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Bis(triphenylphosphine)silver(I) perrhenate, a cyclic dimer

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Received ooth January 2012, Accepted ooth January 2012

DOI: 10.1039/x0xx00000x

www.rsc.org/

The 1:4 and 1:2 complexes of silver perrhenate and triphenylphosphine, [(Ph3P)2Ag] + ReO4 − and [(Ph3P)2AgReO4]2−, have been prepared and their structures determined in the solid state by X-ray diffraction. The former is composed of independent ions, while in the latter the ions are aggregated into cyclic dimers. The silver centers are tetracoordinate including contacts with two bridging perrhenate anions, setting this structure apart from that of the gold analogue [(Ph3P)2Au] + ReO4 − where the gold centers are strictly two-coordinate.

The perrhenate anion ReO4 − is a common component of many salt-like compounds, where it is associated with a large variety of monoatomic or more complex cations M [ReO4] 5−. Owing to very similar structure and charge characteristics of the anions, there are many analogies not only with the congeners permanganate (MnO4 −) and perrhenate anions, setting this structure apart from that of the gold analogue [(Ph3P)2Au] + ReO4 − where the gold centers are strictly two-coordinate.

The combination of perrhenate with the heavy coinage metals, Ag and Au, is poorly represented in the literature. Contrary to silver(I) perrhenate AgReO4, gold(I) perrhenate AuReO4 is still an unknown compound. In work published in 2013 on complexes with triphenylphosphine as a ligand it has been shown that in the 1:2 complex, [(Ph3P)2Au] + ReO4 −, the gold center has no acceptor affinity to the anion and remains strictly linearly two-coordinate. This result has recently been confirmed for a series of other gold(I) complexes with tertiary phosphines, where again the ReO4 − counterion is not part of the coordination sphere of the metal atoms. In subsequent investigations it has now been tried to synthesize the corresponding silver(I) complexes, where perrhenate complexation and hence activation may arise because relativistic effects which strongly favours two-coordination at gold(I), are strongly reduced at silver(I) centres.

However, compounds in which the perrhenate anion is coordinatively attached to acceptor atoms, or entertains covalent bonds with a substituent, are generally rare and in most cases of limited stability. This is particularly true for the highly unstable esters of perrhenic acid ROReO4, showing an analogy with the explosive esters of permanganic, pertechnetic and perchloric acid. An exceptional stability was only found for the silyl esters R3SiOReO4 which can be readily prepared and are stable at ambient temperature. The crystal structure of Me3SiOReO4 has been determined and shown to have a single discrete Si-O-Re linkage. Detailed 185,187 Re NQR measurements have confirmed that in this ester the ReO4 tetrahedron is indeed strongly distorted. Similar overall characteristics were found for organogermainium, -tin and -indium perrhenates.

From the reaction mixture of AgReO4 with PPh3 in the molar ratio 1:2 in dry acetonitrile at reflux temperature under nitrogen and with protection against incandescent light a crystalline product could be isolated in 92 % yield. The pale rosé colour of the primary product vanished upon careful crystal growth from acetonitrile. The expected 1:2 composition of the product was confirmed by an elemental analysis (Electr. Suppl. Inf., ESI). Solutions in acetonitrile-d3 showed a sharp single resonance in the 31P NMR spectrum with δ 11.25 ppm at 25 °C. No couplings 1J(107/109Ag - 31P) were observed even upon lowering the temperature to the solubility limit, probably owing to the rapid ligand exchange very common for silver(I) complexes of tertiary phosphines. The spectrum also suggests...
that the eight-membered ring found in the crystal structure is flexible or subject to partial dissociation in solution which is rapid on the NMR time scale.

The IR spectrum of the solid (on ATR crystals) shows that the prominent ν(Re-O) vibrational mode, which appears as a single band for the undistorted tetrahedral anionic ReO₄⁻ unit near 910 cm⁻¹ (see below), is split into two bands at 896 and 925 cm⁻¹ suggesting a significant distortion. In a single crystal X-ray diffraction analysis it has been shown that the perrhenate anions are indeed strongly coordinated to the silver atoms as shown in Fig. 1 (triclinic, space group P-1, for further crystallographic details see Table 1 in the ESI).

![Molecular structure of [(Ph₅P)₂AgReO₄]²⁻](image)

Figure 1. Molecular structure of [(Ph₅P)₂AgReO₄]²⁻. Thermal displacement parameters are shown at the 70 % level at 123 K. H atoms are omitted and the C atoms are shown as a wire-frame for the sake of clarity. Only one orientation of the disordered O3 and O4 atoms is shown.

