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# $N,N$-Dimethylacetamide Adducts of Mixed Iodo–Ammine Complexes of Platinum(II) and Platinum(IV)

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## Abstract

As a route to purify mixed iodo–ammine complexes of Pt, the $N,N$-dimethylacetamide (DMA) solvates *cis*-$(NH_3)_2PtI_2 \cdot DMA$, *trans*-$(NH_3)_2PtI_2 \cdot 3DMA$, *cis*- and *trans*-$(NH_3)_2PtI_4 \cdot 3DMA$, and the mixed-valence compound *cis*-$(NH_3)_2PtI_2 \cdot$*cis*-$(NH_3)_2PtI_4 \cdot 2DMA$ were prepared. Crystals of *cis*-$(NH_3)_2PtI_2 \cdot DMA$ are monoclinic, $P2_1/c$, $a = 8.443(4)$, $b = 12.691(6)$, $c = 12.150(9)$ Å, $\beta = 105.12(7)$ Å, $Z = 4$. The structure was solved on 2035 unique Mo K$\bar{\alpha}$ reflections to $R = 0.044$. The compound reveals well separated square planar *cis*-$(NH_3)_2PtI_2$ and DMA units. The crystals are unstable to loss of DMA. A three-dimensional hydrogen-bonding network involving the ammines, the iodine atoms, and the carbonyl groups of DMA determines the crystal structure. The infrared spectra indicate that the DMA molecule is not coordinated to platinum in these compounds.

## Introduction

Recrystallization of mixed halogen–ammine complexes of platinum from substituted formamides appears to be a suitable route to effectively purify the complex and/or obtain single crystals for structural work, as has recently been shown by us in the case of the antitumor agent *cis*-$(NH_3)_2PtCl_2$, Cisplatin, and its iodo derivative [1, 2]. In continuation of this work, we have also studied the formation of $N,N$-dimethylacetamide (DMA) adducts of several mixed iodo-ammine complexes of Pt(II) and Pt(IV), which we report here together with the X-ray structure of one DMA adduct, *cis*-diiododiammineplatinum(II)$N,N$-dimethylacetamide solvate, *cis*-$(NH_3)_2PtI_2 \cdot (CH_3)_2NCOCH_3$.

## Experimental

### Preparation

*cis*-$(NH_3)_2PtI_2$ was prepared according to Dhara [3], *trans*-$(NH_3)_2PtI_2$ according to Nakamoto *et al.* [4] from *trans*-$(NH_3)_2PtCl_2$ [5].

*cis-$(NH_3)_2PtI_2 \cdot DMA$ (1)*

250 mg of crude *cis*-$(NH_3)_2PtI_2$ were dissolved in 5.5 ml DMA at room temperature, filtered from any undissoved material and layered with 11 ml of ether. After 24 h at 4 °C, 60 mg of **1** (orange cubes) were collected on a filter and briefly dried in air. After addition of another 20 ml of ether to the resulting solution, a second crop (60 mg) of **1** was obtained. The crystals are air-stable for up to 48 h at room temperature, then gradually lose DMA. *Anal.* Calc. for $(NH_3)_2PtI_2 \cdot C_4H_9NO$: C, 8.43; H, 2.66; N, 7.37. Found: C, 8.59; H, 2.79; N, 7.58%.

*trans-$(NH_3)_2PtI_2 \cdot 3DMA$ (2)*

120 mg of crude *trans*-$(NH_3)_2PtI_2$ were dissolved in 4 ml DMA, and 6 ml ether were added. After 1 d at 4 °C, 80 mg (43% yield) of **2** (yellow needles) were filtered off and briefly dried in air. The crystals rapidly lose DMA when kept in air. *Anal.* Calc. for $(NH_3)_2PtI_2 \cdot 3(C_4H_9NO)$: C, 19.36; H, 4.47; N, 9.41; Pt, 26.21. Found: C, 19.89; H, 4.57; N, 9.50; Pt, 25.7%.

