A novel example of a direct interaction between the carbonyl oxygen, O(6), of a N(7)-bonded 6-oxopurine and copper(II). Preparation, spectroscopic study and crystal structure of bis(8-methylthiotheophyllinato)bis(pyridine)copper(II)

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(Received May 14, 1992; revised July 27, 1992)

Abstract

The preparation, spectroscopic study and crystal structure of the complex bis(8-methylthiotheophyllinato)bis(pyridine)copper(II), $[Cu(L)_2(py)_2]$, are reported. The complex crystallizes in the monoclinic system, space group $P2_1/c$ with $a=7.502(2)$, $b=20.352(4)$, $c=9.757(2)$ Å, $\beta=98.67(3)°$ and $Z=2$. The structure was solved for 4056 non-zero Mo Kα reflections ($R=0.040$). The structure consists of discrete $[Cu(L)_2(py)_2]$ molecules with the copper(II) atom located on a center of symmetry. Each molecule includes two *trans* N(7)/O(6) bidentate ligands and two *trans* pyridine molecules. The copper ligand environment can be described as a highly elongated octahedron with four strong Cu–N bonds forming an exact basal plane (Cu–N(7) = 1.999(2); Cu–N(15) = 2.032 Å) and two weak axial bonds (2.825(2) Å) to O(6) and O(6′) carbonyl oxygen atoms. This Cu–O(6) distance is the shortest observed in a copper(II) complex with a 6-oxopurine. Owing to the N(7)/O(6) bite of the theophyllinato chelate, the Cu–N(7) bond does not lie as the expected lone-pair direction of N(7) (C(8)–N(7)–Cu = 141.8(2); Cu–N(7)–C(5) = 114.9(2)°) and the O(6)–O(6′) axis is tilted 15.6° from the normal to the basal plane. The ESR and electronic spectra of the complex are consistent with the same structure being retained in CH_2Cl_2 solution. The ESR spectra of the complex in CH_2Cl_2 solution show nine lines of nitrogen superhyperfine splitting indicating clearly the coordination of four nitrogen atoms toward copper(II).

Introduction

It is widely accepted that the bifunctional binding modes of platinum antitumour complexes to DNA bases are likely to be responsible for their antitumour activity [1, 2]. Numerous investigations have confirmed that, in particular, *cis*-$[Pt(NH_3)_2Cl_2]$ prefers to form adducts in which the platinum coordinates to the N(7) positions of two adjacent guanine bases or an adenine and a guanine base on a single strand [1, 2]. Among the proposed bifunctional binding modes, the N(7)/O(6) chelate on guanine has been generally rejected on geometric grounds [3]. Recently, however, a semiempirical calculation on the interaction of model antitumour platinum compounds with guanine has shown that N(7)/O(6) chelation is possible [4]. Although so far there are no X-ray crystallographic or NMR results supporting the N(7)/O(6) chelate in platinum(II) complexes [1–3], structural evidence for its formation in Cu^{II}, Ti^{III} and Pt^{IV} complexes has been reported. Thus, in the complex (*N*-3,4-benzosalicylidene-*N*′,*N*′-dimethylethylenediamine)(theophyllinato)copper(II) [5], the O(6) was found to occupy an apical coordination site around copper, the Cu–O(6) distance (2.919(3) Å) being much longer than the Cu–N(7) distance (1.956(3) Å). In this case, even though the two bonding interactions are hardly comparable the values of the exocyclic bond angles at N(7), Cu–N(7)–C(8) and Cu–N(7)–C(5),

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0020-1693/92/$5.00

reveal that the chelate exists. The first crystallographic evidence for the formation of a balanced N(7)/O(6) chelate with a 6-oxopurine was provided by the complex bis(η^5-cyclopentadienyl)(theophyllinato)titanium(III) [6]. In this complex, the deprotonated theophylline is coordinated to Ti^{III} through the N(7) and O(6) atoms, with Ti–N(7) and Ti–O(6) distances of 2.213(3) and 2.278(2) Å, respectively. A further example of an N(7)/O(6) bonded theophylline was reported for a trimethylplatinum–theophylline hexamer [7]. In this complex each monodeprotonated theophylline bridges pairs of Me_3Pt groups through the N(7)/O(6) chelate and the N(9) atom with Pt–N(7), Pt–O(6) and Pt–N(9) distances of 2.17(2), 2.34(2) and 2.21(2) Å, respectively.

