

atoms, to give a polymeric anion structure. More restricted bridging between Cu atoms by chloride ligands is observed in [MoS<sub>4</sub>(CuCl)<sub>4</sub>]<sup>2-</sup>, to give a chain polymer (Nicholson, Flood, Garner & Clegg, 1983), and in [WS<sub>4</sub>(CuCl)<sub>4</sub>]<sup>2-</sup>, to give dimeric units (Clegg, Scattergood & Garner, 1987).

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## Structures of Tetraphenylphosphonium Bis(ethane-1,2-dithiolato)oxorhenium(V) and Tetraphenylphosphonium Bis(benzene-1,2-dithiolato)oxorhenium(V)

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**Abstract.** (1): [P(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>][ReO(C<sub>2</sub>H<sub>4</sub>S<sub>2</sub>)<sub>2</sub>], *M<sub>r</sub>* = 726.0, orthorhombic, *Pbca*, *a* = 19.650 (1), *b* = 18.679 (1), *c* = 15.104 (1) Å, *V* = 5543.8 Å<sup>3</sup>, *Z* = 8, *D<sub>x</sub>* = 1.739 Mg m<sup>-3</sup>, λ(Mo *Kα*) = 0.71073 Å, μ = 4.81 mm<sup>-1</sup>, *F*(000) = 2864, *T* = 293 K, *R* = 0.0279 for 2935 unique reflections with *F* > 4σ(*F*). (2): [P(C<sub>6</sub>H<sub>5</sub>)<sub>4</sub>][ReO(C<sub>6</sub>H<sub>4</sub>S<sub>2</sub>)<sub>2</sub>], *M<sub>r</sub>* = 822.0, monoclinic, *Cc*, *a* = 12.511 (1), *b* = 15.749 (2), *c* = 16.581 (2) Å, β = 93.55 (1)°, *V* = 3260.8 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.674 Mg m<sup>-3</sup>, μ(Mo *Kα*) = 4.10 mm<sup>-1</sup>, *F*(000) = 1624, *T* = 293 K, *R* = 0.0253 for 5431 unique reflections with *F* > 4σ(*F*). In both anions, Re has square-based pyramidal coordination with axial O<sup>2-</sup> and the bidentate edt<sup>2-</sup> (=C<sub>2</sub>H<sub>4</sub>S<sub>2</sub><sup>2-</sup>) and bdt<sup>2-</sup> (=C<sub>6</sub>H<sub>4</sub>S<sub>2</sub><sup>2-</sup>) ligands in basal positions. Mean bond lengths for (1) are: Re–O = 1.673 (4), Re–S = 2.308 (10) Å; for (2): Re–O = 1.663 (4), Re–S = 2.315 (3) Å, the Re–S distances showing significant variations within the anion of (1).

**Experimental.** The compounds were obtained by reaction of [ReOCl<sub>3</sub>(PPh<sub>3</sub>)<sub>2</sub>] with H<sub>2</sub>edt or H<sub>2</sub>bdt in MeOH/Et<sub>3</sub>N solution, followed by addition of [PPh<sub>4</sub>]<sup>+</sup>Br<sup>-</sup>, and were recrystallized from CH<sub>2</sub>Cl<sub>2</sub>/Et<sub>2</sub>O. Crystals were mounted in air on glass fibres and examined on a Siemens AED2 diffractometer with graphite-monochromated Mo *Kα* radiation.

Table 1. Atomic coordinates (×10<sup>4</sup>) and equivalent isotropic thermal parameters (Å<sup>2</sup> × 10<sup>4</sup>) for (1)

$U_{eq} = \frac{1}{3}(\text{trace of the orthogonalized } U_{ij} \text{ matrix}).$

