Synthesis and Crystal Structure Determination of a One-dimensional End-to-end Cyanate-bridged Copper(II) Compound†

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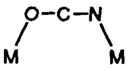
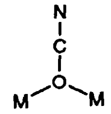
The compound $[\{CuL(\mu\text{-}NCO)\}_n][ClO_4]_n$ **1** (L = *N,N,N',N'',N''*-pentamethyl-3-azapentane-1,5-diamine) was synthesized and characterized. The crystal structure was determined by single-crystal X-ray analysis: orthorhombic, space group $P2_1nb$, a = 6.534(2), b = 10.945(3), c = 22.683(4) Å, Z = 4. The magnetic behaviour was recorded between 290 and 2 K, showing antiferromagnetic coupling. The magnetic susceptibility data were fitted to the expression for a homogeneous $S = \frac{1}{2}$ linear chain, giving the parameters $2J = -1.26$ cm^{-1} and g = 2.10. Polycrystalline powder ESR spectra recorded at 4, 77, 180 and 298 K remained unchanged, showing axial distortion with $g_{\parallel}$ = 2.21 and $g_{\perp}$ = 2.06. The single-crystal ESR spectrum was also recorded at room temperature: g_1 = 2.059, g_2 = 2.055, g_3 = 2.213.

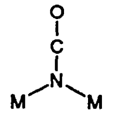
The cyanate ion, like the most widely studied azide, can act as a bridging ligand between two metal atoms in an end-to-end (**a**) or an end-on fashion (**b**, **c**). In cyanate-bridged polynuclear copper(II) compounds the end-on co-ordination mode is usually found. Indeed, all reported dinuclear copper(II) cyanate-bridged compounds exhibit end-on co-ordination,[1-8] three structural examples have been reported of two-dimensional end-to-end cyanate-bridged copper(II) compounds[9-11] and only one structural example of a one-dimensional end-to-end cyanate-bridged compound has been reported, $[\{Cu(NCO)_2(ampy)_2(H_2O)\}_n]$[12] (ampy = 3-aminopyridine), which comprises an alternating $[Cu(ampy)_2(H_2O)_2\text{–}NCO\text{–}Cu(ampy)_2(NCO)_2\text{–}OCN\text{–}]_n$ chain.



a



b



c

We now present the synthesis and structural study of the one-dimensional compound $[\{CuL(\mu\text{-}NCO)\}_n][ClO_4]_n$ (L = *N,N,N',N'',N''*-pentamethyl-3-azapentane-1,5-diamine), the first homogeneous copper(II) end-to-end cyanate-bridged compound. The ligand L was chosen with the aim of continuing the ESR studies started by Hendrickson[13] and Gatteschi and their co-workers[14] on the dinuclear $[Cu_2L_2(\mu\text{-}N_3)_2]^{2+}$ system, but with cyanate as bridging ligand.

Experimental

Synthesis of $[\{CuL(\mu\text{-}NCO)\}_n][ClO_4]_n$ **1**.—Copper(II) perchlorate hexahydrate (0.003 mol), L (0.003 mol) and potassium cyanate (0.003 mol) in water (75 cm^3) were mixed. From this solution blue single crystals of complex **1** suitable for X-ray analysis were collected 2 weeks later (Found: C, 31.7; H, 6.2; Cl, 9.4; N, 14.7. Calc. for $C_{10}H_{23}ClCuN_4O_5$: C, 31.7; H, 6.1; Cl, 9.4; N, 14.8%).

Spectral and Magnetic Measurements.—The IR spectra were recorded on a Nicolet 520 FT-IR spectrometer. Magnetic susceptibility measurements in the range 300–2 K and magnetization measurements at 15 and 2 K were carried out on an MPMS (5.5 T) Quantum Design instrument (with a SQUID detector). Diamagnetic corrections were estimated from Pascal tables. The ESR measurements were made with a Bruker ES200 spectrometer at X-band frequency, and an Oxford liquid-helium cryostat for variable-temperature work.

