

High-yield one-step synthesis in water of $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$ ($n > 6$) and $[\text{Pt}_{38}(\text{CO})_{44}]^{2-}$

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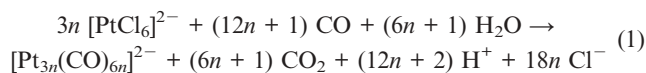
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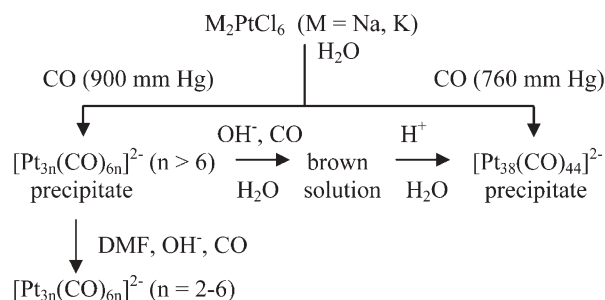
Carbonylation of $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$, as well as K_2PtCl_6 , in water under a CO pressure of 900 mm Hg selectively and quantitatively affords $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$ ($n > 6$) salts; conversely, their corresponding carbonylation at reduced CO pressure of 760–800 mm Hg leads to a convenient one-step synthesis of $[\text{Pt}_{38}(\text{CO})_{44}]^{2-}$.

The poor impact of structurally and compositionally well-defined molecular metal carbonyl clusters of nanometric size in nanotechnologies other than heterogeneous catalysis,¹ in comparison to molecularly less-defined quasi monodispersed ligand-stabilised metal nanoparticles,² is probably a consequence, beyond other considerations, of the widespread opinion that their synthesis and purification are troublesome. The potential of water-soluble metal carbonyl clusters as “printable metals” in molecular electronics^{3,4} and nanolithography^{4,5} prompted a re-investigation of the chemistry of Pt carbonyl clusters with the aim of finding easily-reproducible selective syntheses of some highest nuclearity species.

We wish now to report an extremely simple and quantitative synthesis of a $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$ ($n > 6$),^{6,7} mixture of oligomers, as well as a one-step synthesis of the $[\text{Pt}_{38}(\text{CO})_{44}]^{2-}$ ^{8,9} dianion from $[\text{PtCl}_6]^{2-}$ alkali salts. Both syntheses rely on carbonylation of $[\text{PtCl}_6]^{2-}$ salts in water and the results are summarized in Scheme 1. The efficiency of the carbonylation reaction is only moderately affected by the alkali counterion, the pH of the aqueous solution and the chloride concentration. Typically, aqueous solutions of $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ (ca. 0.1 M) or suspensions of K_2PtCl_6 in water (1–2 g in 50 mL) upon vigorous stirring under a superatmospheric carbon monoxide pressure (900 mm Hg) separate in a few hours a brown-violet precipitate owing to reaction (1).



After filtration of the precipitate, the reaction solution is colourless, displays an acidic pH (< 2) and contains only a trace amount of platinum. The resulting brown-violet precipitates display distinct behaviour according to the alkali counterion and the effectiveness of the drying procedures. In particular, $[\text{Na}(\text{H}_2\text{O})_x]_2[\text{Pt}_{3n}(\text{CO})_{6n}]$ carbonylation products which are still hydrated are soluble in several organic solvents such as THF, acetone and acetonitrile. The solutions are green-brown and



Scheme 1

display IR carbonyl absorptions at ca. 2070 and 1885 cm^{-1} characteristic of $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$ ($n > 6$) clusters.⁷ A typical ESI-MS in THF solution is shown in Fig. 1. It might represent a snapshot of the mixture of $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$ ($n = 3$ –10) oligomers present in the water-insoluble precipitate. However, it is much more likely that the observed bell-shaped distribution centred at $n = 6$ is the result of fragmentation and condensation processes triggered by electrospray ionization. First of all, ESI-MS experiments on spectroscopically pure $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$ ($n = 3$ –5) species also exhibit related distributions mainly arising from the presence of $n \pm 1$

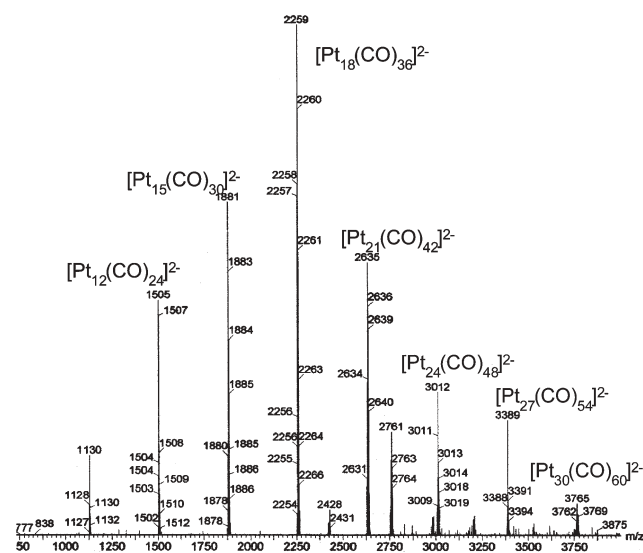


Fig. 1 ESI-MS in THF of the $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$ ($n > 6$) mixture obtained by carbonylation of $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in water under a CO pressure of 850 mm Hg. The weak unattributed peaks centred at 2428 and 2761 m/z are due to $[\text{Pt}_{38}(\text{CO})_{44}]^{2-}$ impurities.

