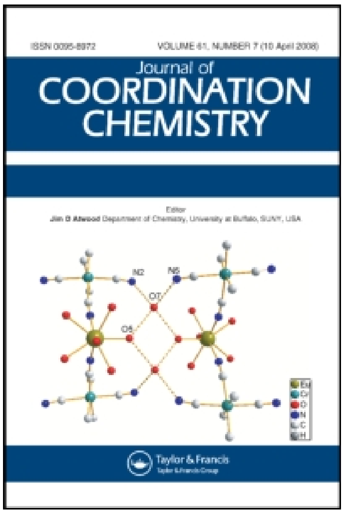

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1,3-DIPOLAR CYCLOADDITION OF CS_2 TO THE COORDINATED AZIDE IN THE CYCLOPALLADATED $[Pd(bzan)(\mu-N_3)]_2$. CRYSTAL AND MOLECULAR STRUCTURE OF DI(μ-N,S-1,2,3,4-THIATRIAZOLE-5-THIOLATE)BIS[(BENZYLIDENEANILINE-C^2,N)PALLADIUM(II)]

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1,3-DIPOLAR CYCLOADDITION OF CS_2 TO THE COORDINATED AZIDE IN THE CYCLOPALLADATED $[Pd(bzan)(\mu\text{-}N_3)]_2$. CRYSTAL AND MOLECULAR STRUCTURE OF DI(μ-N,S-1,2,3,4-THIATRIAZOLE-5-THIOLATE)BIS[(BENZYLIDENEANILINE-C^2,N)PALLADIUM(II)]

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The compound $[Pd(bzan)(\mu\text{-}N_3)]_2$ **1**, *bzan* = benzylideneaniline, was prepared from $[Pd(bzan)(\mu\text{-}OOCCH_3)]_2$ by an anion exchange reaction. The 1,3-dipolar cycloaddition of carbon disulfide to the bridged coordinated azide in the cyclometallated compound **1** was investigated. The species resulting from this reaction, di(μ-N,S-1,2,3,4-thiatriazol-5-thiolate)bis[(benzylideneaniline)palladium(II)] **2**, was characterized by IR spectroscopy and X-ray diffraction. The compound **2** is a dimer containing two [Pd(benzylideneaniline)] moieties connected by two vicinal bridging N,S-1,2,3,4-thiatriazole-5-thiolate anions in a square-planar coordination geometry for the palladium atoms.

Keywords: Cyclopalladated; Azido; Cycloaddition; Carbon disulfide; Infrared spectroscopy; X-ray diffraction

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INTRODUCTION

Cyclometallated species constitute an important class of organometallic compounds [1]. Within this class, there has been considerable interest in cyclopalladated complexes due to their use in areas such as catalysis [2], in the design of metallomesogens [3], photochemistry [4] and antitumor agents [5].

Cyclopalladated compounds can be prepared by the coordination to palladium of tertiary benzylamines, oximes, imines, azines, several *N*-heterocycles and also benzylideneamines [6], whose mechanism of cyclopalladation is well understood. Accordingly, a significant number of halide and acetate-bridged dimers of cyclopalladated compounds containing benzylideneamines have been reported.

Our interest in coordination complexes bearing *pseudo*-halogens [7] and our previous paper [8] where we reported the first X-ray crystal diffraction of a metallated complex bearing the heterocyclic anion $CN_3S_2^-$, $[Pd(dmba)(\mu\text{-}N,S{-}CN_3S_2)]_2$ **3** (*dmba* = *N*,*N*-dimethylbenzylamine), have encouraged us to prepare $[Pd(bzan)(\mu\text{-}N_3)]_2$ **1** (*bzan* = *N*-benzylideneaniline) in which the azido groups can undergo 1,3-dipolar cycloaddition of CS_2 to produce another member of the series of complexes stabilized by the heterocyclic anion. These insertion reactions are important working tools because these types of complexes are inaccessible through other synthetic routes [9]. We therefore report here the synthesis of $[Pd(bzan)(\mu\text{-}N,S{-}CN_3S_2)]_2$ **2**, which was characterized by IR spectroscopy and X-ray crystallography.

