Synthesis and characterisation of rhenium dithiocarbamate complexes. Crystal structures of [ReO{O(OH)C$_6$H$_4$}(S$_2$CNEt$_2$)$_2$], [Re{PPh$_2$(C$_6$H$_4$S-2)}$_2$(S$_2$CNEt$_2$)]·Me$_2$CO and [ReO{PPh-(C$_6$H$_4$S-2)$_2$}(S$_2$CNEt$_2$)]

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The reaction of [Re$_2$O$_3$(S$_2$CNEt$_2$)$_4$] with catechol in acetone yielded the dark orange complex [ReO{O(OH)C$_6$H$_4$}(S$_2$CNEt$_2$)$_2$] **1**. The crystal structure shows a distorted-octahedral geometry with the oxo group *trans* to the monodentate catecholate ligand. The Re–O (catechol) bond length is typical of a Re–O single bond and implies little *trans* influence of the oxo ligand. Reaction of [Re$_2$O$_3$(S$_2$CNEt$_2$)$_4$] with 1,4-dihydroxybenzene yielded the red-brown dimer [{ReO(S$_2$CNEt$_2$)$_2$}$_2$(C$_6$H$_4$O$_2$-1,4)] **2**, in which the dianionic ligand bridges two rhenium centres. With 2-amino-4-methylphenol [ReO(OC$_6$H$_3$NH$_2$-2-Me-4)(S$_2$CNEt$_2$)$_2$] **3** was obtained containing the ligand co-ordinated in a monodentate mode. Reaction of [Re$_2$O$_3$(S$_2$CNEt$_2$)$_4$] with dithiolate proligands such as ethane-1,2-dithiol yielded [NEt$_2$H$_2$][ReOL$_2$], L = C$_2$H$_4$S$_2$-1,2 **4**, C$_6$H$_4$S$_2$-1,2 **5** or MeC$_6$H$_3$S$_2$-3,4 **6**, where degradation of the dithiocarbamate ligands to form the diethylammonium counter ion occurs. Reaction of **1** with bidentate phosphines yielded green complexes of the general formula [Re(S$_2$CNEt$_2$)$_2$L][BPh$_4$], where L = Me$_2$PCH$_2$CH$_2$PMe$_2$ **7** or Ph$_2$PCH$_2$CH$_2$PPh$_2$ **8**. These reactions can be contrasted to the inactivity of these phosphine ligands towards [Re$_2$O$_3$(S$_2$CNEt$_2$)$_4$]. The reaction of [Re$_2$O$_3$(S$_2$CNEt$_2$)$_4$] with the bidentate phosphinothiolate proligand PPh$_2$(C$_6$H$_4$SH-2) in acetone at room temperature yielded the red-orange rhenium(III) complex [Re{PPh$_2$(C$_6$H$_4$S-2)}$_2$(S$_2$CNEt$_2$)]·Me$_2$CO **9**. The crystal structure revealed a distorted-octahedral geometry. The sulfur donors of the phosphinothiolate ligands adopt a *cis* configuration. Reaction of [Re$_2$O$_3$(S$_2$CNEt$_2$)$_4$] with the tridentate phosphinothiolate proligand PPh(C$_6$H$_4$SH-2)$_2$ proceeded at room temperature to yield the red rhenium(v) complex [ReO{PPh(C$_6$H$_4$S-2)$_2$}(S$_2$CNEt$_2$)] **10**. Its crystal structure shows a distorted-octahedral geometry. Reaction of [Re$_2$O$_3$(S$_2$CNEt$_2$)$_4$] with SiMe$_3$Cl yielded the new rhenium(v) precursor [ReCl$_2$(S$_2$CNEt$_2$)$_2$][BPh$_4$] **11** which permits investigation into rhenium dithiocarbamate chemistry without an oxo core.

The dithiocarbamate core, M–S$_2$CNR$_2$, could prove to be of great synthetic utility in radiopharmacology as a wide variety of organic substituents can be incorporated in the stable bidentate ligand. This allows the chemical 'fine-tuning' of the biological properties of the complex by variation of the organic substituent R, and this can be carried out independently of the other ligands on the metal. Also variation of coligands has an effect on the biodistribution of the metal complex. Here we report our attempts to synthesize rhenium dithiocarbamate complexes with a variety of coligands to explore the chemistry of the rhenium–dithiocarbamate core. We are interested in the chemistry of rhenium and technetium dithiocarbamate complexes for their potential use as radiopharmaceuticals for imaging and therapy by using the ^{99m}Tc and $^{186/188}$Re radionuclides. The chemistry of the rhenium–dithiocarbamate core complements on-going work into the chemistry of the technetium-99m–dithiocarbamate core.[1]

Here we report an investigation into the reaction of the 'Re(S$_2$CNEt$_2$)' core with a range of mono-, bi and tri-dentate ligands including catechol, PPh$_2$(C$_6$H$_4$SH-2) and PPh(C$_6$H$_4$SH-2)$_2$. Catechol complexes are well known for most of the transition elements including iron, molybdenum, osmium, manganese and chromium.[2] Catechol and catecholate ligands are of interest due to their significance in certain biological systems as their inherent redox activity plays a central role in intermolecular electron-transfer reactions. Biological applications of catechol include incorporation in iron-sequestering agents (siderophores) and also use as biogenic amines such as the catecholamines adrenaline {4-[1-hydroxy-2-(methylamino)-ethyl]benzene-1,2-diol}, dopamine [4-(2-aminoethyl)-benzene-

1,2-diol] and isoprotenerol [4-{1-hydroxy-2-[(1-methylethyl)-amino]ethyl}-benzene-1,2-diol] which act as neurotransmitters in the brain and nervous system. On co-ordination catechol more commonly binds as a bidentate ligand, however there are examples of monodentate catecholate complexes and the first structures were determined by Heistand II *et al.*[3] A more recent example is of the niobium(v) porphyrin complex [Nb-(tpp){O(OH)C$_6$H$_4$}(O$_2$C$_6$H$_4$)][4] which was found to contain both types of co-ordination geometries (tpp represents the 5,10,15,20-tetraphenylporphyrin dianion). The co-ordination chemistry of bidentate phosphinothiolate ligands such as PPh$_2$(C$_6$H$_4$SH-2) has been explored to some extent[5] but that of the potentially tridentate ligands such as PPh(C$_6$H$_4$SH-2)$_2$ has been less studied. Structures which have been determined of the complexes of these mixed-donor tridentate ligands include [Re{PPh(C$_6$H$_4$S-2)$_2$}$_2$][6] and [Mo(NNPh$_2$){PPh(C$_6$H$_4$S-2)$_2$}$_2$].[7]

