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Structural characterization of 1:2 tris(μ -benzenethiolato)bis[(hexamethylbenzeneruthenium)chloride-chloroform

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Table III. Selected Bond Distances (Å) and Angles (deg) for *catena*-[Ni₂(μ-N₃)₃(dpt)₂](ClO₄)

Distances			
N(1)-Ni	2.194 (4)	C(8)-C(7)	1.517 (9)
N(3')-Ni	2.153 (4)	C(9)-C(8)	1.514 (9)
N(4)-Ni	2.143 (4)	N(10)-C(9)	1.471 (7)
N(6)-Ni	2.076 (4)	C(11)-N(10)	1.479 (7)
N(10)-Ni	2.117 (4)	C(12)-C(11)	1.521 (9)
N(14)-Ni	2.059 (5)	C(13)-C(12)	1.509 (9)
N(2)-N(1)	1.162 (6)	N(14)-C(13)	1.482 (7)
N(5)-N(4)	1.169 (4)	N(3)-N(2)	1.179 (6)
C(7)-N(6)	1.465 (7)		
Angles			
N(4)-Ni-N(1)	98.3 (2)	N(2)-N(3)-Ni	124.4 (3)
N(6)-Ni-N(1)	85.8 (2)	N(5)-N(4)-Ni	119.2 (3)
N(6)-Ni-N(4)	90.4 (2)	N(4)-N(5)-N(4)'	180.0
N(10)-Ni-N(1)	177.9 (2)	C(7)-N(6)-Ni	120.9 (4)
N(10)-Ni-N(4)	90.1 (2)	C(8)-C(7)-N(6)	110.4 (5)
N(10)-Ni-N(6)	96.2 (2)	C(9)-C(8)-C(7)	113.6 (5)
N(14)-Ni-N(1)	85.9 (2)	N(10)-C(9)-C(8)	115.2 (5)
N(14)-Ni-N(4)	91.8 (2)	C(9)-N(10)-Ni	116.5 (3)
N(14)-Ni-N(6)	171.4 (2)	C(11)-N(10)-Ni	115.0 (3)
N(14)-Ni-N(10)	92.1 (2)	C(11)-N(10)-C(9)	108.4 (4)
N(3')-Ni-N(1)	91.7 (2)	C(12)-C(11)-N(10)	114.5 (5)
N(3')-Ni-N(4)	178.3 (2)	C(13)-C(12)-C(11)	115.7 (5)
N(3')-Ni-N(6)	88.3 (2)	N(14)-C(13)-C(12)	110.5 (5)
N(3')-Ni-N(10)	89.0 (2)	C(13)-N(14)-Ni	120.1 (3)
N(3')-Ni-N(14)	89.6 (2)	N(3)-N(2)-N(1)	177.4 (4)

SHELX76 computer program.¹³ The function minimized was $w\|F_o - |F_c|\|^2$, where $w = (\sigma^2(F_o) + 0.0057|F_o|^2)^{-1}$. f , f' , and f'' were taken from ref 14. The coordinates of 16 H atoms were located from a difference synthesis and refined with an overall isotropic factor. Maximum shift/esd = 0.1, and maximum and minimum peaks in the final difference synthesis were 0.4 and -0.4 e Å⁻³, respectively. Final atomic coordinates are given in Table II.

Results and Discussion

IR and Analytical Data. The most characteristic band for the linear amine ligand is that found at 1600 cm⁻¹ (s), in contrast to the analogous band when the ligand is the N₃ macrocycle (1650 cm⁻¹). The ν_{as} azide at 2040 cm⁻¹ (s, broad) and the perchlorate bands at 1100 (s) and 610 cm⁻¹ (m) are also found. The other two bands of the N₃⁻ group (ν_s and δ) are masked by the amine and perchlorate bands. The elemental analyses for the two different syntheses are consistent with the product formulation [Ni₂(N₃)₃(dpt)₂](ClO₄).

