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Bis(guanidinium) bis(oxalato)platinate(II)

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Key indicators

Single-crystal X-ray study
 $T = 296$ K
Mean $\sigma(\text{C}-\text{C}) = 0.006$ Å
 R factor = 0.014
 wR factor = 0.034
Data-to-parameter ratio = 9.4

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

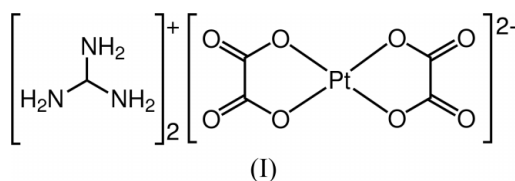
Bis(guanidinium) bis(oxalato)platinate(II)

The title compound, $(\text{CH}_6\text{N}_3)_2[\text{Pt}(\text{C}_2\text{O}_4)_2]$ or (guanidinium)₂- $[\text{Pt}(\text{ox})_2]$ (ox = oxalate), possesses an intriguing three-dimensional hydrogen-bonding network in the crystal structure, where extensive hydrogen bonds are formed between N–H(guanidinium) units and O atoms of oxalates [$\text{N} \cdots \text{O} = 2.913(5)–3.197(5)$ Å]. The $[\text{Pt}(\text{ox})_2]^{2-}$ anions stack weakly in a one-dimensional manner, with an intermolecular Pt \cdots Pt distance of 3.5876(7) Å. The Pt atom is located at an inversion centre.

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Comment

For a long time we have been interested in one-dimensional systems consisting of dimers doubly bridged with amidate or carboxylate ligands (see, for example, Sakai, Tanaka *et al.*, 1998; Sakai, Takeshita *et al.*, 1998; Sakai *et al.*, 2002). All the dimers used thus far have been cationic dimers with a general formula $[\text{Pt}_2L_4(\mu\text{-bridge})_2]^{2+}$ [$L_2 = (\text{NH}_3)_2$, ethylenediamine, 2,2'-bipyridine, 1,10-phenanthroline, *etc.*; bridge = acetamidate, pivalamidate, acetate, benzoate, *etc.*]. In this context, attempts have been made to prepare a Pt(ox) dimer, doubly bridged by guanidinate ligands, $[\text{Pt}_2(\text{ox})_2(\mu\text{-guanidinato})_2]^{2-}$. However, the preparation of such anionic dimers has, so far, been unsuccessful. Here we report the crystal structure of the title compound, which was obtained as a by-product in these studies.



The asymmetric unit of (I) consists of a half unit of the formula (Fig. 1). The Pt atom is located at an inversion centre and therefore the coordination around it has a planar coordination geometry. The $[\text{Pt}(\text{ox})_2]^{2-}$ anion exhibits a distorted square-planar stereochemistry, due to the structural restraint arising from the chelating oxalates (see Table 1).

As shown in Fig. 2, the crystal packing of (I) is stabilized by extensive hydrogen bonds formed between guanidinium cations and O atoms of the oxalates (see also Table 2). Fig. 2*b* shows that the $[\text{Pt}(\text{ox})_2]^{2-}$ anions stack along the a axis, where the Pt1 \cdots Pt1ⁱ [symmetry code: (i) $1 - x, 1 - y, 1 - z$] vector is canted by *ca.* 22° with respect to the orthogonal vector of the mean plane defined by the four coordinated O atoms. The intermolecular Pt \cdots Pt distance [3.5876(7) Å] is much longer than those reported for partially oxidized analogs (Pt \cdots Pt =

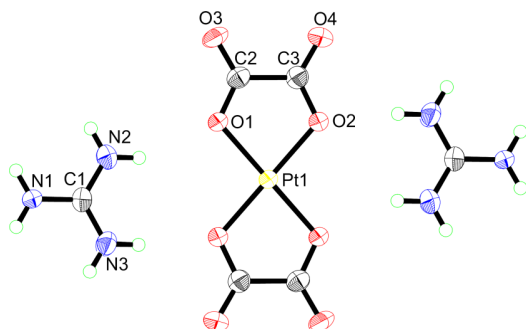


Figure 1
The structure of (I), showing the atom-labeling scheme. Displacement ellipsoids are drawn at the 50% probability level.

