

# Preparation and Characterization of Cr(III) & Cu(II) Complexes With Mixed Ligand Containing Isatinazine and Semicarbazones

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## ABSTRACT

New chromium(III) and copper(II) complexes with mixed ligands isatinazine-IAH<sub>2</sub> and semicarbazone ligands {including benzoinsemicarbazone- B'SCH<sub>2</sub> or isatinsemicarbazone- ISCH<sub>2</sub> or isatinbis (semicarbazone) -ISCH<sub>3</sub>} have been prepared in neutral (or slightly acidic) and basic medium.

The resulted complexes have been characterized using elemental analysis by atomic absorption spectroscopy and by precipitation methods, relative molecular weight determination, molar conductance measurements, molar refraction, magnetic susceptibilities, infrared and electronic spectra. Accordingly, The study suggested that the above ligands form positive ionic complexes having general formula [M(IAH<sub>2</sub>)(LH<sub>2,3</sub>)(NO<sub>3</sub>)<sub>m</sub>](NO<sub>3</sub>)<sub>n-m</sub> or [Cr(IAH<sub>2</sub>)(B'SCH<sub>2</sub>)](NO<sub>3</sub>)<sub>3</sub> in neutral (or slightly acidic) medium, whereas neutral or negative ionic complexes of the general formula [M(IAH<sub>2</sub>-y')(LH<sub>2,3</sub>-y'')] or Na[Cr(IA)(B'SC)] have been resulted in basic medium (where M= Cr<sup>+3</sup> or Cu<sup>+2</sup>; y'=1 or 2; y''=1 or 2; n=2 or 3; m=1; LH<sub>2,3</sub>= the ligands B'SCH<sub>2</sub> or ISCH<sub>2</sub> or ISCH<sub>3</sub>). The ligands acted as neutral or anionic (-1) in neutral (or slightly acidic) or basic medium, respectively. Hexacoordinated mononuclear complexes have been investigated by this study and having octahedral geometries.

## Introduction

A good deal of work has been reported on the preparation, spectral and structural investigation of azines and their complexes, due to their capability of acting as multidentate donor(1-4). Moreover azines and their complexes had important analytical application, photosensitizer in solar cells and biological activities (5,6).

An extremely large number of semicarbazone complexes have been reported(7-11). In addition to their ligational properties, semicarbazones formed an important class of biologically active compounds and they were also used as pigments(12-14).

Mixed ligand complexes were of considerable importance in the field of metallo-enzymes and other biological activities(15-17). Hence a large body of mixed ligand complexes with transition and non-transition metal ions have been reported(18-20).

Due to the importance of such ligands and mixed ligand complexes, we took a modest part in the chemistry of mixed ligands and some articles have

been published on their coordination chemistry with transition and non-transition metal ions(21-24).

In the present work, new chromium (III) and copper(II) complexes with mixed ligands {isatinazine-IAH<sub>2</sub> and semicarbazone ligands {benzoinsemicarbazone-B'SCH<sub>2</sub> or isatinsemicarbazone -ISCH<sub>2</sub> or isatinbis (semicarbazone) -ISCH<sub>3</sub>} (Figure1) have been prepared and characterized physico-chemically.

## Experimental

### 1- Starting Materials:

All the chemicals used were supplied from Fluka, BDH, Aldrich, Merck, Anhydrous LAB-SCAN, U.S.A and Appl:Chem and GCC.

### 2- Synthetic Methods :

Isatinazine-IAH<sub>2</sub> has been prepared according to literature method<sup>(25,26)</sup>. Semi- carbazone ligands have been prepared according to literature method<sup>(25,26)</sup>.

A general procedure has been adopted for the preparation of the complexes in neutral and basic medium .

### In neutral medium:

A solution of 0.5 gm (1.25x10<sup>-3</sup> or 2.07x10<sup>-3</sup>

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mole) of  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  or  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$  in 5 ml water has been added to the solution of 0.48 or 0.60 gm  $\text{IAH}_2$  ( $1.25 \times 10^{-3}$  or  $2.07 \times 10^{-3}$  mole) and  $1.25 \times 10^{-3}$  or  $2.07 \times 10^{-3}$  mole of one of the semicarbazone ligands in a small amount of ethanol and water with heating until a clear solution has been resulted (the amounts in grams were listed in Table 1). The mixtures have been refluxed for three hours followed by evaporation to half their volumes then cooled. The products were separated by filtration, washed with petroleum ether and dried at  $100^\circ\text{C}$ .

### In basic medium:

The complexes have been prepared by applying the same amounts used for neutral medium, and after mixing the metal salts with the ligands and heating, sodium hydroxide solution (1M) has been added until pH of the solutions have been adjusted to about 8-9. The mixtures have been heated on a waterbath for half an hour then allowed to stand then cooled. The products were filtered off and washed with petroleum ether and dried at  $100^\circ\text{C}$ .

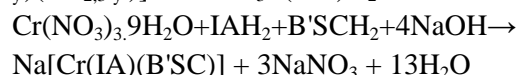
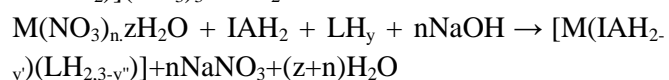
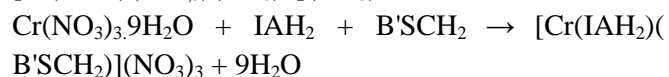
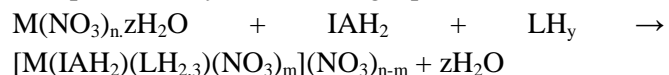
### 3-Analytical and Physical Measurements :

Copper contents have been determined by atomic absorption spectroscopy and chromium contents have been determined by applying precipitation method after the decomposition of the complexes with concentrated nitric acid<sup>(27)</sup>.

Relative molecular weights of the ligands and their complexes have been determined cryoscopically (decrease in freezing point<sup>(28)</sup>). Molar refraction measurements<sup>(28)</sup> have been carried out with Atago Illumination, Atago Co-LTD, Japan using  $10^{-3}$  M dimethylformamide solution. Conductivity measurements have been carried out with an electrolytic conductivity measuring set LF-42 and Multiline f/SET-2WTW Wis-senschaf Technische Werkstattem 82362 Weiheim using  $10^{-3}$  M dimethylformamide solution at  $25^\circ\text{C}$ . The infrared spectra has been recorded on FT-IR Bruker type Tensor 27 in the range  $400-4000\text{ cm}^{-1}$  using KBr pellets. Electronic spectra has been recorded on Shimadzu UV-1650 PC UV-Visible Spectrophotometer for  $10^{-3}$  M solutions of the ligands and their complexes in dimethylformamide at  $25^\circ\text{C}$ , using a 1cm cell. Magnetic susceptibility of the complexes have been measured by Bruker-BM6

## Results and Discussion

The reaction of chromium (III) or copper(II) nitrate, isatinazine and the semicarbazone ligands in 1:1:1 molar ratio in both neutral and basic medium can be represented by the following equations :



(where  $\text{M}=\text{Cr}^{+3}$  or  $\text{Cu}^{+2}$ ;  $\text{LH}_y = \text{B'SCH}_2$ ,  $\text{ISCH}_2$  or  $\text{ISCH}_3$ ;  $n=3,2$ ;  $m=1$ ;  $z=9$  or  $3$ ;  $y'=1$  or  $2$ ,  $y''=1$  or  $2$ ).

