Synthesis and Characterization of Copper(II) Complexes with a Tridentate Schiff Base Ligand Derived from 5-Chloro-2-hydroxyacetophenone and Salicylhydrazide. X-ray Structure of Copper(II) (5-Chloro-2-hydroxyacetophenone-salicylhydrazide) Dimethylformamide

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Abstract

Two copper(II) complexes with the Schiff base derived from the condensation of 5-chloro-2-hydroxyacetophenone and salicylhydrazide have been prepared and characterized by means of IR, electronic and EPR spectroscopies and magnetic measurements. For Cu(II) (5-chloro-2-hydroxyacetophenone-salicylhydrazide) dimethylformamide, Cu(5Cl-OHA-SHZ) DMF, obtained by recrystallizing the anhydrous complex Cu(5Cl-OHA-SHZ) from dimethylformamide solution, the crystal structure was also determined. Crystals of Cu(5Cl-OHA-SHZ) DMF are triclinic, space group $P\bar{1}$, with two molecules in a unit cell of dimensions: $a = 8.012(2)$, $b = 8.359(2)$, $c = 13.906(1)$ Å, $\alpha = 88.80(1)$, $\beta = 88.48(1)$, $\gamma = 82.01(1)^\circ$, and $V = 918(1)$ Å^3. Refinement by full-matrix least-squares gave a final $R_w = 0.058$. In the mononuclear molecule the copper atom is bonded to three ONO donor atoms from the Schiff base ligand and to an oxygen atom from the DMF solvent molecule in a highly distorted square planar geometry. The EPR spectrum of this DMF coordinated complex has been interpreted in terms of the great deviation of the coordination geometry from the idealized square planar one. Cu(5Cl-OHA-SHZ) DMF was found to be a normal paramagnet. Variable temperature magnetic studies on the anhydrous compound suggest a dimeric structure with strong antiferromagnetic interactions ($2J = -439$ cm^{-1}). The IR spectra are discussed in comparison with that of the free ligand.

Introduction

It has been found that the condensation of salicylhydrazide with aldehydes or ketones gives rise to Schiff base ligands which generated principally dinuclear transition complexes involving di-oxo-bridged structures and conform to various stereochemistries [1–3]. Recently we reported the magnetic and EPR study of a Cu(II) compound with the Schiff base derived from salicylhydrazide and *o*-hydroxypropiophenone whose results clearly indicate a dinuclear structure [4]. In order to obtain more information of this group of compounds we synthesized a Cu(II) complex with the Schiff base derived from salicylhydrazide and 5-chloro-2-hydroxyacetophenone, Cu(5Cl-OHA-SHZ). Attempts to grow suitable single crystals of this anhydrous compound gave rise to the formation of a mononuclear species with a DMF solvent molecule coordinated to the metal atom, for which the crystal structure is presented. In this paper we will also describe the electronic, IR, EPR and magnetic properties of both Cu(II) complexes.

Experimental

Syntheses

Salicylhydrazide and 5-chloro-2-hydroxyacetophenone were prepared following methods previously described [5, 6]. The Schiff base ligand was prepared by a typical procedure. A mixture of salicylhydrazide and 5-chloro-2-hydroxyacetophenone (1:1 molar ratio) in ethanol was refluxed with stirring for 3 h after which a pale yellow microcrystalline compound separated. This was filtered off and recrystallized

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from ethanol. *Anal.* Calc. for $C_{15}H_{13}N_2O_3Cl$: C, 59.11; H, 4.27; N, 9.19. Found: C, 59.06; H, 4.18; N, 9.22%.

Cu(5Cl-OHA-SHZ) was prepared by mixing hot ethanolic solutions of copper(II) acetate monohydrate and the ligand (1:1 molar ratio) and refluxing for 3 h. The separated green precipitate was filtered off, washed with hot ethanol and water, dried *in vacuo*, and used without further purification. The compound, which is extremely insoluble in most common organic solvents, but soluble in dimethylsulfoxide and *N,N*-dimethylformamide, does not decompose up to 330 °C. *Anal.* Calc. for $CuC_{15}H_{13}N_2O_3Cl$: C, 49.17; H, 3.00; N, 7.65; Cu, 17.36. Found: C, 49.25; H, 3.00; N, 7.60; Cu, 17.31%.