The present paper is devoted to the spectroscopic and structural studies of a copper(II) complex with a 6-oxopurine (8-methylthiotheophylline), having so far the strongest Cu–O(6) direct interaction. As in the N(7)/O(6) bonded theophyllinato complexes indicated above, the absence of active hydrogen atoms on the ligands precludes interligand hydrogen bonding to the O(6) carbonyl oxygen atom, thus favouring the N(7)/O(6) chelate formation in the complex discussed here.

Experimental

Physical measurements

Microanalyses of C, H and N were performed with a Perkin-Elmer 240 C analyzer. The IR spectrum were recorded in the 4000–180 cm^{-1} range on a Perkin-Elmer 983G spectrophotometer, using KBr and polyethylene pellets. ESR spectra of the compound in powder and CH_2Cl_2 solution were recorded at X-band frequencies with a Bruker 200 TT spectrometer operating at 9.4–9.5 GHz, at room temperature and 90 K. Thermogravimetric studies were carried out with a Mettler TG-50 thermobalance, using samples varying in weight from 9 to 10 mg and a heating rate of 5 °C min^{-1} in air atmosphere.

Preparation of the compounds.

The ligand 8-methylthiotheophylline (abbreviated hereafter as HL) was prepared as described in the literature [8]

Bis(8-methylthiotheophyllinato)bis(pyridine)copper(II)

$Cu(NO_3)_2\cdot 3H_2O$ (2.2 mmol, 0.53 g) was added over a solution of HL (4.4 mmol, 1 g) in concentrated ammonia (50 ml) and the resulting solution boiled for 5 min and then filtered to remove any small amount of copper(II) hydroxide. From the filtrate, after one day at room temperature, a red–brown powder of the complex $[Cu(NH_3)_2(L)_2]$ was obtained. m.p. 180–185 °C dec. *Anal.* Found: C, 34.7; H, 4.4; N, 25.9; Cu, 12.0. Calc. for $C_{16}H_{24}N_{10}O_4S_2Cu$: C, 35.1; H, 4.4; N, 25.6; Cu, 11.6%. NH_3 by TGA, 6.4%; calc. 6.2%. IR (cm^{-1}): 3338 ν_a(NH), 3164 ν_s(NH), 1675 $\nu(C_6{=}O)$, 1630 δ_a(NH), 1614 $\nu(C_2{=}O)$, 1585 ν(C=C), 1516 ν(C=N), 1400 δ_s(NH). To a heated suspension of this complex (1 g, 1.8 mmol) in water (50 cm^3) was added pyridine until a clear red solution was obtained. After filtration, the solution was allowed to stand at room temperature for three days, whereupon red–violet crystals of $[Cu(py)_2(L)_2]$ formed. m.p. 185–190 °C dec. *Anal.* Found: C, 46.8; H, 4.2; N, 20.9; Cu, 9.6. Calc. for $C_{26}H_{28}N_{10}O_4S_2Cu$: C, 46.5; H, 4.2; N, 20.8; Cu, 9.5% IR (cm^{-1}): 3062 ν(C–H), 1684 $\nu(C_6{=}O)$, 1642 $\nu(C_2{=}O)$, 1590 ν(C=C), 1527 ν(C=N).

X-ray data collection and structure determination of $[Cu(py)_2(L)_2]$

Single-crystal data collection was performed at ambient temperature with a Siemens R3m/V diffractometer using monochromatized Mo Kα radiation ($\lambda = 0.71069$ Å). The unit cell parameters for the red–violet crystals were obtained from least-squares refinement of 42 well-centered reflections ($25 > 2\theta > 35°$).

Crystal data

$C_{26}H_{28}N_{10}O_4S_2Cu$, $M = 672.25$, monoclinic, space group $P2_1/c$, $a = 7.502(2)$, $b = 20.352(4)$, $c = 9.757(2)$ Å, $\beta = 98.67(3)°$, $U = 1472.67$ Å^3, $Z = 2$, $D_c = 1.516$ g cm^{-3}, $F(000) = 694.00$, μ(Mo Kα) = 0.93 mm^{-1}.

