A novel one-dimensional Ni(II)–Fe(II) polymer containing μ_3-cyanides: $[Ni(cyclen)]_2[Fe(CN)_6]\cdot 8H_2O$

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Reaction of $K_4[Fe(CN)_6]$ with $Ni(CH_3COO)_2$ and cyclen produced an unusual one-dimensional paramagnetic complex, $[Ni(cyclen)]_2[Fe(CN)_6]\cdot 8H_2O$ (cyclen = 1,4,7,10-tetraazacyclododecane), that consists of $[Ni(cyclen)]_2$ dimers bridged by μ_3-cyanides from $[Fe(CN)_6]^{4-}$. The Ni···Ni distance is 3.303 Å, which is significantly shorter than the corresponding distance of 3.449 Å in $[Ni_2(\mu\text{-}N_3)_2(232\text{-tet})_2](PF_6)_2$. Moderate antiferromagnetic coupling occurs between the Ni^{2+} ions.

The chemistry of cyano-bridged coordination polymers is of current interest due to the remarkable diversity of structural types.[1,2] A wide variety of coordination polymers employing cyanometallate building blocks such as $[Fe(CN)_6]^{3-/4-}$ and $[Cr(CN)_6]^{3-}$ have been reported.[3,4] In these polymers the cyanide ions bridge metal centers in a μ_2-fashion: M–C–N–M′. On the other hand, polymers containing μ_3- or μ_4-cyanides are much less common, and we are aware of only a few examples that were reported recently; these include the layer-type double salts $3AgCN\cdot 3AgF\cdot 3H_2O$ and $AgCN\cdot 2AgF\cdot 3H_2O$;[5] the two-dimensional (2-D) $[Cd(tren)]_2[Fe(CN)_6]$ [tren = *tris*-(2-aminoethyl)amine],[6a] and $[Cu(dmen)]_2[Fe(CN)_6]$ (dmen = 2-dimethylaminoethylamine).[6b] We report here a unique one-dimensional (1-D) paramagnetic complex, $[Ni(cyclen)]_2[Fe(CN)_6]\cdot 8H_2O$ ($\mathbf{1}\cdot 8H_2O$; cyclen = 1,4,7,10-tetraazacyclododecane), that consists of $[Ni(cyclen)]_2$dimers bridged by μ_3-cyanides from $[Fe(CN)_6]^{4-}$. Such a bonding mode results in a moderate antiferromagnetic coupling between Ni^{2+} ions.

Treatment of $K_4[Fe(CN)_6]$ with $Ni(CH_3COO)_2$ and cyclen in a mole ratio of 1:1:1 at room temperature produced $\mathbf{1}\cdot 8H_2O$ as a purple solid. X-ray crystallography revealed that **1** has a 1-D structure consisting of $[Ni(cyclen)]_2$ units bridged by the axial cyanides of $[Fe(CN)_6]^{4-}$ in a μ_3-fashion (Figs. 1 and 2). Each Ni^{2+} center has a distorted octahedral geometry and is coordinated to the four nitrogen atoms of cyclen in a cis configuration, as well as the nitrogen atoms from two μ_3-cyanides. The Ni–N(cyclen) distances range from 2.090(3)–2.113(2) Å and are comparable to those in another 1-D complex, $\{[Ni(cyclen)][Ag(CN)_2]\}[Ag(CN)_2]$.[7] The C–N distance in the μ_3-cyanides [1.164(4) Å] is slightly longer than that in the terminal cyanides [1.151(4) Å]. The angles in the Ni_2N_2 square (84.2 and 95.8°) show deviations from a right angle. The Ni(1)···Ni(1*) distance is 3.303(9) Å, which is significantly shorter than the corresponding distance of 3.449(1) Å in $[Ni_2(\mu\text{-}N_3)_2(232\text{-tet})_2](PF_6)_2$.[8]

