

Transition Metal Complexes of Bidentate Ligand N-aminoquinolino-2-one and Anthranilic Hydrazide

Israa A. Hassan

Department of chemistry, College of Science University of Mosul, IRAQ

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Abstract

This research involves the preparation of some transition metal complexes of Ni(II), Cu(II), Zn(II) and Hg(II) with the ligand N-aminoquinolino-2-one(L) and mixed ligands such as anthranilic hydrazide as a bidentate ligand. Complexes of the general formula $[M(L)_2Cl_2]$, $[M(L)_2Cl_2]$ and $[M(L)_2(L_2)]Cl_2$ were prepared through direct reaction of the above ligand with the metal respectively (1:1), (1:2) and (1:2:1) ligand with anthranilic acid. These complexes were characterized by means of Microanalysis (M) molar conductance measurements, Magnetic measurements, Infrared and electronic spectral techniques.

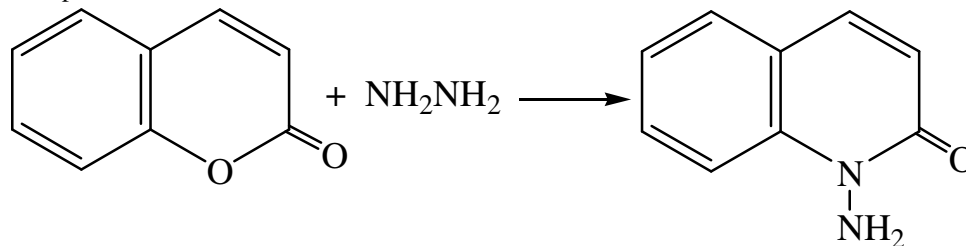
Keywords: Metal complexes, N-aminoquinolino-2-one, spectral study.

Introduction

Interest in coordination chemistry is increasing continuously with the preparation of organic ligands containing a variety of donor groups¹⁻² and it is multiplied many fold when the ligands have biological importance³⁻⁴. Coumarins have stimulated extensive research in biology, organic chemistry and medicine, due to their antibiotic⁵, anti-coagulant⁶⁻⁷, anticancer⁸, anti-inflammatory⁹. Coumarins are now a day an important group of organic compounds that are used as additives to food and cosmetic¹⁰, the derivatives of coumarin usually occur as secondary metabolites present in seeds, roots and leaves of many species. Transition metal has varying utility and interesting chemistry. Coordination compounds are important due to their role in biological and chemical systems in various ways. Al-Amery reported the synthesis and antimicrobial studies of Co(II), Ni(II), Cu(II) complexes with Schiff bases derivative from N-aminoquinolone¹¹.

The present research reports the preparations and characterization of some new complexes formed by the reaction of Ni(II), Cu(II), Zn(II) and Hg(II) with two different donor atoms¹².

Experimental: The ligands (L) have been synthesized according to the reported procedure¹³.



Preparation of the metal complexes

Material and Methods

All chemicals were of reagent grade, were used as supplied (Fluka) or (B.D.H.). Metal estimation was done on a PYE UNICAM SPg atomic absorption spectro-photometer. The chloride was determined using the method in Vogel¹⁴. Conductivity measurements for 10⁻³M solution of the complexes in (DMF) were carried out with a Jenway 4070 conductivity meter and a dip cell with a platinumized electrode. Infrared spectra were recorded on a FTIR Burcker Tensor 27co spectrophotometer in 400-4000 cm⁻¹ range using KBr discs. The UV/Vis spectra were recorded on a Shimadzu UV-160 spectrophotometer for 10⁻³ M solution of complexes in DMF using a 1cm quartz cell. Melting points were measured using an electro-thermal 9300 digital melting point apparatus. Magnetic susceptibility was measured on the solid state by Faraday's method using a Burcker BM6 instrument at 25°C. All magnetic susceptibility values were corrected for diamagnetic using Pascal's constant.

Synthesis of the ligand: Treatment of coumarin (1.46gm, 0.01mol) with excess hydrazine hydrate (99%) (3.2 gm, 0.1 mol) in absolute ethanol (25ml) was refluxed for 12h, it was then cooled and the formed solid was collected and recrystallized from chloroform (m.p. 131-133°C).