The data were collected by ω–2θ scan mode ($3 > 2\theta > 56°$) with variable scan rate from 0.9 to 3.6° min^{-1} depending on the intensity. A total of 4056 reflections with $I > 4\sigma(I)$ was considered to have observable intensity and used in the structure analysis. Intensities of three check reflections measured every 120 min showed only statistical variation. The data were corrected for Lorentz and polarizations effects and for absorption.

The structure was solved by a combination of Patterson and Fourier techniques by using the SHELXTL-Plus program system [9]. In the final refinement, all non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed at calculated positions and then refined isotropically.

The function minimized was $\Sigma w(\Delta F)^2$ ($w = 1/\sigma_F{}^2$), resulting in a final $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ value of 0.040 and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.044$. The goodness-of-fit ratio was 1.30 for 198 parameters. Atomic coordinates for the non-hydrogen atoms are listed in Table 1.

Results and discussion

Crystal structure of $[Cu(L)_2(py)_2]$

The structure consists of discrete $[Cu(L)_2(py)_2]$ molecules. A perspective drawing of the molecule is given

TABLE 1. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($Å^2 \times 10^4$)

	x	y	z	U_{eq}[a]
Cu	0	0	0	296(1)
N(1)	2938(4)	−1881(1)	−1067(3)	432(10)
C(1)	4763(6)	−2028(2)	−360(4)	612(16)
C(2)	2178(6)	−2348(2)	−2050(4)	473(13)
O(2)	3001(4)	−2842(1)	−2288(3)	735(12)
N(3)	462(4)	−2221(1)	−2727(3)	443(10)
C(3)	−374(6)	−2666(2)	−3814(4)	604(15)
C(4)	−432(5)	−1655(1)	−2402(3)	344(10)
C(5)	371(4)	−1216(1)	−1432(3)	321(10)
C(6)	2117(5)	−1292(1)	−704(3)	347(10)
O(6)	2878(3)	−906(1)	165(2)	459(8)
N(7)	−870(4)	−718(1)	−1333(3)	332(8)
C(8)	−2301(4)	−898(1)	−2260(3)	337(10)
S(8)	−4226(1)	−403(1)	−2501(1)	537(3)
N(9)	−2114(4)	−1472(1)	−2943(3)	370(9)
C(9)	−5693(6)	−854(2)	−3785(5)	740(17)
C(10)	187(5)	−677(2)	2690(4)	528(13)
C(11)	−402(6)	−1008(2)	3766(4)	687(16)
C(12)	−2201(6)	−1165(2)	3684(4)	566(14)
C(13)	−3343(5)	−989(2)	2519(4)	461(12)
C(14)	−2660(5)	−653(1)	1478(3)	364(10)
N(15)	−928(4)	−499(1)	1553(3)	346(9)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

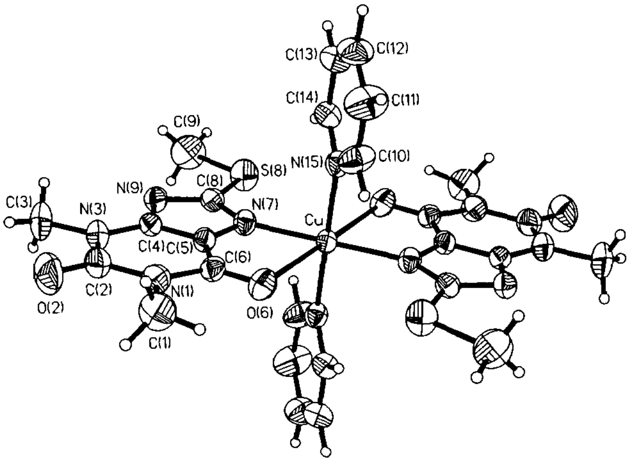

Fig. 1. A perspective view of the $[Cu(L)_2(py)_2]$ molecule with the atom labelling.

