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Caesium *cis*-tetrachloridodioxidorhenate(VII)

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The title crystal structure, Cs[ReCl$_4$O$_2$], consists of *cis*-tetrachloridodioxidorhenate(VII) anions and caesium cations. The distorted octahedral anion has nearly C_{2v} symmetry, with a *cis* arrangement of the oxide ligands. The Re—Cl bond lengths for the Cl atoms *trans* to the oxide ligands are affected by the *trans* influence of the Re—O bonds and are longer than for the Cl atoms *cis* to the oxide ligands [average of 2.472 (2) Å *versus* average of 2.322 (2) Å, respectively]. There are ten Cl atoms from six *cis*-tetrachloridodioxidorhenate(VII) anions in the neighbourhood of the caesium cation.

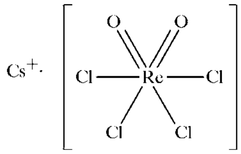
Comment

Tetrachloridodioxidorhenate(VII) anions, [ReCl$_4$O$_2$]$^-$, were initially studied as the first-stage yellow product in the reaction between gaseous hydrogen chloride and rhenate(VII) anions by Jeżowska-Trzebiatowska (1951). Crystal structures containing [ReCl$_4$O$_2$]$^-$ anions were reported recently by Supeł & Seppelt (2007) in the form of the tetraethylphosphonium salt and also as the [NO][ReCl$_4$O$_2$] salt. As far as the present authors are aware, the only other structure report of an [ReX_4O$_2$]$^-$ anion (X = halogen) was published for the [ReF$_4$O$_2$]$^-$ anion as the lithium salt (Casteel *et al.*, 1999).

In this paper, we report a simple method of obtaining unstable crystals of caesium *cis*-tetrachloridodioxidorhenate(VII), (I), and its crystal structure at 110 (2) K. This compound is one of the unstable crystalline products that it is possible to obtain in the reaction of caesium rhenate(VII) with acetyl chloride (see *Experimental*).

The crystal structure of (I) consists of *cis*-[ReCl$_4$O$_2$]$^-$ anions and caesium cations. In the distorted-octahedral *cis*-[ReCl$_4$O$_2$]$^-$ anion of nearly C_{2v} symmetry (Fig. 1), the two oxide ligands (O1 and O2) are in a *cis* arrangement. Such a *cis* arrangement of the oxide ligands is expected for a d^0 electron configuration of the central metal ion (Barea *et al.*, 1998). This is contrary to, for example, the d^2 configuration, where, based on molecular orbital calculations, the *trans* arrangement is favoured (Demachy & Jean, 1997). This symmetry, as well as the geometric parameters of the anion, corresponds very well to the data reported by Supeł & Seppelt (2007). In the tetraethylphosphonium salt (Supeł & Seppelt, 2007), the Re—O bond lengths are 1.692 (1) and 1.707 (1) Å, the Re—Cl$_{cis}$ bond lengths are 2.3225 (5) and 2.3302 (5) Å, the Re—Cl$_{trans}$ bond lengths are 2.4417 (4) and 2.4453 (5) Å, and the O—Re—O bond angle is 102.31 (7)°.

$$\mathrm{ReO_4^- + 4CH_3COCl = ReO_2Cl_4^- + 2(CH_3CO)_2O}$$



(I)

In the original paper reporting the crystal structure of [NO][ReCl$_4$O$_2$] (Supeł & Seppelt, 2007), a difference Fourier peak of 5.28 electrons was present, which could come from partial disorder. Refinement based on the original reflection data obtained from the former authors was performed. Although the inclusion of the highest peak in the new refinement resulted in a drop in the R value, we were unable to propose any disorder model better than the previously published model without disorder. It seems that in the reported crystal structure of [NO][ReCl$_4$O$_2$], only the geometric parameters of the second anion are affected by disorder. Therefore, these parameters will not be taken into account in the summary concerning the geometry of the ReO$_2$ moiety in [ReX_4O$_2$]$^-$ anions.

The Re—O bond lengths reported here [1.695 (3) and 1.704 (3) Å] are also comparable with the corresponding values published for the Re—O bond lengths in the [ReF$_4$O$_2$]$^-$ anion in its lithium salt [the anion can be described with only one Re—O bond length, 1.678 (9) Å, as only half the anion is symmetry independent; Casteel *et al.*, 1999]. All in all, according to the data reported so far, and taking into account the present report, the Re—O bond lengths in the *cis*-ReO$_2$ moiety in [ReX_4O$_2$]$^-$ anions should be approximately 1.70 Å.

