Ferromagnetic Ordering in a Diamond-Like Cyano-Bridged $Mn^{II}Ru^{III}$ Bimetallic Coordination Polymer**

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The field of molecule-based magnetic materials has made significant advances in recent years.[1] A popular approach to the synthesis of these materials has been to use a paramagnetic $[M(CN)_6]^{n-}$ ($M = Cr^{III}$, Mn^{III}, Fe^{III}, or V^{II}) building block in conjunction with another paramagnetic 3d metal ion, and this resulted in the formation of a large number of one-, two-, and three-dimensional polymers that exhibit various magnetic behaviors.[2] We are interested in extending this approach to 4d and 5d metal ions, since their orbitals are more diffuse, and enhanced magnetic interactions can therefore be expected. In general, however, it is much more difficult to construct polymers from 4d or 5d metal complexes, since they are usually much more substitution-inert than 3d metal complexes. Our strategy is to use a 4d or 5d metal cyanide in conjunction with a 3d metal ion to produce 4d–3d and 5d–3d polymers, and we note that examples of such polymers are limited to Mo−C≡N−Mn[3] and $NBu_4[M^{II}Ru^{III}(ox)_3]$ (M = Mn, Fe, Cu; ox = oxalato).[4] We initially planned to use this strategy to prepare $3d-Ru^{III}$ polymers from $[Ru(CN)_6]^{3-}$, since a number of novel Fe^{III}-containing magnetic materials were prepared from $[Fe(CN)_6]^{3-}$. However, whereas $[Fe(CN)_6]^{3-}$ is robust and readily available, $[Ru(CN)_6]^{3-}$ is very unstable, especially in solvents such as water and alcohols.[5] We therefore attempted to design alternative stable cyano complexes of ruthenium(III) as building blocks, and here we report on the synthesis and structure of *trans*-$Ph_4P[Ru^{III}(acac)_2(CN)_2]$ (**1**, Hacac = acetylacetone) and its reaction with Mn^{2+} to produce the novel cyano-bridged $Mn^{II}Ru^{III}$ polymer $\{Mn[Ru(acac)_2(CN)_2]_2\}_n$ (**2**), which has a diamond-like structure and exhibits ferromagnetic ordering below $T_C = 3.6$ K. A diamond-like structure was also proposed for $Mn^{II}[Mn^{II}(CN)_4]$, which is antiferromagnetic.[6]

Reaction of *trans*-$Ph_4P[Ru^{III}(acac)_2Cl_2]$ with KCN in methanol produced **1**. The IR spectrum showed a strong C≡N stretching band at 2099 cm^{-1}. The structure of **1** was determined by X-ray crystallography (Figure 1).[7] The ruthenium atom is octahedrally coordinated by the four oxygen atoms of the two acac ligands and the carbon atoms of the cyanide ions in a *trans* configuration. The four Ru−O distances are almost identical (1.98–2.03 Å) and are also similar to that of $[Ru(acac)_3]$ (av 2.003 Å).[8] The two Ru−CN distances are also similar, as are the two C−N distances. The cyclic voltammogram of **1** in CH_3CN (with 0.1 M Bu_4NPF_6) shows two reversible waves at +0.70 and −1.15 V (vs Ag/Ag$^+$), which are assigned to the Ru^{IV}/Ru^{III} and the Ru^{III}/Ru^{II} couples, respectively. These electrochemical data indicate that $[Ru(acac)_2(CN)_2]^-$ is very stable with respect to oxidation and reduction. Electrospray mass spectrometry (ES-MS) on a methanolic solution of **1** in the anionic mode showed only a peak at *m/z* 352 for $[Ru(acac)_2(CN)_2]^-$, and agreement between calculated and experimental isotopic distribution patterns was excellent. All these results suggest that $[Ru(acac)_2(CN)_2]^-$ is stable in solution and is therefore a suitable precursor for the construction of ruthenium(III)-containing coordination polymers.

