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A dinuclear platinum complex with bridging hydrazine: $(NPr^n_4)_2[PtCl_3(\mu\text{-}N_2H_4)PtCl_3]$

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Abstract

The synthesis, spectroscopic characterization and crystal structure of a dinuclear platinum(II) complex with a simple hydrazine bridge, $(NPr^n_4)_2[PtCl_3(\mu\text{-}N_2H_4)PtCl_3]$ (**1**), is reported. The dioxane solvate of the compound crystallizes in the space group $P\bar{1}$; $a=8.463(3)$, $b=11.174(2)$, $c=23.075(3)$ Å; $\alpha=79.98(1)$, $\beta=80.44(3)$, $\gamma=82.14(3)$°. The coordination of platinum is approximately square planar, with bond lengths (mean values of two independent dianions) Pt–N = 2.04, Pt–Cl(*trans* to N) = 2.29, Pt–Cl(*trans* to Cl) = 2.29 Å. The dinuclear dianion is stabilized by intramolecular NH---Cl hydrogen bonding. Comparison of the crystallographic and spectroscopic data with those of $[PtCl_3(NH_3)]^-$ has shown that the Pt–N bonds have very similar characteristics in the two compounds.

Introduction

Reports on hydrazine complexes of platinum have been scarce so far [1]. The factor limiting the hydrazine chemistry of platinum is doubtlessly the reducing power of hydrazine that makes redox processes compete with ligand substitution reactions. Many platinum complexes are reduced by hydrazine to metallic platinum. In other cases, reactions with hydrazine can serve to prepare zerovalent platinum complexes [2] or platinum hydride complexes [3]. In the present work, we report the synthesis of a dinuclear compound in which two trichloroplatinum(II) units are joined by a simple hydrazine bridge. Spectroscopic as well as crystallographic characterization of the bridged species is presented.

Experimental

Synthesis

The title compound was synthesized from a solution of 30 mg $(NPr^n_4)_2[Pt_2Cl_6]$ [4] in 0.5 ml DMF, adding slowly 1.5 mg hydrazine monohydrate (carcinogenic!) in 0.5 ml DMF. After 2 h of stirring at ambient temperature, the yellow solution was freed of some metallic platinum by filtration over charcoal. Precipitation with ether yielded yellow crystals of the DMF solvate of the compound in 60% yield. *Anal.* Calc. for $C_{24}H_{60}Cl_6N_4Pt_2 \cdot C_3H_7NO$: C, 30.01; H, 6.25; N, 6.48. Found: C, 30.6; H, 6.4; N, 6.5%.

X-ray crystallography

Monocrystals of the dioxane solvate of **1**, $(NPr^n_4)_2[PtCl_3(\mu\text{-}N_2H_4)PtCl_3] \cdot C_4H_8O_2$, were obtained from dichloromethane/dioxane by slow evaporation from a round-bottom flask closed with a non-gasproof parafilm seal. The structure was solved by Patterson and Fourier methods and refined by full matrix least-squares. An absorption correction was applied using the program DIFABS [5] from the CRYSTALS package [6]. All atoms were refined with anisotropic temperature factors. Hydrogen atoms were not included. The details of data collection and refinement are given in Table 1. See also 'Supplementary material'.

Results

Physical and spectroscopic properties

As a solid, the title compound is stable for months at ambient temperature. The UV spectrum in dich-

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TABLE 1. Experimental data for the crystallographic analysis of 1

Formula	$C_{28}H_{68}Cl_6N_4O_2Pt_2$
Molecular weight	1063.8
Crystal system	triclinic
Space group	$P\bar{1}$
a (Å)	8.463(3)
b (Å)	11.174(2)
c (Å)	23.075(3)
α (°)	79.98(1)
β (°)	80.44(3)
γ (°)	82.14(3)
V (Å^3)	2106(3)
Z	2
ρ_{calc} (g cm^{-3})	1.68
Reflections for lattice parameters: no., range	25, 14–15
$F(000)$	1076
μ (cm^{-1})	71.1
Temperature (°C)	18
Crystal size (mm)	0.65×0.20×0.20
Diffractometer	Nonius CAD4
Radiation	Mo Kα
Monochromator	graphite
Scan type	ω–2θ
Scan width	$1+0.34\tan\theta$
θ range (°)	1–25
Standard reflections	two, measured every 2 h
No. measured reflections	7386
No. reflections used $I \geq 3\sigma(I)$	4811
Min.–max. height in final $\Delta\rho$ (e Å^{-3})	−1.40–1.65
No. of refined parameters	372
$R=[\Sigma\lvert\Delta F\rvert/\Sigma F_o]$	0.047
$R_w=[\Sigma w(\Delta F)^2/\Sigma wF_o^2]^{1/2}$	0.055
$w=1$	

