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The first crystal structure of a one-dimensional chain of linked Ru^{II}=Ru^{II} units

Hitoshi Miyasaka, Rodolphe Clérac, Cristian S. Campos-Fernández and Kim R. Dunbar *

Department of Chemistry, Texas A&M University, PO Box 30012, College Station, Texas 77842-3012, USA. Fax: (979) 845-7177; E-mail: dunbar@mail.chem.tamu.edu

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The one-dimensional polymer $[Ru_2(O_2CCF_3)_4(Phz)]_\infty$ **1** (Phz = phenazine) was synthesized by the reaction of $Ru^{II}_2(O_2CCF_3)_4(THF)_2$ with phenazine. An X-ray crystallographic analysis revealed that the compound consists of $Ru_2(O_2CCF_3)_4$ units bridged by phenazine ligands. The Ru–Ru bond distance is 2.3109(10) Å and the axial Ru–N distance is 2.425(2) Å. Magnetic measurements performed in the temperature range 1.8–300 K indicate that the $S = 1$ Ru^{II}_2 units are weakly antiferromagnetically coupled ($zJ = -3.0$ cm^{-1}) with a large zero-field splitting ($D = 277$ cm^{-1}).

Introduction

It has been demonstrated in recent years that dinuclear complexes of Mo, W, Re, Rh and Ru are useful precursors for the design of cyclic architectures[1a–e] as well as one-dimensional chains[1f–l] and two-dimensional networks.[1m,n] One can envisage a variety of interesting phenomena that may be exhibited by materials composed of M–M building blocks; these include unusual optical, electronic and magnetic properties. With regard to magnetic materials, the most interesting members of the metal–metal bonded family of compounds are the "paddle-wheel" molecules $[Ru_2^{II,III}(O_2CR)_4]^+$ and $Ru^{II}_2(O_2CR)_4$ with ground states of $S = 3/2$ and 1 respectively. To date, most of the diruthenium chemistry has been carried out with the more stable mixed-valence $Ru_2^{II,III}$ species. For example various 1-D chains such as $[Ru_2^{II,III}(O_2CR)_4(Cl)]_\infty$,[2–6] $[Ru_2^{II,III}(O_2CEt)_4(Phz)]_\infty^+$ (Phz = phenazine)[7] and $[Ru_2^{II,III}(O_2C^tBu)_4(L)]_\infty^+$ (L = 4,4,5,5-tetramethyl-2-phenyl-4,5-dihydro-1*H*-imidazol-1-oxyl 3-*N*-oxide or 4,4,5,5-tetramethyl-2-(4-pyridyl)-4,5-dihydro-1*H*-imidazol-1-oxyl 3-*N*-oxide)[8–10] have fully been characterized and their magnetic properties elucidated. In contrast to this situation, 1-D compounds of Ru^{II}_2 have not been well investigated, and no X-ray data are available to correlate with the observed physical properties.[11–15] In this paper we report the first X-ray structural determination of a polymer that contains doubly bonded Ru^{II}_2 units. The magnetic behavior of the new compound is also described.

Experimental

Chemicals and reagents

The chemicals used were of reagent grade quality. Reactions were carried out under a dinitrogen atmosphere unless otherwise indicated. Benzene was dried by refluxing over sodium–benzophenone, and dichloromethane was dried by refluxing over P_2O_5. Both solvents were freshly distilled under N_2 before use. $Ru_2(O_2CCF_3)_4(THF)_2$ was synthesized by the literature method.[16]

Preparation of $[Ru_2(O_2CCF_3)_4(Phz)]_\infty$ 1

A dichloromethane solution (25 mL) of $Ru_2(O_2CCF_3)_4(THF)_2$ (80 mg, 0.1 mmol) was placed in a Schlenk tube, and layered with 25 mL of a benzene solution that contained an excess of phenazine (72 mg, 0.4 mmol). The solution was allowed to stand undisturbed for 3 days at room temperature, after which time a crop of brown needle-type crystals was harvested (68 mg, yield 82%). An excess of phenazine is required, as the polymeric product does not form in high yields with a 1 : 1 ratio of Ru_2 to phz. IR (Nujol): 1645s, 1608w, 1526w, 1284w, 1201s, 1167s, 1120w, 910w, 861m, 826w, 775m, 736m, 655w and 598w cm^{-1}.