EXPERIMENTAL

General Comments

The preparation of $[Pd(bzan)(\mu\text{-}N,S{-}CN_3S_2)]_2$ **2** was carried out under purified nitrogen in a Schlenk apparatus. Solvents were purified using standard methods [10]. $[Pd(bzan)(\mu\text{-}OOCCH_3)]_2$ was prepared by literature methods [11]. IR spectra in the range 400 – 4000 cm^{-1} were recorded on a FTIR Nicolet-Impact 400 spectrophotometer and the samples were ground with KBr and pressed into pellets. Central Analítica of IQ-USP (São Paulo – Brazil) performed the elemental analyses.

Synthesis of $[Pd(bzan)(\mu\text{-}N_3)]_2$ 1

To a solution of 0.100 g (0.145 mmol) of $[Pd(bzan)(\mu\text{-}OOCCH_3)]_2$ in 20 mL of acetone was added 0.0177 g (0.272 mmol) of sodium azide.

After stirring the solution for 30 min, the solution was concentrated to give a yellow precipitate which was filtered, washed with *n*-pentane, and then dried *in vacuo*. Recrystallization from a mixture of chloroform and pentane gave yellow crystals. Yield: 0.0943 g (99%). Anal. Calcd. for $PdC_{13}H_{10}N_4$ (%): C, 47.51; H, 3.07; N, 17.05. Found: C, 48.08; H, 3.24; N, 16.76.

Synthesis of $[Pd(bzan)(\mu\text{-}N, S\text{—}CN_3S_2)]_2$ 2

To a solution of 0.132 g (0.200 mmol) of $[Pd(bzan)(\mu\text{-}N_3)]_2$ in 30 mL of dichloromethane was added 0.5 mL (8.3 mmol) of carbon disulfide. After stirring the solution for 8 h, the solution was concentrated to give a rather unstable, orange solid which was filtered, washed with *n*-pentane, and then dried *in vacuo*. Careful recrystallization from a mixture of acetone/chloroform (1 : 1), under nitrogen, gave orange crystals of analytical quality and suitable for X-ray analysis. Yield: 0.0981 g. Anal. Calcd. for

TABLE I Summary of data collection and refinement for $[Pd(bzan)(\mu\text{-}N, S\text{—}CN_3S_2)]_2$

Molecular formula	$[Pd(C_{13}H_{10}N)(CN_3S_2)]_2$
Molecular mass	404.791
Crystal system	orthorhombic
Space group	Pbcn
A (Å)	20.348 (5)
b (Å)	9.128 (3)
c (Å)	16.020 (5)
Z (dimer/unit cell)	4
V(Å^3)	2975.6 (1)
D_c(g · cm^{-3})	1.807
Crystal size (mm)	0.20 × 0.20 × 0.10
Crystal color	orange
μ (cm^{-1})	15.0
λ (Å)	0.71073
Scan mode	$\omega - 2\theta$
Temperature (K)	298
Scan speed (°min^{-1}) max. – min	16.48 – 2.75
θ range (°)	2.5 – 28.0
Range in *hkl*: min.	– 26; – 2; – 2
max.	25; 12; 21
No. reflections collected	4246
Unique reflections; R_{int} (in I)	3569, 0.023
Observed reflections ($I \geq 2\sigma(I)$)	2124
R	0.036
R_w	0.040
R_{all}	0.099
Goodness of fit	1.08
No. of variables	190
Max. density in diff. map (e/Å^3)	0.36 (8)
Min. density in diff. map (e/Å^3)	– 0.23(8)
Weight system (*w*) for observed	Non Poisson

$[Pd(C_{13}H_{10}N)(\mu\text{-}N,S\text{—}CN_3S_2)]_2$ (%): C, 41.54; H, 3.23; N, 13.84. Found: C, 41.32; H, 3.18; N, 13.53.

