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Synthesis and Characterization of Mononuclear and Dinuclear Bis(2,2′-bipyridine)ruthenium(II) Complexes Containing Sulfur-Donor Ligands

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A series of ruthenium(II) bis(bipyridyl) complexes containing sulfur-donor ligands has been synthesized. UV–visible spectroscopy, cyclic voltammetry, and elemental analysis characterize the complexes as containing coordinated WS_4^{2-}, Mo_2S_4(ethanedithiolate)$_2^{2-}$, polysulfide (S_5^{2-}), aliphatic and aromatic thiolate, and dithiolene ligands. Crystal structures of two dinuclear ruthenium bis(bipyridyl) complexes are reported. $\{[Ru(bpy)_2]_2WS_4\}(PF_6)_2$ crystallizes in the space group *Cmca* ($Z = 8$) with unit cell dimensions $a = 20.948$ (5) Å, $b = 18.992$ (3) Å, and $c = 31.701$ (6) Å. The structure shows two octahedral ruthenium bis(bipyridyl) fragments binding through the sulfur atoms of a tetrahedral WS_4 unit, forming a linear trinuclear array. Interatomic distances are as follows: Ru–S = 2.376 (2), 2.369 (3) Å; W–S = 2.222 (2), 2.206 (2) Å; W⋯Ru = 2.838 (1) Å. $\{[Ru(bpy)_2(SC_6H_5)]_2\}(CF_3SO_3)_2$ crystallizes in the space group $P\bar{1}$ ($Z = 2$) with unit cell dimensions $a = 10.997$ (2) Å, $b = 16.276$ (3) Å, $c = 20.020$ (4) Å, $\alpha = 92.93$ (2)°, $\beta = 112.13$ (1)°, and $\gamma = 103.68$ (2)°. The structure shows two octahedral ruthenium bis(bipyridyl) fragments bridged by two μ_2-benzenethiolate sulfur atoms forming an edge-shared bioctahedron. Interatomic distances are as follows: Ru–S = 2.433 (3), 2.432 (2), 2.418 (3), 2.420 (2) Å; Ru⋯Ru = 3.785 (1), 3.771 (1) Å. Cyclic voltammetry was used to compare the electron-donor/acceptor characteristics of the sulfur-donor ligands, and a relative ranking of these ligands is presented. Correlations between the MLCT absorption spectra and the electrochemical properties of the complexes are reported, and a difference is noted for complexes containing monodentate versus bidentate sulfur-donor ligands. Room-temperature EPR spectra of chemically oxidized ruthenium bis(bipyridyl) complexes containing the maleonitriledithiolato and dimethyl dimercaptomaleato ligands were recorded in methylene chloride and exhibited *g* values of 2.057 and 2.055, respectively, with isotropic ruthenium hyperfine splitting of 16 G in each case.

Introduction

Ruthenium(II) bis(bipyridyl) complexes have been the focus of much research since their initial synthesis in 1955.[1] Nearly 100 cis-disubstituted complexes have been synthesized with a wide variety of ligands including amines, phosphines, arsines, stibines, halides, pseudohalides, thiolates, thioethers, and organometallic donors.[2,3] The motivations in synthesizing these complexes have been diverse as well. Several complexes have been exploited in solar energy conversion schemes,[4] while others have performed as oxidation catalysts, for example, in the oxidation of water to dioxygen[5] and in the conversion of chloride ion to chlorine.[6] Still other complexes have been utilized as electrochemical reduction catalysts in converting acetylene to ethane and ethylene.[7] Of equal importance has been the utilization of this family of complexes for studying fundamental chemical processes. Photoactive ruthenium polypyridyl complexes have been used to investigate photochemically induced charge-transfer,[8] ligand substitution,[9] and stereochemical isomerization processes.[10] Dinuclear complexes have been scrutinized to gain further understanding of intervalence electron transfer and the effects of differing bridging ligands upon metal–metal interactions.[11] Finally, the electronic absorption and electrochemical properties of the ruthenium bis(bipyridyl) chromophore make it a highly sensitive spectator ion with which to probe metal–ligand interactions.[12]

In this paper we report the synthesis and characterization of a series of cis-disubstituted ruthenium(II) bis(bipyridyl) complexes containing a variety of sulfur-donor ligands. These ligands are both monodentate and bidentate, with the latter type including the tetrathiometalate donor WS_4^{2-}. All complexes have been characterized by elemental analysis, UV–visible spectroscopy, and cyclic voltammetry. A thiolate-bridged dimer and a tetrathiotungstate-bridged dimer have been structurally characterized by X-ray diffraction. Comparison of the electrochemical properties within this series of compounds has allowed us to rank the sulfur-donor ligands according to their electron-donor/acceptor propensities. Correlations between the electrochemical properties and visible absorption spectra are also discussed, and a signficant difference between complexes containing monodentate and bidentate sulfur-donor ligands is noted. Two of the complexes have been oxidized chemically, and the EPR spectra of the ruthenium(III) complexes are presented. Our motivation for studying these complexes involves the investigation of their potentially interesting redox[3] and catalytic[7] properties.

Experimental Section

Measurements. UV–visible, infrared, and fluorescence spectra were recorded on Perkin-Elmer Model 330, 683, and MPF-44A spectrophotometers, respectively. IR samples were prepared as KBr pellets. UV–visible and fluorescence measurements were conducted in *N*,*N*-dimethylformamide. Cyclic voltammetric studies were performed with a BAS 100 electrochemical analyzer and an IBM voltammetric cell consisting of a glassy-carbon working electrode (area 16 mm^2), a platinum-wire auxiliary electrode, and a saturated calomel reference electrode. A Varian Model 2109 X-band electron spin resonance spectrometer was utilized to obtain ESR spectra. All measurements were conducted at ambient room temperature. Fluorescence measurements were attempted on these complexes, but none exhibited any significant fluorescence at room temperature. Elemental analyses were performed by Galbraith Analytical Laboratory Inc., Knoxville, TN.

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Single-crystal X-ray structural determinations were performed by Dr. C. S. Day of Crystalytics Co., Lincoln, NE.

Materials. Ru(bpy)$_2$Cl$_2$·2H$_2$O was purchased from Strem Chemical Co. or prepared by the method of Meyer et al.[12a] Benzenethiol, ethanethiol, *tert*-butyl mercaptan, *p*-chlorothiophenol, *p*-methylthiophenol, trifluoromethanesulfonic acid, dimethyl acetylenedicarboxylate (dmad), and ammonium hexafluorophosphate were obtained from Aldrich Chemical Co. and used as received. Tetrabutylammonium hexafluorophosphate used in electrochemical studies was obtained from Southwestern Analytical Laboratories. Ammonium tetrathiotungstate from SPEX and sulfur from Fisher Chemical Co. were also used as received. (Et$_4$N)$_2$Mo$_2$S$_4$(edt)$_2$[13] (edt = ethanedithiolate), (Ph$_4$P)$_2$Mo$_2$S$_8$,[14] and disodium maleonitriledithiolate[15] (Na$_2$mnt) were synthesized according to previously published procedures. All solvents used in this study were obtained from Burdick and Jackson and were stored over molecular sieves. Dimethylformamide was stored under argon.

Syntheses. All syntheses were performed under an argon atmosphere by employing standard Schlenk-line techniques. Unless otherwise noted in the Discussion, all solid products are air-stable.

Ru(bpy)$_2$WS$_4$. Ru(bpy)$_2$Cl$_2$·2H$_2$O (0.52 g, 1.0 mmol) and (NH$_4$)$_2$WS$_4$ (0.35 g, 1.0 mmol) were added to 300 mL of ethanol/water (4:1), and the mixture was allowed to stir at room temperature for 18 h. A fine red-brown powder formed and was collected by filtration, washed with water, ethanol, and ether, and then dried under vacuum. Yield: 0.48 g (66%). Anal. Found (calcd): C, 31.55 (31.53); H, 2.25 (2.62); N, 7.58 (7.62).

{[Ru(bpy)$_2$]$_2$WS$_4$}(PF$_6$)$_2$. Ru(bpy)$_2$WS$_4$ (0.36 g, 0.5 mmol) and Ru(bpy)$_2$Cl$_2$·2H$_2$O (0.26 g, 0.5 mmol) were added to 100 mL of ethanol/H$_2$O (4:1), and the mixture was heated to reflux for 4 h. The strawberry red solution was allowed to cool, and its volume was reduced by two-thirds. An excess of NH$_4$PF$_6$ (0.33 g, 2.0 mmol) was dissolved in 20 mL of H$_2$O and the solution slowly added to the rapidly stirring reaction mixture. After 30 min the mixture was filtered, isolating a fine dark maroon powder, which was then washed with H$_2$O and ether and dried under vacuum. Yield: 0.55 g (77%). Anal. Found (calcd): C, 33.81 (33.61); H, 2.43 (2.25); S, 9.18 (8.98); P, 3.99 (4.34); W, 12.58 (12.90); Ru, 14.86 (14.20).

Ru(bpy)$_2$(edt)$_2$. Sodium metal (0.23 g, 10 mmol) was carefully added to 30 mL of absolute ethanol and the mixture stirred at room temperature until completely reacted. Ethanethiol (0.74 mL, 10 mmol) was added. Ru(bpy)$_2$Cl$_2$·2H$_2$O (0.26 g, 0.50 mmol) was dissolved separately in 30 mL of absolute ethanol and the solution transferred by cannula to the thiolate solution. The mixture was then warmed to 75 °C and allowed to stir/react overnight (~18 h). Upon cooling, the dark green mixture was filtered to remove a white solid and then the filtrate was volume-reduced by half. Ether was added dropwise to the point of incipient crystallization and the flask stored in a freezer (−20 °C) for several days. The dark green, almost black crystalline product was isolated by filtration, washed with ether, and dried under vacuum. Yield: 0.12 g (40%). Anal. Found (calcd): C, 53.79 (53.83); H, 5.02 (4.86); N, 10.39 (10.47); S, 12.10 (11.96); Ru, 19.24 (18.88).

