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Novel Infinite Three-Dimensional Networks with Highly Conjugated Polynitrile Ligands: Syntheses, Crystal Structures, and Magnetic Properties of $[Cu\{C[C(CN)_2]_3\}(H_2O)_2]_n$ and $[Cu\{C[C(CN)_2]_3\}(en)]_n$ (en = $NH_2CH_2CH_2NH_2$)

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Many cyanocarbon and cyanocarbanion derivatives are distinguished by unusual physical properties that are attractive for potential applications, for example as organic metals and molecular ferromagnets.[1] As recently noted[2] solids that contain transition metal cations and polycyano units can be grossly divided into two categories: one in which the ligand is σ bonded to the cation, and one which contains stacked anionic organic systems, which are usually obtained from electron acceptors such as tetracyanoethylene (TCNE) and 7,7,8,8-tetracyano-*p*-quinodimethane (TCNQ). As part of our investigations into the first class we described recently the intriguing three-dimensional polymeric structure of the silver complex with the cyanocarbon ligand $\{[C(CN)_2C(CN)]_2N\}^-$.[3] We were thus interested in novel polymeric solids based on transition metal cations and such highly conjugated polynitrile anions that present a plurality of cyano groups juxtaposed in such a way that they cannot all coordinate to the same metal cation.

Our objective is to examine the ability of these organic ligands to create a range of two- or three-dimensional polymeric metallacycle networks. This study will therefore contribute to the understanding of properties of molecular systems, such as binary metal/TCNX (X = E, Q) compounds, which present fascinating properties,[1, 2] but for which the detailed structures are as yet unknown. We focus here on the use of the symmetrical 2-dicyanomethylene-1,1,3,3-tetracyanopropanediide anion $[C\{C(CN)_2\}_3]^{2-}$ (**1**) with copper(II) ions; several studies of the chemical and physical properties of this anion have been reported,[4] but as far as we know no crystal structure of solids containing a transition metal cation σ bonded to this ligand has been reported. We report here the syntheses, crystal structures, and preliminary magnetic properties of compounds **2** and **3**, which have unprecedented three-dimensional polymeric networks.

$[\{Cu\{C[C(CN)_2]_3\}(H_2O)_2\}_n]$ **2**

$[\{Cu\{C[C(CN)_2]_3\}(en)\}_n]$ **3**
(en = ethylenediamine = $NH_2CH_2CH_2NH_2$)

X-ray analyses[5] of **2** and **3** show they have polymeric structures based on networks of octahedrally coordinated Cu^{II} centers linked by $[C\{C(CN)_2\}_3]^{2-}$ ligands (Figures 1a and 2a). In both structures, each $[C\{C(CN)_2\}_3]^{2-}$ ligand acts in a polybridging mode with four of its six nitrogen atoms bound to four different copper cations. Each metal cation in complex **2** has a pseudo-octahedral *trans*-CuO_2N_4 environment with four nitrogen atoms from four different organic ligands and two oxygen atoms from the water molecules (Figure 1a). While the bond angles around the Cu atom only deviate moderately from 90°, the Cu–N bond lengths of the perfectly planar CuN1N2N1N2 unit are significantly different (1.978(5) and 2.051(5) Å). The most important distortion of the octahedron corresponds to an elongation along the pseudo fourfold axis with a Cu–O bond length of 2.191(5) Å.

The molecular unit from which the molecular arrangement can be easily described is the 12-membered metallacycle **A** (Cu ⋯ Cu 7.026 Å) (Figure 1a). These metallacycles are connected to each other through Cu atoms to give the first monodimensional chain **Ch1** (**A-A-A-A**), which runs along the [−110] direction (Figure 1b). Such infinite units form eclipsed stacks parallel to the [100] direction and separated by 8.108 Å. Furthermore, each metallacycle **A** is laterally connected to two metallacycles **A′** by two organic ligands; this affords a second monodimensional chain **Ch2** (**A′-A′-A′-A′**) that is crystallographically equivalent to **Ch1** chain but runs orthogonally (along the [110] direction). This generates the three-dimensional structure represented in Figure 1b.

