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An Unsymmetrical Ligand Arrangement in the Complex $Re_2(\mu\text{-mp})_4Cl_2$ (mp = Monoanion of 2-Mercaptopyridine)

Robert M. Tylicki, Wengan Wu, Phillip E. Fanwick, and Richard A. Walton*

Department of Chemistry, Purdue University,
1393 Brown Building, West Lafayette, Indiana 47907-1393

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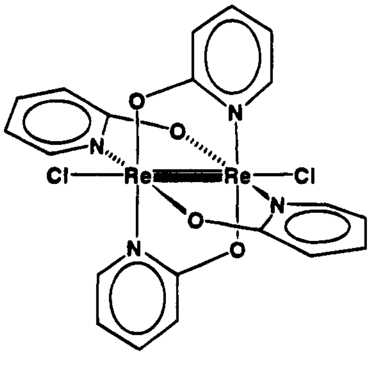
Introduction

In contrast to the large variety of neutral quadruply bonded dimolybdenum(II) and ditungsten(II) complexes that have been prepared and structurally characterized in which unsymmetrical monoanionic bridging ligands with N⌒N, N⌒O, N⌒P, and N⌒S donor sets are present, related compounds derived from the isoelectronic dirhenium(III) core are quite rare.[1] This is the consequence of unfavorable steric effects between relatively bulky nonbonding substituents, that are often an integral part of the organic bridging ligands, and the axial rhenium–halide bonds that are invariably present in dirhenium(III) complexes of the type $Re_2(\mu\text{-LL}')_4X_2$. Axial bonds of this type are absent in the analogous dimolybdenum(II) and ditungsten(II) compounds $M_2(\mu\text{-LL}')_4$. Of further note is the tendency of these unsymmetrical bridging ligands to orientate themselves in 2:2 head-to-tail arrangements so that the two metal centers possess formally equivalent charges (oxidation numbers). However, there are occasional exceptions, such as in the case of the compounds $M_2(\mu\text{-fhp})_4\cdot$THF (M = Mo, W; fhp = monoanion of 2-hydroxy-6-fluoropyridine) in which the four fhp ligands are orientated in the same direction to give a polar O_4M-MN_4 skeleton.[2]

Previously, we described[3] synthetic procedures for the complete series of 2-hydroxypyridinato complexes of dirhenium(III) of the type $Re_2(\mu\text{-hp})_4X_2$ (X = Cl, Br, I; hp = monoanion of 2-hydroxypyridine), as well as details of their spectroscopic and cyclic voltammetric properties, and, more recently, the synthetic and structural details for the "intermediate" species $Re_2(\mu\text{-hp})_2X_4\cdot$Hhp (X = Cl, Br).[4] This work had followed an earlier report[5] of the crystal structure of $Re_2(\mu\text{-hp})_4Cl_2$ (**1**) which



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has a symmetric structure with an identical *cis*-ReN_2O_2 ligand geometry about each of the metal centers, *i.e.*, a cis 2:2 head-to-tail bridging ligand arrangement. In a study of dirhenium(III) complexes that contain monoanionic N⌒S bridging ligands, we have isolated the analogous 2-mercaptopyridine complexes $Re_2(\mu\text{-mp})_4X_2$ (X = Cl, Br) and found that they contain the rarely encountered unsymmetrical 3:1 orientation of bridging ligands. The details of this work are described herein.

Experimental Section

Starting Material and Reaction Procedures. The compounds $(n\text{-}Bu_4N)_2Re_2X_8$ (X = Cl, Br)[6,7] and *cis*-$Re_2(O_2CCH_3)_2X_4(H_2O)_2$ (X = Cl, Br)[8] were prepared according to the published procedures. Solvents were obtained from commercial sources and were deoxygenated by purging with dinitrogen prior to use. The 2-mercaptopyridine (Hmp) ligand was purchased from Aldrich Chemical Co. and used as received. All reactions were performed under an atmosphere of dry dinitrogen.

