ESR magnetic and bonding parameters.

Complex	g_{\parallel}/g_{\perp}	θ_{xx}	θ_{\perp}	g_{yy}	g_{zz}	A_{\parallel}/A_{zz} (G)	A_{xx} (G)	A_{\perp} (G)	A_{yy} (G)	A_{zz} (G)	a^2/β^2
VO(H ₂ saath) ₂ SO ₄	1.9330	—	1.9762	—	1.9618	195.00	—	72.86	—	113.57	0.93
VO(H saath) ₂	1.9433	—	1.9641	—	1.9572	181.43	—	57.14	—	98.57	0.93
Cu(H ₂ saath) ₂ Cl ₂	2.2821	2.0343	—	2.0719	2.1419	166.67	11.66	—	13.33	64.44	0.78
Cu(H saath) ₂	2.2561	2.0095	—	2.0488	2.1172	166.67	14.17	—	15.00	65.56	0.74

Table 4. Important IR bands and their assignments.

Complex	$\nu(\text{OH})$	$\nu(\text{C=O})$	$\nu(\text{C=N})$	$\nu_{\text{sym}}(\text{C-O})$	$\nu_{\text{asym}}(\text{C-O-M})$	$\nu(\text{N-N})$	$\nu(\text{M-O})$	$\nu(\text{M-N})$	$\nu(\text{M-Cl})$
H ₂ saath	3440 b	1660 s	1620 mb	1270 s	—	1010 w	—	—	—
VO(H ₂ saath) ₂ SO ₄	3360-3440 b	1640 m	—	—	—	—	410 w	—	—
Mn(H ₂ saath) ₂ Cl ₂	3320-3440 b	1640 s	1610 w	—	—	1025 w	400 w	350 m	265 m
Co(H ₂ saath) ₂ Cl ₂	3380-3440 b	1640 w	1610 w	—	—	1035 s	400 w	330 s	265 w
Ni(H ₂ saath) ₂ Cl ₂	3300-3440 b	1650 w	1610 m	—	—	1020 w	395 m	335 s	260 m
Cu(H ₂ saath) ₂ Cl ₂	3330-3440 b	1645 w	1605 s	—	—	1020 w	395 m	335 w	265 s
Zn(H ₂ saath) ₂ Cl ₂	3360-3440 b	1650 w	1610 m	—	—	1035 s	400 m	335 m	300 s
VO(H saath) ₂	—	1660 m	1600 s	1305 m	1530 m	1025 s	400 m	325 s	—
Mn(H saath) ₂	—	1660 w	1605 s	1305 w	1535 s	1035 s	400 w	325 w	—
Co(H saath) ₂	—	1660 m	1605 w	1295 m	1535 s	1035 s	400 w	330 s	—
Ni(H saath) ₂	—	1660 m	1600 m	1300 w	1530 s	1035 s	395 s	335 s	—
Cu(H saath) ₂	—	1660 m	1600 m	1305 w	1535 s	1035 s	395 w	335 w	—
Zn(H saath) ₂	—	1660 w	1600 s	1300 m	1530 s	1035 s	400 m	335 m	—

Abbreviations: b - broad; s - strong; m - medium; w - weak.

Table 5. Observed and computed Q and hkl values for copper(II) complexes.

Cu(H ₂ saath) ₂ Cl ₂						Cu(Hsaath) ₂					
2θ	RI*	d	Q_{obs}	Q_{calc}	hkl	2θ	RI*	d	Q_{obs}	Q_{calc}	hkl
9-10	<i>m</i>	9-7099	0-0106	0-0106	100	9-05	<i>vs</i>	9-7592	0-0105	0-0105	100
13-35	<i>w</i>	6-6265	0-0227	0-0227	010	10-40	<i>s</i>	8-4989	0-0138	0-0138	010
15-60	<i>w</i>	5-6743	0-0311	0-0311	001	15-35	<i>w</i>	5-7678	0-0301	0-0301	001
19-05	<i>w</i>	4-6526	0-0462	0-0454	020	16-65	<i>m</i>	5-3177	0-0354	0-0348	210
20-05	<i>m</i>	4-4227	0-0511	0-0523	201	17-65	<i>s</i>	5-0196	0-0397	0-0406	103
27-70	<i>s</i>	3-2164	0-0967	0-0957	122	18-20	<i>s</i>	4-8673	0-0422	0-0414	030
—	—	—	—	—	—	20-90	<i>w</i>	4-2448	0-0555	0-0552	040
—	—	—	—	—	—	22-30	<i>s</i>	3-9814	0-0631	0-0630	600
—	—	—	—	—	—	24-60	<i>w</i>	3-6150	0-0765	0-0762	240
—	—	—	—	—	—	25-95	<i>vs</i>	3-4421	0-0844	0-0845	112
—	—	—	—	—	—	27-10	<i>w</i>	3-2864	0-0926	0-0925	231
—	—	—	—	—	—	27-65	<i>s</i>	3-2231	0-0963	0-0972	440
—	—	—	—	—	—	31-15	<i>m</i>	2-8678	0-1216	0-1218	303
—	—	—	—	—	—	31-70	<i>w</i>	2-8195	0-1258	0-1249	213
—	—	—	—	—	—	32-15	<i>w</i>	2-7808	0-1293	0-1298	422
—	—	—	—	—	—	33-10	<i>m</i>	2-7037	0-1368	0-1364	242
—	—	—	—	—	—	35-70	<i>m</i>	2-5122	0-1584	0-1599	423
—	—	—	—	—	—	37-75	<i>m</i>	2-3802	0-1765	0-1770	343
—	—	—	—	—	—	39-50	<i>m</i>	2-2788	0-1926	0-1922	652

