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A chiral tetranuclear platinum(II) cluster complex, $[Pt_4(O_2CMe)_4(pro)_4]$ (Hpro = L-proline)

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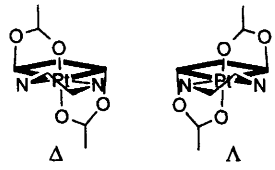
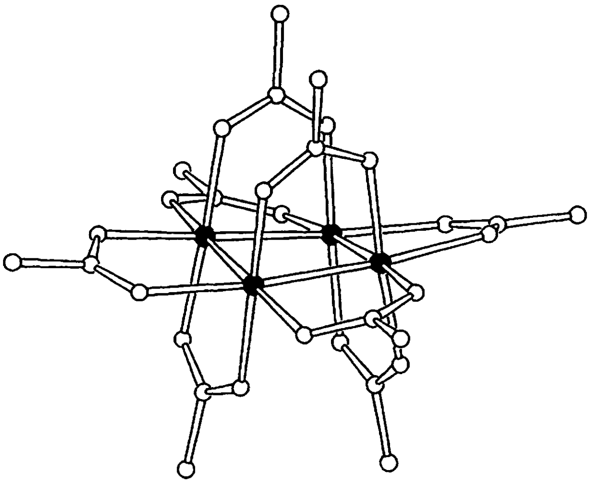
A new optically active tetranuclear platinum(II) cluster complex, which has two diastereotopic platinum centres, was prepared by L-proline substitution for the in-plane acetate ligands in octaacetatotetraplatinum(II).

Octaacetatotetraplatinum(II) $[Pt_4(O_2CMe)_8]$ **1** is a well known cluster complex of unique molecular[1] and electronic structure[2] and reactivity.[2,3] Previously, we reported that the acetate ligands in **1** which are in the plane of the square-planar cluster core are labile, whereas the out-of-plane ligands are inert to substitution.[2] Thus, we prepared derivatives of the type $[Pt^{II}_4(\mu\text{-}O_2CMe)_4L_4]^{n+}$, in which bidentate ligands (L) occupy the in-plane co-ordination sites in either chelating or bridging mode depending on the bite distance.[2,4,5] More interestingly, the in-plane positions can participate in catalytic hydrolysis of acetonitrile to give acetamide[5a] and also catalytic dimerization of acetone to yield 4-hydroxy-4-methylpentan-2-one.[5b] The catalytic activities arise from the high lability of the platinum site *trans* to the Pt–Pt bond.[2,5a] It is of interest to construct a chiral environment around Pt in this type of compound. In $[Pt_4(\mu\text{-}O_2CMe)_4(en)_4]^{4+}$, which has achiral chelating ethane-1,2-diamine (en),[4a] each Pt is in a chiral environment, although the compound is optically inactive as a whole [*meso*(ΔΛΔΛ) form]. The compound has S_4 symmetry and thereby adjacent platinums have opposite chiralities. When four optically active chelate ligands are introduced at the in-plane sites the resulting chiral Pt_4 complex should have two diastereotopic centres.



Complex **1** was allowed to react with an excess of L-proline (Hpro) to yield the tetrasubstituted orange-red complex $[Pt^{II}_4(\mu\text{-}O_2CMe)_4(pro)_4]\cdot 5H_2O$ (**2**·5H$_2$O).† Fig. 1 shows the crystal structure of **2**.‡ Upon substitution, the four in-plane bridging acetates in **1** are replaced by L-prolinates which adopt the *N,O* chelating mode.§ Donor N and O atoms are arranged alternately around the square-planar cluster core. The square-planar cluster core and the out-of-plane acetate bridges of the parent are essentially unchanged. All the pyrrolidine rings are on the same side of the Pt_4 plane and almost vertical to it. Two of the four out-of-plane acetate ligands are on the same side as the pyrrolidine rings and the other two are on the opposite side.



