Transition Metal Complexes with Sulfur Ligands, 131[◇]

Synthesis, Structure, and Properties of Osmium Complexes Containing [Os('S_4')] and [Os('S_2')$_2$] Fragments ('S_4'$^{2-}$ = 1,2-Bis(2-mercaptophenylthio)-ethane(2−), 'S_2'$^{2-}$ = 1,2-Benzenedithiolate)☆

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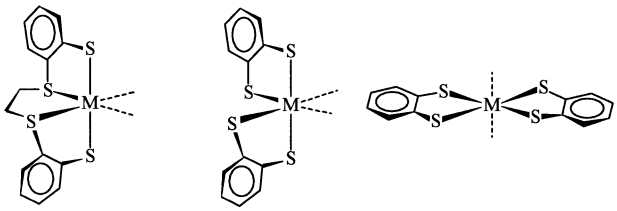
In search for osmium complexes with sulfur-dominated coordination spheres that potentially bind and activate or stabilize nitrogenase relevant small molecules, several osmium−sulfur complexes containing 1,2-bis(2-mercaptophenylthio)ethane(2−) ('S_4'$^{2-}$) and benzenedithiolate ('S_2'$^{2-}$) ligands were synthesized. [Os^{II}(PR_3)$_2$('S_4')] [R = Ph (**1**), Et (**2**)], [Os^{IV}(PR_3)$_2$('S_2')$_2$] [R = Et (**3**), Pr(**4**), Me(**5**), Ph(**6**)], [Os^{IV}(PCy_3)('S_2')$_2$] (**7**), ($PHCy_3$)[Os^{III}('S_2')$_2$] (**8a**), (NMe_4)-[Os^{III}('S_2')$_2$] (**8b**), and (NBu_4)$_2$[Os^{IV}('S_2')$_3$] (**9b**) were obtained in reactions starting from commercially available osmium compounds and the sulfur and phosphane ligands. The presence or absence of reducing solvents strongly influenced these reactions. Octahedral (**3**), (**4**), and ($PHCy_3$)$_2$[Os^{IV}('S_2')$_3$] (**9a**) were characterized by X-ray structure analysis, leading to the conclusion that despite the high oxidation state of the osmium centers, innocent dithiolate ligands are present. The stabilization of the Os^{IV} centers is traced back to S→M π donation. Close inspection of **1** and **2** revealed a large influence of the phosphane ligands on the stability of Os^{II} thioether complexes. While **1** is reasonable stable, **2** readily gives **3** and ethylene via intramolecular 'S_4'$^{2-}$ ligand reduction and Os^{II} → Os^{IV} oxidation. UV-Vis spectra of **3**−**5** indicate phosphane dissociation in solution leading to pentacoordinate [Os(PR_3)('S_2')$_2$] complexes. This was confirmed by the synthesis of pentacoordinate [Os(PCy_3)('S_2')$_2$] (**7**).

Introduction

Transition metals in sulfur-dominated coordination spheres form the active centers of numerous oxidoreductases such as nitrogenases, hydrogenases and CO dehydrogenase[1]. In the search for low-molecular compounds that combine structural and reactivity features of these [MS] enzymes we have found that transition metal complexes containing [M('S_4')] (**A**) or [M('S_2')$_2$] fragments (**B** and **C**) ['S_4'$^{2-}$ = 1,2-bis(2-mercaptophenylthio)ethane(2−); 'S_2'$^{2-}$ = 1,2-benzenedithiolate(2−)] can bind and activate or stabilize a considerable number of small molecules that are key intermediates in enzymatic processes[2]. In a few cases, catalytic reaction cycles could be developed[3]. For example, [Rh(L)('S_4')]$^+$ complexes (L = CO, PCy_3) catalyze the heterolytic cleavage of dihydrogen and D_2/H^+ exchange that are features of hydrogenases[4].

Iron and ruthenium [M('S_4')] complexes bind key intermediates of N_2 fixation such as N_2H_2, N_2H_4 and NH_3[2]. However, attempts to coordinate also dinitrogen to such fragments have as yet remained unsuccessful. In this context it is to be noted that transition metal N_2 complexes with sulfur dominated coordination spheres are conspicuously rare. In fact, [Mo(N_2)$_2$(octamethyltetrathiacyclohexadecane)] is the only example for the coordination of N_2 to a metal center carrying exclusively sulfur coligands[5].



For this reason, we have started to explore the osmium chemistry of 'S_4'$^{2-}$ and 'S_2'$^{2-}$ ligands, anticipating that with [Os('S_4')] or [Os('S_2')$_n$] species complexes could become accessible that proved inaccessible with the iron and ruthenium homologues. [Os('S_4')] complexes have been unknown as yet, the chemistry of osmium benzene-1,2-dithiolate and related ligands is largely unexplored[6]. No benzenedithiolate complex was known, and only a very few complexes with toluenedithiolate, maleonitriledithiolate and similar ligands have been described[7].

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Results

[Os($'S_4'$)] Complexes

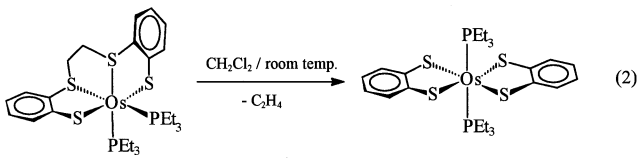
Two target complexes containing [Os($'S_4'$)] cores could be obtained from commercially available $OsCl_3 \cdot x\,H_2O$ by the reaction according to eq. (1).

$$OsCl_3{\cdot}xH_2O + {'S_4'}\text{-}H_2 + PR_3\ \text{exc.} \xrightarrow[\text{reflux}]{\text{THF / MeOH}} [Os(PR_3)_2({'S_4'})] \quad (1)$$

R = Ph (**1**), Et (**2**)

Heating to reflux, an excess of the respective phosphane, and the use of the solvent mixture MeOH/THF proved necessary. The excess of phosphane and the methanol probably serve as reducing reagents for $OsCl_3 \cdot x\,H_2O$. The methanol additionally causes precipitation of the resultant yellow to yellow-green [Os(PR_3)$_2$($'S_4'$)] complexes **1** (PPh_3) and **2** (PEt_3) from the reaction solutions. When pure THF was used as solvent, neither **1** nor **2** could be isolated.