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oligomers. Secondly, comproportionation reactions between non consecutive $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$ dianions^{7,11} should oppose the above spreading in solution.

Conversely, the water-carbonylation products of K_2PtCl_6 (as well as $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ once thoroughly dried) are insoluble in THF and are extracted only by acetonitrile as violet colloidal suspensions, showing unresolved carbonyl absorptions at 2075 and 1887 cm^{-1} . The violet colour is probably due to the Tyndall effect. Their ESI-MS patterns display bell-shaped distributions of $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$ ($n = 3-10$) oligomers differing from that of Fig. 1 only in the relative abundance of the peaks. The most abundant peak is often that corresponding to a $[\text{Pt}_{21}(\text{CO})_{42}]^{2-}$ oligomer rather than $[\text{Pt}_{18}(\text{CO})_{36}]^{2-}$ as in Fig. 1. These violet suspensions turn into green-brown solutions on addition of water owing to re-hydration of alkali cations and reduction to species with $n \sim 6$ (ν_{CO} at *ca.* 2060 and 1870 cm^{-1}). It is, therefore, only possible to conclude that oligomerization of $\text{Pt}_3(\text{CO})_6$ units, generated by carbonylation in water, proceeds to give $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$ mixtures centred at $6 < n < 10$.

Reduction of the water-insoluble $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$ ($n > 6$) precipitates with alkali metals or hydroxides in solutions of organic solvents and under a carbon monoxide atmosphere, according to previously described procedures,^{7,10,11} quantitatively affords the known $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$ ($n = 1-5$) clusters. This prompted new attempts to obtain the structure of $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$ and, as a fallout, we have isolated and structurally characterised $[\text{Nn-Bu}_4]_2[\text{Pt}_{12}(\text{CO})_{24}]$.[†] The $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$ dianion was not previously⁶ characterised owing to poor diffraction patterns and disorder problems of all its crystals with a variety of tetrasubstituted ammonium and phosphonium cations leading to unreliable unit cells with an axis of *ca.* 3.2 Å. In contrast, the unit cell of the always disregarded $[\text{Nn-Bu}_4]_2[\text{Pt}_{12}(\text{CO})_{24}]$ salt contains four discrete $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$ dianions and eight $[\text{Nn-Bu}_4]^+$ cations. Dianions and cations respectively give rise to interpenetrating approximate body-centred-cubic and cubic lattices. As a result, the cations are lodged in tetrahedral cavities individuated by the dianions with an n-butyl arm lying along the crystallographic C_3 axis. Heavy disorder is still present. Indeed, the two inner $\text{Pt}_3(\text{CO})_6$ units give rise to a “Star of David” image with all atoms featuring occupancy fractions of *ca.* 0.5. The outer $\text{Pt}_3(\text{CO})_6$ units are likewise split into two though almost coincident images. The carbon atoms of the n-butyl arm lying along the crystallographic C_3 axis are disordered in two positions and split in six by symmetry. The remaining independent arm of $[\text{NBu}_4]^+$ is ordered. All arms display rather short $\text{C} \cdots \text{O}$ separations (2.71–2.97 Å) with the carbonyl groups of three out of four dianions. Most of the above heavy disorder likely originates from random occupation of the unit cell sites with clockwise and anti-clockwise helicoidally-twisted orientations of the $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$ dianion such as those depicted in Fig. 2. Such a random occupation would give rise to almost ordered superimposition of the outer and twisted images of the inner $\text{Pt}_3(\text{CO})_6$ units, which show the shortest $\text{O} \cdots \text{C}$ contacts with the disordered arm of the cation.

