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Polyhedron 27 (2008) 335–343
POLYHEDRON
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Synthesis, spectroscopic, electrochemical and structural characterization of Cu(II) complexes with asymmetric NN′OS coordination spheres

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Received 24 May 2007; accepted 16 September 2007
Available online 14 November 2007

Abstract

A set of four Cu(II) complexes, [Cu(cdnapen)], [Cu(cdnappd)], [Cu(cdMenappd)] and [Cu(cdMeMeOsalpd)], derived from Schiff base ligands with an asymmetric NN′OS coordination sphere have been synthesized. The molecular and the crystal structures have been determined by X-ray diffractometry. The structural results confirm that the complexes are tetra coordinated. The copper (II) ion coordinates to two nitrogen atoms from the imine moiety of the ligand, a sulfur atom from the methyl dithiocarboxylate moiety and a phenolic oxygen atom. The complexes show an unusual tetrahedral distortion to the square-planar geometry around the metal centre in spite of the pseudomacrocyclic skeleton of the ligand. The complexes were further characterized by cyclic voltammetry and electron paramagnetic resonance spectroscopy. The degree of tetrahedral distortion of the complexes appears to be dependent on the number of carbon atoms of the aliphatic bridge and the nature of the coordinating atoms.

Keywords: Copper Schiff base complexes; X-ray crystal structures; EPR; Electrochemistry; Asymmetric Cu(II) complexes

1. Introduction

Cu(II)/Cu(I) chemistry has received renewed attention since the characterization and the structural elucidation of blue copper proteins [1–4], e.g. hemocyanin, tyrosinase, cytochrome *c* oxidase and laccase. These proteins have been reported to play an important role in electron transfer during biochemical metabolism. The metal centre responsible for the electron transfer has been identified as containing the redox pair Cu(II)/Cu(I) with quite positive reduction potentials. This feature has been attributed to the unusual coordination geometry around the metal centre. Blue copper proteins have an active copper centre with a N_2S_2 or a N_2OS_2 coordination sphere. Several attempts of preparing lower molecular weight compounds for modelling the redox behaviour of this active centre have been made [5–11]. The copper (II) moiety in biological proteins is asymmetric and, for the tetracoordinated active centre, the geometry around the Cu(II) ion seems to have a significant tetrahedral distortion from square planar geometry. We have prepared a series of Cu(II) complexes with a pseudomacrocyclic Schiff base ligand with a N_2OS asymmetric coordination sphere, as depicted in Scheme 1. The complexes have a sulfur donor atom that can act as a π acceptor, an oxygen donor atom as a π donor and the coordination around the copper ion allows for π electronic

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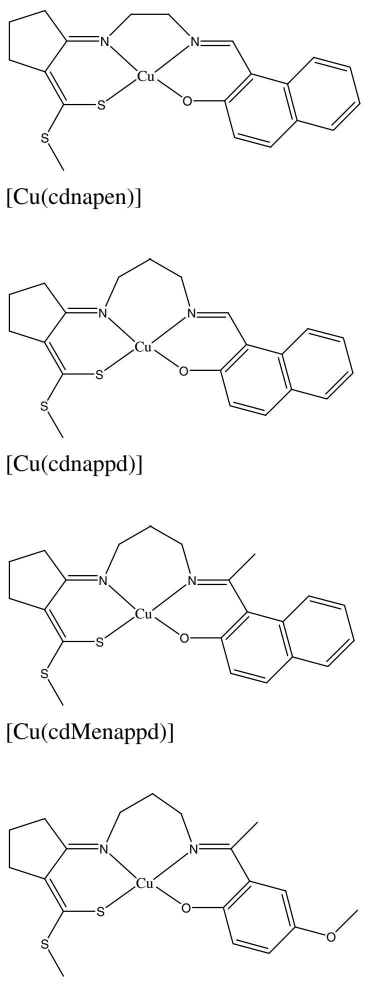
doi:10.1016/j.poly.2007.09.030



[Cu(cdnapen)]

[Cu(cdnappd)]

[Cu(cdMenappd)]

[Cu(cdMeMeOsalpd)]

Scheme 1.

delocalization. These complexes were characterized in the solid state by X-ray diffractometry in order to elucidate their molecular and crystal structures and to evaluate their degree of tetrahedral distortion to the square planar geometry. Also they have been characterized by EPR spectroscopy in solution at 298 K and at 77 K. Further, their electrochemical behaviour was studied by cyclic voltammetry. The structural and the electrochemical results are compared with those obtained for the corresponding symmetric N_2O_2 and N_2S_2 Cu(II) complexes.

2. Experimental

2.1. Reagents and solvents

All solvents and reagents used in the synthesis and characterization were of reagent grade and were used as received. Solvents used in the electrochemical studies (Merk *pro analysis*) were dried by standard methods. Tetra(*n*-butyl)ammonium perchlorate, TBAP, was prepared following published procedures [12]. *CAUTION*: perchlorates may be hazardous and may explode.

2.2. Synthesis of the ligands

Methyl 2-{*N*-(2-aminoethane)}-amino-1-cyclopentenedithiocarboxylate (Hcden) and methyl 2-{*N*-(2-aminopropane)}-amino-1-cyclopentenedithiocarboxylate (Hcdpd) were prepared by published methods [13,14]. The other ligands were prepared following the general published procedure [15,16].