TABLE 2. Bond lengths (Å) of $[Cu(L)_2(py)_2]$

Cu–N(7)	1.999(2)	N(7)–C(5)	1.390(4)
O(6)–Cu	2.825(2)	N(9)–C(4)	1.345(4)
Cu–N(15)	2.032(3)	N(9)–C(8)	1.362(4)
N(1)–C(1)	1.468(5)	S(8)–C(8)	1.748(3)
N(1)–C(2)	1.408(4)	N(7)–C(8)	1.345(4)
O(2)–C(2)	1.221(4)	S(8)–C(9)	1.792(4)
N(3)–C(2)	1.379(5)	C(10)–C(11)	1.375(6)
N(3)–C(3)	1.462(4)	C(12)–C(11)	1.378(7)
N(3)–C(4)	1.393(4)	C(13)–C(12)	1.364(5)
C(5)–C(4)	1.373(4)	C(14)–C(13)	1.385(5)
N(1)–C(6)	1.417(4)	N(15)–C(14)	1.328(4)
C(5)–C(6)	1.401(4)	N(15)–C(10)	1.335(4)
O(6)–C(6)	1.232(4)		

TABLE 3. Bond angles (°) of $[Cu(L)_2(py)_2]$

N(7)–Cu–N(15)	90.3(1)	C(5)–C(4)–N(3)	121.2(3)
N(15)–Cu–N(7′)	89.7(1)	N(9)–C(4)–N(3)	126.6(3)
N(15)–Cu–N(15′)	180.0(1)	N(9)–C(4)–C(5)	112.2(3)
N(7)–Cu–O(6)	74.5(1)	C(4)–C(5)–C(6)	123.8(3)
N(15)–Cu–O(6)	88.6(1)	N(7)–C(5)–C(4)	107.1(3)
N(7′)–Cu–O(6)	105.5(1)	N(7)–C(5)–C(6)	129.1(2)
N(15′)–Cu–O(6)	91.4(1)	C(5)–C(6)–N(1)	112.0(2)
O(6′)–Cu–O(6)	180.0(1)	O(6)–C(6)–N(1)	122.6(3)
Cu–N(7)–C(8)	141.8(2)	O(6)–C(6)–C(5)	125.4(3)
Cu–N(7)–C(5)	114.9(2)	C(5)–N(7)–C(8)	103.3(2)
Cu–N(15)–C(10)	120.8(2)	S(8)–C(8)–N(7)	119.5(2)
Cu–N(15)–C(14)	121.3(2)	N(7)–C(8)–N(9)	115.6(3)
C(2)–N(1)–C(1)	115.9(3)	S(8)–C(8)–N(9)	124.9(2)
C(6)–N(1)–C(2)	126.5(3)	C(8)–S(8)–C(9)	101.9(2)
C(6)–N(1)–C(1)	117.7(3)	C(4)–N(9)–C(8)	101.9(2)
N(3)–C(2)–N(1)	116.9(3)	N(15)–C(10)–C(11)	122.3(4)
N(3)–C(2)–O(2)	121.7(3)	C(12)–C(11)–C(10)	119.6(4)
N(1)–C(2)–O(2)	121.4(3)	C(13)–C(12)–C(11)	118.3(4)
C(2)–N(3)–C(3)	119.9(3)	C(14)–C(13)–C(12)	119.1(4)
C(4)–N(3)–C(2)	119.5(3)	N(15)–C(14)–C(13)	122.9(3)
C(4)–N(3)–C(3)	120.6(3)	C(14)–N(15)–C(10)	117.9(3)

′ = $-x$, $-y$, $-z$.

in Fig. 1 together with the atomic labelling scheme. Selected bond lengths and angles are listed in Tables 2 and 3, respectively. Molecules of $[Cu(L)_2(py)_2]$ have C_i symmetry, with the Cu^{II} atom located on a center of symmetry. Each molecule includes two *trans* N(7)/O(6) bidentate 8-methylthiotheophyllinato ligands and two *trans* pyridine molecules.

The copper ligand environment can be described as a highly elongated octahedron with four strong Cu–N bonds forming an exact basal plane (Cu–N(7) = 1.999(2); Cu–N(15) = 2.032(3) Å) and two weak axial bonds (2.825(2) Å) to O(6) and O(6′) carbonyl oxygen atoms (′ = $-x$, $-y$, $-z$).

