

## Synthesis and structural studies of 2-acetylthiophene-2-thenoylhydrazone complexes of oxovanadium(IV), manganese(II), cobalt(II), nickel(II), copper(II), zinc(II), cadmium(II) and mercury(II)

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**Abstract.** Complexes with chemical compositions  $\text{VO}(\text{Hatth})_2\text{SO}_4$ ,  $\text{VO}(\text{Hatth})_2\text{SO}_4 \cdot \text{py}$ ,  $[\text{M}(\text{Hatth})_2\text{Cl} \cdot \text{H}_2\text{O}]\text{Cl}$  [ $\text{M} = \text{Mn}(\text{II}), \text{Co}(\text{II})$  and  $\text{Ni}(\text{II})$ ],  $[\text{Cu}(\text{Hatth})_2\text{Cl}]_2\text{Cl}_2$ ,  $[\text{Cu}(\text{Hatth})_2 \cdot \text{Cl} \cdot \text{py}]\text{Cl}$ ,  $[\text{Cd}(\text{Hatth})_2\text{Cl}]\text{Cl}$ ,  $\text{M}(\text{Hatth})_2\text{Cl}_2$  [ $\text{M} = \text{Zn}(\text{II})$  and  $\text{Hg}(\text{II})$ ],  $\text{VO}(\text{atth})_2$ ,  $\text{VO}(\text{atth})_2 \cdot \text{py}$ ,  $\text{M}(\text{atth})_2(\text{py})_2$  [ $\text{M} = \text{Mn}(\text{II})$  and  $\text{Cu}(\text{II})$ ],  $\text{M}(\text{atth})_2(\text{H}_2\text{O})_2$  [ $\text{M} = \text{Mn}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Cu}(\text{II})$  and  $\text{Zn}(\text{II})$ ],  $\text{Hatth} = 2\text{-acetylthiophene-2-thenoylhydrazone}$ , and  $\text{atth}$ , its deprotonated form, have been prepared and characterized by analytical data, molar conductance, magnetic susceptibility, electronic and photoacoustic, ESR, IR and NMR spectral studies. X-ray diffraction study has been used to determine the shape and the dimensions of the unit lattice of copper(II) complexes.

**Keywords.** 2-Acetylthiophene-2-thenoylhydrazone; transition metal complexes; orthorhombic unit lattice.

### 1. Introduction

Schiff base metal complexes have broad applications in biological processes (Sorkin *et al* 1952; Ali and Livingstone 1974; Johnson *et al* 1982) and as catalysts in chemical and petrochemical industries (Srinivasan *et al* 1986; Bhattacharya 1990). Catalytic activity is reported to depend on the structure of the Schiff base, the substituted groups on it and the redox potential of the metal ion. Binuclear complexes have been found to be better catalysts than the mononuclear Schiff base complexes. As 2-acetylthiophene-2-thenoylhydrazone can act as a multidentate ligand, in continuation of our previous work (Singh *et al* 1988; Singh and Srivastav 1989–1991), the synthesis and structural studies of OV(IV), Mn(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II) and Hg(II) complexes with the title Schiff base (figure 1) have been carried out. The results of these investigations are presented in this paper.

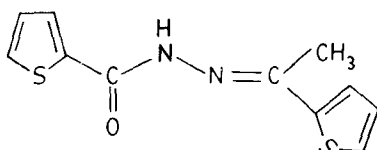


Figure 1. Structure of the Schiff base, 2-acetylthiophene-2-thenoylhydrazone (Hatth).

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## 2. Experimental

### 2.1 Starting materials

All the chemicals used in the present study were of BHD or of equivalent grade. 2-Acetylthiophene and 2-thenoylhydrazine, obtained from Aldrich Chemie, Germany, were used without further purification.

### 2.2 Preparation of ligand

2-Acetylthiophene-2-thenoylhydrazone (Hatth) was prepared by refluxing an ethanolic solution (20 ml) of 2-thenoylhydrazine (6 g) and 2-acetylthiophene (5 ml) for ~ 3 h. On standing overnight, a pale yellow product separated out. This was washed with ethanol and ether. Yield 70%, m.p. 177–178°C;  $C_{11}H_{10}N_2OS_2$  requires: C, 52.8; H, 4.0; N, 11.2;  $N_2H_4$ , 12.8%. Found: C, 52.4; H, 3.9; N, 11.1;  $N_2H_4$ , 12.7%. The Schiff base was also characterized by IR,  $^1H$  and  $^{13}C$  NMR spectra.

### 2.3 Preparation of the complexes

The compounds  $[M(Hatth)_2Cl(H_2O)]Cl$  [ $M = Mn(II), Co(II)$  and  $Ni(II)$ ],  $[Cu(Hatth)_2Cl]_2Cl_2$ ,  $[Cd(Hatth)_2Cl]Cl$  and  $M(Hatth)_2Cl_2$  [ $M = Zn(II)$  and  $Hg(II)$ ] were prepared by mixing together an ethanolic solution (10 ml) of the metal chloride (1 mmol) and Hatth (2 mmol) in the same solvent (20 ml). The complexes were precipitated after reducing the volume and adding ether.  $VO(Hatth)_2SO_4$  was prepared similarly by using a methanolic solution (20 ml) of vanadyl sulphate.

$[Cu(Hatth)_2Cl \cdot py]Cl$  was prepared by mixing ethanolic solutions (10 ml) of copper(II) chloride (1 mmol), Hatth (2 mmol) in ethanol (20 ml) and pyridine (2 mmol). The complex was precipitated by reducing the volume followed by addition of ether.  $VO(Hatth)_2SO_4 \cdot py$  was prepared by mixing methanolic solution (20 ml) of vanadyl sulphate (1 mmol), ethanolic solution (20 ml) of Hatth (2 mmol) and pyridine (2 mmol).

