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Crystal Structures of Diammine(oxalato)platinum(II) and Diammine-(malonato)platinum(II)

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Abstract

$[Pt(NH_3)_2malonate]$ belongs to the monoclinic space group $P2_1/c$, $a = 4.063(2)$, $b = 14.150(2)$, $c = 11.414(2)$ Å, $\beta = 93.27(2)°$, $Z = 4$. The structure was refined on 1274 nonzero CuKα reflections to $R = 0.035$. The crystal contains individual square planar molecules with two *cis* NH_3 ligands at 2.036(9) Å from Pt. The Pt–O distances to the bidentate malonate average 2.022(6) Å and the chelate ring has a boat conformation. The angles around Pt lie in the range 86.0–93.5° ($\sigma = 0.3°$). The molecules are stacked along the a axis and form N–H···O bonds with adjacent molecules. $[Pt(NH_3)_2oxalate]$ is monoclinic, space group $P2_1/m$, $a = 3.865(2)$, $b = 10.703(4)$, $c = 6.774(3)$ Å, $\beta = 94.29(4)°$. $Z = 2$. The structure was refined on 449 non-zero MoKα reflections to $R = 0.045$. The square planar monomeric molecule possesses a crystallographic mirror plane perpendicular to the coordination plane and bisecting the N–Pt–N and O–Pt–O angles. The oxalate imposes an O–Pt–O angle of 82.0° in the chelate ring. The molecules are stacked in columns in the a direction, and form inter-column hydrogen bond in the b and c directions.

Introduction

Since the discovery of the antitumor properties of Cisplatin, $[Pt(NH_3)_2Cl_2]$, efforts have been made in many laboratories to modify this basic structural unit in order to develop more efficient and less toxic analogs. Complexes with chelating carboxylates such as malonate (mal) as leaving ligand are much less toxic than the chloride complexes. The compound $[Pt(NH_3)_2mal]$ has shown good activities against L1210 [1] and ADJ/PC6A tumors [2, 3], and against advanced S180 tumors [1, 2]. Antitumor activity has also been observed for the oxalate (ox) complex $[Pt(NH_3)_2ox]$ [2], but higher toxicity hampered its use as antitumor drug [4].

The crystal structures of $[Pt(NH_3)_2ox]$ and $[Pt(NH_3)_2mal]$ are reported in the present paper. The purpose of this study was to better define the Pt-carboxylate portion of the complex, and its possible influence on the $Pt(NH_3)_2$ region of the molecule. At the time this work was undertaken, no crystal structures were available for Pt(ox) complexes containing amines. For the malonate, the structure of [Pt(mal)(1,3-diamino-2,2-dimethylpropane)] [5] was the only one known. Very recently, Bau *et al.* [6]** have reported the structures of the [Pt(dach)ox] and [Pt(dach)mal] compounds (where dach = 1R,2R-*trans*-1,2-diaminocyclohexane). Other malonate containing Pt complexes have also been recently described [7–10].

Experimental

$[Pt(NH_3)_2malonate]$

Crystal Data

$C_3H_8N_2O_4Pt$, fw = 331.20, monoclinic, $P2_1/c$, $a = 4.063(2)$, $b = 14.150(2)$, $c = 11.414(2)$ Å, $\beta = 93.27(2)°$, $V = 655.14$ Å^3, $Z = 4$, $D_c = 3.357$ g cm^{-1}, $\lambda(CuK\bar{\alpha}) = 1.54178$ Å (graphite monochromator),

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**The x coordinate of Pt in Table III of ref. 6 should read −0.0555 (instead of +0.0555) and the C8–O2–Pt angle (Table II) should be 114° (instead of 141°).

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μ(CuKα) = 40.26 mm^{-1}, T = 296 K, crystal dimensions (mm): 0.080 (01$\bar{1}$–0$\bar{1}$1) × 0.50 (0.11–0$\bar{1}\bar{1}$) × 0.64 (102–$\bar{1}$0$\bar{2}$).