Synthesis of $Re_2(\mu\text{-mp})_4X_2$ (X = Cl, Br). (i) Reactions of $(n\text{-}Bu_4N)_2Re_2X_8$ with Hmp in Refluxing Solvents. A mixture of blue-green $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.100 g, 0.0876 mmol) and yellow Hmp (0.040 g, 0.36 mmol) was treated with acetonitrile (15 mL). The color of the mixture turned to a dark brown immediately following the addition of the solvent. The resulting reaction mixture was heated to reflux for 2 h with stirring. A dark purple solid, $Re_2(\mu\text{-mp})_4Cl_2$, **2a**, precipitated during this period. The solid was collected by filtration and washed with approximately 20 mL of acetonitrile and dried under vacuum; yield 0.045 g (62%). Anal. Calcd for $C_{20}H_{16}Cl_2N_4Re_2S_4$: C, 27.18; H, 1.82. Found: C, 27.69; H, 1.85. Ethanol can be used as the reaction solvent and gives the same result.

The bromo analogue $Re_2(\mu\text{-mp})_4Br_2$, **2b**, was synthesized by a similar procedure. A mixture of 0.200 g (0.134 mmol) of dark olive-green $(n\text{-}Bu_4N)_2Re_2Br_8$, 0.060 g (0.54 mmol) of Hmp, and 20 mL of ethanol was heated to reflux for a reaction period of 4 h; yield 0.101 g (78%). Anal. Calcd for $C_{20}H_{16}Br_2N_4Re_2S_4$: C, 24.69; H, 1.66; N, 5.76. Found: C, 24.56; H, 1.65; N, 5.59.

(ii) Reactions of *cis*-$Re_2(O_2CCH_3)_2X_4(H_2O)_2$ with Hmp in Refluxing Solvents. A mixture of dark blue *cis*-$Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ (0.077 g, 0.12 mmol) and Hmp (0.055 g, 0.50 mmol) was treated with ethanol (12 mL). The color of the mixture changed to dark purple upon the addition of the solvent. The resulting reaction mixture was heated to reflux for 2 h with stirring. A workup procedure similar to that described in (i) was used to afford pure **2a**; yield 0.073 g (72%). When this same reaction was carried out with the use of smaller amounts of the Hmp ligand (2 and 3 equiv), **2a** was still isolated but in lower yields (38% and 42%, respectively).

The bromo analogue **2b** was obtained by the reaction of *cis*-$Re_2(O_2CCH_3)_2Br_4(H_2O)_2$ (0.073 g, 0.086 mmol) with Hmp (0.038 g, 0.34 mmol) in 12 mL of refluxing ethanol; yield 0.008 g (10%). A consistently low product yield was obtained by the use of this procedure. A higher yield of **2b** (36%) was obtained by the use of *cis*-$Re_2(O_2CCH_3)_2Br_4(py)_2$ in place of *cis*-$Re_2(O_2CCH_3)_2Br_4(H_2O)_2$ and with acetonitrile as the reaction solvent.

(iii) Reaction of $(n\text{-}Bu_4N)_2Re_2Cl_8$ with Hmp at Room Temperature. A dark green suspension was obtained when a mixture of $(n\text{-}Bu_4N)_2Re_2Cl_8$ (0.170 g, 0.149 mmol) and Hmp (0.063 g, 0.57 mmol) was treated with 30 mL of acetonitrile. The mixture was stirred at room temperature for 28 h. During this period, a dark brown solid and a dark purple solution were formed. The solid was separated from the solution by filtration, and 0.009 g (7%) of **2a** was obtained as crystals from the filtrate by slow evaporation of the solvent at 25 °C. It is found that the dark brown solid can be converted into **2a** by heating a suspension of it in acetonitrile solvent for 2 h, although attempts to

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Table 1. Crystallographic Data for $Re_2(\mu\text{-mp})_4Cl_2{\cdot}2C_6H_6$ (**2a**·$2C_6H_6$)

chem formula	$Re_2Cl_2S_4N_4C_{32}H_{28}$	Z	2
fw	1040.17	T, °C	20
space group	$P\bar{1}$ (No. 2)	λ, Å (Cu Kα)	1.541 84
a, Å	9.848(2)	ϱ_{calc}, g/cm^3	2.043
b, Å	12.299(1)	μ, cm^{-1}	172.92
c, Å	14.381(2)	transmissn coeff	1.000−0.413
α, deg	86.338(8)	R^a	0.039
β, deg	77.70(1)	$R_w{}^b$	0.052
γ, deg	83.90(1)	GOF	1.680
V, Å^3	1690.7(5)		