*cis-$(NH_3)_2PtI_4 \cdot 3DMA$ (3)*

250 mg (0.52 mmol) of crude *cis*-$(NH_3)_2PtI_2$ were dissolved in 5.5 ml DMA, filtered from undissolved material, and 130 mg (0.52 mmol) solid $I_2$ were added to the yellow solution. Ether (20 ml) was added to the resulting brown solution, which was kept at 4 °C for 2 d. Almost black cubes (320 mg, 62% yield) were then filtered and briefly dried in air. The crystals gradually lose DMA in air. *Anal.* Calc. for $(NH_3)_2PtI_4 \cdot 3(C_4H_9NO)$: C, 14.44; H, 3.33; N, 7.02; I, 50.86; Pt, 19.54. Found: C, 14.66; H, 3.40; N, 7.17; I, 49.17; Pt, 19.5%.

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### *trans*-$(NH_3)_2PtI_4 \cdot 3DMA$ (4)

120 mg (0.25 mmol) of *trans*-$(NH_3)_2PtI_2$ were dissolved in 6 ml DMA and 60 mg (0.25 mmol) of solid $I_2$ was added. From the brown solution, **4** crystallized as tiny, almost black needles. After 1 d at 4 °C, 130 mg (52% yield) of **4** were collected. The crystals rapidly lose DMA in air. *Anal.* Calc. for $(NH_3)_2PtI_4 \cdot 3(C_4H_9NO)$: C, 14.44; H, 3.33; N, 7.02; Pt, 19.54. Found: C, 14.71; H, 3.39; N, 7.12; Pt, 19.4%.

### *cis*-$(NH_3)_2PtI_2 \cdot$*cis*-$(NH_3)_2PtI_4 \cdot 2DMA$ (5)

This compound was prepared in two ways:

(a) 1.14 g (2 mmol) of crude *cis*-$(NH_3)_2PtI_2$ were dissolved in 28 ml DMA and the solution filtered. Then 0.25 g (1 mmol) of solid $I_2$ was added and the brown solution layered with 220 ml ether. After 5 d at 4 °C, 140 mg of crystals having a metallic bronze lustre were collected, washed with 3 ml of ether, and briefly dried in air. Addition of two more portions of ether (80 and 100 ml) and subsequent cooling gave two additional crops of **5**. Total yield: 690 mg (50%). The crystals appear to be stable in air (*c.f.*, however, next section).

(b) 60 mg (0.1 mmol) of **1** and 100 mg (0.1 mmol) of **3** were each dissolved in 3 ml of DMA, the two solutions combined, and layered with 20 ml ether. After 3 d at 4 °C, crystals of **5** were collected on a filter. *Anal.* Calc. for '$(NH_3)_2PtI_3 \cdot C_4H_9NO$': C, 6.89; H, 2.17; I, 54.62; Pt, 27.99. Found: C, 7.24; H, 2.19; I, 53.30; Pt, 28.3%.

### *IR Spectra*

These were recorded on a Perkin-Elmer 580 grating spectrometer (Nujol mulls, CsI windows) between 4000 and 200 $cm^{-1}$.

### *X-ray Measurements*

Of all the compounds prepared, only *cis*-$(NH_3)_2PtI_2 \cdot DMA$ (**1**), proved to be sufficiently stable to permit a structure determination (*vide infra*). From the mixed-valence compound **5**, *cis*-$(NH_3)_2PtI_2 \cdot$*cis*-$(NH_3)_2PtI_4 \cdot 2DMA$, only the crystal data could be obtained prior to decomposition. They are as follows: monoclinic, space group $P2$, $Pm$ or $P2/m$, $a = 10.848$, $b = 6.167$, $c = 10.910$ Å, $\beta = 104.3°$.