In these experiments, it was noted that **2** is rather thermolabile. The reaction leading to its formation according to eq. (1) had to be quenched after ca. one hour of refluxing in order to avoid a drastic decrease in yield. Already at room temperature, [Os(PEt_3)$_2$($'S_4'$)] (**2**) slowly decomposes according to eq. (2).



(2)

2 **3**

An intramolecular redox reaction leads to release of C_2H_4 and formation of the Os^{IV} complex [Os(PEt_3)$_2$($'S_2'$)$_2$] (**3**). The evolving ethylene could be detected by its ^{1}H-NMR signal at $\delta = 5.24$[8].

Complexes **1** and **2** were characterized by the common spectroscopic methods. For example, the ^{1}H-NMR spectra of **1** and **2** exhibit signal patterns that are typical of C_2 symmetrical [ML_2($'S_4'$)][9] complexes. Cyclic voltammetry of **2** further revealed two reversible redox waves at $E_{1/2} = -20$ mV and $E_{1/2} = 950$ mV that can be assigned to the formation of the $[\mathbf{2}]^+$ and $[\mathbf{2}]^{2+}$ cations.

Attempts to substitute one PPh_3 ligand of **1** by N_2H_4 or CO remained unsuccessful. Complex **1** proved substitution inert even at elevated temperatures and pressures. In this respect, **1** contrasts the homologous [Ru(PPh_3)$_2$($'S_4'$)] which readily exchanges one PPh_3 ligand for numerous two electron donors at room temperature[10].

The facile formation of the Os^{IV} complex [Os(PEt_3)$_2$($'S_2'$)$_2$] (**3**) from the Os^{II} complex [Os(PEt_3)$_2$($'S_4'$)] (**2**) and the rareness of osmium benzene dithiolate complexes in higher oxidation states prompted us to investigate these species more closely, which are also potentially suited to yield complexes with [Os($'S_4'$)] cores via template alkylations[9].

Synthesis and Characterization of the Hexa- and Pentacoordinate Os^{IV} Complexes [Os(PR_3)$_2$($'S_2'$)$_2$] (R = Me, Et, Pr, Ph), and [Os(PCy_3)($'S_2'$)$_2$]

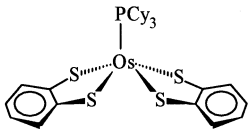
[Os(PR_3)$_2$($'S_2'$)$_2$] complexes were obtained with various PR_3 ligands according to eq. (3).

$$(NH_4)_2[OsBr_6] + 2\ {'S_2'}\text{-}Li_2 + 2\ PR_3 \xrightarrow[\text{reflux / 19 h}]{\text{THF / MeOH}} [Os(PR_3)_2({'S_2'})_2] \quad (3)$$

R = Et (**3**), Pr (**4**), Me (**5**), Ph(**6**)

The resultant complexes **3**–**6** are gray-black to black-violet and diamagnetic. While the PMe_3 and PPh_3 complexes **5** and **6** are only very sparingly soluble, the PEt_3 and PPr_3 complexes **3** and **4** readily dissolve in common organic solvents. The complexes were characterized by elemental analyses and spectroscopic methods, and **3** and **4** also by X-ray structure analyses. The Os^{IV} complexes **3** and **4** each exhibit a characteristic low field shifted ^{31}P-NMR signal in the region of $\delta = -200$ and contrast in this respect the Os^{II} complexes **1** and **2** whose ^{31}P-NMR signals appear at δ ca. -20. No ^{31}P-NMR spectrum could be recorded of the sparingly soluble PMe_3 complex **5**. The ^{31}P-NMR spectrum of the PPh_3 complex **6** revealed one broad signal at $\delta = -46.5$. The shift of this signal indicates dissociation of **6** to give pentacoordinate [Os(PPh_3)($'S_2'$)$_2$] (vide infra).

When the reaction according to eq. (3) was carried out with the sterically very demanding phosphane PCy_3, no hexacoordinate complex but the pentacoordinate [Os(PCy_3)($'S_2'$)$_2$] (**7**) formed. This even occurred when a fourfold excess of PCy_3 was applied. Complex **7** was obtained as violet microcrystals that proved diamagnetic and well soluble in organic solvents. The number and splitting of the ^{1}H- and ^{13}C-NMR signals of **7** indicate that **7** possesses lateral symmetry. The ^{31}P-NMR spectrum exhibits one signal at $\delta = -29.2$ whose chemical shift contrasts the ^{31}P-NMR shifts (-200 ppm) of the bisphosphane complexes **3** and **4**. The FD mass spectrum of **7** revealed the molecular ion at $m/z = 752$ and no ions of higher masses. These results and, in addition, the UV-Vis-NIR spectroscopic properties of **7** versus those of **3**–**5** (vide infra) indicate that **7** is mononuclear possessing the structure indicated by formula **D**.



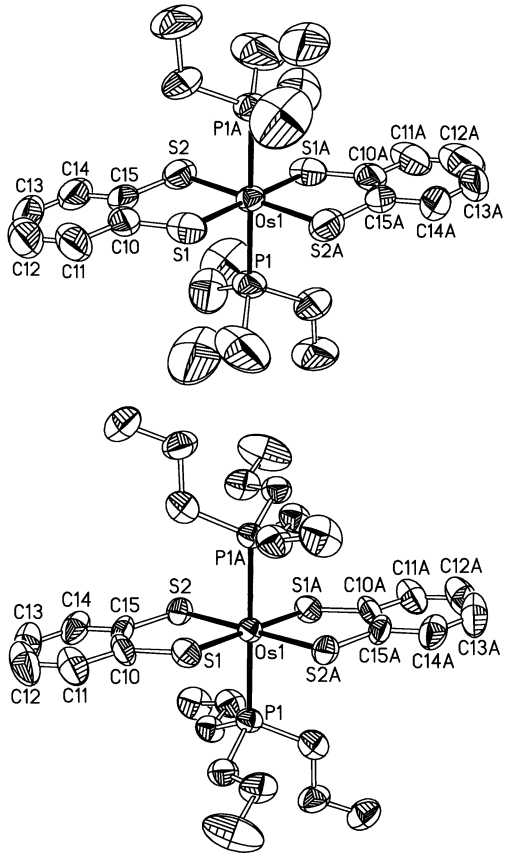
D

X-ray Structure Determination of [Os(PEt_3)$_2$($'S_2'$)$_2$] (3) and [Os(PPr_3)$_2$($'S_2'$)$_2$] (4)

The molecular structures of **3** and **4** are depicted in Figure 1.

