Metal−Metal Bonded Diruthenium(II, III) Assemblies with the Polycyano Anionic Linkers $N(CN)_2^-$, $C(CN)_3^-$, and 1,4-Dicyanamido-2,5-dimethylbenzene (DM-Dicyd^{2-}): Syntheses, Structures, and Magnetic Properties

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The new metal−metal bonded diruthenium(II,III) compounds $[Ru_2(O_2CCH_3)_4(\mu\text{-L})]_\infty$ (L = $N(CN)_2^-$, **1**; $C(CN)_3^-$, **2**) and $[\{Ru_2(O_2CCH_3)_2(mhp)_2\}_2(\mu\text{-DM-Dicyd})]$ (**3**) (mhp = 2-oxy-6-methylpyridinate, DM-Dicyd = 1,4-dicyanamido-2,5-dimethylbenzene dianion) have been synthesized and fully characterized. Compounds **1** and **2** were synthesized by the reaction of $[Ru_2(O_2CCH_3)_4(NCCH_3)_2](BF_4)$ with $NaN(CN)_2$ and $KC(CN)_3$, respectively. The “dimer-of-dimers”, **3**, was synthesized by a 2:1 reaction of $[Ru_2(O_2CCH_3)_2(mhp)_2(MeOH)](BF_4)$ with $[As(Ph)_4]_2$[DM-Dicyd]. Compound **1** crystallizes in the monoclinic space group $C2/m$ with $a = 10.174(2)$ Å, $b = 13.016(3)$ Å, $c = 7.0750(14)$ Å, $\beta = 101.83(3)°$, and $Z = 2$. Compound **2** crystallizes in the orthorhombic space group $Fdd2$ with $a = 29.679(6)$ Å, $b = 31.409(6)$ Å, $c = 7.3660(15)$ Å, $V = 6866(2)$ Å^3, and $Z = 16$. In compound **1**, dicyanamide anions ($N(CN)_2^-$) bridge the $[Ru_2(O_2CCH_3)_4]^+$ units in an end-to-end bridging mode, thereby forming an alternating one-dimensional chain. In compound **2**, two cyano groups of tricyanomethanide anion ($C(CN)_3^-$) are coordinated to independent $[Ru_2(O_2CCH_3)_4]^+$ units to give a chain similar to that found in **1**. The Ru−Ru bond distances in **1** and **2** are 2.2788(14) and 2.2756(5) Å, respectively, which are typical values for $Ru_2(O_2CR)_4Cl$ and $[Ru_2(O_2CR)_4]^+$ compounds. The Ru−N distances are 2.257(8) Å in **1** and 2.259(4) and 2.283(4) Å in **2**. The temperature dependence of the magnetic susceptibilities of compounds **1**−**3** reveals a weak antiferromagnetic interaction between Ru_2 units ($S = {}^3/_2$) through each polycyano anionic linker: $g = 2.16$, $zJ = -0.33$ cm^{-1}, $D = 63.3$ cm^{-1} for **1**; $g = 2.15$, $zJ = -0.22$ cm^{-1}, $D = 58.0$ cm^{-1} for **2**; and $g = 2.10$, $zJ = -0.90$ cm^{-1}, $D = 75.0$ cm^{-1} for **3**.

Introduction

The construction of multidimensional materials and the exploration of such properties as magnetism,[1] conductivity,[2] and gas absorption[3] are active subjects of research in coordination chemistry. Polycyano organic molecules are interesting ligands to use with metal ions in preparing new materials because they possess pπ electronic conjugated systems that facilitate electronic communication between metal centers.[2,4−7] The neutral forms of certain polycyanide molecules, for example, 7,7,8,8-tetracyanoquinodimethane (TCNQ),[5,6] tetracyanoethylene

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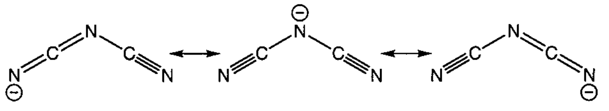
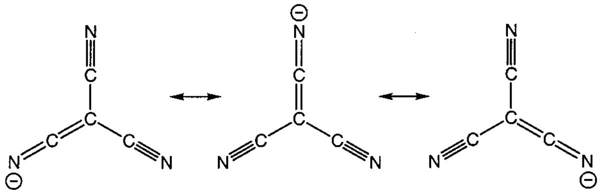
(TCNE),[1a,7] and *N*,*N'*-dicyanoquinone diimine (DCNQI),[2] undergo reversible one-electron reductions to form stable anionic radicals. These open-shell molecules promote stronger magnetic coupling between paramagnetic metals than their neutral counterparts; moreover, the local metal−organic antiferromagnetic coupling induces ferromagnetic coupling between the metal centers.[5−7] In addition to polycyano radicals, anions such as dicyanamide ($N(CN)_2^-$) and tricyanomethanide ($C(CN)_3^-$) also show promise in the design of magnetic materials.[8,9] Their conjugated pπ resonance structures provide coupling pathways for magnetic interactions between paramagnetic metal centers.

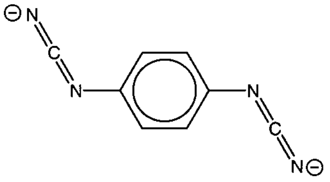


$N(CN)_2^-$



$C(CN)_3^-$

For example, dicyanamide-based metal assemblies of the type $[M\{N(CN)_2\}_2]$ ($M = Cr^{2+}$, Mn^{2+}, Co^{2+}, and Ni^{2+}) with a rutilelike architecture exhibit a spontaneous magnetization in the temperature range 9−47 K,[8a,f] and the tricyanomethanide polymers $[M\{C(CN)_3\}_2]$ ($M = V^{2+}$, Cr^{2+}, and Mn^{2+}) exhibit spin frustration due to their Kagomé type structural topologies.[9a,c] Another application of these ligand types is illustrated by the chemistry of the 1,4-dicyanamidebenzene dianion (Dicyd^{2-}),



which is the two-electron-reduced species of the aforementioned DCNQI molecule. The dianion has been studied by Crutchley et al.[10b] who found that ruthenium(III) compounds bridged by Dicyd^{2-} linkers exhibit strong superexchange coupling between metal ions; for example, in $[\{Ru(NH_3)_5\}_2(\mu\text{-DM-Dicyd})](ClO_4)_4$ the J value is greater than or equal to -400 cm^{-1} (for $H = -2JS_1S_2$).[10]

One class of materials under investigation in our laboratories is a network involving metal−metal bonded units and polycyano acceptor ligands. In terms of paramagnetic systems, paddlewheel complexes of the type $Ru_2^{II,II}(O_2CR)_4$ and $[Ru_2^{II,III}(O_2CR)_4]^+$ are well-documented in the literature.[11] These molecules are good precursors for magnetic systems because of the fact that they exhibit ground states of $S = 1$ and $S = {}^3/_2$, respectively. Various polymeric compounds consisting of these Ru_2 dinuclear species bridged by organic molecules have been prepared and investigated in recent years.[12−15] Among the earliest work in this area are studies by Swanson and co-workers who demonstrated that electron transfer occurs between $Ru_2^{II,II}(O_2CR)_4$ donors and DCNQI acceptors to give what is proposed to be

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an alternating chain of $Ru_2^{II,III}(O_2CR)_4^+$ ($S = {}^3/_2$) and $DCNQI^{\bullet -}$ ($S = {}^1/_2$) units.[16] More recently, we reported the X-ray structure of the novel two-dimensional networks of $M_2^{II,II}(O_2CCF_3)_4$ (M = Ru and Rh) bridged by partially reduced TCNQ ligands $[\{M_2(O_2CCF_3)_4\}_2(\mu^4\text{-TCNQ})]_\infty$ (M = Ru and Rh).[17] In light of the intriguing results reported for single metal ions bridged by cyanamide and dicyanamide ligands, it was a logical step to study the corresponding chemistry with paramagnetic dinuclear metal units.