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

completely characterize the dark brown solid itself have so far been unsuccessful due to its very limited solubility in all common solvents.[9]

Preparation of Single Crystals of 2a. Crystallographic quality crystals of compound **2a** were grown by diffusion of benzene into a solution of **2a** in dichloromethane at 25 °C. Approximately 0.004 g of **2a** was dissolved in 4 mL of CH_2Cl_2 in a small sample vial, and the vial was placed inside a 50 mL bottle that contained benzene. The bottle was sealed to allow for the diffusion of vapors. Dark purple-black crystals of composition **2a**·$2C_6H_6$ were collected after 5 weeks.

X-ray Crystallography. A dark purple chunk of **2a** with approximate dimensions of 0.25 × 0.15 × 0.13 mm was mounted on a glass fiber. The data collection was performed on an Enraf-Nonius CAD4 computer controlled diffractometer with graphite-monochromatized Cu Kα radiation at 20 °C. The cell contents were based on 25 reflections obtained in the range $22 < \theta < 35°$, measured by the computer controlled diagonal slit method of centering. Calculations were performed on a microVAX II computer using the Enraf-Nonius MolEN structure determination package. Lorentz and polarization corrections were applied to the data set, and an empirical absorption correction[10] was also applied.

Compound **2a** crystallized in the triclinic system. The space group $P\bar{1}$ was assumed and subsequently confirmed by the successful solution and refinement of the structure. The structure was solved by the use of the Patterson heavy-atom method, which revealed the positions of the Re atoms. The remaining atoms were located in succeeding difference Fourier syntheses. All non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms were added to the structure factor calculations, but their positions were not refined. The structure was refined in full-matrix least-squares where the function minimized was $\Sigma w = (|F_o| - |F_c|)^2$, where w is the weighting factor defined as $w = 1/\sigma^2(|F_o|)$. Corrections for anomalous scattering were applied to the anisotropically refined atoms.[11] In the final stages of the refinement of **2a**, two molecules of benzene, originating from the crystallization solvents, were found. They were included in the calculations and satisfactorily refined. The final residuals for **2a** were $R = 0.039$ ($R_w = 0.052$) and GOF = 1.680. The highest remaining peak in the final difference Fourier map was 1.78 e/Å^3. The basic crystallographic parameters for **2a**·$2C_6H_6$ are listed in Table 1. Positional parameters and their errors for the non-hydrogen atoms of the dirhenium molecules are listed in Table 2. Important intramolecular bond distances and angles are listed in Table 3.

Table 2. Positional Parameters and Equivalent Isotropic Displacement Parameters for the Important Atoms of **2a**·$2C_6H_6$ and Their Estimated Standard Deviations[a]

