Magnetic and spectroscopic properties of some new complexes of cobalt (II), nickel (II) and copper (II) with α-(2,6-dimethyl anilino)-2,6-dimethyl acetanalide

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الخـــلاصـــة

تـــم تحضـــير عـــدد مـــن معقـــدات جديـــدة ذات الصـــيغ $[NiL_2X_2]$ و $[ML_2]X_2$ و $[ML_2SO_4.H_2O]$ حيث M = Cu(II),Co(II),Ni(II);L=α-(2,6-dimethyl anilino)-6,2 – ثنائي مثيل انيلينو)-6,2 ; X= Cl^-,Br^-,NO_3^- . وتم تشخيص المعقدات باستخدام تقنيات التحليـــل الدقيق للعناصر وقياسات التوصيلية الكهربائية المولارية والقياسات المغناطيسية وقياسات الأشعة تحت الحمراء والطيف الالكتروني . وقد اقترحت تراكيب كيليتية للمعقدات إذ يسلك فيها الليكانـــد بشكل ثنائي السن كيليتي من خلال ذرتي النتروجين.

ABSTRACT

New complexes of the general formulae $[Ni(L)_2X_2]$,$[M(L)_2]X_2$ and $[M(L)_2SO_4.H_2O]$ where M=Ni(II),Co(II),Cu(II);L=α-(2,6-dimethyl anilino)-2,6-dimethyl acetanalide ; X=Cl^-,Br^-,NO_3^-, have been prepared and characterized by elemental analysis,conductivity measurements,magnetic moments and spectral (IR and electronic) studies. Chelated structures have been proposed for the resulting complexes in which the ligand acted as bidentate chelating ligand through the two nitrogen atoms.

INTRODUCTION

N-alkyl and N-aryl substituted acetamide compounds aroused considerable interest with regard to their ability to form complexes with transition metal ions[1,3] . This partially was due to their wide range of different molecular topologies and sets of doner atomes[4]. In addition to their

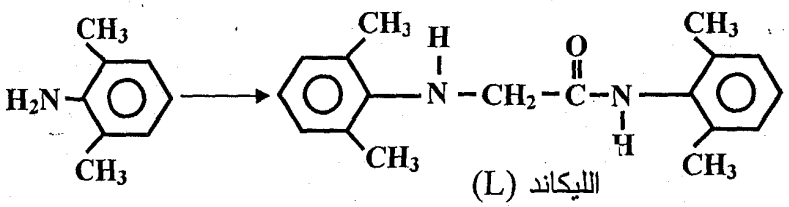
interesting ligational properties, both substituted acetamide ligand and complexes had importance biological and industrial applications,they are of considerable importance in the field of anti-inflammatory action and bacterial growth inhibitors[5].Hence,alarge body of the coordination chemistry of N-alkyl and N-aryl substituted acetamide with transition and non-transition metal ions have been reported preferring derivatives for many biological fundamental systems,such as photosynthesis and transport of oxygen in mamalian and other resperatory systems[6].

In view of the above the synthesis and characterization of new nickel(II),cobalt(II) and copper(II) complexes with α-(2,6-dimethyl anilino) - 2,6-dimethyl acetanalide ligand have been studied .

EXPERIMENTAL SECTION

The ligand has been synthesised according to the following procedure. 2.1g (0.022 mole) of chloroacetic acid and 3.3 g (0.028 mole) of thionyl chloride have been refluxed under anhydrous conditions at (70-78°C) for 30 minutes with continueous stirring. The excess of thionyl chloride was evaporated to obtain chloroacetyl chloride.40 ml of dry benzene have been added to the above product and then cooled to 0°C followed by the addition of 5.32 g (0.044 mole) of 2,6-dimethyl aniline and then refluxed for 1.5 hrs with continuous stirring. After evaporation of benzene, 50 ml of water have been added and the solution was neutralized with (10%) sodium hydroxide solution till be alkaline,the resulting precipitate was filtered off, washed with ice cold water and then recrystallized from ethanol-water to obtain pale yellow powder of 67% yield[8]. The reaction can be represented as followes:

1- $Cl-CH(=O)-C-OH + SOCl_2 \longrightarrow Cl-CH_2-C(=O)-Cl$

2- $Cl-CH_2-C(=O)-Cl + 2$  $+2HCl$

(L) الليكاند

A: Preparation of the metal complexes:

A solution of $NiCl_2.6H_2O$ (0.23 g,0.01 mole) in (10 cm^3) ethanol was mixed with an ethanolic solution of the ligand (0.54,0.02 mole). The mixture was refluxed for 1 hour, then cooled.The precipitate was filtered off, washed

with cold ethanol and diethyl ether several times and then dried under vacuum.