Results and Discussion

Preparation and properties of the dithiocarbamate complexes

The rhenium(v) precursor [Re$_2$O$_3$(S$_2$CNEt$_2$)$_4$] reacts readily with catechol in acetone under reflux to yield the orange, air-stable rhenium(v) complex [ReO{O(OH)C$_6$H$_4$}(S$_2$CNEt$_2$)$_2$] **1** in near-quantitative yield. The ^{1}H NMR spectrum displays a complex series of resonances in the range δ 6.5–6.7 attributable to the phenyl protons of the catecholate ligand. The unexpected co-ordination of catechol as a monodentate ligand was confirmed by the observation of the resonance due to the OH proton at δ 5.8 and a band in the infrared spectrum at 3489 cm^{-1} due to ν(O–H). Confirmation of this co-ordination is provided

by the shift of $\nu(CC)$, due to the ring stretch between C(1) and C(2) of the catecholate ring, from 1620 cm^{-1} for the free catechol[8] to 1471 cm^{-1} for the complex. This shift to lower energy is due to the deprotonation and co-ordination of one of the oxygen donors. Also present at 1271 cm^{-1} is a band which can be attributed to $\nu(C-O)$ of the co-ordinated catecholato anion and indicates that the ligand had no semiquinone character for which the $\nu(C-O)$ would occur around 1500 cm^{-1}.[9] A sharp band at 969 cm^{-1} was observed which is typical of $\nu(Re=O)$.[10] In the ^{1}H NMR spectrum the resonances due to the ethyl protons of the dithiocarbamate ligand are present as a triplet at δ 1.3 and as a quartet at δ 3.8 due to the CH$_3$ and CH$_2$ protons respectively, which confirms the presence of equivalent dithiocarbamate ligands. The red-brown dimeric species [{ReO-(S$_2$CNEt$_2$)$_2$}$_2$(C$_6$H$_4$O$_2$-1,4)] **2** is formed by the reaction of [Re$_2$O$_3$(S$_2$CNEt$_2$)$_4$] with 1,4-dihydroxybenzene. The complex is sparingly soluble in most solvents with the dianionic ligand bridging the two rhenium metal centres. The presence of a strong absorption due to $\nu(C-O)$ at 1248 cm^{-1} and absence of any bands assignable to $\nu(OH)$ confirmed the ligand had completely deprotonated and had no semiquinone character confirming a formal rhenium(v) oxidation state. The ^{1}H NMR spectrum of complex **2** shows the retention of the dithiocarbamate ligand with the resonances due to the CH$_3$ and CH$_2$ protons present as a triplet at δ 1.3 and a quartet at δ 3.8 respectively. The resonances due to the aromatic protons of the dianionic ligand were present as a multiplet between δ 6.5 and 6.7. Room-temperature reaction of [Re$_2$O$_3$(S$_2$CNEt$_2$)$_4$] with 1,2-dithiolate ligands yielded orange anionic complexes of the type [NEt$_2$H$_2$][ReOL$_2$], where L = C$_2$H$_4$S$_2$-1,2 **4**, C$_6$H$_4$S$_2$-1,2 **5** or MeC$_6$H$_3$S$_2$-3,4 **6**. The crystal structure determination of **4** was undertaken and confirmed a square-based pyramidal arrangement of ligands surrounding the central rhenium centre. The structure is analogous to [PPh$_4$][ReO(S$_2$C$_2$H$_4$)$_2$] which has previously been determined.[11] The [NEt$_2$H$_2$]$^+$ cation results from the decomposition of Et$_2$NCS$_2^-$ and similar reactions have been observed previously during the reaction of sodium diethyldithiocarbamate with metal complexes.[12] The resonance due to the NH protons was present at δ 6.1 and could be removed by H/D exchange by shaking with D$_2$O. These reactions with the 1,2-dithiolate ligands can be contrasted with the behaviour of the parent monodentate ligands, phenol and benzenethiol, with [Re$_2$O$_3$(S$_2$CNEt$_2$)$_4$] where no reaction was found to occur even in the presence of base and the use of forcing reaction conditions. The terminal oxo core was found to be retained in all three complexes and the absorption due to $\nu(Re=O)$ was identified in the infrared spectrum as strong bands at 954, 948 and 923 cm^{-1} for complexes **4**, **5** and **6**.

The complex [ReO{O(OH)C$_6$H$_4$}(S$_2$CNEt$_2$)$_2$] reacts readily with bidentate phosphines in boiling acetone to yield green complexes of general formula [Re(S$_2$CNEt$_2$)$_2$L][BPh$_4$] where L = Me$_2$PCH$_2$CH$_2$PMe$_2$ (dmpe) **7** or Ph$_2$PCH$_2$CH$_2$PPh$_2$ (dppe) **8**. In contrast, no reaction was found to occur between the phosphines and the dimeric precursor [Re$_2$O$_3$(S$_2$CNEt$_2$)$_4$]. The IR spectrum confirmed the absence of $\nu(Re=O)$ and the ^{1}H NMR spectra gave the expected resonances assigned to the ethyl protons of the dithiocarbamate ligand and to the protons of the co-ordinated bidentate phosphine. The ^{31}P-{^{1}H} NMR spectra of **7** and **8** gave rise to the expected singlets at δ 44.5 and 12.4 due to the equivalent phosphorus donors in both complexes. The FAB mass spectra show ions at $m/z = 632$ and 881 respectively with the appropriate isotope distribution.

The orange-red rhenium(III) complex [Re{PPh$_2$(C$_6$H$_4$S-2)}$_2$-(S$_2$CNEt$_2$)]·Me$_2$CO **9** was prepared from the overnight room-temperature reaction of [Re$_2$O$_3$(S$_2$CNEt$_2$)$_4$] with the phosphinothiolate proligand PPh$_2$(C$_6$H$_4$SH-2). The terminal oxo ligand had been replaced by the bidentate phosphine/thiolate ligand. The ^{1}H NMR spectrum shows the resonances due to the protons of the dithiocarbamate ligands at δ 0.6 due to the methyl protons and δ 2.9 due to the methylene protons. The resonances
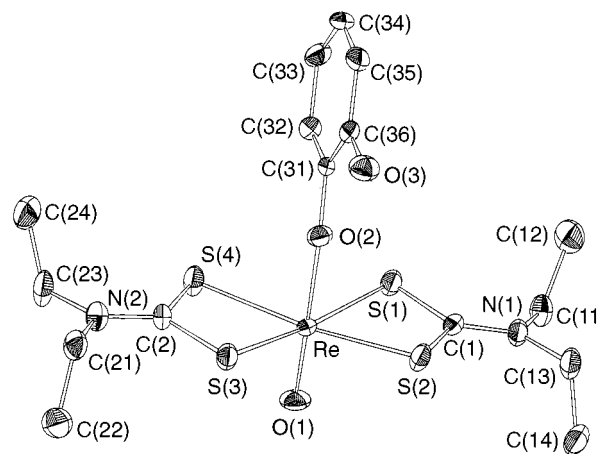

