

Inorganica Chimica Acta

Inorganica Chimica Acta 285 (1999) 145-148

Note

Platinum(II) and palladium(II) saccharinate complexes

William Henderson^{*}, Brian K. Nicholson, Louise J. McCaffrey

Department of Chemistry, University of Waikato, Private Bag 3105, Hamilton, New Zealand

Received 10 April 1998; accepted 17 June 1998

Abstract

A number of platinum(II) and palladium(II) complexes containing the saccharinate ligand (sac⁻), of the type [MCl(sac)L₂] (M = Pt, $L = PPh_3$, $L_2 = Ph_2PCH_2CH_2PPh_2$, dppe; M = Pd, $L = PPh_3$) have been synthesised by reaction of [MCl₂L₂] with sacNa in methanol. A single crystal X-ray diffraction study carried out on *cis*-[PtCl(sac)(PPh_3)₂]·4CHCl₃ shows the N-bonded saccharinate and platinum coordination planes to be nearly orthogonal. The results of an electrospray mass spectrometric study of the dppe complex are also reported. \bigcirc 1999 Elsevier Science S.A. All rights reserved.

Keywords: Crystal structures; Platinum complexes; Palladium complexes; Saccharin complexes

1. Introduction

Platinum-group metal complexes of amide (amidate) ligands are of interest for their fundamental coordination chemistry [1–3] and biological activity [4,5] though to date, relatively few complexes have been reported. We are currently investigating the syntheses and properties of platinum amide complexes [6-8]. Saccharin (also known as 2,3dihydro-3-oxobenzisosulfonazole, 1,2-benzisothiazoline-3-(2H)one 1,1-dioxide, o-benzosulfimide) (1) is an amide widely used as an artificial sweetener, and because of the biological importance of this molecule, there have been many studies on coordination complexes with a range of metal centres, especially first-row transition metals [8,10-16]. However, there has only been one report of a platinum or palladium complex containing the sac ligand; complexes *trans*-[PtH(sac)(EPh₃)₂] (E = As, P) (2) were synthesised by oxidative addition of the N-H bond of saccharin to $[Pt(EPh_3)_4]$ [17]. Here we report the synthesis of platinum and palladium saccharinate complexes formed by reaction of the saccharinate anion with metal-halide complexes.





2. Results and discussion

Reactions of the platinum(II) dichloride complexes *cis*-[PtCl₂L₂] [L = PPh₃ and L₂ = Ph₂PCH₂CH₂PPh₂ (dppe)] with excess sodium saccharinate (sacNa) in refluxing methanol gives the platinum mono(sac) complexes **3a** and **3b** respectively, after addition of water to precipitate the product. A prolonged reaction time (70 h) and a large excess of sacNa did not lead to substitution of the second chlorine of *cis*-[PtCl₂(PPh₃)₂]. In all preparations, the complex *cis*-[PtCl(sac)(PPh₃)₂] was contaminated with a small quantity of unreacted *cis*-[PtCl₂(PPh₃)₂], even after the prolonged reaction. Reaction of [PdCl₂(PPh₃)₂] under analogous conditions yielded the complex *trans*-[PdCl(sac)(PPh₃)₂] (**4**) as shown by the single peak in the ³¹P {¹H} NMR spectrum, and by elemental analysis.



3a; L = PPh₃ **3b**; L = dppe

*Corresponding author: Tel.: +64-7-856-2889; fax: +64-7-838-4219; e-mail: w.henderson@waikato.ac.nz

0020-1693/99/\$ – see front matter \odot 1999 Elsevier Science S.A. All rights reserved. PII: S0020-1693(98)00327-2