Physical measurements

Infrared spectra were recorded as Nujol mulls between KBr plates with a Nicolet 740 FT-IR spectrophotometer. The magnetic susceptibility measurements were made with the use of a Quantum Design SQUID magnetometer MPMS-XL (housed in the Department of Chemistry at Texas A&M University) on a finely ground, polycrystalline sample (20.22 mg) in the range 1.8–350 K at 1000 G. The data were corrected for the sample holder from experimental data and for the diamagnetic contribution of the sample using Pascal's constants.[17]

X-Ray crystallographic analysis

A rectangular crystal of compound **1** was cut from a larger needle crystal and secured on a glass fiber with Dow-Corning grease. Data were collected on a Bruker SMART CCD diffractometer equipped with graphite monochromated Mo-Kα radiation. Of the 4653 reflections that were collected, 2852 were unique. The structure was solved by direct methods (SHELXS 97)[18] and refined by full-matrix least-squares calculations on F^2 (SHELXL 97).[19] All atoms except for hydrogen atoms were refined anisotropically. Data collection parameters and details of the structure determination are summarized in Table 1.

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See http://www.rsc.org/suppdata/dt/b0/b007079n/ for crystallographic files in .cif format.

Results and discussion

Structural determination of $[Ru_2(O_2CCF_3)_4(Phz)]_\infty$ 1

Crystals of $[Ru_2(O_2CCF_3)_4(Phz)]_\infty$ **1** grew as brown needles during slow diffusion of solutions of $Ru_2(O_2CCF_3)_4(THF)_2$ and phenazine. The polymeric product crystallizes in the triclinic space group $P\bar{1}$, with the midpoint of the Ru–Ru vector and the center of the phenazine molecule residing on inversion centers

Table 1 Crystallographic data for $[Ru_2(O_2CCF_3)_4(Phz)]_\infty$ **1**

Formula	$C_{20}H_8F_{12}N_2O_8Ru_2$
M	834.42
Crystal system	Triclinic
Space group	$P\bar{1}$
T/K	100(2)
λ/Å	0.71069
a/Å	8.574(5)
b/Å	8.863(5)
c/Å	9.006(5)
α/°	112.649(5)
β/°	93.209(5)
γ/°	90.088(5)
V/Å^3	630.4(6)
Z	1
μ(Mo-Kα)/cm^{-1}	1.338
R	0.0240 ($I > 2.00\sigma(I)$) 0.0260 (all data)
Rw	0.0623 ($I > 2.00\sigma(I)$) 0.0633 (all data)

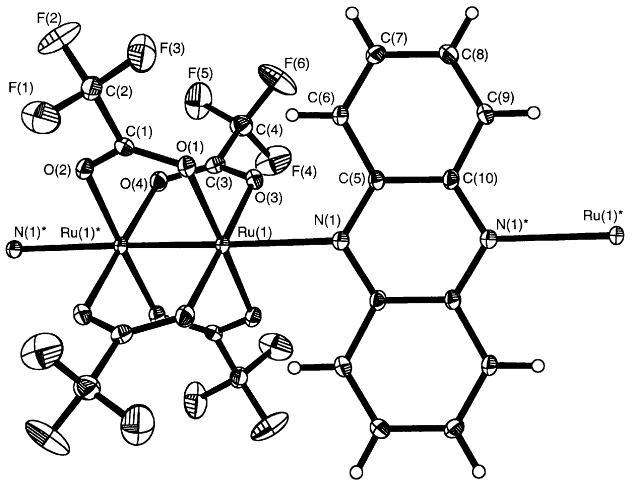

Fig. 1 Thermal ellipsoid drawing at the 50% probability level of the unique portion of $[Ru_2(O_2CCF_3)_4(Phz)]_\infty$ **1** with atom labeling scheme.

($Z = 1$). An ORTEP[20] drawing of the formula unit with the atom numbering scheme is depicted in Fig. 1.

Selected bond distances and angles are given in Table 2. The phenazine molecules bridge the $Ru^{II}_2(O_2CCF_3)_4$ units to form an infinite one-dimensional chain along the [0, 1, 1] direction as shown in Fig. 2. The Ru(1)–N(1) axial interaction is 2.425(2) Å which is very close to the values of 2.436(4) and 2.443(5) Å reported for the mixed-valence analog $[Ru_2^{II,III}(O_2CEt)_4(Phz)][BF_4]$.[7] The phenazine bridges in **1** are canted away from a strictly linear interaction (Ru(1)–N(1) ··· N(1)* 164.6°), a situation that was also noted in $[Ru_2^{II,III}(O_2CEt)_4(Phz)][BF_4]$ by Cotton *et al.* who attributed this feature to the cumulative effects of intermolecular packing forces.[7] A view along the N–Ru–Ru–N axis (Fig. 3) reveals that the phenazine bridges in **1** do not bisect the paddle-wheel arrangement of $O_2CCF_3^-$ ligands at the ideal angle of 45°.