Two formula units are associated into a cyclic dimer in which the ReO₄⁻ anions form triatomic bridges O-Re-O between the silver cations. The silver atoms are thus tetracoordinated with Ag-P and Ag-O bond lengths at 2.3997(8)/2.4227(7) and 2.366(2)/2.511(2) Å, respectively. The P-Ag-P angle of 133.38(3)° shows a strong deviation from the linear geometry observed in the gold analogue.²⁹ The point group symmetry of the cyclic dimer is Cᵥ as it resides around a crystallographic inversion center. The Re-O distances for the Ag-O-Re bridges are observed with Re-O(1) 1.718(2), Re-O(2) 1.705(2) Å. Due to the disorder of the terminal O atoms, a direct comparison of the distances to the terminal oxygen atoms (Re-O(3A/B) 1.60(2)/1.81(2), Re-O(4A/B) 1.78(1)/1.65(2) Å) is not meaningful, but as expected the former Re-O distances are similar to, and the latter shorter than the reference distance in an undistorted ReO₄⁻ tetrahedron which is present in the gold analogue [1.710(7)-1.716(7) Å].²⁶ However, it is interesting to note that in crystals of AgReO₄ (Scheelite-type), where all four oxygen atoms of the anion have intimate contact with the silver cation,² the Re-O distances are as long as 1.732(2) Å showing the strong influence of silver multiple-coordination on the structure of the anion. The strong donor properties of the perrhenate anion for silver(I) are also evident from a comparison with the corresponding tetrafluoroborate [(Ph₅P)₂Ag]BF₄⁻. When this compound is prepared in acetonitrile, its 1:1 solvate [(Ph₅P)₂Ag(NCMe)]⁺ BF₄⁻ with a tricoordinate silver atom is formed.²⁵ By contrast, perrhenate competes favourably with the solvent molecules and only perrhenate complexation is established.

Experiments with a molar ratio 1:4 of the reactants in a mixture of dry acetonitrile and benzene [2:5 v/v] at 25 °C under nitrogen and protection against light led to the formation of the complex [(Ph₅P)₂Ag]²⁻ ReO₂⁻ in 89 % yield. A compound of this composition has been prepared in a previous report, but no structural data are available.²⁸ Crystals grown from the reaction mixture were colourless and stable to air, moisture and light. Their composition was confirmed by elemental analysis (ESI). Solutions in acetonitrile-d₈ at 25 °C showed a singlet resonance at δ 10.8 ppm in the ³¹P NMR spectrum, again without ¹⁰⁷/¹⁰⁹Ag - ³¹P couplings. The crystals (trigonal, space group R3) are related with those of known compounds containing the [(Ph₅P)₂Ag]⁺ cation associated with other tetrahedral anions like ClO₄⁻ or BF₄⁻ (space groups R-3, heavily disordered tetrahedral anions due to site symmetry).²⁵,³⁶ It is possible that for these cases the space group type R3 would be a better choice as well. For crystallographic details, information on the space group choice, crystal structure solution and refinement see the SI.

The bond lengths and angles of the cations are within the range of data collected in earlier studies. The tetrahedron of the anion is largely undistorted as shown also by the IR spectrum of the crystals, where only a single sharp band is observed for the ν(Re-O) mode at 906.8 cm⁻¹. Attempts to prepare crystals of compounds with the 1:1 and 1:3 stoichiometry were unsuccessful.

In summary, in the present work structural details of silver-perrhenate coordination have been provided for a molecular system. The results help to explain the unusual silver-perrhenate affinity suggested by a number of earlier qualitative observations. This affinity causes distinct differences in the structural chemistry of silver(I) and gold(I) compounds. The radii of Ag⁺ and Au⁺ are known to be virtually the same for both the two- and four-coordinate states owing to strong relativistic contraction of the frontier orbitals of the latter.³⁷,³⁸ The differences in the Ag/Au←O-ReO₄⁻ acceptor strength are the result of the distinct preference for two-coordination with high s-character in the two dative bonds at gold(I), which is less pronounced for silver(I). Along the same lines, the higher donor strengths of the perrhenate anion as compared to, e.g. the perchlorate anion (the former is coordinated to Ag, while the latter is not) is related to strong relativistic effects on rhenium which strongly modify the donor properties of the ReO₄⁻ anion through electronegativity enhancement and orbital rehybridization affecting the nature of the Re-O bonds.³⁹,⁴⁰

Notes and references

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Electronic Supplementary Information (ESI) available: Preparation of the described compounds, ATR-IR spectra, NMR and elemental analyses data, selected crystallographic data, details on structure solution and
refinement, additional figures. CCDC 1052824 and 1052825 See
DOI: 10.1039/c000000x/


4. R. D. Peacock, The Chemistry of Technetium and Rhenium, Elsevier,
Amsterdam 1966.


C49, 214.

1992, 47b, 1513.


15. H. Schmidbaur, S. Cronje, B. Djordjevic, O. Schuster, Chemical


6386.


20. E. Herdtweck, P. Kiprof, W. A. Herrmann, J. G. Kuchler, I. A.


