

# Copolymerisation of Pt–carbonyl clusters with Lewis acids: synthesis and crystal structure of the molecular $\{\text{Cd}_2\text{Cl}_4[\text{Pt}_9(\text{CO})_{18}]^{2-}\}_\infty$ 1-D polymer

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Reaction of  $[\text{NBu}_4]_2[\text{Pt}_9(\text{CO})_{18}]$  with the soft Lewis acid  $\text{CdCl}_2$  gives the  $[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]^{2-}$  adduct, which self-assembles upon crystallization into a 1-D  $\{[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]^{2-}\}_\infty$  polymer via the formation of chloride bridges.

The propensity of certain molecules to self-assemble into 1-, 2- and 3-D ordered structures is the basis of the bottom-up approach towards nanotechnologies.<sup>1–3</sup> Applications of metal carbonyl clusters in nanoelectronics<sup>4,5</sup> could be of interest because of their size entering from the bottom end of the nano regime, and their electronic and magnetic properties.<sup>6</sup> So far, only a few examples of self-assembled nanomaterials obtained from metal carbonyl clusters have been reported.<sup>6</sup> Probably the first example was the  $\{\text{Ag}^+[\text{Rh}_6\text{C}(\text{CO})_{15}]^{2-}\}_n$  oligomer, characterised in solution by multi-nuclear NMR.<sup>7</sup> More recently, an infinite  $\{[\text{AgRu}_6\text{C}(\text{CO})_{16}]^-\}_\infty$  superwire has been quantitatively assembled via related heterometallic Ag–Ru bonds upon reacting  $[\text{Ru}_6\text{C}(\text{CO})_{16}]^{2-}$  with  $\text{Ag}^+$ .<sup>8</sup> Miscellaneous 1- and 2-D arrays assembled via  $\eta^2$ -carbonyl groups of the previously unknown  $[\text{Co}_4(\text{CO})_{11}]^{2-}$  dianion and Yb(II) or Eu(II) cations have been obtained by the reaction of  $\text{Hg}[\text{Co}(\text{CO})_4]_2$  with Yb or Eu metals.<sup>9</sup> Finally, the  $[\text{Pt}_{24}(\text{CO})_{48}]^{2-}$  dianion, as its  $[\text{NBu}_4]^+$  salt, self-assembles by the formation of homometallic Pt–Pt bonds into a 1-D  $\{[\text{Pt}_{24}(\text{CO})_{48}]^{2-}\}_\infty$  infinite wire upon crystallisation.<sup>10</sup>

Another possibility to self-assemble 1-D chains stems from the formation of intermolecular chloride bridges. We report here the first example of this possibility, consisting of the synthesis of the 1-D  $\{[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]^{2-}\}_\infty$  polymer by the self-assembly of the bicapped  $[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]^{2-}$  adduct upon crystallisation. The dark-violet  $[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]^{2-}$  adduct has been obtained nearly quantitatively by the reaction of  $[\text{NBu}_4]_2[\text{Pt}_9(\text{CO})_{18}]$  with two equivalents of  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$  in THF. Only very minor amount of an as yet uncharacterised carbonyl by-product precipitates out from the reaction solution. The  $[\text{NBu}_4]^+$  salt of the  $[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]^{2-}$  adduct has been isolated in a crystalline state with yields of up to 80% by layering *n*-hexane onto its filtered THF solution. The resulting  $[\text{NBu}_4]_2[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]$  black crystals are very soluble in polar organic solvents such as THF, acetone and acetonitrile. These solutions show invariant infrared carbonyl absorptions ( $\nu_{\text{CO}}$  at 2047(s) and 1870(ms)  $\text{cm}^{-1}$ ). The great solubility in organic solvents of  $[\text{NBu}_4]_2[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]$  argues against the

maintenance of the polymeric structure in solution that is found in the solid state (see later). To gain a better insight of the nature of the species present in solution, ESI-MS and variable temperature <sup>195</sup>Pt NMR studies were performed. ESI-MS of  $[\text{NBu}_4]_2[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]$  in an acetonitrile solution displays peaks corresponding to  $\{[\text{Pt}_9(\text{CO})_{18}(\text{CdCl}_2)[\text{NBu}_4]\}^-$  (2686),  $[\text{Pt}_9(\text{CO})_{18}(\text{CdCl}_2)_2]^{2-}$  (1313),  $[\text{Pt}_9(\text{CO})_{18}(\text{CdCl}_2)]^{2-}$  (1222) and  $[\text{CdCl}_3]^-$  (219). Even though peaks due to  $[\text{Pt}_{15}(\text{CO})_{30}]^{2-}$  (1883) and  $[\text{Pt}_{12}(\text{CO})_{24}]^{2-}$  (1507) were noticeable, no signals for higher Pt–Cd aggregations were present.