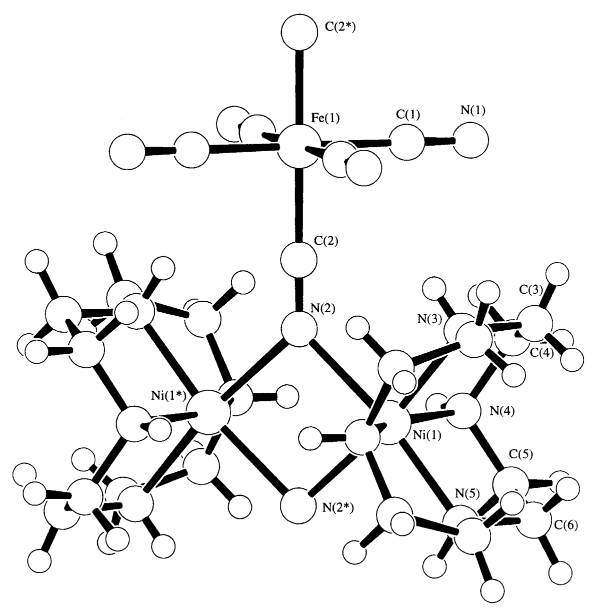

Fig. 1 Perspective view of μ_3-cyano-bridged trimetallic asymmetric unit. Selected bond lengths (Å) and angles (°): Ni(1)–N(2) 2.220(3), Ni(1)–N(2*) 2.234(3), Ni(1)–N(3) 2.090(3), Ni(1)–N(4) 2.113(2), Ni(1)–N(5) 2.093(3), C(1)–N(1) 1.151(4), N(2)–C(2) 1.164(4), N(2)–Ni(1)–N(2*) 84.2(1), Ni(1)–N(2)–Ni(1*) 95.8(1), Fe(1)–C(1)–N(1) 178.3(3), Fe(1)–C(2)–N(2) 179.4(3).

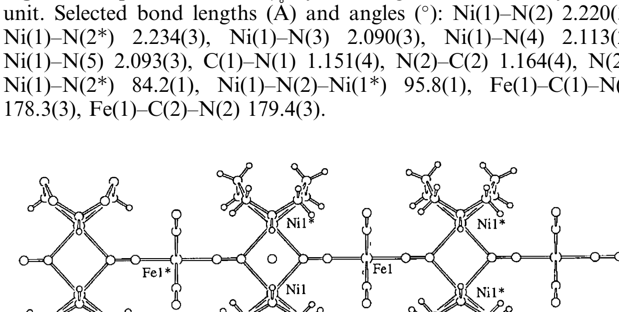

Fig. 2 A view illustrating the μ_3-cyano-bridged chain of **1**.

The temperature dependence of the magnetic susceptibility χ_M of **1** was investigated from 2 to 300 K (Fig. 3). A broad maximum was observed at *ca.* 48 K, indicative of an antiferromagnetic exchange between the Ni^{2+} ions in the $[Ni(cyclen)]_2$ unit. The $\chi_M T$ of **1** decreases continuously on cooling from room temperature and becomes practically zero below 10 K,

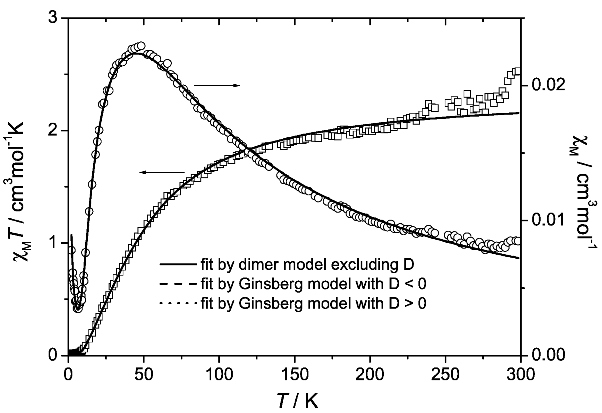

Fig. 3 Temperature dependence of the magnetic susceptibility χ_M (○) and $\chi_M T$ (□) for $[Ni(cyclen)]_2[Fe(CN)_6]\cdot 8H_2O$.

also suggesting a nonmagnetic ground state due to intradimer antiferromagnetic interactions. The increase of χ_M below 7 K could be due to a paramagnetic impurity. To estimate the magnitude of the intradimer exchange coupling constant (J) and the interdimer magnetic interaction (zJ'), the experimental data were initially fitted to a simple analytical expression based on the Hamiltonian $\mathbf{H} = -2JS_1S_2$ with an isotropic interaction between the two $S = 1$ ions and taking into account the molecular field effect. The best fit parameters obtained by minimizing the function $R = \sum (\chi_M^{cal} - \chi_M^{obs})^2/\sum(\chi_M^{obs})^2$ are: $J = -15.59(7)$ cm^{-1}, $zJ' = 2.2(4)$ cm^{-1}, $g = 2.17(1)$, the mole fraction of uncoupled impurity species $\rho = 0.0157(4)$, and $R = 7.7 \times 10^{-4}$. When the zero-field splitting D of the Ni^{2+} ion was considered, a magnetic model derived by Ginsberg *et al.* and corrected by Wen has been used to fit the magnetic data,[9] resulting in almost the same values for the parameters except for uncertain D values: (a) $D = -5(3)$ cm^{-1}, $J = -15.58(7)$ cm^{-1}, $zJ' = 2.2(4)$ cm^{-1}, $g = 2.17(1)$, $\rho = 0.0152(7)$, and $R = 7.7 \times 10^{-4}$; (b) $D = 4(5)$ cm^{-1}, $J = -15.59(7)$ cm^{-1}, $zJ' = 2.2(4)$ cm^{-1}, $g = 2.17(1)$, $\rho = 0.0155(7)$, and $R = 7.7 \times 10^{-4}$. The magnitude of the zero-field splitting seems to be on the order of several wavenumbers, but it is not possible to determine the sign from our data. A similar situation has been documented by Ginsberg *et al.*[9a] In any case, the fit results suggest an antiferromagnetic intradimer coupling through the end-on cyano bridges, and weak ferromagnetic interdimer interactions. The long-range ferromagnetic interdimer interactions are probably mediated by the empty d_σ orbitals of the diamagnetic Fe(II) ions.[3f,10]

