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Spectral, magnetic and thermal characterization of new Ni(II), Cu(II), Zn(II) and Cd(II) complexes with a bischelate Schiff base

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Abstract The Schiff base *N,N′*-bis-(3-methoxy-salicyliden)-*o*-tolidine (H_2L) derived from *o*-vanillin and 3,3‘-dimethylbenzidine has been synthesized and structurally characterized. The crystal structure shows that the planar molecular units are arranged in sheets assembled through hydrogen bonds and π–π stacking interactions. New Ni(II), Cu(II), Zn(II), and Cd(II) complexes with H_2L were synthesized and characterized by microanalytical, molar conductivities, ESI MS, IR, UV–Vis–NIR, and EPR spectra, magnetic data at room temperature as well as thermal analysis. IR data are in accord with divergent bischelate nature of ligand that coordinates as anion through azomethine nitrogen and phenolic oxygen. The electronic spectra correlated with magnetic susceptibility measurements, and EPR data indicate an octahedral stereochemistry for Ni(II) complex and a tetrahedral one for Cu(II) complex. Processes such as water elimination, thermolyses, and oxidative degradation of Schiff base were evidenced during thermal analysis. All these processes lead to the most stable metallic oxides as final products.

Keywords Complex · *N,N′*-bis-(3-methoxy-salicyliden)-*o*-tolidine · Schiff base · Single crystal · Thermal behavior

Introduction

Multidentate Schiff bases are versatile ligands used in many studies to design the structure of complexes in order to obtain species with desired physicochemical or biological properties. This field grows considerably in last year, starting from the idea that such ligands generate stable complexes with transition metal ions in several oxidation states, sometimes even unusual, as was mentioned in several reviews [1–8].

Among these species, a special attention has been paid to the chemistry of Schiff bases containing supplementary donor atoms beside azomethine nitrogen in suitable positions in the molecule that allow a stabile chelate ring formation. Complexes with such ligand usually can be obtained either by direct synthesis [9–28] or by template condensation [29, 30].

Some species derived from functionalised aromatic carbonyl [9–30] and/or aromatic amines derivatives [9, 11, 12, 15–17, 22, 27] behave as effective and stereospecific catalysts for a variety of reactions that involve both inorganic and organic compounds [31–37]. Moreover, some complexes display antimicrobial [13–18, 25–27], cytotoxic [16–30], SOD-like behavior [18, 19] or antiviral [28] activity. The activity was correlated with the ligand and metallic ions specificity. The complexes exhibit an enhanced activity in comparison with the free ligand [13–30].

Thermal behavior was studied, both in dry air and nitrogen, for some complexes with ligands derived from *o*-vanillin [23–29, 38–43] or 3,3‘-dimethylbenzidine [44–47]. These studies show the presence of the (crystallization and/or coordination) water molecules as well as the Schiff base

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pyrolysis in one or more steps depending on metallic ion and Schiff base structure [23–25, 38–47]. The non-isothermal kinetic data were analyzed by means of differential and integral methods, and the possible mechanism for some steps of thermal decomposition was proposed for complexes with Schiff base derived from *p*-toluidine and *o*-vanillin [40].

Data concerning synthesis, structure characterization, and thermochemical parameters calculated by microcalorimetry were recently reported for a praseodymium(III) and copper(II) complex with Schiff bases derived from *o*-vanillin [48, 49].

Results concerning the synthesis of new complexes with the tetradentate bischelate Schiff base *N*,*N*′-bis-(3-methoxy-salicyliden)-*o*-toluidine (H_2L) are reported in this work. The reaction of this ligand with nickel(II), copper(II), zinc(II), and cadmium(II) chloride in 1:2 molar ratio in alkaline medium yield four new polynuclear complexes. The details of synthesis, spectral, magnetic, and thermal behavior of these compounds are described in the following, together with the structure analysis for the ligand.

Experimental

Materials

The high-purity reagents were commercially purchased from Sigma-Aldrich ($NiCl_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $ZnCl_2 \cdot 2H_2O$, $CdCl_2 \cdot 2H_2O$), Merck (*o*-vanillin), ICN Biomedicals (3,3‘-dimethylbenzidine), and Fluka (triethylamine) and were used as received without further purification.

Instruments

Chemical analyses of carbon, nitrogen, and hydrogen were performed using a PerkinElmer PE 2400 analyzer. The metal ion content was determined volumetrically by using complexometric or iodometric method, respectively.

Mass spectra were recorded by electrospray ionization tandem mass spectrometry (ESI–MS) technique operating in the negative ion mode. The sample was dissolved in methanol–water (1:1) containing 0.2 % formic acid and the solution was injected with 0.2 mL min^{-1} flow directly in Agilent triple quadrupole mass spectrometer with an electrospray interface.

