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# Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

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Synthesis and Characterization of N-(o-Vanillinidene)-p-anisidine and N,N'-bis(o-Vanillinidene)ethylenediamine and Their Metal Complexes

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# SYNTHESIS AND REACTIVITY IN INORGANIC AND METAL-ORGANIC CHEMISTRY Vol. 33, No. 5, pp. 817–836, 2003

# Synthesis and Characterization of N-(*o*-Vanillinidene)-*p*-anisidine and N,N'-*bis*(*o*-Vanillinidene)ethylenediamine and Their Metal Complexes

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## ABSTRACT

Two Schiff bases, N-(*o*-vanillinidene)-*p*-anisidine (*o*-VPAH) and N,N'bis(*o*-vanillinidene)ethylenediamine (*o*-VEDH<sub>2</sub>), and eleven complexes of the compositions [M(L)(OAc)(H<sub>2</sub>O)] {where M = Cu(II) (1), Co(II) (2), Mn(II) (3) or Ni(II) (4) and OAcH = CH<sub>3</sub>COOH}, [Zn(L)<sub>2</sub>]·H<sub>2</sub>O (5), [M(L')(H<sub>2</sub>O)<sub>2</sub>] {where M = Cu(II) (6) or Ni(II) (7)}, [Zn(L')]·2H<sub>2</sub>O (8), [Sm(L')(OAc)(H<sub>2</sub>O)] (9), [Th(L')(NO<sub>3</sub>)<sub>2</sub>] (10) and [UO<sub>2</sub>(L')(H<sub>2</sub>O)]· H<sub>2</sub>O (11) (where LH = *o*-VPAH, and L'H<sub>2</sub> = *o*-VEDH<sub>2</sub>), were prepared.

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From the elemental analyses, IR, electronic and NMR spectra, magnetic susceptibility measurements and thermal studies, the mode of chelation of the ligands and geometry of the complex molecules were assigned. In all of the complexes, o-VPAH acts as a monobasic-bidentate ligand and o-VEDH<sub>2</sub> acts as a dibasic-tetradentate ligand. The presence of water is revealed by thermograms and supported by the presence of relevant bands in their IR spectra. Suitable structures have been proposed for these complexes.

*Key Words:* N-(*o*-vanillinidene)-*p*-anisidine; N,N'-bis(*o*-vanillinidene)ethylenediamine; Cu(II); Co(II); Mn(II); Ni(II); Zn(II); Sm(III); Th(IV); UO<sub>2</sub>(VI) complexes.

## **INTRODUCTION**

Chelating ligands containing O and N donor atoms show broad biological activity and are of special interest because of the variety of ways in which they are bonded to metal ions.<sup>[1,2]</sup> Aromatic hydroxyaldehydes form stable complexes and the presence of a phenolic hydroxyl group at their *o*position imparts an additional donor site in the molecule making it bidentate. Such a molecule coordinates with the metal ion through the carbonyl oxygen and deprotonated hydroxyl group. The chelating properties of Schiff bases derived from *o*-hydroxyaldehydes and ketones are well established.<sup>[3–5]</sup>

Chelate complexes of formylferrocene and acetylferrocene salicyloylhydrazones with transition metals have been synthesized and characterized by Xian<sup>[6]</sup> et al. The ligands are bidentate and their complexes in DMF are non-electrolytes. Mononitrosyl derivatives of iron and cobalt complexes of quadridentate ligands derived from 2-hydroxy-1-naphthaldehyde and ethylenediamine, *o*-phenylenediamine and 4-methyl-*o*-phenylenediamine have been synthesized and characterized by Larkworthy<sup>[7]</sup> and coworkers.

In view of the coordinating ability of Schiff bases derived from *o*-hydroxyaromatic aldehydes along with their biological activity, we have synthesized and characterized the two aroyl Schiff bases, 1) N-(*o*-vanillinidene)-*p*-anisidine (o-VPAH), and 2) N,N-bis(*o*-vanillinidene)ethy-lenediamine (o-VEDH<sub>2</sub>). Among the aromatic aldehydes, an isomer of vanillin, *i.e.*, *o*-vanillin is used. It is 3-methoxysalicylaldehyde. Vanillin is a constituent of fruits of the widely occurring plant *Vanilla Planifolia*. It can easily be obtained by the treatment of spent wood pulp with alkali.

In order to explore the ligational behaviour of theses two ligands, we have prepared a series of their metal complexes with Cu(II), Co(II), Ni(II), Mn(II), Zn(II), Sm(III), Th(IV) and UO<sub>2</sub>(VI), and characterized them by various physico-chemical techniques. The results of our studies are included in this paper.

## EXPERIMENTAL

## Materials

*o*-Vanillin, ethylenediamine, *p*-anisidine and dimethylformamide (Sisco Chem. Industry, Bombay), Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O, Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O, Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O and UO<sub>2</sub>-(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (E. Merck, Germany), Th(NO<sub>3</sub>)<sub>4</sub>·6H<sub>2</sub>O and Sm(CH<sub>3</sub>-COO)<sub>3</sub>·3H<sub>2</sub>O (Indian Rare Earth Ltd.) were used as supplied. Ethanol and other solvents employed were of A.R. grade.