Cu(5Cl-OHA-SHZ) DMF was obtained by recrystallizing Cu(5Cl-OHA-SHZ) from DMF solution. Dark green crystals suitable for X-ray analysis were separated and dried in air. The thermogravimetric analysis gives a weight loss of a DMF solvent molecule on heating from 120 to 140 °C. *Anal.* Calc. for $CuC_{18}H_{18}N_3O_4Cl$: C, 49.20; H, 4.10; N, 9.57; Cu, 14.47. Found: C, 49.16; H, 4.04; N, 9.51; Cu, 14.42%.

Chemical analyses of C, H, and N were carried out on a Carlo Erba 1106 microanalyzer. Cu was determined by atomic absorption on a Perkin-Elmer 305 apparatus.

Physical Measurements

Thermal analyses by means of TGA were carried out on a Perkin-Elmer TGS-1 thermobalance. Electronic spectra of the solid compounds were run on a Beckman DU-2 spectrophotometer after dilution of the sample in $BaSO_4$, in the 400–1000 nm spectral range. IR spectra were recorded on a Perkin-Elmer 681 spectrophotometer using KBr pellets as support, in the 625–4000 cm^{-1} spectral range. EPR spectra were recorded at 4.2 and 300 K on a Bruker X-band ER 200D spectrometer equipped with a continuous-flow cryostat. Magnetic susceptibility data were collected on powdered samples on a Faraday type microbalance. Independence of the magnetic susceptibility from the applied field was checked at both room and low temperature. The data were corrected for diamagnetism of the ligand system and for the temperature independent paramagnetism (taken to be 60×10^{-6} emu/mole). Diamagnetic corrections were estimated by use of Pascal constants [7] and found to be -152.54×10^{-6} emu/mole for Cu(5Cl-OHA-SHZ) and -199.23×10^{-6} emu/mole for Cu(5Cl-OHA-SHZ) DMF.

Crystallographic Data Collection and Structure Determination of Cu(5Cl-OHA-SHZ) DMF

With the aid of a polarizing microscope a suitable crystal, with approximate dimensions $0.15 \times 0.20 \times 0.25$ mm, was chosen and mounted on an Enraf-Nonius CAD-4 diffractometer. The following triclinic unit cell dimensions were obtained and refined from the setting angles of 25 reflections: $a = 8.012(2)$, $b = 8.359(2)$, $c = 13.906(1)$ Å; $\alpha = 88.80(1)$, $\beta = 88.48(1)$, $\gamma = 82.01(1)°$, and $V = 918(1)$ Å^3. Using the observed density 1.53 g cm^{-3}, measured by picnometry, the atomic mass calculation indicated the presence of two molecules per unit cell. The three dimensional intensity data were collected by using graphite monochromated Mo Kα ($\lambda = 0.71073$ Å) radiation, up to $2\theta = 50°$ and the ω–2θ scanning mode with varying interval. During the data collection the intensities of 2 standard reflections were measured every hour; significant variations in these standards were not observed. Of the 3229 recorded independent reflections, 2359 were observed above the background $I > 3\sigma(I)$ (where $\sigma(I)$ were based on counting statistics). Lorentz and polarization but not absorption corrections were made ($\mu = 11.50$ cm^{-1} for Mo Kα radiation). The space group $P\bar{1}$ was chosen due to the centrosymmetric intensities statistic distribution.

The copper atoms were deduced from the three dimensional Patterson calculation. All the remainder heavy atoms appeared clearly on the difference Fourier maps. Refinement was made by full-matrix least-squares calculations, with anisotropic thermal parameters for all the atoms except for the hydrogen atoms (taken as 0.06 Å^2). Hydrogen atoms positions were calculated from geometrical considerations, except the initial HO(4) position, carried out by bond valence theory considerations, using the parameters given in ref. 8. The function minimized was $\Sigma w_i(k|F_o| - |F_c|)^2$, where $w_i = k/\sigma^2(F) + |g|F^2$, with $k = 1$ and $g = 0.0008$, values taken at the last calculation. The atomic scattering factors were those of Cromer and Waber [9]. The final R_w value was 0.058 for the significant data (0.071 for all data). All calculations were performed with the SHELX-76 set of programs [11].