2.3. Synthesis of the Cu(II) complexes

2.3.1. General procedure

A solution of copper (II) acetate monohydrate (0.1 mmol in 10 cm^3 of methanol) was added to 0.1 mmol of the appropriate ligand in chloroform/methanol (2:1) v/v solution. The mixture was stirred for about 20 min and allowed to react at room temperature for about 24 h. The resulting green or brown powder was recrystallized from acetonitrile/methanol (1:1) v/v. Single crystals for X-ray diffraction were obtained by slow evaporation of the acetonitrile/methanol (1:1) v/v solution.

Methyl 2-{[3-(2-hydroxynaphthyl)methyleneamino]ethylamino}(cyclopent-1-ene-1-dithiocarboxylato) copper (II), [Cu(cdnapen)]: Yield: 54%. *Anal.* Calc. for $C_{20}H_{20}N_2OS_2Cu$: C, 55.60; H, 4.66; N, 6.48; S, 14.84. Found: C, 55.65; H, 4.92; N, 6.45; S, 14.73%.

Methyl 2-{[3-(2-hydroxynaphthyl)methyleneamino]propylamino}(cyclopent-1-ene-1-dithiocarboxylato) copper (II), [Cu(cdnappd)]: Yield: 61%. *Anal.* Calc. for $C_{21}H_{22}N_2OS_2Cu$: C, 56.54; H, 4.97; N, 6.28; S, 14.37. Found: C, 56.59; H, 5.03; N, 6.30; S, 14.32%.

Methyl 2-{[3-(2-hydroxynaphthyl)-ethyl-1-ene-1-amino] ethylamino}(cyclopent-1-ene-1-dithiocarboxylato) copper (II), [Cu(cdMenappd)]: Yield: 14%. *Anal.* Calc. for $C_{22}H_{24}N_2OS_2Cu$: C, 57.43; H, 5.26; N, 6.09; S, 13.94. Found: C, 57.47; H, 5.29; N, 6.05; S, 13.57%.

Methyl 2-{[3-(2-hydroxy-5-methoxyphenyl)ethyl-1-ene-1-amino]ethylamino}(cyclopent-1-ene-1-dithiocarboxylato) copper (II), [Cu(cdMeMeOsalpd)]: Yield: 68%. *Anal.* Calc. for $C_{19}H_{24}N_2OS_2Cu$: C, 51.85; H, 5.50; N, 6.37; S, 14.57. Found: C, 51.90; H, 5.80; N, 6.38; S, 14.69%.

2.4. Instrumentation and electrochemical measurements

Elemental analysis (C, H and N) were performed at the Micro Analytical Laboratory, University of Manchester.

The electrochemical studies were performed with an EG&G PAR 362 instrument. Cyclic voltammetry was carried at room temperature under nitrogen atmosphere on a three-electrode system cell consisting of a microplatinum electrode, a platinum wire counter electrode and an Ag/AgCl (1 mol dm^{-3} NaCl) reference electrode. The cyclic voltammograms were recorded from $\sim 10^{-3}$ mol dm^{-3} solutions of the complexes in dmf, $(CH_3)SO$ and CH_3CN solutions. The potentials were corrected for the ferrocenium/ferrocene (Fc^+/Fc) couple. The potentials were scanned between 0.0 and −2.0 V at a scan rate of 50 mV s^{-1}. Voltammograms were also obtained with scan rates from 20 to 500 mV s^{-1}, to check the reversibility of the redox process.

The EPR spectra were obtained with a Bruker ESP300E spectrometer (9 GHz) in a dual cavity, using diphenylpicrylhydrazyl ($g = 2.0037$) as an external standard; the magnetic field was calibrated with Mn^{2+} in MgO.

2.5. Structure determination

The data acquisition was made using a Stoe Stadi IV diffractometer for [Cu(cdnapen)] and [Cu(cdMeMeOsalpd)] and an image plate Stoe Ipds diffractometer for [Cu(cdnappd)] and [Cu(cdMenappd)], $\lambda = 0.71073$ nm. Intensities were corrected for Lorentz and polarization effects. Empirical absorption correction was performed for compounds [Cu(cdnapen)] and [Cu(cdMeMeOsalpd)] and numerical absorption correction was performed for [Cu(cdnappd)] and [Cu(cdMenappd)] using the package SADABS [17]. SHELX-97 [18] was used to make the structure solution and refinement. The structures were solved by direct methods and subsequent Fourier difference techniques. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares on F^2. Hydrogen atoms were treated as riding atoms with C–H(aromatic) 0.93 Å, C–H(CH_2) 0.97 Å, C–H(CH_3) 0.96 Å, and given an isotropic displacement parameter equal to 1.2 (CH, CH_2) and 1.5 (CH_3) times the equivalent isotropic displacement parameter of the atom to which it is attached. Details for crystallographic data and refinement of the four complexes are shown in Table 1. Molecular and packing diagrams were generated by ORTEP-32 [19] and PLATON [20].

3. Results and discussion

3.1. Structures of the complexes

The X-ray structure determinations confirmed that the complexes show the expected molecular structure. For compounds [Cu(cdnapen)], [Cu(cdnappd)] and [Cu(cdMenappd)], the metal is bonded to the two imine nitrogen atoms, to the sulfur atom from the methyl dithiocarboxylate residue and to the naphtholic oxygen atom of the ligand, assuming a *cis* configuration. For the complex [Cu(cdMeMeOsalpd)], the ligand is a Schiff base that is formed with a fragment derived from the 5-methoxyketophenone and another one derived from the 2-aminocyclopentenedithiocarboxylate methyl ester. Complex [Cu(cdnapen)] has an ethylenic diimine chain while the remaining complexes have a propylenic one.