X-Ray Crystallography.—A prismatic blue crystal (0.1 × 0.1 × 0.1 mm) was selected and mounted on an Enraf–Nonius CAD4 diffractometer. Unit-cell parameters were determined from automatic centring of 25 reflections ($12 < \theta < 21°$) and refined by the least-squares method. Intensities were recorded with graphite-monochromatized Mo-Kα radiation (λ 0.710 69 Å). 2565 Reflections were measured in the range $2 < \theta < 30°$, 2542 of which were independent (R_{int} = 0.005); 2486 were assumed as observed, applying the condition $I > 2.5\sigma(I)$. Three reflections were measured every 2 h as orientation and intensity controls; no significant intensity decay was observed. The crystallographic data, conditions used for the intensity data collection, and some features of the structure refinement are listed in Table 1. Lorentz-polarization and extinction [coefficient = 0.006(2)] but not absorption corrections were made. The structure was solved by Patterson synthesis, using the SHELXS computer program,[15] and refined by full-matrix least squares with the SHELX 93 program.[16] The function minimized was $\Sigma w||F_o^2| - |F_c^2||^2$, where $w = [\sigma^2(F_o) + (0.1254P)^2 + 2.1781P]^{-1}$ and $P = (F_o^2 + 2F_c^2)/3$: values of f, f' and f'' were taken from ref. 17.

The cyanate and two oxygen atoms of perchlorate were located in disordered positions, an occupancy factor of 0.5 being assigned according to the maximum in the Fourier synthesis. The positions of 24 hydrogen atoms were computed and refined with an overall isotropic thermal parameter, using a riding model. Maximum shift/e.s.d. = 0.1; maximum and minimum peaks in the final difference synthesis 0.7 and −0.7 e Å^{-3}. Final atomic coordinates are given in Table 2.

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.
Non-SI unit employed: G = 10^{-4} T.

Table 1 Crystallographic data for [{CuL(μ-NCO)}$_n$][ClO$_4$]$_n$

Formula	(C$_{10}$H$_{23}$ClCuN$_4$O$_5$)$_n$
M	378.31
Crystal system	Orthorhombic
Space group	*P*2$_1$*nb*
a/Å	6.534(2)
b/Å	10.945(3)
c/Å	22.683(4)
U/Å^3	1622.2(7)
Z	4
D$_c$/g cm^{-3}	1.549
F(000)	788
T/°C	25
μ(Mo-Kα)/cm^{-1}	15.36
Scan method	ω–2θ
Observed reflections [$I \geqslant 2\sigma(I)$]	2468
No. of parameters refined	236
R^a	0.046
wR^b	0.124

^{a} $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR(F_o) = \Sigma w||F_o| - |F_c||/\Sigma|F_o|$.

Table 2 Final atomic coordinates (×10^4) for [{CuL(μ-NCO)}$_n$]-[ClO$_4$]$_n$

Atom	*x*	*y*	*z*
Cu	2 878	1 271(1)	860(1)
Cl	7 905(6)	5 798(1)	1 731(1)
O(1)	6 326(16)	948(12)	622(6)
C(1)	6 764(18)	329(15)	211(8)
N(1)	2 282(23)	360(12)	157(7)
O(1′)	9 365(19)	927(13)	633(6)
C(1′)	9 017(20)	245(14)	222(7)
N(1′)	3 770(18)	257(15)	186(6)
N(2)	3 418(9)	−152(4)	1 431(2)
N(3)	3 477(9)	2 271(4)	1 586(2)
N(4)	2 867(21)	2 944(3)	439(2)
C(2)	2 909(23)	280(5)	2 030(2)
C(3)	2 650(37)	1 621(7)	2 071(3)
C(4)	2 900(38)	3 507(5)	1 472(2)
C(5)	3 175(22)	3 891(5)	873(2)
C(6)	2 285(15)	−1 259(6)	1 301(4)
C(7)	5 618(12)	−457(7)	1 379(3)
C(8)	5 667(12)	2 384(6)	1 730(3)
C(9)	5 386(13)	3 061(6)	269(4)
C(10)	1 956(19)	3 064(8)	−93(3)
O(2)	7 739(20)	4 987(6)	1 247(2)
O(3)	7 844(28)	5 124(6)	2 263(2)
O(4)	10 092(58)	6 029(30)	1 592(20)
O(4′)	9 191(70)	6 738(37)	1 795(16)
O(5)	5 719(21)	6 095(15)	1 698(8)
O(5′)	6 894(49)	6 853(22)	1 650(12)

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Results and Discussion

Infrared Spectrum.—The IR spectrum shows absorption bands corresponding to bonded NCO ions at 2271m, 2204s (CN) and 1323m cm^{-1} (CO). The unco-ordinated perchlorate anion appears at normal frequencies (1147s, 1119s, 1088s and 625m cm^{-1}).