A-1 $[M(L_1)Cl_2]$ or $[M(L_1)_2Cl_2]$: A hot ethanolic (20ml) solution of the ligand (L_1)(1.34 gm. 0.01mol) or(2.68gm 0.02mol) was added hot ethanolic (20ml) solution of the metal salts (0.01 mol) with stirring the mixture was refluxed for hr-cooling gave complexes with different color. They were filtered off washed with cold Etoh and dried in vacuum.

B-2 $[M(L_1)_2(L_2)]Cl_2$: The same above procedure besides the addition of the ligand (L_2)

Results and Discussion

The new bidentate (L_1) was prepared by the reaction of coumarin with excess of hydrazide hydrate to give N-amino quinoline -2- one in high yield. The complexes were prepared through direct reaction of the metal chlorides $NiCl_2 \cdot 6H_2O$,

$CuCl_2 \cdot 6H_2O$, $ZnCl_2$ and $HgCl_2$ with the above ligand in different molar ratio, gave the complexes of the general formula $[M(L_1)Cl_2]$, $[M(L_1)_2Cl_2]$, and some mixed ligand like anthranilic hydrazide as bidentate ligand. The analytical data of the ligand and its complexes are given in table-1. These data were in a good agreement with the proposed formula. All the complexes in the air are stable at room temperature and insoluble in common organic solvents but they are soluble in dimethyl formamide (DMF) or dimethyl sulfoxide (DMSO).

The electrical molar conductance of the complexes no. (1-8) were (14–31) $ohm^{-1} mol^{-1} cm^2$ indicating non-conductive. Where the complexes no. (9–12) gives (151–192) which are corresponding conductivity complexes indicating a 1:2 $ohm^{-1} mol^{-1} cm^2$ electrolytic nature of the complexes¹⁵ (table-1)

Table-1
Physical properties of ligand and its complexes

No	Complex	Color	M.P	Yield	Molar Conductivity $\Omega cm^{-1}, mol^{-1}$	Elemental analysis
	L_1	Orange	131-133	91%		
1.	$[Ni(L_1)Cl_2]$	Light blue	246	80%	22	20.41 (18.92)
2.	$[Cu(L_1)Cl_2]$	Brown	270	81%	29	21.61 (23.26)
3.	$[Zn(L_1)Cl_2]$	Yellow	198.8	73%	15	22.26 (18.99)
4.	$[Hg(L_1)Cl_2]$	Light yellow	218.4	60%	21	50.90 (47.14)
5.	$[Ni(L_1)_2Cl_2]$	Grey	153	86%	26	13.16 (11.50)
6.	$[Cu(L_1)_2Cl_2]$	Brown	182	84%	24	14.01 (14.33)
7.	$[Zn(L_1)_2Cl_2]$	Dark yellow	144	67%	31	14.46 (12.69)
8.	$[Hg(L_1)_2Cl_2]$	White	139	69%	14	36.33 (34.10)
9.	$[Ni(L_1)(L_2)]Cl_2$	Grey	118.9	70%	151	10.93 (9.99)
10.	$[Cu(L_1)(L_2)]Cl_2$	Dark green	143.0	64%	155	11.66 (10.02)
11.	$[Zn(L_1)(L_2)]Cl_2$	Light yellow	124.3	72%	192	12.04 (11.20)
12.	$[Hg(L_1)(L_2)]Cl_2$	Light orange	133.2	57%	159	29.78 (27.15)

Table-2
Infrared spectral data of ligand and their complexes

No.	Compound	$\delta N-H$	$\nu N-N$	$\nu C=O$	$\nu N-H$	M-N	M-O
	L	1683	930	1198	3060		
1.	$[Ni(L_1)Cl_2]$	1640	987	1167	3244	490	450
2.	$[Cu(L_1)Cl_2]$	1645	976	1157	3236	471	461
3.	$[Zn(L_1)Cl_2]$	1625	975	1163	3282	525	462
4.	$[Hg(L_1)Cl_2]$	1641	977	1184	3246	513	423
5.	$[Ni(L_1)_2Cl_2]$	1634	985	1240	3445	471	439
6.	$[Cu(L_1)_2Cl_2]$	1636	969	1157	3381	485	453
7.	$[Zn(L_1)_2Cl_2]$	1628	978	1125	3234	495	441
8.	$[Hg(L_1)_2Cl_2]$	1640	980	1163	3373	503	465
9.	$[Ni(L_1)(L_2)]Cl_2$	1630	957	1161	3373	492	427
10.	$[Cu(L_1)(L_2)]Cl_2$	1641	966	1161	3341	503	435
11.	$[Zn(L_1)(L_2)]Cl_2$	1625	977	1238	3218	512	427
12.	$[Hg(L_1)(L_2)]Cl_2$	1639	945	1230	3415	528	427

