A comparative study of the coordination of saccharinate (sac), thiosaccharinate (tsac) and benzisothiazolate (bit) ligands to *trans*-[PdCl₂(H₂NBz)₂]: molecular structure of *cis*-[Pd(bit)₂(H₂NBz)₂]

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Abstract A comparative study of reactions of saccharinate (sac), thiosaccharinate (tsac) and benzisothiazolate (bit) with *trans*-[PdCl₂(H₂NBz)₂] is reported. While in all cases substitution of both chlorides occurs, product types differ for the three closely related ligands. With sodium saccharinate, *trans*-[Pd(N-sac)₂(H₂NBz)₂] results in which the sac ligands are N-bound. A similar N-bound coordination is observed with sodium benzisothiazolate, but a crystal structure shows that they adopt a mutual *cis* arrangement in *cis*-[Pd(N-bit)₂(H₂NBz)₂]. In contrast, with sodium thiosaccharinate it is proposed that the new ligands adopt an S-bound coordination mode in *trans*-[Pd(S-tsac)₂(H₂NBz)₂].

Introduction

Saccharinate (sac) and thiosaccharinate (tsac) anions (Fig. 1) are versatile poly-functional ligands, shown to adopt a variety of coordination modes, and consequently their coordination chemistry has been widely studied [1, 2]. Palladium(II) and platinum(II) complexes of these ligands

have been detailed [3–18] with some showing promising biological properties [19–24]. In contrast, the coordination chemistry of the related benzisothiazolate (bit) anion (Fig. 1), resulting from deprotonation of the acidic imine hydrogen in benzisothiazolinone, remains virtually unexplored; as far as we are aware, there are only two literature reports concerning the coordination chemistry of this ligand [25, 26]. Griffith and co-workers have reported the synthesis of *cis*-[Pd(N-bit)₂(κ²-en)] (en = ethylenediamine) and [Pt(NH₃)₂(N-bit)₂], the former being characterised by single-crystal X-ray crystallography [25], while we have recently detailed the synthesis of a number of square-planar palladium complexes, *trans*-[Pd(N-bit)₂L₂], with amine, amide and diphosphine co-ligands [26]. The latter can be formed via two synthetic routes, namely reaction of [Pd(bit)₂]·H₂O with neutral ligands or via displacement of both chlorides in *trans*-[PdCl₂L₂]. Herein, we develop further the coordination chemistry of the benzisothiazolate anion in a comparative study of reactions of saccharinate (sac), thiosaccharinate (tsac) and benzisothiazolate (bit) with *trans*-[PdCl₂(H₂NBz)₂]. The surprising outcome of this simple study was the isolation of different product types in each case.

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Experimental

General methods

¹H NMR spectra were recorded on a Varian Unity spectrometer in CDCl₃ or *d*⁶-dms_o. IR spectra were recorded on a Shimadzu FT-IR 8400 spectrophotometer in the 400–4000 cm^{−1} range using KBr discs and in the 200–600 cm^{−1} using CsI discs. Elemental analysis was carried out at Al Al-Bayt University, Jordan, using a Euro-

Fig. 1 Saccharin (sacH), benzisothiazoline (bitH) and thiosaccharin (tsacH)

vector EURO EA 300 elemental analyzer. Melting points were measured on a Gallenkamp melting point apparatus and are uncorrected. Conductivity measurements were carried out on 10^{-3} M solutions using a digital conductivity meter. Na_2PdCl_4 , benzisothiazolinone (Hbit), benzylamine and sodium saccharinate were purchased and used as received. Thiosaccharin [27] and *trans*-[PdCl₂(H₂NBz)₂] (**1**) [28] were prepared by literature methods.

Synthesis of 2

A solution of Nasac (0.285 g, 1.35 mmol) in MeOH (5 cm³) was added to a solution of **1** (0.244 g, 0.62 mmol) in MeOH (10 cm³). The mixture was stirred at room temperature for 3 h. The resulting yellow solid was collected by filtration, washed with MeOH and dried in vacuum. It was recrystallised from CHCl₃/MeOH to afford **2** as a yellow crystalline solid. Yield 0.341 g, 73%. *Anal.* Calc. for C₂₈H₂₆N₄O₆PdS₂: C, 49.1, H, 3.8, N, 8.2. Found: C, 49.2, H, 3.7, N, 8.2. Molar conductivity (DMSO): 0.40 ($\Omega^{-1} \text{ mol}^{-1} \text{ cm}^{-1}$). IR (KBr): 3265w, 3130w, 3029w, 1672s, 1593w, 1451w, 1290s, 1155m, 563m cm⁻¹. ¹H NMR (CDCl₃): δ 7.94–7.92 (m, 2H, sac), 7.87–7.85 (m, 2H, sac), 7.75–7.72 (m, 4H, sac), 7.30–7.22 (m, 10H, Ph), 4.34 (bs, 4H, 2NH₂), 3.97–3.93 (m, 4H, 2CH₂) ppm. Mp: 224–226 °C.