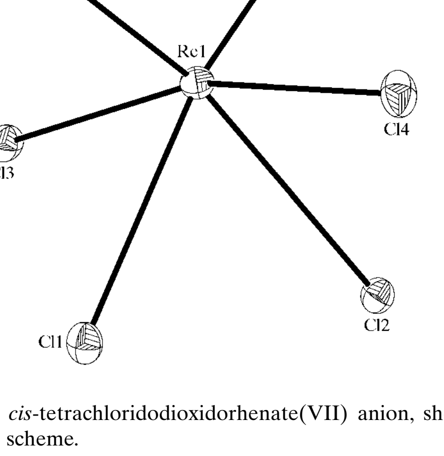


Figure 1
A view of the *cis*-tetrachloridodioxidorhenate(VII) anion, showing the atom-labelling scheme.

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Based on the aforementioned results, some general conclusions concerning the $[ReCl_4O_2]^-$ anion geometry can be made and the obtained values of the geometric parameters can be compared with the analogous rhenium d^2 system having a *trans* arrangement of the oxide ligands. A survey of the current literature on rhenium compounds reveals an example of a compound suitable for this purpose, potassium tetracyanidodioxidorhenate(V). The crystal structure of this complex was first determined by Łukaszewicz & Głowiak (1961), then by Murmann & Schlemper (1971), and finally by neutron diffraction by Fenn *et al.* (1971). The criterion for the suitability of this compound consists of the presence of two oxide ligands in a *trans* arrangement, Re^V as the central metal atom, and four remaining ligands of the same kind and possibly resembling chloride ligands. In this crystal structure, the complex *trans*-$[Re(CN)_4O_2]^{3-}$ anions differ from the *cis*-$[ReCl_4O_2]^-$ anions by the oxidation state of the central Re atom (Re^V instead of Re^{VII}), as well as by the arrangement of the two oxide ligands (*trans* instead of *cis*) and the type of the four remaining ligands (cyanide instead of chloride ligands). The Re—O bond length reported for this compound (Murmann & Schlemper, 1971) is 1.781 (3) Å. This means that in the *trans*-dioxidorhenium(V) moiety the Re—O bond should be 0.06–0.08 Å longer than in the *cis*-dioxidorhenium(VII) moiety.

The Re—Cl bond lengths reported here for the chloride ligands *cis* to the oxide ligands (Cl3 and Cl4) are 2.330 (2) and 2.313 (2) Å, respectively. The distances of the chloride ligands *trans* to the oxide ligands (Cl1 and Cl2) from the central Re1 atom are longer [2.473 (2) and 2.471 (2) Å, respectively]. These values for the Re—Cl_{trans} bond lengths are comparable with the analogous values published for other rhenium(VII) compounds. For *cis*-$[ReCl_4O_2]^-$ anions, Supeł & Seppelt (2007) reported values of 2.4417 (4) and 2.4453 (5) Å in the tetraethylphosphonium salt, and 2.488 (2) and 2.529 (2) Å for $[NO][ReCl_4O_2]$. In caesium *cis*-trichloridotrioxidorhenate(VII) reported by Lis (1983), the Re—Cl_{trans} bond lengths are 2.517 (8) and 2.494 (5) Å. In another example, $ReO_3Cl(THF)_2$, reported by Noh & Girolami (2007), the Re—Cl_{trans} bond length is 2.427 (2) Å. In all these cases, the lengthening of the Re—Cl bond is the result of the *trans* influence of the Re—O bond (Shustorovich *et al.*, 1975). Based on these data, it seems that the Re—Cl_{trans} (to the oxide O atom) bond should be as much as 0.10–0.25 Å longer than the Re—Cl_{cis} bond.

