$Ni^{II}Ru^{II}$ and $Cu^{II}Ru^{II}$ Coordination Polymers Constructed from $[Ru(CN)_6]^{4-}$

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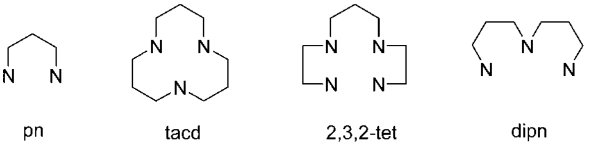
Keywords: Coordination polymers / Cyanides / Magnetic properties / Ruthenium

The dimetallic compounds $[Ni(2,3,2\text{-tet})]_2[Ru(CN)_6]\cdot 8H_2O$ (**1**), $[Ni(pn)_2]_2[Ru(CN)_6]\cdot 5H_2O$ (**2**) $[Ni(tacd)(H_2O)]_2[Ru(CN)_6]\cdot 8H_2O$ (**3**) and $\{[Cu(dipn)]_3[Ru(CN)_6]\}(ClO_4)_2\cdot 4H_2O$ (**4**) [2,3,2-tet = *N*,*N'*-bis(2-aminoethyl)-1,3-propanediamine, pn = 1,3-diaminopropane, tacd = 1,5,9-triazacyclododecane, dipn = dipropylenetriamine] have been prepared from the reaction of $[Ru(CN)_6]^{4-}$ with $[Ni(2,3,2\text{-tet})]^{2+}$, $[Ni(pn)_2]^{2+}$, $[Ni(tacd)(H_2O)]^{2+}$ and $[Cu(dipn)]^{2+}$, respectively. Compounds **1** and **2** contain a two-dimensional square network, compound **3** has a one-dimensional, crossed-double chain structure, while compound **4** has an unusual, two-dimensional, double-edged, honeycomb network. A very weak antiferromagnetic interaction is observed in **2**.

Introduction

In the past decade, metal cyanides such as $[M(CN)_6]^{n-}$ (M = V^{II}, Cr^{III}, Mn^{II}, Mn^{III} or Mn^{IV}, Fe^{II} or Fe^{III}) have been used as building blocks for the construction of a variety of coordination polymers with various interesting structures and properties.[1−28] The use of 4d-metal cyanides as building blocks, however, has not received much attention until more recently. Most of the examples are limited to the heptacyanometallate $[Mo^{III}(CN)_7]^{4-}$ and the octacyanometallates $[M^{IV/V}(CN)_8]^{3/4-}$ (M = $W^{IV/V}$, $Mo^{IV/V}$ or Nb^{IV}).[29] Only a few examples of coordination polymers containing $[Ru(CN)_6]^{4-}$ have been reported.[29p,30−33] We describe here a number of heterodimetallic coordination polymers made from the reaction of $[Ru(CN)_6]^{4-}$ with Cu^{2+} or Ni^{2+} in the presence of an amine ligand such as 2,3,2-tet, pn, tacd, or dipn [2,3,2-tet = *N*,*N'*-bis(2-aminoethyl)-1,3-propanediamine, pn = 1,3-diaminopropane, tacd = 1,5,9-triazacyclododecane, dipn = dipropylenetriamine]. One of our objectives was to compare the structure and magnetic properties of these polymers with the corresponding ones made from $[Fe(CN)_6]^{4-}$. A number of polynuclear cyano-bridged complexes containing $[Fe(CN)_6]^{4-}$ are known. For example, reaction of $[Ni(L)_3]X_2$ with $K_4[Fe(CN)_6]$ in water produces a 3D network, $[Ni(L)_2]_3[Fe(CN)_6]X_2$ [L = ethylenediamine (en), trimethylenediamine (tn); X = PF_6^-, ClO_4^-], which exhibits a ferromagnetic interaction between the nearest Ni^{II} ions through the diamagnetic Fe^{II} ion.[19] On the other hand, reaction of $Cu(ClO_4)_2\cdot 6H_2O$, ept and $K_4[Fe(CN)_6]$ produces the 2D molecule $\{[Cu(ept)]_3[Fe(CN)_6]\}(ClO_4)_2\cdot 5H_2O$ [ept = *N*-(2-aminoethyl)-1,3-diaminopropane], which exhibits little or no coupling between the copper atoms via the −NC−Fe−CN− bridges.[28]



Results and Discussion

Structure of $[Ni(2,3,2\text{-tet})]_2[Ru(CN)_6]\cdot 8H_2O$ (1)

The pale-pink, dimetallic compound **1** was obtained by reacting $Ni(CH_3COO)_2\cdot 4H_2O$ with one molar equivalent of 2,3,2-tet and $K_4[Ru(CN)_6]$. The structure was determined by X-ray crystallography; selected bond lengths and angles are summarized in Table 1. The compound is isomorphous to $[Ni^{II}(diamine)_2]_2[Fe^{III}(CN)_6]X$.[7,17,18] The asymmetric unit of **1** contains a $[Ni(2,3,2\text{-tet})]^{2+}$ cation, one-half of a $[Ru(CN)_6]^{4-}$ anion, and four water molecules (Figure 1a). The four equatorial cyanides of each $[Ru(CN)_6]^{4-}$ unit are coordinated to four *trans*-$[Ni(2,3,2\text{-tet})]^{2+}$ moieties to pro-

