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Simple Preparations of Pd_6Cl_{12}, Pt_6Cl_{12}, and $Q_n[Pt_2Cl_{8+n}]$, $n = 1, 2$ ($Q = TBA^+$, PPN^+) and Structural Characterization of $[TBA][Pt_2Cl_9]$ and $[PPN]_2[Pt_2Cl_{10}]\cdot C_7H_8$

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The hexanuclear Pd_6Cl_{12}, i.e., the crystal phase classified as β-$PdCl_2$, was obtained by reacting $[TBA]_2[Pd_2Cl_6]$ with $AlCl_3$ (or $FeCl_3$) in CH_2Cl_2. The action of $AlCl_3$ on $PtCl_4^{2-}$, followed by digestion of the resulting solid in 1,2-$C_2H_4Cl_2$ (DCE), $CHCl_3$, or benzene, produced $Pt_6Cl_{12}\cdot$DCE, $Pt_6Cl_{12}\cdot CHCl_3$, or $Pt_6Cl_{12}\cdot C_6H_6$, respectively. Treating $[TBA]_2[PtCl_6]$ with a slight excess of $AlCl_3$ afforded $[TBA][Pt_2Cl_9]$, whose anion was established crystallographically to be constituted by two "$PtCl_6$" octahedra sharing a face. Dehydration of $H_2PtCl_6\cdot nH_2O$ with $SOCl_2$ gave an amorphous compound closely analyzing as $PtCl_4$, reactive with [Q]Cl in $SOCl_2$ to yield $[Q][Pt_2Cl_9]$ or $[Q]_2[Pt_2Cl_{10}]$, depending on the [Q]Cl/Pt molar ratio ($Q = TBA^+$, PPN^+). A single-crystal X-ray diffraction study has shown $[PPN]_2[Pt_2Cl_{10}]\cdot C_7H_8$ to contain dinuclear anions formed by two edge-sharing $PtCl_6$ octahedra.

Introduction

In palladium and platinum chemistry, chloro complexes have a remarkable importance, as they are the usual precursors to various derivatives. From a preparative point of view, the most accessible species are those containing the mononuclear anions MCl_4^{2-} and MCl_6^{2-}. These derivatives are usually prepared in water and can be easily extracted in suitable organic solvents (for instance, CH_2Cl_2) in the presence of tetraalkylammonium salts.[1] Finding convenient preparations of the binary chlorides under mild conditions, however, is still an interesting goal.

Palladium(II) and platinum(II) derivatives exist as hexanuclear M_6Cl_{12} (β-$PtCl_2$[2] and β-$PdCl_2$[3]) or extended-structure (α-$PdCl_2$[4] and α-$PtCl_2$[5]) species. Pt_6Cl_{12} was structurally characterized by single-crystal X-ray diffraction measurements in 1965,[2a] and the palladium analogue was found to be isotypical with it through X-ray diffraction experiments on a polycrystalline sample, as prepared by an unspecified method.[3a] Later, the hexanuclear palladium derivative was obtained by treating $Pd_3(O_2CMe)_6$ with gaseous HCl.[3b] Moreover, controlled decarbonylation at room temperature of $Pd_2Cl_4(CO)_2$ in $SOCl_2$, see eq 1, produced Pd_6Cl_{12}, whose crystal and molecular structure was definitely established by single-crystal X-ray diffraction methods.[3c]

$$3Pd_2Cl_4(CO)_2 \rightleftarrows Pd_6Cl_{12} + 6CO \qquad (1)$$

Clathrates of the formula $Pd_6Cl_{12}\cdot A$ (A = arene, fullerene) were independently reported and structurally characterized.[6] Also, Pt_6Cl_{12} was shown[2b] to readily give clathrates including solvent molecules in the interstitial voids. The preparation

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(1) Bagnoli, F.; Belli Dell'Amico, D; Calderazzo, F; Englert, U.; Marchetti, F.; Merigo, A.; Ramello, S *J. Organomet. Chem*. **2001**, *622*, 180.

(2) (a) Brodersen, K.; Thiele, G.; Schnering, H. G. *Z. Anorg. Allg. Chem*. **1965**, *337*, 120. (b) Pilbrow, M. F. *J. Chem. Soc., Dalton Trans*. **1975**, 2432. (c) Schnering, H.G.; Chang, J.-H.; Peters, K.; Peters, E.-M.; Wagner, F. R.; Grin, Y.; Thiele, G. *Z. Anorg. Allg. Chem*. **2003**, *629*, 516.

(3) (a) Schäfer, H.; Wiese, U.; Rinke, K.; Brendel, K. *Angew. Chem*. **1967**, *79*, 244; *Angew. Chem., Int Ed Engl*. **1967**, *6*, 253. (b) Yatsimirski, A.; Ugo, R. *Inorg. Chem*. **1983**, *2*, 1395. (c) Belli Dell'Amico, D.; Calderazzo, F.; Marchetti, F.; Ramello, S. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1331.

(4) Wells, A. F. *Z. Kristallogr*. **1938**, *100*, 189.

(5) Wiese, U.; Schäfer, H.; Schnering, H. G.; Brendel, C.; Rinke, K. *Angew. Chem.* **1970**, *82*, 135; *Angew. Chem., Int. Ed. Engl*. **1970**, *9*, 158.

(6) (a) Olmstead, M. M.; Ginwalla, A. S.; Noll, B. C.; Tinti, D. S.; Balch, A. L. *J. Am. Chem. Soc*. **1996**, *118*, 7737. (b) Olmstead, M. M; Wei, P.; Balch, A. L. *Chem. Eur. J.* **1999**, *5*, 3136. (c) Olmstead, M. M.; Wei, P.; Ginwalla, A. S.; Balch, A. L. *Inorg. Chem*. **2000**, *39*, 4555.