Ru(bpy)$_2$(SC$_6$H$_5$)$_2$. Sodium metal (0.23 g, 10 mmol) was added to 100 mL of absolute ethanol and the mixture stirred at room temperature until completely reacted. Benzenethiol (1.1 mL, 10 mmol) was then added and the mixture allowed to react for 10 min. Ru(bpy)$_2$Cl$_2$·2H$_2$O (0.26 g, 0.50 mmol) was added to the thiolate solution and the mixture heated to 75 °C and left to stir/react overnight. Upon cooling, the dark red mixture was filtered to remove a white solid and then the filtrate was reduced in volume by half. Dark crystals began to appear at this point, and further crystal growth was encouraged by cooling the mixture in a freezer (−20 °C) for several hours. The dark purple-black crystalline product was isolated by filtration and ether-rinsed. A second crop of crystals can be produced by addition of ether to the initial filtrate. Yield: 0.23 g (81%). Anal. Found (calcd): C, 60.64 (60.86); H, 4.28 (4.12); N, 8.60 (8.87); S, 11.23 (10.14); Ru, 16.08 (16.00).

Ru(bpy)$_2$(SC$_6$H$_4$-*p*-CH$_3$)$_2$. Potassium hydroxide (0.43 g, 7.6 mmol) was dissolved in 30 mL of a 1:1 methanol/water mixture. *p*-Methylthiophenol (0.95 g, 7.6 mmol) was added and the mixture allowed to react for 10 min. Ru(bpy)$_2$Cl$_2$·2H$_2$O (0.20 g, 0.38 mmol) was added and the resultant mixture heated to 90 °C for 1 h. Upon cooling, the black-purple crystalline product was isolated by filtration, washed with water and ether, and dried by suction. Yield: 0.16 g (62%). Anal. Found (calcd): C, 61.61 (61.91); H, 4.65 (4.55); N, 8.80 (8.49); S, 9.89 (9.71).

Ru(bpy)$_2$(SC$_6$H$_4$-*p*-Cl)$_2$. The same procedure as described above was used except for the substitution of *p*-chlorothiophenol (1.09 g, 7.6 mmol) for *p*-methylthiophenol. Yield: 0.19 g (71%). Anal. Found (calcd): C, 54.51 (54.86); H, 3.60 (3.42); N, 7.79 (8.00); S, 9.25 (9.14).

Ru(bpy)$_2$(SC$_4$H$_9$)$_2$. The procedure described above was used except for the substitution of *tert*-butyl mercaptan (0.90 mL, 7.6 mmol). Yield: 0.15 g (67%). Anal. Found (calcd): C, 55.35 (56.85); H, 5.87 (5.75); N, 8.86 (9.47); S, 10.82 (10.83).

Ru(bpy)$_2$(mnt). A solution of the disodium salt of maleonitriledithiolate (0.18 g, 1 mmol) in 100 mL of ethanol/water (4:1) was added dropwise to a solution of Ru(bpy)$_2$Cl$_2$·2H$_2$O (0.52 g, 1 mmol) in 200 mL of the same solvent. The reaction mixture was allowed to stir overnight (18 h) at room temperature, over which time a dark red-brown precipitate formed. This solid was isolated by filtration and rinsed with water, ethanol, and ether. Further purification was effected by recrystallization from acetonitrile and ether. Yield: 0.26 g (47%). Anal. Found (calcd): C, 48.40 (48.99); H, 3.31 (3.39); N, 13.92 (14.31); S, 10.70 (10.87).

Ru(bpy)$_2$(F$_3$CSO$_3$)$_2$. Trifluoromethanesulfonic acid (4.5 mL, 5.0 mmol) was added dropwise to a swirling slurry of Ru(bpy)$_2$Cl$_2$·2H$_2$O (0.52 g, 1.0 mmol) in 50 mL of chlorobenzene. After 4 h at ambient temperature the reaction mixture had separated into two immiscible layers. The less dense, dilute yellow layer was decanted away, leaving a dark red-orange solution. This was cooled to 0 °C in an ice bath, and ether was added dropwise with vigorous stirring. Note that a significant quantity of heat is generated upon addition of ether, and all necessary precautions should be taken. Addition of a total of 100 mL of ether produced a fine red solid, which was isolated by filtration, rinsed with ether, and dried under vacuum at 120 °C for 18 h. Yield: 0.68 g (90%). Anal. Found (calcd): C, 36.28 (37.20); H, 2.08 (2.24); N, 7.61 (7.89); S, 9.23 (9.00); Ru, 14.23 (14.20).

[(bpy)$_2$Ru(SC$_6$H$_5$)$_2$Ru(bpy)$_2$](F$_3$CSO$_3$)$_2$. Ru(bpy)$_2$(F$_3$CSO$_3$)$_2$ (71 mg, 0.10 mmol) and Ru(bpy)$_2$(SC$_6$H$_5$)$_2$ (63 mg, 0.10 mmol) were each dissolved in 25 mL of acetone in separate flasks, and then the solutions were mixed. After being stirred overnight at ambient temperature, the dark cherry-red solution was reduced in volume to 10 mL and then placed in a freezer (−20 °C) for 1 h. Filtration isolated a black crystalline solid that when rinsed with ether and vacuum-dried weighed 30 mg. A second crop of product was isolated by addition of ether to the acetone filtrate. Analytically pure material can be obtained by recrystallization from acetone/hexane. Yield: 111 mg (83%). Anal. Found (calcd): C, 47.98 (48.29); H, 3.40 (3.13); N, 8.26 (8.35); S, 9.30 (9.54); F, 8.21 (8.49); Ru, 14.46 (15.05).

Ru(bpy)$_2$S$_5$. Elemental sulfur (80 mg, 2.5 mmol) was added directly to a slurry of Ru(bpy)$_2$(SC$_6$H$_5$)$_2$ (316 mg, 0.50 mmol) in 50 mL of acetonitrile. The reaction mixture was heated to 75 °C for 18 h and filtered while still warm. A purple-black microcrystalline product was obtained, washed with toluene and ether, and air-dried. Yield: 257 mg (90%). Anal. Found (calcd): C, 41.96 (41.88); H, 3.08 (2.79); N, 9.44 (9.77); S, 28.29 (27.92); Ru, 17.80 (17.63).

Ru(bpy)$_2$(dmdmm) (dmdmm = Dimethyl Dimercaptomaleato). Ru(bpy)$_2$S$_5$ (114 mg, 0.20 mmol) was added to 25 mL of dimethylformamide. An excess of dimethyl acetylenedicarboxylate (80 μL, 0.65 mmol) was added by syringe, and the solution was left to stir overnight at ambient temperature. The dark red-orange reaction mixture was filtered, and ca. 30 mL of ether was slowly added to the filtrate, leading to the formation of a red-brown solid. This solid was isolated by filtration and ether-rinsed. Yield: 84 mg (68%). Anal. Found (calcd): C, 50.08 (50.40); H, 3.99 (3.55); N, 8.73 (9.05); S, 10.16 (10.34).

[Ru(bpy)$_2$(CH$_3$CN)$_2$](Mo$_2$S$_8$). Ru(bpy)$_2$(tf)$_2$ (tf = triflate = F$_3$CSO$_3^-$) (0.36 g, 0.50 mmol) was added to 30 mL of acetonitrile and the mixture allowed to stir for 30 min, resulting in complete dissolution. (Ph$_4$P)$_2$Mo$_2$S$_8$ (0.60 g, 0.50 mmol) was dissolved separately in 30 mL of acetonitrile. This molybdenum sulfide containing solution was then added dropwise to the rapidly stirring ruthenium bipyridyl solution. A fine dark powder formed immediately. After being stirred for 1 h, the mixture was filtered and the dark powder was rinsed with acetonitrile and ether and dried under vacuum. Yield: 0.45 g (95%). Anal. Found (calcd): C, 30.17 (30.54); H, 2.52 (2.33); N, 8.99 (8.91); S, 27.94 (27.15); Mo, 20.72 (20.36); Ru, 10.54 (10.71).

Solution and Refinement of Structure of [(bpy)$_2$RuS$_2$WS$_2$Ru(bpy)$_2$](PF$_6$)$_2$. Dark red, needlelike crystals were obtained by layering hexane over an acetone solution of the complex. A single crystal was sealed inside a capillary tube with mother liquor. Molybdenum Kα radiation (λ = 0.71073 Å) was used for the X-ray diffraction study, which was conducted on a computer-controlled four-circle Nicolet autodiffractometer. ω-Scan data collection was used with a scan range of $3.00 < 2\theta < 48.3°$. Other details of the data collection and refinement are given in Table I.