Synthesis of 3

A solution of tsac (0.051 g, 0.26 mmol) in MeOH (5 cm³) was added to a solution of **1** (0.051 g, 0.13 mmol) in MeOH (10 cm³). The mixture was stirred at 30 °C for 2 h. The yellow–orange solid formed was collected by filtration and dried under vacuum. Yield 0.068 g, 75%. *Anal.* Calc. for C₂₈H₂₆N₄O₄PdS₄: C, 46.9, H, 3.7, N, 7.8. Found: C, 46.9, H, 3.8, N, 8.0. Molar conductivity (DMSO): 0.40 ($\Omega^{-1} \text{ mol}^{-1} \text{ cm}^{-1}$). IR (KBr): 3425sb, 3051w, 2922w, 1541m, 1463m, 1384s, 1163s, 1004m, 806m, 370s cm⁻¹. ¹H NMR (DMSO-*d*₆): δ 7.89 (dd, J 8.0, J 3.2, 4H, tsac), 7.71 (t, J 8.0, 2H, tsac), 7.58 (t, J 8.0, 2H, tsac), 7.29 (s, 10H, Ph), 4.58 (bs, 4H, 2NH₂), 3.69 (s, 4H, 2CH₂) ppm.

Synthesis of 4

A solution of Nabit (0.048 g, 0.28 mmol) in MeOH (5 cm³) was added to a solution of **1** (0.055 g, 0.14 mmol) in MeOH (10 cm³) and stirred for 3 h at room temperature to give a yellow–brown solution. The solution was filtered and left to evaporate to afford yellow crystals. These were collected by filtration, washed with water and dried in a vacuum oven. Yield 0.075 g, 87%. *Anal.* Calc. for C₂₈H₂₆N₄O₂PdS₂: C, 53.3, H, 4.1, N, 9.2. Found: C, 53.4, H, 4.4, N, 9.5. Molar conductivity (DMSO): 0.80 ($\Omega^{-1} \text{ mol}^{-1} \text{ cm}^{-1}$). IR (KBr): 3195w, 3112w, 2927w, 1650s, 1539s, 1450m, 1290m, 1155m, 459w, 342m cm⁻¹. ¹H NMR (DMSO-*d*₆): δ 7.76 ppm (d, J 7.7, 2H, bit), 7.66 (d, J 7.7, 2H, bit), 7.57–7.23 (m, 14H, Ph + bit), 5.56 (s, 4H, 2NH₂), 3.56 (s, 4H, 2CH₂) ppm. Mp: 208–210 °C.

X-ray crystallography

Crystals of *cis*-[Pd(bit)₂(H₂NBz)₂] (**4**) suitable for X-ray crystallography were produced by slow evaporation of a methanol solution. A yellow crystal with approximate dimensions 0.10 × 0.10 × 0.10 mm³ was mounted on a glass fibre, and all geometric and intensity data were taken from this sample using a STOE-IPDS diffractometer with Mo-*K* α radiation ($\lambda = 0.7103 \text{ \AA}$, graphite monochromator). Absorption corrections were made using the IPDS software package [29]. All structures were solved by direct methods and refined using full-matrix least-square routines against F^2 with SHELXL-97 [30]. Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were included in the models by calculating the positions (riding model) and refined with calculated isotropic displacement parameters. Illustrations were generated using DIAMOND 3.0 [31].

Results and discussion

Addition of two equivalents of sodium saccharinate to a methanol solution of *trans*-[PdCl₂(H₂NBz)₂] (**1**) resulted in the slow formation of *trans*-[Pd(N-sac)₂(H₂NBz)₂] (**2**) isolated in 73% yield as a yellow solid (Scheme 1). Elemental analysis supports the substitution of both halides in **1**, as does the symmetrical nature of the ¹H NMR spectrum. This simple substitution and formation of the *trans*-saccharinate complexes mirrors behaviour previously noted by us [17, 18] and others [13]. Reaction of **1** with thiosaccharin in methanol at 30 °C resulted in formation of *trans*-[Pd(S-tsac)₂(H₂NBz)₂] (**3**) as a yellow–orange solid in 75% yield (Scheme). Elemental analysis was indicative of the substitution of both chlorides, and this is consistent with

