

# Synthesis and structures of platina- $\beta$ -diketonato complexes of platina- $\beta$ -diketones; organometallic analogues of platinum blue complexes

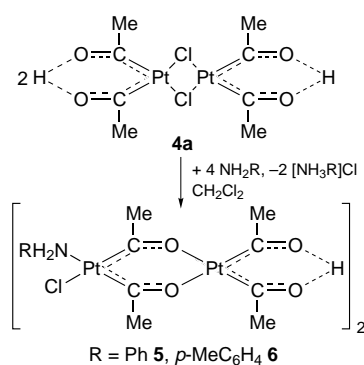
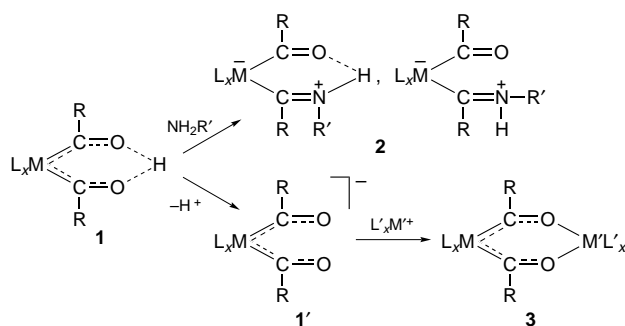
Dirk Steinborn,\* Michael Gerisch, Frank W. Heinemann and Clemens Bruhn

Institut für Anorganische Chemie, Martin-Luther-Universität Halle-Wittenberg, Kurt-Mothes-Str. 2, D-06120 Halle, Germany

The platina- $\beta$ -diketonate  $[\text{Pt}_2(\mu\text{-Cl})_2\{(\text{COMe})_2\text{H}\}_2]$  **4a** reacts with aniline or *p*-toluidine to give the first platina- $\beta$ -diketonato complexes of platina- $\beta$ -diketones  $[(\text{NH}_2\text{R})\text{ClPt}(\mu\text{-COMe})_2\text{Pt}\{(\text{COMe})_2\text{H}\}_2]$  (**R** = Ph **5**, *p*-MeC<sub>6</sub>H<sub>4</sub> **6**), whose X-ray crystal structures reveal the formation of head-to-head dimers with zigzag Pt<sub>4</sub> chains analogous to platinum blue complexes.

Metalla- $\beta$ -diketones **1** are organometallic analogues of the enol tautomers of 1,3-diketones where the methine group is replaced formally by the L<sub>x</sub>M moiety.<sup>1</sup> It is known that complexes **1** react with primary amines NH<sub>2</sub>R' to give the corresponding metalla- $\beta$ -ketoimines **2**.<sup>1,2</sup> The deprotonated complexes **1'** are capable of forming metal complexes of metalla- $\beta$ -diketonates **3** with two bridging acyl ligands.<sup>1,3</sup> Scheme 1. Previously we described the synthesis of  $[\text{Pt}_2(\mu\text{-Cl})_2\{(\text{COR})_2\text{H}\}_2]$  (**R** = Me **4a**, Et **4b**) being the first platina- $\beta$ -diketonates and, indeed, the first dinuclear metalla- $\beta$ -diketonates.<sup>4</sup> Here, we report the reactions of **4a** with aromatic amines to give, unexpectedly, platina- $\beta$ -diketonato complexes of platina- $\beta$ -diketones which were revealed to be of the platinum blue structural type.

