High pressure co-ordination chemistry of a palladium thioether complex: pressure *versus* electrons†

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Received (in Cambridge, UK) 12th May 2006, Accepted 20th June 2006
First published as an Advance Article on the web 6th July 2006
DOI: 10.1039/b606736k

The mononuclear Pd(II) complex *cis*-[PdCl$_2$([9]aneS$_3$)] ([9]aneS$_3$ = 1,4,7-trithiacyclononane) converts at 44 kbar pressure into an intensely coloured chain polymer, which exhibits distorted octahedral co-ordination at the metal centre and an unprecedented [1233] conformation for the thioether crown.

High pressure structural studies have predominantly focused on mineral and mineral-like phases,[1] and the structures of some simple organic molecules at elevated pressures have been reported.[2] In contrast, there are few examples of pressure studies on metal co-ordination complexes[3] and there are no reports of major structural changes in such systems. Pd(II) complexes often adopt a square-planar arrangement of ligands about the d^8 metal centre. However, with macrocyclic thioether ligands Pd(II) centres often incorporate long-range apical interactions to S-donor centres.[4] Such ligands can act as protecting groups for metal centres and have been shown to adopt varying binding modes.[5] We have previously reported that it is possible to tune the length of the long-range apical Pd···S distance in the complexes *cis*-[PdXY([9]aneS$_3$)] by varying the ligands X and Y, with π-donor ligands such as chloride affording long Pd···S distances of greater than 3.1 Å,[6] and π-acceptor ligands such as phosphines leading to a contraction of the distance to about 2.7 Å.[7] The complexes *cis*-[PdXY([9]aneS$_3$)], where X and Y are halides, therefore, provide tuneable examples of [4 + 1] co-ordination at Pd(II) within a neutral complex environment. We report herein a variable pressure study of the structure of *cis*-[PdCl$_2$([9]aneS$_3$)], which involves a dramatic conversion of this mononuclear species to an intensely coloured chain polymer at 44 kbar.

Several factors determined our selection of *cis*-[PdCl$_2$([9]aneS$_3$)] (Fig. 1) as the subject of the present study. The long apical Pd···S distance of 3.159(10) Å was expected to provide an especially sensitive indicator of the effects of pressure. We reasoned that the presence of electron-releasing π-donor chloride ligands coupled with potential π-donor/acceptor thioether donors[8] provides potential stabilisation of any activated or high energy species that might be formed, and, importantly, the choice of *cis*-[PdCl$_2$([9]aneS$_3$)] avoids any possibility of complications resulting from the presence of and interaction with counter-anions.

An orange crystal of *cis*-[PdCl$_2$([9]aneS$_3$)] (0.15 × 0.10 × 0.05 mm) was sealed into a diamond anvil cell (DAC) and an X-ray diffraction dataset collected at ambient pressure.‡ Hydrostatic fluid (methanol–ethanol 4 : 1 v/v) was then added, as was a small ruby crystal to allow measurement of the pressure within the DAC by laser-induced fluorescence.[9] Datasets were then recorded successively at 12.6, 23.5, 36, 73.1, 76.8 and 53.5 kbar using the first crystal and at 46 kbar§ and 42.5 kbar using a second crystal of similar size.¶ Data collection procedures followed those of Dawson *et al.*[2]

Our attempts to determine the structure at pressures of over 80 kbar were unsuccessful due to degradation of the crystals. However, we do not believe that this pressure represents a limit to the compression of the co-ordination sphere at the Pd(II) centre.

At ambient pressure the apical S-donor (S1) lies 3.159(10) Å from the square-planar Pd(II) centre with the thioether ligand adopting the expected [333] conformation.[10] In this structure Pd is positioned 3.525(8) Å from an S-centre (S4) in a neighbouring molecule at (½ + *x*, ½ − *y*, 1 − *z*). As the pressure is increased to 42.5 kbar these distances contract smoothly to 3.009(5) and 3.204(5) Å, respectively (Fig. 2). The colour of the crystal becomes a slightly darker orange as the pressure increases, and the ligand maintains its [333] conformation. The effects of pressure on unit cell lengths, cell volume and various geometric parameters are summarised in Electronic Supplementary Information (ESI).

When the pressure is increased from 42.5 to 46 kbar the structure undergoes a sudden and unexpected first-order isosymmetric phase transition. The Pd···S1 and Pd···S4 distances contract to 2.846(7) and 3.117(8) Å, respectively (Fig. 2), thus

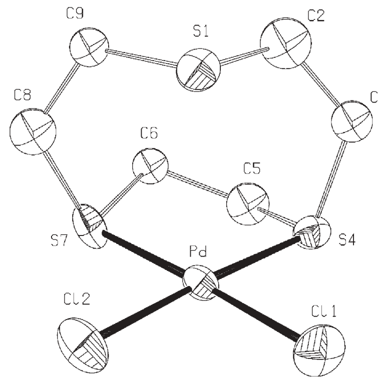

Fig. 1 View of the structure of *cis*-[PdCl$_2$([9]aneS$_3$)] at ambient pressure with atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level. Pd···S1 = 3.159(10) Å.

