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Note

Double cyclometallation of bridging 3,6-bis(2-thienyl)-1,2,4,5-tetrazine in a dinuclear mesityl(dimethylsulfoxide)platinum(II) complex: Structure and properties

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Abstract

3,6-Bis(2-thienyl)-1,2,4,5-tetrazine (bttz) reacts with *trans*-Pt(dmso)$_2$(mes)$_2$, mes = mesityl = 2,4,6-trimethylphenyl, under twofold cyclometallation to yield structurally characterized (μ-bttz-2H$^+$)[Pt(dmso)(mes)]$_2$ with uncoordinated thiophene sulfur atoms and bttz deprotonated in the 3,3′ positions. The structural features include *cis*-positioned carbanionic ligands, twisted mesityl substituents, *S*-coordinated dmso ligands with the S=O bonds lying in the molecular plane, shortened inter-ring bonds, and rather short Pt–C bonds at 1.998(9)/2.00(1) Å (Pt–C$_{\text{mes}}$) and 1.985(9)/1.99(1) Å (Pt–C$_{\text{bttz-2H+}}$). Reversible reduction to $\{(\mu\text{-bttz-2H}^+)[\text{Pt(dmso)(mes)}]_2\}^{\cdot-}$ causes a high-energy shift of the charge transfer bands and the appearance of an unresolved EPR signal at $g = 1.9905$.

Keywords: Crystal structure; Cyclometallation; EPR spectroscopy; Heterocyclic ligand; Platinum complex

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1. Introduction

The cumulation of four electronegative nitrogen atoms in a benzenoid six-membered ring to form 1,2,4,5-tetrazines has a number of remarkable consequences. In addition to their high nitrogen content [1] 1,2,4,5-tetrazines are distinguished by a very low-lying π^* molecular orbital centered on the N atoms which is responsible for facile reduction (electron transfer and hydrogenation) [2] and low-energy electronic transitions [3], observable in absorption and emission [3]. Typically, the low-energy transitions of 1,2,4,5-tetrazines are of internal π–π^* or n-π^* character [3], however, with electron rich metals coordinated via the N lone pairs [4] it is also possible to observe intense metal-to-ligand charge transfer (MLCT, d-π^*) transitions at rather long wavelengths. Most metal complexes of tetrazines have involved derivatives with coordinating groups in 3,6-position [4]. Among the potentially bis-chelating tetrazine acceptor ligands the 3,6-bis(2-thienyl)-1,2,4,5-tetrazine (bttz) [5–7] has occupied a special position (Scheme 1). The dinuclear redox systems $\{(\mu\text{-bttz})[\text{M(bpy)}_2]_2\}^{n+}$, M = Ru or Os, with unusually different features of the mixed-valent intermediates were initially assumed to involve S-bonded thienyl rings [5] but have now been identified as bis-cyclometallated species [7] following C–H activation. On the other hand, [Ru(acac)$_2$(CH$_3$CN)$_2$] reacts with bttz under reductive ring-opening of the tetrazine to yield a complex $\{(\mu\text{-dih-Th})[\text{Ru(acac)}_2]_2\}$ with dih-Th^{2-} = 1,2-bis(2-thienylimino)-hydrazido(2-), i.e. with uncoordinated thiophene [8].

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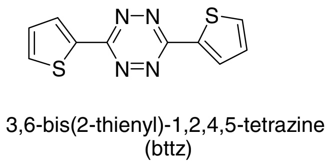

Scheme 1.

In the course of further studies on compounds between bttz and platinum metal containing complex fragments we have now been able to obtain a doubly cyclometallated compound for structural analysis and electron transfer studies. The precursor compound [Pt(dmso)$_2$(mes)$_2$] which exists in a *trans* configuration [9] and not in a *cis* arrangement as earlier believed [10] reacts with bttz to form the dinuclear bis-cyclometallated species (μ-bttz-2H$^+$)- [Pt(dmso)(mes)]$_2$ as evident from a crystal structure determination and from spectroscopy (NMR, EPR of the reduced form), cyclic voltammetry and spectroelectrochemistry.

Whereas mononuclear cyclometallated platinum(II) complexes are well known [11], not in the least due to their photophysical properties [12], there are but a few reports of dinuclear such compounds [13] in which the potential for π conjugatively mediated metal–metal interaction exists. Dinuclear platinum(II) compounds have been discussed in connection with cytostatic behaviour [14], and organometallic compounds containing conjugated bridging ligands were investigated with respect to reduction and oxidation, establishing radical and mixed-valent intermediates [15]. Considering the stabilization of the Pt(III) state by two mesityl substituents [16] and the coordination ambivalence of the bttz ligand [5,7] we have reacted these components in order to probe the coordination behaviour of that ligand.