IR spectra were recorded in KBr pellets with a Bruker Tensor 37 spectrometer in the range 400–4000 cm^{-1}.

Electronic spectra by diffuse reflectance technique, with spectralon as standard, were recorded in the range 200–2000 nm, on a JASCO V670 spectrophotometer.

The molar conductance was determined for 10^{-3}M solutions of complexes in DMSO with a multi-parameter analyzer CONSORT C861.

Magnetic measurements were done by Faraday's method, at room temperature, using $Hg[Co(NCS)_4]$ as standard. The molar magnetic susceptibilities were calculated and corrected for the atomic diamagnetism. EPR spectra were recorded on microcrystalline samples at room temperature with a Varian E-9 spectrometer. The field was calibrated using crystalline diphenylpicrylhydrazyl ($g = 2.0036$).

The heating curves (TG, DTG and DTA) were recorded using a Labsys 1200 SETARAM instrument, with a sample mass of 7–12 mg over the temperature range of 20–900 °C with a heating rate of 10 K min^{-1}. The measurements were carried out in synthetic air atmosphere (flow rate 17 cm^3 min^{-1}) by using alumina crucibles.

The single-crystal X-ray diffraction measurement was made on a diffractometer Rigaku R-AXIS RAPID II, using Mo-Kα radiation. For crystal data collection and refinement, a red platelet crystal of $C_{30}H_{28}N_2O_4$(H_2L) having approximate dimensions of 0.500 × 0.200 × 0.050 mm was mounted on a glass fiber. Cell constants and an orientation matrix for data collection were obtained from a least-squares refinement using the setting angles of 12904 carefully centered reflections in the range $6.00 < 2\theta < 55.00°$ corresponding to a primitive monoclinic cell. The data were collected at a temperature of 22 ± 1 °C using the ω scan technique to a maximum 2θ value of 55.0°. Of the 27889 reflections that were collected, 8291 were unique ($R_{int} = 0.0427$). No decay correction was applied. The linear absorption coefficient, μ, for Mo-Kα radiation is 0.875 cm^{-1}. The data were corrected for Lorentz and polarization effects. The structure was solved by direct methods [50] and expanded using Fourier techniques. The non-hydrogen atoms were refined anisotropically. Some hydrogen atoms were refined isotropically, and the rest were refined using the riding model. The final cycle of full-matrix least-squares refinement on F^2 was based on 8291 observed reflections and 511 variable parameters and converged (largest parameter shift was 0.00 times its esd) with unweighted and weighted agreement factors of: $R_1 = \Sigma||Fo| - |Fc||/\Sigma|Fo| = 0.1005$; $wR_2 = [\Sigma(w(Fo^2 - Fc^2)^2)/\Sigma w(Fo^2)^2]^{1/2} = 0.2305$. The standard deviation of unit weight [least-squares function minimized: (SHELXL97) $\Sigma w(Fo^2 - Fc^2)^2$[where w = least-squares weights] was 0.95. Unit weights were used. The maximum and minimum peaks on the final difference Fourier map correspond to 0.26 and −0.27 e/$Å^3$, respectively. Neutral atom-scattering factors were taken from Cromer and Waber [51]. Anomalous dispersion effects were included in *F*calc [52]; the values for $\Delta f'$ and $\Delta f''$ were those of Creagh and McAuley [53]. The values for the mass attenuation coefficients are those reported by Creagh and Hubbell [54]. All calculations were performed using the Crystal Structure [55] crystallographic software package except for refinement, which was performed using SHELXL-97 [56]. CCDC reference number is 1434413 and contains the supplementary crystallographic data for this compound.

Synthesis and analytical data of ligand and complexes

H_2L: The ligand was synthesized as described in the literature [46] by the following procedure: 10 mmol of 3,3‘-dimethylbenzidine in 50 mL ethanol was added dropwise to an ethanol solution containing 20 mmol of *o*-vanillin and few drops of acetic acid. The yellow solution obtained was refluxed for 2 h. The product resulted after cooling was washed with ethanol, and its purity was checked by elemental analysis, ^{1}H NMR and IR (KBr). Single crystals suitable for X-ray diffraction were obtained from the slow evaporation of a methanolic solution.

$[Ni_2LCl_2(OH_2)_6]$ (**1**): To a solution containing 0.480 g (1 mmol) *N,N′*-bis-(3-methoxy-salicyliden)-*o*-tolidine (H_2L) dissolved in 30 mL tetrahydrofuran in presence of 1 mL triethylamine was dropwise added a solution of 0.475 g (2 mmol) nickel(II) chloride hexahydrate in 20 mL ethanol. The reaction mixture was refluxed for 2 h until the color was modified. A sparingly soluble species brown colored was formed after the solution was cooled at room temperature and the volume was reduced at half by slow evaporation. The solid product formed was filtered off and washed with hot ethanol and benzene and then with cold diethyl ether. The product was dried under vacuum at room temperature. Yield 74 %.Analysis found: Ni, 15.09; C, 46.62; H, 4.86; N, 3.72, $NiC_{30}H_{38}N_2O_{10}Cl_2$ requires: Ni, 15.15; C, 46.50; H, 4.94; N, 3.61 %.