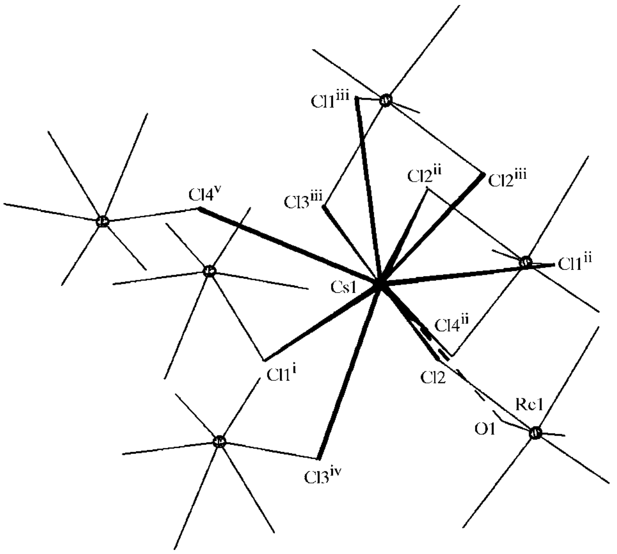

Figure 2
The nearest neighbours of the Cs^+ cation. The debatable contact to atom O1 (see *Comment*) is denoted with a dashed line. [Symmetry codes: (i) $x-1, -y+\frac{3}{2}, z+\frac{1}{2}$; (ii) $x-1, y, z$; (iii) $-x+1, -y+2, -z+1$; (iv) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (v) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$.]

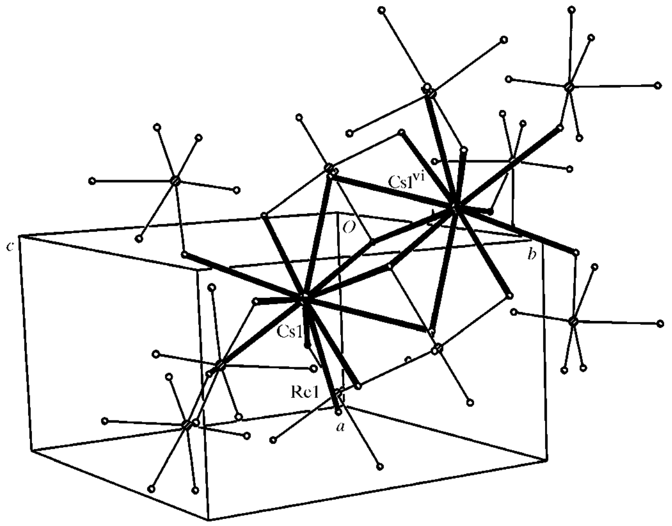

Figure 3
A view of the packing in the crystal structure, showing the three-dimensional network of short Cs···Cl contacts (heavy lines; see *Comment*). [Symmetry code: (vi) $-x, -y+2, -z+1$.]

There are ten Cl atoms from six *cis*-$[ReCl_4O_2]^-$ anions in the neighbourhood of the Cs^+ cation, at distances in the range 3.44–3.73 Å (see Table 2 for symmetry codes and the shortest interatomic distances; Fig. 2). Two anions are in contact with the Cs^+ cation *via* three chloride ligands ($Cl1^{ii}$, $Cl2^{ii}$ and $Cl4^{ii}$, and $Cl3^{iii}$, $Cl1^{iii}$ and $Cl2^{iii}$), while four anions are in contact *via* only one Cl ligand (Cl2, $Cl3^{iv}$, $Cl1^{i}$ and $Cl4^{v}$). For one *cis*-$[ReCl_4O_2]^-$ anion in contact with the Cs^+ cation *via* the Cl2 ligand, an additional contact involving the O1 ligand can be distinguished (Table 1). Thus, the Cs^+ cation is surrounded by 11 ligands from six anions, lying in the vertices of a 'staggered 164 stack' based on the considerations of King (1970).

The crystal structure is stabilized by a three-dimensional network of short Cs···Cl contacts (Fig. 3). The shortest distance between two Cs^+ cations is approximately 4.86 Å. The shortest intermolecular distance between two Re centres from two independent anions is approximately 4.73 Å.

Experimental

All operations were performed at room temperature. Caesium rhenate(VII) (0.05 g) was placed in a glass vessel and acetyl chloride (0.2 ml) was added. The vessel was covered with Parafilm. The mixture turned orange slowly and then red with dissolution of the solid rhenate(VII). At this stage, the vessel was covered with a plastic cap. After 1 d, extremely unstable crystals in the form of plates, which were difficult to handle and reproduce, began to precipitate. Part of the solution with the precipitated crystals was quickly placed on a cool plate, cooled to about 258 K under a nitrogen atmosphere and covered with perfluoroalkyl ether. All these operations were intended to avoid the decomposition of the crystals. A single crystal was selected from the cooled mixture and a preliminary X-ray diffraction measurement showed it likely to be composed of caesium *cis*-tetrachloridodioxidorhenate(VII) acetic anhydride solvate. The measurement provided only the crystal structure model, as the crystals were extremely unstable and some decomposition occurred before they were mounted on the diffractometer. This could lead to the conclusion concerning the apparent reaction shown in the scheme (see *Comment*).