There have been numerous structural determinations of metal-saccharinate complexes of first-row transition metals [11-16], cadmium [18,19], mercury [20-23], and silver [24,25] but no structures of platinum group metals have been reported. Crystals of the triphenylphosphine complex 3a suitable for a single crystal X-ray diffraction study were obtained by allowing a saturated chloroform solution to stand at room temperature for several weeks. The structure of 3a shows an approximately square-planar platinum centre which is coordinated by a chloride and two cis-triphenylphosphine ligands, together with an N-bonded saccharinate ligand. Coordination about the platinum atom is planar to within ± 0.03 Å, and the planar core of the sac ligand forms a dihedral angle of 78° to the coordination plane. As is typical for complexes of this type, the P(1)-Pt(1)-P(2) angle is greater than the idealised 90°, in this case 99.09(8)°. The N(1)-Pt(1)-Cl(1) angle is correspondingly reduced at $87.0(2)^\circ$. The platinum–phosphorus bond lengths are identical (Pt(1)-P(1) 2.266(2), Pt(1)-P(2) 2.264(2) Å). suggesting that the saccharinate and chloride ligands have very similar *trans* influences, though the values of ${}^{1}J(PtP)$ in the ³¹P NMR spectrum of **3a** are significantly different (3770 and 3483 Hz). The platinum(II) complex 5 containing the anion of 5,5-diethylbarbituric acid (H debarb) together with a chloride ligand, provides a useful complex for comparison [7]. The Pt-P bond lengths of 5 are different, with the one *trans* to chloride (2.241(2) Å) being slightly shorter than that trans to the higher trans-influence amide ligand (2.274(2) Å). The Pt(1)–N(1) bond length of the sac complex **3a** (2.064(6) Å) is similar to that of **5**, and to platinum-nitrogen bond lengths in other platinum amidate complexes [6-8].



One feature of the structure is the high level of solvation. There are four molecules of $CHCl_3$ in the asymmetric unit, three ordered and one disordered over two sites. One is hydrogen-bonded to the Cl(1) of the complex, one to O(3) of the sac ligand, while the other two make no unusually short contacts.

Electrospray mass spectrometry (ESMS) has recently been used in the study of a number of different types of platinum-group metal amidate complexes, including complexes derived from 5,5-diethylbarbituric acid, of type **5** [7], which are analogous to the complexes reported in this paper in having *cis* chloride and amidate ligands. For these complexes, the chloride ligand was more readily lost than the amide, by a solvolysis reaction with the MeCN solvent, giving ions of the type [Pt(debarb)(MeCN)L₂]⁺. However, for the saccharinate complex [PtCl(sac)(dppe)] (**3b**) the sac and Cl ligands are both relatively easily lost; the positive-ion spectrum of **3b** recorded in MeCN–H₂O solvent at a cone voltage of 50 V showed two main ions due to [PtCl(dppe)]⁺ (*m*/*z* 629) and [Pt(sac)(dppe)]⁺ (*m*/*z* 775). At the lower cone voltage of 20 V, ions solvated with MeCN were observed, together with a minor ion assigned as [*M* + H]⁺.

The IR spectra of the sac complexes **3** and **4** show the expected features for such complexes [9,10]. Strong CO stretches were observed in the range 1661-1684 cm⁻¹, and strong SO₂ symmetric stretches were observed

Table 1 Crystal data and structure refinement for **3a**·4CHCl₂

crystal data and structure remientent for 5a -4CHCl3	
Crystal data	
Empirical formula	C43H34NClO3P2PtS·4CHCl3
Formula weight	1414.72
Temperature (K)	203(2)
Wavelength (Å)	0.71073
Crystal system	monoclinic
Space group	C2/c
Unit cell dimensions	
a (Å)	43.3254(15)
b (Å)	10.4480(4)
c (Å)	23.9703(8)
$\beta(\hat{c})$	93.444(1)
Volume ($Å^3$)	10830.9(7)
Z	8
Density (calc.) (Mg m^{-3})	1.735
Data collection	
Diffractomator	Sigmons SMART CCD
Diffractometer	Siemens SMART CCD
Crystal to detector distance (cm) (-1)	8.0
E(000)	5.572
F(000)	5568
Crystal size (mm)	$0.43 \times 0.18 \times 0.06$
θ Range for data collection (°)	1.70 to 25.80
Index ranges	$-52 \le h \le 52$
	$0 \le k \le 12$
	$0 \le l \le 29$
Reflections collected	24711
Independent reflections	9274 $[R_{int} = 0.0401]$
Observed reflections $[I > 2\sigma(I)]$	7539
Max., min. transmission	0.8838, 0.5784
Structural analysis and refinement	
Solution by	Patterson methods
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	9274/0/606
Goodness-of-fit on F^2	1.135
Final <i>R</i> indices $[I > 2\sigma(I)]$	$R_1 = 0.0597, wR_2 = 0.1333$
R indices (all data)	$R_1 = 0.0782, wR_2 = 0.1440$
Largest difference peak, hole (e $Å^{-3}$)	2.488, -1.907 (adjacent to Pt atom)
Programs used	SHELXS 86 [29] and SHELXL 93 [30]

