THE STRUCTURE OF TRIS(3',5'-DIMETHYL-PYRAZOL-1-YL)-s-TRIAZINE AND ITS USE AS A LIGAND IN COORDINATION CHEMISTRY

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The crystal and molecular structure of the title compound (Me_2 -TPzT) has been determined by X-ray analysis. The observed molecular conformation presents the nitrogen atoms of three pyrazole rings in the same relative positions. The molecules are joined through intermolecular contacts forming chains that are arranged in a distorted hexagonal symmetry. Two complexes containing this ligand have been prepared: $[{Pd(en)}_3(Me_2-TPzT)](PF_6)_6$ and $[{Ag(PPh_3)}_3(Me_2-TPzT)](ClO_4)_3$, which, due to their insolubility, have been characterized only by microanalysis, IR, ¹H NMR and, in the latter case, by mass spectrometry.

Keywords: X-ray crystallography, pyrazole, s-triazine, palladium and silver complexes.

INTRODUCTION

Following the standard classification of heteroaromatic compounds, ligands used in coordination chemistry can be divided into azoles and azines [1-3]. Trofimenko's scorpionates [4, 5] belong to the first class and pyridine and phenanthroline derivatives to the second one [6-8]. Many groups have successfully used ligands containing both azoles and azines. We have devoted some efforts to explore the structure, properties, and coordinative abilities of 2,4,6-tris(pyrazol-1-yl)-1,3,5-triazines of general formula 1.



2 $R^3 = R^4 = R^5 = H$, TPzT; **3** $R^3 = R^5 = H$, $R^4 = Me$, Me-TPzT; **4** $R^3 = R^5 = H$, $R^4 = Br$, Br-TPzT; **5** $R^3 = R^5 = Me$, $R^4 = H$, Me₂-TPzT; **5** $R^3 = R^5 = Me$, $R^4 = H$, Me₂-TPzT; **7** $R^3 = R^5 = Me$, $R^4 = H$, Me₂-TPzT; **7** $R^3 = R^5 = Me$, $R^4 = H$, Me₂-TPzT; **7** $R^3 = R^5 = Me$, $R^4 = H$, Me₂-TPzT; **7** $R^3 = R^5 = Me$, $R^4 = H$, Me₂-TPzT; **7** $R^3 = R^5 = Me$, $R^4 = H$, Me₂-TPzT; **7** $R^3 = R^5 = Me$, $R^4 = H$, Me₂-TPzT; **7** $R^3 = R^5 = Me$, $R^4 = H$, Me₂-TPzT; **7** $R^3 = R^5 = Me$, $R^4 = H$, Me₂-TPzT; **7** $R^3 = R^5 = Me$, $R^4 = H$, Me₂-TPzT; **7** $R^3 = R^5 = Me$, $R^4 = H$, Me₂-TPzT; **7** $R^3 = R^5 = Me$, $R^4 = H$, Me₂-TPzT; **7** $R^3 = R^5 = Me$, $R^4 = H$, Me₂-TPzT; **7** $R^3 = R^5 = Me$, $R^4 = H$, Me₂-TPzT; **7** $R^3 = R^5 = Me$, $R^4 = H$, $R^4 = Me$, $R^4 = M$

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We have described the structure of tris(pyrazol-1-yl)-s-triazine (TPzT 2), both in the solid state (X-ray) and in the gas phase (electron diffraction) [9], its basicity in water, and the X-ray structure of its picrate [10]. More recently, we reported other azol-1-yl-s-triazines [11] as well as tris-pyrazolyl-s-triazines with the pyrazolyl substituents linked by the carbon [12]. Concerning their properties, we have described the behavior of the palladium(II) complexes of tris(4-methylpyrazol-1-yl)-s-triazine (Me-TPzT, **3**) and tris(4-bromopyrazol-1-yl)-s-triazine (Br-TPzT **4**) [13] and published a review on this topic [14]. Tris(3,5-dimethylpyrazol-1-yl)-s-triazine (Me₂-TPzT **5**, the pyrazole part is usually named dmpz) was used by Orrell to prepare Re fluxional complexes [15, 16] and by Chinese authors to obtain Eu(III) complexes and to demonstrate that their luminescence is sensitive to π - π stacking and H-bonding interactions [17].