The deprotonated complexes,  $M(atth)_2(H_2O)_2$  [ $M = Mn(II), Co(II), Ni(II), Cu(II)$  and  $Zn(II)$ ] and  $VO(atth)_2$  were prepared by mixing the aqueous solutions (10 ml) of the metal chloride/sulphate (1 mmol) and ethanolic solution (20 ml) of Hatth (2 mmol) and raising the pH of the solution to ~ 7 by  $NKOH$  solution.

$VO(atth)_2 \cdot py$  and  $M(atth)_2(py)_2$  [ $M = Mn(II)$  and  $Cu(II)$ ] were prepared by adding aqueous solutions (10 ml) of the metal chloride/sulphate (1 mmol) to the ethanolic solution (20 ml) of Hatth (2 mmol) followed by pyridine (2 mmol), and raising the pH of the solution to ~ 7 by  $NKOH$  solution.

The Hatth complexes were washed with ethanol and ether, while the atth complexes were first washed with water and then with ethanol and ether, and finally dried under vacuum.

### 2.4 Analysis

Metals were analysed using gravimetric procedures (Vogel 1973) while hydrazine was estimated volumetrically by titrating against  $KIO_3$  after submitting the complexes to acid hydrolysis for ~ 4 h. Sulphate and chloride were estimated gravimetrically as barium sulphate and silver chloride, respectively. C, H and N were estimated microanalytically. Water content was determined by heating the complexes in the 100–180°C range and evaluating the weight loss. Analytical data are given in table 1.

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

Compound	Colour	Yield (%)	Found (calcd.)%							Weight loss	$\mu_{\text{eff}}$	Molar conductance*	m.p. (°C)
			M	N <sub>2</sub> H <sub>4</sub>	N	Cl/SO <sub>4</sub>	C	H					
VO(Hatth) <sub>2</sub> SO <sub>4</sub>	Brown	62	7.6 (7.9)	—	8.5 (8.7)	14.4 (14.8)	40.4 (40.8)	3.0 (3.1)	—	1.63	19.2	205–07	
VO(Hatth) <sub>2</sub> SO <sub>4</sub> ·py	Canary yellow	74	6.7 (6.9)	—	9.2 (9.4)	12.2 (12.9)	43.2 (43.7)	3.5 (3.4)	—	1.80	14.7	224–26	
[Mn(Hatth) <sub>2</sub> Cl(H <sub>2</sub> O)]Cl	Dirty yellow	68	8.3 (8.5)	9.5 (9.9)	8.6 (8.7)	10.8 (11.0)	40.5 (40.6)	3.1 (3.1)	2.8 (2.8)	6.20	73.6	234–35	
[Co(Hatth) <sub>2</sub> Cl(H <sub>2</sub> O)]Cl	Ash	76	8.9 (9.1)	9.6 (9.9)	8.5 (8.6)	10.9 (11.0)	40.6 (40.8)	3.0 (3.1)	2.8 (2.8)	5.18	73.6	238–40	
[Ni(Hatth) <sub>2</sub> Cl(H <sub>2</sub> O)]Cl	Dirty green	78	8.9 (9.1)	9.5 (9.9)	8.6 (8.7)	10.9 (11.0)	40.6 (40.8)	3.0 (3.1)	2.7 (2.8)	3.26	83.7	255–56	
[Cu(Hatth) <sub>2</sub> Cl] <sub>2</sub> Cl <sub>2</sub>	Green	82	9.7 (10.0)	—	8.5 (8.8)	10.8 (11.2)	41.1 (41.6)	2.9 (3.2)	—	1.64	118.9	278–80 <sup>d</sup>	
[Cu(Hatth) <sub>2</sub> Cl·py]Cl	Greenish blue	76	8.6 (8.9)	—	9.6 (9.8)	9.6 (10.0)	45.1 (45.1)	3.4 (3.5)	—	2.22	69.6	310–12	
Zn(Hatth) <sub>2</sub> Cl <sub>2</sub>	Light yellow	58	9.9 (10.3)	9.8 (10.1)	8.8 (8.8)	10.6 (11.1)	41.1 (41.5)	3.1 (3.1)	—	dia. <sup>†</sup>	14.7	189–90	
[Cd(Hatth) <sub>2</sub> Cl]Cl	Whitish yellow	72	15.6 (16.5)	9.3 (9.4)	7.8 (8.2)	9.6 (10.4)	38.6 (38.6)	2.8 (2.9)	—	dia.	65.6	222–24	
Hg(Hatth) <sub>2</sub> Cl <sub>2</sub>	Yellow	78	26.3 (26.0)	8.9 (9.2)	7.1 (7.3)	7.8 (8.3)	34.0 (34.2)	2.6 (2.6)	—	dia.	5.3	217–18	
VO(atth) <sub>2</sub>	Greenish yellow	88	8.7 (9.0)	—	9.7 (9.9)	—	46.8 (46.7)	3.5 (3.5)	—	1.61	2.1	208–09	
VO(atth) <sub>2</sub> ·py	Canary yellow	74	7.6 (7.9)	—	10.7 (10.9)	—	49.9 (50.3)	3.8 (3.6)	—	1.74	9.5	235–37	
Mn(atth) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	Brown	78	9.1 (9.3)	10.6 (10.8)	9.2 (9.5)	—	44.6 (44.7)	3.3 (3.4)	6.0 (6.1)	4.48	2.4	> 350	
Mn(atth) <sub>2</sub> (py) <sub>2</sub>	Dirty yellow	66	7.6 (7.7)	8.8 (9.0)	9.6 (9.9)	—	45.7 (45.5)	3.2 (3.2)	—	5.81	19.8	> 350	

(Continued)

Table 1. (Continued)

