

Synthesis And Characterization of Some Transition Metals Complexes of Schiff Base Derived From Benzidine and Acetylacetone

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ABSTRACT

The ligand and its complexes of Cr(III), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) were investigated in terms of synthesis, elemental analysis, molar conductivity, thermal analysis, infrared spectra and magnetic susceptibility measurements. The ligand: 4-[4'-(3-Hydroxy-1-ethyl-but-2-enylideneamino)-biphenyl-4-ylimino]-pent-2-en-ol (C₂₂H₂₄N₂O₂) has been synthesized by the condensation of acetylacetone and benzidine. The complexes have been synthesized by two different methods and their geometries were investigated. A synthesis and characterization of novel complexes of 4-[4'-(3-Hydroxy-1-ethyl-but-2-enylideneamino)-biphenyl-4-ylimino]-pent-2-en-ol has been achieved. The study also confirmed the formation of mono-, di- and novel polynuclear metal complexes. The researcher recommended that the mentioned complexes may have biological activity.

Key Words: Synthesis and Characterization, Benzidine, Novel polynuclear metal complexes

INTRODUCTION

In recent years, metal complexes with salen ligands derived from the condensation of salicylaldehyde with a diamine, have been widely studied. Dinuclear metal complexes have been a fascinating area of research, in view of their significance as biomimetic catalysts in the process of oxygenation (Konsler, Karl, & Jacobsen 1988; Wei, & Atwood 1997; Kolb, Vannieuvenhze, & Sharpless 1994). Discoveries of dinuclear cores at the active sites of some metalloproteins have aroused interest in the investigation of multimetallic systems (Than, Feldmann, & Krebs 1999) Schiff bases have been widely used as ligands because of high stability of the coordination compounds and their good solubility in common solvents. The π -system in a Schiff base often imposes a geometrical constriction and affects the electronic structure as well. Thermo chemical properties of Schiff bases have attracted much researcher attention in view of their ability to coordinate metal ions, acting as bidentate or

tetradentate ligands in metal chelates involving a NO or N₂O₂-Schiff-base donor atom sets. These Schiff base metal derivatives have considerable interest due to their role as model complexes to biological systems, contributing to the knowledge of their structure and behavior (Costamagna, Vargas, Latorre, Alvarado, & Mena 1992; Marchetti, Pettinari, Pettinari, Cingolani, Leonesi, & Lorenzotti, 1999). Catalytic studies reveal that the metal complexes of N₂O₂-Schiff-base donor types of chiral metal complexes are active catalysts for stereoselective organic transformations including hydroxylation of styrene, aldol reactions, alkene epoxidation, trimethylsilylcyanation of aldehydes, and desymmetrization of meso-N-sulfonylaziridine (Che, & Huang 2003). We have previously reported results for the structural study of some Schiff bases derived from β-diketones and diamines and their complexes (Ahmed, BenGuzzi, & El-Hadi 2007). We are now involved in the synthesis and structural investigation of another set of related tetradentate Schiff base ligand, obtained as condensation products of benzidine with acetylacetone, and its complexes with Cr(III), Fe(III), Co(II), Ni(II), Cu(II) ions.

EXPERIMENTAL

All materials and reagents used in this study were laboratory pure chemicals. They include benzidine and acetylacetone. The solvents and metal salts are used as they received from the supplier without further purification. The synthesis of N₂O₂-Schiff-base ligand and its complexes are based on the methods reported previously (Ahmed, BenGuzzi, & El-Hadi 2007).

Synthesis of the Schiff base ligand

Benzidine (1.84g; 0.0051 moles) was refluxed with acetylacetone (20 cm³, 0.0102 moles) in 20 cm³ ethanol for 10-12h. A yellow solid crude product is filtered off, wash several times with small portions of ethanol and finally with diethyl ether. The product was recrystallized from hot ethanol and dried in desiccated over anhydrous CaCl₂.

