

1D Polymeric copper(II) azido complexes. Synthesis, spectral and structural studies of $[\text{Cu}(\text{ethyl isonicotinate})_2(\text{N}_3)_2]_n$ and $[\text{Cu}(\text{methyl isonicotinate})_2(\text{NO}_3)(\text{N}_3)]_n$ complexes

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Summary

Two new 1:2 polymeric complexes of copper(II) azide with ethyl isonicotinate (1) and methyl isonicotinate (2) have been synthesized and characterized by spectroscopic and crystallographic methods. The polymeric structure of complex (1) features six coordinated copper centers, a pair of *trans*-coordinated ligand molecules, and asymmetric μ_2 -1,1 and μ_2 -1,3-azido bridges resulting in a 1D chain structure. In complex (2), each copper atom which is located at an inversion center, is coordinated to a pair of *trans* ligand molecules, to the nitrogen atom of two μ -1,1-azido ligand and to an oxygen atom of a bridging (μ -O,O') nitrogen group. The i.r., electronic and e.s.r. spectra of the complexes are reported.

Introduction

Crystalline polymers containing copper complex units provide not only novel structures and geometries⁽¹⁾ but also interesting properties^(2,3). From the synthesis point of view, literature which has elucidated the relationship between the polymer and monomer structures toward rational synthesis of copper complex polymers in the simple crystal phase is sparse. The azide ligand is a good choice for the design of new polynuclear systems because it is able to act as end-on or as end-to-end coordination modes^(4,5).

Recently, we synthesized and structurally characterized copper(II) azido complexes of the type $\text{CuL}_2(\text{N}_3)_2$. With L = 4-picoline, the complex features an oligomeric edge-sharing chain of polyhedra and contains terminal and μ_2 -1,1 bridging azides⁽⁶⁾. When L = 3-picoline, the complex contains both μ_2 -1,1 and μ_2 -1,3 bridging azides⁽⁷⁾ but the 1:2 complex of 3-benzoylpyridine⁽⁸⁾ possesses only μ_2 -1,3 azido ligands. We have now isolated two new complexes, one of formula $\text{CuL}_2(\text{N}_3)_2$, and the other $\text{CuL}_2(\text{NO}_3)(\text{N}_3)$. The synthesis and characterization of these complexes as elucidated by X-ray crystallography and spectroscopic methods, are presented in this paper.

Experimental

Ethyl isonicotinate and methyl isonicotinate were purchased from Aldrich Company; other chemicals were of analytical grade quality.

Polymeric $[\text{Cu}(\text{ethyl isonicotinate})_2(\text{N}_3)_2]_n$ (1)

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.72 g, 3 mmol) dissolved in ca. 30 cm³ EtOH and ethyl isonicotinate (1.06 g, 7 mmol) were mixed together followed by addition of an aqueous solution (ca. 5 cm³) of NaN_3 (0.52 g, 8 mmol). After filtration, several drops of ethylisonicotinate were added to prevent co-precipitation of the 1:1 complex. The final mixture was allowed to stand in an open beaker for several weeks until black long needle-like crystals of the complex separated. Yield, 47%. (Found: C, 42.4; H, 4.2; N, 25.1; Cu, 14.6; $\text{CuC}_{16}\text{H}_{18}\text{N}_8\text{O}_4$ calcd.: Cu, 42.7; H, 4.0; N, 24.9; Cu, 14.1%).

Polymeric $[\text{Cu}(\text{methyl isonicotinate})_2(\text{N}_3)(\text{NO}_3)]_n$ (2)

$\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (0.96 g, 4 mmol) and methyl isonicotinate (2.06 g, 15 mmol) were mixed together in (40 cm³) EtOH. To this mixture, an aqueous solution (ca. 5 cm³) of NaN_3 (0.48 g, 7.5 mmol) was added with continuous stirring, and a green precipitate formed. The final mixture was boiled until the precipitate completely dissolved. The mixture was then filtered and the filtrate was then allowed to stand in an open beaker over several weeks until dark green long needle like crystals of the complex were separated. Yield, 30%. (Found: C, 38.4; H, 3.0; N, 19.5; Cu, 14.1; $\text{CuC}_{14}\text{H}_{14}\text{N}_6\text{O}_7$ calcd.: Cu, 38.0; H, 3.2; N, 19.0; Cu, 14.4%).