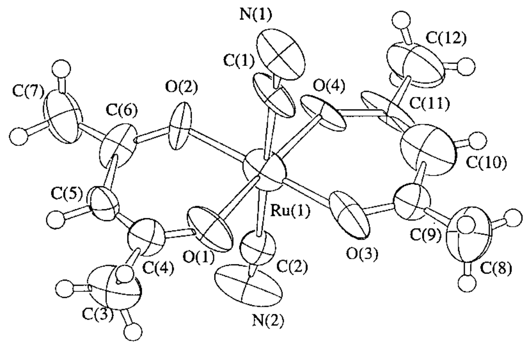

Figure 1. ORTEP plot of the anion of **1**. Selected bond lengths [Å] and angles [°]: Ru(1)-O(1) 2.03(2), Ru(1)-O(2) 1.98(2), Ru(1)-O(3) 1.98(2), Ru(1)-O(4) 2.03(2), Ru(1)-C(1) 2.06(3), Ru(1)-C(2) 2.09(3), N(1)-C(1) 1.15(3), N(2)-C(2) 1.12(3); O(1)-Ru(1)-O(2) 92.1(9), O(1)-Ru(1)-O(3) 87.8(8), O(1)-Ru(1)-O(4) 177.6(10), O(1)-Ru(1)-C(1) 90.3(8), O(1)-Ru(1)-C(2) 89.7(8), C(1)-Ru(1)-C(2) 178(1), Ru(1)-C(1)-N(1) 178(3), Ru(1)-C(2)-N(2) 173(3).

Reaction of **1** with $Mn(ClO_4)_2 \cdot 6H_2O$ in MeOH produced $\{Mn[Ru(acac)_2(CN)_2]_2\}_n$ (**2**) as dark purple crystals. The IR spectrum showed a C≡N stretching band at 2125 cm^{-1}, which is at a higher frequency than that of **1**, consistent with coordination of RuC≡N to Mn. The structure of **2** was determined by X-ray crystallography (Figure 2).[9] Each Mn center is tetrahedrally coordinated by four $[Ru^{III}(acac)_2(CN)_2]^-$ ions through the cyano nitrogen atoms to produce a three-dimensional polymer with a diamond-like structure. The bond lengths of each $[Ru^{III}(acac)_2(CN)_2]^-$ unit in the polymer (Ru−O 1.995, 2.001, Ru−C 2.052, C−N 1.148 Å) are essentially the same as in **1**.

The temperature dependence of the molar magnetic susceptibility χ_M of **1** and **2** was investigated in the range 2–

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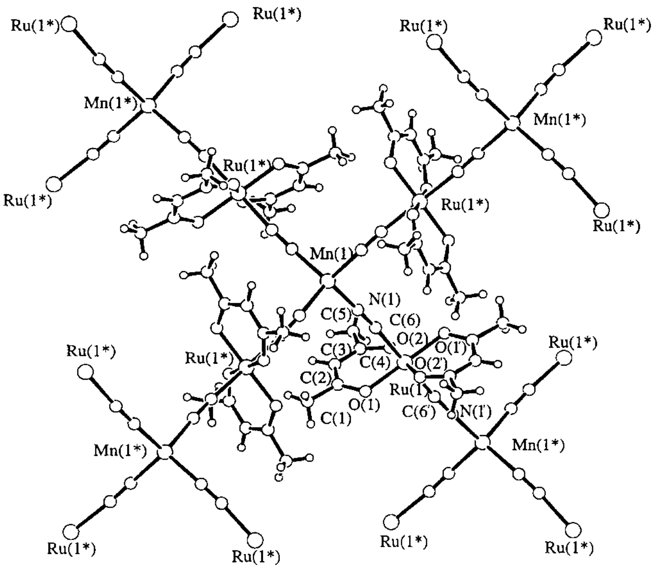