The structure was solved by heavy-atom Patterson techniques and refined with use of the Nicolet SHELXTL interactive crystallographic

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Table I. Summary of Crystallographic Parameters

formula	$[(Ru(N_2C_{10}H_8)_2)_2WS_4](PF_6)_2$	$[(Ru(N_2C_{10}H_8)_2(SC_6H_5))_2](CF_3SO_3)_2$
mol wt	1592.1	1490.6
a, Å	20.948 (5)	10.997 (2)
b, Å	18.992 (3)	16.276 (3)
c, Å	31.701 (6)	20.020 (4)
α, deg	90.00	92.93 (2)
β, deg	90.00	112.13 (1)
γ, deg	90.00	103.68 (2)
V, Å^3	12612 (4)	3186 (1)
space group	$Cmca$-D_{2h}^{18} (No. 64)	$P\bar{1}$-C_i^1 (No. 2)
Z	8	2
d_{calc}, g/cm^3	1.677	1.554
d_{obs}, g/cm^3	1.66	1.54
λ(Mo Kα), Å	0.71073	0.71073
cryst size, mm	0.30 × 0.42 × 0.80	0.19 × 0.30 × 0.52
no. of unique data collcd	5193	10178
no. of data used in refinement	2828	4968
final GOF	1.80	1.46
final R_F	0.037	0.052
final R_{wF}	0.040	0.049
highest peak in final diff map, e/Å^3	<0.53	<0.69

software package. Intensity data were corrected empirically for absorption effects by using ψ scans for five reflections ($9.3 < 2\theta < 31.5°$) and were then reduced to relative squared amplitudes (F^2) incorporating standard Lorentz and polarization corrections. Six standard reflections exhibited no significant loss of intensity throughout the course of data collection, and therefore no time-dependent intensity corrections were necessary. Anomalous dispersion corrections were applied to all nonhydrogen atoms. The hydrogen atoms of the bipyridyl ligands were included in the structure factor calculations as idealized atoms (assuming sp^2 hybridization of the carbon atom and a C–H bond length of 0.96 Å) "riding" on their respective carbons. The isotropic thermal parameters of each hydrogen atom were fixed at 1.2 times the equivalent isotropic thermal parameters of the carbon atoms to which these are covalently bonded.

The refinement converged with final residuals of $R = 0.037$ and $R_w = 0.040$ and a goodness-of-fit indicator equal to 1.80. No parameter was shifted by more than 0.19 times its estimated standard deviation, and the difference Fourier map at the end of the refinement had no peaks present above the noise level (0.53 e/Å^3).

Solution and Refinement of the Structure of $[(bpy)_2Ru(SC_6H_5)_2Ru(bpy)_2](CF_3SO_3)_2$. A single crystal suitable for X-ray diffraction was grown by slow diffusion of ether into a dimethylformamide solution of the complex. A brown-black rectangular parallelepiped was chosen and sealed in a glass capillary with mother liquor and mounted with its long axis parallel to the ϕ axis of the diffractometer.

The crystal structure was solved by using direct methods and the SHELXTL direct-methods program to locate the 89 non-hydrogen atoms. Standard Lorentz and polarization corrections were applied to all reflections. No corrections for either absorption or time-dependent intensity fluctuations were necessary on the basis of the periodic monitoring of six check reflections. Anomalous dispersion corrections were applied to ruthenium and sulfur atoms. The cation hydrogen atoms were included in the structure factor calculations as idealized atoms (assuming sp^2 hybridization of the carbon atoms and a C–H bond length of 0.96 Å) "riding" on their respective carbon atoms. One of the dimethylformamide solvent methyl groups (C_{10} and its hydrogens) was refined as a rigid rotor with sp^3 hybridization and a C–H bond length of 0.96 Å. The initial orientation of the methyl group was determined from the difference Fourier positions for the hydrogen atoms. The final orientation was determined by three rotational parameters. The refined positions for the rigid-rotor methyl group gave N–C–H angles that ranged from 98 to 118°. The isotropic thermal parameter for each hydrogen atom was fixed at 1.2 times the equivalent isotropic thermal parameter for the carbon atom to which it is covalently bonded.

The final refinement converged with residuals of $R = 0.052$ and $R_w = 0.049$ and a goodness-of-fit indicator equal to 1.46. No parameter was shifted more than 0.18 times its estimated standard deviation, and the final difference Fourier map had no peaks present above the noise level (0.69 e/Å^3).

Results and Discussion

Syntheses. The reaction of $Ru(bpy)_2Cl_2{\cdot}2H_2O$ and $(NH_4)_2WS_4$ in an aqueous ethanol solvent mixture produces the red-brown product $Ru(bpy)_2WS_4$ in high yield. This synthesis is directly analogous to the reaction previously reported by Tanaka et al.[7] for the synthesis of $Ru(bpy)_2MoS_4$. As in the molybdenum analogue, $Ru(bpy)_2WS_4$ reacts with a second molecule of $Ru(bpy)_2Cl_2$ to produce the dicationic product, $(bpy)_2RuS_2WS_2Ru(bpy)_2^{2+}$. Addition of NH_4PF_6 to the reaction mixture produced a dark maroon powder, which upon recrystallization provided crystals suitable for an X-ray crystal diffraction study. Unlike its molybdenum analogue, the dicationic tungsten complex is air-stable.

Attempts to extend this reaction to other molybdenum and tungsten sulfide complexes have proven less fruitful. For example, $Ru(bpy)_2Cl_2$ reacts with $Mo_2S_4(edt)_2^{2-}$ only after prolonged heating in acetonitrile (3 days) and produces the product, $Ru(bpy)_2Mo_2S_4(edt)_2$, in low yield. The reasons for the low reactivity are uncertain. The necessary avoidance of aqueous solvents to prevent hydrolysis of the sulfide complexes may preclude a rapid hydrolysis of the $Ru(bpy)_2Cl_2$. In addition, steric and geometric constraints imposed by these larger sulfide complexes may inhibit reaction.

In an attempt to circumvent this low reactivity, we synthesized the complex $Ru(bpy)_2(tf)_2$ (tf = $F_3CSO_3^-$). This was suggested by the work of Meyer et al.,[16] who, along with others,[17] have found that the triflate ion is an excellent leaving group. Dissolving $Ru(bpy)_2(tf)_2$ in a weakly coordinating solvent produces a bis(solvent) complex, which, in turn, should readily be attacked by an added nucleophile, such as a metal sulfide complex. The synthesis of $Ru(bpy)_2(tf)_2$ is straightforward and produces an air-stable product in essentially stoichiometric yield. Caution must be taken upon adding ether during isolation of the product, since a fair amount of heat is generated. Though the compound is air-stable, it is best stored in a desiccator to reduce the formation of the bis(aquo) complex. Unfortunately, the utility of the $Ru(bpy)_2(tf)_2$ complex for reactions with anionic metal sulfides is limited by formation of insoluble salts. For example, dissolution of $Ru(bpy)_2(tf)_2$ in acetonitrile produces the bis(acetonitrile) species, which is dicationic. Subsequent addition of the anionic molybdenum sulfide complex $Mo_2S_8^{2-}$ immediately leads to the formation of the insoluble salt $[Ru(bpy)_2(CH_3CN)_2](Mo_2S_8)$ according to

$$Ru(bpy)_2(tf)_2 \xrightarrow{CH_3CN} Ru(bpy)_2(CH_3CN)_2^{2+}$$

$$Ru(bpy)_2(CH_3CN)_2^{2+} + Mo_2S_8^{2-} \rightarrow [Ru(bpy)_2(CH_3CN)_2](Mo_2S_8)$$

Similar insoluble salts were obtained with other anionic metal sulfide complexes.

While pursuing the synthetic routes outlined above, we knew that although a very wide range of $Ru(bpy)_2L_2$ complexes were known, few contained sulfur donors.[7,18] With this in mind, we undertook the synthesis of a series of thiolate and sulfide complexes. The first two simple bis(thiolate) complexes were produced by the same synthetic route: generation of the thiolate by addition of thiol to a sodium ethoxide solution followed by addition of $Ru(bpy)_2Cl_2{\cdot}2H_2O$ and overnight heating. The dark green bis(ethanethiolate) complex is extremely air-sensitive and care must be taken to exclude all oxygen during synthesis and storage. The dark purple bis(benzenethiolate) complex is air-stable as a solid but decomposes upon prolonged air exposure in solution. An analogous synthesis of this latter thiolate complex has recently been reported by Deutsch et al.[3] We have found their procedure to be superior due to the shorter reaction times and have employed it in the synthesis of three additional bis(thiolate) complexes with *p*-methylthiophenolate, *p*-chlorothiophenolate, and *tert*-butyl mercaptide ligands.

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The synthesis of the $Ru(bpy)_2(mnt)$ complex is analogous to that of the bis(thiolate) complexes, except that the in situ generation of the thiolate is unnecessary due to the availability of the dithiolate as the disodium salt. Our interest in synthesizing this complex stems from the unusual photochemical and redox properties of the maleonitriledithiolate ligand, specifically its capacity to stabilize metal complexes in high formal oxidation states.[19] The synthesis proceeded smoothly, producing a dark red-brown product that is air-stable. Chemical oxidation of this complex in dimethylformamide or methylene chloride produced a stable orange ruthenium(III) species that is EPR active and will be discussed later.

The dimeric, thiolate-bridged complex $(bpy)_2Ru(SC_6H_5)_2Ru(bpy)_2^{2+}$ was prepared in a straightforward fashion by reacting equimolar amounts of $Ru(bpy)_2(tf)_2$ and $Ru(bpy)_2(SC_6H_5)_2$ in acetone. Presumably the reaction proceeds in the following manner:

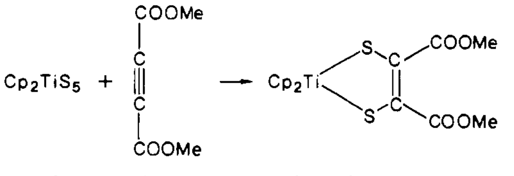
$$Ru(bpy)_2(tf)_2 \xrightarrow{CH_3COCH_3} Ru(bpy)_2(CH_3COCH_3)_2^{2+} + 2tf^-$$

$$(bpy)_2Ru(CH_3COCH_3)_2^{2+} + (C_6H_5S)_2Ru(bpy)_2 \rightarrow [(bpy)_2Ru(SC_6H_5)_2Ru(bpy)_2](tf)_2$$

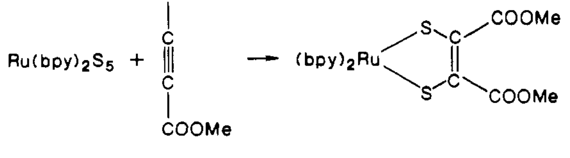
The intermediacy of the bis(solvent) complex was also postulated by Meyer et al. in the synthesis of the related chloro-bridged dimer;[11e] however, the method of generating this species differs. Several other dinuclear species have been reported.[12] This benzenethiolate-bridged dimer is air-stable, and crystals suitable for an X-ray diffraction study were obtained.

