Magnetic measurements and spectral studies on copper(II) complexes of semicarbazones derived from isatin, benzoin and 2-hydroxy-naphthaldehyde

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Summary

The preparation and spectral properties of five copper(II) complexes of semicarbazones, derived from 2-hydroxynaphthaldehyde (NPSCZ), benzoin (BZSCZ) and isatin (ISSCZ) are described. I.r., electronic, e.s.r. ^1H and ^{13}C n.m.r. spectra show that the semicarbazone's coordination is distorted trigonal bipyramidal for $[Cu(BZSCZ\text{-}2H)(H_2O)]$, distorted tetragonal pyramidal for $[Cu(NPSCZ)_2](ClO_4)_2$ and dimeric for the other three complexes.

Introduction

Copper(II) complexes are interesting due to their biological roles(1,2) and medicinal properties(3). Bacteriostatic and bacteriocidal properties of semicarbazides have been reviewed(4). Further, semicarbazones have been widely used as spectrophotometric agents(5,6) for the analysis of metal ions. A theoretical investigation(7) of the structure and chemical properties of semicarbazide has demonstrated its similarity to thiosemicarbazide. Metal complexes of thiosemicarbazides and thiosemicarbazones have been investigated(8,9) extensively, but considerably less information is available on semicarbazide and semicarbazone complexes(9,10). Copper(II) complexes of tridentate thiosemicarbazones have been reviewed(11) with emphasis on their e.s.r. spectra. However, few reports dealing with e.s.r. spectral studies of copper(II) complexes of semicarbazones(12,13) have appeared. This paper describes the preparation and the magnetic and spectral properties of some copper(II) complexes of semicarbazones derived from 2-hydroxynaphthaldehyde (NPSCZ), benzoin (BZSCZ) and isatin (ISSCZ).

Experimental

Synthesis of $[Cu(NPSCZ)_2](ClO_4)_2$, $[Cu(BZSCZ\text{-}H)_2]$ *and* $[Cu(ISSCZ)_2](ClO_4)_2$

Semicarbazones were prepared as reported earlier(14). $Cu(ClO_4)_2 \cdot 6H_2O$ (0.01 mol) and the appropriate semicarbazone (0.02 mol) were dissolved in EtOH and the mixture boiled under reflux for 4 h. On cooling, a microcrystalline complex was separated by filtration and the crystals were washed with H_2O, EtOH and anhydrous Et_2O and kept in a desiccator over fused $CaCl_2$.

Synthesis of $[Cu(BZSCZ\text{-}2H)(H_2O)]$ *and* $[Cu(ISSCZ\text{-}2H)(H_2O)] \cdot H_2O$

$Cu(ClO_4)_2 \cdot 6H_2O$ (0.01 mol), the appropriate semicarbazone (0.01 mol) and NaOAc (0.01 mol) were dissolved in aqueous EtOH and the mixture was boiled under reflux on a H_2O bath for 2 h. On cooling, a powdery product was separated by filtration and washed and dried as above.

Physical measurements

Carbon, hydrogen and nitrogen analyses were carried out by the microanalysis laboratory of R.S.I.C., CDRI, Lucknow, India. Electronic spectra were recorded on a Perkin-Elmer Lambda-15 spectrophotometer. ^1H and ^{13}C n.m.r. spectra were recorded on a W.M.-400 Brucker or Varian Gemini 300 MHz spectrometer in d^6-DMSO or $CDCl_3$ with TMS as the internal standard. The other physical and spectral properties of the complexes were obtained as reported previously(15). All the chemicals were BDH grade except benzoin (Estman) and sodium acetate (Aldrich).

Results and discussion

Table 1 lists colours, partial elemental analyses and magnetic susceptibility values for the complexes. Table 2 lists the i.r. assignments most useful for determining the coordination mode of the semicarbazones. Table 3 lists the electronic spectral bands and their assignments, and Table 4 the e.s.r. parameters for each of the complexes. This information will be discussed for each of the five complexes reported in this study.

