

## Bis(*o*-vanillin)benzidine(*o*-v<sub>2</sub>bzH<sub>2</sub>) as a binucleating ligand: Synthesis, characterization and 3D molecular modeling and analysis of some binuclear complexes of *o*-v<sub>2</sub>bzH<sub>2</sub> with copper(II), nickel(II), cobalt(II), manganese(II), zinc(II), samarium(III) and dioxouranium(VI)

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A binucleating tetra-dentate Schiff base ligand, bis(*o*-vanillin)benzidine (*o*-v<sub>2</sub>bzH<sub>2</sub>), and its seven new binuclear complexes have been synthesized and characterized on the basis of elemental analysis, IR, NMR, electronic, magnetic, thermal studies and conductance measurements. The compositions of these complexes are found to be [M(*o*-v<sub>2</sub>bz)]<sub>2</sub>.nH<sub>2</sub>O, where M = Cu(II), Ni(II), Co(II), Zn(II), Mn(II) or UO<sub>2</sub>(VI), and [Sm(*o*-v<sub>2</sub>bz)(OAc)(H<sub>2</sub>O)]<sub>2</sub>. The <sup>1</sup>H NMR spectrum of one of the compounds, [Zn(*o*-v<sub>2</sub>bz)]<sub>2</sub>, shows the absence of proton signal for phenolic oxygen (-OH). Low magnetic moment values, high thermal stability and insolubility in common organic solvents support the binuclear structure of these complexes. Suitable binuclear structures have been assigned. The 3D molecular modeling and analysis for bond lengths and bond angles have also been carried out of one of the representative compounds, [Ni(*o*-v<sub>2</sub>bz)]<sub>2</sub>.

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The design and synthesis of binucleating ligands and their complexes has been the subject of much interest in the recent past<sup>1</sup>. The studies on binuclear metal complexes in which the two metal centres are held in closed proximity have addressed<sup>2,3</sup> ligand environment, redox behaviour, magnetic exchange interactions and spectroscopic properties. Considerable interest has also been focused on synthesis and biomimetic reactions of model systems related to metalloenzymes<sup>4,5</sup>. Such complexes with extended bridged structures are of current interest due to their application in homogeneous catalysis<sup>6</sup>.

The transition metal and inner transition metals complexes of the Schiff bases derived from acetylacetone and ethylenediamine or benzidine are well known<sup>7</sup>. Synthesis, spectral and electrochemical studies of dioxotungsten(VI) complexes of binucleating Schiff bases derived from various hydrazides have been reported by Gopinathan *et al.*<sup>8</sup> The IR and NMR spectral data suggest an oligomeric structures for these complexes in which each tungsten

atom achieves a pseudo-octahedral structure via W=O→W bridging. Binuclear dioxomolybdenum(VI) complexes of dithio or methylene bridged Schiff bases have also been reported by Gopinathan *et al.*<sup>9</sup> The cyclic voltammetric measurements indicate irreversible to quasireversible reduction of Mo(VI) complexes to Mo(IV).

We have recently reported some diamagnetic ligand-bridged binuclear complexes with the compositions, *cis*-[MoO<sub>2</sub>(OEt)]<sub>2</sub>(L) (LH<sub>2</sub>=binucleating dibasic tetradentate Schiff base of 4-benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one (BMPHP) with *p*-phenylenediamine<sup>10</sup> or binucleating dibasic tetradentate Schiff base of 3-methyl-1-phenyl-4-propionyl-2-pyrazolin-5-one with *m*-phenylenediamine, *p*-phenylenediamine or benzidine<sup>11</sup>, and, *cis*-[MoO<sub>2</sub>(OEt)]<sub>2</sub>(L) (L=binucleating neutral tetradentate Schiff base of BMPHP with benzidine)<sup>10</sup>. Three more ligand-bridged binuclear complexes of compositions, *cis*-[MoO<sub>2</sub>(OMe)]<sub>2</sub>(L) (L = LH<sub>2</sub> = bi-

nucleating dibasic tetradentate Schiff base of salicylaldehyde with *m*-phenylenediamine or *p*-phenylenediamine), and, *cis*-[MoO<sub>2</sub>(OMe)(dmf)<sub>2</sub>(L)] (LH<sub>2</sub> = binucleating dibasic tetradentate Schiff base of salicylaldehyde with benzidine) have been reported by the same research group<sup>12</sup>. In a recent communication<sup>13</sup> from our laboratory, we reported the synthesis, magnetic and spectral studies of some novel binuclear dioxomolybdenum(VI) chelates involving Schiff bases derived from sulfa drugs and BMPHP. Reports are also available on some di- and tri-nuclear dioxouranium(VI) complexes<sup>14</sup> with some binucleating Schiff bases derived from 3-methyl-1-phenyl-4-*p*-nitrobenzoyl-2-pyrazolin-5-one.

The synthesis of a new series of ligand-bridged binuclear dinitrosylmolybdenum(0) complexes of the composition, *trans*-[Mo(NO)<sub>2</sub>(L)]<sub>2</sub> (LH<sub>2</sub> = binucleating dibasic tetradentate Schiff base of 4-Benzoyl-3-methyl-1-phenyl-2-pyrazolin-5-one with benzidine or *p*-phenylenediamine) is reported using [Mo(NO)<sub>2</sub>(acac)<sub>2</sub>] as precursor<sup>15</sup>. The synthesis of a binuclear dinitrosyl complex of molybdenum of the composition, [{Mo(NO)<sub>2</sub>}(L)]<sub>2</sub>·H<sub>2</sub>O (where LH<sub>2</sub> = N, N-(4'-butyrylidene-3'-methyl-1'-phenyl-2'-pyrazolin-5'-one)-*m*-phenylenediamine, a binucleating Schiff base ligand) is claimed in a single step directly from molybdate(VI) is also reported<sup>16</sup>. On the basis of different physico-chemical studies, the compound is found to contain low-spin Mo(0) with NO<sup>+</sup> grouping.

The chelating behaviour<sup>17</sup> of two binucleating Schiff base ligands [prepared by condensation of salicylaldehyde and phenylglyoxal with 4,4'-diaminodiphenylsulphone (DADPS)] and one such carboxamide ligand (obtained by interaction of maleic anhydride and DADPS) towards some bivalent metal salts has been examined in order to design their respective binuclear chelates. We have also examined the ligational<sup>18</sup> behaviour of DADPS as a binucleating ligand in a binuclear mixed-ligand cyanonitrosyl {Mn(NO)}<sup>6</sup> complex of manganese(I) of composition [Mn(NO)(CN)<sub>2</sub>(DADPS)(H<sub>2</sub>O)]<sub>2</sub>.

In view of interesting ligational behaviour of binucleating systems and in continuation of our interest in the synthesis and characterization of binucleating ligands and their complexes, we considered it worthwhile to prepare Cu(II), Ni(II), Co(II), Mn(II), Zn(II), Sm(III) and UO<sub>2</sub>(VI) complexes of dibasic tetradentate bis(*o*-vanillin) benzidine.

## Materials and Methods

*o*-Vanillin, benzidine and dimethylformamide (Sisco Chem, Bombay, India), Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O, Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O, Co(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, 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, Bombay, India) 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 of A.R. grade were used as received.

### Synthesis of Schiff base bis(*o*-vanillin)benzidine

A hot ethanolic solution (50 mL) of *o*-vanillin (7.60 g, 50 mmol) was added to a hot ethanolic solution (50 mL) of benzidine (4.60 g, 25 mmol) and the reaction mixture was refluxed on a water bath for 4-5 h. A solid mass separated out on cooling. It was suction filtered, washed with ethanol, diethyl ether and subsequently dried over anhydrous CaCl<sub>2</sub> in a desiccator. The purity of the ligand was checked by TLC (solvent system: 1:1 ethanol-DMF). The Schiff base ligand is soluble in organic solvents, viz., ethanol, dimethylformamide and dimethylsulfoxide.

