Linear (1-D) Chain Structure of $[\text{Ru}_2(\text{O}_2\text{CMe})_4]^+[\text{Co}^{\text{III}}\text{Pc}(\text{CN})_2]^-$ Determined via Synchrotron Powder Diffraction Data

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ICA-D-14-00370

Keywords: Metal-Metal bonds, Ru complexes, X-ray structure

Abstract

Reaction of $[\text{Ru}_2(\text{O}_2\text{CMe})_4]\text{Cl}$ and $\text{Na}[\text{Co}^{\text{III}}\text{Pc}(\text{CN})_2]$ (H_2Pc = phthalocyanine) forms $[\text{Ru}_2(\text{O}_2\text{CMe})_4][\text{Co}^{\text{III}}\text{Pc}(\text{CN})_2]$ with the targeted linear structure possessing linear $\cdots\text{Ru}-\text{N}\equiv\text{C}-\text{Co}\cdots$ linkages. The magnetic properties of $[\text{Ru}_2(\text{O}_2\text{CMe})_4][\text{Co}^{\text{III}}\text{Pc}(\text{CN})_2]$ can be fit to a zero field splitting model with $D/k_{\text{B}} = 95$ K (66 cm^{-1}). Attempts to prepare the Cr(III) analogue were unsuccessful due to cyanide abstraction by the ruthenium site.

1. Introduction

Mixed-valent, dinuclear, multiple metal-metal bonded $[\text{Ru}_2^{\text{II/III}}(\text{O}_2\text{CR})_4]^+$ has a rich coordination chemistry [1,2,3,4]. The reaction with $\text{R} = \text{Me}, \text{H}$ with octahedral $[\text{M}^{\text{III}}(\text{CN})_6]^{3-}$ ($\text{M} = \text{Cr}, \text{Fe}, \text{Co}$) predictably formed cubic $[\text{Ru}_2(\text{O}_2\text{CR})_4]_3[\text{M}(\text{CN})_6]$ possessing an extended 3-D network structure that magnetically orders as a ferrimagnet for $\text{M} = \text{Cr}, \text{Fe}$ [5,6]. For $\text{R} = \text{tert-Bu}$ an extended 3-D network structure of $[\text{Ru}_2(\text{O}_2\text{CBu}^t)_4]_3[\text{M}(\text{CN})_6]$ composition was also anticipated, however, a layered, 2-D structural motif formed [7, 8]. Using $[\text{Ni}(\text{CN})_4]^{2-}$ layered $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_2[\text{Ni}(\text{CN})_4]$ was sought and characterized [9]. Seeking to make an 1-D analog the reaction of $[\text{Ru}_2(\text{O}_2\text{CMe})_4]^+\text{Cl}^-$ and Na^+ *trans*- $[\text{Co}^{\text{III}}\text{Pc}(\text{CN})_2]^-$ [10] to form

$[\text{Ru}_2(\text{O}_2\text{CMe})_4]^+[\text{Co}^{\text{III}}\text{Pc}(\text{CN})_2]^-$ and the Cr(III) analogue were executed, and herein we report its crystal structure and magnetic properties of $[\text{Ru}_2(\text{O}_2\text{CMe})_4]^+[\text{Co}^{\text{III}}\text{Pc}(\text{CN})_2]$. Due to the low spin nature of $[\text{Fe}^{\text{III}}\text{Pc}(\text{CN})_2]^-$ [11] and facile loss of cyanide, it was not studied.

2. Experimental

2.1 Synthesis

A 10-mL methanol solution of 50 mg (0.0773 mmol) of $\text{Na}[\text{Co}^{\text{III}}\text{Pc}(\text{CN})_2]$ [10] was added in to a 5 mL methanol solution of 36.64 mg (0.0773mmol) of $[\text{Ru}_2(\text{O}_2\text{CMe})_4]\text{Cl}$ at room temperature. A brown precipitate appeared immediately and the mixture was stirred for an additional 30 min. The brown precipitate was collected and washed with water and then methanol and dried in vacuum at room temperature. A dark powder was obtained (Yield: 26 mg, 32%). IR(KBr) 2128 m cm^{-1} (ν_{CN}). While the synthesis did not produce samples usable for single crystal structure determination, it did produce a powder with diffraction peaks sufficiently strong and sharp to determine the structure. The analogous chemistry was carried out using $\text{Na}[\text{Cr}^{\text{III}}\text{Pc}(\text{CN})_2]$ [12].

2.2 Crystal Structure Determination

High-resolution X-ray powder diffraction patterns were collected at the X16C beamline, National Synchrotron Light Source, Brookhaven National Laboratory at ambient temperature. A Si(111) channel cut monochromator selected a highly collimated incident beam of $0.69994(2)\text{ \AA}$. The diffracted X-rays were analyzed by a Ge(111) single-reflection crystal and detected using a NaI scintillation counter. Data were collected in step-scan mode for approximately 5 s per point. The sealed capillary was spun during data collection for better averaging of the powder pattern data. TOPAS-Academic [13] was used to index the lattice, solve the structure by direct space search (simulated annealing), and to refine the structure via the Rietveld method. The crystallographic data for $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_2[\text{Ni}(\text{CN})_4]$ is summarized in Table 1. There are several unidentified impurity peaks, accounting for less than 1% of the total diffracted intensity. Lower space group symmetry could not account for them; refinement using robust statistics did not differ significantly from the straight least-squares results presented here [14].