In the present paper we will discuss the structure of the ligand Me₂-TPzT **5** and its Pd(II)/en (en = ethylenediamine) **6** and Ag(I)/PPh₃ **7** complexes.



RESULTS AND DISCUSSION

X-Ray Crystallographic Study

Since the structure has been deposited at the Cambridge Structural Database (CCDC number 188 400), the geometrical parameters corresponding to Me₂-TPzT **5** are not reported. A perspective drawing of the molecule with the atom-labeling scheme is shown in Fig. 1. The bond lengths and angles are similar to those observed in the TPzT molecule **2** [9]. The only difference concerns the effect of the methyl groups at positions 3 and 5 of the pyrazole ring. Comparison of the internal angles of the five-membered rings in the title compound with those of the not disordered in the TPzT molecule (one out of three) [9] reveals the influence of the methyl substituents [18,19] contracting the *ipso* angle and expanding the adjacent ones.

The nitrogen atoms, N(i2), of the pyrazole rings present the same relative position with respect to the central triazine ring. The whole molecule does not have not planar conformation, because of the twist of one of the dimethyl-3,5-pyrazole rings, 10° between the planes of the pyrazole and triazine rings (the two others are nearly planar). In solution, we have estimated, from its NMR data, that Me₂-TPzT **5** should have a dihedral angle of 4.5° [11], which compares well with the average value of the three torsion angles, 4.0° .

In the crystal structure of the title compound the molecules, related by a glide symmetry plane, form chains along the **a** axis through $\pi \cdots \pi$ and C-H \cdots N interactions (Table 1, Figs. 2a and 2b). These chains pack in a distorted hexagonal topology [20], as we can see in Fig. 2a, that is, leaving out distances and angles, each molecular chain along the **a**-axis is surrounded by another six closer to the first. These chains are joined through methylpyrazole ring contacts to form sheets perpendicular to the direction (001). The crystal is formed by the



Fig. 1. Molecular structure of the title compound showing the atom numbering. Thermal ellipsoids are drawn at 30% probability level and H atoms are represented by spheres of 0.1 Å.

union of these sheets through van der Waals interactions, one sheet slipped with regard to another so as to form the mentioned mode of packing. This mode is very frequent in organic crystal structures, associating molecules as to form the initial chain. It gives rise, when the actual size of the molecules (and so that of the chains) comes into play, to the most frequent space groups appearing in organic structures. There are no voids in the structure, within a 1.4 Å radius ball, and the total packing coefficient is 0.66 [21].

TABLE 1. Geometry Intermolecular Contacts (Distances, Å, and Angles, deg.) for Compound **5**.

c0103 and ci1i5 represent the centroids of the rings (N(1), C(1)…C(3)) and (N(i1), N(i2)…C(i5)) respectively (i = 1-3)

	D–H	Н…А	D…A	D–H…A
c0103…c1115 (<i>x</i> -1/2, 1/2– <i>y</i> , <i>z</i>)			3.607(3)	
c0103c3135 (1/2+x, 1/2-y,z)			3.517(3)	
C37–H373····N2 (1/2+x, 1/2–y,z)	1.11(7)	2.63(7)	3.617(8)	149(5)
C37–H372···N3 (x–1/2, 1/2–y,z)	0.95(7)	2.89(7)	3.764(7)	153(5)
C16–H162···N22 (1/2+x, 1/2–y,z)	0.93(6)	2.94(6)	3.812(8)	157(5)
C17–H171···N12 (1/2+x, 1/2–y,z)	1.00(7)	2.80(7)	3.395(7)	118(5)
C26–H263····c2125 (1/2+ <i>x</i> ,– <i>y</i> –1/2, <i>z</i>)	1.01(5)	2.99(5)	3.797(9)	138(3)



