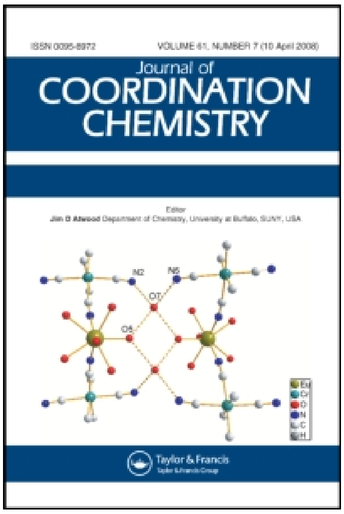

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Pd(thiosaccharinato)$_2$·H$_2$O, the first thiosaccharinato complex of a platinum-group metal

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Pd(thiosaccharinato)$_2\cdot H_2O$, the first thiosaccharinato complex of a platinum-group metal

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A Pd(II) complex of the thiosaccharinato (tsac) anion, of stoichiometry Pd(tsac)$_2\cdot H_2O$ was prepared by interaction of Na_2PdCl_4 with thiosaccharin in methanol and characterized by infrared and ^1H and ^{13}C NMR spectroscopy. These spectral studies confirmed interaction of the metal center with the thiosaccharinate acting as a bidentate ligand through its thiol group and the N-atom. NMR measurements also confirmed that in solution thiosaccharin is mainly present in its thiolate tautomeric form.

Keywords: Palladium(II); Thiosaccharin; IR; NMR

1. Introduction

Although a number of metal complexes of saccharin (o-sulphobenzimide) have been prepared and thoroughly characterized (for a recent review cf [1]), information concerning similar complexes of thiosaccharin remains relatively scarce [2]. We have begun a systematic study of thiosaccharinato complexes, preparing and performing detailed structural and spectroscopic studies of different Cd(II) and Tl(I) complexes containing this ligand alone or together with other coordinating molecules [3–6].

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In order to investigate the differences in chemical behavior between saccharin and thiosaccharin we have also performed a theoretical study, using density functional theory, of the electronic structures of these molecules and their anions [7].

As a continuation of these studies, we have now investigated the possible interaction of thiosaccharin with different platinum-group metals and found that it is possible to isolate a simple thiosaccharinato (tsac) complex of Pd(II) of stoichiometry $Pd(tsac)_2 \cdot H_2O$. In this article we describe the synthesis and spectroscopic characterization of this complex.

2. Experimental

2.1. *Materials*

All common chemicals were purchased from commercial sources and used without further purification. The employed thiosaccharin was prepared by reaction of saccharin with Lawesson's reagent in toluene, according to the procedure of Scheibye *et al.* [8].

2.2. *Synthesis of the complex*

The new complex precipitated after refluxing Na_2PdCl_4 (40 mg, 0.136 mmol) with thiosaccharin (54 mg, 0.272 mmol) in methanol (10 mL) for 5 h. The generated complex was filtered from the hot solution as a yellow brownish solid and was not further purified. Yield: 55 mg, 75%. Anal. Calcd for $C_{14}H_{10}N_2O_5S_4Pd$: C, 32.25; H, 1.92; N, 5.37; S, 24.62%. Found: C, 32.43; H, 2.00; N, 5.31; S, 24.44%.

Unfortunately, it was impossible to obtain single crystals adequate for a crystallographic study. Therefore, we have analyzed the complex on the basis of its infrared and ^1H and ^{13}C NMR spectra.

2.3. *Characterization*

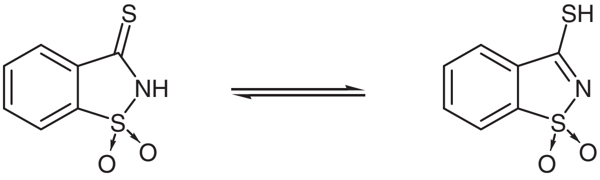
Elemental analysis was performed with a Carlo Erba Model EA 1108 elemental analyzer. FTIR spectra in the spectral range between 4000–400 cm^{-1} were measured as KBr pellets on a Bomen M 102 instrument.