The end-on cyano-bridged $[Ni(cyclen)]_2$ unit in **1** is structurally similar to end-on azido-bridged complexes, which are much more common. These azido complexes usually show ferromagnetic interactions between metal centers,[11] hence the observation of an antiferromagnetic interaction between the two nickel(II) centers in **1** is somewhat surprising. However, we note that the Ni–N–Ni angle of 95.8(1)° in **1** is much smaller than that in end-on azido nickel dimers, which fall in a narrow range of 101–105°.[11a] On the other hand, the Ni–N distances in **1** [2.220(3) and 2.234(3) Å] are much longer than that in end-on azido nickel complexes such as $[Ni_2(\mu\text{-}N_3)_2(232\text{-}N_4)_2](ClO_4)_2$ (2.080 Å).[11b] Such structural differences may result in a different magnetic behavior. Recent DFT calculations have shown that the exchange coupling constant J in the end-on azido complex $[Ni_2(\mu\text{-}N_3)_2(NH_3)_8]^{2+}$ decreases with decreasing bridging angle and increasing Ni–N distance.[11a] Antiferromagnetic interaction is also observed in the end-to-end cyano-bridged complexes $[Ni_2(tetren)_2CN](ClO_4)_3$ and $[Ni_2(tetren)_2CN][Cr(CN)_6]\cdot 5H_2O$ (tetren = tetraethylenepent-tetraethylenepentamine), where coupling occurs through the Ni–C≡N–Ni unit.[12] In the case of $[Cu(dmen)]_2[Fe(CN)_6]$, which contains dicopper(II) units that are also axial cyanides of $[Fe(CN)_6]^{4-}$ in a μ_3-fashion as in **1**,[6b] the Cu–N–Cu angle is 91.3(3)° and a weak ferromagnetic interaction between the two copper(II) ions was observed. This seems to be in line with the magnetic behavior of end-on azido-bridged copper complexes, which show ferromagnetic interactions when the bridging angle is below *ca.* 105°.[11a,c] Apparently, additional new end-on cyano-bridged compounds need to be prepared and examined before a complete magneto-structural correlation can be constructed.

Experimental

Synthesis

Preparation of $[Ni(cyclen)]_2[Fe(CN)_6]\cdot 8H_2O$, **1**. Ten milliliters of an aqueous solution of nickel acetate (0.1 g, 0.4 mmol) was slowly added to 10 ml of an aqueous solution of $K_4[Fe(CN)_6]$ (0.15 g, 0.4 mmol) and cyclen (0.07 g, 0.4 mmol). The resulting clear purple solution was placed in the dark at room temperature. After a few days, purple-blue crystals suitable for X-ray crystallography were collected. Yield: 96 mg (29%). Anal. found: C, 32.49, H, 7.20, N, 23.59. Calcd for $Ni_2FeN_{14}C_{22}H_{56}O_8$, $\mathbf{1}\cdot 8H_2O$: C, 32.30, H, 6.90, N, 23.97. IR (KBr, cm^{-1}): υ_{CN} 1979(s), 2062(s).

X-Ray crystallography

A blue plate crystal of $\mathbf{1}\cdot 8H_2O$ was mounted on a glass fiber. All diffraction data was collected at 296 K on a Bruker SMART 1 K CCD diffractometer equipped with graphite monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). A Lorentz-polarization correction was applied to the intensity data. The structure was solved by direct methods (SIR 92)[13] and expanded using Fourier techniques (DIRDIR94).[14] All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included but not refined. The structure was also refined by full-matrix least-squares analysis. All calculations were performed using the teXsan package.

Crystal data for $\mathbf{1}\cdot 8H_2O$: $Ni_2FeN_{14}C_{22}H_{56}O_8$, $M = 818.02$, monoclinic, $P2/m$ (no. 12), $a = 12.048(2)$, $b = 17.729(2)$, $c = 9.155(1)$ Å, $\beta = 112.08(1)°$, $U = 1812.1(4)$ Å^3, $Z = 2$, μ(Mo-Kα) = 14.85 cm^{-1}, 5669 reflections measured, 2104 unique ($R_{int} = 0.019$), final $R = 0.033$, $R_w = 0.044$ for 1808 [$I > 1.50\sigma(I)$] observed reflections.

CCDC reference number 189240. See http://www.rsc.org/suppdata/nj/b2/b203077b/ for crystallographic files in CIF or other electronic format.

Magnetic measurements

The variable-temperature magnetic susceptibility for a collection of small single crystals was measured in the temperature range of 2–300 K under a 10 kOe field, using an Oxford MagLab 2000 system.

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