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Crystal structure and thermal studies of copper(II) and nickel(II) complexes of 2-hydroxyacetophenoimine as vapour precursors

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ABSTRACT

Schiff's base complexes bis(2-hydroxyacetophenoimine)nickel(II) $[Ni(ohapim)_2]$ and bis(2-hydroxyacetophenoimine)copper(II) $[Cu(ohapim)_2]$ were synthesized and studied for their idealist novel vapour source for chemical vapour deposition (CVD) application. Molecular structure was determined using single crystal X-ray diffraction, FT-IR, and elemental (C, H, N, and O) studies. Upon screening these complexes by dynamic thermogravimetric (TG) analyses, $[Ni(ohapim)_2]$ was found to be completely volatile and suitable for Ni/NiO CVD application. The temperature-dependent vapour pressure of $[Ni(ohapim)_2]$ was measured by using a transpiration apparatus and gave a value of 77.4 ± 0.8 kJ/mol for the enthalpy of sublimation (ΔH°_{sub}) in the temperature range 527.86–584.22 K. Copyright © 2013 VBRI press.

Keywords: Schiff's base complexes; single crystal; volatility; vapour pressure; CVD precursors.

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Introduction

The aim of this study was to develop novel Cu(II) and Ni(II) with Schiff base complexes for chemical vapour deposition (CVD) application. CVD-derived metals and metal alloy thin films, for instance Cu–Ni alloys, have found potential applications in resistive and thermoelectric devices or micro-electrochemical systems, due to their anticorrosion and antifouling properties, electrocatalytic properties, as well as their high tensile strength and reasonably good wear resistance **[1, 2]**. Our present and previous reports **[3,4]** indicated that the replacement of oxygen atom in the $M(sal)_2$-based molecule (O–Cu–O to O–Cu–N) or the reaction of Schiff base ligands with the Cu^{2+} or Ni^{2+} salts led to potential precursors for producing metallic Ni or Cu thin films for technological applications. In fact, for a compound to be ideal for a metallorganic (MO) CVD precursor, it should exhibit thermal stability under ambient temperature, complete volatility, readiness to shed the ligand in the CVD chamber, and good gas phase transportability **[5–7]** for maintaining adequate feed stock of the precursor. While the variety of nickel precursor compounds known today is large and the processes of film deposition are complex, knowledge of the precursor and discussion of their physical and chemical properties within the context of vapour deposition can be useful to MOCVD users.

Many publications aimed to replace the use of highly toxic $Ni(CO)_4$ as precursor by fluorine or diketonate-based sources [**5,8–10**]. Although $Ni(tmhd)_2$ and $Ni(acac)_2en$ seemed to meet the ideal requirements, it was considered essential to synthesize newer sources employing aromatic ligands for a better understanding of what makes the complex volatile. In the past, several β-diketonate and few Schiff's base complexes and their derivatives of various metals have been routinely used as precursors for the MOCVD of thin films **[11,12]**, but to date no thermal and volatility behaviour of the title compounds of Ni and Cu precursors has been reported. Therefore, we report the methodology of synthesis, characterization by single crystal X-ray diffraction, and thermogravimetric (TG) analyses of Ni(II) and Cu(II) complexes with 2-hydroxyacetoimine. The used methodology and starting materials for synthesis of complexes are easy to handle, require less solvent and low cost in process handling. In addition, the complexes can be readily prepared in a single step in laboratories for immediate use in vapour deposition. The yielded products are non-toxic and moisture, air, light and atmosphere stable. From the TG analyses, we found that the Ni(II) complex satisfies most of the salient CVD precursor's criteria than the Cu(II) complex. Hence, the mass fragmentation studies (possible fragments formation) and equilibrium vapour pressure (p_e) measurements are presented here for the Ni(II) complex.

Experimental

Materials

The chemicals, 2-hydroxyacetophenone (ohap, 97%, LOBA Chemie, India), liquor ammonia (about 25%, Qualigens, India), $NiCl_2{\cdot}6H_2O$ (≥97%, LOBA Chemie, India) and $Cu(CH_3COO)_2{\cdot}2H_2O$ (≥97%, LOBA Chemie, India) were used as purchased.