Crystal Structure. The structure consists of the 1D -Ni-(N₃)₂Ni(N₃)-system, isolated by ClO₄⁻ anions. The structure of the chain and the packing diagram are shown in Figure 1. The bond lengths and angles are gathered in Table III. In the packing diagram, only the Ni and azide N atoms are indicated for clarity. In the chain structure, each Ni(II) atom is coordinated by one dpt ligand and three azido ligands in a *mer* arrangement. Two of the azido bridges are shared with one Ni(II) atom (double bridge) and the third is shared with another Ni(II) atom (single bridge) (Figure 1). This structure corresponds to the first fully characterized alternating Ni(II) chain.

Magnetic Results. As has been previously reported by Carlin,¹ in the susceptibility curves of alternating chains, broad maxima are observed for all values of the alternating parameter α . These susceptibility curves vanish exponentially when temperature tends to 0 for all $\alpha < 1$; on the contrary, the uniform ($\alpha = 1$) chain reaches a finite value at $T = 0$ K, depending on the value of S . The case with $\alpha = 0$ is of course simply the isolated curve for a dimer. The magnetic susceptibility of a crystalline sample of *catena*-[Ni₂(μ-N₃)₃(dpt)₂](ClO₄) is plotted in Figure 2 as a function of the temperature. The χ_M value increases when the temperature decreases, reaching a broad maximum ca. 120 K. This maximum clearly indicates strong antiferromagnetic coupling

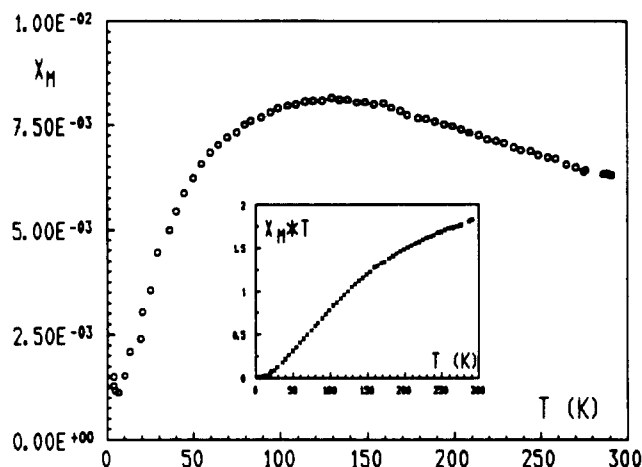


Figure 2. Magnetic susceptibility plots for a polycrystalline specimen for *catena*-[Ni₂(μ-N₃)₃(dpt)₂](ClO₄) (χ_M in cm³ mol⁻¹ and χ_MT in cm³ K mol⁻¹).

between the Ni(II) ions through the N₃⁻ bridge. The χ_MT curve vs T decreases continuously, corroborating this hypothesis. The most important feature is what happens when the temperature is lowered: the molar magnetic susceptibility value tends to zero when T tends to zero, indicating the existence of a nonuniform chain. On the other hand, the shape of the curve does not correspond to an antiferromagnetically coupled nickel(II) binuclear complex such as a structural alternating chain with one of the J parameters equal to zero,¹⁵ because in this case the maximum should be more pronounced. The attempts made to fit this curve with the dimer model¹⁶ were obviously unsuccessful, clearly indicating that this chain is the first true magnetically alternating Ni(II) chain. Further theoretical studies on this kind of alternating Ni(II) chain are in progress in order to account for their magnetic behavior.

Acknowledgment. This work was undertaken with the financial support of CICYT Grant MAT88-0545.

