charinate groups in molecule **1**. Even the angles formed by most of the related atoms are similar in **1** and **2**. All these factors contribute to the relatively easy interconversion of the two compounds in the solid state.

Acknowledgment. We are grateful to the Vicerrectoría, de Investigación, UCR (Grant No. 115-87-516), for support of work at the University of Costa Rica and to the National Science Foundation for support of work at Texas A&M University.

Supplementary Material Available: For structures **1** and **2**, complete tables of crystal data, bond distances and angles, general displacement parameters, and positional parameters of calculated hydrogen atoms (18 pages); tables of observed and calculated structure factors (40 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry and Laboratory for Molecular Structure
and Bonding, Texas A&M University, College Station, Texas 77843

Compounds Containing Linked Multiply-Bonded Dimetal Units. 2. An Antiferromagnetic Compound Containing Infinite Chains of $Ru_2(O_2CR)_4^+$ Units Linked by Bridging Phenazine Molecules

F. Albert Cotton,* Youngmee Kim, and Tong Ren

Received January 24, 1992

The polymeric $[Ru_2(O_2CC_2H_5)_4(phz)]BF_4$ was prepared by reaction of $[Ru_2(O_2CC_2H_5)_4(H_2O)_2]BF_4$ with phz (phenazine). Crystals of $[Ru_2(O_2CC_2H_5)_4(phz)]BF_4$ were obtained by a diffusion technique in which a dichloromethane solution of $[Ru_2(O_2CC_2H_5)_4(H_2O)_2]BF_4$ was carefully layered by a benzene solution containing an excess amount of phz. The compound has been characterized by X-ray crystallography and magnetic susceptibility measurements from ca. 2 to ca. 300 K. The space group is $P\bar{1}$, and there are two formula units per unit cell with $a = 11.669$ (5) Å, $b = 14.471$ (2) Å, $c = 8.963$ (1) Å, $\alpha = 103.96$ (1)°, $\beta = 96.743$ (2)°, and $\gamma = 70.237$ (2)°. The phz ligands connect the dinuclear species into kinked chains that all run parallel to the 111 direction. There are two crystallographically independent $Ru_2(O_2CC_2H_5)_4^+$ cations with Ru(1)–Ru(1)′ = 2.2756 (6) Å, Ru(2)–Ru(2)′ = 2.2747 (7) Å, Ru(1)–N(1) = 2.436 (4) Å, and Ru(2)–N(2) = 2.443 (5) Å. The BF_4^- ions occupy general positions between the chains. The compound is antiferromagnetic with a magnetic moment of ca. 4.3 μ_B at 300 K that tends toward zero as 0 K is approached (1.72 μ_B at 2.7 K).

Introduction

A number of compounds containing $Ru_2(O_2CR)_4^+$ moieties are known, and in general they are well characterized.[1,2] They have three unpaired electrons, and it is generally accepted that this results from an electron configuration $\sigma^2\pi^4\delta^2(\delta^*\pi^*)^3$, where we use the symbol $(\delta^*\pi^*)^3$ to denote the fact that the δ^* and π^* orbitals are nearly degenerate. In several cases,[2] $Ru_2(O_2CR)_4X$ (X = Cl, Br) compounds have been found to have chain structures where shared axial halide ions link the $Ru_2(O_2CR)_4^+$ ions in either linear or kinked chains. The butyrate has been studied magnetically,[1a,c] and it was concluded that magnetic coupling of the Ru_2^{5+} units along the chain (one-dimensional antiferromagnetism, ODAFM) was not occurring.

We undertook the work described here to see if we could find a bridging ligand that would cause the formation of infinite chains displaying ODAFM. In our first effort, we employed the aromatic diamine phenazine (I) as the linking ligand and we have obtained a compound of the desired type, $[Ru_2(O_2CC_2H_5)_4(phz)]BF_4$, where we use phz to represent phenazine.

I

Table I. Crystal Data for $[Ru_2(Pro)_4(phz)]BF_4$

formula	$Ru_2O_8C_{24}$-	Z	2
	$H_{28}N_2BF_4$	d_{calc}, g/cm³	1.831
fw	761.4	μ(Mo Kα), cm⁻¹	11.471
space group	$P\bar{1}$ (No. 2)	radiation monochromated in incident beam (λ, Å)	Mo Kα (0.71073)
a, Å	11.669 (5)	temp, °C	20
b, Å	14.471 (2)	transm factors: max; min	1.00; 0.86
c, Å	8.963 (1)		
α, deg	103.96 (1)		
β, deg	96.743 (2)	R^a	0.045
γ, deg	70.237 (2)	$R_w{}^b$	0.062
V, Å³	1381 (1)		

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

Experimental Section

The starting material, $Ru_2(O_2CC_2H_5)_4Cl$, was prepared by using a literature procedure.[3] Phenazine was purchased from Aldrich Chemical Co. and used as received.

