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1-D polymer containing the [Ru–N–Ru] μ-nitrido moiety: crystal structure and magnetic properties of $\{[Cu(en)_2]_3[Ru_2N(CN)_{10}]\cdot ClO_4\}_n$ (en = 1,2-diaminoethane)†

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A novel (μ-nitrido–diruthenium)-bridged 1-D coordination polymer was formed from reaction of $K_5[Ru_2N(CN)_{10}]$ with $[Cu(en)_2](ClO_4)_2$; a similar reaction with $[Cu(pn)_2][(ClO_4)_2]$ (pn = 1,3-diaminopropane) gave $\{[Cu(pn)_2]_5[Ru_2N(CN)_{10}]_2\}$ as a discrete molecular compound; variable temperature susceptibility measurements show that there is a weak ferromagnetic interaction between the Cu(II) ions in 1-D polymer.

Construction of coordination polymers with transition metal–organic compounds as building blocks has attracted considerable interest in the context of developing new magnetic, electronic and liquid crystalline materials.[1] The cyanide ligand plays an important role in the synthesis of such polymers due to its remarkable coordination ability towards various metal ions.[2] To develop new building blocks for the assembly of ruthenium coordination polymers,[3] which are sparse in the literature,[4] we turned our attention to the μ-nitrido precursor $K_5[Ru_2N(CN)_{10}]$,[5] which has two appealing properties: first, the $[Ru_2N(CN)_{10}]^{5-}$ unit is very stable with regards to thermal dissociation and hydrolytic reactions; secondly, each ruthenium atom has five cyanide ligands which are capable of multi-dimensional coordination. Herein we describe the synthesis and characterisation of a discrete molecule and a 1-D polymer with $[Ru_2N(CN)_{10}]^{5-}$ as the building block. Variable temperature susceptibility measurements of the Cu_3Ru_2 polymer show that there is a weak ferromagnetic interaction between the Cu(II) ions.

The discrete cluster $\{[Cu(pn)_2]_5[Ru_2N(CN)_{10}]_2\}$ (**1**) and 1-D polymer $\{[Cu(en)_2]_3[Ru_2N(CN)_{10}]\cdot ClO_4\}_n$ (**2**)‡ were obtained by a self-assembly process. An aqueous solution of $K_5[Ru_2N(CN)_{10}]$ and $[Cu(pn)_2][(ClO_4)_2]$ (10 equiv.) was stirred for 1 h and filtered. The filtrate was left to stand at room temperature for several weeks to afford green crystals. As depicted in Fig. 1, each $[Ru_2N(CN)_{10}]^{5-}$ moiety in **1** linked to three $[Cu(pn)_2]^{2+}$ fragments and the two $[Ru_2N(CN)_{10}]^{5-}$ are connected by $[Cu(pn)_2]^{2+}$ to an H-type ennea-metallic cluster. The Cu2–N2 distance of 2.42(1) Å is longer than that of Cu1–N1 (2.291(8) Å) and Cu3–N6 (2.251(8) Å). Interestingly, when we changed the pn ligand to en, the 1-D polymer **2** (shown in Fig. 2) was obtained. The Cu2–N1 and Cu2–N1b distances are 2.539(1) Å, thus revealing that there are bonding interactions between Cu2 and the N atoms of the coordinated CN^- ligands, and these interactions link the [Ru(IV)–N–Ru(IV)] units to generate a 1-D polymeric chain. The distances between copper and the bridging CN^- nitrogen atoms compare well with those reported in the literature (normally ranging from 2.402 to 2.662 Å).[6–9] The nitrido ligand forms a linear bridge between the two ruthenium(IV) centers. The distances Ru1–N4 and N4–Ru1a are 1.7640(4) Å, which are similar to those in $K_5[Ru_2N(CN)_{10}]$ (1.760(1) Å),[5b] and $[K_3(Ru_2N(Cl)_8(H_2O)_2)]$ (1.720(4) Å).[10] The C–N distances range from 1.136(6) to 1.157(5) Å, and also compare well with those in $K_5[Ru_2N(CN)_{10}]$ (1.106(22)–1.145(18) Å).[5b] These observations show that the self-assembly reaction has minimal influence on the structure of $[Ru_2N(CN)_{10}]^{5-}$. The IR spectrum of **2** (KBr) shows sharp