Complexes **3** and **4** both possess crystallographically imposed inversion symmetry and exhibit pseudo-octrahedral coordination with the phosphane ligands in *trans* positions. The corresponding Os–P and Os–S distances in **3** and **4**

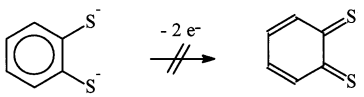
Figure 1. ORTEP plots of a) $[Os(PEt_3)_2(′S_2′)_2]$ (**3**) and b) $[Os(PPr_3)_2(′S_2′)_2]$ (**4**) drawn with 50% probability ellipsoids (H atoms omitted)[a]



[a] Selected distances [pm] and angles [°]: **3**: Os(1)−S(1) 231.1(2), Os(1)−S(2) 232.8(2), Os(1)−P(1) 244.8(2), S(1)−C(10) 174.8(8), S(2)−C(15) 173.1(8), C(10)−C(11) 142.4(10), C(11)−C(12) 138(2), C(12)−C(13) 130(3), C(14)−C(15) 141.2(9), C(10)−C(15) 139.0(11). S(1)−Os(1)−P(1) 90.58(7), S(2)−Os(1)−P(1) 90.46(7), S(1)−Os(1)−S(2) 86.33(7). − **4**: Os(1)−S(1) 231.2(2), Os(1)−S(2) 231.7(2), Os(1)−P(1) 244.2(2), S(1)−C(10) 172.8(11), S(2)−C(15) 172.6(9), C(10)−C(11) 137.9(13), C(11)−C(12) 137(2), C(12)−C(13) 136(2), C(14)−C(15) 138.1(12), C(10)−C(15) 145.3(14), S(1)−Os(1)−P(1) 89.85(8), S(2)−Os(1)−P(1) 90.65(8), S(1)−Os(1)−S(2) 86.29(8).

are identical within the 3σ criterion. The averaged Os−S distances of **3** and **4** [231.7(2) pm] are identical to the Ru−S distances of the analogous $[Ru(PMe_3)_2(′S_2′)_2]$ [231.7(1) pm][11] and are in the usual range of osmium(IV) thiolate complexes. Os−S distances of osmium(IV) thiolate complexes cover a range from 220 to 241 pm and depend on the coordination number and geometry[12].

Detailed inspection of the C−C and C−S bond distances in the $C_6H_4S_2^{2-}$ ligands revealed no evidence for a partial oxidation of the benzenedithiolate ligands to give dithiocyclohexadiene units according to eq. (4).



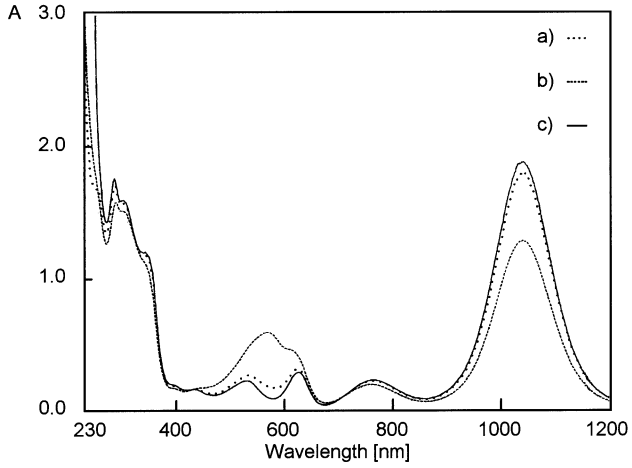
(4)

In this respect, the Os^{IV} complexes **3** and **4** behave identical to the homologous Fe^{IV} complex $[Fe(PMe_3)_2(′S_2′)_2]$ and related species, which have been extensively discussed previously[13]. They allow to conclude that benzenedithiolate behaves as "innocent" dithiolate ligand such that stabilization of higher metal oxidation states is rather due to increasing S→M π donation.

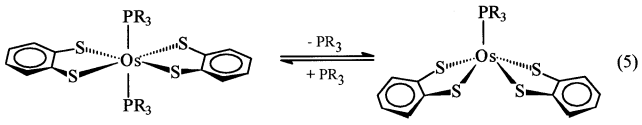
Reversible Dissociation of $[Os(PR_3)_2(′S_2′)_2]$ Complexes; UV-Vis-NIR Spectra

The UV-Vis-NIR spectra of the hexacoordinate complexes **3**−**5** exhibit very intense absorptions (ε > 40000 $l·mol^{-1}·cm^{-1}$) in the region of 950−1050 nm. These bands can be assigned to sulfur-metal LMCT transitions, and they slowly decrease in intensity when dilute solutions of **3**−**5** are kept at room temperature. Simultaneously, the solutions change color from deep red to violet blue. Addition of the respective phosphane reverses these effects (Figure 2).

Figure 2. UV-Vis-NIR spectra of a) **4** in CH_2Cl_2 (λ_{max} = 1043 nm, ε = 42740 $lmol^{-1}cm^{-1}$), b) after 12 h, c) after addition of excessive PPr_3



These observations indicate that the hexa-coordinate complexes reversibly dissociate in solution to yield pentacoordinate species according to eq. (5).



(5)

4

This assumption is supported by the electronic spectrum of the pentacoordinate complex $[Os(PCy_3)(′S_2′)_2]$ (**7**) which does not exhibit an absorption in the NIR region. It is further corroborated by the FD mass spectra of complexes **3**−**5**, which all show intensive signals of the fragment ions $[Os(PR_3)(′S_2′)_2]^+$ in addition to the molecular ions.

