

CRYSTAL STRUCTURE OF DI- μ -AMIDO- bis[DIAMMINEPLATINUM(II)] NITRATE

Q.-S. Ye¹, M.-J. Xie², X.-N. Li³, W.-P. Liu^{1*},
J. Yu¹, Q.-W. Chang¹, J. Jiang¹, C.-X. Yan¹,
and J. Li¹

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Di- μ -amido-bis[diammineplatinum(II)] nitrate (**1**) was synthesized as a byproduct during preparation of tetraammineplatinum(II) nitrate. One possible pathway to produce **1** is that $[(\text{H}_3\text{N})_2\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{NH}_3)_2](\text{NO}_3)_2$, a well-known complex forming on treatment of *cis*-Pt(NH₃)₂I₂ with AgNO₃, reacts with aqueous ammonia. The other possible pathway involves deprotonation of $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$ to form monomeric Pt(NH₃)₃(NH₂)NO₃ followed by elimination of NH₃. Crystals of **1** (from water) are monoclinic (C2/c) with $a = 16.834(2)$ Å, $b = 10.573(1)$ Å, $c = 7.415(1)$ Å, $\beta = 114.846(1)^\circ$, and $Z = 4$. The cationic portion consists of two symmetrical square-planar Pt centers with the inversion center at the midpoint of the Pt(1)···Pt(1A) vector. The Pt(II) ion is coordinated by four N atoms from two ammonia molecules and two bridging amido groups affording a slightly distorted square. The molecules are stacked in such a way that the planes of coordination squares turn out to be parallel to each other with a distance of 3.501 Å. Intermolecular Pt–H interaction between the μ -NH₂ hydrogens and the platinum(II) centers of the adjacent molecule are observed.

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The synthesis and chemistry of platinum(II) amido complexes have attracted interest for their relevance to the formation of C–N bonds in synthesis and catalysis [1-3]. An amido-bridged diplatinum(II) complex, $[(\text{Ph}_3\text{P})_2\text{Pt}(\mu\text{-NH}_2)_2\text{Pt}(\text{PPh}_3)](\text{BPh}_4)_2$, which was obtained by reaction of Pt(PPh₃)Cl₂ with 85% aqueous hydrazine followed by addition of sodium tetraphenylborate, was first reported in 1967 by Mason et al [4]. After this report several amido-bridged diplatinum(II) complexes containing phosphine ligands were synthesized by treatment of L₂PtCl₂ (L = phosphine ligand) with a strong base in liquid ammonia [5, 6], by reaction of hydroxo-bridged diplatinum(II) complexes with ammonia/amine [7-9], or by deprotonation of the corresponding monomeric platinum(II) complexes [10, 11]. As compared to the systematic investigation of amido-bridged diplatinum(II) complexes containing phosphine ligands, less information is available about the platinum(II) complexes containing the ammine ligands. The only reported complex of this type was a tetravalent diplatinum complex, $[(\text{H}_3\text{N})_4\text{Pt}(\mu\text{-NH}_2)_2\text{Pt}(\text{NH}_3)_4]^{6+}$, which was prepared in 1982 by Kretsohmer and Heck and characterized by single-crystal X-ray structural analysis [12, 13]. However, the obvious divalent analog, $[(\text{H}_3\text{N})_2\text{Pt}(\mu\text{-NH}_2)_2\text{Pt}(\text{NH}_3)_2]^{2+}$, to

¹State Key Lab of Advanced Technologies for PGM, Kunming Institute of Precious Metals, Kunming 650106, P. R. China; *liuweiping0917@126.com. ²Department of Chemistry, Yunnan University, Kunming 650031, P. R. China. ³Analysis and Test Center, State Key Laboratory of Phytochemistry and Plant Resources in West China, Kunming Institute of Botany, Chinese Academy of Sciences, Kunming 650201, P. R. China. The text was submitted by the authors in English. *Zhurnal Strukturnoi Khimii*, Vol. 57, No. 4, pp. 882-885, May-June, 2016. Original article submitted April 6, 2015.