The resulting complexes were colored. Chromium and copper contents and relative molecular weights revealed that the complexes in neutral or slightly acidic medium had the composition  $[\text{M}(\text{IAH}_2)(\text{LH}_{2,3})\text{X}_m]\text{X}_{n-m}$  or  $[\text{Cr}(\text{IAH}_2)(\text{B'SCH}_2)](\text{NO}_3)_3$  and  $[\text{M}(\text{IAH}_2 \cdot y')(\text{LH}_{2,3-y''})]$  or  $\text{Na}[\text{Cr}(\text{IA})(\text{B'SC})]$  in basic medium (Table 1). The values of the molar conductivities ( $195.00$ ,  $127.00-127.29$ ,  $77.75-93.98$  and  $0.024-32.74\ \Omega^{-1}\text{cm}^2\text{mol}^{-1}$ ) approached those expected for 1:3 (complex 1), 1:2 (complexes 3 and 5), 1:1 (complexes 7, 9, 11 and 2) and non electrolytes (complexes 4, 6, 8, 10 and 12)<sup>(29)</sup>. The room temperature ( $25^\circ\text{C}$ ) magnetic moments ( $1.58-1.90$  and  $3.22-3.77\text{ B.M}$ ) indicated the presence of one unpaired and three unpaired electrons, for copper(II) and chromium(III) complexes<sup>(3,30)</sup>, assigned to a monomeric structure, having octahedral geometry (Table 1). The refraction of the complexes in  $10^{-3}$  M dimethylformamide solution were in the range  $1.435522 \times 10^{-4} - 1.435585 \times 10^{-4}$ . The molar refraction is an additive and constitutive property. It has been used to construct the correct structure of the compound<sup>(31)</sup>.

The infrared spectra of semicarbazone ligands (Table 3, Figure 2) showed a strong band at  $1685.15-1697.80\text{ cm}^{-1}$  attributed to the  $\text{C}=\text{O}$  group<sup>(32)</sup>. This value shifted towards a lower frequency on coordination in neutral medium, indicating the formation of a chelation between the oxygen of the  $\text{C}=\text{O}$  group and the metal ion<sup>(32)</sup>. Meanwhile, in basic medium, this band was disappeared in the complexes and a new band has been observed at  $1110.64-1207.29\text{ cm}^{-1}$  due  $\text{C}-\text{O}$  group, thereby establishing coordination of the ligand through the enolic oxygen atom<sup>(3,32)</sup>. The next strong band at  $1611.91-1637.93\text{ cm}^{-1}$  attributed to

C=N group<sup>(32)</sup> shifted towards a lower frequency on coordination due to the decrease of the bond order as a result of metal nitrogen bond formation<sup>(32)</sup>. The appearance of strong bands at 1630.00-1635.00 cm<sup>-1</sup> and 1570.00-1580.00 cm<sup>-1</sup> attributed to  $\nu_{(C=N)+\nu_{(O-C=N)}}$  and azine chromophore  $\nu_{(C=N-N=C)}$ , respectively, supported the formation of enolic structure in basic medium<sup>(3,32)</sup>. The position bands of the ligands in the range 3234.21-3235.86 cm<sup>-1</sup> remained unaltered in the complexes prepared in neutral medium indicating that there is no coordination through the NH group<sup>(21,32)</sup>, whereas in basic medium, this band was disappeared due to the enolic form. The other bands at 3390.00-3410.00 cm<sup>-1</sup> and 1450.00 cm<sup>-1</sup> attributed to  $\nu_{NH_2}$  and  $\delta_{NH_2}$ <sup>(32)</sup>. These bands remained unaltered on complexation indicating that there is no coordination through this group and the metal ion<sup>(21,32)</sup>. The infrared spectra of B'SCH<sub>2</sub> ligand showed a wide band at 3552.28 cm<sup>-1</sup> due to the stretching vibration of phenolic hydroxyl shifted to a lower frequency on complexation<sup>(32)</sup>. The other band observed at 1330.37 cm<sup>-1</sup> attributed to the bending vibration of phenolic OH shifted towards a lower frequency on complexation<sup>(32)</sup> indicating the coordination of this group with the metal ion. Moreover the appearance of a band at 1109.16 cm<sup>-1</sup> which belongs to  $\nu_{(C-O)}$  shifted to higher frequency 1130.79-1133.56 cm<sup>-1</sup> on complexation indicating the coordination of oxygen atom<sup>(32)</sup>. The infrared spectra of ISCH<sub>2</sub> showed band at 1720.37 cm<sup>-1</sup> attributed to  $\nu_{C=O}$  observed in the same position in complex 3 and 9 indicating the uncoordination of this group to the metal ion<sup>(30)</sup>. Meanwhile in basic medium this band was disappeared due to the formation of the enol isomer which was supported by the appearance of a band (Table 3) assigned to  $\nu_{C-O}$ <sup>(21,22,32)</sup>.

The infrared spectra of IAH<sub>2</sub> showed band at 1637.96 cm<sup>-1</sup> due to  $\nu_{C=N}$ <sup>(32)</sup>. On coordination this band was splitted into two bands, one appeared at the same position, whereas the other band observed at lower frequency. This demonstrated that only one nitrogen atom was coordinated to the metal ion<sup>(1,30,32)</sup>. Moreover the positive shift in N-N vibration on complexation can be added as a further support to the coordination of the azine nitrogen to the metal ion<sup>(30,32)</sup>. The next band at 1687.14 cm<sup>-1</sup> attributed to  $\nu_{C=O}$  shifted towards a lower frequency (Table 3, Figure 2) for complexes prepared in neutral (or slightly acidic) medium<sup>(32)</sup>. Meanwhile in basic

medium this band disappeared in the complexes and a new band was observed at 1146.27-1198.87 cm<sup>-1</sup> due to  $\nu_{C-O}$ , there-by establishing coordination of the ligand through enolic oxygen atom<sup>(32)</sup>.

On the other hand the spectra of the complexes prepared in neutral (or slightly acidic) medium showed new bands around 1384.50-1389.45 cm<sup>-1</sup> due to ionic nitrate<sup>(32)</sup>. In addition, complexes 3, 5, 7, 9 and 11 showed bands at 1400.51-1455.75 cm<sup>-1</sup>, 1285.51-1340.61 cm<sup>-1</sup> and 900.75-1005.00 cm<sup>-1</sup> due to  $\nu_{s(NO_3)}$ ,  $\nu_{as(NO_3)}$  and  $\nu_{NO}$  ( $\nu_2$ ,  $\nu_1$ ,  $\nu_5$ ), respectively<sup>(32)</sup>. The difference between  $\nu_1$ - $\nu_5$  equal to 115.00-115.14 cm<sup>-1</sup> which supported the bonding of nitrate group as monodentate ligand through the oxygen atom. The spectra of all the complexes showed new bands at 400.00-470.47 and 451.03-534.48 cm<sup>-1</sup> due to  $\nu_{M-N}$  and  $\nu_{M-O}$ , respectively<sup>(22,30,32)</sup>. The presence of these bands supported the formation of the complexes under investigation

