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The versatility of the 1,4-dithiane ligand towards the coordination chemistry of ruthenium-phosphine complexes

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Abstract

The *trans*-[RuCl₂(dppb)(1,4-dt)], *mer*-[RuCl₃(dppb)(1,4-dt)] and [{RuCl₃(dppb)}₂(μ -(1,4-dt))] complexes were synthesized and characterized by spectroscopic and electrochemical techniques. Despite the favorable energy for the C_{2h} conformation, the crystallographic data point for the 1,4-dithiane (1,4-dt) D₂ conformer in the *trans*-[RuCl₂(dppb)(1,4-dt)] complex, where it acts as a bidentate ligand. The $E_{1/2}$ value of this complex is higher than those found for some related pyridine derivative compounds showing that with this thio-ligand, the Ru(II) atom presents a relatively strong π back-bonding interaction. Apart from the phosphine intraligand transitions, the UV/Vis spectrum of the *trans*-[RuCl₂(dppb)(1,4-dt)] complex shows only one band at 457 nm assigned to the MLCT transition. The bands observed in the spectra of the *mer*-[RuCl₃(dppb)(1,4-dt)] and [{RuCl₃(dppb)}₂(μ -(1,4-dt))] complexes, at 530, 420 and 347 nm were attributed to the contribution of the (Ru^{III}) \leftarrow (Cl,S) LMCT transitions. The EPR spectrum of the *mer*-[RuCl₃(dppb)(1,4-dt)] complex shows three *g*-values in 2.87, 2.15 and 1.73, suggesting that the 1,4-dt is coordinated in a monodentate mode. The NMR, EPR, FTIR and crystallographic data point for the ruthenium-phosphine species as the first example of metallic system that form complexes with the 1,4-dt has acting as bidentate, monodentate and bridged ligand.

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Keywords: 1,4-Dithiane; Phosphine; Ruthenium; X-ray structure; Electrochemistry; Crystal structure

1. Introduction

The redox and reactive character of the sulfur combined with that of the transition metal, leads to versatile chemistry that has been exploited both industrially and biologically [1,2]. The literature reports that sulfur atoms of dithioether ligands have a pronounced effect on the transition metals redox potential upon coordination [3]. Usually, it implies in a stability enhancement of the metal center in the reduced state [4]. This effect, however, is not yet fully understood and some reports have addressed the participation of the empty sulfur 3d orbitals and others to explain such unusual properties of sulfur compounds [5–10]. In fact, the stabilities of many polycoordinated sulfur compounds are believed to be due to the added orbital interaction with accessible 3d orbitals [7]. Wolfe et al. [8], with use of ab initio calculations, found that the participation of 3d orbitals of sulfur atom is quite significant in the stabilization of the α -sulfur carbanions. Taube [9] was the first to make use of the $d\pi$ (sulfur) $\leftarrow d\pi$ Ru back-bonding effect to explain the affinity of ruthenium toward neutral sulfur ligands. Although this assignment does not account

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for the difference in affinity of ruthenium for hydrogen sulfide and dimethyl sulfide ligands, this effect has been elegantly applied to explain some unusual features of sulfur based metal complexes including the questions related to the competitive catalysts for metal sulfur enzymes [10].

The 1,4-dithiane (1,4-dt) ligand can bind to a metal center via a variety of bonding modes. This versatility of 1,4dt is attributed to the presence of two S atoms and its proximity. The large size of the S atom makes it easier to adopt different angles at this atom in complexes, which is necessary for different geometries. The 1,4-dithiane can function as a chelating ligand for a single metal center, as a monodentate or yet as bridged ligand in binuclear species [11]. The literature reports that the chair conformation of the 1,4-dt species is preferred [12,13]. Probably, this is the reason why a very few X-ray structures of compounds containing the 1,4-dt molecule as a bidentate ligand are noticed [14–17].

