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A new cyano-bridged one-dimensional polymeric mixed-valence $\mathrm{Cu^{II}/Cu^{I}}$ complex formed from reduction of a binuclear $\mathrm{Cu^{II}}$ complex with sodium cyanide

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Abstract—A new cyano-bridged polymeric mixed-valence $\mathrm{Cu^{II}/Cu^{I}}$ complex, $\mathrm{[Cu(dien)_2(CN)_2Cu(CN)]_n}$ (**2**) (dien = diethylenetriamine) has been prepared by the partial reduction of the OH-bridged binuclear complex $\mathrm{[Cu_2(dien)_2(OH)](ClO_4)_3}$ (**1**) with sodium cyanide. The X-ray crystal structure shows that **1** is a polymeric, linear mixed-valence $\mathrm{Cu^{I}/Cu^{II}}$ complex and consists of a one-dimensional three-coordinated $\mathrm{[Cu^{I}(CN)]_n}$ chain, in which the $\mathrm{Cu^{I}}$ atoms are linked by two disordered CN bonding groups. The structure of each $\mathrm{Cu^{II}}$ atom consists of a square-pyramidal five-coordinate environment, in which the basal plane is formed by the three nitrogen atoms of the dien ligands and one carbon atom of the terminal cyanide group, and the apical position is occupied by the nitrogen atom of a bridging cyano ligand. This is the first example of one $\mathrm{Cu^{II}}$ centre coordinating with two different bonding types of the terminal $\mathrm{Cu^{II}}$—CN and the bridging $\mathrm{Cu^{II}}$—NC in a polymeric complex. The cryomagnetic behaviour has been investigated in the temperature range 4.2–300 K. There is a weak antiferromagnetic interaction between two intrachain copper(II) ions with $J = -0.47\ \mathrm{cm^{-1}}$. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: Copper complexes; mixed-valence $\mathrm{Cu^{I}/Cu^{II}}$ complexes; polymeric copper complexes; X-ray structure; magnetic property.

It is well known that in aqueous solution copper(II) is easily reduced to copper(I) by cyanide and that simple C-bonded cyano complexes of copper(II) are unstable at normal temperatures with respect to reduction and cannot be isolated [1]. Nevertheless, it has been shown that by choosing ligands (e.g. amines) that have good σ-electron donor character and strongly prefer to coordinate to $\mathrm{Cu^{II}}$ rather than $\mathrm{Cu^{I}}$ ions, it is possible to stabilize the $\mathrm{Cu^{II}}$—CN coordination bonding. To date, several such complexes have been reported: the mononuclear, $\mathrm{[Cu^{II}(phen)(CN)](NO_3)}$ [2], $\mathrm{[Cu(bipy)_2(CN)])NO_3]}$ [3], [Cu(cyclps)(CN)] [4], $\mathrm{[Cu(Me_6tren)(CN)](ClO_4)}$ [5], the CN-bridged binuclear, $\mathrm{[Cu_2([14]\text{-}4,11,\text{-}dien\text{-}N_4)(CN)](ClO_4)}$ [6], $\mathrm{[Cu_2(tren)(CN)_2](BPh_4)_2}$ [7], and $\mathrm{[(Cu(Me_6tren))_2(CN)](ClO_4)}$ [5], and the CN-bridged polynuclear $\mathrm{[Cu(Me_5\text{-}dien)(CN)]_n(CF_3SO_3)_n}$ [5]. In addition, a few cyano-bridged $\mathrm{Cu^{I}/Cu^{II}}$ mixed-valence complexes of $\mathrm{[Cu(en)_2][Cu_2(CN)_5H_2O]}$ [8] $\mathrm{[Cu^{II}(en)_2]_3[Cu^{I}_6(CN)_6(SeCN)_6]}$ [9], and $\mathrm{[Cu_2(L)(CN)](ClO_4)_2}$ (L = N,S-containing macrocyclic ligand) [10] have been reported, but there are no cyanide groups directly coordinated to the $\mathrm{Cu^{II}}$ ion as C-bonded $\mathrm{Cu^{II}}$—CN in these complexes. Most recently, a series of model molecular complexes of cytochrome-*c* oxidase containing the $\mathrm{[Fe^{III}}$—CN—$\mathrm{Cu^{II}]}$ bridge unit has been prepared by Holm *et al.* [5,11] and structurally characterized, but there are no stable C-bonded $\mathrm{Cu^{II}}$—CN of $\mathrm{[Fe^{III}}$—CN—$\mathrm{Cu^{II}]}$ fragments reported in this series. Furthermore, to the best of our knowledge, only one example of a $\mathrm{Cu^{II}/Cu^{I}}$ mixed-valence stable polymer complex, $\mathrm{[Cu^{I}_4(CN)_6Cu^{II}(NH_3)_2]_n}$ with cyano-bridged $\mathrm{Cu^{I}}$—CN—$\mathrm{Cu^{II}}$ prepared from the reaction of $\mathrm{[Cu^{I}CN]}$ with $\mathrm{[Cu^{II}(NH_3)_4]^{2+}}$, has been reported [12]. In this example the two copper(I) units, a linear