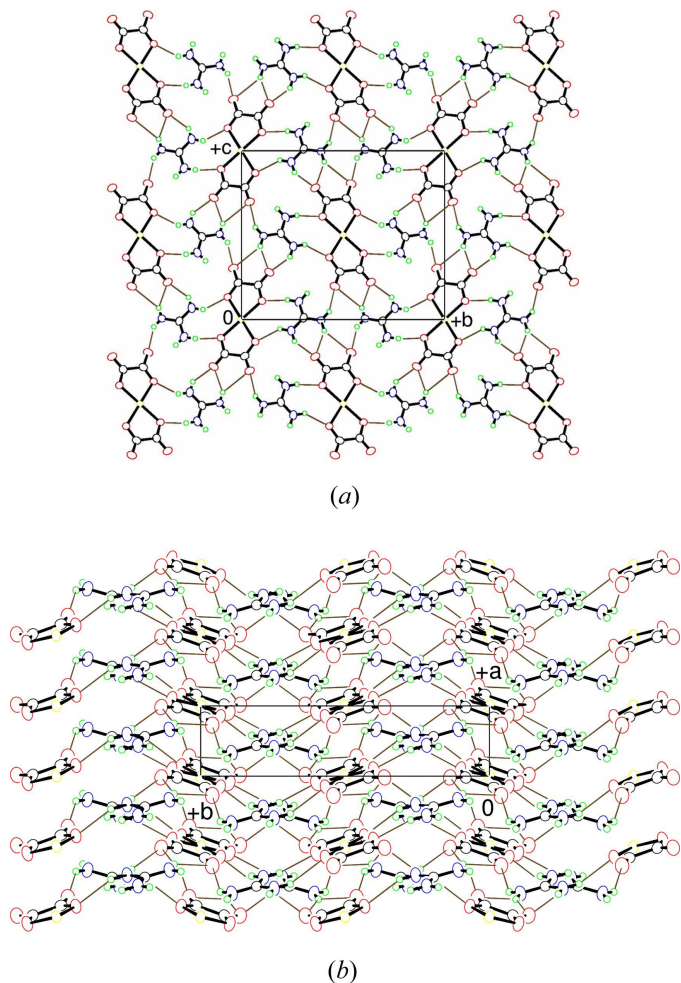


Figure 2
Crystal packing view of (I), showing the hydrogen-bonding network: (a) along the *a* axis and (b) along the *c* axis.

2.717–2.876 Å; Miller, 1982), consistent with our assignment of oxidation level Pt^{II} for (I). However, the deep green color of (I) implies that metal-metal interactions are to some extent promoted in (I). Examples of other Pt^{II} compounds are as follows: K₂[Pt(ox)₂]·2H₂O (Pt···Pt > 8 Å, Mattes & Krogmann, 1964; [Cu(en)₂][Pt(ox)₂] (Pt···Pt = 3.554 and 3.855 Å, Bekaroglu *et al.*, 1976; Ca[Pt(ox)₂]·3.5H₂O (Pt···Pt = 3.18 Å, Krogmann, 1968).

Experimental

A solution of K₂[Pt(ox)₂]·2H₂O (0.20 mmol, 0.098 g; Werner & Grebe, 1899) and guanidine carbonate (0.20 mmol, 0.024 g) in water (5 ml) was refluxed for 3 h, during which the solution became dark green and a small amount of black precipitate deposited. The solution was then filtered while it was hot. Allowing the filtrate to stand at room temperature overnight afforded (I) as dark-green needles, which were collected by filtration and air-dried (yield: 30%). Analysis calculated for C₁₂H₆N₆O₈Pt: C 14.86, H 2.31, N 16.97%; found: C 14.67, H 2.46, N 17.11%.