In this work, we present the first example of a metal center system that form complexes with the 1,4-dithiane acting as bidentate, monodentate and bridged ligand. The electrochemical, spectroscopic and crystallographic data of such complexes highlights the conformational versatility of this ligand towards the coordination chemistry.

2. Experimental

2.1. Materials

All manipulations were carried out under argon atmosphere using Schlenk techniques. The solvents were purified according to standard procedures [18]. The water used throughout was purified by a Milli-Q system (Millipore Co.). The *mer*-[Ru^{III}Cl₃(dppb)H₂O] and [Ru^{II}Cl₂(dppb)-PPh₃] (dppb = 1,4-bis(diphenylphosphino)butane, PPh₃ = triphenylphosphine) complexes were prepared according to the literature [19,20]. Tetrabutylammonium perchlorate (TBAP) was purchased from Fluka, recrystallized twice from absolute ethanol solution, filtered and dried under vacuum. All other chemicals of reagent grade were used as received.

2.1.1. trans- $[RuCl_2(dppb)(1,4-dt)]$

trans-[RuCl₂(dppb)(1,4-dt)] complex was synthesized from the [RuCl₂(dppb)PPh₃] (0.100 g, 0.12 mmol) and 1,4dt (0.014 g, 0.12 mmol) at room temperature in 5 mL of dichloromethane. The mixture was stirred under argon during 30 min and the resulting solution was reduced to near 1 mL volume. The product was precipitated by the addition of diethyl ether, separated by filtration, washed with diethyl ether and dried under vacuum. Yield: 40.0 mg, 80%. *Anal.* Calc. for $C_{32}H_{36}Cl_2P_2S_2Ru$, fw.: 718.69; C, 53.48; H, 5.05; S, 8.92. Found: C, 53.27; H, 5.06; S, 8.87%.

Recrystallization of *trans*-[RuCl₂(dppb)(1,4-dt)] from dichloromethane/diethyl ether solution yielded yellow crystals suitable for single crystal X-ray analysis. Crystal data

Crystal data and structure refinement for the *trans*-[RuCl₂(dppb)(1,4-dt)] complex

•ompien	
Empirical formula	$C_{32}H_{36}Cl_2P_2S_2Ru$
Formula weight	718.69
Temperature (K)	120(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a (Å)	10.7020(1)
b (Å)	12.0660(1)
<i>c</i> (Å)	26.5840(3)
β (°)	99.57(1)
Volume (Å ³)	3385.06(6)
Ζ	2
$D_{\rm c} ({\rm Mg}{\rm m}^{-3})$	1.577
Absorption coefficient (mm ⁻¹)	1.021
<i>F</i> (000)	1640
Crystal size (mm ³)	$0.20 \times 0.04 \times 0.04$
θ Range for data collection (°)	1.55-25.00
Index ranges	$-12 \leqslant h \leqslant 12, \ -14 \leqslant k \leqslant 14,$
	$-31 \leq l \leq 31$
Reflections collected	11 543
Independent reflections $[R_{int}]$	5957 [0.0215]
Completeness to $\theta = 25.00^{\circ}$	100.0%
Maximum and minimum transmission	0.9603 and 0.8219
Refinement method	full-matrix least-squares on F^2
Data/parameters	5957/406
Goodness-of-fit on F^2	1.171
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0373, wR_2 = 0.1077$
R indices (all data)	$R_1 = 0.0581, wR_2 = 0.1534$
Largest difference peak and hole (e $Å^{-3}$)	1.104 and -2.421

and structure refinement for this complex are summarized in Table 1.

2.1.2. $mer-[RuCl_3(dppb)(1,4-dt)]$

mer-[RuCl₃(dppb)(1,4-dt)] complex was prepared from *mer*-[RuCl₃(dppb)H₂O] (0.100 g, 0.15 mmol) and 1,4-dt (0.039 g, 0.32 mmol) dissolved in CH₂Cl₂ (10 mL) with stirring for 12 h, at room temperature. The resulting red dark solution was reduced to near 1 mL volume, by rotary evaporation. A red solid was obtained by the addition of diethyl ether, which was separated by filtration, washed with diethyl ether, and dried and stored under vacuum. Yield: 98.0 mg, 85%. *Anal.* Calc. for C₃₂H₃₆Cl₃P₂RuS₂, fw. 754.16; C, 50.96; H, 4.81; S, 8.50. Found: C, 50.85; H, 4.86; S, 8.54%.