Compound	Yield (%)	Colour	Found (calcd.)%						Weight loss	$\mu_{eff}$	Molar conductance*	m.p. (°C)
			M	N <sub>2</sub> H <sub>4</sub>	N	Cl/SO <sub>4</sub>	C	H				
Co(atth) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	76	Brown	9.6 (9.9)	10.5 (10.8)	9.3 (9.4)	—	44.2 (44.5)	3.3 (3.4)	6.0 (6.1)	5.14	1.7	256–58 <sup>d</sup>
Ni(atth) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	82	Dirty brown	9.5 (10.5)	10.4 (10.8)	9.3 (9.5)	—	44.3 (44.5)	3.3 (3.4)	6.0 (6.1)	2.79	2.9	234–35 <sup>d</sup>
Cu(atth) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	86	Brown	10.5 (10.6)	—	9.3 (9.4)	—	44.0 (44.2)	3.2 (3.4)	6.0 (6.0)	1.62	3.1	> 350
Cu(atth) <sub>2</sub> (py) <sub>2</sub>	74	Dark green	8.6 (8.8)	—	9.6 (9.7)	—	45.6 (45.0)	3.1 (3.2)	—	1.85	7.3	> 350
Zn(atth) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	78	Light yellow	10.8 (10.9)	10.4 (10.7)	9.3 (9.3)	—	43.8 (44.1)	3.1 (3.3)	5.9 (6.0)	dia.	1.2	192–93

<sup>d</sup>Decomposes; \*molar conductance in DMF (ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>); †dia. = diamagnetic.

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

Complex	Bands ( $\text{cm}^{-1}$ )	Assignments
VO(Hatth) <sub>2</sub> SO <sub>4</sub>	12,905(11,110), 16,000(18,180), 25,000	$d_{xy} \rightarrow d_{yz}, d_{xz}, d_{x^2-y^2}$
VO(Hatth) <sub>2</sub> SO <sub>4</sub> ·py	12,660, 23,310	$d_{xy} \rightarrow d_{yz}, d_{xz}; d_{x^2-y^2}$
[Co(Hatth) <sub>2</sub> Cl(H <sub>2</sub> O)]Cl	8 890, 16,130(14,925)	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F), {}^4A_{2g}(F)$
[Ni(Hatth) <sub>2</sub> Cl(H <sub>2</sub> O)]Cl	10,000, 15,875, 24,690	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F), {}^3T_{1g}(F), {}^3T_{1g}(P)$
[Cu(Hatth) <sub>2</sub> Cl] <sub>2</sub> Cl <sub>2</sub>	13,700	${}^2E_g \rightarrow {}^2T_{2g}$
[Cu(Hatth) <sub>2</sub> Cl·py]Cl	14,855	${}^2E_g \rightarrow {}^2T_{2g}$
VO(atth) <sub>2</sub>	10,640, 15,625, 25,000	$d_{xy} \rightarrow d_{yz}, d_{xz}, d_{x^2-y^2}$
VO(atth) <sub>2</sub> ·py	11,390, 23,365	$d_{xy} \rightarrow d_{yz}, d_{xz}; d_{x^2-y^2}$
Co(atth) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	10,050, 16,000	${}^4T_{1g}(F) \rightarrow {}^4T_{2g}(F), {}^4A_{2g}(F)$
Ni(atth) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	9 260, 15,040, 21,055	${}^3A_{2g}(F) \rightarrow {}^3T_{2g}(F), {}^3T_{1g}(F), {}^3T_{1g}(P)$
Cu(atth) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	12,820	${}^2E_g \rightarrow {}^2T_{2g}$
Cu(atth) <sub>2</sub> (py) <sub>2</sub>	15,385	${}^2E_g \rightarrow {}^2T_{2g}$

**Table 3.** ESR magnetic and bonding parameters.

Complex	$g_{\parallel}$	$g_{\perp}$	$g_{av}$	$A_{\parallel}(G)$	$A_{\perp}(G)$	$A_{av}(G)$	$\alpha^2/\beta^2$
VO(Hatth) <sub>2</sub> SO <sub>4</sub>	1-9428	1-9829	1-9695	197-14	67-96	111-02	0-97
[Cu(Hatth) <sub>2</sub> Cl] <sub>2</sub> Cl <sub>2</sub>	2-2929	2-0715	2-1453	183-34	11-67	68-89	0-84
Cu(atth) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	2-2570	2-0406	2-1127	156-66	26-66	69-99	0-72

### 2.5 Physical measurements

Experimental details pertaining to the molar conductance, magnetic susceptibility, electronic and photoacoustic, ESR, IR, NMR (<sup>1</sup>H and <sup>13</sup>C) and X-ray diffraction were the same as described in our earlier papers (Singh *et al* 1988; Singh and Srivastav 1989).

Molar conductance, magnetic susceptibility and C, H, N analyses data are included in table 1 while electronic, ESR, IR, NMR and X-ray diffraction data are listed in tables 2–6.

### 3. Results and discussion

All the complexes are insoluble in water, carbon tetrachloride, chloroform and benzene and soluble in ethanol, methanol, acetonitrile, acetone, DMF and DMSO. Mn(atth)<sub>2</sub>·(H<sub>2</sub>O)<sub>2</sub>, Mn(atth)<sub>2</sub>(py)<sub>2</sub>, Cu(atth)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> and Cu(atth)<sub>2</sub>(py)<sub>2</sub> are non-melting below 350°C. VO(Hatth)<sub>2</sub>SO<sub>4</sub>, [Cu(Hatth)<sub>2</sub>Cl]<sub>2</sub>Cl<sub>2</sub>, Co(atth)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> and Ni(atth)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> complexes decompose in the 205–280°C temperature range whereas the remaining complexes melt in the 189–256°C temperature range. [Cu(Hatth)<sub>2</sub>Cl]<sub>2</sub>Cl<sub>2</sub> is a 1:2 electrolyte (Ginsberg 1971) whereas all adduct complexes are 1:1 electrolytes except VO(Hatth)<sub>2</sub>SO<sub>4</sub>, VO(Hatth)<sub>2</sub>SO<sub>4</sub>·py, Zn(Hatth)<sub>2</sub>Cl<sub>2</sub> and Hg(Hatth)<sub>2</sub>Cl<sub>2</sub>. The deprotonated complexes are nonelectrolytes (Geary 1971). The hydrated complexes lose water at 140–170°C (Fabretti *et al* 1977).

Table 4. Important IR bands ( $\text{cm}^{-1}$ ) and their assignments.

