Template synthesis of a polyiodide belt at a metal complex cation: structure of $[([16]aneS_4)M{-}I{-}M([16]aneS_4)]^{3+}[I_5^-]_2I^-$ (M = Pd, Pt) incorporating a symmetric linear M–I–M bridge ($[16]aneS_4$ = 1,5,9,13-tetrathiacyclohexadecane)

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Reaction of $[M([16]aneS_4)][PF_6]_2$ with $NBu^n{}_4I_3$ affords the binuclear species $[([16]aneS_4)M{-}I{-}M([16]aneS_4)]^{3+}$ (M = Pd, Pt) incorporating a highly unusual linear M–I–M moiety within a conformationally constrained environment: the counter anion, which can be regarded formally as two I_5^- and one I^- or alternatively as two I_3^-, two I_2 and one I^-, forms a belt around the complex cation with the metal-bridging I^- placed at its centre.

The coordination chemistry of thioether crowns has been established over the past decade.[1,2] The complexation characteristics of these ligands with a wide range of transition-metal ions have been investigated.[3] We have been interested in developing the coordination chemistry of thioether crown ligands with main-group centres such as halogens and interhalogens, and have reported the interaction of I_2 with metal-free ligands to form charge-transfer adducts.[4] We have extended these studies recently to the investigation of the interaction(s) of I_2 and polyiodides with metal-containing thioether crowns,[5] and report herein the template synthesis of an extended polyiodide array about a highly unusual iodo-bridged species incorporating a linear M–I–M unit.

Reaction of $NBu^n{}_4I_3$ with $[M([16]aneS_4)][PF_6]_2$ (M = Pd,[1] Pt[6]) in MeCN in 2 : 1 molar ratios affords a red solution from which dark red products can be isolated in 78% (Pd) and 62% (Pt) yield. The FAB mass spectrum of the products shows molecular ion peaks for the mononuclear fragment $[M([16]aneS_4)I]^+$ with the correct isotopic distribution. Recrystallisation of these products from MeCN–$MeNO_2$ affords single crystals and, in order to ascertain their structures, single-crystal X-ray determinations were undertaken. The crystal structures[†] confirm both products to contain the binuclear fragment $[([16]aneS_4)M{-}I{-}M([16]aneS_4)]^{3+}$. The cations $[([16]aneS_4)M{-}I{-}M([16]aneS_4)]^{3+}$ (M = Pd, Pt) (Fig. 1) are isostructural and show a highly unusual *linear* M–I–M (M–I–M 180°) moiety with an I^- bridging the metals symmetrically. The M–I distances are relatively long, 3.135(3) Å for Pd and 3.194(2) Å for Pt. In general, M–I–M bridges are found to lie in the range 60–110° with M–I bond lengths in the range 2.5–2.9 Å depending upon M.[7] The complex $[Au_2(dmpe)_2]I_2{\cdot}MeCN$ (dmpe = $Me_2PCH_2CH_2PMe_2$) shows a particularly wide M–I–M angle of 161.2°.[8] Genuine linear iodo bridges, M–I–M, between metal centres are therefore rare in the literature. The complex $[I(PhNC)_4Co{-}I{-}Co(CNPh)_4I]I$ shows[9] a linear symmetric Co–I–Co bridge with Co–I–Co 180°, Co–I(bridge) 2.891(2) Å, while $[(nas)_3Ni{-}I{-}Ni(nas)_3]BPh_4$ [nas = tris(2-diphenylarsinoethyl)amine] shows a linear Ni–I–Ni bridge, Ni–I(bridge) 2.994(4) Å.[10] Very recently, a new polymorph of PtI containing an asymmetric linear $Pt^{II}{-}I{-}Pt^{IV}$ chain has been reported with Pt^{IV}–I 2.747(2), Pt^{II}–I 3.072(1).[11]

Clearly, the M–I distances in $[([16]aneS_4)M{-}I{-}M([16]aneS_4)]^{3+}$ (M = Pd, Pt) are particularly long. The iodide anion may be regarded as being trapped between two $[M([16]aneS_4)]^{2+}$ cations with a linear M–I–M bridge being imposed by the steric bulk of the tetrathioether crown. Thus, the linear binuclear unit is conformationally locked, as reducing the M–I–M angle would force together the propylene chains of the macrocycles, thereby increasing repulsive forces.