2.1.3. $[{RuCl_3(dppb)}_2(\mu-(1,4-dt))]$

The [{RuCl₃(dppb)}₂(μ -(1,4-dt))] binuclear complex was obtained from stoichiometric amounts (1:1) of *mer*-[Ru-Cl₃(dppb)H₂O] (0.100 g, 0.15 mmol) and *mer*-[RuCl₃-(dppb)(1,4-dt)] (0.115 g, 0.15 mmol) dissolved in CH₂Cl₂ (10 mL), with stirring for 12 h, at room temperature. The solution was then reduced to near 3 mL volume, followed by the addition of diethyl ether (10 mL) to form of a redviolet precipitate that was collected, washed with diethyl ether, dried and stored under vacuum in the absence of light. Yield: 190.0 mg, 89%. *Anal.* Calc. for C₆₀H₆₄Cl₆P₄-Ru2S₂, fw. 1388.08; C, 51.92; H, 4.65; S: 4.62. Found: C, 51.89; H, 4.68; S, 4.59%.

Single crystals were used for data collection and cell parameter determination on an Enraf-Nonius Kappa-CCD diffractometer, using Mo K α radiation ($\lambda = 0.71073$ Å). Data collection was made by using the COLLECT program [21]; integration and scaling of the reflections were performed with the HKL Denzo-Scalepack system of programs [22]. Absorption corrections were carried out by using the multi-scan method [23]. The structure was solved by direct methods with SHELXS-97 [24]. The models were refined by full-matrix least-squares on F^2 with SHELXL-97 [25]. All the hydrogen atoms were stereochemically positioned and refined with the riding model [26]. The NMR spectra were obtained in a T BRUKER DRX400 spectrometer at 298 K, using H₃PO₄ 85% as external reference for ${}^{31}P{}^{1}H{}$ (161 MHz). Elemental analyses were performed on a Fison equipment, EA 1108 model. The electrochemical experiments were carried out at room temperature in freshly distilled dichloromethane containing $0.1 \text{ mol } L^{-1} \text{ TBAP}$ under argon atmosphere. These measurements were performed by using an electrochemical analyzer from Bioanalytical Systems Inc. (BAS), model 100BW, at 25 ± 0.2 °C. A conventional electrochemical glass cell of one compartment containing three electrodes and two gas inlets was used in these experiments. A platinum foil and a pseudo-reference Ag/AgCl electrode prepared at the working day, 1 h before the experiments beginning, were used as working and auxiliary electrodes, respectively. The electrochemical potentials reported in this study were all converted to the normal hydrogen electrode (NHE), based on the ferrocene/ferrocenium ($Fc^{+/0}$) redox couple in CH₂Cl₂, as reported by Koelle et al. [27]. The transmission infrared spectra of the isolated species dispersed in CsI were obtained by using a BOMEM MICHEL-SON instrument, model 102. The electronic spectra, acquired on a HP8452A spectrophotometer, were obtained in CH₂Cl₂ solutions.

3. Results and discussion

The characterization of the *trans*-[RuCl₂(dppb)(1,4-dt)], *mer*-[RuCl₃(dppb)(1,4-dt)] and [{RuCl₃(dppb)}₂(μ -(1,4-dt))] complexes was carried out by cyclic voltammetry, electronic, infrared, NMR and EPR spectroscopies and X-ray diffraction when it was possible.