Physical measurements

The experimental procedures and instruments used for different physical measurements are as described previously⁽⁹⁾.

X-ray crystal structure analysis

A modified STOE four circle diffractometer was used for single crystal X-ray measurements. Orientation matrix and lattice parameters were obtained by least-squares refinement of the diffraction data from 34 reflections in the 4.2–14.0 range (1) and 32 reflections in the 5.2–12.2 range (2), respectively. Data were collected at 298(2) K (1) and at 295(2) K (2) using graphite crystal-monochromatized Mo-K α radiation ($\lambda = 0.71069$) and the ω scan technique. Three reflections [0 1 2, 0 6 0, 1 1 1 (1) and 1000, -221, 40-2 (2)] were collected every hour and used for intensity corrections [Intensities of the three standard reflections dropped continuously during data collections by 13% and 17%, respectively]. Corrections were applied for Lorentz-polarization effects, for intensity decay and for absorption. Crystallographic data and processing parameters are given in Table 1.

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Table 1. Crystallographic data and processing parameters for complexes (1) and (2)

Compound	(1)	(2)
Molecular formula	C ₁₆ H ₁₈ CuN ₈ O ₄	C ₁₄ H ₁₄ CuN ₆ O ₇
Molecular weight	449.92	441.85
Color	Black	Dark green
System, space group	Monoclinic, P2 ₁ /n	Monoclinic, C ₂ /c
a (Å)	3.9932(15)	20.842(9)
b (Å)	21.751(6)	11.575(6)
c (Å)	11.382(3)	7.352(5)
β (°)	96.32(2)	97.97(4)
V (Å ³)	988.3(5)	1757(2)
Z	2	4
μ(M _o Kα) (mm ⁻¹)	1.146	1.671
Normalized transition factors	1.000–0.104	1.000–0.219
D _{calc} /D _{obs} (Mg/m ³)	1.512/1.50(3)	1.671/1.65(4)
Approx. Crystal size (mm)	0.70 × 0.25 × 0.10	0.62 × 0.10 × 0.07
θ range of data collection (°)	3.33–24.99	3.34–25.00
Reflections collected	1881	1937
Independent. Refl./Rint	1585/0.0394	1446/0.0668
Parameters	165	132
Goodness-of-Fit on F _o ²	1.101	1.101
R1/wR2	0.0665/0.1503	0.0759/0.1805
Weighting factors ^a : a/b	0.0861/0.2411	0.1236/0.0000
Largest peak/hole (eÅ ⁻³)	0.915/–0.649	1.159/–0.817

$$^a w^{-1} = [\sigma^2(F_o^2) + (aP)^2 + bP] \text{ and } P = (F_o^2 + 2F_c^2)/3.$$

Table 2. Selected bond lengths (Å) and angles (°) for complex (1)

Bond lengths			
Cu(1)—Cu(1a)	3.993(2)	Cu(1)—N(21b)	1.968(8)
Cu(1)—N(21)	1.968(8)	Cu(1)—N(11b)	1.991(7)
Cu(1)—N(11)	1.991(7)	Cu(1)—N(1)	2.048(3)
Cu(1)—N(1b)	2.048(3)	N(11)—N(12)	1.236(10)
N(12)—N(13)	1.133(10)	N(21)—N(22)	1.22(2)
N(22)—N(23)	1.132(2)	N(11)—Cu(1a)	2.615(7)
N(23)—Cu(1a)	2.706(13)		
Bond angles			
N(21)—Cu(1)—N(1)	88.0(3)	N(11)—Cu(1)—N(1)	91.6(2)
N(12)—N(11)—Cu(1)	120.6(5)	N(13)—N(12)—N(11)	172.0(8)
N(22)—N(21)—Cu(1)	114.1(8)	N(23)—N(22)—N(21)	173.7(14)

Symmetry codes: (a) $x + 1, y, z$; (b) $-x, -y, -z$.

The structure were solved by direct methods and subsequent Fourier analyses. Anisotropic displacement parameters were applied to non-hydrogen atoms in full-matrix least-squares refinements based on F². For (1), nitrogen atoms of disordered azide group were refined with occupation factors of 0.654(4) and 0.346(4), respectively. The hydrogen atoms were assigned with isotropic displacement factors and included in the final refinement cycles by use of geometrical restraints. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. The program DIFABS [1], and the SHELXTL/PC [2] program package were used for computations. Final atomic coordinates are given in Tables 2 and 3, selected bond distances and bond angles are given in Tables 4 and 5, respectively. Supplementary material has been deposited at the Cambridge Crystallographic Data Center (deposition numbers 103046 and 103047, respectively).