Table 1. Summary of the synchrotron crystallographic data for $[\text{Ru}_2(\text{O}_2\text{CMe})_4][\text{Co}^{\text{III}}\text{Pc}(\text{CN})_2]$.

	[Ru ₂ (O ₂ CMe) ₄][Co ^{III} Pc(CN) ₂]
Formula	C ₄₂ H ₂₈ CoN ₁₀ O ₈ Ru ₂
Formula mass	1061.874
Space Group	<i>I</i> 4 ₁ / <i>a</i>
<i>a</i> , Å	17.3647(5)
<i>c</i> , Å	13.0373(4)
<i>Z</i>	4
<i>V</i> , Å ³	3929.8(3)
ρ _{calcd} , g/cm ³	1.79
R _{wp} ^a	6.52%
R _{exp} ^b	3.10%
<i>T</i> , K	297(2)
λ, Å	0.69994(2)

^a $R_{wp} = \sqrt{\frac{\sum_i w_i (y_i^{calc} - y_i^{obs})^2}{\sum_i w_i (y_i^{obs})^2}}$, where y_i^{calc} and y_i^{obs} are the calculated and observed intensities at the

i^{th} point in the profile, normalized to monitor intensity. The weight w_i is $1/\sigma^2$ from counting statistics, with the same normalization factor. N is the number of points in the measured profile.

^b $R_{exp} = \sqrt{\frac{N}{\sum_i w_i (y_i^{obs})^2}}$

2.3 Physical Studies

Infrared spectra were taken as KBr pellets using a Bruker Tensor 37 FT-IR spectrometer (± 1 cm⁻¹). Magnetic measurements were made between 5 and 300 K on a Quantum Design MPMS-5XL 5 T SQUID magnetometer equipped with a reciprocating sample measurement system as previously described [15]. The data were corrected for the diamagnetism of the holders.

3. Results and Discussion

The reaction of [Co^{III}Pc(CN)₂]⁻ and [Ru₂(O₂CMe)₄]⁺ forms [Ru₂(O₂CMe)₄][Co^{III}Pc(CN)₂] whose 2128 cm⁻¹ ν_{CN} absorption is not shifted with respect to the ν_{CN} absorption observed for *trans*-[Co^{III}Pc(CN)₂]⁻. While this is not suggestive of bonding between the cation and anion, powder X-ray diffraction (PXRD) was observed, and high-resolution patterns were collected at the National Synchrotron Light Source at ambient temperature (Figure 1), and the structure was determined. The crystallographic data for [Ru₂(O₂CMe)₄][CoPc(CN)₂] is summarized in Table 1.

Figure 1. High-resolution synchrotron powder diffraction data (•) and Rietveld fit for the refined structure of $[\text{Ru}_2(\text{O}_2\text{CMe})_4][\text{Co}^{\text{III}}\text{Pc}(\text{CN})_2]$ (–). Note successive changes of vertical scale factor. The lower trace is the difference, measured – calculated, plotted to the same vertical scales.

3.1 Crystal Structure

The Rietveld refinement of the synchrotron powder diffraction data (Figure 1) provides a structure consisting of $[\text{Ru}_2(\text{O}_2\text{CMe})_4]^+$ cations bonded to two *trans*- $[\text{Co}^{\text{III}}\text{Pc}(\text{CN})_2]^-$ anions with linear Co-C≡N-Ru linkages (Figure 2). The Ru-NC distance of 2.14(2) Å is within the 2.11 – 2.29 Å range of distances in the literature [16], and the Co-CN distance of 2.14(2) Å is slightly above the 1.82 – 2.09 Å range of literature distances of similarly coordinated Co, and is comparable to that observed for $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_3[\text{M}(\text{CN})_6]$ (M = Cr, Fe, Co) [5] and $\{[\text{Rh}_2(\text{O}_2\text{CMe})_4]_2[\text{Co}(\text{CN})_6]\}^{3-}$ [17]. The Ru•••Ru distance of 2.30(3) Å is in accord with 2.270 Å reported for $[\text{Ru}_2(\text{O}_2\text{CMe})_4]_2[\text{Ni}(\text{CN})_4]$ [9], and falls in the middle of the 2.20 – 2.43 Å range of similar tetra-acetate ruthenium dimers. The intra- and closest interchain Co•••Co separations are 13.04 Å (*c*) and 9.27, 13.08, and 13.90 Å, respectively, Figure 2.