Synthesis and Properties of the Os^{III} Complex $(PHCy_3)[Os(′S_2′)_2]$ (8a)

The $[Os(PR_3)_2(′S_4′)]$ complexes **1** and **2** had shown that the solvent and reaction time could markedly influence the course of synthesis reactions. This was also observed when $(NH_4)_2[OsBr_6]$, $′S_2′$-Li_2 and an excess of PCy_3 were com-

bined not in THF as in the reaction according to eq. (3), but in a mixture of THF and MeOH, and refluxed for three days. In this case, not the Os^{IV} complex **7** but the Os^{III} complex $(PHCy_3)[Os('S_2')_2]$ (**8a**) formed as major product according to eq. (6).

$$(NH_4)_2[OsBr_6] + 2\ 'S_2'\text{-}Li_2 + \text{exc. } PCy_3 \xrightarrow[3\ d,\ reflux]{THF\ /\ MeOH} (PHCy_3)[Os('S_2')_2] \quad (6)$$

8a

Complex **8a** precipitated as orange micro-crystals from the boiling reaction mixture. The violet-blue $[Os(PCy_3)('S_2')_2]$ (**7**) formed only as minor by-product and could be isolated in negligible amounts when the mother liquors were cooled to −20 °C.

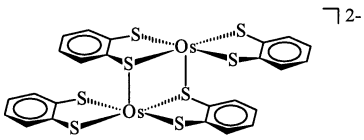
Apparently, in the reaction according to eq. (6) the solvent MeOH and possibly also the excess PCy_3 act as reducing reagents upon $(NH_4)_2[OsBr_6]$. Complex **8a**, whose elemental composition differs from that of the Os^{IV} complex $[Os(PCy_3)('S_2')]$ (**7**) only by one proton, was identified by its spectra, magnetism, and by the metathesis reaction with NMe_4OH yielding the NMe_4^+ salt $(NMe_4)[Os('S_2')_2]$ (**8b**) according to eq. (7).

$$(PHCy_3)[Os('S_2')_2] + \text{exc. } NMe_4OH \xrightarrow{THF} (NMe_4)[Os('S_2')_2] + (PHCy_3)OH \quad (7)$$

8a **8b**

The presence of the $PHCy_3^+$ cation in **8a** could further be concluded from the ^{1}H-NMR spectrum of **8a** which revealed the characteristic ^1J(PH) coupling constant (475 Hz) of the $PHCy_3^+$ cation.

8a is paramagnetic and exhibits a magnetic moment of μ_{eff} = 3.04 μ_B. The magnetic moment is compatible with three unpaired electrons at Os^{III} centers in square planar or tetragonal pyramidal coordination. In contrast octahedral Os^{III} thiolate phosphane complexes with one unpaired electron exhibit magnetic moments in the range μ_{eff} = 1.85−1.98 μ_B[14]. The structure of the anion in **8a** remains unknown, however, the dinuclear structure of the homologous iron complex that was revealed by X-ray structure analysis[15] suggests a similar structure for **8a** as indicated by formula **E.**



E

Complex **8a** is sparingly soluble in THF or MeOH, but readily dissolves in CH_2Cl_2. Also in the absence of air, the resultant orange CH_2Cl_2 solutions are unstable and turn to deep violet in the course of a few hours, because **8a** spontaneously forms **7** according to eq. (8).

$$(PHCy_3)[Os('S_2')_2] \xrightarrow[room\ temp.]{CH_2Cl_2} [Os(PCy_3)('S_2')_2] + H^+ + e^- \quad (8)$$

8a **7**

This reaction involves an $Os^{III} \rightarrow Os^{IV}$ oxidation, but the oxidizing reagent as well as the fate of the formally released proton and electron remain unknown. Evolution of H_2 could not be observed[16].

Synthesis and Properties of $(NBu_4)_2[Os('S_2')_3]$ and $(PHCy_3)_2[Os('S_2')_3]$

Single crystals that precipitated in minor amounts from the mother liquors of the $[Os(PCy_3)('S_2')_2]$ (**7**) synthesis could be characterized by X-ray structure analysis revealing that the crystals contained the salt $(PHCy_3)_2[Os('S_2')_3]$ (**9a**). The NBu_4^+ salt $(NBu_4)_2[Os('S_2')_3]$ (**9b**) was subsequently obtained in the straight forward synthesis according to eq. (9).

$$(NH_4)_2[OsBr_6] + 6\ NBu_4OH + 3\ 'S_2'\text{-}H_2 \xrightarrow[2\ h,\ reflux]{MeOH} (NBu_4)_2[Os('S_2')_3] \quad (9)$$

9b

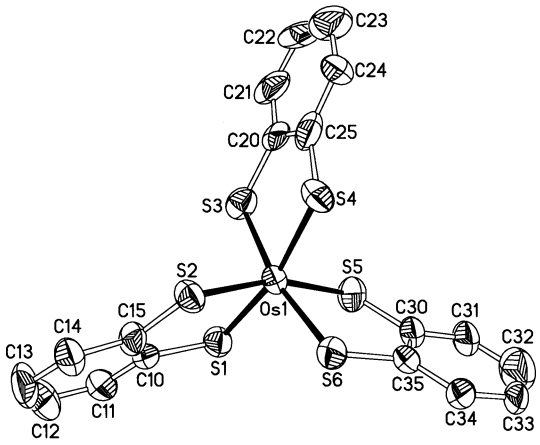
9b was isolated in form of dark red crystals, which were characterized by elemental analysis and spectroscopic methods. **9b** is diamagnetic. Its cyclic voltammogramm shows one irreversible (−580 mV) and two reversible anodic redox waves (−80 mV and 180 mV). They can be assigned to the redox steps indicated by eq. (10).

$$[Os('S_2')_3]^{3-} \underset{-e^-}{\overset{+e^-}{\leftarrow}} [Os('S_2')_3]^{2-} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [Os('S_2')_3]^{-} \underset{+e^-}{\overset{-e^-}{\rightleftharpoons}} [Os('S_2')_3]^{0} \quad (10)$$

- 580 mV - 80 mV 180 mV

Figure 3 depicts the molecular structure of the anion of $(PHCy_3)_2[Os('S_2')_3]$ (**9a**).

