

Preparation and characterization of new complexes for cobalt (II), nickel (II) and copper (II) with ligands derived from 4- hydroxyacridine and 3,6-diaminoacridine.

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Received: 17/5/2009 ; Accepted: 13/5/2010

Abstract:

New cobalt (II) , nickel (II) and copper (II) complexes of Schiff base and xanthato group (OCS_2^-) which is derived from 4-hydroxy acridine and 3,6-diamineacridine, have been synthesized and characterized by using physical and chemical methods such as molar conductance, quantitative analysis of Co, Ni, Cu and the measurement of magnetic moments for the complexes , infrared and electronic spectroscopy. All the results can be taken as an evidence for a high spin octahedral configuration for all the complexes . It has been indicated that the two ligand (L_1) and (L_2) prepared as coordinated tridentate chelating ligands. During the two nitrogen atoms of the two azomethine groups and one nitrogen of acridine for L_1 , also during the two sulphur atoms of the xanthato group and one nitrogen of acridine for L_2 , (where $\text{L}_1 = \text{N,N-dibenzylideneacridine-3,6-diamine}$ and $\text{L}_2 = \text{Potassium o-acridine-4-yl carbonothioate}$).Accordingly, general formulas $[\text{M}(\text{L}_1)(\text{L}_2)] \text{Cl}$, $[\text{M}(\text{L}_1)_2] \text{Cl}_2$ and $[\text{M}(\text{L}_2)_2] \text{Cl}_2$ have been suggested for the complexes .

تحضير وتشخيص معقدات جديدة للكوبلت (II) والنيكل (II) والنحاس (II) مع ليكنيدات مشتقة من 4-هيدروكسي اكريدين و 3،6-ثنائي امينو اكريدين

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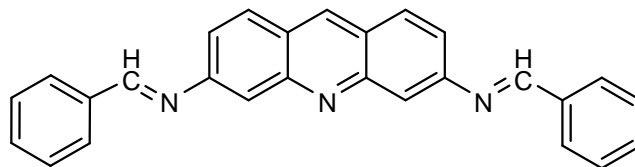
ملخص البحث :

تم تحضير معقدات جديدة للكوبلت (II) والنيكل (II) والنحاس (II) لقواعد شيف ومجموعة الزانثيت المشتقة من (4-هيدروكسي اكريدين و 3،6-ثنائي امينو اكريدين) وتم تشخيصها باستخدام طرق فيزيائية وكيميائية تتضمن التوصيل المولاري وحساب كمية الكوبلت والنيكل والنحاس وقياس العزوم المغناطيسية للمعقدات وطيف الاشعة تحت الحمراء والطيف الالكتروني . أوضحت النتائج أن المعقدات عالية البرم ذات بنية ثمانية السطوح للمعقدات وأن الليكندين L_1 و L_2 تناسقا بشكل ثلاثي السن كيليتي من خلال ذرتي النتروجين لمجموعتي الازوميثان وذرة نتروجين الاكريدين لليكاند الاول L_1 ، وأيضا من خلال ذرتي الكبريت لمجموعة الزانثيت وذرة نتروجين الاكريدين لليكاند الثاني L_2 , (حيث $N, N = L_1$ -ثنائي بنزلدين اكردين-3،6-ثنائي الامين و L_2 = بوتاسيوم اورثو اكريدين -4-يل كاربونوثايويت) واستناداً إلى ذلك اقترحت الصيغ العامة للمعقدات , $[M(L_1)(L_2)] Cl$ و $[M(L_1)_2] Cl_2$ و $[M(L_2)_2] Cl_2$.

Introduction

Metal complexes with Schiff bases and dithiocarbonate (xanthato group), have recently drawn a special attention due to their activities against cancer and antibiological agents (Dove et al., 1999; Craciunescu., 1988; Hassan, 1999; and Sallomi et al., 2000). The antifungal activity of these compounds is due to the presence of both (C=N) and (OCS₂⁻), groups and its derivatives. These ligands among the widely studied have been coordinated with the metal ion through the nitrogen and sulphur atoms.