atom	x	y	z	B, Å^2
Re(1)	0.13094(3)	0.28913(2)	0.25967(2)	1.961(5)
Re(2)	−0.07681(2)	0.24366(2)	0.24222(2)	1.582(4)
Cl(1)	0.3438(2)	0.3896(2)	0.2634(2)	4.10(4)
Cl(2)	−0.2834(2)	0.1328(1)	0.2406(1)	2.95(3)
S(12)	0.0440(2)	0.3627(2)	0.4117(1)	3.11(3)
S(22)	−0.0292(2)	0.0730(1)	0.3242(1)	2.67(3)
S(32)	0.2675(2)	0.2003(2)	0.1245(1)	2.85(3)
S(42)	0.0886(2)	0.4563(1)	0.1729(1)	2.99(3)
N(11)	−0.1960(5)	0.3113(4)	0.3707(4)	2.3(1)
N(21)	0.2095(5)	0.1514(5)	0.3355(4)	2.5(1)
N(31)	0.0071(5)	0.1868(4)	0.1002(3)	2.01(9)
N(41)	−0.1577(5)	0.3825(4)	0.1732(3)	2.00(9)
C(12)	−0.1341(7)	0.3541(5)	0.4350(4)	2.5(1)
C(13)	−0.2135(9)	0.3942(7)	0.5213(5)	3.7(2)
C(14)	−0.353(1)	0.3941(7)	0.5411(5)	4.2(2)
C(15)	−0.4171(8)	0.3545(7)	0.4737(6)	4.0(2)
C(16)	−0.3369(8)	0.3168(6)	0.3923(5)	3.2(1)
C(22)	0.1268(7)	0.0685(5)	0.3621(4)	2.5(1)
C(23)	0.1681(8)	−0.0214(6)	0.4186(5)	3.5(1)
C(24)	0.2949(9)	−0.0292(7)	0.4426(5)	4.2(2)
C(25)	0.3815(9)	0.0512(8)	0.4110(6)	4.6(2)
C(26)	0.3366(8)	0.1404(7)	0.3596(5)	3.7(2)
C(32)	0.1461(7)	0.1695(5)	0.0625(4)	2.6(1)
C(33)	0.1921(8)	0.1303(7)	−0.0293(5)	3.6(2)
C(34)	0.1013(9)	0.1146(7)	−0.0839(5)	4.0(2)
C(35)	−0.0408(9)	0.1385(7)	−0.0482(5)	3.8(2)
C(36)	−0.0835(7)	0.1724(6)	0.0425(4)	2.8(1)
C(42)	−0.0730(7)	0.4649(5)	0.1447(4)	2.4(1)
C(43)	−0.1185(9)	0.5586(6)	0.0935(5)	3.5(2)
C(44)	−0.2498(9)	0.5687(6)	0.0751(5)	3.8(2)
C(45)	−0.3365(8)	0.4862(6)	0.1063(5)	3.4(1)
C(46)	−0.2896(7)	0.3965(5)	0.1540(5)	2.7(1)

[a] Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $(4/3)[a^2\beta(1,1) + b^2\beta(2,2) + c^2\beta(3,3) + ab(\cos\gamma)\beta(1,2) + ac(\cos\beta)\beta(1,3) + bc(\cos\alpha)\beta(2,3)]$. Data for the atoms of the benzene molecules are available as supplementary material.

Table 3. Selected Bond Distances (Å) and Bond Angles (deg) for the Dirhenium Molecule of **2a**·$2C_6H_6$[a]

Distances			
Re(1)−Re(2)	2.2453(4)	Re(2)−Cl(2)	2.572(2)
Re(1)−Cl(1)	2.556(2)	Re(2)−S(22)	2.393(2)
Re(1)−S(12)	2.372(2)	Re(2)−N(11)	2.132(5)
Re(1)−S(32)	2.372(2)	Re(2)−N(31)	2.165(5)
Re(1)−S(42)	2.381(2)	Re(2)−N(41)	2.090(5)
Re(1)−N(21)	2.121(6)		
Angles			
Re(2)−Re(1)−Cl(1)	165.05(5)	Re(1)−Re(2)−Cl(2)	161.95(4)
Re(2)−Re(1)−S(12)	94.83(5)	Re(1)−Re(2)−S(22)	87.85(4)
Re(2)−Re(1)−S(32)	96.83(4)	Re(1)−Re(2)−N(11)	96.5(2)
Re(2)−Re(1)−S(42)	88.14(4)	Re(1)−Re(2)−N(31)	92.9(1)
Re(2)−Re(1)−N(21)	103.5(2)	Re(1)−Re(2)−N(41)	103.3(2)
Cl(1)−Re(1)−S(12)	83.63(7)	Cl(2)−Re(2)−S(22)	74.43(6)
Cl(1)−Re(1)−S(32)	87.27(7)	Cl(2)−Re(2)−N(11)	87.5(2)
Cl(1)−Re(1)−S(42)	77.21(6)	Cl(2)−Re(2)−N(31)	85.7(2)
Cl(1)−Re(1)−N(21)	91.2(2)	Cl(2)−Re(2)−N(41)	94.5(2)
S(12)−Re(1)−S(32)	165.51(6)	S(22)−Re(2)−N(11)	91.2(1)
S(12)−Re(1)−S(42)	94.99(7)	S(22)−Re(2)−N(31)	96.1(1)
S(12)−Re(1)−N(21)	85.4(2)	S(22)−Re(2)−N(41)	168.7(2)
S(32)−Re(1)−S(42)	93.97(7)	N(11)−Re(2)−N(31)	168.3(2)
S(32)−Re(1)−N(21)	83.5(2)	N(11)−Re(2)−N(41)	85.9(2)
S(42)−Re(1)−N(21)	168.2(2)	N(31)−Re(2)−N(41)	85.2(2)

