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NEW COMPLEXES OF COBALT(II) CONTAINING MIXED LIGANDS {ACETYLACETONE BIS(SEMI-CARBAZONE AND SUBSTITUTED PHENOLS)}

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الخلاصة

تمّ تحضير ودراسة التركيب لبعض معقدات الكوبلت (II) مع خليط من ليكاندي الاسيتيل أسيتون بس (سميكاربازون)- $ASCH_2$ وبعض الفينولات المعوّضة { 2-أمينو فينول ($L1H_2$) أو2-كاربوكسي فينول ($L2H_2$) أو 2- نيترو فينول($L3H$) } . شخصت المعقدات الناتجة بطرائق فيزيائية-كيميائية ، ووجد أن لها الصيغ البنائية العامة$[Co(ASCH_2)(LH_2)]X_2$ و$[Co(ASCH)(LH)]$ أو$[Co(ASCH)(L3)]$ في كل من الوسطين المتعادل والقاعدي على التوالي (حيث$LH_2 = L1H_2$ أو $L2H_2$ أو $L3H$ ، $LH = L1H$ أو $L2H$ ، $X = NO_3^-$ أو Cl^-). عززت النتائج أن المعقدات لها شكل ثماني السطوح عالي البرم .

ABSTRACT

The synthesis and structural studies of some cobalt (II) complexes with mixed ligands including acetylacetone bis(semicarbazone) - $ASCH_2$ and substituted phenols {2-aminophenol ($L1H_2$), 2-carboxyphenol ($L2H_2$), 2-nitrophenol ($L3H$)} have been described and characterized using differen different physico-chemical methods . They have been found to have the general formulas $[Co(LH_2)(ASCH_2)]X_2$ and $[Co(L3)(ASCH)]$ or $[Co(LH)(ASCH)]$ in neutral and basic medium , respectively (where $X = NO_3^-$ or Cl^- ; $LH_2 = L1H_2$ or $L2H_2$ or $L3H$; $LH = L1$ or $L2$) . The results supports that the complexes have high spin octahedral geometries .

INTRODUCTION

Recent years witness a growing interest in the chemistry of semicarbazones owing to their ligational properties achieved through several available coordination sites [1,2]. They form an important class of biologically active ligands and provide models for metal-ligand bonding sites in several enzymes [3] .

Substituted phenols are ligands bonding to the central metal ion forming complexes which are used in different purposes [4-6] .

There has been a considerable interest , recently , in the study of mixed ligands complexes of transition and non-transition metal ions due to their important role in biological processes [7-10] .

To the best of available knowledge the synthesis and study of cobalt (II) complexes with mixed ligands have not yet been reported of such ligands . The aim of the present work is , therefore , to investigate the preparation and characterization of some new cobalt (II) complexes with mixed ligands} acetylacetone bis(semicarbazone) and substituted phenols (Figure 1)} .