In this paper we report the use of $[N(CN)_2]^-$ and $[\text{DM-Dicyd}]^{2-}$ linkers to connect the metal−metal bonded complexes $[Ru_2^{II,III}(O_2CCH_3)_4]^+$ and $[Ru_2^{II,III}(O_2CCH_3)_2(mhp)_2]^+$ cations into oligomers and one-dimensional chains. The new polymeric compounds are $[Ru_2(O_2CCH_3)_4(\mu\text{-L})]_\infty$ (L = $N(CN)_2^-$, **1**; $C(CN)_3^-$, **2**), and the new "dimer-of-dimers" is $[\{Ru_2(O_2CCH_3)_2(mhp)_2\}_2(\mu\text{-DM-Dicyd})]$ (**3**) (mhp = 2-oxy-6-methylpyridinate, DM-Dicyd = 1, 4-dicyanamido-2, 5-dimethylbenzene dianion). The single-crystal X-ray structures as well as the magnetic properties of the new compounds are described.

Experimental Section

Chemicals and Reagents. Unless otherwise stated, all reactions were carried out under a nitrogen atmosphere. All chemicals used for the syntheses were of reagent grade quality. Sodium dicyanamide ($NaN(CN)_2$) and potassium tricyanomethanide ($KC(CN)_3$) were purchased from Fluka Chemika Co. Ltd. and Alfa Aesar Co. Ltd., respectively, and used without further purification. The diruthenium(II,III) compounds $Ru_2(O_2CCH_3)_4Cl$ and $Ru_2(O_2CCH_3)_2(mhp)_2Cl$ were synthesized according to literature methods.[18,19] The salt $[As(Ph)_4]_2[\text{DM-Dicyd}]$ was synthesized according to the method reported by Crutchley et al.[10b] Methanol was dried by refluxing over Mg chips and I_2. Acetonitrile and acetone were dried by refluxing over 3 Å molecular sieves. Dichloromethane used for the cyclic voltammetric studies was dried by refluxing over P_2O_5. All solvents were freshly distilled under N_2 before use.

Preparation of $[Ru_2(O_2CCH_3)_4(NCCH_3)_2](BF_4)$. To a methanol (20 mL) suspension of $Ru_2(O_2CCH_3)_4Cl$ (474 mg, 1.0 mmol) was added $AgBF_4$ (195 mg, 1.0 mmol) in 20 mL of methanol. The brown suspension turned to a reddish-brown color with the appearance of gray-white AgCl. The mixture was stirred for 12 h at room temperature and then filtered. The reddish-brown filtrate was evaporated to dryness to yield an orange-brown powder that was dissolved in 5 mL of acetonitrile, placed in a narrow Schlenk tube, and layered with diethyl ether (40 mL). After 2 weeks at room temperature, a crop of reddish-brown microcrystals was harvested. Yield: 462 mg, 76%. IR (Nujol): 2305w, 2276w, 2246w, 1639m, 1102s, 1075s, 1048s, 1021s, 695s cm^{-1}.

Preparation of $[Ru_2(O_2CCH_3)_4\{\mu\text{-N}(CN)_2\}]_\infty$ (1). An acetonitrile solution (16 mL) of $[Ru_2(O_2CCH_3)_4(NCCH_3)_2](BF_4)$ (61 mg, 0.1 mmol) was separated into eight 2 mL portions, each of which was placed in a 3 mm diameter glass tube. In the same manner, an acetonitrile solution (16 mL) containing $NaN(CN)_2$ (9 mg, 0.1 mmol) was separated into eight 2 mL portions and carefully layered on top of the Ru_2 solutions. After 1 day at room temperature, the solutions had yielded reddish-brown crystals. A bulk, polycrystalline sample was obtained by mixing acetonitrile solutions (20 mL each) containing the two precursors. Yield: 47 mg, 93%. IR (Nujol): 2412w, 2312m, 2240m, 2161s, 1680−1639w, 1049w, 691s cm^{-1}. IR spectra of batches of the single crystals and the polycrystalline samples are essentially identical.

Preparation of $[Ru_2(O_2CCH_3)_4\{\mu\text{-C}(CN)_3\}]_\infty$ (2). An acetonitrile solution (10 mL) of $KC(CN)_3$ (13 mg, 0.1 mmol) was added to an acetonitrile solution (10 mL) of $[Ru_2(O_2CCH_3)_4(NCCH_3)_2](BF_4)$ (92 mg, 0.15 mmol) and stirred for 30 min at room temperature. The resulting reddish-brown solution was treated with 20 mL of water and then filtered. The filtrate was allowed to slowly evaporate in air, and after 1 day reddish-brown rectangular platelets were obtained. Yield: 40 mg, 76%. IR (Nujol): 2233w, 2190m, 2168s, 1682−1644w, 1050w, 1025w, 691s cm^{-1}.

Preparation of $[\{Ru_2(O_2CCH_3)_2(mhp)_2\}_2(\mu\text{-DM-Dicyd})]$ (3). To a methanol solution (15 mL) of $Ru_2(O_2CCH_3)_2(mhp)_2Cl$ (114 mg, 0.2 mmol) was added a methanol solution (15 mL) of $AgBF_4$ (39 mg, 0.2 mmol). This was stirred overnight at room temperature. During this time AgCl was observed to form as a grayish precipitate. The resulting blue-purple solution was filtered, and the filtrate was removed in vacuo at room temperature. The blue-purple residue was dissolved in 20 mL of acetone and added to an acetone suspension (20 mL) of $[As(Ph)_4]_2[\text{DM-Dicyd}]$ (95 mg, 0.1 mmol). The cloudy solution was stirred overnight at room temperature to yield a red-purple precipitate of **3**, which was collected by filtration, washed with 3 × 20 mL of acetone, and dried in vacuo. Yield: 107 mg, 85%. Anal. Calcd for $C_{42}H_{44}N_8O_{12}Ru_4$: C, 40.12; H, 3.53; N, 8.91. Found: C, 39.72; H, 3.73; N, 8.18. IR (Nujol): 2102s, 1709w, 1610m, 1548w, 1220w, 1145w, 806w, 782w, 760m, 690s cm^{-1}.

Physical Measurements. Infrared spectra were recorded as Nujol mulls between KBr plates with a Nicolet 740 FT-IR spectrophotometer. The magnetic susceptibility data were measured with the use of a Quantum Design SQUID magnetometer MPMS-XL (housed in the Department of Chemistry at Texas A&M University). Measurements were performed in the temperature range 1.8−300 K at 1000 G on finely divided polycrystalline samples. Data were corrected for the sample holder, and diamagnetic contributions were calculated from Pascal constants.[20] Electrochemical measurements for **3** were recorded in CH_2Cl_2 (1×10^{-3} M) with 0.1 M $[n\text{-Bu}_4N][PF_6]$ as a supporting electrolyte under nitrogen with the use of an HCH Instruments electrochemical analyzer model CH1620A. The working electrode and counter electrodes were Pt, and the reference electrode was Ag/AgCl.