In complex **3** each Cu atom presents a CuN_4N_2 distorted octahedral coordination with four nitrogen atoms from four organic ligand and two nitrogen atoms from a classical bidentate en ligand. The Cu^{II} coordination octahedron is much more severely distorted here than in complex **2**. Whilst the CuN2N5N7N8 fragment is planar within ±0.03 Å and presents almost equivalent Cu–N bond lengths (1.977(4) and 1.980(4) Å from the polynitrile ligand; 2.008(4) and 2.013(5) Å from the en ligand), the two *trans*-CuN1 and CuN6 bonds are much longer (2.437(5) and 2.449(5) Å, respectively). The extended molecular structure of complex **3** represented in Figure 2b is very similar to that of complex **2** described above; the main difference lies in the absence of the monodimensional chain observed in **2**; the fictive chain is destroyed by the coordination of the bidentate en ligand. This leads to linear successions along the [101] direction of metallacycles fairly similar to those described in complex **2**;

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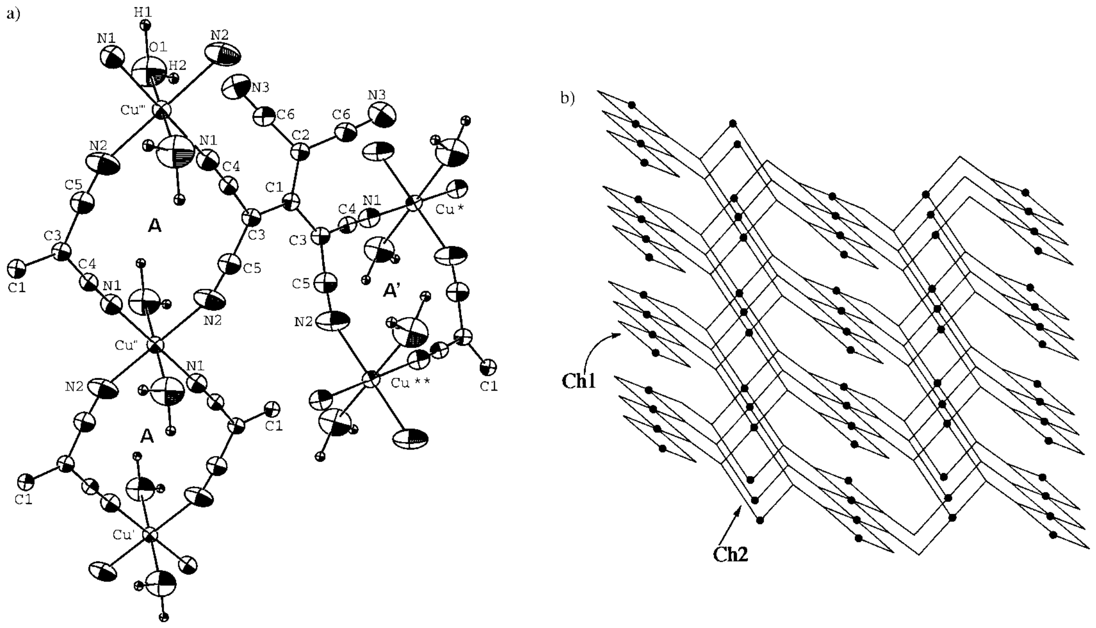

Figure 1. Complex **2:** a) Perspective view showing the polybridging (μ_4-η^4) ligand geometry, the copper environment, and the two metallacycles **A** and **A′**. Selected distances [Å]: C1–C2 1.41(1), C1–C3 1.424(6), C4–N1 1.136(7), C5–N2 1.140(8), C6–N3 1.138(8). Copper positions: Cu′ (–½, ½, ½); Cu″ (0, 0, ½), Cu‴ (½, –½, ½); Cu* (–½, –½, 1); Cu** (0, 0, 1). b) Schematic representation of the extended structure to show the two infinite monodimensionnal chains, **Ch1** and **Ch2**, which run orthogonally along the [–110] and [110] directions, respectively. The water molecules are omitted and only the C3 atom of the organic ligands is represented for clarity.

