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Palladium(II) and platinum(II) complexes of 1-thia-4,7-diazacyclononane (L^1). Crystal structures of [Pd(L^1)$_2$]Cl$_2$·H$_2$O, [Pt(L^1)$_2$](PF$_6$)$_2$ and [Pd$_3$(L^1)$_4$Cl$_2$]Cl$_4$·2H$_2$O

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Abstract

The palladium(II) and platinum(II) complexes of 1-thia-4,7-diazacyclononane (L^1) [Pd(L^1)$_2$]Cl$_2$·H$_2$O, [Pt(L^1)$_2$](PF$_6$)$_2$ and [Pd$_3$(L^1)$_4$Cl$_2$]Cl$_4$·2H$_2$O have been prepared and characterized by X-ray crystallography. In **1** and **2** the metal center is coordinated in a square-planar configuration to the N-donor atoms of two macrocyclic ligands. The thioether groups are non-interacting and dangling away from the metal center. **3** contains the three-nuclear centrosymmetric anion [Pd$_3$(L^1)$_4$Cl$_2$]$^{2+}$. A central [Pd(L^1)$_2$]$^{2+}$ unit is bridged via exo coordination of its thioether groups to two [Pd(L^1)Cl]$^+$ moieties. All thioether groups show long-range apical interactions. Crystal data for [Pd(L^1)$_2$]Cl$_2$·H$_2$O (**1**): monoclinic, space group $C2/c$, $a=15.574(3)$, $b=7.768(2)$, $c=15.310(3)$ Å, $\beta=106.87(7)°$, $Z=4$, $R=0.032$ for 1546 independent reflections with $I \geqslant 1.96\sigma(I)$; [Pt(L^1)$_2$](PF$_6$)$_2$ (**2**): monoclinic, space group $P2_1/c$, $a=8.451(5)$, $b=14.724(5)$, $c=9.055(6)$ Å, $\beta=94.48(3)°$, $Z=2$, $R=0.043$ for 1912 independent reflections with $I \geqslant 1.96\sigma(I)$; [Pd$_3(L^1)_4Cl_2$]Cl$_4$·2H$_2$O (**3**): orthorhombic, space group $Pbca$, $a=19.194(4)$, $b=10.081(2)$, $c=23.819(5)$ Å, $Z=4$, $R=0.0612$ for 3394 independent reflections with $I \geqslant 1.96\sigma(I)$.

Introduction

The coordination chemistry of the small macrocycles 1-thia-4,7-diazacyclononane (L^1), 1,4,7-triazacyclononane (L^2), 1,4,7-trithiacyclononane (L^3) and 1,4-dithia-7-diazacyclononane (L^4) are characterized by their ability to bind to triangular faces of octahedra [1–3]. This property has stimulated studies to elucidate the structures of 2:1 or 1:1 complexes of these ligands with metal ions which prefer square-planar stereochemistry like Pd(II), Pt(II) and Au(III). During these studies it was found, that L^3 forms five or six coordinate complexes with Pd(II) and Pt(II), in which there are long-range apical interactions between the metal ion center and the S-donors of the crown thioether in addition to the square-planar MS$_4$ coordination. Examples herefore are the complexes [M(L^3)$_2$]$^{2+}$ (M = Pd, Pt) [3] or the half-sandwich complexes [M(L^3)(L)]$^{n+}$ (L = 2Cl, 2Br; $n=0$ or L = 2PPh$_3$, $n=2$) [3, 4]. Until recently such long-range interactions to Pd(II) and Pt(II) have not been observed with the polyaza-ligand L^2. The [Pd(L^2)$_2$]$^{2+}$ ion shows square-planar coordination at Pd(II) with the third N-donor of the ligands non-interacting and dangling away from the metal center [5, 6]. But according to a preliminary report [4], apical interaction is present as well in [Pd(L^5)(NCMe)$_2$]$^{2+}$ (L^5 = 1-methyl-1,4,7-triazacyclononane).

We are engaged in studies of the respective properties of the analogous mixed-donor macrocycle L^1. In an earlier paper we reported the structures of [Pd(L^1)$_2$](PF$_6$)$_2$ and [Pt(L^1)$_2$]Br$_2$·H$_2$O [7]. Both complexes contain square-planar MN$_4$ cores; the former shows two long-range apical interactions with the S-donor atom of L^1, whereas in the Pt(II) complex no such interaction is observed. In this paper the preparation and structures of three further complexes of L^1 with platinum group metal ions are described.