After a week, in the remaining reaction mixture among the orange plates, red blocks began to appear with another kind of unstable orange plate. Application of a similar procedure to that described above enabled the performance of X-ray diffraction measurements for both new kinds of crystals. The red blocks consisted of caesium pentachloridooxidorhenate(VI) and the new kind of orange plates consisted of the title compound. Interestingly, the same reaction of acetyl chloride with caesium rhenate(VII) performed at about 267 K yielded orange crystals in the form of needles with the same composition as the title compound. At further reaction stages, the red mixture in contact with air turned violet and underwent decomposition to caesium rhenate(VII).

Crystal data

$Cs[ReCl_4O_2]$
$M_r = 492.91$
Monoclinic, $P2_1/c$
$a = 6.609\ (3)$ Å
$b = 10.322\ (5)$ Å
$c = 11.714\ (5)$ Å
$\beta = 92.04\ (5)^\circ$
$V = 798.6\ (6)$ Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 20.98$ mm^{-1}
$T = 110\ (2)$ K
$0.11 \times 0.11 \times 0.07$ mm

Data collection

Oxford Diffraction XcaliburPX CCD diffractometer
Absorption correction: analytical (*ABSPACK*; Oxford Diffraction, 2006)
$T_{\min} = 0.164$, $T_{\max} = 0.296$
14688 measured reflections
4462 independent reflections
2402 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.057$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.034$
$S = 0.77$
4462 reflections
73 parameters
$\Delta\rho_{\max} = 1.52$ e Å^{-3}
$\Delta\rho_{\min} = -1.59$ e Å^{-3}

The structure was solved using the Patterson method in *SHELXS97* (Sheldrick, 2008).

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2006); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2006); data reduction: *CrysAlis RED*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 2008); program(s) used to refine structure: *SHELXL97* (Sheldrick, 2008); molecular graphics: *XP* in *SHELXTL* (Bruker, 1997) and *DIAMOND* (Brandenburg & Putz, 2005); software used to prepare material for publication: *SHELXL97*.

Table 1
Selected geometric parameters (Å, °).

Re1—O1	1.695 (3)	Cs1—Cl1$^{\rm iii}$	3.6013 (18)
Re1—O2	1.704 (3)	Cs1—Cl2$^{\rm ii}$	3.4357 (19)
Re1—Cl1	2.4728 (14)	Cs1—Cl2	3.4761 (19)
Re1—Cl2	2.4710 (12)	Cs1—Cl2$^{\rm iii}$	3.5847 (15)
Re1—Cl3	2.3299 (13)	Cs1—Cl3$^{\rm iii}$	3.5584 (16)
Re1—Cl4	2.3131 (14)	Cs1—Cl3$^{\rm iv}$	3.5751 (17)
Cs1—O1	3.508 (3)	Cs1—Cl4$^{\rm ii}$	3.6662 (16)
Cs1—Cl1$^{\rm i}$	3.5082 (16)	Cs1—Cl4$^{\rm v}$	3.7314 (16)
Cs1—Cl1$^{\rm ii}$	3.5331 (18)	Cs1—Cs1$^{\rm vi}$	4.856 (2)
O1—Re1—O2	103.18 (13)	Cl4—Re1—Cl2	84.97 (4)
O1—Re1—Cl4	95.05 (10)	Cl3—Re1—Cl2	84.24 (5)
O2—Re1—Cl4	95.40 (10)	O1—Re1—Cl1	168.60 (9)
O1—Re1—Cl3	93.54 (10)	O2—Re1—Cl1	88.20 (10)
O2—Re1—Cl3	93.48 (10)	Cl4—Re1—Cl1	84.37 (5)
Cl4—Re1—Cl3	165.92 (3)	Cl3—Re1—Cl1	85.00 (5)
O1—Re1—Cl2	87.74 (9)	Cl2—Re1—Cl1	80.86 (4)
O2—Re1—Cl2	168.98 (9)		

Symmetry codes: (i) $x-1, -y+\frac{3}{2}, z+\frac{1}{2}$; (ii) $x-1, y, z$; (iii) $-x+1, -y+2, -z+1$; (iv) $x, -y+\frac{3}{2}, z+\frac{1}{2}$; (v) $-x+1, y+\frac{1}{2}, -z+\frac{3}{2}$; (vi) $-x, -y+2, -z+1$.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: IZ3041). Services for accessing these data are described at the back of the journal.

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