## Synthesis of Ligands

An ethanolic solution (30 mL) of *o*-vanillin (50 mmol, 7.60 g) was added to the ethanolic solution (15–20 mL) of *p*-anisidine (50 mmol, 6.15 g)/ethylenediamine (25 mmol, 1.17 mL). The resulting mixture was then refluxed on a water bath for 4–5 h. A coloured solid mass separated out on cooling. It was then filtered by suction, washed with ethanol, diethyl ether and subsequently dried over anhydrous CaCl<sub>2</sub> in a desiccator. The purity of the ligands was checked by TLC. Both Schiff base ligands are insoluble in all common organic solvents, *viz.*, acetone, alcohol, benzene, etc. but soluble in polar solvents, *viz.*, DMF, DMSO, etc.

## Synthesis of Metal Complexes of o-VPAH

Metal complexes of *o*-VPAH were synthesized by mixing a solution of *o*-VPAH (5 mmol, 1.28 g) in the minimum quantity of dimethylformamide (~ 20 mL) and an ethanolic solution (~ 30 mL) of the metal salt  $[Cu(CH_3COO)_2 \cdot H_2O$  (5 mmol, 0.99 g), Co(CH\_3COO)\_2 \cdot 4H\_2O (5 mmol, 1.24 g), Ni(CH\_3COO)\_2 \cdot 4H\_2O (5 mmol, 1.24 g), Mn(CH\_3COO)\_2 \cdot 4H\_2O (5 mmol, 1.22 g)] or Zn(CH\_3COO)\_2 \cdot 2H\_2O (2.5 mmol, 0.55 g)]. The resulting mixture was then refluxed on an electric heating mantle at 80 °C for ~4 h. On cooling a coloured complex precipitated, was filtered, washed with alcohol and finally with diethyl ether and dried over anhydrous CaCl<sub>2</sub>.



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## Synthesis of Metal Complexes of o-VEDH<sub>2</sub>

Metal complexes of N,N'-bis(*o*-vanillinidene)ethylenediamine (*o*-VEDH<sub>2</sub>) were synthesized by mixing a hot solution of *o*-VEDH<sub>2</sub> (5 mmol, 1.64 g) in a minimum quantity of dimethylformamide (~20 mL) and an aqueous-ethanolic (1:1, 30 mL) solution of the metal salt [Ni(CH<sub>3</sub>-COO)<sub>2</sub>·4H<sub>2</sub>O (5 mmol, 1.24 g), Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (5 mmol, 1.10 g), Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O (5 mmol, 0.99 g), Sm(CH<sub>3</sub>COO)<sub>3</sub>·3H<sub>2</sub>O (5 mmol, 1.90 g), of Th(NO<sub>3</sub>)<sub>4</sub>·6H<sub>2</sub>O (5 mmol, 2.94 g) or UO<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O (5 mmol, 2.12 g)]. The resulting mixture was then refluxed on an electric heating mantle at 80 °C for ~4 h. On cooling, the coloured complexes precipitated out which were filtered by suction, washed with ethanol and finally with diethyl ether and dried in vacuo over anhydrous CaCl<sub>2</sub>.



N,N'-Bis(o-vanillinidene)ethylenediamine (o-VEDH<sub>2</sub>)

Figure 1. Synthesis of Schiff base ligands.

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Empirical formula Found (calc.), % M.p. Yield (formula С Ν Ligand weight)  $(^{\circ}C)$ (%) Solubility Color Η o-VPAH  $C_{15}H_{15}N_1O_3$ 230 65 Sol. in Brown 69.72 5.72 5.64 DMF and (70.04)(LH) (257.00)(5.83)(5.44)DMSO o-VEDH<sub>2</sub> 5.76 8.23  $C_{18}H_{20}N_2O_4$ 260 75 Yellow 65.49 Sol. in (L'H<sub>2</sub>) (328.00)DMF and (65.85) (6.09) (8.53) DMSO

*Table 1.* Physical characteristics and microanalytical data of the ligands.

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# **RESULTS AND DISCUSSION**

The Schiff base ligands o-VPAH and o-VEDH<sub>2</sub> were prepared from o-vanillin according to the equations in Figure 1.

The formation of the Schiff bases is consistent with the microanalytical data of the ligands. The microanalytical data, melting points, colours, % yields and other details are given in Table 1. The <sup>1</sup>H NMR spectra of the Schiff base ligands are given in Figures 2 and 3 along with the indexing of various protons. The formation of the Schiff base ligands are confirmed by the appearance of the azomethine proton (-CH=N-) signal at 8.95 ppm in *o*-VPAH and 8.2 ppm in *o*-VEDH<sub>2</sub>.<sup>[8]</sup> This is further supported by the appearance of a band in the IR spectra of the ligands



Figure 2. <sup>1</sup>H NMR spectrum of the ligand o-VPAH.



Figure 3. <sup>1</sup>H NMR spectrum of the ligand o-VEDH<sub>2</sub>.

for v(C=N) (azomethine) at 1610 and 1620 cm<sup>-1</sup> in *o*-VPAH and *o*-VEDH<sub>2</sub>, respectively. Both ligands exhibit signals for aromatic, OCH<sub>3</sub>, and phenolic (OH) protons at 6.7–7.4 ppm, 3.18–3.86 ppm and 13.47 ppm, respectively<sup>[9]</sup> Unfortunately, a signal for the phenolic proton in *o*-VEDH<sub>2</sub> could not be observed due to recording of the spectrum up to only 10 ppm.