### Synthesis of metal complexes: General method

The metal complexes of the *o*-v<sub>2</sub>bzH<sub>2</sub> were synthesized by mixing a DMF-ethanolic (1:1, 30 mL) solution of Schiff base, *o*-v<sub>2</sub>bzH<sub>2</sub> (2.260 g, 5 mmol) with an ethanolic solution (30 mL) of the metal acetate (5 mmol) [0.995 g of Cu(CH<sub>3</sub>COO)<sub>2</sub>·H<sub>2</sub>O; 1.244 g of Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O; 1.245 g of Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O; 1.100 g of Zn(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O; 1.224 g of Mn(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O; 1.906 g of Sm(CH<sub>3</sub>COO)<sub>3</sub>·3H<sub>2</sub>O or 2.120 g of UO<sub>2</sub>(CH<sub>3</sub>COO)<sub>2</sub>·2H<sub>2</sub>O]. The resulting mixture was refluxed with stirring on a magnetic stirrer equipped with heater for 5-6 h. On cooling, the coloured complex precipitated out, which was filtered by suction, washed several times with ethanol and finally with ether, and dried over anhydrous CaCl<sub>2</sub>.

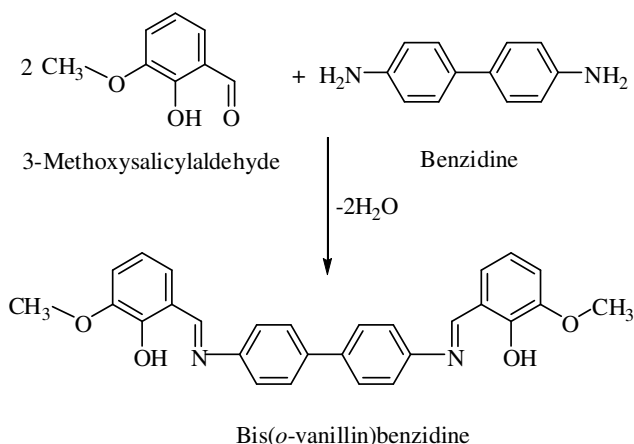
Microanalyses of carbon, hydrogen and nitrogen of the complexes were carried on a Heraeus Carlo Erba 1108 elemental analyzer at the Central Drug Research Institute, Lucknow, India. Copper was determined gravimetrically as copper salicylaldoximate<sup>19</sup>, Cu(C<sub>7</sub>H<sub>6</sub>O<sub>2</sub>N)<sub>2</sub>, while zinc was determined complexometrically<sup>20</sup> using EDTA. The cobalt content in the synthesized complexes was determined gravimetrically as cobaltous sulfate<sup>21</sup>. Nickel was determined gravimetrically as nickel dimethylglyoximate<sup>19</sup>. Samarium and thorium were determined by the oxalate-oxide method<sup>22</sup>. The uranium content

of the complex was determined gravimetrically<sup>23</sup> as U<sub>3</sub>O<sub>8</sub>, after decomposing the complex with concentrated HNO<sub>3</sub> and igniting the residue.

Solid-state IR spectra were recorded on a Perkin-Elmer grating infrared spectrophotometer/FT-IR spectrophotometer in the range 4000-200 cm<sup>-1</sup> at the Central Drug Research Institute, Lucknow. Electronic spectra of the complexes were recorded on a Cary 2300 spectrophotometer at the Central Drug Research Institute, Lucknow. <sup>1</sup>H NMR spectra of the ligands and metal chelates were recorded on a WH-270 FT-NMR spectrometer equipped with an ASPECT 2000 computer at the Indian Institute of Science, Bangalore. Molar conductances were measured at room temperature in DMF using a Toshniwal conductivity bridge fitted with a dip-type cell, having platinum electrodes (cell constant = 1.3 cm<sup>-1</sup>). The room temperature magnetic susceptibility measurements of the resulting complexes were measured by Gouy's method at the Regional Sophisticated Instrumentation Centre, Nagpur, and by a vibrating sample magnetometer, at the Institute Instrumentation Centre, Indian Institute of Technology, Roorkee. The diamagnetic corrections were computed using Pascal's constants in order to get the corrected molar magnetic susceptibilities. Thermograms of the complexes were recorded in the temperature range 50-810°C at the heating rate of 15°C/min. using a TGS2-Perkin Elmer thermal analyzer under N<sub>2</sub> atmosphere at the Regional Sophisticated Instrumentation Centre, Nagpur.

## Results and Discussion

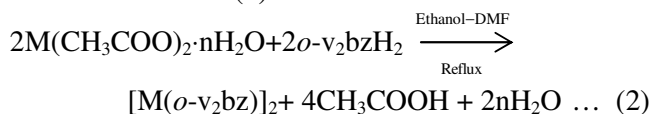
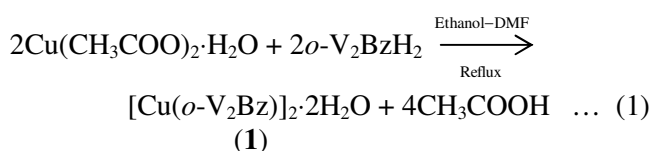
The binucleating Schiff base ligand bis(*o*-vanillin) benzidine was prepared by the condensation reaction of *o*-vanillin and benzidine according to Scheme 1.



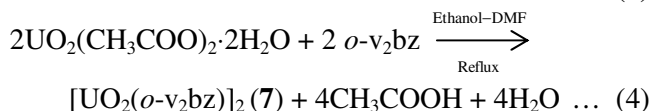
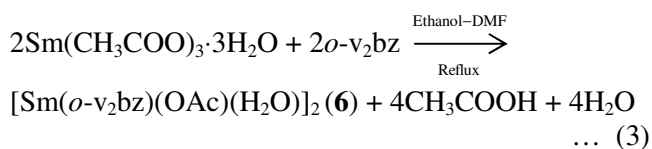
Scheme 1

The formation of Schiff base ligand is inferred by the appearance of a strong band in the IR spectrum at 1614 cm<sup>-1</sup> due to azomethine<sup>24</sup> group. Another strong band appearing at 1466 cm<sup>-1</sup> is assigned to ν(C-O)<sup>25</sup> of the phenolic group in the ligand. The phenolic group deformation mode appears at 1254 cm<sup>-1</sup> in the ligand. The appearance of a band at 2833 cm<sup>-1</sup> in the IR spectrum of Schiff base has been assigned to -OCH<sub>3</sub> group vibration<sup>26</sup>.

The metal chelates in the present investigations were prepared according to the Eqs (1)-(4):



Where, M = Ni(II), n = 4 (2); Co(II), n = 4 (3); Zn(II), n = 2 (4); Mn(II), n = 4 (5)



The observed molar conductances (7.8 to 10.4 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>) of all the complexes in 10<sup>-3</sup> M dimethyl sulfoxide solutions suggest the non-electrolytic<sup>27</sup> nature of these complexes. The resulting complexes are non-hygroscopic, air stable, coloured solids (see Table 1 for colours). Other physical properties of the complexes like decomposition temperatures, % yields and solubility are also given in Table 1. These complexes are characterized by thermal and spectral methods.