The structures of complexes are depicted in Figs. 1–5. The main bond lengths for the compounds studied as well as for the homologous compounds with a symmetric coordination sphere, are shown in Table 2. The bond lengths are within the expected range for copper (II) complexes with

Table 1
Crystallographic parameters for the data acquisition of the studied compounds

Compound	[Cu(cdnapen)]	[Cu(cdnappd)]	[Cu(cdMenappd)]	[Cu(cdMeMeOsalpd)]
Formula	$C_{20}H_{20}CuN_2OS_2$	$C_{21}H_{22}CuN_2OS_2$	$C_{22}H_{24}CuN_2OS_2$	$C_{19}H_{24}CuN_2O_4$
Molecular weight (mol dm^{-3})	432.05	442.07	460.09	440.07
Color	brown	green	green	brown
Crystal size (mm)	0.4 × 0.3 × 0.3	0.4 × 0.2 × 0.1	0.3 × 0.3 × 0.2	0.4 × 0.2 × 0.1
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$	$P2_1/c$
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Temperature (K)	293(2)	203(2)	203(2)	293(2)
Unit cell dimensions				
a (Å)	14.976(7)	19.009(10)	16.104(4)	16.962(13)
b (Å)	14.583(7)	8.302(3)	7.207(4)	8.474(7)
c (Å)	16.829(8)	12.872(10)	17.462(4)	14.283(13)
β (°)	93.54(3)	94.05(6)	94.15(2)	110.72(7)
Volume (Å^3)	3668(3)	2026(2)	2021.4(13)	1920(3)
Z	8	4	4	4
μ (mm^{-1})	1.405	1.274	1.280	1.347
$F(000)$	1784	924	956	916
Minimum to maximum θ collected (°)	1.77–27.07	4.95–28.31	4.95–28.20	2.57–26.00
Index range	$0 \leqslant h \leqslant 16$, $0 \leqslant k \leqslant 18$, $-21 \leqslant l \leqslant 21$	$-22 \leqslant h \leqslant 23$, $-11 \leqslant k \leqslant 10$, $-16 \leqslant l \leqslant 17$	$-20 \leqslant h \leqslant 21$, $-9 \leqslant k \leqslant 9$, $-20 \leqslant l \leqslant 20$	$0 \leqslant h \leqslant 17$, $0 \leqslant k \leqslant 10$, $-20 \leqslant l \leqslant 19$
Absorption correction	empirical	multiscan	multiscan	empirical
Measured reflections (R_{int})	7676 (0.0331)	4747 (0.1633)	4711 (0.0728)	3776 (0,0472)
Data/parameters	7618/469	3735/245	4214/256	3771/238
Goodness-of-fit	1.037	1.056	1.083	1.031
R_1 and wR_2 ($I > 2\sigma I$)	$R_1 = 0.0479$, $wR_2 = 0.0991$	$R_1 = 0.0652$, $wR_2 = 0.1485$	$R_1 = 0.0490$, $wR_2 = 0.1095$	$R_1 = 0.0470$; $wR_2 = 0.1037$
R_1 and wR_2 (all data)	$R_1 = 0.1073$, $wR_2 = 0.1267$	$R_1 = 0.1277$, $wR_2 = 0.1790$	$R_1 = 0.0896$, $wR_2 = 0.1395$	$R_1 = 0.0991$; $wR_2 = 0.1158$
Extinction coefficient	0.013(3)	0.006(8)	0.014(2)	
Major difference (e Å^{-3})	0.474 and −0.629	0.412 and 0.678	0.450 and −0.549	0.041 and −0.613

Table 2
Selected geometric parameters for the some copper (II) complexes with Schiff base ligands

Compound	Cu–N (Å)	Cu–S (Å)	Cu–O (Å)	S–C (Å)	O–C (Å)	Reference
[Cu(cden)]	1.966; 1.925	2.243; 2.258		1.728; 1.680		[26]
[Cu(napen)]	1.925		1.951			[28]
[Cu(cdnapen)]	1.930(4); 1.947(3); 1.940(4); 1.947(4)	2.2374(15); 2.2342(15)	1.921(3); 1.914(3)	1.725(4); 1.718(4)	1.305(5); 1.308(4)	this work
[Cu(salpd)]	1.938(11); 1.958(9)		1.857(10); 1.878(12)		1.293(17)	[31]
[Cu(cdpd)]	1.9498(30)	2.2225(11)		1.723(4)		[25]
[Cu(cdMeMeOsalpd)]	1.949(3); 1.993(3)	2.235(2)	1.888(3)	1.722(4)	1.307(4)	this work
[Cu(nappd)]	1.989(12); 1.971(13)		1.904(11); 1.917(12)			[30]
[Cu(cdnappd)]	1.921(5); 1.944(6)	2.227(3)	1.892(4)	1.697(7)	1.320(7)	this work
[Cu(cdMenappd)]	1.959(3); 2.002(3)	2.2295(11)	1.939(3)	1.713(4)	1.316(5)	this work