* RI – relative intensity; abbreviations are as in table 4; *v* – very.Table 6. Observed and computed Q and hkl values for zinc(II) complexes.

Zn(H ₂ saath) ₂ Cl ₂						Zn(Hsaath) ₂					
2θ	RI*	d	Q_{obs}	Q_{calc}	hkl	2θ	RI*	d	Q_{obs}	Q_{calc}	hkl
9-20	<i>m</i>	9-6009	0-0108	0-0108	100	8-20	<i>w</i>	10-7692	0-0086	0-0086	100
14-75	<i>w</i>	5-9969	0-0278	0-0278	101	10-05	<i>s</i>	8-7899	0-0129	0-0129	101
23-70	<i>s</i>	3-7415	0-0714	0-0710	211	14-30	<i>m</i>	6-1847	0-0261	0-0258	102
25-05	<i>m</i>	3-5500	0-0793	0-0788	102	16-10	<i>s</i>	5-5000	0-0331	0-0344	200
26-20	<i>m</i>	3-3965	0-0866	0-0864	220	18-85	<i>m</i>	4-7008	0-0453	0-0473	211
—	—	—	—	—	—	20-30	<i>m</i>	4-3700	0-0524	0-0516	112
—	—	—	—	—	—	21-80	<i>s</i>	4-0719	0-0603	0-0602	212
—	—	—	—	—	—	23-00	<i>m</i>	3-8616	0-0671	0-0688	220
—	—	—	—	—	—	24-20	<i>m</i>	3-6737	0-0741	0-0731	221
—	—	—	—	—	—	25-45	<i>s</i>	3-4952	0-0819	0-0817	301
—	—	—	—	—	—	31-65	<i>w</i>	2-8236	0-1254	0-1247	313,115
—	—	—	—	—	—	34-45	<i>w</i>	2-6005	0-1479	0-1462	410,304
—	—	—	—	—	—	37-00	<i>w</i>	2-4267	0-1698	0-1720	420,116
—	—	—	—	—	—	42-00	<i>m</i>	2-1484	0-2166	0-2150	500

* Abbreviations as in tables 4 and 5.

3.3 Photoacoustic spectra

The H₂saath does not show any absorption bands in the visible region. Ni(H₂saath)₂Cl₂ absorbs at 16,950 and 24,390(20,835)cm⁻¹ while Ni(Hsaath)₂

shows bands at 16,665 and 24,390 cm^{-1} which are due to $d-d$ transitions (Rosencwaig 1980) and indicate octahedral geometry (Singh and Rao 1981) for both the nickel(II) complexes as inferred from electronic spectra.

3.4 ESR spectra

The DMF glass ESR spectra of oxovanadium(IV) complexes exhibit two sets of eight lines arising from interaction of an unpaired electron with the ^{51}V nucleus due to anisotropy yielding $g_{\parallel} < g_{\perp} < g_e$. This indicates the presence of the unpaired electron in the $d_{xy}(b_{2g}^*)$ orbital (Kon and Sharpless 1965).

The trend in g values is indicative of the unpaired electron in the $d_{x^2-y^2}$ orbital (Goodman and Raynor 1970). Both the copper(II) complexes give three distinct g values indicating rhombic (Hathaway and Billing 1970) symmetry. The σ -bonding parameter, α^2 , indicates the presence of an appreciable amount of covalency in the metal-ligand bond.