Crystal Structure Determination of $[Pd(bzan)(\mu\text{-}N, S\text{—}CN_3S_2)]_2$ 2

A single crystal of the compound was mounted in the Enraf-Nonius CAD4 diffractometer, at room temperature, and using 25 reflections automatically centered, the cell parameters were obtained and refined. Table I shows the data collection and refinement conditions. The intensity data were reduced to F_0 values and corrected by absorption factors $[\mu(Mo-K_\alpha) = 15.0\,cm^{-1}]$. The structure was solved by Patterson function and difference Fourier synthesis, and refined by full matrix least squares, using MolEN system [12]. The hydrogen atoms were located in their ideal positions and not refined, using d(C—H) = 0.96 Å, and with thermal vibration equal to 1.3 times the isotropic equivalent B of the attached carbon. All non-hydrogen atoms were refined anisotropically, and the atomic scattering factors were those from Cromer and Mann [13] with anomalous dispersion from Cromer and Liberman [14] and for hydrogen atoms from Stewart *et al.* [15]. The atomic coordinates of heavy atoms are shown in Table II. The anisotropic thermal parameters, observed and calculated structure factors, hydrogen coordinates, complete angles and distances tables are available from A.E.M.

TABLE II Fractional atomic coordinates and isotropic equivalent temperature factor with e.s.d.'s in parentheses for the $[Pd(bzan)(\mu\text{-}N, S\text{—}CN_3S_2)]_2$

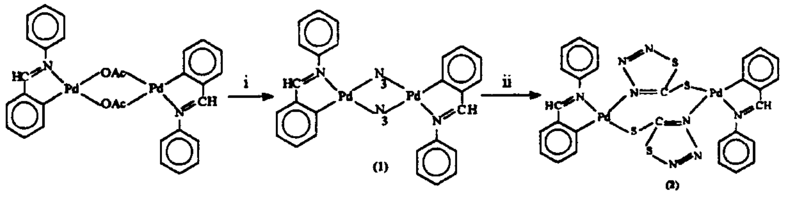
Atom	*x*	*y*	*z*	*Beq*(*Å* ^{2})
Pd	0.96684 (2)	0.41331 (4)	0.66261 (2)	2.810 (6)
S (1)	0.88476 (6)	0.5613 (2)	0.71147 (9)	4.45 (3)
S (2)	1.12057 (7)	0.7890 (2)	0.6562 (1)	4.76 (3)
N (1)	1.0308 (2)	0.2638 (4)	0.6080 (2)	2.98 (7)
N (2)	1.0330 (2)	0.5991 (4)	0.6559 (2)	3.18 (8)
N (3)	1.0232 (2)	0.6873 (5)	0.5888 (3)	4.2 (1)
N (4)	1.0648 (2)	0.7898 (5)	0.5788 (3)	4.8 (1)
C	0.9145 (2)	0.6395 (5)	0.7983 (3)	2.94 (9)
C (1)	0.9066 (2)	0.2407 (5)	0.6582 (3)	3.18 (9)
C (2)	0.8407 (2)	0.2277 (6)	0.6803 (3)	4.3 (1)
C (3)	0.8084 (2)	0.0948 (6)	0.6708 (4)	5.0 (1)
C (4)	0.8387 (2)	−0.0268 (6)	0.6404 (4)	4.7 (1)
C (5)	0.9046 (3)	−0.0172 (6)	0.6171 (4)	4.4 (1)
C (6)	0.9373 (2)	0.1162 (5)	0.6263 (3)	3.4 (1)
C (7)	1.0046 (3)	0.1364 (5)	0.6005 (3)	3.6 (1)
C (8)	1.0978 (2)	0.2862 (5)	0.5828 (3)	2.98 (9)
C (9)	1.1461 (2)	0.1951 (6)	0.6114 (4)	3.9 (1)
C (10)	1.2109 (2)	0.2162 (6)	0.5852 (4)	5.1 (1)
C (11)	1.2251 (2)	0.3289 (7)	0.5316 (4)	5.3 (1)
C (12)	1.1770 (2)	0.4194 (6)	0.5028 (3)	4.6 (1)
C (13)	1.1124 (2)	0.3991 (5)	0.5283 (3)	3.6 (1)