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

Physical Measurements. Infrared spectra were recorded as Nujol mulls between NaCl or KBr plates on a Perkin-Elmer 1800 FT-IR spectrometer. Electronic absorption spectra were recorded with an IBM 9420 UV−visible spectrophotometer. ^1H NMR spectra were obtained with the use of either a Varian Gemini-200 or a GE QE-300 spectrometer. Proton resonances were referenced internally to the residual protons in the incompletely deuteriated solvent. Electrochemical measurements were carried out with use of a BAS Inc. Model CV-27 instrument in conjunction with a BAS Model RXY recorder and were recorded on dichloromethane solutions that contained 0.1 M

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(9) Elemental microanalytical data for this product are consistent with the formulation $Re_2(\mu\text{-mp})_2Cl_4(Hmp)_2$. Anal. Calcd for $C_{20}H_{18}Cl_4N_4Re_2S_4$: C, 25.10; H, 1.90; Cl, 14.82; N, 5.85. Found: C, 25.54; H, 1.95; Cl, 15.01; N, 5.71. However, its poor solubility properties have prevented us from determining its solution properties, and so far, we have not succeeded in converting it to other compounds of the type $Re_2(\mu\text{-mp})_2Cl_4L_2$ (e.g. L = 4-Mepy). The latter transformation would have supported our tentative formulation.

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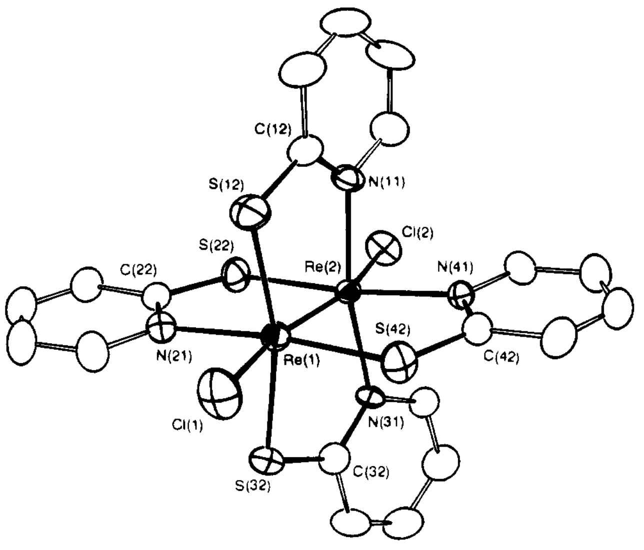


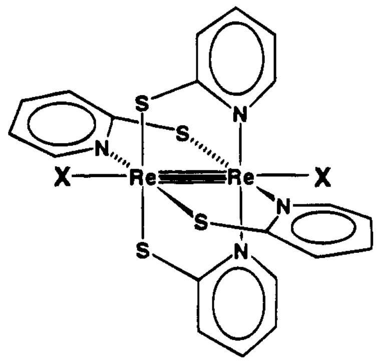
Figure 1. ORTEP representation of the structure of the $Re_2(\mu\text{-mp})_4Cl_2$ molecule as present in $\mathbf{2a}\cdot 2C_6H_6$. The thermal ellipsoids are drawn at the 50% probability level.

tetra-*n*-butylammonium hexafluorophosphate (TBAH) as supporting electrolyte. $E_{1/2}$ values, determined as $(E_{p,a} + E_{p,c})/2$, were referenced to the silver/silver chloride (Ag/AgCl) electrode at 25 °C and were uncorrected for junction potentials. Under our experimental conditions $E_{1/2}$ = 0.47 V vs Ag/AgCl for the ferrocenium/ferrocene couple. Conductivity measurements were obtained by the use of an Industrial Instruments Inc. Model RC-16B2 conductivity bridge.