loromethane did not change during 4 h. In methanol and water, it dissolves under simultaneous reduction to Pt metal. The fresh solution in DMF shows a clean UV spectrum analogous to that in dichloromethane, but after several hours the bands flatten indicating a slow degradation. The absorption bands seen in the DMF spectrum are as follows: 502s (8), 426s (32), 355 (157), 303 (135) (wavelength in nm; s = shoulder; ϵ values in M^{-1} cm^{-1} in parentheses). For comparison, we have synthesized the analogous ammine complex $NH_4[PtCl_3(NH_3)]\cdot H_2O$ [7]. The UV absorption spectrum in DMF is virtually identical with that of 1: 500s (11), 430s (27), 354 (180), 303 (112). The IR spectrum (KBr pellet) of 1 features, in the NH stretching region, a weak band at 3202 cm^{-1} with a shoulder at 3230 cm^{-1}. The fingerprint region is dominated by $NPr^n{}_4{}^+$ bands; assignment of the δNH absorptions was not attempted.

X-ray crystallography

The unit cell of $(NPr^n{}_4)_2[PtCl_3(\mu\text{-}N_2H_4)PtCl_3]\cdot C_4H_8O_2$ (Fig. 1) contains two platinum centers belonging to two crystallographically different, centrosymmetric dimers. The bond lengths and angles in the two dinuclear dianions are similar and are displayed in Fig. 2. See also 'Supplementary material'. There are no short intermolecular contacts.

The coordination geometry of platinum is approximately square planar, with bond angles ranging from 86.3 to 92.9°. The Pt–N and Pt–Cl bond lengths are within experimental error equal to those found in $K[PtCl_3(NH_3)]\cdot H_2O$ [8], except for Pt2–Cl5 (2.273(4) Å) which is slightly shorter than the other Pt–Cl bonds. The angle subtended by the Pt–N–N–Pt plane and the coordination planes is 123.8° for dianion 1 and 134.7° for dianion 2. Both dianions exhibit intramolecular N–H---Cl hydrogen bonding connecting one chloride ligand with the remote NH_2 group (Fig. 3). With hydrogen atoms H11 and H12 (dianion 1), and H21 and H22 (dianion 2) introduced in tetrahedral arrangement at a distance of 1.0 Å from the hydrazine nitrogens, the hydrogen bonding geometries are as follows (see Fig. 2 for atom numbering).

Dianion 1: Cl3′–N1 = 3.24 Å; Cl3′–H12 = 2.61 Å; Cl3′–H12–N1 = 121°; Pt1–Cl3′–H12 = 78°.

Dianion 2: Cl6″–N2 = 3.12 Å; Cl6″–H22 = 2.48 Å; Cl6″–H22–N2 = 122°; Pt2–Cl6″–H22 = 80°.

Discussion

$[PtCl_3L]^-$ complexes have been used for comparisons of the *trans* and *cis* influences of ligands [9] as well as for the calculation of ligand field parameters [10, 11]. $PtCl_3L$ is probably the ideal chromophore for investigations of d–d bands in platinum(II) complexes, since (i) the d–d bands occur at relatively low energies (due to the three Cl ligands keeping the ligand field weak); and, (ii) ligand-to-metal electron transfer as well as Rydberg transitions occur at higher energies than in chromophores with more than one L ligand, and thus do not obscure the d–d bands. The $PtCl_3N$ chromophore is particularly suitable for spectroscopic studies since the ligand field spectrum is completely separated from the high intensity bands. Thus, detailed spectroscopic work on the anions $[PtCl_3(NH_3)]^-$ and $[PtCl_3(NMe_3)]^-$ has shown that trimethylamine produces a weaker ligand field that ammonia [10, 11]. In a similar way, we compared the DMF solution spectrum of 1 with that of $NH_4[PtCl_3(NH_3)]$. In a rough reasoning, we expected that in hydrazine, the electron withdrawing effect of the nitrogen atom, increased by its coordination to platinum, would