Supplementary Material Available: For *catena*-[Ni₂(μ-N₃)₃(dpt)₂](ClO₄), tables of complete crystal data, anisotropic thermal parameters, hydrogen atom coordinates, and distances and angles (3 pages); a listing of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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Structural Characterization of [(Hexamethylbenzene)Ru]₂(μ-SPh)₃Cl·2CHCl₃

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In recent years there has been an increased interest in ruthenium complexes with sulfur donor ligands, in part because of the high catalytic activity of RuS₂ in various hydrotreating processes.^{1,2} As a part of this development, many examples of ruthenium thiolate complexes have been reported.³⁻¹⁴ During the course

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Table I. Crystallographic Data for $[(\text{HMB})\text{Ru}]_2(\mu\text{-SPh})_3\text{Cl}\cdot 2\text{CHCl}_3$ (1)

fw	1128.3	Z	4
space group	monoclinic, $C2/c$	T	22-26
a	14.537 (7) Å	μ	1.174 mm ⁻¹
b	19.378 (9) Å	$\lambda(\text{Mo K}\alpha)$	0.71073 Å
c	17.061 (5) Å	$R(F_o)$	3.89%
β	97.007 (3)°	$R_w(F_o)$	4.67%
V	4770 (3) Å ³		

of work to prepare mononuclear ruthenium complexes with both alkyl and sulfur donor ligands, we have isolated and characterized new dinuclear complexes with bridging thiolate ligands. We report here the synthesis and structural characterization of a ruthenium thiolate complex which contains hexamethylbenzene (HMB) as the supporting ligand. The structure permits a comparison with previously reported analogous structures containing penta-methylcyclopentadienyl ligands.^{3,4}

Experimental Section

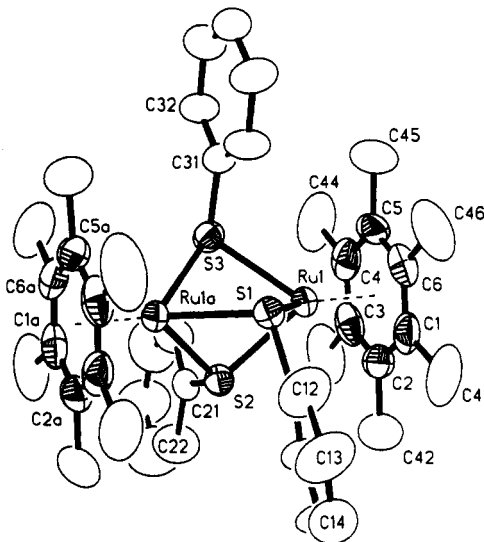
$[(\text{HMB})\text{RuCl}_2]_2$ and $(\text{HMB})\text{RuCl}_2\text{PPh}_3$ were prepared as described in the literature.^{15,16} (Phenylthio)trimethylsilane and thiophenol were purchased from Aldrich and used without purification. Tetrahydrofuran was distilled from sodium/benzophenone ketyl.

¹H NMR and ¹³C NMR spectra were recorded on a Varian VXR-300 NMR spectrometer. Chemical shifts are reported in ppm relative to tetramethylsilane. Mass spectra were obtained on a VG Analytical 7070 EQ-HF mass spectrometer. Elemental analyses were performed by Spang Microanalytical Laboratories.

X-ray Diffraction Study. A crystal of 1 was mounted with epoxy resin, and the data were collected on a Nicolet P3/F diffractometer. The structure was solved using direct methods and Fourier techniques. The molecule sits on a crystallographic 2-fold axis which passes through the midpoint of the Ru-Ru bond. This symmetry axis disorders the sulfur atoms and the phenyl groups of the cation. Fortunately, the disorder was clearly defined and the molecular connectivity was unambiguous. Crystallographic data are given in Table I. A complete listing of crystal data, data collection conditions, and solution and refinement details is given in the supplementary material.

$[(\text{HMB})\text{Ru}(\mu\text{-SPh})_2\text{Ru}(\text{HMB})\text{Cl}]\text{Cl}$ (1). Procedure I. PhSSiMe_3 (0.04 mL, 0.21 mmol) was added to $(\text{HMB})\text{RuCl}_2\text{PPh}_3$ (120 mg, 0.20 mmol) in 40 mL of THF at -78 °C. Over a period of 1 h, the reaction mixture was warmed to room temperature. After 3 h of stirring at room temperature, the solvent was removed at reduced pressure, the residue was dissolved in 10 mL of CH_2Cl_2 , and the solution was filtered. The filtrate was layered with 20 mL of hexane to induce precipitation of orange yellow crystals of 1. Yield: 23 mg, 26%. The crystals for the elemental analyses and the X-ray diffraction study were obtained through a second recrystallization from CHCl_3 /hexane. The crystal mounted for the X-ray study contained two molecules of CHCl_3 .