Preparation of $[Ru_2(O_2CC_2H_5)_4(H_2O)_2]BF_4$. An aqueous solution of $Ru_2(O_2CC_2H_5)_4Cl$ was absorbed on a cation-exchange column (Dowex 50W-X1) and eluated with 0.5 M $NaBF_4$. Evaporation of the eluate gave the brown product and the excess $NaBF_4$. The excess $NaBF_4$ was removed from the product by recrystallization from methanol several times. IR (Nujol mull, cm⁻¹): 3300–3600 (broad), 1300 m, 1000–1150 (several bands), 810 w, 720 m, 635 w, 450 w. UV–vis (CH_2Cl_2 solution; λ, nm (ϵ, M⁻¹ cm⁻¹)): 423 (330).

Preparation of $[Ru_2(O_2CC_2H_5)_4(phz)]BF_4$. A 154-mg sample (0.25 mmol) of $[Ru_2(O_2CC_2H_5)_4(H_2O)_2]BF_4$ was suspended in 10 mL of benzene. A solution of phenazine (phz), 90 mg (0.5 mmol) in 10 mL of benzene, was added to this suspension. The reaction mixture was refluxed for 3 h, and the color of the reaction mixture changed from brown to reddish brown. The precipitate was collected, washed with benzene several times to remove the excess phenazine, and dried under vacuum.

---

(1) (a) Cotton, F. A.; Pedersen, E. *Inorg. Chem.* **1975**, *14*, 388. (b) Clark, R. J. H.; Ferris, L. H. *Inorg. Chem.* **1981**, *20*, 2759. (c) Telser, J.; Drago, R. S. *Inorg. Chem.* **1984**, *23*, 3114. (d) Miskowski, V. M.; Gray, H. B. *Inorg. Chem.* **1988**, *27*, 2501.

(2) (a) Bennett, M. J.; Caulton, K. G.; Cotton, F. A. *Inorg. Chem.* **1969**, *8*, 1. (b) Bino, A.; Cotton, F. A.; Felthouse, T. R. *Inorg. Chem.* **1979**, *18*, 2599. (c) Togano, T.; Mukaida, M.; Nomura, T. *Bull. Chem. Soc. Jpn.* **1980**, *53*, 2085. (d) Martin, D. S.; Newman, R. A.; Vlasnik, L. M. *Inorg. Chem.* **1980**, *19*, 3404. (e) Kimura, T.; Sakurai, T.; Shima, M.; Togano, T.; Mukaida, M.; Nomura, T. *Bull. Chem. Soc. Jpn.* **1982**, *55*, 3927. (f) Cotton, F. A.; Matusz, M.; Zhong, B. *Inorg. Chem.* **1988**, *27*, 4368.

(3) Stephenson, T. A.; Wilkinson, G. *J. Inorg. Nucl. Chem.* **1966**, *28*, 2285.

Table II. Positional Parameters and *B* Values Their Estimated Standard Deviations for $[Ru_2(Pro)_4(phz)]BF_4$[a]