Fig. 1 Perspective view of [ReO{O(OH)C$_6$H$_4$}(S$_2$CNEt$_2$)$_2$] **1** showing the atom labelling scheme

Table 1 Selected bond lengths (Å) and angles (°) for [ReO{O(OH)-C$_6$H$_4$}(S$_2$CNEt$_2$)$_2$] **1**

Re–O(1)	1.666(6)	Re–S(4)	2.444(2)
Re–O(2)	1.969(5)	Re $\cdots$ O(3)	4.462(6)
Re–S(3)	2.411(2)	O(2)–C(31)	1.338(8)
Re–S(2)	2.425(2)	O(3)–C(36)	1.356(10)
Re–S(1)	2.434(2)		
O(1)–Re–O(2)	175.4(2)	S(3)–Re–S(1)	172.05(7)
O(1)–Re–S(3)	97.1(2)	S(2)–Re–S(1)	72.37(7)
O(2)–Re–S(3)	86.1(2)	O(1)–Re–S(4)	91.7(2)
O(1)–Re–S(2)	96.8(2)	O(2)–Re–S(4)	86.1(2)
O(2)–Re–S(2)	85.4(2)	S(3)–Re–S(4)	72.30(7)
S(3)–Re–S(2)	105.97(7)	S(2)–Re–S(4)	171.48(7)
O(1)–Re–S(1)	90.8(2)	S(1)–Re–S(4)	108.15(7)
O(2)–Re–S(1)	86.1(2)	C(31)–O(2)–Re	146.5(5)

due to the aromatic protons were found as a multiplet between δ 7.1 and 7.9. The single phosphorus environment was confirmed by the singlet observed in the ^{31}P-{^{1}H} NMR spectrum at δ 20.2. This reaction can be contrasted to the formation of [ReO{PPh(C$_6$H$_4$S-2)$_2$}(S$_2$CNEt$_2$)] **10** which was obtained from the reaction of [Re$_2$O$_3$(S$_2$CNEt$_2$)$_4$] and the tridentate proligand PPh(C$_6$H$_4$SH-2)$_2$. In complex **10** the oxo ligand was retained which was confirmed by the strong absorption observed in the infrared spectrum at 941 cm^{-1} due to the stretching frequency of the Re=O bond. The ^{1}H NMR spectrum was unremarkable except for the observation of complex multiplets between δ 3.7–4.1 and 1.4–1.5 which were assigned as the methylene and methyl protons of ethyl groups in inequivalent environments. The ^{31}P-{^{1}H} NMR spectrum shows the expected singlet at δ 47.7 due to the co-ordinated phosphine. The new dithiocarbamate precursor [ReCl$_2$(S$_2$CNEt$_2$)$_2$][BPh$_4$] **11** was prepared in high yield by the room-temperature reaction of the oxo precursor with SiMe$_3$Cl. The resonances from the methyl and methylene protons from the co-ordinated dithiocarbamates were present as a triplet at δ 1.5 and a quartet at δ 3.9 respectively indicating equivalence of the dithiocarbamate ethyl groups. The aromatic protons from the counter ion were present as a multiplet between δ 6.9 and 7.5. The new precursor will allow a route into rhenium dithiocarbamate chemistry without involvement of an oxo core.

Crystal and molecular structures of [ReO{O(OH)C$_6$H$_4$}-(S$_2$CNEt$_2$)$_2$] 1, [Re{PPh$_2$(C$_6$H$_4$S-2)}$_2$(S$_2$CNEt$_2$)]·Me$_2$CO 9 and [ReO{PPh(C$_6$H$_4$S-2)$_2$}(S$_2$CNEt$_2$)] 10

A representation of the structure of complex **1** is shown in Fig. 1 along with the associated atom numbering scheme. Selected bond lengths and angles are given in Table 1. The overall geom-
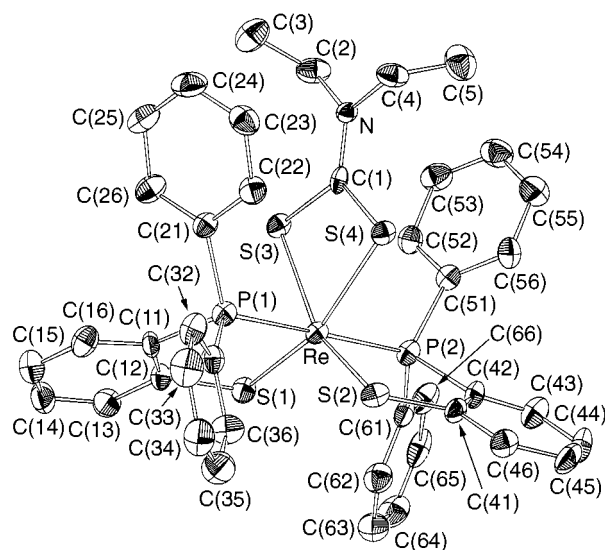
Fig. 2 Perspective view of [Re{PPh₂(C₆H₄S-2)}₂(S₂CNEt₂)]·Me₂CO **9** showing the atom labelling scheme

Fig. 3 Perspective view of [ReO{PPh(C₆H₄S-2)₂}(S₂CNEt₂)] **10** showing the atom labelling scheme

Table 2 Selected bond lengths (Å) and angles (°) for [Re{PPh₂-(C₆H₄S-2)}₂(S₂CNEt₂)]·Me₂CO **9**

Re–S(2)	2.265(2)	Re–S(3)	2.502(2)
Re–S(1)	2.265(2)	S(3)–C(1)	1.723(9)
Re–P(2)	2.371(3)	S(4)–C(1)	1.714(9)
Re–P(1)	2.376(3)	N–C(1)	1.318(13)
Re–S(4)	2.496(2)		
S(2)–Re–S(1)	116.88(9)	P(2)–Re–S(4)	85.15(9)
S(2)–Re–P(2)	85.99(9)	P(1)–Re–S(4)	95.63(9)
S(1)–Re–P(2)	93.48(9)	S(2)–Re–S(3)	155.26(8)
S(2)–Re–P(1)	94.14(9)	S(1)–Re–S(3)	87.71(8)
S(1)–Re–P(1)	85.78(9)	P(2)–Re–S(3)	95.63(8)
P(2)–Re–P(1)	179.22(8)	P(1)–Re–S(3)	84.58(8)
S(2)–Re–S(4)	86.57(8)	S(4)–Re–S(3)	69.03(8)
S(1)–Re–S(4)	156.40(9)		