Fig. 2. Crystal structure of the title compound along the **a** (a) and **b** (b) axis showing hexagonal topology in the

packing of the chains and the herringbone like mode respectively

Formation of Complexes from Compound 5

Complexes [{Pd(en)}₃(Me₂-TPzT)](PF₆)₆ (**6**) and [{Ag(PPh₃)}₃(Me₂-TPzT)](ClO₄)₃ (**7**) were prepared as described in the experimental part. Both have three metallic centers, which has never been previously observed with TPzT-type ligands (the described complexes have one or two metals [13, 15, 16, 17, 22]). They are moderately air-stable in the solid state. Unfortunately, they are very insoluble in organic solvents to the point that, in general, neither ¹³C NMR spectra nor crystals for X-ray crystallography could be obtained. However, a ¹H NMR spectrum has been recorded (saturated solutions, see Table 2). They have been characterized by microanalysis, IR, as well as by FAB⁺/MS (FAB⁺ = fast atom bombardment in the positive mode) in the case of **7**. For compound **6**, the IR characteristic bands of the PF₆⁻ anion (840 cm⁻¹, broad, and 655 cm⁻¹, narrow) and the v(N–H) stretching of the ethylenediamine (en) ligand (3334 and 3341 cm⁻¹) [23] were observed. In FAB⁺/MS this compound is too insoluble in the matrix and no interesting peaks were found. In IR, compound **7**

C	Solvent	¹ H NMR spectrum, δ , ppm (<i>J</i> , Hz)			
Com-		Me ₂ -TPzT			Other ligands
pound		3'-Me	4'-H	5'-Me	
5	CDCl ₃ *	2.09	5.87	$2.59 (J_{4'5'} = 0.75)$	—
	CDCl ₃	2.32	6.09	$2.80 (J_{4'5'} = 0.8)$	—
	CD ₃ CN	2.28	6.20	$2.76 (J_{4'5'} = 0.85)$	—
	Acetone-d ₆	2.26	6.22	$2.84 (J_{4'5'} = 0.9)$	_
6	CD ₃ CN	2.30	6.32	2.58	~2.6 and 3.92 (br, NH ₂);
					2.67 (s, CH ₂ CH ₂)
7	Acetone-d ₆	2.15	6.39	2.76	7.50-7.63 (phenyl)

TABLE 2. ¹H NMR Chemical Shifts of the Free Ligand 5 and Its Two Complexes 6 and 7 at 300 K

* From reference [16] at 303 K (it seems that there was a TMS error of 0.22 ppm in these data).

showed the characteristic bands of the ClO_4^- anion at 1089 cm⁻¹ (broad and intense) and 622 cm⁻¹ (narrow) [24]. In FAB⁺/MS, a low-intensity peak at 1772 Da (M⁺) was observed together with peaks corresponding to the loss of ClO_4^- and AgPPh₃⁺ fragments (see Experimental).

The ¹H NMR data reported in Table 2 help to establish that the complexes have the proposed structures. For instance, in complex **6**, the ratio of en to dmpz is approximately 1:1 and there is only one group of signals corresponding to a C_3 symmetry. The effect of complexation on the chemical shifts (solvent CD₃CN) is small and only noticeable on 5'-Me. The same happens in complex **7** where there are three phenyl groups (15 protons) for each dmpz methyl group (3 protons). Here, the effects are small on all signals (solvent acetone-d₆). These conclusions were supported by the study of the NC vibrations in the aromatic rings: free ligand **5** 1587 and 1541 cm⁻¹, complex **6** 1592 and 1556 cm⁻¹, and complex **7** 1589 and 1534 cm⁻¹. It appears that the complexes are not contaminated with the ligand.

Although we have been unable to grow crystals of 6 and 7, the collection of spectroscopic data we obtained make us confident that the structures proposed for these three metallic derivatives are correct.

EXPERIMENTAL

The synthesis of complexes **6** and **7** was carried out under an atmosphere of dry oxygen-free nitrogen using standard Schlenk techniques. Solvents were distilled from the appropriate drying agents and degassed before use. $PdCl_2(en)$ [25] and $AgClO_4(PPh_3)$ [26] were prepared as described in the literature. **Safety note**: Perchlorate salts of metal complexes with organic ligands are potentially explosive.