The Ru–Ru bond distance in compound **1** is 2.3109(10) Å, the longest distance reported to date for compounds of the type $Ru^{II}_2(O_2CCF_3)_4(L)_2$. One exception to this is $Ru_2(O_2CCF_3)_4(NO)_2$ with a Ru–Ru separation of 2.532(4) Å, but the Ru_2 core is formally reduced by NO to give a singly bonded compound with a ground state electronic configuration of $\sigma^2\pi^2\delta^2\delta^{*2}\pi^{*4}$.[6] The corresponding metal–metal bond distances in $Ru_2(O_2CCF_3)_4(THF)_2$[16] and $[Ru_2(O_2CCF_3)_4(Tempo)_2]$ (Tempo = 2,2,6,6-tetramethylpiperidine-*N*-oxyl) are 2.276(3) and 2.300(2) Å, respectively.[21] The 2-D network compound $[\{Ru^{II}_2(O_2CCF_3)_4\}_2(\mu_4\text{-TCNQ})]_\infty$ (TCNQ = 7,7,8,8-tetracyanoquinodimethane) recently prepared in our laboratories exhibits a Ru–Ru bond distance of 2.2875(7) Å.[22]

Table 2 Pertinent bond distances (Å) and angles (°) for $[Ru_2(O_2CCF_3)_4(Phz)]_\infty$ **1** with estimated standard deviations in parentheses

Ru(1)–O(1)	2.0671(19)	Ru(1)–O(4)*	2.0679(18)
Ru(1)–O(2)*	2.0677(19)	Ru(1)–N(1)	2.425(2)
Ru(1)–O(3)	2.0643(18)	Ru(1)–Ru(1)*	2.3109(10)
O(1)–Ru(1)–O(2)*	178.15(6)	O(2)*–Ru(1)–Ru(1)*	89.15(5)
O(1)–Ru(1)–O(3)	94.55(7)	O(3)–Ru(1)–O(4)*	178.15(6)
O(1)–Ru(1)–O(4)*	85.71(7)	O(3)–Ru(1)–N(1)	86.12(8)
O(1)–Ru(1)–N(1)	93.88(7)	O(3)–Ru(1)–Ru(1)*	88.71(6)
O(1)–Ru(1)–Ru(1)*	89.14(5)	O(4)*–Ru(1)–N(1)	95.68(8)
O(2)*–Ru(1)*–O(3)	86.11(7)	O(4)*–Ru(1)–Ru(1)*	89.47(6)
O(2)*–Ru(1)–O(4)*	93.57(7)	Ru(1)*–Ru(1)–N(1)	174.21(4)
O(2)*–Ru(1)–N(1)	87.88(7)		

Symmetry operation: * $-x, -y, -z$.

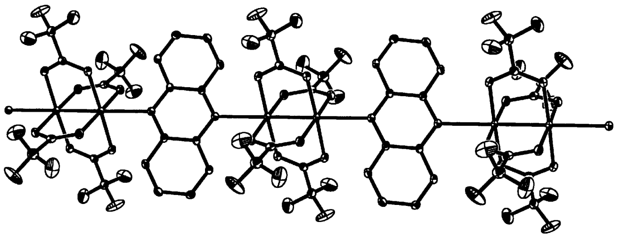

Fig. 2 View of a chain of $[Ru_2(O_2CCF_3)_4(Phz)]_\infty$ **1**.