Table 3 Selected bond lengths (Å) and angles (°) for [ReO{PPh-(C₆H₄S-2)₂}(S₂CNEt₂)] **10**

Re–O(1)	1.679(4)	Re–S(3)	2.430(2)
Re–S(1)	2.326(2)	Re–S(2)	2.624(2)
Re–S(4)	2.378(2)	S(3)–C(1)	1.725(6)
Re–P(1)	2.3847(14)	S(4)–C(1)	1.746(6)
O(1)–Re–S(1)	103.4(2)	S(4)–Re–S(3)	72.70(5)
O(1)–Re–S(4)	108.5(2)	P(1)–Re–S(3)	102.07(5)
S(1)–Re–S(4)	91.97(5)	O(1)–Re–S(2)	162.7(2)
O(1)–Re–P(1)	93.2(2)	S(1)–Re–S(2)	81.74(5)
S(1)–Re–P(1)	86.07(5)	S(4)–Re–S(2)	87.50(5)
S(4)–Re–P(1)	157.97(6)	P(1)–Re–S(2)	70.49(5)
O(1)–Re–S(3)	96.7(2)	S(3)–Re–S(2)	81.66(5)
S(1)–Re–S(3)	157.82(6)		

etry about the central rhenium atom is distorted octahedral with the principal distortions coming from the relatively small bite angles of the chelated dithiocarbamate ligands, S(1)–Re–S(2) 72.37(7) and S(3)–Re–S(4) 72.30(7)°. The four sulfur donors occupy the equatorial plane of the octahedron with the two oxygen donors occupying the remaining sites. The most surprising feature of the structure is the monodentate binding of the potentially bidentate catechol ligand. The Re–O (catecholate) distance of 1.969(5) Å shows no pronounced lengthening as a consequence of the *trans* influence of the oxo group. This bond length can be compared with those found for [ReO₂(O₂C₆H₄)₂]⁻ where the Re–O (catecholate) distances are 1.952(6) and 2.031(7) Å for the bond *cis* and *trans* to the oxo core respectively and with 1.96(1) Å found in the *cis* catecholate complex [ReO(O₂C₆H₄)₂]⁻.[13] The C–O distance of C(31)–O(2) 1.338(8) Å is consistent with the presence of an anionic catecholato ligand rather than the presence of the semiquinone or benzoquinone forms.[4] The Re–O (catechol) distance *trans* to the oxo ligand is typical of an Re–O single bond[14] and implies little bond lengthening due to the *trans* influence. The presence of the unligated OH group is confirmed by the slightly longer C(36)–O(3) bond [1.356(10) Å] and the Re···O(3) distance of 4.462(6) Å also supports the non-bonding of the hydroxyl group.

A representation of the structure of [Re{PPh₂(C₆H₄S-2)}₂-(S₂CNEt₂)]·Me₂CO **9** is shown in Fig. 2 together with the atom-labelling scheme and selected bond lengths and angles are shown in Table 2. The geometry about the rhenium is best described as distorted octahedral. The principal distortions
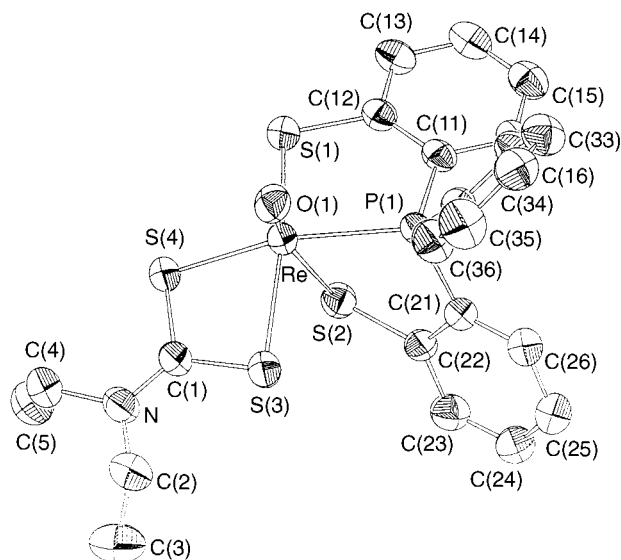
are the result of the bite angles of the bidentate ligands, S(1)–Re–P(1) 85.78(9), S(2)–Re–P(2) 85.99(9)°, with the largest distortion arising from the small bite angle of the dithiocarbamate ligand S(3)–Re–S(4) 69.03(8)°. The sulfur donors of the phosphinothiolate ligands are in a *cis* configuration along with the dithiocarbamate sulfurs resulting in one plane being comprised of only sulfur donors. There is significant opening up of the S(1)–Re–S(2) angle to 116.88(9)° which was also observed in the structure of [Re{PPh₂(C₆H₄S-2)}₃] where the corresponding angle was determined to be 113.0(2)°. The most likely explanation is electronic repulsion between the two negatively charged thiol groups. The Re–S and Re–P distances are typical of those found in rhenium(III) complexes.[15]