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DOI: 10.1002/ejic.200400537

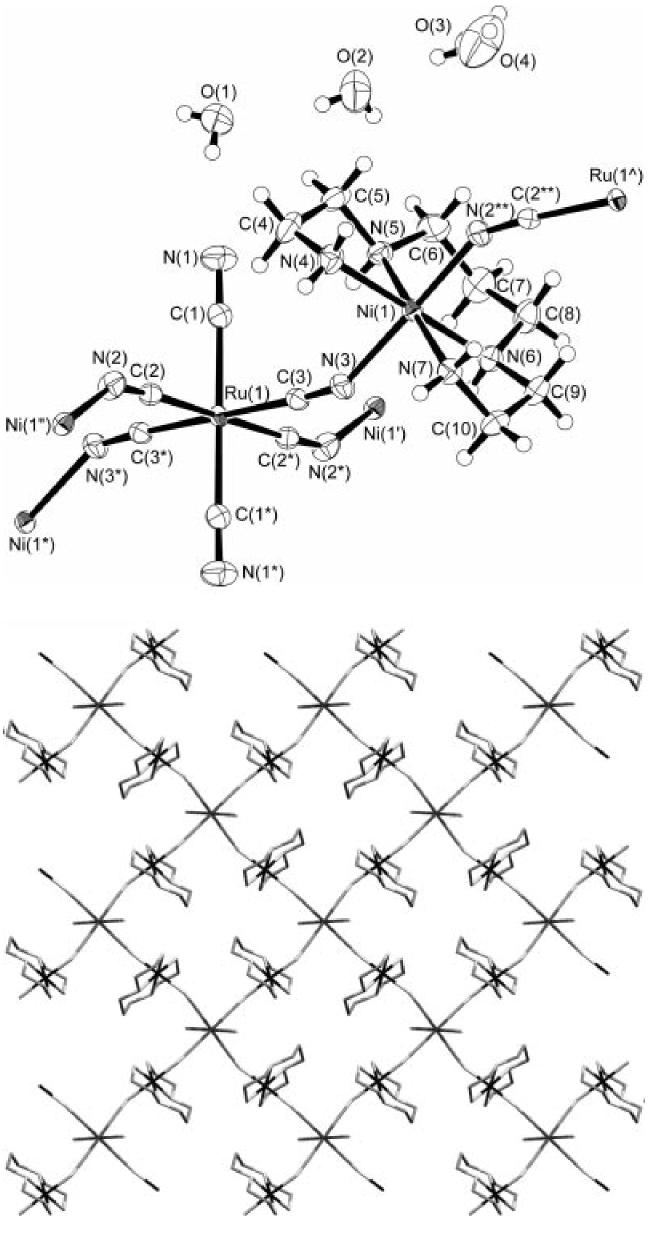


Figure 1. (a) Asymmetric unit of $[Ni(2,3,2\text{-tet})]_2[Ru(CN)_6]\cdot 8H_2O$ (**1**) showing the atom labeling scheme; (b) view of the 2D structure of $[Ni(2,3,2\text{-tet})]_2[Ru(CN)_6]\cdot 8H_2O$ (**1**); water molecules and hydrogen atoms have been omitted for clarity

duce a square 2D network which has an aaa-type sequence (Figure 1b). The average Ru−C bond length of 2.03 Å and C≡N bond length of 1.156 Å are similar to those in $Mn_2[Ru(CN)_6]\cdot 8H_2O$.[30] The bond lengths of bridging [1.156(3) Å] and terminal cyanides [1.154(3) and 1.157(3) Å] are essentially identical. The Ni−N bond lengths in *trans*-$[Ni(2,3,2\text{-tet})]^{2+}$ range from 2.102(2) to 2.109(2) Å, and are similar to those in other *trans*-$[Ni(2,3,2\text{-tet})]^{2+}$ compounds.[34] There are N−H···O, O−H···N, O−H···O hydrogen-bond interactions in the crystal structure which are mainly between the water solvates and two of the amine nitrogens. The O···O distances range from 2.794(4)−2.880(5) Å and the N···O distances are 2.873(6) and 3.064(4) Å (Table S1, Supporting Information). The Ni···Ni separation through -NC−Ru−CN- is 10.06 Å, and the shortest interlayer Ni···Ni distance is 8.91 Å.

Table 1. Selected bond lengths [Å] and angles [°] of **1**

Ru(1)−C(1)	2.041(2)	Ru(1)−C(2)	2.025(2)
Ru(1)−C(3)	2.029(2)	Ni(1)−N(2)	2.085(2)
Ni(1)−N(3)	2.101(2)	Ni(1)−N(4)	2.108(3)
Ni(1)−N(5)	2.109(2)	Ni(1)−N(6)	2.102(2)
Ni(1)−N(7)	2.103(2)	N(1)−C(1)	1.154(3)
N(2)−C(2)	1.157(3)	N(3)−C(3)	1.156(3)
C(1)−Ru(1)−C(2)	89.95(9)	C(1)−Ru(1)−C(3)	90.79(9)
C(2)−Ru(1)−C(3)	90.27(9)	Ru(1)−C(1)−N(1)	178.7(2)
Ru(1)−C(2)−N(2)	176.1(2)	Ru(1)−C(3)−N(3)	176.3(2)
Ni(1)−N(2)−C(2)	148.2(2)	Ni(1)−N(3)−C(3)	145.2(2)

Structure of $[Ni(pn)_2]_2[Ru(CN)_6]\cdot 5H_2O$ (2)