The <sup>195</sup>Pt NMR spectrum of the  $[\text{NBu}_4]_2[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]$  salt in *d*<sub>6</sub>-acetone solution at room temperature only shows the presence of two broad resonances at –4740 and –5069 ppm in the relative ratio 2 : 1. Progressive lowering of the temperature down to 203 K, rather than increasing the peak resolution, causes the appearance of up to seven broad resonances between –4344 and –5205 ppm. Further lowering of the temperature was hampered by the falling solubility of the  $[\text{NBu}_4]_2[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]$  salt. It appears safe to conclude that symmetric  $[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]^{2-}$  (see Fig. 1) building units, rather than unsymmetrical  $[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-Cd}_2\text{Cl}_4)]^{2-}$  fragments (as a result of breaking the chains depicted in Fig. 2a) are present in solution at room temperature. Attributing the resonances at –4740 and –5069 ppm to Pt atoms belonging to the outer and inner triangles of the

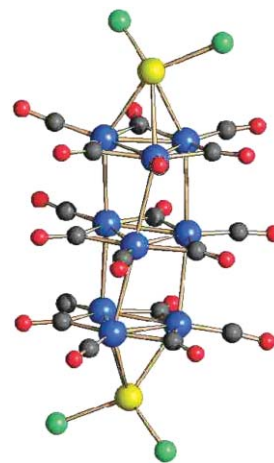
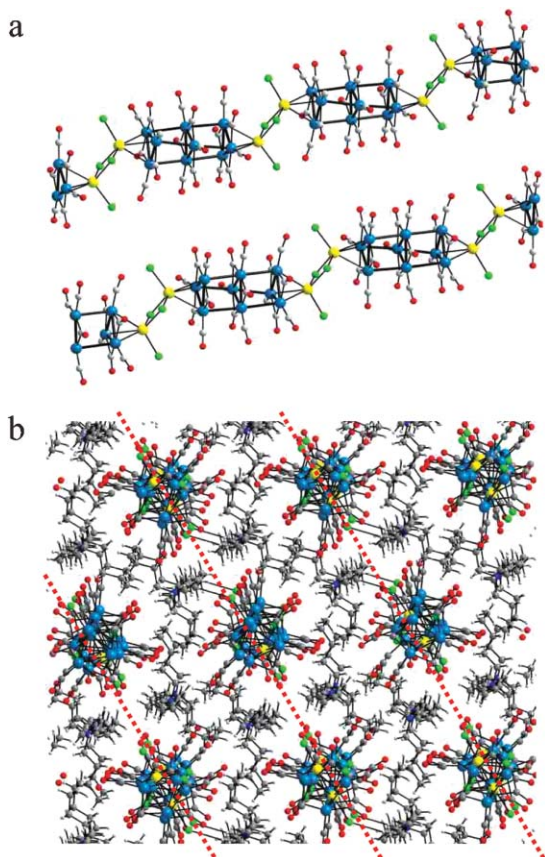


Fig. 1 View of the  $[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]^{2-}$  building unit of the 1-D  $\{[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]^{2-}\}_\infty$  chain (one of the two bridging Cl atoms is omitted), pointing out the structure of the  $[\text{Pt}_9(\text{CO})_{18}]^{2-}$  and the incomplete distorted octahedral geometry of Cd (colour legend: Pt blue, Cd yellow, Cl green, C grey, O red).

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**Fig. 2** (a) Portions of two parallel  $\{[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]^{2-}\}_\infty$  chains (colour legend as in Fig. 1), and (b) view of the crystal packing along the b-axis showing the 2-D hexagonal packing of the  $\{[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]^{2-}\}_\infty$  chains (red dotted lines indicate the 101 planes).

trigonal prismatic  $\text{Pt}_9$  metal core, respectively, seems straightforward in view of their relative intensities and the fact that  $[\text{Pt}_9(\text{CO})_{18}]^{2-}$  shows two well-resolved multiplets with comparable chemical shifts ( $-4440$  and  $-5020$  ppm) under corresponding experimental conditions.<sup>12,13</sup> The broadness of the signals might be indicative of a slowed-down rotation of the  $\text{Pt}_3$  triangles with respect to the parent  $[\text{Pt}_9(\text{CO})_{18}]^{2-}$  dianion.<sup>11,12</sup> The low temperature  $^{195}\text{Pt}$  NMR spectra point out a progressive loss of equivalence of the  $\text{Pt}_3$  triangles, which might be taken as indicative of the incipient self-assembly of  $\{[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]^{2-}\}_n$  ( $n = 2$  and  $3$ ) oligomers. An alternative, less-likely explanation might be the occurrence in solution of equilibria involving the progressive entering of solvent molecules into the coordination sphere of Cd upon decreasing the temperature.