Crystal data

(CH₆N₃)₂[Pt(C₂O₄)₂]
M_r = 491.31
 Monoclinic, *P*2₁/*c*
a = 3.5876 (7) Å
b = 14.684 (3) Å
c = 12.237 (2) Å
 β = 94.686 (3)°
V = 642.5 (2) Å³
Z = 2

D_x = 2.540 Mg m⁻³
 Mo *K*α radiation
 Cell parameters from 1567 reflections
 θ = 2.8–23.3°
 μ = 10.97 mm⁻¹
T = 296 (2) K
 Prism, dark green
 0.15 × 0.15 × 0.04 mm

Data collection

Bruker SMART APEX CCD detector diffractometer
 ω scans
 Absorption correction: Gaussian (*XPREP* in *SAINT*; Bruker, 2001)
T_{min} = 0.288, *T_{max}* = 0.675
 2782 measured reflections
 911 independent reflections

685 reflections with *I* > 2σ(*I*)
R_{int} = 0.033
 θ_{\max} = 23.3°
h = -3 → 3
k = -15 → 16
l = -12 → 13
 58 standard reflections
 frequency: 330 min
 intensity decay: 0.2%

Refinement

Refinement on *F*²
R[*F*² > 2σ(*F*²)] = 0.015
wR(*F*²) = 0.034
S = 0.94
 911 reflections
 97 parameters

H-atom parameters constrained
 $w = 1/[\sigma^2(F_o^2) + (0.0131P)^2]$
 where $P = (F_o^2 + 2F_c^2)/3$
 $(\Delta/\sigma)_{\max} = 0.001$
 $\Delta\rho_{\max} = 0.44 \text{ e } \text{Å}^{-3}$
 $\Delta\rho_{\min} = -0.43 \text{ e } \text{Å}^{-3}$

Table 1

Selected geometric parameters (Å, °).

Pt1—O1	2.016 (3)	Pt1—Pt1 ⁱ	3.5876 (7)
Pt1—O2	2.009 (3)		
O2—Pt1—O1	82.52 (12)	O2 ⁱⁱ —Pt1—O1	97.48 (12)

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

Table 2

Hydrogen-bonding geometry (Å, °).

<i>D</i> —H··· <i>A</i>	<i>D</i> —H	H··· <i>A</i>	<i>D</i> ··· <i>A</i>	<i>D</i> —H··· <i>A</i>
N2—H2A···O1	0.86	2.39	3.120 (5)	143
N1—H1A···O3 ⁱⁱⁱ	0.86	2.49	3.197 (5)	139
N1—H1A···O4 ⁱⁱⁱ	0.86	2.21	2.969 (4)	147
N2—H2B···O4 ⁱⁱⁱ	0.86	2.21	2.971 (5)	147
N1—H1B···O3 ^{iv}	0.86	2.40	3.106 (5)	139
N3—H3B···O3 ^{iv}	0.86	2.15	2.913 (5)	148
N3—H3A···O2 ⁱⁱ	0.86	2.11	2.944 (5)	164

Symmetry codes: (ii) -*x*, 1 - *y*, 1 - *z*; (iii) 1 - *x*, *y* - ½, ½ - *z*; (iv) *x*, ½ - *y*, ½ + *z*.

All H atoms of the guanidinium ion were positioned geometrically as riding atoms (N—H = 0.86 Å).

Data collection: *SMART* (Bruker, 2001); cell refinement: *SAINT* (Bruker, 2001); data reduction: *SAINT*; program(s) used to solve

structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *KENX* (Sakai, 2002); software used to prepare material for publication: *SHELXL97*, *TEXSAN* (Molecular Structure Corporation, 2001), *KENX* and *ORTEPII* (Johnson, 1976).

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