X-ray Data Collection, Reduction, and Structure Determination. Single crystals for the crystallographic analyses were mounted on glass fibers and secured with Dow-Corning grease. The crystal dimensions were 0.08 mm × 0.12 mm × 0.15 mm for **1** and 0.12 mm × 0.22 mm × 0.28 mm for **2**. Data were collected on a Bruker SMART CCD area detector diffractometer in the range $2.58° < 2\theta < 28.31°$ for **1** and $1.89° < 2\theta < 28.28°$ for **2** at 100(2) K with graphite monochromated Mo Kα radiation ($\lambda = 0.710\,69$ Å). Of the total 4357 reflections for **1** and 12 397 reflections for **2** that were collected, 1168 and 3945 are unique, respectively. The structures were solved by direct methods (SHELXS-97)[21] and refined by full-matrix least-squares calculations on F^2 (SHELXL-97).[22] The non-hydrogen atoms were refined anisotropically, while hydrogen atoms were refined isotropically. Full-matrix

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Table 1. Crystallographic Data for $[Ru_2(O_2CCH_3)_4\{N(CN)_2\}]\cdot CH_3CN$ (**1**·CH_3CN) and $[Ru_2(O_2CCH_3)_4\{C(CN)_3\}]$ (**2**)

	1·CH_3CN	**2**
formula	$C_{12}H_{15}N_4O_8Ru_2$	$C_{12}H_{12}N_3O_8Ru_2$
fw	545.613	528.583
space group	*C*2/*m*	*Fdd*2
T/K	100(2)	100(2)
λ/Å	0.71069	0.71069
a/Å	10.174(2)	29.679(6)
b/Å	13.016(3)	31.409(6)
c/Å	7.0750(14)	7.2660(15)
α/deg	90	90
β/deg	101.83(3)	90
γ/deg	90	90
V/Å^3	917.0(3)	6866(2)
Z	2	16
D_{cal}/g cm^{-3}	2.090	2.044
μ(Mo Kα)/cm^{-1}	1.661	1.805
R^a	0.0511 ($I > 2.00\sigma(I)$)	0.0314 ($I > 2.00\sigma(I)$)
R^a	0.0676 (all data)	0.0322 (all data)
$R_w{}^b$	0.1257 ($I > 2.00\sigma(I)$)	0.0781 ($I > 2.00\sigma(I)$)
$R_w{}^b$	0.1356 (all data)	0.0784 (all data)

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

least-squares refinements based on 1168 observed reflections for **1** and 3813 observed reflections for **2** ($I > 2.00\sigma(I)$) were employed. The unweighted and weighted agreement factors of $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$ were used. The crystal data and details of the structure determinations are summarized in Table 1.

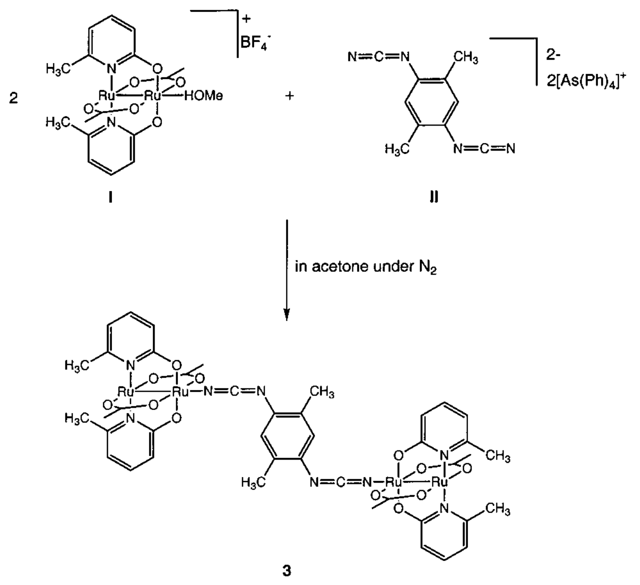
Results and Discussion

Syntheses and General Properties of Compounds 1−3. Starting materials of the type $[Ru_2(O_2CCH_3)_4(S)_2][BF_4]$ (S = solvent) can be obtained by passing $Ru_2(O_2CCH_3)_4Cl$ down a cation-exchange column with a water/$NaBF_4$ eluent.[23a] We have found that a more convenient route is to sequester Cl^- with Ag^+ in MeOH and then to recrystallize the cation from acetonitrile/diethyl ether to obtain high yields of $[Ru_2(O_2CCH_3)_4(NCCH_3)_2][BF_4]$. Samples of $[Ru_2(O_2CCH_3)_4(NCCH_3)_2][BF_4]$ exhibit ν(C≡N) stretches in the infrared region at 2305, 2276, and 2246 cm^{-1} and a broad ν(B−F) stretch of $[BF_4]^-$ in the range 1021−1102 cm^{-1}, in accord with successful exchange of Cl^- with $[BF_4]^-$.[23b]

Compound **1** was prepared in an acetonitrile solution containing $[Ru_2(O_2CCH_3)_4(NCCH_3)_2][BF_4]$ and $NaN(CN)_2$ in a 1:1 reaction ratio. An IR spectrum of **1** revealed three ν(NCN) stretches at 2312, 2240, and 2161 cm^{-1} as well as unreacted $NaN(CN)_2$ (2288, 2235, and 2182 cm^{-1}). Two of the three absorptions are shifted to higher frequencies, and one is shifted to lower energies compared to $NaN(CN)_2$. These shifts reflect the electronic effects of σ donation from $N(CN)_2{}^-$ to Ru_2 units and π back-donation from Ru_2 units to $N(CN)_2{}^-$.

Compound **2** was synthesized from $[Ru_2(O_2CCH_3)_4(NCCH_3)_2][BF_4]$ and $KC(CN)_3$ in a 3:2 ratio in a mixture of acetonitrile and water. This stoichiometry was based on the expectation that all three cyano groups would coordinate, but instead the 1:1 product $[Ru_2(O_2CCH_3)_4\{C(CN)_3\}]$ was obtained. A synthetic route analogous to the one used to prepare **1** did not yield any isolable products. An IR spectrum of **2** revealed three ν(C≡N) stretches located at 2233, 2190, and 2168 cm^{-1}, compared to the strong ν(C≡N) stretch in $KC(CN)_3$ at 2177 cm^{-1}. The number of stretches and the shifts observed for **2** reflect both the lower molecular symmetry and the effect of coordination.

Scheme 1



I: $[Ru_2(O_2CCH_3)_2(mhp)_2(MeOH)](BF_4)$

II: $[As(Ph)_4]_2$[DM-Dicyd]

Table 2. Cyclic Voltammetric Data for **3** and the Parent Complexes $Ru_2(O_2CCH_3)_2(mhp)_2(Cl)$ (**I**) and $[As(Ph)_4]_2$[DM-Dicyd] (**II**)

compd	Ru_2[(II, II)/(II, III)]	Ru_2[(II, III)/(III, III)]	L(−/2−)^a	L(0/−)^a	ref
3^b	−0.311		0.103	0.723	
I^c	−0.10	1.64			19
II^d			−0.545 (−0.322)^e	0.095 (0.318)^e	10b

[a] L = DM-Dicyd. [b] In CH_2Cl_2 solution containing 0.1 M TBAH vs Ag/AgCl at a scan rate of 100 mV/s. [c] In CH_2Cl_2 solution containing 0.1 M TBAH vs Ag/AgCl at a scan rate of 100 mV/s. [d] In acetonitrile solution containing 0.1 M TBAH vs NHE at a scan rate of 100 mV/s. [e] The data for **II** vs Ag/AgCl.