The Cu–O(6) distance in the present compound is similar to those found for the weak Cu^{II}–carbonyl oxygen axial bond in a series of centrosymmetric $Cu^{II}(barb)_2(L)_2$ complexes [10] (barb = 5,5′-diethyl and 5′-allyl-5-(2-bromoallyl)barbiturato anions; L = pyridine and β-picoline), but about 0.2 Å longer than those observed for weakly coordinated axial water or small anions [11]. Nevertheless, that distance is considerably shorter than the average Cu...O(6) distance observed for Cu^{II} complexes of the analogous ligand theophylline in which the O(6) atom is involved in interligand hydrogen bonds (3.75 Å) or does not exhibit any kind of bonding interaction (3.31 Å) [5]. Moreover, it may be pointed out that in the complex (*N*-3,4-benzosalicylidene-*N′N′*-dimethylethylenediammine)(theophyllinato)copper(II) monohydrate [5], the only example reported in the literature with a significant direct interaction between the O(6) carbonyl oxygen atom of a 6-oxopurine and the Cu^{II} atom, the Cu...O(6) distance was 0.1 Å longer than is observed in the present complex.

Even though, the Cu–O(6) bond seems to be weak, the N(7)/O(6) chelation in this complex may be evidenced from the exocyclic bond angles at N(7). As pointed out by some authors for theophylline metal complexes, the formation of interligand hydrogen bonds to O(6) causes a dissymmetry in the exocyclic bond angles at N(7), so that the M–N(7)–C(5) is larger than C(8)–N(7)–M by about 14°. A difference between these angles of 12° has been observed for the related $Zn(L)_2(H_2O)_2$ complex (L = 8-methylthiotheophyllinato anion) [12], in which one hydrogen atom of each water molecule is involved in a intramolecular hydrogen bond of length 2.661(3) Å to the O(6) atom of each N(7)-bonded 8-methylthiotheophyllinato anion. However, when a significant Cu...O(6) interaction exists, just the opposite dissymmetry is observed, the C(5)–N(7)–M angle being smaller than C(8)–N(7)–M. For instance, in the complexes bis(η^5-cyclopentadienyl)(theophyllinato)titanium(III) [6], $[Me_3PtThp]_6 \cdot 12Cl_3CH$ (Thp = theophyllinato anion) [7] and (*N*-3,4-benzosalicylidene-*N′*,*N′*-dimethylethylenediammine)(theophyllinato)copper(II) [5], which contain the theophyllinato monoanion coordinated in the N(7)/O(6) chelate mode, the C(8)–N(7)–M angle is larger than the C(5)–N(7)–M angle by 50, 39.2 and 21°, respectively. In the absence of either interligand hydrogen bonding involving O(6) or M–O(6) interaction, the Cu–N(7) bond lies roughly along the expected lone pair direction of N(7) and, therefore, the exocyclic angles at N(7) have close values. In the present compound, the C(8)–N(7)–Cu angle (141.8(2)°) differs from C(5)–N(7)–Cu (114.9(2)°) by 26.9° indicating N(7)/O(6) chelation of the ligand to Cu^{II}. Furthermore, the small N(7)/O(6) bite of the theophyllinato chelate tilts the O(6)–O(6′) axis *c.* 15.6° from the normal to the basal plane.

In addition to this, when compared with the values of the angles for the N(7)-8-methylthiotheophyllinato $Zn(L)_2(H_2O)_2$ [12] complex, the data for the present compound indicate that the O(6) coordination introduces significant variations in the six-membered ring. Firstly, an in plane motion of O(6) toward N(7) which decreases the C(5)–C(6)–O(6) and C(5)–C(6)–N(1) angles by 2.9 and 0.2°, respectively. The adjoining N(1)–C(6)–O(6) angle is increased in the opposite direction by 3.1°, thereby maintaining the planar environment of O(6). Secondly, a reduction of the other angle in the chelate ring (N(7)–C(5)–C(6)) by 1.5°. Such variation has also been observed for the balanced N(7)/O(6) complex bis(η^5-cyclopentadienyl)(theophyllinato)titanium(III) [6].

The remaining bond lengths and angles of 8-methylthiotheophylline in the present compound do not significantly differ from those reported for the complex $Zn(L)_2(H_2O)_2$ [12] and N(7)-bonded complexes of theophylline [13]. In the pyridine ligand, the C–C and C–N bond lengths and angles are within the expected ranges.