Crystal Structure.—The structure of [{CuL(μ-NCO)}$_n$]-[ClO$_4$]$_n$ **1** consists of the one-dimensional system [{CuL(μ-NCO)}$_n$]$^{n+}$, isolated by ClO$_4^-$ anions. The copper(II) atoms are bridged by cyanate ions in an end-to-end fashion, giving the first end-to-end cyanate-bridged homogeneous copper(II) chain. An ORTEP[18] drawing with the atom-labelling scheme and a view of the unit cell are shown in Fig. 1. The main bond lengths and angles are given in Table 3. The copper atom is five-co-ordinated by the three N atoms of the L ligand, one N atom of cyanate and one O atom of the other bridging cyanate group. The geometry of the structural unit [CuL(μ-NCO)]$^+$ can be described as intermediate between a trigonal bipyramid and a square-planar pyramid, but closer to the latter, since the geometric parameter Γ, an index of the degree of trigonality,[19] is equal to 0.230 (Γ = 1 for an ideal trigonal bipyramid, 0 for an ideal square-planar pyramid). The three N atoms of the ligand L and the copper atom are in the same plane. The Cu–N(1)–C(1^{II}) and Cu–O(1)–C(1) angles in the bridge are, respectively, 169.0(14) and 119.9(10)°. The Cu–N(1) and Cu–O(1) distances are, respectively, 1.920(14) and 2.344(10) Å. The Cu ⋯ Cu distance is 5.80 Å. For comparison, in the one-dimensional compound [{Cu(NCO)$_2$(ampy)$_2$(H$_2$O)}$_n$][12] the Cu–N–C (cyanate) and Cu–O–C (cyanate) angles are, respectively, 161.2 and 118.5° and the Cu–N (cyanate) and Cu–O (cyanate) distances are 1.952(7) and 2.663(6) Å, respectively.

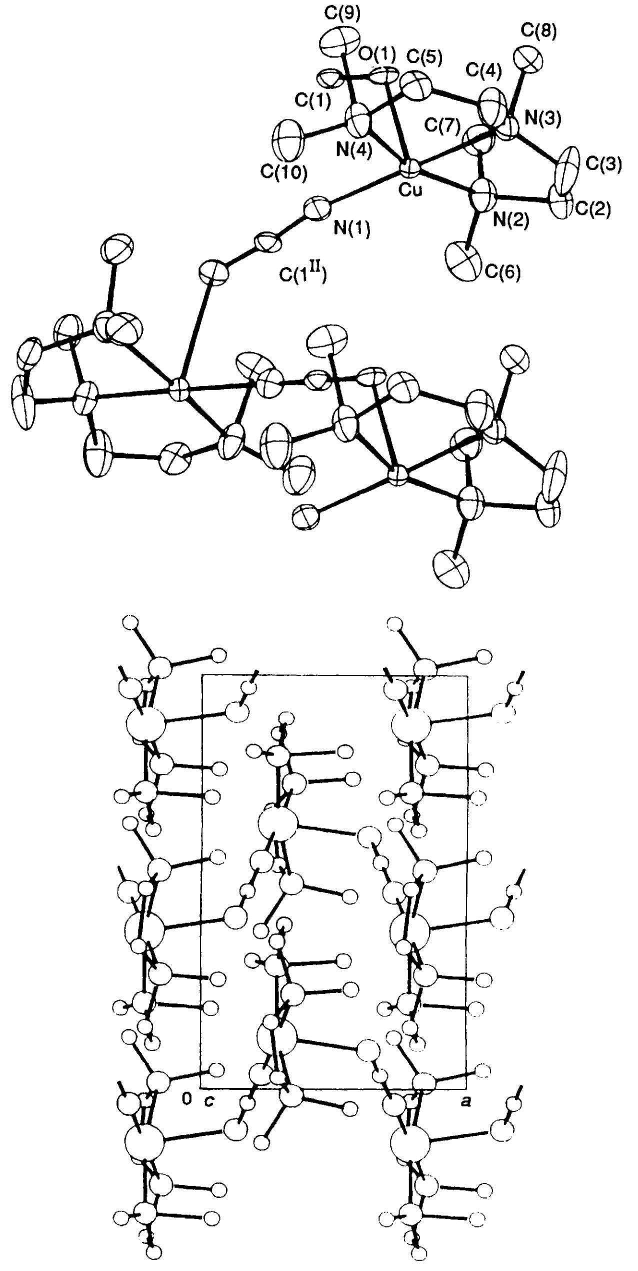

Fig. 1 An ORTEP drawing with the atom-labelling scheme and a view of the unit cell for [{CuL(μ-NCO)}$_n$]$^{n+}$