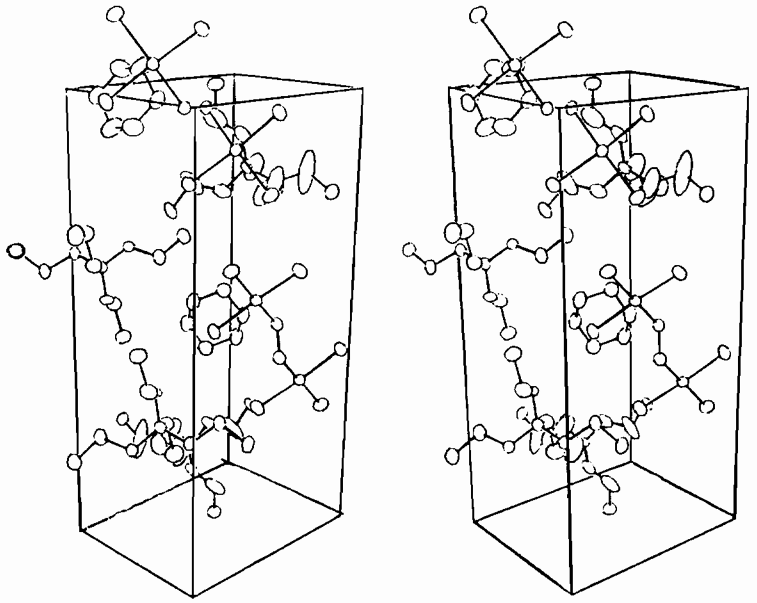

Fig. 1. Stereoview of the unit cell of $(NPr^n_4)_2[PtCl_3(\mu\text{-}N_2H_4)PtCl_3]\cdot C_4H_8O_2$.

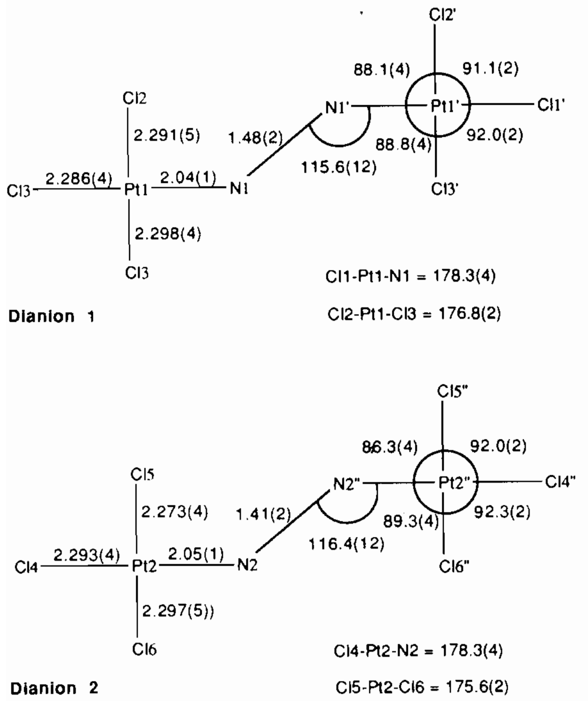

Fig. 2. Bond distances and angles in the two independent dianions of $(NPr^n_4)_2[Pt_2Cl_6(\mu\text{-}N_2H_4)]\cdot C_4H_8O_2$. Atoms X′ are related bo X by $-x$, $1-y$, $1-z$; atoms X″ by $-x$, $-y$, $-z$.

weaken the donor ability of the other nitrogen. Thus, bridging hydrazine would be expected to produce a weaker ligand field than ammonia. In contrast to this prediction, the ligand field spectra of **1** and $NH_4[PtCl_3(NH_3)]$ are virtually identical, demonstrating that the ligand fields of ammonia and bridging hydrazine are within experimental error equal. Related to this finding may be the intramolecular N–H--Cl hydrogen bonding in the hydrazine compound (Fig. 3), which enhances the polarization of the N–H bonds and increases thus the negative charge on the N atoms. This effect could compensate for the aforementioned electron withdrawal.

Similar donor strengths of bridging hydrazine and ammine are also inferred from the Pt–N bond lengths that are not significantly different in **1** (2.045 ± 0.015 Å) and in $K[PtCl_3(NH_3)]\cdot H_2O$ (2.06 ± 0.02 Å). The mean values for Pt–Cl(*trans* to N) and for Pt–Cl(*trans* to Cl) are both 2.29 Å, showing that the *trans* influence of bridging hydrazine is very close to that of chloride. A similar result has been recently found for the hydrazine-bridged complex, *cis,cis*-$[PtCl(PBu^n_3)_2(\mu\text{-}N_2H_4)PtCl(PBu^n_3)_2](ClO_4)_2$ [12], in which the Pt–P(*trans* to N) and Pt–P(*trans* to Cl) bond lengths are also nearly identical.