Infrared spectral studies of the free ligand shows strong band at 1683 cm^{-1} which is assignable $\nu(\text{C}=\text{O})$ of coumarin and other band at $3060, 1198\text{ cm}^{-1}$ belong to $\nu\text{NH}_2, \delta\text{NH}_2$. The spectra bands of complexes at $(1625\text{--}1645)\text{ cm}^{-1}$ were characterized for the carbonyl group which indicates that the oxygen atom of the carbonyl group was coordinated to the metal ion and the prepared complexes exhibited νNH_2 in the range of $(3236\text{--}3445)\text{ cm}^{-1}$, which shows a shifting to the higher frequencies, A medium band at $(1230\text{--}1271)\text{ cm}^{-1}$ maybe assigned to δNH_2 stretching vibration. Weak band located at $(930\text{--}987)\text{ cm}^{-1}$ can be assigned (N-N) group. negative and positive shift in ν (N-N) hydrazide groups¹⁶. The absorption band in the range $(471\text{--}535)$ and $(423\text{--}465)\text{ cm}^{-1}$ were assigned to (M-N) and (M-O) bands (table 3)

Table-3
Magnetic moment and electronic spectral data of the complexes

No.	Complexes	$\mu_{\text{eff}}(\text{B.M})$	$\lambda_{\text{max}}\text{ cm}^{-1}$
1.	$[\text{Ni}(\text{L}_1)\text{Cl}_2]$	3.29	13173,15889,30860
2.	$[\text{Cu}(\text{L}_1)\text{Cl}_2]$	1.34	15330,15514,26042
3.	$[\text{Zn}(\text{L}_1)\text{Cl}_2]$	---	27933,30120
4.	$[\text{Hg}(\text{L}_1)\text{Cl}_2]$	---	25000,34101
5.	$[\text{Ni}(\text{L}_1)_2\text{Cl}_2]$	2.91	10419,16534,25509
6.	$[\text{Cu}(\text{L}_1)_2\text{Cl}_2]$	1.99	13290,17250,25011
7.	$[\text{Zn}(\text{L}_1)_2\text{Cl}_2]$	---	26040,34021
8.	$[\text{Hg}(\text{L}_1)_2\text{Cl}_2]$	---	30131,32000
9.	$[\text{Ni}(\text{L}_1)(\text{L}_2)]\text{Cl}_2$	2.71	10101,18559,26737
10.	$[\text{Cu}(\text{L}_1)(\text{L}_2)]\text{Cl}_2$	1.73	12871,19424,31002
11.	$[\text{Zn}(\text{L}_1)(\text{L}_2)]\text{Cl}_2$	---	30822,32011
12.	$[\text{Hg}(\text{L}_1)(\text{L}_2)]\text{Cl}_2$	---	28212,34120

The magnetic moment of Ni (II) complexes no.1 was 3.29 B.M. The electronic spectra showed broad band in the range at $(13173\text{--}15889)\text{ cm}^{-1}$ assigned to ${}^3\text{T}_{1(\text{F})} \rightarrow {}^3\text{T}_{1(\text{p})}$ transition¹⁷ and another band at 30860 cm^{-1} was absorbed due to charge transfer these values suggested a tetrahedral geometry¹⁸, but another Ni(II) complexes no.(5,9) the magnetic moment were (2.91,2.88) B.M and the electronic spectra of these complexes shows three bands at $(10126\text{--}10149)$ $(16534\text{--}18559)$ $(25509\text{--}25899)\text{ cm}^{-1}$ correspond to three spin allowed transition ${}^3\text{A}_{2\text{g}(\text{F})} \rightarrow {}^3\text{T}_{2\text{g}(\text{Fv1})}$,

${}^3\text{A}_{1\text{g}(\text{F})} \rightarrow {}^3\text{T}_{1\text{g}(\text{v2})}$ and ${}^3\text{A}_{2\text{g}(\text{F})} \rightarrow {}^3\text{T}_{1\text{g}(\text{p}(\text{v3}))}$ ¹⁹.