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of $Pt_6Cl_{12}\cdot 0.1C_2H_5Cl\cdot 5.7H_2O$ under relatively mild conditions requires the action of $BF_3\cdot OEt_2$ on K_2PtCl_4.[7]

Concerning the tetravalent chlorides MCl_4, $PdCl_4$ is unknown, being presumably unstable, while $PtCl_4$ can be prepared from the metal and SO_2Cl_2 under careful control of the temperature.[8] The product was reported to be highly hygroscopic, and an X-ray diffraction study of a polycrystalline sample[9] has shown the compound to be isostructural with α-PtI_4, the latter being constituted by infinite zigzag edge-sharing chains of PtI_6 octahedra. Similar chains have been found in the mixed-valence platinum chloride $PtCl_3$ where edge-sharing $PtCl_6$ octahedra are packed together with Pt_6Cl_{12} in the correct stoichiometric ratio.[5,10]

In the course of previous studies we had found that a brown amorphous product of chemical composition close to $PtCl_4$ (hereafter named "$PtCl_4$") is obtained by treating the commercially available solid hydrated hexachloroplatinic acid with $SOCl_2$.[11] We now report a simple method of preparation of Pd_6Cl_{12} and $Pt_6Cl_{12}\cdot$ solvent (solvent = 1,2-$C_2H_4Cl_2$ (DCE), C_6H_6, $CHCl_3$). Moreover, the preparation and characterization of the derivatives $[Q]_n[Pt_2Cl_{8+n}]$ ($n = 1, 2$; Q = TBA^+, PPN^+) are presented. They were prepared both by extraction of chloride ions from salts containing the $PtCl_6^{2-}$ anion with aluminum chloride or by reaction of "$PtCl_4$" with [Q]Cl or $[Q]_2[PtCl_6]$.

Experimental Section

General Procedures. All manipulations were performed under a dinitrogen atmosphere.

Aqueous solutions of hexachloroplatinic acid (Chimet S.p.A., I-52041 Badia al Pino, Arezzo) and $SOCl_2$ (Aldrich) were commercial products used without further purification. "$PtCl_4$" was prepared as already described[11] (Pt: 55.5%; calcd for $PtCl_4$: 57.9%). The product was amorphous according to a powder X-ray diffraction analysis. DCE was distilled from P_4O_{10}. Toluene and heptane were distilled from sodium. $CDCl_3$ (99.9%, Aldrich) was treated with P_4O_{10} and distilled before use. Tetrabutylammonium chloride [TBA]-Cl and bis(triphenylphosphine)iminium chloride, [PPN]Cl, were dried in vacuo in the presence of P_4O_{10}.

^1H, ^{31}P, and ^{195}Pt NMR spectra were recorded with a Varian Gemini 200BB spectrometer. Chemical shifts were measured in ppm (δ) with external TMS as reference for ^1H and with H_3PO_4 and aqueous (D_2O) hexachloroplatinic acid for ^{31}P and ^{195}Pt, respectively. A sealed capillary containing C_6D_6 was introduced in the NMR tube to lock the spectrometer to the deuterium signal when $SOCl_2$ was used as solvent. Elemental analyses (C, H, N) were performed by Laboratorio di Microanalisi, Dipartimento di Scienze Farmaceutiche, Università di Pisa, with a C. Erba model 1106 elemental analyzer.

Preparation of Pd_6Cl_{12}. A solution of $[TBA]_2[Pd_2Cl_6]$ [1] (746 mg, 0.82 mmol) in CH_2Cl_2 (30 mL) was treated with $AlCl_3$ (207 mg, 1.56 mmol). Solid $AlCl_3$ progressively disappeared, and a red-brown precipitate was observed. The solid was recovered by filtration and dried in vacuo (248 mg, 90% yield). Anal. Calcd for Cl_2Pd: Cl, 40.0; Pd, 60.0%. Found: Cl, 40.9; Pd, 59.9%. Analogous results were obtained by using $FeCl_3$ instead of $AlCl_3$ as halide scavenger.

The X-ray diffraction pattern of the product was collected on a little lump of powder glued at the end of a glass fiber in a Gandolfi camera (114.6 mm) using Ni-filtered Cu K_α radiation (λ = 1.54178 Å). A satisfactory agreement was found between the observed (Å) and calculated (in brackets) d values for β-$PdCl_2$ {1.88 [1.87], 1.94 [1.92], 2.00 [2.00], 2.29 [2.28], 2.37 [2.36], 2.54 [2.53], 3.04 [3.03], 3.26 [3.26], 3.78 [3.83], 4.02 [4.02], 6.53 [6.52], 6.86 [6.84]}.

Preparation of $Pt_6Cl_{12}\cdot$DCE. A solution of $[TBA]_2[PtCl_4]$ (4.36 g, 5.3 mmol) in CH_2Cl_2[1] (100 mL) was treated with $AlCl_3$ (1.55 g, 11.6 mmol), giving a brown suspension which was filtered after 24 h. The solid was then suspended in DCE and refluxed for 6 h, and the resulting suspension was filtered. The solid was washed with CH_2Cl_2 (10 mL) and dried in vacuo (87% yield). Anal. Calcd for $Pt_6Cl_{12}\cdot$DCE, $C_2H_4Cl_{14}Pt_6$: inorganic Cl, 25.1; Pt, 69.1%. Found: inorganic Cl, 25.1; Pt, 69.7%. If the final treatment of the solid was carried out in $CHCl_3$ or in benzene, $Pt_6Cl_{12}\cdot CHCl_3$ or $Pt_6Cl_{12}\cdot C_6H_6$ was obtained, respectively. The X-ray diffraction pattern of $Pt_6Cl_{12}\cdot C_6H_6$ was collected on a two-circle diffractometer with a Bragg−Brentano geometry, equipped with a graphite monochromator on the diffracted beam, using Cu K_α radiation. The specimen was supported on a quartz sample holder. The pattern, collected with steps of 0.02° between 4° and 100°, has been deposited as Supporting Information. The diffraction pattern may be indexed with a trigonal unit cell, and c = 12.396 Å, corresponding to the primitive rhombohedral cell (a = 8.13 Å; α = 96.4°) previously reported.[2b] The CIF files have been deposited with the Cambridge Crystallographic Data Centre, CCDC 656752 and CCDC 656753, respectively.