$[Ru_2(O_2CCH_3)_2(mhp)_2(MeOH)][BF_4]$ was synthesized in the same manner as $[Ru_2(O_2CCH_3)_4(NCCH_3)_2](BF_4)$, by abstraction of Cl^- from $[Ru_2(O_2CCH_3)_2(mhp)_2(Cl)]$ with Ag^+ in MeOH. An IR spectrum of $[Ru_2(O_2CCH_3)_2(mhp)_2(MeOH)][BF_4]$ exhibits a strong, broad ν(B−F) stretch of $[BF_4]^-$ over the range 1025−1109 cm^{-1}. A 2:1 reaction of $[Ru_2(O_2CCH_3)_2(mhp)_2(MeOH)][BF_4]$ with $[As(Ph)_4]_2$[DM-Dicyd] in acetone led to the formation of $[\{Ru_2(O_2CCH_3)_2(mhp)_2\}_2(\mu\text{-DM-Dicyd})]$ (**3**) as a red-purple precipitate (Scheme 1). An IR spectrum of **3** revealed a strong ν(NCN) stretch at 2102 cm^{-1}, which is essentially the energy of the stretch exhibited by $[As(Ph)_4]_2$[DM-Dicyd] at 2098 cm^{-1}. It should be noted that other Ru(III) compounds with Dicyd^{2-} bridges have been reported to show a strong ν(NCN) feature in the range 2082−2106 cm^{-1}.[10]

Electrochemical studies were performed on **3** in CH_2Cl_2 from −1.5 to +1.8 V vs Ag/AgCl. Table 2 lists the redox potentials of **3** together with the cyclic voltammetric data for the precursors $Ru_2(O_2CCH_3)_2(mhp)_2Cl$ and $[As(Ph)_4]_2$[DM-Dicyd]. $[\{Ru_2(O_2CCH_3)_2(mhp)_2\}_2(\mu\text{-DM-Dicyd})]$ (**3**) exhibits three redox waves, namely, one quasi-reversible 2e$^-$ reduction ($E_{1/2}$(red) = −0.31 V, $I_{pa}/I_{pc} \approx 1$, ΔE = 70 mV), one reversible 1e$^-$ oxidation ($E_{1/2}$(ox) = +0.10 V, $I_{pa}/I_{pc} \approx 1$, ΔE = 51 mV), and

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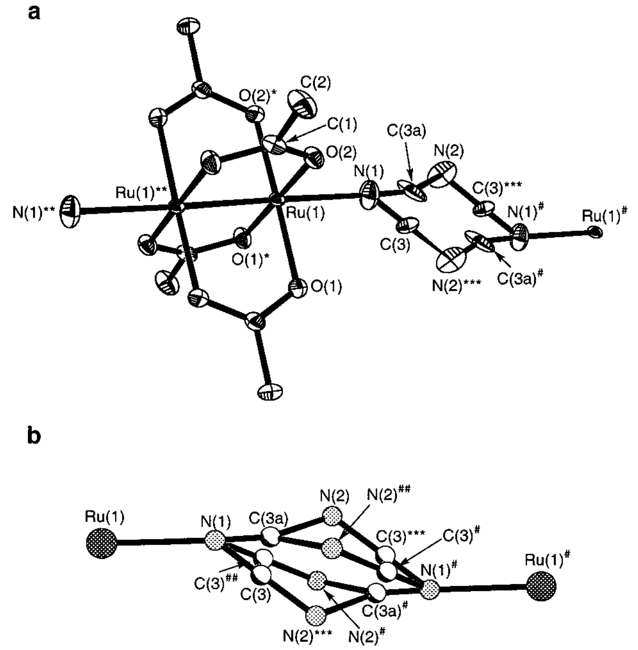

Figure 1. (a) ORTEP drawing of a formula unit of **1** with the atom labeling scheme (50% probability thermal ellipsoids). The hydrogen atoms of the CH_3 groups were omitted for the sake of clarity. (b) Description of the disordered form of the $N(CN)_2^-$ unit. Symmetry operations are the following: (∗) $x, -y - 1, z$; (∗∗) $-x - 1, -y - 1, -z$; (∗∗∗) $-x, 1 - y, 1 - z$; (#) $-x, y, 1 - z$; (##) $x, 1 - y, z$.

an irreversible 1e$^-$ oxidation ($E_{1/2}(\text{ox}) = +0.72$ V, $I_{pa}/I_{pc} \neq 1$, $\Delta E = 146$ mV). The first process at $E_{1/2} = -0.31$ V is attributed to the simultaneous reduction of both Ru_2(II, III) units to Ru_2(II, II) with no significant electronic communication occurring through the bridging ligand DM-Dicyd^{2-}. The corresponding reduction of Ru_2(II, III) to Ru_2(II, II) of the parent compound $Ru_2(O_2CCH_3)_2(mhp)_2Cl$ occurs at -0.10 V.[19] The one-electron process at $E_{1/2} = +0.10$ V is attributed to the DM-Dicyd^{2-}/DM-Dicyd$^{\bullet-}$ oxidation, and the one-electron irreversible wave at $E_{1/2} \approx +0.72$ V is assigned to the second oxidation from DM-Dicyd$^{\bullet-}$ to DM-Dicyd^0. The redox chemistry of $[(NH_3)_5\text{-}Ru^{III}]_2[\mu\text{-DM-Dicyd}][ClO_4]_4$ and related molecules reported by Crutchley et al.[10b] involves a much more accessible reduction of Ru(III) to Ru(II), which can be taken as an indication of lower energy LUMOs. This situation would be expected to lead to a major difference in the superexchange through the bridging DCNQI ligand, which is indeed the case (vide infra).

Single-Crystal X-ray Analysis of 1. Compound **1** crystallizes as a chain compound in the monoclinic space group *C*2/*m*. Although the X-ray experiment was conducted at low temperature, a high degree of disorder in the structure led to a low-quality data set. An ORTEP drawing of the formula unit with the atom numbering scheme is depicted in Figure 1a. Selected bond distances and angles are provided in Table 3. The $N(CN)_2^-$ anions coordinate to the Ru_2 units in an end-to-end bridging mode with Ru(1)−N(1) = 2.257(8) Å, Ru(1)−N(1)−C(3) = 177.8(15)°, and Ru(1)−N(1)−C(3a) = 140.9(14)°, which leads to the one-dimensional chain structure shown in Figure 2. The Ru−Ru bond distance of 2.2788(14) Å is very close to the values observed in $Ru_2(O_2CR)_4(Cl)$ and $[Ru_2(O_2CR)_4(L)_2]^+$ (ranges are 2.27−2.29 Å).[11] It should be pointed out that the $N(CN)_2^-$ moieties are involved in a complicated disorder, wherein the amide nitrogen N(2) and the cyano carbon C(3 and 3a) atoms have four and three different positions, respectively, due to the crystallographically imposed inversion center and the mirror plane located on the $N(CN)_2^-$ bridge (Figure 1b). For the cyano carbons C(3a) and C(3), the situation is slightly different. The atom C(3a) resides on a special position (on the mirror plane), but C(3) resides on a general position that generates a third position C(3)$^{\#\#}$ related by the mirror plane symmetry operation$^{\#\#}$: $x, 1 - y, z$. Although they are less than well determined, the bond angles of N−C−N are N(1)−C(3)−N(2)∗∗∗ ≈ 178(2)° and N(1)−C(3a)−N(2) ≈ 149.1(10)° (∗∗∗ symmetry operation: $-x, 1 - y, 1 - z$). The latter angle is much less than 180°, but this type of distortion has been noted by others who reported N−C−N bends ranging from 144° to 156°.[24,25] The average N(1)−C(3) and C(3)−N(2) distances are 1.125 and 1.395 Å, respectively. The former N≡C bond distance is slightly shorter than previously reported ones (N≡C ≈ 1.13−1.15 Å), while the latter C−N distance is relatively longer (C−N ≈ 1.3−1.4 Å).[24,25,33] These structural aspects are consistent with the characteristic CN vibrations detected by IR spectroscopy, which are influenced by π back-donation from Ru_2 dimers.