The very intense infrared absorption of the free 1,4-dt molecule at 664 cm⁻¹, which is assigned to the C–S stretching mode [12], shifts to lower frequency (650 cm⁻¹) and dramatically decreases in intensity in the spectra of the *trans*-[RuCl₂(dppb)(1,4-dt)] and [{RuCl₃(dppb)}₂(μ -(1,4-dt))] complexes. Similar behavior was observed for some similar systems [28,29]. These downshifts would suggest that in these complexes the 1,4-dithiane ligand is coordinated through both sulfur atoms to the metal center. On the other hand, the IR spectrum of the *mer*-[RuCl₃(dppb)-(1,4-dt)] complex shows two bands at 668 and 655 cm⁻¹

assigned to the C–S stretching modes of the 1,4-dt noncoordinated and coordinated to the Ru(III) ion, respectively [12]. Based on similar systems, these observations suggest that the 1,4-dt is coordinated through only one sulfur atom to the ruthenium in the *mer*-[RuCl₃(dppb)(1,4-dt)] complex [28]. For the *trans*-[RuCl₂(dppb)(1,4-dt)] complex, the Ru–Cl stretching frequency (ν Ru–Cl) is observed at 260 cm⁻¹. The presence of only one ν Ru–Cl band suggests the *trans* configuration for this complex. Conversely, two ν Ru–Cl bands would be expected for the *cis* configuration [30].

The X-ray structure of the *trans*-[RuCl₂(dppb)(1,4-dt)] complex clearly shows that the 1.4-dt ligand is coordinated in a bidentate mode to the ruthenium atom, in a distorted octahedron with the metal on a twofold axis with a trans configuration of the Cl atoms with the sulfur atoms necessarily trans to the phosphorous atoms (Fig. 1). The 1,4-dt molecule normally exists in a C_{2h} conformation similar to the chair form of cyclohexane [13]. The D_2 form of this molecule, similar to a boat, has not been detected in any appreciable amount of complexes since it has a relative unstable energy level, 5 kcal mol⁻¹ higher than the C_{2h} form [12]. Despite the energy difference between the C_{2h} and D_2 configurations, the crystallographic data point for the 1,4-dt D₂ conformer in the trans-[RuCl₂(dppb)(1,4dt)] complex, where 1,4-dt acts as a bidentate ligand. The relevant interatomic bond lengths and angles are listed in Table 2.

As expected for a relatively soft Ru (II) center, the Ru–P distances (2.297(1) and 2.317(1) Å) are shorter than the Ru–S distances (2.404(1) and 2.444(1) Å). The Ru–S, Ru–P and Ru–Cl bond lengths (Table 2) are within the well established range for Ru(II) complexes [31,32]. The S–C distances (ca. 1.824 Å) of the coordinated ligand are slightly elongated compared with the free 1,4-dt molecule (ca. 1.811 Å) [12]. The C–C bonds of the coordinated



Fig. 1. ORTEP view of the *trans*-[RuCl₂(dppb)(1,4-dt)] complex, showing the atoms labeling and the 50% probability ellipsoids.

Table 2
Selected bond lengths (Å) and angles (°) for the trans-[RuCl ₂ (dppb)(1,4-
dt)] complex