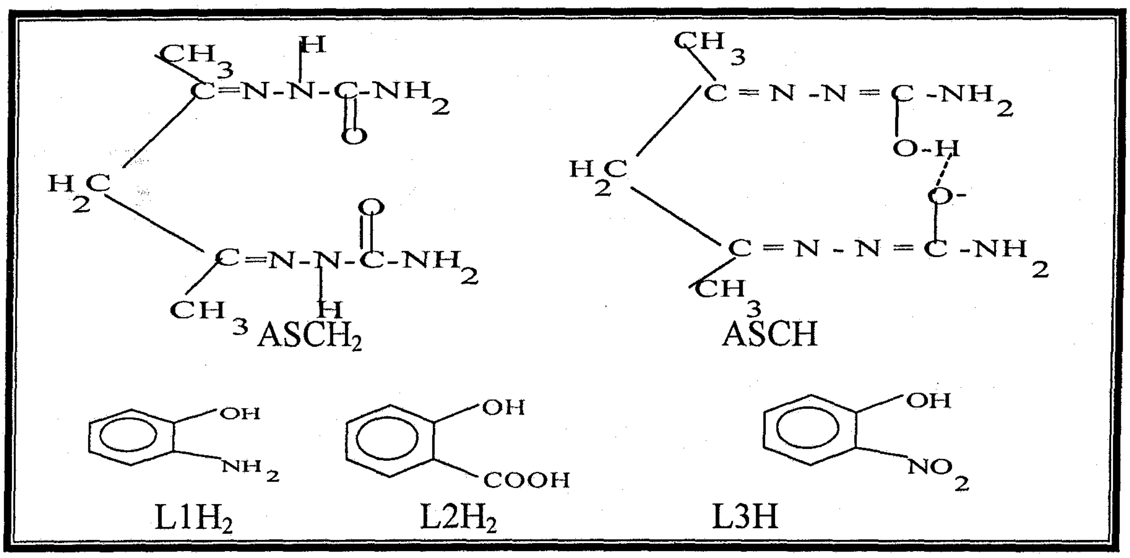

Figure 1 : Model structures of the ligands

EXPERIMENTAL

1 -Synthetic Methods:

Acetylacetone bis(semicarbazone) - $ASCH_2$ has been prepared according to previous method [11] .

Complexes of the type $[Co(LH_2)(ASCH_2)]X_2$ have been prepared by the reaction of aqueous solution of cobalt nitrate or cobalt chloride with ethanolic solution of acetylacetone bis(semicarbazone) and substituted phenols in 1:1:1 molar ratio . The mixture has been refluxed for three hours followed by evaporation to about half it's volume then cooled . The resulting product is separated by filteration , washed with petroleum ether , recrystallized from ethanol and dried .

Complexes of the type [Co(LH)(ASCH] or [Co(L3)(ASCH)] have been prepared by the reaction of aqueous solution of cobalt nitrate or cobalt chloride with hot ethanolic solution of acetylacetone bis(semicarbazone) and substituted phenols in 1:1:1 molar ratio . Potassium hydroxide solution (1M) has been added until the pH of the solution is 8-9 . The mixture has been heated on a waterbath for a few minutes then cooled in ice bath . The product is filtered off , washed with petroleum ether and dried .

2-Analytical and Physical Measurements:

Cobalt contents have been determined by applying precipitation method [12] after the decomposition of the complexes with concentrated nitric acid .

Molar conductivities of the complexes have been measured in an electrolytic conductivity measuring set LF-42 using 10^{-3} M dimethylformamide solutions at room temperature . The infrared spectra has been recorded on a Pye-Unicam 1100 Infrared Spectrophotometer in the 400-4000 cm^{-1} range using KBr pellets . Electronic spectra has been recorded on Shimadzu UV-210A Spectrophotometer for 10^{-4} M solutions of the ligands and their complexes in dimethylformamide at 25 ^{0}c , using a 1cm cell . Magnetic susceptibilities of the complexes have been measured by Bruker B.M 6 .

RESULT AND DISCUSSION

The reaction of cobalt (II) salts with acetylacetone bis (semicarbazone) and substituted phenols in both neutral and basic medium may be represented by the following reactions:

$CoX_2.6H_2O+LH_2+ASCH_2 \rightarrow [Co(LH_2)(ASCH_2)]X_2+6H_2O$

(where $LH_2 = L1H_2$ or $L2H_2$ or $L3H$) in neutral medium

$CoX_2.6H_2O + LH_2 + ASCH_2 + 2KOH \rightarrow [Co(LH)(ASCH)] + 2KX + 8H_2O$

$CoX_2.6H_2O + L3H + ASCH_2 + 2KOH \rightarrow [Co(L3)(ASCH)] + 2KX + 8H_2O$

(where $X=NO_3^-$ or Cl^-, $LH_2 = L1H_2$ or $L2H_2$) in basic medium

The resulted complexes are colored and solids , slightly soluble in water , moderately soluble in ethanol and soluble in dimethylformamide. The values of molar conductivities (Table 1) approach those expected for 1:2 and non electrolytes [13] for complexes prepared in neutral and basic medium , respectively .

The room temperature magnetic moments of Co(II) complexes are in the range of 2.98-3.60 B.M. (Table 1) suggesting the presence of unpaired electrons , the low values of the magnetic moments of some complexes may be due to transfer of electron from cobalt ion to the ligand

[4,14,15] and hence the complexes are spin free with octahedral stereochemistry .

