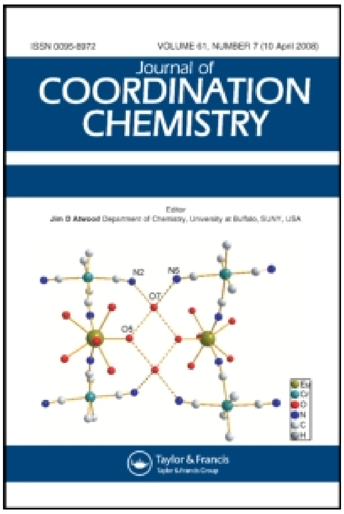

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N. Mincheva[a]; T. Todorov[b]; O. Angelova[b]; P. J. Bailey[c]; M. Mitewa[a]
[a] Departments of Chemistry, University of Sofia, Sofia, Bulgaria [b] Central Laboratory of Mineralogy and Crystallography, Bulgarian Academy of Sciences, Sofia, Bulgaria [c] Department of Chemistry, University of Edinburgh, UK

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SYNTHESIS AND STRUCTURE OF Pd(II) COMPLEXES OF 1,2,3-TRIPHENYLGUANIDINE

N. MINCHEVA[a], T. TODOROV[b], O. ANGELOVA[b],
P.J. BAILEY[c] and M. MITEWA[a,*]

[a]*Department of Chemistry, University of Sofia, 1126 Sofia, Bulgaria;*
[b]*Central Laboratory of Mineralogy and Crystallography,*
Bulgarian Academy of Sciences, 1000 Sofia, Bulgaria;
[c]*Department of Chemistry, University of Edinburgh, EH9 3JJ, UK*

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The formation of two complexes by reaction of $[PdCl_4]^{2-}$ with 1,2,3-triphenylguanidine $(PhNH)_2C{=}NPh$ under different metal/ligand ratios has been observed and the structure of the complex $[(1,2,3\text{-triphenylguanidine})_2PdCl_2]$ has been determined by X-ray diffraction methods. The ligands are coordinated as neutral monodentate molecules to the metal centre through their imine nitrogen atoms. The second Pd(II) complex is $[Pd(1,2,3\text{-triphenylguanidine})_4]^{2+}$ and was isolated by precipitation with ClO_4^-.

Keywords: 1,2,3-Triphenylguanidine; Pd(II) complexes; X-ray structure

INTRODUCTION

It is already well documented that guanidine derivatives $[RN{=}C(NR_2)_2]$ are able to coordinate as monodentate, chelating and bridging ligands, mainly in deprotonated (guanidinate) forms.[1–11] Bailey *et al.*[7] reported the first structures of Rh and Ru complexes with chelating 1,2,3-triphenylguanidinate ligands. Details of molybdenum dimers $[Mo_2\{\mu\text{-}\eta^2\text{-}(PhN)_2CNHPh\}_4]^{0/+}$, bridged by four 1,2,3-triphenylguanidinate ligands, have also been published.[8] Recently, the same authors have reported Co and Ag complexes

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* Corresponding author.

containing monodentate neutral triphenylguanidine coordinated through imine nitrogen atoms.[9] In the present paper we report the synthesis of Pd(II) complexes containing 1,2,3-triphenylguanidine (Pd_3G), and the X-ray crystal structure of one of these complexes.

EXPERIMENTAL

General

The ligand 1,2,3-triphenylguanidine was obtained as previously described.[7] $(NH_4)_2[PdCl_4]$ (Aldrich) was used without further purification. Aqueous solutions were prepared with distilled water. All syntheses were performed under aerobic conditions (open air) at ambient temperature. Pd content was determined gravimetrically after treatment with conc. H_2SO_4 and calcination at 800°C to constant weight. IR spectra were recorded on a Specord 75-IR (Carl-Zeiss, Jena) spectrophotometer.

Synthetic Procedures

Trans-$[Pd(Ph_3G)_2Cl_2]$ (1)

An aqueous solution of $(NH_4)_2[PdCl_4]$ (5×10^{-2} M) was added to an ethanolic solution of Ph_3G (2×10^{-2} M) at molar ratio 1:2 and the reaction mixture was kept in the dark at ambient temperature. After 14–15 h $Pd(NH_3)_2Cl_2$ was precipitated as a side product (yield *ca.* 10%), which was filtered off, and after 25–30 days reddish yellow crystals were formed. The latter were washed repeatedly with methanol, and dried for 10 days over P_4O_{10} (yield ~30%).