$[CuNPSCZ)_2](ClO_4)_2$

The i.r. spectrum of this complex shows a medium intensity band at 1608 cm^{-1} due to ν(C=N) which shifted from 1625 cm^{-1} in the spectrum of NPSCZ, while ν(C=O) shifted from 1665 to 1643 cm^{-1} suggesting a CuO_2N_2 coordination centre(14,16) involving the azomethine nitrogen and the carbonyl oxygen. This conclusion is further supported by the presence of ν(Cu—N) at 452 cm^{-1} and ν(Cu—O) at 411 cm^{-1}, values based upon the assignments of others(17,18). Furthermore, the spectrum of the complex shows a strong, broad band centred at 1075 cm^{-1} (ν_3, ClO_4), a strong band at 615 cm^{-1} (ν_4, ClO_4) and a weak, sharp band at 942 cm^{-1} (ν_1, ClO_4) indicating substantial distortion of the perchlorate ion. This result suggests the presence of weakly coordinated or semicoordinated

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Table 1. Colours, partial elemental analyses and magnetic susceptibilities of selected copper(II) complexes of some semicarbazone derivatives.

Compound	Colour	Found (Calcd.)(%) C	H	N	μ(B.M.)
$[Cu(NPSCZ)_2](ClO_4)_2$	Olive green	40.1(40.0)	3.1(3.1)	11.8(11.7)	1.9
$[Cu(BZSCZ\text{-}2H)(H_2O)]$	Brown	50.7(51.8)	3.8(4.0)	12.0(12.1)	0.8
$[Cu(BZSCZ\text{-}H)_2]$	Green	60.9(60.3)	4.2(4.4)	14.0(14.1)	0.0
$[Cu(ISSCZ\text{-}2H)H_2O]\cdot H_2O$	Olive green	35.3(35.8)	3.2(3.3)	18.5(18.6)	1.1
$[Cu(ISSCZ)_2](ClO_4)_2$	Brown	32.5(32.2)	2.5(2.4)	16.6(16.7)	0.0

Table 2. Selected i.r. absorption frequencies (cm^{-1}) of semicarbazones and their copper(II) complexes.

Compound	ν(C=O)^a	ν(C=O)^b	ν(C=N)	ν(Cu—N)	ν(Cu—O)^c
NPSCZ		1665s	1625s		
$[Cu(NPSCZ)_2](ClO_4)_2$		1643m	1608m	452m	411m 305w
BZSCZ		1685s	1585s		
$[Cu(BZSCZ\text{-}2H)(H_2O)]^d$		1672m	1545sh	438m	425sh 392m
$[Cu(BZSCZ\text{-}H)_2]$		1660m	1570m	455m	410m 327m
ISSCZ	1725s	1695s	1605s		
$[Cu(ISSCZ\text{-}2H)H_2O]\cdot H_2O^d$	1706s	1684s	1572m, br	445m	425w 400sh 370m
$[Cu(ISSCZ)_2](ClO_4)_2$	1719s	1673m 1660sh	1568m	475w	433w 313m

^{a}Isatin; ^{b}semicarbazone; ^{c}bands from 410–433 cm^{-1} due to semicarbazone oxygen, 390–400 cm^{-1} to coordinated H_2O and lower energy bands to other oxygens; ^{d}both compounds' spectra possess a sharp, medium intensity band at ca. 3440 cm^{-1} and a band at ca. 550 cm^{-1} due to ν(OH) and $\rho_{wagg}(H_2O)$ for coordinated H_2O.

Table 3. Mull transmission electronic spectra (cm^{-1}) of copper(II) complexes of semicarbazone derivatives.

Compound	Intraligand and charge transfer bands	d–d
NPSCZ	48080 43290 32790 31650 28380	
$[Cu(NPSCZ)_2](ClO_4)_2$	47350 42230 39810 31550 27470 25840 24810	16580
BZSCZ	48080 36770	
$[Cu(BZSCZ\text{-}2H)(H_2O)]$	49260 38580 30050	14060
$[Cu(BZSCZ\text{-}H)_2]$	49210 39060 30050	14820
ISSCZ	40980 37760 31690	
$[Cu(ISSCZ\text{-}2H)H_2O]\cdot H_2O$	45120 40850 37760 31810	14900
$[Cu(ISSCZ)_2](ClO_4)_2$	41390 31730 30050 27120	15820

perchlorate ion(s)$^{(19,20)}$ and a band at 305 cm^{-1} is in the region assignable to ν(Cu—O) for coordinated perchlorato ligands. The measured magnetic moment is consistent with a monomer copper(II) complex with significant spin orbit coupling which raises the value to 1.90 B.M.