Figure 3. ORTEP plot of the anion of $(PHCy_3)_2[Os('S_2')_3]$ (**9a**) drawn with 50% probability ellipsoids (H atoms omitted)[a]



[a] Selected distances [pm]: Os(1)−S(1) 236.6(2), Os(1)−S(2) 235.7(2), Os(1)−S(3) 235.6(2), Os(1)−S(4) 234.5(3), Os(1)−S(5) 235.0(3), Os(1)−S(6) 236.0(3), S(1)−C(10) 175.8(9), S(2)−C(15) 173.6(9), S(3)−C(20) 177.4(10), S(4)−C(25) 172.7(11), S(5)−C(30) 176.7(11), S(6)−C(35) 177.2(10); average S−S(intra) 3.190, S−S(inter) 3.385. − Selected angles [°]: S(1)−Os(1)−S(4) 167.40(9), S(2)−Os(1)−S(5) 163.53(9), S(3)−Os(1)−S(6) 168.23(8), S(1)−Os(1)−S(2) 85.06(8), S(3)−Os(1)−S(4) 85.40(9), S(5)−Os(1)−S(6) 85.23(10).

The average Os−S distances in **9a** [235.6(3) pm] are longer than those in the neutral $[Os(PR_3)_2('S_2')_2]$ complexes **3** and **4** [231.7(2) pm]. This can be traced back to reduced

S→M π donation in **9a** which unlike **3** and **4** does not exhibit π acceptor phosphane ligands. As for **3** and **4**, scrutinizing the C−C and C−S distances yielded no evidence for cyclohexadienedithioketone-like structures of the $C_6H_4S_2$ ligands.

An important structural feature of numerous dithiolene type $[M(S_2C_2R_2)_3]$ complexes (R = H, Ph) is their trigonal prismatic coordination geometry. Potential factors, e.g., S···S interactions between vicinal S donors, metal-ligand π bonding and the overall charge of the complexes, stabilizing the trigonal pyramidal versus the octahedral coordination geometry have been elucidated[17]. The analysis of the S−Os−S angles in **9a** shows that **9a** is best described to possess pseudo-octahedral geometry. Due to the chelate bite of the $C_6H_4S_2$ units, the ideal S−M−S angle which can be reached for *'trans'* sulfur donors in octahedral complexes is 170° (instead of 180°)[18]. The corresponding angle in trigonal prismatic complexes is 136°. The respective S−Os−S angles in **9a** vary between 163.5(1)° and 168.2(1)° and are thus close to the ideal angle for octahedral coordination.

A literature search revealed that there are only two other dianionic $[M('S_2')_3]^{2-}$ complexes (M = Ti[19], Zr[18]) that exhibit octahedral geometry. The anion in $(AsPh_4)_2[W('S_2')_3]$ shows average S−W−S angles of 151.6°[20]. It thus represents an intermediate between octahedral and trigonal prismatic coordination comparable to the structure of the monoanion in $(AsPh_4)[Nb('S_2')_3]$[21].

Discussion and Summary

The Os^{II} complexes $[Os(PR_3)_2('S_4')]$ (**1**) (R = Ph) and **2** (R = Et) could be directly synthesized from $'S_4'^{2-}$, the respective phosphane and commercially available $OsCl_3 \cdot x\ H_2O$. Complexes **1** and **2** revealed a remarkable influence of the phosphane coligands upon the complex stability and reactivity. **1** proved temperature stable and substitution inert contrasting the homologous $[Ru(PPh_3)_2('S_4')]$, which readily exchanges one PPh_3 ligand. **2** is so labile that already at room temperature it readily releases C_2H_4 and forms the Os^{IV} complex $[Os(PEt_3)_2('S_2')_2]$ (**3**) via an intramolecular redox reaction. Evidently, the strongly electron donating PEt_3 and the a priori high electron density of the Os^{II} center destabilize the $'S_4'^{2-}$-ligand to such an extent that its C_2H_4 bridge is reductively eliminated. Such C_2H_4 eliminations from the $'S_4'^{2-}$-ligand have been observed previously with electron rich Fe and Mo species[22]. In this respect, **2** unexpectedly strongly differs from its iron and ruthenium alkylphosphane $[M(PR_3)_2('S_4')]$ counterparts which are perfectly stable at ambient conditions. Complex **3** and the PMe_3 **5**, PPr_3 **4**, and PPh_3 **6** analogues were directly obtained from $[OsBr_6]^{2-}$, $'S_2'^{2-}$ and the respective phosphanes. X-ray structure analyses of **3** and **4** revealed that these complexes possess planar $[Os('S_2')_2]$ cores and *trans* phosphanes. UV-Vis-NIR spectroscopy further showed that the hexacoordinate complexes **3** to **5** have very intense NIR bands and reversibly dissociate yielding pentacoordinate $[Os(PR_3)('S_2')_2]$ complexes. When PR_3 is the sterically very bulky PCy_3, only the pentacoordinate species $[Os(PCy_3)('S_2')_2]$ (**7**) could be isolated. The influence of solvents upon the course of reactions became particularly evident when the synthesis of (**7**) was tried in MeOH instead of THF. In this case, the Os^{III} complex $(PHCy_3)[Os('S_2')_2]$ (**8a**) formed. Complex **8a** probably possesses a dinuclear anion, is paramagnetic and spontaneously oxidizes in CH_2Cl_2 to give **7**. Cyclic voltammetry revealed redox activity also for **2**, **3**, and $(NBu_4)_2[Os('S_2')_3]$ (**9b**) which forms from stoichiometric amounts of $[OsBr_6]^{2-}$, NBu_4^+, and $'S_2'^{2-}$. X-ray structure analysis of the analogous $(PHCy_3)_2[Os('S_2')_3]$ (**9a**) revealed pseudo-octahedral coordination geometry of the $[Os('S_2')_3]^{2-}$ anion.

Scrutinizing the C−C and C−S distances in the $C_6H_4S_2$ units of **3**, **4**, and **9a** corroborates previous results. They indicate that benzenedithiolate behaves as "normal" dithiolate also when binding to metal centers in higher oxidation states. The stabilization of these oxidation states thus is better traced back to increasing S→M π donation than to a "non-innocence" of benzenedithiolate that involves a break-up of the aromatic benzene system.

In summary, first examples of complexes containing $[Os('S_4')]$ and $[Os('S_2')_2)]$ fragments have been synthesized and characterized. The complexes differ unexpectedly strongly from their iron and ruthenium homologues. While with $'S_4'^{2-}$ or $'S_2'^{2-}$ ligands the metal oxidation state +IV is found only in very few iron and only unsignificantly more ruthenium complexes, it is well accessible with Os complexes.