### Infrared spectra

The important IR spectral bands of the ligand as well as complexes are presented in Table 2. The IR spectra of the metal complexes show significant changes compared to the ligand. In the IR spectrum of the Schiff base ligand, *o*-*v*<sub>2</sub>BzH<sub>2</sub>, a sharp band observed at 1614 cm<sup>-1</sup> is assigned to the ν(C=N) mode of the azomethine group. This shifts to lower wave numbers in all the complexes, suggesting the

Table 1 – Physical characteristics and microanalytical data of *o*-V<sub>2</sub>BzH<sub>2</sub> and the mixed-ligand complexes

No.	Comp. (Emp. for.) (F. W.)	Colour	Decomp. temp. (°C)	Yield (%)	$\mu_{\text{eff}}$ (B.M.)	$\Lambda_M$ (ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup> )	Found (Calc.) (%)			
							C	H	N	M
	<i>o</i> -v <sub>2</sub> bzH <sub>2</sub> (C <sub>28</sub> H <sub>24</sub> N <sub>2</sub> O <sub>4</sub> ) (452)	Orange	285	80	—	—	74.18 (74.34)	5.19 (5.31)	5.97 (6.19)	— —
(1)	[Cu( <i>o</i> -v <sub>2</sub> bz)] <sub>2</sub> .2H <sub>2</sub> O (C <sub>56</sub> H <sub>48</sub> Cu <sub>2</sub> N <sub>4</sub> O <sub>10</sub> ) (1063.08)	Nut brown	320	62	1.71	8.2	63.01 (63.21)	4.38 (4.52)	5.39 (5.27)	12.21 (11.95)
(2)	[Ni( <i>o</i> -v <sub>2</sub> bz)] <sub>2</sub> (C <sub>56</sub> H <sub>44</sub> Ni <sub>2</sub> N <sub>4</sub> O <sub>8</sub> ) (1017.38)	Reddish brown	340	60	3.58	9.5	66.21 (66.05)	4.18 (4.32)	5.38 (5.50)	11.21 (11.54)
(3)	[Co( <i>o</i> -v <sub>2</sub> bz)] <sub>2</sub> (C <sub>56</sub> H <sub>44</sub> Co <sub>2</sub> N <sub>4</sub> O <sub>8</sub> ) (1017.86)	Greenish brown	330	60	4.10	10.4	66.34 (66.02)	4.50 (4.32)	5.36 (5.50)	11.79 (11.58)
(4)	[Zn( <i>o</i> -v <sub>2</sub> bz)] <sub>2</sub> (C <sub>56</sub> H <sub>44</sub> N <sub>4</sub> O <sub>8</sub> Zn <sub>2</sub> ) (1030.78)	Orangish yellow	345	65	Diamag- netic	9.4	65.36 (65.19)	4.16 (4.27)	5.67 (5.43)	12.43 (12.69)
(5)	[Mn( <i>o</i> -v <sub>2</sub> bz)] <sub>2</sub> C <sub>56</sub> H <sub>44</sub> Mn <sub>2</sub> N <sub>4</sub> O <sub>8</sub> (1009.86)	Nut brown	325	60	5.74	7.8	66.25 (66.54)	4.21 (4.36)	5.32 (5.55)	10.56 (10.88)
(6)	[Sm( <i>o</i> -v <sub>2</sub> bz) (OAc)(H <sub>2</sub> O)] <sub>2</sub> (C <sub>60</sub> H <sub>54</sub> N <sub>4</sub> O <sub>14</sub> Sm <sub>2</sub> ) (1354.72)	Brick  red	338	62	1.28	9.6	53.31  (53.15)	3.78  (3.99)	4.06  (4.13)	22.61  (22.20)
(7)	[UO <sub>2</sub> ( <i>o</i> -v <sub>2</sub> bz)] <sub>2</sub> (C <sub>56</sub> H <sub>44</sub> N <sub>4</sub> O <sub>12</sub> U) (1440.04)	Reddish brown	>360	60	Diamag- netic	10.1	46.85 (46.67)	3.15 (3.06)	3.74 (3.89)	33.39 (33.06)

Table 2 – Important IR spectral data (cm<sup>-1</sup>) of LH and its mixed-ligand metal complexes with phen

No.	Comp.	$\nu$ (O-H) (Phenolic)	$\nu$ (C=N) (Azome- thine)	$\nu$ (C-O) (Phenolic)	$\nu$ (M-O)	$\nu$ (M-N)	$\nu$ (O-H) Water	$\nu$ (OCH <sub>3</sub> )	Acetate stretch
	<i>o</i> -v <sub>2</sub> bzH <sub>2</sub>	3380 br	1614 s	1466 m	-	-	-	2833 w	-
(1)	[Cu( <i>o</i> -v <sub>2</sub> bz)] <sub>2</sub> .2H <sub>2</sub> O	-	1585 s	1438 m	540 w	424w	3500 br	2827 w	-
(2)	[Ni( <i>o</i> -v <sub>2</sub> bz)] <sub>2</sub>	-	1595 s	1440 m	525 w	480 w	-	2860 w	-
(3)	[Co( <i>o</i> -v <sub>2</sub> bz)] <sub>2</sub>	-	1590 s	1420 m	560 w	440 w	-	2850 w	-
(4)	[Zn( <i>o</i> -v <sub>2</sub> bz)] <sub>2</sub>	-	1586 s	1430 m	540 w	470 w	-	2840 w	-
(5)	[Mn( <i>o</i> -v <sub>2</sub> bz)] <sub>2</sub>	-	1590 s	1420 m	530 w	460w	-	2940 w	-
(6)	[Sm( <i>o</i> -v <sub>2</sub> bz) (OAc)(H <sub>2</sub> O)] <sub>2</sub>	-	1590 s	1440 m	520 w	410 w	3575 br 3380 br	2840 w	1630 m 1340 m
(7)	[UO <sub>2</sub> ( <i>o</i> -v <sub>2</sub> bz)] <sub>2</sub>	-	1585 s	1435 m	530 w	450 w	-	2940 w	-

coordination of the azomethine nitrogen<sup>25</sup> to the metal centres. This is further substantiated by the presence of a new band at 410-480 cm<sup>-1</sup>, assignable to  $\nu(\text{M-N})$ <sup>28</sup>. The characteristic phenolic  $\nu(\text{O-H})$  mode due to presence of a hydroxy group at ortho position in the ligand was observed at 3380 cm<sup>-1</sup>. A band at 1466 cm<sup>-1</sup> due to  $\nu(\text{C-O})$ <sup>25</sup> phenolic was also observed in the ligand. The disappearance of phenolic  $\nu(\text{O-H})$  band in all the complexes under study suggests the coordination by the phenolic oxygen after deprotonation to the metal ion<sup>25</sup>. This is further supported by the shifting of  $\nu(\text{C-O})$  phenolic to lower<sup>25</sup> wave numbers in all the metal complexes. The appearance of a new non-ligand band at 520-560 cm<sup>-1</sup> in all the complexes due to  $\nu(\text{M-O})$ <sup>28</sup> further substantiates it. The overall IR data suggest the dibasic, tetradentate (OONN) nature of the ligand, *o-v*<sub>2</sub>bzH<sub>2</sub>. The presence of lattice water in the Cu(II) complex (**1**) is revealed by the appearance of a broad band at 3500 cm<sup>-1</sup> due to  $\nu(\text{O-H})$ .

In the samarium complex (**6**), the appearance of two additional bands at 1630 and 1340 cm<sup>-1</sup> due to  $\nu_{\text{as}}(\text{COO})$  and  $\nu_{\text{s}}(\text{COO})$  modes, respectively, of acetato group, suggests its unidentate coordination ( $\Delta = 290 \text{ cm}^{-1}$ )<sup>29</sup>. This is further supported by the non-electrolytic nature of this complex (*vide infra*). This complex also exhibits the  $\nu(\text{OH})$  bands at 3575 and 3385 cm<sup>-1</sup>, and  $\delta\text{H}_2\text{O}$  at 1605 cm<sup>-1</sup> for coordinated water molecule.

The dioxouranium(VI) complex (**7**) exhibits one strong band at 920 cm<sup>-1</sup> and one weak band at 860 cm<sup>-1</sup> in the IR spectrum due to  $\nu_{\text{as}}(\text{O=U=O})$  and  $\nu_{\text{s}}(\text{O=U=O})$  stretches, respectively. This indicates the presence of *trans*-UO<sub>2</sub> group<sup>30</sup> in the complex.

#### Thermogravimetric analyses

The thermograms of two representative compounds, [Cu(*o-v*<sub>2</sub>bz)]<sub>2</sub>·2H<sub>2</sub>O (**1**) and [Sm(*o-v*<sub>2</sub>bz)(OAc)(H<sub>2</sub>O)]<sub>2</sub> (**6**) were recorded in the temperature range from 50°C-910°C at a heating rate of 15°C/min. The first weight loss in the complex (**1**) (Fig. 1a) was observed in the temperature range 75-120°C, which corresponds to 3.4% against a theoretical weight loss of 3.3%. As this weight loss starts at lower temperature (75°C), it suggests the presence of two lattice<sup>31</sup> water molecules in the complex. After this weight loss, the complex remains stable up to 310°C. Thereafter, it shows a weight loss continuously up to 910°C. This weight loss consists of

greatly overlapped decomposition steps, which prevents the accurate correlation of these steps with proper decomposition products.