# **Compositions and Characterization of Metal Complexes**

The metal complexes of o-VPAH and o-VEDH<sub>2</sub> were prepared according to the following equations:

$$\begin{split} M(CH_{3}COO)_{2} \cdot nH2O + LH & \xrightarrow{Ethanol-DMF} & [M(L)(CH_{3}COO)(H_{2}O)] \\ & + CH_{3}COOH + (n-1)H_{2}O & (1) \\ M &= Cu(II) \ (1), \ n &= 1; \\ M &= Co(II) \ (2)/Mn(II) \ (3)/Ni(II) \ (4), \\ n &= 4, \\ LH &= o-VPAH \end{split}$$

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$$Zn(CH_{3}COO)_{2} \cdot 2H_{2}O + 2o \cdot VPAH$$

$$\xrightarrow{\text{Ethanol-DMF}}_{\text{Reflux}} [Zn(o \cdot VPA)_{2}] \cdot 2H_{2}O(5) + 2CH_{3}COOH + H_{2}O \qquad (2)$$

$$\xrightarrow{\text{Ethanol-DMF}}_{\text{Ethanol-DMF}}$$

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(4)

$$M(CH_{3}COO)_{2} \cdot nH_{2}O + L'H_{2} \xrightarrow[Reflux]{Reflux} [M(L')(H_{2}O)_{2}]$$

$$+ 2CH_{3}COOH + (n-1)H_{2}O \qquad (3)$$

$$\mathbf{M} = \mathbf{Cu}(\mathbf{II})(\mathbf{6}), \mathbf{n} = 1; \mathbf{M} = \mathbf{Ni}(\mathbf{II})(\mathbf{7}), \mathbf{n} = 4, \mathbf{L'H}_2 = o - \mathbf{VPAH}_2$$

$$Zn(CH_3COO)_2 \cdot 2H_2O + L'H_2 \xrightarrow{\text{Ethanol-DMF}} [Zn(L')] \cdot 2H_2O$$
 (8)

+2CH<sub>3</sub>COOH

$$Sm(CH_{3}COO)_{3} \cdot 3H_{2}O + L'H_{2} \xrightarrow{\text{Ethanol-DMF}} [Sm(L')-$$

$$(CH_{3}COO)(H_{2}O)] (9) + 2CH_{3}COOH + 2H_{2}O \qquad (5)$$

$$Th(NO_{3})_{4} \cdot 6H_{2}O + L'H_{2} \xrightarrow{\text{Ethanol-DMF}} [Th(L')(NO_{3})_{2}] (10)$$

$$+2HNO_3+6H_2O$$
(6)

$$UO_2(CH_3COO)_2 \cdot 2H_2O + L'H_2 \xrightarrow[Reflux]{Ethanol-DMF} [UO_2(L')(H_2O)]-$$

 $\cdot \mathrm{H}_{2}\mathrm{O}\left(\mathbf{11}\right) + 2\mathrm{CH}_{3}\mathrm{COOH} \tag{7}$ 

The microanalytical data, some physical properties, such as, decomposition temperatures and colours as well as % yields of the complexes are given in Table 2. All the complexes are soluble in DMF and DMSO. They were characterized by the following physical studies.

# **Infrared Spectra**

The ligand o-VPAH contains two potential donor sites: 1) the azomethine nitrogen and 2) the phenolic oxygen while the ligand o-VEDH<sub>2</sub> has four potential donor sites: 1) two azomethine nitrogens and 2) two phenolic oxygens.

Both of the ligands (Table 3) show a characteristic band at 1610 and 1620 cm<sup>-1</sup>, respectively, due to v(C=N) of the azomethine group. Bonding of this nitrogen is indicated by the shifting of v(C=N) to lower

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	Table 2. Physical cl	naracteristics	and microans	alytical d	lata of ti	he o-VPA	H and o	-VEDH <sub>2</sub> c	omplexe	ċ	
	Compound								Found (c	:alc.), %	
Sr. no.	(empirical formula) (F. W)	Color	Decomp. temp. (°C)	Yield (%)	C.N.	μ <sub>eff</sub> (B.M.)	$\Lambda_{M}{}^{a}$	C	Н	z	Μ
(1)	[Cu( <i>o</i> -VPA)(OAc)(H <sub>2</sub> O)] (C <sub>17</sub> H <sub>19</sub> CuN <sub>1</sub> O <sub>6</sub> ) (396.54)	Green	> 360	70	4	2.05	11.2	51.62 (51.44)	4.86 (4.79)	3.82 (3.53)	15.68 (16.02)
(2)	$\begin{array}{l} [Co(o-VPA)(OAc)(H_2O)] \\ (C_{17}H_{19}CoN_1O_6) \\ (391.93) \end{array}$	Brown	270	60	4	4.30	6.9	52.18 (52.05)	4.49 (4.84)	3.18 (3.57)	14.60 (15.03)
(3)	$[Mn(o-VPA)(OAc)(H_2O)] (C_{17}H_{19}MnN_1O_6) (387.93)$	Reddish brown	260	60	4	5.94	10.5	52.26 (52.58)	4.38 (4.89)	3.36 (3.61)	13.88 (14.16)
(4)	[Ni(o-VPA)(OAc)(H <sub>2</sub> O)] (C <sub>17</sub> H <sub>19</sub> NiN <sub>1</sub> O <sub>6</sub> ) (391.69)	Yellow	> 360	65	4	3.82	9.9	51.84 (52.08)	4.52 (4.85)	3.28 (3.57)	14.56 (14.98)
(5)	[Zn((o-VPA) <sub>2</sub> ]·H <sub>2</sub> O (C <sub>30</sub> H <sub>30</sub> N <sub>2</sub> O <sub>7</sub> Zn) (595.39)	Brown	265	60	4	Dia.	8.6	60.14 ( $60.46$ )	4.82 (5.04)	4.63 (4.70)	10.92 (10.98)