The same procedure has been followed to prepare the Co(II),Ni(II) and Cu(II) complexes using (0.01 mole) and the weights of the metal salts are listed in table 1.

B: Physical measurements

Analysis of the complexes were carried out with a CHN analyzer type (Carlo Erba) in Chemistry Department, Science College, Mosul University.Cobalt,nickel and copper content in all the complexes were determined gravimetrically[7]. IR spectra in the region 200-4000 cm^{-1} was recorded on a PYE Unicam SP2000 recording spectrophotometer using KBr pellets. The electronic spectral measurements were carried out using PYE Unicam SP1800 spectrometer in DMF 10^{-3}M solution in the region 200-1100 nm. The magnetic measurements have been determined at room temperature by Farady method, using Bruker-BM6.

Conductance measurements were carried out at room temperature in DMF solution (10^{-3} M) using bridge conductivity type MC1.

RESULTS AND DISCUSSION

Chemical analysis (CHN and the metal contents) supported the proposed formulations (values have been listed in Table 1 with some of their pertinent physical-chemical properties).

The magnetic moment values at room temperature of the cobalt (II) complexes $[Co(L)_2]X_2$ (X = Cl^-,Br^-,NO_3^- and ½ SO_4^{-2}) (Table 2) were in the range 3.72-3.95 BM. These values were simillar to those reported for four coordinate spin only value (3.89 BM) tetrahedral cobalt (II) complexes[9,10,11].

The electronic spectra of cobalt (II) complexes showed one band located at 14880-15152 cm^{-1} which may be attributed to the transition $^4A_2(F) \longrightarrow {}^4T_1(P)\ \upsilon_3$ in an average field of tetrahedral (Td) symmetry.

On the other hand, the υ_2 and υ_1 bands can not be observed due to instrumental limitation

Conductivity measurement showed a 1:2 and 1:1 electrolytes for cobalt (II) complexes which supported the tetrahedral configuration[12].

The non electrolyte nickel (II) complexes $[Ni(L)_2X_2]$ (X = Cl^-,Br^- and NO_3^-) and $[Ni(L)_2(SO_4)(H_2O)]$ showed magnetic moment values of 2.89-3.13 BM.(Table1) which were quite typical to six-coordination spin free octahedral species[9,10].

The electronic spectra of the nickel (II) complexes showed two absorption maxima at 24800-25641 cm^{-1} and 13157-13931 cm^{-1} assigned to $^3A_2g \longrightarrow {}^1T_2g(P)\ (\upsilon_3)$ and $^3A_2g \longrightarrow {}^3T_1g(P)\ (\upsilon_2)$ transitions, respectively,

in octahedral symmetry[12]. The υ_2 & υ_3 band positions were used to calculate the third transition band (at 7774-8300 cm^{-1}) which was attributed to $^3A_2g \longrightarrow {}^3T_2g(P)(\upsilon_1)$ transition. The values of B and β (Table 2) also supported the octahedral geometry of the nickel (II) complexes and suggested a moderate configuration interaction between the high spin T_1g (P) and T_1g(F) excited states[9,10,12,15].The calculated values of Racah parameter (B)(Table 2) lied in the range 957-978 cm^{-1} for these complexes. The results are in a good agreement with those reported for nickel (II) complexes (8,13). The calculated values of β (Table 2) indicated a strong degree of covalent characters among the hexa-coordinated complexes.

The magnetic moment values at room temperature (1.53 BM., 1.66 BM.,1.69 BM.,1.82 BM.) for the copper (II) complexes were well in accord with those having distorted octahedral structure[13].The electronic spectra showed a band at 19000cm^{-1} which could be assigned to a tetragonally distorted octahedral structure. The non electrolytic nature of those complexes were in accord with their tentative structures.

The important IR bands with their assignments were listed in Table 3. The IR data for the present ligand and its complexes were some what complicated. However, careful comparison of the IR spectra of the ligand with its metal complexes gave positive information about the coordination.

The υ_s(N-H) and υ_{as}(N-H) of the ligand appeared around 3250 and 3000 cm^{-1} respectively,have been disappeared with the appearance of a new broad band around 3100-3000 cm^{-1} on complexation. The broadening of this band may be attributed to the inter or intra-molecular interaction of the metal complexes[16].