Crystallographic Measurements and Structure Resolution

The crystal used for X-ray work was an elongated plate obtained as described elsewhere [11]. The crystal was mounted with a random orientation on an Enraf-Nonius CAD4 diffractometer and a list of 25 reflections was created by the search routine of the CAD4 software. These reflections were centered four times and the autoindexing routine yielded the above monoclinic cell. The Niggli parameters clearly indicated that the lattice could not be described in higher symmetry. As a check on the cell so obtained, long-exposure oscillation photographs were recorded along each of the three axes. They showed the expected layer-line separation without interleaving layers, and the mirror in the 2/m Laue symmetry was observed for the oscillation about *b*. The cell parameters given above were determined by least-squares fit on the setting angles for the 25 reflections. Space group $P2_1/c$ was uniquely determined from the systematic absences ($h0l$, $l \neq 2$n; $0k0$, $k \neq 2$n) noted in the complete data set.

The intensity data were collected witn an Enraf-Nonius CAD4 diffractometer, following a procedure described elsewhere [12]. Three standard reflections fluctuated within ±1.8% during the experiment. All hkl and $hk\bar{l}$ reflections contained in a sphere limited by 2θ = 140° were collected. Among the 1343 CuKα reflections so obtained, 1274 had intensities significantly above background ($I \geqslant 3.0\sigma(I)$) and they were retained for structure determination. They were corrected for the Lorentz effect and polarization. An absorption correction based on crystal geometry was applied at a later stage (Gaussian integration, grid 10 × 10 × 10, transmission range = 0.016–0.257).

The position of the Pt atom was determined by using MULTAN [13]. The remaining nonhydrogen atoms were located from a subsequent difference Fourier (ΔF) map phased on Pt. Isotropic refinement on the data uncorrected for absorption converged to R = 0.152. The absorption correction reduced R to 0.071. After anisotropic refinement of the known atoms, a ΔF map revealed the positions of the eight hydrogens, which were isotropically refined. Convergence was reached for R = 0.035 and R_w = 0.048. The goodness-of-fit ratio was 2.12. The final ΔF map showed a general background < ±0.7 e/Å^3. The highest residual (1.3 e/Å^3) was found at (0.95, 0.30, 0.40) and could not be related to any reasonable atomic position. The remaining peaks above background were all found near Pt.

[Pt(NH$_3$)$_2$oxalate]

Crystal Data

$C_2H_6N_2O_4Pt$, fw = 317.17, monoclinic, $P2_1/m$, a = 3.865(2), b = 10.703(4), c = 6.774(3) Å, β = 94.29(4)°, V = 279.4 Å^3, Z = 2, D_c = 3.768 g cm^{-3}, λ(MoKα) = 0.71069 Å, μ(MoKα) = 25.30 mm^{-1}, T = 296 K, crystal dimensions (mm): 0.059 (001–00$\bar{1}$) × 0.146 (101–$\bar{1}$0$\bar{1}$) × 0.0064 (010–0$\bar{1}$0).

Crystallographic Measurements and Structure Determination

The crystals were prepared as described elsewhere [11]. Laue symmetry, cell parameters and space group were determined as above. The systematic absences ($0k0$, $k \neq 2$n) were consistent with the $P2_1$ and $P2_1/m$ space groups. The latter was found to be correct after structure refinement.

A set of 518 unique MoK$\bar{\alpha}$ hkl and $hk\bar{l}$ reflections ($2\theta \leqslant 50°$) was collected as described above (standard fluctuations within ±1.4%). The 449 reflections with $I/\sigma(I) > 3.0$ were retained for structure determination. They were corrected for the Lorentz effect, polarization and absorption (transmission range: 0.08–0.72).

The Patterson map was consistent with the two Pt atoms occupying crystallographic mirror planes (equipoint 2e) in space group $P2_1/m$. Successive ΔF maps revealed the positions of the remaining atoms, including the hydrogens. The nonhydrogen atoms were refined anisotropically, the hydrogens isotropically. The final results are: R = 0.045, R_w = 0.054, goodness-of-fit ratio = 2.32, maximum residuals ± (0.6–1.5) e/Å^3 near Pt, general background < ±0.5 e/Å^3.