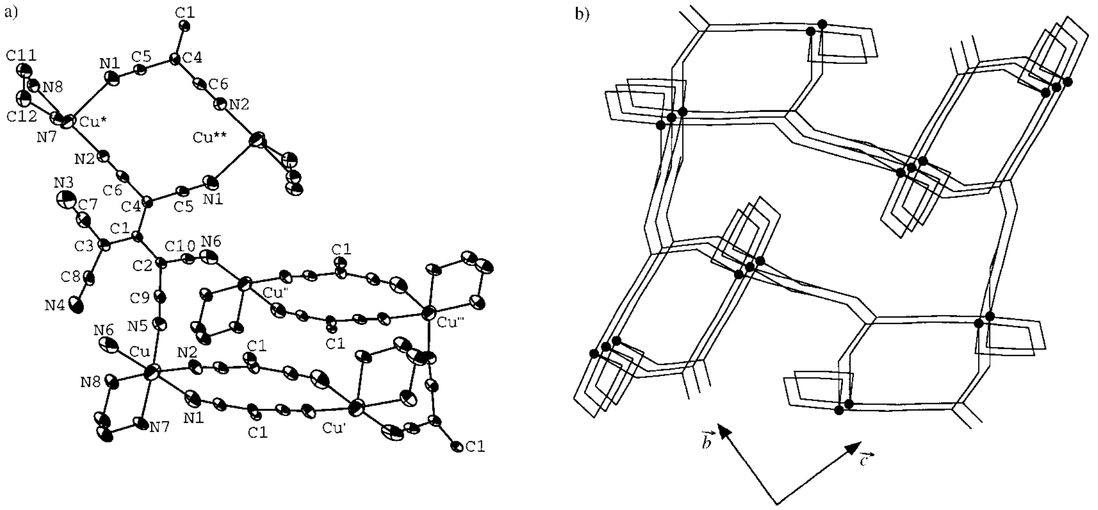

Figure 2. Complex **3**: a) Perspective view that shows the polybridging (μ_4-η^4) ligand geometry and the copper environment. Selected distances [Å]: C5–N1 1.144(6), C6–N2 1.146(6), C7–N3 1.146(7), C8–N4 1.158(7), C9–N5 1.142(6), C10–N6 1.148(6), C1–C2 1.424(6), C1–C3 1.412(6), C1–C4 1.419(6). Symmetry code of copper positions: Cu′ = $-x, -y, -z$; Cu″ = $-1+x, y, z$; Cu‴ = $-1-x, -y, -z$; Cu* = $-\tfrac{1}{2}+x, \tfrac{1}{2}-y, \tfrac{1}{2}+z$; Cu** = $-\tfrac{1}{2}-x, \tfrac{1}{2}+y, \tfrac{1}{2}-z$. b) Schematic representation of the extended structure to show the 12-membered metallacycles and the bidentate en ligand. Only the two coordinated $C(CN)_2$ arms of the organic ligands are represented for clarity.

the intra-metallacycle Cu···Cu distances of 7.434 Å is longer than that observed in complex **2**. As in the first complex (**2**), the metallacycles stack in an eclipsed way along the [100] direction with an inter-planar distance of 7.214 Å. In both complexes, as in previously studied derivatives,[4, 6] the $[C\{C(CN)_2\}_3]^{2-}$ unit has a propeller-shaped geometry of approximate D_3 symmetry since the axis that passes through the central carbon atom appears as a pseudo threefold axis. The three $C(CN)_2$ arms are tilted out of the plane that contains the four central carbon atoms; the mean tilt angle is slightly greater in **2** (26.9(1)°) than in **3** (22.7(7)°). These values are of the same order of magnitude as that observed in the calcium derivative (24°).[6]

The magnetic behavior of complex **2** follows a Curie–Weiss law with $\theta = 0.8$ K, which indicates the presence of a weak ferromagnetic exchange interaction between copper(II) ions. This observation is confirmed by the $\chi_M T$ versus T plot, which shows an increase in $\chi_M T$ below 50 K to 0.54 emu K mol^{-1} at 4 K (Figure 3). Complex **3** follows a Curie law with $C = 0.40$ emu K mol^{-1} (Figure 3). The weak ferromagnetic behav-

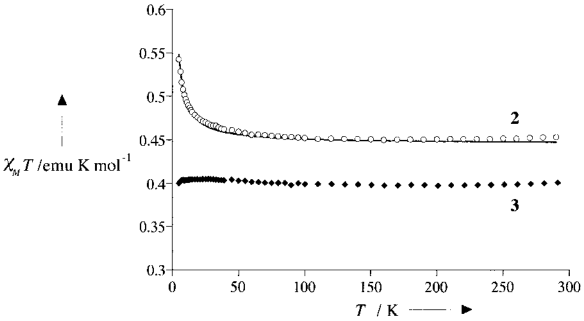

Figure 3. Variable-temperature magnetic data for **2** and **3**. The solid line represents the best fit obtained with the parameters reported in the text.

ior obtained for **2** can be explained on the basis of the structural results by intra-chain interaction between neighboring copper cations in the metallacycles. A further analysis was then restricted to the one-dimensional model; the experimental data were fitted by using the empirical expression proposed by Baker[7, 8] for ferromagnetic one-dimensional isotropic Heisenberg chains with $S = ½$. The solid curve in Figure 3 represents the best fit for the experimental data obtained with $J = 0.6$ K and $g = 2.18$ (from deconvolution of the powder EPR spectra from reference [9]: $g_x = 2.095$, $g_y = 2.180$, $g_z = 2.260$).

The polycyanocarbanion $[C\{C(CN)_2\}_3]^{2-}$ appears to have a sophisticated bridging mode toward copper cations but structural comparison with uncoordinated $[C\{C(CN)_2\}_3]^{2-}$ anions shows that the coordination does not greatly affect the geometry of this moiety. Extension of this study to other polynitrile anions and to other magnetic metal cations is in progress to obtain a more unified view of the bonding/electronic structure relationship in these highly conjugated systems. This might lead to a rationale of their properties of interest: electronic delocalization within the ligand, conduction, and magnetism.