The compound (**6**) (Fig. 1b) is stable up to 250°C. Thereafter, a weight loss of 2.75% was recorded at 280 °C (calcd. weight loss = 2.65%), which is due to removal of two coordinated<sup>32</sup> water molecules from the complex. This compound shows a steep weight loss of 51.18% in the temperature range 310-435°C (calcd. weight loss for 1.5 *o-v*<sub>2</sub>bz, 51.75%). This suggests the elimination of one and half molecule of the Schiff base ligand (*o-v*<sub>2</sub>bz) from the coordination sphere of the complex. Thereafter, it registers a weight loss continuously up to 910°C. This weight loss consists of greatly overlapped decomposition steps, which prevents the accurate correlation of these steps with proper decomposition products. The final residue roughly corresponds to Sm<sub>2</sub>O<sub>3</sub> (observed residual mass, 34%; calcd. residual mass, 25.74%). This shows that weight loss is not constant at 910°C but still continues beyond this temperature.

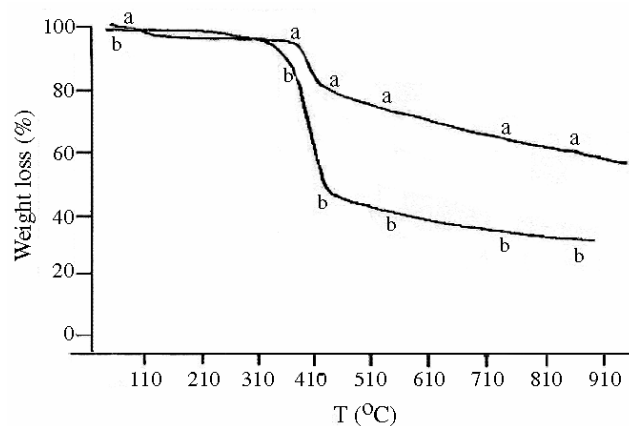


Fig. 1 – Thermogram of (a) [Cu(*o-v*<sub>2</sub>bz)]<sub>2</sub>·2H<sub>2</sub>O (**1**); and, (b) [Sm(*o-v*<sub>2</sub>bz)(OAc)(H<sub>2</sub>O)]<sub>2</sub> (**6**). [Atm.: N<sub>2</sub>; Heating rate: 5°C/min; Chart speed: 5 mm/min; Sample weight: a, 2.62 mg; b, 2.46 mg].

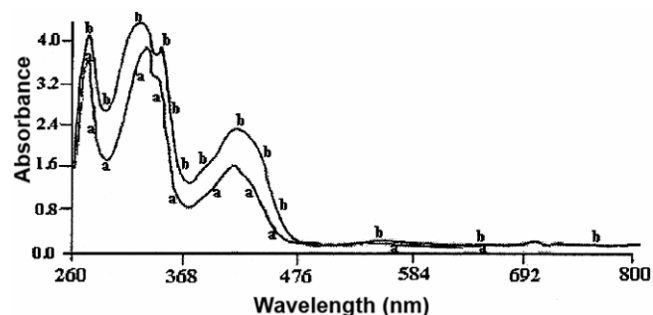


Fig. 2 – Diffuse reflectance spectrum of (a) [Mn(*o-v*<sub>2</sub>bz)]<sub>2</sub> (**5**); and, (b) [Sm(*o-v*<sub>2</sub>bz)(OAc)(H<sub>2</sub>O)]<sub>2</sub> (**6**).

### Magnetic susceptibility

Cu(II) has a  $d^9$  electronic configuration and its complexes contain one unpaired electron in the  $d$ -shell. The majority of Cu(II) complexes<sup>33</sup> are formed by involvement of  $d$ -orbitals and they are square-planar or distorted-octahedral. The formation of tetrahedral complexes of Cu(II) without using  $d$ -orbital is also reported to be formed. In the case of square planar, tetrahedral or distorted-octahedral Cu(II) complexes, the room temperature magnetic moment values are usually observed in the range<sup>34</sup> of 1.8-2.2 B.M., and are not affected appreciably by the temperature and magnetic field. In practice, compounds whose geometry approaches octahedral usually exhibit magnetic moments at the lower end of the range, while those approaching square-planar or tetrahedral geometry are at the higher end. In case of square-planar dimeric or polynuclear species, the complexes display subnormal<sup>34</sup> magnetic moments. The observed room temperature magnetic moment of Cu(II) complex in the present case is 1.71 B. M. The spacer<sup>35</sup> nature of the ligand in question, being two azomethyne nitrogens of benzidine moiety far apart, and the analytical data coupled with the magnetic moment, suggest that the complex is magnetically dilute, binuclear<sup>17</sup> with square planar geometry at each metal center.

The Ni(II) complex (**2**) shows a magnetic moment of 3.88 B.M., which is in the range (~3.6-4.0 B.M.) of magnetic moments, expected for tetrahedral<sup>36</sup> Ni(II) complexes. Again, the spacer nature of the ligand, absence of any Ni-Ni actual bond length value in the 3D molecular modeling data of this compound, and the analytical data coupled with the magnetic moment value suggest that the complex is magnetically dilute, ligand bridged binuclear with tetrahedral geometry at each nickel center. The magnetic moment of Co(II) complex (**3**) was found to be 4.10 B.M. This value, which is at the lower end of magnetic moments expected for tetrahedral<sup>36</sup> Co(II) complex, suggests a dimeric nature of the complex (on account of the same reasoning given above) where the geometry around each cobalt(II) center is tetrahedral. The magnetic moment of manganese(II) complex is 5.74 B.M., which is consistent with high-spin Mn(II). Manganese(II) generally forms high-spin complexes because of the additional stability of the half filled  $d$ -shell. The magnetic moment of both octahedral and tetrahedral complexes should be the same since a  $^6S$  ground state persists in both symmetries. Thus, the

magnetic result gives no specific information about the geometry of this compound. However, the analytical data of the complex suggest that the complex is tetra-coordinated.

The magnetic moment value of the Sm(III) complex is found to be 1.28 B.M., which shows a small deviation from the Van Vleck<sup>37</sup> values. The Zn(II) and UO<sub>2</sub>(VI) complexes are found to be diamagnetic as expected.

### Electronic spectra

The diffuse reflectance spectra (drs) of two representative compounds (Figs 2a and 2b) were recorded in the range 260-800 nm. The drs spectrum

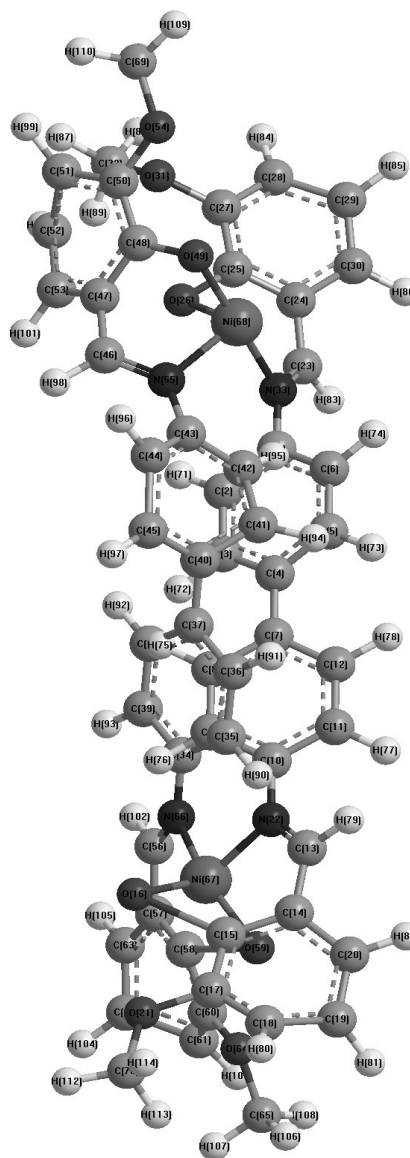


Fig. 3 – 3D Molecular structure of compound (**1**).

of Mn(II) complex (**5**) exhibits four spectral peaks at 271 nm (36,900 cm<sup>-1</sup>), 325 nm (30,769 cm<sup>-1</sup>), 410 nm (24,390 cm<sup>-1</sup>) and 558 nm (17,921 cm<sup>-1</sup>). The first two spectral peaks of high intensities ( $\epsilon = 3595$  and 3809 L cm<sup>-1</sup> mol<sup>-1</sup>, respectively) are due to charge transfer transitions. The peaks at 410 and 558 nm, which may be assigned to  ${}^6A_1 \rightarrow {}^4A_1(G)$  and  ${}^6A_1 \rightarrow {}^4E(G)$ , respectively, are characteristic of four coordinated tetrahedral<sup>38</sup> Mn(II) complex.