Schiff base ligands [21]. The analysis of the bond length within the metallocyclic part of the molecule is indicative of a strong delocalization of the π-electron density through the six member rings. For the cyclopentene fragment, the mean value for the S21–C221 bond length is 1.7150(7) Å, which is considerably lower than what is usually found for a single S–Csp^3 bond, 1.808(10) Å, and similar to the 1.712(17) Å attributed to the S–Csp^2 bond in thiophene, showing a high delocalization of the π-electron density in this part of the molecules [22]; in addition, the distances found between the C21/C41 and C22/C42 carbon atoms of the cyclopentene ring have a mean value within the range 1.439(5)–1.443(9) Å that is similar to the mean value for the Csp^2–Csp^2 bond in conjugated systems [22]. Finally, the similarity of the C21–N2 and C1–N1 bond length values is indicative that this fragment coordinates in a Schiff base mode. This electronic delocalization was reported for complexes containing this type of ligand with other metals [23,24] and for complexes of related ligands [25,26].

The cyclopropene ring defined by the atoms Cn1–Cn2–Cn3–Cn4–Cn5 (where n is 2 or 4) is puckered in all cases except the compound [Cu(cdMenappd)]. This puckering can be quantified in terms of the pseudorotation parameters P and τ [27]. In all cases the reference bond is Cn1–Cn2. For [Cu(cdnapen)], the pucker values P and τ are $P = 296.8(19)°$, $\tau = 11.5(4)°$ corresponding to a twist on C24 and C25 for molecule **A**, and $P = 80.9(19)°$, $\tau = 10.4(4)°$ corresponding to an envelope on C44 for molecule **B**. For [Cu(cdnappd)] these values are $P = 98.6(12)°$, $\tau = 23.2(5)°$ corresponding to an envelope on C24 and for [Cu(cdMeMeOsalpd)] $P = 89.4(6)°$, $\tau = 29.8(3)°$ corresponding to an envelope on C24.

All the Cu(II) complexes show a square planar geometry but with different degrees of tetrahedral distortion. The degree of the distortion will be quantified by measuring the dihedral angle, θ, between planes formed by the N/Cu/O and N/Cu/S atoms of the two semi-coordination spheres.

3.1.1. [Cu(cdnapen)]

The ORTEP representation of the structure of this complex, including the atom numbering scheme is shown in Fig. 1. The crystal structure determination revealed the existence of two independent molecules in the asymmetric unit. These are assigned as molecule **A** (labelled as Cu1) and molecule **B** (labelled as Cu2). The two molecules have different tetrahedral distortions relative to the square-planar geometry. Molecule **A** presents a dihedral angle of 5.28(17)° and molecule **B** of 11.52(9)°. In both of them, the geometry around the coordination centre is more planar than that in the homologous N_2S_2 complex [Cu(cden)] that presents an dihedral angle of about 20° [21]. On the other hand, the analogous N_2O_2 [Cu(napen)] seems to be more planar with $\theta \approx 7°$ [28].

The minimum distance between the copper atoms is 3.879 Å which rules out the existence of an interaction between them. This observation contrasts with that described for the homologous symmetric N_2O_2 complex, [Cu(napen)], for which the crystallographic results pointed to the existence of an interaction between the copper ion (placed in an apical position) of the complex and the donor oxygen atom of the above one.

3.1.2. [Cu(cdnappd)]

The molecular diagram of this complex, together with the atom numbering scheme is depicted in Fig. 2. The molecular structure revealed that the geometry around the coordination centre is a square planar one with a tetrahedral distortion. The dihedral angle is 37.36(25)°, higher than that reported for [Cu(nappd)], 6.1° [30], the analogous symmetric N_2O_2 complex, but lower than that shown by the analogous N_2S_2 complex, [Cu(cdpd)], which has a value of ca. 50° [25]. The aliphatic chain is in the *twist* conformation.

In this compound C18 acts as a hydrogen bond donor to atom O12 in the molecule at (x, $1.5 - y$, $0.5 + z$), so forming a C(6) chain [29] which runs parallel to the c-axis (Fig. 3). The C–H distance is 0.93 Å, the H···O distance is 2.48 Å and the C—O distance is 3.397(7) Å. The angle at H is 171°. The same O12 oxygen atom establishes a short contact with H1–C1 of the c-glide related complex, O12···H1–C1 (distance 2.64 Å).

3.1.3. [Cu(cdMenappd)]

The structure of [Cu(cdMenappd)] is depicted in Fig. 4. The propylenic aliphatic chain of the ligand assumes a

