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Crystal structure and magnetic properties of *catena*-μ-(pyrazine-*N*,*N*′)bis[(*p*-nitrobenzoyl)-trifluoroacetonato-*O*,*O*′]copper(II)

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Abstract

The X-ray crystal structure, variable-temperature magnetic susceptibilities and e.s.r. spectra are reported for the title complex. The complex crystallises as infinite chains in which the copper(II)-β-diketonate units are bridged axially by ambidentate pyrazine ligands with a Cu···Cu separation of 7.6700(2) Å. The magnetic susceptibility measurements in the range 5–325 K are consistent with the ferromagnetic intrachain exchange. The $S = 1/2$ Heisenberg ferromagnetic linear chain analysis results in magnetic parameters of $g = 2.12$ and $J/k = 0.6$ K. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

We reported earlier [1] that the 1:1 dioxane adduct of copper(II) *para*-substituted benzoyltrifluoroacetate, $[Cu(nbtfa)_2]_n$ possesses a linear chain structure and shows unusual, well resolved, nine line e.s.r. spectrum as a result of a combination of magnetic dipole coupling with the unpaired electron spins of the copper ions bridged by dioxane molecules and the copper hyperfine interaction. A simple point-dipole approximation used for the interpretation of the unusual splitting allowed to estimate the optimal values for the interdipole separation and the angle between the dipole–dipole vector and the z molecular axis in reasonable agreement with the values of 7.59 Å and 7° suggested for $[Cu(nbtfa)_2diox]_n$ by the X-ray structural analysis. The absence of any rich splitting in the e.s.r. spectrum of the related 1:1 pyrazine adduct in which the copper atoms might be similarly separated as in $[Cu(nbtfa)_2 diox]_n$, and a particular interest in pyrazine-bridged copper(II) complexes because of the potential for the propagation of exchange interactions over extended distances, prompted us to study the crystal structure and magnetic properties of the title compound. A perusal of literature shows that only few examples exists of structurally characterised pyrazine-bridged copper complexes in which the Cu···Cu separation exceeds 7.2 Å. The extended Cu···Cu distances of 7.867(7), 7.490(4) and 8.193 Å were found in polymers comprising axially bound pyrazine: $Cu(pyz)(hfac)_2$ [2], $Cu(pyz)(ttfa)_2$ [3] and along the axial direction in the two-dimensional polymer $Cu(pyz)_2(CH_3SO_3)_2$ [4], where pyz, hfac and ttfa denote pyrazine, hexafluroacetylacetonate and thenoilotrifluroacetonate anions, respectively. Magnetic susceptibility measurements of copper(II) complexes bridged axially by pyrazine molecules revealed either antiferromagnetic [5] or no exchange coupling [2,6].

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2. Experimental

2.1. Syntheses

The title compound was prepared by mixing of the copper(II) bis(*p*-nitrobenzoyl-trifluoroacetonate) (584 mg, 0.001 mmol) dissolved in boiling benzene (25 ml) with an equimolar solution of pyrazine (70 mg, 0.001mol) in the same solvent (20 ml). The solid adduct which separated after cooling was recrystallised from benzene to yield dark green crystals of X-ray quality. Yield 68%. *Anal.* Found: C, 43.2; H, 2.0; N, 8.2. Calc. for $C_{24}H_{14}F_6N_4O_8Cu$: C, 43.4; H, 2.1; N, 8.4%.

2.2. Instruments

Microanalyses were performed with a Carlo Erba MOD 1106 elemental analyser. Magnetic susceptibility data were recorded on powdered samples with the use of a Faraday type magnetometer fitted with a helium continuous flow cryostat. All data were corrected of diamagnetism of the ligands estimated from Pascal constants and temperature independent paramagnetism (TIP) equal to 60×10^{-6} cm^3 mol^{-1}. E.s.r. spectra were obtained using a JES-ME-3X spectrometer working at 9 GHz.