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$[Cu(CN)_2]$ chain and a trigonal $[Cu(CN)_3]$ chain are bridged by cyanide ligands and there was no magnetic interaction between the Cu^{II} ions.

Undoubtedly the stable copper(II)–cyanide linkage formation is dependent on the chemical reduction process and the types of ligands that will stabilize coordination of cyanide [1]. The aim of this paper is to deal with the first example of the cyano-bridged polymeric mixed-valence complex $[Cu^{II}(dien)(CN)_2Cu^{I}(CN)]_n$ (**2**) (dien = diethylenetriamine) with a very unusual five-coordination of Cu^{II} containing a terminal C-bond Cu^{II}—CN and a bridging Cu^{II}—NC—Cu^{I} bonding. This compound was prepared by the reduction of the known OH-bridged binuclear complex $[Cu^{II}(dien)_2(OH)](ClO_4)_3$ (**1**) with sodium cyanide in methanol. The preparation, structural and cryomagnetic studies of this binuclear complex **1** have been reported [13,14]. The structure of $[Cu^{II}(dien)_2(OH)](ClO_4)_3$ consists of a discrete binuclear molecule where the two copper(II) atoms are bridged by a single OH group with Cu^{II}—OH—Cu^{II} angles of 128° and an intramolecular Cu^{II}—Cu^{II} distance of 3.43 Å and weaker interactions with oxygens from three perchlorate ions, with a strong antiferromagnetic interaction between two copper(II) ions. We chose this OH-bridged binuclear copper(II) complex for reduction with NaCN since from the viewpoint of the dien ligand in **1** it has the capability to stabilize Cu^{II}—CN bonding and also because such a complex would be relevant to the development of model systems for active sites of biological interest [15]. Additionally, cyanide is an irreversible inhibitor of the copper-oxidized enzymes; specifically, its toxicity has been traced to bimetallic oxidases such as cytochrome-*c* oxidase [16] and a haemocyanin [17]. Herein the preparation, X-ray crystal structure, spectroscopic and magnetic properties of the complex **2** are reported. In addition, for comparison, the structure of the OH-bridged binuclear complex **1** was reconfirmed by X-ray crystallographic analysis.

EXPERIMENTAL

Preparation of complexes

$[Cu_2(dien)_2(OH)](ClO_4)_3$ (**1**) was prepared following the method initially described by Curtis and Powell [13]. To a solution of $Cu(ClO_4)\cdot 6H_2O$ (1 mmol) in water (10 cm^3) were added diethylenetriamine (dien) in ethanol (15 cm^3). The resulting blue solution changed to blue-violet on adding of $Na_2CO_3\cdot 10H_2O$ (5 mmol). Deep blue-violet crystals of $[Cu_2(dien)_2(OH)](ClO_4)_3$ were obtained by slow evaporation at room temperature. These were collected by filtration, washed with water and air dried. Found: C, 15.0; H, 4.0; N, 12.9. Calc. for $C_8H_{17}N_6O_{13}Cl_3Cu_2$: C, 14.8; H, 4.2, N, 13.0%.