The structure of [ReO{PPh(C₆H₄S-2)₂}(S₂CNEt₂)] **10** is shown in Fig. 3 and selected bond distances and angles are shown in Table 3. The overall geometry about the central rhenium atom is best described as distorted octahedral with the tridentate ligand, PPh(C₆H₄S-2)₂, bound in a facial co-ordination. The oxo group is *trans* to a sulfur of the phosphinothiolate ligand. The principal distortions arise from the small bite angles of the polydentate ligands, S(3)–Re–S(4) 72.70(5)° in the dithiocarbamate ligand, and due to the constraints of the P–C–C–S chelate rings the S–Re–P bond angles are significantly reduced from the ideal octahedral values of 90° to 86.07(5) and 70.49(5)°. The Re–S(2) bond shows significant lengthening due to the *trans* influence of the oxo group, 2.624(2) Å, as compared with the more usual bond length of 2.326(2) Å for Re–S(1). The Re–S and Re–P distances are unremarkable and are similar to those found for complexes of phosphinothiolate ligands.[6]
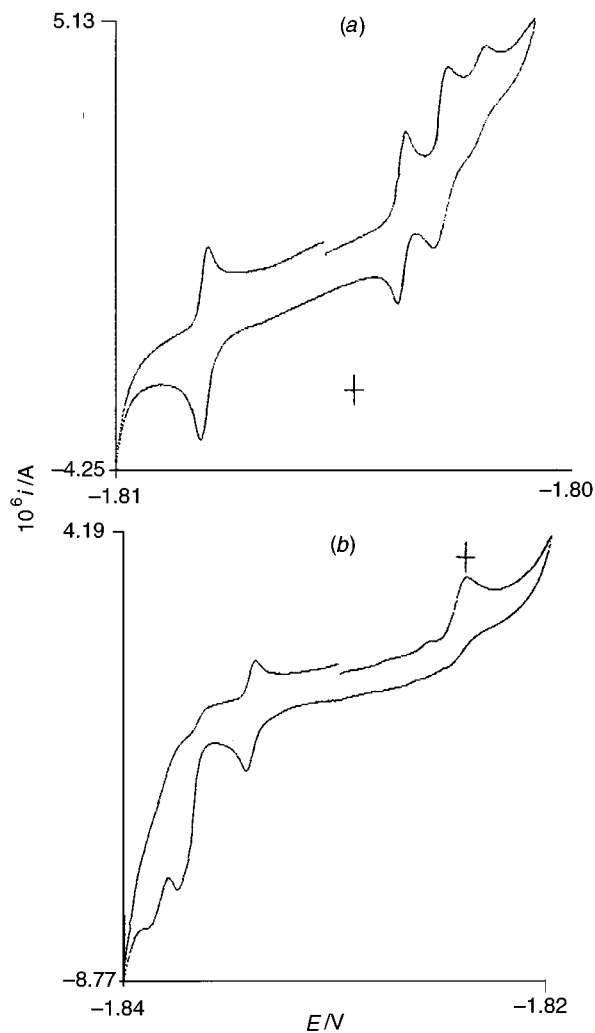
Fig. 4 Cyclic voltammograms for [Re{PPh$_2$(C$_6$H$_4$S-2)}$_2$(S$_2$CNEt$_2$)]·Me$_2$CO **9** (*a*) and [ReO{PPh(C$_6$H$_4$S-2)$_2$}(S$_2$CNEt$_2$)] **10** (*b*) recorded at room temperature in CH$_2$Cl$_2$ at a platinum-wire auxiliary electrode and silver-wire pseudo-reference electrode

Electrochemistry of [Re{PPh$_2$(C$_6$H$_4$S-2)}$_2$(S$_2$CNEt$_2$)]·Me$_2$CO 9 and [ReO{PPh(C$_6$H$_4$S-2)$_2$}(S$_2$CNEt$_2$)] 10

The cyclic voltammetry data for complexes **9** and **10** are summarised in Table 4. The complex [Re{PPh$_2$(C$_6$H$_4$S-2)}$_2$(S$_2$CNEt$_2$)]·Me$_2$CO **9**, Fig. 4(*a*), shows two reversible and one irreversible oxidation which could be accounted for by the reversible oxidation of the rhenium(III) complex to Re^{IV} and Re^V and an irreversible oxidation to Re^{VI}. The first oxidation was a simple reversible one-electron process whilst the second reversible oxidation appeared to have slow electron transfer. The electrochemical behaviour of the complex during reduction showed a reversible one-electron transfer. The complex [ReO{PPh(C$_6$H$_4$S-2)$_2$}(S$_2$CNEt$_2$)] **10**, Fig. 4(*b*), shows an irreversible oxidation which can be accounted for by an oxidation of Re^V to Re^{VI}. On the negative sweep one reversible and two irreversible reductions were identified. The reversible reduction, Re^V to Re^{IV}, exhibited an ideal one-electron transfer. The two reversible reductions involve conversion of Re^{IV} into Re^{III} and a further reduction to Re^{II}.

Conclusion

We have described the syntheses and properties of some new rhenium dithiocarbamato-complexes. The complex [ReO{O-(OH)C$_6$H$_4$}(S$_2$CNEt$_2$)$_2$] **1** represents a relatively rare example of a complex containing a monodentate catecholate ligand. Reaction with the analogous bidentate ligands unexpectedly

Table 4 Cyclic voltammetric data for complexes **9** and **10**

Complex	Process	i_{pa}/i_{pc}	E_{pa}*/V	E_{pc}*/V	E_p/mV	$E_{\frac{1}{2}}$/V
9	Oxidation 1	1.03	+0.61	+0.69	71	+0.65
	Oxidation 2	1.10	+0.93	+1.05	120	+0.99
	Oxidation 3	—	+1.37	—	—	—
	Reduction	0.96	−1.02	−1.08	63	−1.05
10	Oxidation	—	+1.39	—	—	—
	Reduction 1	1.06	−0.74	−0.81	72	−0.78
	Reduction 2	—	−1.39	—	—	—
	Reduction 3	—	−1.63	—	—	—

* All potentials are quoted relative to the ferrocenium–ferrocene couple taken as 0.0 V. Ferrocene was added to the cell for each measurement. Scan rate 0.2 V s^{-1}.

yielded complexes of the general type [NEt$_2$H$_2$][ReOL$_2$], where L = C$_2$H$_4$S$_2$-1,2 **4**, C$_6$H$_4$S$_2$-1,2 **5** and MeC$_6$H$_3$S$_2$-3,4 **6**. Degradation of the dithiocarbamate ligand by the thiolate ligands is the source of the counter ion. The dimeric oxo-bridged precursor was found to be unreactive towards both mono- and bi-dentate phosphines. Complexes such as [Re(S$_2$CNEt$_2$)$_2$L]-[BPh$_4$], where L = dmpe **7** or dppe **8**, could only be prepared from the reaction of the catecholate complex [ReO{O(OH)-C$_6$H$_4$}(S$_2$CNEt$_2$)$_2$] **1** with these ligands. The mixed phosphine–thiolate complexes [Re{PPh$_2$(C$_6$H$_4$S-2)}$_2$(S$_2$CNEt$_2$)]·Me$_2$CO **9** and [ReO{PPh(C$_6$H$_4$S-2)$_2$}(S$_2$CNEt$_2$)] **10** could be prepared in high yield from the room-temperature reaction of [Re$_2$O$_3$-(S$_2$CNEt$_2$)$_4$] with the mono- and bi-dentate ligands respectively. The new rhenium dithiocarbamate precursor [ReCl$_2$-(S$_2$CNEt$_2$)$_2$][BPh$_4$] **11** was prepared in high yield and will allow a route into rhenium dithiocarbamate chemistry without involvement of the oxo core.