Figure 2. View of **2**. Selected bond lengths [Å] and angles [°]: Ru(1)-O(1) 2.001(3), Ru(1)-O(2) 1.995(3), Ru(1)-C(6) 2.052(4), Mn(1)-N(1) 2.076(3), N(1)-C(6) 1.148(5); O(1)-Ru(1)-O(1′) 180.0, O(1)-Ru(1)-O(2) 89.5(2), O(1′)-Ru(1)-C(6) 94.6(2), O(1)-Ru(1)-O(2) 90.5(2), O(1)-Ru(1)-C(6) 85.4(2), O(2)-Ru(1)-O(2′) 180.0, O(2)-Ru(1)-C(6) 89.9(1), C(6)-Ru(1)-C(6′) 180.0, N(1)-Mn(1)-N(1) 103.49(8), N(1)-Mn(1)-N(1) 122.2(2), Mn(1)-N(1)-C(6) 170.8(4), Ru(1)-C(6)-N(1) 175.6(4).

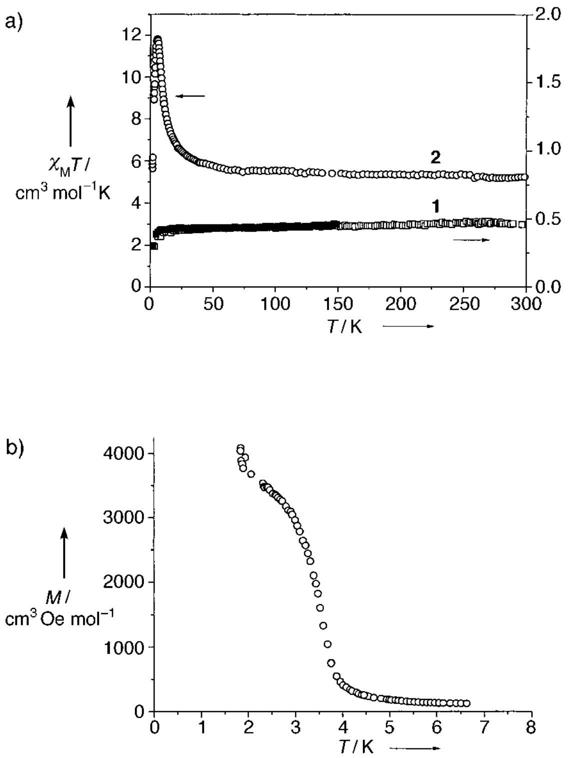

Figure 3. a) Temperature dependence of $\chi_M T$ for **1** (right axis) at 10 kOe (■) and 50 kOe (□), and for **2** (left axis) at 10 kOe (○). b) Temperature dependence of magnetization for **2** at 100 Oe.

300 K on an Oxford Instruments Maglab2000 magnetometer, and plots of $\chi_M T$ versus T are shown in Figure 3a. At room temperature $\chi_M T$ of **1** is 0.46 cm^{3}mol^{-1} K (1.91 μ_B), which is comparable to that of [Ru(acac)$_3$],[10] and is consistent with the low-spin configuration $(t_{2g})^5$ with $S = 1/2$. The magnetic susceptibility above 10 K obeys the Curie–Weiss law $[\chi_M = C/(1-\theta)]$ with $C = 0.46$ cm^{3}mol^{-1}K and $\theta = -3.3$ K. The slight decrease in $\chi_M T$ below 10 K and the negative θ do not necessarily imply antiferromagnetic interaction between Ru^{III} ions, but are more likely due to complicated spin–orbital coupling that combines the effects of ligand-field and thermally populated excited states.[11]

