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Bis{di-μ-isobutyrato-bis[*cis*-diammine-platinum(II)]} tetraperchlorate

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The title compound, $[Pt_2(\mu\text{-}C_4H_7O_2)_2(NH_3)_4]_2(ClO_4)_4$, involves two independent diplatinum(II) units. For each unit, a pair of dimeric units located around an inversion center are associated with one another to give a tetranuclear Pt^{II}_4 cation, in which the interdimer association is stabilized by four hydrogen bonds formed between the ammines and the butyrate O atoms. The intradimer and interdimer Pt—Pt distances within these tetraplatinum(II) chain cations are, respectively, 2.9881 (4) and 3.2619 (6) Å for one set of dimers, and 3.0246 (4) and 3.3049 (6) Å for the other set of dimers.

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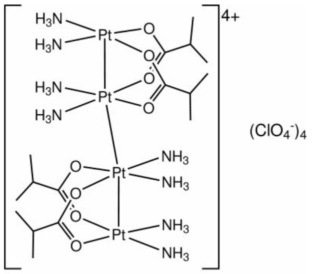
Key indicators

Single-crystal X-ray study
T = 296 K
Mean σ(C–C) = 0.015 Å
H-atom completeness 97%
Disorder in solvent or counterion
R factor = 0.043
wR factor = 0.102
Data-to-parameter ratio = 20.2

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

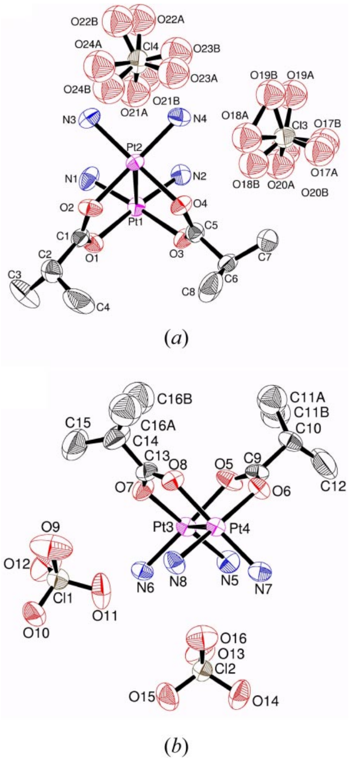
Comment

We recently reported that *cis*-diammineplatinum dimers doubly bridged with carboxylate ligands, $[Pt_2(NH_3)_4(\mu\text{-carboxylato})_2]^{2+}$ (carboxylate = acetate, glycolate, propionate *etc*), afford one-dimensional platinum chain systems based on linear stacks of diplatinum entities. The attractive feature lies in their ability to form quadruple hydrogen bonds at both sides of the dimer unit, leading to the achievement of an infinite Pt chain in the crystal structure (Sakai, Takeshita *et al.*, 1998). In addition, we also found that electrochemical oxidation of the compounds results in the formation of black mixed-valence compounds which show relatively high electrical conduction properties (Sakai *et al.*, 2002). On the other hand, we also reported that extended linear platinum chains are not formed when hydrophobic interactions between the bridging ligands play a major role in the stabilization of the crystal packing; benzoate (Sakai, Takeshita *et al.*, 1998) and pivalate (Sakai *et al.*, 2003*a*,*b*) are known to give discrete dimers in the crystal structure. We report here the crystal structure of a butyrate-bridged *cis*-diammineplatinum(II) complex, $[Pt^{II}_2(NH_3)_4(\mu\text{-butyrato})_2]_2(ClO_4)_4$, (I). This is the first example of a tetranuclear platinum chain complex obtained for the compounds derived from carboxylate-bridged *cis*-diammineplatinum dimers.



(I)

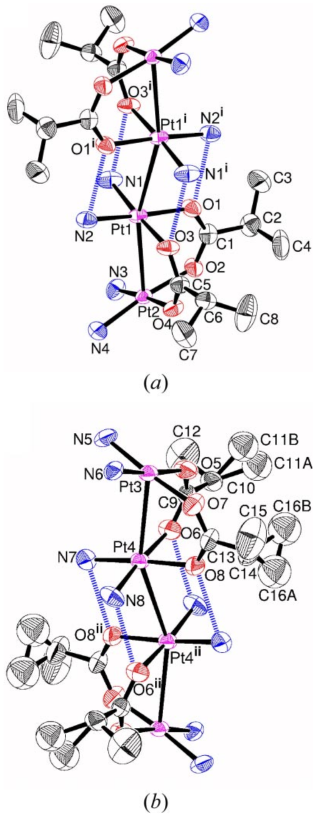
The asymmetric unit of (I) consists of two diplatinum(II) cations and four perchlorate anions (Fig. 1). Two of the four



(*a*)

(*b*)

Figure 1
The cations and anions (*a* and *b*) involved in the asymmetric unit of (I), together with the atom-labeling scheme. Displacement ellipsoids are shown at the 50% probability level. H atoms are omitted for clarity.