Appropriate single crystals were grown by slow diffusion of an aqueous solution of $(NH_4)_2[PdCl_4]$ through an ethanolic Ph_3G solution for 2–3 weeks. *Anal.* Calcd. for *trans*-$[Pd(Ph_3G)_2Cl_2]$ (%): C, 60.7; H, 4.6; N, 11.2; Cl, 9.4; Pd, 14.1. Found: C, 60.2; H, 4.5; N, 10.9; Cl, 9.8; Pd, 14.5.

$[Pd(Ph_3G)_4](ClO_4)_2$ (2)

Reaction of aqueous $(NH_4)_2[PdCl_4]$ (5×10^{-2} M) and ethanolic Ph_3G (2×10^{-2} M) solution (molar ratio 1:4) in the dark at ambient temperatures for 2 weeks results in the formation of $[Pd(Ph_3G)_4]^{2+}$. The latter was precipitated by addition of excess $NaClO_4$. The yellow complex was filtered off, washed repeatedly with distilled water, and dried over P_4O_{10} for 10 days (yield 60%). *Anal.* Calcd. for $[Pd(Ph_3G)_4](ClO_4)_2$ (%): C, 62.7; H, 4.7; N, 11.5; Cl, 4.9; Pd, 7.3. Found: C, 62.7; H, 4.8; N, 11.5; Cl, 4.5; Pd, 7.8.

X-Ray Crystallographic Data

A prismatic reddish yellow single crystal with dimensions 0.25 × 0.16 × 0.16 mm was mounted on a glass capillary and examined on an Enraf-Nonius CAD-4 diffractometer (Mo$K\alpha$, $\lambda = 0.71073$ Å, graphite monochromator). The compound *trans*-$[Pd(Ph_3G)_2Cl_2]$ crystallizes in the orthorhombic crystal system, space group $P2_12_12_1$ with $Z = 4$. Cell parameters $a = 12.731(2)$, $b = 14.850(5)$, $c = 18.641(5)$ Å, $V = 3524(3)$ Å^3 were obtained from a least-squares fit of 25 reflections with $20° < \theta < 22°$. All 11053 reflections ($\sin\theta/\lambda < 0.703$, h: 0–17, k: 0–20, l: −26 to 26) were collected at 292°C in the $\omega/2\theta$ scan mode. Three standard reflections monitored every 2 h revealed no intensity decay. The structure was solved by direct methods using *SHELXS*86.[13] An anisotropic model including all non-hydrogen atoms was refined by full-matrix least-squares methods. The hydrogen atoms were placed in calculated positions and refined with fixed $U_{iso} = 0.05$ Å^2 using a riding model (N–H, C–H = 0.95 Å). Final agreement parameters $R = 0.035$ and $R_w = 0.044$ were reached using 4847 reflections with $I > 2.5\sigma(I)$. Atomic scattering factors were taken as quoted in the SDP/PDP V3.0 package.[14] Crystal data and experimental details are summarized in Table I. The coordinates of non-hydrogen atoms are listed in Table II. An ORTEP[15] diagram with the atom numbering scheme is shown in Figure 1.

RESULTS AND DISCUSSION

The extended reaction (*ca.* 1 month) of $(NH_4)_2[PdCl_4]$ with 1,2,3-triphenylguanidine (molar ratio 1 : 2) in aqueous ethanol provided red/brown crystals of *trans*-$[Pd(Ph_3G)_2Cl_2]$ (**1**) in 30% yield. The molecular structure of (**1**) has been determined by single-crystal X-ray diffraction techniques. The Pd^{2+} ion is coordinated by two imine N atoms and two Cl ions in *trans* positions (mean Pd–Cl and Pd–N bond lengths of 2.310(2) and 2.029(7) Å respectively; (Figure 1). The bond angles at the metal centre are within the range 88.77(20)°–91.63(20)° (Table III). Until recently this ligand had been shown to coordinate to metal centres either in mono-$[(PhNH)C(NPh)_2]^-$ or dianionic $[C(NPh)_3]^{2-}$ form acting as a chelating[5–7,10–12] or bridging[1,3,8] ligand. There is an early structurally characterized example of the similar coordination of a 1,1,2,2-tetramethylguanidine ligand[2] and two previous examples of