The magnetic moment of Cu(II) complexes (2, 6, and 10) has been found to be (1.34, 1.99, and 1.73) B.M the lower value suggested the presence one unpaired electron. The electronic spectra of this complex showed a band at $(15330\text{--}15514)\text{ cm}^{-1}$ were assigned to ${}^2\text{T}_{2\text{g}} \rightarrow {}^2\text{E}_{\text{g}}$ transition in tetrahedral environment²⁰, where the electronic spectra of two copper (II) complexes display bands at $(13290\text{--}17250)$ and $(12871\text{--}19424)\text{ cm}^{-1}$ assigned to the ${}^3\text{G}_{\text{g}} \rightarrow {}^3\text{T}_{2\text{g}}$ transition in distorted octahedral structure around the Cu(II) ions²¹⁻²².

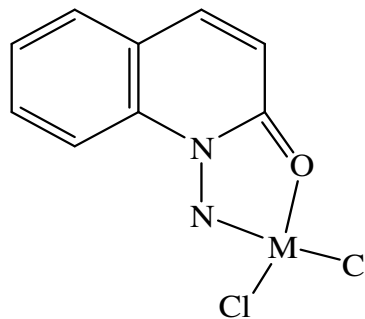


Figure-1

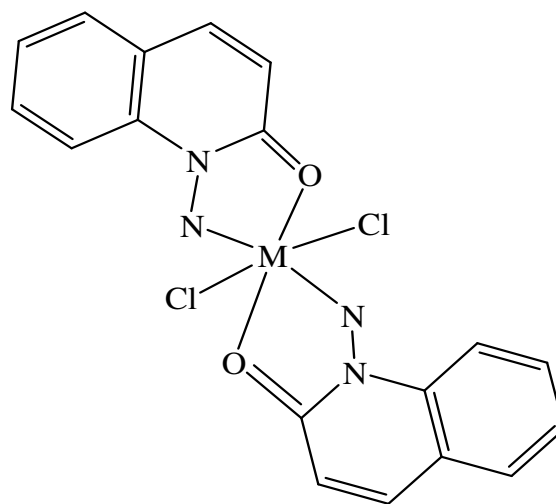


Figure-2

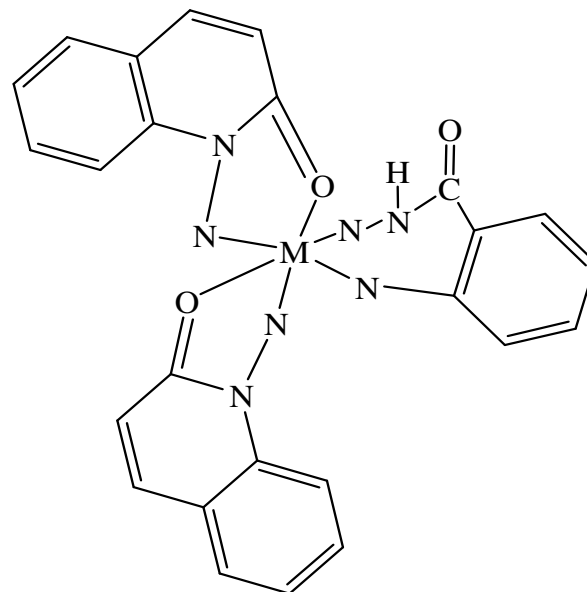


Figure-3

Suggested structure of complex, where $\text{M} = \text{Ni}^{+2}, \text{Cu}^{+2}, \text{Zn}^{+2}, \text{Hg}^{+2}$

Conclusion

The electronic spectra of Zn(II), Hg(II) complexes give only charge transfer in the range (25000–34211)cm⁻¹ and the magnetic susceptibility showed that all these complexes were diamagnetic²³.

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