The other complexes of the series were obtained by the same method.

$[Cu_2LCl_2]$ (**2**): Yield 72 %. Analysis found: Cu, 18.63; C, 53.32; H, 4.08; N, 3.92, $CuC_{30}H_{26}N_2O_4Cl_2$ requires: Cu, 18.79; C, 53.26; H, 4.14; N, 3.87 %.

$[Zn_2LCl_2]$ (**3**): Yield 68 %. Analysis found: Analysis found: Zn, 19.19; C, 53.02; H, 3.86; N, 4.17, $ZnC_{30}H_{26}N_2O_4Cl_2$ requires: Zn, 19.23; C, 52.97; H, 3.85; N, 4.12 %.

$[Cd_2LCl_2]$ (**4**): Yield 65 %. Analysis found: Cd, 28.96; C, 46.60; H, 3.36; N, 3.72, $CdC_{30}H_{26}N_2O_4Cl_2$ requires: Cd, 29.04; C, 46.54; H, 3.38; N, 3.62 %.

Several crystallization methods were applied for the obtained complexes without any results in obtaining suitable single crystals.

Results and discussions

Synthesis and physicochemical characterization of ligand and complexes

Tetradentate ligand (H_2L) having a divergent ONNO donor atom set was synthesized by [1 + 2] condensation of 3,3′-dimethylbenzidine with *o*-vanillin in ethanol as reported [32]. Nickel(II), copper(II), zinc(II), and cadmium(II) complexes with Schiff base were obtained from refluxing an ethanol solution of ligand and hydrated metal(II) (M: Ni, Cu, Zn, Cd) chloride in a 1:2 molar ratio, in the presence of triethylamine. The elemental analyses (experimental part) confirm the 1:2 ligand to metal stoichiometry for all complexes. All complexes behave as non-electrolytes in DMSO [57]. The compounds were formulated as $[Ni_2LCl_2(OH_2)_6]$ (**1**), $[Cu_2LCl_2]$ (**2**), $[Zn_2LCl_2]$ (**3**), and $[Cd_2LCl_2]$ (**4**), respectively on the basis of IR, UV–Vis–NIR, EPR, magnetic susceptibility at room temperature as well as thermal analysis data.

Description of *N,N′*-bis-(3-methoxy-salicyliden)-*o*-tolidine structure

A summary of the crystallographic data and structure refinement is given in Table 1. The asymmetric unit (Fig. 1) contains one disordered molecule (Fragment 1) and half of another molecule which, based on the symmetry operations, generates another, more symmetric, species (Fragment 2). In the Fragment 1 the central phenyl rings are mutually tilted by 34.31° and form with the o-vanillin unit torsion angles of 31.17° (C8–N1–C9–C10) and 30.86° (C23–N2–C19–C20), respectively. In the

Table 1 Summary of crystallographic data

Chemical formula	$C_{30}H_{28}N_2O_4$
M_w	480.56
Crystal system	Monoclinic
Space group	$P2_1/n$ (#14)
a/Å	7.1157 (4)
b/Å	27.862 (2)
c/Å	18.496 (2)
β/°	96.987 (7)
Volume/Å^3	3639.9 (4)
Z	6
R_1	0.0562
wR_2	0.1997
Goodness of fit	0.949

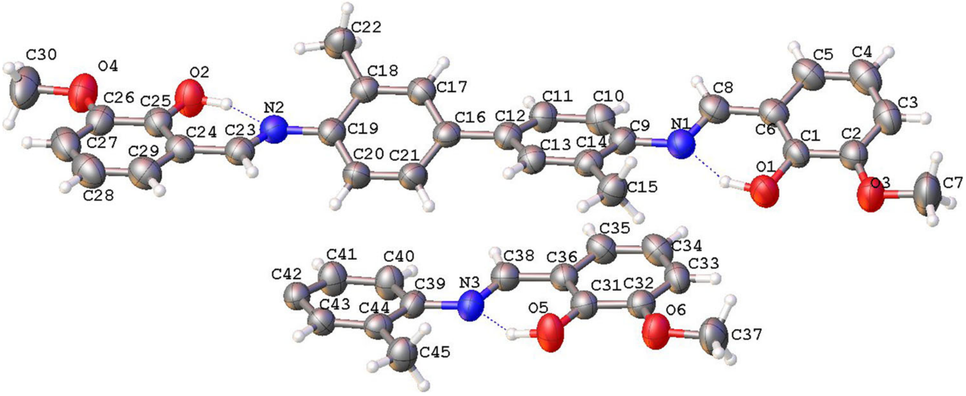


Fig. 1 ORTEP view of the asymmetric unit for *N,N′*-bis-(3-methoxy-salicyliden)-*o*-tolidine with the atom numbering scheme (50 % probability of thermal ellipsoids)