The scattering curves used were from standard sources [14]. The f′ and f″ contributions of Pt to anomalous dispersion [15] were included in structure factor calculations. The refined coordinates for both structures are listed in Table I. The temperature factors, structure factor amplitudes and least-squares plane calculations for both compounds are part of the supplementary material available from the authors.

Description of the Structures

[Pt(NH$_3$)$_2$malonate]

Figure 1 contains representations of the molecule with the coordination plane viewed from above (Fig. 1a) and edgewise (Fig. 1b). Platinum exhibits the usual square planar coordination and the molecule possesses an approximate mirror plane perpendicular to the coordination plane, through Pt and the malonate methylene group. The Pt–N bond lengths (Table II, av. 2.036(9) Å) are similar to those observed in other Pt-ammine compounds

TABLE I. Refined Fractional Coordinates.

Atom	x	y	z
[Pt(NH$_3$)$_2$malonate] (×10^4, Pt × 10^5, H × 10^3)			
Pt	64165(7)	17331(2)	85554(2)
O(1)	8576(15)	2026(4)	7046(5)
O(2)	11135(20)	1556(5)	5510(6)
O(3)	8647(15)	458(4)	8721(4)
O(4)	11224(16)	−721(4)	7922(5)
N(1)	4334(19)	3031(5)	8382(5)
N(2)	4306(19)	1463(5)	10105(6)
C(1)	9518(21)	1392(5)	6357(6)
C(2)	8518(22)	381(5)	6614(7)
C(3)	9585(20)	12(5)	7838(6)
H(1)	944(16)	−4(5)	607(6)
H(2)	612(16)	36(6)	650(5)
H(11)	597(18)	348(4)	821(7)
H(12)	267(21)	297(6)	775(8)
H(13)	356(18)	325(3)	907(6)
H(21)	359(11)	205(3)	1043(4)
H(22)	587(21)	117(6)	1064(7)
H(23)	247(36)	106(11)	996(14)
[Pt(NH$_3$)$_2$oxalate] (×10^3, Pt × 10^4, H × 10^2)			
Pt(1)	1509(2)	2500	1016(1)
O(1)	323(3)	127(1)	−92(2)
O(2)	575(3)	120(1)	−374(2)
N(1)	−13(4)	115(2)	279(2)
C(1)	458(5)	178(2)	−236(2)
H(1)	18(4)	8(2)	35(2)
H(2)	−14(3)	5(1)	20(3)
H(3)	−16(3)	15(2)	37(2)

TABLE II. Interatomic Distances and Bond Angles in [Pt(NH$_3$)$_2$malonate].

Distances (Å)	
Pt–O(1)	2.020(6)
Pt–O(3)	2.023(5)
Pt–N(1)	2.027(7)
Pt–N(2)	2.045(7)
C(1)–O(1)	1.267(9)
C(1)–O(2)	1.222(10)
C(1)–C(2)	1.520(11)
C(2)–C(3)	1.531(11)
C(3)–O(3)	1.266(9)
C(3)–O(4)	1.233(9)
Angles (deg)	
O(1)–Pt–O(3)	92.8(2)
O(1)–Pt–N(1)	86.0(3)
O(1)–Pt–N(2)	178.5(3)
O(3)–Pt–N(1)	178.0(3)
O(3)–Pt–N(2)	87.7(3)
N(1)–Pt–N(2)	93.5(3)
Pt–O(1)–C(1)	123.1(5)
Pt–O(3)–C(3)	121.6(5)
O(1)–C(1)–O(2)	123.5(7)
O(1)–C(1)–C(2)	117.0(7)
O(2)–C(1)–C(2)	119.6(7)
C(1)–C(2)–C(3)	115.6(6)
C(2)–C(3)–O(3)	118.3(7)
C(2)–C(3)–O(4)	118.8(7)
O(3)–C(3)–O(4)	122.9(7)

[16]. The Pt–O distances (av. 2.022(6) Å) compare well with the average value (2.029 Å) computed for Pt-malonate complexes [5–10]. The metal atom is only 0.026 Å above the plane defined by the four donor atoms. The angles (Table II) between *cis* bonds are all in the range 86.0–93.5° (σ = 0.3°). The O–Pt–O angle (92.8(2)°) is only slightly greater than the mean value (91.3°) for other Pt-malonates, indicating that the malonate ring does not impose severe constraints on the coordination geometry around platinum. The 'bite' of the malonate (O···O = 2.928 Å) lies within the range previously found (2.78–2.99 Å) [5–10].