RESULTS AND DISCUSSION

The metathesis reaction of the compound [Pd(bzan)(μ-OOCCH$_3$)]$_2$ with sodium azide in acetone gave the corresponding azido-bridged complex [Pd(bzan)(μ-N$_3$)]$_2$ **1**, which could be characterized by elemental analyses and by IR and ^{1}H NMR spectroscopy. Thus, the characteristic asymmetric stretching vibration [16], ν_{as}(N$_3$), of the bridging azide group appeared at 2056 cm^{-1}; the coordination of the C=N moiety of *bzan* to the palladium through the nitrogen lone pair was confirmed by the shift of the ν(C=N) frequency from 1623 cm^{-1} for the free ligand to 1580 cm^{-1} for **1**. The orthometallation of *bzan* can be verified by the observation of the imine proton NMR resonance at $\delta = 8.59$ which is shifted downfield, ca. 0.2 ppm, relative to that of free ligand.

The compound [Pd(bzan)(μ-N$_3$)]$_2$ **1** is interesting because it allows the preparation of various derivatives, like the mononuclear [Pd(bzan)(N$_3$)(*L*)] and the binuclear [Pd(bzan)(N$_3$)(μ-*L*')]$_2$ by reactions of **1** with phosphines or tertiary amines, (*L*), or bidentated phosphines (*L*'), [17] all of them effectively cleave the azido bridge. In spite of the bridging behavior of the coordinated azido group in **1**, it is capable of undergoing a 1,3-dipolar cycloaddition reaction with a carbon-heteroatom multiple bond [8]. It was observed in this work that the heterocumulene carbon disulfide cycloadded to the azido bridging group of **1** under very mild conditions, to give [Pd(bzan)(μ – N, S—CN$_3$S$_2$)]$_2$ **2** in accordance to the following scheme:

i-NaN$_3$, acetone, 30 min.
ii-CS$_2$, dichloromethane, N$_2$, 8h.



The orange complex **2** is insoluble in the reaction medium and its IR spectrum allowed us to get the first insights on its structural features. For instance, no band assignable to ν_{as}(N$_3$) was detected in the IR spectrum; but new bands clearly associated to the anion CN$_3$S$_2^-$ appeared. These were found at 1248, ν(C=S); 1101, ν(CN)+ν(CS); 911, δ(NCS), cm^{-1}, which compare well to those of our previously reported [8]

[Pd(dmba)(μ-N, S—CN_3S_2)]$_2$ **3**, 1247, ν(C=S); 1101, ν(CN) +ν(CS); 908, δ(NCS), cm^{-1}, in which the bridging nature of the heterocyclic anion was confirmed by X-ray diffraction.

The anion $CN_3S_2^-$ is quite interesting since it may coordinate to a metallic center in different ways, such as a monodentate N- or S-bonded ligand, as an N,S chelate or, finally, as an N,S-bridging anion [18].

The similarity in the IR spectra of **2** and **3** indicated clearly that the coordination mode of $CN_3S_2^-$ in **2** should be similar. However, since there is only one report in the literature with crystallographic data on this interesting palladium based family of complexes, it was important to further define the correlation between IR data and the mode of coordination of the anion within the complex. In order to further clarify this point we decided to undertake the full X-ray crystallographic analysis of **2**. The structure of **2** with the atom numbering scheme is depicted in Figure 1. Selected bond lengths and bond angles with estimated standard deviations are listed in Table III.

