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Polymeric anionic networks using dibromine as a crosslinker; the preparation and crystal structure of $[(C_4H_9)_4N]_2[Pt_2Br_{10}]\cdot(Br_2)_7$ and $[(C_4H_9)_4N]_2[PtBr_4Cl_2]\cdot(Br_2)_6$

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The reaction of $M[PtX_3(CO)]$ ($M^+ = [(C_4H_9)_4N]^+$, X = Br, Cl) with an excess of Br_2 gives the new platinum(IV) salts, $[(C_4H_9)_4N]_2[Pt_2Br_{10}]\cdot(Br_2)_7$, 1, and $[(C_4H_9)_4N]_2[PtBr_4Cl_2]\cdot(Br_2)_6$, 2, which, in the solid state, contain strong Br Br interactions resulting in the formation of polymeric networks; they could provide useful solid storage reservoirs for elemental bromine.

A vast variety of solid state structures have been described, which contain anionic polyiodide frameworks. The main building blocks are I^- and I_3^-, which act as electron donors, and I_2, which acts as an electron acceptor;[1,2] recent research has focused on how to increase the amount of iodine per formula unit. Tebbe *et al.* have recently reported the crystal structure of the largest polyiodide, $(Fc)_3I_{29}$,[3] but the ability to form polyhalides decreases dramatically in the order I > Br > Cl > F.[4] A number of halometalate derivatives have been prepared in order to obtain further structural information about different linking motifs of halogen rich compounds.[2,5,6]

During our recent investigations of carbonyl substituted bromoplatinates, we attempted to prepare $[(C_4H_9)_4N][PtBr_5(CO)]$ by oxidative bromination of $[(C_4H_9)_4N][PtBr_3(CO)]$ with elemental bromine in CH_2Cl_2 at *ca.* 240 K. A red crystalline solid was obtained, which was structurally characterised as $[(C_4H_9)_4N]_2[Pt_2Br_{10}]\cdot(Br_2)_7$, **1**.† We assume that the excess of Br_2 reacts with the initially formed $[(C_4H_9)_4N][PtBr_5(CO)]$, which was first observed by Crocker *et al.*,[7] by elimination of CO and subsequent dimerisation to form $[Pt_2Br_{10}]^{2-}$. Salts containing $[Pt_2Br_{10}]^{2-}$ were first prepared in 1991 by Hollmann and Preetz *via* the reaction of $[(C_4H_9)_4N][PtBr_6]$ with CF_3COOH which resulted in elimination of HBr and formation of $[(C_2H_5)_4N][CF_3COO]$.[8] Presently, there are several known examples containing either $[Se_2X_{10}]^{2-}$ (X = Cl, Br) or complex antimony anions linked into polymeric chains by *one* or *two* Br_2 molecules.[9–14] We now report that the crystal structure of **1** contains an unprecedented *seven* Br_2 molecules per formula unit; the Br_2 molecules link with the $[Pt_2Br_{10}]^{2-}$ anions to form an anionic host framework, which accommodates the tetrabutylammonium ions. There are significant Br Br interactions between the $[Pt_2Br_{10}]^{2-}$ anions and Br_2 molecules ranging from 2.990 to 3.317 Å and between Br_2 molecules amounting to 3.342 Å. The $[Pt_2Br_{10}]^{2-}$ anions are linked by Br_2 molecules to form a complicated 3-dimensional anionic network (Fig. 1). The intermolecular Br Br contacts can be described as donor (Br^- in $[Pt_2Br_{10}]^{2-}$) and acceptor (Br_2) interactions.[15] The structure of the $[Pt_2Br_{10}]^{2-}$ anions consist of two edge-shared $PtBr_6$-octahedra bridged by two bromides. The average terminal Pt–Br bond lengths are 2.455(2) Å and the bridging Pt–Br bonds are (2.496(2) and 2.517(2) Å).[16] To our knowledge, **1** contains the largest number of Br_2 molecules per formula unit in a structurally characterised compound.