Synthesis of Schiff base Complexes

Schiff base complexes under investigation were synthesized as follows; the ligand was dissolved in (20 cm³) ethanol and added to a metal chloride salts ethanolic solution (20 cm³). The reaction molar ratio is (1:1) or (1L: 2M). The mixture was refluxed for 10h; the volume of the mixture was reduced to one-third. On cooling a crude product was formed, which is collected by filtration and washed several times with ethanol and dried over anhydrous CaCl₂.

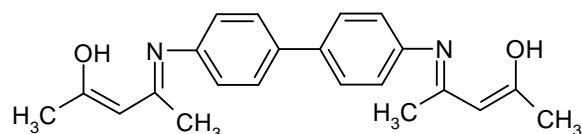
Measurements

The Schiff base ligand and its complexes under investigation were subjected to (C, H and N) elemental analysis which performed at analytic unit of the central laboratory of Tanta University (Egypt) and laboratories of RASCO Company Libya. The melting points were measured in capillary tubes Philip Harris, Shenston-England, serial NO.B/A_211. The molar conductance values were calculated in (10⁻³M) in DMF or Chloroform solution by using digital conductivity meter CMD 650. The magnetic moment measurements were determined by using a modified Goy type magnetic balance Hertz SG8 SHJ, England. The IR spectra were recorded using a Perkin-Elmer 1430 spectrophotometer using KBr

Discs, at Menofia University, Shibin El-Kom (Egypt). Thermal analysis, differential thermal analysis (DTA) and thermogravimetric analysis (TGA) measurements were recorded on Shimadzu DT-30 thermal analyzer with heating rate of 10°C/min. at Menofia University, Shibin El-Kom (Egypt).

RESULT AND DISCUSSION

The 4-[4'-(3-Hydroxy-1-methyl-but-2-enylideneamino)-biphenyl-4-ylimino]-pent-2-en-2-ol ligand was formed by the condensation of benzidine with acetylacetone. The structure of Schiff base ligand is shown below.



Elemental analysis

Physical characteristics and elemental analysis of C, H and N of the compounds considered are listed in Table 1. The results of C, H and N percentage are in accordance with the composition suggested for the ligand and the complexes.

Table 1: Elemental analysis, Color, M.P, and molar conductivity of the compounds under investigation.

Compound	M.w _t	Color	Cond. scm ² mol ⁻¹	M.P. C°	Found (Cal.)		
					%C	%H	%N
C ₂₂ H ₂₄ N ₂ O ₂	348	Yellow	-	275	74.90 (75.83)	7.06 (6.94)	8.30 (8.04)
C ₄₄ H ₅₂ O ₈ N ₄ Cl ₄ Cu ₄	1160	Black	4.1	240	46.1 (45.52)	4.1 (4.48)	5.40 (4.83)
C ₄₄ H ₄₆ N ₄ O ₄ Ni	753	Red	2.2	185	71.50 (70.12)	7.00 (6.11)	7.50 (7.44)
C ₄₄ H ₄₆ N ₄ O ₄ Co	753	Brown	3.6	170	71.58 (70.12)	7.00 (6.11)	7.50 (7.44)
C ₄₄ H ₄₄ O ₄ N ₄ Cl ₂ Fe ₂	874.6	Black	3.4	200	59.14 (60.37)	5.40 (5.07)	6.80 (6.40)
C ₄₄ H ₄₆ O ₅ N ₄ Cl ₂ Cr ₂	884	Gray	4.0	180	59.80 (59.73)	5.00 (5.43)	6.70 (6.33)
C ₂₂ H ₃₄ O ₈ N ₂ Cl ₂ Ni ₂	642	Yellow	3.4	300<	40.50 (41.12)	4.30 (5.30)	4.10 (4.36)
C ₂₂ H ₂₈ O ₄ N ₂ Cl ₂ Zn	517	Gray	3	210	51.49 (51.04)	4.52 (4.87)	5.40 (5.41)

$C_{22}H_{30}O_6N_2Cl_2Cu_2$	616	Brown	3.1	300<	42.70 (42.86)	6.50 (4.87)	4.50 (4.55)
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Molar conductance

The molar conductance has been demonstrated to be a very useful tool in the investigation of geometrical structure of inorganic compounds. The molar conductance for the complexes is measured in $10^{-3}M$ solution in DMF and chloroform as solvents at room temperature (25-30C°). The molar conductivity was applied to investigate the existence of anions outside the coordination sphere for the complexes. The molar conductivity values are given in Table 1. The complexes showed a lower molar conductivity values in the range 2.2-4.1 Scm^2mol^{-1} which indicated their non-electrolytic nature. Our results are in good agreements with those reported earlier, (Osman 2006).