(b) (ammuche) Complexes	N-(	0-V	anill	inid	ene)	Com	plexes
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(9)	$[Cu(o-VED)(H_2O)_2] (C_{18}H_{22}CuN_2O_6) (425.54)$	Green	300	65	9	1.88	8.3	51.08 (50.76)	4.90 (5.17)	6.84 (6.58)	14.50 (14.93)
6	$\begin{array}{l} [\mathrm{Ni}(o\mathrm{-VED})(\mathrm{H_2O})_2] \\ (\mathrm{C}_{18}\mathrm{H_{22}}\mathrm{NiN_2O_6}) \\ (420.69) \end{array}$	Reddish brown	240	65	9	3.01	10.3	50.90 (51.34)	4.87 (5.23)	6.24 (6.65)	13.62 (13.95)
(8)	$[Zn(o-VED)] \cdot 2H_2O$ ( $C_{18}H_{18}N_2O_4Zn$ ) (391.39)	Yellow	> 360	65	4	Dia.	7.6	54.88 (55.19)	4.28 (4.59)	6.88 (7.15)	16.19 (16.70)
(6)	$[Sm(o-VED)(OAc)(H_2O)] (C_20H_{23}N_2O_7Sm) (553.36)$	Yellow	285	60	9	1.62	6.8	43.14 (43.37)	3.76 (4.15)	4.87 (5.06)	26.87 (27.17)
(10)	$[Th(o-VED)(NO_3)_2] (C_{18}H_{18}N_4O_{10}Th) (682.00) (682.00)$	Reddish brown	> 360	75	9	Dia	8.4	31.18 (31.67)	2.28 (2.64)	7.88 (8.21)	33.84 (34.01)
(11)	[UO <sub>2</sub> (0-VED)(H <sub>2</sub> O)]·H <sub>2</sub> O (C <sub>18</sub> H <sub>22</sub> N <sub>2</sub> O <sub>8</sub> U) (632.03)	Reddish brown	280	60	٢	Dia.	6.9	34.89 (34.17)	3.96 (3.48)	4.26 (4.43)	37.69 (37.66)
<sup>a</sup> Ohm <sup>-1</sup>	$cm^2 mole^{-1}$ .										

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Sr. no.	Compound	v(O-H) (phenolic)	Acetate-stretch	v(C=N) (azomethine)	v(C-O) (phenolic)	v(M-O)	v(M-N)
	o-VPAH	3400 br	I	1610 s	1450 m	I	I
(1)	$[Cu(o-VPA)(OAc)(H_2O)]$	I	1605 s 1320 m	1600 m	1440  m	520 w	400 w
(2)	$[Co(o-VPA)(OAc)(H_2O)]$	I	1612 s 1330 m	1585 s	1430  m	510 w	435 w
(3)	$[Mn(o-VPA)(OAc)(H_2O)]$	I	1640 s 1300 s	1600 s	1440  m	510 w	450 w
(4)	$[Ni(o-VPA)(OAc)(H_2O)]$	I	1620 s 1300 s	1590 m	1430 m	510 w	400 w
(2)	$[Zn((o-VPA)_2]\cdot H_2O$	I	I	1600 s	1430  m	515 w	405 w
	o-VEDH <sub>2</sub>	3300 br	I	1620 s	1450  m	I	I
(9)	$[Cu(o-VED)(H_2O)_2]$	I	I	1600 s	1440  m	530 w	460 w
6	$[Ni(o-VED)(H_2O)_2]$	I	Ι	1600 m	1420 m	520 w	450 w
(8)	$[Zn(o-VED)] \cdot 2H_2O$	I	I	1595 s	1425 m	510 w	460 w
(6)	$[Sm(o-VED)(OAc)(H_2O)]$	I	1605 s 1325 m	1600 s	1425 m	540 w	485 w
(10)	$[Th(o-VED)(NO_3)_2]$	I	I	1600 s	1440  m	520 w	450 w
(11)	[UO <sub>2</sub> ( <i>o</i> -VED)(H <sub>2</sub> O)]·H <sub>2</sub> O	I	I	1585 s	1418 m	510 w	460 w

**Table 3.** Important IR spectral bands  $(cm^{-1})$  of o-VPAH, o-VEDH<sub>2</sub> and their metal complexes.

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 $(10-25 \text{ cm}^{-1})$  wave numbers in the complexes.<sup>[10]</sup> The characteristic phenolic v(OH), due to the presence of an hydroxy group at the *o*-position, was observed in *o*-VPAH and *o*-VEDH<sub>2</sub> at 3400 and 3300 cm<sup>-1</sup>, respectively.<sup>[2]</sup> A band at 1450 cm<sup>-1</sup> due to v(C–O) of the phenolic group was also observed in both ligands. The sharp band due to the phenolic (O–H) of the two ligands should be absent in all of the complexes under study to indicates the coordination of the phenolic oxygen, after deprotonation, to the metal ion. But due to the presence of a broad band (vide infra) for lattice and coordinated water, it is difficult to confirm with certainty the coordination is supported by the shifting of the phenolic v(C–O) band to lower wave numbers (see Table 3) in the complexes.<sup>[2]</sup> The coordination of the azomethine nitrogen and phenolic oxygen is further supported by the appearance of two non-ligand bands at 510–540 and 400–460 cm<sup>-1</sup>, due to v(M–O)<sup>[11]</sup> and v(M–N),<sup>[12]</sup> respectively.