Results and discussion

The interaction between copper(II) nitrate and ethyl isonicotinate or methyl isonicotinate in the presence of azide ions yielded two different complexes; a 1:2 cop-

Table 3. Selected bond lengths (Å) and angles (°) for complex (2)

Bond lengths			
Cu(1)—N(1a)	2.025(6)	Cu(1)—N(1)	2.025(6)
Cu(1)—N(11)	2.071(4)	Cu(1)—N(11a)	2.071(4)
Cu(1)—O(3)	2.399(6)	Cu(1)—O(3a)	2.399(6)
N(11)—N(12)	1.218(8)	N(11)—Cu(1b)	2.071(4)
N(12)—N(13)	1.135(9)	O(3)—N(2)	1.259(7)
N(2)—O(4)	1.174(14)	N(2)—O(3b)	1.259(7)
Cu(1b)—Cu(1b)	3.676(3)		
Bond angles			
N(1)—Cu(1)—N(11)	88.3(2)	N(1)—Cu(1)—O(3)	93.5(2)
N(11)—Cu(1)—O(3)	92.8(3)	N(12)—N(11)—Cu(1)	117.4(2)
Cu(1b)—N(21)—Cu(1b)	125.1(4)	N(13)—N(12)—N(11)	180
N(2)—O(3)—Cu(1)	125.9(5)	O(4)—N(2)—O(3)	120.4(5)
O(4)—N(2)—O(3b)	120.4(5)	O(3)—N(2)—O(3b)	119.2(10)

Symmetry codes: (a) $-x + 1, -y + 1, -z + 1$; (b) $-x + 1, y, -z + 1/2$.

Table 4. I.r. spectra (cm⁻¹) for complexes (1) and (2)

(1)	(2)	Assignments
2070vs	2065vs,sh 1470ms 1280s(sh) 1015m	$\nu_{as}(N_3)$ νNO_3
1270ms 640sh 605wm 365m 350m	645wm 598wm 370m	$\nu_s(N_3)$ $\delta(N_3)$
	310ms 285m	$\nu Cu-N(N_3)$
265ms	270ms 240m	$\nu Cu-O(NO_3)$ $\nu Cu-N(L)$

^a masked by the ligand absorption.

Table 5. Electronic absorption spectra (cm⁻¹) for complexes (1) and (2)

Complex	Solvent	N ₃ →Cu ^{II} CT(ε) λ _{max} (cm ⁻¹)	d-d(ε) λ _{max} (cm ⁻¹)
(1)	NM	25400sh 22300s,v br 24390(1800)	15750
	DMF	24390(2220)	13812(207)
	DMSO	24390(2220)	13140(320)
(2)	NM	24,400 22,200s,br	15400 14200br
	DMF	24946(2500)	12515(180)
	DMSO	25000(2200)	12060(180)

per(II) azide complex in case of ethylisonicotinate and the [Cu(methylisonicotinate)₂(N₃)(NO₃)] complex for the methyl ester. Both complexes are black needle-like crystals and are insoluble in many non-polar solvents, *e.g.* benzene, carbon tetrachloride, *etc.*, and many polar solvents, *e.g.* methanol, chloroform and water. They are slightly soluble in acetone and ethanol but soluble in DMF and DMSO, giving non-conducting solvents. The complexes change to brown immediately in the last two solvents.

Figure 1 illustrates the principle structural features of complex (1) for which selected bond distances and bond angles are collected in Table 2. This compound crystallizes in monoclinic space group P2₁/n with 2 formula per unit cell. The *trans* coordinated ethyl isonicotinate molecules have normal occupancy whereas the azido ligands show positional disorder. N(11), N(12) and