Attempts to produce a simple sulfide complex $Ru(bpy)_2S_x$ by reaction of $Ru(bpy)_2Cl_2$ with disodium tetrasulfide produced purple powders with varying sulfur content. However, a simple and essentially stoichiometric synthesis of $Ru(bpy)_2S_5$ was achieved by adding elemental sulfur to a slurry of $Ru(bpy)_2(SC_6H_5)_2$ in acetonitrile. The sulfide ligand is presumed to chelate the ruthenium atom as a bidentate pentasulfide dianion, forming a stable six-membered ring. Several examples of such pentasulfide ligation have been reported.[20] The displaced benzenethiolate ligands provide the reducing power needed to convert the elemental sulfur to polysulfide and are presumably oxidized to organic disulfide in the process.

Polysulfide ligands such as the one described above have been found to exhibit a wide range of chemical reactivities that have recently been reviewed.[20] Possibly the most thoroughly studied compound in this class is Cp_2TiS_5, in which a bidentate pentasulfide ligand of the type postulated here is found. A known reaction of the polysulfide ring was undertaken to assess the effects of the metal and other ligands upon the reactivity of the pentasulfide ligand and to further substantiate its presence in the purple $Ru(bpy)_2S_5$ complex. The addition of dimethyl acetylenedicarboxylate (dmad) to metal complexes that contain polysulfide rings leads to the formation of metal dithiolene complexes:[21]



Reaction of $Ru(bpy)_2S_5$ with dmad produced an analogous dithiolene species:



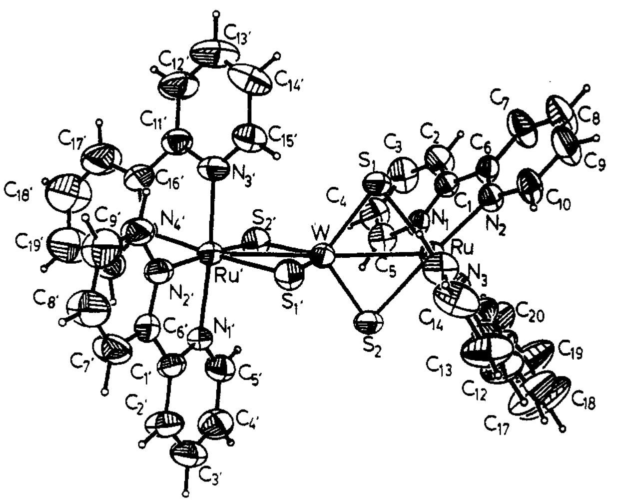


Figure 1. ORTEP drawing of $[(Ru(bpy)_2)_2WS_4]^{2+}$ with thermal ellipsoids showing 50% electron probability distributions for non-hydrogen atoms.

Table II. Interatomic Distances (Å) and Esd's for the Cation $[(Ru(bpy)_2)_2WS_4]^{2+}$

$Ru-S_1$	2.376 (2)	$Ru-N_1$	2.078 (6)
$Ru-S_2$	2.369 (3)	$Ru-N_2$	2.073 (7)
W-Ru	2.838 (1)	$Ru-N_3$	2.082 (7)
$W-S_1$	2.222 (2)	$Ru-N_4$	2.083 (7)
$W-S_2$	2.206 (2)		

Table III. Interatomic Angles (deg) and Esd's for the Cation $[(Ru(bpy)_2)_2WS_4]^{2+}$

Ru-W-Ru'	176.4 (1)	$W-Ru-N_4$	133.3 (2)
$Ru-W-S_1$	54.4 (1)	S_1-Ru-S_2	98.5 (1)
$Ru-W-S_2$	54.3 (1)	S_1-Ru-N_1	86.1 (2)
$Ru-W-S_1'$	123.1 (1)	S_1-Ru-N_2	86.8 (2)
$Ru-W-S_2'$	128.4 (1)	S_1-Ru-N_3	96.9 (2)
S_1-W-S_2	108.5 (1)	S_1-Ru-N_4	174.6 (2)
S_1-W-S_1'	108.6 (1)	S_2-Ru-N_1	96.8 (2)
S_1-W-S_2'	111.9 (1)	S_2-Ru-N_2	172.6 (2)
S_2-W-S_2'	107.4 (1)	S_2-Ru-N_3	87.3 (2)
$W-S_1-Ru$	76.2 (1)	S_2-Ru-N_4	84.7 (2)
$W-S_2-Ru$	76.6 (1)	N_1-Ru-N_2	78.3 (3)
$W-Ru-S_1$	49.5 (1)	N_1-Ru-N_3	174.5 (3)
$W-Ru-S_2$	49.1 (1)	N_1-Ru-N_4	97.9 (3)
$W-Ru-N_1$	94.9 (2)	N_2-Ru-N_3	97.2 (3)
$W-Ru-N_2$	136.3 (2)	N_2-Ru-N_4	90.4 (3)
$W-Ru-N_3$	90.5 (2)	N_3-Ru-N_4	78.8 (3)

This dithiolene complex was found to have electrochemical properties similar to those of the previously discussed maleonitriledithiolate complex and exhibits a nearly identical EPR spectrum when oxidized with iodine. Further chemical reactivity studies of the $Ru(bpy)_2S_5$ complex are in progress.

Structure of $[(bpy)_2RuS_2WS_2Ru(bpy)_2](PF_6)_2$. The dicationic complex $(bpy)_2RuS_2WS_2Ru(bpy)_2^{2+}$ possesses approximate D_2 symmetry with a tetrahedral tetrathiotungstate molecule serving to bridge two octahedral $Ru(bpy)_2$ fragments (Figure 1). This complex is capable of exhibiting diastereoisomerism. The crystal is found to contain a racemic mixture of Δ,Δ and Λ,Λ isomers, though this does not preclude the existence of the meso isomer in different crystals or in solution. Many examples of bidentate ligation by tetrathiotungstate are known, and several include simultaneous bonding to two metal centers.[22] The S-W-S angles are close to the angles expected for a regular tetrahedron (Table III). The W-S bond lengths of 2.222 (2) and 2.206 (2) Å are slightly longer than the bond lengths observed in $(NH_4)_2WS_4$, 2.177 Å (Table II).[22] Apparently the bonding to ruthenium through sulfur has only a minor effect upon the tungsten-to-sulfur bonding. The relatively short Ru-W distance of 2.838 Å is suggestive of some binding interaction and is in accord with

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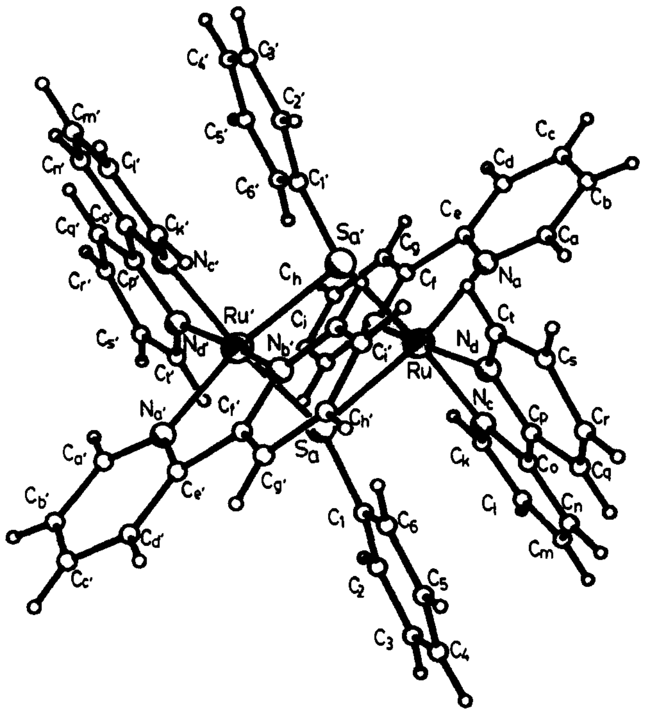

Figure 2. ORTEP drawing of $[(Ru(bpy)_2(SPh))_2]^{2+}$ (cation 2) with thermal ellipsoids showing 50% electron probability distributions for ruthenium atoms only.

calculations on related systems that predict such an interaction.[23]

The $Ru(bpy)_2S_2$ fragments of the molecule are distorted from perfect octahedral geometry due to the acute "bite" angle of the bipyridyl ligand. The N_1–Ru–N_2 and N_3–Ru–N_4 angles are 78.3 (3) and 78.8 (3)°, respectively. These values are typical for the bipyridyl ligand bound to ruthenium(II). The Ru–N bond lengths are all equal within experimental error and are similar to previously reported values for other $Ru(bpy)_2L_2$ complexes.[24] Sulfur ligation trans to bipyridyl nitrogen appears to have little effect upon the Ru–N bond length. Several recent structural studies have reported significant variation in Ru–N bond lengths in related $Ru(bpy)_2L_2$ complexes and have attributed the observed variations to a trans influence of the L_2 ligands.[16c,d] The absence of this effect in the present structure implies that the sulfur atoms in the tetrathiotungstate ligand are similar to the bipyridyl ligands in their electronic demands upon the ruthenium center. Further discussion of this trans influence is presented in the discussion of the subsequent structure. The Ru–S bond lengths of 2.376 (2) and 2.369 (3) Å are nearly equal within experimental error and are in the range of previously reported bond lengths for other ruthenium–sulfur complexes.[25]

The bond lengths and bond angles of the bipyridyl ligands are all within the ranges normally observed. In addition, each bipyridyl ring is planar with a maximum deviation from the 12-membered least-squares plane of 0.024 (4) Å.