The presence of coordinated water<sup>[13]</sup> in the complexes (1), (2), (3), (4), (6), (7), (9) and (10) is indicated by the presence of either a broad band at  $3550-3200 \text{ cm}^{-1}$  or two broad bands at 3490-3550, and  $3350-3400 \text{ cm}^{-1}$ . The other characteristic bands for coordinated water could not be definitively characterized. The presence of lattice/coordinated water<sup>[14]</sup> in the complexes (5), (8) and (11) is revealed by the presence of a broad band in the region  $3600-3400 \text{ cm}^{-1}$ .

The unidentate coordination of acetate ion in the complexes (1), (2), (3), (4) and (9) is supported by the presence of two bands at 1605–1640 cm<sup>-1</sup> and 1300–1330 cm<sup>-1</sup>, due to  $v_{as}(COO)$  and  $v_{sy}(COO)$  modes, respectively<sup>[15]</sup> ( $\Delta v = \sim 300 \text{ cm}^{-1}$ ).

In the spectrum of the complex  $[Th(o-VED)(NO_3)_2]$  three additional bands which are not present in the spectrum of the free ligand o-VEDH<sub>2</sub> are observed. Of these, the band at 1015 cm<sup>-1</sup> is assigned to the v<sub>2</sub> mode of the NO<sub>3</sub> group. The bands at 1480 and 1380 cm<sup>-1</sup> are the two split bands v<sub>4</sub> and v<sub>1</sub>, respectively, of the coordinated nitrate ion. The magnitude of  $\Delta v = (v_4 - v_1) = 100$  cm<sup>-1</sup> shows the unidentate coordination of the nitrate ion.<sup>[16]</sup>

The IR spectrum of the uranium complex (11) exhibits two bands at 920 and 840 cm<sup>-1</sup> which are assignable to  $v_{as}(O=U=O)$  and  $v_{sy}(O=U=O)$  modes, respectively. This observation indicates that the linearity of the O=U=O group is maintained in the complex.<sup>[17]</sup>

The force constant (f) for the  $v_{as}(O=U=O)$  mode was calculated for complex (11) by following the method of McGlynn et al.<sup>[18]</sup> It was found to be 7.03 m dyne/Å, and agrees well with the force constant values of similar dioxouranium(VI) complexes.<sup>[19]</sup> From this value, the U–O bond distance  $R_{U-O}$  was calculated by using Jone's equation,<sup>[20,21]</sup>  $R_{U-O} = 1.08f^{-1/3} + 1000$ 

1.17, where f is the force constant for the  $v_{as}$ (O=U=O). It was found to be 1.73 Å, and this is in the usual range (1.60–1.92 Å) observed for dioxouranium(VI) complexes.<sup>[17,19]</sup>

# **Conductance Measurements**

The observed molar conductances of the complexes in  $10^{-3}$  molar solutions in DMSO lie in the range 6.9–11.2 ohm<sup>-1</sup> cm<sup>2</sup> mole<sup>-1</sup> (Table 2). This is consistent with the non-electrolytic nature of these complexes.<sup>[22]</sup>

## **Magnetic Susceptibility Measurements**

In the present investigation, complexes (1) and (6) of Cu(II) exhibit magnetic moments of 2.05 and 1.88 B.M., respectively. These data indicate tetrahedral geometry for compound (1) and octahedral geometry for compound (6). The Co(II)-*o*-VPA complex in the present study displays a magnetic moment of 4.30 B.M. suggesting a tetrahedral geometry for this complex.<sup>[23,24]</sup> Nickel(II) forms complexes of the coordination numbers 4, 5 and 6. The complexes (4) and (7) display magnetic moment values of 3.82 and 3.01 B.M., respectively. These results suggest a tetrahedral geometry for complex (4) and an octahedral one for complex (7). The observed room temperature magnetic moment value of the Mn-*o*-VPA complex is 5.94 B.M., which is consistent with high-spin manganese(II). Because of the additional stability of the half filled d-shell, manganese(II) generally forms high-spin complexes.

The observed room temperature magnetic moment value of the Sm-o-VED complex (9) is found to be 1.62 B.M. This agrees well with the theoretical value calculated from the Van Vleck equation,<sup>[25]</sup> which suggests that the 4f electrons play a negligible role in bonding. In both the cases, the Zn-o-VPA (5) and Zn-o-VED (8) complexes, a tetrahedral structure is proposed and the diamagnetic behaviour was confirmed. The Th-o-VED (10) and UO<sub>2</sub>(VI)-o-VED (11) complexes were found to be diamagnetic as expected.