The infrared spectra of ASCH$_2$ ligand (Figure 2) shows a strong band at 1585 cm^{-1} attributed to C=N group [1,2] shifts towards a lower frequency region on coordination due to the decrease of the bond order as a result of metal nitrogen bond formation [1,2,16] . The next strong band at 1685 cm^{-1} attributed to C=O group [7,16] . This value shifts towards a lower frequency on coordination for complexes 1, 2, 3, 7, 8 and 9 indicating the coordination of the two carbonyl oxygen to the metal ion [1,2] in neutral medium . Meanwhile , in basic medium , this band disappears in the complexes and a new band is observed at 1240-1250 cm^{-1} for complexes 4, 5, 6, 10, 11 and 12 due to C-O group , thereby establishing coordination of the ligand through the two enolic oxygen atoms [1,2] . The appearance of strong bands at 1630-1635 and 1570-1580 cm^{-1} which are attributed to ʼ$_{(C=N)}$ + ʼ$_{(O-C=N)}$ and azine chromophore ʼ$_{(C=N-N=C)}$, respectiveively, support the formation of enolic structure in basic medium [14] . The position of the ligand in the range 3200-3300 cm^{-1} due to ʼ$_{NH}$ remains unaltered in the complexes prepared in neutral medium indicating that there is no coordination through the NH group [1,2,16,17]. Meanwhile in basic medium , because of the presence of hydrogen bonding it is more difficult to notice the absence of NH group , but it is well known that this band is disappeared in basic medium due to the enolic form . The other strong bands at 3390 , 3410 and 1450 cm^{-1} due to ʼ$_{NH_2}$ remain unaltered in all the complexes indicating that there is no coordination through this group .

The infrared spectra of substituted phenols (Figure 2) show a band at about 1230 cm^{-1} attributed to C-O group [18] shifts towards higher frequency region on coordination demonstrates that the phenolic oxygen is coordinated to the metal ion . The next band at 3300-3400 cm^{-1} attributed to OH group [18] shifts towards a lower frequency on coordination in the complexes prepared in neutral medium . Whereas in basic medium , this band is disappeared due to the deprotonation . L1H$_2$ shows band at 3200-3250 cm^{-1} due to NH$_2$ group shifts towards a lower frequency indicating the formation of a chelation between the nitrogen of NH$_2$ group and the metal ion [18] . L2H$_2$ ligand shows bands at 1365 and 1600 cm^{-1} attributed to the symmetric and asymmetric stretching frequencies of carboxylic group , respectively . On coordination these two bands shift to 1390 and 1560 cm^{-1} , respectively [18,19] . The difference between the symmetry and asymmetry stretching frequencies of COO$^-$ group ($\Delta\upsilon$ which equal to 170 cm^{-1}) indicate that the carboxylic group act as monodentate [18] . L2H$_2$ ligand shows a band at 3100-3200 cm^{-1} due to OH group , this low value is due to the hydrogen bonding , shifts towards a lower frequency for complexes in neutral medium due to the chelation, meanwhile in basic medium this band is disappeared due to the deprotonation . L3H ligand shows bands at 1525 and 1355 cm^{-1} attributed to the NO_2 group [20] shift towards lower frequencies indicating the coordination of this group with the metal ion . Complexes 1-3 (Table-2) show band at 570-590 cm^{-1} due to ionic chloride [18] . These bands are not observed in the spectra of the complexes prepared in basic medium (complexes 4-6) indicating the absence of this ion . Complexes 7-9 show band at 1380-1385 cm^{-1} attributed to the ionic nitrate [18] . In basic medium (complexes 10-12) these bands are not observed indicating the absence of this group .

On the other hand the spectra of all the complexes show new bands around 430-500 cm^{-1} and 600-750 cm^{-1} due to $'_{M-N}$ and $'_{M-O}$ respectively [17,18] . The presence of these bands strongly support the formation of the complexes under investigation (Figure 2) .