The crystal data for compound **1** are: $C_4H_{15}I_2N_3OPt$, $M_r = 570.1$, monoclinic, $P2_1/c$, $a = 8.443(4)$, $b = 12.691(6)$, $c = 12.150(9)$ Å, $\beta = 105.12(7)°$, $V = 1256.8$ Å$^3$, $Z = 4$, $D_m = 3.01(1)$ g cm$^{-3}$, $D_c = 3.012$ g cm$^{-3}$, $F(000) = 1008$, $\lambda$(Mo K$\alpha$) = 0.71069 Å (graphite-monochromated), $\mu$(Mo K$\alpha$) = 161.2 cm$^{-1}$, $T = 296$ K, crystal faces and dimensions (in mm from an arbitrary point: $01\bar{1}$ (0.148), $0\bar{1}1$ (0.131), $\bar{1}\bar{1}0$ (0.000), 110 (0.442), $10\bar{2}$ (0.238), $\bar{1}02$ (0.000), $0\bar{1}\bar{1}$ (0.136), 011 (0.153), $\bar{1}12$ (0.000), $1\bar{1}\bar{1}$ (0.326).

The $P2_1/c$ space group was uniquely determined from the Laue symmetry and systematic absences ($h0l$, $l \neq 2n$; $0k0$, $k \neq 2n$) noted on precession photographs. The crystal was transferred to an Enraf-Nonius CAD-4 diffractometer, which was used to obtain accurate cell parameters and collect the intensity data. The autoindexing procedure on 25 centered Mo K$\alpha$ reflections ($6.1 < 2\theta < 30.5°$) randomly distributed in the reflection sphere yielded the same unit cell as deduced from films. The cell parameters given above were obtained by least-squares fit on the setting angles for these 25 reflections.

The intensity data were collected as described elsewhere [6]. The three standard reflections measured every hour showed random fluctuation (esd = 2.5%) during data collection. A total of 2486 Mo K$\alpha$ intensity data were collected, including 310 zero or systematically absent reflections. The remaining 2176 measurements included 141 pairs of symmetry equivalent reflections which were averaged (agreement factor = 4.2%). The final data set consisted of 2035 unique non-zero reflections, of which 299 having $I/\sigma(I) < 3$ were not used in the refinement. The data were corrected for the Lorentz effect, polarization and absorption (Gaussian integration, transmission range = 0.042–0.095).

The Pt atom was located from a Patterson synthesis, whereas the remaining non-hydrogen atoms were determined by standard structure-factor and difference-Fourier ($\Delta F$) calculations. The non-hydrogen atoms were anisotropically refined on $|F_o|$ by full-matrix least squares. Five H atoms each bound to a different atom were found in the $\Delta F$ map weighted with low-angle data. The remaining H-atom positions were calculated. The hydrogen coordinates were refined in conjunction with one isotropic hydrogen temperature factor for each molecule. These hydrogen parameters were then fixed at the refined values for the final cycles of refinement. Weights $w = (\sigma_F^2 + 0.00146|F_o|^2)^{-1}$ were applied in the final stage. Convergence was reached with $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.044$, $R_w = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2} = 0.061$, and a goodness-of-fit ratio of 1.37 for 101 parameters varied. The maximum and average shift/error ratio in the final cycle were 0.028 and 0.006, respectively. The final $\Delta F$ map showed a maximum residual peak of 3.0 e Å$^{-3}$ and deepest valley of $-1.5$ e Å$^{-3}$, both near Pt. Calculations were carried out using the SHELX package [7]. ORTEP II [8] was used for the drawings. The atomic scattering factors not supplied in the program were from International Tables [9], as were the anomalous-dispersion corrections [10]. The final atomic positional coordinates and equivalent isotropic temperature factors are listed in Table I*.

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*See also Supplementary Material.