atom	*x*	*y*	*z*	*B*, Å^2
Ru(1)	0.08268 (4)	0.43532 (3)	0.02463 (5)	2.07 (1)
Ru(2)	0.49008 (4)	0.03605 (3)	0.39757 (5)	1.86 (1)
F(1)	0.9125 (5)	0.2157 (5)	0.7301 (7)	8.8 (2)
F(2)	0.7469 (6)	0.3449 (4)	0.6968 (9)	8.8 (2)
F(3)	0.7289 (5)	0.1976 (4)	0.7098 (7)	7.1 (2)
F(4)	0.8101 (5)	0.2134 (4)	0.5081 (6)	7.1 (2)
O(11)	−0.0306 (4)	0.3688 (3)	0.0721 (5)	2.7 (1)
O(12)	0.0789 (4)	0.5042 (3)	0.2483 (5)	2.7 (1)
O(13)	0.1920 (4)	0.5057 (3)	−0.0230 (5)	2.6 (1)
O(14)	0.0833 (4)	0.3689 (3)	−0.2020 (5)	2.7 (1)
O(21)	0.4514 (4)	0.1713 (3)	0.5424 (5)	2.36 (9)
O(22)	0.3118 (3)	0.0497 93)	0.3807 (5)	2.48 (9)
O(23)	0.5305 (4)	−0.1012 (3)	0.2563 (4)	2.27 (9)
O(24)	0.6678 (3)	0.0215 (3)	0.4187 (5)	2.30 (9)
N(1)	0.2516 (4)	0.2950 (3)	0.0891 (6)	2.1 (1)
N(2)	0.4279 (4)	0.1352 (3)	0.1993 (6)	2.3 (1)
C(11)	−0.1443 (6)	0.4101 (5)	0.0617 (8)	2.8 (1)
C(12)	−0.0032 (6)	0.5876 (4)	0.2936 (8)	2.8 (1)
C(13)	−0.2285 (7)	0.3612 (5)	0.098 (1)	4.5 (2)
C(14)	−0.1671 (18)	0.2555 (6)	0.123 (1)	5.9 (2)
C(15)	0.0020 (7)	0.3639 (6)	−0.4590 (8)	3.8 (2)
C(16)	0.1281 (8)	0.6169 (7)	−0.526 (1)	5.5 (2)
C(21)	0.5497 (5)	−0.1772 (4)	0.3146 (7)	2.4 (1)
C(22)	0.7333 (5)	−0.0198 (4)	0.5253 (7)	2.3 (1)
C(23)	0.4253 (8)	0.2775 (5)	0.7961 (9)	4.0 (2)
C(24)	0.4329 (8)	0.3633 (5)	0.730 (1)	5.2 (2)
C(25)	0.8655 (6)	−0.0360 (5)	0.5365 (8)	3.4 (2)
C(26)	0.0741 (6)	0.0539 (6)	0.3073 (9)	4.2 (2)
C(31)	0.2506 (5)	0.1987 (4)	0.0406 (7)	2.0 (1)
C(32)	0.1577 (6)	0.1773 (5)	−0.0651 (8)	2.8 (1)
C(33)	0.1557 (6)	0.0813 (5)	−0.1136 (8)	3.0 (2)
C(34)	0.2466 (6)	0.0013 (5)	−0.0619(8)	3.4 (2)
C(35)	0.3350 (6)	0.0186 (4)	0.0415 (7)	2.7 (1)
C(36)	0.3388 (5)	0.1187 (4)	0.0967 (6)	2.0 (1)
C(37)	0.4394 (5)	0.2273 (4)	0.2331 (6)	1.9 (1)
C(38)	0.5423 (5)	0.2437 (5)	0.3216 (7)	2.6 (1)
C(39)	0.5532 (6)	0.3379 (4)	0.3584 (8)	2.9 (1)
C(40)	0.4604 (6)	0.4194 (4)	0.3127 (8)	3.1 (2)
C(41)	0.3609 (6)	0.4066 (4)	0.2279 (8)	2.8 (1)
C(42)	0.3489 (5)	0.3088 (4)	0.1799 (7)	2.1 (1)
B	0.7981 (8)	0.2440 (7)	0.664 (1)	4.2 (2)

[a] *B* values for anisotropically refined atoms are given in the form of the equivalent isotropic displacement parameter defined as $(4/3)[a^2\beta_{11} + b^2\beta_{22} + c^2\beta_{33} + ab(\cos\gamma)\beta_{12} + ac(\cos\beta)\beta_{13} + bc(\cos\alpha)\beta_{23}]$.

Yield: 175 mg (92%). It is slightly soluble in CH_2Cl_2. IR (Nujol mull, cm^{-1}): 1520 w, 1300 m, 1000–1150 (several bands), 830 w, 810 w, 770 w, 755 m, 720 m, 650 w, 630 w, 600 w, 550 w, 520 w, 450 w, 430 w, 370 w. The single crystal for X-ray data collection was prepared by a diffusion technique in which a dichloromethane solution of $[Ru_2(O_2CC_2H_5)_4(H_2O)_2]BF_4$ was carefully layered by a benzene solution containing an excess of phenazine.

Measurements. Infrared spectra were recorded from 4000 to 400 cm^{-1} on a Perkin-Elmer 783 spectrophotometer. The electronic spectrum was recorded as a solution on a Cary 17D UV–vis spectrophotometer. Magnetic susceptibility measurements were carried out on polycrystalline samples in the 2.7–300 K temperature range with a SQUID (superconducting quantum interference device) at Northwestern University. The samples were all quenched in a field of 5 kG.