Elemental microanalyses were performed by Dr. H. D. Lee of the Purdue University Microanalytical Laboratory.

Results and Discussion

The quadruply bonded dirhenium(III) complexes $Re_2(\mu\text{-mp})_4X_2$ (X: Cl, **2a**; Br, **2b**) were prepared in good yield (62–78%) from the reactions of $(n\text{-}Bu_4N)_2Re_2X_8$ with 4 equiv of 2-mercaptopyridine (Hmp) in refluxing acetonitrile or ethanol solvent. The analogous reactions of *cis*-$Re_2(O_2CCH_3)_2X_4(H_2O)_2$ with 4 equiv of Hmp under similar reaction conditions also yielded **2a** and **2b**, although the yield of **2b** by this procedure was low (10%). Attempts to obtain intermediates of the type $Re_2(\mu\text{-mp})_2X_4$ from the reactions of *cis*-$Re_2(O_2CCH_3)_2X_4(H_2O)_2$ with <4 equiv of Hmp were unsuccessful, although the analogous 2-hydroxypyridinato complexes, viz., *cis*-$Re_2(\mu\text{-hp})_2X_4\cdot Hhp$, have been prepared[4] by the use of such a procedure.



2a (X = Cl)

2b (X = Br)

A single-crystal X-ray structure determination on a crystal of composition $Re_2(\mu\text{-mp})_4Cl_2\cdot 2C_6H_6$ ($\mathbf{2a}\cdot 2C_6H_6$) confirmed the structural identity of **2a** (Figure 1 and Tables 1–3). Compounds **2a** and **2b** were further characterized on the basis of elemental microanalyses (see Experimental Section), and their IR, electronic absorption, and ^1H NMR spectra and electrochemical properties (Table 4). The similarity between the spectroscopic and electrochemical data of **2a** and **2b** implies a very close structural relationship between these two complexes. Their nonionic nature was confirmed by a conductivity measurement on an acetone solution of **2a** ($\Lambda_m = 6\ \Omega^{-1}\ mol^{-1}cm^2$ for $c_m = 1.0 \times 10^{-3}$ M).

The first clue that we were dealing with an unusual arrangement of μ-mp ligands was gleaned from the ^1H NMR spectrum of **2a**, which was of considerable complexity (Table 4). There are 12 identifiable proton resonances for the four bridging mp ligands, some of which overlap, that integrate for the 16 H's. This accords with a 3:1 orientation of the four μ-mp ligands rather than a cis or trans 2:2 arrangement and makes **2a** different structurally from its more symmetrical μ-hp analogue, $Re_2(\mu\text{-hp})_4Cl_2$ (**1**).[5] The ^1H NMR spectrum of the bromo analogue **2b** is very similar to that of **2a**.[12]

The conclusions from the ^1H NMR spectral study were confirmed by a single-crystal X-ray structure determination. An ORTEP representation of the molecular structure of **2a** is shown in Figure 1. As anticipated from the ^1H NMR results, there is a 3:1 orientation of the four mp ligands which leads to N_3S and NS_3 donor sets at the two disparate Re centers. This is the first example of its type for a quadruply bonded dimetal species. The more commonly encountered symmetrical 2:2 arrangements are seen, for example, in $Re_2(\mu\text{-hp})_4Cl_2$,[5] where there are *cis*-ReN_2O_2 geometries, in $Mo_2(mhp)_4$ (mhp = the monoanion of 6-methyl-2-hydroxypyridine),[13] with *trans*-MoN_2O_2 geometries, and in a series of dirhenium(III) amidato-bridged complexes which can be of either of these types depending upon the choice of bridging ligand.[14]

