

Synthesis and Spectral Characterization of Mono- and Homodinuclear Complexes of Co(II), Ni(II), and Cu(II) with a Compartmental Hexadentate Schiff Base Ligand Derived from 3-Formylsalicylic Acid

ESAM ABD EL-MALEK ABD-ALLAH ORABI

Chemistry Department, Faculty of Science, Assiut University, Assiut, 71516, Egypt.

(Received on 13th March 2010, accepted in revised form 5th May 2010)

Summary: Reaction between 3-formylsalicylic acid and 4,5-dichloro-1,2-phenylenediamine gave a compartmental hexadentate Schiff base ($H_4fsacph$) with an N_2O_4 donor frame involving an inner N_2O_2 set of donors and an outer set of O_2O_2 donors. Three mononuclear complexes of the form $M(H_2fsacph)(H_2O)_2$ ($M = Co(II), Ni(II), Cu(II)$), and three homodinuclear complexes $M'_2(fsacph)(H_2O)_2$ ($M' = Co(II), Ni(II)$) and $Cu_2(fsacph)$ were isolated and analyzed by physico-chemical techniques. The metal ions have been found to occupy the outer coordination site in the mononuclear complexes and occupy both sites in the dinuclear complexes.

Introduction

Interest in multidentate acyclic/macrocyclic compounds is continually increasing [1-14] because of their unique properties and use in the synthesis of polynuclear metal complexes. The chemistry of metal complexes of Schiff base ligands has been extensively studied since late 19th century [15-18]. Recently much attention has been focused in the synthesis and characterization of multimetallic complexes involving polydentate and compartmental ligands [19-25]. The compartmental ligands are capable of forming both mono and poly-nuclear metal complexes by binding one metal ion in any compartment and one or more metal ions in close proximity in the other compartment [14, 25-31]. 3-Formylsalicylic acid has been used to prepare compartmentalized Schiff bases of amines, diamines and other amines for the last three decades [12-14, 32-35]. The polymetallic complexes of these Schiff bases can show their profound activity in different fields like bioinorganic chemistry, materials science, and catalysis [36-42]. In present days the polynuclear complexes are being used as luminescent compounds [43].

In view of the above facts and in continue to our studies on 3-formylsalicylic acid [44-46] we report here the synthesis, characterization and magnetic properties of the mono- and homodinuclear metalcomplexes of the compartmental hexadentate Schiff base ligand synthesized *via* condensation of 3-formylsalicylic acid with 4,5-dichloro-1,2-phenylenediamine. It should be mentioned that, despite our best efforts we could not grow suitable crystals to study the X-ray crystal structures of the complexes.

Results and Discussion

The ligand was obtained by condensation of 4,5-dichloro-1,2-phenylenediamine and 3-formylsalicylic acid and is abbreviated as $H_4fsacph$. It acts as a hexadentate ligand of N_2O_4 donor centers with two imine nitrogens, two phenolato oxygens, and two carboxylato oxygens as coordinating agents. All the mononuclear complexes were synthesized *via* the reaction of the dilithium salt of the ligand, $Li_2H_2fsacph$, and corresponding metal(II) chloride in 1:1 molar ratio in methanol. The homodinuclear complexes were synthesized by reacting the tetralithium salt of the ligand, $Li_4fsacph$, with the metal(II) chloride in 1:2 molar ratio in methanol. The formation of the mono- and dinuclear complexes is supported by the analytical and spectral data. The complexes are insoluble in common organic solvents, but soluble in coordinating solvents like DMSO and DMF. Two molecules of water are lost on heating the mononuclear complexes and the homodinuclear complexes of Co(II) and Ni(II) in the temperature range 120–150 °C, while no loss of water molecules occurs in case of the homodinuclear complex of Cu(II) complex. These data are in good agreement with the elemental analyses of these complexes (Table-1). The complexes are all found to be non-conducting in DMF solution (10^{-3} M) (Table-1). The slightly higher molar conductance of the mononuclear complexes relative to the dinuclear complexes is attributed to the weak acidic character of the phenolic group in the mononuclear complexes. Molecular weights of the complexes (Table-1) were estimated following Rast method [47], and are also in conformity with the formulations.