$[Cu(dien)(CN)_2Cu(CN)]_n$ (**2**). To a solution of $[Cu_2(dien)_2(OH)](ClO_4)_3$ (**1**) (30 mg, 0.04 mmol) in methanol were added 15 cm^3 of methanol containing an excess amount (18 mg) of NaCN. During the addition of NaCN the solution turned to light blue with subsequent precipitation of a white substance. The mixture was filtered off and the light blue filtrate was transferred to a beaker and allowed to stand at ambient temperature. After several days well-formed light blue crystals suitable for X-ray analysis were isolated, filtered off and dried *in vacuo*. Found: C, 31.4; H, 4.1; N, 22.6. Calc. for $C_7H_{13}N_6Cu_2$: C, 31.4; H, 4.3; N, 22.6%.

Physical measurements

Infrared spectra were recorded on a Bio-Rad FTS-40FTIR spectrophotometer as KBr pellets in the 4000–400 cm^{-1} region. *X*-band (9.8 GHz) EPR spectra at 298 K were recorded on a Bruker ECS-106 spectrometer. Cryomagnetic susceptibilities of the polycrystalline samples were measured between 4.2 and 300 K at a field of 1 T using a Quantum Design Model MPMS computer-controlled SQUID magnetometer. Diamagnetic corrections were made using Pascal's constants.

Crystal structure determinations for **1** *and* **2**

The X-ray crystallographic data of a dark blue crystal (0.40 mm × 0.45 mm × 0.60 mm) of **1** and a light blue plate (0.35 mm × 0.45 mm × 0.45 mm) of **2**, were collected with graphite-monochromatized Mo-K_α radiation at 25°C using an Enraf–Nonius CAD-4 diffractomer, and are given in Table 1. Cell parameters were calculated from the least-squares fitting of setting angles for 25 reflections. The ω–2θ scan technique to

Table 1. Crystallographic data for **1** and **2**

Formula	$C_8H_{17}N_6Cl_3O_{13}Cu_2$	$C_8H_{13}N_5Cu_2$
F.w.	638.70	306.317
Size, mm	0.4 × 0.45 × 0.60	0.35 × 0.45 × 0.45
Temp., K	298	298
Crystal system	Monoclinic	Orthorhombic
Space group	$P2_1$	*Pnma*
a, Å	11.4382(20)	19.184(6)
b, Å	9.402(3)	8.6917(24)
c, Å	11.849(3)	7.124(3)
β, °	117.928(20)	
V, $Å^3$	1125.9(5)	1187.9(7)
D_c, g cm^{-3}	1.884	1.578
Z	2	4
$F(000)$	640	616
μ, cm^{-1}	23.22	35.685
N	2736	1830
N_0 $[I > 2.0\sigma(I)]$	2156	1367
R^a	0.054	0.026
$R_w{}^b$	0.065	0.026

[a] $R_f = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$.

[b] $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$.

Table 2. Bond distances (Å) and angles (°) for **1**

Cu(1)—O(1)	1.893(10)	Cu(1)—O(7)	2.894(21)
Cu(1)—N(1)	2.180(14)	Cu(1)—N(2)	2.004(8)
Cu(1)—N(3)	1.993(10)	Cu(2)—O(1)	1.960(11)
Cu(2)—O(2)	2.481(9)	Cu(2)—O(7)	2.746(14)
Cu(2)—N(4)	2.158(15)	Cu(2)—N(5)	2.014(8)
Cu(2)—N(6)	1.960(11)	Cu(1)—Cu(2)	3.420(17)
Cu(1)—O(1)—Cu(2)	129.1(4)	Cu(1)—O(7)—Cu(2)	74.9(4)
N(1)—Cu(1)—N(3)	163.5(5)	N(1)—Cu(1)—O(1)	94.8(9)
N(3)—Cu(1)—O(1)	96.6(8)	N(4)—Cu(2)—O(1)	91.7(9)
O(1)—Cu(2)—O(2)	93.7(3)	Cu(2)—O(2)—Cl(1)	128.1(7)