Experimental

Syntheses

L^1·2HBr was prepared as described previously [8]. To obtain the free ligand, NaOH (1 g) was added to an aqueous solution (10 ml) of L^1·2HBr (0.34 g, 1.1 mmol), which was extracted several times with CHCl$_3$. The solutions were combined and dried over Na$_2$SO$_4$. The solvent was distilled off, and the resultant yellow oil dissolved in the suitable solvent.

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cis-[Pd(L¹)Cl₂]

L^1 (0.15 g, 1 mmol) was added to a suspension of $PdCl_2$ (0.18 g, 1 mmol) in nitromethane/dichloromethane (3:1). The mixture was refluxed for 8 h under N_2. From the clear solution the product crystallized in the form of orange, very thin platelets during slow cooling.

Anal. Calc. for $C_6H_{14}N_2SCl_2Pd$: C, 22.28; H, 4.36; N, 8.66. Found: C, 21.62; H, 4.39; N, 8.35%. IR (KBr disc): 3210vs, 993vs, 800s, 315m, 290m (νPd–Cl) cm^{-1}.

[Pd(L¹)₂]Cl₂·H₂O (1)

L^1 (0.15 g, 1 mmol) was added to a suspension of $PdCl_2$ (0.18 g, 1 mmol) in nitromethane/dichloromethane (3:1). The mixture was irradiated for 5 h with ultrasonic sound at room temperature. The white–yellow solids were filtered off and dissolved in a minimum of water. The solution was layered with ethanol to grow large, slightly yellow coloured, rhombic crystals.

Anal. Calc. for $C_{12}H_{30}N_4S_2Cl_2OPd$: C, 29.54; H, 6.10; N, 11.49. Found: C, 29.44; H, 6.61; N, 11.28%. Yield: 120 mg (25%). IR (KBr disc): 3460m, 3047vs,b, 1394s, 1090s, 1031s cm^{-1}.

[Pt(L²)₂](PF₆)₂ (2)

Solid K_2PtCl_4 (0.2 g, 0.5 mmol) and $NaPF_6$ (0.5 g, 3 mmol) were added to a solution of L^1 (0.33 g, 2.2 mmol) in water (20 ml). A yellow precipitate, which appeared after several minutes, was filtered off. Slow evaporation of the filtrate yielded colourless, hexagon-shaped crystals.

Anal. Calc. for $[Pt(C_6H_{14}N_2S)_2](PF_6)_2$: C, 18.54; H, 3,63; N, 7.21. Found: C, 19.14; H, 3.51; N, 7.66%. Yield 50 mg (13%). IR (KBr disc): 3295s, 3280s, 1400s, 1028s, 840vs,b, 750s, 554vs cm^{-1}.

[Pd₃(L¹)₄Cl₂]Cl₄·2H₂O (3)

cis-$[Pd(L^1)Cl_2]$ (360 mg, 0.75 mmol) was dissolved in the minimum amount of water. The solution was carefully layered with ethanol. After several days, dark red crystals of X-ray quality appeared.

Anal. Calc. for $C_{24}H_{60}N_8S_4Cl_6O_2Pd_3$: C, 25.00; H, 5.25; N, 9.72. Found: C, 23.39; H, 5.43; N, 9.06%. Yield 100 mg (35%). IR (KBr disc): 3050s,b, 1090s, 1000s, 805m cm^{-1}.

X-ray crystallography

Measurements were made at room temperature on a Nonius CAD4 diffractometer with graphite-monochromated Mo Kα radiation $\lambda = 0.71073$ Å. Cell parameters were refined from 2θ values of 25 reflections. Intensity data were collected in the 2θ range 4–54° using the ω-2θ scan technique. Two check reflections were measured at constant intervals. No crystal decay was observed. Empirical absorption corrections (Ψ-scan) were applied to the data sets of **2** and **3**. The structures were solved and refined by standard methods using the SHELXTL PLUS [9] program system. Anisotropic thermal parameters were refined for non-H atoms; the positions of H atoms were calculated (C–H, 0.96; N–H, 0.90 Å) and refined using the riding model ($U_H = 0.08$ Å^2). The weighting scheme $w^{-1} = \sigma^2(F) + gF^2$ (for g see Table 1) was used in the least-squares refinement. Table 1 contains the crystal data and further details concerning the individual compounds. Refined atomic coordinates are given in Tables 2–4, and selected bond lengths and angles in Tables 5 and 6. See also 'Supplementary material'.