Table-1: Some characterization data of the uni- and dinuclear complexes.

Compound	Colour	Mol. wt. found (calculated)	Elemental analyses, found (calculated) (%)				Λ_M^a ($\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$)
			C	H	N	M	
[Co(H ₄ fsacph)(H ₂ O) ₂] C ₂₂ H ₁₆ N ₂ O ₈ Cl ₂ Co	Brown	573 (566.21)	46.61(46.67)	2.91(2.85)	5.05(4.95)	10.54(10.41)	35.6
[Ni(H ₄ fsacph)(H ₂ O) ₂] C ₂₂ H ₁₆ N ₂ O ₈ Cl ₂ Ni	Reddish-brown	581 (565.97)	46.75(46.69)	2.81(2.85)	4.90(4.95)	10.35(10.41)	36.8
[Cu(H ₄ fsacph)(H ₂ O) ₂] C ₂₂ H ₁₆ N ₂ O ₈ Cl ₂ Cu	Green	561 (570.83)	46.13(46.29)	2.78(2.83)	4.84(4.91)	10.96(11.13)	37.5
[Co ₂ (fsacph)(H ₂ O) ₂] C ₂₂ H ₁₄ N ₂ O ₈ Cl ₂ Co ₂	Dark brown	630 (623.13)	42.28(42.40)	2.18 (2.26)	4.48(4.50)	19.06(18.92)	5.4
[Ni ₂ (fsacph)(H ₂ O) ₂] C ₂₂ H ₁₄ N ₂ O ₈ Cl ₂ Ni ₂	Dark red	614 (622.65)	42.23(42.44)	2.34(2.27)	4.52(4.50)	18.78(18.85)	6.2
[Cu ₂ (fsacph)] C ₂₂ H ₁₀ N ₂ O ₈ Cl ₂ Cu ₂	Dark Green	588 (596.33)	44.29(44.31)	1.71(1.69)	4.77(4.70)	21.16(21.31)	3.5

^a 10⁻³ M in DMF

Mononuclear Complexes

Analytical data support the formation of the mononuclear complexes having the metal ion in the outer O₂O₂ compartment while the inner N₂O₂ is unoccupied.

Infrared Spectra of Mononuclear Complexes

The important infrared bands for the three mononuclear complexes are summarized in Table-2. No free carboxyl group band is observed in the region 1690–1720 cm⁻¹ in all the mononuclear complexes which is located at 1705 cm⁻¹ in the free ligand. Instead, a new band appeared in the region 1580–1590 cm⁻¹, which may be attributed to the stretching frequency of the coordinated carboxylate group [48, 49]. The $\nu(\text{C}-\text{O})$ (phenolic) appears at 1520 cm⁻¹ in the free Schiff base and at 1540–1560 cm⁻¹ in the mononuclear complexes indicating that the phenolato-O is single bonded to the metal ions [50, 51]. The three complexes show a sharp stretch assigned to $\nu(\text{C}=\text{N})$ at ~1655 cm⁻¹ which is close to the free ligand band, supporting no coordination of azomethine nitrogen. All the complexes exhibit a broad band in the 3400–3470 cm⁻¹ region, indicating the presence of coordinated water molecules. This band disappeared in the spectra of the complexes when heated up to 170 °C which can be used as evidence for the presence of coordinated water molecules in all of the mononuclear complexes. Thus it may be concluded that in the mononuclear complexes the ligand H₄fsacph functions as a dibasic tetradentate ligand having the O₂O₂ outer compartment being occupied by the metal ions (Fig. 1). Previous studies [9, 51-54] on structurally similar