X-ray Crystallography. A reddish brown block-shaped crystal of $[Ru_2(O_2CC_2H_5)_4(phz)]BF_4$ was mounted on a glass fiber. Data collection was carried out at room temperature on an Enraf-Nonius CAD-4 diffractometer. The determination of the crystal system, data collection procedure, structure solution, and refinement were all carried out by procedures that have been described before.[4,5] The unit cell parameters and orientation matrix were refined by a least-squares fit to the positions of 25 reflections in the range of $18 < 2\theta < 32°$. The 2θ–ω scan technique was used to collect data in the range of $4 < 2\theta < 46°$. A set of reflections monitored regularly showed an overall change in intensity during the period of data collection of −9.2%. A correction was applied.[6] The ruthenium atoms were located from the Petterson map, and the other non-hydrogen atoms were obtained by an alternating series of difference

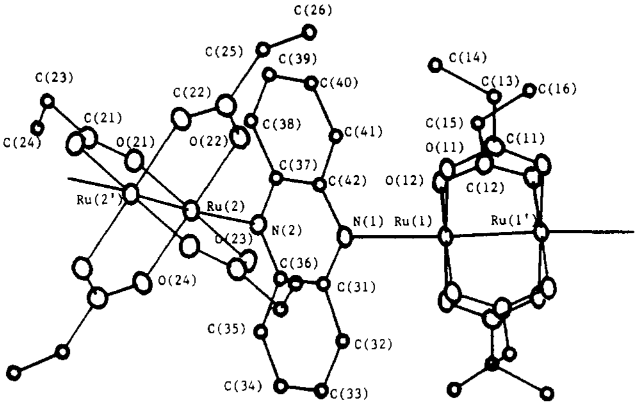

Figure 1. ORTEP drawing of the asymmetric unit (including additional atoms at each end but omitting the BF_4^- ions) for the $[Ru_2(O_2CC_2H_5)_4(phz)]BF_4$ crystal. The atoms are represented by arbitrarily small circles for clarity.

Table III. Selected Bond Distances (Å) and Angles (deg) for $[Ru_2(Pro)_4(phz)]BF_4$[a]

Bond Distances			
Ru(1)–Ru(1)′	2.2756 (6)	Ru(2)–O(24)	2.004 (4)
Ru(1)–O(11)	2.011 (5)	Ru(2)–N(2)	2.443 (5)
Ru(1)–O(12)	2.010 (4)	O(11)–C(11)	1.261 (7)
Ru(1)–O(13)	2.016 (5)	O(12)–C(12)	1.269 (6)
Ru(1)–O(14)	2.027 (4)	O(21)–C(21)	1.265 (8)
Ru(1)–N(1)	2.436 (4)	O(22)–C(22)	1.267 (9)
Ru(2)–Ru(2)′	2.2747 (7)	N(1)–C(31)	1.359 (8)
Ru(2)–O(21)	2.009 (3)	N(1)–C(42)	1.359 (8)
Ru(2)–O(22)	2.013 (4)	N(2)–C(36)	1.350 (7)
Ru(2)–O(23)	2.015 (3)	N(2)–C(37)	1.343 (8)
Bond Angles			
Ru(1)′–Ru(1)–O(11)	88.9 (1)	O(22)–C(22)–O(24)	121.9 (5)
Ru(1)′–Ru(1)–O(12)	89.5 (1)	C(33)–C(34)–C(35)	120.8 (6)
Ru(1)′–Ru(1)–O(13)	89.4 (1)	C(34)–C(35)–C(36)	119.8 (5)
Ru(1)′–Ru(1)–O(14)	89.1 (1)	Ru(1)–N(1)–C(31)	121.2 (4)
Ru(1)′–Ru(1)–N(1)	176.2 (1)	Ru(1)–N(1)–C(42)	122.1 (4)
O(11)–Ru(1)–O(12)	87.2 (2)	Ru(2)–N(2)–C(36)	117.4 (4)
O(11)–Ru(1)–O(13)	178.3 (1)	Ru(2)–N(2)–C(37)	117.9 (4)
O(11)–Ru(1)–O(14)	93.0 (2)	N(1)–C(31)–C(32)	119.9 (5)
O(12)–Ru(1)–O(13)	92.5 (2)	N(1)–C(31)–C(36)	121.4 (5)
O(12)–Ru(1)–O(14)	178.6 (2)	C(31)–C(32)–C(33)	120.2 (5)
O(11)–C(11)–O(13)	122.4 (7)	C(31)–N(1)–C(42)	116.6 (5)
O(12)–C(12)–O(14)	122.4 (5)	O(22)–Ru(2)–O(24)	178.7 (2)
C(31)–C(32)–C(33)	120.2 (5)	O(23)–Ru(2)–O(24)	89.2 (2)
C(32)–C(33)–C(34)	120.9 (6)	Ru(1)–O(11)–C(11)	120.1 (5)
O(21)–Ru(2)–O(22)	89.4 (2)	Ru(1)–O(12)–C(12)	119.7 (4)
O(21)–Ru(2)–O(23)	178.7 (2)	Ru(2)–O(21)–C(21)	119.5 (4)
O(21)–Ru(2)–O(24)	90.4 (2)	Ru(2)–O(22)–C(22)	120.4 (4)
O(22)–Ru(2)–O(23)	90.9 (2)	C(32)–C(33)–C(34)	120.9 (6)
O(21)–C(21)–O(23)	123.2 (5)	C(33)–C(34)–C(35)	120.8 (6)
O(22)–C(22)–O(24)	121.9 (5)	C(34)–C(35)–C(36)	119.8 (5)
C(33)–C(34)–C(35)	120.8 (6)	C(36)–N(2)–C(37)	118.0 (5)
C(34)–C(35)–C(36)	119.8 (5)	N(2)–C(36)–C(35)	119.4 (5)
C(32)–C(31)–C(36)	121.1 (5)	C(31)–C(36)–C(35)	119.5 (5)
O(13)–Ru(1)–O(14)	87.3 (2)	N(2)–C(37)–C(38)	119.7 (5)
Ru(2)′–Ru(2)–O(21)	89.1 (1)	N(2)–C(37)–C(42)	119.8 (6)
Ru(2)′–Ru(2)–O(22)	88.6 (1)	C(38)–C(37)–C(42)	119.8 (6)
Ru(2)′–Ru(2)–O(23)	89.7 (1)	C(37)–C(38)–C(39)	119.7 (5)
Ru(2)′–Ru(2)–O(24)	90.2 (1)	C(38)–C(39)–C(40)	120.3 (6)
Ru(2)′–Ru(2)–N(2)	168.1 (1)	C(39)–C(40)–C(41)	121.6 (6)
O(21)–Ru(2)–O(22)	89.4 (2)	C(40)–C(41)–C(42)	120.0 (5)
O(21)–Ru(2)–O(23)	178.7 (2)	N(1)–C(42)–C(37)	121.5 (5)
O(21)–Ru(2)–O(24)	90.4 (2)	N(1)–C(42)–C(41)	120.2 (5)
O(22)–Ru(2)–O(23)	90.9 (2)	C(37)–C(42)–C(41)	118.3 (5)
O(21)–C(21)–O(23)	123.2 (5)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits.