The electronic spectra in the ultraviolet region (Table 4, Figure 3) of the ligands showed two bands in the region 400000.00 -43859.65 cm<sup>-1</sup> and 30120.48 - 33112.58 cm<sup>-1</sup> corresponding to  $\pi \rightarrow \pi^*$  and  $n \rightarrow \pi^*$  transitions<sup>(33)</sup>. On complexation a blue shift was observed due to the polarization in the C=N bond caused by the elemental ligand electron interaction during the chelation. The electronic spectra of chromium (III) complexes (Table 5, Figure 3) showed bands ( $\nu_1$ ,  $\nu_2$  and  $\nu_3$ ) at 10204.08-11764.71 cm<sup>-1</sup>, 12309.23- 25510.20 cm<sup>-1</sup> and 25510.20-29761.90 cm<sup>-1</sup> due to the transitions  ${}^4A_{2g}(F) \rightarrow {}^4T_{2g}(F)$ ,  ${}^4A_{2g}(F) \rightarrow {}^4T_{1g}(F)$  and  ${}^4A_{2g}(F) \rightarrow {}^3T_{1g}(P)$ , respectively<sup>(33,34)</sup>. The ligand field parameter B and the ligand field splitting energy (10Dq) in case of chromium(III) complexes have been calculated<sup>(34,35)</sup>. The values of  $\beta$  of chromium(III) complexes were 0.85-0.97 clearly indicated the covalent character of the bond concerned. The values of Dq/B which were in the range 1.145-1.490 suggested octahedral geometry for all the chromium(III) complexes. The electronic spectra of copper(II) complexes (Table 6, Figure 3) showed bands ( $\nu_1$ ,  $\nu_2$  and  $\nu_3$ ) at 10000.00-11764.70 cm<sup>-1</sup>, 12500.00-14815.00 cm<sup>-1</sup> and 23148.14-24271.84 cm<sup>-1</sup> due to the transitions  ${}^2B_{1g} \rightarrow {}^2A_{1g}$ ,  ${}^2B_{1g} \rightarrow {}^2B_{2g}$  and  ${}^2B_{1g} \rightarrow {}^2E_g$ , respectively<sup>(33,34)</sup>. The value of CFSE of chromium(III) complexes have been also determined which were in the range 12219.96-14018.69 cm<sup>-1</sup>. However, the electronic spectral data suggested octahedral geometry for all the complexes<sup>(33-35)</sup>.

According to the analytical, physical and spectral data, some observations have been achieved that lead to establish the following points:

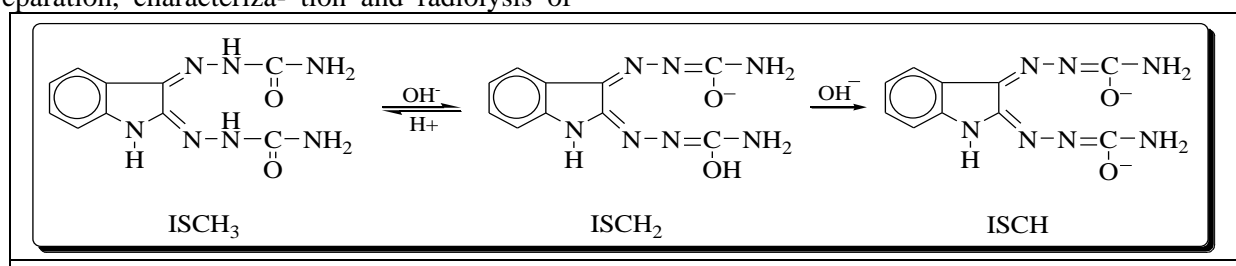
1. IAH<sub>2</sub> ligand acted as tridentate chelating ligand joint to the metal ion through the azomethine nitrogen and the two oxygen atoms of the carbonyl groups.
2. B'SCH<sub>2</sub> ligand acted as either bidentate or tridentate chelating ligand joint to the metal ion through N atom and one or two O atoms.
3. ISCH<sub>2</sub> ligand acted as either bidentate or tridentate chelating ligand joint to the metal ion through N atom and one or two O atoms.
4. ISCH<sub>3</sub> ligand acted as either bidentate or tridentate chelating ligand joint to the metal ion through the two N atoms or through the two N and one O atoms.
5. Chromium(III) and copper(II) ions have been probably hexacoordinated, leading to octahedral geometries (Figure 4).

## References

- 1- S. Satapathy and B. Sahoo, (1970). Salicylaldazine metalchelates and their LR. Spectra. *J. Inorg Nucl. Chem.* 23: 2223-2227.
- 2- S. K. Mandal, L.K. Thompson and M.J. Newlands, (1986). Binuclear copper (II) complexes of tetradentate (N<sub>4</sub>) diazine ligands crystal complexes of [ $\mu$ -1,4Bis(4,6-dimethyl-2-pyridylthio)pyridazine-N, $\mu$ -N1, $\mu$ -N2,N]( $\mu$ -dichloro)dichlorodicyclopentadiene-copper(II) ethanol, and 3,6-Bis(2-pyridylthio)pyridazine. *J. Inorg. Chem. Acta.* 122: 199-205.
- 3- L.K. Thompson, S.K. Mandel, J.P. Charland and E.J. Gobe, (1988). Magnetism and structure in a series of halogen and hydroxo-bridged binuclear copper(II) diazine complexes structure of a dibromobridged derivative [Cu<sub>2</sub>(C<sub>14</sub>H<sub>10</sub>N<sub>4</sub>S<sub>2</sub>)Br<sub>4</sub>] *Can. J. Chem.*, 66 (2): 348-354.
- 4- S.You, Ch. Xue-Tai, Z. Chang-Ge, Z. Dun-Ru, Y. Xiao-Zeng and W. Lin-Hong,(2001).Synthesis, crystal structure and properties of the dimeric copper(II) complex, [Cu<sub>2</sub>(Hboa)<sub>2</sub>(H<sub>2</sub>O)<sub>2</sub>](ClO<sub>4</sub>)<sub>2</sub> (H<sub>2</sub>boa =biacetylloximeazine). *Trans. Met. Chem.* 26 (3): 247-251.
- 5- C.R. Hauer, G.S. King, E.L. McCool, W.B. Euler, J.D. Ferrara and W.J. Youngs, (1987). The structure of 2,3-Butanedionedi-hydrazone and IR study of higher polyazines: A new class of polymeric conductors. *J. Am. Chem. Soc.* 109: 5760.
- 6- K. Kalyanasundaram, (1997). Use of azine dye as a photosensitizer in solar cell: Different reductants-safranin. *Int. J. Energy Res.* 21 (14): 1345-1350.
- 7- C.B. Mahto, (1980). Studies on Complexes of Ni(II), Pd(II) and Cu(II) with benzaldehydesemicarbazone. *J. Indian Chem. Soc.* 57 (5): 553.
- 8- C. Georg and L. Paul, (1987). Copper or nickel complexes of ligand containing an azomethime, semicarbazone or hydrazone moiety. United States Patent 4775747. <http://www.freepatentsonline.com>.
- 9- L. Hong, Ch. Xiongbin, H. Ruixiang, Ch. Zhenfeng and Y. Kaibei, (2002). Synthesis, crystal structure and spectroscopic properties of a copper(II) complex of the Schiff base derived from picolinaldehyde N-oxide and semicarbazone. *Acta Chem. Sinica*, 60 (5): 939-946.
- 10- J. Zhou, X. Liu, J. Dai, D. Li, Z. Huang, Z. Chen and H. Liang, (2006). Synthesis and crystal structure of a two-dimensional bilayered supramolecular network compound [Cu<sub>2</sub>(C<sub>7</sub>H<sub>8</sub>N<sub>4</sub>O)<sub>4</sub>](ClO<sub>4</sub>)<sub>2</sub> (C<sub>7</sub>H<sub>8</sub>N<sub>4</sub>O=Pyridine-3-carbaldehyde-semicarbazone). *J.Coord. Chem.* 59 (15): 1711-1717.
- 11- J. Joseph and B. Mehta, (2007). Synthesis, characterization and thermal analysis of transition metal complexes of polydentate ONO donor schiff base ligand. *Russian J.Coord. Chem*33(2):124-129.
- 12- Z. Jian, L. Xing, Ch. Zhenfeng and L. Hong, (2006). Synthesis and crystal structure of cobalt(II) complex of Schiff base from pyridine-4-aldehyde and semicarbazide. *Chinese J. Synth. Chem.* 14 (5): 471-475.
- 13- P. Noblia, M. Vieites, B.S. Parajon-Costa, E.J. Baran, H. Cerecetto, P. Draper, M. Gonzalez, O.E. Piro, E.E. Castellano, A. Azqueta, A.L. Cerain, A. Monge-Vega and D. Gambino, (2005). Vanadium(V) complexes with Salicylaldehydesemicarbazone derivatives bearing in vitro anti-tumor activity toward kidney tumor cell (TK-10): crystal structure of [VO<sub>2</sub>(5-bromosalicylaldehydesemicarbazone)]. *J. Inorg. Biochem.* 99 (2): 443-451.
- 14- Z.H. Chohan, H. Pervcz, K.M. Khan and C.T. Supuran, (2005). Organometallic-based antibacterial and antifungal compounds: transition metal complexes of 1,1-diacylferrocene-derived thiocarbohydrazone, carbohydrazone, thiosemicarbazone and semicarbazone. *J. Enzyme Inhib Med. Chem.* 20 (1): 8-81.
- 15- R.K. Hussain, R.P. Sambasiva and B.P. Ravindra, (2000). Nuclease activity of mixed ligand complexes of copper(II) with heteroaromatic derivatives and picolin. *Trans. Met. Chem.* 25 (5): 505-510.