$[TBA]_2PtCl_6$ by Solvent Extraction. An aqueous solution (0.147 M) of hexachloroplatinic acid (35 mL, 5.14 mmol) was shaken with a solution of [TBA]Cl (2.847 g, 10.24 mmol) in CH_2Cl_2 (50 mL). The aqueous solution rapidly discolored, and the orange layer was evaporated to dryness in vacuo. The yellow-orange residue was treated with heptane (30 mL), and the suspension was filtered. The solid was dried in vacuo for 2 h (4.25 g, 93% yield). Anal. Calcd for $C_{32}H_{72}Cl_6N_2Pt$: C, 43.0; H, 8.1; N, 3.1%. Found: C, 42.2; H, 8.2; N, 2.5%. ^{195}Pt NMR (in $CH_2Cl_2/CDCl_3$): 237 ppm.

Preparation of $[TBA][Pt_2Cl_9]$. (a) From "$PtCl_4$" and [TBA]-Cl. To a suspension of "$PtCl_4$" (709 mg, 2.02 mmol) in $SOCl_2$ (20 mL) a solution of [TBA]Cl (281 mg, 1.01 mmol) in $SOCl_2$ (5 mL) was added. The suspension rapidly turned deep red and, after stirring at 25 °C for 2 h and at 80 °C for an additional 2 h, complete dissolution was observed. After addition of heptane (20 mL) and cooling down to −30 °C for 24 h, a red hygroscopic microcrystalline solid separated out, which was filtered and dried in vacuo (472 mg, 49.8% yield). Anal. Calcd for $C_{16}H_{36}Cl_9NPt_2$: Pt, 41.0%. Found: Pt, 41.5%. ^{195}Pt NMR ($SOCl_2$): 220 and 177 ppm, see the Results and Discussion section.

(b) From $[TBA]_2PtCl_6$ and $AlCl_3$. To a solution of $[TBA]_2PtCl_6$ (1.890 g, 2.12 mmol) in CH_2Cl_2 (25 mL), $AlCl_3$ (564 mg, 4.23 mmol) was added. After 4 h of stirring at room temperature, solid $AlCl_3$ had completely disappeared and the solution was of an intense red color. After cooling at −30 °C for 4 days, red crystals separated out and were filtered and dried in vacuo (537 mg, 53% yield). Some crystals were selected and sealed in Lindemann capillaries under N_2 to perform X-ray diffraction measurements. Anal. Calcd for $C_{16}H_{36}Cl_9NPt_2$: C, 20.2; H, 3.8; N, 1.5; Pt, 41.0%. Found: C, 20.0;

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(7) Kukushkin, V. Yu.; Tkachuk, V. M.;Vorobiov-Desiatovsky, N. V. *Inorg. Syn.* **1998**, *32*, 145, and references therein.

(8) Dillamore, I. M.; Edwards, D. A. *J. Inorg. Nucl. Chem.* **1969**, *31*, 2427.

(9) Pilbrow, M. F. *J. Chem. Soc., Chem. Commun.* **1972**, 270.

(10) Schnering, H. G.; Chang, J.-H.; Freiberg, M.; Peters, K.; Peters, E.-M.; Ormeci, A.; Schröder, L.; Thiele, G.; Röhr, C. *Z. Anorg. Allg. Chem.* **2004**, *630*, 109.

(11) Belli Dell'Amico, D.; Calderazzo, F.; Dell'Amico, G. *Gazz. Chim. Ital.* **1977**, *107*, 101.

H, 3.6; N, 1.3; Pt, 40.8%. ^{195}Pt NMR ($SOCl_2$): 220 and 177 ppm, see the Results and Discussion section.

Preparation of [Q]$_2$[Pt$_2$Cl$_{10}$]. (a) From "PtCl$_4$" and [Q]Cl. A solution of [PPN]Cl in $SOCl_2$ was added to a suspension of "$PtCl_4$" in $SOCl_2$, corresponding to a Pt/[Q]Cl molar ratio of 1. Toluene was added to the resulting yellow-brown solution, and crystals of $[PPN]_2[Pt_2Cl_{10}]\cdot C_7H_8$ precipitated out within about 24 h at room temperature. The product was collected by filtration and dried in vacuo (29% yield). Anal. Calcd for $\{N[P(C_6H_5)_3]_2\}[Pt_2Cl_{10}]\cdot C_7H_8$, $C_{79}H_{68}Cl_{10}N_2P_4Pt_2$: C, 49.6; H, 3.6; N. 1.5%. Found: C, 49.5; H, 4.0; N. 1.3%. ^{195}Pt NMR ($SOCl_2$): 385 ppm. ^{31}P NMR ($SOCl_2$) 22.5 ppm. Some crystals, suitable for X-ray diffraction measurements, were selected (vide infra).

The analogous product $[TBA]_2[Pt_2Cl_{10}]$ was obtained (66% yield) from equimolar amounts of "$PtCl_4$" and [TBA]Cl.