Complex	$\nu(\text{OH})$	Amide I	Amide II	$\nu(\text{C}=\text{N})$	$\nu(\text{N}=\text{N})$	$\nu(\text{M}=\text{O})$	$\nu(\text{M}=\text{N})$	$\nu(\text{M}=\text{Cl})$
Hatth	—	1695 m	1530 m	1645 m	1000 w	—	—	—
VO(Hatth) <sub>2</sub> SO <sub>4</sub>	—	1680 w	1515 w	1645 w/	—	415 w	—	—
VO(Hatth) <sub>2</sub> SO <sub>4</sub> ·py	—	1655 s	1515 w	1645 w	—	405 w	315 w	—
[Mn(Hatth) <sub>2</sub> Cl(H <sub>2</sub> O)]Cl	3400 b	1680 m	1515 w	1640 m	1015 w	370 w	320 m	295 m
[CO(Hatth) <sub>2</sub> Cl(H <sub>2</sub> O)]Cl	3400 b	1680 w	1515 w	1635 s	1010 w	385 m	320 m	285 m
[Ni(Hatth) <sub>2</sub> Cl(H <sub>2</sub> O)]Cl	3440 b	1680 w	1515 m	1625 w	1010 m	390 w	320 w	290 m
[Cu(Hatth) <sub>2</sub> Cl] <sub>2</sub> ·Cl <sub>2</sub>	—	1680 m	1520 w	1615 m	1015 w	385 w	315 w	295 w
[Cu(Hatth) <sub>2</sub> Cl·py]Cl	—	1655 m	1510 w	1630 w	1020 w	390 w	320 w	285 w
Zn(Hatth) <sub>2</sub> Cl <sub>2</sub>	—	1655 w	1515 w	1640 m	1025 m	410 w	325 w	290 w
[Cd(Hatth) <sub>2</sub> Cl]Cl	—	1675 w	1515 w	1640 m	1015 w	385 w	320 w	285 w
Hg(Hatth) <sub>2</sub> Cl <sub>2</sub>	—	1675 w	1515 w	1640 m	1025 s	385 s	325 w	290 w
VO(atth) <sub>2</sub>	—	1565 w	1310 w	1635 w	1015 w	425 m	315 w	—
VO(atth) <sub>2</sub> py	—	1560 w	1310 w	1620 m	1030 m	400 m	320 w	—
Mn(atth) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	3400 b	1565 w	1300 w	1635 w	1020 w	385 w	315 w	—
Mn(atth) <sub>2</sub> ·py <sub>2</sub>	—	1545 w	1290 s	1630 s	1030 s	385 w	320 w	—
Co(atth) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	3460 b	1565 w	1315 w	1625 w	1015 w	405 w	300 s	—
Ni(atth) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	3400 b	1570 w	1315 w	1625 w	1015 w	425 m	320 w	—
Cu(atth) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	3470 b	1575 w	1300 w	1620 w	1025 w	375 w	330 w	—
Cu(atth) <sub>2</sub> py <sub>2</sub>	—	1555 w	1330 m	1620 m	1030 w	395 w	330 w	—
Zn(atth) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	3440 b	1575 w	1300 w	1625 w	1020 w	385 w	315 m	—

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

Table 5. <sup>13</sup>C NMR spectral bands (in ppm) and their assignments.

Complex	C=O	C=N	CH <sub>3</sub>	C <sub>2</sub>	C <sub>3</sub>	C <sub>4</sub>	C <sub>5</sub>	C <sub>6</sub>	C <sub>7</sub>	C <sub>8</sub>	C <sub>9</sub>
Hatth	161.55	143.16	14.47	134.60	129.21	128.26	126.67	130.12	128.58	127.94	126.04
Zn(Hatth) <sub>2</sub> Cl <sub>2</sub>	161.86	142.84	14.47	134.28	128.89	128.26	127.47	131.11	128.42	128.10	126.83
[Cd(Hatth) <sub>2</sub> Cl]Cl	162.18	142.84	14.53	134.44	128.89	128.42	127.79	131.59	128.58	128.26	126.83
Hg(Hatth) <sub>2</sub> Cl <sub>2</sub>	161.86	142.84	14.42	134.28	129.21	127.19	126.83	131.75	128.42	127.63	125.88
Zn(atth) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>	162.18	143.00	14.47	134.44	129.21	128.42	126.99	131.59	128.58	127.79	125.72

Table 6. Observed and calculated Q and hkl values of copper(II) complexes.

