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Some Tetragonally Distorted Copper(II) Complexes of 4-Benzylamidothiosemicarbazide and Its Thiosemicarbazone

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Some copper(II) complexes of the type CuL_2X_2 *(where L = BTSC and FBTS and X = Cl, Br,* NO_3 *and NCS) have been prepared with 4-benzylamidothiosemicarbazide (BTSC) and 1-(α-)-furyl-4-benzylamidothiosemicarbazone (FBTS) and characterized by conventional chemical and physical measurements. The complexes possess tetragonally distorted octahedral stereochemistry as evidenced by their electronic spectra. The infrared spectra (4000–200 cm*$^{-1}$*) reveal that both BTSC and FBTS act as bidentate ligands while nitrate and thiocyanato groups are coordinated through oxygen and nitrogen atoms, respectively. The M–N, M–S and M–X frequencies have been located in their far infrared spectra and assigned. The polycrystalline E.S.R. spectra suggest tetragonal symmetry for the copper(II) ion involving* $d_{x^2-y^2}$ *(or* d_{xy}*) ground state except chloride complexes where isotropic spectra are observed.*

Introduction

Although thiosemicarbazides and thiosemicarbazones have been known to give stable complexes with transition metal ions [1–5], it is only very recently that the detailed stereochemistry and reactions of these complexes have been investigated [6]. A reason for this renewed interest is the proved anti-tumor activity [7]. Their pharmacological [8], anti-bacterial [9] and fungicidal [10] properties are also well known. Two series, $Cu(tScH)_2X_2$ (X = Cl, Br, NO_3, ClO_4, 1/2 SO_4) and $Cu(tScH)X_2$ (X = Cl, Br), of copper(II) complexes with thiosemicarbazone have been reported [11–13], the former conforming to distorted octahedral stereochemistry whereas in the latter the halide ions are coordinated in square-planar arrangement about the copper(II) ion giving infinite polymeric chains [12]. The present communication describes a number of copper(II) complexes derived from 4-benzylamidothiosemicarbazide (BTSC) and 1-(α)-furyl-4-benzylamidothiosemicarbazone (FBTS) which have been found to be tetragonally distorted.

Results and Discussion

The interaction of BTSC and FBTS with copper(II) ions yields complexes corresponding to the general formula CuL_2X_2 (where L = BTSC and FBTS and X = Cl, Br, NO_3 and NCS). All the complexes, as expected for a nitrogen–sulphur donor set [13], are sparingly soluble in non-polar solvents and possess no sharp melting point. They do, however, decompose on heating above 250 °C.

The magnetic moments of all these complexes at room temperature have been found in the range 1.72–1.82 B.M. which are very close to spin-only for one unpaired electron and are in the range normally observed for copper(II) complexes having an orbitally non-degenerate B_{1g} ground state, thereby indicating no metal–metal interaction. In fact, no significant conclusion can be drawn from the magnetic data regarding the stereochemistry of copper(II) complexes. As a representative complex, the chloro complex of the BTSC was subjected to low temperature magnetic measurements. These data obey the Curie–Weiss law ($\theta = -2$ °K).

TABLE I. Magnetic Data of $Cu(BTSC)_2Cl_2$ Complex at Various Temperatures.

Temperature (°K)	$\chi_M' \times 10^6$ c.g.s.	μeff B.M.
80	4,538	1.71
98	3,904	1.73
117	3,184	1.75
152	2,534	1.76
204	1,943	1.78
295.5	1,403	1.81

The electronic spectra of all the complexes show one broad strong band in the region 18,600–16,100 cm^{-1} with a more or less pronounced low energy shoulder. On this basis all the complexes seem to be tetragonally distorted [11]. For copper(II) ion in tetragonal environment three principal absorption bands are expected but only in few complexes [15–17] have these absorption bands been resolved either

TABLE II. Magnetic, E.P.R. and Electronic Spectral Data of Cu(II) Complexes of BTSC and FBTS.