Table 3. Selected bond distances (Å) and angles (°) for **2**

Cu(1)—C(4)	1.919(3)	Cu(1)—NC	1.9358(22)
Cu(2)—N(1)	2.0517(21)	Cu(2)—C(3)	1.971(3)
Cu(2)—N(4)	2.171(3)	NC—NCb	1.138(4)
C(4)—N(4)	1.127(4)	C(3)—N(3)	1.133(5)
C(4)—Cu(1)—NC	120.36(17)	NC—Cu(1)—NC	119.08(10)
N(4)—Cu(2)—C(3)	98.77(13)	N(1)—Cu(2)—C(3)	94.81(6)
N(1)—Cu(2)—N(1)	158.84(18)	N(2)—Cu(2)—C(3)	163.12(12)
Cu(1)—C(4)—N(4)	178.1(3)	Cu(2)—N(4)—C(4)	171.3(3)
Cu(2)—C(3)—N(3)	177.9(3)	Cu(1)—NC—NCb	176.84(21)

a $2\theta_{max}$ value of 55.0° for **1** and 160.0° for **2** was used. A total of 2736 reflections for **1** and 1830 for **2** were measured, of which 2730 for **1** and 1830 for **2** with $I > 2.0\sigma(I)$, were used in further calculations. The structures were solved by the heavy-atom method. Full-matrix least-squares anisotropic refinement for all non-hydrogen atoms yielded $R_f = 0.054$, $R_w = 0.065$ and *GOF* (goodness-of-fit) = 2.11 for **1** and $R_f = 0.026$, $R_w = 0.026$ and *GOF* = 16 at convergence. All calculations were performed using the NRCVAX computer crystallographic software package [18]. Disorder was observed in the chain-bridging cyano groups of **2**. Selected bond distances and angles for **1** and **2** are given in Tables 2 and 3, respectively. Complete crystal data, atomic coordinates, full listings of bond distances and angles and the anisotropic thermal parameters for **1** and **2** are available as supplementary material, and have been deposited at the Cambridge Crystallographic Data Centre.

RESULTS AND DISCUSSION

The chemical reduction of $[Cu_2(dien)_2(OH)](ClO_4)_3$ (**1**) in excess methanolic solution of NaCN yielded a one-dimensional chain structured Cu^{I}/Cu^{II} mixed-valence complex, $[Cu^{II}(dien)(CN)_2Cu^{I}(CN)]_n$ (**2**) and some white solid identified as $NaClO_4$. Complex **2** was isolated in low yield (*ca* 20%), but was air stable in solution and in the solid state for a long period.

IR spectra

The most relevant IR feature is the presence of bridging and terminally bound CN stretching vibrations. In general, the ν(CN) frequency should be significantly greater for the bridging case than for the terminal one. Therefore, complex **2** exhibits very sharp double ν(CN) bands at 2133 and 2118 cm^{-1} in KBr, suggestive of the absorptions for the bridging CN and the terminal CN stretching vibrations, respectively [5–7,11].

Description of the structures

The structure of **1** (as shown in Fig. 1) consists of a binuclear $[Cu_2(dien)_2(OH)]^{3+}$ cation with three ClO_4^- anions, which is the same as previously found [14]. Nevertheless, in our system, only one ClO_4^- group oxygen atom was coordinated to the Cu^{II} centre with a Cu(2)—O(2) bond distance of 2.481(9) Å and the oxygens of the other two ClO_4^- groups interact