Experimental

All manipulations were carried out under an inert atmosphere of dry dinitrogen gas using conventional Schlenk techniques and all solvents were freshly distilled from appropriate drying agents prior to use. Elemental analyses were performed by S. Hodder and S. Ridgeway at the University of Essex or Medac Ltd., University of Brunel. Infrared spectra were measured in the range 200–4000 cm^{-1} as Nujol mulls (KBr plates) on a Perkin-Elmer 1600 Series FTIR spectrophotometer, ^{1}H and ^{31}P-{^{1}H} NMR using a JEOL EX270 MHz instrument. Fast atom bombardment mass spectra (3-nitrobenzyl alcohol as matrix) were recorded at the University of Essex, by E. Potter, on a MS 50 instrument or by the EPSRC at the University of Swansea facility. The electrochemical measurements were recorded in dichloromethane solution at a platinum-wire working electrode and silver-wire pseudo-reference electrode with 0.2 M [NBu$^n_4$][BF$_4$] as the supporting electrolyte. Potentials are quoted relative to the ferrocene–ferrocenium couple, which was taken as 0.0 V. All other materials and reagents were obtained commercially (Aldrich, Fisons) and used without further purification. The compounds [Re$_2$O$_3$(S$_2$CNEt$_2$)$_4$],[16] PPh$_2$-(C$_6$H$_4$SH-2) [17] and PPh(C$_6$H$_4$SH-2)$_2$ [17] were prepared using published procedures.

Preparation of the complexes

[ReO{O(OH)C$_6$H$_4$}(S$_2$CNEt$_2$)$_2$] 1. The complex [Re$_2$O$_3$(S$_2$C-NEt$_2$)$_4$] (0.31 g, 0.31 mmol) and C$_6$H$_4$(OH)$_2$-1,2 (0.30 g, 2.72 mmol) were heated under reflux in acetone (20 cm^3) for 30 min. A deep orange-brown solution and a dark orange crystalline solid were formed on completion of the reaction. The solid was filtered off, washed with Et$_2$O and dried under vacuum. Yield 0.17 g, 94%. Recrystallisation from acetone–Et$_2$O afforded dark orange prisms. IR (KBr): ν(C–O) 1271s, ν(O–H) 3489w, ν(C–S) 761s and ν(Re=O) 969s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.3 (t, 12 H, CH$_3$), 3.8 (q, 8 H, CH$_2$), 5.8 (s, 1 H, OH) and 6.5–6.7 (m, 4 H,

aromatic). ^{13}C-$\{^1H\}$ NMR (CDCl$_3$): δ 12.6 (CH$_3$), 46.1 (CH$_2$), 114.5, 118.1, 118.5, 120.0, 148.8, 149.0 (ring) and 235.6 (CS) (Found: C, 31.6; H, 4.1; N, 4.6. C$_{16}$H$_{25}$N$_2$O$_3$ReS$_4$ requires C, 31.6; H, 4.1; N, 4.6%). FAB mass spectrum: m/z, 499 {100%, [ReO(S$_2$CNEt$_2$)$_2$]$^+$}.

[{ReO(S$_2$CNEt$_2$)$_2$}$_2$(C$_6$H$_4$O$_2$-1,4)] 2. The complex [Re$_2$O$_3$-(S$_2$CNEt$_2$)$_4$] (0.30 g, 0.30 mmol), C$_6$H$_4$(OH)$_2$-1,4 (0.33 g, 0.30 mmol) and NEt$_3$ (0.41 cm^3, 0.30 mmol) were heated under reflux in acetone (20 cm^3) for 1 h. The dark yellow-green suspension yielded a red-brown solid on completion of the reaction. The solid was filtered off and washed with Et$_2$O. Yield 0.23 g, 70%. IR (KBr): ν(C−O) 1248 and ν(Re=O) 960s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.3 (t, 12 H, CH$_3$), 1.4 (t, 12 H, CH$_3$), 3.8 (q, 16 H, CH$_2$), 6.5 (d, 2 H, aromatic) and 6.7 (d, 2 H, aromatic) (Found: C, 28.3; H, 4.1; N, 4.9. C$_{26}$H$_{44}$N$_4$O$_4$ReS$_8$ requires C, 28.2; H, 4.0; N, 5.1%). FAB mass spectrum: m/z, 605 {50, [ReO(OC$_6$H$_4$O)-(S$_2$CNEt$_2$)$_2$]$^+$} and 499 {100%, [ReO(S$_2$CNEt$_2$)$_2$]$^+$}.

[ReO(OC$_6$H$_3$NH$_2$-2-Me-4)(S$_2$CNEt$_2$)$_2$] 3. The complex [Re$_2$O$_3$(S$_2$CNEt$_2$)$_4$] (0.46 g, 0.45 mmol) and 2-amino-4-methylphenol (0.29 g, 2.35 mmol) were heated under reflux in acetone (20 cm^3) for 1 h. The dark yellow-green suspension yielded a dark orange solution which was filtered and the solvent removed under vacuum to yield a dark orange oil. Recrystallisation from CH$_2$Cl$_2$–Et$_2$O yielded a dark orange microcrystalline powder. Yield 0.19 g, 68%. IR (KBr): ν(C−S) 674s, ν(N−H) 3365w, 3468w and ν(Re=O) 964s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.3 (t, 12 H, CH$_3$), 2.1 (s, 3 H, CH$_3$), 3.1 (br s, 2 H, NH), 3.8 (q, 8 H, CH$_2$), 6.3, 6.7 (d, 2 H, aromatic) and 6.4 (s, 1 H, aromatic) (Found: C, 33.2; H, 4.6; N, 6.7. C$_{17}$H$_{28}$N$_3$O$_2$ReS$_4$ requires C, 32.9; H, 4.6; N, 6.8%).

[NEt$_2$H$_2$][ReO(C$_2$H$_4$S$_2$-1,2)$_2$] 4. The complex [Re$_2$O$_3$(S$_2$C-NEt$_2$)$_4$] (0.30 g, 0.30 mmol) and C$_2$H$_4$(SH)$_2$-1,2 (0.20 ml, 2.12 mmol) were stirred at room temperature for 1 h in acetone (20 cm^3). The green suspension yielded an orange solution on completion of the reaction. The solution was filtered and the solvent removed under vacuum which yielded an orange solid which was filtered off and washed with Et$_2$O. Cubic crystals were obtained from slow evaporation of a solution of the complex in CH$_2$Cl$_2$. Yield 0.11 g, 78%. IR (KBr): ν(C−S) 772m, ν(Re=O) 954s and ν(N−H) 3444w cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.2 (t, 6 H, CH$_3$), 2.6, 2.73 (2 s, 8 H, CH$_2$), 3.0 (q, 4 H, CH$_2$) and 6.1 (m, 2 H, NH) (Found: C, 20.9; H, 4.4; N, 3.1. C$_8$H$_{20}$NOReS$_4$ requires C, 20.9; H, 4.4; N, 3.0%).