---

(4) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.

(5) Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227.

(6) North, A. C. T.; Phillips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1968**, *24A*, 351.

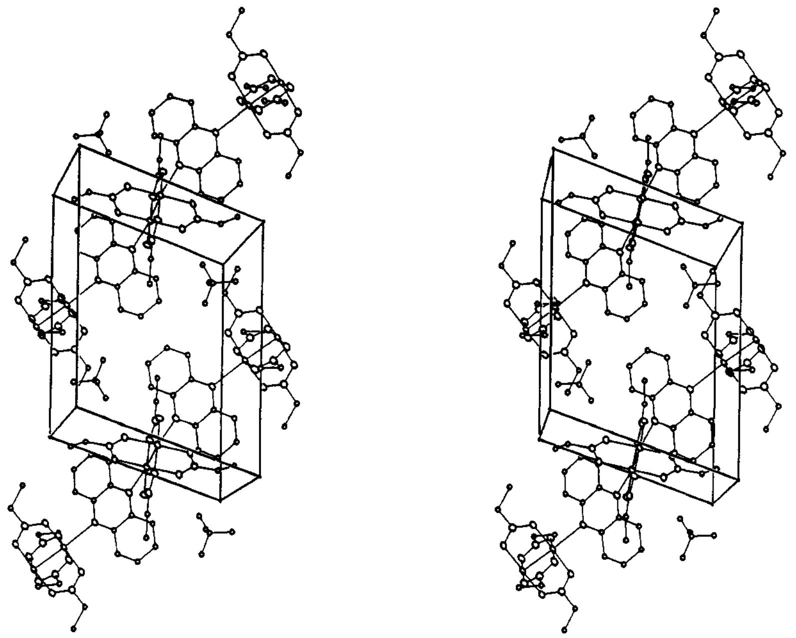

Figure 2. Stereo ORTEP drawing of the unit cell of $[Ru_2(O_2CC_2H_5)_4(phz)]BF_4$, showing the alignment of the chains and the BF_4^- ions lying between them.

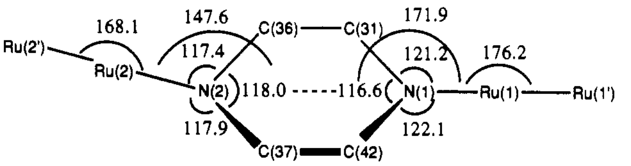

Figure 3. Diagram of all angles (deg) along the chain.