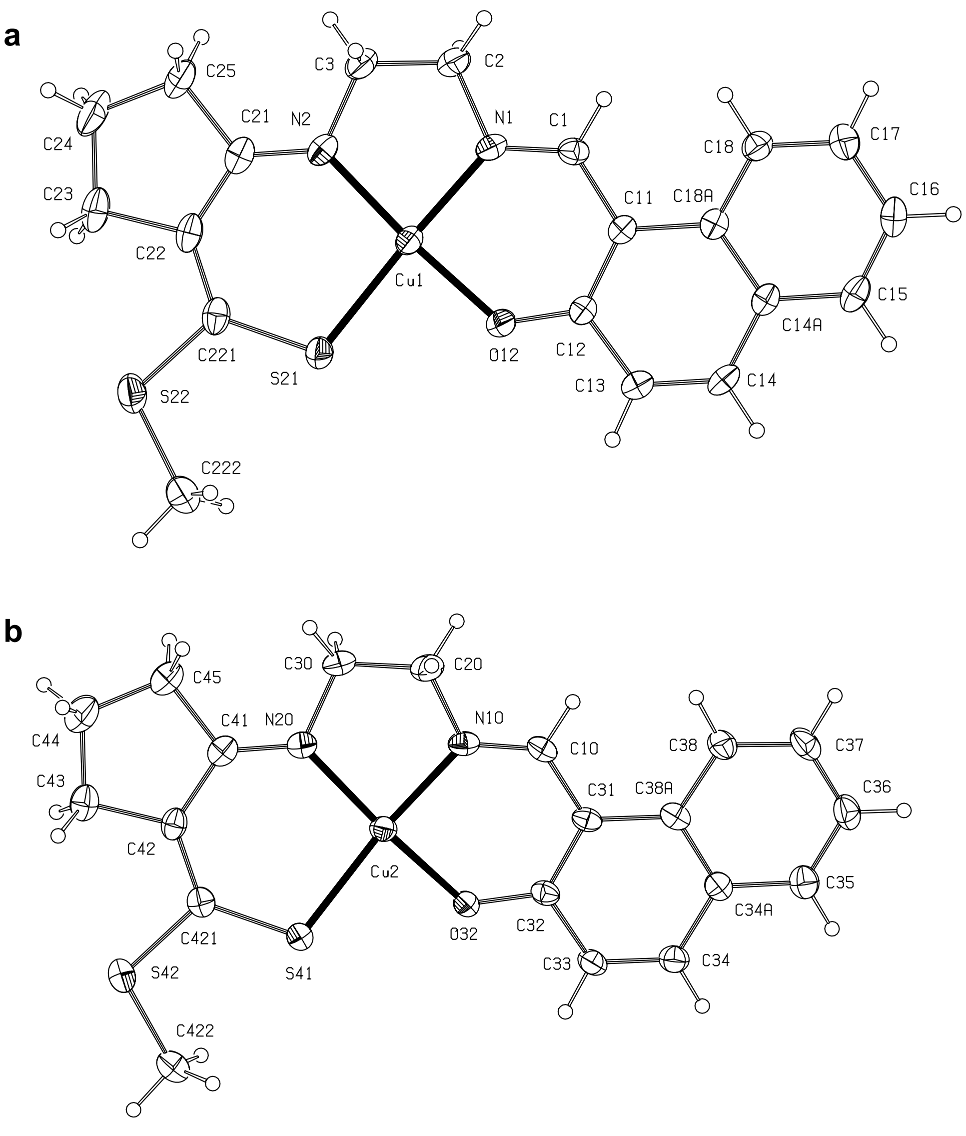


Fig. 1. A view of [Cu(cdnapen)] **A** (labelled with Cu1) and **B** (labelled with Cu2) with the adopted numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

"*boat*"-shape conformation in the complex. The coordination around the Cu(II) ion is square planar with a tetrahedral distortion. For this compound $\theta = 28.44(15)°$. This value is lower than that of 50° reported for [Cu(cdpd)] [25], and higher than the dihedral angle for the symmetric [Cu(nappd)], with a reported value of 6.1° [30].

3.1.4. [Cu(cdMeMeOsalpd)]

Fig. 5 shows the perspective view and the atomic numbering scheme for the [Cu(cdMeMeOsalpd)] complex. The trimethylenic chain of the ligand is *twisted* and the chelating rings assume an *umbrella* conformation relative to each other. The complex also presents some degree of tetrahedral distortion around the metal centre relative to the square-planar geometry. The dihedral angle between the N/Cu/S and N/Cu/O planes is 41.79(10)°. This complex is more tetrahedrally distorted than [Cu(salpd)] [31], for which the θ angle is ca. 21.0°, but the distortion value is similar to that for [Cu(Me$_2$salpd)], which is 43.8° [32]. Anyhow, the symmetric homologous N_2S_2 complex [Cu(cdpd)] [25] exhibits even higher distortion ($\theta = 50°$) showing that the presence of the sulfur atom also plays an important role in the geometrical distortion from the square planar shape in these complexes.

Our structural results point out some factors that can change the degree of tetrahedron distortion of these Cu(II) complexes, namely, (i) the number of ethylene groups in the ligand bridge and (ii) the type of donor atoms. Comparing the theta values for the [Cu(salen)]/[Cu(salpd)] (1.7° and 21°), [Cu(cden)]/[Cu(cdpd)] (20° and 50°) and [Cu(cdnapen)]/[Cu(cdnappd)] (5.5°/11.6° and 37.3°) set of pairs, it is clear that the three carbon atom chain induces a higher distortion than the two carbon atom chain. This has been reported for several other studies on Schiff base metal complexes that have even lower electronic preferences for square planar geometries.