from 1303 to 1310 cm⁻¹. The CO stretching frequencies are notably higher than those of first-row transition metal complexes of the type [M(sac)₂(H₂O)₄], which occur at ca. 1610 cm⁻¹ [9,10]. Two bands were observed for all three complexes in the SO₂ asymmetric stretching region, at 1155 and 1172 cm⁻¹, and a definitive assignment has not been made.

3. Experimental

General experimental procedures were as described previously [7,8]; reactions were carried out in air, using LR grade solvents which were not further purified. Electrospray mass spectra were recorded in positive-ion mode, in MeCN– H_2O (1:1, vol./vol.) solvent, and cone voltages were varied between 20 and 50 V. Assignment of ions was assisted by comparison of experimental and calculated isotope patterns, the latter obtained by means of the ISOTOPE program [26].

Sodium saccharinate hydrate (Aldrich) was used as supplied. The complexes $[PtCl_2(cod)]$ [27] and $[PdCl_2(cod)]$ [28] were prepared by the literature procedures, and the complexes *cis*- $[PtCl_2(PPh_3)_2]$, $[PtCl_2(dppe)]$, and $[PdCl_2(PPh_3)_2]$ prepared from them by reaction with the appropriate molar amount of the phosphine in dichloromethane, followed by precipitation with petroleum spirits (b.p. 40–60°C).

3.1. Synthesis of cis-[PtCl(sac)(PPh₃)₂] (3a)

The complex *cis*-[PtCl₂(PPh₃)₂] (259 mg, 0.327 mmol) with sodium saccharinate hydrate (337 mg, 1.64 mmol) was refluxed for 65 min in methanol (45 ml). Water (70 ml) was added, and the white solid filtered and washed with water (20 ml), ether (20 ml), and dried under vacuum. Yield 271 mg (88%), m.p. > 230°C. Found: C, 53.9; H, 3.75; N, 1.5%. C₄₃H₃₄NClO₃P₂PtS requires: C, 55.1; H, 3.7; N, 1.5% ³¹P {¹H} NMR (CDCl₃ + 10% DMSO), δ 15.2 (d, P *trans* Cl, ¹*J*(PtP) 3770, ²*J*(PP) 17) and 7.9 (d, P *trans* N, ¹*J*(PtP) 3483). IR: ν (CO) 1673; ν _{sym}(SO₂) 1310 cm⁻¹. Recrystallisation from a saturated chloroform solution at room temperature gave X-ray quality crystals of the tetra(chloroform) solvate, which lose chloroform on exposure to air.