Scheme 1 Reactions of *trans*-[PdCl₂(H₂NBz)₂] (**1**) with two equivalents of Na(sac), tsacH and Na(bit)

the ¹H NMR spectrum. On the basis of the observation of an IR band at 1004 cm^{−1}, which is attributed to the C–S vibration and is shifted some 35 cm^{−1} from the corresponding vibration in thiosaccharin, we propose that binding of the tsac ligands occurs through sulphur. This is not unexpected and is in accord with the established chalcogenophilic nature of Pd(II) and also with previous

work from our laboratory [18]. While we have been unable to crystallographically characterise **2** and **3**, we strongly believe that the *trans* arrangement confirmed in **1** is maintained upon chloride substitution. The basis of this is the relatively simple nature of their IR spectra and the aromatic region of the ¹H NMR spectra, both being consistent with retention of the (approximate) *D*_{2h} symmetry.

Fig. 2 Molecular structure of *cis*-[Pd(N-bit)₂(H₂NBz)₂] (**4**) with selected bond lengths (Å) and angles (°): Pd–N(1) 2.022(2), Pd–N(2) 2.015(3), Pd–N(3) 2.045(2), Pd–N(4) 2.056(3), N(1)–Pd–N(2) 90.3(1), N(3)–Pd–N(4) 90.1(1), N(1)–Pd–N(3) 178.5(1), N(2)–Pd–N(4) 177.8(1)

Table 1 Crystallographic data for *cis*-[Pd(bit)₂(H₂NBz)₂] (**4**)

Empirical formula	C ₂₈ H ₂₆ N ₄ O ₂ Pd S ₂
Formula weight	621.05
Temperature	200(2) K
Wavelength	0.71073 Å
Crystal system, space group	Monoclinic, <i>P</i> 2 ₁ / <i>c</i>
Unit cell dimensions	<i>a</i> = 9.8581(4) Å, α = 90° <i>b</i> = 23.7295(8) Å, β = 102.856(3)° <i>c</i> = 11.6318(5) Å, γ = 90°
Volume	2652.79(18) Å ³
Z, Calculated density	4, 1.555 mg/m ³
Absorption coefficient	0.890 mm ⁻¹
F(000)	1264
Crystal size	0.10 × 0.10 × 0.10 mm
Theta range for data collection	1.72–29.30°
Limiting indices	−13 ≤ <i>h</i> ≤ 13, −32 ≤ <i>k</i> ≤ 32, −15 ≤ <i>l</i> ≤ 14
Reflections collected/unique	19,921/7115 [<i>R</i> (int) = 0.0597]
Completeness to θ = 25.00	97.9%
Max. and min. transmission	0.9162 and 0.9162
Refinement method	Full-matrix least-squares on <i>F</i> ²
Data/restraints/parameters	7115/0/350
Goodness-of-fit on <i>F</i> ²	1.052
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> ₁ = 0.0377, <i>wR</i> ₂ = 0.0732
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0696, <i>wR</i> ₂ = 0.0851
Largest diff. peak and hole	0.605 and −0.628 e Å ⁻³

This assignment is also made on the basis of the chemical shifts of the amine protons at δ 4.34 and 4.58, respectively (see below).

Reaction of two equivalents of sodium benzisothiazolate with **1** in methanol gave a yellow–brown solution and, unlike previous reactions with sodium saccharinate and thiosaccharin, no solids initially precipitated from the solution. However, after filtration and upon standing for a few days, slow evaporation of the methanol led to the growth of yellow crystals identified as *cis*-[Pd(N-bit)₂(H₂NBz)₂] (**4**) in 87% yield. The ¹H NMR spectrum was significantly different to those of **1–3**, being more complicated with overlapping signals in the aromatic region (indicative of a lowering of the D_{2h} symmetry), while the amine protons appeared at δ 5.56. We have recently reported [Pd(H₂NBz)₃Cl][Cl] and note that its ¹H NMR spectrum shows two amine resonances in an approximate 2:1 ratio at δ 4.70 (4H) and 5.26 (2H) [34] assigned to the mutual *trans* amines and that lying *trans* to the chloride, respectively. This suggested to us that the amines in **4** adopted a relative *cis* orientation. A single-crystal analysis was carried out in order to determine the coordination mode of the bit ligands and relative arrangement of amines. The results of this are shown in Fig. 2 and its caption (Table 1).