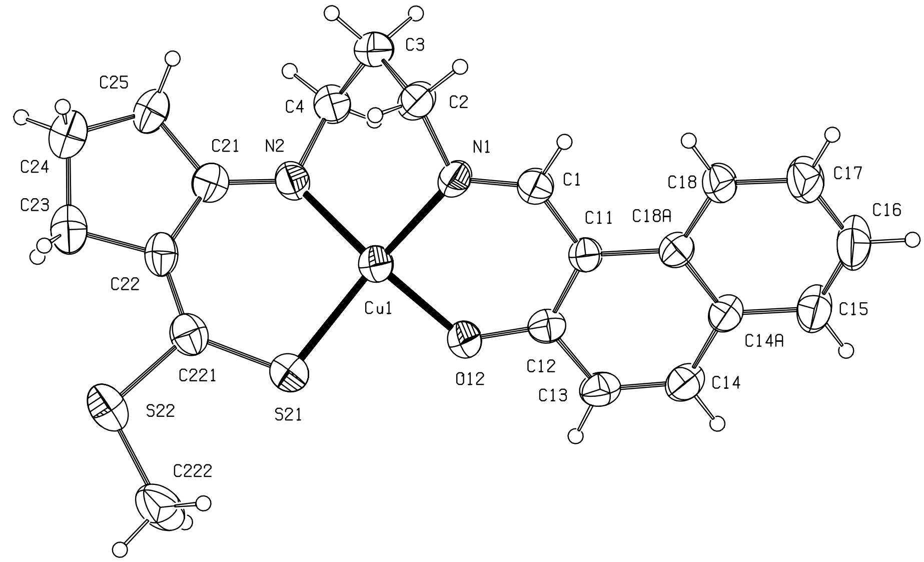


Fig. 2. A view of [Cu(cdnappd)] with the adopted numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

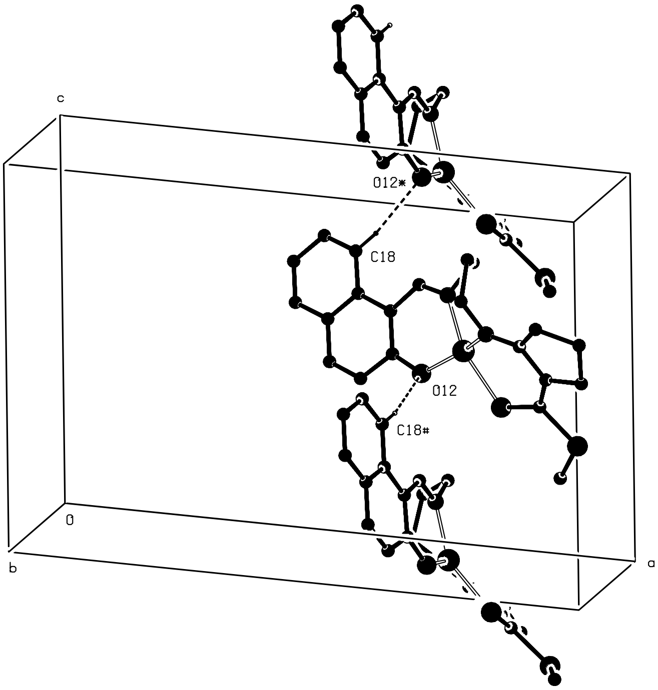


Fig. 3. Part of the structure of compound [Cu(cdnappd)] showing a C(6) chain running parallel to the *c*-axis. Hydrogen atoms not involved in the hydrogen bonding are omitted for clarity. The atom marked with an asterisk, (*), and hash, (#), are at symmetry positions (x, $1.5 - y$, $0.5 + z$) and (x, $1.5 - y$, $-0.5 + z$), respectively.

The complexes with an N_2O_2 coordination sphere are more planar than those with a N_2OS coordination sphere, that are, on the other hand, more planar than those with N_2S_2. A larger difference is observed for [Cu(nappd)]/[Cu(cdnappd)] and [Cu(cdpd)], which have 6.1°, 37° and 50° theta angles values, respectively. A sulfur donor, which gives a lower ligand field strength, shows a higher tendency than oxygen towards tetrahedral distortion.

3.2. Electron paramagnetic resonance spectroscopy

The EPR characterization of the complexes in dmf solution was made at room temperature and at 77 K. In Table 3, EPR parameters that were obtained after computational simulation of the experimental spectra are presented and in Fig. 6 a typical spectrum obtained for the complexes, together with the graphic computational simulation is shown.

The EPR parameters are in the range expected for tetra-coordinate copper (II) complexes with N_2S_2 and N_2O_2 coordination spheres and show the typical hyperfine splitting with the ^{63}Cu and ^{65}Cu nuclei. Super-hyperfine coupling with the two magnetically equivalent nitrogen nuclei (^{14}N, $I = 1$) is also observed either at room temperature or in frozen solution, in accordance with the similarity between the two nitrogen donor atoms revealed in the molecular structures of the complexes.

A comparison of the EPR parameters shows that the g and A values are very sensitive to the tetrahedral distortion of the complexes, as usually observed for tetra-coordinated copper (II), with a marked decrease of A values and an increase in g_1 with the tetrahedral distortion [33–36]. The dependence of the EPR parameters on the coordination sphere is not so important, and in fact the ERP parameters obtained for the N_2OS complexes are more similar to the N_2S_2 parent complexes than to the N_2O_2 copper (II) Schiff base complexes [37,38].