TABLE 1. Bond Lengths (d , Å), Bond Angles (ω , deg) for Complex **1**

Bond	d	Angle	ω
Pt(1)–N(1)	2.051(7)	N(1)–Pt(1)–N(2)	89.9(3)
Pt(1)–N(2)	2.065(7)	N(1)–Pt(1)–N(3)	94.3(3)
Pt(1)–N(3)	2.032(6)	N(2)–Pt(1)–N(3A)	94.9(3)
Pt(1)–N(3A)	2.049(6)	N(3)–Pt(1)–N(3A)	80.8(3)
Pt(1)–Pt(1A)	3.1074(6)	N(1)–Pt(1)–N(3A)	174.3(3)
N(4)–O(1)	1.229(9)	N(2)–Pt(1)–N(3)	175.7(3)
N(4)–O(2)	1.255(9)	Pt(1)–N(3)–Pt(1A)	99.2(3)
N(4)–O(3)	1.226(9)	O(1)–N(4)–O(2)	119.5(9)
		O(1)–N(4)–O(3)	120.0(8)
		O(2)–N(4)–O(3)	120.5(8)

Symmetry transformations used to generate equivalent atoms: A: $-x, -y+1, -z$.

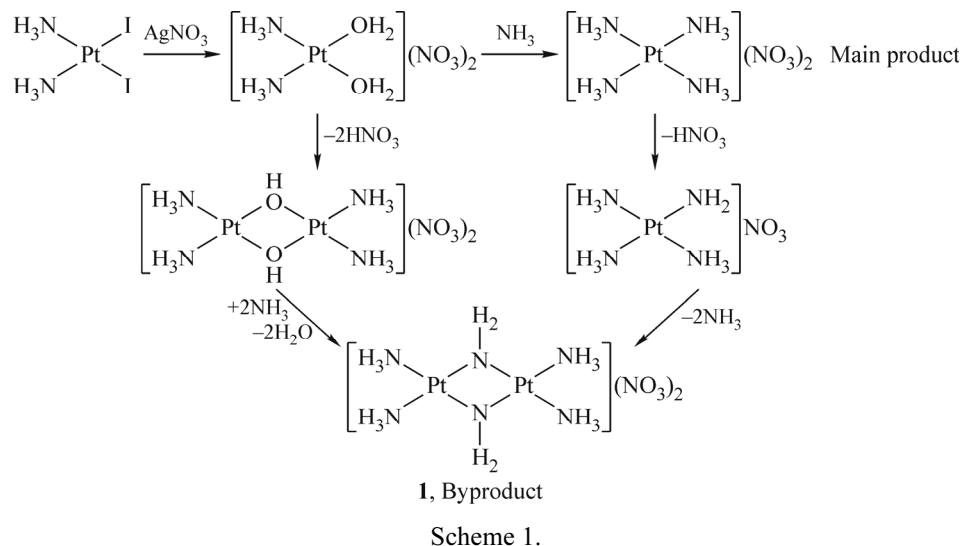
the best of our knowledge, has not been reported until now. This is surprising since the similar hydroxo-bridged complex, $[(\text{H}_3\text{N})_2\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{NH}_3)_2]^{2+}$, has been widely studied in the literature [14–16]. In the present paper, we report the synthesis and crystal structure of $[(\text{H}_3\text{N})_2\text{Pt}(\mu\text{-NH}_2)_2\text{Pt}(\text{NH}_3)_2](\text{NO}_3)_2$ (**1**).

Synthesis of di- μ -amide-bis[diammineplatinum(II)] nitrate (1**).** The complex was accidentally obtained in the preparation of tetraammineplatinum(II) nitrate. Namely, a solution of 14.0 g of AgNO_3 (41.2 mmol) in 30 mL of deionized water was added to a suspension of *cis*- $\text{Pt}(\text{NH}_3)_2\text{I}_2$ (20.0 g, 41.4 mmol) in 100 mL of deionized water, and the mixture was stirred at 40° for 5 h. After AgI formed was filtered off, 50 mL of concentrated aqueous ammonia solution ($\geq 25\%$) was added to the yellowish filtrate. The solution was stirred for 30 min at room temperature and then concentrated to 20 mL at 50° under reduced pressure. The white $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ precipitated was filtered off. The yellow filtrate was allowed to evaporate slowly at room temperature. In two weeks white crystals along with a small amount of brownish-yellow prisms precipitated. The brownish-yellow prisms were mechanically separated from the mixture. Yield: 65 mg (0.5%). Anal. Calcd. for $\text{H}_{16}\text{N}_8\text{O}_6\text{Pt}_2$: H 2.63, N 18.24. Found: H 2.6, N 18.1.