The $\chi_M T$ value of **2** at room temperature is 5.25 cm^{3}mol^{-1}K, which is slightly larger than the uncoupled, spin-only value of 5.12 for one Mn^{II} ($S = 5/2$) and two Ru^{III} ($S = 1/2$) centers, but is very close to the value of 5.29 calculated from the measured $\chi_M T$ value for Ru^{III} in **1**. The monotonic increase in $\chi_M T$ on cooling indicates the presence of ferromagnetic coupling between Mn^{II} and Ru^{III} via the cyano bridges. The $\chi_M T$ value increases abruptly below 50 K and reaches a maximum (11.8 cm^{3}mol^{-1}K) at 5.5 K, which is much higher than the value of 7.88 cm^{3}mol^{-1}K for the ferromagnetic spin state $S_T = 7/2$, assuming $g_T = 2.0$;[4] this suggests long-range ferromagnetic ordering. The magnetic susceptibility above 10 K obeys the Curie–Weiss law with $C = 5.16$ cm^{3}mol^{-1}K and a positive Weiss constant $\theta = +5.4$ K, which also proves the presence of ferromagnetic coupling in **2**. The onset of a long-range magnetic phase transition is evidenced by the low-field temperature dependence of the magnetization (Figure 3b), which increases abruptly below 4 K, characteristic of a long-range magnetic ordering. The ferromagnetic ordering temperature $T_C = 3.6$ was further determined from the maximum of χ'_M as shown in Figure 4, where χ'_M and χ''_M are the in-phase and out-of-phase alternating current (ac) susceptibilities at zero external magnetic field and an oscillating field frequency range of 111–1111 Hz. No frequency dependence was observed, and this rules out the presence of glassy behavior.

The field dependence of the magnetization for **1** and **2** was measured at 2.0 and 1.86 K, respectively. The saturation value for **1** is 1.06 $N\mu_B$, consistent with the value for low-spin Ru^{III} ($S = 1/2$). The magnetization of **2** at 1.86 K increases rapidly at low field, as expected for a magnet, and reaches 6.8 $N\mu_B$ at

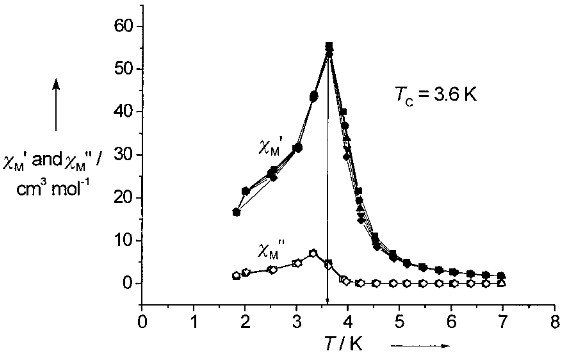

Figure 4. Temperature dependence of ac susceptibility measured at zero external magnetic field and $H_{ac} = 2$ Oe and different frequencies: 111 Hz (□), 199 Hz (○), 355 Hz (△), 633 Hz (▽), 1111 Hz (◇); in-phase susceptibility χ'_M (filled symbols) and out-of-phase susceptibility χ''_M (open symbols). Further magnetic measurements can be found in the Supporting Information.

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60 kOe, which is very close to the expected value of 7.0 $N\mu_B$ for a parallel alignment of the magnetic moments of two Ru^{III} and one Mn^{II} ion. Furthermore, a characteristic hysteresis loop is observed at 1.85 K but with negligible remanent magnetization (0.06 $N\mu_B$) and coercive field (6 Oe). Although ferromagnetic $Ru^{III}-Mn^{II}$ interaction was also observed in two-dimensional $(NBu_4)[Mn^{II}Ru^{III}(ox)_3]$ via the oxalato bridges, no long-range ordering occurs down to 2 K.[4] We are currently investigating related 3d–4d and 4d–5d systems in order to understand the origin of the ferromagnetic behavior in **2**.

Experimental Section

1: *trans*-$Ph_4P[Ru^{III}(acac)_2Cl_2]$[12] (355 mg, 0.5 mmol) and KCN (325 mg, 5.0 mmol) were heated in refluxing methanol (30 mL) for 24 h. The solution was evaporated to dryness, and the residue was dissolved in CH_2Cl_2 (10 mL). After filtration, the product was precipitated as a dark purple solid by adding diethyl ether. Yield: 225 mg (65%). Crystals suitable for X-ray crystallography were obtained by slow diffusion of diethyl ether into a solution of **1** in CH_2Cl_2. IR (KBr): $\tilde{\nu}_{CN} = 2099\ cm^{-1}$; UV/Vis ($CH_3CN$): λ_{max} (lgε) = 349 (3.76), 407 sh (3.16), 540 (3.22); elemental analysis (%) calcd for $C_{36}H_{34}N_2O_4RuP$: C 62.60, H 4.96, N 4.06; found: C 62.96, H 5.05, N 4.21.