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Experimental Section

General Methods: Unless noted otherwise, all reactions were carried out under an atmosphere of dinitrogen at room temperature by using standard Schlenk techniques. Solvents were dried and distilled before use. − Physical measurements were carried out with the following instruments: IR spectra, Perkin Elmer 16PC FTIR spectrometer (IR spectra of solutions were recorded in CaF_2 cuvettes with compensation of the solvent bands, solids were measured as KBr pellets); mass spectra, Varian MAT 212; UV/Vis/NIR spectra, Shimadzu UV3101 PC spectrometer; NMR spectra, Jeol FT-JNM-GX 270, EX 270 and LA 400; Magnetic susceptibility: Johnson Matthey susceptibility balance; Cyclic voltammograms, EG&G potentiostat PAR model 264A with glassy carbon working electrode, Pt counter electrode and Ag/AgCl reference electrode. Conducting electrolyte: 0.1 M NBu_4PF_6. Potentials are referred to NHE via $Cp_2Fe^{0/+}$ as internal standard. $Cp_2Fe^{0/+}$ = 0.40 V vs. NHE[23]. − 1,2-benzenedithiol[24] and 1,2-bis(2-mercaptophenylthio)ethane $'S_4'$-H_2[25] were prepared as described in the literature.

[Os(PPh$_3$)$_2$('S$_4$')] (**1**): $OsCl_3 \cdot x\ H_2O$ (335 mg, 1.1 mmol), PPh_3 (1 g, 3.8 mmol), and $'S_4'$-H_2 (350 mg, 1.1 mmol) were suspended in MeOH (20 ml) and THF (40 ml) and refluxed for 24 h. The resultant suspension was cooled to room temperature, the precipitating yellow-green crystals were separated, recrystallized from CH_2Cl_2 (20 ml), and dried in vacuo. Yield: 500 mg of **1**·0.25 CH_2Cl_2 (44%). − $C_{50.25}H_{42.5}OsP_2S_4$ (1044.5): calcd. C 57.78, H 4.10, S 12.28; found C 57.55, H 4.15, S 12.22. − ^{1}H NMR (CD_2Cl_2): δ = 6.4−7.5 (m, 38 H, C_6H_4, C_6H_5), 2.15−2.4 (m, 2 H,

C_2H_4), 1.6−1.8 (m, 2 H, C_2H_4). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ = 159.6, 136.2 (m), 135.4 (t), 133.1, 130.8, 129.8, 129.2, 128.1, 126.7 (t), 121.6 (C_6H_4, C_6H_5), 43.3 (C_2H_4). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2) δ = −14.4 (s, *P*Ph_3).

[Os(PEt$_3$)$_2$('S$_4$')] (**2**): $OsCl_3 \cdot x\ H_2O$ (360 mg, 1.2 mmol), PEt_3 (4 ml, 26 mmol), and 'S$_4$'-H_2 (380 mg, 1.2 mmol) were suspended in MeOH (35 ml) and THF (20 ml) and refluxed for 1 h. The resultant solution was filtered and cooled to −20°C. Yellow crystals precipitated that were separated after one week, washed with MeOH (50 ml) and *n*-hexane (20 ml), and dried in vacuo. Yield: 550 mg of **2** (62%). − $C_{26}H_{42}OsP_2S_4$ (735.0): calcd. C 42.49, H 5.76, S 17.45; found C 42.85, H 5.75, S 17.54. − FD MS (CH_2Cl_2); *m/z*: 736 [M^+]. − ^1H NMR (CD_2Cl_2), δ = 7.3−7.6 (m, 4 H, C_6H_4), 6.65−7.0 (m, 4 H, C_6H_4), 2.45−2.7 (m, 2 H, C_2H_4), 1.7−2.2 (m, 12 H, CH_2), 1.4−1.7 (m, 2 H, C_2H_4), 0.8−1.2 (m, 18 H, CH_3). − ^{31}P NMR (CD_2Cl_2), δ = −26.3 (s, *P*Et_3). − CV (CH_2Cl_2, room temp., [mV]); *E* = −20 (rev.), −950 (rev.).

[Os(PR$_3$)$_2$('S$_2$')$_2$] with R = Me, Et, Pr, Ph

General Procedure: At −78°C, 2.5 M *n*BuLi in *n*-hexane (0.8 ml, 2 mmol) was added to a solution of 'S$_2$'-H_2 (0.12 ml, 1 mmol) in THF (10 ml). The solution was warmed to room temperature and added to a suspension of $(NH_4)_2[OsBr_6]$ (350 mg, 0.5 mmol) and PR_3 (0.15 ml, 1 mmol) in MeOH or THF (10 ml). The resultant suspension was heated under reflux for 19 h, filtered, and cooled to room temperature or −20°C. The resultant complexes precipitated as black crystals or gray-black powders that were collected after one week, washed with MeOH (20 ml) and dried in vacuo. Complex **6** required recrystallization from THF (20°C → −20°C) in order to obtain correct elemental analyses.

[Os(PEt$_3$)$_2$('S$_2$')$_2$] (**3**): Yield: 225 mg of **3** (50%). − $C_{24}H_{38}OsP_2S_4$ (707.0): calcd. C 40.78, H 5.42, S 18.14; found C 40.66, H 5.72, S 18.10. − FD MS (CH_2Cl_2); *m/z*: 590 [M^+ − PEt_3]. − ^1H NMR (CD_2Cl_2), δ = 7.5−7.7 (m, 4 H, C_6H_4), 5.3−5.5 (m, 4 H, C_6H_4), 0.4−0.6 (quint, 18 H, CH_3), −0.7 (m, 12 H, CH_2). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ = 148.0, 125.0, 120.7 (C_6H_4), 10.7 (t, CH_2), 6.7 (s, CH_3). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2), δ = −195.4 (s, *P*Et_3). − UV/VIS/NIR (CH_2Cl_2): λ_{max} (lg ε) = 1043 nm (4.61), 765 (3.64), 626 (3.78), 531 (3.67). − CV (CH_2Cl_2, room temp., [mV]); *E* = 340 (rev.), −760 (rev.), 1030 (irrev.).