- 16- B.K. Rai, P. Choudhary, S. Rana and P. Sahi, (2006). Structural characterization and antifungal studies of some mixed ligand Schiff base complexes with 6-bromo-2-thio-3-phenylquinazoline-4(3H)onethio-semicarbazone. *Orient. J. Chem.* 23: 1.
- 17- M.M. Ajaily, A.A. Maihub, S.F. Ben-Gweirif, A.M. Belazi and R.S. El-Zweay, (2007). Characterization and antibacterial activity of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) mixed ligand complexes. *Orient. J. Chem.* 23: 1.
- 18- M.T.H. Tarafder and S.C. Pal, (1995). Mixed ligand complexes of chromium(III) containing some bi-dentate amines and quadridentate Schiff base ligands. *J. Indian Chem. Soc.* 72: 581.
- 19- N. Samus, A. Gulya, V. Tsapkov, Y. Chumakov and T. Roshu, (2006). Coordination compounds of cobalt, nickel, copper and zinc with thiosemicarbazone and 3-phenylpropenalsemicarbazone. *Russ. J. Gen. Chem.*, 76 (7): 1100-1105.
- 20- R.K. Agarwal, B. Prakash, V. Kumar and A. Khan, (2007). Synthesis, physico-chemical and thermal characteristics of seven and ten coordinated complexes of trivalent lanthanids derived from 4[N-(cinnamalidene)amino]antipyrinesemicarbazone and diphenyl-sulfoxide. *J. Iran Chem. Soc.*, 4 (1): 114-125.
- 21- Z.F. Dawood, (2000). New complexes of indium(III) containing mixed ligands (semicarbazones and benzaldazine. *Sci. & Tech.* 4: 47-50.
- 22- Z.F. Dawood, (2002). Zr(IV) complexes of some nitrogen-oxygen donor ligands (semicarbazones and salicylaldazine). *Sci. & Tech.* 17: 36-38.
- 23- Z.F. Dawood, A.Y. Shareef and M.A. Al-Shames, (2007). Preparation, characterization and biological activity of new nickel(II) complexes containing mixed ligands. *J. Edu & Sci. The first conf. Biology.* 20 (3): 105-115.
- 24- Z.F. Dawood and Y.T. Mahmood, (2007). Preparation, characterization and radiolysis of copper(II) complexes containing mixed ligands. *Nat. J. Chem.* 25: 206-216.
- 25- A.I. Vogel, (1964). *Textbook of Practical Organic Chemistry.* 3rd ed., 344. Longman Green, London.
- 26- F.J.A. Al-Moula, (2008). Preparation and characterization of some complexes of 3d transition elements containing mixed ligands. M. Sc. Thesis. Mosul University.
- 27- A.I. Vogel, (1978). *Textbook of Quantitative Inorganic Analysis.* 3rd ed., 344, 722. Longman Green, London.
- 28- J.W. Daniels, (1962). *Experimental Physical Chemistry.* 6th ed., 81. McGraw-Hill, London.
- 29- W.J. Geary, (1971). Use of conductivity measurements inorganic solvents for the characterization of coordination compounds. *Coord. Chem. Rev.* 7: 81-87.
- 30- K.M. Daoud, Z.F. Dawood and M.A. Mohammad, (1992). Complexes of V(III) and Nb(V) with furfuraldazine, 2-thiophenaldazine and 2-pyridinealdazine. 7 (1): 325-333.
- 31- A.M. James and F.E. Prichard (1985). *Practical physical chemistry.* Translated by M.S. Saeed, N. S. Al-Chalabi and L.S.M. Al-Jomard. 157. University of Mosul, Iraq.
- 32- K. Nakamoto, (1976). *Infrared and Raman Spectra of Inorganic and Coordination Compound.* 3rd ed., 166-322. John Wiley and Sons, New York.
- 33- D. Sutton, (1968). *Electronic Spectra of transition metal complexes.* 11-21, 146-149. McGraw-Hill publishing Co., London,
- 34- D. Nicolls, (1984). *Complexes and first-row transition elements.* Translated by Wissam Ibrahim, 167-257. University of Mosul Iraq.
- 35- A.B.P. Lever, (1968). *Electronic spectra of some transition metal Complexes.* *J. Chem.Edu.* 45: 711-712.