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† Electronic supplementary information (ESI) available: Graphs showing the structural trends in *cis*-[PdCl$_2$([9]aneS$_3$)] as a function of pressure; details of literature structural studies on coordination complexes. See DOI: 10.1039/b606736k

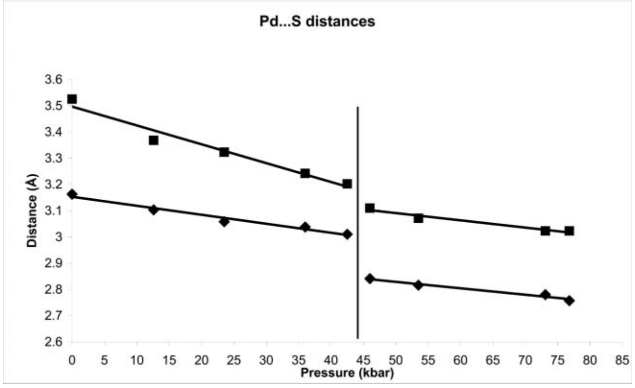

Fig. 2 The variation of the Pd$\cdots$S1 (bottom) and Pd$\cdots$S4 (top) distances as a function of pressure. The transition at 44 kbar is indicated by a vertical line.

conferring a distorted [4 + 2] octahedral co-ordination on the Pd(II) centre. The complex now forms a zigzag chain polymer, which runs along the *a* axis (Fig. 3). The crystal colour changes abruptly at the transition, becoming so dark as to appear completely black. At this pressure the macrocycle begins to adopt a previously unobserved [1233] conformation[11] which at the highest pressures contains a highly unfavourable eclipsed arrangement for S4–C5–C6–S7. While the S1–C9–C8–S7–C6 section of the ring is largely unchanged, the S1–C2–C3–S4–C5–C6 linkage adopts a more extended conformation in order to encapsulate the Pd(II) cation more effectively. This asymmetry in the macrocyclic ring leads to S1 adopting an asymmetric position over the metal (Fig. 4), as illustrated by the differing S1–Pd–Cl1 and S1–Pd–Cl2 angles of 110.2(3) and 94.6(3)°, respectively. The S_2Cl_2 equatorial plane around the Pd centre is distorted: although the metal lies precisely in the plane defined by Cl2, S4 and S7, the remaining chloride Cl1 lies 0.594(15) Å out of this plane in the opposite direction to that of S1. We estimate that these major changes in the structure occur at 44 kbar, and marked discontinuities in unit cell dimensions, unit cell volume and various geometric parameters (see ESI) are observed at this pressure. Moreover, the gradients of the lines on either side of the transition differ, suggesting that the bonds are becoming less compressible at higher pressures and indicating a change in the potential around the metal centre. Intriguingly, the shorter axial Pd$\cdots$S distances do not occur at the expense of the Pd–Cl and equatorial Pd–S bond distances, which contract only marginally over the pressure range studied.

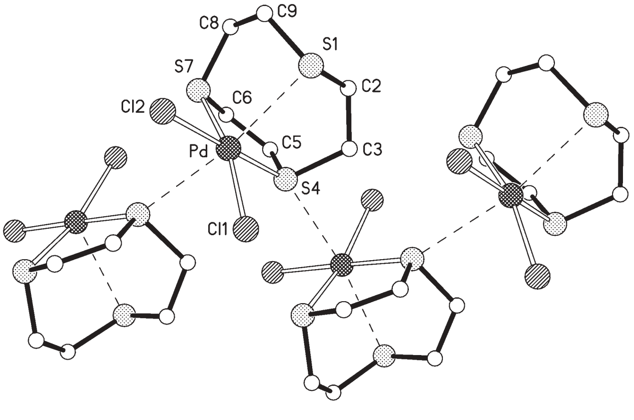

Fig. 3 A view of the high pressure structure at 46 kbar, showing the distorted octahedral co-ordination around Pd(II) and the formation of a zigzag one-dimensional polymeric chain. The equatorial Pd–S and Pd–Cl are shown as open bonds while the axial Pd–S bonds are drawn as dashed lines. Atoms are identified as follows: Pd, cross-hatched; Cl, shaded; S, dotted; C, open circles.