TABLE I Crystal data and refinement details*

Formula	$C_{38}H_{34}Cl_2N_6Pd$
Formula weight	752.04
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
Z	4
a (Å)	12.731(2)
b (Å)	14.850(5)
c (Å)	18.641(5)
V (Å^3)	3524(3)
F(000)	1536
Calculated density (g cm^{-3})	1.417
Crystal size (mm)	0.25 × 0.16 × 0.16
Absorption coefficient (cm^{-1})	0.70
Data collection limits (°)	$0 < h < 17, 0 < k < 20, -26 < l < 26$
Total number of reflections	11053
$I > n\sigma(I)$	4847, $I > 2.5\sigma(I)$
Weighting scheme	$1/[\sigma^2(F) + (0.40F)^2]$
R	0.035
R_w	0.044
Goodness of fit	1.245
(Δ/σ)max	0.006
$(\Delta\rho)$min, max (e/Å^3)	−1.198, 1.114

*Further details of the structure determination and refinement, full list of displacement parameters, H atom positions and observed and calculated structure factors are available from the authors.

the monodentate coordination of 1,2,3-triphenylguanidines as neutral ligands.[9] Metrical parameters for the present example are in close agreement with those reported for these latter two complexes.

Coordination around the palladium in (1) is square planar within 0.080(2) Å. In each of the ligand molecules the sums of angles around the central carbons C(11) and C(22) of 359.97(78)° and 359.99(75)° reveal the essential planarity of the corresponding CN_3 groups. As is expected for a non-centrosymmetric molecule, the dihedral angles between the bridging plane and CN_3 planes from both ligand molecules are different with values of 97.57(25)° and 75.62(26)°. The C(11)–N(11) [1.309(11) Å] and C(21)–N(21) [1.312(11) Å] bond lengths (N(11) and N(21) being the coordinated N atoms) are shorter than the other C–N bonds (C(11)–N(12) 1.348(11) Å; C11–N13 1.360(12) Å; C21–N22 1.362(11) Å; C21–N23 1.364(11) Å). These results indicate the double character of the C(11)–N(11) and C(21)–N(21) bonds, while the lengths of other C–N bonds are typical for single C–N bonds.

For the two triphenylguanidine ligands, the phenyl rings are in different conformations with respect to the CN_3 planes of both triphenylguanidine molecules in the complex. While Ph(12) and Ph(13) are mutually *cis* and

TABLE II Atomic coordinates and equivalent isotropic displacement parameters (Å^2) for non-hydrogen atoms with e.s.d.'s in parentheses