(*a*)

(*b*)

Figure 2
Views showing the structures of two independent tetranuclear platinum(II) complex cations (*a* and *b*) in (I), where dashed lines denote hydrogen bonds. Counter-ions and H atoms are omitted for clarity. [Symmetry codes: (i) $-x$, 1-y, 1-z; (ii) 1 $-x$, -y, -z.]

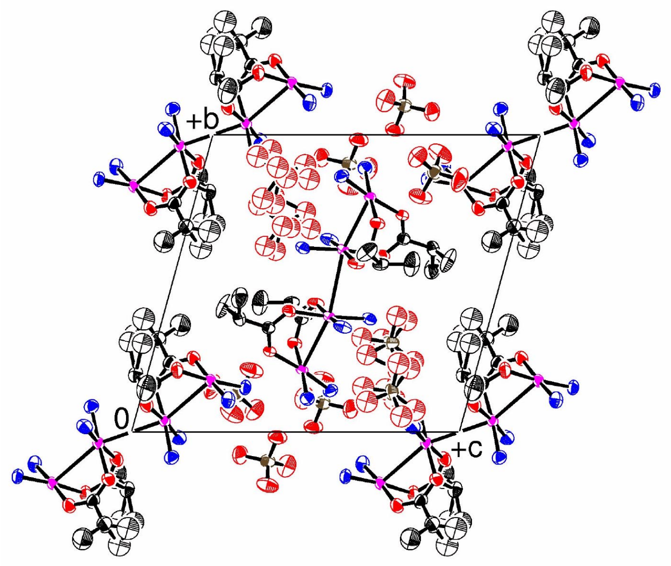


Figure 3
Crystal packing of (I), viewed along the *a* axis, where H atoms have been omitted for clarity. Hydrogen bonds are not drawn.

isopropyl units and two of the four perchlorate anions are disordered over two sites (see *Experimental*). As shown in Fig. 2, each dimer unit is associated with the crystallographically identical dimer unit through an inversion center to give a tetranuclear platinum(II) chain structure. Therefore, it is considered that two crystallographically different tetranuclear platinum chain cations are involved in the unit cell of (I) (see Fig. 3). The dimer–dimer interactions are stabilized by a weak metal–metal association between the dimers, as well as four hydrogen bonds formed between the ammines and the O atoms of butyrates [$Pt1—Pt1^i$ = 3.2619 (6), $N1\cdots O3^i$ = 3.105 (8), $N2\cdots O1^i$ = 3.093 (8), $Pt4—Pt4^{ii}$ = 3.3049 (6), $N7\cdots O8^{ii}$ = 3.167(9), $N8\cdots O6^{ii}$ = 3.109(9) Å; symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1-x, -y, -z$; see also Table 2]. The intradimer Pt—Pt distances are Pt1—Pt2 = 2.9881 (4) and Pt3—Pt4 = 3.0246 (4) Å in (I). The intra- and interdimer Pt—Pt distances [respectively abbreviated as Pt—Pt(intra) and Pt—Pt(inter)] are comparable to those reported for $[Pt^{II}_2(NH_3)_4(\mu\text{-acetato})_2](SiF_6)\cdot 4H_2O$ [Pt—Pt(intra) = 2.9713 (8) Å and Pt—Pt(inter) = 3.176 (1) and 3.2265 (9) Å], $[Pt^{II}_2(NH_3)_4(\mu\text{-glycolato})_2](SiF_6)\cdot 4H_2O$ [Pt—Pt(intra) = 2.9892 (9) Å and Pt—Pt(inter) = 3.2735 (9) Å], and $[Pt^{II}_2(NH_3)_4(\mu\text{-benzoato})_2]_2[\textit{cis}\text{-}Pt^{II}(NH_3)_2(\text{benzoato})_2](SiF_6)(BF_4)_2\cdot 3H_2O$ [Pt—Pt(intra) = 2.952 (1) and 2.990 (1) Å; Sakai, Takeshita *et al.*, 1998]. However, two pivalate-bridged compounds which give discrete dimers in the crystal structure show somewhat exceptional Pt—Pt distances; Pt—Pt(intra) = 2.9011 (9) Å for $[Pt^{II}_2(NH_3)_4(\mu\text{-pivalato})_2](SO_4)\cdot H_2O$ (Sakai *et al.*, 2003*a*) and Pt—Pt(intra) = 3.0928 (9) Å for $[Pt^{II}_2(NH_3)_4(\mu\text{-pivalato})_2](ClO_4)_2\cdot C_5H_{10}O_2$ ($C_5H_{10}O_2$ = pivalic acid; Sakai *et al.*, 2003*b*).