Results and Discussion

Description of the Structure of Cu(5Cl-OHA-SHZ) DMF

Final positional parameters are given in Table 1. A view of the molecule and labeling scheme of the atoms are shown in Fig. 1. The asymmetric unit consists of a discrete molecule of the complex. The coordination around the Cu atom is planar and made up by the O(1), N(1) and O(2) atoms from the Schiff base ligand molecule and by the O(3) atom from the DMF solvent molecule. Tables 2 and 3 contain the interatomic lengths and angles. In the coordination plane bond lengths vary for Cu–O bonds from 1.874(3) to 1.971(3) Å, while the Cu–N bond length is 1.933(3) Å. The angles and bond lengths

TABLE 1. Fractional atomic coordinates and equivalent isotropic temperature factors [10] in Cu(5Cl-OHA-SHZ) DMF[a]

Atom	x/a	y/b	z/c	B_{eq} (Å^2)
Cu	0.4351(1)	0.1607(1)	0.0990(0)	2.37(2)
Cl	1.0100(3)	0.2569(3)	0.4585(1)	8.6(1)
O(1)	0.4218(4)	0.1986(4)	−0.0378(2)	3.9(1)
O(2)	0.4642(4)	0.1289(4)	0.2305(2)	4.1(1)
O(3)	0.2282(4)	0.0562(4)	0.1092(2)	3.8(1)
O(4)	0.7542(4)	0.5167(4)	−0.1506(3)	4.6(2)
N(1)	0.6289(4)	0.2754(4)	0.0765(3)	3.0(1)
N(2)	0.6477(5)	0.3338(5)	−0.0177(3)	3.1(1)
N(3)	0.0511(5)	−0.0949(5)	0.1941(3)	3.4(2)
C(1)	0.5353(5)	0.2873(5)	−0.0702(3)	2.8(2)
C(2)	0.5464(5)	0.3392(5)	−0.1723(3)	3.0(2)
C(3)	0.4464(6)	0.2774(6)	−0.2378(4)	3.8(2)
C(4)	0.4570(7)	0.3192(7)	−0.3340(4)	4.4(2)
C(5)	0.5671(7)	0.4295(7)	−0.3679(4)	4.5(2)
C(6)	0.6636(7)	0.4924(7)	−0.3060(4)	4.3(2)
C(7)	0.6552(6)	0.4496(6)	−0.2086(3)	3.3(2)
C(8)	0.5898(6)	0.1663(5)	0.2774(3)	3.2(2)
C(9)	0.5888(6)	0.1212(6)	0.3751(3)	3.8(2)
C(10)	0.7121(7)	0.1499(7)	0.4319(4)	4.4(2)
C(11)	0.8444(7)	0.2278(7)	0.3895(4)	4.6(2)
C(12)	0.8500(6)	0.2777(6)	0.2957(3)	3.7(2)
C(13)	0.7227(5)	0.2502(5)	0.2360(3)	2.9(2)
C(14)	0.7348(6)	0.3103(5)	0.1373(3)	3.1(2)
C(15)	0.8687(6)	0.4139(7)	0.1023(4)	4.1(2)
C(16)	0.1770(6)	−0.0084(6)	0.1869(4)	3.5(2)
C(17)	−0.0037(7)	−0.1662(7)	0.2858(4)	4.6(2)
C(18)	−0.0422(7)	−0.1201(7)	0.1114(4)	4.4(2)

[a] e.s.d.s are given in parentheses.

relevant to the coordination sphere give an impression of the degree of distortion of the coordination geometry from the idealized square planar. The shortest intermolecular contacts were found at Cu–O(1)′ ($1-x, -y, -z$ symmetry), 3.159(4) Å, and Cu–O(4)″ ($1-x, 1-y, -z$ symmetry) 2.970(4) Å. These two oxygen atoms from adjacent molecules complete a highly distorted octahedron around the Cu atom. The molecule is essentially planar, with the maximum deviation from the mean plane, calculated by least-squares methods, located at the O(4) atom (−0.401(4) Å). The Cu–Cu′ ($1-x, -y, -z$ symmetry) is 3.855(1) Å.