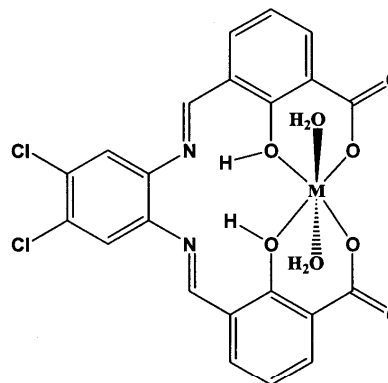


Fig. 1: Proposed structural formula for the mononuclear complexes, M = Co²⁺, Ni²⁺, or Cu²⁺.

ligands to H₄fsacph indicated that the metal in the mononuclear complexes occupies the N₂O₂ inner compartment. The presence of the metal ion in the outer compartment in the mononuclear complexes in our case can be attributed to two structural factors. First preparation of the mononuclear complexes in this work has been done *via* reacting the metal ion with the dilithium salt of the ligand. The presence of the carboxylate ion rather than the carboxylic group may thus enhance the binding of the metal to the carboxylate oxygen and leads to an outer compartmental type of complexes. The second factor is the presence of the two chlorine atoms attached to the benzene ring holding the two nitrogen atoms. This results in lowering the electron density on the two nitrogen atoms and favors the coordination of the metal to the outer coordination site.

Table-2: Important infrared bands, electronic absorption spectral data and magnetic moment values of the mononuclear complexes.

Compound	Infrared spectral data (ν/cm^{-1})				Absorption data ($\lambda_{\text{max}}/\text{cm}^{-1}$)	μ_{eff} (B.M.) ^a
	O-H	C=O	C=N	C-O		
H ₄ fsacph	3280	1705	1655	1520	38460, 32258, 30303, 2564	-
[Co(H ₄ fsacph)(H ₂ O) ₂]	3430	1585	1655	1555	38300, 32250, 30450, 20500, 15400	4.53
[Ni(H ₄ fsacph)(H ₂ O) ₂]	3400	1590	1653	1540	38460, 32510, 30350, 25000, 16000, 10000	3.48
[Cu(H ₄ fsacph)(H ₂ O) ₂]	3450	1580	1655	1560	38700, 32250, 30300, 25300, 14925	1.93

^a At room temperature

Electronic Spectra and Magnetic Moments of Mononuclear Complexes

The UV-Vis spectra of ligand and its complexes have been taken in DMSO at room temperature. The spectral data are given in Table 2. The Schiff base ligand $H_4fsacph$ exhibits four bands at 38460 cm^{-1} , 32258 cm^{-1} , 30303 cm^{-1} , and 25641 cm^{-1} . These are inner ligand transitions such as $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ which are common due to the presence of C=N, C=O, C=N, C-O, and C=C groups in the ligand structure. All the mononuclear complexes showed absorption close to the first three bands of the ligand and are thus intra ligand transition bands. In addition the following bands have been observed. The electronic absorption spectrum of the cobalt(II) complex, **1**, shows two additional bands at $15,400\text{ cm}^{-1}$ and $20,500\text{ cm}^{-1}$ which corresponds to ${}^4T_{1g}(F) \rightarrow {}^4A_{2g}$ and ${}^4T_{1g}(F) \rightarrow {}^4T_{1g}(P)$ transitions, respectively, which clearly indicate the octahedral stereochemistry of the complex [55]. The electronic spectra of the nickel(II) complex, **2**, shows three additional bands. The band at $10,000\text{ cm}^{-1}$ is due to ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transition, the band at $16,000\text{ cm}^{-1}$ corresponds to ${}^3A_{2g} \rightarrow {}^3T_{1g}$ transition, and the band at $25,000\text{ cm}^{-1}$ is due to ${}^3A_{2g} \rightarrow {}^3T_{2g}$ transition which also clearly indicates the octahedral stereochemistry of the complex [55]. The green copper(II) complex, **3**, shows two additional bands, one at $25,300\text{ cm}^{-1}$ and another at $14,925\text{ cm}^{-1}$ which is consistent with an octahedral geometry [52].