Table 1
Selected bond length (Å) and angles (°) for $[Cu(nbtfa)_2pyz]_n$

Bond lengths			
Cu–O(1)	1.953(1)	Cu–N(1')	2.445(2)
Cu–O(2)	1.950(1)		
Bond angles			
O(2) # 1–Cu–O(1)	88.17(6)	C(2)–O(1)–Cu	122.0(1)
O(2)–Cu–O(1)	91.83(6)	C(4)–O(2)–Cu	125.6(1)
O(1)–Cu–N(1′) # 1	92.24(6)	O(1)–C(2)–C(3)	129.5(2)
O(2) # 1–Cu–N(1′)	95.25(6)	O(2)–C(4)–C(3)	123.6(2)
O(2)–Cu–N(1′)	84.75(6)	O(2)–Cu–N(1′)–C(1′)	−43.8(2)
O(1)–Cu–N(1′)	87.76(6)	O(1)–Cu–N(1′)–C(1′)	−135.9(2)

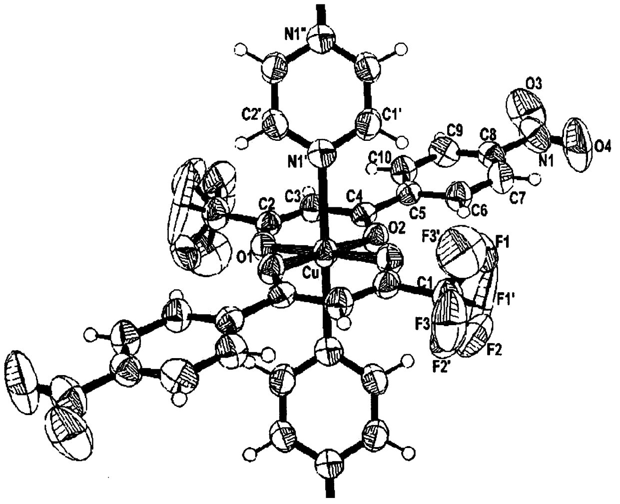

Fig. 1. An ORTEP drawing of the crystal structure of $[Cu(nbtfa)_2pyz]_n$ illustrating copper environment with the atomic numbering scheme.

2.3. Crystal data for the title compound

A crystal of $Cu(nbtfa)_2pyz$ with dimensions $0.45 \times 0.15 \times 0.10$ mm^3 was selected for the studies. Chemical formula for the monomeric unit is $C_{24}H_{24}F_6N_4O_8$. Cell parameters are $a = 7.6700(2)$, $b = 10.6700(3)$, $c = 15.9490(8)$ Å, $\beta = 95.443(1)°$, $V = 1299.36(7)$ Å^3. Crystal system is monoclinic, space group $P2_1/n$, number of formulae per unit cell $Z = 2$. All the intensity data were collected on a Kappa CCD diffractometer using graphite monochromatised Mo K_α radiation of wavelength $\lambda = 0.71073$ Å, with a scan mode $\omega–2\theta$. Reflections (5325) were collected in the range $3.07 < \theta < 27.51$, 2939 of which were unique ($R_{int} = 0.24$). Coverage of the unique set up to $\theta = 27.51°$ is in 98.8% complete. The crystal structure was solved by direct methods and refined by full matrix least squares technique with program systems SHELXS-97 [7] and SHELXL-97 [8], respectively. Non-hydrogen atoms were treated anisotropically. Hydrogen atoms were introduced at calculated positions and allowed to ride with isotropic displacement factors 1.2 times larger than those of their hosts. The refinement of F^2 was carried out against all (2939) reflections. The number of refined parameters is 225. The agreement factors defined as $R = [\Sigma(|F_o| - |F_c|)/\Sigma|F_o|]$ and $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]$ where $w = 1/[\sigma^2(F_o)^2 + (0.0529P)^2 + 0.4165P]$ and $P = (F_o^2 + 2F_c^2)/3$ were as follows: $R = 0.0516$ and $R_w = 0.1048$ for all (2939) reflections, but $R = 0.0388$ and $R_w = 0.0989$ for 2409 reflections with $I > 2\sigma(I)$. Selected geometric parameters are listed in Table 1.

3. Results and discussion

X-ray diffraction studies have shown that the title compound forms a linear coordination polymer with $Cu(nbtfa)_2$ moieties bridged by pyrazine (pyz) molecules. The view of a part of the chain polymeric structure with the numbering scheme is shown in Fig. 1.