TABLE I. Atomic Positional Parameters ($\times 10^3$, Pt $\times 10^5$, I $\times 10^4$) and Equivalent Isotropic Temperature Factors ($Å^2$) ($\times 10^3$)

| Atom | $x$ | $y$ | $z$ | $U_{eq}$[a] |
|---|---|---|---|---|
| Pt | 86764(6) | 11956(4) | 45727(4) | 38 |
| I(1) | 8252(1) | 521(1) | 2500(1) | 57 |
| I(2) | 10568(1) | 2716(1) | 4310(1) | 62 |
| N(1) | 894(2) | 169(1) | 622(1) | 57 |
| N(2) | 721(2) | −4(1) | 487(1) | 54 |
| O(1) | 591(1) | 419(1) | 171(1) | 74 |
| N(3) | 538(2) | 346(1) | 323(1) | 74 |
| C(1) | 607(2) | 413(2) | 280(2) | 79 |
| C(2) | 712(3) | 502(2) | 359(2) | 88 |
| C(3) | 439(2) | 266(2) | 252(2) | 77 |
| C(4) | 546(3) | 342(2) | 447(1) | 84 |

[a] $U_{eq} = (1/3)(U_{11} + U_{22} + U_{33} + 2U_{13} \cos \beta)$

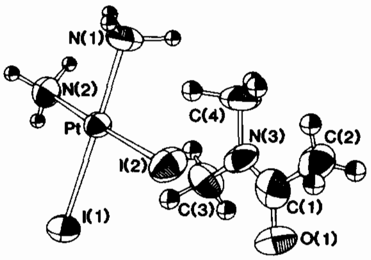

Fig 1. The labelling of the $cis$-$(NH_3)_2PtI_2$ and the dimethylacetamide molecules The ellipsoids correspond to 50% probability, except for the hydrogen atoms (unlabelled), which have been reduced by a factor of 14. The projection corresponds to the lower left corner of Fig. 2.

## Discussion

The Pt complex **1**, $cis$-$(NH_3)_2PtI_2 \cdot DMA$, is illustrated in Fig. 1 with the atom labels defined. The interatomic distances and bond angles are listed in Table II. The DMA moiety is neutral and planar (maximum deviation is for C(4) and C(1). 0.03(2) Å), and is not coordinated to the Pt atom. The interatomic distances and angles are all within the ranges of previously published values for non-coordinated DMA [11–15].

The $(NH_3)_2PtI_2$ molecule has a slight tetrahedral distortion, with the ammines ±0.04(1) Å out of the plane. The Pt–N bond distances (2.05(1) and 2.10(1) Å) are normal [16], as are the Pt–I distances (2.595(1) and 2.577(1) Å [17]. The I(1)–Pt–I(2) angle (93.40(4)°) is significantly greater than 90°, which aids in increasing the intramolecular I(1)···I(2) separation to 3.765(1) Å.

The crystal packing is shown in Fig. 2. It reveals stable groups of two $Pt(NH_3)_2I_2$ and two DMA molecules bound via hydrogen-bonding of the O(1) atoms to the ammines (shown in top face of cell). These dimeric units are bound to one another with weaker iodine–ammine intermolecular hydrogen-bonds. A Pt complex of one 'dimer' is hydrogen-bonded to another Pt complex which is related by an inversion center (0, 1/2, 0) or (0, 0, 1/2) as shown on the left side of Fig. 2. This type of $cis$-$Pt(NH_3)_2X_2$ pairing has been previously discussed [18, 19]. The H-bonded bridging by N(1) of the I(1) and I(2) atoms of a Pt complex in a third dimeric unit completes the three-dimensional hydrogen-bonding network.