Table 3. Pertinent Bond Distances (Å) and Angles (deg) for **1** with the Estimated Standard Deviations in Parentheses[a]

Ru(1)−O(1)	2.021(4)	N(1)−C(3)	1.15(2)
Ru(1)−O(2)	2.019(4)	N(1)−C(3a)	1.10(2)
Ru(1)−N(1)	2.257(8)	N(2)−C(3)	1.36(3)
Ru(1)−Ru(1)**	2.2788(14)	N(2)−C(3a)	1.43(2)
O(1)*−Ru(1)−O(2)	178.62(14)	N(1)−Ru(1)−Ru(1)**	178.8(2)
O(1)*−Ru(1)−O(2)*	90.92(17)	Ru(1)−N(1)−C(3)	140.9(14)
O(1)−Ru(1)−O(2)	90.92(17)	Ru(1)−N(1)−C(3a)	177.8(15)
O(1)−Ru(1)−O(2)*	178.62(14)	N(1)−C(3)−N(2)***	178(2)
O(1)*−Ru(1)−O(1)	88.4(2)	N(1)−C(3a)−N(2)	149.1(10)
O(1)−Ru(1)−N(1)	89.8(2)	C(3)***−N(2)−C(3a)	119.9(17)
O(1)−Ru(1)−Ru(1)**	89.35(11)	C(3)***−N(2)−C(3)	111.0(19)
O(2)−Ru(1)−O(2)*	89.7(2)		
O(2)−Ru(1)−N(1)	91.4(2)		
O(2)−Ru(1)−Ru(1)**	89.45(11)		

[a] Symmetry operations: (∗) $x, -y - 1, z$; (∗∗) $-x - 1, -y - 1, -z$; (∗∗∗) $-x, 1 - y, -z + 1$.

Single-Crystal X-ray Analysis of 2. Compound **2** crystallizes in the orthorhombic space group *Fdd*2. An ORTEP drawing of the asymmetric unit with the atom labeling scheme is depicted in Figure 3. Selected bond distances and angles are given in Table 4. The Ru−Ru bond distance of 2.2756(5) Å is very close to that observed in **1**, and both values are typical of $Ru_2(O_2CR)_4(Cl)$ and $[Ru_2^{II,III}(O_2CR)_4]^+$ compounds as noted earlier.[11] Two cyano groups of the $[C(CN)_3]^-$ anion are coordinated to the axial positions of Ru_2 molecules at distances of Ru(1)−N(1) = 2.259(4) Å and Ru(2)−N(2) = 2.283(4) Å and angles of Ru(1)−N(1)−C(9) = 164.4(4)° and Ru(2)−N(2)−

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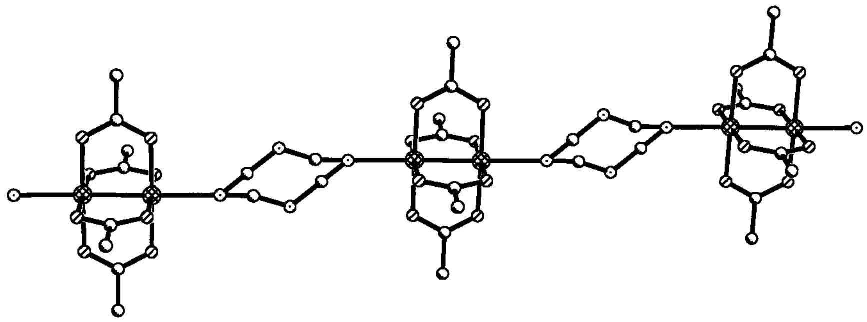

Figure 2. View of an alternating one-dimensional chain of **1**.

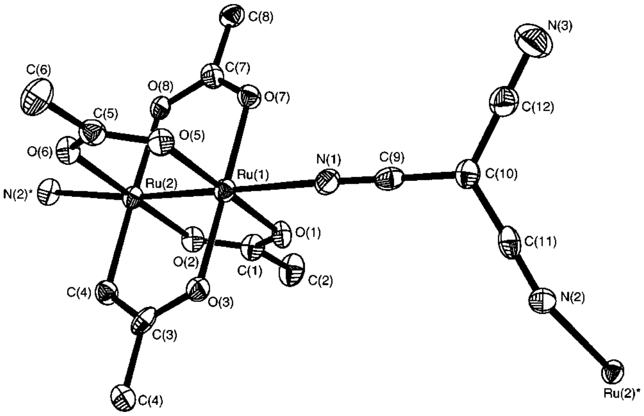

Figure 3. ORTEP drawing of an asymmetric unit of **2** with the atom labeling scheme (50% probability thermal ellipsoids). The hydrogen atoms of the CH_3 groups were omitted for the sake of clarity.

Table 4. Pertinent Bond Distances (Å) and Angles (deg) for **2** with the Estimated Standard Deviations in Parentheses

Ru(1)−O(1)	2.024(3)	N(1)−C(9)	1.146(6)
Ru(1)−O(3)	2.023(3)	N(2)−C(11)	1.158(6)
Ru(1)−O(5)	2.014(3)	N(3)−C(12)	1.155(7)
Ru(1)−O(7)	2.025(3)	C(9)−C(10)	1.413(6)
Ru(1)−N(1)	2.259(4)	C(10)−C(11)	1.407(6)
Ru(2)−O(2)	2.020(3)	C(10)−C(12)	1.410(7)
Ru(2)−O(4)	2.026(3)	Ru(1)−Ru(2)	2.2756(5)
Ru(2)−O(6)	2.033(3)		
Ru(2)−N(2)	2.283(4)		
O(1)−Ru(1)−O(3)	90.97(13)	O(5)−Ru(1)−O(7)	91.25(13)
O(1)−Ru(1)−O(5)	179.26(14)	O(5)−Ru(1)−N(1)	92.09(13)
O(1)−Ru(1)−O(7)	89.04(14)	O(5)−Ru(1)−Ru(2)	89.96(9)
O(1)−Ru(1)−N(1)	88.59(13)	O(6)−Ru(2)−O(8)	91.30(13)
O(1)−Ru(1)−Ru(2)	89.36(9)	O(6)−Ru(2)−N(2)	88.44(13)
O(2)−Ru(2)−O(4)	90.32(13)	O(6)−Ru(2)−Ru(1)	89.17(9)
O(2)−Ru(2)−O(6)	178.88(14)	O(7)−Ru(1)−N(1)	88.24(13)
O(2)−Ru(2)−O(8)	88.56(13)	O(7)−Ru(1)−Ru(2)	90.12(9)
O(2)−Ru(2)−N(2)	92.66(13)	O(8)−Ru(2)−N(2)	85.46(13)
O(2)−Ru(2)−Ru(1)	89.71(9)	O(8)−Ru(2)−Ru(1)	88.93(8)
O(3)−Ru(1)−O(5)	88.73(13)	N(1)−Ru(1)−Ru(2)	177.40(11)
O(3)−Ru(1)−O(7)	179.33(14)	Ru(1)−Ru(2)−N(2)	173.85(10)
O(3)−Ru(1)−N(1)	92.42(14)	Ru(1)−N(1)−C(9)	164.4(4)
O(3)−Ru(1)−Ru(2)	89.22(9)	Ru(2)−N(2)−C(11)	140.3(4)
O(4)−Ru(2)−O(6)	89.79(13)	N(1)−C(9)−C(10)	179.3(5)
O(4)−Ru(2)−O(8)	178.37(13)	N(2)−C(11)−C(10)	178.1(5)
O(4)−Ru(2)−N(2)	95.77(13)	N(3)−C(12)−C(10)	179.3(6)
O(4)−Ru(2)−Ru(1)	89.89(9)	C(9)−C(10)−C(11)	118.4(4)
		C(9)−C(10)−C(12)	119.8(4)
		C(11)−C(10)−C(12)	121.7(4)