Structure of $[(bpy)_2Ru(SC_6H_5)_2Ru(bpy)_2](F_3CSO_3)_2$. The complex $[(bpy)_2Ru(SC_6H_5)_2Ru(bpy)_2](F_3CSO_3)_2$ crystallizes in the space group $P\bar{1}$ with two crystallographically independent cations in the unit cell. The dication can be viewed as an edge-sharing bioctahedron with approximate C_2 symmetry (Figure 2). Two μ_2-benzenethiolate ligands serve to bridge the two $Ru(bpy)_2$ fragments. Syn and anti conformers for such thiolate bridges are possible, but in this case, only the anti conformer is observed in the solid state. The syn conformer would likely be precluded by severe steric crowding between the bipyridyl and benzenethiolate rings. As in the case of the previous dimer, diastereoisomerism is possible. In the crystal used for the structure determination, only the meso isomer was found, though the other isomer could exist in solution and/or in other crystals.

Table IV. Interatomic Distances (Å) and Esd's for the Cation $[(Ru(bpy)_2(SC_6H_5))_2]^{2+}$

	cation 1	cation 2		cation 1	cation 2
Ru···Ru	3.785 (1)	3.771 (1)	Ru–N_b	2.075 (8)	2.041 (8)
Ru–S_a	2.433 (3)	2.418 (3)	Ru–N_c	2.084 (8)	2.070 (8)
Ru–S_a'	2.432 (2)	2.420 (2)	Ru–N_d	2.069 (8)	2.083 (8)
Ru–N_a	2.046 (8)	2.066 (9)	S_a–C_1	1.78 (1)	1.80 (1)

Table V. Interatomic Angles (deg) and Esd's for the Cation $[(Ru(bpy)_2(SC_6H_5))_2]^{2+}$

	cation 1	cation 2		cation 1	cation 2
Ru–S_a–Ru'	102.1 (1)	102.4 (1)	N_b–Ru–N_c	93.3 (3)	91.4 (3)
S_a–Ru–N_a	171.7 (2)	170.1 (2)	N_b–Ru–N_d	167.3 (2)	168.0 (2)
S_a–Ru–N_b	95.2 (2)	95.3 (2)	N_c–Ru–N_d	77.8 (2)	79.0 (3)
S_a–Ru–N_c	92.8 (2)	94.4 (2)	S_a–Ru–S_a'	77.9 (1)	77.6 (1)
S_a–Ru–N_d	94.3 (2)	92.6 (2)	N_a–Ru–S_a'	97.1 (2)	96.2 (2)
N_a–Ru–N_b	78.9 (3)	78.0 (3)	N_b–Ru–S_a'	98.1 (2)	99.8 (2)
N_a–Ru–N_c	93.3 (3)	93.1 (3)	N_c–Ru–S_a'	165.8 (2)	166.7 (2)
N_a–Ru–N_d	92.5 (3)	95.2 (3)	N_d–Ru–S_a'	92.2 (2)	90.7 (2)

The coordination geometry about each ruthenium is again imperfectly octahedral with bipyridyl "bite" angles of 78.9 (3) and 77.8 (3)° in cation 1 and 78.0 (3) and 79.0 (3)° in cation 2 (Table V). Unlike those in the tetrathiotungstate-bridged dimer discussed above, the Ru–N bond lengths do show significant variations of 2.046 (8)–2.084 (8) Å in cation 1 and 2.041 (8)–2.083 (8) Å in cation 2, possibly indicating a trans influence due to sulfur (Table IV). The expected influence due to ligation of a π-acceptor ligand in a coordination site trans to a bipyridyl ligand would be a lengthening of the Ru–N bond due to loss of Ru (d) → bpy (π*) bonding. Conversely, ligation of a poor π-acceptor or a π- and σ-donor ligand in a coordination site trans to a bipyridyl ligand would be expected to produce a shortened Ru–N bond. These effects have recently been discussed for the complex $Ru(bpy)_2(CO)Cl^+$.[24] Here the Ru–N bond length involving the bipyridyl nitrogen trans to the π-acceptor ligand CO was found to be 2.18 Å, whereas the Ru–N bond length for the bipyridyl nitrogen trans to the π-donating chloride anion measured 2.07 Å. This same trans influence has been invoked to explain the observed Ru–N bond length variations in $Ru(bpy)_2Cl_2$[24c] and $Ru(bpy)_2(NCCH_3)_2^{2+}$.[24d]

Surprisingly, in cation 1 of $[(bpy)_2Ru(SC_6H_5)_2Ru(bpy)_2](F_3CSO_3)_2$ both the shortest (2.046 (8) Å) and the longest (2.084 (8) Å) Ru–N bonds are trans to sulfur atoms of benzenethiol, whereas in cation 2 both the longest (2.083 (8) Å) and the shortest (2.041 (8) Å) Ru–N bonds are trans to bipyridyl nitrogens. This would not be as puzzling if the Ru–S bond lengths were significantly different in each cation, therefore explaining the differing degrees of trans influence, but these bond lengths are equal in each cation: 2.433 (3) and 2.432 (3) Å in cation 1 and 2.418 (3) and 2.420 (2) Å in cation 2. Since we cannot rationalize the trend in Ru–N distances, we must conclude that other effects, such as crystal packing, may be operative.

A notable feature of this structure is the relation of the benzene rings of the thiolate ligands to the aromatic rings of the bipyridyl ligands. One might expect that each benzenethiol ring would lie on the imaginary mirror plane that lies between the $Ru(bpy)_2$ fragments in order to minimize steric crowding. In actuality these two benzenethiol rings are not coplanar with the mirror plane. It appears that each benzenethiol ring has adopted a conformation that allows it to "stack" with a bipyridyl ring. This intramolecular ring-stacking is reminiscent of that observed for other inorganic

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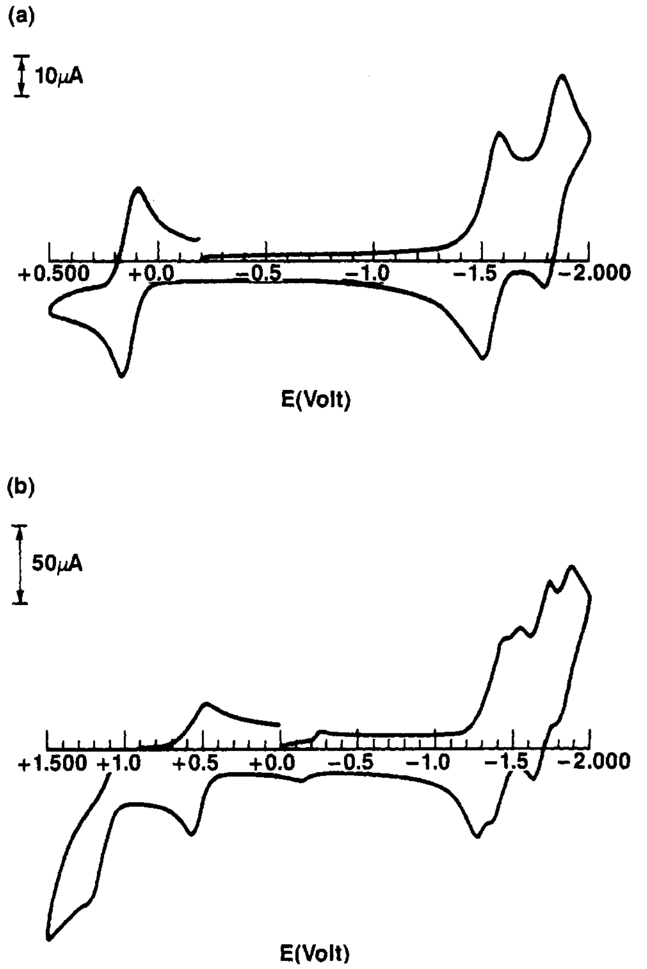

Figure 3. Cyclic voltammograms of (a) $Ru(bpy)_2(mnt)$ and (b) $[((Ru(bpy)_2(SPh))_2](tf)_2$ in dmf, 0.1 M $(Bu_4N)PF_6$ vs SCE with a scan rate of 100 mV/s.