The platina- $\beta$ -diketonate **4a** reacts with aniline and *p*-toluidine in a molar ratio 1 : 2.1 in dichloromethane as solvent to give the dimeric bis(acyl)-bridged platinum complexes **5** and **6** in high yield (73 and 68%, respectively), Scheme 2.<sup>†</sup> Intermediates in these reactions might include the monomeric complexes

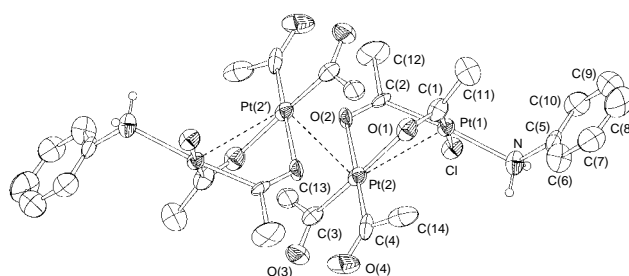


$[\text{PtCl}\{(\text{COMe})_2\text{H}\}(\text{NH}_2\text{R})]$  (**R** = Ph, *p*-MeC<sub>6</sub>H<sub>4</sub>), of which half is deprotonated with substitution of the chloro ligand to give **5** and **6**, respectively. An indication of this is the formation of  $[\text{NMe}_4][\text{Cl}_2\text{Pt}(\mu\text{-COMe})_2\text{Pt}\{(\text{COMe})_2\text{H}\}_2]^{5-}$  in the reaction of **4a** with  $[\text{NMe}_4]\text{OH}$ .

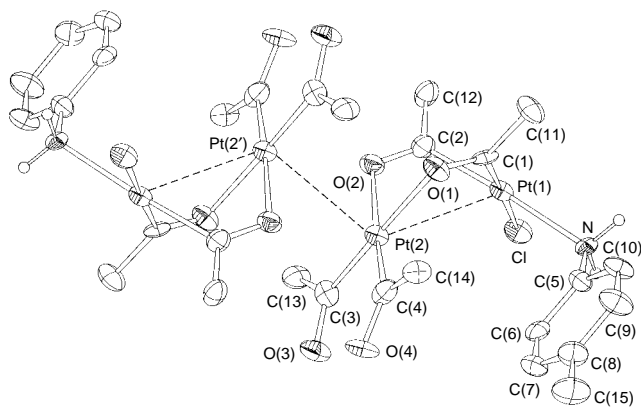
Compounds **5** and **6** crystallize from dichloromethane as well shaped, yellow and red, air-sensitive crystals of  $[(\text{NH}_2\text{R})\text{ClPt}(\mu\text{-COMe})_2\text{Pt}\{(\text{COMe})_2\text{H}\}_2] \cdot x\text{CH}_2\text{Cl}_2$  (**R** = Ph, *p*-MeC<sub>6</sub>H<sub>4</sub>; *x* = 2), respectively, which lose 1 mol of CH<sub>2</sub>Cl<sub>2</sub> upon drying *in vacuo* (*x* = 1).<sup>‡</sup> They melt with decomposition at 90–91 °C (**5**·CH<sub>2</sub>Cl<sub>2</sub>) and 92–93 °C (**6**·CH<sub>2</sub>Cl<sub>2</sub>). Solutions of **5** and **6** are quite unstable at room temperature. Complex **6** is monomeric in chloroform solution (found: 692.1 g mol<sup>-1</sup>; calc. for  $[(\text{NH}_2(p\text{-MeC}_6\text{H}_4))\text{ClPt}(\mu\text{-COMe})_2\text{Pt}\{(\text{COMe})_2\text{H}\}_2]$  706.0 g mol<sup>-1</sup>). The C–O stretching vibrations for the bridging acyl ligands appear at lower wavenumbers (1514s, 1535vs cm<sup>-1</sup>) than those in **4a** (1548 cm<sup>-1</sup>) which is in agreement with the series: acyl {e.g.  $\nu(\text{C}=\text{O})$  1639 cm<sup>-1</sup> in *trans*- $[\text{PtCl}(\text{COMe})(\text{PPh}_3)_2]^{6-}$ } >  $\beta$ -diketonate (**4a**) >  $\mu\text{-COMe}$  (**5**, **6**). As expected, all four methyl groups of the organo ligands in **6** are chemically inequivalent in the <sup>1</sup>H NMR spectrum. In **5** two methyl groups are isochronous by chance.