Bond length (\mathring{A})			
Ru–P(2)	2.297(1)	P(1)–C(111)	1.828(4)
Ru-P(1)	2.317(1)	P(1)–C(121)	1.844(4)
Ru-S(1)	2.404(1)	P(1)–C(131)	1.845(4)
Ru–Cl(2)	2.414(9)	P(2)–C(221)	1.836(4)
Ru–Cl(1)	2.439(9)	P(2)–C(231)	1.840(4)
Ru-S(2)	2.444(1)	P(2)–C(211)	1.855(4)
S(1)-C(11)	1.821(4)	C(11)–C(21)	1.540(5)
S(1)-C(12)	1.825(4)	C(12)-C(22)	1.537(6)
S(2)-C(22)	1.822(4)	C(111)–C(112)	1.392(6)
S(2)-C(21)	1.828(4)	C(111)-C(116)	1.393(6)
Bond angle (°)			
P(2)-Ru-P(1)	93.88(4)	S(1)-Ru-S(2)	74.80(3)
Cl(2)-Ru-S(2)	83.63(3)	P(1)-Ru-S(1)	171.32(4)
Cl(1)-Ru-S(2)	88.62(3)	P(1)-Ru-S(2)	96.79(4)
P(2)-Ru-Cl(2)	93.96(3)	C(11)-S(1)-C(12)	95.42(19)
P(1)-Ru-Cl(2)	87.73(3)	C(11)–S(1)–Ru	101.40(13)
S(1)-Ru-Cl(2)	93.35(3)	C(12)-S(1)-Ru	103.09(13)
P(2)-Ru-Cl(1)	94.44(3)	C(22)-S(2)-C(21)	94.97(19)
P(1)-Ru-Cl(1)	89.02(3)	C(22)-S(2)-Ru	101.31(14)
S(1)-Ru-Cl(1)	88.65(3)	C(21)–S(2)–Ru	101.49(13)
Cl(2)-Ru-Cl(1)	171.18(3)	C(111)–P(1)–C(121)	100.65(18)
P(2)-Ru-S(2)	168.95(4)	C(111)–P(1)–C(131)	101.97(18)

1,4-dt (average value of 1.54 Å) are elongated comparatively with the free species, 1.490(18) Å [12].

The angles of the bonds involving the ruthenium atom indicate that the chloride atoms are in the *trans* configuration (see Table 2). The observation that the C–S–C angles of the 1,4-dt change from ca. 99.0° (6) in the free molecule to 95.42° (19) in the coordinated ligand [13], strongly suggests that electronic density of the sulfur atoms was withdrawn upon coordination. The S–M–S angle is smaller for the ruthenium complex, 74.80(3)°, comparatively to the [PtI₂(1,4-dt)] compound, 79.74 (8)° [15]. This result is attributed to the size difference between these atoms, i.e. 134 pm for ruthenium and 138 pm for platinum [33].

The ³¹P{¹H} spectrum of the *trans*-[RuCl₂(dppb)(1,4dt)] complex showed one single signal, at δ 33.0 ppm, indicating that the symmetrical arrangement of the two phosphorous atoms is maintained in solution [30]. This signal presents a downshift in comparison with similar complexes in which the metal centers are bonded to a nitrogen atoms where the ³¹P{¹H} NMR chemical shifts are close to 42 ppm [30].

The electronic absorption spectrum data are shown in the Table 3. Apart from the transitions involving the phosphine ligands, observed at 240 nm [34], the UV/Vis spectrum of the *trans*-[RuCl₂(dppb)(1,4-dt)] complex, presents one band at 452 nm ($\varepsilon = 290 \text{ L mol}^{-1} \text{ cm}^{-1}$), in CH₂Cl₂ solution. This absorption band is sensitive toward solvent changes (425 nm in *N*,*N'*-dimethylformamide) and was assigned to the metal-to-ligand charge transfer transition, (1,4-dt) $\pi \leftarrow d\pi$ (Ru). Charge transfer transitions of low extinction coefficients were also observed for the [Ru(NH₃)₅L]²⁺ type complexes, where L = dithioether ligands (see Table 3) [4].

Table 3

Electronic absorptions	data, λ (nm), a	$\varepsilon (L \text{ mol}^{-1} \text{ cm})$	$^{-1}$), and R	a ^{III/II} half-
wave formal potential,	$E_{1/2}$ (V vs. NF	HE), for some	ruthenium	complexes

Complex	λ	$\varepsilon \times (10^{-3})$	$E_{1/2}$	Reference
mer-[RuCl ₃ (dppb)(1,4-dt)]	530	2.0	0.45	this work
	420	1.6		
	347	2.2		
$[{RuCl_3(dppb)}_2(\mu-(1,4-dt))]$	530	3.8	0.45	this work
	420	3.2		
	347	4.2		
$\mathit{mer}\text{-}[RuCl_3(dppb)H_2O]$	533	1.6	0.34	[19]
	420	1.3		
	350	1.7		