A mull transmission spectrum (Table 3) shows a d–d composite band at 16580 cm^{-1}, which compares quite favourably with 16200 cm^{-1}, the value suggested for tetragonal coordination of a CuO_2N_2 centre$^{(21)}$ with weak axial coordination. The e.s.r. parameters (Table 4), $g_{\parallel} = 2.226$ and $g_{\perp} = 2.058$ with $g_{av} = 2.114$, are in excellent agreement with a CuO_2N_2 centre in a tetragonal field with weak axial bonding$^{(21,22)}$, and the signal is sufficiently intense to be associated with a monomer. At liquid nitrogen temperature, the values change to $g_{\parallel} = 2.213$,

Table 4. E.s.r. spectral parameters for copper(II) complexes of semicarbazones derived from 2-hydroxynaphthaldehyde and benzoin.

Complex	Matrix	Temperature	g_1 or $g_{\parallel}$	g_2	g_3 or $g_{\perp}$	g_{av}
$[Cu(NPSCZ)_2](ClO_4)_2$	Solid	RT	2.226		2.058	2.114
		77K	2.213		2.054	2.107
	DMSO	RT			$A_0 = 66G$	$g_0 = 2.128$
		77K	2.276	2.065	2.040	2.127
			$A_1 = 168G$	$A_2 = 15G$	$A_3 = 15G$	
$[Cu(BZSCZ\text{-}2H)H_2O]$	Solid	RT	2.027		2.216	2.153
		77K	2.024		2.211	2.149

RT = room temperature.

$g_\perp = 2.054$ and $g_{av} = 2.107$, suggesting that axial bonding is lessened, or that any tetrahedral distortion of the semicarbazone coordination is flattened. Dimethyl sulphoxide must substitute for the weakly coordinated perchlorate ions in the axial positions, since $g_0 = 2.128$ in the room temperature spectrum and $g_{av} = 2.127$ in frozen solution with the spectrum becoming slightly rhombic on freezing. $A_0 = 66$ G at room temperature and for the frozen solution spectrum $g_1 = 2.276, g_2 = 2.065, g_3 = 2.040$ and $A_1 = 168$ G, which is close to the 175 G that is proposed for a CuO_2N_2 centre in a tetragonal field[(21,22)]. Therefore, from $3A_0 - A_1/2, A_2$ and A_3 are approximately equal to 15 G.

[Cu(BZSCZ-2H)(H$_2$O)]

Based on its low magnetic susceptibility, this complex is likely to be dimeric. The e.s.r. spectrum is reversed, suggesting a d_{z^2} ground state which could arise from the presence of an additional coordinating atoms or groups to give a distorted trigonal bipyramid. Therefore, this dimeric complex is probably five-coordinate with a bridging oxygen atom and a plausible structure is shown in Figure 1.

The g-values (Table 4) for the copper(II) complex are $g_\perp = 2.216$ and $g_\parallel = 2.027$ with $g_{av} = 2.153$ at room temperature and change on cooling to 77 K to $g_\perp = 2.211$, $g_\parallel = 2.024$ and $g_{av} = 2.149$. These e.s.r. parameters support the proposed trigonal bipyramidal structure for this copper(II) complex; similar observations have been reported by others[(23,24)]. A mull transmission spectrum (Table 3) shows a very broad d–d band at 14060 cm^{-1} further supporting the proposed structure. It has been reported[(25)] that trigonal bipyramidal (distorted) copper(II) complexes show a d–d band at 14827 cm^{-1} (CuN_3Cl_2), 14285 cm^{-1} (CuN_3Br_2) and 15271 cm^{-1} (CuN_3O_2, one chelating NO_3), while distorted tetragonal pyramidal copper(II) complexes have a band at 15479 cm^{-1} (CuN_3O_2 with two H_2O ligands). Ali *et al.*[(26)] and Singh and Rao[(20)] have also made similar observations.