The identities of **5** and **6** were confirmed by X-ray structure determinations.<sup>§</sup> The molecular structures are shown in Figs. 1 and 2, with selected bond lengths and angles. They reveal the presence of head-to-head dimers in the solid state with a crystallographically imposed inversion centre (*C*<sub>i</sub>). Both structures are very similar apart from the orientations of the amine ligands {torsion angle C(5)–N–Pt(1)–Pt(2) 105.9° [18.0°]}.<sup>¶</sup>

The coordination of Pt(1) [Cl, N, C(1), C(2)] and Pt(2) [C(3), C(4), O(1), O(2)] is square planar. These coordination planes are inclined at an angle of 95.7(6) [103.6(4)°]. Thus, the six-membered rings [Pt(1), C(1), O(1), Pt(2), C(2), O(2)] exhibit boat conformations with Pt(1)⋯Pt(2) distances of 3.284(1) [3.160(1) Å]. There are no significant differences between the four Pt–C {*d*(Pt–C) = 1.89(3)–1.98(2) [1.93(2)–2.00(2) Å]}



**Fig. 1** Molecular structure in the solid state with atomic labelling scheme for **5**; thermal ellipsoids are drawn at the 30% probability level, H-atoms are omitted for clarity. Selected distances (Å) and angles (°): Pt(1)–Pt(2) 3.284(1), Pt(2)–Pt(2') 3.186(2), Pt(1)–C(1) 1.95(2), Pt(1)–C(2) 1.98(2), Pt(1)–Cl 2.409(6), Pt(1)–N 2.18(2), Pt(2)–O(1) 2.15(2), Pt(2)–O(2) 2.18(2), Pt(2)–C(3) 1.89(3), Pt(2)–C(4) 1.97(3), C(1)–O(1) 1.25(3), C(2)–O(2) 1.21(3), C(3)–O(3) 1.24(3), C(4)–O(4) 1.22(4), O(3)–O(4) 2.28(4); Cl–Pt(1)–N 84.0(5), Cl–Pt(1)–C(2) 93.6(7), N–Pt(1)–C(1) 98.5(9), C(1)–Pt(1)–C(2) 84(1), O(1)–Pt(2)–O(2) 85.0(7), C(3)–Pt(2)–C(4) 89(1), O(1)–Pt(2)–C(4) 94(1), O(2)–Pt(2)–C(3) 92(1), Pt(1)–Pt(2)–Pt(2') 119.80(5).



**Fig. 2** Molecular structure in the solid state with atomic labelling scheme for **6** with details as in Fig. 1. Selected distances (Å) and angles (°): Pt(1)–Pt(2) 3.160(1), Pt(2)–Pt(2') 3.152(2), Pt(1)–C(1) 1.95(2), Pt(1)–C(2) 2.00(2), Pt(1)–Cl 2.390(4), Pt(1)–N 2.23(1), Pt(2)–O(1) 2.15(1), Pt(2)–O(2) 2.18(1), Pt(2)–C(3) 1.93(2), Pt(2)–C(4) 1.95(2), C(1)–O(1) 1.24(2), C(2)–O(2) 1.24(2), C(3)–O(3) 1.30(2), C(4)–O(4) 1.29(2), O(3)–O(4) 2.37(2); Cl–Pt(1)–N 86.0(3), Cl–Pt(1)–C(2) 91.9(5), N–Pt(1)–C(1) 95.8(6), C(1)–Pt(1)–C(2) 86.2(7), O(1)–Pt(2)–O(2) 84.6(4), C(3)–Pt(2)–C(4) 93.8(8), O(1)–Pt(2)–C(4) 89.5(7), O(2)–Pt(2)–C(3) 92.2(6), Pt(1)–Pt(2)–Pt(2') 127.52(3)°.

and C–O bonds [ $d(\text{C}–\text{O}) = 1.21(3)–1.25(3)$  [1.24(2)–1.30(2) Å]] nor significant differences to those in **4a** [ $d(\text{Pt}–\text{C}) = 1.95(1)$  Å,  $d(\text{C}–\text{O}) = 1.23(1)$ , 1.26(1) Å]. The O–H–O bridge in the remaining platina- $\beta$ -diketone unit [ $d(\text{O}(3)\cdots\text{O}(4)) = 2.28(4)$  [2.38(2) Å]] is comparable to that in **4a** [ $d(\text{O}\cdots\text{O}) = 2.37(1)$  Å].

