

# $[\text{ReS}_4]^\ominus$ , $[\text{ReS}_9]^\ominus$ , $[\text{ReOS}_8]^\ominus$ : Simple Synthesis with $\text{S}_x^{2\ominus}$ Solutions, Structural Data, and $^{185/187}\text{Re}$ -NMR Studies\*\*

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**Abstract:** Simple preparation procedures for the compounds  $[(\text{C}_2\text{H}_5)_4\text{N}][\text{ReS}_4]$  and  $[(\text{C}_6\text{H}_5)_4\text{P}][\text{ReS}_9]_{0.7}[\text{ReOS}_8]_{0.3}$  – the latter containing new simple polysulfido complexes – together with their structural data and the  $^{185/187}\text{Re}$ -NMR spectra of  $[\text{ReO}_4]^\ominus$  and  $[\text{ReS}_4]^\ominus$  are reported.

Though there has been a tremendous number of studies on the coordination chemistry and properties of the thioanions of molybdenum and tungsten (like  $[\text{MoS}_4]^{2\ominus}$ ) since we introduced these species

as ligands in coordination chemistry<sup>[1]</sup>, there is not much known about the corresponding chemistry of rhenium. Thiometalates are unique ligands and their complexes have been used as starting materials for heterogeneous catalysts<sup>[2]</sup> as well as in the preparation of models of the active site of the MoFe protein of nitrogenase<sup>[1]</sup>.

In this note we present very simple and convenient preparation methods for  $[\text{ReS}_4]^\ominus$  and the new interesting ions  $[\text{ReS}_9]^\ominus$  and  $[\text{ReOS}_8]^\ominus$  (using polysulfide solutions) as well as their structures. We think that the rhenium sulfur chemistry is as interesting and versatile as that of molybdenum.

Thiometalates and oxothiometalates including those of Re are usually prepared

by bubbling  $\text{H}_2\text{S}$  through a solution containing the corresponding oxoanions  $[\text{MO}_4]^{n\ominus}$ <sup>[1,3]</sup>. We have now found that thioperrhenates can be obtained much easier by using a polysulfide solution rather than  $\text{H}_2\text{S}$ . This is an interesting result as the reaction of  $[\text{MoO}_4]^{2\ominus}$  with  $\text{S}_x^{2\ominus}$  yields disulfido complexes, e.g.  $[\text{Mo}_2^{\text{V}}(\text{S}_2)_6]^{2\ominus}$  or  $[\text{Mo}_3^{\text{IV}}\text{S}(\text{S}_2)_6]^{2\ominus}$ <sup>[2,4]</sup>. On the other hand, the rhenium(v)-sulfur species like the new anionic complexes  $[\text{ReS}_9]^\ominus$  and  $[\text{ReOS}_8]^\ominus$  (cf. the structures shown in Fig. 1) can also be obtained by reducing  $\text{Re}^{\text{VII}}$ -species with a polysulfide solution upon more pronounced heating. The only known species of that type are  $[\text{MoS}_9]^{2\ominus}$  and  $[\text{MoOS}_8]^{2\ominus}$ <sup>[1,5]</sup>.

Structural data of the compounds  $[(\text{C}_2\text{H}_5)_4\text{N}][\text{ReS}_4]$  and  $[(\text{C}_6\text{H}_5)_4\text{P}][\text{ReS}_9]_{0.7}[\text{ReOS}_8]_{0.3}$ <sup>[14]</sup> are presented in Table 1 and Fig. 1. The Re-S1-S2-S3-S4 ring in the latter compound has *half-chair* conformation and the Re-S5-S6-S7-S8 one has a conformation between *half-chair* and *envelope* (for torsional angles see Fig. 1). The mean Re–S bond distance of the tetrahedral  $[\text{ReS}_4]^\ominus$  is 212.5 pm.

The  $^{185/187}\text{Re}$ -NMR spectra of  $[(\text{C}_2\text{H}_5)_4\text{N}][\text{ReS}_4]$  are shown in Fig. 2 in relation to the corresponding spectra of  $\text{Na}[\text{ReO}_4]$  and of  $[(\text{C}_6\text{H}_5)_4\text{P}][\text{ReO}_4]$ ; the data are filed in Table 2.