^1H and ^{13}C NMR spectra of the free ligand and of the complex were recorded on a Bruker DPX-400 instrument (at 400 and 100 MHz, respectively). Experiments were performed at 303 K in deuterated dimethylsulfoxide, DMSO-d_6. Heteronuclear correlation experiments (2D-HETCOR), HMQC (multiple quantum) and HMBC (multiple bond), were performed with the same instrument. Tetramethylsilane was used as the internal standard and the chemical shifts are reported in ppm. The stability of the complex in such medium was monitored by ^1H-NMR at 303 K in DMSO-d_6 during the NMR experiments, to examine possible ligand substitution by DMSO. Special attention was paid to the emergence of DMSO signals, that must appear if DMSO enters the coordination sphere of the metal atom (cf [9] and references therein), and the emergence of signals due to the free ligand.

3. Results and discussion

3.1. *Infrared spectra*

Thiosaccharin has two tautomeric forms in solution:



As shown by our theoretical analysis [7] and confirmed by the NMR measurements performed during the present study (see below), the thiol form (right side of the depicted equilibrium) predominates. Therefore, and as it has been found in previously investigated thiosaccharinato complexes [3–6], one may expect interaction of the Pd(II) cation with the **S** and **N** atoms of the deprotonated ligand. This expectation was clearly confirmed by the analysis of IR spectrum of $Pd(tsac)_2 \cdot H_2O$.

As discussed in our previous papers on different thiosaccharinato complexes [3–6] the most important and interesting vibrational modes for structural analysis, correspond to vibrations of the five-membered ring localized between 1500 and 400 cm^{-1} and which involve, in particular, the $\nu(CN)$, $\nu(CS)$, $\nu(NS)$ and $\nu(SO_2)$ motions. In table 1 these and other characteristic vibrations of free thiosaccharin [3] and of the $Pd(tsac)_2 \cdot H_2O$ are compared. Data for the [Tl(tsac)] [6] and $[Cd(tsac)_3(H_2O)]^-$ [4] complexes, in which relatively strong M^{II}–S bonds and secondary M^{II}–N interactions have been established by complete crystallographic structural analyzes, are also included.

The data presented in this table show the same trends for $Pd(tsac)_2 \cdot H_2O$ as those observed for the other two complexes. In particular, it is evident that after coordination, the C–N bond is strengthened, in good agreement with the results of theoretical calculations [7]. The $\nu(CS)$ stretching mode is not a good group vibration because it is coupled with other motions of the sulfothioamide skeleton [3,10]; the band mainly related to this motion, located at 1039 cm^{-1} in thiosaccharin, should be displaced to lower energies in the complexes, as also observed from the data of table 1. The $\nu(NS)$ stretching motion is less affected after coordination in all cases, but presents

Table 1. IR-spectroscopic data for free thiosaccharin, $Pd(tsac)_2 \cdot H_2O$, [Tl(tsac)] and $[Cd(tsac)_3(H_2O)]^-$ (band positions in cm^{-1}).

Thiosaccharin	[Tl(tsac)]	$[Cd(tsac)_3(H_2O)]^-$	$Pd(tsac)_2 \cdot H_2O$	Assignment
1247m	1382m	1420vs	1421s	$\nu(CN)$
1376vs	1269vs	1299vs	1241vs	$\nu_{as}(SO_2)$
1156vs/1120m	1148vs/1112m	1159vs/1151vs	1129s	$\nu_s(SO_2)$
1039m	1005s	1005vs	1022s/1011s	$\nu(CS)$
817vs	819s/815s	817vs	805s	$\nu(NS)$
591s	625w	623m	597s	$\gamma(SO_2)$
		3557sh/3485m	3440s,br	(O–H) (H_2O)
		1627sh/1613m	1617m	$\delta(H_2O)$
			470m	$\rho(H_2O)$ (?)

vs, very strong; s, strong; m, medium; sh, shoulder; br, broad.

its lowest value in the new Pd-complex, pointing to a stronger Pd–N interaction in the present case.

On the other hand, and taking into account that four-membered chelate rings are relatively unstable, we cannot exclude the formation of a polymeric complex in which the thiosaccharinato moieties act as bidentate bridging ligands.

Regarding the stretching vibrations of the SO_2 groups, the antisymmetric motion is more affected than the symmetric one, upon complex formation. The higher shifts observed for $Pd(tsac)_2 \cdot H_2O$, in comparison with the other complexes, can probably be related to the involvement of the O-atoms of this group in H-bonding with the water molecule, or may be an indirect consequence of the formation of the Pd–N bond.