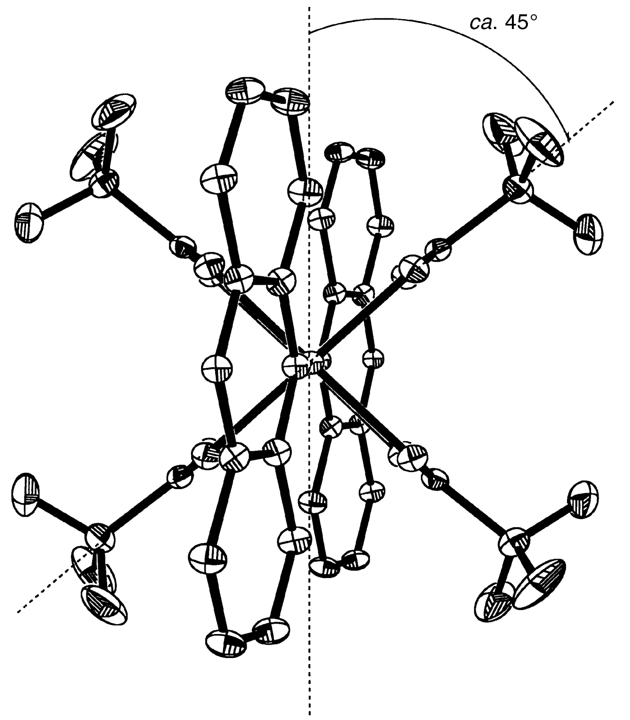

Fig. 3 View of compound **1** looking down the N–Ru–Ru–N vector.

Magnetic properties

The temperature dependence of the magnetic susceptibility of compound **1** measured between 1.8 and 300 K is shown in Fig. 4. The overall behavior is very similar to that of the parent $Ru^{II}_2(O_2CR)_4$ compounds whose magnetic properties have been reported.[13,15,21,23] The nature of the ground state of such compounds has been a matter of debate over the years. The first theoretical calculation on this series was performed by Norman *et al.*[24] at the SCF-Xα-SW level on $Ru_2(O_2CH)_4$. The results predicted the presence of a Ru–Ru double bond with a $(\pi^*)^3(\delta^*)^1$ ground-state configuration and a $(\pi^*)^2(\delta^*)^2$ excited-state configuration. Later, *ab initio* Hartree–Fock (RHF) calculations[25] led to the conclusion that the ground-state

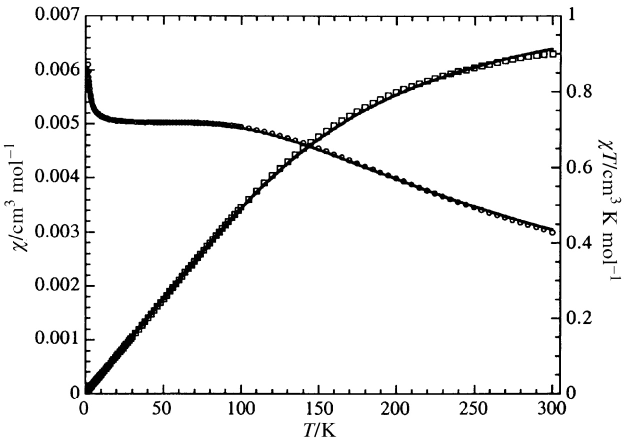

Fig. 4 Temperature dependence of χ (circle) and χT (square) of $[Ru_2(O_2CCF_3)_4(Phz)]_\infty$ **1**. The solid line represents the theoretical fit with $g = 2.0$, $D = 277$ cm^{-1}, $zJ = -3.0$ cm^{-1}, TIP = 9.9×10^{-5} cm³ mol^{-1}, and $\rho = 0.1\%$.

configuration is most likely $(\pi^*)^2(\delta^*)^2$, in accord with reports of the magnetic properties of $Ru_2(hp)_4$ (Hhp = 2-hydroxypyridine) compounds.[26] X-Ray photoelectron spectroscopic studies performed by Green *et al.* on $Ru^{II}_2(O_2CCF_3)_4$ apparently do not allow for a definitive assignment of the ground state.[27] With the data currently in hand, however, it is reasonable to state that Ru^{II}_2 complexes are doubly bonded species with the π^* and δ^* HOMO orbitals being nearly degenerate. The ground state electronic configuration is $(\pi^*)^2(\delta^*)^2$ which is an $S = 1$ state with an appreciable zero-field splitting (ZFS).