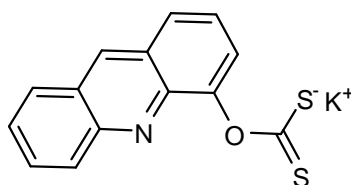
The ligand L₍₁₎: (N,N-dibenzylideneacridine-3,6-diamine) have two azomethine groups which are derived from 3,6- diamine acridine after its reaction with benzaldehyde to obtain the structure 1.



***N,N*-dibenzylideneacridine-3,6-diamine**

(L₁) (structure 1)

Ligand (L₂)(potassium *o*-acridine-4-yl carbonodithioate) have one xanthato group prepared by the reaction of 4-hydroxy acridine and CS₂ in presence of ethanol and potassium hydroxide, (Structure 2).



potassium *o*-acridine-4-yl carbonodithioate

(L₂) (structure 2)

Chemicals :

All the chemicals used in this work are CoCl₂.6H₂O, (98%), NiCl₂.6H₂O (99%), CuCl₂.2H₂O (98%), NaOH, 4-hydroxyacridine and 3,6- diamineacridine and the solvents such as dimethylformamide (DMF), absolute ethanol , were supplied from (B.D.H.and Fluka).

Experimental methods:

Melting points were recorded by Electrothermal 9300, conductivity measurements were measured, for 10⁻³ M solution of the complexes in DMF solvent at room temperature, by conductive model 4070 Jenway. Magnetic moments measurement was carried out at 25 C° on the solid

state using Faraday method by Bruker BM6 Co. Infrared data obtained by using F.T.I.R- Tensor 27-Bruker in the range of $(200 - 4000) \text{ cm}^{-1}$, using CsI discs. Electronic spectra were obtained by using shimadzu UV/VIS Spectrophotometer UV-160 for 10^{-3} M solution of the complexes in (DMF) using 1 cm cell quartz, Metals Cobalt, nickel and copper. Determination of Co, Ni and Cu elements by using quantitative analysis method (Vogel, 1971) by standard methods.

Preparation of N,N-dibenzylideneacridine (L_1):

This ligand N,N-dibenzylideneacridine was prepared mixing (0.01) mole of 3,6-diaminoacridine in 100 ml absolute ethanol with (0.02) mole of benzaldehyde in 100 ml absolute ethanol. After three hours refluxed reddish – brown crystals appeared. The mixture was cooled to room temperature and filtered off and the crystals were washed with ethanol and dried.

Preparation of potassium *o*-acridine-4-yl-carbonodithioate (L_2):

This ligand was synthesized by refluxing the mixture of (0.01) mole of 4-hydroxyacridine in 100 ml absolute ethanol and (0.01) of CS_2 (the CS_2 solution added drop wise). The reaction was continued for 2 hours and left overnight to form shining yellow crystals which were separated from ethanol and dried.

1-Preparation of the complexes with ratio (1:1:1) M: L_1 : L_2

These complexes were synthesized by mixing (0.01) mole of metal salt in 50 ml in distilled water with (0.01) mole of ligand (L_1) and (L_2) in 100 ml of absolute ethanol. The mixture was refluxed for three hours, on cooling colored crystals were separated out, filtered, washed with ethanol and then dried.

2- Preparation of the complexes with ratio (1:2) M: L₁

These complexes have been synthesized by mixing (0.02) mole of ligand (L₁) in 100 ml absolute ethanol and (0.01) mole of metal salt. The mixture was refluxed for three hours, then left to cool to room temperature and colored crystals were separated out, filtered, washed with absolute ethanol and then dried

3- Preparation of the complexes with ratio (1:2) M: L₂

These complexes were prepared and isolated by a similar method 2 above. They were synthesized by mixing (0.01) mole of metal salt in 50 ml distilled water with the mixture was one mole of L₂ refluxed for three hours, then left to cool to room temperature, filtered, washed with absolute ethanol and dried.