[Cu(Hatth) <sub>2</sub> Cl] <sub>2</sub> Cl <sub>2</sub>												Cu(atth) <sub>2</sub> (H <sub>2</sub> O) <sub>2</sub>											
2θ	d	R1*	Q <sub>obs</sub>	Q <sub>calc</sub>	hkl	2θ	d	R1*	Q <sub>obs</sub>	Q <sub>calc</sub>	hkl	2θ	d	R1*	Q <sub>obs</sub>	Q <sub>calc</sub>	hkl						
11.519	7.6818	78	0.0169	0.0169	100	6.374	13.8670	106	0.0052	0.0052	100	6.374	13.8670	106	0.0052	0.0052	100						
16.196	5.4726	322	0.0334	0.0334	010	9.599	9.2136	112	0.0118	0.0118	010	9.599	9.2136	112	0.0118	0.0118	010						
19.835	4.4760	141	0.0499	0.0499	001	11.910	7.4308	174	0.0181	0.0181	001	11.910	7.4308	174	0.0181	0.0181	001						
27.931	3.1941	130	0.0980	0.0998	002	12.818	6.9061	119	0.0210	0.0208	400	12.818	6.9061	119	0.0210	0.0208	400						
30.911	2.8928	118	0.1195	0.1183	700	17.255	5.1395	470	0.0379	0.0389	401	17.255	5.1395	470	0.0379	0.0389	401						
32.706	2.7380	136	0.1334	0.1336	040	18.387	4.8252	134	0.0430	0.0417	021	18.387	4.8252	134	0.0430	0.0417	021						
34.778	2.5795	149	0.1503	0.1505	320	19.285	4.6025	212	0.0472	0.0469	121	19.285	4.6025	212	0.0472	0.0469	121						
43.783	2.0676	125	0.2339	0.2338	070	19.802	4.4835	184	0.0497	0.0493	601	19.802	4.4835	184	0.0497	0.0493	601						
45.314	2.0012	148	0.2497	0.2495	005	23.084	3.8529	171	0.0674	0.0677	521	23.084	3.8529	171	0.0674	0.0677	521						
48.439	1.8792	105	0.2832	0.2841	180	24.492	3.6342	147	0.0757	0.0751	403	24.492	3.6342	147	0.0757	0.0751	403						
51.484	1.7750	126	0.3174	0.3175	190	25.436	3.5016	386	0.0816	0.0820	232	25.436	3.5016	386	0.0816	0.0820	232						
54.441	1.6853	137	0.3521	0.3525	960	26.894	3.3151	386	0.0910	0.0907	703	26.894	3.3151	386	0.0910	0.0907	703						
62.287	1.4906	111	0.4501	0.4491	009	28.312	3.1521	189	0.1006	0.1011	903	28.312	3.1521	189	0.1006	0.1011	903						
68.602	1.3680	119	0.5343	0.5343	509	34.356	2.6102	118	0.1468	0.1459	462	34.356	2.6102	118	0.1468	0.1459	462						
—	—	—	—	—	—	36.876	2.4375	154	0.1683	0.1692	564	36.876	2.4375	154	0.1683	0.1692	564						
—	—	—	—	—	—	46.348	1.9590	125	0.2606	0.2616	996	46.348	1.9590	125	0.2606	0.2616	996						
—	—	—	—	—	—	48.384	1.8812	105	0.2826	0.2822	698	48.384	1.8812	105	0.2826	0.2822	698						

\*R1 - relative intensity.

### 3.1 Magnetic measurements

The magnetic moment of  $[\text{Mn}(\text{Hatth})_2\text{Cl}(\text{H}_2\text{O})]\text{Cl}$  and  $\text{Mn}(\text{atth})_2(\text{py})_2$  are 6.20 and 5.81 BM respectively. This shows the presence of five unpaired electrons but gives no definite information about their stereochemistry (Cotton and Wilkinson 1976). The  $\mu_{\text{eff}}$  values of cobalt(II) and nickel(II) complexes are indicative of octahedral geometry around the metal ions (Figgis and Lewis 1964). The  $\mu_{\text{eff}}$  values of  $\text{VO}(\text{Hatth})_2\text{SO}_4 \cdot \text{py}$ ,  $\text{VO}(\text{atth})_2\text{py}$ ,  $[\text{Cu}(\text{Hatth})_2\text{Cl} \cdot \text{py}]\text{Cl}$  and  $\text{Cu}(\text{atth})_2(\text{py})_2$  correspond to the presence of one-unpaired electron (Cotton and Wilkinson 1976). The magnetic moment of  $[\text{Cu}(\text{Hatth})_2\text{Cl}]_2\text{Cl}_2$  and  $\text{Cu}(\text{atth})_2(\text{H}_2\text{O})_2$  are anomalous (1.64 and 1.62 BM, respectively) which may be attributed to metal-metal interaction (Ginsberg 1971, Yamada *et al* 1960) while that of  $\text{VO}(\text{Hatth})_2\text{SO}_4$  and  $\text{VO}(\text{atth})_2$  (1.63 and 1.61 BM) may be ascribed to spin-orbit coupling (O'Connor 1964) and/or  $\text{V} = \text{O} \dots \text{V}$  interaction and  $\text{Mn}(\text{atth})_2(\text{H}_2\text{O})_2$  (4.48 BM) may be attributed to metal-metal and/or antiferromagnetic exchange between two adjacent Mn(II) ions in dimeric/polymeric species (Hewkin and Lewis 1964; Lewis *et al* 1968). The pyridine compounds having normal  $\mu_{\text{eff}}$  values indicate that dimeric/polymeric complexes change to monomeric complexes. This may be considered as evidence that the parent complexes are involved in the interactions proposed above.

### 3.2 Electronic spectra

The stereochemistry of the complexes deduced from magnetic susceptibility studies are further confirmed by the electronic spectral (nujol mull) studies. The number, position and assignments of bands observed in the spectra of cobalt(II) and nickel(II) complexes are consistent with octahedral geometry (Dunn 1960; Lever 1964; Mathews and Walton 1971) as evidenced by their magnetic moment values. Three bands are observed in the electronic spectra of oxovanadium(IV) complexes indicating square pyramidal geometry (Farmer and Urbach 1974; Stoklosa *et al* 1974), while the two bands observed in the spectra of the respective pyridine complexes are commensurate with octahedral geometry (Dutta and Sengupta 1971). The band position in the copper(II) complexes are indicative of octahedral coordination around the copper(II) ion.

### 3.3 Photoacoustic spectra

The assignment of the electronic spectral bands to  $d-d$  transitions in the nickel(II) complexes is further confirmed from photoacoustic spectral studies. The photoacoustic spectrum (recorded in the  $13,335-25,000 \text{ cm}^{-1}$  region) of the title Schiff base does not show any absorption bands in this region. The observed bands at  $16,000$  and  $24,390 \text{ cm}^{-1}$  for  $[\text{Ni}(\text{Hatth})_2\text{Cl}(\text{H}_2\text{O})]\text{Cl}$  and at  $14,925$  and  $21,275 \text{ cm}^{-1}$  for  $\text{Ni}(\text{atth})_2 \cdot (\text{H}_2\text{O})_2$  are assigned to  $d-d$  transitions (Rosencwaig 1980) on the basis of octahedral (Singh and Rao 1981) geometry for the complexes.