The drs spectra of compound (**6**) shows six spectral peaks at 274, 324, 340, 410, 539 and 692 nm. The first three spectral peaks of high intensities are most probably due to charge transfer transitions while the three absorption bands in the visible region at 410, 539 and 692 nm are assigned to  ${}^6H_{5/2} \rightarrow {}^4F_{9/2}$ ,  ${}^6H_{5/2} \rightarrow {}^6P_{5/2}$ ,  ${}^6H_{5/2} \rightarrow {}^4I_{13/2}$ , respectively<sup>39</sup>. The appearance of these peaks indicates the metal-ligand interactions in the complex.

#### <sup>1</sup>H NMR spectra

The <sup>1</sup>H NMR spectrum of the compound [Zn(*o*-v<sub>2</sub>bz)]<sub>2</sub> (**4**) was recorded in DMSO-*d*<sub>6</sub>. The

proton signals at 3.35, 3.85, 6.9 to 7.9 and 9.1 ppm are due to the solvent, -OCH<sub>3</sub> group, aromatic protons and azomethine (-CH=N-) proton, respectively. The absence of proton signal around 13 ppm for phenolic (-OH) proton of vanillin<sup>41</sup> built-in in the ligand understudy suggests the coordination of phenolic oxygen after deprotonation to the metal ion in the complex. Such a result we have already reported<sup>40</sup> in complexes [Zn(*o*-vpa)<sub>2</sub>].H<sub>2</sub>O and [Zn(*o*-ved)].2H<sub>2</sub>O (where *o*-vpaH = N-(*o*-vanillinidene)-*p*-anisidine and *o*-vedH<sub>2</sub> = N,N'-bis(*o*-vanillinidene)-ethylenediamine).

#### Molecular modeling and analysis

In view of the tetra-coordination of the present Ni(II) complex, [Ni(*o*-v<sub>2</sub>bz)]<sub>2</sub> (**2**) (vide infra), the molecular modeling of this compound as a representative, is based on its tetrahedral structure. The details of bond lengths and bond angles as per the 3D structure (Fig. 3) are given in Tables 3 and 4, respectively. For convenience of looking over the different bond lengths and bond angles, the various atoms in the compound in question are numbered in

Table 3 – Various bond lengths of compound [Ni(*o*-v<sub>2</sub>bz)]<sub>2</sub> (**2**)

No.	Atoms	Actual bond length	Optimal bond length	No.	Atoms	Actual bond length	Optimal bond length
1	H(113)-C(70)	1.113	1.111	24	Ni(68)-N(55)	1.826	-
2	H(109)-C(69)	1.113	1.111	25	N(22)-Ni(67)	1.826	-
3	H(107)-C(65)	1.113	1.111	26	O(59)-Ni(67)	1.79	-
4	C(53)-H(101)	1.1	1.1	27	O(16)-Ni(67)	1.79	-
5	C(52)-H(100)	1.1	1.1	28	N(66)-Ni(67)	1.826	-
6	C(51)-H(99)	1.1	1.1	29	C(56)-N(66)	1.266	1.266
7	C(46)-H(98)	1.1	1.1	30	H(108)-C(65)	1.113	1.111
8	H(96)-C(44)	1.1	1.1	31	H(106)-C(65)	1.113	1.111
9	H(93)-C(39)	1.1	1.1	32	C(60)-O(64)	1.355	1.355
10	H(89)-C(32)	1.113	1.111	33	O(64)-C(65)	1.402	1.396
11	H(88)-C(32)	1.113	1.111	34	H(105)-C(63)	1.1	1.1
12	H(87)-C(32)	1.113	1.111	35	C(63)-C(57)	1.337	1.42
13	C(28)-H(84)	1.1	1.1	36	C(62)-H(104)	1.1	1.1
14	C(12)-H(78)	1.1	1.1	37	C(62)-C(63)	1.337	1.42
15	H(75)-C(8)	1.1	1.1	38	C(61)-C(62)	1.5947	1.42
16	H(74)-C(6)	1.1	1.1	39	C(61)-H(103)	1.1	1.1
17	C(3)-H(72)	1.1	1.1	40	C(60)-C(61)	1.337	1.42
18	H(114)-C(70)	1.113	1.111	41	C(60)-C(58)	1.337	1.42
19	H(112)-C(70)	1.113	1.111	42	O(59)-C(58)	2.4294	1.355
20	C(70)-O(21)	1.402	1.396	43	C(57)-C(58)	1.337	1.42
21	H(111)-C(69)	1.113	1.111	44	C(56)-H(102)	1.1	1.1
22	H(110)-C(69)	1.113	1.111	45	C(56)-C(57)	1.337	1.503
23	C(69)-O(54)	1.402	1.396				

(Contd)

Table 3 – Various bond lengths of compound  $[\text{Ni}(o\text{-v}_2\text{bz})_2]$  (2)—Contd

No.	Atoms	Actual bond length	Optimal bond length	No.	Atoms	Actual bond length	Optimal bond length
46	C(43)-N(55)	1.266	1.462	87	C(27)-C(25)	1.337	1.42
47	C(46)-N(55)	1.266	1.266	88	Ni(68)-O(26)	1.79	-
48	C(50)-O(54)	1.355	1.355	89	O(26)-C(25)	1.3243	1.355
49	C(53)-C(52)	1.337	1.42	90	C(30)-C(24)	1.337	1.42
50	C(51)-C(52)	1.5327	1.42	91	C(25)-C(24)	1.337	1.42
51	C(51)-C(50)	1.337	1.42	92	H(83)-C(23)	1.1	1.1
52	Ni(68)-O(49)	1.79	-	93	N(33)-C(23)	1.266	1.266
53	O(49)-C(48)	1.3807	1.355	94	C(23)-C(24)	1.337	1.503
54	C(50)-C(48)	1.337	1.42	95	C(10)-N(22)	1.266	1.462
55	C(47)-C(48)	1.337	1.42	96	H(82)-C(20)	1.1	1.1
56	C(47)-C(53)	1.337	1.42	97	C(19)-H(81)	1.1	1.1
57	C(46)-C(47)	1.337	1.503	98	C(19)-C(20)	1.337	1.42
58	H(97)-C(45)	1.1	1.1	99	C(18)-H(80)	1.1	1.1
59	C(40)-C(45)	1.337	1.42	100	C(18)-C(19)	1.6096	1.42
60	C(44)-C(45)	1.5458	1.42	101	C(17)-C(18)	1.337	1.42
61	C(43)-C(44)	1.337	1.42	102	C(17)-O(21)	1.355	1.355
62	C(42)-H(95)	1.1	1.1	103	C(17)-C(15)	1.337	1.42
63	C(42)-C(43)	1.337	1.42	104	C(15)-O(16)	2.0332	1.355
64	C(42)-C(41)	1.4363	1.42	105	C(14)-C(20)	1.337	1.42
65	H(94)-C(41)	1.1	1.1	106	C(14)-C(15)	1.337	1.42
66	C(40)-C(41)	1.337	1.42	107	H(79)-C(13)	1.1	1.1
67	H(92)-C(38)	1.1	1.1	108	N(22)-C(13)	1.266	1.266
68	C(39)-C(38)	1.337	1.42	109	C(14)-C(13)	1.337	1.503
69	C(40)-C(37)	1.337	1.503	110	C(12)-C(7)	1.337	1.42
70	C(38)-C(37)	1.337	1.42	111	C(11)-H(77)	1.1	1.1
71	C(36)-C(37)	1.337	1.42	112	C(12)-C(11)	1.337	1.42
72	C(36)-H(91)	1.1	1.1	113	C(10)-C(11)	1.337	1.42
73	H(90)-C(35)	1.1	1.1	114	C(9)-H(76)	1.1	1.1
74	C(36)-C(35)	1.3371	1.42	115	C(9)-C(10)	1.337	1.42
75	C(34)-N(66)	1.266	1.462	116	C(9)-C(8)	1.3373	1.42
76	C(39)-C(34)	1.337	1.42	117	C(8)-C(7)	1.337	1.42
77	C(35)-C(34)	1.337	1.42	118	C(6)-C(5)	1.337	1.42
78	N(33)-Ni(68)	1.826	-	119	H(73)-C(5)	1.1	1.1
79	C(1)-N(33)	1.266	1.462	120	C(4)-C(7)	1.337	1.503
80	C(27)-O(31)	1.355	1.355	121	C(4)-C(5)	1.337	1.42
81	C(32)-O(31)	1.402	1.396	122	C(4)-C(3)	1.337	1.42
82	C(30)-H(86)	1.1	1.1	123	H(71)-C(2)	1.1	1.1
83	H(85)-C(29)	1.1	1.1	124	C(3)-C(2)	1.3371	1.42
84	C(30)-C(29)	1.337	1.42	125	C(1)-C(2)	1.337	1.42
85	C(28)-C(29)	1.4388	1.42	126	C(1)-C(6)	1.337	1.42
86	C(28)-C(27)	1.337	1.42				