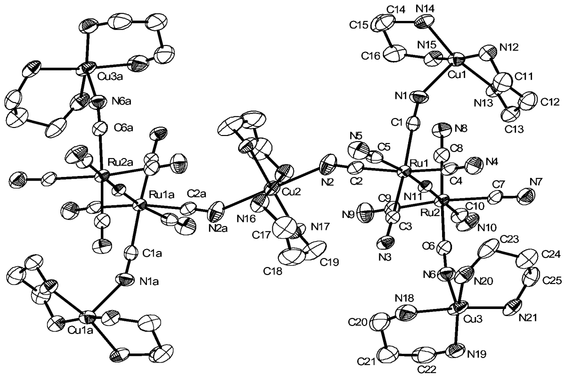

Fig. 1 Molecular structure of **1**. Selected bond distances (Å) and angles (°): Ru1–N11 1.778(6), Ru2–N11 1.758(6), Ru1–C1 2.07(1), Ru1–C2 2.034(11), Ru2–C6 2.056(10), C1–N1 1.15(1), C2–N2 1.15(1), C3–N3 1.16(1), C6–N6 1.16(1), Cu1–N1 2.291(8), Cu2–N2 2.42(1), Cu3–N6 2.251(8); Ru1–N11–Ru2 174.6(4), Ru1–C1–N1 177.9(8), Ru1–C2–N2 177.5(9), Ru2–C6–N6 177.3(9).

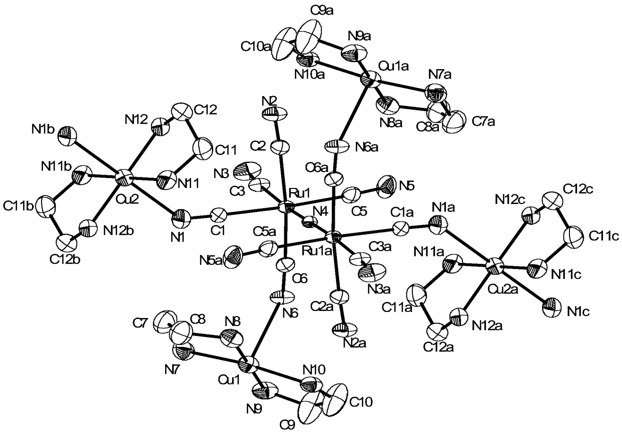

Fig. 2 Crystal structure of the complex cation in **2**. Selected bond distances (Å) and angles (°): Ru1–N4 1.7640(4), Ru1a–N4 1.7640(4), Ru1–C1 2.060(4), Ru1–C3 2.148(4), C1–N1 1.136(6), C2–N2 1.143(6), C3–N3 1.142(6), C6–N6 1.157(5), Cu2–N1 2.539(1), Cu2–N1b 2.539(1), Cu1–N6 2.497(1); Ru1–C1–N1 178.4(4), Ru1–C2–N2 177.3(4), Ru1–C3–N3 175.6(5), Ru1–C6–N6 176.1(4).

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† Electronic supplementary information (ESI) available: field dependence of magnetisation for cluster **1** and polymer **2**. See http://www.rsc.org/suppdata/cc/b2/b205534c/

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peaks at 2121, 2131 and 2149 cm^{-1}, which are assigned to ν(C≡N) of the cyanide ligands.[6,11]

In contrast to the extensive body of work on magnetic properties of 3d and 4f metal coordination polymers, the magnetic nature of ruthenium polymers are less developed.[12] The temperature dependence of molar magnetic susceptibility χ_M of **1** and **2** were investigated on a Quantum Design SQUID, and plots of χ_M^{-1} and $\chi_M T$ *vs.* T are shown in Fig. 3(a) for **1** (Cu_5Ru_4 unit) and Fig. 3(b) for **2** (Cu_3Ru_2 unit), respectively. The magnetic susceptibility obeys the Curie–Weiss law ($\chi_M = C/(T - \theta)$) with $C = 1.97(1)$ cm^3 mol^{-1} K and $\theta = +0.32(2)$ K for **1**, and $C = 1.18(1)$ cm^3 mol^{-1} K and $\theta = +3.2(2)$ K for **2**. The Curie constants C correspond to five paramagnetic Cu(II) ions in **1** or three Cu(II) ions in **2** (with $S = 1/2$ and $g = 2.05$), and diamagnetic Ru(IV) ions. The slight increase of $\chi_M T$ upon cooling and the positive Weiss constant θ suggest a weak ferromagnetic interaction between the Cu(II) ions, and this is more clearly in **2**. The slight decrease of $\chi_M T$ below *ca.* 10 K for both compounds might be due to field saturation effect in the 5 kOe applied field. The field dependence of magnetisation for **1** and **2** was measured at 2.0 K. The experimental magnetisation values for **2** in the 0–50 kOe range are mostly slightly larger than the calculated values using a Brillouin function based on three non-interacting Cu(II) ions with $S = 1/2$, $g = 2.05$. This also supports the weak ferromagnetic coupling between the Cu(II) ions in **2**, notwithstanding the long separations of Cu2–Cu2a (~ 15 Å by 8 bonds; –NCRuNRuCN– bridge) and Cu1–Cu2 (~ 11.5 Å by 6 bonds; –NCRuCN– bridge). Compound **1** has similar Cu–Cu separations, but the coupling between Cu(II) ions seems much weaker than that in **2** based on the θ values.