The HO(4) atom is bonded to the N(2) atom in an intramolecular hydrogen interaction, with O(4)–N(2), O(4)–HO(4) and HO(4).....N(2) distances of 2.534(5), 1.33(6) and 1.41(6) Å respectively, and the O(4)–HO(4)....N(2) angle equal to 134(4)°. The bond lengths and angles of the ligand and DMF coordinated molecule are normal.

Magnetic Properties and EPR Spectra

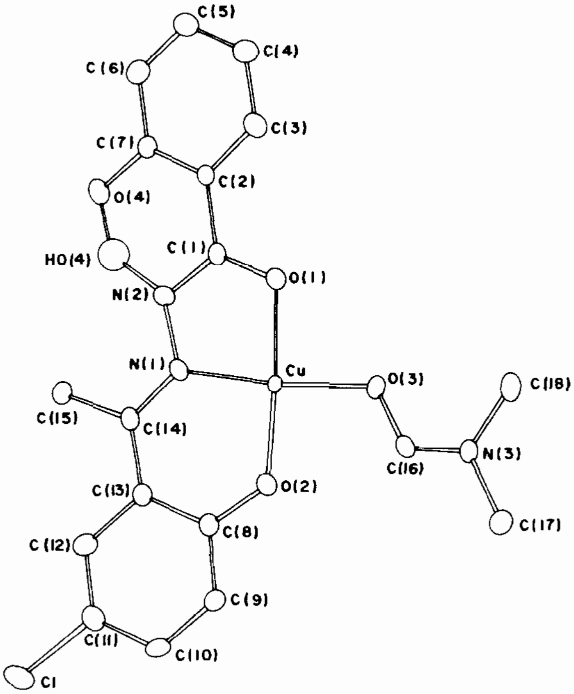

Fig. 1. ORTEP drawing showing the atom-numbering scheme for Cu(5Cl-OHA-SHZ) DMF.

TABLE 2. Interatomic distances (Å) for Cu(5Cl-OHA-SHZ) DMF[a]

Cu–O(1)	1.933(3)	Cu–O(2)	1.874(3)
Cu–O(3)	1.971(3)	Cu–N(1)	1.933(4)
Cl–C(11)	1.756(6)	O(1)–C(1)	1.294(5)
O(2)–C(8)	1.326(6)	O(3)–C(16)	1.257(6)
N(1)–N(2)	1.390(5)	N(1)–C(14)	1.318(6)
N(2)–C(1)	1.316(6)	O(4)–HO(4)	1.33(6)
N(2)–O(4)	2.534(5)	N(2)–HO(4)	1.41(6)
C(1)–C(2)	1.474(6)	C(2)–C(3)	1.419(7)
C(2)–C(7)	1.409(6)	C(3)–C(4)	1.373(7)
C(4)–C(5)	1.407(8)	C(5)–C(6)	1.369(8)
C(6)–C(7)	1.391(7)	C(7)–O(4)	1.364(6)
C(8)–C(9)	1.402(7)	C(8)–C(13)	1.425(6)
C(9)–C(10)	1.372(7)	C(10)–C(11)	1.397(8)
C(11)–C(12)	1.360(7)	C(12)–C(13)	1.421(7)
C(13)–C(14)	1.451(6)	C(16)–C(15)	1.509(7)
C(16)–N(3)	1.316(6)	N(3)–C(17)	1.452(7)
N(3)–C(18)	1.465(7)		

[a] e.s.d.s are given in parentheses.

The room temperature effective magnetic moment of Cu(5Cl-OHA-SHZ), 1.10 μ_B, markedly lower than the spin-only value expected for a $S = 1/2$ system, suggests an appreciable metal–metal interaction in the solid state. The temperature dependence of the molar magnetic susceptibility for this complex is plotted in Fig. 2. A mononuclear impurity was only detected at very low temperatures and was calculated to represent about 2% of the amount (assuming a $\chi_{imp} = C/T$ law). The maximum in the susceptibility near 390 K is indicative of antiferromagnetic inter-

TABLE 3. Interatomic angles (°) for Cu(5Cl-OHA-SHZ) DMF[a]