Complex	Temp. (°K)	$\chi'_M \times 10^6$ c.g.s.	μ_{eff} B.M.	$g_{\parallel}$	$g_{\perp}$	$^2B_{1g} \rightarrow {}^2A_{1g}$	$^2B_{1g} \rightarrow {}^2E_g$
$Cu(C_9H_{12}N_4OS)_2Cl_2$	302	1,370	1.81		2.117[a]	12,900	16,000
$Cu(C_9H_{12}N_4OS)_2Br_2$	302	1,216	1.72	2.277	2.131	13,330	16,670
$Cu(C_9H_{12}N_4OS)_2(NO_3)_2$	302	1,256	1.74	2.262	2.14	14,290	17,390
$Cu(C_9H_{12}N_4OS)_2(NCS)_2$	302	1,187	1.69	2.126	2.128	14,930	18,520
$Cu(C_{14}H_{14}N_4O_2S)_2Cl_2$	291	1,362	1.78		2.104[a]	12,990	16,130
$Cu(C_{14}H_{14}N_4O_2S)_2Br_2$	302	1,375	1.82	2.28	2.131	13,420	16,810
$Cu(C_{14}H_{14}N_4O_2S)_2(NO_3)_2$	302	1,340	1.79	2.331	2.14	14,490	17,540
$Cu(C_{14}H_{14}N_4O_2S)_2(NCS)_2$	302	1,249	1.73	2.28	2.10	15,040	18,690

[a] Average g value.

by Gaussian analysis or single crystal polarization studies and are assigned to transitions $^2B_{1g} \rightarrow {}^2A_{1g}$; $^2B_{1g} \rightarrow {}^2B_{2g}$ and $^2B_{1g} \rightarrow {}^2E_g$ in order of increasing energy. The low energy shoulder in the present complexes can be assigned [15, 16] to the transition $^2B_{1g} \rightarrow {}^2A_{1g}$, this being equal to the splitting of the ^2E_g term. Because of the low intensity of $^2B_{1g} \rightarrow {}^2B_{2g}$ (being equal to 10 Dq), this band is usually not observed as a separate band in tetragonal compounds [15, 16]. The splitting of the E_g level is a measure of the difference between the in-plane and axial fields, and since the in-plane field is constant in all the cases, hence any change in the position of these bands would be due to axial field only. In the electronic spectra the absorption bands shifted to higher energy in the order $Cl^- < Br^- < NO_3^- < NCS^-$. This, of course, is the order of decreasing interaction. A similar sequence has been reported in the literature [24].

E.S.R. powder spectra usually do not yield accurate molecular g-values but in most cases it is possible to distinguish unambiguously between $d_{x^2-y^2}$ (or d_{xy}) ground state on the one hand and d_{z^2} ground state on the other hand. Thus a $d_{x^2-y^2}$ (or d_{xy}) ground state gives a spectrum $g_{\parallel} > g_{\perp} > 2.04$ in most cases whilst a d_{z^2} ground term usually gives a spectrum with $g_{\perp} > g_{\parallel} \approx 2.00$. The g values of all the complexes are given in Table II. The 'g' values of bromo, nitrato and thiocyanato complexes of both the ligands have been found in accordance with the above statement and conform to the tetragonal symmetry of these complexes having $d_{x^2-y^2}$ ground state. However, the e.s.r. spectra of the chloro-complexes of both the ligands are surprisingly isotropic which suggest the possible presence of copper(II) ions in the complexes containing grossly misaligned tetragonal axes [18].

Infrared Spectral Studies

Band assignments for thiosemicarbazide and thiosemicarbazone complexes are difficult to arrive at because of the extensive mixing of internal modes of the ligand, *e.g.* deformation modes involving $-NH_2$ are mixed with skeletal bending and stretching modes. The absorption bands in the region 3,290–3,040 cm^{-1} in the infrared spectra of BTSC only have been assigned to the NH_2 and NH frequencies on the basis of similar observations by Mashima [19]. Most of these bands are shifted to lower frequency as a result of the drainage of electrons from the terminal nitrogen atom of the $NHNH_2$ group to the metal ion which indicates that this terminal nitrogen is taking part in coordination.

A strong band at 1625 cm^{-1} in BTSC has been observed due to the amide I and NH_2 bend [4]. On complexation this band shifts slightly (10–20 cm^{-1}) to lower frequency, as the contribution of NH_2 group to this band is reduced, which suggests the participation of the NH_2 group in coordination. On the other hand since the NH_2 group disappears during the thiosemicarbazone formation the amide I band is expected to be relatively free from the contribution of the NH_2 bend and therefore it is observed at 1615 cm^{-1} in FBTS (instead of 1625 cm^{-1} as in BTSC). Furthermore no change in the position of this band has been observed in FBTS complexes.