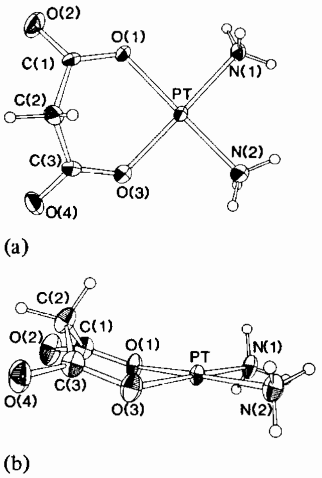

Fig. 1. ORTEP drawings of the [Pt(NH$_3$)$_2$malonate] molecule. The ellipsoids correspond to 50% probability. The hydrogens are represented by spheres of arbitrary size. The coordination plane is viewed from above in (a) and edgewise in (b).

The structure of the coordinated malonate compares well with similar cases [5–10]. The C–C bond lengths (av. 1.526(11) Å) are little affected by coordination. On the other hand, the C–O distances, which are ideally equal in the free malonate dianion, exhibit significant differences in the present complex: the free C–O bonds have become shorter (av. 1.227(10) Å) by acquiring some double bond character at the expense of the metal-bonded C–O bonds, which are longer (1.266(9) Å). The central C(1)–C(2)–C(3) angle (115.6(6)°) corresponds to the average found for platinum compounds. In ~50 known crystal structures in which ~20 metal ions are chelated by a malonate ligand, this angle is always appreciably above 109.5° (mean 117.0°) [17].

The torsion angles in the chelate ring are listed in Table III, together with those found in the other available platinum compounds. The ring generally adopts a boat conformation. If all bond angles were tetrahedral as in cyclohexane, the pattern of torsion angles for an ideal boat conformation would be 0, 60, −60, 0, 60, −60. The Pt–O–C–C and C–C–C–O angles follow this pattern fairly well, with values generally in the range ±(0 to 9)° and ±(44 to 63)°, respectively. The square planar coordination of platinum requires an O–Pt–O angle of 90°, which flattens the boat and reduces the O–Pt–O–C angles in the range ±(26 to 45)°. One of the two independent molecules in the isopropylamine complex has a more distorted, although still resembling, boat conformation. However, in [$Pt(NH_3)_2(OH)_2mal$], the ring assumes a totally different conformation [9].

A diagram of the unit cell down the *a* axis is shown in Fig. 2. The molecules are stacked in the direction of the *a* axis, forming infinite columns between which hydrogen bonds are formed. Details are given in Table IV. Interestingly, all three hydrogen atoms on both NH_3 ligands are involved

TABLE III. Torsion Angles (deg) in Various Pt(malonate) Units.

Bonds	$(NH_3)_2$ this work	en[a] [7]	Me_2pn[b] [5]	dach[c] [6]	$(en)(OH)_2$[a,d] [10]	$i\text{-}C_3H_7NH_2$ [8]		$(NH_3)_2(OH)_2$[d] [9]
Pt–O(1)–C(1)–C(2)	9	−3	−4	1	4	16	−9	40
O(1)–C(1)–C(2)–C(3)	−57	60	−52	−55	44	43	63	6
C(1)–C(2)–C(3)–O(2)	58	−60	52	53	−48	−65	−54	−41
C(2)–C(3)–O(2)–Pt	−10	3	4	7	3	21	−4	18
C(3)–O(2)–Pt–O(1)	−26	38	−43	−45	31	30	43	18
O(2)–Pt–O(1)–C(1)	26	−38	43	40	−35	−48	−36	−47

[a] Ethylenediamine. [b] 2,2-Dimethyl-1,3-diaminopropane. [c] *trans*-1,2-diaminocyclohexane. [d] Pt(IV).