Syntheses of bis(2-hydroxyacetophenoimine)nickel(II), Ni(ohapim)$_2$

The aqueous solution of $NiCl_2{\cdot}6H_2O$ (1 mol) was added gradually to a solution of 2-hydroxyacetophenone (ohap) (2 mol) in ethanol with constant stirring until a clear green colour solution was obtained (Scheme 1). Excess aqueous ammonia was added to the clear solution and refluxed for 3 h at 323 K with constant stirring, and a reddish precipitate was obtained. The obtained reddish precipitate was filtered, washed with ethanol and dried in a vacuum desiccator. Melting point: 627 K. *Anal. Calc.* for $C_{16}H_{16}N_2NiO_2$ (M = 327.02 g/mol) CHN analysis: Ni: 15.57%: C, 58.82%; H, 6.77 %; N, 8.81%; O, 9.89%. FT-IR (per cm): 3220.57 (N–H), 3026.53 (aromatic–CH), 1605.97 (C=N), 1437.86 (aromatic C=C), 1336.19 (C–O), 771.92–747.01 (C–H out of plane, 1,2 disubstituted compounds), 591.31 (M–O), 457.97 (M–N).

Syntheses of bis(2-hydroxyacetophenoimine)copper(II), Cu(ohapim)$_2$

An aqueous solution of $Cu(CH_3COO)_2{\cdot}2H_2O$ (1 mol) was added gradually to a solution of 2-hydroxyacetophenone (ohap) (2 mol) in ethanol with constant stirring until a clear blue colour solution was obtained (**Scheme 1**). Excess aqueous ammonia was added to the clear solution and refluxed for 3 h at 323 K with constant stirring, resulting in the formation of a dark green precipitate. The resulting dark green precipitate was filtered, washed with ethanol and dried in a vacuum desiccator. Melting point: 572 K. *Anal. Calc*. for $C_{16}H_{16}N_2CuO_2$ (M = 331.85 g/mol): CHN analysis: Cu, 17.36%; C, 58.42%; H, 5.56%; N, 8.92%; O, 9.75%. FT-IR (per cm): 3194.51 (N–H), 3053.22 (aromatic–CH), 1603.07 (C=N), 1438.42 (aromatic C=C), 1337.54 (C–O), 776.13–750.23 (C–H out of plane, 1,2–disubstituted compounds), 573.89 (M–O), 441.95 (M–N).

Spectral characterization

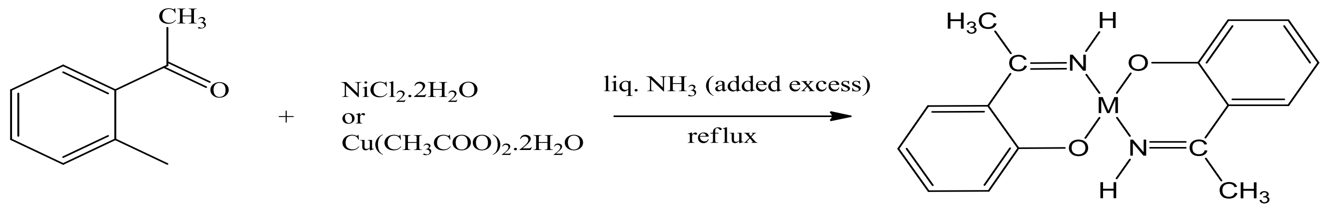
The C, H, N and O analyses for Ni(II) and Cu(II) complexes were carried out by employing the rapid elemental analyser model (CARLO–ERBA–11008). Fourier-transform infrared (FTIR) spectra were recorded to infer the various stretching frequencies using a Perkin–Elmer FTIR spectrometer at room temperature in the region of 4000−450/cm. The mass spectrum of the Ni(II) complex was recorded by using a fast atom bombardment mass spectrometer (FABMS) model (JEOL SX 102/DA-6000) using argon/xenon as the FAB gas at an accelerating voltage of 10 kV with *m*-nitrobenzyl alcohol (NBA) as the matrix at ambient temperature.