2: A mixture of $MnClO_4 \cdot 6H_2O$ (36 mg, 0.1 mmol) and **1** (69 mg, 0.1 mmol) was stirred in methanol (30 mL) at room temperature. The solution was filtered after 3 h, and slow evaporation of the filtrate afforded dark purple crystals. Yield: 34 mg (45%). IR (KBr): $\tilde{\nu}_{CN} = 2125\ cm^{-1}$; elemental analysis (%) calcd for $Ru_2MnN_4C_{24}O_8H_{28}$: C 38.05, H 3.73, N 7.40; found: C 38.24, H 3.82, N 7.56.

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[1] O. Kahn, *Molecular Magnetism*, VCH, Weinheim, **1993**.

[2] a) K. R. Dunbar, R. A. Heintz, *Prog. Inorg. Chem.* **1997**, *45*, 283–373; b) T. Iwamoto in *Comprehensive Supramolecular Chemistry, Vol. 6* (Eds.: J. L. Atwood, J. E. D. Davies, D. D. MacNicol, F. Vögtle, F. Toda, R. Bishop), Pergamon, Oxford, **1996**, pp. 643–690; c) W. D. Grieber, D. Babel, *Z. Naturforsch. B* **1982**, *87*, 832; d) V. Gadet, T. Mallah, I. Castro, P. Veillet, M. Verdaguer, *J. Am. Chem. Soc.* **1992**, *114*, 9213; e) T. Mallah, S. Thiébaut, M. Verdaguer, P. Veillet, *Science* **1993**, *262*, 1554; f) H. Miyasaka, H. Ieda, N. Matsumoto, N. Re, R. Crescenzi, C. Floriani, *Inorg. Chem.* **1998**, *37*, 255; g) K. V. Langenberg, S. R. Batten, K. J. Berry, D. C. R. Hockless, B. Moubaraki, K. S. Murray, *Inorg. Chem.* **1997**, *36*, 5006; h) H. Miyasaka, N. Matsumoto, N. Re, E. Gallo, C. Floriani, *Inorg. Chem.* **1997**, *36*, 670; i) N. Re, E. Gallo, C. Floriani, H. Miyasaka, N. Matsumoto, *Inorg. Chem.* **1996**, *35*, 5964; j) M. Ohba, H. Ōkawa, N. Fukita, Y. Hashimoto, *J. Am. Chem. Soc.* **1997**, *119*, 1011; k) H. Miyasaka, N. Matsumoto, H. Okawa, N. Re, E. Gallo, C. Floriani, *J. Am. Chem. Soc.* **1996**, *118*, 981; l) M. Ohba, N. Maruono, H. Ōkawa, T. Enoki, J.-M. Latour, *J. Am. Chem. Soc.* **1994**, *116*, 11566; m) M. S. El Fallah, E. Rentschler, A. Caneschi, R. Sessoli, D. Gatteschi, *Angew. Chem.* **1996**, *108*, 2081; *Angew. Chem. Int. Ed. Engl.* **1996**, *35*, 1947; n) H. Miyasaka, N. Matsumoto, H. Ōkawa, N. Re, E. Gallo, C. Floriani, *Angew. Chem.* **1995**, *107*, 1565; *Angew. Chem. Int. Ed. Engl.* **1995**, *34*, 1446; o) S. Ferlay, T. Mallah, J. Vaissermann, F. Bartolomé, P. Veillet, M. Verdaguer, *Chem. Commun.* **1996**, 2481; p) M. Ohba, H. Ōkawa, T. Ito, A. Ohto, *J. Chem. Soc. Chem. Commun.* **1995**, 1545.