The i.r. spectrum (Table 2) of the BZSCZ complex shows strong bands at 1685 and 1585 cm^{-1} due to ν(C=O) and ν(C=N), respectively. Ferrari *et al.* have reported[(27)] that ν(C=N) shifts to lower energy on coordination of the azomethine nitrogen atom and accordingly, the band is found at 1545 cm^{-1} in the complex's spectrum. The ν(C=O) band also shifts to lower energy, 1672 cm^{-1}, in the complex supporting bonding to copper(II) by the carbonyl oxygen[(14)]. A band at 1240 cm^{-1} in the spectrum of the ligand is assigned to the benzyl oxygen ν(C—O)[(28,29)], and changes to 1225 cm^{-1} in the spectrum of the complex indicating the probable involvement of the benzyl oxygen in coordination[(29)]. The mode of coordination[(29)]. The mode of coordination of this semicarbazone can be supported by assignments of ν(Cu—N) and ν(Cu—O) at 438 and 425 cm^{-1}, respectively[(28,30)]. Similar assignments have also been reported for copper(II) complexes of methylglycine and phenylglycine[(17)]. T.g.a. studies show that the H_2O molecule is not lost until 170° C is reached, suggesting that it is coordinated H_2O, rather than hydrate H_2O. Bands at 3440, 550 and 392 cm^{-1} are assignable to ν(OH), $\rho_{wagg}(H_2O)$ and ν(CuO), respectively, for coordinated H_2O[(31)]. One of the two donor oxygens must bridge to a second copper(II) centre in order for both metal ions to achieve coordination number five. Bridging by the semicarbazone carbonyl oxygen would probably lead to a dimer in which the copper(II) centres would be closer to square pyramidal, as is often found[(32)]. Therefore, it seems more likely that the benzyl oxygen is the bridging oxygen.

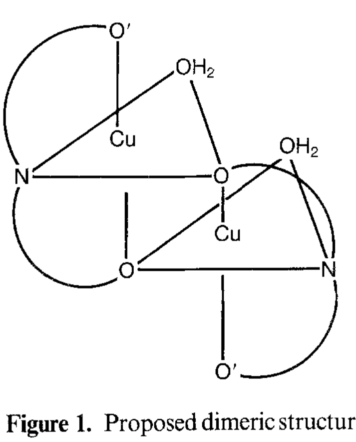


Figure 1. Proposed dimeric structure of [Cu(BZSCZ-2H)(H$_2$O)].

[Cu(BZSCZ-H)$_2$]

This copper(II) complex is diamagnetic and is probably dimeric; the very weak e.s.r. spectrum indicates the presence of a monomeric impurity. The 1685 cm^{-1} band in the spectrum of BZSCZ, due to ν(C=O), is found at 1660 cm^{-1} in the spectrum of the complex supporting involvement of the carbonyl oxygen in coordination. Also, BZSCZ's spectrum has a strong band at 1585 cm^{-1} due to ν(C=N) which shifts to 1570 cm^{-1} indicating coordination through the azomethine nitrogen. Both coordination modes are further confirmed by the presence of ν(Cu—N) and ν(Cu—O) at 455 and 410 cm^{-1}, respectively. These copper-ligand bond assignments are in conformity with the results obtained by other workers[(17,22,33)]. The band at 327 cm^{-1} may be due to ν(CuO) for a bridging oxygen, and it is likely that the alkoxy oxygen serves as the bridging atom. The d–d composite maximum at 14820 cm^{-1} in the mull transmission spectrum (Table 3) of the complex is consistent with strong axial bonding, suggesting a distorted square pyramidal or trigonal bipyramidal structure. The n.m.r. spectra, discussed later, provides more information about this complex.

[Cu(ISSCZ)$_2$](ClO$_4$)$_2$

The ν(C=O) band at 1725 cm^{-1} in the ISSCZ spectrum is assigned to the isatin moiety's carbonyl group[(34)], and occurs at 1719 cm^{-1} in the spectrum of the copper(II) complex, suggesting that it remains uncoordinated or is weakly coordinated. The band assigned to the carbonyl function by Chandra *et al.*[(14)] shifts from 1695 to 1673 cm^{-1} with a shoulder at 1660 cm^{-1} on complexation, indicating its involvement in the coordination sphere. In the i.r. spectra of ISSCZ and this complex ν(C=N) at 1605 cm^{-1} changes to 1580 cm^{-1}, confirming coordination via the azomethine nitrogen[(14)]. Thus, ISSCZ acts as a bidentate ligand for one copper centre and one of the carbonyl oxygens probably bridges to a second copper(II) (Figure 2). Further support is provided by ν(Cu—N) and ν(Cu—O), observed at 475 and 433, 313 cm^{-1}, respectively[(17)].