The N–N distances in the two crystallographically distinguished dianions are significantly different (1.48 ± 0.02 and 1.41 ± 0.02 Å, respectively); we have no explanation for this difference. In the only other two metal compounds featuring a single hydrazine bridge crystallographically characterized so far, $(NBu^n_4)_2[Fe(S_2C_6H_4)_2(\mu\text{-}N_2H_4)Fe(S_2C_6H_4)_2]$ [13] and *cis,cis*-$[PtCl(PBu^n_3)_2(\mu\text{-}N_2H_4)PtCl(PBu^n_3)_2](ClO_4)_2$ [12], the N–N distances are 1.42 ± 0.02 and

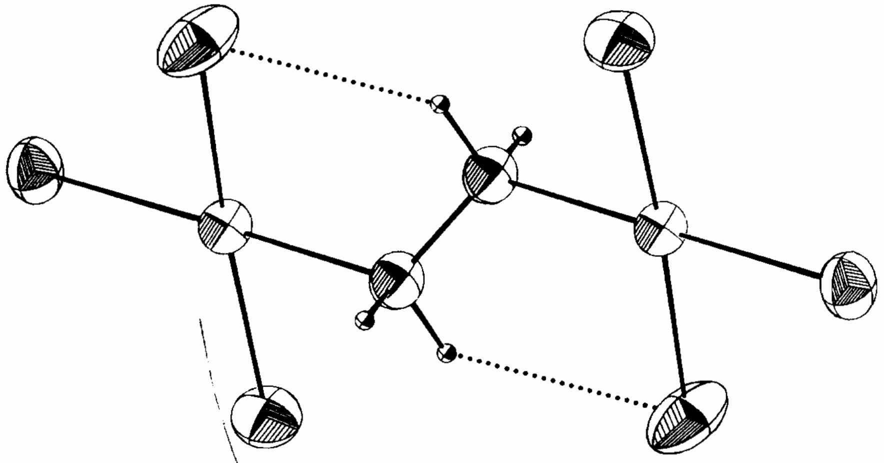

Fig. 3. ORTEP drawing (30% ellipsoids) of dianion 2 displaying the N–H---Cl hydrogen bonding.

1.41 ± 0.02 Å, respectively. The N–N separations in the latter two structures are thus similar to the shorter distance found in 1. On the other hand, in complex compounds with multiple hydrazine bridges, of which several examples are known, the N–N bond length ranges between 1.45 and 1.48 Å [14]. There seems thus to exist a fair variance in the N–N bond length in metal complexes with bridging hydrazine.

If a hydrazine molecule is attached to a metal atom bearing a chloride ligand, the β nitrogen of the hydrazine molecule can form a hydrogen bond to that chloride. Such a hydrogen bond is observed in both dianions present in the crystals of 1. It seems to constrain the dihedral angle between the Pt–N–N–Pt plane and the platinum coordination planes to a value near 120°. In *cis,cis*-$[PtCl(PBu^n_3)_2(\mu\text{-}N_2H_4)PtCl(PBu^n_3)_2](ClO_4)_2$, where a similar hydrogen bonding is present, this dihedral angle is 123° [12].

We wish to emphasize the formal similarity between dinuclear complexes containing a $Pt(\mu\text{-}NH_2\text{-}NH_2)Pt$ core and previously reported $Pt(\mu\text{-}NH_2)_2Pt$ complexes [15]. The two classes of compounds differ in the oxidation state of the bridging nitrogens and in the number of bridges. In one reported case, a diamido-bridged complex has been obtained from *cis*-$[PtCl_2(PPh_3)_2]$ and hydrazine hydrate [16]. In fact, in view of the structural similarity between the two classes, one may ask whether it would not be possible to convert one class into the other, e.g. to obtain a hydrazine-bridged compound by a mild oxidation of a diamido-bridged complex.

Platinum complexes have been used as potent anticancer drugs, the major cellular target of which is believed to be DNA [17]. One idea behind the synthesis of platinum hydrazine compounds was to create species with interesting DNA-binding properties. A dinuclear platinum complex with a short bridge could bind to two adjacent nucleobases of DNA without major structural perturbation of the helix, a binding mode that is not possible with mononuclear complexes. Unfortunately, the instability of the present compound in water precludes its utilization in biological systems.

Supplementary material

Fractional atomic coordinates, thermal parameters, and calculated and observed structure factors can be obtained from the authors on request.

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