Letter

A novel heterobimetallic Ni(II)–Ag(I) cyano-bridged coordination polymer incorporating Ag···Ag interactions: {[Ni(cyclen)][Ag(CN)$_2$]}[Ag(CN)$_2$]

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Reaction of nickel(II) acetate with cyclen (cyclen = 1,4,7,10-tetraazacyclododecane) and K[Ag(CN)$_2$] gave {[Ni(cyclen)]-[Ag(CN)$_2$]}[Ag(CN)$_2$], which consists of *cis*-[Ni(cyclen)]$^{2+}$ units bridged by [Ag(CN)$_2$]$^-$ to form a zig-zag chain; the Ag atoms of the free and bridging [Ag(CN)$_2$]$^-$ also align together to form an infinite zig-zag chain with short Ag···Ag distances.

The chemistry of cyano-bridged coordination polymers is of current interest due to the remarkable diversity of structural types that may be obtained from these systems.[1,2] The majority of these materials were prepared by using [M(CN)$_x$]$^{n-}$ (n = 2, 4 or 6) building blocks in conjunction with a transition metal ion complex. We are particularly interested in the use of the linear rigid-rod dicyanometalate anions [Au(CN)$_2$]$^-$ and [Ag(CN)$_2$]$^-$ as building blocks, since apart from being able to act as bridging ligands using the cyanide groups, these anions can also produce polymeric structures *via* strong metal–metal interactions.[3–5] [Ag(CN)$_2$]$^-$ has been shown to bridge metal centres such as Cd(II),[6] Zn(II),[7] Eu(III)[8] and Cu(II)[9] to form a variety of multi-dimensional coordination polymers. Although short Ag···Ag distances were observed in a number of cases, we are aware of only one example, {Cu(bpy)$_2$[Ag(CN)$_2$]}[Ag(CN)$_2$][9], where Ag···Ag interactions play a significant role in the formation of the polymer. We report here the synthesis and structure of a novel heterobimetallic Ni(II)–Ag(I) cyano-bridged coordination polymer, {[Ni(cyclen)][Ag(CN)$_2$]}[Ag(CN)$_2$] (cyclen = 1,4,7,10-tetraazacyclododecane), where apart from the bridging [Ag(CN)$_2$]$^-$ groups, strong Ag···Ag interactions are also utilized in the formation of the polymer.

Treatment of K[Ag(CN)$_2$] with Ni(CH$_3$COO)$_2$ and cyclen at room temperature produced **1** as a purple solid.† The IR spectrum (KBr) shows ν_{CN} bands at 2130 and 2169 cm^{-1}, which are assigned to free and coordinated [Ag(CN)$_2$]$^-$, respectively. The structure of **1**·H$_2$O was determined by X-ray crystallography,‡ and a perspective view is shown in Fig. 1(a). It consists of *cis*-[Ni(cyclen)]$^{2+}$ units bridged by [Ag(CN)$_2$]$^-$ to form positively charged zig-zig chains. There are also [Ag(CN)$_2$]$^-$ counter-ions and uncoordinated water molecules. The Ag atoms of the free and bridging [Ag(CN)$_2$]$^-$ also align to form an infinite zig-zag chain with short Ag···Ag distances of 3.0270(5) and 3.0371(5) Å [Fig. 1(b)]. These short Ag···Ag distances suggest the presence of strong Ag···Ag interactions that appear to play a significant role in the formation of the polymer.

Each nickel atom is coordinated to four nitrogens of cyclen and two nitrogens of [Ag(CN)$_2$]$^-$ in a distorted octahedral geometry. The Ni–N(cyclen) distances are normal and range from 2.080 to 2.141 Å, while the Ni–N(≡C) distances are iden-