A mull transmission spectrum shows only a shoulder at ca. 15820 cm^{-1}, but the relatively higher energy may indicate that this purple brown solid has a *trans*-CuO_2N_2 centre[(35)] as suggested in Figure 2. The copper(II) complex

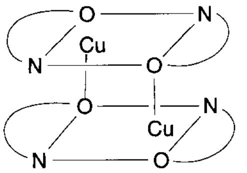


Figure 2. Proposed dimeric structure of $[Cu(ISSCZ)_2](ClO_4)_2$.

is diamagnetic and shows an extremely weak signal in the e.s.r. spectrum at room temperature, which is presumably due to a monomer impurity. The n.m.r. spectra discussed in the next section provides additional information about this complex.

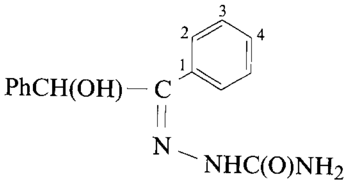
$[Cu(ISSCZ\text{-}2H)(H_2O)]\cdot H_2O$

The decrease in ν(C=O) from 1695 to 1684 cm^{-1} and decrease in ν(C=N) from 1605 to 1572 cm^{-1} when comparing the spectrum of ISSCZ with this copper(II) complex (Table 2) indicate coordination through the semicarbazone azomethine nitrogen and carbonyl oxygen atoms(14). The i.r. band due to ν(C=O) of the isatin moiety(34) also decreases from 1725 to 1706 cm^{-1} in the spectrum of its complex. Therefore, this semicarbazone is a ONO tridentate ligand. The ν(Cu—N) band is assigned to 445 cm^{-1} with ν(CuO) at 425 cm^{-1} (semicarbazone), 400 cm^{-1} (aqua) and 370 cm^{-1} (isatin), respectively(17). The composite d–d band has been observed at 14900 cm^{-1} by mull transmission spectrum, which suggests considerable axial bonding in the solid state. Coordination probably involves the carbonyl oxygen atom of the semicarbazone moiety acting as a bridge between two copper(II) centres. There are similar reports in the literature of Schiff base oxo-bridging(36) as well as phenoxo bridging(37,38), consistent with the low magnetic moment and the extremely weak signal for the e.s.r. spectrum at room temperature.

^1H and ^{13}C n.m.r. spectral studies

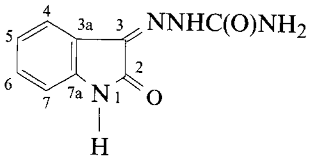
The ^1H n.m.r. spectra of BZSCZ, ISSCZ and their diamagnetic complexes have been recorded in d^6-DMSO and

Table 5. ^1H and ^{13}C n.m.r. chemical shifts (δ) for BZSCZ and its complex, $[Cu(BZSCZ\text{-}H)_2]$, in d^6-DMSO.



^{13}C	BZSCZ	$[Cu(BZSCZ\text{-}H)_2]$	^1H	BZSCZ	$[Cu(BZSCZ\text{-}H)_2]$
C(1)	140.02s 136.88s	132.09s			
C(2)	128.73d 128.51d	129.33d	C(2)*H*	7.78 7.26	7.76 7.20
C(3)	126.94d 126.43d	135.30d	C(3)*H*	7.32	7.32 7.60
C(4)	127.89d	129.33d	C(4)*H*	6.20	7.40
C=N	146.35s	132.49s	O*H*	10.20	
C=O	156.91s	194.64s	N*H*	7.02	
*C*H—OH	71.63d		NH_2	6.54	7.88

Table 6. ^1H and ^{13}C n.m.r. chemical shifts (δ) for ISSCZ and its complex, $[Cu(ISSCZ)_2](ClO_4)_2$, in d^6-DMSO.



^{13}C	ISSCZ	$[Cu(ISSCZ)_2](ClO_4)_2$	^1H	ISSCZ	$[Cu(ISSCZ)_2](ClO_4)_2$ (br)
C(2)	156.71s	153.17s	C(4)*H*	6.90d	6.9
C(3)	143.09s	139.15s	C(5)*H*	7.02t	7.04
C(3a)	115.78s	117.98s	C(6)*H*	7.30t	7.30
C(4)	125.42d	119.90d	C(7)*H*	8.10d	7.60
C(5)	122.13d	117.91d	C—N*H*	10.20s	11.06
C(6)	131.98d	128.17d	N—N*H*	10.80s	11.70
C(7)	110.96d	108.52d	NH_2	4.15s	9.25
C(7a)	133.58s	128.98s			
C=O	165.73s	160.45s			

$CDCl_3$ (Tables 5 and 6). A comparison of the spectra of the semicarbazones with those of the complexes leads to the conclusions that the $\delta = 10.2$ singlet is exchangeable with D_2O and may be assigned to OH in the BZSCZ spectrum and it disappears in the spectrum of $[Cu(BZSCZ\text{-}H)_2]$ supporting coordination through the phenoxy oxygen upon deprotonation (Figure 2)(39).