### 3.4 Electron spin resonance spectra

The electronic structure of some copper(II) and oxovanadium(IV) complexes is further elucidated from electron spin resonance studies. DMF glass electron spin resonance spectra of copper(II) complexes have characteristic axial symmetry and yield



well-resolved signals in parallel and perpendicular  $^{63}\text{Cu}$  regions of the spectra. The trend  $g_{\parallel} > g_{\perp} > g_e$  (2.0023) (table 3), shows that the unpaired electron is localized in the  $d_{x^2-y^2}$  orbital (Goodman and Raynor 1970) of the copper(II) ion. The additional peaks observed at 1470 G for  $[\text{Cu}(\text{Hatth})_2\text{Cl}]_2\text{Cl}_2$  and 1510 G for  $\text{Cu}(\text{atth})_2(\text{H}_2\text{O})_2$  may be due to singlet-triplet transition (Smith and Pilbrow 1974; O'Young *et al* 1978; Churchill *et al* 1980) ( $\Delta M_s = 2$ ) suggesting that the complexes are dimeric in nature. These findings agree with information gathered about the structure of  $[\text{Cu}(\text{Hatth})_2\text{Cl}]_2\text{Cl}_2$ ,  $\text{Cu}(\text{atth})_2(\text{H}_2\text{O})_2$  and  $\text{VO}(\text{Hatth})_2\text{SO}_4$  from anomalous magnetic moments.

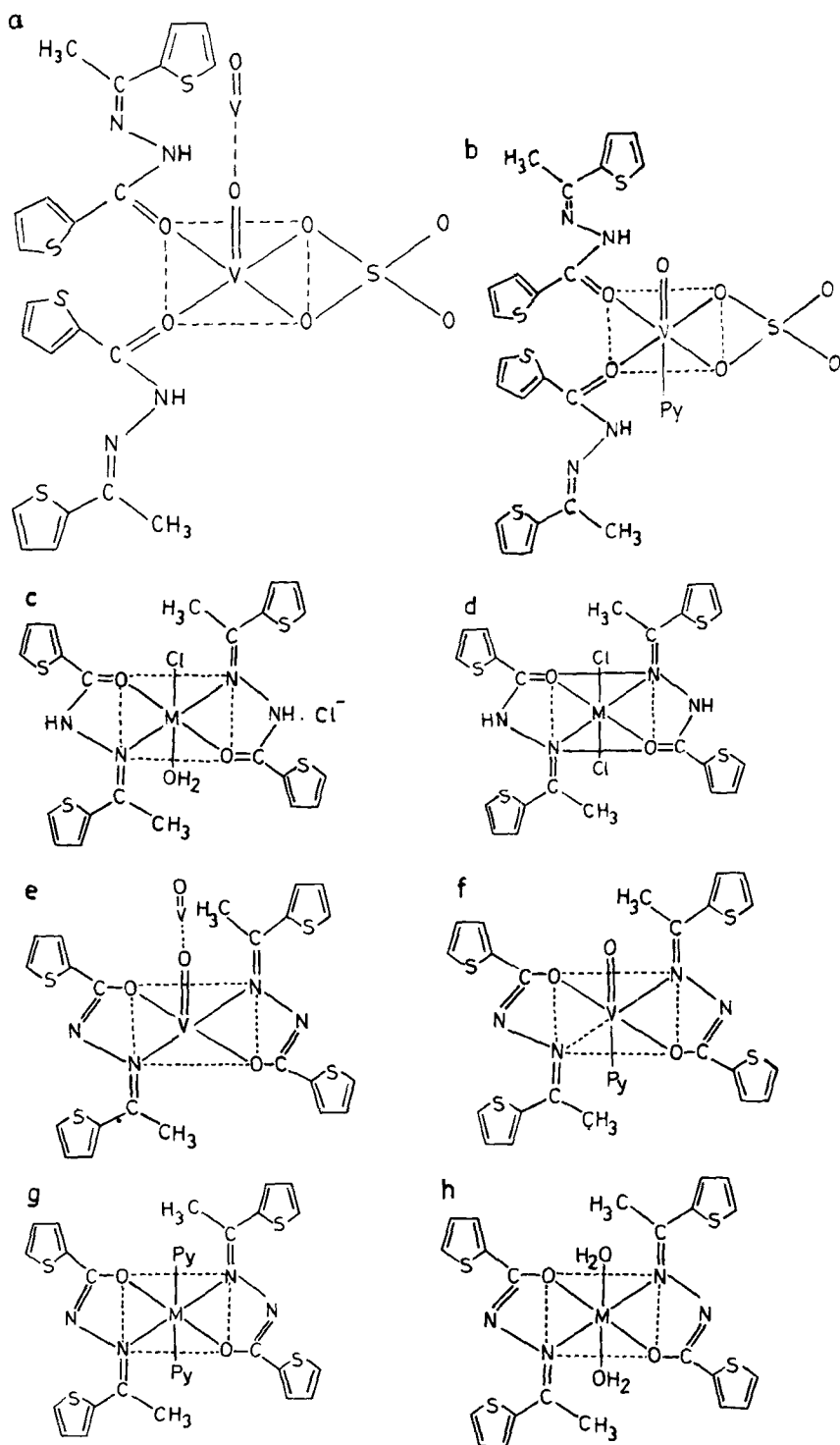
The spectrum of  $\text{VO}(\text{Hatth})_2\text{SO}_4$  gives two sets of eight lines arising from interaction of the unpaired electron with  $^{51}\text{V}$  nucleus yielding  $g_{\parallel} > g_{\perp} > g_e$ . The trend in  $g$  values indicates the presence of unpaired electron in the  $d_{xy}$  ( $b_{2g}^*$ ) orbital (Kon and Sharpless 1965; Rani *et al* 1982). This spectrum gives a half-field signal at 1505 G due to a  $\Delta M_s = 2$  transition characteristic of magnetic exchange interaction in dimeric species. The spectrum of  $\text{VO}(\text{atth})_2$  is not clearly resolved but the spectrum shows bands at 2640, 2810, 2960, 3070, 3220 and 3260 G and hence it is not possible to calculate the magnetic parameters for this complex.