Elemental analyses were performed with a Perkin–Elmer 2400 microanalyzer. IR spectra were recorded as KBr pellets with a Perkin–Elmer PE 883 IR spectrometer. Mass spectra were recorded in a VG Autospec instrument using FAB ionization and a nitrobenzyl alcohol matrix. Melting points were determined on a hot-stage microscope and are uncorrected. The NMR spectra of the ligand were recorded on a Bruker DRX 400 spectrometer working at 400 (for ¹H), 100 (for ¹³C), and 40 MHz (for ¹⁵N). The ¹H NMR spectrum of **6** and **7** were recorded on a Varian Unity 300 instrument (¹H at 300 MHz). Tetramethylsilane was used as external standard for ¹H and ¹³C NMR and external nitromethane for ¹⁵N NMR. The usual NMR sequences have been used [27].

Tris(3,5-dimethylpyrazol-1-yl)-s-triazine (5). In a three-necked round bottomed flask provided with a reflux condenser, argon atmosphere, and magnetic stirring, NaH (2.0 g, 60%, 50 mmol) washed with anhydrous pentane to remove the mineral oil in anhydrous THF (150 ml) was placed. 3,5-Dimethylpyrazole (4.33 g, 45 mmol) was added to this mixture in small portions and the reaction mixture stirred at room temperature for 2 h. Then 2,4,6-trichloro-1,3,5-triazine (2.65 g, 14.5 mmol) in dry THF (50 ml) was added dropwise, and the orange-reddish reaction mixture stirred overnight. After evaporation of the solvent, the crude residue was washed with water and the insoluble orange solid obtained by filtration dried. Column chromatography over Merck silica gel 60 afforded pure compound 5, mp 241-244°C (although this compound 5 has been described three times [15-17] no melting point was reported). $R_f 0.71$ (chloroform–methanol, 10:1) on TLC aluminium sheets of silica gel Merck 60 F_{254} (layer thickness 0.2 mm). Yield 30%. Mass spectra (*m/e*, relative intensity higher than 10%): 363 ($[M]^+$, 52), 348 (28), 268 (25), 242 (15), 227 (12), 201 (13), 149 (15), 122 (13), 120 (15), 107 (17), 106 (17), 97 (16), 96 (26), 95 (100). ¹³C NMR spectrum (CDCl₃), δ, ppm (J, Hz): 164.3 (C(2), C(4), C(6), of triazine ring; 14.0 (${}^{1}J = 127.9$, 3'-Me); 153.3 (${}^{2}J = {}^{2}J = 5.9$, C(3')); 111.9 (${}^{1}J = 174.2$, C(4')); 15.5 $({}^{1}J=130.3, 5'-Me)$; 144.4 $({}^{2}J={}^{2}J=7.4, C(5'))$. ¹⁵N NMR spectrum (CDCl₃), δ , ppm: -167.1 (N(1), N(3), N(5), of triazine ring); -166.5 (N(1), pyrazole); -81.6 (N(2'), pyrazole (inverse gate)); ¹⁵N NMR spectrum (DMSO-d₆): N-triazine, not observed, pyrazole: 165.4 (N(1'), 77.5 (N(2'), (gs-HMBC). Assignments made on the basis of gs-HMQC (^{1}J) and gs-HMBC (^{n}J) correlations and analogy with other reported pyrazole and triazine derivatives [11-13]. Found, %: C 59.55; H 5.92; N 34.29. C₁₈H₂₁N₉. Calculated, %: C 59.49; H 5.82; N 34.69.