The down field signals at $\delta = 10.8$ and $\delta = 10.2$ in the spectrum of ISSCZ can be assigned to the two NH groups and they both move further downfield (i.e., $\delta = 11.70$ and $\delta = 11.06$, respectively) in the spectrum of $[Cu(ISSCZ)_2](ClO_4)_2$. This change is likely due to the coordination of the oxo group oxygen of the isatin moiety, and the azomethine nitrogen and carbonyl oxygen of the semicarbazone moiety. In order for the complex to be diamagnetic, these coordinated semicarbazones must act as bridging tridentate ONO ligands with the carbonyl oxygens serving as the bridging atoms. The large downfield change in the NH_2's chemical shift for one of the protons in the spectrum of the complex compared to its position in the spectrum of ISSCZ is due to this function's enhanced involvement in intermolecular hydrogen bonding to the solvent(40,41).

The ^{13}C n.m.r. spectral assignments for BZSCZ, ISSCZ and their diamagnetic copper(II) complexes are included in Tables 5 and 6, respectively. The salient features of the spectra are: the carbonyl peak is assigned at $\delta = 156.9$ for BZSCZ, in agreement with data for other semicarbazones(42). This signal moves downfield to $\delta = 194.6$ in the spectrum of $[Cu(BZSCZ\text{-}H)_2]$ due to loss of hydrogen bonding and, apparently, lack of or weakened coordination in DMSO solution. This peak is at a similar δ to the carbonyl carbon's $\delta = 193.8$ in fluorenone(43) as well as other carbonyl carbons(44), prompting us to suggest that the semicarbazone's carbonyl function does not remain coordinated in DMSO solutions of $[Cu(BZSCZ\text{-}H)_2]$. Thus, DMSO is substituting for this donor atom making the benzyl oxygen the likely bridging oxygen for this complex. Singh and Rao(29) have reported the downfield shift of the carbonyl carbon signal caused by pyridoxal isonicotinoyl hydrazone complexing with zinc, and an upfield shift in the cobalt(II) complex of this ligand. Mishra *et al.*(45) have reported an upfield shift of $-C(=N)H$ in titanium and zirconium complexes involving Schiff base derivatives of 2-formylthiophene. The ^{13}C chemical shift assignments for thiosemicarbazone complexes have been reported to be both upfield(46,47) or downfield(46,48,49) depending on the nature of the thiosemicarbazone and the metal ions involved. The upfield shift due to CN group signal, $\delta = 146.4$ to $\delta = 132.5$, supports f coordination through the azomethine nitrogen. The CH signal at $\delta = 71.6$ must have been affected considerably upon coordination and we were not able to establish its presence in the spectrum of $[Cu(BZSCZ\text{-}H)_2]$.

The ^{13}C n.m.r. chemical shift assignments for ISSCZ are in good agreement with the reported values for semicarbazones(42), isatin(50) and isatin derivatives(51). The chemical shift due to the azomethine carbon, C-3, at $\delta = 143.1$ moves upfield to $\delta = 139.2$ with the corresponding downfield shift of the peak assignable to C-3a at $\delta = 115.8$ to $\delta = 118.0$ on complexation, clearly suggesting coordination by the azomethine nitrogen. The chemical shift assignable to C-2 ($\delta = 156.7$) and CO ($\delta = 165.73$) carbons change to $\delta = 153.17$ and $\delta = 160.45$, respectively. These observations and our other spectral findings support bridging via one of the semicarbazone function's oxygen atoms and ISSCZ acting as a bidentate NO ligand for $[Cu(ISSCZ)_2](ClO_4)_2$ as suggested by Figure 2.

Antifungal activity

In contrast to numerous copper(II) thiosemicarbazone complexes(52), none of the semicarbazone complexes studied here show any activity against *Paecilomyces variotii*. This is in agreement with an earlier report indicating the inactivity of semicarbazones compared with their active thiosemicarbazone analogues(27).