C(11) = 140.3(4)°. The arrangement of Ru_2 units and $[C(CN)_3]^-$ anions leads to the alternating one-dimensional chain structure shown in Figure 4. The Ru−N bond distances are essentially the same as those in **1** but somewhat shorter than the value of 2.323(7) Å observed in $[\{Ru_2^{II,III}(O_2CCMe_3)_4(H_2O)\}_2(\mu^2\text{-}TCNQ)](BF_4)_2$ with a neutral TCNQ bridge.[26] The shorter Ru−N bond is most likely associated with the stronger σ donation expected for the anionic ligands $N(CN)_2^-$ and $C(CN)_3^-$. The bond distances for the coordinated C≡N groups are C(9)−N(1) = 1.146(6) Å and C(11)−N(2) = 1.158(6) Å, and for the noncoordinated C≡N group, C(12)−N(3) = 1.155(7) Å. The bond distances of C−C in the $C(CN)_3^-$ moiety are C(9)−C(10) = 1.413(6) Å, C(11)−C(10) = 1.407(6) Å, and C(12)−C(10) = 1.410(7) Å. These bond distances are typical of $C(CN)_3^-$ (C−N, ca. 1.15 Å; C−C, ca. 1.41 Å).[9,27]

Magnetic Properties of 1 and 2. The magnetic susceptibilities of **1** and **2** were measured over the range 1.8−300 K (Figure 5). For **1**, the χT product at 300 K of 2.12 cm^3 K mol^{-1} (4.12 μ_B) gradually decreases upon cooling and finally reaches a minimum value of 0.37 cm^3 K mol^{-1} (1.72 μ_B) at 1.8 K. Similar behavior is observed for **2**; at 300 and 1.8 K the χT products are 2.10 cm^3 K mol^{-1} (4.10 μ_B) and 0.51 cm^3 K mol^{-1} (2.02 μ_B), respectively. The room temperature χT values for both compounds are typical for this class of compounds; for example, the moments for $[Ru_2(O_2CR)_4]^+$ and $Ru_2(O_2CR)_4Cl$ are in the range 4.0−4.3 μ_B. The overall behavior is also very similar to that observed for the discrete cations $[Ru_2^{II,III}(O_2CR)_4]^+$.[13,28] The electronic ground state for $Ru_2^{II,III}(O_2CR)_4^+$ is predicted to be $^4B_{2u}$, which undergoes a substantial zero-field splitting (ZFS).[29] Norman et al. explained that the large ZFS is due to high-order spin−orbit terms in the $^4B_{2u}$ ground state.[30,31] If one considers that the main contribution to the decrease of the magnetic moment is due to ZFS effects, the following expressions for the magnetic susceptibility for $S = {}^3/_2$ are applicable:[32]

$$\chi_{\parallel} = \frac{Ng^2\beta^2}{k_BT}\,\frac{1 + 9e^{-2x}}{4(1 + e^{-2x})} \tag{1}$$

$$\chi_{\perp} = \frac{Ng^2\beta^2}{k_BT}\,\frac{4 + \frac{3}{x}(1 - e^{-2x})}{4(1 + e^{-2x})} \tag{2}$$

where x is $D/(k_BT)$ and D is the magnitude of the ZFS. The average molar magnetic susceptibility for a powder sample is given by the well-known relationship

$$\chi' = \frac{\chi_{\parallel} + 2\chi_{\perp}}{3} \tag{3}$$

Although in some cases, temperature-independent paramagnetism (TIP) needs to be included in eq 3, it was found to be negligible by the best fit to the data. The decrease in χT observed at very low temperatures (~10 K) may include some weak magnetic interactions superimposed on the dominant ZFS contribution. The presence of weak intermolecular interactions was introduced into eq 3 by using the molecular field approximation:[32]

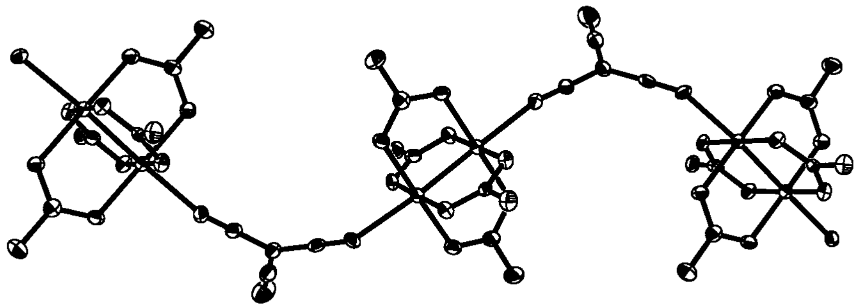

Figure 4. View of an alternating one-dimensional chain of **2**.

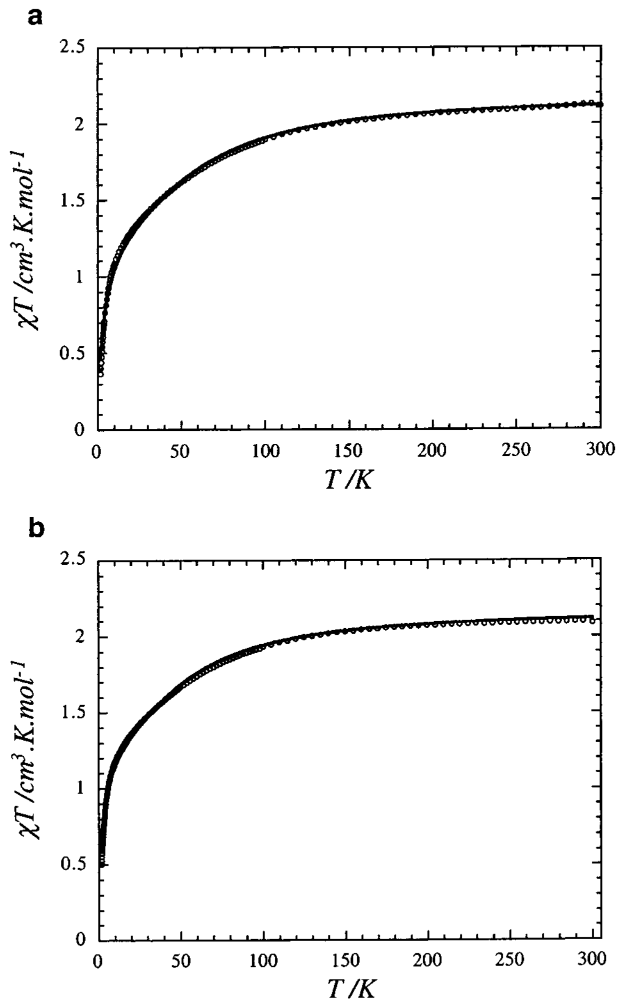

Figure 5. Temperature dependence of χT for **1** (a) and **2** (b). The solid line represents the theoretical fitting with the following parameters: $g = 2.16$, $D = 63.3$ cm^{-1}, $zJ = -0.33$ cm^{-1} for **1**; $g = 2.15$, $D = 58.0$ cm^{-1}, $zJ = -0.22$ cm^{-1} for **2**.