(b) From "PtCl$_4$" and [TBA]$_2$[PtCl$_6$]. Substantially equimolar quantities of "$PtCl_4$" (199 mg, 0.56 mmol) in $SOCl_2$ (10 mL) and $[TBA]_2[PtCl_6]$ (463 mg, 0.52 mmol) in $SOCl_2$ (5 mL) were stirred at room temperature (12 h), giving an orange solution. The solvent was evaporated to dryness, and the orange residue was treated with toluene (10 mL). The suspension was filtered, and the product $[TBA]_2[Pt_2Cl_{10}]$ was dried in vacuo (528 mg, 83% yield). Anal. Calcd for $C_{32}H_{72}Cl_{10}N_2Pt_2$: Pt, 31.7%. Found: Pt, 31.0%. ^{195}Pt NMR ($SOCl_2$): 385 ppm.

(c) From [TBA]$_2$PtCl$_6$ and AlCl$_3$. From equimolar quantities of $[TBA]_2[PtCl_6]$ and $AlCl_3$ in 1,2-dichloroethane, a yellow-brown solution was obtained after 4 h whose ^{195}Pt NMR spectrum showed the signal at 384 ppm, due to the $[Pt_2Cl_{10}]^{2-}$ anion, while the resonance of $PtCl_6^{2-}$ at 233 ppm had disappeared.

Reaction of [PPN][Pt$_2$Cl$_9$] with [PPN]Cl. A solution of [PPN]-$[Pt_2Cl_9]$ was obtained by reacting "$PtCl_4$" (0.80 mmol) with [PPN]-Cl (0.40 mmol) in $SOCl_2$ (12 mL): ^{195}Pt NMR: 220 and 177 ppm. A solution of [PPN]Cl in $SOCl_2$ (0.40 mmol in 3 mL) was then added. A rapid color change was observed (from red to brown-yellow). After 2 h, the ^{195}Pt NMR spectrum of the solution showed the resonance due to $[Pt_2Cl_{10}]^{2-}$ at 384 ppm only. Toluene (20 mL) was added, and the solution was stored at about 0 °C. Brown-yellow crystals separated out. The suspension was filtered after 5 days, and the solid was recovered (65% yield).

Reaction of [TBA]$_2$[Pt$_2$Cl$_{10}$] with [TBA]Cl. To a brown solution of $[TBA]_2[Pt_2Cl_{10}]$ (352 mg, 0.29 mmol) in $SOCl_2$ (10 mL), a solution of [TBA]Cl (0.57 mmol) in 5 mL of $SOCl_2$ was added and the reaction was monitored by ^{195}Pt NMR spectroscopy. After 24 h of stirring at 25 °C, only the unconverted precursor was observed. The solution, after 4 h of reflux, turned golden yellow. A ^{195}Pt NMR spectrum at room temperature showed no signal due to $Pt_2Cl_{10}^{2-}$, while the $PtCl_6^{2-}$ anion, characterized by the resonance at 183 ppm, was present. The solvent was evaporated to dryness, and the product was recovered (70% yield). Anal. Calcd for $C_{32}H_{72}Cl_6N_2Pt$: Pt, 21.9%. Found: Pt, 22.9%.

Single-Crystal X-ray Diffraction Studies. The X-ray diffraction experiments were carried out at 293 K by means of a Bruker P4 diffractometer equipped with graphite-monochromated Mo K$_\alpha$ radiation. The samples were sealed in glass capillaries under an atmosphere of dinitrogen. The intensity data collection with the $\omega/2\theta$ scan mode gave a redundant set of data. Three standard reflections, measured every 97 measurements, were used to check sample decay. The intensities were corrected for Lorentz and polarization effects and for absorption by the ψ-scan method.[12] The structure solution was obtained by means of the automatic direct methods contained in SHELXS97[13] for $[TBA][Pt_2Cl_9]$ and in SIR92[14] for $[PPN]_2[Pt_2Cl_{10}]\cdot C_7H_8$. The refinements, based on full-matrix least-squares on F^2, were carried out by means of the SHELXL97 program.[13] Some other utilities contained in the WINGX suite[15] were also used. The more relevant crystal parameters are listed in Table 1.

Table 1. Crystal Data and Structure Refinements

compound	[TBA][Pt$_2$Cl$_9$]	[PPN]$_2$[Pt$_2$Cl$_{10}$]$\cdot$C$_7$H$_8$
empirical formula	$C_{16}H_{36}Cl_9NPt_2$	$C_{79}H_{68}Cl_{10}N_2P_4Pt_2$
fw	951.69	1913.91
cryst syst	monoclinic	triclinic
space group	$P2_1/m$ (No. 11)	$P\bar{1}$ (No. 2)
a/Å	10.637(2)	12.124(1)
b/Å	11.156(2)	13.253(2)
c/Å	14.006(2)	13.678(1)
α/deg	-	102.209(9)
β/deg	111.86(1)	94.790(7)
γ/deg	-	112.662(8)
U/Å^3	1542.5(5)	1948.7(4)
Z	2	1
D_{calcd}/Mg$\cdot$m^{-3}	2.049	1.631
μ/mm^{-1}	9.845	4.055
measured reflns	2785	9098
unique reflns [R_{int}]	2109 [0.051]	7923 [0.027]
no. of params	121	442
R1, wR2 (all data)	0.065, 0.188	0.036, 0.107
GOF on F^2	1.023	1.055

The crystals of $[TBA][Pt_2Cl_9]$ gave rather broad reflections whose intensity decreased by increasing the diffraction angle 2θ. The intensity data collection was thus discontinued at $2\theta_{max} = 45°$. Systematic absences suggested $P2_1$ or $P2_1/m$ as possible space groups. The structure solution was found in the centrosymmetric one. Both the cation and the anion were found to be placed on the mirror planes, although the chains of TBA do not perfectly comply with the mirror symmetry. This results in some degree of disorder in the position of the C atoms, which were in part described as distributed in two different sites and refined with isotropic thermal parameters and some geometrical constraints. The hydrogen atoms were placed in calculated positions and let ride on the connected carbon atoms. The final refinement cycles were performed with anisotropic thermal parameters for the Pt, Cl, and N atoms and isotropic for the others, giving the reliability factors listed in Table 1.