Thermal analysis

Thermal analysis methods namely differential thermal analysis (DTA) and thermogravimetric analysis (TGA) have been used to investigate the tetranuclear copper complex ($C_{44}H_{52}O_8N_4Cl_4Cu_4$). The Thermal analysis data are collected in Table 2. The DTA curve exhibited broad endothermic peaks, the elimination of hydrated water molecules showed peaks at (21-70C°). The lattice water (coordinated water) are stable and volatilized above 130C°. The Thermal analysis data are in accordance with that of (Osman 2006). The endothermic peak at (100-250C°) is assigned the lost of HCl molecules. Finally the endothermic peak (450-700C°) which is attributed to the final species CuO. The TGA of the complex confirmed the lost of weight at temperature range (21-70C°) corresponding to the loss of hydrated water molecules which is assigned to (Calc. 4.7%) corresponding to 3H₂O (found 5.03%) which are in conformity with the endothermic peak at temperature range (21-70C°) in the DTA curve. In addition the peak at (130-250C°) for the complex may be due to the decomposition of partial organic ligand with four coordinated water molecules. The curve of the complex confirmed the lost of weight at temperature range (100-250C°) corresponding to the lost of HCl molecules which assigned to (Calc. 11.7%) corresponding to 4HCl (found 11.5%). The final peak at temperature range (450-700C°), corresponds to the lost of 4CuO molecules (Calc. 11.7%; found 11.5%) which indicates the tetranuclear nature of the complex.

Table 2. Thermal analysis (DTA and TGA) of the $C_{44}H_{52}O_8N_4Cl_4Cu_4$ complex.

complex	species	Tmep.- range C°	DTA peaks	TGA (loss %)	
				Found	Calc.
$C_{44}H_{52}O_8N_4Cl_4Cu_4$	3H ₂ O	21-70	Endo.	5.03	4.7
	4HCl	100-250	Endo.	11.5	11.7
	4CuO	450-700	Endo.	14.7	14.5

Infrared spectra

The infrared spectral data of the ligand and its complexes are listed in Table 3. The compounds under investigation showed broad bands at 3132-3445 cm^{-1} region, these bands are associated with the coordinated or solvated water. The free ligand exhibited bands at 1741 cm^{-1} and 1551 cm^{-1} which are attributed to $\nu(\text{C}=\text{N})$ and $\nu(\text{C}-\text{O})$ respectively. On complexation the $\nu(\text{C}=\text{N})$ band was shifted to lower frequency while the $\nu(\text{C}-\text{O})$ band was shifted to a higher frequency indicates that the ligand was coordinated to the metal ions through the nitrogen atom of the azomethine group ($\text{C}=\text{N}$) and through the oxygen atom ($\text{C}-\text{O}$). Finally, the complexes showed bands at lower frequencies region 513-583 cm^{-1} and at 360-414 cm^{-1} which are assigned to $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ respectively. The IR spectra of diagnostic importance of the complexes are given in Table 3. The solid state IR spectra of complexes compared with those of ligands indicated that the $\nu(\text{C}=\text{N})$ stretching vibration band at region 1531-1664 cm^{-1} was shifted to lower frequencies in most complexes as expected. In contrast there are three complexes shifted to higher frequencies, which indicated that the ligands coordinated to the metal ions through nitrogen atom of the azomethine group.