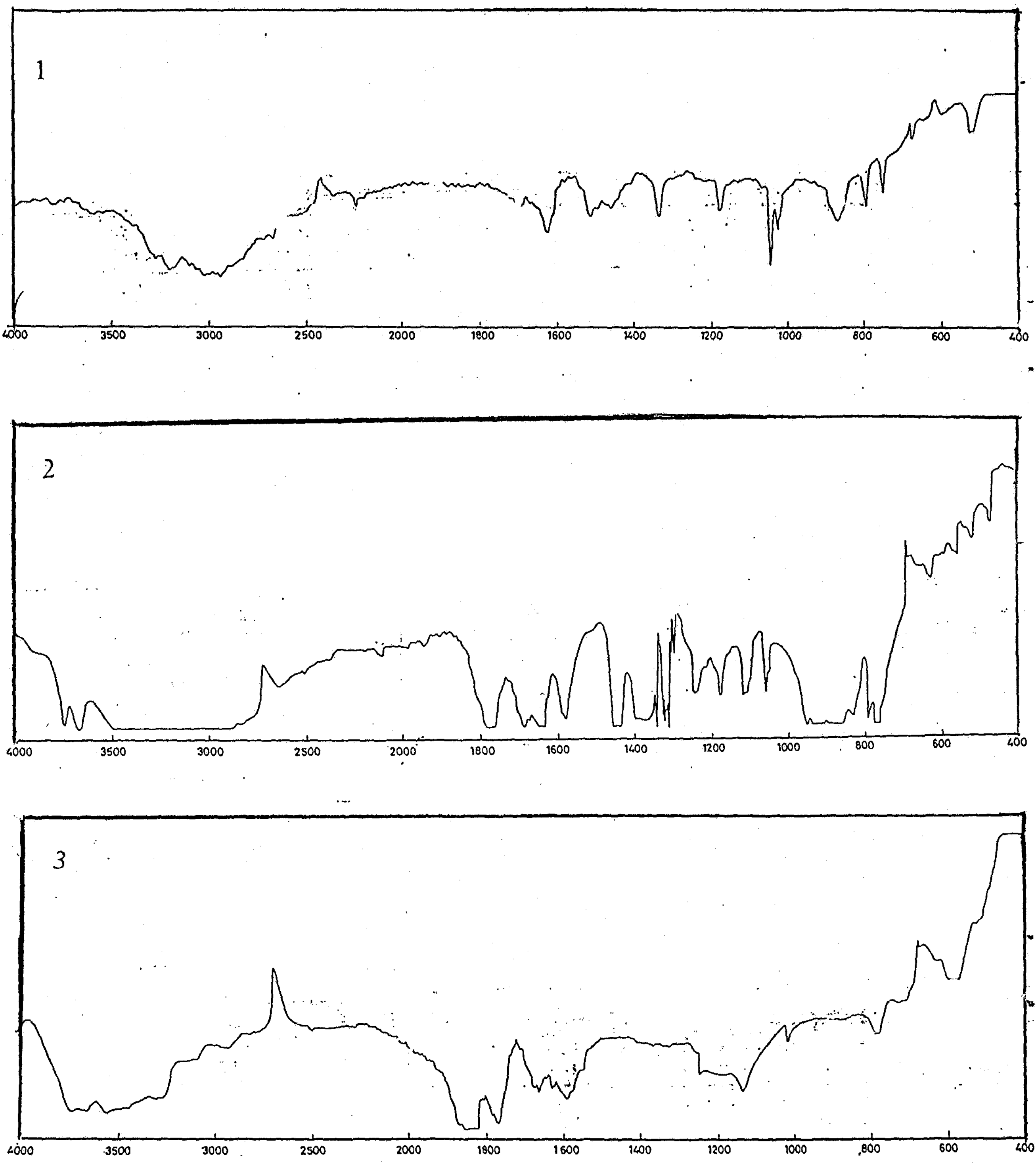

Fig. 2 : Infrared spectra of : (1) $ASCH_2$ ligand . (2) $L2H_2$ ligand.
(3) [Co(ASCH)(L2)]

The electronic spectra of the ligand and some of their complexes in DMF solution have been recorded giving d-d spectra and charge transfer spectra . Cobalt (II) complexes show only two absorption bands at 10526-11428 cm^{-1} and 1869-20790 cm^{-1} due to the transitions $^{4}T_{1}g$ (F)› $^{4}T_{2}g$ (F)-$'_{1}$ and $^{4}T_{1}g$ (F)› $^{4}T_{1}g$ (P) - $'_{3}$ expected for d^{7} system in octahedral field . $'_{2}$ (attributed to $^{4}T_{1}g$(F)› $^{4}A_{2}g$(F) transition) has been not observed due to instrumental limitation , it is calculated by the literature method [21] . The ligand field parameter B and the ligand field splitting energy (10Dq) have been calculated [21] . The values of β of the complexes are between 0.71 - 0.80 clearly indicate the partial covalent character of the bond concerned . However , the electronic spectral data (Table 3) suggest octahedral geometry for all the complexes [15,21] .