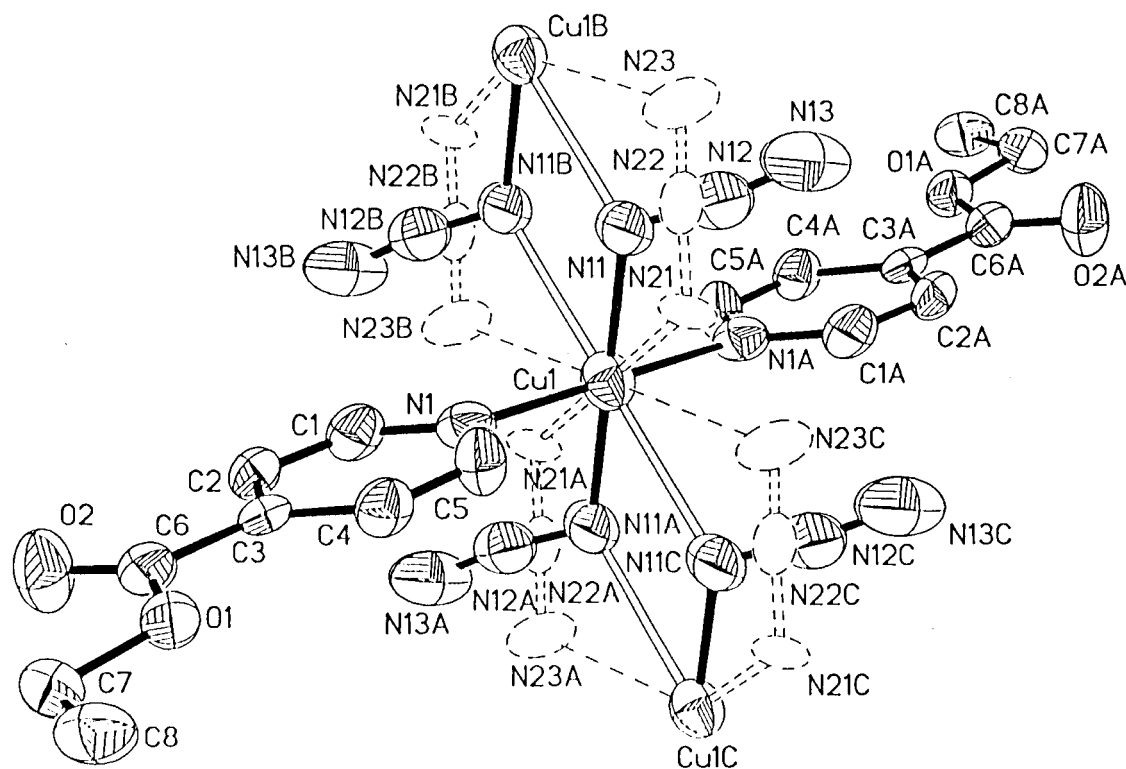


Figure 1. $[\text{Cu}(\text{ethyl isonicotinate})_2(\text{N}_3)_2]_n$ (1): molecular geometry and atom labels. Hydrogen atoms are omitted for clarity. Broken ellipsoids indicate disordered azide groups with minor occupancy.

N(13) have occupation factors of 0.654(4), the remaining N(21), N(22) and N(23) have occupation factors of 0.346(4), *i.e.* the ratio is close to 2:1. As can be seen from Figure 1, the azide group N(11)—N(12)—N(13) may be described as asymmetric μ_2 -1,1 bridge [$\text{Cu}-\text{N} = 1.991(7)$ and $2.615(7)$ Å], whereas azide group N(21)—N(22)—N(23) acts as asymmetric μ_2 -1,3 bridge [$\text{Cu}-\text{N} = 1.968(8)$ and $2.706(13)$ Å], resulting in a one-dimensional (1D) chain structure oriented along the *a*-axis of the unit cell. Assuming an occupation ratio of 2:1 for the azide groups, the “average azide bridging sequence” may be two times simultaneous μ_2 -1,3 and μ_2 -1,1 related by inversion center at a metal site followed by one di- μ_2 -1,1 bridge. Such a bridging sequence has been observed in the structure of $[\text{Cu}(\text{3-picoline})_2(\text{N}_3)_2]_n$ ⁽⁷⁾. The corresponding coordination figure of the copper center in case of the simultaneous μ_2 -1,3 and μ_2 -1,1 sequence may be described as distorted square bipyramidal with N(1), N(1a), N(11) and N(11a) at basal sites [$\text{Cu}-\text{N} = 1.991(7)$ and $2.048(3)$ Å] and N(23), N(23c) at apices [$\text{Cu}-\text{N} = 2.706(13)$ Å], whereas for copper centers with other azide bridges more distorted six-coordinated environments are expected. For the di-1,1 bridge the N(11)—Cu(1)—N(11) angles are close to 120 and 60.