The two tetranuclear Pt^{II}_4 cations in (I) are hydrogen bonded with one another [$N5\cdots O2$ = 3.110 (8) Å and $N6\cdots O4$ = 3.248 (8) Å; see also Table 2] to give a one-

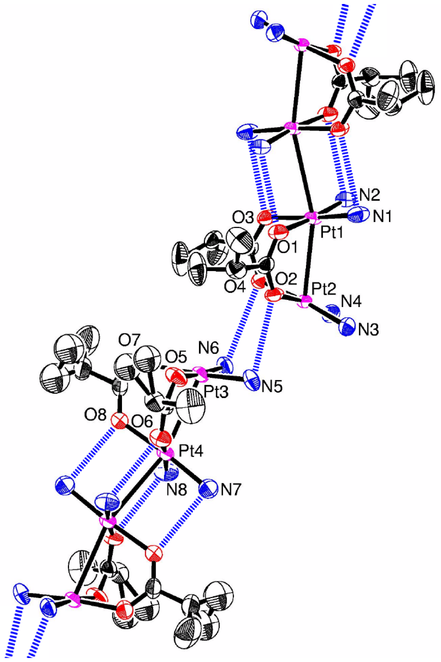


Figure 4

A view showing the inter-dimer interactions leading to a one-dimensional hydrogen-bonding network; dashed lines denote hydrogen bonds. Counter-ions and H atoms have been omitted for clarity.

dimensional network (Fig. 4), even though there is no Pt—Pt interaction between the tetramers [Pt2···Pt3 = 4.5478 (5) Å]. The crystal packing is stabilized by extensive hydrogen bonds formed between the ammines and the O atoms of butyrates and perchlorates (Table 2).

The two Pt atoms within each dimeric unit are displaced from their individual Pt coordination planes in such a manner that they have an attractive interaction with one another. Atoms Pt1 and Pt2 are displaced by 0.081 (3) and 0.102 (3) Å, respectively, where the four-atom r.m.s. deviations estimated in the mean-plane calculations are 0.003 and 0.013 Å, respectively. Similarly, atoms Pt3 and Pt4 are displaced by 0.088 (3) and 0.084 (3) Å, respectively, where the four-atom r.m.s. deviations estimated in the mean-plane calculations are 0.012 and 0.014 Å, respectively. Structural features of this type of dimers have also been evaluated by use of two structural parameters as follows. One is a dihedral angle between the two Pt coordination planes within the dimeric unit (τ), and the other is an average torsional twist of these planes about the Pt—Pt axis (ω). The dimer unit involving Pt1 and Pt2 has τ = 37.2 (2)° and ω = 2.0°, while that involving Pt3 and Pt4 has τ = 40.4 (2)° and ω = 11.7°.

It must be finally noted that the fundamental structural features of the present tetranuclear $\mathrm{Pt^{II}}_4$ compound agree well with those previously reported for the amidate-bridged tetranuclear $\mathrm{Pt^{II}}_4$ analogs (Sakai & Takahashi, 2003; Sakai, Tanaka *et al.*, 1998).

Experimental

To an aqueous solution of *cis*-$[\mathrm{Pt(NH_3)_2(OH_2)_2}](\mathrm{ClO_4})_2$ (0.2 mmol/1.4 ml H_2O), prepared as previously described (Sakai, Takeshita *et al.*, 1998; Sakai *et al.*, 2002), was added $(\mathrm{CH_3})_2\mathrm{CHCO_2Na}$ (0.2 mmol). The solution was left in a refrigerator (*ca* 278 K) for a week to give the product as pale yellow prisms, which were collected by filtration and air-dried (yield: 30%). Analysis calculated for $\mathrm{C_{16}H_{52}Cl_4N_8O_{24}Pt_4}$: C 11.56, H 3.15, N 6.74%; found: C 11.72, H 3.22, N, 6.72%.