[Os(PPr$_3$)$_2$('S$_2$')$_2$] (**4**): Yield: 290 mg of **4** (73%). − $C_{30}H_{50}OsP_2S_4$ (791.1): calcd. C 45.55, H 6.37, S 16.21; found C 45.50, H 6.40, S 15.75. − FD MS (CH_2Cl_2); *m/z*: 792 [M^+], 632 [M^+ − PPr_3]. − ^1H NMR (CD_2Cl_2), δ = 7.5−7.7 (m, 4 H, C_6H_4), 5.35−5.55 (m, 4 H, C_6H_4), 0.6−0.9 (m, 12 H, $^{\beta}CH_2$), 0.5 (t, 18 H, CH_3), −0.75−(−0.6) (m, 12 H, $^{\alpha}CH_2$). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ = 147.9, 124.9, 120.7 (C_6H_4), 21.1 (t, $^{\alpha}CH_2$), 16.3 (s, CH_3), 16.0 (t, $^{\beta}CH_2$). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2), δ = −201.1 (s, *P*Pr_3). − UV/VIS/NIR (CH_2Cl_2, λ_{max} (lg ε) = 1043 nm (4.63), 761 (3.74), 625 (3.88).

[Os(PMe$_3$)$_2$('S$_2$')$_2$] (**5**): Yield: 155 mg of **5** (50%). − $C_{18}H_{26}OsP_2S_4$ (622.8): calcd. C 34.71, H 4.21; found C 34.96, H 4.17. − ^1H NMR (C_6D_6), δ = 7.9−8.1 (m, 4 H, C_6H_4), 5.4−5.6 (m, 4 H, C_6H_4), −1.2 (t, 18 H, CH_3). − UV/VIS/NIR (CH_2Cl_2): λ_{max} (lg ε) = 985 nm (4.53), 750(3.71), 622(3.56).

[Os(PPh$_3$)$_2$('S$_2$')$_2$] (**6**): Yield: 410 mg of **6** (82%). − $C_{48}H_{38}OsP_2S_4$ (995.2): calcd. C 57.93, H 3.85; found C 57.90, H 3.84. − ^1H NMR (CD_2Cl_2), δ = 7.5−7.6 (m, 4 H, C_6H_4), 6.9−7.25 (m, 30 H, C_6H_5), 5.9−6.05 (m, 4 H, C_6H_4). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ = 134.1 (d), 132.3 (d), 132.2, 129.4, 128.8 (d), 128.1, 122.8, 134.1 (d) (C_6H_4, C_6H_5). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2), δ = −46.5 (s, *P*Ph_3).

*[Os(PEt$_3$)$_2$('S$_2$')$_2$] (**3**) from OsCl$_3$·x H$_2$O, 'S$_4$'-H$_2$ and PEt$_3$*: $OsCl_3 \cdot x\ H_2O$ (360 mg, 1.2 mmol), PEt_3 (4 ml, ca. 25 mmol), and 'S$_4$'-H_2 (380 mg, 1.2 mmol) were combined in MeOH (35 ml) and THF (20 ml) and heated under reflux for 3 d. The resultant solution was filtered while hot and cooled to room temperature. Black crystals precipitated that were collected after 7 d, washed with MeOH (40 ml) and *n*-hexane (20 ml) and dried in vacuo. They were identified by comparison with an authentic sample of **3**. Yield: 620 mg of **3** (73%). − $C_{24}H_{38}OsP_2S_4$ (707.0): calcd. C 40.78, H 5.42, S 18.14; found C 40.80, H 5.67, S 18.36.

[Os(PCy$_3$)('S$_2$')$_2$] (**7**): At −78°C, 2.5 M *n*BuLi in *n*-hexane (0.4 ml, 1 mmol) was added to a solution of 'S$_2$'-H_2 (0.16 ml, 0.5 mmol) in THF (10 ml). The solution was warmed to room temperature and added to a suspension of $(NH_4)_2[OsBr_6]$ (176 mg, 0.25 mmol) and PCy_3 (280 mg, 1 mmol) in THF (20 ml). The resultant violet suspension was heated under reflux for 19 h, filtered and cooled to −20°C. The precipitating violet crystals were collected after 8 d, washed with MeOH (20 ml) and dried in vacuo. When the THF/MeOH mother liquor was kept at −20°C, a few single crystals separated in the course of 14 d, which were identified as $(PHCy_3)_2[Os('S_2')_3]$ (**8a**) by X-ray structure determination. Yield: 125 mg of **7** (67%). − $C_{30}H_{41}OsPS_4$ (751.1): calcd. C 47.98, H 5.50, S 17.08; found C 47.88, H 5.51, S 17.27. − FD MS (CH_2Cl_2); *m/z*: 752 [$M]^+$. − ^1H NMR (CD_2Cl_2), δ = 8.25−8.45 (m, 4 H, C_6H_4), 6.55−6.75 (m, 4 H, C_6H_4), 0.7−2.0 (m, 33 H, C_6H_{11}). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2), δ = 164.4, 129.0, 123.7 (C_6H_4), 28.8, 28.1, 28.0, 26.4 (C_6H_{11}). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2), δ = −29.2 (s, *P*Cy_3). − UV/VIS/NIR (CH_2Cl_2, λ_{max} (lg ε) = 563 nm (3.66), 753 (3.22).

(PHCy$_3$)[Os('S$_2$')$_2$] (**8a**): At −78°C, 2.5 M *n*BuLi in *n*-hexane (0.8 ml, 2 mmol) was added to a solution of 'S$_2$'-H_2 (0.12 ml, 1 mmol) in THF (10 ml). The solution was warmed to room temperature and added to a suspension of $(NH_4)_2[OsBr_6]$ (355 mg, 0.5 mmol) and PCy_3 (560 mg, 2 mmol) in MeOH (10 ml) and THF (10 ml). The resultant violet suspension was heated under reflux for 3 d and cooled to room temperature. Orange crystals precipitated that were separated, washed with MeOH (20 ml) and Et_2O (40 ml) and dried in vacuo. Yield: 195 mg of (**8a**) (52%). − $C_{30}H_{42}OsPS_4$ (752.1): calcd. C 47.91, H 5.63, S 17.05; found C 47.83, H 5.68, S 16.96. − ^1H NMR (CD_2Cl_2), δ = 7.4−7.6 (m, 4 H, C_6H_4), 6.55−6.75 (m, 4 H, C_6H_4), 5.46 (d, $^1J_{PH}$ = 475 Hz, 1 H, P*H*Cy_3), 0.8−1.9 (m, 33 H, C_6H_{11}). − $^{13}C\{^1H\}$ NMR (CD_2Cl_2, −70°C), δ = 148.3, 127.7, 121.8 (C_6H_4), 26.1, 25.8, 25.5, 24.2 (C_6H_{11}). − $^{31}P\{^1H\}$ NMR (CD_2Cl_2), δ = 20.7 (s, *P*HCy_3).