The crystals of $[PPN]_2[Pt_2Cl_{10}]\cdot C_7H_8$ were of good quality with sharp reflections. The intensity data collection was carried out up to $2\theta_{max} = 53°$. The structure solution was found in the centrosymmetric $P\bar{1}$ space group. The asymmetric unit contained one cation, half an anion being placed near an inversion center, and half a solvent molecule (toluene) placed near the other inversion center. Disorder results in the toluene molecule orientation due to incompatibility between the molecular symmetry and the site symmetry ($\bar{1}$): it was refined with the methyl group placed at 50% on two opposite carbon atoms of the ring. The hydrogen atoms were placed in calculated positions. The final refinement cycle was done by using anisotropic thermal parameters for all the heavy atoms, letting the hydrogen atoms 'ride' on the connected carbon atoms. The resulting reliability factors are listed in Table 1.

Results and Discussion

The step-by-step construction of a polynuclear or extended structure starting from a molecular species is an interesting

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(12) Sheldrick, G. M. *SHELXTL-Plus*, *Rel. 5.1*; Bruker AXS Inc.: Madison, WI, 1997.

(13) Sheldrick, G. M. *SHELX97, Programs for Crystal Structure Analysis (Release 97-2)*; University of Göttingen: Göttingen, Germany, 1998.

(14) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A. *J. Appl. Crystallogr*. **1993**, *26*, 343.

(15) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837.

subject. The preparation of anhydrous metal halides, MX_n, under mild conditions can be carried out by the progressive subtraction of neutral ligands, L, from halo complexes MX_nL_m or by elimination of halides from $[MX_{n+m}]^{m-}$. Starting from a mononuclear complex, the first steps of the process will produce dinuclear or oligonuclear complexes, which can constitute the building blocks of the subsequent aggregation step.

Let us first compare the dichloro complexes of palladium(II) with those of platinum(II). Earlier we have found that $Pd_2Cl_4(CO)_2$ is the precursor to Pd_6Cl_{12}, eq 1, in solution depending on the CO partial pressure.[3c] We have now found that Pd_6Cl_{12} is also obtained by treating $[TBA]_2[Pd_2Cl_6]$ (easily prepared[1] from aqueous $PdCl_4^{2-}$) with $AlCl_3$ in CH_2Cl_2. Abstraction of chloride ions by aluminum chloride converts the dinuclear anionic palladium chloro complex to the hexanuclear species, easily recovered by filtration of the reaction mixture. The nature of the product has been checked by elemental analysis and by powder X-ray diffraction methods on a polycrystalline sample.

It is well established that Pd_6Cl_{12} and its clathrates can readily be prepared under mild conditions.[3b,c,6] On the other hand, the corresponding hexanuclear derivatives of platinum(II) normally require more drastic conditions for their synthesis. As a matter of fact, a recent paper reports that "the thermal decomposition of commercial hexachloroplatinum(IV) acid in an atmosphere of streaming Cl_2 (T about 800 K) is the best and most simple way to synthesize β-$PtCl_2$".[2c] We have now found that the hexanuclear derivative of platinum(II) can be prepared at room temperature in DCE as solvent by treatment of $[TBA]_2[PtCl_4]$ with $AlCl_3$ in the molar ratio 1:2. The resulting brown solid, by digestion in DCE, $CHCl_3$, or benzene gives the microcrystalline adducts $Pt_6Cl_{12}\cdot$solvent. A X-ray powder diffraction study of the benzene clathrate confirmed the identity of the product.[2b]

The present preparation of Pt_6Cl_{12} appears to be a simple and attractive one to a useful precursor in platinum chemistry, thus improving the known art in this field.

The treatment with halide scavengers was extended to platinum(IV) halo complexes. The reaction of $[TBA]_2[PtCl_6]$ with $AlCl_3$ in a 1:2 molar ratio in CH_2Cl_2 as solvent at room temperature produced a red solution, from which red crystals of $[TBA][Pt_2Cl_9]$ were obtained at low temperature (see eq 2).

$$2[TBA]_2[PtCl_6] + 3AlCl_3 \rightarrow 3[TBA][AlCl_4] + [TBA][Pt_2Cl_9] \quad (2)$$

According to X-ray structural determination, this compound is constituted by dinuclear $[Pt_2Cl_9]^-$ anions where the two platinum atoms are connected by three bridging chlorides with a geometry corresponding to two $PtCl_6$ octahedra sharing a face. The structure is shown in Figure 1 together with some significant bond distances and angles. The ion possesses a mirror plane passing through the platinum atoms and Cl(1), Cl(3), and Cl(5). The coordination geometry is pseudo-octahedral, the deformation being mainly due to face sharing, the average Pt−Cl distances being 2.254 and 2.379 Å for terminal and bridging chlorides, respectively. The Cl−Pt−Cl angles range between 89.7° and 91.6° and between 81.5° and 82° for terminal and bridging chlorides, respectively.