O(1)–Cu–O(2)	175.7(2)	O(1)–Cu–O(3)	91.4(2)
O(1)–Cu–N(1)	83.0(2)	O(2)–Cu–O(3)	92.7(2)
O(2)–Cu–N(1)	92.9(2)	O(3)–Cu–N(1)	173.9(2)
Cu–O(1)–C(1)	109.5(3)	Cu–O(2)–C(8)	127.4(4)
Cu–O(3)–C(16)	121.4(4)	Cu–N(1)–N(2)	111.6(3)
Cu–N(1)–C(14)	130.0(4)	N(2)–N(1)–C(14)	118.3(4)
N(1)–N(2)–C(1)	112.0(4)	N(1)–N(2)–O(4)	129(1)
N(1)–N(2)...HO(4)	116.1(1)	O(1)–C(1)–N(2)	123.4(5)
O(1)–C(1)–C(2)	120.3(4)	N(2)–C(1)–C(2)	116.2(4)
C(1)–C(2)–C(3)	120.3(5)	C(1)–C(2)–C(7)	122.3(5)
C(3)–C(2)–C(7)	117.4(5)	C(2)–C(3)–C(4)	121.8(5)
C(3)–C(4)–C(5)	119.1(6)	C(4)–C(5)–C(6)	120.4(6)
C(5)–C(6)–C(7)	121.7(6)	C(2)–C(7)–C(6)	119.5(5)
C(2)–C(7)–O(4)	121.6(5)	C(6)–C(7)–O(4)	118.8(5)
C(7)–O(4)–HO(4)	118(1)	N(2)...HO(4)–O(4)	134(4)
O(2)–C(8)–C(9)	117.1(5)	O(2)–C(8)–C(13)	124.8(5)
C(9)–C(8)–C(13)	118.2(5)	C(8)–C(9)–C(10)	123.8(5)
C(9)–C(10)–C(11)	117.2(6)	Cl–C(11)–C(10)	118.7(5)
Cl–C(11)–C(12)	119.7(5)	C(10)–C(11)–C(12)	121.5(6)
C(11)–C(12)–C(13)	121.7(6)	C(8)–C(13)–C(12)	117.6(5)
C(8)–C(13)–C(14)	124.1(5)	C(12)–C(13)–C(14)	118.3(5)
N(1)–C(14)–C(13)	120.4(5)	N(1)–C(14)–C(15)	118.9(5)
C(13)–C(14)–C(15)	120.8(5)	O(3)–C(16)–N(3)	123.5(5)
C(16)–N(3)–C(17)	121.0(5)	C(16)–N(3)–C(18)	121.9(5)
C(17)–N(3)–C(18)	117.1(5)		

[a] e.s.d.s are given in parentheses.

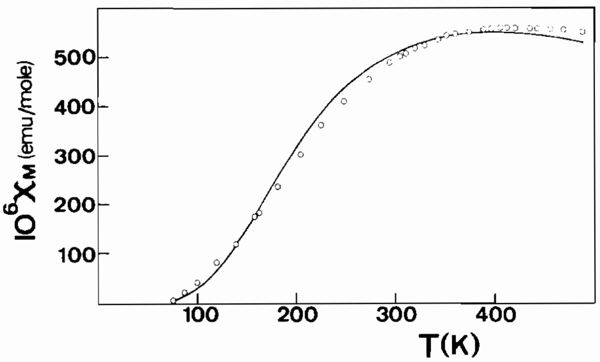

Fig. 2. Experimental (○○○) and calculated (——) thermal variation of the magnetic susceptibility for Cu(5Cl-OHA-SHZ).

actions. The full line in Fig. 2 is the best least-squares fit of the data to the Bleaney–Bowers equation for exchange coupled Cu(II) dimers [12], which yielded a singlet–triplet splitting, $2J$, of -439 cm^{-1}, and a Lande splitting factor of 2.16. The function that was minimized in the curve fitting was $F = \Sigma(\chi_{calc} - \chi_{obs})^2/(\Sigma\chi_{obs})^2$. The refinement converged to a R value, defined as square root of F, equal to 0.019. The exchange integral calculated for this complex agrees closely with that observed for a related Cu(II) complex prepared with salicylhydrazide and *o*-hydroxypropiophenone, whose EPR and magnetic properties are fully consistent with a di-oxo-bridged dimeric structure [4], and with those reported for structurally known Cu(II) dimers with the same type of structure [13].

The DMF coordinated complex is characterized by having a room temperature effective magnetic moment of 1.84 μ_B. The temperature dependence of the inverse molar magnetic susceptibility (between 4.2 and 100 K) exhibits a Curie behaviour, with a Curie constant $C = 0.397$ cm^3 K mol^{-1}. No indication of any magnetic interaction was detected down to 4.2 K.