In summary, a 1-D polymer containing the first μ-nitrido Ru–N–Ru unit has been prepared through a self-assembly process and characterised by X-ray crystallography.[13] The $[Ru_2N(CN)_{10}]^{5-}$ moiety is a potentially versatile building block for the construction of multi-functional polymers.

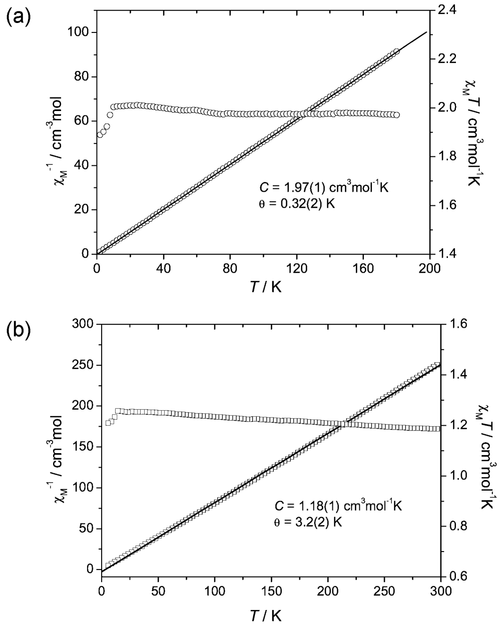

Fig. 3 Temperature dependence of χ_M^{-1} and $\chi_M T$ of **1** (a) and **2** (b).

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Notes and references

‡ To a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (370 mg, 1 mmol) and 1,3-diaminopropane (or 1,2-diaminoethane for **2**) (2 mmol) in water (20 mL) was added $K_5[Ru_2N(CN)_{10}] \cdot 3H_2O$ (72 mg, 0.1 mmol). The mixture was stirred for 1 h at room temperature. The resulting purple solution was filtered. The filtrate was stand for about two weeks, and single crystals suitable for X-ray crystal analysis were obtained. **CAUTION***: Perchlorate salts are potentially explosive and should be handled with care.* **1**: Yield: 40%. Elemental analysis: Calc. for **1**$\cdot 10H_2O$ ($C_{50}H_{100}Cu_5N_{42}Ru_4 \cdot 10H_2O$), C, 27.40, H, 5.52, N, 26.84. Found, C, 27.28, H, 5.14, N, 26.48%. IR (KBr): 2116, 2125, 2142 cm^{-1} (C≡N). *Crystal data* for **1**$\cdot 30H_2O$: $C_{50}H_{160}Cu_5N_{42}O_{30}Ru_4$, $M = 2552.09$, orthorhombic, *Pbca*, $a = 29.462(6)$, $b = 12.660(2)$, $c = 30.697(6)$ Å, $V = 11450(4)$ Å^3, $Z = 2$, $D_c = 1.457$ g cm^{-3}, μ(Mo-Kα) = 1.50 mm^{-1}, $F(000) = 5100$, $T = 293(2)$ K, $2\theta_{max} = 51.18°$, 8684 independent reflections, 517 variable parameters, $R_1 = 0.056$ ($I > 2\sigma(I)$), $wR_2 = 0.15$, GOF(F^2) = 0.91. CCDC 178399. **2**: Yield: 30%. Elemental analysis: Calc. for **2**$\cdot 5H_2O$ ($C_{22}H_{48}ClCu_3N_{23}O_4Ru_2 \cdot 5H_2O$), C, 21.71, H, 4.77, N, 26.48. Found, C, 21.41, H, 4.44, N, 26.67%. IR (KBr): 1090, 1040 cm^{-1} (ClO_4^-), 2121, 2131, 2149 cm^{-1} (C≡N). *Crystal data* for **2**$\cdot 2H_2O$: $C_{22}H_{52}ClCu_3N_{23}O_6Ru_2$, $M = 1163.08$, monoclinic, $P2_1/a$ (No. 14), $a = 9.502(2)$, $b = 22.567(4)$, $c = 11.189(3)$ Å, $\beta = 95.29(2)$, $V = 2389.1(9)$ Å^3, $Z = 4$, $D_c = 1.617$ g cm^{-3}, μ(Mo-Kα) = 2.05 mm^{-1}, $F(000) = 1170$, $T = 300(2)$ K, $2\theta_{max} = 51.12°$, 4396 independent reflections, 272 variable parameters, $R_1 = 0.045$ ($I > 2\sigma(I)$), $wR_2 = 0.138$, GOF(F^2) = 1.14. CCDC 178400. See http://www.rsc.org/suppdata/cc/b2/b205534c/ for crystallographic data in CIF or other electronic format.

