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Synthesis, Magnetic and Spectral Investigations of Copper Metal Ion Complexes of 2–Substituted Benzaldehyde Semicarbazones and Thiosemicarbazones

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Abstract

The paper reports the synthesis of copper (II) complexes by refluxing the metal salts with the ligands 2–bromobenzaldehyde semicarbazone / thiosemicarbazone (bass, bbtsc) and 2–methoxybenzaldehyde semicarbazone/ thiosemicarbazone (mbsc, mbtsc) with general composition ML_2X_2 (L→ bbsc, bbtsc, mbsc and mbtsc, X→ Cl, Br, CH_3COO^- and SO_4^{-2}). All these complexes are characterized by elemental analysis, magnetic susceptibility measurements, infrared and electronic spectral studies. The infrared spectral data of the complexes reveals bidentate complexating nature of the ligands coordinating through oxygen atom of carbonyl group/sulphur atom of thioketo form and azomethine nitrogen atom. High spin configuration has been suggested by magnetic moment of the complexes. The most probable geometry for all the metal complexes is proposed here.

Keywords: Semicarbazone, Thiosemicarbazone, Benzaldehyde, Ligands

1. Introduction

The chemistry of the transition metal complexes of semicarbazones and thiosemicarbazones have been receiving considerable attention largely because of their wide synthetic and analytical applications as well as biological activities [1]. In recent years thiosemicarbazones have been evaluated for the analytical determination of metals and received attention in view of their variable bonding modes, structural diversity and ion-sensing ability [2-4]. Occurrence of Copper (II) in human body as also in other living beings and plants in the form of cuproprotein is known since long [5]. The cytotoxic studies of copper (II) salicylaldehyde semicarbazone complexes on a number of human tumor cell lines were conducted [6]. Copper bis (thiosemicarbazone) complexes bearing methyl, phenyl and hydrogen on diketo backbone of the ligand have been synthesized, characterized and study in vitro and vivo anticancer activity [7]. Several copper (II) complexes of bis (thiosemicarbazone) show promise as therapeutics for the treatment of neurological diseases, cancer and bacterial infections [8]. In the present study, we report the synthesis of complexes of divalent copper with the ligands 2–bromobenzaldehyde semicarbazone/ thiosemicarbazone (bbsc, bbtsc) and 2–methoxybenzaldehyde semicarbazone/ thiosemicarbazone (mbsc, mbtsc), magnetic and spectral studies of these complexes on the basis of various physico-chemical techniques and probable geometry for all the complexes.

2. Experimental

All the chemical and solvents used were of analytical reagent grade.

2.1Preparation of Ligands

The ligands 2–methoxybenzaldehyde semicarbazone/ thiosemicarbazone (mbsc, mbtsc)

and 2–bromobenzaldehyde semicarbazone/ thiosemicarbazone (bbsc, bbtsc) were prepared according to the literature[9] procedure by condensing 2–methoxybenzaldehyde and 2–bromobenzaldehyde with semicarbazide hydrochloride and thiosemicarbazide respectively and conformed by elemental analysis and IR spectral studies.

2.2General method for synthesisation of metal complexes

A hot ethanolic solution (20 ml) of metal salt (0·05 mol) was refluxed with a hot ethanolic solution (20 ml) of the respective ligands (0·10 mol) keeping the molar ratio 1:2 for 3–4 hours. The colored complexes were separated out on cooling the contents. The same was filtered, washed with 50% ethanol, dried in the electric oven, analyzed and the data is reported in table–1.

2.3Physical and analytical measurements

The analysis of C, H and N were done by micro analytical techniques. Metal contents were determined [10] by the precipitation of copper extract with dilute Hydrochloric acid as cuprous thiocynate. IR spectral data of the ligands and their complexes were recorded on perkin-Elmer 1600 FTIR automatic recording spectrophotometer in potassium bromide. Electronic spectra of the complexes were scanned in ethanol on Shimadzu U.V. and visible spectrophotometer 1601 C.P. The Magnetic susceptibility measurements of the complexes were determined by Guoy's method using Hg $[Co(CNS)_4]$ as calibrant.

3. Results and Discussion

Synthesized metal complexes were insoluble in water and most of the organic solvents with the exception of polar solvents such as DMF and DMSO. The analytical data of all the complexes correspond to 1: 2 (M : L) stoichiometric ratio indicating coordination of anions and have the general formula CuL_2X_2 (L → bbsc, mbsc, bbtsc and mbtsc, X → Cl^-, Br^-, CH_3COO^- and ½SO_4^{-2}). The complexes exhibit different stereo-chemistry varying from four coordinate tetrahedral, five coordinate square pyramidal & trigonal bipyramidal and six coordinate octahedral.