3.2. Synthesis of cis-[PtCl(sac)(dppe)] (3b)

The complex [PtCl₂(dppe)] (300 mg, 0.451 mmol), with sodium saccharinate hydrate (464 mg, 2.26 mmol) in methanol (20 ml) was refluxed for 60 min. Water (70 ml) was added, the mixture stirred overnight, and the white product filtered off, washed with water (20 ml), ether (20 ml), and dried under vacuum. Yield 240 mg (66%), m.p. > 230°C. Found: C, 48.0; H, 3.7; N, 1.6%. C₃₃H₂₈NClO₃P₂PtS requires: C, 48.9; H, 3.5; N, 1.7% ³¹P {¹H} NMR, δ 42.4 (d, P *trans* Cl, ¹*J*(PtP) 3623, ²*J*(PP) 45) and 35.7 (d, P *trans* N, ¹*J*(PtP) 3457). IR



Fig. 1. Molecular structure of the complex *cis*-[PtCl(sac)(PPh₃)₂]-4CHCl₃ (**3a**-4CHCl₃), showing the atom numbering scheme. The chloroform molecules of crystallisation have been omitted. Selected bond lengths (Å) and angles ($^{\circ}$): Pt(1)–N(1) 2.064(6), Pt(1)–P(2) 2.264(2), Pt(1)–P(1) 2.266(2), Pt(1)–Cl(1) 2.340(2), N(1)–Pt(1)–P(2) 89.8(2), N(1)–Pt(1)–P(1) 170.8(2), P(2)–Pt(1)–P(1) 99.09(8), N(1)–Pt(1)–Cl(1) 87.0(2), P(2)–Pt(1)–Cl(1) 176.71(7), P(1)–Pt(1)–Cl(1) 84.17(7). The inset shows the orthogonality of the sac ligand and platinum coordination planes; PPh₃ carbons are omitted.

 ν (CO) 1684; ν_{sym} (SO₂) 1303 cm⁻¹. ESMS: cone voltage 20 V (*m*/*z*, %) [*M*-sac + MeCN]⁺ (670, 100), [*M*-Cl + MeCN]⁺ (816, 62), [*M*-Cl]⁺ (775, 17), [*M*-sac]⁺ (629, 10), [*M* + H]⁺ (812, 5), plus several other minor unassigned ions. Cone voltage 50 V: [*M*-sac]⁺ (629, 100), [*M*-Cl]⁺ (775, 85), [*M*-sac + MeCN]⁺ (670, 13).

3.3. Synthesis of trans-[PdCl(sac)(PPh₃)₂] (4)

The complex [PdCl₂(PPh₃)₂] (300 mg, 427 mmol) with sodium saccharinate hydrate (439 mg, 2.14 mmol) in methanol (25 ml) was refluxed for 65 min. Water (70 ml) was added, and the orange product filtered off, washed with water (20 ml) and ether (20 ml), and dried under vacuum. Yield 247 mg (68%), m.p. > 230°C, decomp. > ca. 195°C. Found: C, 60.3; H, 4.1; N, 2.3%. C₄₃H₃₄NClO₃P₂PdS requires: C, 60.9; H, 4.0; N, 1.65%. ³¹P {¹H} NMR (CDCl₃), δ 24.1 (s). ¹³C {¹H} NMR (CDCl₃), δ 165.09 (s, CO), 142.9–119.4 (m, Ph). IR: ν (CO) 1661; ν_{sym} (SO₂) 1305 cm⁻¹.

3.4. X-ray structure determination of cis-[PtCl(sac)(PPh₃)₂]·4CHCl₃ (**3b**)

Crystals were obtained from a saturated chloroform solution and were rapidly transferred to the diffractometer and cooled to -70° C to prevent loss of solvent. Details of the structure determination are given in Table 1, and selected bond parameters are included in the caption to Fig. 1, which illustrates the complex.

4. Supplementary material

Additional data available from the Cambridge Crystallographic Data Centre comprise full tables of bond lengths and angles, atomic coordinates, thermal parameters and hydrogen atom coordinates.

Acknowledgements

We thank the University of Waikato for financial support of this work, the New Zealand Lottery Grants Board for a grant-in-aid towards the mass spectrometer. The loan of platinum from Johnson Matthey plc is gratefully acknowledged. Wendy Jackson and Ralph Thomson are thanked for technical assistance and literature searches respectively.