$$\chi = \frac{\chi'}{1 - \left(\frac{2zJ}{Ng^2\beta^2}\right)\chi'} \qquad (4)$$

where z is the number of neighbors and J is the magnitude of the intermolecular interactions, which are assumed to be intrachain through the bridging linker, $N(CN)_2^-$ for **1** and $C(CN)_3^-$ for **2**. We obtained the best agreement between model and experiment by fitting χT with eq 4 ($g = 2.16$, $D = 63.3$ cm^{-1}, $zJ = -0.33$ cm^{-1}, $R = 0.9985$ for **1**; and $g = 2.15$, $D = 58.0$ cm^{-1}, $zJ = -0.22$ cm^{-1}, $R = 0.9983$ for **2**; ($R = 1 - \sum\{(\chi T_{calc} - \chi T_{obs})/\sum(\chi T_{obs})\}^2$). The ZFS values of both compounds are in good agreement with the previously reported values.[26] These magnetic data and fitting parameters point to very weak antiferromagnetic interactions between $Ru_2(O_2CCH_3)_4^+$ units through the $N(CN)_2^-$ and $C(CN)_3^-$ linkages.

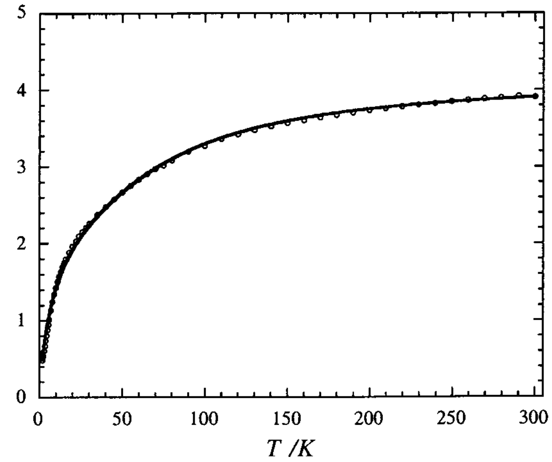

Figure 6. Temperature dependence of χT for **3**. The solid line represents the theoretical fitting with the following parameters: $g = 2.10$, $D = 75.0$ cm^{-1}, $zJ = -0.90$ cm^{-1}.

Magnetic Properties of 3. Temperature-dependent magnetic susceptibility data were measured for **3** between 1.8 and 300 K, the result of which is shown in Figure 6. The χT product at 300 K of 3.92 cm^3 K mol^{-1} (5.6 μ_B per $[Ru_2(II, III)]_2$) gradually decreases upon cooling and finally reaches 0.46 cm^3 K mol^{-1} (1.92 μ_B) at 1.8 K. Since the overall behavior is very similar to that of **1** and **2**, it is assumed that the decrease of χT is primarily due to ZFS from the $[Ru_2(O_2CCH_3)_2(mhp)_2]^+$ units with only weak antiferromagnetic interactions occurring through the DM-Dicyd^{2-} bridges. The best fit was obtained with eq 4 based on two $[Ru_2(II, III)]_2$ units ($S = {}^3/_2 + {}^3/_2$) with $g = 2.10$, $D = 75.0$ cm^{-1}, $zJ = -0.90$ cm^{-1}, and $R = 0.9995$. These magnetic data and parameters support the conclusion that weak antiferromagnetic exchange occurs between Ru_2(II, III) units through the DM-Dicyd^{2-} linkage.

Consideration of Superexchange Mechanism in 1−3. The use of the $N(CN)_2^-$ molecule as an end-to-end bridged ligand was reported by Escuer et al. who described the one-dimensional chain compounds *trans*-$[Mn(4\text{-bzpy})_2\{N(CN)_2\}_2]_n$ and *cis*-$[Mn(bpy)\{N(CN)_2\}_2]_n$ (4-bzpy = 4-benzoylpyridine; bpy = 2,2′-bipyridyl).[33] In addition, Miller et al. reported one-dimensional chain compounds of Mn(II), Fe(II), and Co(II) ions of the type $M[\{N(CN)_2\}_2(bpym)]\cdot H_2O$ (M = Mn, Fe, Co; bpym = 2,2′-bipyrimidine).[24] In these studies, the magnetic exchange interactions through the $N(CN)_2^-$ linkages were estimated to be weakly antiferromagnetic ($J = -0.3$ to -0.99 cm^{-1}). Escuer et al. performed MO calculations in an effort to understand the superexchange mechanism for $N(CN)_2^-$ bridges. Their results

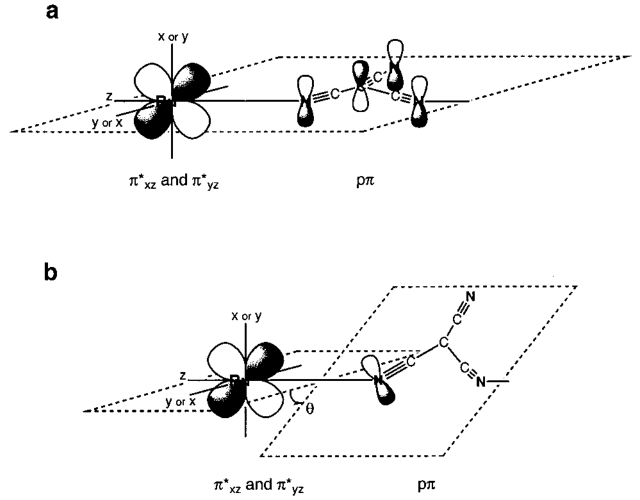

Figure 7. (a) Schematic representation of orbital arrangements between π^* orbital (π^*_{xz} and π^*_{yz}) in $[Ru_2(O_2CCH_3)_4]^+$ and the pπ orbital in the tricyanomethanide anion and (b) orbital arrangements in a rotation based on the N−Ru−Ru−N vector. The orbital arrangements between π^* orbital in $[Ru_2(O_2CCH_3)_4]^+$ and the pπ orbital in the dicyanamide anion are similar to (a) and (b) representations.

indicate that the exchange interactions occur through HOMO π orbitals and σ orbitals lying on a nearly degenerate energy level with HOMO π orbitals.[33] The interaction through the pπ orbitals of dicyanamide is reduced when bound in the end-to-end mode because of the lower electronic density on the terminal nitrogen atoms (~25% probability on terminal nitrogen atoms).[33] In the diruthenium(II,III) systems, the three unpaired electrons reside in one δ^* and two π^* orbitals ($\delta^{*1}\pi^{*2}$), but because of symmetry, the π^* orbitals are expected to be the main contributors to magnetic exchange through the axial position of the $[Ru_2(O_2CCH_3)_4]^+$ cations (Figure 7a). The lower electronic density of pπ orbitals on the terminal nitrogen atoms of dicyanamide will affect the extent of the magnetic interactions in our system as well as Escuer's compounds.