The present structure differs from that of the brownish-green $[\text{Cu}(\text{pyridine})_2(\text{N}_3)_2]_n$ complex (3)⁽¹²⁾ although (3) possesses six-coordination copper centers, μ_2 -1,1 and μ_2 -1,3 azido bridges. These μ_2 -1,1 and μ_2 -1,3, however, are *trans* to each other in complex (3), and therefore it does not contain the di- μ_2 -1,1 azide bridges. Complex (1) differs also from the structure of $[\text{Cu}(\text{3-chloropyridine})_2(\text{N}_3)_2]_n$ (4)⁽¹³⁾. Complex (4) was found to contain chains of copper atoms bridged by two different kinds of azido bridges in alternating fashion: twice simultaneous μ -1,1- N_3 and μ -1,3- N_3 double bridges.

A plot of the molecular structure of complex (2) and the atom labeling scheme is given in Figure 2. Selected bond distances and angles are collected in Table 3. In complex (2) the copper(1) atom is located at inversion center, whereas N(11), N(12), N(13) of the azide group and N(2) and O(4) of the nitrate anion are located at special positions $1/2, y, 1/4$ with site symmetry 2. The coordination geometry around copper atoms may be described as a distorted square bipyramidal with N(1) and N(1a) of *trans* coordinated methyl isonicotinate

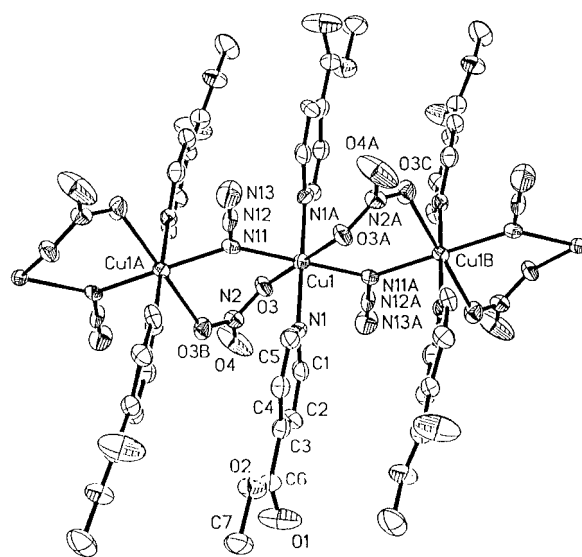


Figure 2. $[\text{Cu}(\text{methyl isonicotinate})_2(\text{N}_3)_2]_n$ (2): molecular geometry and atom labels. Hydrogen atoms are omitted for clarity. Azide groups and nitrate ions act as bridging ligands to form a 1D chain structure oriented along the *c*-axis of unit cell.

molecules and N(11) and N(11a) of azido groups at basal sites [Cu–N = 2 × 2.025(6) and 2 × 2.071(4) Å], and O(3) and O(3a) at apical positions [Cu–O = 2.399(6) Å]. The azido groups behave in the μ_2 -1,1 fashion and the nitrate anions act as μ -O,O' bridging ligands, thus forming a one-dimensional (1D) chain structure oriented along the c-axis of the unit cell.

The structure of complex (2) differs from those of [Cu(3-acetylpyridine)₂(NO₃)(N₃)₂] (5)⁽¹⁴⁾, and [Cu(3-picoline)₄(NO₃)₂(N₃)₂(H₂O)] (6)⁽¹⁵⁾. In the dimeric molecule, (5) which contains di- μ_2 -1,1 bridging azides, each copper atom in the cyclic Cu₂N₂ ring is coordinated by two oxygen atoms from a bidentate chelating nitrate group with Cu–O = 2.022(8) and 2.571(9) Å. The structure of (6) contains anionic and bridging nitrate groups in addition to the μ_2 -1,1 azido ligands giving rise to cyclic Cu₂N₂ units.