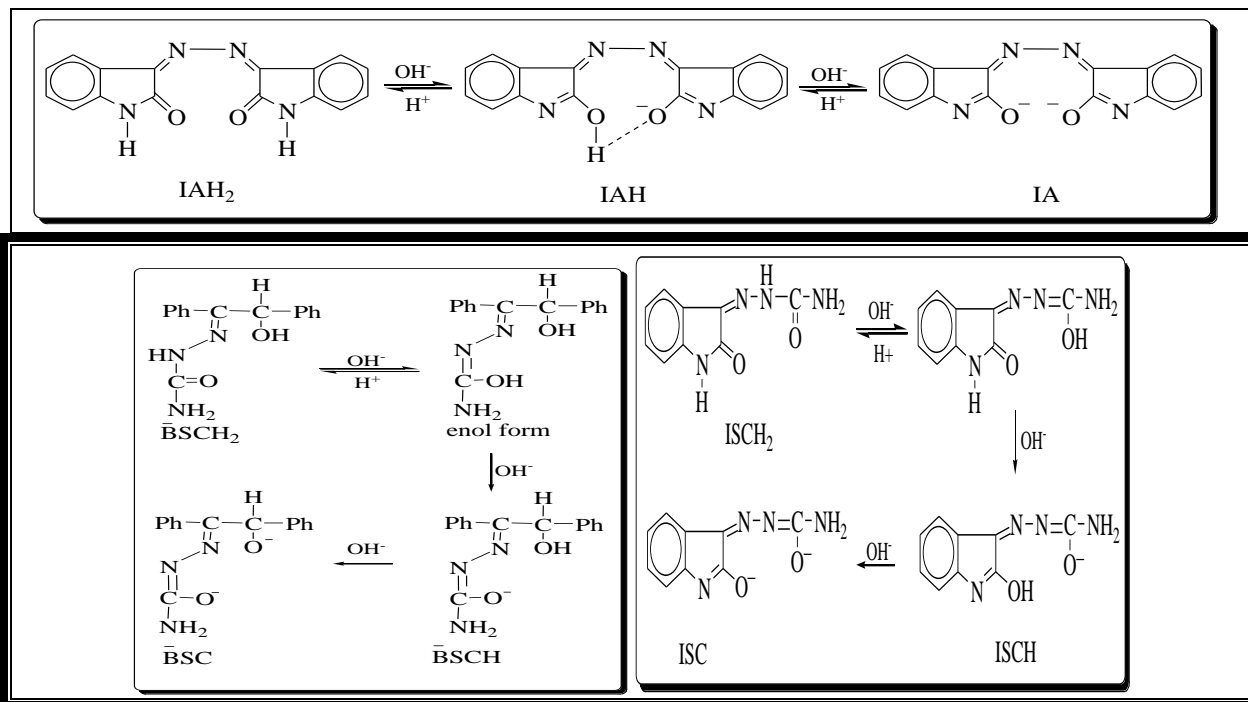


Figure 1: Model structures of the ligands

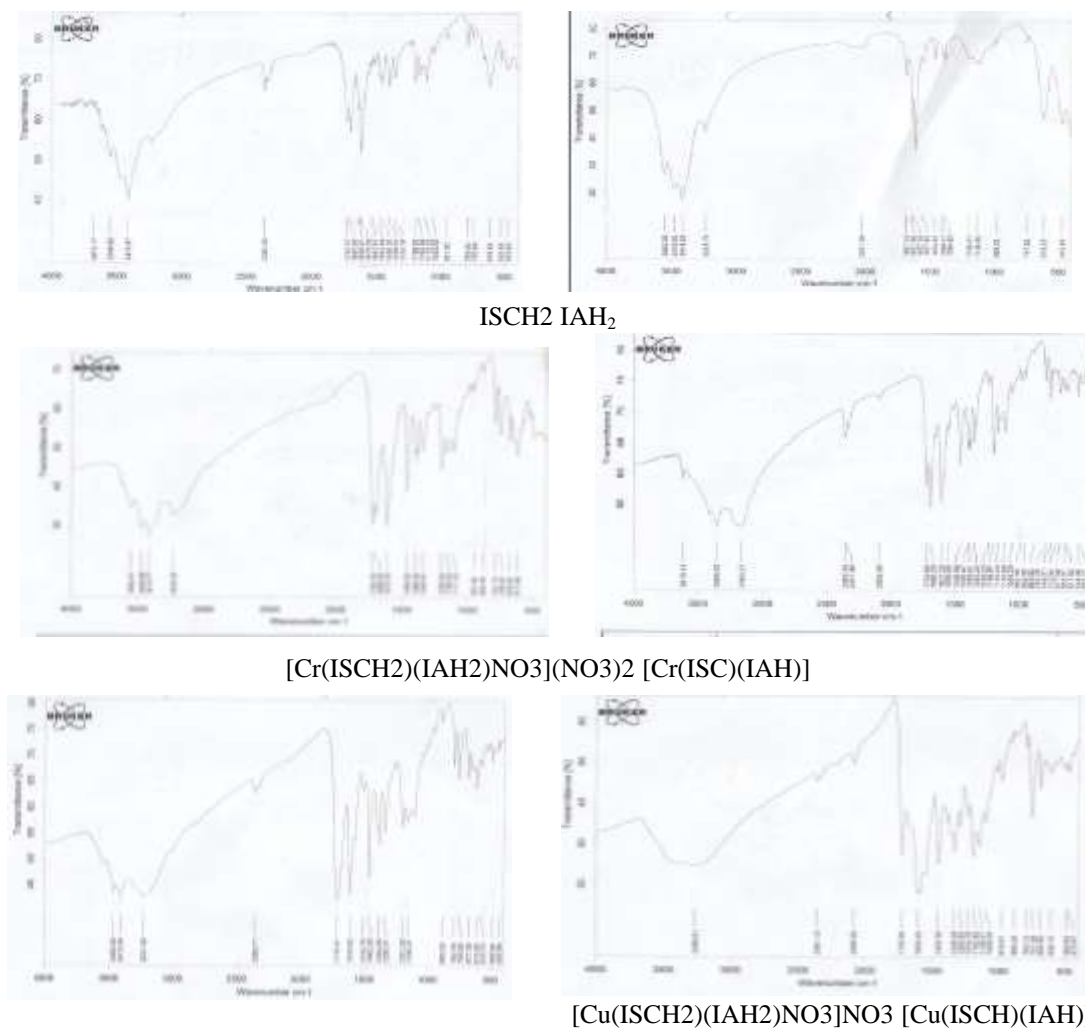
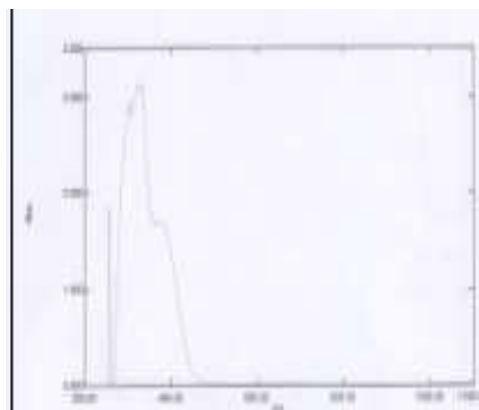
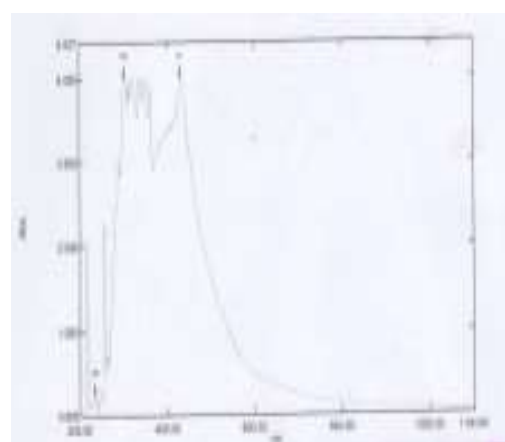
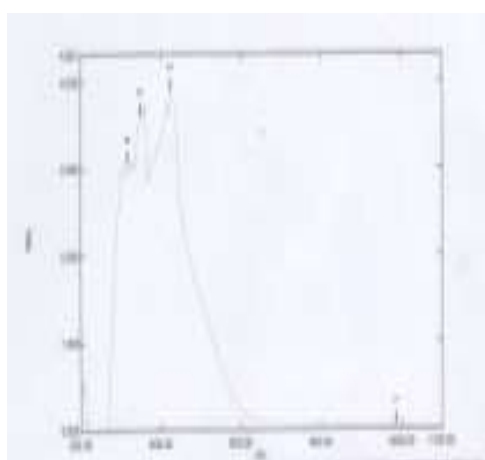