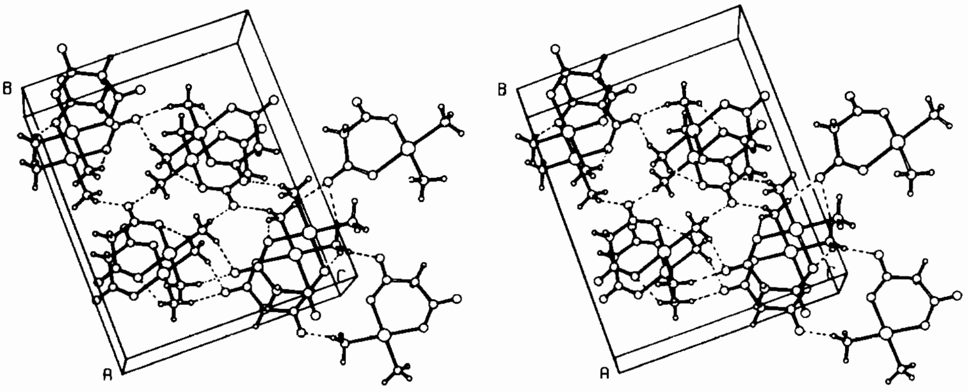

Fig. 2. Stereoview of the unit cell of [$Pt(NH_3)_2$malonate] down the *a* axis. The atoms are shown as spheres of arbitrary size and can be identified from Fig. 1. Dashed lines correspond to hydrogen bonds.

TABLE IV. Geometry of the Hydrogen Bonds in [$Pt(NH_3)_2$malonate].

Bonds	Transformation	Distances (A)			Angle (deg) N–H···O
		N–O	N–H	H···O	
N(1)–H(11)···O(4)	2 − x, ½ + y, 3/2 − z	2.983(9)	0.95(7)	2.10(7)	154(6)
N(1)–H(12)···O(1)	−1 + x, y, z	3.068(9)	0.96(9)	2.25(9)	143(7)
N(1)–H(13)···O(2)	−1 + x, ½ − y, ½ + z	2.880(10)	0.92(6)	1.98(7)	165(6)
N(2)–H(22)···O(4)	2 − x, −y, 2 − z	3.001(9)	0.95(9)	2.07(8)	167(8)
N(2)–H(21)···O(2)	−1 + x, ½ − y, ½ + z	3.130(10)	0.96(4)	2.21(4)	159(4)
N(2)–H(23)···O(3)	−1 + x, y, z	3.064(9)	0.95(15)	2.21(16)	150(13)

in moderate to strong hydrogen bonding interactions with free or coordinated carboxylate oxygens in adjacent columns.

[Pt(NH$_3$)$_2$oxalate]

The molecule is also monomeric and square planar (Fig. 3). The Pt atom occupies a crystallographic mirror plane perpendicular to the coordination plane and bisecting the N–Pt–N and the O–Pt–O angles. The Pt–N and the Pt–O distances, all equal to 2.01(1) Å (Table V), compare well with those found in the above malonate complex. The N–Pt–N angle (91.8(6)°) is only slightly above the ideal 90° value, presumably because of hydrogen bonding in the solid. The small O–Pt–O angle (82.0(5)°) imposed by the chelating oxalate group is similar to those found in a series of Pt-oxalate complexes [18]. The non-hydrogen atoms in the molecule are coplanar within 1σ (0.014 Å).

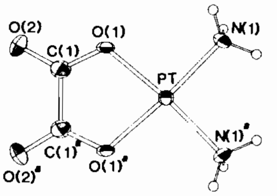

Fig. 3. ORTEP drawing of the [Pt(NH$_3$)$_2$oxalate] molecule. The ellipsoids correspond to 50% probability and the hydrogens are represented by spheres of arbitrary size. Atoms with superscript 'a' are related to the others by the crystallographic mirror plane.

TABLE V. Interatomic Distances and Bond Angles in [Pt(NH$_3$)$_2$oxalate].