## **Thermogravimetric Analysis**

Two representative compounds of each ligand system, *o*-VPAH and *o*-VEDH<sub>2</sub>, were subjected to thermogravimetric analyses. The compound (1) shows a weight loss in the temperature range 195 °C to 228 °C to be 5.0% (calcd. weight loss for 1 mole of H<sub>2</sub>O: 4.5%) corresponding to the elimination of one molecule of coordinated water.<sup>[13]</sup> Further decomposing occurs at 315 °C and continues up to 360 °C. This weight loss is found to be

15.0% against a theoretical weight loss of 15.6% due to removal of one coordinated acetate group from the complex (Figure 4). These weight loss data thus agree with the IR results for this complex.

The thermogravimetric curve of compound (5) exhibits a weight loss of 3.0% (calcd. weight loss for H<sub>2</sub>O, 3.0%) in the temperature range 99 °C to 141 °C. As this weight loss starts at lower temperature (99 °C), it suggests the presence of one lattice water<sup>[26]</sup> molecule in this compound. This corroborates the IR results (vide supra). The thermogram shows a steep weight loss of 63% in the temperature range 255 °C to 420 °C that could not be correlated. Beyond 420 °C no significant weight loss could be observed.

The thermogram of compound (9) registers a weight loss of 3.0% (calcd. weight loss for one mole H<sub>2</sub>O, 3.2 %) in the temperature range 95–120 °C, suggesting the loss of one coordinated water<sup>[14]</sup> molecule. The further weight loss shown by this compound could not be correlated. Finally, the residue attains a constant composition corresponding to  $Sm_2O_3$  at 890 °C (calcd. mass retained 62.9 %; observed = 60.0%).

The thermogravimetric curve of compound (11) shows a weight loss of 6.0 % (calcd. 5.9%, assuming a weight loss for two moles of H<sub>2</sub>O molecules), which starts from 78 °C and is completed at 141 °C. This may be



Figure 4. TG curve of  $[Cu(o-VPA)(OAc)(H_2O)]$  (1).

due to the presence of one lattice and one coordinated water<sup>[14]</sup> molecule in this complex, which is consistent with the IR spectral data (vide supra). A second weight loss of 42% (calcd. 42.1%, assuming weight loss for one *o*-VED molecule) was observed in the temperature range 213 to 261 °C. This corresponds to the elimination of one coordinated *o*-VED group. The decomposition continues with the gradual weight loss, and it ceases at about 800 °C. The final residue (observed 35.2 %) corresponds to  $U_3O_8^{[27]}$  (calcd. 35.6).

## **Electronic Spectra**

The electronic spectra of four representative compounds,  $[Cu(o-VPA)-(OAc)(H_2O)]$  (1),  $[Ni(o-VPA)(OAc)(H_2O)]$  (4),  $[Cu(o-VED)(H_2O)_2]$  (6) and  $[UO_2(o-VED)(H_2O)] \cdot H_2O$  (11) were recorded in the range 260–800 nm.

The diffuse reflectance spectrum of the compound [Cu(o-VPA)(OAc)-(H<sub>2</sub>O)] (1) exhibits three absorption bands at 304 nm (32,894 cm<sup>-1</sup>), 403 nm (24,813 cm<sup>-1</sup>) and 580 nm (17,241 cm<sup>-1</sup>). The appearance of the last two broad bands is indicative of a modified (square-planar) stereochemistry due to Jahn-Teller distortion, as reported elsewhere.<sup>[8]</sup> The first band of relatively high intensity is assigned as ligand  $\rightarrow$  metal charge transfer transition.<sup>[28]</sup> This result, coupled with the magnetic data of this complex (2.05 B.M.), suggests a square-planar geometry.

The diffuse reflectance spectrum of  $[Ni(o-VPA)(OAc)H_2O]$  (4) (Figure 5) shows two absorption bands at 319 nm (31,347 cm<sup>-1</sup>) ( $\epsilon = 972 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) and 416 nm (24,038 cm<sup>-1</sup>) ( $\epsilon = 370 \text{ L mol}^{-1} \text{ cm}^{-1}$ ). The first band, which is of relatively high intensity, is attributed to a



Figure 5. Diffuse reflectance spectrum of [Ni(o-VPA)(OAc)(H<sub>2</sub>O)] (4).

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ligand  $\rightarrow$  metal charge transfer transition.<sup>[28]</sup> The second broad band corresponds to the transition  ${}^{3}T_{1}(P) \leftarrow {}^{3}T_{1}(F)$  for a tetrahedral complex, which is of much lower energy as compared with octahedral complexes.<sup>[29]</sup> The magnetic moment value (3.82 B. M.) also ruled out the possibility of octahedral complexes.

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The diffuse reflectance spectrum of  $[Cu(o-VED)(H_2O)_2]$  (6) shows three spectral peaks at 280 nm (35,714 cm<sup>-1</sup>), 317 nm (26,954 cm<sup>-1</sup>) and 568 nm (17,605  $\text{cm}^{-1}$ ). The third broad peak at 568 nm is most probably due to the  ${}^{2}T_{2g} \leftarrow {}^{2}E_{2g}$  transition suggesting a distorted octahedral geometry for this complex.<sup>[30]</sup> The first and second spectral peaks of relatively higher intensities are due to ligand  $\rightarrow$  metal charge transfer transitions.