Another strong band at 1565 in BTSC and 1575 cm^{-1} in FBTS has been assigned to the amide II and ν(CN) stretch vibrations [19]. In case of BTSC there is no change in the position of this band on complexation whereas in FBTS complexes this band shifts either to low frequency (up to 20 cm^{-1}) or weakens in intensity (in few cases both weakening and shift occur). This indicates that the contribution of CN stretch has been reduced as the nitrogen of CN group is involved in the bond formation to the metal ion. The bands observed at ~1230, ~750 and 650 cm^{-1} have been assigned to the amide III [4], amide IV [20] (due to the major contribution of NCO) and amide IV [20] (due to the contribution of C=O out-of-plane bending), respectively. The coordination through amino group can be excluded as no appreciable change in the position of all the bands due to this vibration has been observed in the infrared spectra of all the complexes of both the ligands.

The bands around 1290 and 730 cm^{-1} which may be assigned to ν(CS) vibrations do change either in

TABLE III. Important Infrared Spectral Bands of The Ligands (BTSC and FBTS) and Their Copper(II) Complexes.

Compound	νNH & νNH_2	Amide I & NH_2 bend	Amide II & ν(CN)	ν(CS) & ν(CN)	Amide III	δ(NCO)	ν(Cu–N)	ν(Cu–S)	ν(Cu–X)
BTSC	3290 to 3040(s)	1625(s)	1565(s)	1290(s) 730(s)	1230(m)	755(m)	–	–	–
$Cu(BTSC)_2Cl_2$	3240 to 3045(m)	1610(s)	1570(s)	1270(m) 735(s)	1235(w)	752(m)	425(w)	322(m)	269(m)
$Cu(BTSC)_2Br_2$	3270 to 3015(m)	1605(s)	1562(s)	1272(m) 730(s)	1230(w)	750(m)	435(w)	325(m)	212(m)
$Cu(BTSC)_2(NO_3)_2$	3230 to 3050(m)	1612(s)	1578(s) 1545(m)	1275(s) 725(s)	1225(m)	758(m)	430(w)	324(m)	1755(m)
$Cu(BTSC)_2(NCS)_2$	3260 to 3025(m)	1605(s)	1570(s)	1260(m) 727(s)	1237(m)	760(m)	430(w)	320(m)	2070(s) 290(w)
FBTS	3140 to 3040(s)	1615(s)	1575(s)	1280(s) 735(s)	1235(w)	750(s)	387(m)	–	–
$Cu(FBTS)_2Cl_2$	3125 to 3030(s)	1610(s)	1550(m)	1265(m) 730(s)	1240(sh.m)	752(s)	388(m) 378(sh.w)	320(m)	270(m)
$Cu(FBTS)_2Br_2$	3135 to 3060(s)	1617(s)	1555(s)	1267(m) 728(s)	1230(w)	755(s)	390(w) 380(sh.w)	322(m)	212(w)
$Cu(FBTS)_2(NO_3)_2$	3135 to	1617(s)	1547(s)	1267(m) 728(s)	1220(m)	747(s)	385(w) 370(w)	320(m)	1750(m)
$Cu(FBTS)_2(NCS)_2$	3130 to 3035(m)	1612(s)	1550(s)	1265(m) 725(s)	1232(w)	752(s)	390(w)	324(m)	2070(m) 300(w)

TABLE IV. Analytical Data of Copper(II) Complexes.

Complex	Observed Percentage of					Calculated Percentage of				
	C	H	N	M	X	C	H	N	M	X
$Cu(C_9H_{12}N_4OS)_2Cl_2$	37.01	4.10	19.20	10.99	12.01	37.08	4.12	19.23	10.91	12.19
$Cu(C_9H_{12}N_4OS)_2Br_2$	28.19	3.09	14.67	8.17	20.73	28.44	3.16	14.75	8.37	21.07
$Cu(C_9H_{12}N_4OS)_2(NO_3)_2$	29.98	3.30	19.39	8.72	–	29.85	3.32	19.35	8.78	–
$Cu(C_9H_{12}N_4OS)_2(NCS)_2$	33.98	3.42	19.80	8.79	–	33.54	3.35	19.57	8.88	–
$Cu(C_{14}H_{14}N_4O_2S)_2Cl_2$	45.40	3.75	15.23	8.58	9.86	45.50	3.79	15.17	8.60	9.61
$Cu(C_{14}H_{14}N_4O_2S)_2Br_2$	40.60	3.32	13.48	7.59	20.02	40.61	3.38	13.54	7.68	19.34
$Cu(C_{14}H_{14}N_4O_2S)_2(NO_3)_2$	42.55	3.48	17.58	7.98	–	42.45	3.54	17.69	8.03	–
$Cu(C_{14}H_{14}N_4O_2S)_2(NCS)_2$	46.06	3.59	17.93	8.02	–	45.94	3.57	17.86	8.11	–

