Chain Compound of Mixed-Valent Ruthenium Dimers Linked by Hydrogen-Bonding between the Axially Coordinated Nitronyl Nitroxide and Water Molecules

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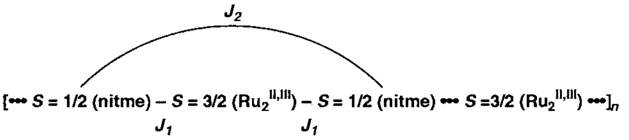
An adduct of ruthenium(II,III) dimer with nitronyl nitroxide, $[\{Ru_2(O_2CCMe_3)_4(nitme)_2\}\{Ru_2(O_2CCMe_3)_4(H_2O)_2\}]_n(BF_4)_{2n}$ (nitme = 2,4,4,5,5-pentamethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide), which has a chain structure formed by hydrogen bonds between the axial nitme and water molecules, has been prepared and characterized by the X-ray crystallography, magnetic susceptibility, and EPR measurements.

There has been considerable interest in one-dimensional chain compounds.[1] One of the fascinating strategies towards the design of chain compounds is the use of metal carboxylates with metal–metal bonds as a building block.[2-5] Recently some efforts to produce magnetic chain compounds have been done with a combination of metal carboxylates and nitroxide radicals.[5-9] However, none of them was successful in producing one-dimensional ferro- or ferrimagnetic behavior based on the interaction between the paramagnetic metal carboxylates and nitroxide radicals, expect for one example.[9] We report here a new chain compound of $Ru_2^{II,III}$ carboxylate and nitronyl nitroxide, $[\{Ru_2(O_2CCMe_3)_4(nitme)_2\}\{Ru_2(O_2CCMe_3)_4(H_2O)_2\}]_n(BF_4)_{2n}\bullet 2nCH_2Cl_2$ (**1**) (nitme = 2,4,4,5,5-pentamethyl-4,5-dihydro-1*H*-imidazolyl-1-oxyl 3-oxide), in which hydrogen bonds between the axial nitme and water molecules work as a junction to connect the $Ru_2^{II,III}$ dimers and radicals to form a unique chain structure.

Complex **1** was prepared by a reaction of $[Ru_2(O_2CCMe_3)_4(H_2O)_2]BF_4$[7] and nitme[10] in a ratio of 1:1 in dichloromethane—hexane under Ar.[11]

The X-ray crystal structure of **1** shows that the crystal contains two kinds of $Ru_2^{II,III}$ cation units, $[Ru_2(O_2CCMe_3)_4(nitme)_2]^+$ and $[Ru_2(O_2CCMe_3)_4(H_2O)_2]^+$.[12] This situation is similar to that of adduct of ruthenium(II,III) dimer with tempo (2,2,6,6-tetramethylpiperidine-1-oxyl), $[Ru_2(O_2CCMe_3)_4(tempo)_2][Ru_2(O_2CCMe_3)_4(H_2O)_2](BF_4)_2$ (**2**).[7] The two $Ru_2^{II,III}$ cations of **1** are not discrete. The N-O groups of $[Ru_2(O_2CCMe_3)_4(nitme)_2]^+$ are hydrogen bonded to the water molecules of $[Ru_2(O_2CCMe_3)_4(H_2O)_2]^+$, resulting in a zig-zag chain as shown in Figure 1. The O(10)···O(11) distance is 2.81(1) Å. The crystallographic inversion center is located at the midpoint of the Ru-Ru bond of each $Ru_2^{II,III}$ dimer. The Ru(1)-Ru(1)' and Ru(2)-Ru(2)" bond distances are 2.275(1) and 2.262(1) Å, respectively, both of which are in the range of those reported for $[Ru_2(O_2CR)_4]^+$ compounds (2.24—2.30 Å).[13] The axial bond distances of the two $Ru_2^{II,III}$ dimers are 2.269(8) and 2.248(7) Å for nitme and water molecules, respectively. The Ru(1)'-Ru(1)-O(9), Ru(2)"-Ru(2)-O(11), Ru(1)-O(9)-N(1) and Ru(2)-O(11)···O(10) angles are 177.7(2), 174.3(2), 121.5(6), and 120.7(4)°, respectively. The N-O bond distances [1.31(1) (N(1)-O(9)) and 1.28(1) Å (N(2)-O(10))] confirm the free radical character of the nitme ligand.[14]