1 Recent reviews: (*a*) P. Nguyen, P. Gomez-Elipe and I. Manners, *Chem. Rev.*, 1999, **99**, 1515; (*b*) B. Moulton and M. J. Zaworotko, *Chem. Rev.*, 2001, **101**, 1629.
2 K. R. Dunbar and R. A. Heintz, *Prog. Inorg. Chem.*, 1997, **45**, 283.
3 M.-Y. Choi, M. C. W. Chan, S.-M. Peng, K.-K. Cheung and C.-M. Che, *Chem. Commun.*, 2000, 1259.
4 (*a*) S. Kelch and M. Rehahn, *Macromolecules*, 1999, **32**, 5818; (*b*) C. M. Barnes, D. S. Bohle, R. E. Dinnebier, S. K. Madsen and P. W. Stephens, *Inorg. Chem.*, 1997, **36**, 5793; (*c*) Y. Hoshino and Y. Hagihara, *Inorg. Chim. Acta*, 1999, **292**, 64.
5 (*a*) W. P. Griffith and D. Pawson, *J. Chem. Soc., Dalton Trans.*, 1973, 1315; (*b*) W. P. Griffith, M. J. Mockford and A. C. Skapski, *Inorg. Chim. Acta*, 1987, **126**, 179.
6 P. S. Mukherjeee, T. K. Maji, T. Mallah, E. Zangrando, L. Randaccio and N. R. Chaudhuri, *Inorg. Chim. Acta*, 2001, **315**, 249.
7 M. S. E. Fallah, J. Ribas, X. Solans and M. Font-Bardia, *J. Chem. Soc., Dalton Trans.*, 2001, 247.
8 E. Colacio, J. M. Dominguez-Vera, M. Ghazi, R. Kivekas, J. M. Moreno and A. Pajunen, *J. Chem. Soc., Dalton Trans.*, 2000, 505.
9 H.-Z. Kou, H.-M. Wang, D.-Z. Liao, P. Cheng, Z.-H. Jiang, S.-P. Yan, X.-Y. Huang and G.-L. Wang, *Aust. J. Chem.*, 1998, **51**, 661.
10 M. Ciechanowicz and A. C. Skapski, *J. Chem. Soc. A*, 1971, 1792.
11 I. K. Chu, I. P. Y. Shek, K. W. M. Siu, W.-T. Wong, J.-L. Zuo and T.-C. Lau, *New J. Chem.*, 2000, **24**, 765.
12 (*a*) W.-F. Yeung, W.-L. Man, W.-T. Wong, T.-C. Lau and S. Gao, *Angew. Chem., Int. Ed.*, 2001, **40**, 3031; (*b*) L. F. Chibotaru, V. S. Mironov and A. Ceulemans, *Angew. Chem., Int. Ed.*, 2001, **40**, 4429.
13 (*a*) M. H. Chisholm, *Angew. Chem., Int. Ed.*, 1991, **30**, 673; (*b*) M. H. Chisholm, D. M. Hoffman and J. C. Huffman, *Inorg. Chem.*, 1983, **22**, 2903.