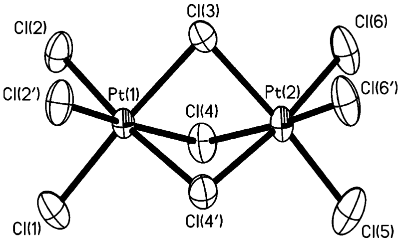

Figure 1. Structure of the $Pt_2Cl_9^-$ anion in $[TBA][Pt_2Cl_9]$. Ellipsoids are at 20% probability. Bond distances (Å) and angles (deg): Pt(1)−Cl(1) 2.255(9), Pt(1)−Cl(2) 2.261(6), Pt(1)−Cl(3) 2.376(8), Pt(1)−Cl(4) 2.381(6), Pt(2)−Cl(3) 2.383(9), Pt(2)−Cl(4) 2.375(6), Pt(2)−Cl(5) 2.233(12), Pt(2)−Cl(6) 2.266(7), Pt(1)−Cl(3)−Pt(2) 81.6(3), Pt(1)−Cl(4)−Pt(2) 81.7(2). ′ = x, $3/2 - y$, z.

Although the Pt···Pt distance of 3.111(2) Å is rather short, this is no evidence of a metal−metal interaction. In fact, for an ideal bi-octahedral face-sharing geometry, the angles subtended by the bridging chlorides (β angles) are expected to be 70.5°.[16] Deviations from the ideal geometry due to attraction or repulsion between the two metal centers correspond to a decrease or an increase, respectively, of this value. In $[Pt_2Cl_9]^-$ these angles are about 82°, corresponding to a platinum−platinum repulsion. For instance, in $[M_2Cl_9]^{3-}$ with M = Cr, Mo, W the metal−metal distances are 3.1, 2.7, and 2.4 Å, respectively and the β angles are 82°, 66°, and 59°, respectively. Magnetic susceptibility data suggest the presence of a metal−metal bond in the molybdenum and tungsten derivatives but not in the chromium one.[17] $[M_2Cl_9]^{x-}$ anions with three chloride bridges have frequently been found in early transition metals. Of special interest are the $[M_2Cl_9]^-$ anions with M = Ti, Zr, Hf: in these systems of d^0 electronic configuration, where no metal−metal bond interaction of any sort can be expected, the metal atoms are situated at a nonbonding distance of 3.39, 3.62, and 3.58 Å, respectively, with β angles of 86°, 88°, and 87°, respectively.[18] Chloride-bridged dinuclear anions of this type are less frequent in late transition metal anions, well-defined cases being known only for Ru(II)−Ru(III),[19] Ru(III),[20] Rh(III),[21] and Ir(III).[22] While

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(16) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1979**, *101*, 3821.

(17) Several data are reported in the literature; here only three papers are reported dealing with chromium, molybdenum, and tungsten derivatives, in that order. (a) Dyer, P. W.; Gibson, V. C.; Jeffery, J. C. *Polyhedron* **1995**, *14*, 3095. (b) Stranger, R.; Smith, P. W.; Grey, I. E. *Inorg. Chem.* **1989**, *28*, 1271. (c) Dunbar, K. R.; Pence, L. E. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1991**, *47*, 23.

(18) Selected papers on titanium, zirconium, and hafnium compounds are, respectively. (a) Solari, E.; Floriani, C.; Schenk, K.; Chiesi-Villa, A.; Rizzoli, C.; Rosi, M.; Sgamellotti, A. *Inorg. Chem.* **1994**, *33*, 2018. (b) Schormann, M.; Garratt, S.; Hughes, D. L.; Green, J. C.; Bochmann, M. *J. Am. Chem. Soc.* **2002**, *124*, 11266. (c) Calderazzo, F.; Ferri, I.; Pampaloni, G.; Troyanov, S. *J. Organomet. Chem.* **1996**, *518*, 189.

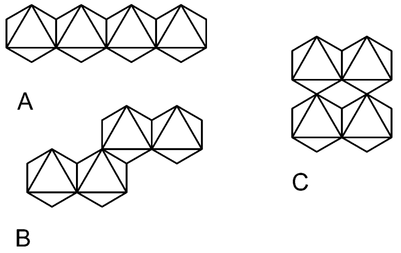
(19) Bino, A.; Cotton, F. A. *J. Am. Chem. Soc.* **1980**, *102*, 608.

(20) Efimenko, I. A.; Balakaeva, T. A.; Kurbakova, A. P.; Kanishcheva, A. S.; Chuvaev, A. V.; Stepanovich, V. M.; Mikhailov, Yu. N. *Zh. Neorg. Khim.* **1992**, *37*, 1312.

(21) Cotton, F. A.; Ucko, D. A. *Inorg. Chim. Acta* **1972**, *6*, 161.

(22) Yellowlees, L.; Elliot, M.; Parsons, S.; Messenger, D. Cambridge Crystallographic Data Centre, Private Communication, CCDC 278284.

Scheme 1. Some Possible Chains of Edge-Sharing Octahedra



$Rh_2Cl_9^{3-}$ and $Ir_2Cl_9^{3-}$ are similar to $Pt_2Cl_9^{-}$ (with M$\cdots$M distances of 3.121 and 3.124 Å, respectively, and β angles of 80.2° and 82.1°, respectively), $Ru_2Cl_9^{3-}$ has been found to have a short Ru$-$Ru distance of 2.716 Å and β angles of 70°, compatible with the presence of a metal$-$metal bond. On the other hand, the Pt(μ-Cl)$_3$Pt core has been found in the $[(CH_3COCH_2)_3Pt(\mu\text{-}Cl)_3Pt(CH_2COCH_3)_3]^-$ anion,[23] which, however, shows a rather long Pt$\cdots$Pt distance of 3.275 Å that is related to Pt$-$Cl bond distances in the $Pt_2(\mu\text{-}Cl)_3$ core of 2.51 Å. In [PPN][Pt_2Br_9], belonging to the class of the $[M_2X_9]^{n-}$ anions, the intermetallic distance is 3.23 Å, the β angle is 79°, and the Pt$-$Br bond distances in the $Pt_2(\mu\text{-}Br)_3$ core are 2.50 Å.[24] It is of note that the geometrical and electronic properties of the dinuclear face-sharing $[M_2X_9]^{n-}$ anions have stimulated several theoretical studies.[16,25]

As has been shown, a rather large number of species containing the face-sharing bi-octahedral dinuclear anions $M_2X_9^{n-}$ have been structurally characterized. On the other hand, different nuclearities and geometries can be hypothesized for an anion with this stoichiometry, for instance, linear or zigzag tetranuclear complexes $M_4X_{18}^{2-}$ formed by MCl_6 octahedra sharing edges, see A and B in Scheme 1.