The solid state nature of the  $[\text{NBu}_4]_2[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]$  salt has been elucidated by single crystal X-ray analysis.<sup>†</sup> The unit cell contains two  $[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]^{2-}$  dianions and four  $[\text{NBu}_4]^+$  cations. The molecular structure of the dianionic building unit (Fig. 1) consists of a distorted trigonal-prismatic  $[\text{Pt}_9(\text{CO})_{18}]^{2-}$  moiety, capped on both sides by  $\mu_3\text{-CdCl}_2$  groups. The  $[\text{Pt}_9(\text{CO})_{18}]^{2-}$  moiety retains the original structure of the  $[\text{Pt}_9(\text{CO})_{18}]^{2-}$  dianion,<sup>13</sup> consisting of three stacked  $\text{Pt}_3(\text{CO})_3(\mu\text{-CO})_3$  units similarly twisted away from an ideal trigonal prismatic geometry by  $13$  and  $18^\circ$ . The intra-layer Pt–Pt bonds [ $2.685(4)$ – $2.701(5)$  Å] are considerably shorter than the

inter-layer Pt–Pt contacts [ $3.046(5)$ – $3.080(5)$  Å], as found in the parent  $[\text{Pt}_9(\text{CO})_{18}]^{2-}$  cluster and in other oligomers of the  $[\text{Pt}_{3n}(\text{CO})_{6n}]^{2-}$  series.<sup>13</sup> The two external triangular faces of the distorted trigonal prismatic  $[\text{Pt}_9(\text{CO})_{18}]^{2-}$  moiety are capped by two cadmium atoms, with Pt–Cd distances ranging from  $2.931(4)$  to  $3.023(4)$  Å. We are not aware of a previously reported Pt(0)–Cd(II) bond. The observed bond lengths are comparable to the alkynyl-supported Pt(II)–Cd(II) interactions found, for instance, in the  $\{[\text{Pt}(\mu\text{-CCPh})_4]_2(\text{CdCl}_2)_2\}^{2-}$  dianion (av.  $2.96$  Å),<sup>14</sup> but significantly longer than other unsupported Pt(II)–Cd(II) bonds determined in cationic species such as  $[\{\text{Pt}(\text{NH}_3)_2(\mu\text{-NHCO}^t\text{Bu})_2\}_2\text{Cd}]^{2+}$  (av.  $2.67$  Å).<sup>15</sup> Each cadmium atom displays a distorted octahedral stereochemistry, also being bonded to one terminal ( $2.503(9)$ – $2.504(9)$  Å) and two unsymmetrical bridging Cl ligands ( $2.577(8)$ – $2.629(8)$  Å). These bridges join the  $\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2$  moieties of adjacent unit cells and give rise to  $\{[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]^{2-}\}_\infty$  chains extending throughout the crystal. In each  $\text{Cd}_2\text{Cl}_2(\mu\text{-Cl})_2$  moiety, the terminal chloride ligands adopt a *trans* geometry with respect to the  $\text{Cd}_2(\mu\text{-Cl})_2$  plane, in order to minimise steric repulsions.

Several short contacts exist between the  $\text{CH}_3$  groups of the cations and the Cl and CO ligands of  $\{[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]^{2-}\}_\infty$ . As a result, the 1-D  $\{[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]^{2-}\}_\infty$  chains are arranged into 2-D ordered suprastructures. As shown in Fig. 2b, viewing the crystal along the b-axis, reveals a 2-D hexagonal packing of the anion chains. The  $\{[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]^{2-}\}_\infty$  anions lie in parallel, alternately slightly above and below the 101 planes (Fig. 2b). The two independent  $[\text{NBu}_4]^+$  cations are arranged into planes parallel to the ones containing the anions, forming a double layer in between two adjacent sheets of cluster chains.

The Lewis base donor ability of the neutral  $\text{Pt}_3\text{L}_3(\mu\text{-CO})_3$  cluster ( $\text{L} =$  phosphine) has been discovered and exploited by Imhof and Venanzi.<sup>16</sup> Relevant to the present work is the  $\text{Pt}_3(\text{PPh}^i\text{Pr})_3(\mu\text{-CO})_3(\mu_3\text{-ZnI}_2)$  mono-adduct.<sup>17</sup> The increased donor ability of  $[\text{Pt}_9(\text{CO})_{18}]^{2-}$  towards a soft Lewis acid such as  $\text{CdCl}_2$  enables the formation of a bis-adduct, which self-assembles into a  $\{[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]^{2-}\}_\infty$  chain *via* the formation of Cl bridges. To our knowledge, the above feature of  $[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]^{2-}$  is unprecedented in metal carbonyl clusters and opens up perspectives of nanopatterning surfaces with 1-D arrays of molecular metal clusters.