The most noticeable structure feature of **5** and **6** is the zigzag chain of the Pt<sub>4</sub> unit with an angle between the Pt(1)–Pt(2) and Pt(2)–Pt(2') vectors of 119.80(5) [127.52(3)°]. As expected for a Pt<sup>II</sup>–Pt<sup>II</sup> (d<sup>8</sup>–d<sup>8</sup>) interaction,<sup>7</sup> the distance Pt(2)–Pt(2') [3.186(2) [3.152(2) Å]] is rather long but comparable with those in Pt<sup>II</sup> complexes with columnar structures (3.09–3.60 Å)<sup>8</sup> and with those of amidate-bridged tetranuclear platinum complexes (platinum blue complexes<sup>9</sup>) with platinum in the +2.0 average oxidation state (3.13–3.24 Å).<sup>10</sup>

Besides **5** and **6**, the platinum blue complexes are the only ones with chain-like Pt<sub>4</sub> units. But there are important differences in the structures: in **5** and **6**, the Pt–Pt distances in the ligand bridging units [ $d[\text{Pt}(1)–\text{Pt}(2)] = 3.284(1)$  [3.160(1) Å]] are longer than those between the dinuclear units [ $d[\text{Pt}(2)–\text{Pt}(2')] = 3.186(2)$  [3.152(2) Å]]. In the platinum blue complexes, the amidate-bridged Pt–Pt distances are the shortest ones (2.88–3.03 Å). Furthermore, the tilt angles between the platinum coordination planes in the ligand bridging units are between 30 and 40° in platinum blue complexes but 95.7(6)° in **5** and 103.6(4)° in **6**. Correspondingly, the Pt–Pt–Pt zigzag angles are greater by ca. 35–40° in platinum blue complexes than in **5** and **6**. Summarizing, the platina- $\beta$ -diketonate complexes of platina- $\beta$ -diketones **5** and **6** can be regarded as organometallic analogues of platinum blue complexes.

We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for financial support and the companies Merck (Darmstadt) and Degussa (Hanau) for loans of chemicals.

## Footnotes

\* E-mail: steinborn@chemie.uni-halle.de

† *Syntheses*: To a stirred solution of [Pt<sub>2</sub>( $\mu$ -Cl)<sub>2</sub>{(COMe)<sub>2</sub>H<sub>2</sub>}<sub>2</sub>] (200 mg, 0.32 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (5 cm<sup>3</sup>), aniline (61 mg, 0.66 mmol) or *p*-toluidine (71 mg, 0.66 mmol) was added at 20 °C. The pale yellow solution turned deep yellow immediately. After stirring for 2 h at room temp., a precipitate of **5/6** and [NH<sub>3</sub>R]Cl was filtered off and extracted with CH<sub>2</sub>Cl<sub>2</sub> (10 cm<sup>3</sup>).

At –30 °C, **5** and **6** crystallized within 2 days as yellow and red crystals, respectively, which were filtered off and dried *in vacuo*.