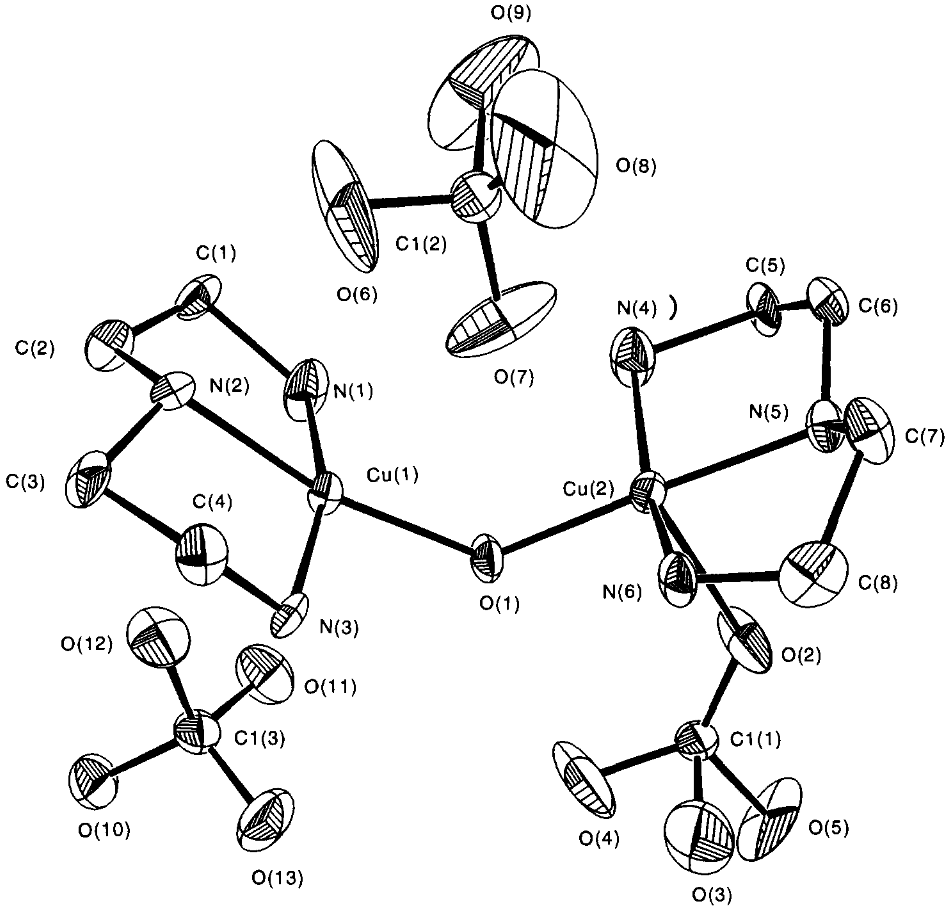

Fig. 1. ORTEP stereoview of $[Cu_2(dien)_2(OH)](ClO_4)_3$ (**1**) with atom-numbering scheme and vibrational ellipsoids at the 30% probability level.

only with Cu^{II}. These $Cu \cdots OClO_3$ interactions are very weak, at 2.608(10) [Cu(1)—O(12)], 2.746(14) [Cu(2)—O(7)] and 2.894(21) Å [Cu(1)—O(7)], and are probably electrostatic rather than covalent. The two copper atoms are bridged by a hydroxo group with the Cu(1)—OH—Cu(2) angle of 129.1(4)° and the intermolecular Cu(1)—Cu(2) separation of 3.4320(17) Å being close to those previously reported by Julve and co-workers [14]. The bridging Cu—O distances of 1.893(10) and 1.960(7) for Cu(1)—O(1) and Cu(2)—O(1), respectively agree closely with those previously reported [14].

The structure of the title compound $[Cu^{II}(dien)(CN)_2Cu^{I}(CN)]_n$ (**2**) consists of a one-dimensional skeleton formed by the polymeric mixed-valence Cu^{I}/Cu^{II} chain through the cyanide bridges as shown in Figs 2 and 3. The layer structure of this polymer is illustrated in Fig. 4. As shown in Fig. 2, the copper(II) atom, Cu(2), takes a distorted square-pyramidal coordination with three nitrogen atoms of the dien ligand, one carbon atom of the terminal CN ion and a nitrogen atom of CN in the apical position, which is linked with the copper(I) atom of the polymer chain. In the polymer chain, the copper atom, Cu(1), is in trigonal-planar coordination (three C—Cu^{I}—C bond angles are 120°) with D_{3h} symmetry.