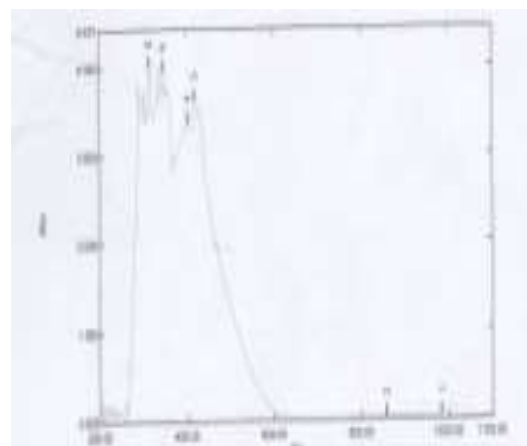
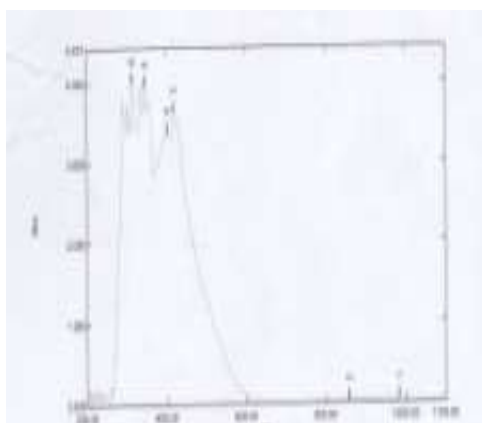
Figure 2: Infrared spectra of the ligands ISCH<sub>2</sub>, IAH<sub>2</sub> and their complexes



ISCH<sub>2</sub> IAH<sub>2</sub>



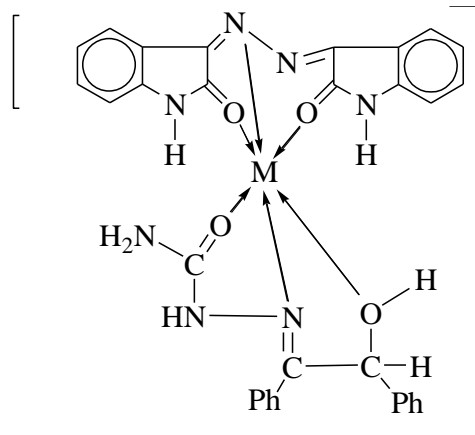
[Cu(ISCH<sub>2</sub>)(IAH<sub>2</sub>)NO<sub>3</sub>]NO<sub>3</sub> [Cu(ISCH)(IAH)]



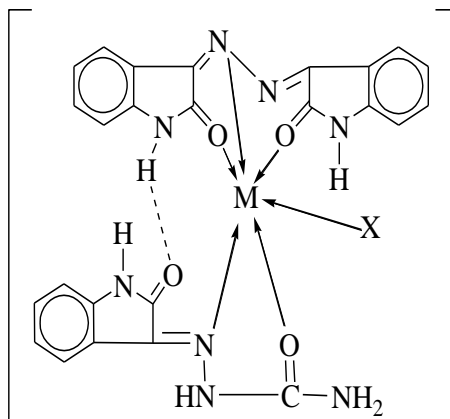
[Cr(ISCH<sub>2</sub>)(IAH<sub>2</sub>)NO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub> [Cr(ISC)(IAH)]

Figure 3: Electronic spectra of the ligands ISCH<sub>2</sub>, IAH<sub>2</sub> and their complexes

+3

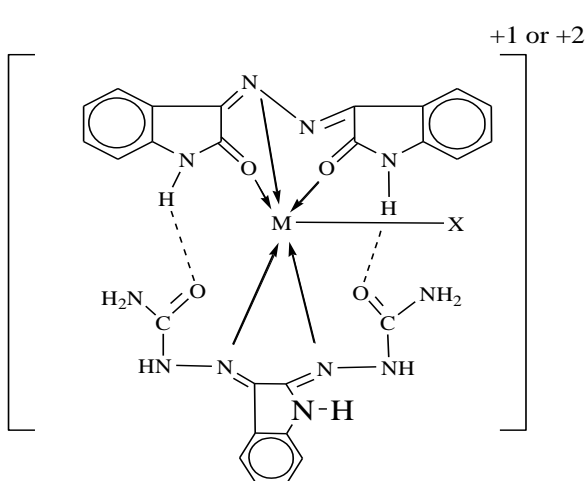


+1 or +2

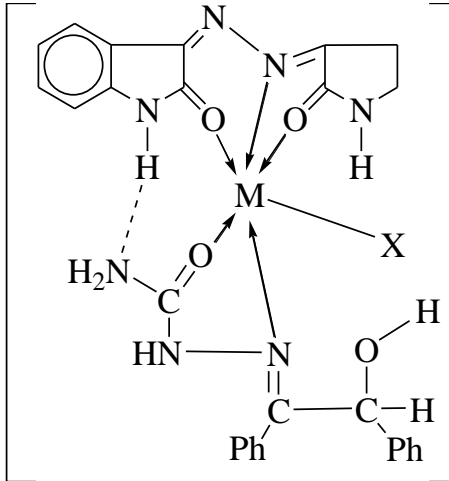


[Cr(B'SCH<sub>2</sub>)(IAH<sub>2</sub>)](NO<sub>3</sub>)<sub>3</sub> [Cr(ISCH<sub>2</sub>)(IAH<sub>2</sub>)NO<sub>3</sub>](NO<sub>3</sub>)<sub>2</sub> ; [Cu(ISCH<sub>2</sub>)(IAH<sub>2</sub>)NO<sub>3</sub>]NO<sub>3</sub>  
13,9

+1

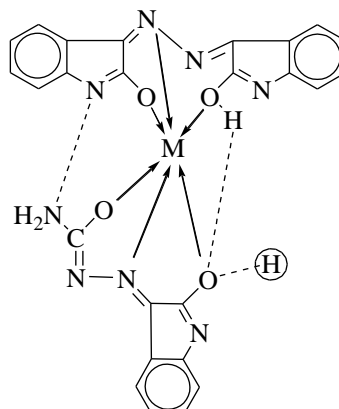
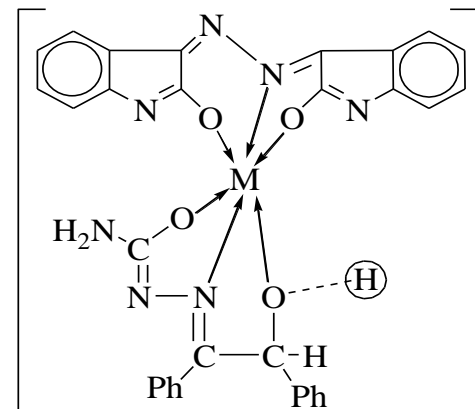