The tetradentate thioether macrocycle $[16]aneS_4$ is bound *via* all four S-donors to the M^{II} centres which are five coordinate in each complex. As expected the Pd–S distances in $[([16]aneS_4)Pd{-}I{-}Pd([16]aneS_4)]^{3+}$ lie in the range 2.347(2)–2.351(2) Å, slightly elongated compared to those of the parent $[Pd([16]aneS_4)]^{2+}$, Pd–S 2.300(10)–2.315(9) Å.[1] Likewise, the Pt–S distances in $[([16]aneS_4)Pt{-}I{-}Pt([16]aneS_4)]^{3+}$ [2.332(3)–2.339(3) Å] are elongated compared to those in $[Pt([16]aneS_4)]^{2+}$, Pt–S 2.310(2) Å.[6] The Pd and Pt metal centres lie 0.352 and 0.306 Å out of the least-squares mean plane of their respective S_4 donor sets, in the direction of the bridging iodide ion I(1): the lower displacement observed for Pt may reflect the smaller ionic radius of Pt^{II} compared with Pd^{II}. Interestingly, the metal ions are displaced to the opposite of the thioether macrocycle compared to the structures of $[M([12]aneS_4)]^{2+}$ and $[M([14]aneS_4)]^{2+}$.[1]

Significantly, the same counter polyanion structure is present in both crystal structures consistent with analytical data. FT-Raman spectroscopy shows two strong peaks for both complexes at 157 and 149 cm^{-1} (for Pd) and 158 and 153 cm^{-1} (for Pt). This is in agreement with the presence of a slightly perturbed I_2 and asymmetric I_3^- or I_5^- anions.[12] Indeed, the crystal structures confirms the formation of a highly unusual