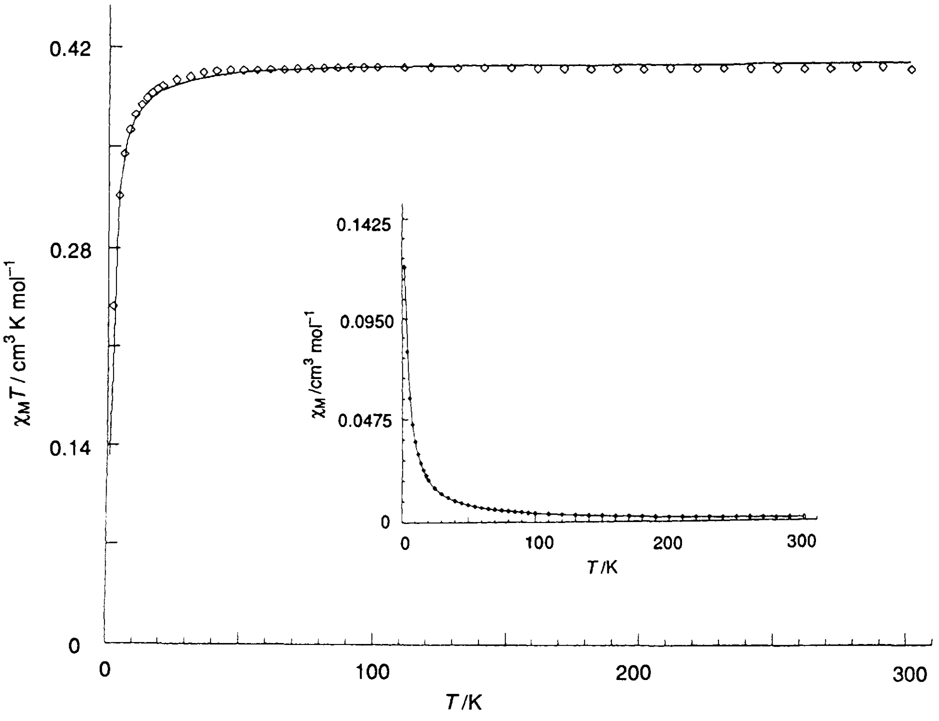

Fig. 2 Magnetic susceptibility plots of a polycrystalline sample of $[\{CuL(\mu\text{-}NCO)\}_n][ClO_4]_n$, solid line shows the best fit using the expression for the magnetic susceptibility of isotropically coupled $S = \frac{1}{2}$ ions in antiferromagnetic linear chains (see text)

Table 3 Selected bond lengths (Å) and angles (°) for $[\{CuL(\mu\text{-}NCO)\}_n][ClO_4]_n$

Cu–N(1′)	1.918(12)	O(1)–C(1)	1.19(2)
Cu–N(1)	1.920(14)	N(1)–C(1^{II})	1.18(2)
Cu–N(3)	2.016(4)	O(1′)–C(1′)	1.22(2)
Cu–N(2)	2.056(4)	O(1′)–Cu^{IV}	2.382(12)
Cu–N(4)	2.065(4)	C(1′)–N(1′)^{III}	1.15(2)
Cu–O(1)	2.344(10)	N(1′)–C(1′)^{II}	1.15(2)
N(1′)–Cu–N(3)	151.1(4)	N(1′)–Cu–O(1′)^{I}	92.2(5)
N(1)–Cu–N(3)	178.4(4)	N(1)–Cu–O(1′)^{I}	62.8(5)
N(1′)–Cu–N(2)	93.1(5)	O(1)–Cu–O(1′)^{I}	148.5(2)
N(1)–Cu–N(2)	99.5(4)	C(1)–O(1)–Cu	119.9(10)
N(3)–Cu–N(2)	82.1(2)	N(1^{III})–C(1)–O(1)	174(2)
N(1′)–Cu–N(4)	95.5(5)	C(1^{II})–N(1)–Cu	169.0(14)
N(1)–Cu–N(4)	94.4(4)	C(1′)–O(1′)–Cu^{IV}	116.3(10)
N(3)–Cu–N(4)	84.1(2)	N(1′)^{IV}–C(1′)–O(1′)	176(2)
N(2)–Cu–N(4)	164.5(3)	C(1′)^{II}–N(1′)–Cu	170.2(12)
N(1)–Cu–O(1)	85.7(5)		