Single crystal analyses

X-ray intensity data for the Ni(II) and Cu(II) complexes were collected on a Bruker APEX2 diffractometer equipped with graphite monochromated Mo (Kα) radiation (λ = 0.71073 Å). The used software programs for the data collection, cell refinement and data reduction are APEX2 **[13]**, SAINT-Plus **[13]** and XPREP **[13]** respectively. The structure was solved by direct methods (SHELXS-97) **[14]**, and the non-hydrogen atoms were refined anisotropically using full-matrix least squares on $|F|^2$ with all unique reflections (SHELXL-97). The riding model was employed in the refinement of the hydrogen atoms.

Non-isothermal thermogravimetric (TG) study

The non-isothermal TG runs on the Ni(II) and Cu(II) complexes were recorded at a linear heating rate of 0.17 K/s using a thermo-analyser (Perkin–Elmer, Pyris–Diamond). High-purity nitrogen (purity >99.99%; 6 dm^3/h) dried by passing through refrigerated molecular sieves (Linde 4A) was used as the carrier gas. The samples were dried in vacuum desiccators with anhydrous calcium chloride as the desiccant prior to the TG runs. The purpose of these runs was to observe the mass loss steps besides identifying the final temperature to attain nil residue or constant weight. Based on the TG–DTA results, the Ni(II) and Cu(II) complexes were further characterized after identifying them to be completely volatile, which also



Scheme 1. Reaction scheme.

helped to infer the temperature range for the vapour pressure measurements.

Isothermal TG-transpiration: Vapour pressure measurement

A horizontal thermal analyser was adopted as a transpiration set-up for vapour pressure measurements. The details of the precise flow calibration for the carrier gas, temperature measurements, and corrections for apparent weight losses in isothermal mode are described elsewhere **[15–18]**. Ni(ohapim)$_2$ was finely powdered by using an agate mortar and pestle, spread out on a shallow alumina crucible, mounted for vapour pressure measurements and flushed with N_2 at a rate of 6 dm^3/h at ambient temperature. The initial heating to 525 K was rather rapid (0.17 K/s) and after allowing for temperature stabilization, the samples were subsequently heated (0.03 K/s) in steps of 10 K to isothermal temperatures in the range of 527.86–584.22 K. The accuracy of the temperature measurements was adjusted to ±0.05 K using the recommended melting point standards, namely indium, tin and aluminium. The reproducibility of the *T*–scale was assessed to be better than ±0.2 K.

Results and discussion

Usually, salicylaldehyde or ortho-hydroxyacetophenone-based Schiff base transition metal complexes are prepared by the following steps: (i) synthesis of hydrated M(sal)$_2$ followed by the addition of nitrogen-containing organic molecules or (ii) synthesis of (sal) or (ohap)-based ligands and finally the addition of a metal salt. Here, we synthesized complexes in a single step as with template synthesis (**Scheme 1**). Template-directed synthesis is an assembly of atoms with respect to one or more geometric arrangements to achieve a particular linking of atoms. The advantage of the currently adopted methodology for the synthesis of title compounds is enhanced yield of product with lesser time compared with other possible methodologies. Basically, aldehydes react with a variety of amines to produce imines, which are often referred to as Schiff bases [**19**]. The resultant imines participate in binding with metal ions via nitrogen lone pair electrons. The Schiff base Cu(II) and Ni(II) complexes described in this paper have been derived by a single step from the electrophilic carbon atom of ortho-hydroxyacetopheneone, nucleophilic nitrogen (from liquid ammonia added excess in the reaction mixture) and respective metal (Scheme 1). The evolved possible by-products (HCl or CH_3COOH) are condensed simultaneously by cold trap.