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U<sub>eq</sub></i>
Re	5347.9 (1)	7948.5 (1)	4302.9 (2)	399 (1)
O	5509 (3)	7183 (2)	4837 (3)	745 (19)
S(1)	5971 (1)	8020 (1)	3010 (1)	634 (6)
S(2)	4435 (1)	7714 (1)	3375 (1)	548 (6)
S(3)	4571 (1)	8615 (1)	5077 (1)	637 (6)
S(4)	6124 (1)	8793 (1)	4785 (1)	780 (8)
C(1)	5426 (4)	7694 (5)	2127 (5)	933 (36)
C(2)	4828 (4)	7327 (5)	2406 (5)	876 (34)
C(3)	5021 (4)	9214 (4)	5815 (4)	692 (28)
C(4)	5757 (4)	9205 (5)	5748 (5)	956 (37)
P	3499 (1)	5361 (1)	3895 (1)	374 (5)
C(11)	3363 (3)	5820 (3)	4924 (3)	383 (19)
C(12)	2959 (3)	5518 (3)	5579 (4)	517 (22)
C(13)	2813 (3)	5902 (3)	6328 (4)	627 (25)
C(14)	3067 (4)	6582 (4)	6439 (5)	735 (30)
C(15)	3458 (4)	6887 (3)	5792 (4)	648 (27)
C(16)	3610 (3)	6518 (3)	5025 (4)	550 (24)
C(21)	3102 (3)	5882 (3)	3033 (3)	406 (20)
C(22)	3305 (3)	5809 (3)	2158 (4)	544 (23)
C(23)	2953 (3)	6174 (4)	1506 (4)	652 (27)
C(24)	2409 (4)	6599 (4)	1714 (5)	637 (28)
C(25)	2207 (3)	6669 (4)	2579 (4)	642 (26)
C(26)	2554 (3)	6316 (3)	3241 (4)	572 (23)
C(31)	3075 (3)	4509 (3)	3939 (3)	382 (19)
C(32)	3404 (3)	3896 (3)	4228 (4)	445 (20)
C(33)	3041 (3)	3261 (3)	4299 (4)	537 (22)
C(34)	2365 (3)	3242 (3)	4088 (4)	542 (24)
C(35)	2039 (3)	3851 (3)	3797 (4)	534 (22)
C(36)	2392 (3)	4484 (3)	3725 (4)	485 (22)
C(41)	4379 (3)	5235 (3)	3628 (4)	400 (19)
C(42)	4888 (3)	5662 (3)	3978 (4)	488 (21)
C(43)	5545 (3)	5593 (4)	3689 (4)	615 (26)
C(44)	5707 (3)	5100 (4)	3061 (4)	586 (25)
C(45)	5216 (3)	4661 (3)	2711 (4)	593 (25)
C(46)	4547 (3)	4727 (3)	2993 (4)	478 (21)

For (1) [for (2) in square brackets where different]: crystal size  $0.4 \times 0.4 \times 0.4$  mm [ $0.15 \times 0.2 \times 0.6$  mm], unit-cell parameters from  $2\theta$  values of 32 reflections measured on both sides of the direct beam ( $20 < 2\theta < 22^\circ$ ), intensity collection in  $\omega/\theta$  scan mode, scan range =  $0.51^\circ$  [ $0.43^\circ$ ] below  $\alpha_1$  to  $0.51^\circ$  [ $0.43^\circ$ ] above  $\alpha_2$ , scan time = 14–56 s [14–70 s],  $2\theta_{\max} = 45^\circ$  [ $50^\circ$ ],  $h$  0→21,  $k$  0→20,  $l$  -16→0 [ $h$  -14→14,  $k$  0→18,

$l$  -19→19], no significant variation for three standard reflections, semi-empirical absorption correction, transmission 0.056–0.100 [ $0.155$ – $0.244$ ]. 3620 [5730] reflections measured, all unique, 2935 [5431] with  $F > 4\sigma(F)$ . Initial atomic coordinates taken from the isostructural Mo complexes (Ellis, Collison, Garner & Clegg, 1986; Boyde, Ellis, Garner & Clegg, 1986), blocked-cascade refinement on  $F$ ,  $w^{-1} = \sigma^2(F) + gF^2$  with  $g = 0$  [0.00036], anisotropic thermal parameters,

Table 2. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^4$ ) for (2)