Fourier maps and least-squares refinements in the VAX-SDP package.[7] All atoms were refined with anisotropic thermal parameters. The fluorine atoms have relatively large thermal displacements but are ordered and gave no difficulty during the refinement. The crystallographic data are summarized in Table I, and the final positional parameters are listed in Table II.

Results

Preparation. To get a polymeric complex $[Ru_2(O_2CC_2H_5)_4(phz)]BF_4$, the axial chloride ligand of the starting material had to be eliminated by using a cation-exchange column. The $[Ru_2(O_2CC_2H_5)_4(H_2O)_2]BF_4$ obtained was characterized by its IR spectrum in which there is a broad O–H stretching band at 3300–3600 cm^{-1}. The axial water molecules were easily substituted by an axial phenazine ligand when $[Ru_2(O_2CC_2H_5)_4(H_2O)_2]BF_4$ was added to the phenazine ligand, producing the polymeric complex, $[Ru_2(O_2CC_2H_5)_4(phz)]BF_4$.

Structure. The triclinic unit cell contains two formula units. The BF_4^- ions and the phenazine (phz) molecules are located on 2-fold general positions. The $Ru_2(O_2CC_2H_5)_4$ units have their midpoints on inversion centers at $^1/_2$, 0, $^1/_2$ and 0, $^1/_2$, 0, so that each is rigorously centrosymmetric but they are not equivalent. The phz molecules connect the Ru_2 units into infinite chains. Figure 1 shows one $Ru_2(O_2CC_2H_5)_4$–phz–$Ru_2(O_2CC_2H_5)_4$ group, and Figure 2 shows the spatial arrangement of the chains through one unit cell and its neighbors. The chains (i.e., the ···N–Ru–Ru–N···N–Ru–Ru– sequences) are not strictly linear, as will be explained shortly, but the mean lines through them (e.g., from the center of one Ru_2 unit to the center of the next) are oriented in the [111] direction. This can easily be appreciated if the origin of the unit cell is shifted by $^1/_2$, 0, $^1/_2$ so that the Ru_2 units are at (0, 0, 0), ($^1/_2$, $^1/_2$, $^1/_2$), (1, 1, 1), etc.

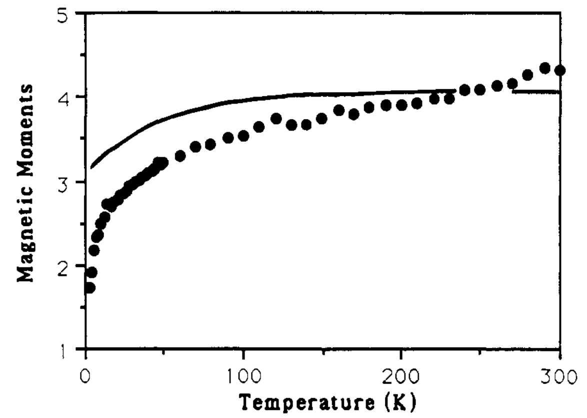

Figure 4. Plot of the magnetic moment (per Ru_2 unit) of $[Ru_2(O_2CC_2H_5)_4(phz)]BF_4$ vs temperature (●) from 300 to 2.7 K. Also shown, as a solid line, is the temperature dependence of the magnetic moment of $Ru_2(O_2CC_3H_7)_4Cl$ from 300 to 5 K, as previously reported by Telser and Drago.[1c]

Each $Ru_2(O_2CC_2H_5)_4^+$ unit has essentially the same dimensions (Table III), and these are similar to those found in other compounds containing $Ru_2(O_2CR)_4^+$ units.[1,2] The Ru(1)–Ru(1)′ and Ru(2)–Ru(2)′ distances are 2.2756 (6) and 2.2747 (7) Å, respectively. The axial Ru–N bonds have two crystallographically independent values as well, but again they are virtually identical, namely, 2.436 (4) and 2.443 (5) Å.

The phz molecule is slightly distorted from planarity. The nature of this distortion is mainly a bending along the N(1)···N(2) line so that the mean planes of the two halves make a dihedral angle of 7.7 ± 0.7°.

Returning now to the nonlinearity of the chains, this can best be appreciated by noting the angles shown in Figure 3. The Ru–N bonds are not strictly colinear with the adjacent Ru–Ru bonds, although the deviations are not large or unusual. The Ru(1)–N(1)···N(2) angle, 171.9°, is also not a major deviation from linearity. Moreover, the N(1) atom has a locally planar environment, with the sum of the three bond angles around it equaling 359.9°. The major cause of nonlinearity occurs at N(2), where the sum of its bond angles is 353.3° and the Ru(2)–N(2) bond makes an angle of 147.6° with the N(2)···N(1) line. There is no obvious reason for this, and we assume it is simply the result of the cumulative effect of many intermolecular packing forces.