Results and discussion

In a 3:1 mixture of nitromethane and dichloromethane two different compounds can be prepared from $PdCl_2$ and L^1 depending on the reaction temperature. At room temperature $[Pd(L^1)_2]Cl_2 \cdot H_2O$ (**1**) is obtained, and at 80 °C the 1:1 complex *cis*-$[Pd(L^1)Cl_2]$, both in moderate yields. During attempts to grow X-ray quality crystals from the latter compound, we obtained the dark red three-nuclear complex $[Pd_3(L^1)_4Cl_2]Cl_4 \cdot 2H_2O$ (**3**). $[Pt(L^1)_2](PF_6)_2$ (**2**) can be prepared in small yields from K_2PtCl_4 and L^1 in water. The main product is a yellow precipitate of varying composition, which has not been characterized so far.

1 and **2** contain isolated $[M(L^1)_2]^{2+}$ (M = Pd, Pt) ions sitting across crystallographic inversion centers. **1** and the related platinum(II) complex $[Pt(L^1)_2]Br_2 \cdot H_2O$ are isotypic, but **2** and the analogous palladium compound $[Pd(L^1)_2](PF_6)_2$ have different structures (*vide infra*) [7]. The structure of **1** (see Fig. 1) shows the Pd(II) ion coordinated to the four N-donors of the two ligands in a square-planar configuration. The Pd–N distances 2.05–2.06 Å and the N–Pd–N angles are in the usual range [6, 7]. The thioether donor atoms are non-interacting and dangling away from the metal center. This contrasts with the structure of the $[Pd(L^1)_2]^{2+}$ ion in the PF_6^- salt $[Pd(L^1)_2](PF_6)_2$. Here the sulfur donor atoms of both ligands are involved in weak apical interactions with Pd–S equal 3.034(1) Å. The remaining bond parameters in **1** are normal. Anions, cations and water of crystallization are linked to a three-dimensional network through hydrogen bonds of medium strength (N···Cl 3.175(2) and 3.171(2), O···Cl 3.248(4) Å).

In **2** the metal center is coordinated exactly as in **1** (see Fig. 2). The S-donor atoms are also dangling away from the metal center. The Pt–N distances are 2.08(1) and 2.08(1) Å. But in contrast to this compound, 1,4,7-trithiacyclononane complexes of Pt(II), e.g. $[Pt(L^3)_2]^{2+}$ show apical interactions of thioether groups with Pt–S distances of approximately 3 Å [4, 10]. As we have

TABLE 1. Crystallographic data

	$[Pd(L^1)_2]Cl_2 \cdot H_2O$	$[Pt(L^1)_2](PF_6)_2$	$[Pd_3(L^1)_4Cl_2]Cl_4 \cdot 2H_2O$
Formula	$C_{12}H_{28}N_4S_2Cl_2OPd$	$C_{12}H_{28}F_{12}N_4S_2P_2Pt$	$C_{24}H_{60}N_8S_4Cl_6O_2Pd_3$
Molecular weight	485.6	777.5	1152.6
Crystal system	monoclinic	monoclinic	orthorhombic
Space group	*C2/c*	$P2_1/c$	*Pbca*
a (Å)	16.574(3)	8.451(5)	19.194(4)
b (Å)	7.768(2)	14.724(5)	10.081(2)
c (Å)	15.310(3)	9.055(6)	23.819(5)
β (°)	106.87(7)	94.48(3)	90
V (Å^3)	1886.3	1123.4	4608.7
D_x (g cm^{-1})	1.71	2.30	1.66
$F(000)$	992	752	2320
μ(Mo Kα) (mm^{-1})	1.476	6.736	1.787
Crystal size (mm)	0.12×0.22×0.18	0.13×0.18×0.27	0.13×0.24×0.19
Octants	$h, -k, \pm l$	$h, k, \pm l$	$h, k, \pm l$
Reflections measured	4409	2725	9889
Unique reflections	2052	2450	4524
Reflections with $I \geqslant 1.96\sigma(I)$	1546	1912	3394
g in weighting scheme	0.0004	0.0003	0.0003
No. parameters	102	151	214
R (R_w)	0.032(0.033)	0.043(0.043)	0.062(0.066)