$U_{\text{eq}} = \frac{1}{3}(\text{trace of the orthogonalized } U_{ij} \text{ matrix}).$

	x	y	z	$U_{\text{eq}}$
Re	5000		5000	391 (1)
O	4110 (3)	3592.5 (1)	5094 (2)	567 (13)
S(11)	4111 (1)	2820 (2)	5086 (1)	510 (4)
S(12)	5058 (1)	3915 (1)	3642 (1)	539 (4)
C(11)	3670 (4)	5144 (3)	4088 (3)	492 (16)
C(12)	2923 (5)	5794 (4)	3930 (4)	574 (19)
C(13)	2600 (6)	5992 (5)	3125 (5)	648 (25)
C(14)	3022 (6)	5569 (4)	2509 (4)	704 (24)
C(15)	3778 (5)	4935 (4)	2654 (4)	650 (22)
C(16)	4097 (4)	4713 (3)	3447 (3)	505 (17)
S(21)	5700 (1)	3932 (1)	6282 (1)	515 (4)
S(22)	6649 (1)	2970 (1)	4831 (1)	504 (4)
C(21)	6866 (4)	3304 (3)	6446 (3)	487 (16)
C(22)	7366 (5)	3244 (4)	7230 (4)	593 (20)
C(23)	8259 (5)	2750 (4)	7355 (4)	688 (23)
C(24)	8690 (5)	2333 (4)	6730 (4)	711 (23)
C(25)	8227 (5)	2401 (4)	5950 (5)	672 (22)
C(26)	7289 (4)	2888 (3)	5818 (3)	489 (17)
P	4367 (1)	895 (1)	7624 (1)	371 (3)
C(31)	5098 (4)	410 (3)	6852 (3)	412 (15)
C(32)	5921 (5)	842 (4)	6517 (3)	541 (19)
C(33)	6417 (5)	498 (4)	5872 (4)	653 (22)
C(34)	6099 (5)	-271 (4)	5560 (3)	629 (21)
C(35)	5263 (5)	-702 (4)	5870 (3)	586 (19)
C(36)	4764 (5)	-372 (4)	6518 (3)	536 (18)
C(41)	5201 (4)	1655 (3)	8180 (3)	437 (15)
C(42)	6246 (5)	1398 (3)	8412 (4)	501 (18)
C(43)	6882 (5)	1907 (4)	8921 (3)	607 (20)
C(44)	6472 (5)	2666 (4)	9176 (3)	659 (22)
C(45)	5445 (6)	2918 (4)	8955 (4)	694 (23)
C(46)	4791 (5)	2403 (4)	8444 (3)	574 (19)
C(51)	3997 (4)	138 (3)	8373 (3)	427 (15)
C(52)	3170 (5)	329 (4)	8849 (3)	562 (19)
C(53)	3005 (5)	-163 (4)	9516 (4)	619 (20)
C(54)	3661 (5)	-849 (4)	9698 (3)	610 (20)
C(55)	4473 (5)	-1050 (4)	9221 (4)	582 (19)
C(56)	4666 (5)	-547 (4)	8548 (4)	546 (20)
C(61)	3203 (4)	1366 (3)	7131 (3)	392 (14)
C(62)	2276 (5)	887 (4)	7004 (5)	553 (22)
C(63)	1413 (5)	1211 (4)	6548 (4)	607 (21)
C(64)	1464 (4)	2013 (4)	6217 (3)	558 (18)
C(65)	2387 (5)	2483 (3)	6328 (3)	514 (17)
C(66)	3269 (4)	2165 (3)	6774 (3)	447 (15)

Table 3. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for (1)

Re–O	1.673 (4)	Re–S(1)	2.309 (2)
Re–S(2)	2.318 (2)	Re–S(3)	2.291 (2)
Re–S(4)	2.312 (2)	S(1)–C(1)	1.815 (8)
S(2)–C(2)	1.807 (8)	S(3)–C(3)	1.810 (7)
S(4)–C(4)	1.797 (8)	C(1)–C(2)	1.424 (11)
C(3)–C(4)	1.449 (11)		
O–Re–S(1)	111.0 (2)	O–Re–S(2)	106.1 (2)
S(1)–Re–S(2)	84.8 (1)	O–Re–S(3)	110.1 (2)
S(1)–Re–S(3)	138.9 (1)	S(2)–Re–S(3)	84.0 (1)
O–Re–S(4)	107.8 (2)	S(1)–Re–S(4)	82.9 (1)
S(2)–Re–S(4)	146.1 (1)	S(3)–Re–S(4)	84.7 (1)
Re–S(1)–C(1)	106.8 (3)	Re–S(2)–C(2)	103.6 (3)
Re–S(3)–C(3)	108.9 (3)	Re–S(4)–C(4)	106.4 (3)
S(1)–C(1)–C(2)	115.6 (5)	S(2)–C(2)–C(1)	113.6 (6)
S(3)–C(3)–C(4)	116.0 (5)	S(4)–C(4)–C(3)	117.5 (6)