With the aim of obtaining similar Br_2 networks, $[(C_4H_9)_4N][PtCl_3(CO)]$ was treated with excess bromine.‡ Again, a dark red solid was obtained and X-ray structural analysis revealed the formation of a further bromine rich complex, $[(C_4H_9)_4N]_2[PtBr_4Cl_2]\cdot(Br_2)_6$, **2**. The $[PtBr_4Cl_2]^{2-}$ anion has previously been isolated as both *cis-* and *trans-*isomers, which were characterised by vibrational and NMR spectroscopy.[17–19] The crystal structure of **2** only contains the *trans* isomer. The anion has D_{4h} symmetry with Pt–Cl bond lengths of 2.358(4) Å and Pt–Br bond lengths of 2.449(2) and 2.471(2) Å. It is interesting to note that, in contrast to most other mixed halometallate anions, the $[PtBr_4Cl_2]^{2-}$ anions in **2** show no disorder in the solid state. Indeed, all four Br atoms of the complex anion undergo Br Br interactions with Br_2 molecules, which determines the orientation of the $[PtBr_4Cl_2]^{2-}$ anions in the crystal lattice (Fig. 2). The lengths of Br Br contacts range from 2.816(4) to 3.271(5) Å. The structure can be described as 2-dimensional networks of Br_2 molecules, which are interlinked by $[PtBr_4Cl_2]^{2-}$ anions to form a 3-D framework which hosts the tetrabutylammonium cations.

The unusually high number of Br_2 molecules included in **1** and **2** leads us to expect that more solid state network structures of this novel class of polyhalides based on bromine await discovery. Future work will show if **1** and **2** can be synthesised by simply treating $[(C_4H_9)_4N]_2[Pt_2Br_{10}]$ or

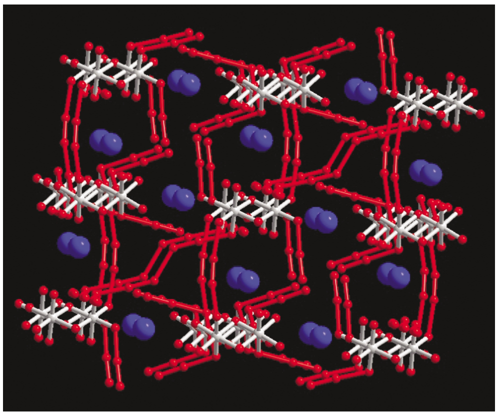

Fig. 1 Crystal structure of **1**. Pt (grey), Br (red), N (blue), butyl groups have been omitted.

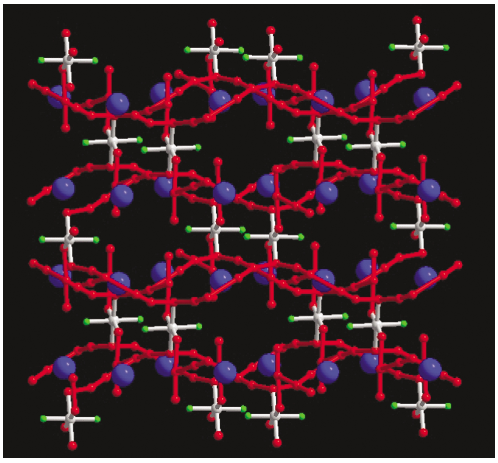

Fig. 2 Crystal structure of **2**. Pt (grey), Br (red), Cl (green), N (blue), butyl groups have been omitted.

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$[(C_4H_9)_4N]_2[PtBr_4CI_2]$ with bromine at low temperatures. Besides promising new coordination modes and new structural motifs, polybromides can provide useful solid-state materials, for example as reservoirs for bromine storage or catalysts for bromination reactions.