TABLE 2. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) in $[Pd(L^1)_2]Cl_2 \cdot H_2O$

	x	y	z	U_{eq}[a]
Pd	2500	2500	0	21(1)
Cl	1479(1)	244(2)	7190(1)	50(1)
O(1)	0	2211(8)	2500	90(3)
N(2)	3507(2)	2286(4)	1157(2)	31(1)
C(2)	4317(3)	2584(7)	925(3)	50(2)
C(4)	3249(3)	−940(5)	1096(3)	37(1)
C(3)	3548(3)	656(6)	1670(3)	40(1)
S	3823(1)	−1629(2)	319(1)	43(1)
C(6)	3592(3)	978(6)	−1068(3)	41(2)
C(5)	3263(3)	−676(6)	−778(3)	40(2)
N(1)	3428(2)	2611(4)	−636(2)	28(1)
C(1)	4164(3)	3377(8)	37(3)	50(2)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 3. Atomic coordinates (×10^4) and equivalent isotropic displacement parameters (Å^2×10^3) in $[Pt(L^1)_2](PF_6)_2$

	x	y	z	U_{eq}[a]
Pt	0	0	0	18(1)
S	−45(4)	−2609(2)	939(4)	33(1)
P(1)	4978(4)	8860(3)	6954(4)	33(1)
F(1)	5345(12)	9251(8)	8598(10)	72(4)
F(2)	4620(12)	8485(9)	5354(11)	80(5)
F(3)	3194(9)	8660(7)	7345(11)	60(3)
F(4)	6759(11)	9062(8)	6621(13)	81(4)
F(5)	5459(12)	7881(7)	7503(15)	80(5)
F(6)	4472(17)	9841(7)	6468(14)	92(5)
N(1)	−1531(11)	−343(7)	1608(10)	24(3)
N(2)	1687(11)	−555(7)	1535(10)	24(3)
C(1)	−1790(14)	−1923(8)	401(14)	32(4)
C(2)	−2350(13)	−1246(9)	1483(14)	31(4)
C(3)	−540(16)	−218(9)	3026(13)	34(4)
C(4)	956(15)	−760(9)	2975(12)	30(4)
C(5)	2563(13)	−1364(9)	1034(14)	30(4)
C(6)	1582(14)	−2032(9)	122(14)	30(4)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

found recently, this type of interaction occurs also in *cis*-$[Au(L^1)Cl_2]^+$ (Au–S = 2.929(2) Å) [2].

Compound **3** contains an unique centrosymmetric three-nuclear cation with the composition $[Pd_3(L^1)_4Cl_2]^{2+}$. A central $[Pd(L^1)_2]^{2+}$ group is bridged via its thioether donor atoms to two $[Pd(L^1)Cl]$ moieties (see Fig. 3). Four additional Cl^- ions act as counterions. The central Pd(II) is coordinated to four N-donors of two ligands in the usual square-planar configuration. But in contrast to **1** and **2** the thioether groups of both ligands (S(1), S(1a)) show apical interactions with Pd···S equal 3.008(2) Å. The Pd–S vectors forms angles of 72.7° with the PdN_4 plane. S(1) and S(1a) form also short exodentate bonds (2.308(3) Å) to Pd(1) and Pd(1a). Exodentate coordination of L^1 has been observed so far only in $[Ag_4(L^1)_4](CF_3SO_3)_4$ [2]. The square-planar configuration of Pd(1) and Pd(1a) is completed by the N,N′-coordinated L^1 and a chloro ligand. The distances within the PdN_2SCl plane agree well with the values found in dinuclear $[Pd_2Cl_2([18]aneN_2S_4)]$ [11] with a similar $PdNS_2Cl$ configuration. The thioether group of L^1 at Pd(1) and Pd(1a) also shows apical interaction (S2–Pd(1) = 3.008(2) Å). As a consequence, Pd(1) is shifted 0.07 Å off the mean plane containing the N_2SCl donor set toward S(2). The Cl^- counterions are fixed through