Blue crystals of compound **2** were obtained by treating $Ni(CH_3COO)_2\cdot 4H_2O$ with 2 mol-equiv. of pn and 1 mol-equiv. of $K_4[Ru(CN)_6]$ in water. The structure was determined by X-ray crystallography; selected bond lengths and angles are summarized in Table 2. The asymmetric unit of **2** consists of a $[Ni(pn)_2]^{2+}$ cation, one-half of a $[Ru(CN)_6]^{4-}$ anion, and two and a half water molecules (Figure 2a). The four equatorial cyanides of each $[Ru(CN)_6]^{4-}$ unit are coordinated to four *trans*-$[Ni(pn)_2]^{2+}$ moieties to produce a square 2D network that is similar to that of compound **1** (Figure 2b). Bridging of the cyano group leads to only a small deviation of the C(cyanide)−Ru−C(cyanide) angles [89.63(11)−90.37(11)°] from a right angle, as in compound **1**. The average Ru−C bond length of 2.03 Å and C≡N bond length of 1.15 Å are similar to those in compound **1**; the bond lengths of bridging (1.152 Å) and terminal cyanides (1.146 Å) also show little difference. The separation of neighboring nickel atoms through −NC−Ru−CN− is 10.30 Å.

Table 2. Selected bond lengths [Å] and angles [°] of **2**; symmetry transformations used to generate equivalent atoms: $-x + 1$, $-y$, $-z$

Ru−C(1)	2.029(3)	Ni(2)−N(1)	2.104(3)
Ru−C(2)	2.025(3)	Ni(2)−N(6)	2.125(3)
Ru−C(3)	2.036(3)	Ni(2)−N(7)	2.117(3)
Ni(1)−N(2)	2.070(3)	N(1)−C(1)	1.151(4)
Ni(1)−N(4)	2.103(3)	N(2)−C(2)	1.154(4)
Ni(1)−N(5)	2.118(3)	N(3)−C(3)	1.146(5)
C(2′)−Ru−C(1)	90.37(11)	N(1)−C(1)−Ru	178.1(3)
C(2)−Ru−C(1)	89.63(11)	N(2)−C(2)−Ru	177.8(2)
C(1)−Ru−C(3′)	90.17(14)	N(3)−C(3)−Ru	178.8(4)
C(1′)−Ru−C(3′)	89.83(14)	C(1)−N(1)−Ni(2)	154.6(3)
C(2′)−Ru−C(3)	88.92(12)	C(2)−N(2)−Ni(1)	158.0(2)
C(2)−Ru−C(3)	91.08(12)		

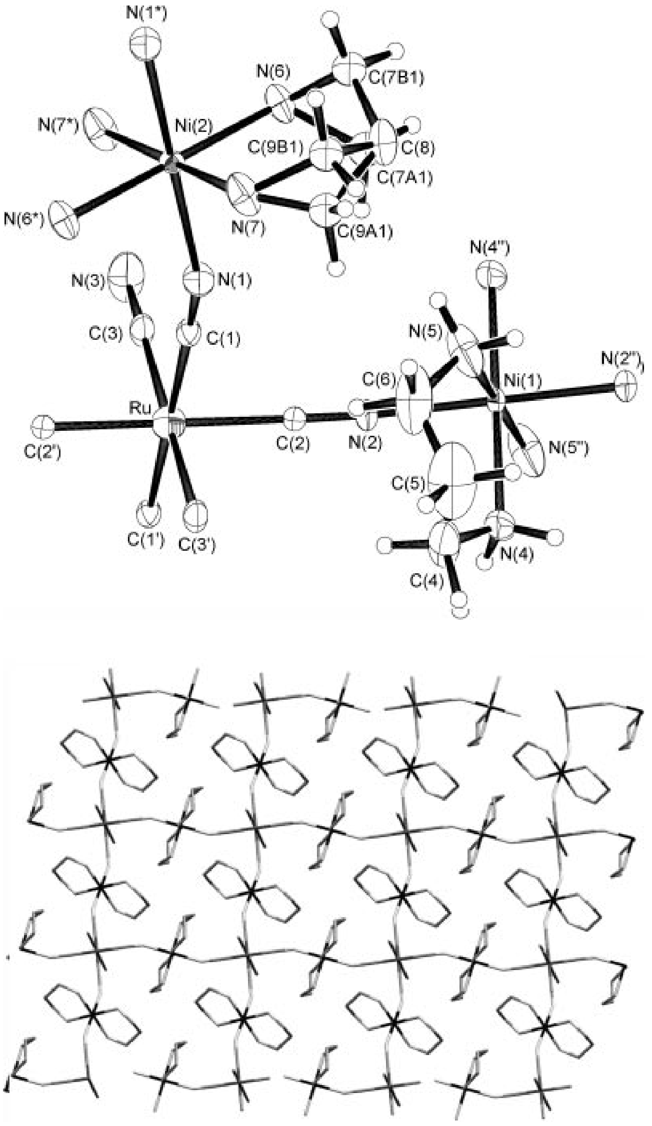


Figure 2. (a) Asymmetric unit of $[Ni(pn)_2]_2[Ru(CN)_6]\cdot5H_2O$ (**2**) showing the atom labeling scheme; water molecules have been omitted for clarity; (b) view of the 2D structure of $[Ni(pn)_2]_2[Ru(CN)_6]\cdot5H_2O$ (**2**); water molecules and hydrogen atoms have been omitted for clarity