It is important to note that due to static disorder, in the bridging CN groups with Cu^{I} the Cu^{I} atom bonded as Cu—CN, and the other bonded as Cu—NC, are almost identical; this means that discrimination between the N and C atoms of the N group linking the Cu^{I} centres is impossible, and they are assumed to have 50% probability for each of the C and N designated as NC, in the structure refinement. The bond length of NC—NCb 1.138(4) Å is slightly longer than that of 1.127(4) Å for C(4)—N(4) which link with the Cu^{II} atom. In the Cu^{II} site, the Cu^{II}—C(3) distance of 1.971(3) Å found here compares favourably with the distances found in the other C-bond Cu^{II}—CN complexes mentioned above [2–7]. The Cu(2)—N(CN) bond length of 2.171 Å is significantly longer than the mean Cu(2)—N(dien) bond length

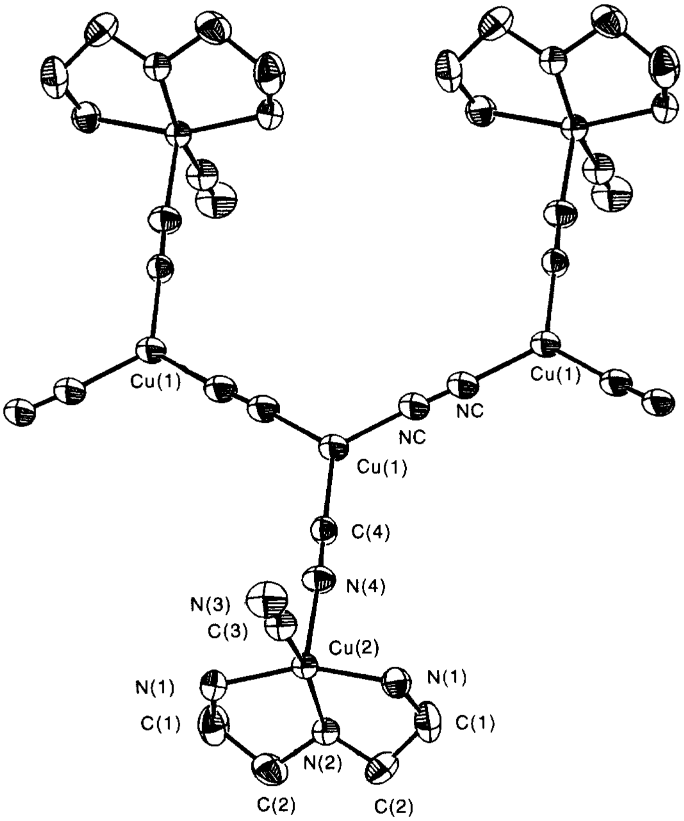

Fig. 2. ORTEP stereoview of $[Cu(dien)(CN)_2Cu(CN)]_n$ (**2**) with atom-numbering scheme and vibrational ellipsoids at the 30% probability level.

of 2.038 Å, which is within the normal range. The C(3)—N(3) bond length of 1.133(5) Å of the bridging CN is slightly longer than the terminal N(4)—C(4) distance of 1.127(4) Å. The nearest intrachain and interchain Cu^{II}—Cu^{II} separations are 6.2214(13) and 7.124(3) Å, respectively, and are likely to cause a very weak magnetic interaction between two copper(II) ions.

Magnetic properties

The *X*-band (9.8 GHz) polycrystalline EPR spectrum at 298 K for **2** was found to exhibit an axially elongated pyramidal copper(II) centre, with $g_{\parallel} = 2.21$ and $g_{\perp} = 2.03$. Magnetic susceptibility measurements from 300 to 4.2 K have been made for complex **2** as shown in Fig. 5, as the effective moments μ_{eff} and χ_m *vs* *T*. In the temperature range studied, the μ_{eff} value of 2.10 μ_B at 300 K is slightly lower than the value of 2.45 μ_B expected for a non-coupled, two $S = \frac{1}{2}$ spin system, and decreases slowly with decreasing temperature, reaching 1.44 μ_B at 4.2 K. This decrease can be owing to intramolecular and/or intermolecular antiferromagnetic exchange interactions between the nearest Cu^{II} ions. Although there is not a detailed model for our complex mixed-valence system, we tried to reproduce the susceptibility of this compound by a modified Bleaney–Bowers susceptibility expression for the two-spin systems of $S = \frac{1}{2}$

$$\chi_m = 2Ng^2\beta^2/k(T-\theta)[\{1/(3+x^{-1})](1-\rho)\} + \rho/4] + N_\alpha \quad (1)$$