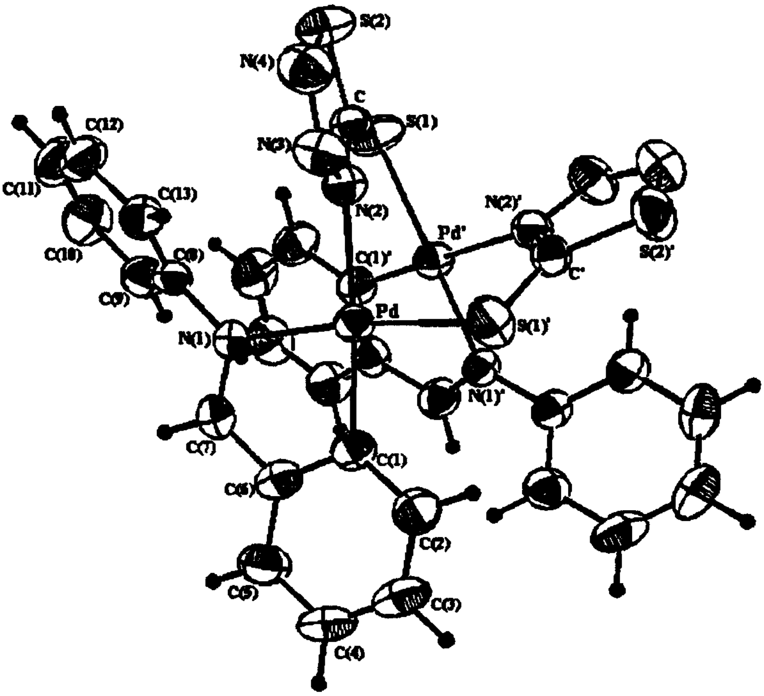


FIGURE 1 ***ORTEP*** drawing of [Pd(bzan)(μ-N, S—CN_3S_2)]$_2$ showing the labeling of atoms.

TABLE III Selected distances (Å) and angles (°) for the $[Pd(bzan)(\mu\text{-}N,S—CN_3S_2)]_2$

Pd—C(1)	1.997 (5)	S(1)'—Pd—N(1)	171.6 (1)
Pd—N(2)	2.168 (3)	N(1)—Pd—N(2)'	96.0 (1)
Pd—S(1)'	2.286 (1)	N(1)—Pd—C(1)	81.4 (2)
Pd—N(1)	2.078 (4)	S(1)'—Pd—C(1)	91.7 (1)
N(2)—N(3)	1.358 (6)	S(1)'—Pd—N(2)'	90.5 (1)
N(3)—N(4)	1.272 (6)	N(2)'—Pd—C(1)	175.1 (2)
S(1)—C	1.677 (5)	N(2)—N(3)—N(4)	116.0 (4)
S(2)—C	1.704 (5)	S(2)—N(4)—N(3)	110.7 (3)
S(2)—N(4)	1.680 (5)	N(4)—S(2)—C	92.1 (2)
N(2)—C	1.347 (6)	S(1)—C—N(2)	128.4 (3)
Pd—Pd'	3.1081 (5)	N(3)—N(2)—C	112.6 (4)

In the evaluation of the parameters of **2**, it is interesting to compare the data with those found for **3**. For instance, in both structures the nitrogen atom of the anion $CN_3S_2^-$ is located *trans* to the orthometallated carbon, therefore leaving the sulfur atom of the anion *trans* to the amine nitrogen of the metallated ligand. This particular disposition is probably electronic in origin, which may be in control of the $PdN_3—CS_2$ cycloaddition process.

In fact, comparison of both sets of data suggest more electronic effects, when one considers the principal difference of both compounds, *i.e.*, the basicity of the orthometallated ligand's nitrogen atoms and the characteristics of the newly formed bidentated anion $CN_3S_2^-$.

On both structures **2** and **3** the anion rings were found to be strictly planar with no atom-plane deviation bigger than 0.009 Å. The alleged aromatic character of the anion's ring implies, in a greater *s* character of the nitrogen lone pair, which assists a strong N—Pd dative covalent bond.

The difference in the basicity of the nitrogen atom of the orthometallated ligand should affect the bond lengths within the anion ring *via* inductive effects or *trans*-influence, since on both structures the orthometallated carbon–palladium bonds are almost equal, 1.997(5) and 1.987(6) Å for **2** and **3** respectively, suggesting that the orthometallation process induces essentially the same overall structural, and electronic effects upon the complexes.