### 3.5 Infrared spectra

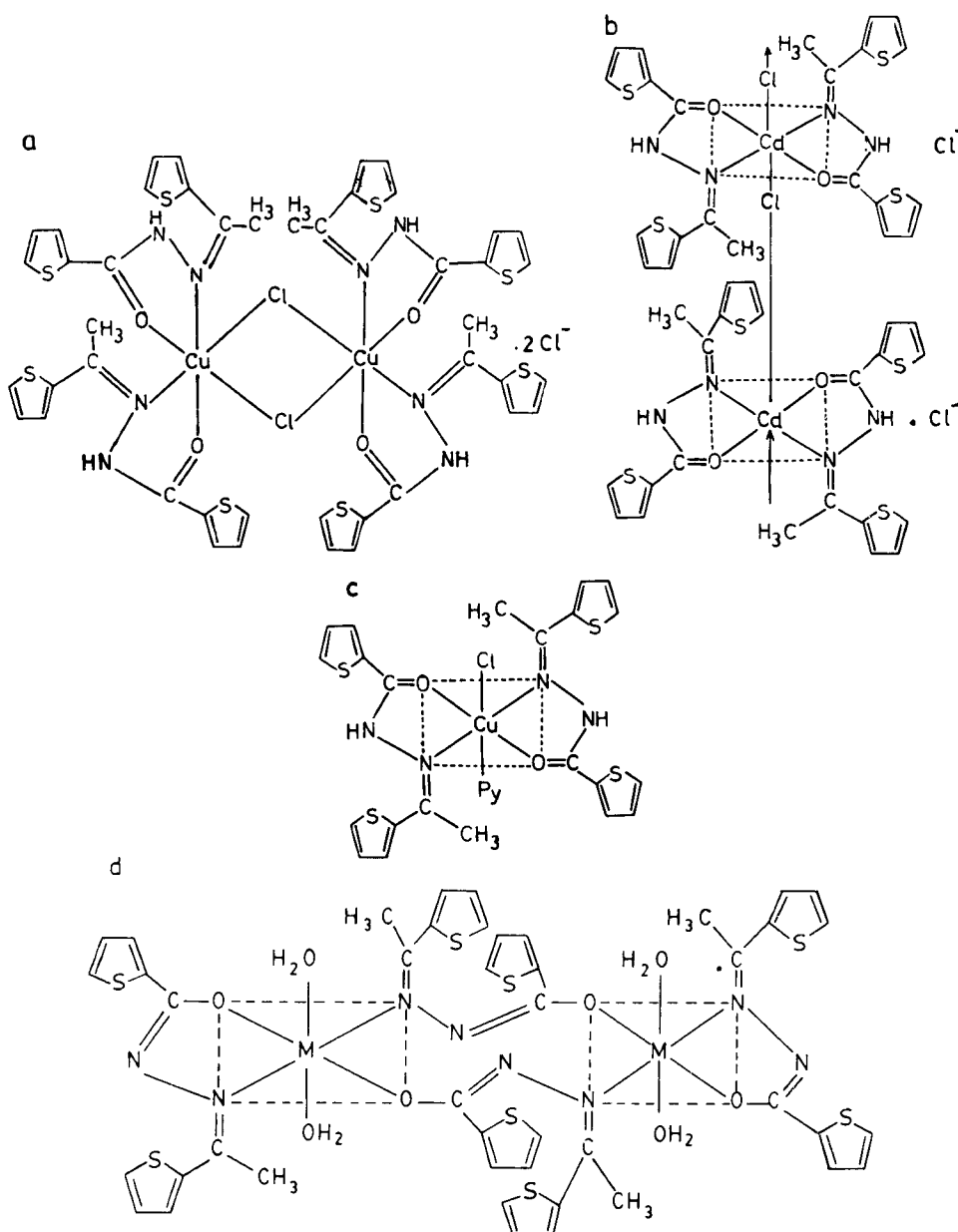
The bonding sites of the 2-acetylthiophene-2-thenoylhydrazone have been adduced from infrared studies. The bands appearing in the spectrum of the Schiff base at 1695, 1945, 1530 and  $1000\text{ cm}^{-1}$  are attributed to amide I [ $\nu(\text{C}=\text{O})$ ],  $\nu(\text{C}=\text{N})$ , amide(II) [ $\beta(\text{N}-\text{H}) + \nu(\text{C}-\text{N})$ ] and  $\nu(\text{N}-\text{N})$  modes, respectively. A broad band observed in the  $3400-3470\text{ cm}^{-1}$  region in the spectra of hydrated complexes may be assigned to the  $\nu(\text{OH})$  of the water molecules. The amide I and amide II bands shift to lower frequencies in the spectra of all the complexes. The  $\nu(\text{C}=\text{N})$  shifts to lower frequencies and  $\nu(\text{N}-\text{N})$  to higher frequencies (Aggarwal and Narang 1973) in all the complexes except  $\text{VO}(\text{Hatth})_2\text{SO}_4$  and  $\text{VO}(\text{Hatth})_2\text{SO}_4 \cdot \text{py}$ . These changes in the spectra of the complexes suggest coordination (Nagano *et al* 1964) of the carbonyl oxygen to the metal ions in all the complexes and that of azomethine nitrogen (Rao 1970) in all except  $\text{VO}(\text{Hatth})_2\text{SO}_4$  and  $\text{VO}(\text{Hatth})_2\text{SO}_4 \cdot \text{py}$ .