[3] a) J. Larionova, R. Clérac, J. Sanchiz, O. Kahn, S. Golhen, L. Ouahab, *J. Am. Chem. Soc.* **1998**, *120*, 13088; b) G. Rombaut, S. Golhen, L. Ouahab, C. Mathonière, O. Kahn, *J. Chem. Soc. Dalton Trans.* **2000**, 3609.

[4] J. Larionova, B. Mombelli, J. Sanchiz, O. Kahn, *Inorg. Chem.* **1998**, *37*, 679.

[5] F. M. Crean, K. Schug, *Inorg. Chem.* **1984**, *23*, 853.

[6] J. L. Manson, W. E. Buschmann, J. S. Miller, *Angew. Chem.* **1998**, *110*, 815; *Angew. Chem. Int. Ed.* **1998**, *37*, 783.

[7] a) Crystal data for **1** ($C_{36}H_{34}N_2O_4RuP$): $M_r = 690.72$, dark purple prisms, monoclinic, space group $P2_1/c$ (no. 14), $a = 7.727(8)$, $b = 27.541(8)$, $c = 15.645(9)$ Å, $\beta = 103.13(8)^\circ$, $V = 3242(3)$ Å^3, $F(000) = 1420.00$, $Z = 4$, $\rho_{calcd} = 1.415\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 5.74\ cm^{-1}$. Data were measured on a Rigaku AFC7R diffractometer with graphite-monochromatized $Mo_{K\alpha}$ radiation and a 12-kW rotating anode generator at 28.0 °C. Of the 3670 reflections measured, 3298 were unique ($R_{int} = 0.053$), and 1403 with $I > 2\sigma(I)$ were observed. Data were corrected for Lorentzian and polarization effects. The structure was solved by direct methods (SHELXS86), and the full-matrix least-squares refinement converged to $R = 0.094$ and $R_w = 0.077$ with a GOF of 3.91. b) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-161807 (**1**) and -161808 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB21EZ, UK (fax: (+44) 1223-336-033; e-mail: deposit@ccdc.cam.ac.uk).

[8] H. Matsuzawa, Y. Ohashi, Y. Kaizu, H. Kobayashi, *Inorg. Chem.* **1988**, *27*, 2981.

[9] Crystal data for **2** ($Ru_2MnN_4C_{24}O_8H_{28}$): $M_r = 757.59$, dark purple blocks, tetragonal, space group $P4_2/n$ (no. 86), $a = 13.6900(7)$, $c = 8.1530(5)$ Å, $V = 1528.0(1)$ Å^3, $F(000) = 747.00$, $Z = 2$, $\rho_{calcd} = 1.646\ g\,cm^{-3}$, $\mu(Mo_{K\alpha}) = 14.31\ cm^{-1}$. Data were collected at 25.0 °C. Of the 9457 reflection measured, 1862 were unique ($R_{int} = 0.034$), and 1091 with $I > 1.50\sigma(I)$ were observed. Data were corrected for Lorentzian and polarization effects. The structure was solved by direct methods (SIR92), and the full-matrix least-squares refinement converged to $R = 0.036$ and $R_w = 0.021$ with a GOF of 1.18.[7b]

[10] B. N. Figgis, P. A. Reynolds, K. Murray, B. Moubaraki, *Aust. J. Chem.* **1998**, *51*, 229, and references therein.

[11] R. L. Carlin, *Magnetochemistry*, Springer, Berlin, **1986**, p. 228.

[12] T. Hasegawa, T. C. Lau, H. Taube, W. P. Schaefer, *Inorg. Chem.* **1991**, *30*, 2912. Ph_4PCl was used instead of $Ph_4AsCl \cdot xH_2O$.

A Silyl Cation with a Three-Center Si-H-Si Bond**

Thomas Müller*

Three-center, two-electron bonds involving hydrogen as a bridging atom are a common feature in the chemistry of early main group metals. Several hydrido-bridged carbocations were identified by low-temperature NMR spectroscopy.[1] It was predicted that the isoelectronic silylium ions will even interact with methane,[2] and it was suggested that such interactions between a positively charged silicon atom and appropriately arranged alkyl groups on its substituents can be

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