Within the orthometallated ring, the angle N(1)—Pd—C(1) in **2** was found to be 81.4(2)°, with a Pd—N(1) bond length of 2.078(4) Å, whereas in **3** the angle was 81.7(2)°, with a Pd—N(1) bond of 2.114(4) Å. The smaller Pd—N(1) bond length in **2** may be related to the sp^2 nature of the *bzan's* N atom.

The anion rings in both structures have small inner angles deviations from each other, with those centered in N(3) being the widest, the value of 116.0(4)° in **2** being only slightly smaller than the 117.2(5)° in **3**. The smaller angle of the ring is that centered in the internal sulfur atom: 91.9(3)° in **3** and

92.1(2)° in complex **2**. In both cases the other internal angles vary around 110°. The angles centered at all atoms, except sulfur, are therefore close to the sp^2 angle of 120°. The angle of the inner sulfur atom is almost perfect for a non-hybridized sulfur, ideal for $3p$ overlap with the remaining $2p$ orbital of carbon and nitrogen atoms of the ring, to enhance its aromatic character.

The relevant bond distances within the $CN_3S_2^-$ ligand in the two complexes so far examined are interesting. Following the actual numbering scheme, the bonds between N(2)—N(3), C—S(1) and C—S(2) are identical in both structures. All other bonds of the anions in the two compounds vary around the value 0.02 Å in a very interesting fashion: for the *dmba* complex the shortening of 0.02 Å happens between the pairs C—N(2) and N(3)—N(4). This compound also possesses the shorter Pd—N(2) bond, 2.140(5) Å. The bonds which shorten the anion $CN_3S_2^-$ in **2** are those involving the inner S atom, albeit the noted small difference of 0.011 Å between S(2)—C between the two structures, as pointed out before. This particular trend may suggest that *dmba* induces an electronic density surplus over the three nitrogen atoms and the carbon atom of the anion $CN_3S_2^-$, increasing the sp^2 character of the nitrogen lone pair and therefore strengthening the Pd—N(2) bond. In the present case where the orthometallated ligand derives from *bzan*, the anion ring seems to have a concentration of electron density, as seen through the small bond distances, over the C, S(2) and the N(4) atoms, causing a longer Pd—N(2) bond, 2.168(3) Å, compatible with less sp^2 character of the N(2) lone pair. It is necessary to emphasize that the difference in length of the Pd—S(1)′ bond in both complexes, 2.286(1) Å for **2**, and 2.300(2) Å for **3**, may be related to the basicity of the N atom of the orthometallated fragment, which increases from *dmba* to *bzan*.

These suppositions are all in accordance with the bonding of the anion as that shown in Figure 1, with the external sulfur atom having an essentially σ S—Pd bond. Accordingly, each palladium atom in **2** or **3** could be considered to be members of the *cis* NNPdCS family, with CS being the cyclopalladated carbon and the anion's S *sigma* bonded atoms. The preference for this *cis* geometry at the metal center could be the determining factor for the way that the cycloaddition occurs and for the preferential mode of bonding of the ring-like anion.

Finally, it is worth mentioning that the remaining bond lengths and bond angles found for **2** agree well with those in **3** and in other cyclometallated species whose X-ray crystal structures have been determined [19–21]. In addition, the successful determination of the molecular structure of two related compounds such as **2** and **3** provides a direct relationship between the techniques of X-ray diffraction and IR spectroscopy. We therefore suggest that the presence of three IR bands at ca. 1248, 1101 and 911 cm^{-1} in the IR spectra of compounds of this family should be assigned to the N,S bridging coordination mode of the aromatic $CN_3S_2^-$ ion in binuclear cyclopalladates, of planar *cis* NNPdCS geometry.

Current studies are underway to examine the synthesis and reactivity of other azide-cyclopalladated complexes towards CS_2, since metal assisted 1,3-dipolar cycloadditions generally yield thermally and photochemically unstable compounds which decompose readily into isothiocyanate compounds. It will also be an opportunity to probe more deeply into the aromatic characteristics of the new ligand found by cycloaddition and its spectroscopic characteristics.

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