**5**·CH<sub>2</sub>Cl<sub>2</sub>: yield 159 mg (73%). **6**·CH<sub>2</sub>Cl<sub>2</sub>: yield 155 mg (68%).

‡ *Selected spectroscopic data*: **5**·CH<sub>2</sub>Cl<sub>2</sub>: IR (CsBr):  $\nu(\text{C}–\text{O})$  1545sh, 1535vs, 1514s;  $\nu(\text{Pt}–\text{Cl})$  275m cm<sup>–1</sup>. <sup>1</sup>H NMR (200 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  2.39 (s, 3 H, CH<sub>3</sub>), 2.44 (s, 6 H, 2 × CH<sub>3</sub>), 2.49 (s, 3 H, CH<sub>3</sub>), 4.92 (s, 2 H, NH<sub>2</sub>), 6.75 (m, 3 H, *m*-, *p*-CH), 7.15 (m, 2 H, *o*-CH). <sup>195</sup>Pt NMR [86 MHz, 293 K, CD<sub>2</sub>Cl<sub>2</sub>; relative to  $\delta(^{195}\text{Pt}) = 4521$  for Na<sub>2</sub>[PtCl<sub>6</sub>]]:  $\delta$  1639 [s + d, <sup>3</sup>J(PtPt) 372 Hz, Pt(2)], 1479 [br, Pt(1)].

**6**·CH<sub>2</sub>Cl<sub>2</sub>: IR (CsBr):  $\nu(\text{C}–\text{O})$  1553sh, 1535vs, 1514s;  $\nu(\text{Pt}–\text{N})$  450w;  $\nu(\text{Pt}–\text{Cl})$  273m cm<sup>–1</sup>. <sup>1</sup>H NMR (500 MHz, 298 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  2.07 (s, 3 H, COCH<sub>3</sub>), 2.14 (s, 3 H, COCH<sub>3</sub>), 2.26 (s, 3 H, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 2.38 (s, 3 H, COCH<sub>3</sub>), 2.47 (s, 3 H, COCH<sub>3</sub>), 5.00 (s, 2 H, NH<sub>2</sub>), 6.89 (d, 2 H, *J* 7.9 Hz, CH), 7.01 (d, 2 H, *J* 7.9 Hz, CH). <sup>195</sup>Pt NMR (86 MHz, 293 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1640 [s + d, <sup>3</sup>J(PtPt) 326 Hz, Pt(2)], 1481 [br, Pt(1)].

§ *Crystal data*: **5**·2CH<sub>2</sub>Cl<sub>2</sub>, C<sub>15</sub>H<sub>22</sub>Cl<sub>3</sub>NO<sub>4</sub>Pt<sub>2</sub>, *M* = 776.87, monoclinic, space group *P*2<sub>1</sub>/*n*, *a* = 9.964(2), *b* = 21.219(3), *c* = 10.633(2) Å,  $\beta$  = 98.61(2)°, *U* = 2222.8(6) Å<sup>3</sup>, *T* = 297 K, *D*<sub>c</sub> = 2.321 g cm<sup>–3</sup>, *Z* = 4, Stoe IPDS diffractometer, Mo-K $\alpha$  radiation,  $\lambda$  = 0.71073 Å,  $\mu$  = 12.951 mm<sup>–1</sup>, numerical absorption correction (*T*<sub>min</sub> = 0.75, *T*<sub>max</sub> = 1.00), 10112 reflections measured ( $\theta_{\text{min}}$  = 2.16,  $\theta_{\text{max}}$  = 22.50°) of which 2911 independent (*R*<sub>int</sub> = 0.172), 2050 observed [*I* > 2 $\sigma$ (*I*)], 226 parameters, *R* = 0.0763, *wR*<sub>2</sub> = 0.2028, GOF = 1.045, the residual electron density lies near the Pt atoms; 2.67, –2.68 e Å<sup>–3</sup>.