The diffuse reflectance spectrum of complex  $[UO_2(o-VED)(H_2O)] \cdot H_2O$ (11) exhibits two spectral bands at 263 nm (38,022 cm<sup>-1</sup>) ( $\epsilon = 556 \text{ L mol}^{-1}$ cm<sup>-1</sup>) and 333 nm (30,030 cm<sup>-1</sup>) ( $\epsilon$  = 412 L mol<sup>-1</sup> cm<sup>-1</sup>) assignable to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transition, respectively, of the azomethine linkage. The third band appearing at 421 nm (23,752 cm<sup>-1</sup>) ( $\epsilon = 398 \text{ L mol}^{-1} \text{ cm}^{-1}$ ) in this complex is assigned to the  ${}^{1}\Sigma^{+}{}_{g} \rightarrow {}^{3}\pi_{u}$  transition typical of the O–U–O symmetric stretching frequency,  $v_{s}$ (O=U=O), for the first excited state.<sup>[2]</sup>



*Figure 6.* <sup>1</sup>H NMR spectrum of  $[Zn(o-VPA)_2] \cdot H_2O$  (5).



*Figure 7.* <sup>1</sup>H NMR spectrum of  $[Zn(o-VED)] \cdot 2H_2O$  (8).

# <sup>1</sup>H NMR Spectral Data

<sup>1</sup>H NMR spectra of the Zn-o-VPA (Figure 6) and Zn-o-VED (Figure 7) complexes were recorded in DMSO-d<sub>6</sub>. Comparison of the chemical shifts of the ligands (Figures 2 and 3) with those of the complexes shows that the signal due to the phenolic proton (OH) is absent in the complexes, suggesting the coordination of the phenolic oxygen to the metal ion after deprotonation. The azomethine proton (-CH=N-) undergoes a significant shift, indicating the coordination of the azomethine nitrogen to the metal ion.<sup>[8]</sup> Thus, the <sup>1</sup>H NMR data confirm the monobasic, bidentate (ON) nature of o-VPAH and the dibasic, tetradentate (OONN) nature of (o-VEDH<sub>2</sub>), which already have been suggested by the IR spectral data.

## CONCLUSIONS

Satisfactory analytical data as well as all the studies presented above suggest that the present complexes may be formulated as  $[M(L)(OAc)(H_2O)]$  {where M = Cu(II), Co(II), Mn(II) or Ni(II) and OAcH = CH<sub>3</sub>COOH}, [Zn-(L)<sub>2</sub>]·H<sub>2</sub>O,  $[M(L')(H_2O)_2]$  {where M = Cu(II) or Ni(II)},  $[Zn(L')]·2H_2O$ ,  $[Sm(L')(OAc)(H_2O)]$ ,  $[Th(L')(NO_3)_2]$  and  $[UO_2(L')(H_2O)]·H_2O$  (where LH = *o*-VPAH, and L'H<sub>2</sub> = *o*-VEDH<sub>2</sub>). From the analytical data and the



Figure 8. Proposed structures of complexes.

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physical studies discussed above, the ligand *o*-VPAH has been shown to act as a bidentate, monobasic ligand which coordinates through the enolic oxygen and azomethine nitrogen and forms complexes with copper(II), nickel(II), cobalt(II) and manganese(II) in 1:1 stoichiometric ratio and with zinc(II) in 1:2 ratio. *o*-VEDH<sub>2</sub> acts as a tetradentate, dibasic ligand coordinating through two azomethine nitrogens and two enolic oxygens and forms complexes with Cu(II), Ni(II), Zn(II), Sm(II), Th(IV) and U(VI)O<sub>2</sub> in 1:1 stoichiometric ratio. The proposed structures of these complexes are shown in Figure 8. The coordination numbers of the complexes are given in Table 2.

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## REFERENCES

- Syamal, A.; Maurya, M.R. Coordination chemistry of Schiff base complexes of molybdenum. Coord. Chem. Rev. 1989, 95, 183–238.
- Maurya, R.C.; Maurya, M.R. Coordination chemistry of Schiff base complexes of uranium. Rev. Inorg. Chem. 1995, 15, 1–107.
- Maurya, M.R.; Gopinathan, S.; Gopinathan, C.; Maurya, R.C. Reactivity of bis(acetylacetonato)dinitrosylmolybdenum(0) towards Schiff bases derived from salicylaldehyde or *o*-vanillin and benzoylhydrazide or isonicotinoylhydrazide. Polyhedron **1993**, *12*, 159–163.
- Maurya, R.C.; Mishra, D.D.; Rao, N.S.; Rao, N.N. Synthesis and characterization of some *cis*-dioxomolybdenum(VI) Schiff bases complexes derived from salicylaldehyde and aromatic amines. Synth. React. Inorg. Met.-Org. Chem. **1995**, *25*, 437–449.
- Agarwala, B.V.; Hingorani, S.; Puri, V.; Khetrapal, C.L.; Naganagowda, G.A. Physico-chemical studies of (*o*-vanillin thiosemicarbazonato)nickel(II) chelate. Transit. Met. Chem. **1994**, *19*, 25–27.
- Xiang, M.Y.; Zhong-Lin, L.; Quing-Bao, S.; Li, W.X. Chelate complexes of formylferrocene and acetylferrocene salicylhydrazone with transition metals. J. Coord. Chem. 1994, 32, 353–359.