Table 4 – Various bond angles of compound [Ni(*o*-V<sub>2</sub>Bz)]<sub>2</sub> (3)

No.	Atoms	Actual bond angles	Optimal bond angles	No.	Atoms	Actual bond angles	Optimal bond angles
1	H(113)-C(70)-H(114)	109.52	109	52	C(35)-C(36)-C(37)	119.9938	-
2	H(112)-C(70)-H(114)	109.4618	109	53	H(93)-C(39)-C(38)	120	120
3	H(114)-C(70)-O(21)	109.4618	106.7	54	H(93)-C(39)-C(34)	120	120
4	H(112)-C(70)-H(113)	109.4418	109	55	C(38)-C(39)-C(34)	120	-
5	H(113)-C(70)-O(21)	109.4418	106.7	56	C(36)-C(35)-H(90)	120.0006	120
6	H(112)-C(70)-O(21)	109.5	106.7	57	H(90)-C(35)-C(34)	120.0006	120
7	H(110)-C(69)-H(111)	109.52	109	58	C(36)-C(35)-C(34)	119.9988	-
8	H(109)-C(69)-H(111)	109.4618	109	59	C(63)-C(62)-H(104)	125.4173	120
9	H(111)-C(69)-O(54)	109.4618	106.7	60	C(61)-C(62)-H(104)	125.4173	120
10	H(109)-C(69)-H(110)	109.4418	109	61	C(61)-C(62)-C(63)	109.1654	-
11	H(110)-C(69)-O(54)	109.4418	106.7	62	C(62)-C(61)-H(103)	125.3465	120
12	H(109)-C(69)-O(54)	109.5	106.7	63	C(60)-C(61)-H(103)	125.3465	120
13	H(107)-C(65)-H(108)	109.52	109	64	C(60)-C(61)-C(62)	109.307	-
14	H(106)-C(65)-H(108)	109.4618	109	65	C(61)-C(60)-O(64)	120	124.3
15	H(108)-C(65)-O(64)	109.4618	106.7	66	O(64)-C(60)-C(58)	120	124.3
16	H(106)-C(65)-H(107)	109.4418	109	67	C(61)-C(60)-C(58)	120	120
17	H(107)-C(65)-O(64)	109.4418	106.7	68	C(58)-O(59)-Ni(67)	52.7608	-
18	H(106)-C(65)-O(64)	109.5	106.7	69	H(105)-C(63)-C(62)	120	120
19	H(88)-C(32)-H(89)	109.52	109	70	H(105)-C(63)-C(57)	120	120
20	H(87)-C(32)-H(89)	109.4618	109	71	C(62)-C(63)-C(57)	120	-
21	H(89)-C(32)-O(31)	109.4618	106.7	72	O(59)-C(58)-C(60)	89.4545	124.3
22	H(87)-C(32)-H(88)	109.4418	109	73	C(60)-C(58)-C(57)	120	120
23	H(88)-C(32)-O(31)	109.4418	106.7	74	O(59)-C(58)-C(57)	147.0226	124.3
24	H(87)-C(32)-O(31)	109.5	106.7	75	C(63)-C(57)-C(58)	119.9988	120
25	C(60)-O(64)-C(65)	120	110.8	76	C(63)-C(57)-C(56)	119.9988	120
26	C(69)-O(54)-C(50)	120	110.8	77	C(56)-C(57)-C(58)	120	120
27	C(27)-O(31)-C(32)	120	110.8	78	N(66)-C(56)-H(102)	120	113.5
28	C(70)-O(21)-C(17)	120	110.8	79	C(57)-C(56)-H(102)	120	120
29	H(96)-C(44)-C(45)	118.2972	120	80	C(57)-C(56)-N(66)	120	119
30	H(96)-C(44)-C(43)	118.2972	120	81	H(81)-C(19)-C(20)	125.681	120
31	C(43)-C(44)-C(45)	123.4056	-	82	C(18)-C(19)-H(81)	125.681	120
32	H(95)-C(42)-C(43)	124.8781	120	83	C(18)-C(19)-C(20)	108.638	-
33	H(95)-C(42)-C(41)	124.8781	120	84	C(19)-C(18)-H(80)	125.6086	120
34	C(43)-C(42)-C(41)	110.2438	-	85	C(17)-C(18)-H(80)	125.6086	120
35	H(97)-C(45)-C(44)	127.6651	120	86	C(17)-C(18)-C(19)	108.7829	-
36	C(40)-C(45)-H(97)	127.6651	120	87	C(18)-C(17)-O(21)	120	124.3
37	C(40)-C(45)-C(44)	104.6699	-	88	C(15)-C(17)-O(21)	120	124.3
38	C(42)-C(41)-H(94)	122.435	120	89	C(18)-C(17)-C(15)	120	120
39	C(40)-C(41)-H(94)	122.435	120	90	C(15)-O(16)-Ni(67)	74.3516	-
40	C(40)-C(41)-C(42)	115.13	-	91	H(82)-C(20)-C(19)	120	120
41	C(39)-C(38)-H(92)	120	120	92	C(14)-C(20)-H(82)	120	120
42	H(92)-C(38)-C(37)	120	120	93	C(14)-C(20)-C(19)	120	-
43	C(39)-C(38)-C(37)	120	-	94	C(17)-C(15)-O(16)	112.1579	124.3
44	C(45)-C(40)-C(41)	119.9988	120	95	C(14)-C(15)-C(17)	119.999	120
45	C(45)-C(40)-C(37)	119.9988	120	96	C(14)-C(15)-O(16)	127.8413	124.3
46	C(37)-C(40)-C(41)	120	120	97	C(15)-C(14)-C(20)	119.9988	120
47	C(40)-C(37)-C(38)	120	120	98	C(13)-C(14)-C(20)	119.9988	120
48	C(40)-C(37)-C(36)	119.9988	120	99	C(15)-C(14)-C(13)	120	120
49	C(36)-C(37)-C(38)	119.9988	120	100	N(22)-C(13)-H(79)	120	113.5
50	H(91)-C(36)-C(37)	120.0031	120	101	C(14)-C(13)-H(79)	120	120
51	H(91)-C(36)-C(35)	120.0031	120				

(Contd)

