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Bis[(2,2-dimethyl-1,3-propanediamine-κ^2N,N')(piperidine-2-carboxylato-κ^2N,O)platinum(II)] sulfate

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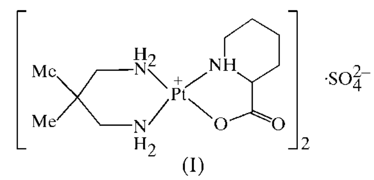
The title compound, $[Pt(C_6H_{10}NO_2)(C_5H_{14}N_2)]_2(SO_4)$, crystallizes with two cations in the asymmetric unit. The two complex cations, which have a square-planar Pt^{II} coordination, are chemically identical but differ slightly in the conformations of their amine groups. A neutral complex, *viz.* (2,2-dimethyl-1,3-propanediamine-κ^2N,N')bis(2-piperidinecarboxylato-κN)platinum(II), is shown to form in solution and to change rapidly into the title compound.

Comment

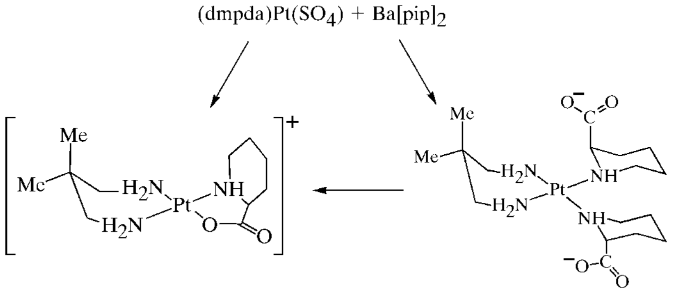
The structural and chemical properties of metal complexes of piperidinecarboxylates have not been studied widely, while those of pyridinecarboxylates have (Gonzales-Vergara *et al.*, 1982; Strearns & Armstrong, 1992). Diaminoplatinum(II) complexes of pyridinecarboxylates exhibit significant anticancer activity *in vitro* (Song *et al.*, 1999, 2000), even though they do not obey the generally accepted structure–activity relationships (Reedijk, 1992) for tumor-active platinum compounds. One molecule of 2-pyridinecarboxylate binds a diaminoplatinum(II) molecule *via N*,*O*-coordination, giving a cationic complex, while two molecules of 3- or 4-pyridinecarboxylate bind a diaminoplatinum(II) molecule *via N*,*N*-coordination, giving a neutral zwitterionic complex. We investigate here the structure of a Pt^{II} complex, (I), of a piperidinecarboxylate ligand that has N and carboxylate O-atom donors similar to those found in pyridinecarboxylate complexes.

The reaction of (dmpda-k^2N,N')platinum(II) sulfate (dmpda is 2,2-dimethyl-1,3-propanediamine) and two equivalents of 2-piperidinecarboxylate in D_2O produces a mixture of a neutral complex, [(dmpda-κ^2N,N')bis(pip-κN)platinum(II)] (pip is piperidinecarboxylate), (II), and a cationic complex, [(dmpda-κ^2N,N')(pip-κ^2N,O)platinum(II)]$^+$, in an initial molar ratio of ~1:0.3 (see scheme below). This ratio can be assessed by integration of the ^{1}H NMR peak at 3.64 p.p.m., corresponding to two methine protons in the neutral complex, and the peak at 3.90 p.p.m., which is due to the methine proton in the cationic complex. The signal intensity of the peak at 3.64 p.p.m. decreases, while that at 3.90 p.p.m. increases, so that the molar ratio is reversed after 3 d. This change is faster at higher temperatures, and certainly signifies the transformation of the neutral complex to the cationic complex, accompanied by the loss of one pip ligand. The cationic complex is so stable that its ^{1}H NMR signals do not change thereafter.