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- Larkworthy, L.F.; Sengupta, S.K. Mononitrosyl derivatives of iron and cobalt complexes of quadridentate ligands derived from 2-hydroxy-1naphthaldehyde and ethylenediamine, *o*-phenylenediamine or 4-methyl*o*-phenylenediamine. Inorg. Chim. Acta **1991**, *179*, 157–160.
- Agarwala, B.V.; Hingorani, S.; Puri, V. Structural elucidation of o-vanillin isonicotinoyl hydrazone and its metal complexes. Transit. Met. Chem. 1993, 18, 576–578.
- Agarwala, B.V.; Hingorani, S.; Puri, V.; Naganagowda, G.A. Synthesis and physico-chemical studies of uranium complexes with semicabazone and hydrazone. Inorg. Chim. Acta **1990**, *176*, 149–154.
- Maurya, R.C.; Mishra, D.D.; Rao, N.S.; Rao, N.N. Synthesis and characterization of some ruthenium(II) Schiff bases complexes derived from 1-phenyl-3-methyl-4-benzoyl-5-pyrazolone. Polyhedron 1992, 11, 2837–2840.
- Singh, H.R.; Agarwala, B.V. Co(II), Ni(II) and Cu(II) complexes with benzoic acid hydrazones. J. Indian Chem. Soc. 1988, 35, 591–593.
- 12. Ferraro, J.R. Low Frequency Vibrations of Inorganic and Coordination Compounds; Plenum Press: New York, 1971.
- 13. Duggal, H.K.; Agarwala, B.V. Metal complexes of aroylhydrazones: preparation and structural characterization. Asian J. Chem. **1992**, *4*, 1–14.
- Maurya, R.C.; Mishra, D.D.; Mukherjee, S.; Dubey, J. Metal cyanonitrosyl complexes: synthesis, magnetic and spectral studies of some novel mixed-ligand cyanonitrosyl {CoNO}<sup>8</sup> complexes of Co(I) with heterocyclic bases. Polyhedron **1995**, *14*, 1351–1358.
- Nakamoto, K. Infrared Spectra of Inorganic and Coordination Compounds; Wiley Interscience: New York, 1970; 232.
- Yadava, H.D.S.; Sengupta, S.K.; Tripathi, S.C. Synthesis and spectroscopic studies on dioxouranium(VI), oxovanadium(IV) and oxozirconium(IV) complexes with tetradentate macrocyclic ligands. Inorg. Chim. Acta 1987, 128, 1–6.
- 17. Maurya, R.C.; Jayaswal, M.N.; Verma, R. The coordination chemistry of dioxouranium(VI): studies on some novel bi- and trinuclear dioxouranium(VI) complexes with pyrazolone based Schiff bases. Synth. React. Inorg. Met.-Org. Chem. **1998**, *28*, 1265–1281.
- McGlynn, S.P.; Smith, J.K.; Neely, W.C. Electronic structure, spectra, and magnetic properties of oxocations. III. Ligation effects on the infrared spectrum of the uranyl ions. J. Chem. Phys. **1961**, *35*, 105–116.
- Syamal, A.; Maurya, M.R. Synthesis and characterization of nickel(II), cobalt(II), copper(II), manganese(II), zinc(II), zirconium(IV), dioxouranium(VI) and dioxomolybdenum(VI) complexes of a new Schiff base

derived from salicylaldehyde and 5-methylpyrazole-3-carboxaldehyde. Transit. Met. Chem. **1986**, *11*, 172–176.

- 20. Jones, L.H. Determination of uranium-oxygen bond distance in uranyl complexes from their IR spectra. Spectrochim. Acta **1958**, *10*, 395–402.
- Jones, L.H. Determination of uranium-oxygen bond distance in uranyl complexes from their IR spectra. Spectrochim. Acta 1959, 11, 409– 415.
- Geary, W.J. The use of conductivity measurements in organic solvents for the characterization of coordination compounds. Coord. Chem. Rev. 1971, 7, 81–122.
- Kuble, R.C.; Bhoon, V.K.; Singh, R.P. Cu(II), Ni(II), Co(II) and Mn(II) complexes of bis-quinolylhydrazones of biacetyl. J. Indian Chem. Soc. 1984, 61, 194–198.
- 24. Dutta, R.L.; Syamal, A. *Elements of Magnetochemistry*, 2nd Ed.; Affiliated East-West Press Pvt Ltd: New Delhi, 1993; 57, 153.
- Van Vleck, J.H.; Frank, N. The effect of second order Zeeman terms on magnetic susceptibilities in the rare earths and iron group. Phys. Rev. 1929, 34, 1494–1505.
- Dodd, J.W.; Tonge, K.H.; Currell, B.R. *Thermal Methods: Analytical Chemistry by Open Learning*; John Wiley & Sons: New York, 1987; 73.
- 27. Agarwal, R.K. Thorium(IV) and dioxouranium(VI) complexes of 4-[(N-acetyl)amino]antipyrine. Pol. J. Chem. **1988**, 62, 369–377.
- Maurya, R.C.; Sharma, P.; Sutradhar, D. Metal thiocyanato complexes: synthesis, magnetic and spectral studies of some mixed-ligand thiocyanato complexes of nickel(II) involving benzothiazole and benzimidazole derivatives. Synth. React. Inorg. Met.-Org. Chem. *in press.*
- 29. Greenwood, N.N.; Earnshaw, A. *Chemistry of the Elements*, 1st Ed.; Pergamon Press: Oxford, 1984; 1345.
- Dianzhong, F.; Bo, W. Complexes of cobalt(II), nickel(II), copper(II), zinc(II) and manganese(II) with tridentate Schiff base ligands. Transit. Met. Chem. 1993, 18, 101–103.

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