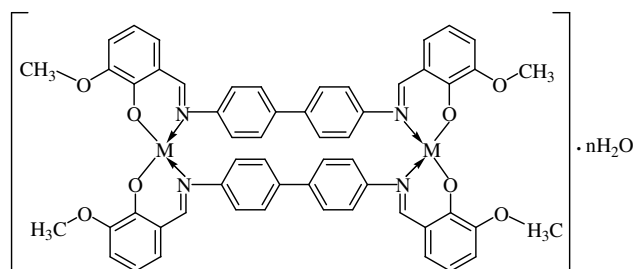
Table 4 – Various bond angles of compound  $[\text{Ni}(o\text{-V}_2\text{Bz})_2]_2$  (3)—*Contd*

No.	Atoms	Actual bond angles	Optimal bond angles	No.	Atoms	Actual bond angles	Optimal bond angles
102	C(14)-C(13)-N(22)	120	119	147	C(1)-C(6)-C(5)	120	-
103	C(12)-C(11)-H(77)	120	120	148	C(3)-C(2)-H(71)	120.0006	120
104	C(10)-C(11)-H(77)	120	120	149	C(1)-C(2)-H(71)	120.0006	120
105	C(12)-C(11)-C(10)	120	-	150	C(3)-C(2)-C(1)	119.9988	-
106	C(39)-C(34)-N(66)	119.9988	120	151	C(53)-C(52)-H(100)	124.2815	120
107	C(35)-C(34)-N(66)	120	120	152	C(51)-C(52)-H(100)	124.2815	120
108	C(39)-C(34)-C(35)	119.9988	120	153	C(51)-C(52)-C(53)	111.437	-
109	C(56)-N(66)-Ni(67)	108.9992	109	154	C(52)-C(51)-H(99)	124.2161	120
110	C(34)-N(66)-Ni(67)	118	109	155	C(50)-C(51)-H(99)	124.2161	120
111	C(56)-N(66)-C(34)	132.9979	124	156	C(50)-C(51)-C(52)	111.5678	-
112	O(59)-Ni(67)-N(66)	159.2606	-	157	C(51)-C(50)-O(54)	120	124.3
113	N(22)-Ni(67)-N(66)	90	-	158	O(54)-C(50)-C(48)	120	124.3
114	O(16)-Ni(67)-N(66)	109.5	-	159	C(51)-C(50)-C(48)	120	120
115	O(59)-Ni(67)-N(22)	90	-	160	Ni(68)-O(49)-C(48)	97.8273	-
116	O(59)-Ni(67)-O(16)	90	-	161	C(52)-C(53)-H(101)	120	120
117	N(22)-Ni(67)-O(16)	109.5	-	162	C(47)-C(53)-H(101)	120	120
118	C(13)-N(22)-Ni(67)	108.9992	109	163	C(47)-C(53)-C(52)	120	-
119	C(10)-N(22)-Ni(67)	118	109	164	C(50)-C(48)-O(49)	122.7169	124.3
120	C(10)-N(22)-C(13)	132.9979	124	165	C(47)-C(48)-C(50)	119.9987	120
121	C(11)-C(10)-N(22)	120	120	166	C(47)-C(48)-O(49)	117.2816	124.3
122	C(9)-C(10)-N(22)	119.9988	120	167	C(53)-C(47)-C(48)	119.9988	120
123	C(9)-C(10)-C(11)	119.9988	120	168	C(46)-C(47)-C(53)	119.9988	120
124	H(76)-C(9)-C(10)	120.0081	120	169	C(46)-C(47)-C(48)	120	120
125	H(76)-C(9)-C(8)	120.0081	120	170	H(98)-C(46)-N(55)	120	113.5
126	C(10)-C(9)-C(8)	119.9839	-	171	H(98)-C(46)-C(47)	120	120
127	C(11)-C(12)-H(78)	120	120	172	C(47)-C(46)-N(55)	120	119
128	C(7)-C(12)-H(78)	120	120	173	C(30)-C(29)-H(85)	122.385	120
129	C(11)-C(12)-C(7)	120	-	174	C(28)-C(29)-H(85)	122.385	120
130	C(9)-C(8)-H(75)	120.0081	120	175	C(28)-C(29)-C(30)	115.23	-
131	H(75)-C(8)-C(7)	120.0081	120	176	H(84)-C(28)-C(29)	122.3335	120
132	C(9)-C(8)-C(7)	119.9839	-	177	H(84)-C(28)-C(27)	122.3335	120
133	H(73)-C(5)-C(6)	120	120	178	C(27)-C(28)-C(29)	115.333	-
134	C(4)-C(5)-H(73)	120	120	179	C(28)-C(27)-O(31)	120	124.3
135	C(4)-C(5)-C(6)	120	-	180	C(25)-C(27)-O(31)	120	124.3
136	C(12)-C(7)-C(8)	119.9988	120	181	C(28)-C(27)-C(25)	120	120
137	C(4)-C(7)-C(12)	119.9988	120	182	Ni(68)-O(26)-C(25)	96.9318	-
137	C(4)-C(7)-C(8)	120	120	183	H(86)-C(30)-C(29)	120	120
139	C(5)-C(4)-C(7)	120	120	184	H(86)-C(30)-C(24)	120	120
140	C(3)-C(4)-C(7)	119.9988	120	185	C(29)-C(30)-C(24)	120	-
141	C(3)-C(4)-C(5)	119.9988	120	186	C(27)-C(25)-O(26)	120.7725	124.3
142	C(4)-C(3)-H(72)	120.0031	120	187	C(27)-C(25)-C(24)	119.9987	120
143	H(72)-C(3)-C(2)	120.0031	120	188	O(26)-C(25)-C(24)	119.2262	124.3
144	C(4)-C(3)-C(2)	119.9938	-	189	C(30)-C(24)-C(25)	119.9988	120
145	H(74)-C(6)-C(5)	120	120	190	C(30)-C(24)-C(23)	119.9988	120
146	C(1)-C(6)-H(74)	120	120	191	C(23)-C(24)-C(25)	120	120
				192	H(83)-C(23)-N(33)	120	113.5

*(Contd)*

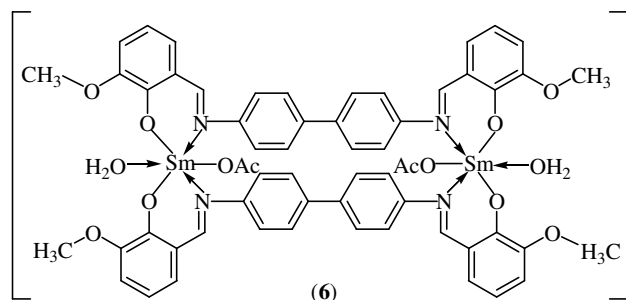
Table 4 – Various bond angles of compound [Ni(*o-v*<sub>2</sub>Bz)]<sub>2</sub> (3)—*Contd*

No.	Atoms	Actual bond angles	Optimal bond angles	No.	Atoms	Actual bond angles	Optimal bond angles
193	H(83)-C(23)-C(24)	120	120	203	O(26)-Ni(68)-N(55)	90	-
194	N(33)-C(23)-C(24)	120	119	204	N(33)-Ni(68)-O(49)	179.4271	-
195	N(55)-C(43)-C(44)	120	120	205	O(26)-Ni(68)-O(49)	90	-
196	C(42)-C(43)-N(55)	119.9988	120	206	N(33)-Ni(68)-O(26)	90	-
197	C(42)-C(43)-C(44)	119.9988	120	207	Ni(68)-N(33)-C(23)	108.9992	109
198	C(46)-N(55)-Ni(68)	108.9992	109	208	C(1)-N(33)-Ni(68)	118	109
199	Ni(68)-N(55)-C(43)	118	109	209	C(1)-N(33)-C(23)	132.9979	124
200	C(46)-N(55)-C(43)	132.9979	124	210	N(33)-C(1)-C(6)	119.9988	120
201	N(55)-Ni(68)-O(49)	89.4271	-	211	N(33)-C(1)-C(2)	120	120
202	N(33)-Ni(68)-N(55)	90	-	212	C(6)-C(1)-C(2)	119.9988	120

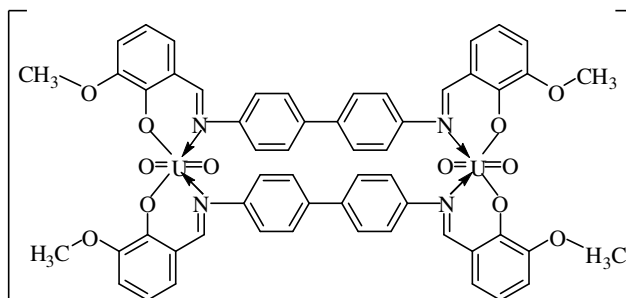


M = Cu(II), n = 2 (1); Ni(II), n = 0 (2); Co(II), n = 0 (3)

Zn(II), n = 0 (4); Mn(II), n = 0 (5)



(6)



(7)

Fig. 4 – Proposed structures of complexes.