Table VI. Electrochemical Parameters for $Ru(bpy)_2(L_s)_2$[a]

complex	$E_{1/2}$- (Ru(II/III)), V	$E_{1/2}$- (ligand redns), V
$Ru(bpy)_2(SC_2H_5)_2$	−0.34	−1.28,[b] −1.68, −2.03
$Ru(bpy)_2(SC_4H_9)_2$	−0.31	−1.67, −2.08
$Ru(bpy)_2(SC_6H_4CH_3)_2$	−0.18	−1.68, −2.00
$Ru(bpy)_2(SC_6H_5)_2$	−0.15	−1.47,[b] −1.63, −1.94
$Ru(bpy)_2(dmdmm)$	−0.15	−1.58, −1.89
$Ru(bpy)_2(SC_6H_4Cl)_2$	−0.08	−1.58, −1.89
$Ru(bpy)_2(mnt)$	+0.13	−1.54, −1.82
$Ru(bpy)_2(S_5)$	+0.45	−1.40, −1.54, −1.77, −1.89
$Ru(bpy)_2(MoS_4)$[c]	+0.54[b]	−1.50, −1.75
$Ru(bpy)_2$-$Mo_2S_4(S_2C_2H_4)_2$	+0.60[b]	−1.10, −1.38, −1.64
$Ru(bpy)_2(WS_4)$	+0.65[b]	−1.38, −1.63
$\{[Ru(bpy)_2(SC_6H_5)]_2\}(tf)_2$	+0.53	−1.37, −1.46, −1.69, −1.83
$\{[Ru(bpy)_2]_2MoS_4\}(PF_6)_2$[c]	+0.90	−1.24, −1.39, −1.54, −1.75
$\{[Ru(bpy)_2]_2WS_4\}(PF_6)_2$	+0.94, +1.50[b]	−1.24, −1.39, −1.65, −1.74

[a] All redox potentials were measured in dmf, 0.1 M Bu_4NPF_6 (scan rate 100 mV/s vs SCE; glassy-carbon working electrode). [b] Irreversible wave. [c] Reference 7.

complexes containing planar aromatic ligands.[26]

The ruthenium–sulfur bond lengths of 2.432 (3) and 2.433 (2) Å in cation 1 and 2.418 (3) and 2.420 (2) Å in cation 2 are within the reported range for other sulfur-containing ruthenium complexes.[25]

Electrochemistry. The cyclic voltammograms obtained in *N*,*N*-dimethylformamide for the neutral sulfur-containing complexes resemble those of previously reported *cis*-$Ru(bpy)_2L_2$ complexes.[2] One oxidation and two reversible reduction waves are observed for all complexes (Figure 3). The oxidation wave is presumably due to a metal-centered oxidation of ruthenium(II) to ruthenium(III), whereas the two reduction waves are ligand-centered and reflect addition of electrons to the two bipyridyl ligands. In addition, for the bis(thiolate) complexes, two irreversible waves are observed that may correspond to the two irreversible processes observed in the cyclic voltammograms of the free thiol. The observed anodic to cathodic peak separations in the quasi-reversible waves of 70–90 mV are typical of similar $Ru(bpy)_2L_2$ complexes and, while larger than the theoretical 59-mV Nernstian value, are attributed to uncompensated solution resistance. For comparison, the anodic to cathodic peak separation for the one-electron oxidation of ferrocene was 75 mV with this electrode configuration. Anodic to cathodic peak current ratios were 1.0 and the half-wave redox potentials were independent of scan rate.

The observed potential should be influenced by the overall charge of the complex, the nature of the ligand set, and the change in the solvation shell. It is clearly more difficult to remove an electron from a positively charged complex than from a neutral complex. For example, the potential for the Ru(II/III) couple in monocationic versus dicationic $Ru(bpy)_2L_2$ complexes differed by 0.8–0.9 and 0.4–0.5 V with phosphine[12a] and thioether[3] ligands, respectively. Oxidation of the metal ion is also influenced by the electron donor/acceptor characteristics of the coordinated ligands, being facilitated by electron-donating and retarded by electron-withdrawing ligands. These donor/acceptor effects are generally smaller in magnitude than the electrostatic effects described above. Within the families of $Ru(bpy)_2L_2$ complexes with the same charge, variations of 0.10 and 0.25 V in the Ru(II/III) potentials were observed for thioether[3] and phosphine[12a] ligands, respectively. In addition, ligands indirectly affect the potential of metal ion redox by altering the solvation sphere about the ion. Ligands with differing hydrophobicity/hydrophilicity can in principle cause differing solvation energy contributions to the overall redox potential. Effects of this type have not been observed for the $Ru(bpy)_2L_2$ complexes studied to date. Apparently, for $Ru(bpy)_2L_2$ complexes, the overall charge of a complex has the largest influence upon the oxidation potential of the Ru(II) ion, with smaller differences attributable to electron donation/withdrawal by the ligands.

Comparison of redox potentials for Ru(II/III) couples in the series of neutral $Ru(bpy)_2(L_s)_2$ complexes provides a means of assessing net electron withdrawal or donation by the sulfur-donor ligands (L_s). Comparisons are limited to one charge type to avoid making corrections for the electrostatic effects described above. This allows changes in the redox potential for the Ru(II/III) couples to be attributed to electron withdrawal or donation by the ligands at the ruthenium atom. The observed Ru(II/III) couple varies over a wide range of 1.00 V from +0.70 to −0.30 V vs SCE (Table VI). The observed order in decreasing potential is $WS_4 > Mo_2S_4(edt)_2 > MoS_4 > S_5 >$ mnt > dmdmm $\sim 2SC_6H_5 > 2SEt$. For comparison, the neutral complex $Ru(bpy)_2(CN)_2$ with the good π-acceptor ligand CN^- exhibits a Ru(II/III) couple at +0.85 V[27] in contrast to $Ru(bpy)_2Cl_2$, with the weak π- and σ-donor chloride ligand, in which the Ru(II/III) couple is at +0.32 V vs SCE.[28] This ordering implies that the tetrathiometalate anions are electron-withdrawing but less so than two cyanide anions, while the thiolate and dithiolate ligands are better electron donors than the chloride ion.

The ordering of the sulfur-containing ligands within the above series is a function of the electronic structure of the ligands. The occurrence of the two tetrathiometalate ligands at the electron-

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Table VII. UV-Visible Spectral Data for $Ru(bpy)_2(L_s)_2$ Complexes

complex	abs max, nm ($10^{-3}\epsilon$, M^{-1} cm^{-1})[a] band IV	band III	band II	band I
$Ru(bpy)_2WS_4$	284 (37)	345 sh	415 sh, 450 (6.3)	555 (3.0)
$Ru(bpy)_2MoS_4$[b]		346	420, 445 sh	570
$Ru(bpy)_2S_5$	302 (34)	364 (8.4), 380 sh	560 (5.1)	625 sh
$Ru(bpy)_2Mo_2S_4(S_2C_2H_2)_2$	294 (29)	375 sh	450 (6.6)	530 (5.6)
$Ru(bpy)_2(SC_6H_5)_2$	288 (27)	370 (6.5), 420 (6.0)	570 (3.9)	660 sh
$Ru(bpy)_2(SC_2H_5)_2$	295 (30)	390 (6.9)	440 (6.5)	650 sh, 720 sh
$Ru(bpy)_2(S_2C_2(CN)_2)$	289 (46)	390 (9.4), 420 (9.5)	460 (9.6), 490 (9.6)	700 (2.2)
$Ru(bpy)_2(S_2C_2(COOCH_3)_2)$	292 (40)	367 (9.3), 390 sh	495 (6.4), 540 (6.0)	800 (2.6)
$Ru(bpy)_2(SC_6H_4CH_3)_2$	285 (33)	375 (8.3), 420 (7.8)	575 (5.1)	650 sh
$Ru(bpy)_2(SC_6H_4Cl)_2$	285 (32)	365 (8.4), 410 sh	565 (4.4)	640 sh
$Ru(bpy)_2(SC(CH_3)_3)_2$	295 (29)	392 (7.4)	440 (7.3)	620 (3.8), 740 sh
$[(Ru(bpy)_2)_2WS_4](PF_6)_2$	285 (61)	350 sh, 395 (14)	520 (11), 555 sh	595 sh
$[(Ru(bpy)_2(SPh))_2](CF_3SO_3)_2$	295 (34), 300 sh	345 (8.3), 375 (8.4)	480 sh, 510 (5.1)	560 sh

[a] In dimethylformamide. [b] Reference 5.

withdrawing extreme of the series is not surprising if one notes that the sulfur atoms are bonded to the strongly electrophilic, high-oxidation-state metals Mo(VI) and W(VI).[22] The same is true for the molybdenum sulfide dimer.[23] The aromatic benzenethiolate ligands would be expected to be poorer σ-donor ligands than the aliphatic thiolates by virtue of the former's ability to delocalize electron density throughout the aromatic π-system. This is reflected in the higher potential Ru(II/III) couple for the bis(benzenethiolate) complex (−0.15 V) relative to the bis(ethanethiolate) complex (−0.34 V).

The occurrence of the dithiolene complexes (mnt and dmdmm) in the electron-donating part of the series indicates that these ligands are stabilizing Ru(III) relative to Ru(II), which is in accord with their ability to stabilize metals in high formal oxidation states. That given pairs of ligands within this series produce electrochemical effects that are consistent with reasonable chemical predictions is encouraging. Moreover, the existence of this series allows for a semiquantitative comparison of the overall electron-donor/acceptor propensities for a diverse series of sulfur-containing ligands. For example, it would be difficult to state, a priori, the relative donor/acceptor abilities of a coordinated pentasulfide ring relative to a tetrathiomolybdate ligand. This series places S_5^{2-} between MoS_4^{2-} and mnt^{2-} in its interaction with Ru(II).

The potentials of the bipyridyl ring reductions also vary, though over a much smaller range compared to the potentials of the Ru(II/III) couples discussed above. The two reversible reductions are presumed to involve addition of electrons to π* orbitals on each bipyridyl ring. Others have observed correlations between the potentials for these reduction processes and the donor/acceptor properties of the non-bpy ligands.[3,5,12] Electron withdrawal by a ligand increases the effective nuclear charge on the ruthenium atom, which lowers the π* bipyridyl level through charge delocalization. Addition of an electron to this lowered π* bipyridyl orbital occurs at a less negative potential than that for addition to the unperturbed orbital. In keeping with this rationale, the reduction potentials for the WS_4 complex are −1.38 and −1.63 V and for the mnt complex, −1.54 and −1.82 V. The sulfur-donor ligands exert a greater influence upon the oxidation of the Ru(II) ion than upon bipyridyl reduction, with ranges of 1000 mV in the Ru(II/III) couples compared with 200–250 mV for bipyridyl reduction potentials. A similar effect has been observed for other $Ru(bpy)_2L_2$ complexes.[3,12] The difference in the magnitude of ligand influence is attributable to the direct ligand orbital interaction with the atomic orbitals of ruthenium compared to the indirect effects (through the metal) upon the molecular orbitals of the bipyridyl ligands.