X-ray diffraction analysis. Single crystals of **1** were obtained as described above. Intensity data for a single crystal (size $0.23 \times 0.17 \times 0.10$ mm) were collected at room temperature on a BRUKER SMART APEX II equipped with a CCD detector using graphite-monochromated MoK_α radiation ($\lambda = 0.071073$ nm) in the θ range from 2.34° to 28.0° . In total, 4380 reflections were measured. Crystallographic data: $a = 16.834(2)$ Å, $b = 10.573(1)$ Å, $c = 7.415(1)$ Å, $\beta = 114.846(1)^\circ$, space group $C2/c$, $V = 1197.6(2)$ Å³, $Z = 4$, $d_{\text{calc}} = 3.408$ g/cm³. The crystal structure was solved by the direct method. The crystalline phase has the composition $\text{Pt}_2(\text{NH}_3)_4(\text{NH}_2)_2(\text{NO}_3)_2$. Final full-matrix refinement on 1383 independent reflections led to $R_1 = 0.0358$ ($wR_2 = 0.0947$). For 1233 reflections with $I > 2\sigma(I)$: $R_1 = 0.0400$ ($wR_2 = 0.0976$). The S -factor against F^2 is 1.069. All calculations were made using the SHELXTL-97 software [17]. The CIF file with complete information about the structure was deposited at CCDC (No. 1039311), from which it is available free of charge on request at <https://summary.ccdc.cam.ac.uk/structure-summary-form>. Selected bond lengths and angles are given in Table 1.

Results and discussion. In our preparation process of $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ (Scheme 1), a yellow solution was always found at the final stage of the reaction, along with the white $\text{Pt}(\text{NH}_3)_4(\text{NO}_3)_2$ product contaminated with brownish yellow byproduct. So we tried to separate the brownish yellow byproduct by recrystallization from water. After several attempts we obtained a mixture of brownish yellow crystal prisms and white crystals. The prisms (**1**) were mechanically picked out as much as possible.

Two possible pathways to form **1** are illustrated in Scheme 1. The first pathway begins with *cis*- $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$, which is partially converted to the hydroxo-bridged diplatinum(II) complex $[(\text{H}_3\text{N})_2\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{NH}_3)_2](\text{NO}_3)_2$, then the hydroxo-bridged complex reacts with aqueous ammonia to afford **1**. This pathway is supported by the well-known formation of $[(\text{H}_3\text{N})_2\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{NH}_3)_2](\text{NO}_3)_2$ from *cis*- $[\text{Pt}(\text{NH}_3)_2(\text{H}_2\text{O})_2](\text{NO}_3)_2$ aqueous



solution [14, 15] and several reports on conversion of hydroxo-bridged diplatinum(II) complexes to amido-bridged diplatinum(II) complexes with aqueous ammonia [7-9]. The second pathway begins with $[\text{Pt}(\text{NH}_3)_4](\text{NO}_3)_2$, where the ammine ligand is deprotonated to produce monomeric $\text{Pt}(\text{NH}_3)_3(\text{NH}_2)\text{NO}_3$ followed by elimination of NH_3 to form the dimer **1**. Some support is found in the fact that two amido-bridged diplatinum(IV) complexes, $[(\text{H}_3\text{N})_4\text{Pt}(\mu\text{-NH}_2)_2\text{Pt}(\text{NH}_3)_4]\text{Cl}_6$ [12, 13] and $[(\text{H}_3\text{N})_4\text{Pt}(\mu\text{-NH}_2)_2\text{Pt}(\text{NH}_3)_4][\text{Au}(\text{CN})_2]_6$ [18], were obtained from aqueous solution of $[\text{Pt}(\text{NH}_3)_6]\text{Cl}_4$ in the presence or absence of strong bases. Both pathways are plausible and are supported by several observations of similar reactions. Currently, we are not sure which pathway is correct. But in the absence of detailed mechanism for the second pathway, we favor the formation of amido-bridged complex **1** through the first pathway.