The copper(II) atom is hexacoordinate where the sphere about any copper atom includes four short (1.95 Å) in plane bonds to the oxygen atoms of the β-diketonate ligands and two longer (2.445(2) Å) out of plane bonds to the pyrazine nitrogens and moreover a range of angles around the metal centre (from 84.75(6) to 95.25(6)°) giving rise to the distorted tetragonal 4 + 2 coordination. Copper atoms are disposited in crystallographic inversion centres, their relative positions being (0,1/2,0). Pyrazine molecules bridge the copper atoms to give a polymeric chain propagating in the crystallo-

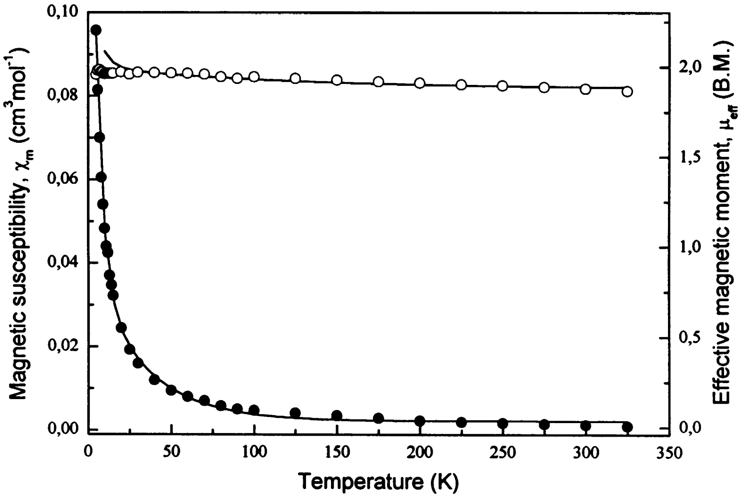

Fig. 2. Temperature dependence of the molar susceptibility (●) (the product of gram susceptibility and molecular weight of the monomeric unit) corrected for diamagnetism and TIP, and of the effective magnetic moment (○) for $[Cu(nbtfa)_2pyz]_n$. Calculated dependences are shown as solid lines.

graphic direction [100]. The plane of pyrazine ring is oriented at nearly right angle (92.4°) to the equatorial plane defined by Cu, O(1), O(2), O(1) # 1, and O(2) # 1 atoms and twisted with respect to the Cu–O(1) and Cu–O(2) bonds what can be seen from the torsion angles − 43.8(2)° [O(2)–Cu–N(1′)–C(1′)] and − 135.9(2)° [O(1)–Cu–N(1′)–C(1′)]. The projection of the normal to the pyrazine plane on the CuO_4 plane is at 43.27(9) and 48.63(8)° to the Cu–O(1) and Cu–O(2) bonds, respectively. These angles are much different from the 8.5° angle at which the pyrazine ring is oriented with respect to the Cu–O bond in $[Cu(hfac)_2pyz]$. The conjugated C_3O_2 fragments of β-diketonate fragments are each closely coplanar (maximum deviation from the least squares plane defined by these atoms is 0.0130(2) Å) and are more canted to the basal plane (dihedral angle 16.46(7)°) than these fragments in $[Cu(nbtfa)_2diox]_n$ (dihedral angle 10.9(4)°). There is a considerable asymmetry of the six-membered chelate ring incorporating this fragment reflected by the external angles at O(1), O(2), C(2) and C(4) atoms. The C_6 skeleton of the aromatic ring is oriented at 17.13(6)° to the basal plane, while the nitro group has a dihedral angle of 10.9(4)° for its associated C_6 aromatic plane. The trifluoromethyl groups are disordered and each occurs at two different orientations. High thermal parameters for fluorine atoms are consistent with a rapid interconversion between these orientations. The Cu–O(1) and Cu–O(2) bond lengths of 1.953(2) and 1.950(2) Å, respectively differ only marginally from the average values of Cu–O bond lengths found in analogous linear polymers comprising axially coordinated bifunctional ligands being 1.949(4) Å in $[Cu(nbtfa)_2diox]_n$, 1.964(7) Å in $[Cu(hfac)_2pyz]_n$ and 1.956(4) Å in $[Cu(ttfa)_2pyz]$. The insignificant difference in Cu–O(1) and Cu–O(2) bond lengths is conspicuous in comparison with the apparent differences of 0.080 Å and 0.026 Å found in $[Cu(hfacac)_2pyz]_n$ and $[Cu(ttfa)_2pyz]_n$, respectively. The Cu–N bond length of 2.445(6) Å is apparently shorter than that of 2.529(9) Å in $Cu(hfacac)_2pyz]_n$ and significantly longer than that of 2.337(3) Å in $[Cu(ttaca)_2pyz]_n$. The bonds and angles of the pyrazine systems agree with the observed values in $[Cu(hfac)_2pyz]_n$ and in $[Cu(pyz)_2(ClO_4)_2]_n$ [9].

Magnetic susceptibilities of $Cu(nbtfa)_2pyz$ were measured in the temperature range 5–325 K. The χ_m and μ_{eff} versus T plots for the compound are shown in Fig. 2.