The presence of sharp band corresponding to the remaining hydroxyl group at 3400 cm^{-1} but it is obscured by the presence of water molecules bands. This was appeared for the most complexes and a very broad band at about 3100-3500 cm^{-1} region, which was associated with coordinated or solvent water molecules. The other bands appeared at 1323-1427 cm^{-1} region assigned to the $\nu(\text{C}-\text{O})$, which are shifted to a higher frequency after complexation with central metal ions, compared to the free ligands in which was noted at 1261-1315 cm^{-1} . In addition the two bands at 729-511 and 531-442 cm^{-1} , was attributed to the $\nu(\text{M}-\text{O})$ and $\nu(\text{M}-\text{N})$ respectively. Generally the infrared results are in agreements with those reported previously for similar complexes. The infrared frequencies are in agreement with our previous finding, (Ahmed, BenGuzzi, & El-Hadi 2007).

Table 3. Infrared bands assignments (cm^{-1}) of the compounds under investigation.

The compound	$\nu(\text{C}=\text{N})$ cm^{-1}	$\nu(\text{C}-\text{O})$ cm^{-1}	$\nu(\text{OH})$ cm^{-1}	$\nu(\text{M}-\text{O})$ cm^{-1}	$\nu(\text{M}-\text{N})$ cm^{-1}
$\text{C}_{22}\text{H}_{24}\text{N}_2\text{O}_2$	1741	1551	3442	-	-
$\text{C}_{44}\text{H}_{52}\text{O}_8\text{N}_4\text{Cl}_4\text{Cu}_4$	1614	1688	3132	582	445
$\text{C}_{44}\text{H}_{46}\text{N}_4\text{O}_4\text{Ni}$	1503	1742	3440	513	440
$\text{C}_{44}\text{H}_{46}\text{N}_4\text{O}_4\text{Co}$	1502	1774	3426	517	360
$\text{C}_{44}\text{H}_{44}\text{O}_4\text{N}_4\text{Cl}_2\text{Fe}_2$	1492	1727	3360	581	498
$\text{C}_{44}\text{H}_{46}\text{O}_5\text{N}_4\text{Cl}_2\text{Cr}_2$	1529	1794	3411	581	365
$\text{C}_{22}\text{H}_{34}\text{O}_8\text{N}_2\text{Cl}_2\text{Ni}_2$	1614	1758	3399	583	514
$\text{C}_{22}\text{H}_{28}\text{O}_4\text{N}_2\text{Cl}_2\text{Zn}$	1546	1741	3332	516	448
$\text{C}_{22}\text{H}_{30}\text{O}_6\text{N}_2\text{Cl}_2\text{Cu}_2$	1601	1823	3336	518	446

Magnetic moment

The magnetic moment values are useful in the evaluation of results provided by the other techniques of the structural investigation. The geometry assessment of the complexes around the Co(II) and Ni(II) and Cu(II) ions was supported further from the results of the magnetic moments. The magnetic moments measurements of the complexes are listed in Table 4. The value of magnetic moment 1.16 B.M is due to one unpaired of $3d^9$ electronic configuration in an octahedral complex ($\text{C}_{44}\text{H}_{52}\text{O}_8\text{N}_4\text{Cl}_4\text{Cu}_4$) of Cu(II) ion. The lower values of magnetic moment at room temperature are 0.0 and 1.2 B.M is consistent with square planar geometry around the metal ions. The magnetic moment values of 3.3 and 4.1 B.M are compatible with a tetrahedral complex. Generally, the low magnetic moment values of bi- and polynuclear copper complexes are attributed to the anti-ferromagnetic moment interaction between two central metal ions; this is an indication of the formation binuclear complex. These results are in accordance with our previous ones, (Ahmed, BenGuzzi, & El-Hadi 2007) . The structures of some complexes are shown below.