For the mer-[RuCl₃(dppb)(1,4-dt)] complex, the absorption at 530 nm is observed with higher intensity ($\varepsilon = 2.0 \times$ $10^3 \,\mathrm{L}\,\mathrm{mol}^{-1}\,\mathrm{cm}^{-1}$) when compared with the band at 533 nm for the *mer*-[RuCl₃(dppb)H₂O] complex ($\varepsilon = 1.6 \times$ $10^3 \,\mathrm{L}\,\mathrm{mol}^{-1}\,\mathrm{cm}^{-1}$), in the same experimental conditions [19]. The band at 533 nm in the spectrum of mer-[RuCl₃-(dppb)H₂O] complex has been assigned as a ligand-to-metal charge transfer (LMCT), (Ru^{III}) $d\pi \leftarrow p\pi$ (Cl) [12]. For the *mer*-[RuCl₃(dppb)(1,4-dt)] and [{RuCl₃(dppb)}₂-(μ -(1,4dt))] complexes, the absorption bands at 530 nm occur with higher intensity than that of mer-[RuCl₃-(dppb)H₂O] complex probably due to the contribution of the (Ru^{III}) $d\pi \leftarrow p\pi$ (S) LMCT [26]. As expected, for the [{RuCl₃-(dppb)₂(μ -(1,4-dt))] binuclear complex the extinction coefficient of the band at 530 nm is almost two times more intense ($\varepsilon = 3.8 \times 10^3 \text{ L mol}^{-1} \text{ cm}^{-1}$) than that observed for the *mer*-[$RuCl_3(dppb)(1,4-dt)$] mononuclear complex.

The EPR spectrum of the *mer*-[RuCl₃(dppb)(1,4-dt)] complex, in CH₂Cl₂, differently of that acquired for the aqua-complex that presents zero field signals [14], shows three *g*-values in 2.87, 2.15 and 1.73. This result is typical of Ru(III) species with rhombic distortions [35], suggesting that the 1,4-dt is coordinated in a monodentate mode.

The EPR spectrum of the binuclear $[{RuCl_3(dppb)}_2(\mu-(1,4-dt))]$ complex, in CH₂Cl₂, shows a large signal (g = 2,31) which is characteristic of complexes with exchange interaction between the ruthenium atoms [36].

The cyclic voltammograms obtained for the *trans*-[RuCl₂(dppb)(1,4-dt)] complex in CH₂Cl₂ evidenced a redox process with half-wave formal potential, $E_{1/2} =$ 0.77 V. This value was observed to be independent of the sweep rate from 0.05 to 0.5 V s⁻¹. In addition, it was observed that the ratio between the anodic and cathodic currents is almost unit, the difference between the anodic and cathodic potentials, ΔE , is approximately equals to 0.07 V, and plots of ip versus $v^{1/2}$ are linear. These results indicate that the Ru^{III}/Ru^{II} redox process of this complex is reversible, involving one-electron transfer and diffusioncontrolled [37]. The $E_{1/2}$ value observed for the *trans*-[RuCl₂-(dppb)(bipy)], $E_{1/2} = 0.66$ V, where bipy = 2,2'-bipyridine, in the same experimental conditions [30]. This difference reflects the stronger π -acid property of the 1,4-dt compared

Table 4 $E_{1/2}$ values (in V vs. NHE) for Ruthenium complexes.

System	L	$E_{1/2}$	Reference
[RuCl ₂ (dppb)(L)]	NH ₃ ^a	0.59	[23]
	Pyridine ^b	0.68	[23]
	Bipy	0.66	[23]
	1,4-Dithiane	0.77	this work
$[Ru(NH_3)_5(L)]^{2+}$	Pyridine	0.30	[38]
	4,4'-Dithiodipyridine	0.40	[39]
	Dimethyl sulfide	0.50	[40]
	1,4-Dithiane	0.52	[4]
	1,3-Dithiane	0.55	[4]
	1,2-Dithiane	0.66	[4]

^a [RuCl₂(dppb)(NH₃)₂].