There are only two reports on rhenium NMR spectra dealing with aqueous solutions of  $\text{Na}[\text{ReO}_4]$ <sup>[6,7]</sup> and tetrahydrofuran (THF) solutions of  $[\text{Re}(\text{CO})_6]\text{Cl}\cdot\text{HCl}$ <sup>[7]</sup>. Apparently this limitation is due to the ex-

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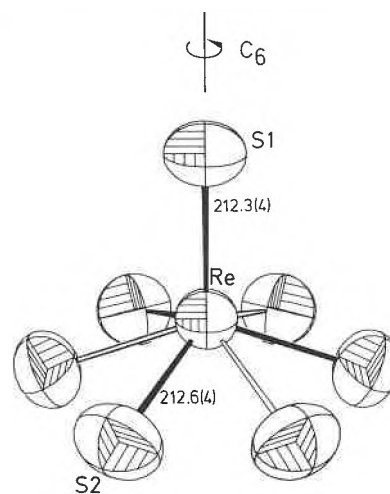
tremely large nuclear quadrupole moments of the two spin 5/2 nuclei <sup>185</sup>Re and <sup>187</sup>Re ( $Q = 2.8$  and  $2.6 \cdot 10^{-28}$  m<sup>2</sup>, respectively), which give rise to very effective quadrupole relaxation and hence to broad lines in all but cubic environments. On the other hand, the rhenium isotopes exhibit a high NMR receptivity (2.6 relative to 1 of <sup>1</sup>H at constant frequency) and one should expect reasonably sharp lines in complexes of T<sub>d</sub> symmetry.

Nonetheless, for the tetrahedral anions [ReO<sub>4</sub>]<sup>⊖</sup> and [ReS<sub>4</sub>]<sup>⊖</sup> in organic solvents and with large non-polarizing counterions, the resonances are broadened to a considerable extent (half widths ca. 2–3.5 kHz), which might be due to distortions of the tetrahedra caused by the formation of short-lived collision complexes<sup>[8]</sup>. Lines are still broader (around 20 kHz) in the spectra of aqueous solutions of Na[ReO<sub>4</sub>]. Contact-ion formation as an explanation has been ruled out by Dwek et al.<sup>[6]</sup> on the grounds that the line widths are independent of concentration and addition of excess Na<sup>⊕</sup>. However, the high polarizing effect of Na<sup>⊕</sup> upon the perrhenate ion has been well established by NQR measurements<sup>[9]</sup>. An alternative explanation of the broad lines observed in H<sub>2</sub>O solution would be the considerably increased molecular reorientation time in the polar solvent.

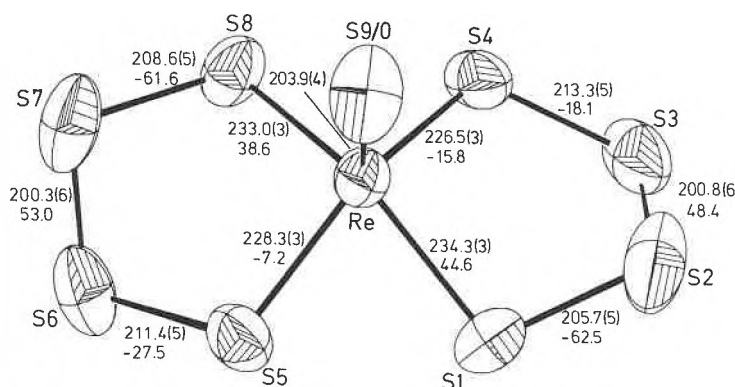
Another interesting observation is the substantial down-field shift of ca. 3300 ppm for the thioperrhenate relative to the oxoperrhenate. This deshielding of the rhenium nuclei is in accordance with the so-called inverse dependence of metal shielding upon the electronegativity (or polarizability) of the ligand set in a d<sup>0</sup> system<sup>[10]</sup>. The shielding difference is about 1.5 times that of [MoO<sub>4</sub>]<sup>2⊖</sup>/[MoS<sub>4</sub>]<sup>2⊖</sup><sup>[11]</sup> and 2.2 times that of [VO<sub>4</sub>]<sup>3⊖</sup>/[VS<sub>4</sub>]<sup>3⊖</sup><sup>[12]</sup>, which compares to an appropriate shielding difference for the pairs [MO<sub>4</sub>]<sup>n⊖</sup>/[M(CO)<sub>6</sub>]<sup>n⊖</sup> (M = Re: Δδ = 3400, see Table 2; M = Mo: 1860; M = V: 1410<sup>[10]</sup>) and has been referred to differing intrinsic shielding sensitivities of the nuclei<sup>[10]</sup>. Quite interestingly, there is a slight but significant difference (primary isotope effect) of 235 ppm for the shift values of the two rhenium isotopes in [ReS<sub>4</sub>]<sup>⊖</sup> relative to [ReO<sub>4</sub>]<sup>⊖</sup>.