Symmetry transformations used to generate equivalent atoms: I $x - 1, y, z$; II $x - \frac{1}{2}, -y, -z$; III $x + \frac{1}{2}, -y, -z$; IV $x + 1, y, z$.

Magnetic Properties.—The magnetic susceptibility data, $\chi_M T$ *vs.* T and χ_M *vs.* T for $[\{CuL(\mu\text{-}NCO)\}_n][ClO_4]_n$ are plotted in Fig. 2. The $\chi_M T$ value is approximately constant (0.41 cm^3 K mol^{-1}) in the range 300–70 K, but below 60 K it decreases slightly, reaching a minimum of 0.24 cm^3 K mol^{-1} at 2 K. This behaviour indicates a slightly antiferromagnetically coupled one-dimensional compound. The susceptibility data were fitted by the expression (1) for the magnetic susceptibility of isotropically coupled $S = \frac{1}{2}$ ions in antiferromagnetic linear chains,[20] where $x = |J|/kT$, derived from the Hamiltonian (2) using as the criterion of best fit the minimum value of $R = \Sigma_i(\chi_i^{calc} - \chi_i^{obs})^2/(\chi_i^{obs})^2$. The results of the fit, shown as the solid lines in Fig. 2, were $2J = -1.26$ cm^{-1}, $g = 2.10$ with $R = 3.4 \times 10^{-5}$. This $2J$ value is the first reported for an end-to-end cyanate-bridged copper(II) one-dimensional complex, and no magneto-structural correlations can be given. The low value may be related to the copper(II) environment in the $[CuL(\mu\text{-}NCO)]^+$ unit, which is described above as intermediate between a trigonal bipyramid and a square-planar pyramid, but principally the latter. In an ideal regular square-planar pyramidal geometry the $x^2 - y^2$ magnetic orbitals are mainly located in the basal plane, and J would be zero. The distortion towards trigonal-bipyramidal co-ordination allows the magnetic orbitals to acquire some z^2 character, and a usually weak magnetic interaction is possible.[21]

$$\chi_M = (Ng^2\mu_B^2/kT)(0.25 + 0.149\,95x + 0.300\,94x^2) \times (1.0 + 1.9862x + 0.688\,54x^2 + 6.0626x^3)^{-1} \quad (1)$$

$$H = -2J\Sigma_i(S_i^z S_{i+1}^z + S_i^x S_{i+1}^x + S_i^y S_{i+1}^y) \quad (2)$$

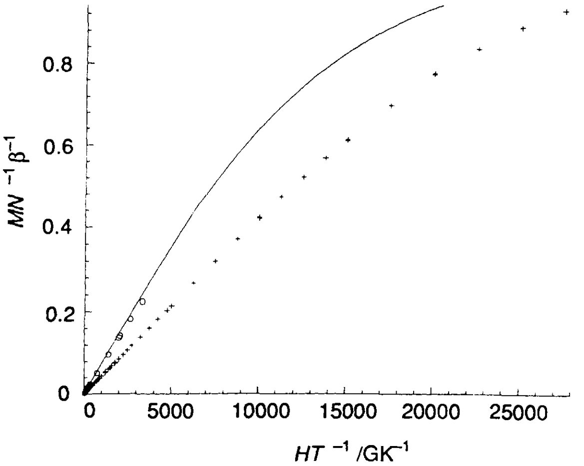

Fig. 3 Magnetization isotherms at 15 K (○) and 2 K (+) up to 51 kG for $[\{CuL(\mu\text{-}NCO)\}_n][ClO_4]_n$. The solid line shows the result obtained by applying the Brillouin formula with $S = \frac{1}{2}$ and $g = 2.11$