CONCLUSION

This work in fact is a continuation of our studies including mixed ligand complexes . In this work some observations have been achieved that lead to establish the following points :

1- Acetylacetone bis(semicarbazone) acts as tetradentate chelating ligand joint to cobalt (II) ion through the two nitrogen atoms and the two oxygen atoms .

2- Substituted phenols $L1H_2$, $L2H_2$ and L3H act as bidentate chelating ligands .

3- The chloride and nitrate ions (in the complexes prepared in neutral medium) joint to the metal ion in ionic manner for .

4- Cobalt (II) ion is probably hexa-coordinated having high spin octahedral geometry .

From the present study we can conclude that the complexes having the following proposed geometries (Figure 3) :

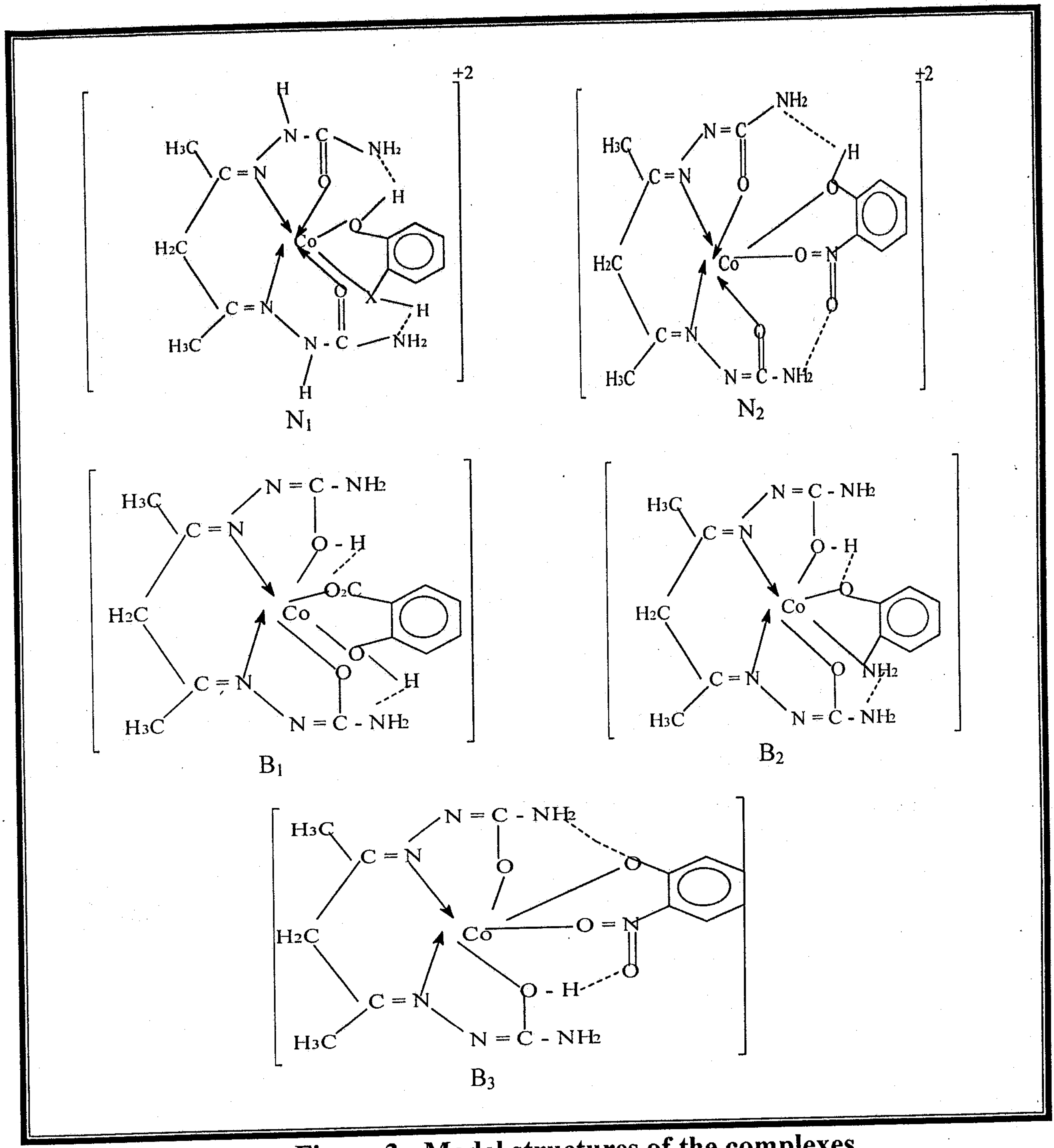

Figure 3 : Model structures of the complexes A_1, A_2 = complexes in neutral medium ; B_1, B_2, B_3 = complexes in basic medium ; X = COO or NH