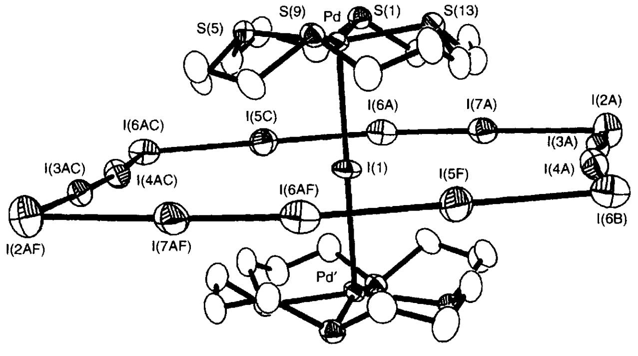

Fig. 1 View of the structure of $[([16]aneS_4)Pd{-}I{-}Pd([16]aneS_4)]^{3+}$ with numbering scheme adopted. Selected bond distances (Å) and angles (°): Pd–S(1) 2.347(2), Pd–S(5) 2.349(2), Pd–S(9) 2.348(3), Pd–S(13) 2.351(2), Pd–I(1) 3.135(3) Å; S(1)–Pd–S(9) 161.70(7), S(1)–Pd–S(5) 90.72(9), S(1)–Pd–S(13) 86.48(8), S(5)–Pd–S(9) 87.14(10), S(5)–Pd–S(13) 163.86(7), S(9)–Pd–S(13) 90.54(9), S(1)–Pd–I(1) 98.73(11), S(5)–Pd–I(1) 98.36(8), S(9)–Pd–I(1) 99.57(10), S(13)–Pd–I(1) 97.78(8), Pd–I(1)–Pd(1′) 180. I(6ac)–I(5c) 3.285, I(5c)–I(6a) 3.285, I(6a)–I(7a) 2.798, I(7a)–I(2a) 3.409, I(2a)–I(3a) 3.044, I(3a)–I(4a) 2.836, I(4a)–I(6b) 3.806. For $[([16]aneS_4)Pt{-}I{-}Pt([16]aneS_4)]^{3+}$: Pt–S(1) 2.336(3), Pt–S(5) 2.332(3), Pt–S(9) 2.339(3), Pt–S(13) 2.334(3), Pt–I(1) 3.194(2) Å, S(1)–Pt–S(9) 165.81(8), S(1)–Pt–S(5) 90.79(9), S(1)–Pt–S(13) 87.74(9), S(5)–Pt–S(9) 86.79(9), S(5)–Pt–S(13) 164.04(8), S(9)–Pt–S(13) 90.76(9), S(1)–Pt–I(1) 97.31(7), S(5)–Pt–I(1) 97.67(6), S(9)–Pt–I(1) 96.87(10), S(13)–Pt–I(1) 98.27(6), Pt–I(1)–Pt(1′) 180. Primed atom related to unprimed equivalent by $-x$, $1 - y$, $1 - z$.

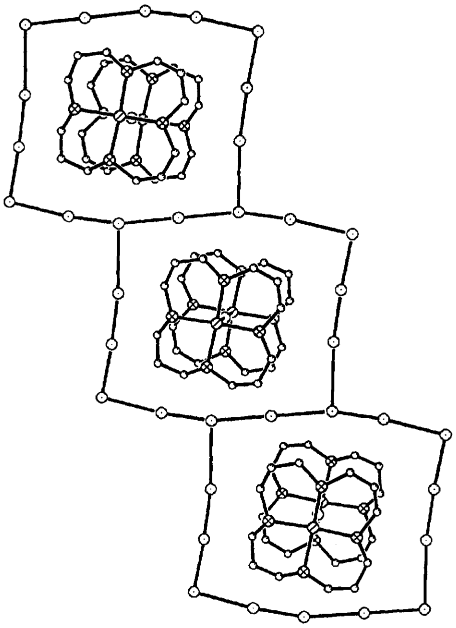

Fig. 2 View of the structure of $[([16]\text{aneS}_4)\text{Pd–I–Pd}([16]\text{aneS}_4)][\text{I}_5^-]_2\text{I}^-$

polyhalide ring surrounding the $[([16]\text{aneS}_4)\text{M–I–M}([16]\text{aneS}_4)]^{3+}$ cations. This is illustrated in Fig. 2 where I(6a)–I(7a)–I(2a)–I(3a)–I(4a) and I(6af)–I(7af)–I(2af)–I(3ac)–I(4ac) define two distorted I_5^- fragments consisting of I^-–$(\text{I}_2)_2$ moieties in which the (I_2)–I–(I_2) angle is approximately 90° as found in discrete I_5^- units.[13] Each binuclear metal cation is therefore surrounded by a 14-membered polyhalide ring with the bridging I^- placed at the centre of this ring. The 14-membered polyanion rings measure 9.657 × 12.640 Å, and 16.383 Å across and are linked to form infinite two-dimensional sheets (Fig. 2). Therefore, the central complex cation may be regarded as acting as a template for the synthesis of this unique cyclic polyhalide array into which the central complex cation sits.

Current work is aimed at investigating further the role of macrocyclic complexes in the template synthesis and self-assembly of these and related polyanion arrays and sheets.