2. Results and discussion

Reaction of bttz with 2 equiv. of Pt(dmso)$_2$(mes)$_2$ for 5 days in refluxing toluene produced (μ-bttz-2H$^+$)-[Pt(dmso)(mes)]$_2$ in 28% isolated yield. In addition to elemental and crystal structure analysis (see below) the IR and ^{1}H NMR spectrum clearly point to the composition indicated, the C–H activation of thienyl rings to effect cyclometallation is a known kind of reactivity [11–13].

Table 1
Selected bond lengths (Å) and angles (°) for {(μ-bttz-2H$^+$)[Pt(dmso)-(mes)]$_2$}

Bond lengths			
Pt1–N1	2.091(7)	C1–C2	1.406(13)
Pt1–C3	1.985(9)	N1–N2	1.316(10)
Pt1–C6	1.998(9)	C1–N1	1.363(11)
Pt1–S2	2.274(3)	C1–N2A	1.362(11)
Bond angles			
C3–Pt1–C6	91.1(4)	S2–Pt1–N1	97.6(2)
C3–Pt1–N1	80.3(3)	C2–C3–Pt1	113.5(7)
C3–Pt1–S2	176.7(3)	C3–C2–C1	118.5(8)
C6–Pt1–S2	91.0(3)	C2–C1–N1	114.3(8)
C6–Pt1–N1	171.4(3)	C1–N1–Pt1	113.4(6)

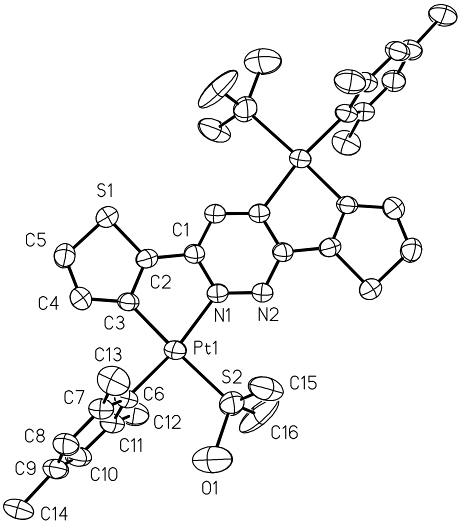

Fig. 1. Molecular structure of {(μ-bttz-2H$^+$)[Pt(dmso)(mes)]$_2$} in the crystal.

Crystallization of the greenish-brown compound gave single crystals of suitable quality for X-ray diffraction. Table 1 contains the bond parameters and Fig. 1 shows a representation of the molecule in the crystal.

The crystal structure analysis confirms the binding of both equivalent platinum(II) centers to the 3 or 3′ positions of the thienyl rings, leaving the sulfur atoms uncoordinated. Whereas the doubly deprotonated bttz bridge and the C,C,N,S donor sets around the platinum centers are largely coplanar, the mesityl ligand is almost orthogonally positioned, reflecting the steric repulsion of the *ortho*-methyl substituents [16]. The dmso ligand is bound through the sulfur atom in such a way that the S=O bond comes to lie within the main molecular plane [17]. Expectedly, the carbanionic ligands at each platinum center are oriented in *cis* position, the Pt–C bond lengths are rather similar and relatively short at about 1.99 Å (Table 1).

The bond parameters *within* the heterocycles of (μ-bttz-2H$^+$)[Pt(dmso)(mes)]$_2$ can be compared with those of free bttz [5c,7]: The main differences are the shortened inter-ring distance (1.448(3) Å → 1.406(13) Å) and the diminished intra-chelate angle N1–C1–C2 (117.9(2)° → 114.3(8)°). Whereas the latter is caused by the formation of the short C3–Pt bond, the increased inter-ring bond order reflects the charge shift from the deprotonated thienyl rings to the strongly [4a] electron accepting tetrazine.

Electron acceptance is also obvious from electrochemical experiments: The reversible reduction of the diplatinum(II) complex as determined by cyclic voltammetry occurs at −0.76 V vs. ferrocenium/ferrocene, i.e. at distinctly less negative values than the reduction of the free bttz ligand at −1.26 V [5,7]. This result, observed in spite of the double deprotonation of the bridging ligand, confirms