Table –1
Amounts, composed formula, analytical and physical properties of some complexes

No.	Complexes	Med.	Wt. $ASCH_2$ gm	Wt. LH gm	% Yield	% Co calc/ obs.	Color	M.P or d. ^{0}C	Λ_M *	μ_{eff} **
1	$[Co(L1H_2)(ASCH_2)]Cl_2$	Neutral	0.90	0.48	74	13.00 12.57	Brown	222	148	3.41
2	$[Co(L2H_2)(ASCH_2)]Cl_2$	Neutral	0.90	0.58	61	12.22 12.84	Pale Violet	250d	134	3.54
3	$[Co(L3H)(ASCH_2)]Cl_2$	Neutral	0.90	1.18	67	12.19 11.13	Pale Blue	258d	171	3.11
4	$[Co(L1H)(ASCH)]$	Basic	0.90	0.48	74	15.49 15.11	Dark Violet	260d	24	3.60
5	$[Co(L2H)(ASCH)]$	Basic	-.90	0.58	75	14.39 14.22	Pale Violet	259d	33	3.57
6	$[Co(L3)(ASCH)]$	Basic	0.90	1.18	67	14.36 14.01	Violet	252d	27	3.02
7	$[Co(L1H_2)(ASCH_2)](NO_3)_2$	Neutral	0.94	0.48	78	11.63 12.07	Dark Brown	257d	115	3.22
8	$[Co(L2H_2)(ASCH_2)](NO_3)_2$	Neutral	0.94	0.60	72	11.00 11.33	Blue	252d	143	3.32
9	$[Co(L3H)(ASCH_2)](NO_3)_2$	Neutral	0.94	1.22	73	10.98 10.32	Pale Blue	251d	140	2.98
10	$[Co(L1H)(ASCH)]$	Basic	0.94	0.48	77	15.49 15.03	Dark Violet	260d	20	3.22
11	$[Co(L2H)(ASCH)]$	Basic	0.94	0.60	75	14.39 14.11	Pale Violet	260d	32	3.98
12	$[Co(L3)(ASCH)]$	Basic	0.94	1.22	70	14.36 14.13	Violet	253d	29	3.17

* Λ_M: Molar conductivities in $\Omega^{-1} cm^2 mol^{-1}$
**μ_{eff}: Magnetic moment in Bohr Magneton
d=decomposition points

Table -2
IR spectra of complexes (values in cm^{-1})

No.	υC=N semi	υ C=O semi	$\upsilon_{C=O}$ semi	υNH_2 semi	υ NH υ OH ph	υ C-O ph	$_{M-N}$	υ M-O
$ASCH_2$	1585	1685	-	145o 3400	3200-3300 3350	1230	-	-
1	1540	1650	-	145o 3400	3200-3300 3350	1330	450 490	600 675
2	1500	1645	-	145o 3400	3200-3300 3350	1340	450	625 , 650 675
3	1530	1655	-	1455 3395	3200-3300 3350	1335	440	625 700, 735
4	1510	-	1240	145o 3400	3200-3300 3350	1350	430 470	630 700
5	1520	-	1245	145o 3400	3200-3300 3350	1350	475	635 , 650 690
6	1530	-	1240	1455 3395	3200-3300 3350	1350	445	640 700, 750
7	1530	1655	-	145o 3400	3200-3300 3350	1340	450 500	640 690
8	1510	1640	-	145o 3400	3200-3300 3350	1345	500	640 , 675 700
9	1510	1655	-	1455 3395	3200-3300 3350	1330	500	630 700, 735
10	1520	-	1250	145o 3400	3200-3300 3350	1345	440 480	650 700
11	1500	-	1250	145o 3400	3200-3300 3350	1340	500	640 , 670 690
12	1500	-	1245	1455 3395	3200-3300 3350	1335	490	635 690,750