3.5 Infrared spectra

The bands appearing in the hydrazone at 1660, 1620 and 1010 cm^{-1} are due to the $\nu(\text{C}=\text{O})$, $\nu(\text{C}=\text{N})$ and $\nu(\text{N}-\text{N})$ modes, respectively. In the H_2 saath complexes the $\nu(\text{C}=\text{O})$ shift to lower frequencies suggesting coordination through the carbonyl oxygen. The intensity of the $\nu(\text{C}=\text{N})$ band decreases and a splitting of the band is also noticed in all the complexes except $\text{VO}(\text{H}_2\text{saath})_2\text{SO}_4$. This observation may be taken as indicative of involvement of one or both $>\text{C}=\text{N}$ nitrogen(s) in bonding. However, $\nu(\text{N}-\text{N})$ is observed at higher frequencies in comparison to its position in the free hydrazone. This favours the involvement of the azomethine nitrogen in bonding. The $\nu(\text{OH})$ observed at 3440 cm^{-1} in the ligand is localized in the 3300–3440 cm^{-1} region in the H_2 saath complexes indicating its noninvolvement in bonding.

In the deprotonated (H saath) complexes no shift is observed in the $\nu(\text{C}=\text{O})$ band. Weakening, splitting and shifting of $\nu(\text{C}=\text{N})$ to lower frequencies is observed together with shifting of the $\nu(\text{N}-\text{N})$ (Aggarwal and Narang 1973) to higher frequencies. The $\nu(\text{OH})$ disappears and new bands due to $\nu_{\text{asym}}(\text{C}-\text{O})$ appear in conjunction with the shifting of $\nu_{\text{sym}}(\text{C}-\text{O})$ to higher frequencies (Sinn and Harris 1969). These changes in spectrum of the hydrazone are indicative of uninegative tridentate bonding behaviour through both the $\nu(\text{C}=\text{N})$ and phenolic oxygens. The square pyramidal geometry for $\text{VO}(\text{H saath})_2$ as inferred from electronic and ESR studies suggests that only one of the $>\text{C}=\text{N}$ nitrogens is involved in bonding. The chelating bidentate bonding of SO_4^{2-} in the vanadyl complex is inferred (Nakamoto 1978) from the appearance of bands at 1240, 1125, 1040 and 975 cm^{-1} . However, the band at 975 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 but the band at 980 cm^{-1} in $\text{VO}(\text{H saath})_2$ may be unequivocally assigned to $\nu(\text{V}=\text{O})$.

The bands observed in the 395–410, 325–350 and 260–300 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.

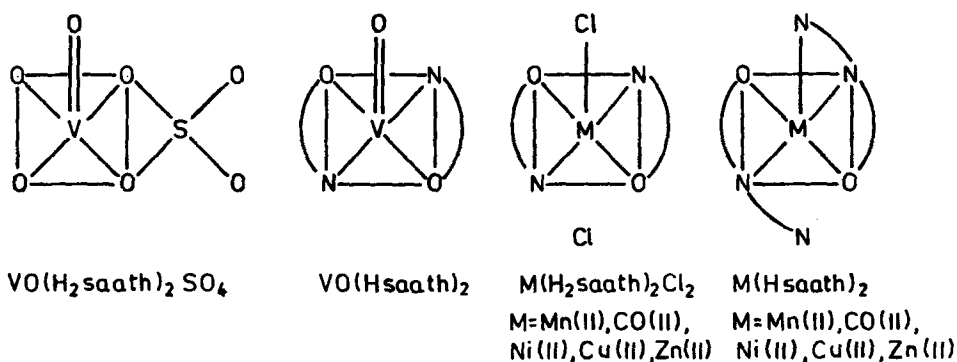


Figure 2. The proposed structures for the complexes.

3.6 X-ray diffraction

X-ray diffraction patterns of copper(II) and zinc(II) complexes have been successfully indexed (Azaroff and Buerger 1958). The lattice parameters are $a = 9.71$, $b = 6.63$ and $c = 5.67$ Å for $\text{Cu}(\text{H}_2\text{saath})_2\text{Cl}_2$, $a = 9.76$, $b = 8.49$ and $c = 5.77$ Å for $\text{Cu}(\text{Hsaath})_2$, $a = b = 9.60$ and $c = 7.67$ Å for $\text{Zn}(\text{H}_2\text{saath})_2\text{Cl}_2$ and $a = b = 10.77$ and $c = 15.25$ Å for $\text{Zn}(\text{saath})_2$. The parameters (Azaroff and Buerger 1958) are commensurate with an orthorhombic unit lattice for copper(II) and a tetragonal one for the zinc(II) complexes.

Based on chemical compositions and physicochemical studies, square pyramidal geometry for oxovanadium(IV) complexes and octahedral stereochemistry for the remaining complexes may be tentatively proposed (figure 2).

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