$x = \exp(-J/kT)$, the parameter θ is the Curie–Weiss constant, which accounts the intermolecular interaction between Cu^{II}—Cu^{II} of the interchain, let $\theta = zJ'$ (interchain coupling parameter) [19], ρ is the fraction of mononuclear paramagnetic impurity, N_α is the temperature-independent paramagnetism and the other symbols have their usual meaning. Where we have assumed the isotropic g value in calculation, the best result of the least squares fitting to Eq. (1) gives $g_i = 2.12$ (obtained from averaged g value of EPR data), $J = -0.47$ cm^{-1}, $zJ' = -0.26$ cm^{-1}, $\rho = 0.06$ and $N_\alpha = 200 \times 10^{-6}$ cm^3 mol^{-1}. Figure 5 illustrates a plot of χ_m and μ_{eff} *vs*. *T* for **2**, with the solid line corresponding to the fitted parameters quoted above. The values of $J = -0.47$ cm^{-1} and $zJ' = -0.26$ cm^{-1}

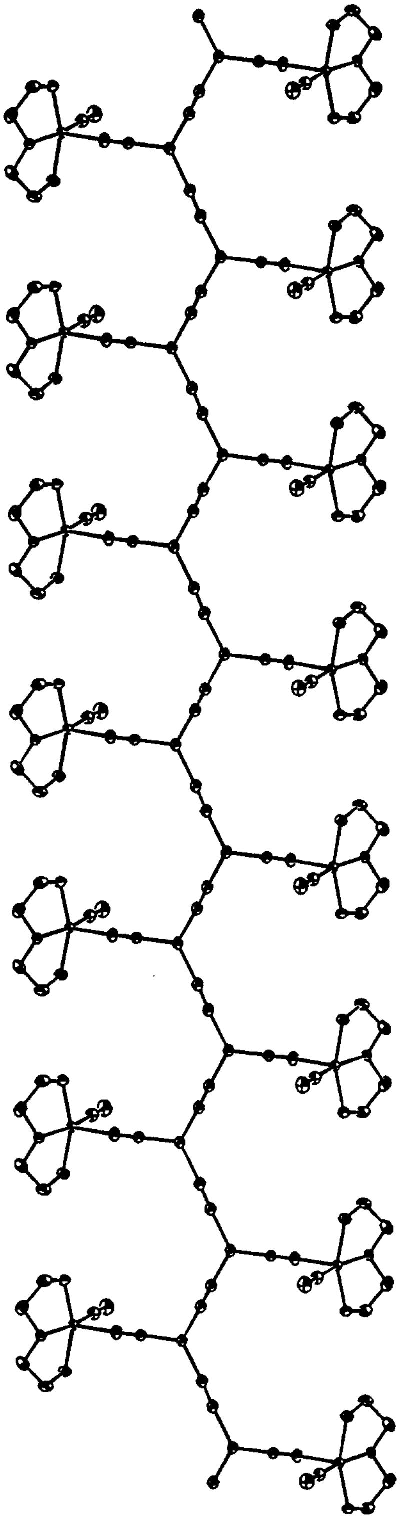

Fig. 3. View of the one-dimensional polymeric chain of 2.