It is interesting to note that [TBA][Pt_2Cl_9] in solution of $SOCl_2$ shows two ^{195}Pt NMR resonances at 220 and 177 ppm whose intensity varies with time, the former being less intense in the freshly prepared solution, becoming the prevailing one after 12 h. As both signals do not present satellites, this allows us to exclude the formation of complexes containing magnetically nonequivalent platinum atoms. We propose the presence of an equilibrium between the dinuclear anion $[Pt_2Cl_9]^-$ and a cyclic tetranuclear species, $[Pt_4Cl_{18}]^{2-}$ (see C in Scheme 1), where the platinum centers are alternately connected by double and single chloride bridges. The $[Bi_4Cl_{18}]^{6-}$ anion shows this architecture,[26] and a similar tetranuclear core $Pt_4(\mu\text{-}Cl)_6$ has been found in $[CPh_3]_2[Pt_4(C_6H_4)_2Cl_{14}]$.[27] The formation of the tetranuclear anion $[Pt_4Cl_{18}]^{2-}$ would allow the system to release the strain associated with the triple chloride bridge. A lower solubility of [TBA][Pt_2Cl_9], probably related to its higher lattice energy with respect to $[TBA]_2[Pt_4Cl_{18}]$, may explain its separation in the solid state.

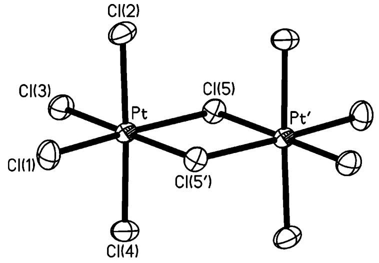


Figure 2. Structure of the $Pt_2Cl_{10}^{2-}$ anion as found in $[PPN]_2[Pt_2Cl_{10}]\cdot C_7H_8$. Ellipsoids are at 30% probability. Bond distances (Å): Pt(1)$-$Cl(1) 2.272(2), Pt(1)$-$Cl(2) 2.310(2), Pt(1)$-$Cl(3) 2.280(2), Pt(1)$-$Cl(4) 2.316(2), Pt(1)$-$Cl(5) 2.374(2), Pt(1)$-$Cl(5′) 2.379(2), ′ = $-x$, $1 - y$, $1 - z$.

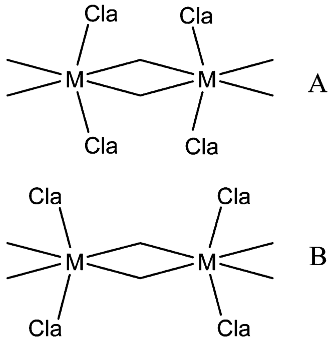


Figure 3. (A) Schematic structure of the $M_2Cl_{10}^{2-}$ anion in Ti, Zr, Hf, Mo, and Os derivatives. (B) Structure of the $M_2Cl_{10}^{2-}$ ion as found in the W and Pt derivatives.

[TBA][Pt_2Cl_9] has been prepared also through an alternative route, i.e., by treating "$PtCl_4$" with the stoichiometric amount of [Q]Cl. In $SOCl_2$ the reaction proceeds in a few hours with formation of a red solution whose ^{195}Pt NMR spectrum shows the two resonances at 220 and 177 ppm. Workup of the solution led to a microcrystalline product of composition [TBA][Pt_2Cl_9], which shows the same color and crystal habit as the species obtained by treating $[TBA]_2[PtCl_6]$ with $AlCl_3$.

By reacting equimolar quantities of "$PtCl_4$" and [Q]Cl (or $[Q]_2[PtCl_6]$) (Q = TBA, PPN), a species analyzed as $[Q]_2[Pt_2Cl_{10}]$ was obtained that is well soluble in chlorinated hydrocarbons and in $SOCl_2$. The same type of product was obtained from equimolar quantities of $[Q]_2PtCl_6$ and $AlCl_3$. The resulting solution, independent of the nature of the cation, exhibits one ^{195}Pt NMR resonance at 385 ppm in $SOCl_2$ (384 ppm in DCE). As only one resonance was observed and the nature of the solvent has a negligible influence on the chemical shift, it can be concluded that only one type of chloro complex is present in solution and that it does not contain coordinated solvent. The derivative $[PPN]_2[Pt_2Cl_{10}]\cdot C_7H_8$ has been characterized by single-crystal X-ray diffraction measurements and shown to contain dinuclear anions formed by two edge-sharing $PtCl_6$ octahedra, see Figure 2.

The structure of the anion is centrosymmetric and, as reported in the caption, contains three types of Pt$-$Cl distances: the longer ones (2.376 Å) for bridging ligands, the intermediate ones (2.313 Å) for axial ligands, and the

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[23] (a) Vicente, J.; Arcas, A.; Fernández-Hernández, J. M.; Sironi, A., Masciocchi, N. *Chem. Commun.*, **2005**, 1267. (b) Vicente, J.; Arcas, A.; Fernández-Hernández, J. M.; Bautista, D. *Organometallics*, **2006**, *25*, 4404.