Table 4. Selected bond lengths ( $\text{\AA}$ ) and angles ( $^\circ$ ) for (2)

Re–O	1.663 (4)	Re–S(11)	2.319 (2)
Re–S(12)	2.314 (2)	Re–S(21)	2.311 (2)
Re–S(22)	2.317 (2)	S(11)–C(11)	1.762 (5)
S(12)–C(16)	1.755 (6)	C(11)–C(12)	1.400 (8)
C(11)–C(16)	1.395 (6)	C(12)–C(13)	1.404 (10)
C(13)–C(14)	1.354 (11)	C(14)–C(15)	1.387 (10)
C(15)–C(16)	1.395 (8)	S(21)–C(21)	1.770 (6)
S(22)–C(26)	1.782 (6)	C(21)–C(22)	1.409 (8)
C(21)–C(26)	1.364 (8)	C(22)–C(23)	1.366 (9)
C(23)–C(24)	1.365 (10)	C(24)–C(25)	1.388 (10)
C(25)–C(26)	1.408 (8)		
O–Re–S(11)	107.9 (1)	O–Re–S(12)	108.2 (1)
S(11)–Re–S(12)	85.0 (1)	O–Re–S(21)	107.5 (1)
S(12)–Re–S(21)	84.1 (1)	S(12)–Re–S(21)	144.2 (1)
O–Re–S(22)	107.9 (1)	S(11)–Re–S(22)	144.2 (1)
S(21)–Re–S(22)	83.9 (1)	S(21)–Re–S(22)	85.4 (1)
Re–S(11)–C(11)	105.8 (2)	Re–S(12)–C(16)	105.9 (2)
S(11)–C(11)–C(12)	121.1 (4)	S(11)–C(11)–C(16)	119.1 (4)
C(11)–C(11)–C(16)	119.7 (5)	C(11)–C(12)–C(13)	119.3 (6)
C(12)–C(13)–C(14)	120.3 (7)	C(13)–C(14)–C(15)	121.1 (7)
S(12)–C(15)–C(16)	119.8 (6)	S(12)–C(16)–C(11)	119.9 (4)
S(12)–C(16)–C(15)	120.4 (5)	C(11)–C(16)–C(15)	119.7 (5)
Re–S(21)–C(21)	105.9 (2)	Re–S(22)–C(26)	105.8 (2)
S(21)–C(21)–C(22)	119.6 (5)	S(21)–C(21)–C(26)	120.4 (4)
C(22)–C(21)–C(26)	120.0 (5)	C(21)–C(22)–C(23)	119.4 (6)
C(22)–C(23)–C(24)	121.0 (6)	C(23)–C(24)–C(25)	120.6 (6)
C(24)–C(25)–C(26)	118.8 (6)	S(22)–C(26)–C(21)	119.5 (4)
S(22)–C(26)–C(25)	120.4 (5)	C(21)–C(26)–C(25)	120.1 (5)

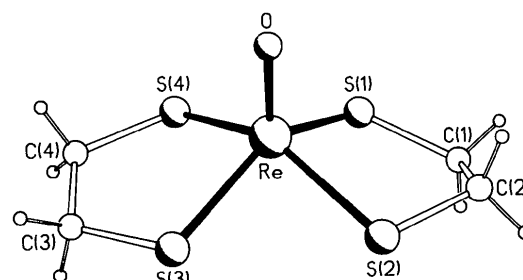


Fig. 1. Structure of the  $[\text{ReO}(\text{edt})_2]^-$  anion with the labelling scheme.

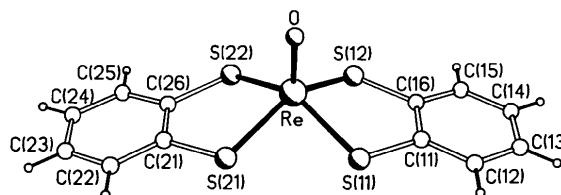


Fig. 2. Structure of the  $[\text{ReO}(\text{bdt})_2]^-$  anion with the labelling scheme.