3.1 IR Spectral Studies

The main vibrational bands (cm^{-1}) of the ligands and complexes are reported. The ligands show main absorption bands in the region ~3020–3045 cm^{-1} due to ν(C–H), ~1615 cm^{-1} due to ν (C=C), 740–755 cm^{-1} (Ortho substitution) diagnostic of aromatic character[11]. The strong bands at ~1664 cm^{-1} and ~1535 cm^{-1} are assignable to ν(C=O) and ν(C=N) stretching vibrations[12] respectively. The bands in the region 3380–3130 cm^{-1} are assigned to ν(NH) and ν(NH_2) stretching vibrations[13] of free ligand and remain practically unchanged or shift slightly to higher side indicating no coordination. The medium intensity bands occur at ~818 cm^{-1} ν(C=S) and ~998–1005 cm^{-1}ν(N–N) vibrations[14 but the former shifts to lower side suggesting the sulphur atom is taken part in coordination with metal ion[15]. The absence of the bands above 3408 cm^{-1} due to ν(O–H) or in the region 2512–2610 cm^{-1} due to ν(S– H) vibrations suggests the presence of ligands in the keto/thione form[16] respectively.

The shifting of characteristic bands of free ligands in the complex formation indicates the bidentating behaviour of the ligands in all the complexes. The strong bands observed at ~1664 cm^{-1} shift to lower wave number side by about 25-50 cm^{-1} in all the complexes indicating the oxygen atom is involved in complexation[12]. The position of ν(C=N) band appeared at 1535 cm^{-1} is shifted toward lower wave number by about 35-60 cm^{-1} in all the complexes indicating coordination via the azomethine nitrogen[17].The appearance of a new band in the range 452-488 cm^{-1} probably arising from ν(M-N) stretching vibration[18]. In the acetato complexes $\nu_a(COO^-)$ and $\nu_s(COO^-)$ are observed at 1670 cm^{-1} and 1442 cm^{-1} respectively indicating bridging nature of the acetate ion as the separation

between two frequencies is much larger in unidentate complexes that in the free ion[19]. The IR spectral data of sulphato complexes exhibit bands at 1098–1129 cm^{-1}, ~957–963 cm^{-1} and ~565 cm^{-1} corresponding monodentate behaviour of sulphate group[20].

Table–1

Elemental analysis data of Copper (II) Complexes

Complexes	Colour	% found (Calculated)			
		Cu	C	H	N
$Cu(mbsc)_2Cl_2$	Light Blue	12.29 (12·21)	41·57(41·49)	4·32(4·23)	16·19(16·14)
$Cu(mbsc)_2Br_2$	Bluish Green	10·49(10·43)	35·36(35·45)	3·73(3·61)	13·87(13·78)
$Cu(mbsc)_2SO_4$	Bluish Green	11·58(11·65)	39·73(39·84)	4·09(4·03)	15·45(15·40)
$Cu(mbtsc)_2Br_2$	Greenish Blue	9·98(9·91)	33·74(33·68)	3·34(3·43)	12·97(13·10)
$Cu(mbtsc)_2SO_4$	Green	10·89(11·00)	37·61(37·40)	3·95(3·81)	14·41(14·54)
$Cu(mbtsc)_2(CH_3COO)_2$	Brown	10·79(10·60)	36·15(36·03)	3·76(3·67)	14·09(14·01)
$Cu(bbsc)_2Cl_2$	Light Green	10·14(10·28)	31·19(31·05)	2·70(2·59)	13·69(13·58)
$Cu(bbsc)_2Br_2$	Greenish Black	9·11(8·99)	27·08(27·15)	2·29(2·26)	11·81(11·88)
$Cu(bbsc)_2SO_4$	Light Green	9·76(9·88)	29·97(29·84)	2·57(2·49)	13·18(13·06)
$Cu(bbsc)_2(CH_3COO)_2$	Brownish Green	9·69(9·55)	28·77(28·86)	2·58(2·40)	12·50(12·62)
$Cu(bbtsc)_2Cl_2$	Light Orange	9·71(9·77)	29·63(29·52)	2·65(2·46)	12·99(12·92)
$Cu(bbtsc)_2Br_2$	Red Black	8·79(8·60)	25·81(25·97)	2·22(2·16)	11·49(11·36)
$Cu(bbtsc)_2SO_4$	Reddish Brown	9·34(9·41)	28·59(28·43)	2·28(2·37)	12·58(12·44)
$Cu(bbtsc)_2(CH_3COO)_2$	Red	9·23(9·11)	27·67(27·53)	2.49(2.29)	12·19(12·05)