The variation of the effective magnetic moment with temperature (2—300 K) for complex **1** is shown in Figure 2. The room temperature magnetic moment of **1** is 6.63 B.M., appreciably higher than the value (6.00 B.M.) expected for non-interacting spins, two $S = 3/2$ ($Ru_2^{II,III}$ core) and two $S = 1/2$ (nitme). The effective magnetic moment of **1** slightly increases from room temperature (6.63 B.M.) to 140 K (6.68 B.M.) and is almost constant down to 100 K. Then, the magnetic moment gradually decreases with lowering of temperature, and reaches a value of 4.71 B.M. at 2.0 K. The magnetic behavior was analyzed by the van Vleck equation based on the Heisenberg model,



assuming that the magnetic interaction through the hydrogen bonds are negligible and g value of nitme is 2.00 in order to avoid an overparameterization, where J_1 and J_2 are spin coupling constants in this model.[7] The best fit with $J_1 = 20$, $J_2 = -50\ cm^{-1}$, $D_1 = 20$, $D_2 = 45\ cm^{-1}$, and $g_{Ru} = 2.20$ was obtained for **1** as the solid line in Figure 2.[15] The magnetic behavior can not be simulated by the equation for this system without the positive J_1 value. This result shows that a ferromagnetic interaction is operative between the $Ru_2^{II,III}$ core and nitroxide radical, in addition to an antiferromagnetic interaction between the two nitroxides through the metal–metal bond. Antiferromagnetic interaction through the metal–metal bond was observed in nitroxide complexes of $Rh_2(O_2CCF_3)_4$.[6] In these complexes,

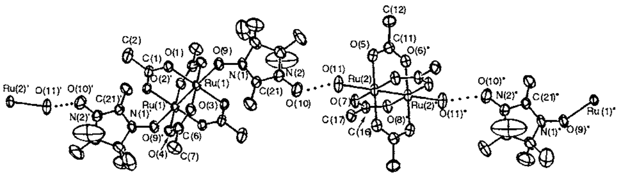


Figure 1. ORTEP view of the chain structure of $[\{Ru_2(O_2CCMe_3)_4(nitme)_2\}\{Ru_2(O_2CCMe_3)_4(H_2O)_2\}]_n(BF_4)_{2n}\bullet 2nCH_2Cl_2$ (**1**). Methyl groups of pivalic acid moieties, BF_4^- ions, and CH_2Cl_2 molecules are omitted for clarity. Selected bond distances (l/Å) and angles (ϕ/°): Ru(1)-Ru(1)' 2.275(1), Ru(1)-O(1) 2.015(7), Ru(1)-O(2) 2.021(7), Ru(1)-O(3) 2.013(7), Ru(1)-O(4) 2.031(7), Ru(1)-O(9) 2.269(8), O(9)-N(1) 1.31(1), O(10)-N(2) 1.28(1), Ru(2)-Ru(2)" 2.262(1), Ru(2)-O(5) 2.014(8), Ru(2)-O(6) 2.024(8), Ru(2)-O(7) 2.024(8), Ru(2)-O(8) 2.037(8), Ru(2)-O(11) 2.248(7); Ru(1)'-Ru(1)-O(9) 177.7(2), Ru(2)"-Ru(2)-O(11) 174.3(2), Ru(1)-O(9)-N(1) 121.5(6).