Compound **1** exhibits a continuous decrease of χT at lower temperatures from 0.900 cm³ K mol^{-1} at 300 K to 0.011 cm³ K mol^{-1} at 1.8 K, which is primarily due to the zero-field splitting arising from the $^3A_{2g}$ ground state. The magnetic susceptibility for $S = 1$ centers with ZFS and a temperature independent paramagnetic (TIP) contribution can be expressed as in eqn. (1)[21]

$$\chi = (2Ng^2\beta^2/3k_BT)[\{e^{-x} + (2/x)(1 - e^{-x})\}/(1 + 2e^{-x})] + \mathrm{TIP} \qquad (1)$$

where $x = D/k_BT$ and D is the magnitude of ZFS. Superexchange in these chains can be considered by the molecular field approximation (2)[28] where z is the number of neighbors

$$\chi' = \chi/\{1 - (2zJ/Ng^2\beta^2)\chi\} \qquad (2)$$

and J the magnitude of the intermolecular interaction, which is assumed to be intrachain magnetic interactions of the $S = 1$ centers. The abrupt increase of χ at low temperature that can be observed in Fig. 4 is attributed to an extrinsic paramagnetic impurity (ρ) of a ubiquitous $Ru_2^{II,III}$ species ($S = 3/2$). This is taken into account by eqn. (3). The value of g_{imp} is assumed to

$$\chi'' = (1 - \rho)\chi' + \rho(5Ng_{imp}^2\beta^2/4k_BT) \qquad (3)$$

be 2.0 by convention. In order to minimize the usual problems of refining many parameters (g, D, zJ, TIP, ρ), the least-squares calculation was performed in a parameter range of $g = 2.0$ and $D = 250$–300 cm^{-1} based on previously reported magnetic data.[13,15,21,23] The best fitting parameters for the magnetic behavior of **1** were determined from eqn. (3). The best χT fitting to the molecular field approximation led to $g = 2.0$, $D = 277$ cm^{-1}, $zJ = -3.0$ cm^{-1}, TIP = 9.9×10^{-5} cm³ mol^{-1}, and $\rho = 0.001$. Expected magnitudes for the temperature independence paramagnetism (TIP) of a $^3A_{2g}$ ground state are in the range $(10$–$30) \times 10^{-5}$ cm³ mol^{-1}.[21]

Although any fitting of the aforementioned kind must be interpreted with caution, one point emerges very clearly. Superexchange interactions between the Ru^{II}_2 units through the phenazine bridges is very weak, of the order of $zJ = -3.0$ cm^{-1}. This conclusion is in accord with the magnetic interactions reported for the 1-D chain $\{[Ru_2^{II,III}(O_2CCH_3)_4(Pyz)]^+\}_\infty$ with pyrazine bridges in which $zJ = -2.3$ cm^{-1}.[7] As mentioned earlier, the phenazine linkers are not lined up perfectly with the Ru–Ru unit (the bending angle $\delta = 15.4°$ as depicted in Fig. 5), furthermore they do not bisect the paddle-wheel arrangement of $O_2CCF_3^-$ groups at a 45° angle (rotation angle θ in Fig. 5). This canting reduces the pπ overlap of the axial nitrogen atoms with the two π^* orbitals in which the unpaired spins of $Ru_2(O_2CCF_3)_4$ reside. The σ pathway for communication would be the main exchange mechanism available in this case, and this is known to be weak for pyrazine, phenazine and related ligands.[7]

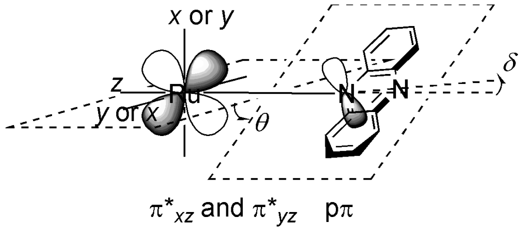

Fig. 5 Schematic representation of orbital arrangements between a π^* orbital (π^*_{xz} or π^*_{yz}) on $Ru_2(O_2CCF_3)_4$ and the pπ orbital of phenazine. The angle θ is *ca.* 45° and δ is 15.4° in $[Ru_2(O_2CCF_3)_4(Phz)]_\infty$ **1**.

In summary, a new one-dimensional compound consisting of $Ru^{II}_2(O_2CCF_3)_4$ molecules linked by axially coordinated phenazine ligands was prepared and fully characterized. $[Ru_2(O_2CCF_3)_4(Phz)]_\infty$ **1** is the first example of a structurally characterized polymeric $Ru^{II}_2(O_2CR)_4$ compound. The magnetic data reveal weak antiferromagnetic interactions between the paramagnetic Ru^{II}_2 $S = 1$ centers *via* the phenazine bridges which is not entirely unexpected, given the orientation of the axial phenazine unit.

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