**Preparation of [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N][ReS<sub>4</sub>]:** 4 g of [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N]Br are dissolved with stirring in 50 mL of methanolic ammonium polysulfide<sup>[13]</sup> (100 mL Erlenmeyer flask). After addition of 1 g Re<sub>2</sub>O<sub>7</sub>, the mixture is heated *shortly* (1 min) to 45°C and quickly filtered. The red-brown filtrate is stored in a closed flask under argon at room temperature. After 1–2 days the precipitated red-violet crystals are filtered off and washed with isopropanol (a.r.), CS<sub>2</sub>, and Et<sub>2</sub>O; yield 1.3 g (71%).

[(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>P][ReS<sub>9</sub>]<sub>0.7</sub>[ReOS<sub>8</sub>]<sub>0.3</sub> has been prepared correspondingly in acetonitrile but upon heating to 60°C.



(a)



(b)

Fig. 1. (a) Structure of the disordered ReS<sub>4</sub><sup>⊖</sup> ion (two superimposed tetrahedra on the C<sub>6</sub> axis sharing the atom S1 and the central Re-atom) as found in the substructure of [(C<sub>2</sub>H<sub>5</sub>)<sub>4</sub>N][ReS<sub>4</sub>] (see Table 1) with bond lengths (pm); bond angles (°): S-Re-S 109.4 (1), 109.5 (1). – (b) Structure of the [ReS<sub>9</sub>]<sup>⊖</sup>/[ReOS<sub>8</sub>]<sup>⊖</sup> ion in crystals of [(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>P][ReS<sub>9</sub>]<sub>0.7</sub>[ReOS<sub>8</sub>]<sub>0.3</sub> with bond lengths (pm) and torsion angles (°); selected bond angles (°): S9/O-Re-S 105.6 (1)–111.7 (1), S1-Re-S4 89.4 (1), S1-Re-S5 75.9 (1), S1-Re-S8 143.5 (1), Re-S1-S2 101.7 (2), S1-S2-S3 100.2 (2), S2-S3-S4 100.6 (2), Re-S4-S3 112.0 (2).

Table 1. Crystal, Intensity Collection, and Refinement Parameters.

Compound	[(C <sub>2</sub> H <sub>5</sub> ) <sub>4</sub> N][ReS <sub>4</sub> ] <sup>a</sup>	[(C <sub>6</sub> H <sub>5</sub> ) <sub>4</sub> P][ReS <sub>9</sub> ] <sub>0.7</sub> [ReOS <sub>8</sub> ] <sub>0.3</sub> <sup>b</sup>
empirical formula	C <sub>8</sub> H <sub>20</sub> NReS <sub>4</sub>	C <sub>24</sub> H <sub>20</sub> O <sub>0.3</sub> PReS <sub>8.7</sub>
molecular weight	444.71	809.36
space group	P6mm	P2 <sub>1</sub> /n
a [pm]	814.9 (2)	1074.8 (3)
b [pm]		1542.8 (4)
c [pm]	653.8 (1)	1742.1 (4)
β [°]		91.54 (2)
V [pm <sup>3</sup> ]	376.0 · 10 <sup>6</sup>	2887.8 · 10 <sup>6</sup>
ρ <sub>calc</sub> [g · cm <sup>-3</sup> ]	1.96	1.86
Z	1	4
crystal dimensions [mm]	0.4 × 0.1 × 0.1	0.3 × 0.3 × 0.3
absorption coefficient	87.0	49.4
μ (Mo-K <sub>α</sub> ) [cm <sup>-1</sup> ]		
F (000), electrons	214	1582.4
ω-scan		ω-scan
scan range (2θ) [°]	4–52	4–50
scan width		1° in ω bisected by K <sub>α1,2</sub> maximum
scan speed [°/min]	2.9–29.3	3.5–29.3
background scan time ratio	0.66	0.66
check reflections		1 reflection after every 39 reflections
no. of measured reflections	1609	5751
no. of unique observed reflections (F <sub>0</sub> > 3.92σ(F <sub>0</sub> ))	329	3770
no. of variables	28	148
R = Σ  F <sub>0</sub>   -  F <sub>c</sub>   /Σ F <sub>0</sub>	0.019	0.047

<sup>a</sup>) A 1:1 disorder of both anion and cation and the presence of additional reflections in between the a\*c\* (and b\*c\*) layers in the reciprocal lattice indicate the presence of a superstructure in [NEt<sub>4</sub>][ReS<sub>4</sub>]. However, as the additional reflections were very weak and only the bonding parameters of the anion were of interest at the moment, the structure was solved within the subcell given in this table. – <sup>b</sup>) The anions [ReS<sub>9</sub>]<sup>⊖</sup> and [ReOS<sub>8</sub>]<sup>⊖</sup> occupy the same position in the crystal lattice in a 0.7:0.3 ratio.