Complex **1** was first characterized by single-crystal X-ray structural analysis. The complex contains a dimer of square-planar $(\text{NH}_3)_2\text{Pt}(\text{NH}_2)_2$ units, the Pt(II) atoms being held together by bridging NH_2 units (Fig. 1), which is very similar to the hydroxo-bridged dimer $[(\text{H}_3\text{N})_2\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{NH}_3)_2](\text{NO}_3)_2$. However, the single-crystal X-ray diffraction study does not provide unequivocal evidence that **1** is not actually the hydroxo-bridged dimer $[(\text{H}_3\text{N})_2\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{NH}_3)_2](\text{NO}_3)_2$, although there are obvious differences of color and crystal system between **1** and $[(\text{H}_3\text{N})_2\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{NH}_3)_2](\text{NO}_3)_2$ (white color and triclinic for $[(\text{H}_3\text{N})_2\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{NH}_3)_2](\text{NO}_3)_2$; brownish-yellow color and monoclinic for **1**) [14]. In order to confirm the presence of bridging amido groups in **1**, its elemental analysis for H and N was carried out. The results are in good agreement with the calculated values, what offers strong evidence for the amido-bridging groups rather than hydroxo-bridging groups in **1**.

A view of the cationic portion of **1**, $[(\text{NH}_3)_2\text{Pt}(\text{NH}_2)_2\text{Pt}(\text{NH}_3)_2]^{2+}$ with the atomic labeling scheme is given in Fig. 1. The Pt(II) atom is coordinated by four N atoms constituting a slightly distorted square, the atoms belonging to two amines

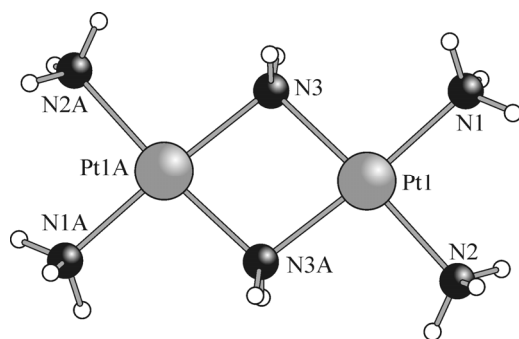


Fig. 1. A view of $[(\text{NH}_3)_2\text{Pt}(\text{NH}_2)_2\text{Pt}(\text{NH}_3)_2]^{2+}$ cation with the atomic labeling scheme.

and two amides, with the platinum atom at 0.033 Å out of the mean plane defined by the four donor atoms. In fact, all the non-hydrogen atoms of the cation $[(\text{NH}_3)_2\text{Pt}(\text{NH}_2)_2\text{Pt}(\text{NH}_3)_2]^{2+}$ are in the mean plane since the molecule is centrosymmetric at the midpoint of the Pt(1)···Pt(1A) vector. This is different from the amido-bridged diplatinum(II) complexes with phosphine ligands, which have a fold angle of 136–148° between the two coordination planes [5–7, 11], but is similar to the structure of the diplatinum(IV) complex containing $[(\text{H}_3\text{N})_4\text{Pt}(\mu\text{-NH}_2)_2\text{Pt}(\text{NH}_3)_4]^{6+}$ core [13].

As shown in Table 1, the Pt–N–Pt bridge distances are slightly unsymmetrical with the Pt(1)–N(3) and Pt(1)–N(3A) distances of 2.032(6) and 2.049(6) Å, respectively. The average Pt–N (ammine) distance (2.058 Å) is 0.017 Å longer than the Pt–N (amido) distance (2.041 Å), consistent with the lower electron density of NH_3 as compared to NH_2 . The Pt(1)–Pt(1A) distance is 3.1074(6) Å, what is longer than expected for any significant Pt–Pt interaction. The N–Pt–N angles are close to 90° and the sum of the four bond angles is 359.9°.