Atom	*x/a*	*y/b*	*z/c*	U_{eq}*
Pd	0.00139(6)	0.20767(4)	−0.11591(3)	0.0317(1)
Cl1	0.0211(2)	0.1613(2)	−0.2336(1)	0.0530(7)
Cl2	−0.0242(2)	0.2353(1)	0.0047(1)	0.0490(6)
N11	−0.1568(5)	0.2162(5)	−0.1304(4)	0.036(2)
N12	−0.3043(6)	0.1228(5)	−0.1529(4)	0.048(2)
N13	−0.1670(6)	0.0749(5)	−0.0826(4)	0.044(2)
N21	0.1584(5)	0.1967(4)	−0.1019(4)	0.034(2)
N22	0.2972(6)	0.1080(5)	−0.0594(4)	0.039(2)
N23	0.1422(5)	0.0435(5)	−0.1070(4)	0.039(2)
C11	−0.2095(7)	0.1410(6)	−0.1240(5)	0.039(2)
C111	−0.2027(7)	0.3009(6)	−0.1460(5)	0.041(2)
C112	−0.3039(8)	0.3232(7)	−0.1248(6)	0.054(3)
C113	−0.344(1)	0.4074(8)	−0.1383(7)	0.074(4)
C114	−0.285(1)	0.470(1)	−0.1733(7)	0.076(4)
C115	−0.183(1)	0.4500(9)	−0.1928(7)	0.077(4)
C116	−0.1418(9)	0.3645(7)	−0.1801(6)	0.055(3)
C121	−0.3447(7)	0.1509(6)	−0.2203(5)	0.039(2)
C122	−0.2794(8)	0.1766(7)	−0.2766(6)	0.056(3)
C123	−0.3237(8)	0.1972(7)	−0.3422(6)	0.061(3)
C124	−0.4301(8)	0.1911(7)	−0.3528(6)	0.058(3)
C125	−0.492(1)	0.1662(7)	−0.2968(5)	0.062(3)
C126	−0.4519(7)	0.1467(6)	−0.2302(5)	0.051(3)
C131	−0.1687(7)	−0.0190(6)	−0.0991(5)	0.041(2)
C132	−0.1701(8)	−0.0461(7)	−0.1706(6)	0.057(3)
C133	−0.1692(9)	−0.1387(8)	−0.1844(6)	0.064(3)
C134	−0.1653(9)	−0.2010(8)	−0.1313(6)	0.066(3)
C135	−0.1619(9)	−0.1716(8)	−0.0607(6)	0.061(3)
C136	−0.1639(8)	−0.0813(7)	−0.0446(6)	0.049(3)
C21	0.2003(6)	0.1175(6)	−0.0895(5)	0.035(2)
C211	0.2217(6)	0.2738(5)	−0.1163(5)	0.035(2)
C212	0.3101(7)	0.2684(7)	−0.1603(6)	0.050(3)
C213	0.3659(9)	0.3462(7)	−0.1769(6)	0.059(3)
C214	0.3331(8)	0.4266(7)	−0.1525(6)	0.061(3)
C215	0.2440(8)	0.4343(7)	−0.1115(7)	0.067(3)
C216	0.1881(8)	0.3571(7)	−0.0926(6)	0.054(3)
C221	0.3729(7)	0.0413(6)	−0.0764(5)	0.037(2)
C222	0.4537(8)	0.0281(7)	−0.0285(6)	0.056(3)
C223	0.5340(9)	−0.0306(8)	−0.0465(6)	0.065(4)
C224	0.5322(9)	−0.0787(7)	−0.1078(6)	0.067(3)
C225	0.4499(8)	−0.0685(7)	−0.1547(6)	0.058(3)
C226	0.3703(8)	−0.0076(6)	−0.1393(5)	0.048(3)
C231	0.1410(7)	−0.0425(6)	−0.0752(5)	0.041(2)
C232	0.1008(7)	−0.1124(7)	−0.1169(6)	0.051(3)
C233	0.0937(8)	−0.1974(8)	−0.0889(6)	0.061(3)
C234	0.1234(8)	−0.2136(8)	−0.0205(7)	0.065(3)
C235	0.1649(9)	−0.1445(8)	0.0212(6)	0.067(3)
C236	0.1748(8)	−0.0586(7)	−0.0064(6)	0.054(3)

*Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

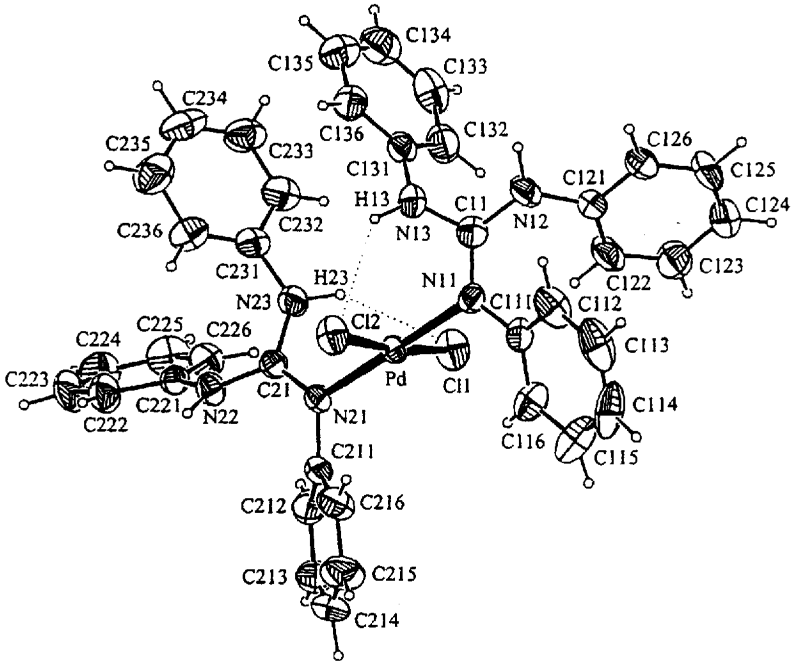

FIGURE 1 The molecular structure of the title complex showing 50% probability displacement ellipsoids. H atoms are shown as circles of arbitrary radii. Intramolecular hydrogen bonds are represented as dotted lines.