Fragment 2, the *o*-tolidine moiety is planar and forms with the *o*-vanillin unit a torsion angle of 15.35° (C38–N3–C39–C40). Selected bond distances and angles for *N,N′*-bis-(3-methoxy-salicyliden)-*o*-tolidine are listed in Table 1S (Supplementary material). The single N–C bonds (N1–C9: 1.426(3) Å; N2–C19: 1.415(3) Å; N3–C39: 1.419(3) Å) are longer than the O–C ones (O1–C1: 1.352(4) Å; O2–C25: 1.342(4) Å; O5–C31: 1.348(4) Å). The double N=C bonds from the azomethine groups (N1–C8: 1.277(4) Å; N2–C23: 1.295(4) Å; N3–C38: 1.282(4) Å) agree well with those reported for other Schiff bases containing the *o*-vanillin moiety [58–60].

The structure consists of layers containing the Schiff base molecules connected through hydrogen bonds and π–π stacking interactions (see packing details and comments in the Supplementary material).

Infrared, NMR and ESI MS spectral data

The IR selected bands of Schiff base and complexes are listed in Table 2. The fundamental stretching mode of the azomethine moiety *ν*(C=N) from 1615 cm^{-1} in the spectrum of Schiff base was assigned based on comparison with the infrared spectra of 3,3‘-dimethylbenzidine and *o*-vanillin. A strong band around 1600 cm^{-1} can be observed in all complexes spectra, shifted to lower wavenumbers in comparison with the spectrum of the free ligand. Such a modification supports the fact that the azomethine nitrogen is involved in coordination [19–47].

At 1253 cm^{-1} appears a strong band in the ligand spectrum that arises from stretching vibration ν(C–O) of the phenolic group. This band is also shifted by 6–14 cm^{-1} to lower wavenumbers in complexes spectra suggesting that this deprotonated group is involved also in coordination [11, 19–43]. Furthermore, the band at 3444 cm^{-1} in the Schiff base spectrum disappears in anhydrous complexes spectra as result of ligand deprotonation at both phenolic groups. Instead, a broad band about 3420 cm^{-1} in the spectrum of complex (**1**) was assigned to ν(OH) stretching vibration of water molecules [61], their presence being confirmed otherwise by both elemental and thermal analyses.

New bands of low intensity in the ranges 430–450 and 506–530 cm^{-1} can be assigned to stretching vibrations ν(M–O) and ν(M–N), respectively [11, 45].

Table 2 Absorption maxima (cm^{-1}) from IR spectra and assignements for the Schiff base and complexes (**1**)–(**4**)

Compound	ν(OH)	ν(C=N)	ν(C–O)	ν(M–O)	ν(M–N)
H_2L	3440m	1615s	1253vs	–	–
$[Ni_2LCl_2(OH_2)_6]$ (**1**)	3420s	1610vs	1239vs	446w	420w
$[Cu_2LCl_2]$ (**2**)	–	1609vs	1245vs	475w	419w
$[Zn_2LCl_2]$ (**3**)	–	1609vs	1247vs	490w	448w
$[Cd_2LCl_2]$ (**4**)	–	1604vs	1242vs	485w	434w

vs very strong, *s* strong, *m* medium, *w* weak

Table 3 Absorption maxima (cm^{-1}) from electronic spectra of ligand and complexes (**1**)–(**4**), assignments, and magnetic moments

Compound	Absorption maxima/cm^{-1}	Assignment	Crystal field parameters			Magnetic moment/B.M.
			10Dq	*B*	*β*	
H_2L	42,550	$\pi \rightarrow \pi^*$	–	–	–	–
	25,345					
	19,800					
$[Ni_2LCl_2(OH_2)_6]$ (**1**)	37,040	$\pi \rightarrow \pi^*$				
	25,640					
	20,000	$^3A_{2g} \rightarrow {}^3T_{1g}$ (P)	8440	887	0.85	3.18
	15,270	$^3A_{2g} \rightarrow {}^3T_{1g}$ (F)				
	8440	$^3A_{2g} \rightarrow {}^3T_{2g}$				
$[Cu_2LCl_2]$ (**2**)	37,740	$\pi \rightarrow \pi^*$	–	–	–	2.12
	25,975					
	19,600					
	10,420	$d_{xy} \rightarrow d_{xz}, d_{yz}$				
$[Zn_2LCl_2]$ (**3**)	38,460	$\pi \rightarrow \pi^*$	–	–	–	–
	26,660					
	21,050					
$[Cd_2LCl_2]$ (**4**)	39,215	$\pi \rightarrow \pi^*$	–	–	–	–
	24,100					
	18,870					