Tris(ethylenediaminepalladium)tris(3,5-dimethylpyrazol-1-yl)-s-triazine Hexafluorophosphate [{Pd(en)}₃(Me₂-TPzT)](PF₆)₆ (6). The compound was prepared in two steps. First, to a solution of PdCl₂(en) (75 mg, 0.32 mmol) in THF (20 ml) was added AgPF₆ (199 mg, 0.79 mmol). The mixture was stirred 12 h at room temperature protected from light. Then, the white precipitate of AgCl was filtered off over cellite and washed with THF till the solution remained perfectly transparent. The solution was evaporated under vacuum to isolate the [Pd(en)(THF)₂](PF₆)₂ adduct in the form of a beige solid that was washed with diethyl ether, yield 97%. In the second step, to a solution of the adduct (180 mg, 0.30 mmol) in THF (20 ml) was added Me₂-TPzT **5** ligand (36.3 mg, 0.10 mmol) and immediately a white precipitate appeared, which was filtered off, washed with diethyl ether, and dried. Beige solid, yield 82% (143 mg). Found, %: C 17.09; H 3.15; N 12.67. C₂₄H₄₅F₃₆N₁₅P₆Pd₃. Calculated, %: C 16.64; H 2.62; N 12.13. Maybe the compound contains some ethylene-diamine of crystallization.

Tris(triphenylphosphinesilver)tris(3,5-dimethylpyrazol-1-yl)-s-triazine Perchlorate [{**Ag(PPh_3)**}]**(Me₂-TPzT)**](**ClO₄**)**3** (7). To a solution of Me₂-TPzT **5** (49 mg, 0.13 mmol) in freshly distilled acetone (20 ml) was added AgClO₄(PPh₃) (194 mg, 0.41 mmol), taking care to protect the reaction from light. After 2 h under stirring, a beige precipitate appeared, the stirring was continued for 3 h, then the solution was filtered and the solid washed with diethyl ether and dried. Yield 90% (207 mg). FAB⁺/MS (*m/e*, relative intensity): 1772 (M⁺, 11), 1672 ([M - ClO₄]⁺, 47), 1202 ([M - Ag(PPh_3) - 2 ClO₄]⁺, 22), 1103 ([M - Ag(PPh_3) - 3ClO₄]⁺, 61), 732 ([M - 2Ag(PPh_3) - 3 ClO₄]⁺, 100), 740 ([M - 2 Ag - 3 PPh_3 - 3 ClO₄]⁺, 81). Found, %: C 49.13; H 3.65; N 7.58. C₇₂H₆₆Ag₃Cl₃N₉O₁₂P₃. Calculated, %: C 48.80; H 3.75; N 7.11.

X-Ray Analysis

Data collection was carried out at room temperature on a four-circle diffractometer (Seifert XRD3000-S), using graphite monochromated CuK α radiation. A summary of data collection and refinement details is given in Table 3. The structure was solved by direct methods, SIR92 [28], and refined with full matrix least squares procedures on Fobs. Owing to the low value of the ratio of freedom (3.6), we refined alternatively non-hydrogen and hydrogen atoms so as to use ratios of freedom of above 4.8. The atomic scattering factors were taken from the International Tables for X-Ray Crystallography [29] and most of the calculations were carried out with the XTAL [30], PESOS [31], and PARST [32] programs running on an AXP 600 computer.

Chemical formula	C18H21N9	<i>R</i> , %	4.1
Formula weight	363.4	wR, %	5.0
Crystal habit	Colorless needle	Crystal system	Orthorhombic
Crystal size, mm	0.78×0.13×0.13	Space group	$Pna2_1$
$Dc \ (g \cdot cm^{-3}), F(000)$	1.281, 768	θ range for lattice	4-35
		parameters (°)	
Wavelength, Å	1.5418	No. of reflections for	57
		lattice parameters	
Absorption coefficient, cm ⁻¹	6.77	<i>a</i> , Å	7.9413(8)
θmax	66.6	<i>b</i> , Å	12.5552(15)
No. Reflex. Independent	1623	<i>c</i> , Å	18.9006(19)
No. Reflex. Observed	1172	<i>V</i> , Å ³	1884.5(4)
$[2\sigma(l) \text{ criterion}]$		Ζ	4
Secondary extinction (10 ⁴)	0.187(7)	Final shift/error	0.001
Maximal thermal value, Å ²	U11(C26) = 0.131(6)	ΔF peaks, eÅ ⁻³	±0.25

TABLE 3. Crystal Data and Structure Determination Details at Room Temperature for **5**

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