Magnetization isotherm measurements *vs.* applied field were carried out at 15 and 2 K up to 50 kG. The normalized plots of $MN^{-1}\beta^{-1}$ *vs.* HT^{-1} (where N is the Avogadro constant and β the Bohr magneton) at the two temperatures are shown in Fig. 3. At 15 K the complex exhibits Brillouin behaviour[22] with $S = 0.47$, slightly lower than the expected value of 0.5 (g fixed at the

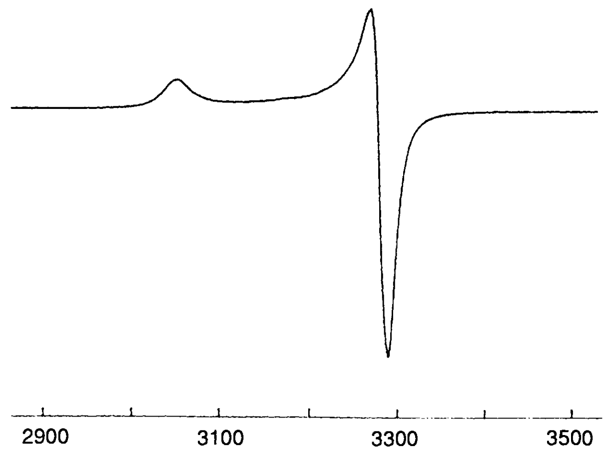

Fig. 4 The ESR spectrum (X-band) of a polycrystalline sample of $[\{CuL(\mu\text{-}NCO)\}_n][ClO_4]_n$ at 77 K

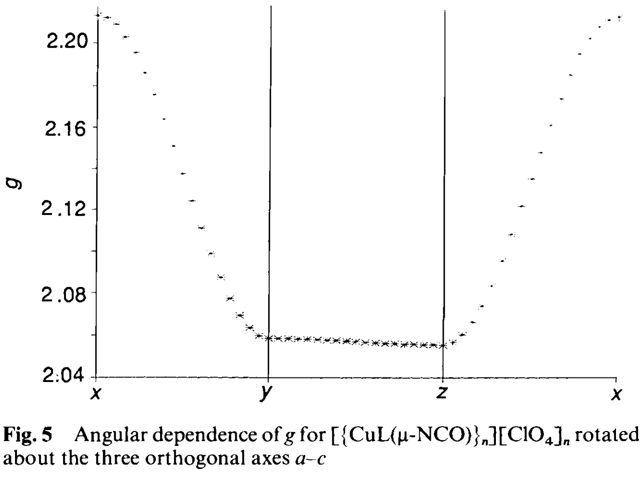

Fig. 5 Angular dependence of g for $[\{CuL(\mu\text{-}NCO)\}_n][ClO_4]_n$ rotated about the three orthogonal axes *a–c*

experimental value of 2.11). At 2 K the magnetization measurements clearly deviate from the Brillouin formula assuming $S = \frac{1}{2}$, $g = 2.11$ with lower $MN^{-1}\beta^{-1}$ values than those at 15 K, in accordance with the antiferromagnetic coupling found for complex **1** from the magnetic susceptibility measurements.

Electron Spin Resonance Spectra.—The ESR spectra of polycrystalline samples of the new complex at X-band frequency were recorded at temperatures from 280 to 4 K. In this range no change was detected. Fig. 4 shows the spectrum at 77 K, displaying axial distortion with $g_{\parallel} = 2.21$ and $g_{\perp} = 2.06$.

The single-crystal ESR spectrum was recorded at room temperature at X-band frequency by rotating around the *a*, *b* and *c* axes. The angular dependence of g is shown in Fig. 5. The usual analysis[23] gave the principal g values: $g_1 = 2.059$, $g_2 = 2.055$, $g_3 = 2.213$ along the axes *a*, *b* and *c*. From the structure, Fig. 1, two values of g_3 along the *a* axis can be expected, but due to the magnetic exchange only one is found along the chain direction; g_3 forms an angle of 16.03° with the Cu–O(1) bond direction (Fig. 6). The monocrystal g_i values are in accordance with the polycrystalline $g_{\parallel}$ and $g_{\perp}$ values.