Crystal data

$[\mathrm{Pt_2(C_4H_7O_2)_2(NH_3)_4}]_2(\mathrm{ClO_4})_4$
M_r = 1662.82
Triclinic, $P\overline{1}$
a = 10.1557 (6) Å
b = 14.5963 (8) Å
c = 15.5209 (9) Å
α = 74.354 (1)°
β = 84.621 (1)°
γ = 85.052 (1)°
V = 2201.3 (2) Å^3

Z = 2
D_x = 2.509 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 5928 reflections
θ = 2.2–28.3°
μ = 13.00 mm^{-1}
T = 296 (2) K
Prism, yellow
0.31 × 0.14 × 0.05 mm

Data collection

Bruker SMART APEX CCD-detector diffractometer
ω scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
$T_{\min}$ = 0.205, $T_{\max}$ = 0.536
21380 measured reflections

10024 independent reflections
7784 reflections with $I > 2\sigma(I)$
R_{int} = 0.058
$\theta_{\max}$ = 27.5°
$h = -13 \rightarrow 13$
$k = -18 \rightarrow 18$
$l = -20 \rightarrow 20$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.043
$wR(F^2)$ = 0.102
S = 0.96
10024 reflections
497 parameters

H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0372P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} < 0.001$
$\Delta\rho_{\max}$ = 2.97 e Å^{-3}
$\Delta\rho_{\min}$ = −2.16 e Å^{-3}

Table 1

Selected geometric parameters (Å, °).

Pt1—Pt2	2.9881 (4)	Pt2—O2	2.031 (6)
Pt1—Pt1^{i}	3.2619 (6)	Pt2—O4	2.023 (5)
Pt3—Pt4	3.0246 (4)	Pt3—N5	2.017 (7)
Pt4—Pt4^{ii}	3.3049 (6)	Pt3—N6	2.011 (7)
Pt2···Pt3	4.5478 (5)	Pt3—O5	2.035 (6)
Pt1—N1	2.037 (7)	Pt3—O7	2.027 (6)
Pt1—N2	2.023 (7)	Pt4—N7	2.020 (7)
Pt1—O1	2.034 (6)	Pt4—N8	2.033 (7)
Pt1—O3	2.044 (5)	Pt4—O6	2.055 (6)
Pt2—N3	2.016 (6)	Pt4—O8	2.032 (6)
Pt2—N4	2.002 (7)		
Pt2—Pt1—Pt1^{i}	161.515 (18)	O4—Pt2—O2	90.0 (2)
Pt3—Pt4—Pt4^{ii}	155.255 (19)	N6—Pt3—N5	91.4 (3)
N2—Pt1—O1	175.1 (2)	N6—Pt3—O7	88.9 (3)
N2—Pt1—N1	91.1 (3)	N5—Pt3—O7	175.7 (3)
O1—Pt1—N1	90.0 (3)	N6—Pt3—O5	174.3 (3)
N2—Pt1—O3	89.2 (3)	N5—Pt3—O5	87.8 (3)
O1—Pt1—O3	89.3 (2)	O7—Pt3—O5	91.5 (3)
N1—Pt1—O3	175.6 (2)	N7—Pt4—O8	176.0 (3)
N4—Pt2—N3	89.8 (3)	N7—Pt4—N8	91.5 (3)
N4—Pt2—O4	89.1 (3)	O8—Pt4—N8	88.1 (3)
N3—Pt2—O4	174.8 (2)	N7—Pt4—O6	88.8 (3)
N4—Pt2—O2	173.4 (2)	O8—Pt4—O6	91.2 (3)
N3—Pt2—O2	90.5 (3)	N8—Pt4—O6	174.5 (3)
N2—Pt1—Pt2—N4	−2.2 (3)	N5—Pt3—Pt4—N7	−12.4 (3)
N1—Pt1—Pt2—N3	−2.1 (3)	O7—Pt3—Pt4—O8	−11.4 (3)
O3—Pt1—Pt2—O4	−1.2 (3)	N6—Pt3—Pt4—N8	−12.0 (3)
O1—Pt1—Pt2—O2	−2.5 (2)	O5—Pt3—Pt4—O6	−10.9 (3)

Symmetry codes: (i) $-x, 1-y, 1-z$; (ii) $1-x, -y, -z$.