The disappearance of amide I and amide II bands and the appearance of new bands characteristic (Braibanti 1968) of  $\nu(\text{NCO}^-)$  in the spectra of the deprotonated complexes, the absence of original anions and their 1:2 metal-ligand stoichiometry show the destruction of the keto group presumably via enolization and bonding of the Schiff base through the resulting enolate oxygen. The presence of four bands at 1235, 1120, 1045 and  $970\text{ cm}^{-1}$  in the spectrum of  $\text{VO}(\text{Hatth})_2\text{SO}_4$  indicates the chelating nature (Nakamoto 1978) of the sulphato group. A band at  $975\text{ cm}^{-1}$  is tentatively assigned to  $\nu(\text{V}=\text{O})$  (Selbin *et al* 1963). However, the  $\nu_{\perp}$  band of the  $\text{SO}_4^{2-}$  also occurs at the same position but a band at  $970\text{ cm}^{-1}$  [ $\text{VO}(\text{atth})_2$ ] may be unequivocally assigned to the  $\text{V}=\text{O}$  stretching mode. The bands observed at 953 and  $958\text{ cm}^{-1}$  in  $\text{VO}(\text{Hatth})_2\text{SO}_4 \cdot \text{py}$  and  $\text{VO}(\text{atth})_2 \cdot \text{py}$ , respectively, at lower frequencies compared to their parent complexes, suggest addition of pyridine *trans* to  $\text{V}=\text{O}$ . The presence of the in-plane ( $640-660\text{ cm}^{-1}$ ) and out-of-plane ( $420-450\text{ cm}^{-1}$ ) vibrations due to the pyridine ring (Nagano *et al* 1964) suggest the involvement of the ring nitrogen in bonding.

The non-ligand bands occurring in the region 370–425, 300–325 and 285–295  $\text{cm}^{-1}$



**Figure 2.** Proposed square pyramidal geometry of  $\text{VO}(\text{Hatth})_2\text{SO}_4$  and  $\text{VO}(\text{atth})_2$  complexes. (a)  $\text{VO}(\text{Hatth})_2\text{SO}_4$ ; (b)  $\text{VO}(\text{Hatth})_2\text{SO}_4 \cdot \text{py}$ ; (c)  $[\text{M}(\text{Hatth})_2\text{ClH}_2\text{O}]\text{Cl}$ ,  $\text{M} = \text{Mn}(\text{II}), \text{Co}(\text{II}), \text{Ni}(\text{II})$ ; (d)  $\text{M}(\text{Hatth})_2\text{Cl}_2$ ,  $\text{M} = \text{Zn}(\text{II}), \text{Hg}(\text{II})$ ; (e)  $\text{VO}(\text{atth})_2$ ; (f)  $\text{VO}(\text{atth})_2\text{py}$ ; (g)  $\text{M}(\text{atth})_2(\text{py})_2$ ,  $\text{M} = \text{Mn}(\text{II}), \text{Cu}(\text{II})$ ; (h)  $\text{M}(\text{atth})_2(\text{H}_2\text{O})_2$ ,  $\text{M} = \text{Co}(\text{II}), \text{Ni}(\text{II}), \text{Zn}(\text{II})$ .



**Figure 3.** Proposed octahedral stereochemistry for complexes other than those shown in figure 2. (a)  $[\text{Cu}(\text{Hatth})_2\text{Cl}]_2\text{Cl}_2$ ; (b)  $[\text{Cd}(\text{Hatth})_2\text{Cl}]\text{Cl}$ ; (c)  $[\text{Cu}(\text{Hatth})_2\text{Clpy}]\text{Cl}$ ; (d)  $\text{M}(\text{atth})_2(\text{H}_2\text{O})_2$ ,  $\text{M} = \text{Mn}(\text{II}), \text{Cu}(\text{II})$ .

are tentatively 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.

### 3.6 Nuclear magnetic resonance spectra

In order to confirm further the bonding sites of the Hatth involved in the complexes, the  $^1\text{H}$  nuclear magnetic resonance spectra of  $\text{Zn}(\text{II})$ ,  $\text{Cd}(\text{II})$  and  $\text{Hg}(\text{II})$  complexes

have been recorded in DMSO- $d_6$  and their spectral features are compared with those of the hydrazone recorded in the same solvent. Hatth exhibits signals at 10.80, 6.96–8.43 and 2.44  $\delta$  assignable to –NH, aromatic and CH<sub>3</sub> protons respectively.

Downfield shifting of –NH protons from 10.80 (hydrazone) to 10.93, 11.09 and 11.13  $\delta$  in Zn(Hatth)<sub>2</sub>Cl<sub>2</sub>, [Cd(Hatth)<sub>2</sub>Cl]Cl and Hg(Hatth)<sub>2</sub>Cl<sub>2</sub>, respectively, suggests the coordination of the carbonyl oxygen with the metal ions. The –NH proton disappears from the spectrum of Zn(atth)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> and thus indicates deprotonation of the hydrazone. There is a slight change in positions of signals in CH<sub>3</sub>, which may be due to the nearby thiophene ring, while the ring protons remain unchanged.

The 22.49 MHz proton noise decoupled <sup>13</sup>C nuclear magnetic resonance spectral data of Hatth and its Zn(II), Cd(II) and Hg(II) complexes, have been shown in table 5. The <sup>13</sup>C assignments for Hatth have been made on the basis of thiophene-2-carboxaldehyde (Silverstein *et al* 1981) and 2-thenoylhydrazine (Singh and Singh 1990). In the complexes, both in the adducts and in the deprotonated forms, bonding through the carbonyl oxygen has been inferred from the deshielding observed for the carbonyl carbon atoms (Howorth *et al* 1981). Surprisingly, shielding (Domiano *et al* 1984) of azomethine carbon is observed which may be due to the presence of anion/electron-donating CH<sub>3</sub> groups in the adducts and of the latter in the deprotonated compounds.

### 3.7 X-ray powder diffraction

X-ray diffraction lines of copper(II) complexes have been satisfactorily indexed (Azaroff and Buerger 1958) for orthorhombic symmetry. The lattice parameters computed for [Cu(Hatth)<sub>2</sub>Cl]<sub>2</sub>Cl<sub>2</sub> is  $a = 7.68$ ,  $b = 5.47$  and  $c = 4.48$  Å and for Cu(atth)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub> is  $a = 13.87$ ,  $b = 9.21$  and  $c = 7.43$  Å.

Based on chemical compositions and physicochemical studies, square pyramidal geometry for VO(Hatth)<sub>2</sub>SO<sub>4</sub> and VO(atth)<sub>2</sub> complexes and octahedral stereochemistry for the remaining complexes may be proposed (figures 2 and 3).

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