It may be noted that in all complexes containing N(7)/O(6) coordinated theophyllinato derivative anions, the metal ion is hard (class a): either Ti^{III}, Pt^{IV} or Cu^{II}. In view of this, it seems to be that the existence of significant O(6)...M metal interaction requires the presence of a hard metal ion. This is not surprising since the hard O(6) oxygen atom must show preference for hard metal ions.

Both crystallographically unique purine and pyridine molecules are essentially planar, as expected. The purine/pyridine dihedral angle of 90.7° indicates that these molecules are perpendicular to each other. This purine/pyridine angle value together with the twisting of the purine molecule 91.7° away from the coordination plane, is to relieve close interligand contacts. In good accord with this, the shortest intramolecular purine–pyridine contact distances of 3.206 Å (C(10)...N(7′)) and 3.233 (C(14)...N(7)) are approximately the sum of their van der Waals radii, which indicates that significant interligand steric crowding does not remain in the structure. This might be the reason by which within the CuN_4 plane, the N–Cu–N angles are very close to 90° (90.3(1)°, 89.7(1)°).

Finally, the shortest intermolecular contact distance N(9)–C(12″) of 3.340 Å (″ = *x*, *y*, *z* − 1), indicates that only van der Waals forces are present between molecules.

Infrared spectroscopy

The IR spectrum of the complex shows no bands due to NH stretching vibrations in the 2800–3200 cm^{-1} region, as expected. The bands for the ligand assigned to C=O stretching vibrations, at 1698 and 1646 cm^{-1}, as well as, C=C and C=N stretching vibrations at 1602 and 1547 cm^{-1}, respectively, undergo shifts to lower frequency upon complex formation. These bands are primarily sensitive to the loss of the imidazolic proton, and they occur practically at the same positions for the $Zn(L)_2(H_2O)_2$ complex [12] (L = 8-methylthiotheophyllinato anion) and all N(7)-bonded 8-substituted theophyllinato complexes [13]. Therefore, it seems to be that the N(7)/O(6) chelation in the present complex compared with the unidentate N(7)-binding introduces no significant changes in the 1500–1700 cm^{-1} region of the IR spectrum.

ESR spectroscopy

The polycrystalline ESR spectrum of $[Cu(L)_2(py)_2]$ at 90 K (Fig. 2(a)) is typical of a monomeric tetragonal Cu^{II} complex with either a $d_{x^2-y^2}$ or d_{xy} ground state [14] ($g_{\parallel}=2.25$, $g_{\perp}=2.07$, $A_{\parallel}{}^{Cu}=193\times10^{-4}$ cm^{-1}). Because it exhibits Cu^{II} hyperfine structure in the $g_{\parallel}$ region there is no significant exchange coupling between the Cu^{II} ions. This is due to the large distances between magnetic centres in the unit cell (the shortest Cu–Cu distance being 7.502(2) Å along the *a* axis).

The room temperature spectrum of the complex in CH_2Cl_2 solution (Fig. 2(b)) is isotropic, being characterized by the parameters $g_0=2.13$ and $A_0=79\times10^{-4}$ cm^{-1}. This spectrum indeed exhibits nine lines superimposed on the high-field copper hyperfine line. Such lines correspond to the ligand nuclear superhyperfine structure produced by the interaction of the unpaired electron with the ^{14}N nuclear spin ($I=1$) of pyridine and purine coordinated nitrogen atoms. The value of the isotropic nitrogen hyperfine splitting, $A^{N}{}_{iso}$, is *c.* 13×10^{-4} cm^{-1}.

The frozen-solution spectrum recorded at 90 K (Fig. 2(c)) seems to be also axial. From this, the parameters $g_{\parallel}=2.24$ and $A_{\parallel}=188\times10^{-4}$ cm^{-1} can be obtained. Owing to the overlap between $g_{\parallel}$ and $g_{\perp}$ regions, a value of $g_{\perp}=2.07$, is estimated by application of the relationship $g_{\perp}=1/2(3\ g_0-g_{\parallel})$. The nitrogen hyperfine interaction is *c.* 13×10^{-4} cm^{-1} in the perpendicular region.