Results and discussion:

The resulted complexes in this work were insoluble in most organic solvents, such as ethanol and chloroform but soluble in dimethylformamide. The molar conductance (Table 1) of the complexes in (DMF) were in the range (68-81) ohm⁻¹.mole⁻¹. cm² due to complexes (1,2,3) that having the ratio 1:1:1, metal :L₍₁₎:L₍₂₎ indicating 1:1 electrolyte, and in the range (146 – 165) ohm⁻¹. mole⁻¹. cm² due to complexes (4,5,6) that having the ratio 1:2, metal: 2 (L₍₁₎) indicating 1:2 electrolyte, and in the range (8-18) ohm⁻¹. mole⁻¹. cm² due to complexes (7,8,9) that having the ratio 1: 2, metal: 2 (L₍₁₎), These complexes are non- electrolytes (Geary., 1971).

Infrared spectra:

The Ligand (L_1) showed band at 1632 cm^{-1} due to $\nu(\text{C}=\text{N})$ shifted by $(18-30)\text{ cm}^{-1}$ towards lower frequencies. This behaviour suggested that N atom in Schiff base take part in coordination (Jon et al., 2007). (Table 2).

Xanthato group in ligand (2) showed one band at $(1025)\text{ cm}^{-1}$ due to $\nu(\text{C}-\text{S})$ shifted towards a lower frequency by $(35-50)\text{ cm}^{-1}$ on complication. This behavior suggested that both sulphur atoms in the xanthato group take part in coordination (Rai. et al., 1986). In all the complexes new bands were observed in the range $(410-430)\text{ cm}^{-1}$ for complexes having the ratio 1:1:1, metal : $L_{(1)}$: $L_{(2)}$ and ratio 1:2, metal: 2 ($L_{(1)}$) , and in the range $(400-420)\text{ cm}^{-1}$ for complexes having the ratio 1:1:1, metal : $L_{(1)}$: $L_{(2)}$ These bands gave proof to the coordination of the ligand with metal ion, $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{S})$, respectively (Abd-Elzاهر., 2001, and Pancchai et al., 2007).

Magnetic measurements and electronic spectra:

The electronic spectrum for the Schiff base for $L_{(1)}$ and its complexes in DMF were recorded. Two bands at 25630 cm^{-1} and 31610 cm^{-1} were observed in the spectrum of the ligand which was attributed to $n \rightarrow \pi^*$ and $\pi \rightarrow \pi^*$ transitions in the $(\text{C}=\text{N})$ chromophore and aromatic ring , respectively (Williams and Fleming, 1989).

Cobalt (II) complexes:

The values of magnetic moment for Co (II) complexes (1,4,7) in the range $(3.78-3.82)$ B.M. were in accordance with the high spin Co(II) (John et al.,2007). The electronic spectra for Co (II) complexes showed three bands between $(7500-12000)\text{ cm}^{-1}$ $(16350-15410)\text{ cm}^{-1}$, and $(19650-21500)\text{ cm}^{-1}$ assigned to ${}^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}(\text{F}) (\nu_1)$, ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{2g}(\text{F}) (\nu_2)$ and ${}^4T_{1g}(\text{F}) \rightarrow {}^4T_{1g}(\text{p}) (\nu_3)$.The (ν_1) transition, ${}^4T_{1g}(\text{F}) \rightarrow {}^4A_{2g}(\text{F})$ lies outside

the range of the spectrometer used but was calculated (Jon et al., 2006) . These are typical for octahedral structure (Aggoral and Saxena.,1984; Rai et al.,1986).

Ni (II) Complexes:

The Ni (II) complexes (2,5,8) showed a magnetic moment (3.26-3.35) B.M at 25 °C . Which indicated octahedral environment around Ni (II) ion (Ali et al., 2005). The electronic spectra of the complexes showed three bands between (11150 – 11500) cm^{-1} , (13000 – 16000) cm^{-1} , and (24500 - 25400) cm^{-1} due to three spin-allowed transition $^3A_{2g}(F) \rightarrow ^3T_{2g}(F)$ (ν_1), $^3A_{2g}(F) \rightarrow ^3T_{1g}(F)$ (ν_2) and $^2A_{2g}(F) \rightarrow ^2T_{1g}(P)$ (ν_3), these bands suggested octahedral geometry (Giannis et al., 2007).