energy or intensity, generally intensity decreases as the energy is also lowered on complexation. These vibrations are not free from the other vibrations, especially CN vibration. The contribution of CN is smaller to the band observed at ~1290 cm^{-1} and greater to that observed at ~730 cm^{-1} since the former changes to a larger extent than the latter. These changes in the ν(CS) vibrations are suggestive of the participation of thioketosulphur in chelation [21, 22].

Metal–ligand vibrations are difficult to assign on an empirical basis, since their frequencies are sensitive to both the metal and the ligand, and often they couple with other low frequency modes in metal chelate compounds. A comparison of i.r. spectra between a free ligand and its metal complex fails to give a clear cut assignment since some ligand vibrations activated by complex formation may appear in the same region as the metal–ligand vibrations. Of the several bands observed in the low energy i.r. region, some of them may be tentatively assigned to ν(Cu–S), ν(Cu–N) vibrations [24]. A band at 387 cm^{-1} in FBTS is split into two bands in all of its complexes, which may be due to the formation of a coordinate bond between metal and nitrogen. However, in BTSC complexes this band appears at about 430 cm^{-1}. In present studies the bands around 270 cm^{-1} and 212 cm^{-1} have been assigned as ν(Cu–Cl) [23, 24] and ν(Cu–Br) [25], respectively. In nitrato complexes bands of medium intensity have been observed around 1545, 990 and 810 cm^{-1} which have been assigned to asymmetric NO_2 stretching, NO stretching and out-of-plane NO_2 rocking vibrations, respectively. The N-bonded mode of coordination of the thiocyanato group [26] is confirmed by the appearance of the bands around 2070, 870 and 485 cm^{-1} which are assigned to ν(CN) of NCS, ν(C–S) of NCS and NCS bending vibrations, respectively. This conclusion is further supported by the fact that an additional ν(Cu–N) [24] vibration has been found to appear in the region 200–300 cm^{-1}.

Experimental

Dihalobis (BTSC) and Dinitrobis (DTCS) Complexes and Corresponding Complexes of FBTS

A general procedure was followed for the preparation of halo and nitrato complexes of copper(II) with both ligands.

50 ml of (1.0 mmol) of the copper(II) salt in ethanol were mixed with 125 ml of (2.5 mmol) ethanolic solution of the ligand, a bluish–green colour was found to develop. The mixture was refluxed for about two hours and then concentrated over a water-bath. After cooling a precipitate was obtained which was filtered, washed with hot ethanol and ether and dried at 110 °C for a couple of hours. Attempts to isolate the iodo complexes of the copper(II) ion were unsuccessful since the cupric iodide immediately disproportionated and yielded cuprous iodide.

Dithiocyanatobis (BTSC) Copper(II) and Dithiocyanatobis (FBTS) Copper(II)

To the bluish–green colour obtained as a result of mixing of copper(II) chloride with ligand as above, an ethalonic solution of ammonium thiocyanate (3.5 g) was added. The colour of the solution immediately turned deep green and a precipitate of ammonium chloride settled down in the flask after stirring the mixture for about 15 minutes. This was filtered and the filtrate was refluxed for about two hours, whereby a deep green precipitate was obtained. It was filtered off, washed thoroughly with hot ethanol and ether and dried at 110 °C.

Physical Measurements

All magnetic measurements were made on powder forms of the complexes employing Guoy's balance using mercury(II) tetrathiocyanatocobaltate(II) as calibrant. The electronic spectra of all the complexes were recorded on a D.M.R.-21 in nujol mull and the vibrational spectra in the range 4000–200 cm^{-1} of the ligands and as well as of their complexes on a Perkin Elmer-471 in KBr discs. The Beckmann I.R. -12 instrument was used for recording the exclusive low energy vibrational spectra in the range 650–200 cm^{-1} in nujol mull. All E.S.R. spectra were recorded on a Varian Spectrometer in solid state as polycrystalline sample using DPPH as reference material. The sparingly soluble nature of these complexes have prevented the determination of molecular weight, conductivity and solution absorption spectral measurements which might have given more information regarding their structures.

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