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*B*···O21*A*	0.89	2.36	3.222 (17)	162
N1—H1*B*···O24*B*	0.89	2.60	3.117 (19)	118
N2—H2*A*···O18*B*	0.89	2.22	3.065 (17)	159
N2—H2*A*···O20*A*	0.89	2.37	3.135 (18)	144
N2—H2*B*···O21*A*	0.89	2.29	3.135 (18)	158
N3—H3*C*···O13	0.89	2.47	3.128 (9)	131
N3—H3*B*···O24*A*	0.89	2.13	2.970 (16)	157
N3—H3*B*···O24*B*	0.89	1.92	2.768 (16)	159
N4—H4*A*···O18*A*	0.89	2.11	2.716 (11)	125
N4—H4*C*···O23*A*	0.89	2.07	2.963 (16)	176
N5—H5*A*···O2	0.89	2.71	3.110 (8)	108
N5—H5*B*···O13	0.89	2.31	3.057 (11)	141
N6—H6*C*···O4	0.89	2.38	3.248 (8)	165
N6—H6*A*···O11	0.89	2.36	2.943 (10)	123
N6—H6*A*···O12	0.89	2.50	3.348 (11)	160
N6—H6*B*···O16	0.89	2.41	3.231 (10)	154
N8—H8*B*···O11	0.89	2.16	2.963 (11)	149
N1—H1*C*···O14^{i}	0.89	2.21	3.005 (9)	149
N1—H1*A*···O3^{ii}	0.89	2.34	3.105 (8)	144
N2—H2*C*···O1^{ii}	0.89	2.28	3.093 (8)	152
N3—H3*C*···O10^{iii}	0.89	2.29	3.041 (11)	142
N3—H3*A*···O10^{iv}	0.89	2.16	2.998 (11)	157
N4—H4*B*···O11^{iii}	0.89	2.59	3.151 (11)	122
N4—H4*A*···O15^{iii}	0.89	2.48	3.013 (10)	119
N5—H5*C*···O22*B*^{i}	0.89	2.30	3.133 (19)	156
N5—H5*C*···O24*A*^{i}	0.89	2.40	3.172 (16)	145
N5—H5*A*···O9^{iv}	0.89	2.44	3.213 (13)	146
N7—H7*B*···O22*A*^{i}	0.89	2.34	3.185 (17)	160
N7—H7*B*···O22*B*^{i}	0.89	2.16	2.91 (2)	142
N7—H7*A*···O8^{v}	0.89	2.47	3.167 (9)	135
N7—H7*A*···O19*A*^{iii}	0.89	2.39	2.938 (15)	120
N8—H8*C*···O6^{v}	0.89	2.39	3.109 (9)	138
N8—H8*A*···O19*A*^{iii}	0.89	2.44	3.155 (14)	138
N8—H8*A*···O19*B*^{iii}	0.89	1.92	2.759 (12)	156

Symmetry codes: (i) $-x, -y, 1-z$; (ii) $-x, 1-y, 1-z$; (iii) $1-x, -y, 1-z$; (iv) $x-1, y, z$; (v) $1-x, -y, -z$.

Two of the four ClO_4^- anions show orientational disorder. Around each Cl atom there are two sets of possible positions as follows: O17*A*, O18*A*, O19*A*, O20*A*, and O17*B*, O18*B*, O19*B*, O20*B* around Cl3; O21*A*, O22*A*, O23*A*, O24*A*, and O21*B*, O22*B*, O23*B*, O24*B* around Cl4. It was assumed that the disordered O atoms around each Cl atom have the same isotropic displacement parameter. Furthermore, Cl—O distances were restrained to 1.43 (1) Å and the six O···O distances within each perchlorate anion were restrained as equal. The occupation factors of sites *A* and *B* were assumed to be 50%, since the preliminary least-squares experiments suggested that they were equally populated. Two of the four propyl units were also judged to be partially disordered. In each case, one of the two methyl units was assumed to be disordered over two sites (C11*A* and C11*B* for one case; C16*A* and C16*B* for the other case) with 50% occupancy each.

All H atoms, except for two methine H atoms on C atoms adjacent to the disordered methyl units, were located at their idealized positions [C—H(methyl) = 0.96 Å, C—H(methine) = 0.98 Å and N—H(ammine) = 0.89 Å], and included in the refinement in a riding-model approximation, with $U_{\rm iso}$(methyl H) = $1.5U_{\rm eq}$(C), $U_{\rm iso}$(methine H) = $1.2U_{\rm eq}$(C), and $U_{\rm iso}$(ammine H) = $1.5U_{\rm eq}$(N). Two H atoms on C atoms adjacent to the disordered methyl groups were not located. In the final difference Fourier synthesis, 32 residual peaks in the range 1.03–2.97 e Å^{-3} were observed primarily within 1.2 Å of the Pt atoms. The highest peak (2.97 e Å^{-3}) was located 0.94 Å from atom Pt2, while the deepest hole (−2.16 e Å^{-3}) was located 0.93 Å from atom Pt3.

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *KENX* (Sakai, 2002) and *ORTEP*II (Johnson, 1976); software used to prepare material for publication: *SHELXL*97, *TEXSAN* (Molecular Structure Corporation, 2001) and *KENX*.

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