Cu(II) Complexes:

The Cu(II) complexes (3,6,9) had the magnetic moment (1.78 – 2.00) B.M, which is corresponding to one unpaired electron $t_{2g}^6 e_g^3$. The electronic spectra of Cu(II) complexes showed one a broad band due to $^2B_{1g} \rightarrow ^2A_{1g}$ (ν_1), $^2B_{1g} \rightarrow ^2B_{2g}$ (ν_2) and $^2B_{1g} \rightarrow ^2E_g$ (ν_3) recorded between (13088- 14750) cm^{-1} which referred to two or three or combined transitions irregular octahedral structure around Cu(II), and caused by Jahn-Teller effect (Atsushi et al.,2005 ; Bechor et al., 1982).

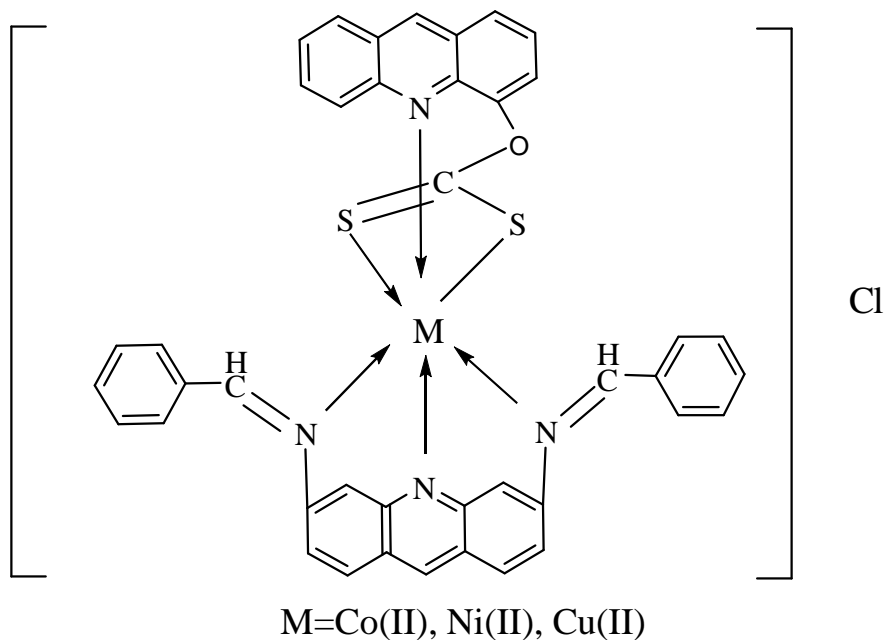


Fig-1: Complexes having the ratio 1:1:1 metal 1: (L_1) 1: (L_2)