TABLE II. Interatomic Distances (Å) and Angles (deg)

| | | | |
|---|---|---|---|
| Bonds | | | |
| Pt–I(1) | 2.595(1) | N(3)–C(1) | 1.23(2) |
| Pt–I(2) | 2.577(1) | C(1)–O(1) | 1.29(2) |
| Pt–N(1) | 2.05(1) | C(1)–C(2) | 1.59(3) |
| Pt–N(2) | 2.10(1) | N(3)–C(3) | 1.45(2) |
| | | N(3)–C(4) | 1.48(2) |
| Angles | | | |
| I(1)–Pt–I(2) | 93.40(4) | C(1)–N(3)–C(3) | 119(2) |
| I(1)–Pt–N(1) | 177.9(4) | C(1)–N(3)–C(4) | 124(2) |
| I(1)–Pt–N(2) | 89.0(3) | C(3)–N(3)–C(4) | 117(2) |
| I(2)–Pt–N(1) | 88.6(4) | N(3)–C(1)–O(1) | 123(2) |
| I(2)–Pt–N(2) | 177.1(3) | N(3)–C(1)–C(2) | 119(2) |
| N(1)–Pt–N(2) | 88.9(5) | O(1)–C(1)–C(2) | 118(2) |
| Possible hydrogen-bonds | | | |
| O(1)···N(1)$^{i}$ | 3.00(3) | I(1)···N(1)$^{i}$ | 3.97(2) |
| O(1)···N(2)$^{i}$ | 2.94(3) | I(1)···N(1)$^{iii}$ | 3.75(2) |
| O(1)···N(2)$^{ii}$ | 2.99(3) | I(2)···N(1)$^{i}$ | 3.73(2) |
| | | I(2)···N(2)$^{iii}$ | 3.88(2) |

Atoms related to those in Table I by:
(i) $x, -y, z -$ (ii) $1 - x, y +, -z$ (iii) $2 - x, -y, 1 - z$

The IR spectra of the five compounds prepared essentially represent superpositions of the spectra of the solvent-free complexes and of liquid DMA. Minor changes refer to shifts of DMA modes (*vide infra*) and of $NH_3$ modes, e.g. the deformation modes around 1300 $cm^{-1}$ (usually shifted by 10–20 $cm^{-1}$ to higher energy in the adducts), the rocking modes in the 750–800 $cm^{-1}$ range (shifted to higher energy in the adducts), and the Pt–$NH_3$ stretching modes below 500 $cm^{-1}$ (no uniform shift pattern). In $trans$-$(NH_3)_2PtI_2 \cdot 3DMA$, (**2**), the IR-active $\nu(Pt–NH_3)$ mode is shifted from 498 $cm^{-1}$ (solvent-free compound) to *ca* 482 $cm^{-1}$ (superimposed with DMA mode), while in $cis$-$(NH_3)_2PtI_2 \cdot DMA$, (**1**), the two IR-active $\nu(Pt–NH_3)$ modes at 496 and 482 $cm^{-1}$ (the latter superimposed with a DMA mode) are at higher energy relative to the solvent-free compound (488 and 469 $cm^{-1}$). This behaviour probably is a consequence of the fact that $NH_3$···O-(DMA) and $NH_3$···I hydrogen bonds affect the

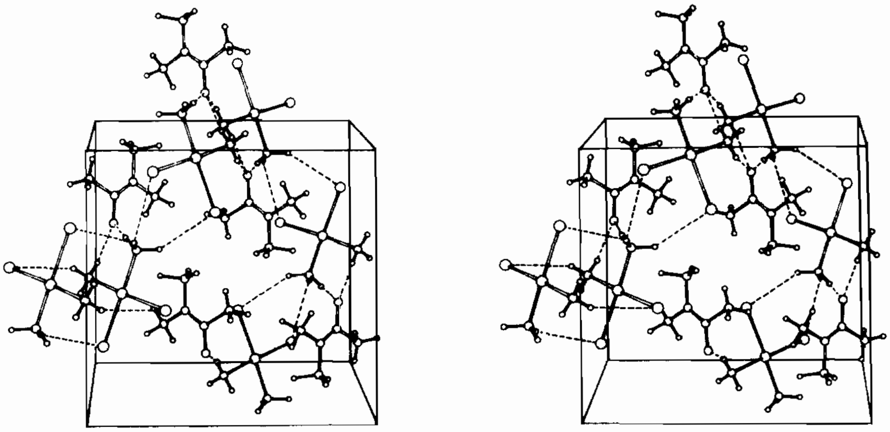

Fig. 2. Stereoview of the unit cell down the *a** axis with *b* parallel to the bottom of the page. Hydrogen-bonds are represented by dashed lines.