Magnetic Properties. Figure 4 shows the dependence of the magnetic moment of $[Ru_2(O_2CC_2H_5)_4(phz)]BF_4$ on temperature and also, for comparison, the previously published[1c] results for

---

(7) Calculations were done on a local area VAX cluster (VMS V4.6) and the commercial package SDP/V V3.0.

$Ru_2(O_2CC_3H_7)_4Cl$. For the latter compound, as we noted earlier, the conclusion drawn from the magnetic data was that "in spite of its polymeric structure, [it] is a complex in which the $Ru_2(but)_4^+$ units can be treated as isolated $S = ^3/_2$ systems." A slight temperature dependence of the magnetic moments, as can be seen in Figure 4, is expected for this type of system, as explained in ref 1a,c, because of zero-field splitting. The contrast between the two temperature dependencies in Figure 4 is obvious and of such a nature as to imply that there is in $[Ru_2(O_2CC_2H_5)_4(phz)]BF_4$ an antiferromagnetic interaction between the $[Ru_2(O_2CC_2H_5)_4]^+$ units. From the structure, which has been described above, we would find it difficult to attribute this to *inter*chain interactions since the chains are well separated by intervening BF_4^- ions. We therefore find it reasonable to conclude that what is occurring is *intra*chain coupling; that is, we have here an ODAFM system.

It should be recalled that in the previous paper in this series we compared the $[Ru_2(chp)_4(pyrazine)Ru_2(chp)_4]^{2+}$ ion with $[Ru_2(chp)_4(pyridine)]^+$, and from the close similarity of the magnetic behavior of the two species, it was concluded that no significant magnetic coupling across the pyrazine bridge occurs in the first cation. To account for the different result in the present case, we must ask what structural and/or chemical differences exist. The bridging ligands are different but similar. Phenazine (phz) is simply pyrazine with benzene rings fused to both sides. However, this could conceivably alter the shapes and energies of the π and π^* orbitals enough to change significantly the strength of interaction with the Ru_2 units. Another difference concerning the bridging is that the Ru–N distances are appreciably different, being 2.275 (5) Å for pyrazine and 2.44 Å for phenazine. The sense of this difference is such that, by itself, it would tend to lessen the coupling in the phenazine compound, contrary to observation.

Finally, however, we must recognize that the $Ru_2(chp)_4^+$ and $Ru_2(O_2CC_2H_5)_4^+$ units may also have significant differences, despite their grossly similar nature. It is possible that molecular orbital calculations could show that the differences are more enabling in one case than in the other with respect to interaction through the bridges. However, it might be more direct and convincing to carry out an experimental study in which we reverse the pairings of Ru_2 units and bridging ligand; that is, we prepare and study $[Ru_2(chp)_4(phz)Ru_2(chp)_4](BF_4)_2$ and $[Ru_2(O_2CC_2H_5)(pyz)]BF_4$. We have, in fact, already initiated such a study.

Acknowledgment. We thank the National Science Foundation for support and Professor T. J. Marks and Douglas Schulz of Northwestern University for the magnetic susceptibility measurements.

Supplementary Material Available: Full tables of crystal data, anisotropic thermal parameters, bond length and angle data, and variable-temperature magnetic susceptibility data (8 pages); a listing of observed and calculated structure factors (17 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
University of Louisville, Louisville, Kentucky 40292

A Pentavalent W_4S_4 Cuboidal Cluster

Michael L. Sampson, John F. Richardson,* and Mark E. Noble*

Received January 29, 1992

The W(V) complex $[W(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)(\mu_3\text{-}S)]_4$ was prepared and characterized. The compound, in solution, is engaged in an associative equilibrium from two dimers, with $K_{eq} = 1600\ M^{-1}$. When this compound is in solution with $[Mo(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)(\mu_3\text{-}S)]_4$, the mixed-metal cluster $[W_2Mo_2(NC_6H_4CH_3)_4(S_2P(OC_2H_5)_2)_4(\mu_3\text{-}S)_4]$ is formed. The crystal structure of $[W(NC_6H_4CH_3)(S_2P(OC_2H_5)_2)(\mu_3\text{-}S)]_4$ was determined: $a = 14.650$ (3) Å, $b = 19.133$ (4) Å, $c = 13.073$ (3) Å, $\alpha = 101.82$ (2)°, $\beta = 104.61$ (2)°, $\gamma = 75.92$ (2)°; triclinic; $P\bar{1}$; $Z = 2$. The crystallography showed a distorted W_4S_4 cubic arrangement.