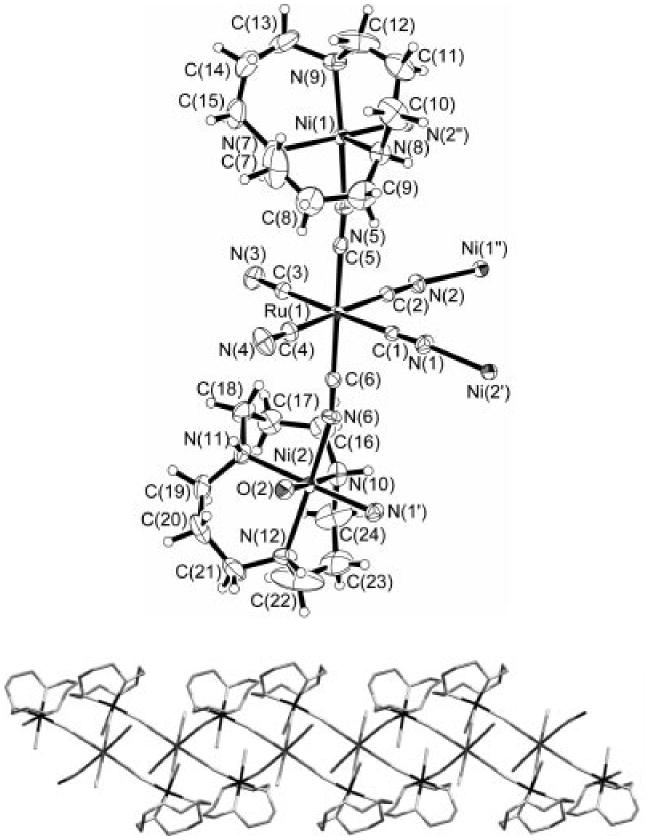


Figure 3. (a) Asymmetric unit of $[Ni(tacd)(H_2O)]_2[Ru(CN)_6]\cdot8H_2O$ (**3**) showing the atom labeling scheme; water molecules have been omitted for clarity; (b) view of the 1D structure of $[Ni(tacd)(H_2O)]_2[Ru(CN)_6]\cdot8H_2O$ (**3**); water molecules and hydrogen atoms have been omitted for clarity

Table 3. Selected bond lengths [Å] and angles [°] of **3**

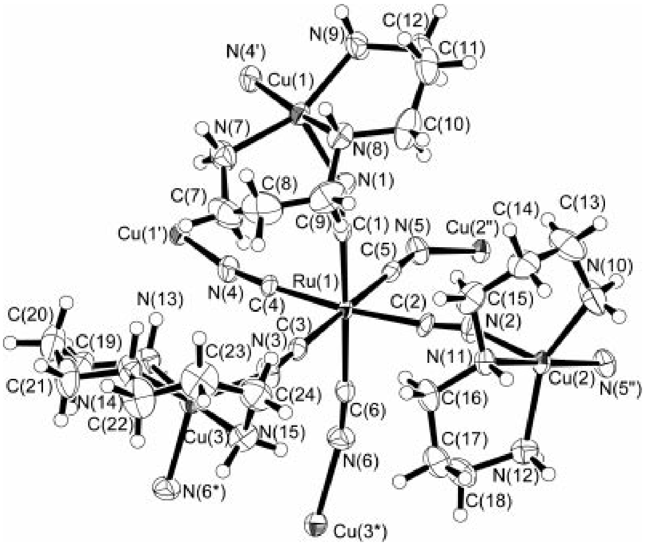
Ru(1)–C(1)	2.025(4)	Ru(1)–C(4)	2.043(5)
Ru(1)–C(2)	2.024(5)	Ru(1)–C(5)	2.028(5)
Ru(1)–C(3)	2.038(5)	Ru(1)–C(6)	2.032(5)
Ni(1)–O(1)	2.272(3)	Ni(2)–O(2)	2.217(3)
Ni(1)–N(2)	2.063(4)	Ni(2)–N(1)	2.055(4)
Ni(1)–N(5)	2.040(4)	Ni(2)–N(6)	2.067(4)
Ni(1)–N(7)	2.101(4)	Ni(2)–N(10)	2.089(4)
Ni(1)–N(8)	2.099(4)	Ni(2)–N(11)	2.095(4)
Ni(1)–N(9)	2.106(4)	Ni(2)–N(12)	2.124(4)
N(1)–C(1)	1.144(6)	N(4)–C(4)	1.155(7)
N(2)–C(2)	1.142(6)	N(5)–C(5)	1.153(6)
N(3)–C(3)	1.147(6)	N(6)–C(6)	1.151(6)
Ru(1)–C(1)–N(1)	178.0(4)	Ru(1)–C(2)–N(2)	176.9(4)
Ru(1)–C(3)–N(3)	177.6(5)	Ru(1)–C(4)–N(4)	177.3(5)
Ru(1)–C(5)–N(5)	177.9(4)	Ru(1)–C(6)–N(6)	177.8(4)
C(1)–Ru(1)–C(6)	91.5(2)	C(2)–Ru(1)–C(5)	89.7(2)
C(1)–Ru(1)–C(3)	177.8(2)	C(2)–Ru(1)–C(4)	176.5(2)
C(5)–Ru(1)–C(6)	178.4(2)	Ni(1)–N(2)–C(2)	168.0(4)
Ni(1)–N(5)–C(5)	170.3(4)	Ni(2)–N(1)–C(1)	163.5(4)
Ni(2)–N(6)–C(6)	163.8(4)	N(1)–Ni(2)–N(6)	89.7(2)
N(2)–Ni(1)–N(5)	90.7(2)		