^b [RuCl₂(dppb)(py)₂], where py = pyridine.

with bipy ligand, when bonded to Ru(II) in the *trans*-[RuCl₂(dppb)(LL)] type complexes. For comparison, the electrochemical data for a series of $[Ru(NH_3)_5(L)]^{2+}$ and *trans*-[RuCl₂(dppb)(LL)] type complexes are displayed in Table 4.

For both type of complexes, the $E_{1/2}$ values show the stability enhancement of the reduced Ru(II) state when the metal center is coordinated through sulfur instead of nitrogen pyridine ring atom [41,42]. This data reflect the pronounced π -acid effect of the sulfur atom, especially for the dithiane isomers (see Table 4). In these cases, the higher values are assigned to the extra interaction between the coordinated and noncoordinated sulfur atoms which decreases as the S–S distance increases [4].

4. Conclusion

The data collected in this work for the *trans*-[RuCl₂-(dppb)(1,4-dt)], *mer*-[RuCl₃(dppb)(1,4-dt)] and [{RuCl₃-(dppb)}₂(μ -(1,4-dt))] complexes where the 1,4-dithiane ligand acts as bidentate, monodentate and ambidentate forms, respectively, exemplify the conformational versatility of this ligand towards the coordination chemistry. The *trans*-[RuCl₂(dppb)(1,4-dt)] complex consists in the first example of an hexacoordinated ruthenium complex with 1,4-dithiane as a bidentate ligand, in a D₂ conformation.

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Center, CCDC No. 279648. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or http://www. ccdc.cam.ac.uk).