The room temperature EPR spectrum of Cu(5Cl-OHA-SHZ) exhibits an axial signal with $g_\parallel = 2.30$ and $g_\perp = 2.04$. According with these EPR parameters the ground state can be described as essentially x^2-y^2 or xy in nature, with some admixture of other d orbitals [14]. At 4.2 K a weak signal with non-resolved structure at g *c.* 4 is also observed and could be associated with transitions within the triplet state of spin coupled Cu(II) ions.

The room temperature EPR spectrum of a powdered sample of Cu(5Cl-OHA-SHZ) DMF, Fig. 3, shows a rhombic signal with $g_3 = 2.31$, $g_2 = 2.12$ and a g_1 factor surprisingly lower than 2 i.e. $g_1 = 1.99$. The large nonaxiality of the g tensor can be explained in terms of the highly distorted coordination geometry around the Cu atom and suggests that the ground state wave function must contain an important admixture of excited orbital states. If bond angle and bond length distortions are

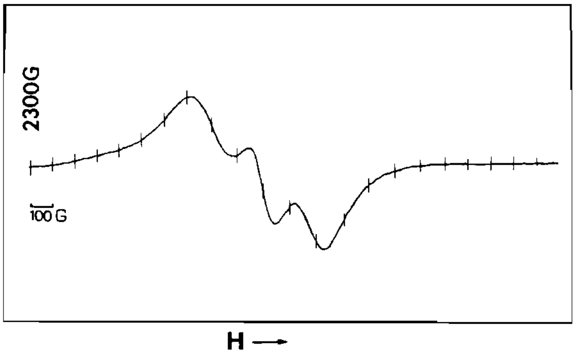

Fig. 3. Room temperature X-band EPR spectrum of Cu(5Cl-OHA-SHZ) DMF.

ignored, an approximate C_{2v} symmetry can be assumed for the CuO_3N chromophore. In C_{2v} symmetry, mixing is allowed between the d_{z^2} and $d_{x^2-y^2}$ orbitals, and following McGarvey [15] the ground state may be written as:

$$\Psi_1 = a(d_{x^2-y^2}) + b(d_{z^2}) \qquad a^2 + b^2 = 1$$

where a and b are the normalized orbital mixing coefficients of the Cu(II) ion.

The unusual lowest g value observed for this complex may be explained as resulting from an important admixture of the excited state d_{z^2} into the ground state. The calculated R value $[R = (g_2 - g_1)/(g_3 - g_2)]$ [16] of 0.63 further supports an essentially $d_{x^2-y^2}$ or d_{xy} ground state.

Electronic and IR Spectra

The diffuse reflectance spectra of both Cu(II) complexes are similar and show a very broad maximum at about 635 nm in agreement with a square-based geometry [17, 18].

Studies in the IR spectral range are performed by comparing the free ligand spectrum with those of its Cu(II) complexes. The spectrum of the free ligand shows a band at *c.* 3260 cm^{-1} which is assignable to ν(N–H) absorption. The disappearance of ν(N–H) in the spectra of both complexes agrees with the enolization of the ligand and the coordination of the amide group through deprotonation. The very broad band appearing at 2500–3000 cm^{-1}, which is observed in either the free ligand and the complexes spectra, but with lower intensity in the latter, is associated with the presence of intramolecular hydrogen bonding OH·····N, as was confirmed by the X-ray crystallographic data for Cu(5Cl-OHA-SHZ) DMF. The coordination of the ligand in the enolic form is further supported by the disappearance in the complexes spectra of the strong band at 1625 cm^{-1} attributed to ν(C=O) absorption in the free ligand spectrum. The ν(C=O) absorption due to the coordinated DMF molecule in the Cu(5Cl-OHA-SHZ) DMF spectrum must be the band observed at 1635 cm^{-1}. A strong band at 1605 cm^{-1} in the free ligand spectrum is attributed to ν(C=N) absorption. In the complexes spectra the ν(C=N) frequency shows a downward shift of *c.* 15 cm^{-1} indicating the coordination of the azomethine group nitrogen atom. A sharp band at 1590 cm appearing in both complexes spectra is associated with the presence of >C=N–N< [19].