Procedure II. $[\text{Ru}(\text{HMB})\text{Cl}_2]_2$ (80 mg, 0.12 mmol) and PhSH (0.4 mL, 4 mmol) were stirred in 80 mL of THF for 14 h. A 0.1 M MeLi solution in diethyl ether (0.2 mL) was then added. After 2 h, the solvent was removed at reduced pressure. The product was purified as in procedure I. Yield: 38 mg, 36%. Mp: 248 °C. ¹H NMR (CDCl_3): δ 1.55 (s, 36 H, HMB), 7.34-7.90 (m, 15 H, Ph). ¹³C NMR (CDCl_3): δ 14.98 (CH_3), 94.92 ($\text{C}_{\text{Ar-HMB}}$), 128.65 (SPh-*p*), 128.67 (SPh-*o*), 129.07 (SPh-*m*), 134.95 (CS). MS (FAB): m/e 855 (P^+ , base), 778 ($\text{P} - \text{Ph}$), 746 ($\text{P} - \text{SPh}$), 693 ($\text{P} - \text{HMB}$). Anal. Calcd for $\text{C}_{42}\text{H}_{51}\text{Cl}_2\text{Ru}_2\text{S}_3$: C, 56.70;

**Figure 1.** Perspective drawing and numbering scheme for the cation of $[(\text{HMB})\text{Ru}]_2(\mu\text{-SPh})_3\text{Cl}\cdot 2\text{CHCl}_3$ (1). For the sake of clarity, disordered S-Ph atoms are shown in only one of their positions. Thermal ellipsoids are shown at the 50% probability level.**Table II.** Selected Bond Distances and Angles for $[(\text{HMB})\text{Ru}]_2(\mu\text{-SPh})_3\text{Cl}\cdot 2\text{CHCl}_3$ (1)

Distances, Å			
Ru(1)-S(1)	2.450 (2)	Ru(1A)-S(1)	2.435 (2)
Ru(1)-S(2)	2.404 (2)	Ru(1A)-S(2)	2.363 (2)
Ru(1)-S(3)	2.400 (2)	Ru(1A)-S(3)	2.372 (2)
S(1)-C(11)	1.798 (11)	S(3)-C(31)	1.783 (8)
S(2)-C(21)	1.790 (9)		
Angles, deg			
S(1)-Ru(1)-S(2)	74.7 (1)	Ru(1)-S(1)-Ru(1A)	86.7 (1)
S(2)-Ru(1)-S(3)	77.3 (1)	Ru(1)-S(2)-Ru(1A)	89.4 (1)
S(1)-Ru(1)-S(3)	76.4 (1)	Ru(1)-S(3)-Ru(1A)	89.3 (1)
Ru(1)-S(1)-C(11)	114.8 (4)	Ru(1)-S(2)-C(21)	112.9 (4)
Ru(1)-S(3)-C(31)	114.2 (3)		

Table III. Selected Atomic Coordinates^a ($\times 10^4$) and Equivalent Isotropic Displacement Parameters ($\text{\AA}^2 \times 10^3$) for $[(\text{HMB})\text{Ru}]_2(\mu\text{-SPh})_3\text{Cl}\cdot 2\text{CHCl}_3$ (1)

	x/a	y/b	z/c	$U(\text{eq})$
Ru(1)	9316 (1)	3014 (1)	1635 (1)	38 (1)
S(1)*	10995 (1)	3099 (1)	1998 (1)	40 (1)
S(2)*	9674 (1)	2197 (1)	2688 (1)	40 (1)
S(3)*	9467 (1)	3734 (1)	2787 (1)	44 (1)
C(1)	9332 (3)	2688 (3)	386 (2)	61 (2)
C(2)	8679 (4)	2282 (3)	725 (3)	61 (2)
C(3)	7958 (3)	2604 (3)	1087 (3)	63 (2)
C(4)	7907 (3)	3335 (3)	1119 (3)	65 (2)
C(5)	8572 (4)	3741 (3)	770 (3)	61 (2)
C(6)	9288 (3)	3413 (3)	420 (3)	61 (2)