[NEt$_2$H$_2$][ReO(C$_6$H$_4$S$_2$-1,2)$_2$] 5. As for complex **4**, with [Re$_2$O$_3$(S$_2$CNEt$_2$)$_4$] (0.33 g, 0.33 mmol) and C$_6$H$_4$(SH)$_2$-1,2 (0.50 cm^3, 4.34 mmol). Yield 0.18 g, 86%. IR (KBr): ν(C−S) 746s, ν(N−H) 3440w and ν(Re=O) 948s cm^{-1}. ^{1}H NMR (CD$_3$OCD$_3$): δ 1.3 (t, 6 H, CH$_3$), 3.1 (q, 4 H, CH$_2$), 6.1 (s, 2 H, NH) and 6.7–7.8 (m, 8 H, aromatic). ^{13}C-$\{^1H\}$ NMR (CD$_3$OCD$_3$): δ 11.6 (CH$_3$), 43.5 (CH$_2$), 123.1, 124.7, 128.3, 129.9, 152.7 (ring) and 237.2 (CS) (Found: C, 34.4; H, 3.6; N, 2.5. C$_{16}$H$_{20}$NOReS$_4$ requires C, 34.5; H, 3.6; N, 2.5%). FAB mass spectrum: m/z, 483 {20, [ReO(S$_2$C$_6$H$_4$)$_2$]$^+$} and 465 {35%, [Re(S$_2$C$_6$H$_4$)$_2$]$^+$}.

[NEt$_2$H$_2$][ReO(MeC$_6$H$_3$S$_2$-3,4)$_2$] 6. As for complex **4**, with [Re$_2$O$_3$(S$_2$CNEt$_2$)$_4$] (0.30 g, 0.30 mmol) and MeC$_6$H$_3$(SH)$_2$-3,4 (0.23 cm^3, 2.17 mmol). Yield 0.14 g, 78%. IR (KBr): ν(C−S) 770w, ν(Re=O) 923s and ν(NH) 3390w cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.9 (t, 6 H, CH$_3$), 2.3 (s, 6 H, CH$_3$), 2.5 (q, 4 H, CH$_2$), 3.0 (br, 2 H, NH) and 6.8–7.7 (m, 6 H, aromatic) (Found: C, 37.2; H, 4.2; N, 2.5. C$_{18}$H$_{24}$NOReS$_4$ requires C, 36.9; H, 4.1; N, 2.4%). FAB mass spectrum: m/z, 511 {20, [ReO(S$_2$C$_6$H$_3$-CH$_3$)$_2$]$^+$}.

[Re(S$_2$CNEt$_2$)$_2$(dmpe)][BPh$_4$] 7. The complex [ReO{O(OH)-(C$_6$H$_4$)}(S$_2$CNEt$_2$)$_2$] (0.25 g, 0.41 mmol) and Me$_2$P(CH$_2$)$_2$PMe$_2$ (0.71 cm^3, 4.73 mmol) were heated under reflux in acetone (20

cm^3) for 2 h. The dark orange suspension yielded a green solution on completion of the reaction. The solvent was removed under vacuum and the resulting oil taken up in methanol (10 cm^3). Immediately on addition of NaBPh$_4$ (0.13 g, 0.38 mmol) a green precipitate was formed which was filtered off and washed with Et$_2$O. Yield 0.27 g, 69%. IR (KBr): ν(CN) 1543m cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.3 (2 s, 12 H, CH$_3$), 1.5 (t, 12 H, CH$_3$), 2.0 (m, 8 H, CH$_2$), 3.6 (m, 8 H, CH$_2$) and 7.1–7.4 (m, 20 H, aromatic). ^{31}P-$\{^1H\}$ NMR (CDCl$_3$): δ 44.5 (s) (Found: C, 50.4; H, 6.0; N, 2.9. C$_{40}$H$_{56}$BN$_2$P$_2$ReS$_4$ requires C, 50.4; H, 5.9; N, 2.9%). FAB mass spectrum: m/z, 632 {100, [Re(S$_2$CNEt$_2$)$_2$(dmpe)]$^+$} and 482 {100%, [Re(S$_2$CNEt$_2$)$_2$]$^+$}.

[Re(S$_2$CNEt$_2$)$_2$(dppe)][BPh$_4$] 8. The complex [ReO{O(OH)-(C$_6$H$_4$)}(S$_2$CNEt$_2$)$_2$] (0.30 g, 0.49 mmol) and Ph$_2$P(CH$_2$)$_2$PPh$_2$ (0.98 g, 2.46 mmol) were heated under reflux in acetone (20 cm^3) for 2 h. The dark orange suspension yielded a green solution on completion of the reaction. The solvent was removed under vacuum and the resulting oil taken up in methanol (10 cm^3). Immediately on addition of NaBPh$_4$ (0.15 g, 0.44 mmol) a green precipitate was formed which was filtered off and washed with Et$_2$O. Yield 0.49 g, 84%. IR (KBr): 1518 ν(CN) and ν(C−S) 746s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.3 (t, 12 H, CH$_3$), 1.7 (m, 2 H, CH$_2$), 3.5 (q, 8 H, CH$_2$) and 6.9–7.9 (m, 20 H, aromatic). ^{31}P-$\{^1H\}$ NMR (CDCl$_3$): δ 12.4 (s) (Found: C, 59.9; H, 5.4; N, 2.3. C$_{60}$H$_{64}$BN$_2$P$_2$ReS$_4$ requires C, 60.0; H, 5.4; N, 2.3%). FAB mass spectrum: m/z, 881 {100%, [Re(S$_2$CNEt$_2$)$_2$(dppe)]$^+$}.

[Re{PPh$_2$(C$_6$H$_4$S-2)}$_2$(S$_2$CNEt$_2$)]·Me$_2$CO 9. The complex [Re$_2$O$_3$(S$_2$CNEt$_2$)$_4$] (0.30 g, 0.30 mmol) and PPh$_2$(C$_6$H$_4$SH-2) (0.46 g, 1.57 mmol) were stirred at room temperature overnight in acetone (20 cm^3). A red-orange solid was formed on completion of the reaction. The solid was filtered off, washed with Et$_2$O and dried under vacuum. Yield 0.27 g, 90%. Recrystallisation from acetone–Et$_2$O afforded red-orange prisms. IR (KBr): 1708w cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 0.6 (t, 12 H, CH$_3$), 2.9 (q, 8 H, CH$_2$) and 7.1–7.9 (m, 28 H, aromatic). ^{31}P-$\{^1H\}$ NMR (CDCl$_3$): δ 20.2 (s) (Found: C, 53.9; H, 4.4; N, 1.4. C$_{44}$H$_{44}$NO-P$_2$ReS$_4$ requires C, 54.0; H, 4.5; N, 1.4%). FAB mass spectrum: m/z, 917 {100%, [Re{PPh$_2$(C$_6$H$_4$S-2)}$_2$(S$_2$CNEt$_2$)]$^+$}.