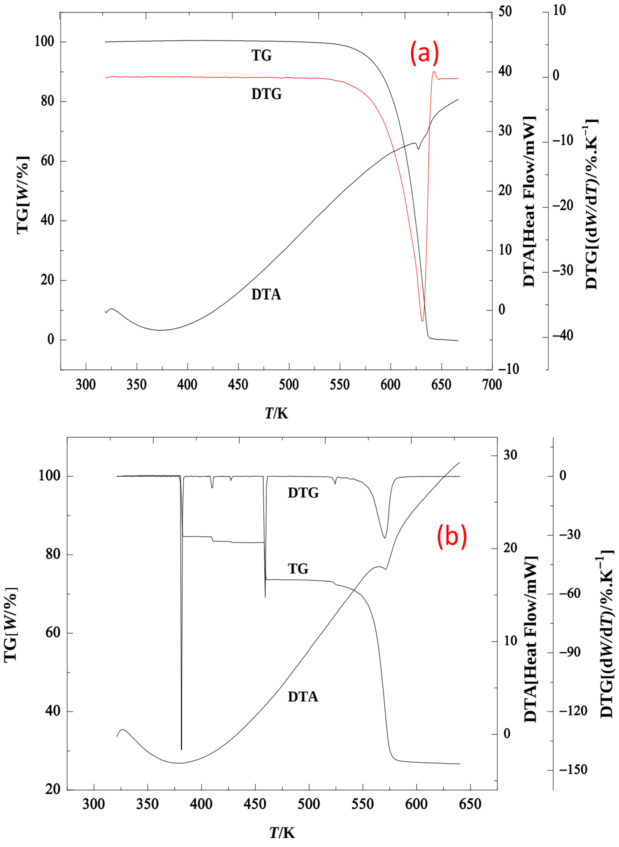


Fig. 1. Thermal analysis of (a) Ni(ohapim)$_2$ and (b) Cu(ohapim)$_2$

Thermal analyses of Ni(II) and Cu(II) complexes

Fig. 1 shows the weight loss that occurred in the TG of Ni(ohapim)$_2$ – a single step commencing from 520 K ending up with the total weight loss at ~630 K, at the heating rate of 0.17 K/s. Even though the ligand environment for both the complexes is the same, the thermogram of the Cu(II) complex shows **(Fig. 1)** two steps of decomposition in the temperature range of 380–460 and 460–560 K. A similar TG trend was observed in the case of Ni(acac)$_2$ and Cu(acac)$_2$ as well, which was due to the octahedral coordination of Ni(II) with the water molecule in Ni(acac)$_2$ **[19]**. The TG behaviour of the complexes is related to the packing of molecules and the same is described in the following section.

Table 1. Crystal data and structure refinement for compound Ni(ohapim)$_2$ and Cu(ohapim)$_2$.

Crystal data	Ni(ohapim)$_2$	Cu(ohapim)$_2$
Empirical formula	$C_{16}H_{16}N_2NiO_2$	$C_{16}H_{16}CuN_2O_2$
Formula weight	327.02	331.85
Temperature		293(2) K
Wavelength	293(2) K	0.71073 Å
Crystal system, space group	0.71073 Å	Triclinic, P$\bar{1}$
Unit cell dimensions	Triclinic, P$\bar{1}$	a = 9.4156(3) Å
-	a = 9.2479(4) Å	b = 11.3975(3) Å
Volume	b = 11.3373(5) Å	c = 12.3237(6) Å
Z, Calculated density	c = 12.3217(6) Å	α = 102.718(2)°
Absorption coefficient	α = 102.972(2)°	β = 103.910(2)°
F(000)	β = 103.455(2)°	γ = 111.097(2)°
Crystal size	γ = 110.217(2)°	1126.91(7) Å^3
Theta range for data collection	1111.28(9) Å^3	3, 1.467 mg/m^3
Limiting indices	3, 1.466 mg/m^3	1.458 mm^{-1}
Reflections collected / unique	1.314 mm^{-1}	513
Completeness to theta	510	0.25 x 0.20 x 0.15 mm
Absorption correction	0.30 x 0.25 x 0.20 mm	1.81 to 26.00°
Max. and min. transmission	1.80 to 25.06°	−11<=h<=11,
Refinement method	−10<=h<=10,	−14<=k<=14,
Data / restraints / parameters	−13<=k<=13,	−15<=l<=15
Goodness-of-fit on F^2	−14<=l<=14	23877 / 4430
Final R indices [I>2sigma(I)]	16734 / 3866	R(int) = 0.0285]
R indices (all data)	[R(int) = 0.0451]	100.0 %
Largest diff. peak and hole	98.1 %	Semi-empirical from
	Semi-empirical from	equivalents
	equivalents	0.820 and 0.662
	0.7790 and 0.6939	4430 / 3 / 301
	Full-matrix least-squares on	1.055
	F^2	R1 = 0.0255, wR2 = 0.0667
	3866 / 3 / 298	R1 = 0.0336, wR2 = 0.0736
	1.137	0.265 and −0.199 e. Å^{-3}
	R1 = 0.0395, wR2 = 0.1052	
	R1 = 0.0546, wR2 = 0.1217	
	0.640 and -0.540 e. Å^{-3}	