TABLE 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) in $[Pd_3(L^1)_4Cl_2]Cl_4 \cdot 2H_2O$

	x	y	z	U_{eq}[a]
Pd(1)	355(1)	1558(1)	1621(1)	31(1)
Pd(2)	0	5000	0	26(1)
S(1)	32(1)	2780(2)	844(1)	30(1)
S(2)	1585(2)	−90(3)	1265(2)	56(1)
Cl(1)	−567(2)	103(3)	1531(1)	50(1)
Cl(2)	503(2)	5725(3)	1692(1)	56(1)
Cl(3)	6964(3)	2554(5)	170(3)	140(3)
N(1)	−1012(4)	5021(9)	254(4)	34(3)
N(2)	−318(5)	3333(8)	−437(4)	33(3)
N(3)	1161(5)	2815(9)	1772(4)	43(3)
N(4)	680(5)	736(14)	2368(4)	200(6)
C(1)	5(7)	1568(10)	280(4)	37(3)
C(2)	95(7)	2103(11)	−323(5)	41(4)
C(3)	−1095(6)	3110(11)	−380(5)	41(4)
C(4)	−1436(6)	4347(13)	−185(5)	46(4)
C(5)	−1095(6)	4534(12)	847(5)	43(4)
C(6)	−874(5)	3143(11)	976(5)	37(3)
C(7)	1104(10)	1645(20)	2675(7)	92(7)
C(8)	1354(13)	2686(18)	2372(7)	111(9)
C(9)	1742(7)	2682(14)	1368(7)	62(5)
C(10)	2098(7)	1340(15)	1340(8)	73(6)
C(11)	1545(8)	−873(18)	1955(7)	80(6)
C(12)	926(9)	−686(14)	2301(7)	74(6)
O(1)	8206(8)	602(14)	325(7)	128(7)

[a]Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor.

TABLE 5. Selected bond distances (Å) and angles (°) in $[Pd(L^1)_2]Cl_2 \cdot H_2O$ (**1**) and $[Pt(L^1)_2](PF_6)_2$ (**2**)

1		2	
Pd–N(1)	2.047(4)	Pt–N(1)	2.08(1)
Pd–N(2)	2.058(3)	Pt–N(2)	2.08(1)
Pd···S	3.836(1)	Pt···S	3.936(2)
S–C(5)	1.822(4)	S–C(1)	1.82(1)
S–C(4)	1.808(5)	S–C(6)	1.82(1)
N(1)–C(1)	1.475(5)	N(1)–C(2)	1.50(2)
N(2)–C(2)	1.502(6)	N(1)–C(3)	1.49(2)
N(2)–C(3)	1.481(6)	N(2)–C(4)	1.52(2)
C(2)–C(1)	1.446(7)	N(2)–C(5)	1.49(2)
C(4)–C(3)	1.517(6)	C(1)–C(2)	1.50(2)
C(6)–C(5)	1.512(7)	C(3)–C(4)	1.50(2)
C(6)–N(1)	1.492(6)	C(5)–C(6)	1.49(2)
N(1)–Pd–(N1a)	180.0	N(1)–Pt–N(2)	82.4(4)
N(1)–Pd–(N2a)	97.0(1)	N(1)–Pt–N(1a)	180.0(0)
N(2)–Pd–(N1)	83.0(1)	N(1)–Pt–N(2a)	97.6(4)
Pd–N(1)–C(1)	105.6(3)	Pt–N(1)–C(2)	118.1(7)
Pd–N(1)–C(6)	115.7(3)	Pt–N(1)–C(3)	103.6(7)
C(1)–N(1)–C(6)	115.6(3)	C(2)–N(1)–C(3)	113.6(9)
Pd–N(2)–C(2)	110.0(3)	Pt–N(2)–C(4)	110.4(7)
Pd–N(2)–C(3)	115.2(2)	Pt–N(2)–C(5)	116.2(7)
C(2)–N(2)–C(3)	110.6(3)	C(4)–N(2)–C(5)	116.2(7)
C(4)–S–C(5)	105.2(2)	C(1)–S–C(6)	104.7(6)

TABLE 6. Selected bond distances (Å) and angles (°) in $[Pd_3(L^1)_4Cl_2]Cl_4 \cdot 2H_2O$ (**3**)