Table – 3
Electronic spectral data of some complexes

No.	$_1$ cm^{-1}	υ_3 cm^{-1}	υ_2 * cm^{-1}	C.T. cm^{-1}	B cm^{-1}	10Dq cm^{-1}	Dq/B	β	C.F.S.E. cm^{-1}
1	11111	18691	15555	29325	776	11252	1.45	0.80	9001
2	10905	20790	14394	29239	700	10360	1.48	0.72	8288
3	11325	20123	15809	28409	698	10121	1.45	0.72	8096
4	10729	19417	15021	28653	698	10400	1.49	0.72	8320
5	10526	19120	13999	29069	695	10216	1.47	0.72	8173
6	10976	19801	14818	28490	690	10350	1.50	0.71	8280
7	10695	19569	15508	28985	700	10220	1.46	0.72	8176
8	11173	19920	15754	28169	690	10074	1.46	0.71	8059
9	11312	20533	15837	28571	700	10430	1.49	0.72	8344
10	10593	19920	15889	28635	770	11473	1.49	0.80	9178
11	11086	19531	15853	28653	697	10245	1.47	0.72	8196
12	11428	20366	15542	28409	699	10385	1.49	0.72	8308

* calculated

REFERENCES

1. Kumar Y. and Tolani S.P., Croat. Chem. Acta., 62 (1), 73 (1989).
2. Maurya P.L., Agarwala B.V. and Dey A., J. Indian Chem. Soc., 55, 418 (1978).
3. Wayland B.B., Abid Elmageed M.F. and Mohns L.P., Inorg. Chem., 14, 1456 (1975).
4. Wilkinson G., Gillard R.D. and McCleverty J.A.; "Comprehensive coordination chemistry", Pergamon Press, Great Britain, 4th ed., 1184 (1987).
5. Kannappan R., Mahahkshmy R., Rajendiran T.M., Venkatesan R. and Sambasiva P.; Proceedings (Chem. Sci.), 115, 1 (2003).
6. Bayly S.R., Humphrey E.R., de Chair H, Parcdes C.G., Bell Z.R., Jeffery J.C., McCleverty J.A., Ward M.D., Totti F., Gatleschi D., Courric S., Barry R.S.C., Steele B.R. and Serettas C.G., J. Chem. Soc. Dalton Trans., 1401 (2001).
7. Dawood Z.F. and Sheet A.A.M., J. Sci. Tekreet Univ., 7 (3), 37 (2001).
8. Dawood Z.F., Sci. & Tech., 14, 47 (2000).
9. Casas Js, Castineira A., Rodrigues A.M.C., Sanchez A., Sordo J., Vazqueztopez A., Pinelli S., Lungli P., Ciancianaini P., Bonati A., Dall Aglio P. and Albertini P., J. Inorg. Biochem., 76 (3-4), 277 (1999).
10. Kamaraj K., Kim E., Galliker B., Zakharov L.N., Rheingold A.L., Zuberbühler A.D. and Karlin K.D., J. Am. Chem. Soc., 125, 6028 (2003).
11. Vogel A.I., "Textbook of practical organic chemistry", Longmans Green, London, 3th ed., 344 (1964).
12. Vogel A.I., "Textbook of quantitative inorganic analysis", Longman Inc., New York, 4th ed., 461 (1981).
13. Geary W.J., Coord. Chem. Rev., 7, 81 (1971).
14. Aggarwal R.C., Singh N.K. and Singh R.P., J. Indian Chem. Soc., 63, 466 (1986).
15. Bhaskare C.K. and More P.G., J. Indian Chem. Soc., 63, 270 (1986).
16. Dawood Z.F., Hessein S.H. and Al-Shama'a M.A., Sci. & Tech. A, 12, 71 (2004).
17. Ali M.W.I., M. Sc. Thesis, Mosul University (2002).
18. Nakamoto K., "Infrared and raman spectra of inorganic and coordination compound", Part B, John Wiley and Sons, Inc., 5th ed. (1997).
19. Singh P.K., Koacher J.K. and Tandon J.P., J. Inorg. Nucl. Chem., 43, 1755 (1981).
20. Parik V.M., "Absorption spectroscopy of organic molecules", Addison-Wesley (1974).
21. Lever A.B.P., J. Chem. Edu., 45, 711 (1968).