Single crystal analysis of Ni(II) and Cu(II) complexes

A saturated chloroform solution of Ni(ohapim)$_2$ and dichloromethane and an ethanolic solution of Cu(ohapim)$_2$ were allowed to evaporate slowly to obtain shiny red and dark green needles of the complexes. Single crystals of the compound with dimensions of 0.30 mm × 0.25 mm × 0.2 mm (Ni) and 0.25 mm × 0.20 mm × 0.15 mm (Cu) were chosen for X-ray diffraction studies.

The Cu(II) complex crystallizes in a triclinic system with P$\bar{1}$ space group and 1.5 molecules in the asymmetric unit. **Fig. 2** and **3** show the ORTEP representation of the molecule with the atoms drawn as 40% probability ellipsoids. **Fig. 4** shows the intermolecular hydrogen bonding interaction of the Cu(ohapim)$_2$ complex. **Table 1** gives the data collection and refinement details of the Ni(II) and Cu(II) complexes.

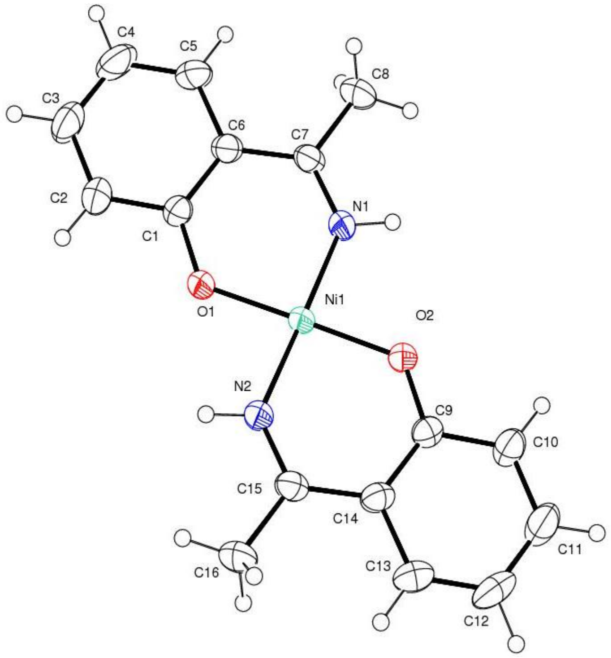


Fig. 2. ORTEP diagram for Ni(ohapim)$_2$.

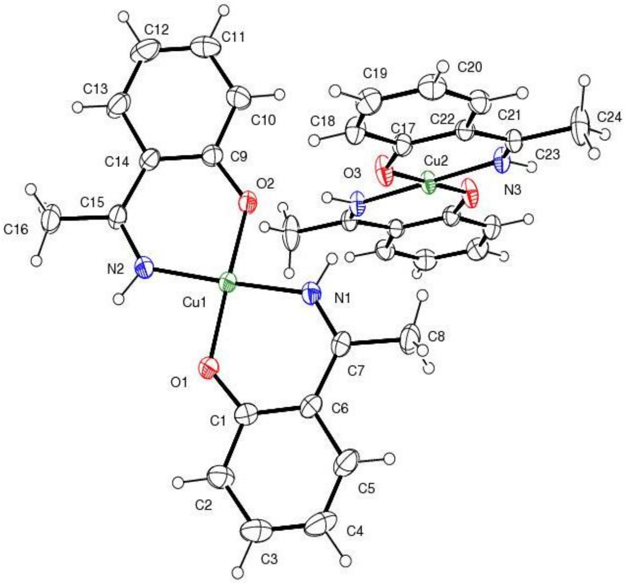


Fig. 3. ORTEP diagram for Cu(ohapim)$_2$.

The coordination around copper is nearly square planar. However, the least squares mean plane calculation shows that there is a small tetrahedral deviation of the coordinating atom from the ideal planarity. The metal atom stays at the centroid of the four coordinating atoms. **Table 2** gives the intermolecular hydrogen bonding interaction.