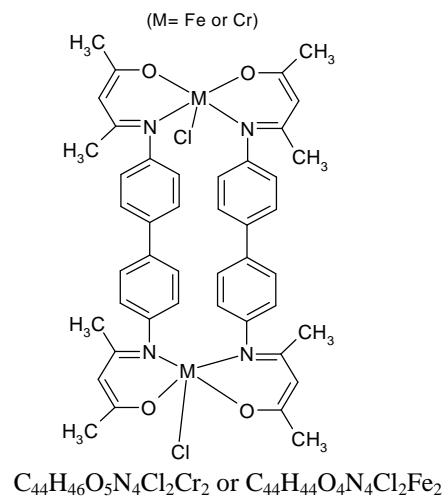
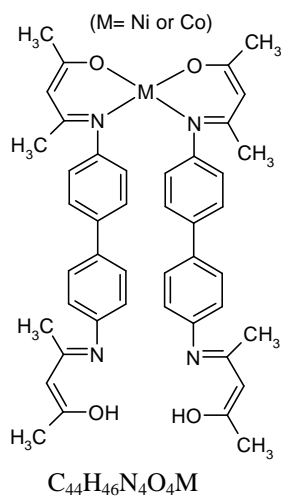
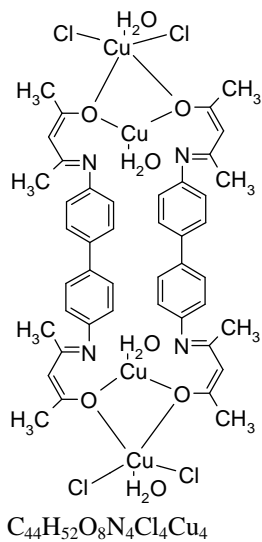


Table 4. Magnetic moment measurements of the complexes under investigation.

The complex	μ_{eff} B.M	Geometry
$C_{44}H_{52}O_8N_4Cl_4Cu_4$	1.16	Octahedral
$C_{44}H_{46}N_4O_4Ni$	0.0	Square planar
$C_{44}H_{46}N_4O_4Co$	4.1	Tetrahedral
$C_{22}H_{30}O_6N_2Cl_2Cu_2$	1.2	Square planar
$C_{22}H_{34}O_8N_2Cl_2Ni_2$	3.3	Tetrahedral

CONCLUSION

The synthesized of novel complexes were examined in terms of elemental analysis, molar conductivity, thermal analysis, infrared spectra, and magnetic susceptibility measurements. The analysis confirmed the formation of mon-, di- and polynuclear metal complexes.

REFERENCES

- Konsler, R. G., Karl, J., Jacobsen, E. N. (1998), Cooperative z asymmetric Catalysis with Dimeric Salen Complexes. *Journal of American Chemical Society*, 120 10780.
- Wie, P., Atwood, D. A. (1997), Bimetallic Borate Derivatives of the Salen Ligands. *Inorganic Chemistry*, 36, 4060.
- Kolb, H. C., VanNieuwenhze, M. S., Sharpless, K. B. (1994), Catalytic Asymmetric Dhydroxylation. *Chemical Review*, 94, 2483.
- Than, R., Feldmann, A. A., Krebs, B. (1999). Structural and functional studies on model compounds of purple acid phosphatases and catechol oxidases. *Coordination Chemistry Reviews*, 182, 211.
- Costamagna, J., Vargas, J., Latorre, R., Avlvarado, A., Mena, G., (1992). Coordination compounds of copper, nickel and iron with Schiff bases derived from hydroxynaphthaldehydes and salicylaldehydes. *Coordination Chemistry Reviews*, 119, 67.
- Marchetti, F., Pettinari, C., Pettinari, R., Cingolani, A., Leonesi, D., Lorenzotti, A, (1999). Group 12 metal complexes of Tetradentate N₂O₂-Schiff-base ligands incorporating pyrazole Synthesis, characterisation and reactivity toward S-donors, N-donors, copper and tin acceptors. *Polyhedron*, 18, 3041.
- Che, C., Huang, J. (2003). Metal complexes of chiral binaphthyl Schiff-base ligands and their application in stereoselective organic transformations. *Coordination Chemistry Reviews*, 242, 97.
- Ahmed, A. A., BenGuzzi, S. A., El-Hadi, A. A., (2007). Synthesis and Characterization of Divalent Transition Metals Complexes of Schiff Bases Derived From O-Phenylenediamine and Benzoylacetone and Related Species. *Journal of Science and Its Applications*. 1, 79.
- Osman, A. H., (2006). Synthesis and characterization of cobalt(II) and nickel(II) complexes of some Schiff bases derived from 3-hydrazino-6-methyl[1,2,4] triazin-5-(4H)one. *Transition Metal Chemistry*, 31, 35.