3.3. Electrochemistry

The results obtained in the electrochemical studies are summarized in Table 4. The symmetric N_2S_2 Cu(II) complexes were also studied under the same conditions for a direct comparison of the results. For all the complexes one anodic peak is observed in the potential range from

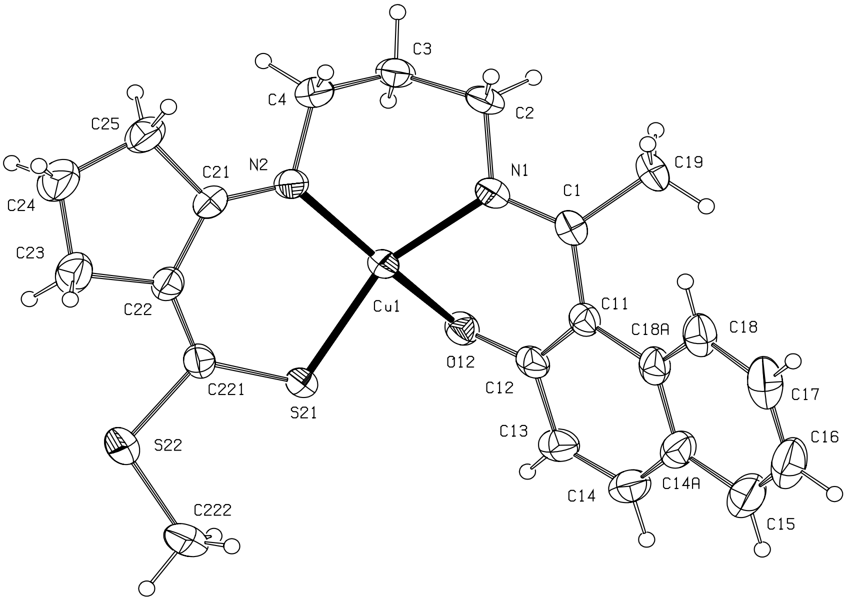


Fig. 4. A view of [Cu(cdMenappd)] with the adopted numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

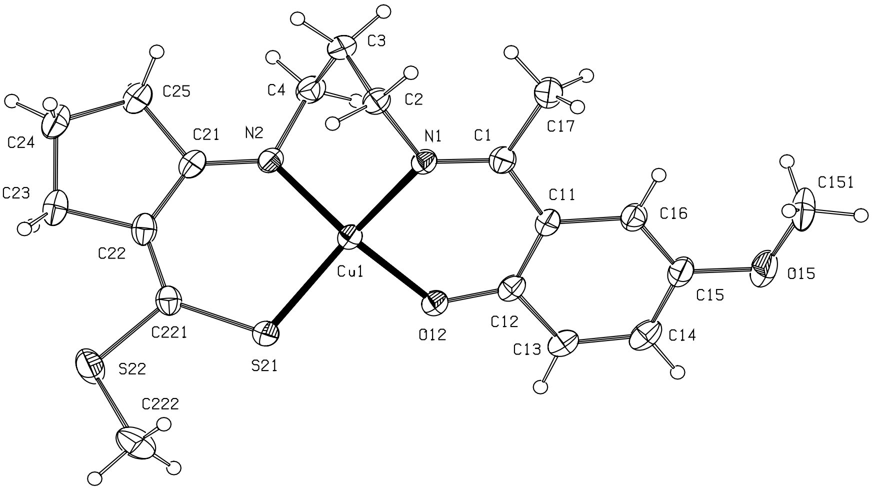


Fig. 5. A view of [Cu(cdMeMeOsalpd)] with the adopted numbering scheme. Displacement ellipsoids are drawn at the 30% probability level.

Table 3
EPR parameters for the studied complexes[a]

Complex	g_{iso}	A_{iso}	$A_{\mathrm{iso}}(\mathrm{N})$	g_1	g_2	g_3	A_1	A_2	A_3	$A_1(\mathrm{N})$	$A_2(\mathrm{N})$	$A_3(\mathrm{N})$
[Cu(cdnapen)]	2.076	84.0	14.5	2.186	2.117	2.060	208.0	[b]	38.0	14.5	[b]	[b]
[Cu(cdnappd)]	2.084	77.0	12.0	2.188	2.049	2.012	186.0	20.0	[b]	[b]	9.0	[b]
[Cu(cdMenappd)]	2.084	77.0	12.0	2.168	2.053	2.036	189.0	37.6	[b]	[b]	12.7	[b]
[Cu(cdMeMeOsalpd)]	2.085	74.5	12.2	2.169	2.051	2.028	180.0	25.0	[b]	12.5	12.5	[b]

[a] Hyperfine coupling constants in 10^{-4} cm^{-1}.

[b] The spectral resolution did not allow the determination of this value.

+0.7 V to +0.9 V, but no evidence for a corresponding cathodic peak is observed, except for the compound [Cu(cdnapen)]. The voltammograms are not repeatable, and a dark material precipitates at the electrode. For the compound [Cu(cdnapen)], the $i_{\mathrm{pc}}/i_{\mathrm{pa}}$ ratio increases with the scan rate, showing that the irreversible voltammetric behaviour is due to a slow chemical reaction after electron-transfer. In addition, in the negative potential scan, a cathodic peak is detected for all the complexes in the potential range from −0.8 V to −1.1 V. In this case, the corresponding anodic peaks are observed in the range from −0.6 V to −1.0 V, except for the compound