The interest in the i.r. spectra of these complexes lies mainly in the bands due to the nitrate groups in complex (2), in addition to those due to azido groups in both complexes. As seen from Table 4, the i.r. spectrum of complex (1) shows a very strong band at 2070 cm⁻¹ due to the $\nu_{as}(\text{N}_3)$ mode. This result is inconsistent with the X-ray structural results as well as the δd versus $\nu_{as}(\text{N}_3)$ relationship given earlier⁽¹⁶⁾ (δd is the difference between the two N–N distances in an azide group), both of which suggest two $\nu_{as}(\text{N}_3)$ bands due to the existence of two asymmetric μ_2 -1,1 and μ_2 -1,3 bridging azides. This result, however, is not unusual as a similar observation has been reported for [Cu(pyridine)₂(N₃)₂]_n complex containing terminal and μ_3 -1,1,3 bridging azides⁽¹⁷⁾. The i.r. spectrum of complex (2) exhibits a strong band related to $\nu_{as}(\text{N}_3)$ mode of the azide. Unfortunately the $\nu_s(\text{N}_3)$ bands, which are good evidence for the asymmetric nature of azide ligand, are masked by the strong absorption of the ligand in both complexes. The separation value of the two bands due to the nitrate group Table is consistent with a bidentate ligand⁽¹⁸⁾. In the far i.r. region we tentatively assigned the bands in the 400–300 cm⁻¹ and 270–200 cm⁻¹ range due to $\nu\text{M-N}(\text{N}_3)$ and $\nu\text{M-N(L)}$, respectively.

The electronic spectrum (Figure 3 and Table 5) of the complex (1) exhibits one d-d absorption band at 15750 cm⁻¹, whereas that of complex (2) shows a split

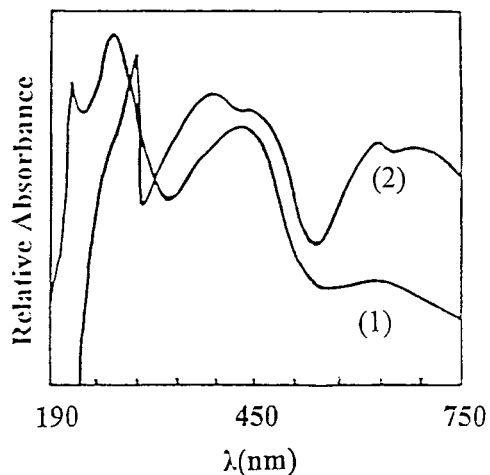


Figure 3. Electronic spectra of solid complexes: (1) [Cu(ethyl isonicotinate)₂(N₃)₂]_n; (2) [Cu(methyl isonicotinate)₂(N₃)₂]_n.

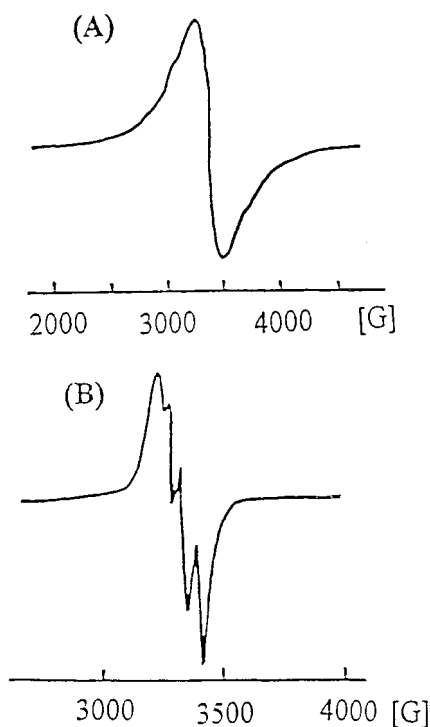


Figure 4. E.s.r. spectra of [Cu(ethyl isonicotinate)₂(N₃)₂]_n complex (1): (A) Solid (B) DMF solution.

d-d band with maxima at 15400 and 14200 cm⁻¹. These results are consistent with distorted octahedral^(20,21) and five-coordinated^(22,23) copper environments for complexes (1) and (2) respectively. The spectra of both also show at least two very strong bands in the 25000–22000 cm⁻¹ range assigned as N₃⁻ → Cu^{II} LMCT transitions, as found in copper(II) azido complexes of similar ligands^(12–15). In DMF and DMSO both complexes show the N₃⁻ → Cu^{II} CT transitions as a very strong single band for each in the 24000–25000 cm⁻¹ range, in addition to the d-d absorption bands shifted to lower wave numbers. The change of these complexes in both solvents from green to brown may be associated with a partial reduction of copper(II) to copper(I) leading to mixed-valence compounds which are well known to be brown.