The room temperature magnetic moments of the mononuclear complexes are given in Table 2. The observed magnetic moments support the proposed octahedral structures. The observed moment of 4.53 BM for the Co(II) complex lie in the range of the magnetic moments of six-coordinate cobalt(II) complexes (1.8 to 5.2 BM) [56]. The magnetic moment of the Ni(II) complex, 3.48 BM, and Cu(II) complex, 1.93 BM, are also confirming the octahedral environments around the two metals [52].

Thermal Studies

A thermal study was carried out in air under non-isothermal conditions. The mass loss starts at $120\text{ }^\circ\text{C}$, continues up to $150\text{ }^\circ\text{C}$ and corresponds to two moles of coordinated water in complexes **1-3** supporting our formulation. All the complexes finally produce their oxides as residue on heating at $500\text{-}800\text{ }^\circ\text{C}$.

Homodinuclear Complexes

Analytical data for all the homodinuclear complexes (Table-1) correspond to 2:1 mole ratio of metal ion to ligand. In these complexes two identical metal ions occupy both the inner N_2O_2 and the outer O_2O_2 compartments.

Infrared Spectra and Molar Conductance of Homodinuclear Complexes

The important infrared bands of the dinuclear complexes are summarized in Table 3. Similar to the mononuclear complexes, no free carboxyl band is observed in the region $1680\text{-}1720\text{ cm}^{-1}$ in all the dinuclear complexes, instead a new band appeared in the region $1580\text{-}1595\text{ cm}^{-1}$, which can be attributed to the stretching frequency of the coordinated carboxylate group [48, 49]. The bridging phenolic $\nu(C-O)$ appear in the region, $1560\text{-}1580\text{ cm}^{-1}$, which appears at 1520 cm^{-1} in the free Schiff base and the range $1540\text{-}1560\text{ cm}^{-1}$ when attached to single metal ion (non-bridging) [50, 51]. The higher energy shift of this $\nu(C-O)$ band has been used for a diagnosis of the formation of the phenolic oxygen bridge. Therefore, it may be concluded that in the present bimetallic complexes the two metal atoms (Co-Co, Ni-Ni, Cu-Cu) are bridged by the phenolic oxygen (Fig. 2). All these complexes exhibit a sharp band in the range $1620\text{-}1630\text{ cm}^{-1}$ due to the coordinated azomethine group, which is $25\text{-}35\text{ cm}^{-1}$ lower than that observed in the free ligand indicating the coordination of nitrogen in these complexes and thus indicates the bimetallic nature of the complexes.

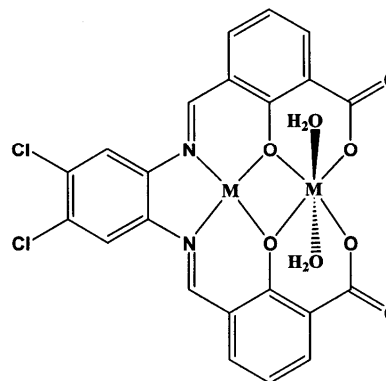


Fig. 2: Proposed structural formula for the homodinuclear complexes, $M = \text{Co}^{2+}$, Ni^{2+} , or Cu^{2+} (for Cu^{2+} , no water exists).

Table-3: Important infrared bands, electronic absorption spectral data and magnetic moment values of the homodinuclear complexes.