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References

- [1] H. Beinert, Eur. J. Biochem. 267 (2000) 5657.
- [2] E.I. Stiefel, In: Transition Metal Sulfur Chemistry, Biological and Industrial Significance, ACS Symposium Series, Washington, 1996.
- [3] C.A. Stein, H. Taube, J. Am. Chem. Soc. 100 (1978) 1635.
- [4] C.G. Kuehn, S.S. Isied, Prog. Inorg. Chem. 27 (1979) 153.
- [5] A. Streitweiser Jr., S.P. Ewing, J. Am. Chem. Soc. 97 (1975) 190.
- [6] A. Streitweiser Jr., J.G. Williams, J. Am. Chem. Soc. 97 (1975) 191.
- [7] S. Oae, T.D. Joyce, Organic Sulfur Chemistry: Structure and Mechanism, CRC Press Inc., London, 1991.
- [8] S. Wolfe, F. Bernardi, I.G. Csizmadia, A. Mangini, Organic Sulfur Chemistry, Elsevier, Amsterdam, 1985, pp. 133.
- [9] C.G. Kuehn, H. Taube, J. Am. Chem. Soc. 98 (1976) 689.
- [10] D. Sellmann, J. Sutter, Acc. Chem. Res. 30 (1997) 460.
- [11] J.C. Bayo'n, C. Claver, A.M. Masdeu-Bultó, Coord. Chem. Rev. 193 (1999) 73.
- [12] T.E. Rosso, M.W. Ellzy, J.O. Jensen, H.F. Hameka, D. Zeroka, Spectrochim. Acta A 55 (1999) 121.
- [13] R.E. March, Acta Crystallogr. 8 (1955) 91.
- [14] R.D. Adams, L. Chen, J.H. Yamamoto, Inorg. Chim. Acta 229 (1995) 47.
- [15] M.H. Johansson, H.P. Engelbrecht, Acta Crystallogr. E 57 (2001) m114.
- [16] M. Green, M. Draganjac, Y. Jiang, P.M. Nave, A.W. Cordes, C.D. Bryan, J.K. Dixon, S.L. Folkert, C.-H. Yu, J. Chem. Crystallogr. 33 (2003) 473.
- [17] U. Frey, S. Elmroth, B. Moullet, L.I. Elding, A.E. Merbach, Inorg. Chem. 30 (1991) 5033.
- [18] D.D. Perrin, W.L.F. Armarego, Purification of Laboratory Chemicals, 3rd ed., Pergamon Press, Oxford, 1988.
- [19] L.R. Dinelli, A.A. Batista, K. Wohnrath, M.P. de Araujo, S.L. Queiroz, M.R. Bonfadini, G. Oliva, O.R. Nascimento, P.W. Cyr, K.S. MacFarlane, B.R. James, Inorg. Chem. 38 (1999) 5341.
- [20] C.W. Jung, P.E. Garrou, P.R. Hoffman, K.G. Caulton, Inorg. Chem. 23 (1984) 726.
- [21] Enraf-Nonius, COLLECT, Nonius BV, Delft, The Netherlands, 1997– 2000.
- [22] Z. Otwinowski, W. Minor, HKL Denzo and Scalepack, in: C.W. CarterJr., R.M. Sweet (Eds.), Methods in Enzimology, vol. 276, Academic Press, New York, 1997, p. 307.
- [23] R.H. Blessing, Acta Crystallogr. A 51 (1995) 33.
- [24] G.M. Sheldrick, SHELXS-97. Program For Crystal Structure Resolution, University of Göttingen, Göttingen, Germany, 1997.
- [25] G.M. Sheldrick, SHELXL-97. Program for Crystal Structures Analysis, University of Göttingen, Göttingen, Germany, 1997.
- [26] L.J. Farrugia, J. Appl. Cryst. 30 (1997) 565.
- [27] U. Koelle, F. Khouzami, Angew. Chem., Int. Ed. 19 (1980) 640.
- [28] S.S.S. Borges, A.L. Coelho, I.S. Moreira, M.A.B. Araujo, Polyhedron 13 (1994) 1015.
- [29] S.R. Wade, G.R. Willey, Inorg. Chim. Acta 72 (1983) 201.
- [30] S.L. Queiroz, A.A. Batista, G. Oliva, M.T.P. Gambardella, R.H.A. Santos, K.S. MacFarlane, S.J. Rettig, B.R. James, Inorg. Chim. Acta 267 (1998) 209.
- [31] D.T.T. Yapp, S.J. Rettig, B.R. James, K.A. Skov, Inorg. Chem. 36 (1997) 5635.
- [32] D.C. Mudalige, E.S. Ma, S.J. Rettig, B.R. James, W.R. Cullen, Inorg. Chem. 36 (1997) 5426.
- [33] S.-X. Xiao, W.C. Trogler, D.E. Ellis, Z. Berkovitch-Yellin, J. Am. Chem. Soc. 105 (1983) 7033.
- [34] A.A. Batista, E.A. Polato, S.L. Queiroz, O.R. Nascimento, B.R. James, S.J. Rettig, Inorg. Chim. Acta 230 (1995) 111.
- [35] Q.A. Paula, A.A. Batista, O.R. Nascimento, A.J. Costa-Filho, M.S. Schultz, M. Bonfadini, G. Oliva, J. Braz. Chem. Soc. 11 (2000) 530.
- [36] A.J. Bard, L.R. Faulkner, Electrochemical Methods, Fundamentals and Applications, Wiley, New York, 1980.

- [37] T. Matsubara, P.C. Ford, Inorg. Chem. 15 (1976) 1107.
- [38] D.W. Franco, I.S. Moreira, Inorg. Chem. 33 (1994) 1607.
- [39] C.G. Kuehn, S.S. Isied, J. Am. Chem. Soc. 98 (1976) 689.
- [40] D. Sellmann, J. Sutter, Acc. Chem. Res. 30 (1997) 460.
- [41] A. Wu, D.C. Kennedy, B.O. Patrick, B.R. James, Inorg. Chem. Comm. 6 (2003) 996.
- [42] M.O. Santiago, C.L. Donnici, I.S. Moreira, R.M. Carlos, S.L. Queiroz, A.A. Batista, Polyhedron 22 (2003) 3205.