It is useful to compare the structure of **1** with the previous study of $[(\text{H}_3\text{N})_2\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{NH}_3)_2](\text{NO}_3)_2$ [14]. Of considerable interest is the fact that the two complexes crystallize in different unit cells (monoclinic vs. triclinic), although their structural parameters are very close. Moreover, the average Pt–N (ammine) distance of **1** (2.058 Å) significantly increases by 0.043 Å as compared to the value in $[(\text{H}_3\text{N})_2\text{Pt}(\mu\text{-OH})_2\text{Pt}(\text{NH}_3)_2](\text{NO}_3)_2$ (2.015 Å) [14], indicating the relative trans influence $\text{NH}_2 > \text{OH}$.

The crystal packing of **1** is stabilized by N–H···O hydrogen bonds. All hydrogen atoms of NH_3 ligands are involved in moderate to strong hydrogen bonding interactions with nitrate oxygen atoms, linking the molecules in stacks in such a way that the planes of coordination squares turn out to be parallel to each other with the distances of 3.501 Å; they are connected by additional N–H···O interactions to afford a three dimensional network. Moreover, a long-range intermolecular agostic interaction between the $\mu\text{-NH}_2$ hydrogens and the platinum(II) centers of the adjacent molecule (Pt(1)···H(3B), 2.8054(5) Å) further stabilize the stacking.

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REFERENCES

1. J. L. McBee, A. T. Bell, and T. D. Tilley, *J. Am. Chem. Soc.*, **130**, 16562–16571 (2008).
2. H. E. Bryndza and Tam W., *Chem. Rev.*, **88**, 1163–1188 (1988).
3. M. D. Fryzuk and C. D. Montgomery, *Coord. Chem. Rev.*, **95**, 1–40 (1989).
4. G. C. Dobinson, R. Mason, and G. B. Robertson, *Chem. Commun.*, 739–741 (1967).
5. N. W. Alcock, P. Bergamini, T. J. Kemp, and P. G. Pringle, *J. Chem. Soc., Chem. Commun.*, 235/236 (1987).
6. C. A. O'Mahoney, I. P. Parkin, D. J. Williams, and J. D. Woollins, *Polyhedron*, **8**, 1979–1981 (1989).
7. N. W. Alcock, P. Bergamini, T. J. Kemp, P. G. Pringle, S. Sostero, and O. Traverse, *Inorg. Chem.*, **30**, 1594–1598 (1991).
8. J. J. Li, W. Li, A. J. James, T. Holbert, T. P. Sharp, and P. R. Sharp, *Inorg. Chem.*, **38**, 1563–1572 (1999).
9. S. Kannan, A. J. James, and P. R. Sharp, *Polyhedron*, **19**, 155–163 (2000).
10. S. Park, A. L. Rheingold, and D. M. Roundhill, *Organometallics*, **10**, 615–623 (1991).
11. S. Park, D. M. Roundhill, and A. L. Rheingold, *Inorg. Chem.*, **26**, 3972–3974 (1987).
12. V. M. Kretschmer and L. Heck, *Z. Anorg. Allg. Chem.*, **490**, 205–214 (1982).
13. V. M. Kretschmer and L. Heck, *Z. Anorg. Allg. Chem.*, **490**, 215–229 (1982).
14. R. Faggiani, B. Lippert, C. J. L. Lock, and B. Rosenberg, *J. Am. Chem. Soc.*, **99**, 777–781 (1977).
15. B. Lippert, C. J. L. Lock, B. Rosenberg, and M. Zvagulis, *Inorg. Chem.*, **16**, 1525–1529 (1977).
16. B. Lippert, C. J. L. Lock, B. Rosenberg, and M. Zvagulis, *Inorg. Chem.*, **17**, 2971–2975 (1978).
17. G. M. Sheldrick, *Acta Crystallogr.*, **A64**, 112–122 (2008).
18. D. M. Pham, D. Rios, M. M. Olmstead, and A. L. Balch, *Inorg. Chim. Acta*, **358**, 4261–4269 (2005).