+1 or +2



[Cr(ISCH<sub>3</sub>)(IAH<sub>2</sub>)(NO<sub>3</sub>)](NO<sub>3</sub>)<sub>2</sub> [Cu(B'SCH<sub>2</sub>)(IAH<sub>2</sub>)NO<sub>3</sub>]NO<sub>3</sub>  
[Cu(ISCH<sub>3</sub>)(IAH<sub>2</sub>)NO<sub>3</sub>]NO<sub>3</sub> 7  
5, 11

-1



Na[Cr(B'SC)(IA)] [Cr(ISC)(IAH)] ; [Cu(ISCH)(IAH)]  
2 4,10



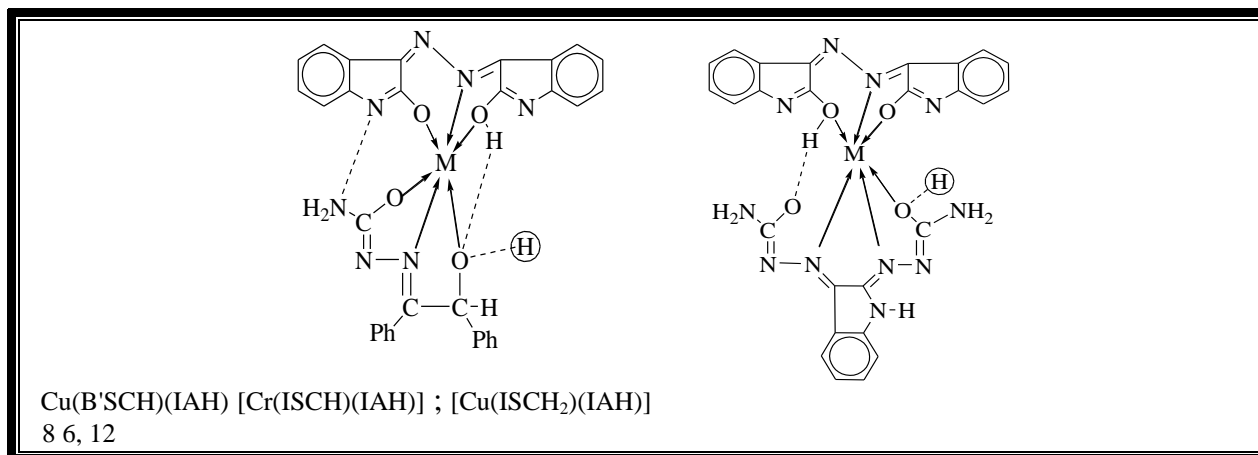


Figure 4: Proposed structures of the complexes

Table 1- Amounts, medium for the preparation of the complexes

No.	Wt. of B'SCH <sub>2</sub>	Wt. of ISCH <sub>2</sub>	Wt. of ISCH <sub>3</sub>	Wt. of IAH <sub>2</sub>	Medium	% yield	Complex
1	0.44	.	.	0.48	Neutral	74.24	[Cr(B'SCH <sub>2</sub> )(IAH <sub>2</sub> )](NO <sub>3</sub> ) <sub>3</sub>
2	0.44	.	.	0.48	Basic	78.75	Na[Cr(B'SC)(IA)]
3	.	0.34	.	0.48	Neutral	81.14	[Cr(ISCH <sub>2</sub> )(IAH <sub>2</sub> NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>
4	.	0.34	.	0.48	Basic	89.00	[Cr(ISC)(IAH)]
5	.	.	0.60	0.48	Neutral	74.98	[Cr(ISCH <sub>3</sub> )(IAH <sub>2</sub> )(NO <sub>3</sub> )](NO <sub>3</sub> ) <sub>2</sub>
6	.	.	0.60	0.48	Basic	85.34	[Cr(ISCH)(IAH)]
7	0.55	.	.	0.60	Neutral	86.83	[Cu(B'SCH <sub>2</sub> )(IAH <sub>2</sub> )NO <sub>3</sub> ]NO <sub>3</sub>
8	0.55	.	.	0.60	Basic	91.40	Cu(B'SCH)(IAH)
9	.	0.42	.	0.60	Neutral	72.85	[Cu(ISCH <sub>2</sub> )(IAH <sub>2</sub> NO <sub>3</sub> )]NO <sub>3</sub>
10	.	0.42	.	0.60	Basic	80.70	[Cu(ISCH)(IAH)]
11	.	.	0.74	0.60	Neutral	71.17	[Cu(ISCH <sub>3</sub> )(IAH <sub>2</sub> NO <sub>3</sub> )]NO <sub>3</sub>
12	.	.	0.74	0.60	Basic	81.42	[Cu(ISCH <sub>2</sub> )(IAH)]

Table 2- Some analytical and physical properties

No.	Color	M.P or d °C	$\Lambda_M^*$	M% calc.(obs.)	Na% calc.(obs.)	M.Wt calc.(obs.)	Ref. x10 <sup>-4</sup>	M <sub>eff</sub> **
1	Brown	130	195	6.52 (6.64)	-	797 (783)	1.435522	3.74
2	Pale green	183	88.49	7.93 (8.10)	3.63 (3.75)	655 (644)	1.435550	3.42
3	Yellowish orange	195	127.00	7.10 (6.85)	-	732 (759)	1.435541	3.47
4	Yellowish brown	165	10.00	9.18 (9.02)	-	566 (578)	1.435552	3.22
5	Cumminy	205	127.29	5.84 (6.50)	-	889 (841)	1.435550	3.77
6	Greenish brown	189	0.024	7.42 (7.10)	-	700 (734)	1.435574	3.54
7	Dark brown	147	77.75	8.50 (8.10)	-	747 (783)	1.435563	1.79
8	Dark brown	170	11.38	10.23 (9.61)	-	621 (661)	1.435577	1.82
9	Redish brown	206	79.22	9.31 (9.05)	-	681 (701)	1.435555	1.90
10	Dark brown	166	17.00	11.43 (11.29)	-	555 (562)	1.435585	1.58
11	Redish brown	154	93.98	7.57 (7.34)	-	838 (865)	1.435563	1.88
12	Dark brown	215	32.74	8.91 (8.55)	-	712 (742)	1.435569	1.75

\* AM : Molar conductivities in  $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$  ; \*\* $\mu_{\text{eff}}$ : Magnetic moment in Bohr Magneton; d=decomposition point

Table 3- Some important bands in the infrared spectra of the ligands and their chromium(II) and copper(II) complexes