Table 4 Thermal behavior data (in air) for Schiff base and complexes

Compound	Step	Thermal effect	Temperature range/°C	Δm_{exp}/%	Δm_{calc}/%	Process
$[Ni_2LCl_2(OH_2)_6]$ (**1**)	1.	Endothermic	100–180	14.8	14.6	Water elimination
	2.	Endothermic	180–264	9.5	9.6	Chloride elimination
	3.	Exothermic	264–425	14.3	14.2	Oxidative degradation of C_6H_2–OCH_3 fragment
	4.	Exothermic	425–665	34.3	34.5	Oxidative degradation of C_6H_4–OCH_3 and $(C_6H_3$–$CH_3)_2$ fragments
	5.	Exothermic	665–835	6.8	7.0	Oxidative degradation of CN fragment
$[Cu_2LCl_2]$ (**2**)	1.	Exothermic	175–230	5.3	5.2	Chloride elimination
	2.	Exothermic	230–900	71.5	71.3	Chloride elimination and oxidative degradation of Schiff base
$[Zn_2LCl_2]$ (**3**)	1.	Exothermic	265–345	12.3	12.6	Chloride elimination and oxidative degradation of Schiff base
	2.	Exothermic	345–485	21.4	21.9	Oxidative degradation of C_6H_4–OCH_3, OCH_3 and CH_3 fragments
	3.	Exothermic	485–850	42.4	41.6	Oxidative degradation of the rest of Schiff base
$[Cd_2LCl_2]$ (**4**)	1.	Exothermic	258–350	11.0	11.1	Chloride elimination and oxidative degradation of Schiff base
	2.	Exothermic	350–565	18.9	19.3	Oxidative degradation of C_6H_4–OCH_3, OCH_3 and CH_3 fragments
	3.	Exothermic	565–900	37.0	36.4	Oxidative degradation of the rest of Schiff base

The Schiff base structure was confirmed by the ^1H NMR and ^{13}CNMR spectra.

Due to the low solubility of complexes in all deuterated solvents, it was not possible to acquire any information for the diamagnetic complexes.

ESI–MS data for complexes were acquired in negative mode and confirmed both the composition of the complexes core and the stoichiometric ratio. The pseudomolecular ions for complexes were found as $[M + 3OH–3H_2O]^-$ (*m/z*, calc./exp: 717.20/717.85) for (**1**), $[M + 3OH + 2CH_3OH]^-$

(*m/z*, calc./exp: 823.67/823.85) for (**2**), $[M + 3OH]^-$ (*m/z*, calc./exp: 823.67/823.85) for (**3**) and $[M + 3OH + CH_3CN]^-$ (*m/z*, calc./exp: 866.35/866.62) for (**4**), respectively.

Electronic, EPR spectra, and magnetic moments

Electronic spectra correlated with magnetic moments at room temperature provide useful information concerning the oxidation state of the metallic ion, the stereochemistry, and the ligand field strength. Table 3 lists the absorption bands observed in the solid state electronic spectra and magnetic moments of complexes at room temperature.

In the Schiff base spectrum, three bands appear in 19,800–42,000 cm^{-1} range and are assigned to intraligand $\pi \rightarrow \pi^*$ transitions. These bands are different shifted in complexes spectra as result of coordination.

Electronic spectrum of Ni(II) complex (**1**) show the pattern of the octahedral geometry. The two bands usually observed in the NIR and visible regions assigned to spin allowed transitions $^3A_{2g} \rightarrow {}^3T_{2g}$ and $^3A_{2g} \rightarrow {}^3T_{1g}$ (F) are broad as result of distortion generated by the different nature of donor atoms. The small value of the splitting parameter indicates a low field created by oxygen and chloride as donor atoms [62]. The value of nephelauxetic