The X-band e.s.r. spectra (Figure 4) of solid samples of both complexes at room temperature exhibit a broad signal with a poor resolution of the hyperfine structure on both sides of the main signal; average g values are 2.08 and 2.07 for (1) and (2) respectively. This may be due to a Cu–Cu interaction. However, the absence of half-field signals for the two complexes suggests a very weak interaction. In DMSO, spectra of both compounds are similar to those in DMF, and show four hyperfine lines of uncoupled copper(II) with average hyperfine splitting factor A_o(Cu) = 52.6 and 71.5 for complexes (1) and (2) respectively.

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References

- (1) B. J. Hathaway, in G. Wilkinson, (Ed), *Comprehensive Coordination Chemistry*, Pergamon; London, 1988 Vol. 15, p. 533.
- (2) A. Aumuller, P. Erk, G. Klebe, S. Hunig, J. U. Ven Schutz, and H. P. Werner, *Angew. Chem. Int. Ed. Engl.*, **25**, 740, (1986).
- (3) H. Urayama, H. Yamochi, G. Saito, K. Nozawa, T. Sugano, M. Kinoshita, S. Sato, K. Oshima, A. Kawamoto, and J. Tanaka, *Chem. Lett.*, **55**, (1988), A. M. Kini, U. Geiser, H. H. Wang, K. D. Carlson, J. M. Williams, W. K. Kwok, K. G. Vandervoot, J. D. Thompson, D. L. Stupka, D. Jung, M. H. Whangba, *Inorg. Chem.*, **29**, 2555, (1990).
- (4) M. L. Arriortua, A. R. Cortes, L. Lezama, T. Rojo and X. Soons, *Inorg. Chem. Acta*, **174**, 263 (1990); M. A. S. Goher and T. C. W. Mak, *Inorg. Chem. Acta*, **89**, 119 (1984); Z. Dori and R. F. Ziolo, *Chem. Rev.*, **73**, 247 (1973).
- (5) F. Wagner, M. T. Mocella, M. J. D'Aniello, A. J. H. Wang and E. K. Barefield, *J. Am. Chem. Soc.*, **96**, 2625 (1974); C. G. Pierpont, D. N. Hendrickson, D. M. Doggan, F. Wagner and E. K. Barefield, *Inorg. Chem.* **14**, 604 (1975).
- (6) F. A. Mautner and M. A. S. Goher, *Polyhedron*, **11**, 2537 (1992).
- (7) M. A. S. Goher and F. A. Mautner, *Cryst. Res. Technol.*, **27**, 817 (1992).
- (8) M. A. S. Goher, F. A. Mautner, *Polyhedron*, **17**, 1561 (1998).
- (9) M. A. S. Goher, F. A. Mautner and M. A. M. Abu-Youssef, *Transition Met. Chem.* in press. (TMC 4167).
- (10) N. Walker and D. Stuart, *Acta Crystallogr.*, **A39**, 158 (1983).
- (11) *SHELXTL/PC v. 5.03*, Siemens Analytical Automation Inc., Madison, WI, (1986).
- (12) F. A. Mautner and M. A. S. Goher, *Polyhedron*, **14**, 1805 (1995).
- (13) A. Escuer, R. Vicente, M. A. S. Goher and F. A. Mautner, *Inorg. Chem.*, **37**, 4455 (1998).
- (14) M. A. S. Goher and F. A. Mautner, *J. Coord. Chem.*, **34**, 221 (1995).
- (15) F. A. Mautner and M. A. S. Goher, *Polyhedron*, **12**, 2823 (1993).
- (16) I. Agrell, *Acta Chem. Scand.*, **25**, 1630 (1971).
- (17) M. A. S. Goher, *Acta Chim. Hung.*, **127** 2139 (1990).
- (18) I. Agrell, *Acta Chem. Scand.*, **23**, 1667 (1969), I. Agrell, *Acta Chem. Scand.*, **25**, 2965 (1971).
- (19) K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds.*, I. Wiley, New York, 1984.
- (20) J. Kohoret, M. Hvastijova, M. Kohhotova and J. Gazo, *Monatsh. Chem.*, **102**, 350 (1971).
- (21) J. Kohoret, M. Hvastijova, M. Kohhotova and J. Gazo, *Monatsh. Chem.*, **104**, 799 (1973).
- (22) L. Sacconi and L. Bertini, *Inorg. Chem.*, **5**, 1520 (1966).
- (23) A. Mangia, M. Naradilli, C. Pelizzi and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 2483 (1972).

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