The compound has the 325 K temperature effective magnetic moment of 1.84 μ_{BM}. However, when the temperature is lowered the μ_{eff} value increases and reaches a maximum of 2.00 μ_{BM} at 10 K and then decreases. The variation of magnetic susceptibility with temperature in the 10–325 K range is consistent with a weak ferromagnetic coupling between copper atoms within any chain and could satisfactorily be fitted following the Baker et al. [10] equation:

$$\chi_m = (N\beta^2 g^2/4kT)[(1 + Ax + Bx^2 + Cx^3 + Dx^4 + Ex^5)/(1 + Fx + Gx^2 + Hx^3 + Ix^4)]^{2/3}$$

obtained from an expansion for the $S = 1/2$ Heisenberg ferromagnetic linear chain model, where $x = 2J/kT$ and $A = 5.7979916$, $B = 16.902653$, $C = 29.376885$, $D = 29.832959$, $E = 14.036918$, $F = 2.7979916$, $G = 7.0086780$, $H = 8.6538644$, $I = 4.5743114$, and the ferromagnetic interaction is represented by positive J value.

The best fit to the ferromagnetic $S = 1/2$ Heisenberg regular chain model was obtained for $g = 2.12$ and $J/k = 0.60$. The decrease of μ_{eff} below 10 K is most likely due to an intrachain antiferromagnetic interaction. The magnetic properties of the title complex reflect a ferromagnetic exchange coupling between the copper ions not encountered in unsubstituted pyrazine-bridged copper complexes. A different magnetic behaviour of $[Cu(nbtfa)_2pyz]_n$ to that of $[Cu(nbtfa)_2diox]_n$ in spite of similarities in the shortest Cu···Cu intrachain (7.6700(2) vs 7.587(2) Å) and interchain (10.0478(2) vs 11.262(3) Å) separations suggests that the exchange of the unpaired electron spin states in the title compound occurs via the π-electron system of pyrazine and results in from an d–π overlap. Richardson et al. [11] pointed out that for an axially bridged copper(II) complex, in which the site symmetry around the copper atom is C_{2h}, the only symmetry allowed overlap with the pyrazine π-system arises from $d_{xy}-\pi$ (b_{1g}) overlap and that under that symmetry some of the unpaired spin density may be incorporated in the d_{xy} orbital. Some structural features of the title compound like a more favourable orientation of the pyrazine ring with respect to the d_{xy} orbital and a shorter axial Cu–N bond than in $[Cu(hfac)_2pyz]_n$ can result in an efficient $d_{xy}-\pi$ overlap and a $d_{xy}-\pi-d_{xy}$ superexchange not observed in $[Cu(hfac)_2pyz]_n$. The axial bridging of pyrazine nitrogens, a long Cu–N bond and parallelism of pyrazine rings form a different bridging arrangement than that in Cu(pzdc)HCl [12], the only reported so far ferromagnetic pyrazine-bridged copper(II) complex in which nitrogen atoms of disubstituted pyrazine ligands (pzdc denotes the 2,3-pyrazinedicarboxylate anion) are coordinated equatorially, the Cu–N bond length of 2.0 Å is normal, pyrazine ring is approximately perpendicular to the next pyrazine ring in the chain, and the geometry about pentacoordinated copper(II) is square pyramidal.

The X-band e.s.r. spectrum was recorded for undoped and powdered sample. In contrast to the well-resolved unusual nine-line splitting in the $g_\parallel$ region of the powder spectra for the similarly magnetic diluted $[Cu(nbtfa)_2diox]_n$, the title compound gave a extremely broad axial spectrum with $g_\parallel = 2.34$, $g_\perp = 2.10$, $A_\parallel = 1.66 \times 10^{-2}$ T. Its pattern suggests that at the room temperature there is a predominance of non-coupled over coupled copper ions due to a significant reduction of spin–spin interactions by thermal motions, evident also from the negligibly small value of $|J|/kT = 0.002$ at 300 K. Broad spectrum in comparison with that resolved in the already mentioned dioxane adduct suggests a great influence of extremely weak spin–spin interactions on various dynamical processes involving magnetic exchange and dipole–dipole interactions within the chain and throughout the solid.

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 152154 for compound *catena*-μ-(pyrazine-*N*,*N′*)bis[(*p*-nitrobenzoyl)trifluoroacetonato-*O*,*O′*]copper(II). Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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