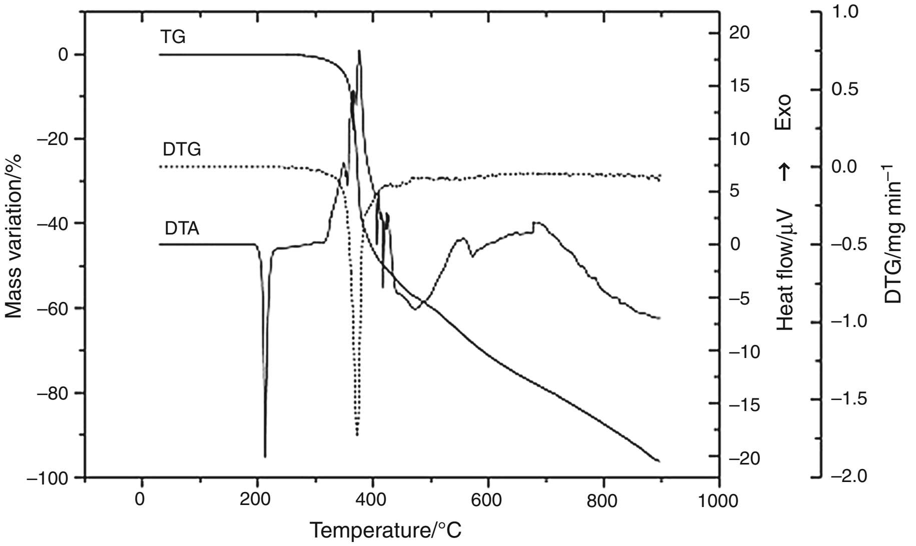


Fig. 2 TG, DTG, and DTA curves for *N,N′*-bis-(3-methoxy-salicyliden)-*o*-tolidine

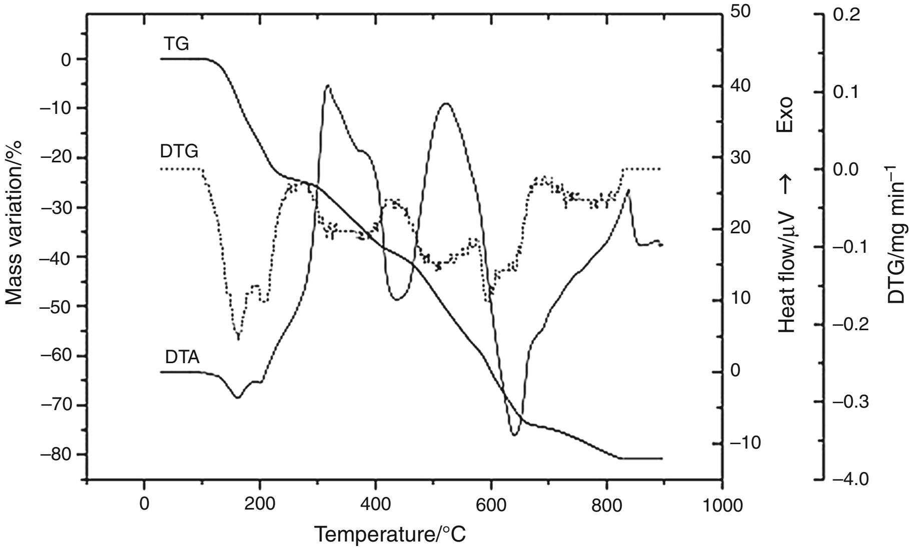


Fig. 3 TG and DTA curves for $[Ni_2LCl_2(OH_2)_6]$ (**1**)

Fig. 4 TG and DTA curves for $[Cu_2LCl_2]$ (**2**)

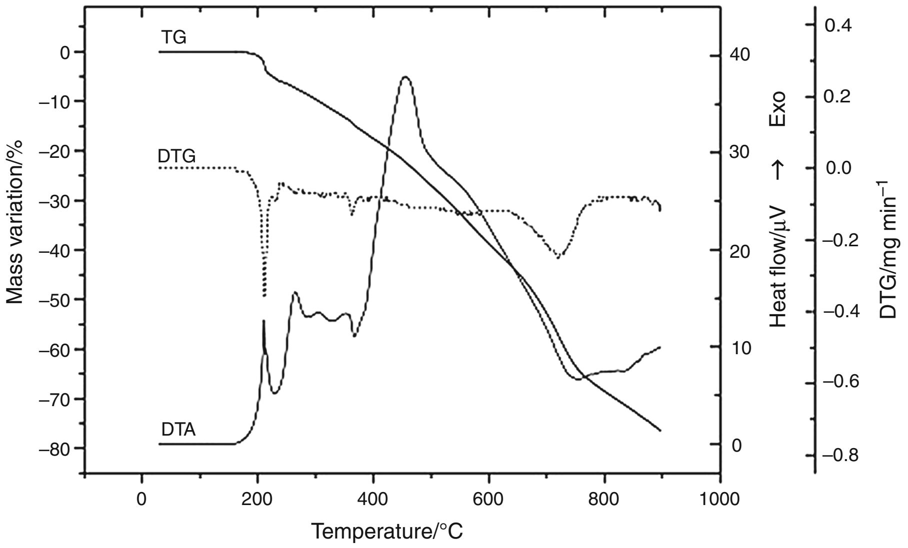
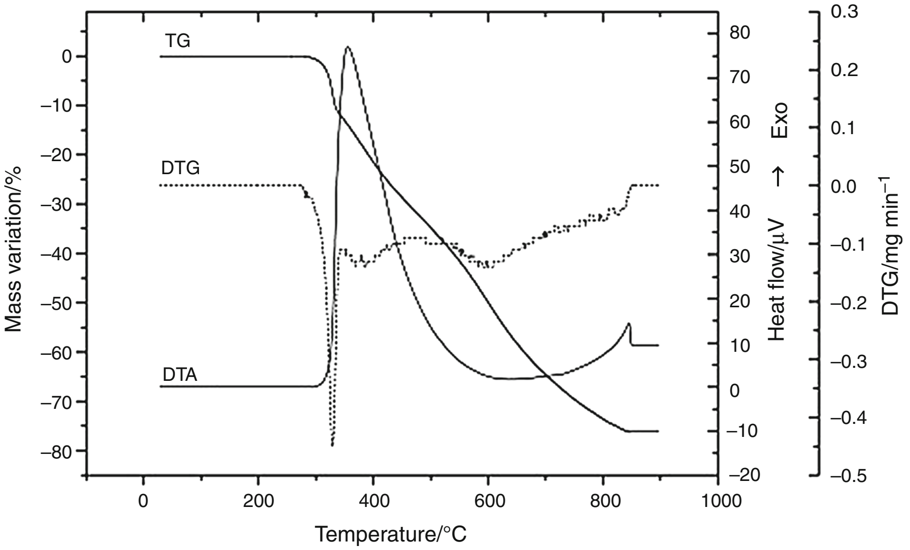