Acknowledgement

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References

(1) E. I. Solomon, *J. Am. Chem. Soc.*, **104**, 7392 (1982).

(2) E. I. Solomon in K. Karlin (Ed.), *Bioinorganic Perspective in Copper Co-ordination Chemistry, in Biochemical and Inorganic Perspective in Copper Co-ordination Chemistry*, I, New York, Adenine Press, 1983.

(3) H. Umezawa and T. Takita, *Structure and Bonding*, **40**, 73 (1980).

(4) B. Murzubraimou, *Sov. J. Coord. Chem., Eng. Ed.*, 903 (1986).

(5) R. B. Singh, B. S. Garg and R. P. Singh, *Talanta*, **25**, 619 (1978).

(6) A. K. Singh, M. Katyal and K. Lal, *Rasayan Samiksha*, **2**, 41 (1986), *Chem. Abstr.*, **110**, 50225n (1989).

(7) R. Benassi, F. Taddel and M. Nardelli, *J. Mol. Struct.*, **164**, 275 (1988).

(8) M. J. M. Campbell, *Coord. Chem. Rev.*, **15**, 279 (1975); S. B. Padhye and G. B. Kauffman, *Coord. Chem. Rev.*, **63**, 127 (1985).

(9) D. X. West, S. B. Padhye and P. B. Sonawane, *Struct. Bond.*, **76**, 1 (1991).

(10) D. Q. Phung and N. M. Samus, *Tap. Chi. Hoa. Hoc.*, **26**, 25 (1988), *Chem. Abstr.*, **112**, 110765s (1990); U. K. Pandey, O. P. Pandey, S. K. Sengupta and S. C. Tripathy, *Synth. React. Inorg. Met.-org. Chem.*, **17**, 567 (1987); M. M. Bekeit, K. M. Ibrahim and T. H. Rakha, *Bull. Soc. Chim. Fr.*, 785 (1989); P. Perez-Dubois, P. Souza, J. R. Masaguer and A. Arquero, *Transition Met. Chem.*, **12**, 200 (1987); P. Souza, F. Sanchez-Kaiser, J. R. Masaguer and A. Arquero, *Transition Met. Chem.*, **12**, 128 (1987); R. C. Mishra, B. K. Mohapatra and D. Panda, *J. Indian Chem. Soc.*, **59**, 836 (1982).

(11) D. X. West, S. B. Padhye, P. B. Sonawane and R. C. Chikate, *Asian J. Chem. Rev.*, **1**, 125 (1990).

(12) A. El-Dissouky and L. S. Rafaat, *Transition Met. Chem.*, **9**, 112 (1984).

(13) Y. Kumar, S. Chandra, R. P. Singh and A. K. Singh, *Synth. React. Inorg. Met.-org. Chem.*, **14**, 185 (1984).

(14) S. Chandra and Y. Kumar, *Proc. Indian Acad. Sci. (Chem. Sci.)*, **92**, 249 (1983).

(15) D. X. West and N. C. Lewis, *Transition Met. Chem.*, **12**, 365 (1987).

(16) M. Nonoyama, *J. Inorg. Nucl. Chem.*, **42**, 299 (1980).

(17) Y. Inomata, A. Shibata, Y. Yukawa, T. Takeuchi and T. Moriwaki, *Spectrochim. Acta*, **44A**, 97 (1988).

(18) D. X. West and J. N. Albert, *Transition Met. Chem.*, **16**, 1 (1991) and references therein.

(19) D. X. West, C. S. Carlson and A. E. Liberta, *Transition Met. Chem.*, **16**, 53 (1991).

(20) R. S. Singh and L. V. K. N. R. Rao, *Polyhedron*, **3**, 137 (1984).

(21) G. Formicka-Kozlowska, H. Kozlowski and B. Jezowska-Trzebiatowska, *Inorg. Chim. Acta*, **25**, I (1977).

(22) S. V. Deshpande and T. S. Srivastava, *Polyhedron*, **2**, 761 (1983).

(23) R. Kirmse and U. Abram, *Z. Anorg. Allg. Chem.*, **608**, 184 (1992).

(24) E. I. Solomon, *Comments Inorg. Chem.*, **3**, 236 (1984).

(25) A. Castineiras, R. Carballo and C. Vasquez, *Polyhedron*, **10**, 1675 (1991).