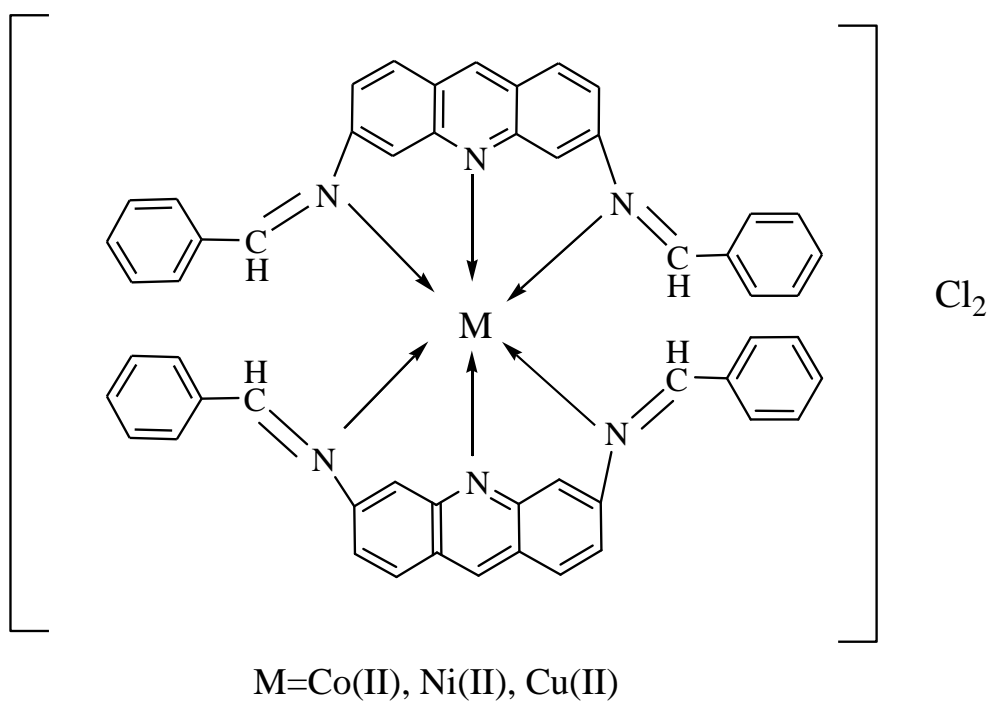
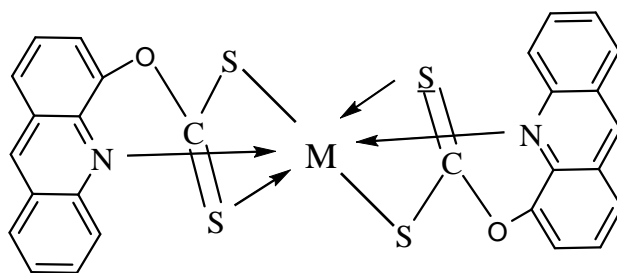


Fig-2: Complexes having the ratio 1:2 metal 1: 2(L_1)



M = Co(II), Ni(II) and Cu(II)

Fig-3: Complexes having the ratio 1:2 metal : 2(L₂)

Table (1): Some analytical data and physical properties

No.	Compound	m.p ° C	Colour	Yield %	Metal % Found (calc)	Λ _M (DMF) ohm ⁻¹ . mole ⁻¹ . cm ²	μ _{eff} B.M
-	L ₁	221	Brown	76	-	-	-
-	L ₂	210	Yellow	72	-	-	-
1	[Co(L ₁)(L ₂)]Cl	254	Dark blue	69	8.42 (8.06)	72	3.78
2	[Ni(L ₁)(L ₂)]Cl	268	Green	74	7.95 (8.11)	68	3.26
3	[Cu(L ₁)(L ₂)]Cl	245	Brown	70	8.58 (8.64)	81	2.00
4	[Co(L ₁) ₂]Cl ₂	256	Blue	72	6.30 (5.80)	165	3.81
5	[Ni(L ₁) ₂]Cl ₂	270	Dark yellow	78	6.25 (6.40)	160	3.28
6	[Cu(L ₁) ₂]Cl ₂	264	Black	81	6.27 (5.12)	146	1.78
7	[Co(L ₂) ₂]	264	Dark yellow	71	10.33 (10.56)	8	3.82
8	[Ni(L ₂) ₂]	273	Green	70	10.25 (10.18)	18	3.35
9	[Cu(L ₂) ₂]	260	Yellow	72	11.03 (10.85)	12	1.82

Table (2): Characteristic infrared bands (cm^{-1}) of the ligands and their complexes:

Compound	ν (C=N)	ν (C-S)	ν (M-N)	ν (M-S)
L ₁	1632	-	-	-
L ₂	-	1025	-	-
(1)	1610	985	415	408
(2)	1614	975	430	400
(3)	1608	982	416	418
(4)	1602	-	410	-
(5)	1612	-	427	-
(6)	1604	-	422	-
(7)	-	984	-	420
(8)	-	987	-	412
(9)	-	990	-	415

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