The Re–Re distance of 2.2453(4) Å is typical for a quadruply bonded dirhenium(III) unit[1] and can be compared with distances of 2.206(2) Å for $Re_2(\mu\text{-hp})_4Cl_2$[5] and 2.210(1) Å for $Re_2(\mu\text{-mhp})_2Cl_4\cdot Hmhp$.[4] While $\mathbf{2a}\cdot C_6H_6$ has no crystallographically imposed symmetry, the virtual symmetry approximates to C_s, although the rotational geometry reveals some staggering of the ReN_3S and $ReNS_3$ units one from the other. The torsional angles about the Re–Re bond range from 0.8° for N(21)–Re(1)–Re(2)–S(22) to 11.8° for S(32)–Re(1)–Re(2)–N(31). While there is doubtless some disparity in charge at the two Re centers, the differences between the Re(1)–ligand and Re(2)–ligand distances are small. The distance Re(2)–Cl(2) is longer than Re(1)–Cl(1) by ca. 0.02 Å, while the greatest disparity within the sets of Re–N and Re–S distances is Re(2)–N(41) = 2.090(5) Å. This is the shortest of the four Re–N bonds and is trans to the lone Re–S bond at the Re atom which contains the N_3S donor set; the bond distance for Re(2)–S(22) is 2.393(2) Å and is the longest of the four Re–S bonds. This is the clearest evidence for a structural trans effect in this complex.

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(12) Most preparative samples of **2a** contained small amounts (a few percent at most) of a contaminant that was very difficult to remove. The most characteristic resonances for this contaminant were at δ +8.58 (dm) and +7.65 ("t"), although other features could be obscurred by the peaks of the majority species. The presence of this contaminant was also seen in the IR spectrum (extra peaks at 1578, 1508, and 1124 cm^{-1}), but its presence was not discernible in the electronic absorption spectrum, in the cyclic voltammogram, or from the elemental microanalyses of **2a**. This contaminant may be a different stereoisomer of $Re_2(\mu\text{-mp})_4Cl_2$ (perhaps the cis or trans 2:2 isomer), but our failure to obtain it in a pure form has prevented us from pursuing its characterization. The purest samples of **2a**, *completely free of any contamination*, were obtained reproducibly from the filtrate of the reaction between $(n\text{-}Bu_4N)_2Re_2Cl_8$ and Hmp in acetonitrile at room temperature (see Experimental Section). Small quantities of a similar contaminant(s) were also detected in the ^1H NMR spectrum of **2b**.

(13) Cotton, F. A.; Fanwick, P. E.; Niswander, R. H.; Sekutowski, J. C. *J. Am. Chem. Soc.* **1978**, *100*, 4725.

(14) Cotton, F. A.; Lu, J.; Ren, T. *Polyhedron* **1994**, *13*, 807.

Table 4. Electrochemical and Spectroscopic Data for **2a** and **2b**

complex	CV half-wave potentials, V[a]	electronic, nm[b]	IR, cm^{-1} [c]	^{1}H NMR spectra, δ[d]
2a	$E_{1/2}$(ox) = +1.21 (110) $E_{1/2}$(red) = −0.54 (80)	782 (2100), 610 (2200), 525 (9500), 490 (sh), 440 (sh), 384 (14 000), 365 (14 000)	1596 (s), 1536 (w), 1406 (m), 1272 (m), 1148 (s), 1090 (w), 1056 (w), 1012 (w), 766 (s), 752 (sh), 730 (m)	8.87 (dm, 1H), 8.80 (dm, 2H), 8.50 (dm, 1H), 7.80 (dm, 1H), 7.76 (dm, 1H), 7.53 (dm, 2H, overlapping tm, 1H), 7.43 (tm, 1H, overlapping tm, 2H), 7.28 (td, 1H), 7.14 (td, 1H), 6.98 (td, 2H)
2b	$E_{p,a} \approx +1.30$ $E_{1/2}$(red) = −0.51 (130)	785 (2600), 610 (2700), 533 (10 000), 495 (sh), 445 (sh), 385 (sh), 367(18 000)	1596 (s), 1534 (w), 1406 (m), 1270 (m), 1146 (s), 1090 (w), 1054 (w), 1016 (w), 754 (s, br), 728 (m)	9.13 (dm, 1H), 9.02 (dm, 1H), 8.78 (dm, 2H), 7.79 (dm, 1H), 7.74 (dm, 1H), 7.53 (dm, 2H, overlapping tm, 1H), 7.44 (tm, 1H, overlapping tm, 2H), 7.30 (m, 1H), 7.13 (tm, 1H), 6.97 (m, 2H)