Fig. 5 TG and DTA curves for $[Zn_2LCl_2]$ (**3**)



parameter indicates a high degree of covalency as result of interaction with nitrogen and chloride donor atoms. The room-temperature magnetic moment of this complex was found to be 3.18 B.M. as is usual observed for two unpaired electrons and an A ground term.

The electronic spectrum of complex (**2**) shows a broad band at 10,420 cm^{-1} with a shoulder at lower value, pattern characteristic for a tetrahedral distorted geometry. The experimental value of the magnetic moment for Cu(II) complex of 2.12 B.M. is typical found for Cu(II) compounds with isolated paramagnetic ions [63].

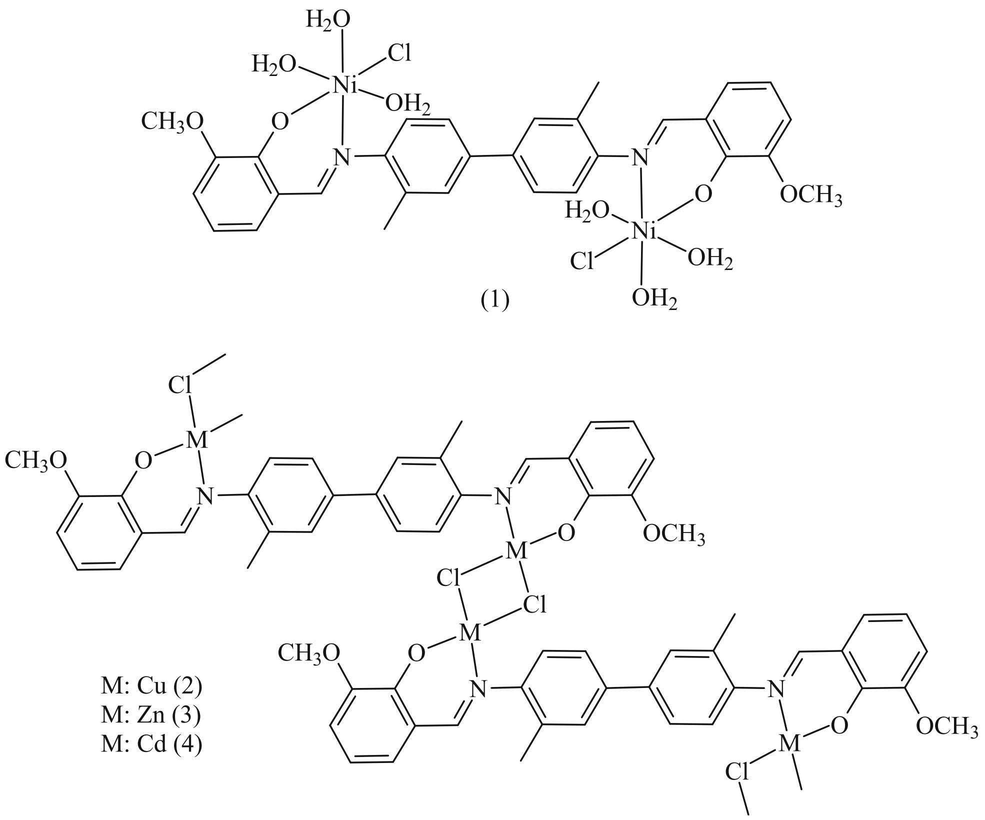
The EPR spectrum of Cu(II) complex was recorded both at room temperature (293 K) and at liquid nitrogen one (77 K). Since the signals are similar, the geometry around the copper ion is not drastically affected by cooling. The EPR signal at room temperature is wide (300 G) and centered at g_{iso} of 2.117 and on cooling becomes $g_{iso} = 2.123$. These features are specific for Cu(II) ions in a pseudo-tetrahedral surrounding [64].