The structure confirms that the two bit ligands bind in a monodentate fashion through nitrogen, but the main

surprise was their relative *cis* arrangement. All four palladium–nitrogen bond lengths are similar, although those to the benzisothiazolate ligands [Pd–N(1) 2.022(2), Pd–N(2) 2.015(3) Å] are slightly shorter than to the benzyamine groups [Pd–N(3) 2.045(2), Pd–N(4) 2.056(3) Å]. The latter compare well with the related bonds in *trans*-[PdCl₂(H₂NBz)₂] [Pd–N 2.050(4) and 2.046(2) Å] [32, 33] and [PdCl(H₂NBz)₃]Cl·H₂O [Pd(1)–N(1) 2.061(2), Pd(1)–N(2) 2.053(2), Pd(1)–N(3) 2.063(2) Å] [34]. Both Pd–N(bit) bond lengths in **4** are significantly shorter than those in [Pd(N-bit)₂(κ²-Ph₂PCH₂CH₂PPh₂)] [Pd–N 2.070(3) & 2.100(3) Å] [26], being closer to [Pd(N-bit)₂(κ²-H₂NCH₂CH₂NH₂)] [Pd–N 2.029(2) & 2.031(2) Å] [25], suggesting that they may be sensitive to a *trans*-influence.

Complex **4** is the third example of a palladium-bis(benzisothiazolate) complex, and like the diphosphine and diamine derivatives, it also contains a *cis* arrangement of benzisothiazolate ligands. Thus, it may be that these ligands inherently prefer to adopt a relative *cis* orientation, although in **4** this is the first example where the arrangement is not imposed by a chelating co-ligand. A possible explanation for the *cis* geometry in **4** comes from inspection of the intermolecular packing of the individual molecules. Thus, as shown in Fig. 3, pairs of molecules are strongly associated by hydrogen bonds between the amine protons and the oxygen atoms of the benzisothiazolate

Fig. 3 Packing of two molecules of **4** with intermolecular bond lengths (Å). Symmetry operator: i : $-x + 2, -y, -z$. We located the protons on nitrogen from Fourier difference maps and acknowledge that this leads to abnormally short N–H distances but we favour this approach over that of using computationally generated positions.

	D–H / Å	H...A / Å	D...A / Å	<(DHA) / °
N3–H16...O2	0.97(3)	1.95(3)	2.826(4)	150(2)
N3–H17...O1 ⁱ	0.82(3)	2.02(3)	2.813(3)	162(3)
N4–H25...O1 ⁱ	0.78(4)	2.18(4)	2.882(3)	151(3)
N4–H26...O2 ⁱ	0.76(4)	2.45(4)	3.102(3)	145(4)

ligands. This arrangement brings the two palladium atoms in close proximity [Pd...Pd 3.839 Å].

Conclusion

In this contribution, we have shown that simple exchange of both chlorides in *trans*-[PdCl₂(H₂NBz)₂] (**1**) for the related mono-anionic (X) N-heterocyclic saccharinate, thiosaccharinate and benzisothiazolinate ligands in all cases affords the expected palladium(II) complexes [PdX₂(H₂NBz)₂]. The molecular structure of the product is, however, sensitive to the nature of the incoming ligand with products *trans*-[Pd(N-sac)₂(H₂NBz)₂] (**2**), *trans*-[Pd(S-tsac)₂(H₂NBz)₂] (**3**) and *cis*-[Pd(N-bit)₂(H₂NBz)₂] (**4**) resulting, respectively. Formation of N-coordinated saccharinate and S-bound thiosaccharinate ligands to the same metal fragments has been previously noted [18] and likely results from a preference of Pd(II) to bind to a soft sulphur centre when available. Palladium(II) bis(benzisothiazolinate) complexes are far less common [25, 26] but the three crystallographically characterised examples all contain a *cis* arrangement of benzisothiazolinate ligands. In [Pd(N-bit)₂(H₂NBz)₂] (**4**), this is the first time that this *cis* arrangement has not been imposed by the presence of a chelating co-ligand and the preferential precipitation of *cis*-**4** over its *trans* isomer (which may be

initially formed) may result from the ability of the *cis* complex to form strong intermolecular hydrogen bonds with a neighbour, thus favouring crystallisation of this isomer.

Supplementary information

CCDC 1503153 contains the supplementary crystallographic data for **4**. These data can be obtained free of charge from the Cambridge Crystallographic Data Center via www.ccdc.cam.ac.uk/data-request/cif.

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