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† A methanolic solution (10 cm^3) of L-proline (100 mg) was added to an acetonitrile solution (10 cm^3) of complex **1** (50 mg). The solution was allowed to stand for 30 min at room temperature and then evaporated to dryness. The residue was dissolved in dichloromethane (*ca.* 20 cm^3), filtered and evaporated again to dryness. A methanolic solution of the residual solid was passed through a gel-filtration column (Sephadex LH-20, methanol eluent) to remove the excess of L-proline. An orange eluate was collected and evaporated to dryness. The residue was recrystallized from acetonitrile to give **2**·5H$_2$O (Found: C, 21.6; H, 3.45; N, 3.5. $C_{28}H_{54}N_4O_{21}Pt_4$ requires C, 21.5; H, 3.5; N, 3.6%). δ_H(270 MHz, CDCl$_3$) 1.90, 1.98 (s, CH$_3$), 2.10–2.80, 3.35, 3.80–4.20, 5.72, 6.87 (m, ring H). δ_C(67.9 MHz, CDCl$_3$) 21.5, 21.6 (CH$_3$), 24.1, 25.0, 30.0, 31.5, 49.2, 49.4, 64.2 (ring C), 182.1, 184.0 (CO$_2$ of pro), 192.6, 194.1 (CO$_2$ of acetate). λ_{max}/nm (ε/dm^3 mol^{-1} cm^{-1}) (water) 388 (10 300) and 263 (62 400). CD spectrum: λ_{max}/nm ($\Delta\varepsilon$/dm^3 mol^{-1} cm^{-1}) (water) 341 (+0.055), 280 (+0.17), 253 (−0.24) and 215 (+0.41).

‡ A specimen recrystallized from acetonitrile was used. Crystal data: **2**·5H$_2$O, $C_{28}H_{54}N_4O_{21}Pt_4$, $M = 1563.12$, prismatic orange-red crystal, size 0.35 × 0.20 × 0.15 mm, orthorhombic, space group $P2_12_12_1$ (no. 19), $a = 20.775(3)$, $b = 21.353(2)$, $c = 9.897(3)$ Å, $U = 4390(1)$ Å^3, $Z = 4$, $F(000) = 2920$. The intensity data were collected at room temperature with Mo-Kα ($\lambda = 0.710\,69$ Å) radiation up to $2\theta = 55.0°$ on a Rigaku AFC-7S diffractometer and were corrected for absorption by the analytical method.[7] With the use of 4593 unique reflections [$I > 3\sigma(I)$], the structure was refined on F by full-matrix least squares with anisotropic thermal parameters for non-hydrogen atoms to final R and R' values of 0.044 and 0.049. The weighting scheme used was $w = 1/[\sigma^2(F_o) + 0.0001|F_o|^2]$. Hydrogen atoms were not found in the Fourier-difference map, and therefore not included in the calculation, although R was very slightly improved to 0.043 by including them at calculated positions. The absolute configuration was assigned to agree with the known chirality of L-proline; R and R' values for the inverted structure were 0.049 and 0.055. All the calculations were performed by the TEXSAN crystallographic program package.[7] Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/267.

§ Prolinate ion has potentially two bidentate sites, two carboxylate oxygens or the pyrrolidine nitrogen and carboxylate oxygen which form a five-membered chelate ring. The former would give rise to the bridging co-ordination which other carboxylates usually adopt. We have no experimental evidence for a carboxylate-bridged isomer. The same behaviour has been observed for the pyridine-2-carboxylate derivative.[4a]