Structure of $[Ni(tacd)(H_2O)]_2[Ru(CN)_6]\cdot8H_2O$ (3)

Red crystals of **3** were obtained from the reaction of $Ni(CH_3COO)_2\cdot4H_2O$ with tacd and $K_4[Ru(CN)_6]$. Compound **3** has a 1D crossed double-chain structure (Figure 3b), as determined by X-ray crystallography. Selected bond lengths and angles are summarized in Table 3. The asymmetric unit consists of two $[Ni(tacd)(H_2O)]^{2+}$ cations, one $[Ru(CN)_6]^{4-}$ anion, and eight water molecules (Figure 3a). Each $[Ru(CN)_6]^{4-}$ unit is connected to four $[Ni(tacd)(H_2O)]^{2+}$ units through two axial and two equatorial cyanides, and each $[Ni(tacd)(H_2O)]^{2+}$ unit is connected to two $[Ru(CN)_6]^{4-}$ units in a *cis* fashion. This produces Ru–Ni squares. Each square is perpendicular to adjacent squares and this arrangement results in a zig-zag structure. The angles C(1)–Ru(1)–C(6), C(2)–Ru(1)–C(5), N(2)–Ni(1)–N(5) and N(1)–Ni(2)–N(6) are 91.5(2)°, 89.7(2)°, 90.7(2)° and 89.7(2)°, respectively. Each nickel(II) atom is coordinated to the three nitrogen atoms of tacd, two nitrogen atoms of cyanide and one oxygen atom of a water molecule, forming a distorted octahedral geometry. The Ni−N(tacd) distances range from 2.099(4) to 2.106(4) Å for Ni(1) and 2.089(4) to 2.124(4) Å for Ni(2), which are within the normal range of Ni−N(amine) distances. The Ni−N(cyanide) distances range from 2.040(4) to 2.067(4) Å. The bridging C≡N distances of 1.142(6)−1.153(6) Å are similar to those in $Mn_2[Ru(CN)_6]\cdot 8H_2O$ [1.152(9)−1.165(8) Å].[30] The Ru−C bond lengths are 2.024(5)−2.043(5) Å. The Ru−C≡N bond angles are close to linear [176.9(4)−178.0(4)°] while the Ni−N≡C angles are bent [163.5(4)−170.3(4)°]. There is intramolecular hydrogen bonding between the coordinated water molecules, with an O(1)···O(2) distance of 2.847(5) Å. The uncoordinated water molecules are positioned between the chains and are hydrogen-bonded to the terminal cyanides of $[Ru(CN)_6]^{4-}$; the N···O distances range from 2.800(6) to 3.523(6) Å. The Ni···Ni separation through -NC−Ru−CN- is 10.38 Å, and the shortest interchain Ni···Ni distance is 9.56 Å.

Structure of $\{[Cu(dipn)]_3[Ru(CN)_6]\}(ClO_4)_2\cdot 4H_2O$ (4)

Green crystals of **4** were obtained from the reaction of $Cu(CH_3COO)_2\cdot H_2O$ with dipn, $K_4[Ru(CN)_6]$ and $NaClO_4$. The structure of **4** was determined by X-ray crystallography; selected bond lengths and angles are summarized in Table 4. The asymmetric unit consists of three $[Cu(dipn)]^{2+}$, one $[Ru(CN)_6]^{4-}$, two ClO_4^-, and four water molecules (Figure 4a). The Cu^{II} in each $[Cu(dipn)]^{2+}$ unit is five-coordinate and is bonded to two nitrogen atoms of two $[Ru(CN)_6]^{4-}$ and the three nitrogen atoms of a dipn. Each $[Ru(CN)_6]^{4-}$ is connected to six $[Cu(dipn)]^{2+}$ units through cyano bridges to form an unusual 2D double-edged honeycomb network (Figure 4b), which is similar to that of $\{[Cu(ept)]_3[Fe(CN)_6]\}(ClO_4)_2\cdot 5H_2O$.[28] The Ru−C bond lengths lie in the range 2.018(7)−2.044(8) Å. The bridging C≡N distances range from 1.144(10) to 1.159(9) Å, and are similar to those in $Mn_2[Ru(CN)_6]\cdot 8H_2O$.[30] The Cu−N(amine) bond lengths [2.007(7)−2.090(7) Å] are similar to those in $\{[Cu(ept)]_3[Fe(CN)_6]\}(ClO_4)_2\cdot 5H_2O$ (2.000−2.050 Å). The Cu−N≡C angles [153.7(6)−168.3(7)°] show significant deviations from 180°, and the Cu atom in each $[Cu(dipn)]^{2+}$ moiety has a distorted square-pyramidal geometry, with τ values of 0.16 for Cu(1), 0.38 for Cu(2) and 0.61 for Cu(3). There are N−H···O interactions in the crystal structure which involve mainly the water solvates and the amine nitrogen, with N···O distances ranging from 3.077(12) to 3.240(13) Å. Hydrogen bonding involving the perchlorate ion is also observed, with N···O distances ranging from 3.071(19) to 3.211(15) Å (Table S2, Supporting Information). The adjacent Cu···Cu separations are 6.590−8.270 Å, and the Cu···Cu distance through −NC−Ru−CN− is 10.093−10.318 Å.