Pd(2)–N(1)	2.034(9)	Pd(1)–N(3)	2.03(1)
Pd(2)–N(2)	2.070(8)	Pd(1)–N(4)	2.06(1)
Pd(2)–S(1)	3.008(2)	Pd(1)–S(1)	2.308(3)
		Pd(1)–Cl(1)	2.308(3)
		Pd(1)–S(2)	3.008(2)
N(1)–Pd(2)–N(2)	82.9(3)	S(1)–Pd(1)–Cl(1)	93.4(1)
N(1)–Pd(2)–N(2a)	97.1(3)	S(1)–Pd(1)–N(3)	90.8(3)
		S(1)–Pd(1)–N(4)	171.4(4)
Pd(1)–S(1)–C(1)	104.0(3)	Cl(1)–Pd(1)–N(3)	175.1(3)
Pd(1)–S(1)–C(6)	103.1(4)	Cl(1)–Pd(1)–N(4)	93.2(3)
		N(3)–Pd(1)–N(4)	82.4(4)

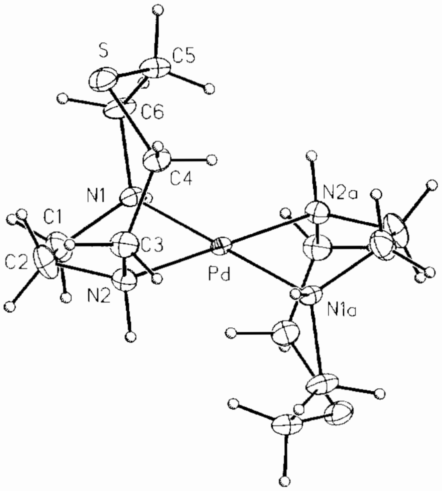

Fig. 1. Perspective view of the cation $[Pd(L^1)_2]^{2+}$ in **1** and atom labelling scheme.

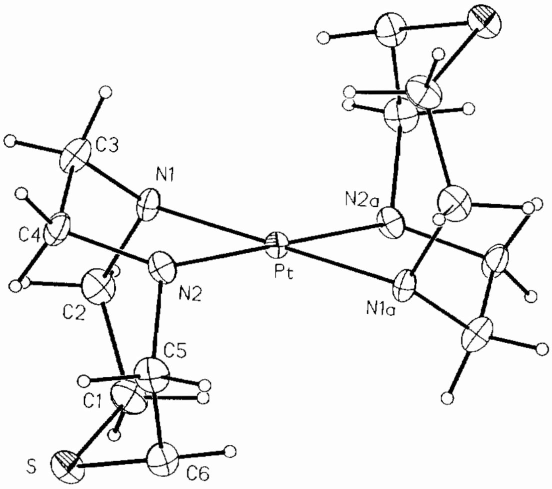

Fig. 2. Perspective view of the cation $[Pt(L^1)_2]^{2+}$ in **2** and atom labelling scheme.

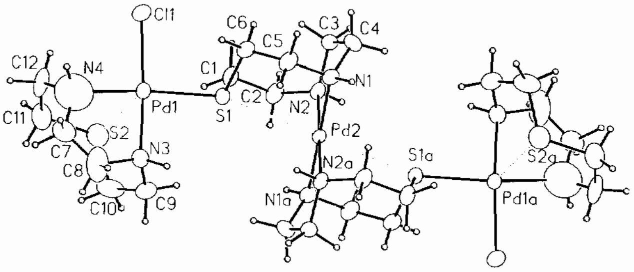

Fig. 3. Perspective view of the cation $[Pd_3(L^1)_4Cl_2]^{4+}$ in **3** and atom labelling scheme.

hydrogen bonds of medium strength (3.112–3.199 Å) to the N–H groups and the solvate H_2O molecule.

As already mentioned, the structures of the $[Pd(L^1)_2]^{2+}$ ion in the compounds $[Pd(L^1)_2](PF_6)_2$ [7] and $[Pd(L^1)_2]Cl_2 \cdot H_2O$ (this work) differ with respect to the coordination of the thioether group. The S-donor is dangling away in **1**, but weakly donating in the PF_6^- salt (and also in the three-nuclear complex **3**). In complexes with apical interaction the ligand L^1 adopts a [234] conformation; without apical interaction the conformation changes to [333]. The small difference in energy between these two conformations [12] is probably compensated by gaining ligand field stabilization energy through the apical interactions. The $[Pd(L^1)_2]^{2+}$ ion is reported to show fluxional behaviour in solution [6]. This can now be correlated to an isomerization process between the [234] and [333] conformation of the ligands. In the solid state the individual isomers are stabilized by electrostatic forces originating from the different counterions Cl^- and PF_6^-.

Supplementary material

Tables of complete crystallographic data, bond distances and angles, and thermal parameters are available from the authors on request.

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