The stretching mode ($\upsilon C = O$) observed at about 1650 cm^{-1} in the IR spectra of the ligand should be lowered upon complexation. The position of this band have been remained unchanged in the spectra of the complexes suggesting the non involvement of the carbonyl oxygen in bonding.

The IR spectra of the complexes showed a distinct band around 450 cm^{-1} which was attributed to M-N stretching vibration providing additional evidence that nitrogen atoms were bonded to the metal ion[16,17] .

The IR spectra of the nitrate complexes $[Ni(L)_2(NO_3)_2]$ and $[Cu(L)_2(NO_3)_2]$ exhibited a split absorption bands, a sharp band at about 1450 cm^{-1} , and a broad at about 1345 cm^{-1} . A simillar splitting of such band has been observed in nitrate complexes indicating the weakly monodentate manner of NO_3^- coordination[18]. The IR spectra of the complexes $[Co(L)_2](NO_3)_2$ showed a strong band around 1370 cm^{-1} which was assigned to ionic NO_3^- group[19].

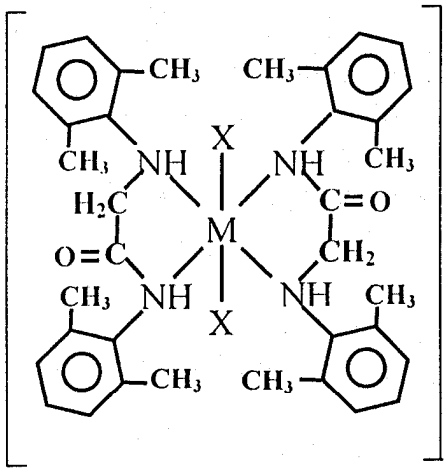
The (M-X) (X = Cl^-,Br^-) stretching vibration observed at 320 and 290 cm^{-1} for the complexes $[Ni(L)_2(Cl)_2]$ and $[Ni(L)_2(Br)_2]$ respectively, supported the formation of such complexes , these values were simillar to those reported for other simillar complexes[19].

The sulphate complexes $[M(L)_2(SO_4).(H_2O)]$ (M = Ni (II) or Cu (II)) showed three bands in the regions 950, 1100 and 654 cm^{-1} , these bands were assigned to υ_1 , υ_3 and υ_4 ,respectively, which supported that sulphate group acted as monodentate ligand[15]. The IR spectrum of the sulphate complexes showed a broad band in the region 3300-3500 cm^{-1} and an additional band at 1005 cm^{-1} which were assigned to the rocking mode of the coordinated water[17].

CONCLUSION

The ligand α-(2,6-dimethyl anilino)-2,6-dimethyl acetanalide acted as bidentate chelating ligand joint to the central metal ions Co(II),Ni(II) and Cu(II) through the two nitrogen atoms.

The physico-chemical analysis of the complexes (Table 1,2,3) are in agreement with the suggested formula Figure 1.