Compound	Infrared spectral data (ν/cm^{-1})				Absorption data ($\lambda_{\text{max}}/\text{cm}^{-1}$)	$\mu_{\text{eff}}/\text{mole}$ (B.M.) ^a
	O-H	C=O	C=N	C-O		
H ₄ fsacph	3280	1705	1655	1520	38460, 32258, 30303, 25641	–
[Co ₂ (fsacph)(H ₂ O) ₂]	3450	1595	1630	1570	38550, 32025, 30303, 20100, 15200, 8750	5.97
[Ni ₂ (fsacph)(H ₂ O) ₂]	3500	1580	1620	1565	38420, 32450, 30500, 25500, 18900, 16240, 10200	4.10
[Cu ₂ (fsacph)]	–	1590	1625	1580	38335, 32105, 30150, 17500	3.79

^a At room temperature

Complexes **4** and **5** exhibit a broad band in the 3400–3500 cm^{-1} region indicating the presence of coordinated water molecule while this band has not been observed in the copper complex **6** indicating the anhydrous nature of this complex. Thus it may be concluded that the ligand H₄fsacph functions as a tetrabasic hexadentate compartmental ligand with both the N₂O₂ inner compartment and the O₂O₂ outer compartment being fully occupied by metal ions.

Electronic Spectra and Magnetic Moments of Homodinuclear Complexes

Electronic spectra of the homodinuclear complexes have been recorded in DMSO at room temperature and the obtained spectral data are summarized in Table 3. The electronic spectra of **4** and **5** showed absorption bands similar to those in **1** and **2** in addition to new bands that are characteristic to the stereochemistry of the second metal ion. Complex **4** showed a band at 8750 cm^{-1} . This lower energy band is due to the second cobalt ion and is due to the $a_{1g} \rightarrow b_{2g}$ transition in a square planar stereochemistry [57, 58]. The electronic spectrum of complex **5** consists of the three bands that have been observed in the mono-nuclear complex with a little shift in their positions together with a band at 18,900 cm^{-1} due to $^1A_{1g} \rightarrow ^1A_{2g}$ transition which indicate a square planar geometry for the second metal ion in the inner coordination site [58]. The other transition, $^1A_{1g} \rightarrow ^1B_{1g}$ (around 25,000 cm^{-1}), that is expected for the square planar geometry of the second Ni(II) ion is almost overlapped with the lowest energy transition of the octahedral metal. The homodicopper complex **6** on the other hand showed a different behavior in its absorption spectrum. No bands have been observed at the absorption wavelengths of the mononuclear complex. Instead, an asymmetric band at 17,500 cm^{-1} has been observed which indicates the presence of the two metal ions in a square planar structure [59]. The slight change in the characteristic absorption wavelengths of the mononuclear complexes of Co(II) and Ni(II) in presence of the second metal ion indicates that the two compartments are not coplanar.

The observed magnetic moment (per mole of compound), for the three dinuclear complexes are given in Table-1. The observed values of the magnetic moment indicate very little interaction between the two metal ions. Hence it may be concluded that in these dinuclear complexes, the two coordination compartments are not coplanar which results in decreased interaction between the two metal ions in the homodinuclear complexes.

Thermal Studies

Similar to mononuclear complexes, the thermal study was carried out in air under non-isothermal conditions. The mass loss starts at 125 °C, continues up to 155 °C and corresponds to two moles of coordinated water in complexes **4** and **5**. For complex **6**, no mass loss occurs until 185 °C indicating the absence of coordinated water in this complex. All the complexes finally produce their oxides as residue on heating at 500-800 °C.

Experimental

Physical Measurements

Microanalysis (C, H, N) were performed using a Gmbh Vario El elemental analyser. The electronic spectra (in DMSO) were recorded on a Shimadzu UV-Vis double-beam spectrophotometer equipped with a constant-temperature cell holder. Spectra were recorded at room temperature in 1 cm quartz cuvettes with a slit width of 2 nm, and infrared spectra (KBr) on a Shimadzu 470 infrared spectrophotometer (4000–400 cm^{-1}). The molar conductance (10^{-3} M in DMF) was measured using a CDM216 conductivity meter Meterlab. Thermo gravimetric analyses were carried in a dynamic oxygen atmosphere using a Shimadzu DTG 60 H thermal analyzer at heating rate 10 °C min^{-1} . Magnetic susceptibility measurements were carried out using a magnetic susceptibility balance, MSB-Auto.