No.	Semi			Azine				$\nu_{NO_3}$ ionic	$\nu_{NO_3}$ (s)	$\nu_{NO_3}$ (as)	$\nu_{N-O}$	$\nu_{M-N}$	$\nu_{M-O}$	Other bands
	$\nu_{C=N}$	$\nu_{C=O}$	$\nu_{C-O}$	$\nu_{C=N}$	$\nu_{C=O}$	$\nu_{C-O}$	$\nu_{N-N}$							
IAH <sub>2</sub>	-	-	-	1637.96	1687.14	-	950.00	-	-	-	-	-	-	-
B'SCH <sub>2</sub>	1637.93	1685.15	-	-	-	-	-	-	-	-	-	-	-	$\nu_{C-O}$ (1109.16) $\nu_{O-H}$ (3552.28)
ISCH <sub>2</sub>	1635.91	1697.80	-	-	-	-	-	-	-	-	-	-	-	$\nu_{C-O}$ (1720.37)
ISCH <sub>3</sub>	1611.91	1697.50	1399.82	-	-	-	-	-	-	-	-	-	-	-
1	1617.32	1638.04	-	1599.01 1638.12	1638.04	-	984.27	1384.94	-	-	-	405.00 400.00	474.62 481.31	$\nu_{C-O}$ (1130.79) $\nu_{O-H}$ (3549.65)
2	1551.43	-	1152.80 1207.29	1616.64 1638.30	-	1155.91 1167.31	981.87	-	-	-	-	445.60 400.03	481.31 492.33	-
3	1616.30	1635.11	-	1598.31 1637.96	1652.30	-	982.71	1389.45	1455.75	1340.61	951.82	405.12 443.00	505.01 521.32	$\nu_{C-O}$ (1720.53)
4	1556.09	-	1110.64 1163.43	1607.33 1638.13	-	1198.87	982.90	-	-	-	-	400.00 445.83	502.11 534.48	-
5	1563.12	1617.08	-	1599.11 1638.40	1638.40	-	990.02	1385.25	1400.51	1285.51	900.75	410.21 401.32	474.87 451.03	$\nu_{C-O}$ (1718.93)
6	1552.53	-	1191.31 1111.80	1617.44 1639.10	-	1159.32	981.96	-	-	-	-	444.32 400.00	452.12 481.21	-
7	1617.62	1638.05	-	1599.00 1638.00	1638.05	-	982.31	1384.90	1420.20	1315.20	1005.00	405.32 400.00	471.94 492.33	$\nu_{C-O}$ (1133.56) $\nu_{O-H}$ (3547.21)
8	1615.94	-	1185.27	1598.32 1637.71	-	1160.29	998.30	-	-	-	-	443.21 409.33	471.89 493.21	-
9	1616.96	1638.10	-	1596.31 1638.15	1630.92	-	979.93	1386.70	1453.55	1338.55	960.00	412.01 400.00	474.64 492.13	$\nu_{C-O}$ (1707.03)
10	1605.43	-	1192.83	1599.70	-	1146.27	979.61	-	-	-	-	470.47 400.00	490.64 501.32	-
11	1589.31	1637.12	-	1616.92 1637.96	1630.92	-	985.73	1384.85	1454.05	1339.01	965.50	435.99 400.00	490.64 530.22	-
12	1586.22	-	1145.71	1615.24 1637.11	-	1194.75	980.40	-	-	-	-	409.12 400.05	493.55 502.91	-

Table 4- Electronic spectral data in the ultraviolet region of ligands and their complexes

No.	$n \rightarrow \pi^*$ cm <sup>-1</sup>	$\pi \rightarrow \pi^*$ cm <sup>-1</sup>
B'SCH <sub>2</sub>	33112.582	40000.000
ISCH <sub>2</sub>	30120.481	37037.037
ISCH <sub>3</sub>	31446.540	43859.649
IAH <sub>2</sub>	30864.197	40000.000
1	24510.050	28750.500
2	24500.100	29500.250
3	24875.621	28735.632
4	24800.050	28901.734
5	25257.625	32786.880
6	27777.778	31645.569
7	28089.887	31750.500
8	26666.667	32000.000
9	24850.100	31446.540
10	26666.667	33333.333
11	25859.790	30487.804
12	29940.119	31847.133

Table 5- Electronic spectral data of chromium(III) complexes

No.	$\nu_1$	$\nu_2$	$\nu_3$	B	$\nu_3/B$	Dq	10Dq	Dq/B	$\beta$	C.T	C.F.S.E
1	11709.60	25510.20	29761.90	892.946	33.33	1170.960	11709.60	1.30	0.97	31645.569	14051.52
2	10204.08	13358.25	25906.74	890.550	29.09	1020.408	10204.08	1.15	0.97	28089.887	12244.90
3	11682.24	23809.52	28735.63	782.987	36.70	1168.224	11682.24	1.49	0.85	31645.569	14018.69
4	10869.57	12309.23	27173.91	820.615	33.114	1086.960	10869.60	1.32	0.89	39370.078	13043.48
5	11764.71	23148.15	29600.00	845.714	35.00	1176.411	11764.11	1.39	0.92	31645.569	12219.96

6	10628.80*	12996.23	25510.20	866.415	29.443	1062.880	10628.80	1.22	0.94	29069.767	12754.56
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Table 6- Electronic spectral data of copper(II) complexes

No.	$\nu_1$	$\nu_2$	$\nu_3$	C.T
7	10183.30	14285.71	24038.46	28089.89
8	10000.00	12500.00	24271.84	32679.14
9	10162.60	14286.00	23584.90	28571.43
10	11111.11	14815.00	23148.15	32894.74
11	10120.41	12500.00	23148.15	28571.43
12	11764.70	14705.00	23148.14	29940.12

## مع مزيج من الليكنات الحاوية على (II) والنحاس(III) تحضير وتشخيص معقدات الكروم الازاتين آزين والسميكاربازونات

زهور فتحي داود فادية جلال المولى

### الخلاصة

حضرت مُعقدات جديدة للكروم(III) و النحاس(II) مع مزيج من الليكنات التي تشمل إزاتين آزين-IAH2 وليكنات السميكاربازون (المتضمنة بنزوين سميكاربازون- B'SCH2 أو إزاتين سميكاربازون-ISCH2 أو إزاتين بس(سميكاربازون)- ISCH3 في كل من الوسطين المتعادل (أو الحامضي قليلاً) والقاعدي. شخّصت المُعقدات الناتجة باستخدام التحليل العنصري باستخدام جهاز طيف الامتصاص الذري و الطريقة الترسيبية وحساب الوزن الجزيئي النسبي وقياس التوصيلية الكهربائية والإنكسار المولاري والمغناطيسية واطيف الأشعة تحت الحمراء والإلكترونية. وإستنتج من هذه الدراسة ان الليكنات تعطى مُعقدات أيونية موجبة ذات صيغ عامة  $[M(IAH_2)(LH_{2,3})(NO_3)_m](NO_3)_{n-m}$  أو  $[Cr(IAH_2)(B'SCH_2)](NO_3)_3$  في الوسط المتعادل (أو الحامضي قليلاً)، في حين تتكون مُعقدات مُتعادلة أو سالبة الشحنة ذات صيغ عامة  $[M(IAH_2-y')(LH_{2,3}-y'')]$  أو  $Na[Cr(IA)(B'SC)]$  في الوسط القاعدي (حيث  $M = Cr+3$  أو  $Cu+2$  و  $y' = 1$  أو  $2$  و  $y'' = 1$  أو  $2$  و  $m = 1$  و  $3$  و  $LH_{2,3} = B'SCH_2$  أو  $ISCH_2$  أو  $ISCH_3$ )، إذ تسلك فيها الليكنات بشكل ليكنات مُتعادلة أو ذات شحنة سالبة أحادية أو ثنائية في الوسط المتعادل (أو الحامضي قليلاً) والقاعدي على التوالي. أثبتت الدراسة أنّ المُعقدات تكون سداسية التناسق ذات أشكال ثمانية السطوح أحادية النواة.