3.2 Study of Magnetic moment and Electronic spectral bands

The observed magnetic moments at room temperature for divalent copper complexes are in the range 1·73–2·05 B.M. (Table-2) corresponding

to one unpaired electron around the metal ion [21]. The only exception being acetate complexes of semicarbazones (bbsc, 1.57 B.M. and mbsc, 1.54 B.M.) indicate polymeric structure for complexes. Irrespective of the stereochemistry involved, bivalent copper complexes contain one unpaired spin [22] per copper atom. So, there should be some correlation between the magnitude of orbital contribution and coordination geometry.Lower magnetic moment or even diamagnetism results [23] to antiferromagnetic interactions which are absent in present case [24]. All the semicarbazone complexes except sulphato may be assigned to have tetragonal structure in planar configuration of the two semicarbazone molecules around metal ion with the anions occupying axial positions as the results resemble to that of semicarbazide chloro complex of copper (II) for which crystal structure is known[25].

The electronic spectra of complexes reported here except sulphato complexes exhibit only a broad absorption band ranging 13435–15400 cm^{-1} and a well defined shoulder in the range 15510–18350 cm^{-1} (Table–2). These spectral bands correspond to the transitions $^2B_{1g} \rightarrow {}^2A_{1g}$ ($d_{x^2-y^2} \rightarrow d_{z^2}$) and $^2B_{1g} \rightarrow {}^2E_g$ ($d_{x^2-y^2} \rightarrow d_{xz}$) transitions respectively. The low intensity bands due to $^2B_{1g} \rightarrow {}^2B_{2g}$ is usually not observed as a separate band in an octahedral field [26-27]. The splitting of the ^2E_g state is a measure of the planar and axial fields.The change of position of the bands would be due to axial field only. Electronic spectra of these complexes were found to have tetragonal configuration with planar arrangement of two ligand molecules around copper (II) ion and the anions occupying axial position[28]. Therefore the complexes may be considered to possess a tetragonal geometry [29].The electronic spectra of 2–bromobenzaldehyde/2–methoxybenzaldehyde sulphato complexes of semicarbazone ligands show only one intense absorption band at 11400 cm^{-1} and 10970 cm^{-1} respectively which may be assigned to $^2A_1 \rightarrow {}^2E^{II}$ transition. These absorption bands are similar to earlier reported trigonal bipyramidal copper (II) complexes [30]. Electronic spectra of 2–bromobenzaldehyde/ 2–methoxybenzaldehyde thiosemicarbazone sulphato complexes exhibit two absorption bands at 13698, 14560 cm^{-1} and 16385, 18350 cm^{-1} respectively. These absorption bands are characteristic for square pyramidal geometry [31] of Copper (II) complexes.

4. Conclusion

Based on Elemental analysis, Magnetic moment, Infrared and Electronic spectral studies tetragonal planar configuration with two ligands around metal ion and anion occupying axial position have been proposed for complexes reported here except sulphato complexes. Five coordinated trigonal bipyramidal geometry has been suggested for semicarbazone sulphato complexes whereas square pyramidal geometry is proposed for thiosemicarbazone sulphato complexes under study.

Table–2
Magnetic Moment and electronic spectral bands of Copper (II) Complexes

Complexes	μ_{eff} (B.M.)	$\nu_2(cm^{-1})$ $^2B_{1g} \rightarrow {}^2A_{1g}$	$\nu_3(cm^{-1})$ $^2B_{1g} \rightarrow {}^2E_g$
Cu $(mbsc)_2$ Cl_2	1·95	13435	15790
Cu $(mbsc)_2$ Br_2	1·91	13680	15805
Cu $(mbsc)_2$ SO_4	2·01	10970	—
Cu $(mbsc)_2$ $(CH_3COO)_2$	1·54	13500	15510
Cu $(mbtsc)_2$ Cl_2	1·83	13510	15785
Cu $(mbtsc)_2$ Br_2	1·80	13705	17400
Cu $mebtsc)_2$ SO_4	2·03	14560	18350
Cu $(mbtsc)_2$ $(CH_3COO)_2$	1·96	15400	18230
Cu $(bbsc)_2$ Cl_2	1·73	13725	16870

Cu $(bbsc)_2$ Br_2	2·01	14220	16955
Cu $(bbsc)_2$ SO_4	2·04	11400	—
Cu $(bbsc)_2$ $(CH_3COO)_2$	1·57	14285	17060
Cu $(bbtsc)_2$ Cl_2	1·97	14600	17380
Cu $(bbtsc)_2$ Br_2	2·05	15350	17900
Cu $(bbtsc)_2$ SO_4	2·02	13698	16385
Cu $(bbtsc)_2$ $(CH_3COO)_2$	2·00	15240	18310

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REFERENCES:

[1] R.Bohra and A. Gupta, *J. Ind. Chem. Soc.*, **80,** 2003, 281.