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Footnote

† *Crystal data*: $[([16]\text{aneS}_4)\text{Pd–I–Pd}([16]\text{aneS}_4)][\text{I}_5^-]_2\text{I}^-$. $\text{C}_{24}\text{H}_{48}\text{I}_{12}\text{Pd}_2\text{S}_8$, M = 2328.7, triclinic, space group $P\bar{1}$ with a = 10.492(11), b = 11.899(4), c = 12.729(3) Å, α = 64.80(2), β = 70.24(7), γ = 87.97(8)°, U = 1342 Å^3 (from setting angles of 25 reflections with $30 \leq 2\theta \leq 32°$, λ = 0.71073 Å, T = 295 K), D_c = 2.881 g cm^{-3}, Z = 1, μ = 7.901 mm^{-1}, $F(000)$ = 1048. Diffraction data were collected on an Enraf-Nonius CAD4 diffractometer using graphite-monochromated Mo-KαX-radiation and ω–2θ scans. Of 3726 reflections collected ($2\theta_{\text{max.}}$ = 45°, $-10 \leq h \leq 11$, $-11 \leq k \leq 12$, $0 \leq l \leq 13$), 3501 were unique (R_{int} = 0.021 after absorption correction based on ψ scans) and 3457 were used in all calculations. The structure was solved by a combination of heavy and direct methods (P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla. The DIRDIF program system, Technical Report of the Crystallography Laboratory, University of Nijmegen, 1992). All non-hydrogen atoms were then refined anisotropically and H atoms were included in fixed, calculated positions and allowed to ride on their parent C atoms with a common $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ (G. M. Sheldrick, SHELXL-93: University of Göttingen, 1993). At final convergence $R[F \geq 4\sigma(F)]$ = 0.0329, $wR(F^2$, all data) = 0.0903, $S(F^2)$ = 1.151 for 212 refined parameters and the final ΔF synthesis showed no peaks outside ±1.06 e Å^{-3}.

$[([16]\text{aneS}_4)\text{Pt–I–Pt}([16]\text{aneS}_4)][\text{I}_5^-]_2\text{I}^-$. $\text{C}_{24}\text{H}_{48}\text{I}_{12}\text{Pt}_2\text{S}_8$, M = 2506.1, triclinic, space group $P\bar{1}$ with a = 10.453(6), b = 11.795(6), c = 12.626(8) Å, α = 64.77(2), β = 70.33(3), γ = 87.94(2)°, U = 1315 Å^3 (from 2θ values for 53 reflections measured at ±ω, $29 \leq 2\theta \leq 32°$, λ = 0.71073 Å, T = 150 K), D_c = 3.164 g cm^{-3}, Z = 1, μ = 7.901 mm^{-1}, $F(000)$ = 1112. Diffraction data for the isomorphous Pt analogue were collected as above, using a Stoe Stadi-4 four-circle diffractometer equipped with an Oxford Cryosystems open-flow nitrogen cryostat (J. Cosier and A. M. Glazer, *J. Appl. Crystallogr.*, 1986, **19**, 105) operating at 150 K. Of 4102 reflections collected, 3457 were unique (R_{int} 0.016 after absorption correction based on ψ scans) and 3495 were used in all calculations. Structure solution and refinement were carried out as above: At final convergence $R[F \geq 4\sigma(F)]$ = 0.0309, $wR(F^2$, all data) = 0.0908, $S(F^2)$ = 1.295 for 212 refined parameters and the final ΔF synthesis showed no peaks outside the range +1.38 to −1.45 e Å^{-3}. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/203.