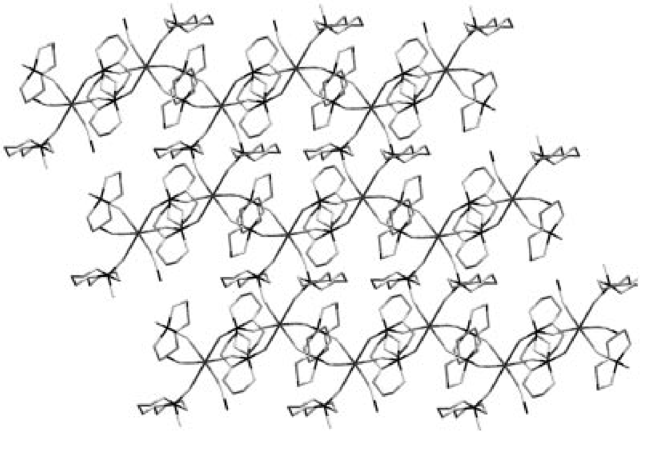


Figure 4. (a) Asymmetric unit of $[Cu(dipn)]_3[Ru(CN)_6](ClO_4)_2\cdot 4H_2O$ (**4**) showing the atom labeling scheme; water molecules and perchlorate ions have been omitted for clarity; (b) view of the 2D honeycomb structure of $[Cu(dipn)]_3[Ru(CN)_6](ClO_4)_2\cdot 4H_2O$ (**4**); water molecules and perchlorate ions have been omitted for clarity

Table 4. Selected bond lengths [Å] and angles [°] of **4**

Cu(1)−N(1)	2.155(7)	Cu(1)−N(4)	2.006(7)
Cu(1)−N(7)	2.009(7)	Cu(1)−N(8)	2.067(7)
Cu(1)−N(9)	2.018(7)	Cu(2)−N(2)	2.166(7)
Cu(2)−N(5)	2.009(7)	Cu(2)−N(10)	2.023(8)
Cu(2)−N(11)	2.060(6)	Cu(2)−N(12)	2.032(7)
Cu(3)−N(3)	2.039(7)	Cu(3)−N(6)	2.116(7)
Cu(3)−N(13)	2.007(7)	Cu(3)−N(14)	2.090(7)
Cu(3)−N(15)	2.015(7)	Ru(1)−C(1)	2.019(8)
Ru(1)−C(2)	2.030(8)	Ru(1)−C(3)	2.026(8)
Ru(1)−C(4)	2.020(8)	Ru(1)−C(5)	2.018(8)
Ru(1)−C(6)	2.044(8)	N(1)−C(1)	1.158(10)
N(2)−C(2)	1.144(10)	N(3)−C(3)	1.159(9)
N(4)−C(4)	1.147(10)	N(5)−C(5)	1.149(9)
N(6)−C(6)	1.153(10)		
C(1)−Ru(1)−C(6)	177.6(3)	C(2)−Ru(1)−C(4)	174.0(3)
C(3)−Ru(1)−C(5)	178.2(3)	Ru(1)−C(1)−N(1)	179.4(7)
Ru(1)−C(2)−N(2)	173.6(7)	Ru(1)−C(3)−N(3)	176.5(7)
Ru(1)−C(4)−N(4)	174.5(7)	Ru(1)−C(5)−N(5)	179.4(6)
Ru(1)−C(6)−N(6)	174.4(7)	Cu(1)−N(1)−C(1)	155.3(7)
Cu(1)−N(4)−C(4)	161.0(7)	Cu(2)−N(2)−C(2)	159.4(7)
Cu(2)−N(5)−C(5)	153.7(6)	Cu(3)−N(3)−C(3)	157.1(7)
Cu(3)−N(6)−C(6)	168.3(7)		

Magnetic Properties

Figure 5 illustrates the temperature dependence of $\chi_M T$ and χ_M^{-1} per Ni_2Ru unit of compound **1**. The $\chi_M T$ value remains more or less constant from 300 K to 10 K. Below 10 K the $\chi_M T$ value decreases rapidly with decreasing temperature. A plot of χ_M^{-1} vs. *T* obeys the Curie–Weiss law with a Curie constant, *C*, of 2.468 $cm^3·K·mol^{-1}$ and a Weiss constant, *θ*, of 0.01 K. The *C* value is slightly larger than the expected value of 2.00 $cm^3·K·mol^{-1}$ for non-coupled, spin-only Ni ($S = 1$) and diamagnetic Ru ions. The very small Weiss constant suggests there is negligible magnetic interaction between the Ni^{II} centers through the diamagnetic $[Ru^{II}(CN)_6]^{4-}$ bridges.