**6**·2CH<sub>2</sub>Cl<sub>2</sub>, C<sub>16</sub>H<sub>24</sub>Cl<sub>3</sub>NO<sub>4</sub>Pt<sub>2</sub>, *M* = 790.89, triclinic, space group *P* $\bar{1}$ , *a* = 9.563(3), *b* = 10.317(3), *c* = 11.665(3) Å,  $\alpha$  = 78.75(2),  $\beta$  = 87.59(2),  $\gamma$  = 83.80(2)°, *U* = 1121.9(6) Å<sup>3</sup>, *T* = 200 K, *D*<sub>c</sub> = 2.341 g cm<sup>–3</sup>, *Z* = 2, Stoe Stadi4 diffractometers, Mo-K $\alpha$  radiation,  $\lambda$  = 0.71073 Å,  $\mu$  = 12.832 mm<sup>–1</sup>, empirical absorption correction via  $\psi$ -scans (*T*<sub>min</sub> = 0.29, *T*<sub>max</sub> = 1.00), 4136 reflections measured ( $\theta_{\text{min}}$  = 1.78,  $\theta_{\text{max}}$  = 22.50°) of which 2942 independent (*R*<sub>int</sub> = 0.0741), 2293 observed [*I* > 2 $\sigma$ (*I*)], 240 parameters, *R* = 0.0494, *wR*<sub>2</sub> = 0.1388, GOF = 1.008, the residual electron density lies near the Pt atoms; 2.62, –2.43 e Å<sup>–3</sup>.

Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/417.

¶ Data relating to **6** given in square brackets.

## References

- C. M. Lukehart, *Acc. Chem. Res.*, 1981, **14**, 109; *Adv. Organomet. Chem.*, 1986, **25**, 45.
- C. M. Lukehart and J. V. Zeile, *J. Am. Chem. Soc.*, 1978, **100**, 2774; *Inorg. Chem.*, 1978, **17**, 2369; K. P. Darst and C. M. Lukehart, *Inorg. Chim. Acta*, 1980, **41**, 239; C. M. Lukehart and M. Raja, *Inorg. Chem.*, 1982, **21**, 1278; D. Afzal and C. M. Lukehart, *Inorg. Chem.*, 1983, **22**, 3954.
- C. M. Lukehart and G. P. Torrence, *Inorg. Chem.*, 1979, **18**, 3150; C. M. Jensen, Y. J. Chen and H. D. Kaesz, *J. Am. Chem. Soc.*, 1984, **106**, 4046; D. Xu, H. D. Kaesz and S. I. Khan, *Inorg. Chem.*, 1991, **30**, 1341; E. Lippmann, C. Robl, H. Berke, H. D. Kaesz and W. Beck, *Chem. Ber.*, 1993, **126**, 933.
- D. Steinborn, M. Gerisch, K. Merzweiler, K. Schenzel, K. Pelz, H. Bögel and J. Magull, *Organometallics*, 1996, **15**, 2454.
- M. Gerisch, C. Bruhn and D. Steinborn, to be published.
- M. Kubota, S. C. Boegeman, R. N. Keil and C. G. Webb, *Organometallics*, 1989, **8**, 1616.
- K. Krogmann, *Angew. Chem.*, 1969, **81**, 10; *Angew. Chem., Int. Ed. Engl.*, 1969, **8**, 35.
- J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, 1976, **20**, 1; J. M. Williams, *Adv. Inorg. Chem. Radiochem.*, 1983, **26**, 235.
- K. A. Hofmann and G. Bugge, *Ber. Dtsch. Chem. Ges.*, 1908, **41**, 312; J. K. Barton and S. J. Lippard, *Ann. N. Y. Acad. Sci.*, 1978, **313**, 686 and references therein; S. J. Lippard, *Science (Washington, DC)*, 1982, **218**, 1075; G. Bernardinelli, P. Castan and R. Soules, *Inorg. Chim. Acta*, 1986, **120**, 205; T. V. O'Halloran, P. K. Mascharak, I. D. Williams, M. M. Roberts and S. J. Lippard, *Inorg. Chem.*, 1987, **26**, 1261.
- L. S. Hollis and S. J. Lippard, *J. Am. Chem. Soc.*, 1981, **103**, 1230; *Inorg. Chem.*, 1983, **22**, 2600; J.-P. Laurent, P. Lepage and F. Dahan, *J. Am. Chem. Soc.*, 1982, **104**, 7335.

Received in Basel, Switzerland, 20th January 1997; Com. 7/00427C