(26) M. A. Ali, C. M. Haroon, M. Nazimuddin and S. M. M. Majumder, *Transition Met. Chem.*, **17**, 133 (1992).

(27) M. B. Ferrari, G. G. Fava, C. Pelizzi, P. Tarasconi and G. Tosi, *J. Chem. Soc. Dalton Trans.*, 227 (1987) and references theirein.

(28) D. X. West, C. S. Carlson, A. C. Whyte and A. E. Liberta, *Transition Met. Chem.*, **15**, 43 (1990).

(29) G. Singh, P. S. Shastry, R. K. Loniwal and T. R. Rao, *Synth. React. Inorg. Met.-org. Chem.*, **22**, 1041 (1992).

(30) K. Balkrishnan and K. K. Aravindakshan, *J. Indian Chem. Soc.*, **68**, 187 (1991).

(31) N. M. Karayannis, C. M. Mikulsi, S. D. Sonsins, E. E. Bradshaw and L. L. Pytlewski, *Inorg. Chim. Acta*, **14**, 195 (1975).

(32) D. A. Krost and G. L. McPherson, *J. Am. Chem. Soc.*, **100**, 987 (1978); H. Muhonen, *Acta Chem. Scand.*, **A34**, 79 (1980); S. F. Pavkovic and S. L. Wille, *Acta Crystallogr.*, **B38**, 1605 (1982).

(33) D. X. West, D. S. Galloway and D. A. Case, *Transition Met. Chem.*, **13**, 415 (1988).

(34) A. R. Katritzky, *Physical Methods in Heterocyclic Chemistry*, Academic Press, London, 1963, Vol. 2, p. 197.

(35) D. X. West and W.-H. Wang, *J. Inorg. Nucl. Chem.*, **41**, 1719 (1979); S. F. Pavkovic, J. N. Brown and D. X. West, *Acta Crystallogr.*, **B36**, 143 (1980); D. X. West and W.-H. Wang, *J. Inorg. Nucl. Chem.*, **42**, 985 (1980).

(36) P. W. Ball, *Coord. Chem. Rev.*, **4**, 361 (1969).

(37) S. Mondal, P. Paul, R. Roy and K. Nag, *Transition Met. Chem.*, **9**, 247 (1984).

(38) F. Calderazzo, F. Marchetti, G. Dell'-Amico, G. Pelizzi and A. Colligiani, *J. Chem. Soc., Dalton Trans.*, 1419 (1984).

(39) P. K. Biswas and N. R. Chaudhori, *J. Chem. Soc., Dalton Trans.*, 2385 (1981).

(40) J. Easman, G. Heinisch and W. Holzer, *Heterocycles*, **29**, 1399 (1989).

(41) M. G. B. Drew, B. Vickery and G. R. Willey, *J. Chem. Soc., Dalton Trans.*, 1297 (1982).

(42) G. Heinisch and W. Holzer, *Monatsch Chem.*, **121**, 837 (1990).

(43) J. A. G. Drake and D. W. Jones, *Spectrochim. Acta*, **36A**, 23 (1980).

(44) D. X. West, Y.-H. Yang and T. L. Klein, unpublished observations.

(45) K. D. Mishra, R. Rai, O. P. Pandey and S. K. Sengupta, *Transition Met. Chem.*, **17**, 127 (1992).

(46) N. T. Akinchan, R. Akinchan, U. J. Ibok, L. B. Battaglia, A. B. Corradi and P. Drozdzewski, *J. Cryst. Spec. Rec.*, **22**, 741 (1992).

(47) P. Umpathy, A. P. Bhudhkar and C. S. Dorai, *J. Indian Chem. Soc.*, **63**, 714 (1986).

(48) A. El-Shekeil and A. Z. El-Sonbati, *Transition Met. Chem.*, **17**, 420 (1992).

(49) D. X. West, B. L. Mokijewski, H. Gebremedhin and T. J. Romack, *Transition Met. Chem.*, **17**, 382 (1992).

(50) V. Galasso, G. Pellizer and G. C. Pappalardo, *Org. Mag. Res.*, **9**, 401 (1977).

(51) E. C. Angell, D. St. C. Black, N. Kumar, *Mag. Res. Chem.*, **30**, 1 (1992).

(52) A. E. Liberta and D. X. West, *BioMetals*, **5**, 121 (1992).

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