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Notes and references

† Single crystals were placed on glass fibres using paraffin oil. X-ray structure determinations were carried out at 150 K on a Bruker Smart APEX CCD diffractometer. Experimental absorption correction was performed (SADABS). Structures were solved by Direct Methods and refined by full matrix least-squares against F^2 (SHELXTL). *Crystal data* for $[(C_4H_9)_4N]_2[Pt_2Br_{10}]\cdot(Br_2)_7$: $C_{32}H_{72}Br_{24}N_2Pt_2$, M = 2792.94, triclinic space group $P1$, a = 11.3186(12), b = 17.1659(19), c = 18.7430(20) Å, α = 103.257(2), β = 101.864(2), γ = 93.605(2)°, V = 3445.7(7) Å^3, Z = 2, μ = 17.997, T = 150(2) K; refinement of 534 parameters against 8953 reflections. R_1 = 0.0641 [$I > 2\sigma(I)$], wR_2 = 0.1883 [all data]. *Crystal data* for $[(C_4H_9)_4N]_2[PtBr_4Cl_2]\cdot(Br_2)_6$: $C_{32}H_{72}Br_{16}Cl_2N_2Pt$, M = 2029.43, monoclinic space group $P2_1/c$, a = 11.604(6), b = 15.530(8), c = 17.764(9) Å, β = 108.671(11)°, V = 3033(3) Å^3, Z = 2, μ = 12.965, T = 150(2) K; refinement of 243 parameters against 3949 reflections. R_1 = 0.0822 [$I > 2\sigma(I)$], wR_2 = 0.2057 [all data].

CCDC reference numbers 187954 ($[(C_4H_9)_4N]_2[Pt_2Br_{10}]\cdot(Br_2)_7$) and 187953 ($[(C_4H_9)_4N]_2[PtBr_4Cl_2]\cdot(Br_2)_6$). See http://www.rsc.org/suppdata/cc/b2/b205712n/ for crystallographic data in CIF or other electronic format.

‡ *Synthesis* of $[(C_4H_9)_4N]_2[Pt_2Br_{10}]\cdot(Br_2)_7$

All synthetic work and sample manipulation was performed using standard Schlenck techniques. Non-volatile materials were handled under dry nitrogen. $[(C_4H_9)_4N][PtBr_3(CO)]$ (140 mg, 0.2 mmol) was dissolved in CH_2Cl_2 (*ca.* 10 mL) and cooled to 243 K. Bromine (320 mg, 2 mmol) was then added dropwise and the formation of a red precipitate was observed. The solvent was removed in vacuum at *ca.* 240 K over 6 h. The resulting red solid was stored under nitrogen at 243 K. It decomposes at temperatures higher than 263 K to a presently unidentified solid, with evolution of bromine. Samples were characterised by Raman spectroscopy and are similar to the Raman spectrum of $[(C_2H_5)_4N]_2[Pt_2Br_{10}]$.[8] Observed bands due to the anion [cm^{-1}]: 262 $\nu(Br_2)$, 237 $\nu_s(PtBr_{2t})$, 208 $\nu_s(Br_t\text{-}Pt\text{-}Br_t)$, 190 $\nu_s(Pt_2Br_{2b})$.

Synthesis of $[(C_4H_9)_4N]_2[PtBr_4Cl_2]\cdot(Br_2)_6$

$[(C_4H_9)_4N][PtCl_3(CO)]$ (105 mg, 0.2 mmol) was dissolved in CH_2Cl_2 (*ca.* 10 mL) and cooled to 243 K. Bromine (320 mg, 2 mmol) in CH_2Cl_2 (2 mL) was added to this solution which resulted in the formation of a red precipitate and evolution of CO. The solvent was removed in vacuum at about 240 K over 8 h. The resulting dark red solid is a mixture of **2** and a presently unidentified platinum salt. It was stored under nitrogen at 243 K. Compound **2** is stable at room temperature. Further investigations to separate **2** from the other side products are presently underway.

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