(NMe$_4$)[Os('S$_2$')$_2$] (**8b**): An orange-brown suspension of (**8a**) (75 mg, 0.1 mmol) in THF (5 ml) was treated with a 2.2 M solution of NMe_4OH in MeOH (0.1 ml, 0.2 mmol). The resultant orange-brown powder was separated, washed with MeOH (5 ml) and dried in vacuo. Yield: 50 mg of (**8b**) (92%). − $C_{16}H_{20}NOsS_4$ (544.8): calcd. C 35.28, H 3.70, N 2.57; found C 35.52, H 3.46, N 2.47. − ^1H NMR ([D$_6$]DMSO), δ = 7.30−7.45 (m, 4 H, C_6H_4), 6.55−6.70 (m, 4 H, C_6H_4), 3.1 (s, 12 H, NMe_4^+).

(NBu$_4$)$_2$[Os('S$_2$')$_3$] (**9b**): NBu_4OH (3 ml of 1 M solution in MeOH, 3 mmol) 'S$_2$'-H_2 (0.18 ml, 1.5 mmol), and $(NH_4)_2[OsBr_6]$ (355 mg, 0.5 mmol) were combined in MeOH (50 ml) and heated under reflux for 2 h. The resultant brown-red solution was filtered while hot, and cooled to room temperature. Brown-red crystals precipitated that were separated after 4 h, washed with MeOH (30 ml) and Et_2O (30 ml), and dried in vacuo. Yield: 500 mg of (**9b**) (91%). − $C_{50}H_{84}N_2OsS_6$ (1095.8): calcd. C 54.80, H 7.73, N 2.56, S 17.56; found C 54.61, H 7.97, N 2.54, S 17.84. − ^1H NMR (CD_2Cl_2), δ = 6.55−7.90 (m, C_6H_4), 3.00 (m, 16 H, CH_2), 1.70 (m, 16 H, CH_2), 1.42 (m, 16 H, CH_2), 1.0 (t, 24 H, CH_3), 0.22 (s, C_6H_4), −0.90 (s,

Table 1. Selected crystallographic data for $[Os(PEt_3)_2('S_2')_2]$ (**3**), $[Os(PPr_3)_2('S_2')_2]$ (**4**), and $(PHCy_3)_2[Os('S_2')_3]$ (**9a**)

compound	$[Os(PEt_3)_2('S_2')_2]$ (**3**)	$[Os(PPr_3)_2('S_2')_2]$ (**4**)	$(PHCy_3)_2[Os('S_2')_3]$ (**9a**)
Formula	$C_{24}H_{38}P_2S_4Os$	$C_{30}H_{50}P_2S_4Os$	$C_{54}H_{78}P_2S_6Os$
MW [g/mol]	706.92	791.08	1171.66
Crystal size. [mm]	0.4 × 0.3 × 0.2	0.3 × 0.2 × 0.1	0.5 × 0.2 × 0.2
$F(000)$	704	800	2416
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/n$
a [pm]	968.9(7)	1001.5(5)	1801.7(4)
b [pm]	1163.7(6)	1320.8(6)	1705.4(5)
c [pm]	1285.6(7)	1354.7(4)	1942.4(5)
β [°]	93.38(5)	95.09(3)	112.72(2)
Cell volume [nm³]	1.447(2)	1.785(1)	5.505(3)
Z	2	2	4
$d_{calcd.}$ [g/cm³]	1.622	1.472	1.414
μ [mm^{-1}]	4.817	3.913	2.636
Temperature [K]	293(2)	293(2)	200(2)
θ-range	2.36−27.04	2.04−27.05	2.27−27.06
Measured reflections	5442	4852	14605
Independent reflections	3177	3354	11812
Observed reflections	2169	1943	4086
Refined parameters	145	169	605
R_1 [$F_0 \geq 4\sigma(F)$]	0.0330	0.0434	0.0488
wR_2 (all data)	0.0865	0.1074	0.1115

C_6H_4). − CV (CH_2Cl_2, room temp., [mV]); E_1 = −80 (rev.), 180 (rev.), −580 (irrev.).

X-ray Structure Analysis of $[Os(PEt_3)_2('S_2')_2]$ (**3**), $[Os(PPr_3)_2('S_2')_2]$ (**4**), *and* $(PHCy_3)_2[Os('S_2')_3]$ (**9a**): Black single crystals of $[Os(PEt_3)_2('S_2')_2]$ (**3**) and $[Os(PPr_3)_2('S_2')_2]$ (**4**) were grown from MeOH (**3**) or MeOH/THF (**4**) solutions at −20°C. A few black single crystals of $(PHCy_3)_2[Os('S_2')_3]$ (**9a**) were obtained as minor by-product from the THF/MeOH mother liquor resulting from the synthesis of $[Os(PCy_3)('S_2')_2]$ (**7**). Suitable single crystals were sealed under N_2 in glass capillaries. The data were collected using a Siemens P4 diffractometer. The structures were solved with direct methods and refined using full-matrix least-squares procedures on F^2 values (SHELXTL 5.03)[26]. Non-hydrogen atoms were refined anisotropically, hydrogen positions were taken from the difference Fourier synthesis and fixed on their positions with a common isotropic thermal parameter in case of **4**, while for **3** and **9a** all H-atoms are geometrically positioned. One cyclohexyl group (C70−C75) of the cation in **9a** is disordered. Two different orientations were refined, with a site occupancy of 50%. Table 1 lists selected crystallographic data of **3**, **4**, and **9a**[27].

☆ Dedicated to Professor *Heinrich Nöth* on the occasion of his 70th birthday.

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[27] Further details of the crystal structure investigations are available on request from Cambridge Crystallographic Data Centre, The Director, 12 Union Road, Cambridge CB2 1EZ (Telefax: Int. + 1223/336-033; E-mail: deposit@chemcrys.cam.ac.uk), on quoting the "supplementary publication no. CCDC-100408", the names of the authors, and the journal citation.
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