Magnetic properties of μ^3-tricyanomethanide-bridged first-row transition metal compounds with an interpenetrated rutile-like structure were recently described.[9] For the two compounds $[Cr\{C(CN)_3\}_2]$ and $[V\{C(CN)_3\}_2]$, the exchange coupling was estimated to be $J/k_B = -1.9$ K ($J = -1.32$ cm^{-1}) and -2.7 K ($J = -1.88$ cm^{-1}), respectively.[9e] The MO calculation for free tricyanomethanide indicates that the HOMO consists of out-of-plane π orbitals on the D_{3h} symmetrical $C(CN)_3^-$ molecule.[27] The electronic populations of the HOMO level on each atom are similar to those of the $N(CN)_2^-$ anion, with electron density residing mainly on the central carbon and less contribution from the terminal nitrogen atoms. In compound **2**, two of three cyano groups are associated with coordination and one cyano group is free, leading to deviation from D_{3h} symmetry. Despite this, the metric parameters in **2** reveal no remarkable distinctions between the coordinated and noncoordinated part of the tricyanomethanide moieties. Consequently, the superexchange mechanism should be through the HOMO pπ orbitals in a manner akin to dicyanamide, but it may be that the electronic density on the two coordinated nitrogen atoms of tricyanomethanide is even lower because of the presence of the additional dangling cyano group.

In any consideration of the magnetic exchange interactions in the diruthenium-bridged systems, it is important to consider the rotation angle θ defined in Figure 7b. When θ is near 0°, significant overlap occurs between the π^*_{xz} or π^*_{yz} of the Ru_2 units and the pπ orbtial on the terminal nitrogen atoms of $N(CN)_2^-$ and $C(CN)_3^-$. Conversely, when θ is near 45 °, there is minimum overlap between the same sets of orbitals. Although the complicated disorder of the dicyanamide moieties in **1** renders it difficult to define an exact value for θ, the angles are ~11° and ~45° based on the N−Ru−Ru−N vector and N(2) positions as shown in Figure 8a. The alternation of these angles in each $N(CN)_2^-$ linkage is expected to lead to a decrease of the magnetic communication between Ru_2 units. In compound **2**, the θ angle is ca. 25° as indicated in Figure 8b, which would also lead to poor overlap and hence weak magnetic exchange interaction in this compound as well.

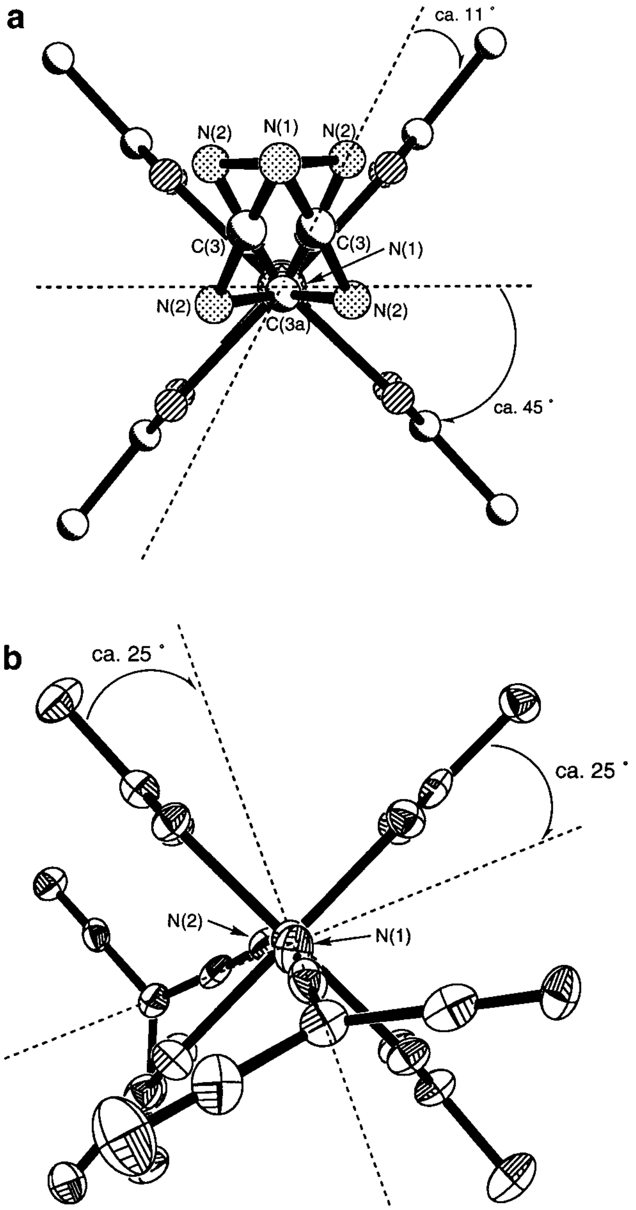

Figure 8. Perspective view of the one-dimensional chain looking down the N−Ru−Ru−N vector of (a) **1** and (b) **2**.

The superexchange mechanism for mononuclear Ru(III) centers through Dicyd^{2-} spacers has been investigated.[10] It is recognized that the Dicyd^{2-} anions are interesting bridging ligands because they lead to strong magnetic and electronic communication. Crutchley and co-workers described the superexchange coupling between monoruthenium(III) ions as occurring by hole transfer via HOMO pπ orbitals of Dicyd^{2-}. This mechanism explains the strong magnetic coupling ($|J| > 400$ cm^{-1}) found in [Ru(III)−(Dicyd^{2-})−Ru(III)] despite the long-range pathway. For this to occur, the relatively high-energy pπ HOMO level in Dicyd^{2-} would have to be energetically well-matched with the dπ orbital of Ru(III) ions. This appears to be the case because a systematic variation of the HOMO energy level according to substituent changes on the Dicyd^{2-} unit led to variations in the magnitude of the magnetic interactions over the range of $|J|$ from 62 to $\geq$400 cm^{-1}.[10b] If we consider these studies as a backdrop for analyzing the magnetic properties of **3**, one may conclude that the energies of the HOMO orbitals ($\delta^{*1}\pi^{*2}$) in the building block $[Ru_2(O_2CCH_3)_2(mhp)_2]^+$ are inaccessible for extensive π overlap with the HOMO level of Dicyd^{2-}. Consequently, the *hole transfer* as Crutchley's compounds will not be operative.

Conclusions

Metal−metal bonded Ru$_2$(II, III) assemblies with three different polycyano anion bridges have been synthesized and fully characterized. One-dimensional chains of **1** and **2** consist of $[Ru_2(O_2CCH_3)_2]^+$ and the linkers $N(CN)_2^-$ and $C(CN)_3^-$, respectively. The temperature dependence of the magnetic susceptibilities of **1** and **2** reveals weak antiferromagnetic interactions between Ru$_2$ units ($S = {}^3/_2$) via $N(CN)_2^-$ and $C(CN)_3^-$ with $g = 2.16$, $zJ = -0.33$ cm^{-1}, $D = 63.3$ cm^{-1} for **1**, and $g = 2.15$, $zJ = -0.22$ cm^{-1}, $D = 58.0$ cm^{-1} for **2**. The Ru$_2$(II, III) "dimer-of-dimers" compound, **3**, bridged by DM-Dicyd^{2-}, was also prepared. The magnetic data of **3** revealed a weak antiferromagnetic interaction ($g = 2.10$, $zJ = -0.90$ cm^{-1}, $D = 75.0$ cm^{-1}), in contrast to the previously reported series of compounds based on the [Ru(III)−(Dicyd^{2-})−Ru(III)] unit, which exhibit strong magnetic interactions ($J = -62$ to ≥ -400 cm^{-1}) via LMCT pathways. The fact that the new compounds in this study exhibit only weak antiferromagnetic superexchange is attributed to poor overlap of the π^* orbitals (π^*_{xz} and π^*_{yz}) of the Ru$_2$(II, III) units with the HOMO delocalized pπ orbitals on the polycyano molecules.

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Supporting Information Available: X-ray crystallographic files, in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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