Introduction

Sulfidomolybdenum(V) dimers of the general form $[Mo_2(NAr)_2(S_2P(OEt)_2)_2(\mu\text{-}S)_2(\mu\text{-}O_2CR)]^n$ (for abbreviations, see footnote 1) have been shown to display a versatile sulfur-centered reactivity at the bridge sulfur positions. Both an anionic ($n = -1$) and a radical ($n = 0$) form have been demonstrated, and observed reactions therewith include nucleophilic and radical chemistry, with strong parallels to that of organic thiols, thiolates, and thiyls.[2-5]

Much of the interest in this system and in many other metallosulfur complexes which display sulfur-centered reactivity derives from the roles of metal sulfides in catalytic processes, both biological and industrial. This is especially true for molybdenum, since molybdenum–sulfur compounds comprise active sites in several key enzymes[6,7] and in hydrotreating catalysts.[8] Of particular interest in the area of catalysis is the possible involvement of the sulfur sites in the catalytic mechanism, in addition to catalytic activity of the metal sites therein. Various notions for catalytic mechanisms have considered a covalent role for sulfur,[7-10] although for the most part exact mechanistic details remain unknown.

While sulfur-centered reactivity of several molybdenum–sulfur complexes has been very well documented,[2-5,9-11] considerably less is known for tungsten–sulfur complexes.[12] The interest here is decidedly more than that of a simple parallel, since tungsten compounds are also used in some hydrodesulfurization[8] systems, and tungsten analogues of molybdenum enzymes are known,[13] although in many cases these are inactive. Because of this, studies of sulfur-centered reactivity in sulfidotungsten complexes are of interest per se. There is also the inherent interest in the comparison of sulfur reactivity between Mo–S and W–S complexes, especially in cases where isostructural complexes of both metals are available. For these reasons, synthesis of tungsten analogues, $[W_2(NAr)_2$-

---

(1) Abbreviations used in this paper: Me, methyl; Et, ethyl; Bu, *n*-butyl; To, *p*-tolyl; Ar, aryl.

(2) Noble, M. E. *Inorg. Chem.* **1986**, *25*, 3311.

(3) Noble, M. E. *Inorg. Chem.* **1987**, *26*, 877.

(4) Lizano, A. C.; Noble, M. E. *Inorg. Chem.* **1988**, *27*, 747.

(5) Lizano, A. C.; Munchhof, M. G.; Haub, E. K.; Noble, M. E. *J. Am. Chem. Soc.* **1991**, *113*, 9204.

(6) Spiro, T. G. *Molybdenum Enzymes*; Wiley: New York, 1985.

(7) Burgmayer, S. J. N.; Stiefel, E. I. *J. Chem. Educ.* **1985**, *62*, 943.

(8) Prins, R.; De Beer, V. H. J.; Somorjai, G. A. *Catal. Rev.* **1989**, *31*, 1.

(9) Rakowski DuBois, M. *Chem. Rev.* **1989**, *89*, 1.

(10) Hadjikyriacou, A. I.; Coucouvanis, D. *Inorg. Chem.* **1989**, *28*, 2169.

(11) Coucouvanis, D.; Toupadakis, A.; Koo, S.-M.; Hadjikyriacou, A. *Polyhedron* **1989**, *8*, 1705.

(12) For example: Kubas, G. J.; Wasserman, H. J.; Ryan, R. R. *Organometallics* **1985**, *4*, 419. Shaver, A.; Hartgerink, J. *Can. J. Chem.* **1987**, *65*, 1190. Ansari, M. A.; Chandrasekaran, J.; Sarkar, S. *Polyhedron* **1988**, *7*, 471.

(13) Hales, B. J.; Case, E. E. *J. Biol. Chem.* **1987**, *262*, 16205 and references therein. Tungsten enzymes per se are also known (Cramer, S. P.; Liu, C.-L.; Mortenson, L. E.; Liu, S.-M.; Yamamoto, I.; Ljungdahl, L. G. *J. Inorg. Biochem.* **1985**, *23*, 119. White, H.; Strobl, G.; Feicht, R.; Simon, H. *Eur. J. Biochem.* **1989**, *184*, 89. Mukund, S.; Adams, M. W. W. *J. Biol. Chem.* **1990**, *265*, 11508), but it is not clear as to whether these are sulfidotungsten systems.

0020-1669/92/1331-2726$03.00/0 © 1992 American Chemical Society