Thermal behavior of *N,N′*-bis-(3-methoxy-salicyliden)-*o*-tolidine and complexes

Thermal analyses data (TG, DTG and DTA) of the Schiff base and its complexes were used to obtain information about the thermal stability of these species as well as to verify the presence and status of water molecules. The thermal decomposition data are summarized in Table 4 and will be discussed as follows.

The Schiff base melts at 186 °C, is stable up to 295 °C and then decomposes in one step (Fig. 2). The decomposition occurs

Fig. 6 Coordination proposed for complexes



in several overlapped processes accompanied by exothermic effects according with DTA curve. The small amount of black final residue results by unoxidized aromatic moieties.

The TG, DTG and DTA curves corresponding to complex (**1**) indicate that decomposition follows five well defined steps (Fig. 3). Chemical analysis indicates the presence of three water molecules per metal ion and this is furthermore confirmed by the thermal behavior. The water molecules elimination occurs in one well defined step in the range 100–180 °C showing that they are involved in coordinative sphere [65]. Anhydrous species is not stable and its decomposition proceeds immediately with chloride anion elimination. Differential thermal analysis (DTA) curve shows two strong exothermic events for the third step. According to the mass loss, one methoxybenzyl moiety is eliminated from the ligand in this step. The decomposition proceeds with oxidative degradation of the organic matrix up to azomethine bonds and a strong exothermic effect can be noticed on DTA curve. In the last step occurs the oxidative degradation of the remaining part of Schiff base and as result, several overlapped processes can be observed on DTA curve in 677–835 °C range. According to overall mass loss the final residue is NiO (found/calcd. overall mass loss: 79.7/79.9 %).

Complex (**2**) is anhydrous and is stable up to 175 °C, after this temperature one chloride anion being eliminated in one step process accompanied by an endothermic effect (Fig. 4). The other chloride anion elimination is overlapped with fragmentation and oxidative degradation of the Schiff base. The small exothermic peaks observed at the beginning of this step can be assigned to the competition of both endothermic and exothermic reactions that occur simultaneously such as cleavage and rearrangement of the bonds as well as some moieties oxidative degradation. According with DTA curve, at least six overlapped processes occur until the CuO is formed (found/calcd. overall mass loss: 76.2/76.5 %).

The decomposition of complex (**3**) starts with both chloride and methyl elimination according with the mass loss (Fig. 5). The step is well delimitated on DTG curve, but the effects are overlapped on DTA curve by the strong exothermic effect that accompany the oxidative degradation of the Schiff base, which starts immediately. This second step consists in oxidative degradation of methyl, methoxy, and methoxybenzyl groups, respectively. The decomposition proceeds with oxidative degradation of the rest of organic matrix and leads to ZnO as residue at 865 °C (found/calcd. overall mass loss: 76.1/76.1 %).

For Cd(II) complex (**4**) thermal decomposition follows the same pattern as for the Zn(II) one, the processes being not well delimitated on the DTA curve. The chloride elimination, fragmentation and oxidative degradation of Schiff base end with CdO formation (found/calcd. overall mass loss: 66.9/66.8 %).

Based on these data complexes can be formulated as presented in Fig. 6.

Conclusions

Direct reaction of metal chloride with Schiff base *N,N′*-bis-(3-methoxy-salicyliden)-*o*-tolidine(H_2L) in alkaline medium allows the synthesis of new complexes $[M_2LCl_2(OH_2)_n]$ (M:Ni, $n = 6$; Cu, Zn, Cd, $n = 0$).

The Schiff base acts as chelate through azomethine nitrogen and phenolic oxygen as IR spectra indicate. Complexes display octahedral or tetrahedral stereochemistry in accordance with UV–Vis–NIR spectra features, magnetic data at room temperature and EPR spectrum, respectively.

Thermal investigations evidenced the presence of coordinated water molecules for complex (**1**) and the anhydrous nature for the others. Anhydrous species suffer oxidative degradation of Schiff base leading to the most stable metal oxide as final product.

For the anhydrous species the beginning temperature of the thermal decomposition increases in order Cu(II) < Ni(II) < Zn(II) < Cd(II). This behavior could be correlated with the ionic radius increasing which leads to relaxation of the steric impediments in a tetrahedral stereochemistry.

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