Materials

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, and 4,5-dichloro-1,2-phenylenediamine were purchased from Aldrich and used as such. 3-Formylsalicylic acid was prepared according to literature procedure [60]. The Schiff base ligand (H_4fsacph) was prepared through condensation of 3-formylsalicylic acid with 4,5-dichloro-1,2-phenylenediamine, as described below. Spectrograde solvents were used for physical measurements.

Synthesis of the Ligand (H_4fsacph)

To a stirred methanolic solution (50 mL) of 3-formylsalicylic acid (4.0 g, 22.6 mmol) was added 4,5-dichloro-1,2-phenylenediamine (7.51 g, 11.3 mmol) in the same solvent (50 mL) dropwise and stirred for 2 h at room temperature. The yellow solid formed was filtered, washed with cold MeOH-water (1:1, v/v, 5 mL \times 3) and dried in vacuo. Yield: 9.1 g (85%).

*Preparation of the Mononuclear Complexes**[Co(H_2fsacph)(H_2O)₂], 1, and [Ni(H_2fsacph)(H_2O)₂], 2*

The ligand, H_4fsacph (1.0 g, 2.12 mmol) was dissolved in 15 mL methanolic solution of lithium hydroxide mono-hydrate (0.18 g, 4.3 mmol). To this hot solution, a hot 15 mL methanolic solution of the metal chloride hexahydrate (0.5 g, 2.12 mmol) was added dropwise with stirring and the reaction mixture was refluxed for 1 h. The brown Co(II) complex and the reddish-brown Ni(II) complex were filtrated, washed with hot methanol, and dried under vacuum over fused CaCl_2 . Yield 76%, 81%, respectively.

[Cu(H_2fsacph)(H_2O)₂], 3

Preparation of the mononuclear Cu(II) complex was performed through drop wise addition of hot 15 mL methanolic solution of copper (II) chloride dihydrate (0.36 g, 2.12 mmol) to hot 15 mL methanolic solution of lithium hydroxide mono-hydrate (0.18 g, 4.3 mmol) containing H_4fsacph (1.0g, 2.12 mmol). The reaction mixture was refluxed for 6 h. the green crystalline complex was then filtered, washed thoroughly with hot methanol, and dried under vacuum over fused CaCl_2 . Yield 85%.

Preparation of the Homodinuclear Complexes

The three homodinuclear complexes, $[\text{Co}_2(\text{fsacph})(\text{H}_2\text{O})_2]$, 4, $[\text{Ni}_2(\text{fsacph})(\text{H}_2\text{O})_2]$, 5, and $[\text{Cu}_2(\text{fsacph})]$, 6, can be synthesized *via* two methods. The first is the interaction of the ligand with the metal ion in a 1:2 mole ratio following the exact procedures for the synthesis of the mononuclear complexes. The other method is based on the reaction of the mononuclear complexes with the corresponding metal ion in a 1:1 mole ratio. However, the first one was found to be of higher yield and was thus applied for synthesis of the homodinuclear complexes.

Preparation of Complexes 4, 5, and 6

The three complexes were identically synthesized. H_4fsacph (1.0 g, 2.12 mmol) was dissolved in 15 mL methanolic solution of lithium hydroxide mono-hydrate (0.368 g, 8.8 mmol). To this hot solution, a hot 15 mL methanolic solution of the metal chloride (4.25 mmol), was added drop wise with stirring. The reaction mixture was refluxed for 1–3 h. A dark brown precipitate in case of Co(II), dark red in case of Ni(II), and dark green in case of Cu(II) formed. The precipitates were filtrated, washed with hot methanol, and dried under vacuum over fused CaCl_2 . Yield: 4, 66%; 5, 85%; 6, 74%.

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