(I)

In the crystal structure of (I) there are two chemically identical [(dmpda-κ^2N,N')(pip-κ^2N,O)platinum(II)]$^+$ ions (Fig. 1). The dmpda ligands in these two molecules have slightly different conformations, which reflects the structural flexibility of the dmpda ligand. One pip ligand chelates a Pt atom *via* a carboxylate O atom and the ring N atom, thus forming a five-membered ring. The sulfate ion is not coordinated to the Pt atom. Pt—N and Pt—O distances (Table 1) fall in the ranges found in other platinum compounds (Goto *et al.*, 1992; Kuroda *et al.*, 1983). The coordination geometries around the Pt atoms are slightly distorted square planar, with the O1—Pt1—N1 [81.50 (17)°] and N4—Pt2—O3 [82.0 (2) °] angles exhibiting the maximum deviations (Table 1). The Pt atom and four coordinated atoms of each Pt complex ion form a well defined plane, to which the piperidine ring stands almost orthogonal.



(I) (II)

Strong hydrogen bonds are observed not only between each of the platinum complex ions and the sulfate anion but also between complex cations. All N atoms serve as hydrogen-bond donors. Sulfate atoms O5, O6 and O7, and the carboxylate O atoms (O1 and O3) coordinated to the Pt atoms, serve as hydrogen-bond acceptors. This net of hydrogen bonds helps construct a layer whose orientation includes the *a* direction and the *bc* diagonal. Short interatomic distances that might accommodate hydrogen-bonding interactions are listed in Table 2.

It is noticeable that the distance across the platinum coordination plane in (I), between a methyl group in the amine and

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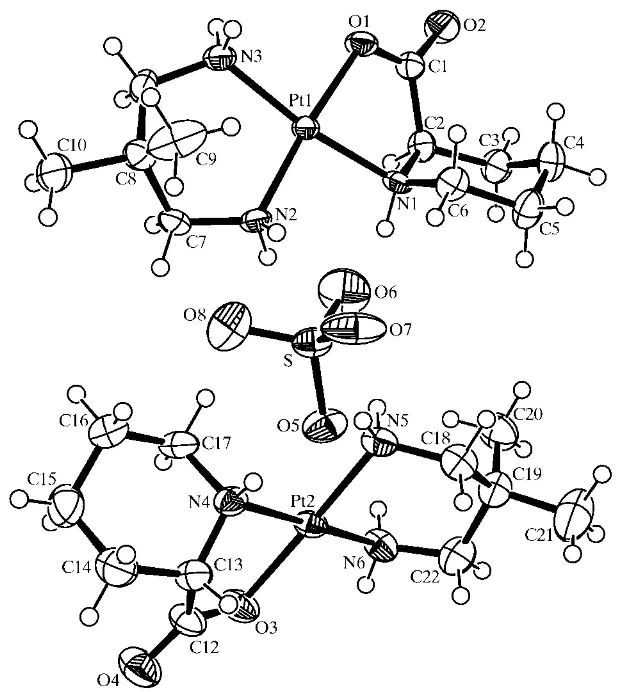

Figure 1
The molecular structure of (I). Displacement ellipsoids are shown at the 50% probability level.

methylene groups in the pip ligand, is 5–6 Å. It is unlikely that significant steric hindrance occurs in this distance, even though the thermal motion of the dmpda ligand is considered. However, the steric hindrance is expected to increase severely in the case of the *N*,*N*-coordinated complex, (II), the hindrance involving a methyl group of the dmpda ligand and the carboxylate group of a pip ligand across the platinum coordination plane (see second scheme above). This steric hindrance is possibly an important reason for the transformation of (II) into (I), since this transformation would significantly diminish the steric hindrance occurring across the platinum coordination plane of the *N*,*N*-coordinated complex. Thus, this study of the crystal structure of (I) suggests that the transformation of the neutral complex to the cationic complex may be induced by the steric interaction between the amine and piperidinecarboxylate ligands.