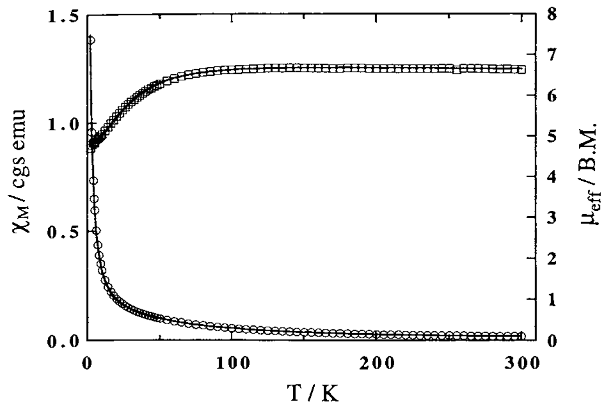


Figure 2. Magnetic susceptibility data (○) and effective magnetic moments (□) of **1**. The solid line was calculated from the van Vleck equation based on the Heisenberg model with parameters in the text.

the Rh-O-N bond angles close to 120° were considered to be suitable for the antiferromagnetic interaction through the σ or σ^* orbitals of the diamagnetic Rh–Rh core. Thus, the Ru1-O9-N1 angle (121.5(6)°) of **1** must be responsible to the antiferromagnetic interaction between the two radical spins through the Ru–Ru bond with the σ pathway mechanism. The correlation between the Ru-O-N angle and the spin coupling parameters is listed in Table 1 together with those of other metal carboxylates with nitroxide radicals. In the case of the Ru complexes, the bond angle close to 120° may be also favorable for the ferromagnetic interaction between the $Ru_2^{II,III}$ core and radical spin. The ferromagnetic interaction in **1** and $[Ru_2(O_2CCMe_3)_4(p\text{-pynit})]_n(BF_4)_n$, may come from the the orthogonality of the $Ru_2^{II,III}$ π^* (and/or δ^*) and nitroxide π^* orbitals as a consequence of the small bond angle.[9] On the other hand, complexes which have larger Ru-O-N angles show antiferromagnetic interaction between the $Ru_2^{II,III}$ core and nitroxide radical. The Ru-O-N angles of **2** is 151.5(3)°, which leads to a significant antiferromagnetic interaction between the π^* orbitals in the Ru_2 core and nitroxide radical because of the considerable overlap between the metal and nitroxide π^* orbitals.[7]

ESR spectrum of **1** (powder at 30 K) shows a signal around g = 4.0, signal for nitme radical being washed out due to the antiferromagnetic interaction through the Ru–Ru bond between the radicals. In the case of **2**, the $Ru_2^{II,III}$–tempo interaction gives the signals at $g_\perp$ = 2.33 and $g_{//}$ = 1.92.[7] These different features support that the two nitroxide radicals are antiferromagnetically coupled through the Ru_2 core in **1**.

Table 1. Structural and magnetic parameters of metal carboxylates with nitroxide radicals

Complexes	M-O-N/°	J_1 / cm^{-1}	J_2 / cm^{-1}	ref.
$Rh_2(O_2CCF_3)_4$(nitme)	118.3(4)	—	-98.8	5
	121.3(4)			
$Rh_2(O_2CCF_3)_4(nitph)_2$	122.7(3)	—	-83.6	5
1	121.5(6)	20	-50	This work
$[Ru_2(O_2CCMe_3)_4(p\text{-pynit})]_n(BF_4)_n$	125.3(6)	20	—	9
$[Ru_2(O_2CCMe_3)_4(nitph)]_n(BF_4)_n$	131.7(7)	0	—	8
	147.5(7)	-100	—	
2	151.5(3)	-130	—	7
$Ru_2(O_2CCF_3)_4(tempo)_2$	158.2(3)	-263	0	6

The Ru-O-N angle closed to 120° may allow the presence of the ferro- and antiferromagnetic interactions in the NO-Ru–Ru-ON moiety. To our knowledge, this is the first example that shows the opposite interactions through the metal-nitroxide bond. Further studies are in progress in our laboratories.

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