Conclusions

The $|J|$ value calculated for Cu(5Cl-OHA-SHZ) is quite comparable to those reported for structurally known Cu(II) dimers containing four membered Cu_2O_2 rings [12], for which a superexchange coupling mechanism has been proposed [20]. Since the elemental analyses indicate a 1:1 ligand:metal stoichiometry and the Schiff base acts as a tridentate dibasic ligand, the way by which the Cu atom can attain a four-coordination is presumably by the dimerization of two Cu(II) units through oxygen bridging atoms. A superexchange coupling can then occur via two possible alternatives. One of them is via the bridging phenolic oxygen atoms, and the second should involve the bridging azomethine oxygen atoms.

In agreement with the electronic and EPR properties, in any of these two possible rearrangements the ground state of the Cu(II) ion must be predominately d_{xy} or $d_{x^2-y^2}$, and the coordination geometry an effective square-planar one.

The large nonaxiality of the g tensor for the magnetically diluted DMF coordinated complex, in conjunction with the lowest g value, are probably related with its structural properties and are compatible with a great admixture of the excited d_{z^2} state into the d_{xy} or $d_{x^2-y^2}$ ground state.

The magnetic susceptibility data for Cu(5Cl-OHA-SHZ) DMF do not indicate any magnetic interaction down to 4.2 K. An appreciable superexchange coupling must occur via the O(1)′ atom, but the Cu–O(1)′ distance, 3.159(4) Å, is too large to consider this possibility.

Supplementary Material

Lists of anisotropic thermal parameters, H atom parameters, least-squares mean planes and observed and calculated structure factors are available from the authors on request.

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References

1 M. F. Iskander, L. El Sayed, A. F. M. Hefny and S. E. Zayan, *J. Inorg. Nucl. Chem., 38* (1976) 2209.
2 P. P. Teopatía, J. N. Gurtu and V. B. Rana, *J. Inorg. Nucl. Chem., 42* (1980) 821.
3 M. N. Patel, M. M. Patel and C. B. Patel, *J. Indian Chem. Soc., LVI* (1979) 1255.
4 M. S. Palacios and J. M. Dance, *Polyhedron, 7* (1988) 543.
5 M. S. Kachhawaha and A. K. Bhattacharya, *J. Inorg. Nucl. Chem., 25* (1963) 361.
6 A. H. Blatt, *Organic Reactions,* Vol. 1, Wiley, New York, 1942, p. 342.
7 P. W. Selwood, *Magneto Chemistry,* Interscience, New York, 2nd edn., 1956.
8 I. D. Brown, *Structure and Bonding in Crystal,* Vol. 11, Academic Press, New York, 1981, p. 1.
9 O. T. Cromer and J. T. Waber, *International Tables for X-ray Crystallography,* Vol. IV, Kynoch Press, Birmingham, U.K., 1974, p. 71.
10 W. C. Hamilton, *Acta Crystallogr., 12* (1959) 609.
11 G. M. Sheldrick, *SHELX-76, a program for crystal structure determination,* University of Cambridge, Cambridge, U.K., 1976.
12 Van Vleck, *The Theory of Electric and Magnetic Susceptibilities,* Oxford University Press, London, 1932, Ch. IX.
13 M. Milan, *Coord. Chem. Rev., 42* (1982) 259.
14 B. J. Hathaway and A. A. G. Tomlinson, *Coord. Chem. Rev., 5* (1970) 1; B. J. Hathaway and D. E. Billing, *Coord. Chem. Rev., 5* (1970) 143.
15 B. R. McGarvey, in R. L. Carlin (ed.), *Transition Metal Chemistry,* Vol. 3, M. Dekker, New York, 1966, p. 180.
16 R. J. Dudley and B. J. Hathaway, *J. Chem. Soc. A,* (1970) 2799.
17 A. B. Lever, *Inorganic Electronic Spectroscopy,* Elsevier, Amsterdam, 1984.
18 B. J. Hathaway, *Coord. Chem. Rev., 42* (1982) 259.
19 L. El Sayed and M. F. Iskander, *J. Inorg. Nucl. Chem., 33* (1970) 435.
20 D. W. Smith, *Struct. Bonding (Berlin), 12* (1972) 49.