Experimental

To a suspension of (dmpda)PtI_2 (1.17 g, 2.0 mmol) in water (35 ml) was added silver sulfate (0.62 g, 2.0 mmol) in water (65 ml). The reaction mixture was stirred for 6 h, with protection from light. After the precipitated AgI had been filtered off, Ba[pip]$_2$ (0.78 g, 2.0 mmol) was added to the filtrate. The reaction mixture was stirred for 3 d, at which point the precipitated $BaSO_4$ was filtered off and the filtrate was evaporated to dryness under reduced pressure. The product was finally recrystallized from methanol and ether. Crystals suitable for X-ray analysis were obtained by slow evaporation of the methanol solution at room temperature over a period of 1 week. After filtration, the crystals were washed with ether. Analysis calculated for $C_{22}H_{48}N_6O_8Pt_2S$: C 27.88, H 5.07, N 8.87%; found: C 27.78, H 5.02, N 8.75%. ^{1}H NMR (D_2O): δ 3.90 (*t*, 1H, CH), 2.94 (*m*, 2H, CH_2), 2.42 (*m*, 4H, CH_2-dmpda), 2.25 (*m*, 1H, CH_2), 2.10 (*m*, 1H, CH_2), 1.89 (*m*, 1H, CH_2), 1.60 (*m*, 3H,CH_2), 0.96 (*d*, 6H, CH_3-dmpda).

Crystal data

$[Pt(C_6H_{10}NO_2)(C_5H_{14}N_2)]_2(SO_4)$
$M_r = 946.90$
Triclinic, $P\overline{1}$
$a = 6.0043$ (13) Å
$b = 11.0480$ (18) Å
$c = 23.763$ (3) Å
$\alpha = 101.882$ (14)°
$\beta = 91.135$ (13)°
$\gamma = 95.216$ (12)°
$V = 1535.0$ (5) Å^3
$Z = 2$
$D_x = 2.049$ Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
$\theta = 10.5$–14.3°
$\mu = 9.22$ mm^{-1}
$T = 293$ (2) K
Block, pale yellow
0.25 × 0.20 × 0.12 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: empirical (*CADDAT*; Enraf–Nonius, 1989)
$T_{min} = 0.12$, $T_{max} = 0.33$
5955 measured reflections
5387 independent reflections
4241 reflections with $I > 2\sigma(I)$
$R_{int} = 0.021$
$\theta_{max} = 25.0°$
$h = 0 \rightarrow 7$
$k = -13 \rightarrow 13$
$l = -28 \rightarrow 28$
3 standard reflections
frequency: 3600 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.027$
$wR(F^2) = 0.065$
$S = 1.09$
5387 reflections
352 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0187P)^2 + 2.3696P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.74$ e Å^{-3}
$\Delta\rho_{min} = -0.73$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Pt1—N2	2.025 (5)	Pt2—N5	2.010 (5)
Pt1—N1	2.028 (5)	Pt2—N4	2.029 (5)
Pt1—O1	2.034 (4)	Pt2—N6	2.035 (5)
Pt1—N3	2.044 (5)	Pt2—O3	2.038 (5)
N2—Pt1—N1	93.06 (19)	N5—Pt2—N4	95.0 (2)
N1—Pt1—O1	81.50 (17)	N5—Pt2—N6	87.4 (2)
N2—Pt1—N3	95.47 (19)	N4—Pt2—O3	82.0 (2)
O1—Pt1—N3	90.01 (18)	N6—Pt2—O3	95.6 (2)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1*D*···O7^{i}	0.91	1.85	2.745 (7)	169
N2—H2*D*···O7^{i}	0.90	2.18	2.987 (7)	150
N2—H2*E*···O6	0.90	2.03	2.882 (8)	158
N3—H3*D*···O1^{ii}	0.90	2.15	3.022 (7)	163
N3—H3*E*···O2^{iii}	0.90	2.12	2.974 (7)	158
N4—H4*D*···O5	0.91	1.91	2.787 (7)	161
N5—H5*D*···O7^{i}	0.90	1.95	2.817 (7)	160
N5—H5*E*···O5	0.90	2.05	2.877 (7)	152
N6—H6*D*···O3^{iv}	0.90	2.20	3.074 (7)	163
N6—H6*E*···O5^{i}	0.90	2.31	3.100 (8)	147

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

The locations of all the H atoms were constrained to ideal positions and refined using a riding model.

Data collection: *CD4CA0* (Enraf–Nonius, 1989); cell refinement: *CD4CA0*; data reduction: *CADDAT* (Enraf–Nonius, 1989); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3 for Windows* (Farrugia, 1998).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: TA1426). Services for accessing these data are described at the back of the journal.

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