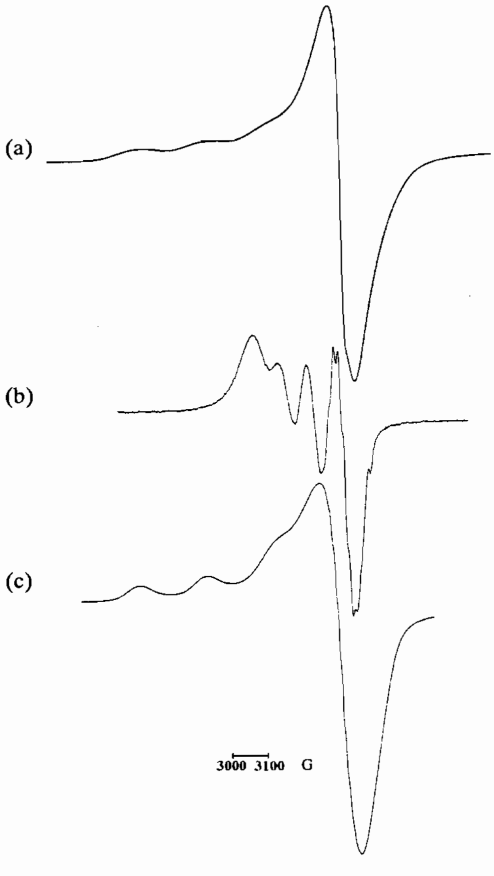

Fig. 2. X-band ESR spectra of $[Cu(L)_2(py)_2]$: (a) powder at 90 K; (b) CH_2Cl_2 solution at 298 K; (c) CH_2Cl_2 solution at 90 K.

As pointed out by some authors [15, 16], the observed tendencies for $A_{\parallel}$ to increase and $g_{\parallel}$ to decrease, with a more important relative variation for $A_{\parallel}$ than for $g_{\parallel}$, have been taken as parameters for the measure of the strength of in plane ligand fields under tetragonal geometry in Cu^{II} complexes. Bearing this in mind, the relatively large value of $A_{\parallel}=193\times10^{-4}$ cm^{-1} observed for the present complex is indicative of a high elongated tetragonal geometry around copper, in accord with the structural results. In fact, the $A_{\parallel}$ value is consistent with those observed for planar CuN_4 and elongated tetragonal octahedral CuN_4O_2 complexes [16–19].

It must be noted that the change from solid state to solution practically does not affect the values of $g_{\parallel}$ and $A_{\parallel}$, pointing out that the copper environment is not modified in CH_2Cl_2 solution. Also consistent with the ESR results is the similarity between the solid state and solution electronic spectra of the complex. For the solid complex, the reflectance spectrum exhibits, in the 10 000–20 000 cm^{-1} range, one absorption maximum at 19 500 cm^{-1} with a well-defined shoulder on the low-energy side at *c.* 15 900 cm^{-1}. The spectrum of the complex in CH_2Cl_2 solution exhibits bands at 16 000 ($\epsilon=62$) and *c.* 20 000 ($\epsilon=85$) cm^{-1}. The energies of these bands are appropriate for ligand field transitions of planar or tetragonal complexes with equatorial CuN_4 environment [17, 20, 21]. Tetragonal distortion from octahedral symmetry splits the lower E_g doublet into two singlets (B_{1g} and A_{1g}) and the upper T_{2g} triplet into a singlet (B_{2g}) and a higher lying doublet E_g. Therefore, the bands observed for our complex around 16 000 and 20 000 cm^{-1} may be tentatively assigned to the transitions $^2B_{1g}\leftarrow{}^2A_{1g}$ and $^2B_{1g}\leftarrow{}^2E_{g1}$, respectively.

Work is in progress to obtain complexes of the type $[Cu(L)_2(N)_2]$ (where N = nitrogen heterocyclic ligands), which might exhibit a stronger Cu–O(6) interaction.

Supplementary material

Hydrogen atom coordinates, thermal parameters, least-square planes and deviations of individual atoms from these planes, tables of observed and calculated structure factors and remaining bond distances and angles, are available from the authors on request.

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