Interestingly, reduction with sodium hydroxide in water suspension of the $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$ ($n > 6$) precipitates, rather than in organic solvents, follows a different course. It leads to mixtures of water-soluble brown Pt carbonyl anions at present under characterisation. Acidification of the above aqueous solutions separates a brown precipitate of the $[\text{Pt}_{38}(\text{CO})_{44}]^{2-}$ dianion in high

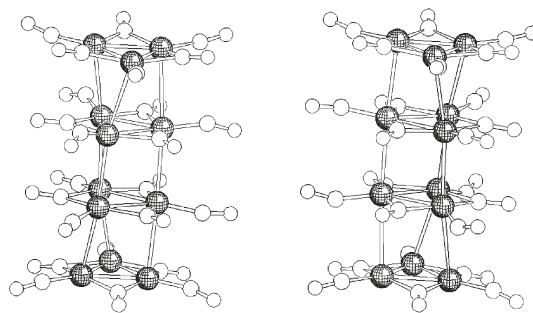


Fig. 2 The clockwise and anti-clockwise helicoidally-twisted $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$ dianions, which give rise to almost perfect superimposition of the outer and a “Star of David” image of the inner $\text{Pt}_3(\text{CO})_6$ units (average intra-plane Pt–Pt bonds 2.69 Å, average inter-plane Pt–Pt bonds 3.05 Å).

yields. Its nature has been unambiguously confirmed by complete X-ray analysis of its $[\text{PPh}_4]^+$ salt.[‡] The cubic close packed $[\text{Pt}_{38}(\text{CO})_{44}]^{2-}$ dianion was synthesized a long time ago,¹² by thermal decomposition of $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$ ($n = 3$) to $[\text{Pt}_{19}(\text{CO})_{22}]^{4-}$ ¹³ followed by reaction with H^+ or NO^+ .⁸ The full elucidation of the structure of its $[\text{N}(\text{PPh}_3)_2]^+$ salt has only recently been achieved.⁸

As shown in Scheme 1, a yet more simple synthesis of this nanosized cluster consists of the direct carbonylation of $\text{Na}_2\text{PtCl}_6 \cdot 6\text{H}_2\text{O}$ in aqueous solution under reduced CO pressures (800–760 mm Hg). At the highest pressure limit, the resulting brown carbonylation product is made by $[\text{Pt}_{38}(\text{CO})_{44}]^{2-}$ and some $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$ ($n > 6$) side-products. At the lowest pressure limit, the resulting $[\text{Pt}_{38}(\text{CO})_{44}]^{2-}$ brown precipitate is contaminated by small amounts of THF-insoluble, as yet unknown clusters and Pt metal. The most convenient synthesis of $[\text{Pt}_{38}(\text{CO})_{44}]^{2-}$ salts, however, starts from K_2PtCl_6 . Its carbonylation at 800 mm Hg affords a mixture of THF-soluble $[\text{Pt}_{38}(\text{CO})_{44}]^{2-}$ and THF-insoluble $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$ ($n > 6$) salts. As a result, $[\text{Pt}_{38}(\text{CO})_{44}]^{2-}$ can be quantitatively separated in up to *ca.* 70% yields (based on K_2PtCl_6) by extraction in THF.

All the above described procedures represent significant improvements in terms of simplicity and yields over the original syntheses.⁷⁻¹¹ The water-insoluble $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$ ($n > 6$) mixture of oligomers and the $[\text{Pt}_{38}(\text{CO})_{44}]^{2-}$ cluster are available through simple one-step syntheses from commercial reagents. That could hopefully prompt the isolation and characterisation of other discrete $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$ ($n > 6$) oligomers or new Pt clusters deriving from $[\text{Pt}_{38}(\text{CO})_{44}]^{2-}$, as well as the major consideration in nanoscience of these structurally and compositionally well-defined nanosized molecules.⁵

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Notes and references

[†] *Crystal data* for $[\text{Nn-Bu}_4]_2[\text{Pt}_{12}(\text{CO})_{24}]$. $M = 3498.24$, cubic, $a = 19.844(16)$ Å, $U = 7815(11)$ Å³, $T = 100(2)$ K, space group $Pa-3$ (no. 205), $Z = 4$, $\mu = 21.452$ mm⁻¹, graphite-monochromatized Mo-K α radiation ($\lambda = 0.71073$). Final R indices were $R = 0.0503$ and $wR = 0.1308$ for 2298 independent reflections having $I > 2\sigma(I)$. ($R_{\text{int}} = 0.2863$).

[‡] *Crystal data* for $[\text{PPh}_4]_2[\text{Pt}_{38}(\text{CO})_{44}] \cdot 4\text{THF}$. $M = 9613.02$, tetragonal, $a = 15.6156(5)$, $c = 14.0477(9)$ Å, $U = 3425.5(3)$ Å³, $T = 100(2)$ K, space group $P-4$ (no. 81), $Z = 1$, $\mu = 38.712$ mm⁻¹, graphite-monochromatized Mo-K α

radiation ($\lambda = 0.71073$). Final R indices were $R = 0.0489$ and $wR = 0.1164$ for 7694 independent reflections having $I > 2\sigma(I)$. ($R_{\text{int}} = 0.0350$). Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC 284955 for $[\text{Nn-Bu}_4]_2[\text{Pt}_{12}(\text{CO})_{24}]$ and no. CCDC 284956 for $[\text{PPh}_4]_2[\text{Pt}_{38}(\text{CO})_{44}]\cdot 4\text{THF}$. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b513507a

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