[ReO{PPh(C$_6$H$_4$S-2)$_2$}(S$_2$CNEt$_2$)] 10. The complex [Re$_2$O$_3$-(S$_2$CNEt$_2$)$_4$] (0.31 g, 0.31 mmol) and PPh(C$_6$H$_4$SH-2)$_2$ (0.30 g, 2.72 mmol) were stirred in acetone (20 cm^3) for 30 min at room temperature. A deep orange-brown solution and a dark orange crystalline solid was formed on completion of the reaction. The solid was filtered off, washed with Et$_2$O and dried under vacuum. Yield 0.17 g, 94%. Recrystallisation from acetone–Et$_2$O afforded dark orange prisms. IR (KBr): ν(C−S) and ν(Re=O) 941s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.4 (t, 12 H, CH$_3$), 3.7–4.1 (q, 8 H, CH$_2$) and 7.0–8.0 (m, 13 H, aromatic). ^{31}P-$\{^1H\}$ NMR (CDCl$_3$): δ 47.7 (s) (Found: C, 40.9; H, 3.5; N, 2.1. C$_{23}$H$_{23}$NO-PReS$_4$ requires C, 40.9; H, 3.4; N, 2.1%). FAB mass spectrum: m/z, 595 {100%, [ReO{P(C$_6$H$_4$S-2)$_2$}(S$_2$CNEt$_2$)]}.

[ReCl$_2$(S$_2$CNEt$_2$)$_2$][BPh$_4$] 11. The complex [Re$_2$O$_3$(S$_2$-CNEt$_2$)$_4$] (0.13 g, 0.13 mmol) and SiMe$_3$Cl (0.1 cm^3, 0.79 mmol) were stirred in methanol (10 cm^3) for 20 min at room temperature. The green-brown suspension yielded a green solution on completion of the reaction. The solvent was removed under vacuum and addition of Et$_2$O yielded a green precipitate, the chloride salt, which was filtered off and washed with Et$_2$O. The precipitate was then dissolved in methanol (5 cm^3) and NaBPh$_4$ (0.04 g, 0.12 mmol) was added which resulted in the immediate precipitation of an orange solid. Yield 0.09 g, 82%. IR (KBr): ν(C−S) 705s cm^{-1}. ^{1}H NMR (CDCl$_3$): δ 1.5 (t, 12 H, CH$_3$), 3.8, 4.0 (q, 8 H, CH$_2$) and 6.9–7.5 (m, 20 H, aromatic) (Found: C, 46.7; H, 4.8; N, 3.1. C$_{34}$H$_{40}$BCl$_2$N$_2$ReS$_4$ requires C, 46.8; H, 4.6; N, 3.2%).

Table 5 Crystallographic data for complexes for $[ReO\{O(OH)C_6H_4\}(S_2CNEt_2)_2]$ **1**, $[Re\{PPh_2(C_6H_4S-2)\}_2(S_2CNEt_2)]\cdot Me_2CO$ **9** and $[ReO\{PPh(C_6H_4S-2)_2\}(S_2CNEt_2)]$ **10**

	1	**9**	**10**
Formula	$C_{16}H_{25}N_2O_3ReS_4$	$C_{44}H_{44}NOP_2ReS_4$	$C_{23}H_{23}NOPReS_4$
M	607.82	979.18	674.83
Crystal size/mm	$0.50 \times 0.50 \times 0.25$	$0.35 \times 0.39 \times 0.21$	$0.52 \times 0.50 \times 0.20$
a/Å	10.092(3)	12.572(2)	9.0340(7)
b/Å	10.325(2)	13.774(6)	9.8391(5)
c/Å	12.144(2)	14.366(3)	14.365(2)
α/°	80.69(1)	103.98(2)	101.503(6)
β/°	74.05(2)	97.880(10)	102.875(8)
γ/°	62.71(2)	115.39(2)	93.653(6)
U/Å³	1080.3(4)	2097.1(11)	1211.9(2)
D_c/g cm⁻³	1.869	1.551	1.849
Reflections collected	3995	7644	4448
Unique data	3764	7322	4259
Observed reflections $[F_o \geqslant 3\sigma(F_o)]$	3590	6486	4084
h, k, l Ranges	−10 to 11, 0–12, −14 to 14	−14 to 14, −15 to 15, 0–16	−10 to 10, −11 to 11, 0–17
θ Range for data/°	1.75–24.98	1.52–25.01	2.13–25.00
$F(000)$	596	984	660
R_{int}	0.0424	0.1546	0.0187
$\mu(Mo\text{-}K\alpha)$	6.029	3.208	5.441
Absorption correction factors	0.642–0.997	0.37–1.000	0.799–0.999
$R1$	0.0448	0.0726	0.0303
$wR2$	0.1186	0.2028	0.0909
Largest difference peak and hole/e Å⁻³	2.53, −3.00	4.18, −3.67	2.66, −1.50

Details in common: intensity data collected on a Enraf-Nonius CAD4 diffractometer [20] with monochromated Mo-Kα radiation ($\lambda = 0.710\ 73$ Å) in the scan mode ω–2θ at 293(2)K; plate crystal; triclinic, space group $P\bar{1}$; $Z = 2$. Weighting schemes used: $w = 1/[\sigma^2(F_o)^2 + (XP)^2 + YP]$, where $X = 0.0961$, $Y = 2.2605$ for complex **1**, $X = 0.1746$, $Y = 7.2905$ for **9** and $X = 0.0492$, $Y = 4.4767$ for **10** and $P = [max(F_o^2 + 2F_c^2)]/3$; $R1 = \Sigma|F_o - F_c|/F_o$ and $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{\frac{1}{2}}$.

X-Ray crystallography

Structures **1**, **9** and **10** were solved by direct methods[18] and refined on F_o^2 by full-matrix least squares[19] using all unique F_o^2 data corrected for Lorentz polarisation factors. An absorption correction was applied using ψ scans of nine reflections with the χ angle range 85–95°.[20] The hydrogen atoms were included in idealised positions with U_{iso} free to refine. The experimental details of the data collections and structure solutions are summarised in Table 5. The program ZORTEP was used to represent the structures.[21]

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Acknowledgements

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