at the same time *trans* positioned to Ph(11), in the other ligand molecule Ph(23) is arranged *trans* to the mutually *cis* Ph(21) and Ph(22).

Three of the symmetrically non-equivalent hydrogen atoms bonded to nitrogen participate in normal hydrogen bonds of the type N–H···Cl. H(13) and H(23) form intramolecular bonds to Cl(2) and Cl(1), respectively, while H(22) is involved in an intermolecular hydrogen bond to Cl(2) $(1/2+x,\ 1/2-y,\ -z)$, which stabilizes the three-dimensional framework. More detailed information about the geometry of the hydrogen bonds is presented in Table III. The closest potential acceptor atom to H(12) is N(13) at 2.461(8) Å, but the N(12)–H(12)···N(13) angle of 68.87(49)° does not permit this configuration to be assigned as a hydrogen bond. Therefore, only three different N–H bonds exist in the structure and giving rise to three ν_{NH} bands at 3350, 3300, 3260 cm^{-1} in the IR spectrum of the complex (Table IV).

Treatment of $(NH_4)_2[PdCl_4]$ with Ph_3G in neutral water–ethanolic medium at M : L ratio 1 : 4 provides a second Pd(II) complex, $[Pd(Ph_3G)_4]^{2+}$

TABLE III Selected interatomic distances (Å) and bond angles (°)

Pd coordination			
Pd–Cl1	2.312(3)	Cl1–Pd–N11	90.01(20)
Pd–Cl2	2.308(3)	Cl1–Pd–N21	89.47(20)
Pd–N11	2.036(7)	Cl2–Pd–N11	88.77(20)
Pd–N21	2.023(7)	Cl2–Pd–N21	91.63(20)
Hydrogen bonds			
D–H···A	H···A	D···A	D–H···A
N13–H13···Cl2	2.64(2)	3.409(8)	139(1)
N22–H22···Cl2ⁱ	2.69(2)	3.409(7)	133(1)
N23–H23···Cl1	2.50(2)	3.317(7)	144(1)

Symmetry codes: (i) $1/2 + x$, $1/2 - y$, $-z$.

TABLE IV Selected IR data for the complexes (cm^{-1})

Ph$_3$G	*trans-Pd(Ph$_3$G)$_2$Cl$_2$* (1)	*[Pd(Ph$_3$G)$_4$](ClO$_4$)$_2$* (2)	*Assignment*
3390s	3350s 3300m 3260s	3350m	ν(NH)
1640sh			ν(C=N)
1625s	1615s	1615s	
1595m	1585m	1595m	
1580s	1570s	1580s	ν(C–N),
1535m	1520s	1530w	δ(NH),
1495s	1480m	1480m	ν(C=C)
		1070 620	ν(ClO_4^-)

which was isolated by precipitation on addition of excess $NaClO_4$. Selected IR data obtained for the free ligand and both Pd(II) complexes (1) and (2) are given in Table IV.

It is evident that IR data indicate the same coordination mode of the ligand in both complexes since the spectra are very similar. Bands at 3350 and 1615 cm^{-1} are observed in both of them and are assigned to ν_{NH} and $\nu_{C=N}$, respectively. Significant shifts of these bands are observed compared with the uncoordinated ligand molecule. The only difference is the presence of two extra bands in the NH range for the *trans*-$Pd(Ph_3G)_2Cl_2$ complex. Their presence is ascribed to NH groups involved in different types of H-bonding as mentioned above. The two strong bands at 1070 and 620 cm^{-1} in the spectra of the perchlorate complex suggest the presence of ClO_4^- groups outside the coordination sphere in the complex.

The ready formation of these complexes provides further evidence that guanidines are flexible ligands capable of coordination to a wide range of metals in a range of coordination modes. We will report further examples in due course.

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