References

- [1] A. Shaver, R.D. Lai, Inorg. Chem. 27 (1988) 4664.
- [2] A. Shaver, H. Boily, A.-M. Lebuis, Inorg. Chem. 35 (1996) 6356.
- [3] D. Michalska, B. Morzyk, W. Wojciechowski, T. Glowiak, Inorg. Chim. Acta 248 (1996) 159.
- [4] Y. Dohta, M. Kodaka, T. Okada, K. Okamoto, H. Okuno, Inorg. Chim. Acta 252 (1996) 5.
- [5] J. Matsunami, H. Urata, K. Matsumoto, Inorg. Chem. 34 (1995) 202.
- [6] W. Henderson, M. Sabat, Polyhedron 16 (1997) 1663.
- [7] J. Fawcett, W. Henderson, R.D.W. Kemmitt, D.R. Russell, A. Upreti, J. Chem. Soc., Dalton Trans. (1996) 1897.
- [8] J.M. Law, W. Henderson, B.K. Nicholson, J. Chem. Soc., Dalton Trans. (1997) 4587.
- [9] F.A. Cotton, E. Libby, C.A. Murillo, G. Valle, Inorg. Synth. 27 (1990) 306.
- [10] S.Z. Haider, K.M.A. Malik, K.J. Ahmed, Inorg. Synth. 23 (1985) 47.
- [11] S.Z. Haider, K.M.A. Malik, K.J. Ahmed, H. Hess, H. Riffel, M.B.
- Hursthouse, Inorg. Chim. Acta 72 (1983) 21. [12] B. Kamenar, G. Jovanski, Cryst. Struct. Commun. 11 (1982) 257.
- [12] D. Ramenar, G. Jovanski, eryst. Stude. Commun. 11 (1962) 257. [13] F.A. Cotton, G.E. Lewis, C.A. Murillo, W. Schwotzer, G. Valle,
- Inorg. Chem. 23 (1984) 4038.
- [14] F.A. Cotton, L.R. Falvello, R. Llusar, E. Libby, C.A. Murillo, W. Schwotzer, Inorg. Chem. 25 (1986) 3423.
- [15] F.A. Cotton, L.R. Falvello, C.A. Murillo, G. Valle, Z. Anorg. Allg. Chem. 540 (1986) 67.
- [16] E.W. Ainscough, E.N. Baker, A.M. Brodie, R.J. Cresswell, J.D. Ranford, J.M. Waters, Inorg. Chim. Acta 172 (1990) 185.
- [17] D.M. Roundhill, Inorg. Chem. 9 (1970) 254.
- [18] S.Z. Haider, K.M.A. Malik, S. Das, M.B. Hursthouse, Acta Crystallogr., Sect. C 40 (1984) 1147.
- [19] I. Pascual, Acta Crystallogr. Sect. C 51 (1995) 2028.
- [20] G. Jovanovski, B. Kamenar, G. Ferguson, B. Kaitner, Acta Crystallogr., Sect. C 44 (1988) 616.
- [21] G. Jovanovski, B. Kamenar, Acta Crystallogr., Sect. A 37 (1981) C171.
- [22] B. Kamenar, G. Jovanovski, D. Grdenic, Cryst. Struct. Commun. 11 (1982) 263.
- [23] A. Hergold-Brundic, B. Kamenar, G. Jovanovski, Acta Crystallogr., Sect. C 45 (1989) 556.
- [24] R. Weber, M. Gilles, G. Bergerhoff, Z. Kristallogr. 206 (1993) 273.
- [25] S.W. Ng, Z. Kristallogr. 210 (1995) 206.
- [26] L.J. Arnold, J. Chem. Educ. 69 (1992) 811.
- [27] J.X. McDermott, J.F. White, G.M. Whitesides, J. Am. Chem. Soc. 98 (1976) 6521.
- [28] D. Drew, J.R. Doyle, Inorg. Synth. 13 (1972) 52.
- [29] G.M. Sheldrick, sheLxs 86, Program for solving crystal structures, University of Göttingen, 1986.
- [30] G.M. Sheldrick, SHELXL 93, Program for refining crystal structures, University of Göttingen, 1993.