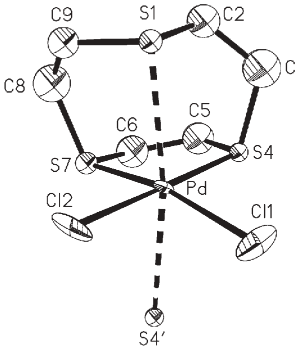

Fig. 4 The disposition of S1 is asymmetric relative to the metal, and Cl1 is displaced from the equatorial plane, at 46 kbar. Displacement ellipsoids are drawn at the 50% probability level.

Increasing the pressure from 46 to 76.8 kbar results in further smooth decreases in the Pd$\cdots$S1 and Pd$\cdots$S4 distances to 2.771(13) and 3.006(10) Å, respectively (Fig. 2), confirming the distorted octahedral co-ordination in this pressure region. These decreasing axial distances clearly demonstrate that increasing pressure is capable of overcoming the electron-releasing π-effects of the chloride ligands which tend to elongate the apical Pd$\cdots$S separation. The geometry observed in this system is also distinct from that of other complex cations such as $[Pd([9]aneS_3)_2]^{2+}$ [12] or in Pd complexes of thioether ligands tethered with extremely bulky substituents,[13] where the approaches of the axial S donors are the result of the internal geometric constraints of the ligand. At this pressure, S4–C5–C6–S7 adopts a fully eclipsed arrangement.

The unit cell volume falls from 1128.2(4) $Å^3$ at ambient pressure to 938.0(7) $Å^3$ at 42.5 kbar, 923.5(2) $Å^3$ at 46 kbar and finally to 869.6(2) $Å^3$ at 76.8 kbar, an overall contraction of 23%. The corresponding crystal densities are 2.105, 2.532, 2.572 and 2.732 g cm^{-3}. Measurements on the second crystal were recorded first at 46 kbar then at 42.5 kbar; the regeneration at the lower pressure of both the initial structure and the orange colour of the crystal confirms that the transition at 44 kbar is fully reversible.

Attempts have been made to measure the optical spectrum of the crystals at pressures above 44 kbar, but so far our efforts have been unsuccessful owing to the very intense absorption by even very thin crystals. The change from isolated, square-planar Pd(II) centres to a one-dimensional co-ordination polymer with distorted octahedral geometry at Pd(II), which is accompanied by an abrupt change in colour, clearly leads to a change in the electronic environment of the metal ion. The almost black appearance of the crystals suggests a broad absorption in the visible region and may signal the switching on of allowed charge-transfer and intervalence transitions due to conjugated S–Pd–S interactions.

Current work seeks to elucidate further the structural and electronic properties of these and related thioether macrocyclic complexes as a function of pressure. This represents a potential route to a range of unusual metal stereochemistries, including high spin octahedral Pd(II) species.

We thank CCLRC for access to Station 16.2smx on the Daresbury SRS, and acknowledge the use of the EPSRC Chemical Database Service at Daresbury Laboratory. We thank EPSRC for support and for an Advanced Research Fellowship (to DRA), and the CVCP for an ORS award (to DH). MS gratefully acknowledges receipt of a Royal Society Wolfson Merit Award and of a Royal Society Leverhulme Trust Senior Research Fellowship. We thank Professor G. A. Lawrance, University of Newcastle, New South Wales, Australia, for helpful discussions.

Notes and references

‡ Crystal data for structure at ambient pressure: $C_6H_{12}Cl_2PdS_3$, M = 357.64, orthorhombic, space group $P2_12_12_1$, a = 7.5626(11), b = 12.1894(15), c = 12.239(4) Å, U = 1128.2(4) Å^3, Z = 4, D_c = 2.105 g/cm^3, μ = 2.619 mm^{-1}, T = 298(2) K. 550 unique reflections (R_{int} = 0.058). Final R_1 [509 $I > 2\sigma(I)$] = 0.0384, wR_2 (all data) = 0.0817. An absolute structure parameter refined to 0.00(13). CCDC 607262. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606736k

§ Crystal data for structure at 46 kbar: $C_6H_{12}Cl_2PdS_3$, M = 357.64, orthorhombic, space group $P2_12_12_1$, a = 7.0624(12), b = 11.5835(9), c = 11.2892(12) Å, U = 923.5(2) Å^3, Z = 4, D_c = 2.572 g/cm^3, μ = 3.200 mm^{-1}, T = 298(2) K. 449 unique reflections (R_{int} = 0.036). Final R_1 [439 $I > 2\sigma(I)$] = 0.0408, wR_2 (all data) = 0.103. An absolute structure parameter refined to 0.00(18). CCDC 607267. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606736k

¶ CCDC 607262–607270. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606736k

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