H atoms constrained to give C–H = 0.96 Å, H–C–H = 109.5°, aromatic H on ring-angle external bisectors,  $U(H) = 1.2U_{eq}(C)$ , isotropic extinction parameter  $x = 3.6(2) \times 10^{-7}$  [ $1.42(4) \times 10^{-6}$ ] to give  $F'_c = F_c / (1 + xF_c^2 / \sin^2\theta)^{1/4}$  [absolute structure determination by refinement of  $\eta = -1.04(1)$ , followed by inversion to give the results here (Rogers, 1981)]. 317 [387] parameters,  $R = 0.0279$  [0.0253],  $wR = 0.0283$  [0.0318], mean  $\Delta/\sigma = 0.010$  [0.006], max. = 0.047 [0.018], max.  $\Delta\rho = 0.57$  [0.97], min. = -0.45 [-1.59] e Å<sup>-3</sup>, slope of normal probability plot = 1.72 [1.20]. Scattering factors from *International Tables for X-ray Crystallography* (1974), *SHELXTL* programs (Sheldrick, 1985).

Atomic parameters are given in Tables 1 and 2,\* selected bond lengths and angles in Tables 3 and 4.

\* Lists of structure factors, anisotropic thermal parameters, H-atom parameters and complete lists of bond lengths and angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 44334 (45 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Atomic numbering for the anions is shown in Figs. 1 and 2.

**Related literature.** The two Re complexes are isostructural with their Mo analogues (Ellis *et al.*, 1986; Boyde *et al.*, 1986), and can thus be used as diamagnetic hosts for single-crystal ESR studies of the paramagnetic Mo complexes.

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## Hexaaquatriss(oxalato)dipraseodymium(III) Pentahydrate (a Redetermination)

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**Abstract.** [Pr<sub>2</sub>(C<sub>2</sub>O<sub>4</sub>)<sub>3</sub>(H<sub>2</sub>O)<sub>6</sub>].5H<sub>2</sub>O,  $M_r = 744.0$ , monoclinic,  $P2_1/c$ ,  $a = 11.236(2)$ ,  $b = 9.634(3)$ ,  $c = 10.320(2)$  Å,  $\beta = 114.55(1)^\circ$ ,  $V = 1016.1$  Å<sup>3</sup>,  $Z = 2$ ,  $D_x = 2.44$  Mg m<sup>-3</sup>,  $F(000) = 720$ ,  $\lambda(\text{Mo } K\alpha) = 0.71069$  Å,  $\mu = 4.60$  mm<sup>-1</sup>,  $T = 293$  K,  $R = 0.046$  for 2162 unique reflexions [ $F > 3\sigma(F)$ ]. This work is a redetermination of an earlier photographic structural investigation [Ollendorff & Weigel (1969). *Inorg. Nucl. Chem. Lett.* **5**, 263–269] for which  $R = 0.130$ . The nine O atoms which make up the praseodymium coordination sphere are derived from three water and three oxalate ligands. Each oxalate group lies on a crystallographic inversion centre, thereby linking the Pr atoms into infinite hexagonal nets parallel to the *ac* plane. An interplanar separation of  $b/2$  is sufficient to accommodate 'zeolitic' water, which shows minor

differences in hydrogen bonding compared to an otherwise isostructural neodymium analogue {structure determined at 223 K by Hansson [*Acta Chem Scand.* (1973), **27**, 2852–2860], reported with a different choice of *c* relative to the title compound}.

**Experimental.** The title compound was prepared by diffusion of an aqueous solution of a Pr<sup>3+</sup> salt in silica gel containing oxamic acid at pH 5.5 to 7.5. Single crystals suitable for X-ray work formed as the oxamate anions were slowly hydrolysed to oxalate.

Colourless trapezoid 0.26 × 0.1 × 0.1 mm, Enraf-Nonius CAD-4 diffractometer, graphite-monochromatized Mo *K*α radiation, unit-cell dimensions from setting angles of 25 accurately centred reflexions ( $6.1 < \theta < 17.1^\circ$ ),  $\omega/2\theta$  scan mode used to measure