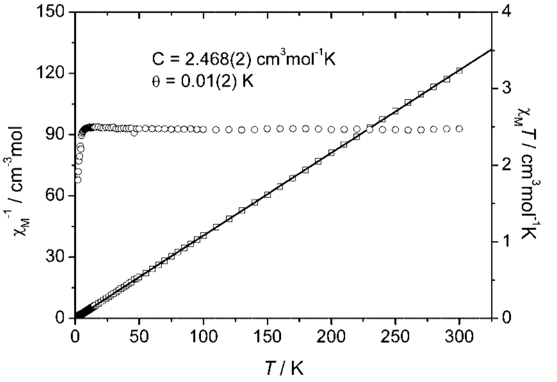


Figure 5. Temperature dependence of $\chi_M T$ (squares) and χ_M^{-1} (circles) for compound **1** per Ni_2Ru unit

The plot of χ_M^{-1} vs. *T* for compound **2** (Figure S1, Supporting Information) obeys the Curie–Weiss law with a Curie constant of 2.56 $cm^3·K·mol^{-1}$ and a small negative Weiss constant of −2.95 K. The *C* value is slightly larger than the expected value (2.00 $cm^3·K·mol^{-1}$) for non-coupled, spin-only Ni ($S = 1$) and diamagnetic Ru ions. The negative Weiss constant suggests that a very weak antiferromagnetic interaction between the Ni^{II} centers through the diamagnetic $[Ru^{II}(CN)_6]^{4-}$ bridges may be present.

For compound **3**, the plot of χ_M^{-1} vs. *T* in the range of 2–300 K (Figure S2; Supporting Information) obeys the Curie–Weiss law, with a small positive Weiss constant of 1.0 K and a Curie constant of 2.17 $cm^3·K·mol^{-1}$. For compound **4**, the plot of χ_M^{-1} vs. *T* in the range of 2–300 K (Figure S3, Supporting Information) also obeys the Curie–Weiss law, with a small positive Weiss constant of +1.1 K and a Curie constant of 1.16 $cm^3·K·mol^{-1}$. The small positive Weiss constants in compounds **3** and **4** do not necessarily imply ferromagnetic interaction between the Ni atoms through the −NC−Ru−CN− bridge, since we have no other supporting data available.

Conclusion

In this work four dimetallic assemblies made from $K_4[Ru(CN)_6]$ are reported. Although 3D NiFe assemblies have been obtained from the reaction of $[Ni(L)_3]X_2$ (L = en, tn; X = PF_6^-, ClO_4^-) with $K_4[Fe(CN)_6]$, similar reactions using $K_4[Ru(CN)_6]$ produce only either 2D (**1**, **2**) or 1D (**3**) compounds. In the case of CuM, however, both $[Cu(dipn)]_3[Ru(CN)_6]\}(ClO_4)_2·4H_2O$ (**4**) and $\{[Cu(ept)]_3[Fe(CN)_6]\}(ClO_4)_2·5H_2O$ have the same unusual, double-edged honeycomb structure.

In all the compounds there is little or no magnetic interaction between the paramagnetic metal centers through the diamagnetic $[Ru^{II}(CN)_6]^{4-}$ bridge. Compounds **1** and **3** involve interesting octahedral Ni^{II} coordination compounds, and it is notable that the magnetic moments of the less deformed NiN_6 octahedra in **1** and **2** reflect more spin-orbit coupling than the clearly more distorted octahedron in **3**.

Experimental Section

Reagents and Physical Measurements: *N,N′*-Bis(2-aminoethyl)-1,3-propanediamine (2,3,2-tet), 1,3-diaminopropane (pn), and dipropylenetriamine (dipn) were purchased from Acros. 1,5,9-Triazacyclododecane (tacd) was obtained from Aldrich. All other reagents and solvents were of reagent grade and used without further purification. Potassium hexacyanoruthenate(II) was prepared according to a literature method.[35] Infrared spectra were recorded as KBr discs in the region of 400–4000 cm^{-1} with an Avatar 360 FTIR spectrophotometer. Elemental analyses were carried out with an Elementar Vario EL Analyser. The variable-temperature magnetic susceptibilities for a collection of small single crystals of **1**–**4** were measured in the temperature range of 2–300 K using either an MPMS XL-5 SQUID (for **1**, **3**, **4**) or an Oxford MagLab 2000 system (for **2**).

Preparation of $[Ni(2,3,2\text{-}tet)]_2[Ru(CN)_6]·8H_2O$ (1): An aqueous solution (10 mL) of 2,3,2-tet (38.7 μL, 0.24 mmol) and $K_4[Ru(CN)_6]$ (0.1 g, 0.24 mmol) was slowly added to a methanolic solution (10 mL) of $Ni(CH_3COO)_2·4H_2O$ (0.06 g, 0.24 mmol). The resulting solution was filtered to remove some pale-pink precipitate and the filtrate was then allowed to stand in the dark at room temperature for a few days. The resulting pale-pink crystals were collected by filtration and washed with methanol and then diethyl ether (79 mg, 76%). $C_{20}H_{56}N_{14}Ni_2O_8Ru$ (839.22): calcd. C 28.62, H 6.73, N, 23.37; found C 28.38, H 6.81, N 23.51. IR (KBr): $\tilde{\nu}$ = 2066 s (C≡N) cm^{-1}.

Preparation of $[Ni(pn)_2]_2[Ru(CN)_6]·5H_2O$ (2): An aqueous solution (10 mL) containing pn (0.06 g, 0.8 mmol) and $K_4[Ru(CN)_6]$ (0.2 g, 0.48 mmol) was added dropwise to an aqueous solution (10 mL) of $Ni(CH_3COO)_2·4H_2O$ (0.2 g, 0.8 mmol). The resulting blue solution was placed in the dark at room temperature for several days. The resulting blue crystals were filtered, washed with methanol and diethyl ether, and dried in air (225 mg, 74%). $C_{18}H_{50}N_{14}Ni_2O_5Ru$ (761.22): calcd. C 28.40, H 6.62, N 25.76; found C 28.49, H 6.51, N 25.52. IR (KBr): $\tilde{\nu}$ = 2062, 2094 (C≡N) cm^{-1}.