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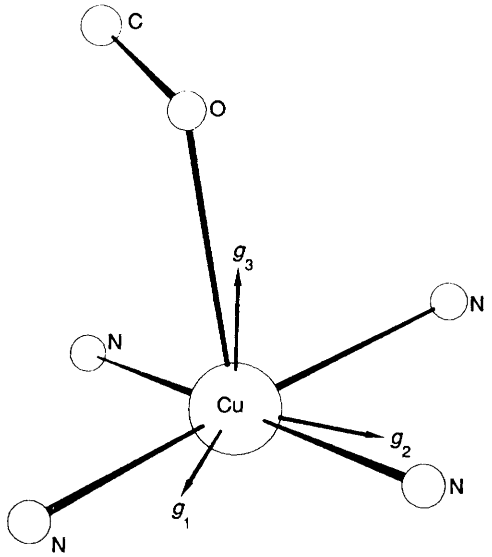

Fig. 6 Principal directions of the g tensor in the $[CuL(\mu\text{-}NCO)]^+$ unit

References

1 T. Mallal, M.-L. Boillot, O. Kahn, J. Gouteron, S. Jeannin and Y. Jeannin, *Inorg. Chem.*, 1986, **25**, 3058.
2 M.-L. Boillot, O. Kahn, C. J. O'Connor, J. Gouteron, S. Jeannin and Y. Jeannin, *J. Chem. Soc., Chem. Commun.*, 1985, 178.
3 M. Mikuriya, S. Kida and I. Murase, *Bull. Chem. Soc. Jpn.*, 1987, **60**, 1355.
4 T. Mallal, O. Kahn, J. Gouteron, S. Jeannin, Y. Jeannin and C. J. O'Connor, *Inorg. Chem.*, 1987, **26**, 1375.
5 O. Kahn, T. Mallal, J. Gouteron, S. Jeannin and Y. Jeannin, *J. Chem. Soc., Dalton Trans.*, 1989, 1117.
6 T. Rojo, R. Cortes, L. Lezama, J. L. Mesa, J. Via and M. I. Arrioortua, *Inorg. Chim. Acta*, 1989, **165**, 91.
7 A. E. Mauro, S. I. Klein, J. S. Saldaña, C. A. De Simone, J. Zukerman-Schpector and E. E. Castellano, *Polyhedron*, 1990, **9**, 2937.
8 J. Zukerman-Schpector, E. E. Castellano, C. A. De Simone, G. Oliva and A. E. Mauro, *Acta Crystallogr., Sect. C*, 1991, **47**, 957.
9 L. Walz and W. Haase, *J. Chem. Soc., Dalton Trans.*, 1985, 1243.
10 M. Julve, M. Verdaguer, G. de Munno, J. A. Real and G. Bruno, *Inorg. Chem.*, 1993, **32**, 795.
11 F. Valach, M. Dunaj-Jurco and M. Handlovic, *J. Cryst. Mol. Struct.*, 1980, **10**, 61.
12 F. Valach and N. Dunaj-Jurco, *Acta Crystallogr., Sect. B*, 1982, **38**, 2145.
13 T. R. Felthouse and D. N. Hendrickson, *Inorg. Chem.*, 1978, **17**, 444.
14 L. Banci, A. Bencini and D. Gatteschi, *Inorg. Chem.*, 1984, **23**, 2138.
15 G. M. Sheldrick, SHELXS 86, A program for crystal structure determination, University of Göttingen, 1986.
16 G. M. Sheldrick, SHELX 93. A computer program for crystal structure determination, in the press.
17 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4, pp. 99, 100 and 149.
18 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.
19 A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn and G. C. Verschoor, *J. Chem. Soc., Dalton Trans.*, 1984, 1349.
20 J. C. Bonner and M. E. Fisher, *Phys. Rev. A*, 1964, **135**, 640; J. W. Hall, Ph.D. Dissertation, University of North Carolina, Chapel Hill, NC, 1977; *Extended Linear Chain Compounds*, ed. S. Miller, Plenum, New York, 1983, vol. 3, p. 45.
21 O. Kahn, *Molecular Magnetism*, VCH, Weinheim, 1993, pp. 167–174 and refs. therein; O. Kahn, I. Morgensten-Badarau and R. Block, *Chem. Phys. Lett.*, 1984, **108**, 457.
22 R. L. Carlin, *Magnetochemistry*, Springer, Berlin, 1986, pp. 14–18.
23 D. S. Schonland, *Proc. Phys. Soc.*, 1958, **73**, 788; W. Gordy, *Theory and Applications of Electron Spin Resonance*, Wiley, New York, 1980.

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