Arabic numerals. In all, 338 measurements of the bond lengths (126 in numbers), plus the bond angles (212 in numbers) are listed in the Tables 3 and 4. Except few cases, optimal values (most favourable) of both the bond lengths and the bond angles are given in the Tables along with the actual ones. The actual bond lengths/bond angles given in Tables 3 and 4 are calculated values as a result of energy optimization in CHEM 3D Ultra, while the optimal bond length/optimal bond angle values are the most desirable/favourable (standard) bond lengths/bond angles established by the builder unit of the CHEM 3D. The missing of some values of standard bond lengths/bond angles may be due to the limitations of the software, which we had already noticed in modeling of other systems<sup>41,42</sup>. In most of the cases, the actual bond lengths and bond angles are close to the optimal values, and thus the proposed structure of the compound (2) is acceptable.

Satisfactory analytical data as well as the studies presented above suggest that the complexes under study may be formulated as [Cu(*o-v*<sub>2</sub>bz)]<sub>2</sub>.2H<sub>2</sub>O, [M(*o-v*<sub>2</sub>Bz)]<sub>2</sub> (where M = Ni(II), Co(II), Zn(II), Mn(II) or UO<sub>2</sub>(VI) and [Sm(*o-v*<sub>2</sub>bz)(OAc)(H<sub>2</sub>O)]<sub>2</sub>. From the physical studies discussed above, the ligand *o-v*<sub>2</sub>bz has been shown to act as a dibasic tetradentate ligand which coordinates through both azomethine nitrogens and both phenolic oxygens after deprotonation, and forms binuclear complexes with Cu(II), Ni(II), Co(II), Zn(II), Mn(II), Sm(III) and UO<sub>2</sub>(VI) in 1:1 stoichiometric ratio. The proposed binuclear structures of these complexes are shown in Fig. 4.

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### References

- Shakir M, Begum N, Azim Y & Parveen S, *Synth React Inorg Met-org Chem*, 33 (2003) 1367, and references therein.
- Adhikari B, Biswas A K, Nag K, Zanello P & Cinquantini A, *Polyhedron*, 6 (1987) 897, and references therein.
- Karlin K D & Tyeklar Z, *Advances in Inorganic Biochemistry*, Vol. 9, edited by G L Eichhorn & L Marzilli (Prentice Hall, Englewood Cliffs, NJ) 1994.
- Bioinorganic Chemistry of Copper*, edited by K D Karlin & Z Tyeklar, (Chapman and Hall, New York) 1993.
- Bioinorganic Catalysis*, edited by J Reedijk (Marcel Dekker, New York) 1993.
- Gengxiu, Z, Guangyou, Z, Qiufen, W & Zhenwei B Z, *Synth React Inorg Met-org Chem*, 28 (1998) 1079, and references therein.
- Sayed A M, Iftikhar K & Ahmad N, *Indian J Chem*, 22A (1983) 259.
- Maurya M R, Antony D C, Gopinathan S & Gopinathan C, *Bull Chem Soc Japan*, 68 (1995) 554.
- Maurya M R, Antony D C, Gopinathan S, Gopinathan C & Mohanan, K V, *Indian J Chem*, 34A (1995) 360.
- Maurya R C, Mishra D D, Rao N S, Jayaswal M N & Rao N N, *Polyhedron*, 12 (1993) 2045.
- Maurya R C, Jayaswal M N & Verma R, *Indian J Chem*, 36A (1997) 406.
- Maurya R C, Mishra D D, Rao N S & Rao N N, *Synth React Inorg Met-org Chem*, 25 (1995) 437.
- Maurya R C, Pandey A & Sutradhar D, *Indian J Chem*, 43A (2004) 763.
- Maurya R C, Jayaswal M N & Verma R, *Synth React Inorg Met-org Chem*, 28 (1995) 1265.
- Maurya R C, Mishra D D, Rao N S & Rao N N, *Polyhedron*, 13 (1994) 2653.
- Maurya R C, Pandey A & Singh T, *Synth React Inorg Met-org Chem*, 32 (2002) 247.
- Ganesh K S & Krishnan C N, *Synth React Inorg Met-org Chem*, 24 (1994) 1789.
- Maurya R C & Batalia S, *Indian J Chem*, 40A (2001) 652.
- Vogel A I, *A Text Book of Quantitative Inorganic Analysis*, (ELBS, Longman Green & Co. Ltd.) 1962, p. 498.
- Maurya R C, Mishra D D & Pillai V, *Synth React Inorg Met-org Chem*, 25 (1995) 139.
- Maurya R C, Mishra D D & Pillai S, *Synth React Inorg Met-org Chem* 27 (1997) 1453.
- Vogel A I, *A Text Book of Quantitative Inorganic Analysis*, (ELBS, Longman Green & Co. Ltd.) 1962, p. 4480.
- Maurya R C, Jaiswal M N, Verma R & Shukla B, *Synth React Inorg Met-org Chem*, 28 (1998) 1265.
- Maurya R C & Patel P, *Synth React Inorg Met-org Chem*, 33 (2003) 801.
- Singh K, Patel P & Agarwala B V, *Spect Lett*, 28 (1995) 751.
- Chatterjee P & Agarwala B V, *Bull Chem Soc Ethiopia*, 4 (1990) 39.
- Geary W J, *COORD chem Rev*, 7 (1971) 81.
- Syamal A & Maurya M R, *Indian J Chem*, 24A (1985) 836
- Nakamoto K, *Infrared Spectra of Inorganic and Coordination Compounds* (Wiley Interscience, New York) 1970, p. 232.
- Maurya M R & Maurya R C, *Rev Inorg Chem*, 15 (1995) 1.
- Dodd J W, Tonge K H & Currell B R, *Thermal Methods: Analytical Chemistry by Open Learning* (John Wiley & Sons, New York) 1987, p. 73.
- Maurya R C, Mishra D D, Mukherjee S & Dubey J, *Polyhedron*, 14 (1995) 1351.
- Patel K S & Woods J A O, *Synth React Inorg Met-org Chem*, 20 (1990) 909.
- Maurya R C, Verma R & Singh H, *Synth React Inorg Met-org Chem*, 33 (2003) 1063.
- Choudhary H, Ghosh R, Sarkar B N, Banerjee S P & Gosh B K, *Indian J Chem*, 46A (2007) 1393.
- Dutta R L & Syamal A, *Elements of Magnetochemistry*, 2<sup>nd</sup> Edn, (Affiliated East-West Press Pvt Ltd, New Delhi) 1993, pp. 152,153.
- Van Vleck J H & Frank N, *Phys Rev*, 34 (1929) 1494.
- Ali S M, Iftikhar K & Ahmad N, *Synth React Inorg Met-org Chem*, 14 (1984) 1031.
- Agarwal R K, Agarwal H & Sarin R K, *Synth React Inorg Met-org Chem*, 24 (1994) 1681.
- Maurya R C, Patel P & Rajput S, *Synth React Inorg Met-org Chem*, 33 (2003) 817.
- Maurya R C & Rajput S, *J Mol Struct*, 687 (2004) 35.
- Maurya R C, Pandey A, Chourasia J & Martin H, *J Mol Struct*, 798 (2006) 89.