[2] T. Kumajai, T. Nagahiro and H. Nishioka, *Microchem. J.*, **50,** 1994, 88.

[3] J.S. Casas, M.S. Garcia-Tasende, J. Sordo, Main group metal complexes of semicarbazones and thiosemicarbazones, *Coordination chemistry reviews*, **209(1),** 2000, 197-261.

[4] D. Mishra, S. Naskar, M.G.B. Drew, S.K.Chattopadhyay, *Inorganica Chimica Acta*, **359(2),** 2006, 585-592.

[5] S.J. Adelstein and B.L. Vallee, *New Eng. J. Med.*, **265,** 1961, 892.

[6] Wan Yen Lee, Lee Peter Peng Foo, Yaw Kai Yan and Mathew Lau, *Metallomics*, **2,** 2010, 694-705.

[7] Duraippandi Palanimuthum, Sridevi Vijay Shinde, Kumaravel Somasundaram and Ashoka G. Samuelson, *J. Med. Chem*, **56(3),** 2013, 722-734.

[8] Karrera Y. Dioko, Paul S. Donnelly and Alastair G. Mcewan, *Metallomics*, **6,** 2014, 2250-2259.

[9] A. I. Vogel "Practical Organic Chemistry", 3rd ed., Longman, ELBS, London, 344, 1973,

[10] A.I. Vogel "Quantitative Inorganic Analysis" 3rd ed., Longman, ELBS, London, 479,1962.

[11] G.C. Bassler and R.M. Silvertein, "Spectrometric Identifications of Organic Compounds", John Wiley, New York, 1367,1968.

[12] M.M. Bekheit and S.I. Mostafa, *Chem. Pharm.Bull. Jpn.*, **48,** 2000, 266.

[13] Dixit, B. Surjit, P. Karla, Achintya Aas and B. Jayaram, *Ind. J. Chem.*, **39A,** 2000, 262.

[14] H. Beraldo, L.P. Boyd. and D.X. West, *Trans. Met. Chem.*, **23,** 1998, 67.

[15] N.S. Youssef, K.H. Hegab, *Synthesis And Reactivity In Inorganic, Metal Organic And Nanometal Chemistry*, **35(5),** 2005, 391-99.

[16] M.P. Teotia, J.N. Gurtu and V.B. Rana, *Ind. J. Chem.*, **19,** 1980,133.

[17] M. Joseph, A. Sreekanth, V.Suni, M.R.P. Kurup, *Spectrochimica Acta part A*, **64(3),** 2006, 637-641.

[18] S.Chandra, L.K.Gupta, EPR, Mass, IR, Electronic and Magnetic studies on Copper (II) complexes of semicarbazones and thiosemicarbazones, *Spectrochimica Acta part A*, **61(1-2),** 2005, 269-275.

[19] B.J. Hathway, "Essay in Chemistry" eds. J.N. Bardly and R.D. Gillan, Academic Press, New York, P. 61,1971.

[20] K. Nakamoto, "Infrared and Raman spectra of Inorganic and Coordination compounds" 3rd ed. John wiley, New York, 1978.

[21] R.A. Earnshaw, "Introduction to Magneto Chemistry". Academic Press, New York, 1966.

[22] B.N. Figgis and J. Lewis, *Proc. Inorg. Chem.*, **6,** 1964,37.

[23] S.B. Padhye, S. Chandra and R.P. Singh, *J. Ind. Chem. Soc.*, **58,** 1981,1097.
[24] M. Kato, H. Johansen and F. Fanning, *Chem. Rev.*, **64,** 1964, 99.
[25] A. Chiesi Villa, H.G. Manfredo and C. Guastini, *Cryst. Struc. Commun.*, **125,** 1972, 207.
[26] Y. Nishida and S. Kida, *Coord. Chem., Rev.*, **27,** 1979, 275.
[27] D. Sutton, "Electronic Spectra of Transition Metal Chemistry", Langmann, London, 344,1973.
[28] B.A. Gingras, R.L. Samerjai and C.H. Bailey, *Can. J. Chem.*, **40,** 1962, 1053.
[29] S.Chandra, A.Kumar, Spectral studies on Co(II), Ni(II) and Cu(II) complexes with thiosemicarbazone (L_1) and semicarbazone (L_2) derived from 2-acetyl furan, *Spectrochimica Acta part A*, **66(4-5),** 2007, 1347-1351.
[30] G.A. Barclay, B.F. Hoskins and C.H.I. Cannard, *J. Chem. Soc.*, **56,** 1963, 91.
[31] L. Sacconi, "Transition Metal Chemistry" Vol. 4, Marcel Dakker, New York, 1978.

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