[24] Hollmann, P.; Preetz, W.; Hillebrecht, H.; Thiele, G. *Z. Anorg. Allg. Chem.* **1992**, *611*, 28.

[25] Cavigliasso, G.; Lovell, T.; Stranger, R. *Dalton Trans.* **2006**, 2017, and references therein.

[26] Aurivillius, B.; Stålhandske, C. *Acta Chem. Scand. A* **1978**, *32*, 715.

[27] Cook, P. M.; Dahl, L. F.; Dickerhoof, D. W *J. Am. Chem. Soc.* **1972**, *94*, 5511.

shorter ones (2.276 Å) in the equatorial positions. The $[Pt_2Cl_{10}]^{2-}$ anion was reported earlier in $[CPh_3]_2[Pt_2Cl_{10}]$,[27] but no geometric parameters were described. Several other $M_2Cl_{10}{}^{2-}$ anions of similar geometry have been reported for tetravalent metal cations (M = Ti,[28] Zr,[29] Hf,[30] Mo,[31] W,[32] Os[33]). In all cases, except for W(IV) where a metal−metal bond is involved, the M···M distances are greater than the $Cl_a \cdots Cl_a$ ones, as shown in Figure 3A. The $[d(M \cdots M) - d(Cl_a \cdots Cl_a)]$ difference ranges between 0.35 Å observed in $Zr_2Cl_{10}{}^{2-}$ [29f] and 0.06 Å in $Os_2Cl_{10}{}^{2-}$.[33] In contrast, in $Pt_2Cl_{10}{}^{2-}$, although the metal−metal distance is not associated with a chemical bond, the Pt atoms approach each other up to 3.518 Å, while the Cl(2)···Cl(4′) distance is 3.629 Å, with a geometry as that sketched in Figure 3B.

Edge-shared systems like $[M_2Cl_{10}]^{n-}$ have been the subject of theoretical studies aimed at correlating the electronic configuration of the metal centers with the presence of metal−metal interactions and comparisons with the face-shared $[M_2Cl_9]^{n-}$ anions have also been made.[34]

The reactivity of the two types of salts toward [Q]Cl has been studied: $Pt_2Cl_9{}^-$ reacts rapidly with 1 equiv of Cl^- producing $[Pt_2Cl_{10}]^{2-}$, while $[Pt_2Cl_{10}]^{2-}$ reacts slowly yielding $[PtCl_6]^{2-}$. These results show that for the doubly bridged $[Pt_2Cl_{10}]^{2-}$ anion, the typical inertness of platinum(IV) is observed, while $[Pt_2Cl_9]^-$ behaves anomalously. The previously discussed structural features of the dinuclear anion, containing a strained triple chloride bridge, accounts for the observed reactivity.

Conclusions

Simple preparations of the hexanuclear complexes of palladium(II) and platinum(II) M_6Cl_{12} under mild conditions have been detected starting from their chloro complexes. The identification in both cases of a specific crystalline form adds significance to these syntheses. The new halide-bridged complexes of platinum(IV) $[Pt_2Cl_9]^-$ and $[Pt_2Cl_{10}]^{2-}$ have been obtained by several synthetic routes, and their structural characterization enlarges the set of metrical data on the dinuclear face-sharing and edge-sharing species, respectively. Further interest originates from the observation that such structures, which are rather common for early and middle transition metals, are relatively rare for the late ones.

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Supporting Information Available: X-ray crystallographic data for $[TBA][Pt_2Cl_9]$ and $[PPN]_2[Pt_2Cl_{10}] \cdot C_7H_8$ in CIF format and the XRD pattern of $Pt_6Cl_{12} \cdot C_6H_6$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(28) Köhn, R. D.; Kampe, P.; Kociok-Köhn, G. *Eur. J. Inorg. Chem.* **2005**, 3217.

(29) (a) Eicher, J.; Müller, U.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1985**, *521*, 37. (b) Brusilovets, A. I.; Rusanov, E. B.; Chernega, A. N. *Zh. Obshch. Khim.* **1995**, *65*, 1819. (c) Krut'ko, D. P.; Borzov, M. V.; Veksler, E. N.; Churakov, A. V.; Howard, J. A. K. *Polyhedron* **1998**, *17*, 3889. (d) Coles, S. J.; Hursthouse, M. B.; Kelly, D. G.; Walker, N. M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1999**, *55*, 1789. (e) Sarsfield, M. J.; Said, M.; Thornton-Pett, M.; Gerrard, L. A.; Bochmann, M. *J. Chem. Soc., Dalton Trans.* **2001**, 822. (f) Hart, R.; Levason, W.; Patel, B.; Reid, G. *J. Chem. Soc., Dalton Trans.* **2002**, 3153. (g) Centore, R.; Tuzi, A.; Liguori, D. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **2003**, *59*, m241.

(30) (a) Calderazzo, F.; Pallavicini, P.; Pampaloni, G.; Zanazzi, P. F. *J. Chem. Soc., Dalton Trans.* **1990**, 2743. (b) Neumüller, B.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2004**, *630*, 2576.

(31) Hey, E.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **1984**, *508*, 86.

(32) Kolesnichenko, V.; Swenson, D. C.; Messerle, L. *Chem. Commun.* **1998**, 2137.

(33) Krebs, B.; Henkel, G.; Dartmann, M.; Preetz, W.; Bruns, M. *Z. Naturforsch., B :Chem. Sci.* **1984**, *39*, 843.

(34) McGrady, J. E.; Stranger, R.; Lovell, T. *Inorg. Chem.* **1998**, *17*, 3802, and references therein.