The selected bond length (Å) and bond angles (°) are given in **Table 3**.

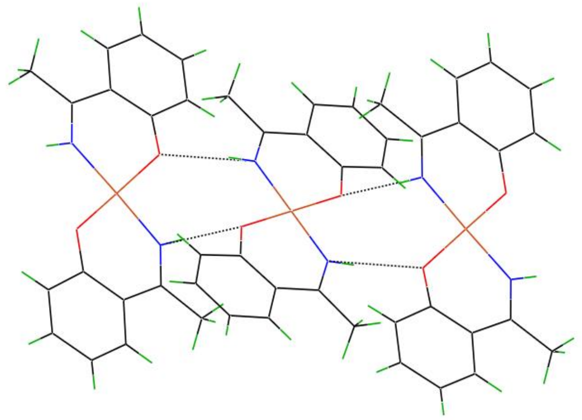


Fig. 4. Intermolecular hydrogen bonding in Cu(ohapim)$_2$.

Table 2. Bond distance and bond angle in hydrogen bonding (Å, °) in Ni(ohapim)$_2$ and Cu(ohapim)$_2$.

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
Ni(ohapim)$_2$				
N(3)-H(3A)...O(1)#1	0.895(10)	2.175(14)	3.057(4)	168.0(4)
	0.889(10)	2.194(12)	3.080(4)	175.0(4)
N(2)-H(2A)...O(3)	0.878(9)	2.146(10)	3.015(2)	170.1(19)
Cu(ohapim)$_2$	0.875(10)	2.178(10)	3.051(2)	176.0(2)
N(3)-H(3A)...O(2)#2				
N(1)-H(1A)...O(3)				

#1: -*x*, -*y*+1, -*z*; #2: -*x*+2, *y*, -*z*+1.

The asymmetric unit along with its inversion form a hydrogen bonded trimer. The hydrogen bonding does not extend through the lattice. Except for the above-mentioned hydrogen bonding, packing is featureless and hence not given. The Ni(II) complex is almost isostructural with that of the Cu(II) complex. The unit cell parameters, packing and hydrogen bonding patterns all remain the same. The coordination around Ni(II) shows less deviation from planarity as compared to the Cu(II) complex. In both complexes, all the hydrogen atoms except the ones belonging to the nitrogen atoms were geometrically fixed at chemically meaningful positions and were allowed to ride over the parent atoms during refinement. The fixed aromatic hydrogen was assigned isotropic parameters, which were 1.2 times the equivalent thermal parameters of the respective parent carbon atoms. The methyl hydrogens were assigned 1.5 times U_{eq} of the parent carbon atoms. The N–H hydrogen atoms were located in the difference Fourier map were refined with N–H distances restrained as 0.90(1) Å. The nitrogen coordination to the nickel centre caused the reduction **(Table 3)** in bond length compared to the copper centre, i.e. Ni(1)-O(1) is 1.823(2) Å and Cu(1)-O(1) is 1.8947(13) Å. The reduction in Ni(1)-O(1) bond length of the Ni(II) complex was effected by the nitrogen coordination for the increase in covalent nature and volatility when compared with the Cu(II) complex.

Table 3. Selected bond length (Å) and angles (°) of Ni(ohapim)$_2$ and Cu(ohapim)$_2$.