[a] Measured on 0.1 M TBAH−CH_2Cl_2 solutions and referenced to the Ag/AgCl electrode with a scan rate (ν) of 200 mV/s at a Pt-bead electrode. Values of ΔE_p ($E_{p,a} - E_{p,c}$) in mV are given in parentheses. [b] Measured on CH_2Cl_2 solutions; ϵ_{max} values are given in parentheses. [c] Spectra recorded as Nujol mulls. [d] Spectra recorded on CD_2Cl_2 solutions. Abbreviations for the approximate descriptions of the multiplets are as follows: dm = doublet of multiplets, m = multiplet, td = triplet of doublets, tm = triplet of multiplets.

Measurement of the cyclic voltammograms of solutions of $Re_2(\mu\text{-hp})_4X_2$ (X = Cl, Br) in TBAH−CH_2Cl_2 had shown[3] that these complexes possess a reversible one-electron reductions with $E_{1/2}$(red) values of −0.73 and −0.67 V vs Ag/AgCl for X = Cl and Br, respectively. Similar behavior is found in the case of **2a** and **2b**, for which the corresponding $E_{1/2}$(red) values are −0.54 and −0.51 V (Table 4). In addition, the mercaptopyridine complexes have an accessible oxidation at ca. +1.3 V (Table 4).

Concluding Remarks

In the absence of any obvious steric effects, it is unclear why the *predominant* stereoisomer in the case of $Re_2(\mu\text{-mp})_4X_2$ (**2a** and **2b**) is the one with a 3:1 orientation of μ-mp ligands, when the cis 2:2 isomer is isolated in the case of $Re_2(\mu\text{-hp})_4Cl_2$.[15] For **2a** and **2b**, there is no perceptible difference in the products that are isolated with the use of different starting materials ($(n\text{-}Bu_4N)_2Re_2X_8$ or *cis*-$Re_2(O_2CCH_3)_2X_4(H_2O)_2$) or different reaction times or reaction solvents, so we presume that the particular stereoisomer of **2a** and **2b** that is obtained reflects some subtle electronic factor or is the consequence of solubility differences between the different stereoisomers in the reaction solvents. In this same context, we note that Lebuis and Beauchamp[16] have described an NMR spectral study of the product $Re_2(\mu\text{-dmad})_4Cl_2$ (dmad = the monoanion of the unsymmetrical $N\frown N$ bridging ligand 6-(dimethylamino)purine), which is apparently formed as a mixture of all four possible stereoisomers (cis 2:2, trans 2:2, 3:1, and 4:0).

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Supplementary Material Available: Tables giving full details of the crystal data and data collection parameters (Table S1), complete atomic positional parameters (Tables S2 and S3), anisotropic thermal parameters (Table S4), bond distances (Table S5), and bond angles (Table S6) for **2a**·$2C_6H_6$ (14 pages). Ordering information is given on any current masthead page.

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(15) The ^{1}H NMR spectra of the crude reaction products that are formed in the reactions between $(n\text{-}Bu_4N)_2Re_2Cl_8$ or *cis*-$Re_2(O_2CCH_3)_2Cl_4(H_2O)_2$ and Hhp indicate that the predominant cis-2:2 stereoisomer of $Re_2(\mu\text{-hp})_4Cl_2$ is contaminated with small quantities of at least two other species. Wu, W.; Walton, R. A. unpublished observations.

(16) Lebuis, A.-M.; Beauchamp, A. L. *Inorg. Chim. Acta*, **1994**, *216*, 131.