The electrochemistry of the dimeric ruthenium species is similar to that of the monomeric neutral complexes, but with differences resulting from their dimeric and dicationic nature. The dipositive charge on these dimers leads to a 100-mV positive shift in the potentials for the first two bipyridyl reductions relative to those for the corresponding neutral homonuclear complexes. In addition, four reversible reduction waves are observed and are assignable to the successive reduction of the four bipyridyl ligands in each dimer.

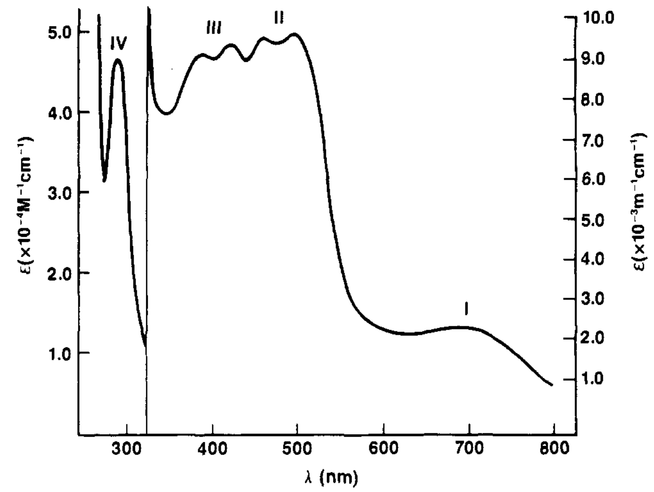

Figure 4. Electronic spectrum of $Ru(bpy)_2(mnt)$ in dmf.

The oxidative half of the cyclic voltammograms of these dimeric complexes reflect the dicationic dinuclear nature of these complexes as well. Two oxidation waves are observed, one of which is electrochemically reversible. The midpoint potential of the first oxidation wave is shifted by +240 to +360 mV relative to the Ru(II/III) couple in the corresponding neutral monomeric species, reflecting the increased difficulty in oxidizing the dicationic species. The appearance of two oxidation waves suggests stepwise removal of an electron from each ruthenium atom, as has been observed for other ruthenium bipyridyl dimers.[7,11c]

Electronic Spectra. The ultraviolet and visible absorption spectra of the neutral monomeric species are complex, containing up to six maxima in the wavelength range 275–1000 nm (see Figure 4). For convenience, these bands have been labeled I–IV, with the two closely spaced intermediate-wavelength bands being grouped together as bands II and III (Table VII). For the complexes with ligands other than maleonitriledithiolate, these two pairs of peaks are not as well resolved but are still discernible.

Comparison with the electronic spectra of previously reported phosphine,[12a] amine,[29] and thioether[3] complexes of ruthenium bis(bipyridyl) allows for the tentative assignments of these bands. Band IV, which is fairly constant throughout this entire series (290 ± 12 nm), has previously been assigned as arising from intraligand bipyridyl transitions. The three longer wavelength bands are assumed to be metal to ligand charge transfer in origin, corresponding to transitions from metal t_{2g} levels to bipyridyl π* orbitals. Greater electron withdrawal by the bipyridyl ligands relative to that by the sulfur-donor ligands results in the stabilization of two filled metal orbitals of the t_{2g} set (d_{xz}, d_{yz}) relative to the third

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(29) Brown, G. M.; Weaver, T. R.; Keene, F. R.; Meyer, T. J. *Inorg. Chem.* **1976**, *15*, 190.

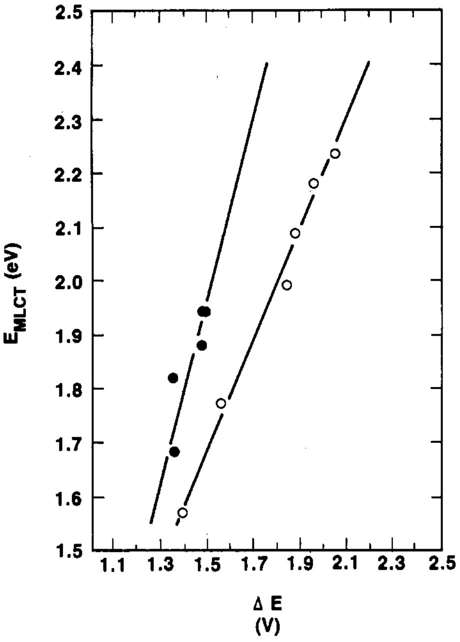

Figure 5. Plot of the metal-to-ligand charge-transfer energy (E_{MLCT}) versus the difference in potential between the Ru(II/III) couple and the first bipyridyl reduction (ΔE). The open circles are bidentate ligand data, and the filled circles are monodentate ligand data.

(d_{xy}). (The coordinate system is defined with the non-bipyridyl ligands along the $+x$ and $+y$ axes.) These metal-based orbitals are the highest occupied molecular orbitals (HOMO's) in these complexes. At higher energy are the bipyridyl π^* orbitals, which are the lowest unoccupied orbitals (LUMO's). These are split into an antisymmetric and a symmetric orbital with respect to the C_2 axis of the molecule.[30] Four metal-to-ligand charge-transfer (MLCT) bands would be expected to arise from transitions from the two HOMO levels into the two LUMO levels. The observation of three relatively intense, broad composite absorption bands in the visible region is consistent with this qualitative ordering of the energy levels in the molecule. Band I, which is very broad and asymmetric, is presumed to arise from the convolution of two of the MLCT bands. Though d–d transitions are possible, detection would not be expected due to the presence of the more intense MLCT transitions. The origins of the splittings in bands II and III are uncertain.

Spectral/Electrochemical Correlations. UV–visible absorption spectroscopy and cyclic voltammetry can be complementary probes of charge-transfer processes within metal complexes.[31] MLCT bands in the UV–visible spectrum arise from an electronic excitation, which is equivalent to oxidation of the metal ion and reduction of the ligand. The energy of the MLCT transition should equal the absolute difference in potential between the corresponding oxidation and reduction processes, as a first approximation. Several authors have successfully applied this simple correlation to metal complexes,[32] including ruthenium bis(bipyridyl) complexes.[33] Recently, Lever and co-workers have demonstrated excellent linear correlations between the MLCT energies (E_{op}) and the difference in electrochemical potential (ΔE) for metal oxidation and ligand reduction for 32 ruthenium bis(bipyridyl) complexes.[2] The equation of the linear correlation is

$$E_{op} = 0.86\Delta E + 0.54 \text{ eV}$$

with a linear regression of 0.95.

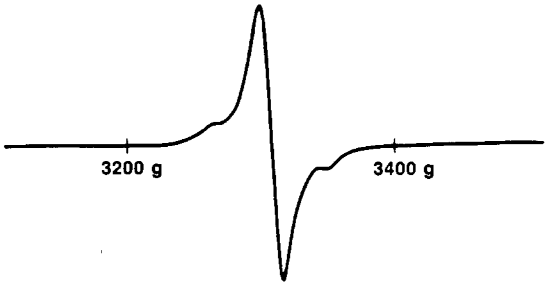

Figure 6. EPR spectrum of Ru(bpy)$_2$(mnt)$^+$ in methylene chloride at 298 K.

This same analysis was applied to the new ruthenium bipyridyl complexes reported in this paper and produced the least-squares line

$$E_{op} = 0.77\Delta E + 0.66 \text{ eV}$$

but with a poor linear regression of 0.75. Inspection of the plot revealed that the data appear to divide into two distinct sets corresponding to complexes containing either monodentate or bidentate sulfur donor ligands. Much better linear correlations are obtained when these two data sets are plotted separately, as illustrated in Figure 5. The two least-squares lines obtained are as follows:

$$\text{bidentate:} \quad E_{op} = 1.19\ \Delta E - 0.17 \text{ eV}$$

$$\text{monodentate:} \quad E_{op} = 1.45\ \Delta E - 0.25 \text{ eV}$$

with linear regressions of 0.92 and 0.95, respectively. The chemical basis for the division of the two data sets may be significantly different solvation and reorganizational energy contributions for the two classes of ligands. Lever attributed the scatter about his least-squares line to such factors.[2]

Electron Paramagnetic Resonance. The electron paramagnetic resonance (EPR) spectrum of [Ru(bpy)$_2$(mnt)]$^+$ generated in situ by the chemical oxidation of Ru(bpy)$_2$(mnt) with iodine is reproduced in Figure 6. The spectrum was recorded at ambient temperature in *N*,*N*-dimethylformamide and in methylene chloride. The chemical oxidation is reversible, with the chemical regeneration of the original Ru(II) complex easily effected by the addition of benzenethiol as reductant. Though addition of iodine to solutions containing other ruthenium bis(bipyridyl) complexes did lead to dramatic color changes, only one other solution was found to be EPR-active at room temperature. This solution contained the dmdsm dithiolene complex of bis(bipyridyl) ruthenium. It appears that dithiolene species such as maleonitriledithiolate and dimethyl disulfidomaleate are required to stabilize the oxidized forms. The observed g values for these EPR signals were as follows: dmdmm, $g = 2.055$; mnt, $g = 2.057$. Both complexes exhibited ruthenium hyperfine coupling with $\langle A \rangle = 16$ G.