Distances (Å)	
Pt–O(1)	2.01(1)
Pt–N(1)	2.01(2)
O(1)–C(1)	1.26(2)
C(1)–O(2)	1.24(2)
C(1)–C(1)^a	1.54(3)
Angles (deg)	
O(1)–Pt–O(1)^a	82.0(5)
N(1)–Pt–O(1)^a	91.8(6)
O(1)–Pt–N(1)	93.1(6)
O(1)–Pt–N(1)^a	175.1(6)
Pt–O(1)–C(1)	113.4(11)
O(2)–C(1)–C(1)^a	120.2(16)
O(1)–C(1)–O(2)	124.2(16)
O(1)–C(1)–C(1)^a	115.6(15)

^{a}x, 1/2 – y, z.

The packing pattern (Fig. 4) shows [Pt(NH$_3$)$_2$-ox] molecules stacked in columns along the *a* direction. The columns are held by hydrogen bonds in the *b* and in the *c* directions. Details on hydrogen bonds are provided in Table IV. All three hydrogens of NH$_3$ form moderately strong hydrogen bonds with oxalate oxygens.

Discussion

Both compounds exist as monomeric species with the dicarboxylate acting as a chelating ligand. The

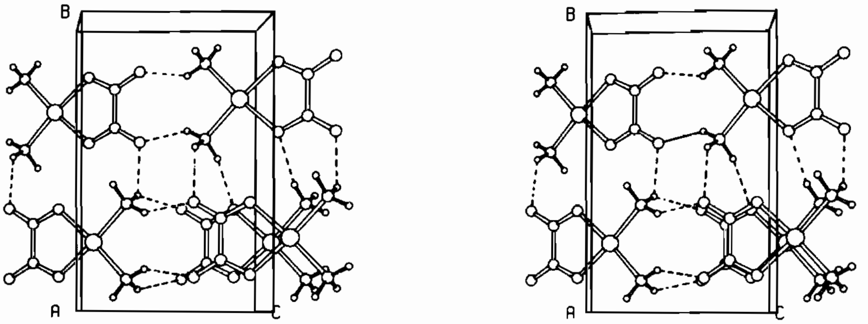

Fig. 4. Stereoview of the unit cell of [Pt(NH$_3$)$_2$oxalate] down the *a* axis. The atoms are shown as spheres of arbitrary size and can be identified from Fig. 3. Dashed lines correspond to hydrogen bonds.

TABLE VI. Geometry of the Hydrogen Bond in [Pt(NH$_3$)$_2$oxalate].

	Transformation	Distances (Å)			Angles (deg)
		N···O	N–H	H···O	N–H···O
N(1)–H(1)···O(2)	1 – x, –y, –z	3.07(2)	0.94(15)	2.34(17)	135(12)
N(1)–H(2)···O(1)	–x, –y, –z	3.09(2)	0.99(16)	2.13(14)	162(14)
N(1)–H(3)···O(2)	–1 + x, y, 1 + z	2.94(2)	0.95(13)	2.10(11)	146(11)

'bite' of the oxalate ion reduces the O–Pt–O angle to 82.0°, thereby introducing an element of strain not found in the malonate complex, where the O–Pt–O angle is 92.8°. There is no dramatic effect of the O–Pt–O angle on the opposite N–Pt–N angle; the latter angle is close to 90° in both compounds, and the small difference is probably due to H-bonding in the solid.

The Pt–oxalate chelate ring (Fig. 3) is roughly planar but the malonate ring is not (Fig. 1). Interestingly, among eight different Pt-malonate rings observed in seven crystal structures, only one does not possess the boat conformation, and six show remarkably symmetrical flattened boat patterns. It is noteworthy that this regular conformation is not commonly observed with other metals. Out of ~50 structures of malonate rings known with ~20 metal ions [17], only a few have a regular boat shape similar to the one found here [19]. This can be ascribed to the fact that Pt(II) has little tendency to increase its coordination above 4, by forming intermolecular coordinative bonds or contacts with 'free' carboxyl oxygens. In a number of metal malonates, this free oxygen fills a coordination position in the sphere of a nearby metal ion, thereby producing a polymeric, generally insoluble, solid. In the present case, the free oxygens only act as hydrogen bond acceptors and this only to a limited extent, because of the overall requirements of crystal packing. Therefore, by dissolving this compound in water, both the NH_3 and free oxalate oxygens act as solubilizing groups by hydrogen bonding with water.

Acknowledgements

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