Experimental Section

2: A hot solution of $CuCl_2 \cdot 2H_2O$ (340 mg, 2 mmol) in water (50 mL) was added to a hot solution of $K_2[C\{C(CN)_2\}_3] \cdot H_2O$[10] (600 mg, 2 mmol). The mixture was refluxed for about 30 minutes and then maintained at room temperature. The black prismatic crystals were filtered, and recrystallized from hot water. Yield approximately 80%. IR (Kbr): $\tilde{\nu} = 2240$ (sh), 2220 (s), 2200 (s), 2180 cm^{-1} (sh).

3: A solution of ethylenediamine (60 mg, 1 mmol) and $CuCl_2 \cdot 2H_2O$ (170 mg, 1 mmol) in water (40 mL) was added to a solution of monohydrated potassium salt of $K_2[C\{C(CN)_2\}_3] \cdot H_2O$ (300 mg, 1 mmol) in water (40 mL). The green product was filtered, and recrystallised from hot water. Yield approximately 90%. IR (Kbr): $\tilde{\nu} = 3420$ (w), 3350 (w), 3270 (sh), 3250 (s), 3150 (w), 2240 (sh), 2220 (s), 2200 (s), 2180 cm^{-1} (sh).

Physical measurements: IR spectra were recorded in the range 4000–200 cm^{-1} on a Perkin–Elmer 1430 spectrometer with samples prepared as KBr pellets. The magnetic susceptibility measurements were performed at 0.1 T between 5 and 300 K with a SQUID magnetometer "MPMS-5" from Quantum Design Corporation. The X-band ESR spectra were performed on a Bruker ER 200D-SRC spectrometer in the range 100–360 K. The molar susceptibility was corrected from the sample holder and diamagnetic contributions of all atoms.

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[5] Crystal structure analysis: **2**: Black prisms: $0.05 \times 0.07 \times 0.08$ mm^3, Enraf–Nonius CAD4 diffractometer, with graphite monochromatized $Mo_{K\alpha}$ radiation ($\lambda(Mo_{K\alpha}) = 0.71073$ Å), $M_r = 303.7$ g mol^{-1}, monoclinic, space group $C2/c$, $a = 8.108(3)$, $b = 11.477(4)$, $c = 12.466(6)$ Å, $\beta = 94.15(3)°$, $V = 1157$ Å^3, $Z = 4$, $\rho_{calcd} = 1.74$ g cm^{-3}, $\mu = 18.97$ cm^{-1}, $F(000) = 604$, $T = 294$ K, $R_{int} = 0.014$, 769 observed reflections ($I > 3\sigma(I)$). **3**: Green prisms: $0.15 \times 0.15 \times 0.20$ mm^3 , $M_r = 327.8$ g mol^{-1}, monoclinic, space group $P2_1/n$, $a = 7.214(5)$, $b = 13.418(2)$, $c = 14.154(4)$ Å, $\beta = 94.00(4)°$, $V = 1367$ Å^3, $Z = 4$, $\rho_{calcd} = 1.593$ g cm^{-3}, $\mu = 16.06$ cm^{-1}, $F(000) = 660$, $T = 294$ K, $R_{int} = 0.033$, 1253 observed reflections ($I > 3\sigma(I)$). The structures were solved by direct methods and successive Fourier difference syntheses, and were refined by weighted anisotropic full-matrix least-squares methods. The hydrogen atoms of both structures were observed in the Fourier difference syntheses and refined isotropically to give $R = 0.039$, $R_\omega = 0.045$, $\Delta\rho_{max} = 0.84$ e Å^3, and GOF = 1.129 for **2**; $R = 0.028$, $R_\omega = 0.031$, $\Delta\rho_{max} = 0.278$ e Å^3, and GOF = 1.29 for **3**. Further details on the crystal structure investigations may be obtained from the Fachinformationszentrum Karlsruhe, D-76344 Eggenstein-Leopoldshafen, Germany (fax: (+49) 7247-808-666, on quoting the depository numbers CSD-408624 and -408625.

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[8] To the best of our knowledge no analytical expression has yet been proposed for a uniform ferromagnetic copper(II) chain. The fit of the experimental data for **2** was performed with the expression given in Equation (1) with $N = 1 + 5.7979916x + 16.902653x^2 + 29.376885x^3 + 29.832959x^4 + 14.036918x^5$, $D = 1 + 2.7979916x + 7.0086780x^2 + 8.6538644x^3 + 4.5743114x^4$ and $x = J/kT$

$$\chi_M = \frac{N g^2 \beta^2}{4kT}\left[\frac{N}{D}\right]^{2/3} \qquad (1)$$

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