Conclusions

In this paper we have reported the synthesis and characterization of a series of cis-disubstituted ruthenium(II) bis(bipyridyl) complexes containing sulfur-donor ligands. Cyclic voltammetry has been utilized to probe the electron-donor/acceptor ability of the sulfur-donor ligands. Using the potential of the Ru(II/III) couple as the criterion, we ranked the sulfur-donor ligands according to their electronic donor/acceptor interactions with Ru(II). In addition, comparisons between the energies of the MLCT absorption spectra and the electrochemical redox potentials of these complexes produced linear correlations in accord with other

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$Ru^{II}(bpy)_2L_2$ complexes. However, significantly better linear correlations are obtained when the monodentate and bidentate bonding types of sulfur-donor ligands are considered separately. This distinction is thought to arise from "chelation effect" contributions to the reorganizational energy terms and has not been as clearly demonstrated previously. Two dimeric complexes have been structurally characterized, and in both cases there is no discernible trans influence due to sulfur ligation.

Registry No. $Ru(bpy)_2WS_4$, 118831-60-0; $\{[Ru(bpy)_2]_2WS_4\}(PF_6)_2$, 118831-83-7; $Ru(bpy)_2(edt)_2$, 118831-61-1; $Ru(bpy)_2(SC_6H_5)_2$, 97279-25-9; $Ru(bpy)_2(SC_6H_4\text{-}p\text{-}CH_3)_2$, 118831-62-2; $Ru(bpy)_2(SC_6H_4\text{-}p\text{-}Cl)_2$, 118831-63-3; $Ru(bpy)_2(SC_4H_9)_2$, 118831-64-4; $Ru(bpy)_2(mnt)$, 118831-65-5; $Ru(bpy)_2(F_3CSO_3)_2$, 104474-95-5; $[(bpy)_2Ru(SC_6H_5)_2Ru(bpy)_2](F_3CSO_3)_2$, 118831-67-7; $Ru(bpy)_2S_5$, 118831-68-8; $Ru(bpy)_2(dmdmm)$, 118831-69-9; $[Ru(bpy)_2(CH_3CN)_2](Mo_2S_8)$, 118831-70-2; $Ru(bpy)_2Cl_2$, 15746-57-3; $(NH_4)_2WS_4$, 13862-78-7; $Ru(bpy)_2(SC_4H_9)_2^+$, 118831-71-3; $Ru(bpy)_2(SC_6H_4\text{-}p\text{-}CH_3)_2^+$, 118831-72-4; $Ru(bpy)_2(SC_6H_5)_2^+$, 97279-44-2; $Ru(bpy)_2(dmdmm)^+$, 118831-73-5; $Ru(bpy)_2(SC_6H_4\text{-}p\text{-}Cl)^+$, 118831-74-6; $Ru(bpy)_2(mnt)^+$, 118831-75-7; $Ru(bpy)_2(S_5)^+$, 118831-76-8; $Ru(bpy)_2(Mo_2S_4(S_2C_2H_4)_2)^+$, 118831-77-9; $Ru(bpy)_2(WS_4)^+$, 118831-81-5; $[Ru(bpy)_2(SC_6H_5)]_2^{4+}$, 118831-78-0; $\{[Ru(bpy)_2]_2WS_4\}^{4+}$, 118831-84-8; $Ru(bpy)_2(SC_5H_5)_2^+$, 118831-79-1; $Ru(bpy)_2(Mo_2S_4(S_2C_2H_4)_2)$, 118831-80-4; sulfur, 7704-34-9; dimethyl acetylenedicarboxylate, 762-42-5.

Supplementary Material Available: For both structures tables containing atom positional and thermal parameters, anisotropic thermal parameters, bond distances and angles, hydrogen atomic coordinates, and least-squares planes (58 pages); tables of structure factors (18 pages). Ordering information is given on any current masthead page.

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Synthesis and Structural Investigation of Polyoxomolybdate Coordination Compounds Displaying a Tetranuclear Core. Crystal and Molecular Structures of $[n\text{-}Bu_4N]_2[Mo_4O_{10}(OMe)_4X_2]$ (X = –OMe, –Cl) and Their Relationship to the Catecholate Derivative $[n\text{-}Bu_4N]_2[Mo_4O_{10}(OMe)_2(OC_6H_4O)_2]$ and to the Diazenido Complexes of the *o*-Aminophenolate and the Naphthalene-2,3-diolate Derivatives $[n\text{-}Bu_4N]_2[Mo_4O_6(OMe)_2(HNC_6H_4O)_2(NNC_6H_5)_4]$ and $[n\text{-}Bu_4N]_2[Mo_4O_6(OMe)_2(C_{10}H_6O_2)_2(NNC_6H_5)_4]$. Comparison to the Structure of a Binuclear Complex with the $[Mo_2(OMe)_2(NNC_6H_5)_4]^{2+}$ Core, $[Mo_2(OMe)_2(H_2NC_6H_4O)_2(NNC_6H_5)_4]$

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The tetranuclear methoxooxomolybdate $[MePPh_3]_2[Mo_4O_{10}(OCH_3)_6]$ ($[MePPh_3]_2$[I]) provides a synthetic precursor and a structural prototype for a class of tetranuclear polyoxomolybdate coordination complexes. Reaction of I with Me_3SiCl yields $[Mo_4O_{10}(OCH_3)_4Cl_2]^{2-}$ (II), which in turn may be reduced by thiols to yield a mixed-valence Mo(VI)/Mo(V) species, $[n\text{-}Bu_4N]_2[Mo_4O_8(OCH_3)_4Cl_4]$ ($[n\text{-}Bu_4N]_2$[III]). In the presence of chelating ligands, I reacts to give tetranuclear derivatives of the class $[n\text{-}Bu_4N]_2[Mo_4O_{10}(OCH_3)_2(LL)_2]$, where LL = catecholate ($[n\text{-}Bu_4N]_2$[IVa]), 3-*tert*-butylcatecholate ($[n\text{-}Bu_4N]_2$[IVb]), naphthalene-2,3-diolate ($[n\text{-}Bu_4N]_2$[IVc]), *o*-aminophenolate ($[n\text{-}Bu_4N]_2$[IVd]). Peripheral oxo groups of complexes IVa–d may be replaced by diazenido groups in condensation type reactions to give the tetranuclear complexes $[n\text{-}Bu_4N]_2[Mo_4O_6(OCH_3)_2(LL)_2(NNC_6H_5)_4]$ ($[n\text{-}Bu_4N]_2$[Va–d]). The related binuclear class of complexes $[Mo_2(OCH_3)_2(NNC_6H_5)_4(LL)_2]^n$ (VIa–d) has also been synthesized. Crystal data: I, triclinic, space group $P\bar{1}$, $a = 10.185$ (2) Å, $b = 10.848$ (2) Å, $c = 11.686$ (2) Å, $\alpha = 92.55$ (2)°, $\beta = 107.15$ (2)°, $\gamma = 96.79$ (2)°, $V = 1220.8$ (6) Å^3, $Z = 1$, 2798 reflections (Mo Kα, $\lambda = 0.71073$ Å in all cases), $R = 0.0246$; II, triclinic, space group $P\bar{1}$, $a = 10.186$ (4) Å, $b = 11.722$ (3) Å, $c = 13.173$ (4) Å, $\alpha = 109.35$ (2)°, $\beta = 107.43$ (1)°, $\gamma = 96.99$ (1)°, $V = 1372.6$ (6) Å^3, $Z = 1$, 3020 reflections, $R = 0.0407$; III, monoclinic, space group $P2_1/n$, $a = 10.653$ (3) Å, $b = 13.184$ (4) Å, $c = 12.703$ (4) Å, $\beta = 98.12$ (1)°, $V = 1766.1$ (8) Å^3, $Z = 2$, 2424 reflections, $R = 0.0469$; IVa, monoclinic, space group $P2_1/a$, $a = 18.494$ (3) Å, $b = 16.192$ (4) Å, $c = 20.411$ (3) Å, $\beta = 107.51$ (1)°, $V = 5822.6$ (10) Å^3, $Z = 4$, 3832 reflections, $R = 0.0566$; Vc, rhombohedral, space group $R\bar{3}$ (hexagonal indices), $a = 26.609$ (4) Å, $c = 31.844$ (7) Å, $V = 19519.4$ (9) Å^3, $Z = 9$, 2730 reflections, $R = 0.0616$; Vd, monoclinic, space group $P2_1/n$, $a = 24.675$ (2) Å, $b = 19.937$ (3) Å, $c = 17.295$ (4) Å, $\beta = 112.62$ (2)°, $V = 7854.3$ (11) Å, $Z = 4$, 4015 reflections, $R = 0.0781$; VId, triclinic, space group $P\bar{1}$, $a = 9.500$ (2) Å, $b = 11.942$ (3) Å, $c = 12.026$ (2) Å, $\alpha = 61.94$ (1)°, $\beta = 81.80$ (2)°, $\gamma = 86.11$ (2)°, $V = 1191.7$ (10) Å^3, $Z = 1$, 2059 reflections, $R = 0.0441$.

Introduction

The interest in the chemistry of early-transition-metal polyanions derives in part from the structural analogies of these clusters to metal oxide surfaces[1,2] and from their industrial application as catalysts for selective air oxidation of organic molecules.[3] Furthermore, the chemistry of these polyoxometalate anions poses fundamental questions with respect to the elucidation of their reactivity and general coordination chemistry, of the mechanisms of interconversion of various structural types, and of their structural interrelationships. The recent expansion of the coordination chemistry of the polyoxometalates is a consequence of the availability of polyoxoanions soluble in organic solvents, displaying characteristic metal–ligand or organometallic reaction chemistry.[1] The reaction chemistry of polyoxometalate anion in nonaqueous solvents has been characterized by the replacement of peripheral oxo groups by organometallic units,[4-11] by a variety

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