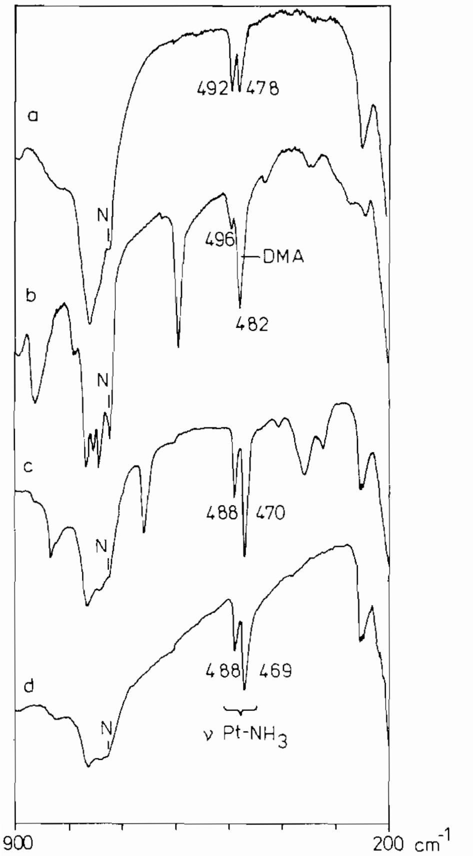

Fig. 3. IR spectra (Nujol, CsI) of (a) crude *cis*-$(NH_3)_2PtI_2$ prepared according to Dhara [3], (b) title compound *cis*-$(NH_3)_2PtI_2$•DMA (1), (c) *cis*-$(NH_3)_2PtI_2$•2DMF [2], and (d) *cis*-$(NH_3)_2PtI_2$, obtained from DMF and acetone as described in [2].

$PtN_2I_2$ skeleton as a whole rather than the individual groups.

While shifts of DMA modes in the adducts as compared to free DMA as a gas [20] or as a liquid in Nujol (e.g. shift of νCO to lower energy (30–50 $cm^{-1}$) in the solvates or shift of δ(OCN) from *ca.* 590 $cm^{-1}$ in liquid DMA to 600 $cm^{-1}$ in the solvates) are consistent with O acting as a donor (*cf.* also [21]), we are aware that changing the physical state from liquid to solid (in the solvates) may also contribute to the shifts observed.

In Fig. 3, IR spectra (between 900 and 200 $cm^{-1}$) of several representative samples of *cis*-$(NH_3)_2PtI_2$ (crude material, DMF- and DMA-solvates, solvent-free material) are compared.

Compound 5, '*cis*-$(NH_3)_2PtI_3$•DMA' is of particular interest since, according to its appearance (lustrous, bonze crystals), it should be formulated as the mixed-valence, linear chain complex *cis*-$(NH_3)_2PtI_2$•*cis*-$(NH_3)_2PtI_4$•2DMA. As compared to charged (anionic [22] or cationic [23]) mixed-valence Pt(II)–Pt(IV) complexes, which are known in large numbers, neutral analogs of this kind appear to be considerably less common [24].

Preliminary synthetic work, e.g. preparation of nucleobase complexes of *cis*-$(NH_3)_2Pt^{II}$, has shown that, unlike crude *cis*-$(NH_3)_2PtI_2$, which gives rise to a number of undesired side reactions, the well-characterized DMA-adduct is an excellent starting material.

## Supplementary Material

The supplementary material, including lists of structure factors, anisotropic thermal parameters and H-atom coordinates, can be obtained upon request from A. L. Beauchamp.

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