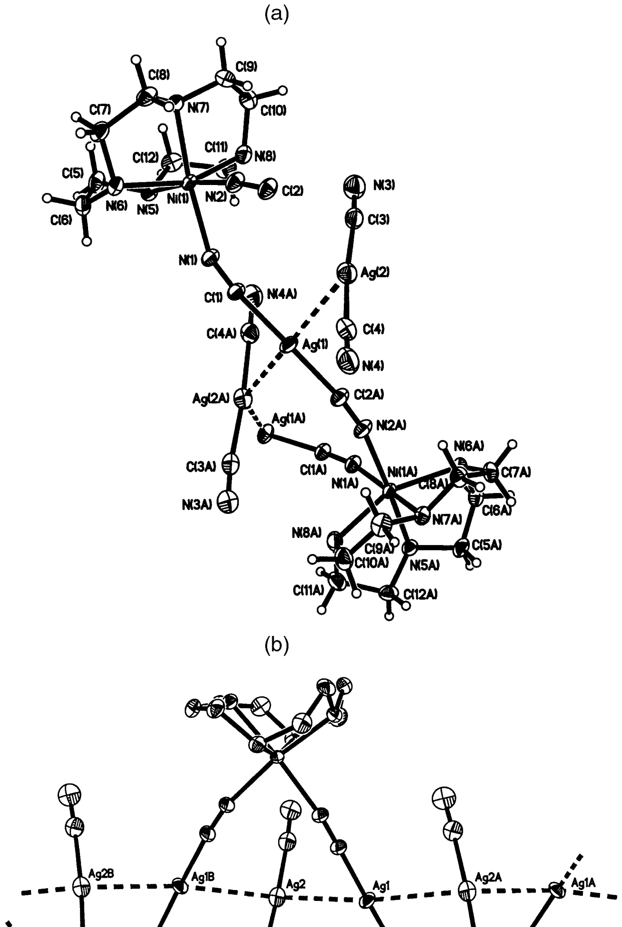

Fig. 1 (a) The molecular structure of {[Ni(cyclen)][Ag(CN)$_2$]}-[Ag(CN)$_2$], **1**. Selected bond lengths (Å) and angles (°): Ag(1)–Ag(2) 3.0270(5), Ag(1)–Ag(2A) 3.0371(5), Ag(1A)–Ag(2A) 3.0372(5), Ag(1)–C(1) 2.053(3), Ag(2)–C(4) 2.050(5), Ag(2)–C(3) 2.052(5), Ag(1)–C(2A) 2.070(4), N(1)–Ni(1) 2.093(3), N(2)–Ni(1) 2.093(3), N(5)–Ni(1) 2.080(3), N(6)–Ni(1) 2.134(3), N(7)–Ni(1) 2.088(3), N(8)–Ni(1) 2.141(3); Ag(2)–Ag(1)–Ag(2A) 169.04(1), Ag(1)–Ag(2A)–Ag(1A) 141.06(1), Ag(2A)–Ag(1A)–C(1A) 101.6(1), C(1)–Ag(1)–C(2A) 178.84(17), C(4)–Ag(2)–C(3) 174.2(2), N(5)–Ni(1)–N(7) 97.4(1), N(5)–Ni(1)–N(2) 172.5(1), N(7)–Ni(1)–N(2) 90.1(1), N(5)–Ni(1)–N(1) 88.1(1), N(7)–Ni(1)–N(1) 173.7(1), N(2)–Ni(1)–N(1) 84.5(1), N(6)–Ni(1)–N(8) 156.0(1). (b) A view showing the zig-zag chains of **1**.

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tical (2.093 Å). Each silver is bonded to two cyanide carbon atoms in an almost linear fashion (C–Ag–C = 178.84°), but the Ni–N≡C units are bent (158.1 and 165.3°). The Ag–C and C–N distances of the bridging $[Ag(CN)_2]^-$ are similar to those of the uncoordinated $[Ag(CN)_2]^-$.

As far as we are aware, this is the first example of a cyano-bridged Ni(II)–Ag(I) complex. It is also the first example of a polymer that contains the bulky macrocyclic ligand cyclen. This polymer clearly demonstrates the unique features of $[Ag(CN)_2]^-$ as a bridging ligand, namely its ability to bridge bulky metal centres and the utilization of strong Ag···Ag interactions to assist in the formation of polymeric materials. With suitable design, a large variety of unique supramolecular structures can be anticipated based on this anion.

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Notes and references

† Preparation of $\{[Ni(cyclen)][Ag(CN)_2]\}[Ag(CN)_2]\cdot H_2O$, **1**, cyclen (0.07 g, 0.4 mmol) was added to a solution of $Ni(CH_3COO)_2\cdot 4H_2O$ (0.1 g, 0.4 mmol) in water (15 cm^3), and the mixture was stirred at room temperature for 15 min. A solution of $K[Ag(CN)_2]$ (0.08 g, 0.4 mmol) in water (5 cm^3) was then added. The resulting purple precipitate was filtered, washed with methanol and then diethyl ether. Slow evaporation of the filtrate gave purple crystals suitable for X-ray crystallography. Yield 44%. Anal. calc. for $C_{12}H_{18}Ag_2N_8NiO$: C, 25,52; H, 3.21; N, 19.84. Found: C, 25.81; H, 3.01; N, 19.45%. IR (KBr, cm^{-1}): ν_{OH} 3431(s); ν_{NH} 3278(m), 3317(m); ν_{CN} 2130(s), 2169(s).

‡ Crystal data for **1**: $C_{12}H_{18}Ag_2N_8NiO$, $M = 564.79$, orthorhombic, $Pna2_1$, $a = 15.930(1)$, $b = 10.8486(7)$, $c = 11.3797(7)$ Å, $U = 1966.6(2)$ Å^3, $Z = 4$, $T = 293(2)$ K, μ(Mo-Kα) = 29.35 cm^{-1}, 10892 reflections measured, 4255 unique ($R_{int} = 0.020$), final $R_1 = 0.0228$, $wR_2 = 0.0637$ (based on F^2) for 4255 $[I > 2\sigma(I)]$ observed reflections. CCDC reference number 440/205. See http://www.rsc.org/suppdata/nj/b0/b004939p/ for crystallographic files in .cif format.

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