Bond length		Bond angle	
	Ni(ohapim)$_2$		
C(1)–O(1)	1.322(4)	**C(7)–N(1)–Ni(1)**	131.4(3)
C(7)–N(1)	1.298(4)	**Ni(1)–N(1)–H(1A)**	120.0(3)
C(17)–O(3)	1.312(4)	**Ni(1)–N(2)–H(2A)**	114.0(3)
N(1)–Ni(1)	1.848(3)	**C(1)–O(1)–Ni(1)**	127.6(2)
N(1)–H(1A)	0.897(10)	**O(1)–Ni(1)–O(2)**	178.06(11)
O(1)–Ni(1)	1.823(2)	**O(1)–Ni(1)–N(2)**	86.38(11)
C(5)-C(6)	1.404(5)	**N(2)–Ni(1)–N(1)**	177.76(13)
C(6)-C(7)	1.444(5)	**O(2)–Ni(1)–N(2)**	93.52(11)
C(7)-C(8)	1.500(5)	**O(1)–Ni(1)–N(1)**	92.79(12)
N(2)-Ni(1)	1.846(3)	**O(2)–Ni(1)–N(1)**	87.38(11)
	Cu(ohapim)$_2$		
C(1) –O(1)	1.310(2)	**C(7)–N(1)–Cu(1)**	130.94(15)
C(7)–N(1)	1.286(3)	**Cu(1)–N(1)–H(1A)**	112.7(15)
C(17)–O(3)	1.306(2)	**Cu(1)–N(2)–H(2A)**	118.1(15)
N(1)–Cu(1)	1.9111(16)	**C(1)–O(1)–Cu(1)**	128.25(13)
N(1)–H(1A)	0.875(10)	**O(1)–Cu(1)–O(2)**	173.49(7)
O(1)–Cu(1)	1.8947(13)	**O(1)–Cu(1)–N(1)**	91.46(7)
C(5)-C(6)	1.416(3)	**N(1)–Cu(1)–N(2)**	175.68(8)
C(6)-C(7)	1.449(3)	**O(2)–Cu(1)–N(2)**	90.58(7)
C(7)-C(8)	1.506(3)	**O(1)–Cu(1)–N(2)**	89.72(7)
N(2)-Cu(1)	1.9207(17)	**O(2)–Cu(1)–N(1)**	88.72(7)

FAB mass spectral study of Ni(II) complex

The mass spectrum of Ni(ohapim)$_2$ shows the pattern of ionized/fragmented species. The mass spectral analysis was carried out to confirm the monomeric nature of the Ni(II) complex in the solid state. The isotopic pattern at m/z = 327 (100%) confirmed the monomeric structure of the complex along with the isotopic abundance (^{58}Ni, ^{60}Ni, ^{61}Ni, ^{62}Ni, ^{64}Ni) of natural nickel. The peaks observed at m/z = 136, 154, 289 and 307 values are due to the m-NBA matrix.

Vapour pressure measurements

The obtained molecular mass of the monomeric precursor vapour species (M = 327 g/mol) was used to calculated equilibrium vapour pressure (p_e) by the following relation by known flow rate of the inert gas:

$$p_e = WRT_c / MV_c \qquad (1)$$

where W is the mass loss (mg) at temperature T (K) due to vaporization, T_c the temperature at which the carrier gas flow rate is measured, V_c (dm^3) the volumetric flow rate of the carrier gas, R is the universal gas constant (8.314 J mol/K) and M (g/mol) is the molecular mass of the monomeric precursor vapour species. When Eq. (1) is used, it is implied that only a single metal precursor species is predominant in the vapour phase and the congruent nature of vaporization is confirmed by their volatility in a smooth single step weight loss to nil residue. The monomeric nature is confirmed by mass spectral analysis. Vapour pressure measurements were then carried out under equilibrium conditions.

The equilibrium vapour pressure (p_e) at each saturation temperature was calculated from the mass of the sample collected within a definite period according to the above relation (eq 1) and the results are summarized in **Table 4**.

Table 4. Vapor pressure data of Ni(ohapim)$_2$.

Run No.	***T*/K**	***W*/mg**	**p_e/Pa**	***ln p_e***	
				Exp.	Cor.*
1	527.86	0.607	0.77	−0.2654	−0.2953
2		0.676	0.85	−0.1578	−0.1056
3	533.02	0.799	1.01	0.0094	0.0743
4	538.13	0.953		0.1856	0.2388
5	543.00	1.158	1.20	0.3805	0.4043
6	548.10	1.380	1.46		0.5627
7	553.18	1.629	1.74	0.5558	0.7176
8	558.35	1.894	2.06	0.7217	0.8654
9	563.48	2.172	2.39	0.8724	1.0071
10	568.59	2.464	2.74	1.0094	1.1423
11	573.65	2.765			1.2759
12	578.84	3.094	3.11	1.1355	1.4094
	584.22		3.49	1.2508	
			3.91	1.3632	

* Correlation based on Antoine coefficients A = 8.45; B = 2033.90; C = −295.19, which are derived from non-linear regression analysis using Solver package in MS-Excel with the initial values of A = 9.3, C =−37 and B = 2000 based on ASTM methods E1719 and E1782 (pressure is in Pa and temperature is in K).