References

1 A. J. Blake and M. Schröder, *Adv. Inorg. Chem.*, 1990, **35**, 1.

2 S. R. Cooper and S. C. Rawle, *Struct. Bonding* (*Berlin*), 1990, **72**, 1.

3 For recent papers see: C. Landgrafe and W. S. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1996, 989; K. Brandt and W. S. Sheldrick, *J. Chem. Soc., Dalton Trans.*, 1996, 1237; A. J. Blake, D. W. Bruce, I. A. Fallis, S. Parsons, H. Richtzenhain, S. A. Ross and M. Schröder, *Philos. Trans. R. Soc. London Ser. A*, 1996, **354**, 395; A. J. Blake, Y. V. Roberts and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1996, in the press; R. D. Adams, S.B. Falloon, J. L. Perrin, J. A. Queisser and J. H. Yamamoto, *Chem. Ber.*, 1996, **129**, 313; G. J. Grant, K. E. Rogers, W. N. Setzer and D. G. Van Derveer, *Inorg. Chim. Acta*, 1995, **234**, 35; H.-J. Kim, J.-H. Lee, I.-H. Suh and Y. Do, *Inorg. Chem.*, 1995, **34**, 796; M. Munakata, L. P. Wu, M. Yamamoto, T. Kuroda-Sowa and M. Maekawa, *J. Chem. Soc., Dalton Trans.*, 1995, 3215.

4 A. J. Blake, R. O. Gould, C. Radek and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1993, 1191; F. Cristiani, F. A. Devillanova, F. Isaia, V. Lippolis, G. Verani and F. Demartin, *Heteroatom Chem.*, 1993, **4**, 571; F. Cristiani, F. A. Devillanova, A. Garau, F. Isaia, V. Lippolis, G. Verani, F. Demartin, A. J. Blake, R. O. Gould, C. Radek and M. Schröder, *Synth. Methodol. in Inorg. Chem., New Compounds and Mater.*, 1994, **4**, 406.

5 A. J. Blake, R. O. Gould, S. Parsons, C. Radek and M. Schröder, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2374.

6 A. J. Blake, A. J. Holder, G. Reid and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1994, 627; A. J. Blake, M. J. Bywater, R. D. Crofts, A. M. Gibson, G. Reid and M. Schröder, *J. Chem. Soc., Dalton Trans.*, 1996, 2979.

7 For example see: D. V. Toronto and A. L. Balch, *Inorg. Chem.*, 1994, **33**, 6132; T. Adatia, H. Curtis, B. F. G. Johnson, J. Lewis, M. McPartlin and J. Morris, *J. Chem. Soc., Dalton Trans.*, 1994, 1109; L. Brunet, F. Mercier, L. Ricard and F. Mathey, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 742; A. Bacchi, W. Baratta, F. Calderazzo, F. Marchetti and G. Pelizzi, *Angew. Chem., Int. Ed. Engl.*, 1994, **33**, 193.

8 H.-R. C. Jaw, M. M. Salvas, R. D. Rogers and W. R. Mason, *Inorg. Chem.*, 1989, **28**, 1028.

9 D. Baumann, H. Endres, H. J. Keller, B. Nuber and J. Weiss, *Acta Crystallogr., Sect. B*, 1975, **31**, 40.

10 L. Sacconi, P. Dapporto and P. Stoppioni, *Inorg. Chem.*, 1977, **16**, 224.

11 B. Scott, B. L. Bracewell, S. R. Johnson, B. I. Swanson, J. F. Bardeau, A. Bulou and B. Hennion, *Chem. Mater.*, 1996, **8**, 321.

12 P. Deplano, F. A. Devillanova, J. R. Ferraro, V. Lippolis, M. L. Mercuri and E. F. Trogu, *Appl. Spectrosc.*, 1994, **48**, 1236.

13 J. Broekema, E. E. Havinga and E. H. Wiebenga, *Acta Crystallogr.*, 1957, **10**, 596; R. J. Hach and R. E. Rundle, *J. Am. Chem. Soc.*, 1951, **73**, 4321; K. Neupert-Laves and M. Dobler, *Helv. Chim. Acta*, 1975, **58**, 432; M. A. Beno, U. Geiser, K. L. Kostka, H. H. Wang, K. S. Webb, M. A. Firestone, K. D. Carlson, L. Nuñez, M.-H. Whangbo and J. M. Williams, *Inorg. Chem.*, 1987, **26**, 1912; R. Thomas and F. H. Moore, *Acta Crystallogr., Sect. B*, 1981, **37**, 2156; F. H. Herbstein, M. Kapon and G. M. Reisner, *Acta Crystallogr., Sect. B*, 1985, **41**, 348.

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