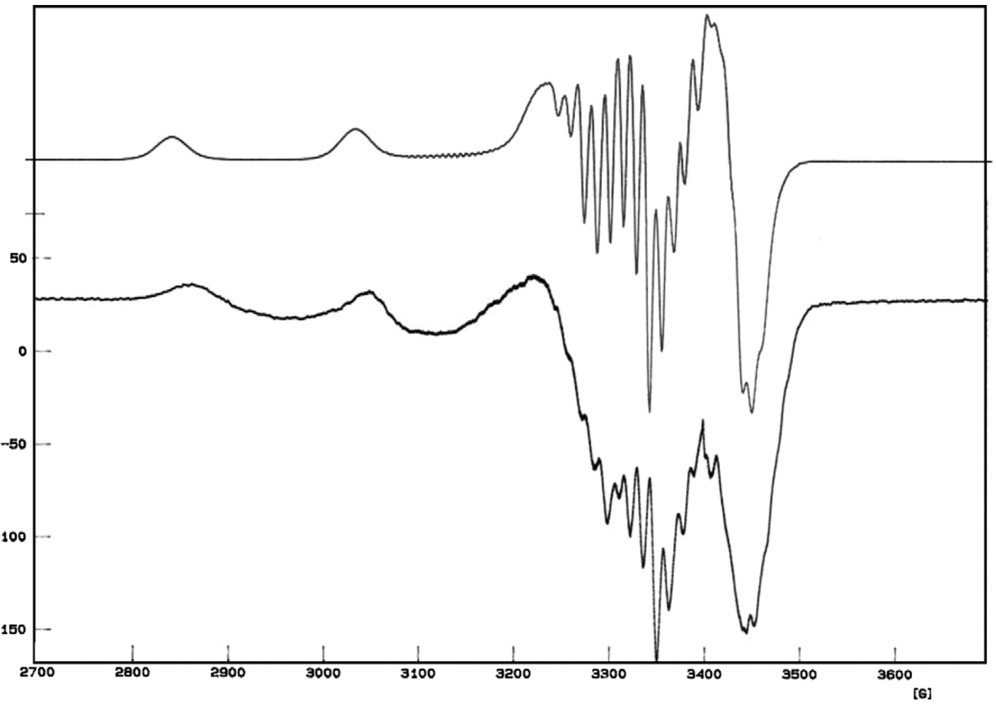


Fig. 6. EPR spectrum of [Cu(cdMenappd)] in DMF at 77 K (bottom) and simulation (top) using the software Symphonia WIN-EPR (Bruker).

Table 4
Voltammetric parameters obtained for the copper (II) complexes

Complex	E_{pa} (V)	E_{pc} (V)	ΔE (V)	i_{pa}/i_{pc}
[Cu(cdnapen)]	−0.978	−1.073	0.095	0.92[a]
[Cu(cdnappd)]	−0.780	−0.880	0.100	0.99[a]
[Cu(cdMenappd)]	−0.64	−0.80	0.16	[b]
[Cu(cdMeMeOsalpd)]	−0.770	−0.900	0.130	0.76[b]
[Cu(cden)]	−0.992	−1.070	0.078	0.93[a]
[Cu(cdpd)]	−0.80	−0.86	0.06	[b]

Potentials are reported in V relative to the Ag/AgCl (1 mol dm^{-3} NaCl) reference electrode and corrected for the Fc$^+$/Fc couple ($E_{1/2} = 0.485$ V). i_{pa} and i_{pc} values are base line corrected. Scan rate: 0.050 V s^{-1}.

[a] The i_{pa}/i_{pc} ratio decreases with the increase of scan rate.

[b] The i_{pa}/i_{pc} ratio increases with the increase in scan rate.

[Cu(cdMeMeOsalpd)], which shows totally irreversible behaviour. The variation of the CV parameters with scan rate shows that in all the other compounds the redox behaviour is not reversible. For compounds [Cu(cdnapen)], [Cu(cdnappd)] and [Cu(cden)], the i_{pc}/i_{pa} ratio decreases with the scan rate, typical of an irreversible electron transfer, whereas for compounds [Cu(cdMenappd)], [Cu(cdMeMeOsalpd)] and [Cu(cdpd)], the i_{pc}/i_{pa} ratio increases with the scan rate, showing that the reduced form undergoes a slow chemical reaction.

Due to the irreversible redox behaviour, it is not possible to correlate the redox potentials with the coordination spheres of the complexes, Nevertheless, the cathodic peak potential corresponding to the reduction of the copper (II) complexes seems to be lower for complexes with a dimethylene bridge than for those with propylene bridges. This trend is also observed for the reduction potentials for the Ni(II)/Ni(I) couple of the analogous Ni(II) complexes [15,16]. These observations have been attributed to the fact that the trimethylene bridge complexes are more tetrahedrally distorted and the distortion could favour the lower oxidation states for the metal complex. This is confirmed also for the compounds under study by the X-ray structural data. The reduction potentials obtained for the asymmetric complexes are similar to those obtained for homologous symmetric ones with the same number of ethylene residues in the bridge. This data is in agreement with the EPR results, and suggests that the change of a soft sulfur donor for a hardest oxygen donor does not significantly affect the properties of the complexes.

Acknowledgements

We thank the Institut fur Anorganische Chemie, Universitat Karlsruhe for allowing X-ray data collection. Lígia Gomes thanks financial support from the Fundação para a Ciência e Tecnologia (POCI/QUI/61873/2004).

Appendix A. Supplementary material

CCDC 640665, 640666, 640667 and 640668 contain the supplementary crystallographic data for [Cu(cdnapen)], [Cu(cdnappd)], [Cu(cdMenappd)] and [Cu(cdMeMeOsalpd)]. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2007.09.030.

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