^a Atoms have occupancies of 1.0 except as marked with * above: S(1), 0.50; S(2), 0.50; S(3), 0.50.

H, 5.78; S, 10.81; Cl, 3.98. Found: C, 56.85; H, 5.81; S, 11.04; Cl, 3.82.

$[(\text{HMB})\text{Ru}(\mu\text{-SPh})_2(\mu\text{-Cl})\text{Ru}(\text{HMB})\text{Cl}]\text{Cl}$. $[\text{Ru}(\text{HMB})\text{Cl}_2]_2$ (200 mg, 0.30 mmol) and HSPH (0.2 mL, 2.0 mmol) were stirred for 10 h in 15 mL of CH_2Cl_2 at room temperature. The solution was filtered, and 40 mL of hexane was added to precipitate the product in the form of orange needles. Yield: 140 mg, 57%. Mp: 196 °C. ¹H NMR (CDCl_3): δ 1.66 (s, 36 H, HMB), 7.26-7.98 (m, 10 H, Ph). ¹³C NMR (CDCl_3): δ 14.84 (CH_3), 92.96 ($\text{C}_{\text{Ar-HMB}}$), 129.00 (SPh-*p*), 129.10 (SPh-*o*), 131.47 (SPh-*m*), 135.08 (CS). MS (FAB): m/e 781 (P^+), 672 ($\text{P} - \text{SPh}$), 595 ($\text{P} - \text{SPh}_2$).

Results and Discussion

The reaction of $(\text{HMB})\text{RuCl}_2\text{PPh}_3$ with ~ 1 equiv of PhSSiMe_3 was carried out in THF at -78 °C in an attempt to prepare a mononuclear thiolate complex. Crystallization of the product mixture from CH_2Cl_2 /hexane led to the isolation of orange-yellow crystals, which were ultimately identified as $[(\text{HMB})\text{Ru}]_2(\mu\text{-SPh})_3\text{Cl}\cdot 2\text{CHCl}_3$.

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$\text{SPh}_3\text{]Cl}$ (**1**). Complex **1** could also be prepared in slightly higher yield (36%) by the addition of excess benzenethiol and base to a THF solution of $[(\text{HMB})\text{RuCl}_2]_2$. The ^1H and ^{13}C NMR spectra of **1** confirmed the presence of hexamethylbenzene and phenyl rings in **1** in a ratio of 2:3. The FAB mass spectrum also provided support for the formation of the product. An envelope centered at m/e 855, which was the base signal in the spectrum, corresponded to the mass of the cation $((\text{HMB})\text{Ru})_2(\text{SPh})_3^+$. Elemental analyses were also consistent with the proposed composition.

An X-ray diffraction study was carried out on a single crystal of **1** in order to confirm the bonding mode(s) of the benzenethiolate ligands. An Ortep plot of the cation with its numbering scheme is shown in Figure 1, selected bond distances and angles are given in Table II, and selected atomic coordinates are given in Table III. The compound contains discrete dinuclear units in which the Ru(II) ions are unsymmetrically bridged by three thiolate sulfurs. The Ru(1A)–S bonds are 0.02–0.04 Å shorter than the Ru(1)–S distances. The disordered thiolate ligands showed 50% occupancy at each of two positions related by a mirror plane that passes through the metal–metal vector. The gross structure is similar to that reported for the pentamethylcyclopentadienyl analogue of Ru(III), $[(\text{Cp}^*\text{Ru})_2(\mu\text{-SPh})_3]\text{Cl}$ (**2**).³ In both structures, the arrangement of the thiolate substituents is symmetrical so that the metal–metal vector lies on a pseudo-3-fold rotation axis. The major structural differences between **1** and **2** arise from the differences in formal oxidation states of the ruthenium ions. While the Ru(III) ions in **2** undergo a significant metal–metal interaction (Ru–Ru = 2.630 (1) Å), the Ru(II) ions in **1** are not expected to participate in metal–metal bonding. The Ru–Ru distance of 3.354 Å in **1** is similar to those of other triply bridged Ru(II) dimers.^{5,6} The Ru–S–Ru angles in **1** average 88.5°, which is also similar to those observed for other ruthenium(II) dimers and significantly larger than the same angles in **2** (68°).