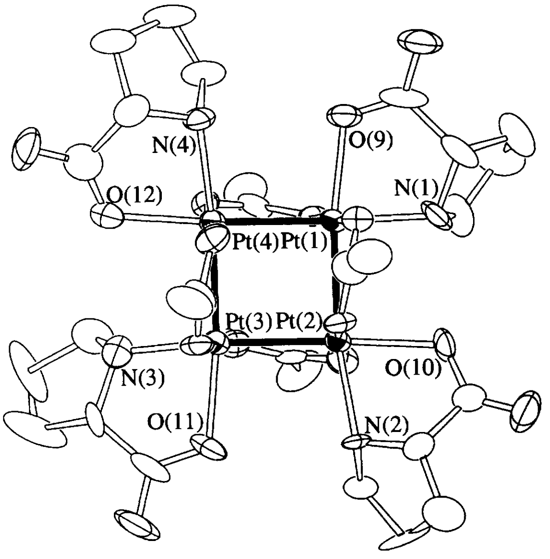

Fig. 1 An ORTEP[6] drawing of complex **2**. Selected bond lengths (Å) and angles (°): Pt(1)–Pt(2) 2.532(1), Pt(2)–Pt(3) 2.531(1), Pt(3)–Pt(4) 2.536(1), Pt(4)–Pt(1) 2.537(1), Pt(1)–O(9) 2.19(1), Pt(1)–N(1) 2.17(2), Pt(2)–O(10) 2.21(1), Pt(2)–N(2) 2.17(1), Pt(3)–O(11) 2.18(1), Pt(3)–N(3) 2.09(2), Pt(4)–O(12) 2.18(2), Pt(4)–N(4) 2.20(1), out-of-plane Pt–O 1.96–2.04; Pt(2)–Pt(1)–Pt(4) 90.41(3), Pt(1)–Pt(2)–Pt(3) 88.10(3), Pt(2)–Pt(3)–Pt(4) 90.46(3), Pt(1)–Pt(4)–Pt(3) 87.88(3), O(9)–Pt(1)–N(1) 81.1(6), O(10)–Pt(2)–N(2) 77.3(6), O(11)–Pt(3)–N(3) 80.0(6), O(12)–Pt(4)–N(4) 78.8(6)

Thus the compound has approximate C_2 symmetry, though the four Pt atoms are crystallographically independent. The platinums occupy two diastereotopic sites: Pt(1) and Pt(3) are in one site, Pt(2) and Pt(4) in the other. The two sites differ in the Pt–Pt–Pt angles: 90.41(3) and 90.46(3)° for the former and 88.10(3) and 87.88(3)° for the latter. There was little difference in bond distances around the two types of Pt probably due to intra- and inter-molecular hydrogen bonding. The Pt–Pt distances of 2.531(1)–2.537(1) Å are longer than those of **1** [2.492(1)–2.501(1) Å],[1] which reflects the effect of the chelate and bridge co-ordination mode on the cluster core structure.

The ^1H and ^{13}C NMR spectra of complex **2**·5H$_2$O show that the prolinate and out-of-plane acetate ligands are pairwise equivalent consistent with the C_2 symmetry. Fig. 2(*a*) shows the ^{195}Pt NMR spectrum which consists of two intense peaks (at δ 922.8 and 789.3 *vs.* K_2PtCl_4–D_2O) and many other satellites. Although the spectral pattern is rather complicated because of large Pt–Pt couplings compared with the chemical shift difference and the existence of nine isotopomers,¶ it has been completely analysed as is seen in the good agreement between the observed and calculated[8] spectra. The above chemical shifts correspond to the two diastereotopic platinum sites. The difference of 133.5 ppm is fairly large although both types of Pt have the same donor atom set. Two kinds of Pt–Pt couplings have been observed, in reflecting the C_2 symmetry of **2**. Their values, 6096 and 5916 Hz, are within the normal range for similar tetraplatinum cluster complexes.[4b]

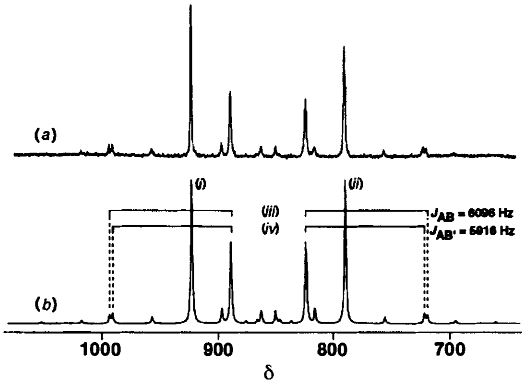

Fig. 2 The ^{195}Pt NMR spectrum of complex **2** in $CDCl_3$: (*a*) observed, (*b*) simulated. Roman numerals denote assignments to isotopomers:¶ (*i*) A and A_2, (*ii*) B and B_2, (*iii*) AB, (*iv*) AB′. Other weak peaks are due to remaining isotopomers having more than two ^{195}Pt nuclei

We have successfully created chiral environment around Pt in this tetranuclear cluster. Other amino acids such as L-alanine, L-hydroxyproline, L-phenylalanine and L-valine form similar compounds. Application of the chiral, labile and multimetal site(s) in these clusters to asymmetric reactions is now being studied in this laboratory.

Acknowledgements

This work was supported by Grants-in-Aid for Scientific Research (Nos. 06740503, 07740517 and 04241102) from the Ministry of Education, Science and Culture, Japan.

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Received 1*st July* 1996; *Communication* 6/04528F

¶ Since the four platinums are in an AA′BB′ type arrangement and the natural abundance of ^{195}Pt is 33.8%, the experimentally observed spectrum consists of the summation of spectra due to nine isotopomers (A, A_2, B, B_2, AB, AB′, AA′B, ABB′ and AA′BB′) with relative intensity ratio corresponding to their natural abundances.