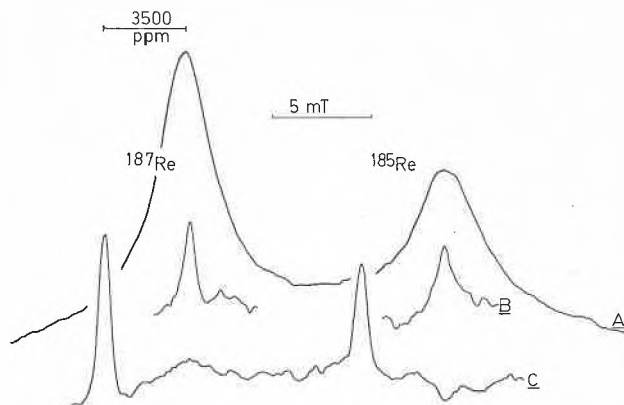


Fig. 2. 8 MHz  $^{187/185}\text{Re}$ -NMR spectra of  $\text{Na}[\text{ReO}_4]$  in  $\text{H}_2\text{O}$  (A),  $[(\text{C}_6\text{H}_5)_4\text{P}][\text{ReO}_4]$  in  $\text{HCONMe}_2/\text{toluene}$  (B), and  $[(\text{C}_2\text{H}_5)_4\text{N}][\text{ReS}_4]$  in  $\text{MeCN}/\text{CH}_2\text{Cl}_2/\text{Me}_2\text{SO}$  (C) at 305 K. The sweep range is 20 mT, the modulation amplitude 0.2 mT. Number of scans: 8 (A), 20 (B), and 15 (C); 2 min per scan; time constant 0.3 s; central field  $B = 0.83$  T.

Table 2.  $^{187,185}\text{Re}$ -NMR parameter<sup>a)</sup>.

Compound	Concentration and medium	$\delta(^{187,185}\text{Re})^b)$	$W_{1/2}(^{187}\text{Re})^c)$ [kHz]	$W_{1/2}(^{185}\text{Re})^c)$ [kHz]	Ref.
$[(\text{C}_2\text{H}_5)_4\text{N}][\text{ReS}_4]$	0.2 M MeCN/ $\text{CH}_2\text{Cl}_2$ / $\text{Me}_2\text{SO}$ (4:4:1)	+3435/+3200	1.96 (10)	1.96 (10)	
$\text{Na}[\text{ReO}_4]$	0.8 M $\text{H}_2\text{O}$ 2.0 M $\text{H}_2\text{O}$	0	13.5 <sup>d)</sup> 20.0 (6)	14.2 <sup>d)</sup> 23.2 (6)	[6]
$[(\text{C}_6\text{H}_5)_4\text{P}][\text{ReO}_4]$	saturated DMF/toluene (4:1)	<sup>e)</sup>	3.3 (2)	3.6 (5)	
$[\text{Re}(\text{CO})_6\text{Cl} \cdot \text{HCl}^f)$	0.3 M MeCN	-3400	2.3 (3) <sup>e)</sup>	2.6 (5) <sup>e)</sup>	[7]

<sup>a)</sup> Data from this work were obtained at 305 (2) K on a Varian DP 60 wide-line instrument equipped with a Varian V-4230 B probe head (4–8 MHz) and a Bruker B-HS 90 VAR magnet. Measuring frequency  $\nu_0 = 8$  MHz (exact), maximum rf power (0.1 mT); central field  $B_0$  ca. 0.83 T; modulation amplitude for the determination of line widths = 0.02 mT. <sup>b)</sup> Relative to 2 M aqueous  $\text{Na}[\text{ReO}_4]$ ; estimated error:  $\pm 40$  ppm. <sup>c)</sup> Width at half-height of the resonance signal; errors are given in parentheses. <sup>d)</sup> At ca. 1.4 T; calculated from  $T_2$ . <sup>e)</sup> Solvent and counter-ion effects are within the limits of error. <sup>f)</sup>  $\nu_0 = 9.70$  MHz ( $B_0$  ca. 1.01 T) at 295 K. <sup>g)</sup> Calculated from the peak-to-peak width.

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- [14] Note added in proof: Pure  $[(\text{C}_6\text{H}_5)_4\text{P}][\text{ReSg}]$  could be obtained too.