Because of the relatively large separation between (HMB)Ru centers in **1**, the three phenyl rings of the thiolate ligands are not constrained to a coplanar arrangement as they were in **2**. With respect to the plane defined by S(1)–C(11), S(2)–C(21), and S(3)–C(31), the plane of the phenyl ring of C(11) is rotated by an angle of 18.8° and that of C(21) by an angle of 7.9°. The third phenyl ring is nearly coplanar, with a dihedral angle of 1.1°.

The two parallel hexamethylbenzene rings are in an eclipsed conformation, while the more sterically hindered structure of **2** led to staggered pentamethylcyclopentadienyl ligands. The mixed-valence dimer $(\text{Cp}^*\text{Ru})_2(\mu\text{-S-}i\text{-Pr})_3$ has also been structurally characterized.⁴ In this complex the metal–metal distance was 2.968 (2) Å and the Cp* ligands were found to be oriented between an eclipsed and a staggered arrangement.

The reaction of $[(\text{HMB})\text{RuCl}_2]_2$ with about a 3-fold excess of benzenethiol in dichloromethane led to the formation of a second dinuclear complex which was tentatively formulated as $[(\text{HMB})\text{Ru})_2(\mu\text{-SPh})_2(\mu\text{-Cl})]\text{Cl}$ on the basis of spectroscopic data. Under these reaction conditions, which were only slightly different from those of the reaction described for the preparation of **1**, the bis(thiolate) dimer was isolated in 60% yield and **1** was not detected. The result suggests that these synthetic reactions are highly dependent on solvent and on reactant stoichiometry. Similar effects have been observed in the reactions of the Cp*Ru systems.^{3,4}

Conclusion. The factors which determine the geometry and metal–metal separation of triply bridged dinuclear complexes have been found in both theoretical and experimental work to be a complex function of ligand–ligand interactions as well as of metal–metal interactions.¹⁷ In many cases, electron-counting conventions have not been a reliable indicator of structural variations in the dimers. Nevertheless, the series of Ru(II/II–II/III–III/III) dimers discussed here provide a good example of systematic compression of the dimer structure as the expected metal–metal interaction increases.

Acknowledgment. This work was supported by the Division of Chemical Sciences, Office of Basic Energy Sciences, Office of Energy Research, U.S. Department of Energy.

Supplementary Material Available: A figure showing the disordered thiolate ligands in the structure of **1** and complete tables of data collection parameters, bond distances and angles, atomic coordinates, and displacement parameters for **1** (14 pages); a listing of observed and calculated structure factors for **1** (14 pages). Ordering information is given on any current masthead page.

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Additions and Corrections

1992, Volume 31

Johann W. Buchler,* Jürgen Löffler, and Mark Wicholas*: Metal Complexes with Tetrapyrrole Ligands. 62. ^{13}C NMR Spectra of Dicerium(III) and Diprasedymium(III) Tris(octaethylporphyrinate).

Page 524. The assignments for the methylene and methyl resonances in Figure 2 have been mislabeled and should read from left to right as $\text{CH}_2(\text{o})$, $\text{CH}_3(\text{o})$, $\text{CH}_3(\text{i})$, $\text{CH}_2(\text{i})$, thus corresponding to the correct assignments listed in Table I.—Mark Wicholas