In the refinement, the phthalocyanine structure was parameterized as a “rigid body” in Topas-Academic [13], with all bond lengths and angles refined; each indole unit was constrained

to be planar and axially symmetric. The -4 point symmetry allows them to tilt and rotate out of the *ab* plane, leading to a deviation from planarity of 0.15 Å rms for the entire phthalocyanine. While phthalocyanines are generally more planar than that, there are a few comparable values in the literature, *e.g.*, 0.10 Å for LiPc [18]. The Ru-O and Co-N directions of the two molecular ions are rotated with respect to the unit cell axes and each other.

Figure 2. Interdigitated packing of adjacent chains of $[\text{Ru}_2(\text{O}_2\text{CMe})_4][\text{Co}^{\text{III}}\text{Pc}(\text{CN})_2]$ viewed parallel to the layers and along the *c*-axis. Chain structure of $[\text{Ru}_2(\text{O}_2\text{CMe})_4][\text{Co}^{\text{III}}\text{Pc}(\text{CN})_2]$ viewed perpendicular to the layer (Ru: orange, Co: dark blue, O: red, N: light blue, C: dark gray, H: light gray).

3.2 Magnetic Properties

The magnetic susceptibility, χ , of $[\text{Ru}_2(\text{O}_2\text{CMe})_4][\text{Co}^{\text{III}}\text{Pc}(\text{CN})_2]$ was studied between 5 and 300 K at 1 kOe applied field, and plotted as $\chi(T)$ and $\chi T(T)$, Figure 3. The 300-K value of χT is 2.14 emuK/mol. This is in accord with the spin-only value of 2.16 emuK/mol for an $S = 3/2$ $[\text{Ru}_2(\text{O}_2\text{CMe})_4]^+$ including the temperature-independent paramagnetism (*TIP*) (vide infra) [5,19]. After correcting $\chi T(T)$ for a 23 ppm Co impurity, the $\chi T(T)$ data was fit to eq (1) [20], which includes zero-field splitting (*D*), *TIP*, and a Weiss constant, θ , to account for inter-

molecular magnetic interactions, Figure 3. A good fit has been obtained for the effective moment measured as a function of temperature with $g = 2.00$, $D/k_B = 95$ K (66 cm^{-1}), $\theta = 0$ K and $TIP = 950 \times 10^{-6} \text{ emu/mol}$. The D and TIP values agree with previous reports for related $[\text{Ru}_2(\text{O}_2\text{CR})_4]^+$ cations [2,20,21].

$$C_{\text{Ru}_2} = \frac{Ng_{\text{Ru}_2}^2 m_B^2}{k_B (T - \theta)} \left[\frac{1}{3} \cdot \frac{1 + 9e^{\frac{-2D}{k_B T}}}{4(1 + e^{\frac{-2D}{k_B T}})} + \frac{2}{3} \cdot \frac{1 + \frac{3k_B T}{4D} (1 - e^{\frac{-2D}{k_B T}})}{1 + e^{\frac{-2D}{k_B T}}} \right] + TIP \quad (1)$$

Figure 3. $\chi T(T)$ (o) and $\chi(T)$ (•) for $[\text{Ru}_2(\text{O}_2\text{CMe})_4][\text{Co}^{\text{III}}\text{Pc}(\text{CN})_2]$ (•), and the fits to the data (—) with eq 1.

To develop materials with more complex magnetic behavior substitution of the Cr(III) with a $S = 3/2$ Cr(III) was sought. The reaction of $[\text{Ru}_2(\text{O}_2\text{CMe})_4]\text{Cl}$ and $\text{Na}[\text{Cr}^{\text{III}}\text{Pc}(\text{CN})_2]$, however, led to cyanide abstraction by the Ru, as has been reported also to occur for the reaction of $[\text{Ru}_2(\text{O}_2\text{CH})_4]\text{Cl}$ and $[\text{M}^{\text{III}}(\text{CN})_6]^{3-}$ ($\text{M} = \text{Cr}, \text{Fe}$) [6], and the desired product could not be isolated.

Acknowledgement. The authors gratefully acknowledge the support from the NSF (Grant No. 1063630). The synthesis, spectroscopic, and magnetic characterization were done at the University of Utah, and the structural data and analysis were executed at Stony Brook University. Use of the National Synchrotron Light Source, Brookhaven National Laboratory, was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, under Contract No. DE-AC02-98CH10886.

Supporting Information Available: The X-Ray CIF file for $[\text{Ru}_2(\text{O}_2\text{CMe})_4][\text{Co}^{\text{III}}\text{Pc}(\text{CN})_2]$ has been deposited with the Cambridge Crystallographic Data Center, ref# CCDC-999604.

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Graphical Abstract

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$[\text{Ru}_2(\text{O}_2\text{CMe})_4][\text{Co}^{\text{III}}\text{Pc}(\text{CN})_2]$ forms from the reaction of $[\text{Ru}_2(\text{O}_2\text{CMe})_4]^+$ and $[\text{Co}^{\text{III}}\text{Pc}(\text{CN})_2]^-$ and possesses the targeted chain structure with linear $\text{Ru}-\text{N}\equiv\text{C}-\text{Co}$ linkages. Adjacent chains form an interdigitated structural motif.