The vapour pressure (Pa) as a function of temperature (K) was fitted into an Antoine expression. The vapour pressure (p_e) obtained from the mass loss of Ni(ohapim)$_2$ yielded a straight line when $\ln p_e$ was plotted against $1/T$ shown in **Fig. 5**. The temperature dependence vapour pressure (p_e) could be represented by the least squares expression:

$$\ln p_e = \frac{-9311.8 \pm 94.5}{T/\mathrm{K}} + 17.4 \pm 0.2 \qquad (2)$$

Multiplying the slope of the Clausius–Clapeyron linear fit expression by $-R$ (8.314 J/mol/K), a value of 77.4 ± 0.8 kJ/mol is derived for the standard molar enthalpy of sublimation ($\Delta_{\mathrm{sub}}H°$) of Ni(ohapim)$_2$. Using the Clausius–Clapeyron expression, the intercept of the resulting straight line gives the standard molar entropies of sublimation ($\Delta_{\mathrm{sub}}S°$). The high entropy of sublimation (144.6 ± 1.7 J/mol/K) and low enthalpy of sublimation of the compound revealed that the compound has appreciable vapour pressure for vapour phase applications. Higher entropy of sublimation and lower enthalpy of sublimation would both contribute towards a higher vapour pressure at constant temperature as observed in the present study. The above equilibrium vapour pressure data will be utilized in the vapour deposition process to calculate the molar flow rate of the precursor material **[20]**. The growth of metal oxide (NiO) or metallic nickel (Ni) thin films in a plasma-assisted MOCVD reactor will constitute the future part of our work using Ni(ohapim)$_2$ as the potential source.

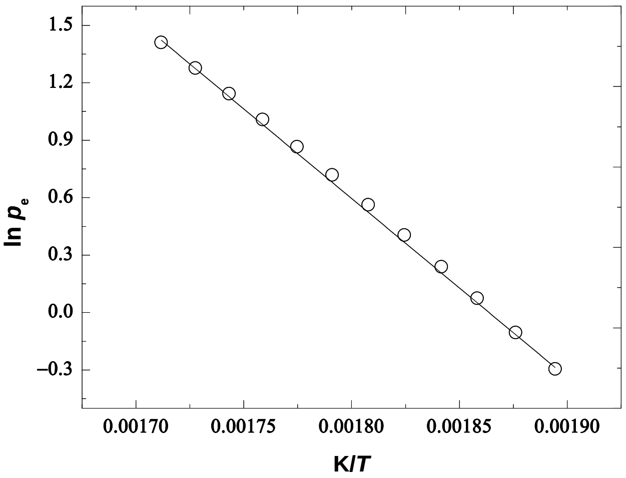


Fig. 5. Clausius–Clapeyron plot for Ni(ohapim)$_2$.

Conclusion

The Schiff's base coordination complexes Ni(ohapim)$_2$ and Cu(ohapim)$_2$ were prepared and crystal structure X-ray analysis was carried out. The complexes were further characterized by using FT-IR, CHN analyses and FABMS studies. The volatility behaviour of the Ni(II) and Cu(II) complexes was elucidated systematically using TG analyses. The reduction in bond lengths of the nickel(II) complex of O(1)–Ni(1) and N(1)–Ni(1) to 1.823(2) and 1.848(3) Å from that of 1.8937(11) and 1.9111(14) Å in the copper(II) complex makes the nickel complex completely volatile than the copper one. Thermal stability (up to 500 K), single-stage weight loss ~520 < T < 630 K, good vapour pressure $p_e = 0.07$–8.81 Pa, low enthalpies of sublimation (77.4 ± 0.8 kJ/mol), and high entropies of sublimation (144.6 ± 1.7 J/mol/K), certified Ni(ohapim)$_2$ as an ideal precursor in the vapour deposition of MOCVD.

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Supplementary Materials

CCDC 787641 and CCDC 826117 contain the supplementary crystallographic data for Cu(ohapim)$_2$ and Ni(ohapim)$_2$ respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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