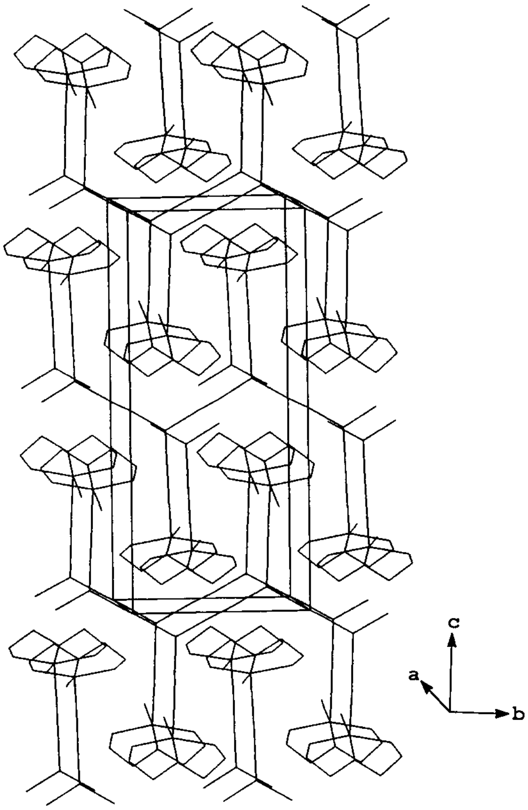

Fig. 4. Interchain molecular arrangement in the crystal of **2**, showing the layer structure.

are relatively much smaller, these may be due to a large separation, 6.22 and 7.12 Å, of the nearest magnetic Cu^{II} ions of the intrachain (through —NC—Cu^{I}—CN—bridge) and the interchain [through Cu^{II}—CN ··· NH(dien)Cu^{II} interaction] respectively, in **2**.

In summary, **2** is a new example of a mixed-valence Cu^{I}/Cu^{II} polymeric complex with the stable Cu^{II}—CN and Cu^{II}—NC bondings that resulted from the direct partial reduction of the OH-bridged binuclear copper(II) complex **1** by NaCN. The terminal C-bonded Cu^{II}—CN is stabilized by three nitrogen atoms of the dien ligand and one nitrogen atom of the bridged NC—Cu^{I}. Although the detailed mechanistic aspects for the partial reduction for the present system and related systems were not elucidated at present, this work is in progress.

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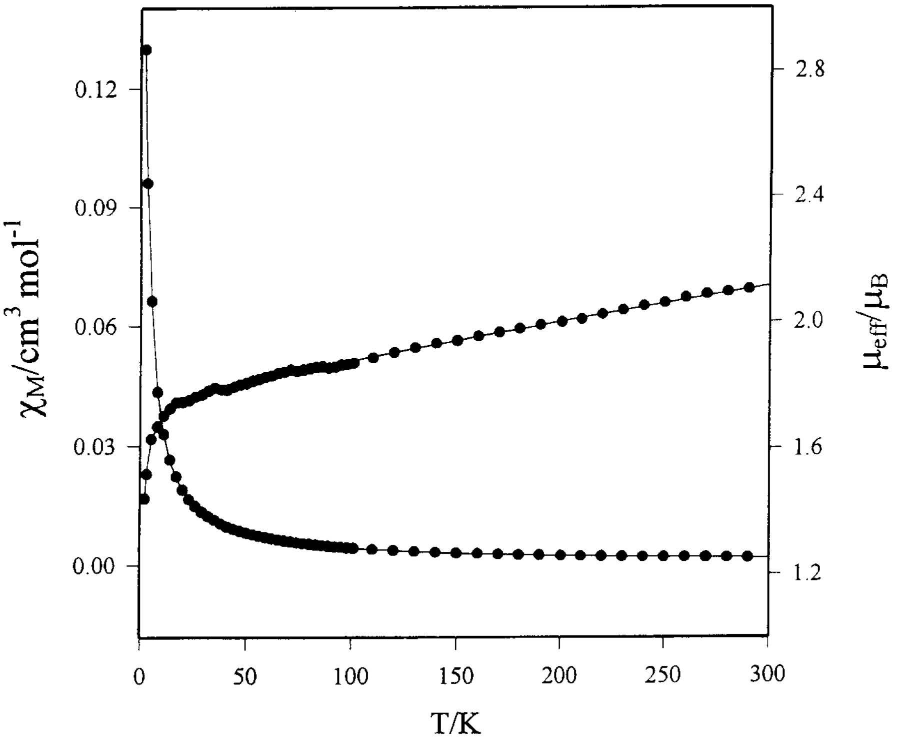

Fig. 5. Temperature dependence of the molar magnetic susceptibility and magnetic moment for **2**. The solid lines represent a fit based on Eq. (1).

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