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## Notes and references

<sup>†</sup> Crystal data for  $[\text{NBu}_4]_2[\text{Pt}_9(\text{CO})_{18}(\mu_3\text{-CdCl}_2)_2]$ :  $\text{C}_{50}\text{H}_{72}\text{Cd}_2\text{Cl}_{14}\text{N}_{20}\text{I}_{18}\text{Pt}_9$   $M = 3111.51$ , triclinic, space group  $P\bar{1}$  (no. 2),  $a = 13.49(2)$ ,  $b = 13.74(2)$ ,  $c = 23.62(4)$  Å,  $\alpha = 77.03(2)^\circ$ ,  $\beta = 84.52(3)^\circ$ ,  $\gamma = 70.26(2)^\circ$ ,  $U = 4013(11)$  Å<sup>3</sup>,  $T = 293(2)$  K,  $Z = 2$ ,  $\mu = 16.321$  mm<sup>-1</sup>, graphite-monochromatized Mo-K $\alpha$  radiation ( $\lambda = 0.71073$  Å). Final  $R$  indices were  $R_1 = 0.0668$  and  $wR_2 = 0.1476$  for 14106 independent reflections having  $I > 2\sigma(I)$ . ( $R_{\text{int}} = 0.1479$ ). Restraints were applied to bond distances and anisotropic displacement parameters of C, O and N atoms. CCDC 299651. For crystallographic data (excluding structure factors) in CIF or other electronic format see DOI: 10.1039/b602593e

- G. Schmid and U. Simon, *Chem. Commun.*, 2005, 697.
- R. L. Whetten, J. T. Khoury, M. M. Alvarez, S. Murthy, I. Vezmar, Z. L. Wang, P. W. Stephens, C. L. Cleveland, W. D. Luedtke and U. Landman, *Adv. Mater.*, 1996, **8**, 428.

- 3 A. Yu. Obydenov, S. P. Gubin, V. V. Khanin, S. N. Polyakov, A. N. Sergeev-Cherenkov, E. S. Soldatov, A. S. Trifonov and G. B. Khomutov, *Colloids Surf., A*, 2002, **198–200**, 389.
- 4 R. L. Carroll and C. B. Gorman, *Angew. Chem., Int. Ed.*, 2002, **41**, 4379.
- 5 D. Wouters and U. S. Schubert, *Angew. Chem., Int. Ed.*, 2004, **43**, 2480.
- 6 C. Femoni, M. C. Iapalucci, F. Kaswalder, G. Longoni and S. Zacchini, *Coord. Chem. Rev.*, 2006, DOI: 10.1016/j.ccr.2006.03.011.
- 7 B. T. Heaton, L. Strona, S. Martinengo, D. Strumolo, V. G. Albano and D. Braga, *J. Chem. Soc., Dalton Trans.*, 1983, 2175.
- 8 T. Nakajima, A. Ishiguro and Y. Wakatsuki, *Angew. Chem., Int. Ed.*, 2001, **40**, 1066.
- 9 C. E. Plechnik, S. Liu, X. Chen, E. A. Meyers and S. G. Shore, *J. Am. Chem. Soc.*, 2004, **126**, 204.
- 10 C. Femoni, F. Kaswalder, M. C. Iapalucci, G. Longoni, M. Mehlstäubl, S. Zacchini and A. Cerotti, *Angew. Chem., Int. Ed.*, 2006, **45**, 2060.
- 11 C. Brown, B. T. Heaton, P. Chini, A. Fumagalli and G. Longoni, *J. Chem. Soc., Chem. Commun.*, 1977, 309.
- 12 C. Brown, B. T. Heaton, A. D. C. Towl, P. Chini, A. Fumagalli and G. Longoni, *J. Organomet. Chem.*, 1979, **181**, 233.
- 13 J. C. Calabrese, L. F. Dahl, P. Chini, G. Longoni and S. Martinengo, *J. Am. Chem. Soc.*, 1974, **96**, 2614.
- 14 J. P. H. Charmant, L. R. Falvello, J. Forniés, J. Gómez, E. Lalinde, M. T. Moreno, A. G. Orpen and A. Rueda, *Chem. Commun.*, 1999, 2045.
- 15 W. Chen, F. Liu, T. Nishioka and K. Matsumoto, *Eur. J. Inorg. Chem.*, 2003, 4234 and references therein.
- 16 D. Imhof and L. M. Venanzi, *Chem. Soc. Rev.*, 1994, 185.
- 17 A. Stockhammer, K.-H. Dahmen, T. Gerfin, L. M. Venanzi, V. Gramlich and W. Petter, *Helv. Chim. Acta*, 1991, **74**, 989.



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