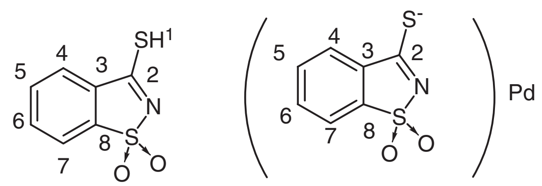
Ligand-to-metal vibrations are probably located below 300 cm^{-1} [4]. No spectral evidence was found for H_2O participation in bonding. The position of the ν(OH) band of this molecule and its broadening, suggests participation in formation of H-bonds of intermediate length [11].

3.2. *NMR studies*

The complex was stable in DMSO. Neither coordination of DMSO to palladium nor liberation of free thiosaccharin was detected by ^{1}H-NMR in DMSO-d_6 during the time involved in the NMR experiments at 303 K. Table 2 shows the ^{1}H and ^{13}C NMR chemical shifts (δ) of the ligand and the complex, and the chemical shift differences between complex and ligand, expressed as $\Delta\delta$. The attached figure shows the numbering scheme.

^{1}H NMR integrations and signal multiplicities are in agreement with the proposed formula and structure. HETCOR experiments allowed assignment of all signals of the free ligand and the complex.

Table 2. ^{1}H and ^{13}C NMR chemical shift values (δ) in ppm, of the ligand and the $Pd(tsac)_2 \cdot H_2O$ complex, in DMSO-d_6 at 303 K.



Proton	δ_H Ligand	δ_H Complex	$\Delta\delta$ (Complex–Ligand)	Carbon	δ_C Ligand	δ_C Complex	$\Delta\delta$ (Complex–Ligand)
1	6.42	–	–				
				2	161.53	189.69	28.16
				3	128.21	128.00	0.21
4	8.04	8.10	0.06	**4**	126.38	122.51	−3.87
5	7.81	7.86	0.05	**5**	135.68	138.00	2.32
6	8.02	7.95	−0.07	**6**	136.50	137.00	0.50
7	8.17	8.14	−0.03	**7**	122.05	121.93	−0.12
				8	140.10	139.00	−0.90

The free ligand exists, in the NMR experimental conditions, as the thiol tautomer. This is confirmed by the detection of proton **1** and by the chemical shift observed for carbon **2** [12, 13]. When the ligand is coordinated to the Pd(II) cation, the signal corresponding to the thiol proton (proton **1**) is not observed, in agreement with the deprotonation of thiosaccharin. In addition, a low deshielding effect of the metal is apparent for those protons that are located relatively close to the coordinating atoms (protons **4** and **5**), causing a downfield shift of these ^{1}H NMR resonances [9, 14]. Upon coordination, the most distinguishing feature of the ^{13}C NMR spectra is the change in the chemical shift of carbon **2**, which falls near 190 ppm. This chemical shift lies near the value commonly observed for the thiocarbonyl moiety ($\delta_{C=S} = \sim 200$ ppm [12]). However, the results of previously reported NMR experiments for other metal coordination compounds showed that carbon atoms located near the metal could suffer significant downfield displacements due to electronic effects [9, 15]. Therefore, taking into account previous NMR results, the predominant tautomeric form of the ligand in the thiosaccharinato complexes [7] and the IR data of the new Pd-complex, we considered that the enthiol carbon **2** could be significantly deshielded in the complex, owing to an electron attractive effect of the metal.

The other carbons, located far from the metal center, suffered only a low effect in their chemical shifts.

4. Conclusions

A new Pd(II) complex of thiosaccharine, of stoichiometry $Pd(tsac)_2 \cdot (H_2O)$, was prepared and spectroscopically characterized. The position of the IR bands (mainly ν(CN), ν(CS) and ν(NS) vibrations) clearly reflect coordination of the ligand through its thiocarbonyl sulfur atom, with great delocalization of the negative charge over the thionate group [7], and generation of Pd–N interactions, i.e. the anion acts as a bidentate ligand generating two S–Pd–N bonds. The Pd–S interaction is also supported by ^{1}H and ^{13}C NMR spectra. These NMR studies also confirmed that in solution the ligand is mainly present in its thiol form.

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