M = Co(II), Ni(II) & Cu(II)
X = Cl^-, Br^-&NO_3^-

Fig.1: Suggested structure of the complexes

Table (1): Analytical, magnetic and other physical properties

No	Compound	Weight of salt used	m.p °C	Color	Analysis % : Found (Calculated)				μ_{eff} B.M (303 K)	Molar conductaus ($\Omega^{-1}cm^2$ mol^{-1})
					C	H	N	M		
1	$[Co(L)_2]Cl_2$	0.23	124	Green	68.11 (68.25)	6.32 (6.45)	8.56 (8.84)	8.98 (9.10)	2.89	149
2	$[Co(L)_2]Br_2$	0.21	131	Brown	58.33 (58.87)	5.11 (5.39)	6.89 (7.63)	7.90 (8.03)	2.84	158
3	$[Co(L)_2](NO_3)_2$	0.29	124	Blue	57.31 (57.83)	5.81 (5.89)	11.02 (11.24)	7.61 (7.88)	2.92	155
4	$[Co(L)_2]SO_4$	0.28	128	Blue	65.76 (68.03)	6.08 (6.12)	7.29 (7.48)	8.00 (8.19)	3.13	79
5	$[Ni(L)_2(Cl)_2]$	0.23	143	Light Green	67.84 (68.27)	6.35 (6.45)	8.80 (8.85)	9.10 (9.27)	3.72	8
6	$[Ni(L)_2(Br)_2]$	0.22	148	Green	58.54 (58.97)	6.80 (6.86)	7.33 (7.64)	8.51 (8.81)	3.83	11
7	$[Ni(L)_2(NO_3)_2]$	0.29	135	Yellowish Green	57.44 (57.85)	5.82 (5.89)	11.01 (11.24)	7.66 (7.86)	3.95	14
8	$[Ni(L)_2(SO_4)(H_2O)]$	0.28	128	Green	58.14 (58.63)	6.15 (6.24)	7.33 (7.60)	7.21 (7.46)	3.81	9
9	$[Cu(L)_2(Cl)_2]$	0.17	145	Gray	64.13 (64.75)	6.31 (6.40)	8.35 (8.48)	9.30 (9.46)	1.53	14
10	$[Cu(L)_2(Br)_2]$	0.22	141	Redish brown	58.29 (58.49)	5.41 (5.46)	7.39 (7.49)	7.36 (7.46)	1.66	8
11	$[Cu(L)_2(NO_3)_2]$	0.24	153	Yellow	57.42 (57.46)	5.80 (5.85)	11.05 (11.17)	8.17 (8.44)	1.69	12
12	$[Cu(L)_2(SO_4)(H_2O)]$	0.25	128	Green	57.95 (58.26)	6.02 (6.20)	7.34 (7.45)	8.22 (8.46)	1.82	16

Table (2):Electronic spectral bands and data

No.	Compund	Charge trans for bands cm^{-1}	υ_3 cm^{-1}	υ_2 cm^{-1}	υ_1 cm^{-1}	B	β
1	$[Ni(L)_2(Cl)_2]$	31347,37174	24960	13157	7824	978.05	0.90
2	$[Ni(L)_2(Br)_2]$	37174	24800	13200	7774	971.78	0.9
3	$[Ni(L)_2(NO_3)_2]$	30303,38131	25641	13931	8300	976.42	0.90
4	$[Ni(L)_2(SO_4)(H_2O)]$	30303,37174	25125	13550	8133	956.77	0.88
5	$[Co(L)_2]\ Cl_2$	29154,37174	14900				
6	$[Co(L)_2]\ Br_2$	28985,37174	14880				
7	$[Co(L)_2](NO_3)_2$	28409,37174	15152				
8	$[Co(L)_2]SO_4$	28985,37131	14987				
9	$[Cu(L)_2(Cl)_2]$	29154,37174					
10	$[Cu(L)_2(Br)_2]$	29154,37174					
11	$[Cu(L)_2(NO_3)_2]$	28571,29850,37174					
12	$[Cu(L)_2(SO_4)(H_2O)]$	30581,37174					

$\beta = B/B_o = B/1080$ (where B = the Recah parameter value in the free ion state).

Table (3):Selected IR bands and their assignment

No.	Compund	υ (M-Cl)	υ (M-Br)	υ (M-N)	SO_4			υ_{as} (NO_3)	υ_{as} (N-H)	υ_{ss} (N-H)
					υ_1	υ_2	υ_3			
	ligand								3000_{br} 2930_w	3245_{br} 3175_{br}
1	$[Co(L)_2]Cl_2$			440_S						3045_m
2	$[Co(L)_2]Br_2$			445_S						3050_{br}
3	$[Co(L)_2](NO_3)_2$			440_S				1370_S		3000_m
4	$[Co(L)_2]SO_4$			445_S						3075_m
5	$[Ni(L)_2(Cl)_2]$	310_w		450_m						3100_m
6	$[Ni(L)_2(Br)_2]$		290_w	448_S						3050_{br}
7	$[Ni(L)_2(NO_3)_2]$			450_S				1450_{brm} 1345_{brm}		3065_m
8	$[Ni(L)_2(SO_4)(H_2O)]$			445_S	950_S	1100_m	645_S			3125_m
9	$[Cu(L)_2(Cl)_2]$	320_w		450_S						3080_m
10	$[Cu(L)_2(Br)_2]$		290_w	445_S						3100_m
11	$[Cu(L)_2(NO_3)_2]$			440_S				1400_{brm} 1350_{brm}		3050_m
12	$[Cu(L)_2(SO_4)(H_2O)]$			460_S	950_S	3050_m	650_S			3080_m

(s) = sharp
(m) = medium
(w) = weak
(br) = broad
ss=symmetric
as = assymmetric

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