Preparation of $[Ni(tacd)(H_2O)]_2[Ru(CN)_6]·8H_2O$ (3): An aqueous solution (5 mL) of tacd (0.1 g, 0.24 mmol) and $K_4[Ru(CN)_6]$ (0.1 g, 0.24 mmol) was added dropwise to an aqueous solution (3 mL) of $Ni(CH_3COO)_2·4H_2O$ (0.06 g, 0.24 mmol). The resulting blue solution was placed in the dark at room temperature for several days. The resulting red crystals were filtered, washed with methanol and diethyl ether, and dried in air. (178 mg, 83%). $C_{24}H_{62}N_{12}Ni_2O_{10}Ru$ (897.30): calcd. C 32.13, H 6.96, N 18.73; found C 32.14, H 6.91, N 18.75. IR (KBr): $\tilde{\nu}$ = 2066 s (C≡N) cm^{-1}.

Table 5. Crystal data and structure refinements for compounds **1**–**4**

	1	**2**	**3**	**4**
Empirical formula	$C_{20}H_{56}N_{14}O_8Ni_2Ru$	$C_{18}H_{50}N_{14}O_5Ni_2Ru$	$C_{24}H_{62}N_{12}O_{10}RuNi_2$	$C_{24}H_{59}Cl_2N_{15}O_{12}Cu_3Ru$
Formula mass	839.22	761.22	897.30	1112.44
Crystal system	monoclinic	triclinic	triclinic	triclinic
Space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no.2)
a [Å]	8.907(2)	8.6964(17)	12.016(1)	13.436(7)
b [Å]	13.815(3)	9.2072(18)	12.635(2)	14.570(5)
c [Å]	14.607(3)	10.289(2)	15.111(1)	12.92(1)
α [°]	90	86.06(3)	68.60(1)	94.30(8)
β [°]	99.66(1)	84.32(3)	72.62(1)	118.24(4)
γ [°]	90	70.14(3)	83.75(2)	81.13(6)
V [Å^3]	1771.9(7)	770.5(3)	2038.5(4)	2201(2)
Z	2	1	2	2
$D_{calcd.}$ [g cm^{-3}]	1.573	1.641	1.462	1.678
T [K]	298(1)	293(2)	298(2)	298(2)
μ [cm^{-1}]	15.33	17.46	13.40	19.56
F_{000}	876.00	396	940.00	1138.00
Measured/independent reflections	21830/4085	15727/3521	12836/8856	8097/7738
R_{int}	0.027	0.0295	0.021	0.072
R,[a] R_w[b]	0.024, 0.021	0.032,0.095	0.048, 0.068	0.059, 0.067
Goodness of fit	0.994	1.053	1.97	1.97

[a] $\Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $[(\Sigma w(|F_o| - |F_c|)^2/\Sigma(wF_o^2)]^{0.5}$.

Preparation of {[Cu(dipn)]$_3$[Ru(CN)$_6$]}(ClO$_4$)$_2$·4H$_2$O (4): An aqueous solution (10 mL) of $Cu(CH_3COO)_2 \cdot H_2O$ (0.1 g, 0.5 mmol) was added to an aqueous solution (5 mL) of $K_4[Ru(CN)_6]$ (0.21 g, 0.5 mmol) and dipn (65 µL, 0.5 mmol). An aqueous solution (2 mL) of $NaClO_4$ (0.06 g, 0.5 mmol) was then added dropwise to the resulting solution. After filtration, the filtrate was allowed to stand in the dark at room temperature for two weeks. The resulting green crystals were collected and washed with a small amount of methanol and then diethyl ether (79 mg, 76%). $C_{24}H_{59}Cl_2Cu_3N_{15}O_{12}Ru$ (1112.4): calcd. C 25.91, H 5.35, N 18.89; found C 25.72, H 5.30, N 18.76. IR (KBr): $\tilde{\nu}$ = 2075 s (C≡N) cm^{-1}.

Crystallographic Data Collection and Structure Determination: Diffraction data for a crystal of **1** or **3** were collected with a Bruker SMART CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å) at 298 K. Data for a crystal of **2** was collected with a Nonius Kappa CCD diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71073 Å) at 293 K. Data for a crystal of **4** was collected with a Rigaku AFC7R diffractometer with graphite-monochromated Mo-K_α radiation (λ = 0.71069 Å) at 298 K. The structure of **1** was solved by direct methods with PATTY,[36] the structure of **2** was solved by direct methods and refined by a full-matrix least-squares technique based on F^2 using the SHELXL 97 program,[37] and the structures of **3** and **4** were solved by direct methods with SIR92[38] and refined by a full-matrix least-squares technique based on F^2 using teXsan.[39] Hydrogen atoms were included but not refined. All calculations were performed with a Silicon Graphic computer, using the teXsan crystallographic software package from Molecular Structure Corporation. All crystallographic data and other details and parameters are summarized in Table 5. CCDC-242152 (**1**), -242160 (**2**), -242151 (**3**), and -242150 (**4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: + 44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

The work described in this paper was supported by grants from the City University of Hong Kong (7001180) and NSFC 20318001, 20490210 (China).

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Received June 18, 2004
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