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Metal−Purine Interactions: Homo- and Heterodinuclear Platinum(II) and/or Palladium(II) Complexes of 8-Thiotheophylline. Crystal Structures of [Pt(μ-TT)(dppm)]$_2$·2DMSO and [(dppm)Pt(μ-TT)$_2$Pd(dppm)]·7H$_2$O

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The reaction of *cis*-[MCl$_2$(dppm)] (M = Pt(II) and Pd(II); dppm = bis(diphenylphosphino)methane) with H$_2$TT and NaOH (H$_2$TT = 8-thiotheophylline) yields neutral mononuclear [M(HTT-*S*(8))$_2$(dppm)] complexes. Homodinuclear [M(μ-TT-*N*(7),*S*(8))(dppm)]$_2$ (M = Pt(II) and Pd(II)) are prepared either by the reaction of [M(HTT)$_2$(dppm)] with *cis*-[MCl$_2$(dppm)] and NaOH or by the direct reaction of *cis*-[MCl$_2$(dppm)] with Na$_2$TT, prepared in situ from H$_2$TT and NaOH. The crystal structure of the Pt derivative is reported: [Pt(μ-TT)(dppm)]$_2$·2DMSO (**3**) crystallizes in the triclinic space group $P\bar{1}$ with a = 12.949(3) Å, b = 13.009(3) Å, c = 22.980(5) Å, α = 96.89(3)°, β = 103.53(3)°, γ = 106.43(3)°, Z = 2, and R_1 = 0.045. Heterodinuclear [(dppm)Pt(μ-TT)$_2$Pd(L-L)] complexes are obtained by reaction of [Pt(HTT)$_2$(dppm)] with [PdCl$_2$(L-L)] in basic medium (L-L = dppm and 2,2′-bipyridine). The crystal structure of [(dppm)Pt(μ-TT)$_2$Pd(dppm)]·7H$_2$O (**5**) is reported. The complex crystallizes in the orthorhombic space group $P2_12_12_1$ with a = 16.560(5) Å, b = 17.063(5) Å, c = 24.428(5) Å, Z = 4, and R_1 = 0.042. The structures of **3** and **5** are almost identical, by which **5** can be seen as an isomorphic substitution of one of the Pt(II) ions of **3** by a Pd(II) ion. The structures consist of dinuclear units having a pseudo-2-fold axis perpendicular to that defined by the metal atoms. The two metal atoms are bibridged by two μ-TT-*N*(7),*S*(8) ligands, in a head to tail arrangement. The square-planar coordination of the metal atoms is completed by a chelate dppm ligand. The steric repulsions between the bulky dppm ligands must be the main factor precluding metal−metal interaction in these compounds.

Introduction

Thiolated purines are of interest because some of them, such as 6-mercaptopurine and 6-mercaptoguanine, are established clinical agents for the therapy of human leukemias.[1] In some cases metal complexes of these bases, especially those of Pt(II) and Pd(II), show higher anticancer activity than the free ligand.[2] On the other hand, phosphines and phosphine metal containing complexes have received much attention during the past few years due to their potential use as antitumor agents.[3] Particularly, 1,2-bis(diphenylphosphino)ethane (dppe) and some of its analogues have been shown to have antitumor activity against a wide range of tumors, and, moreover, their activity is enhanced upon coordination to metal ions, such as gold(I).

The possibility that thiolated purines may act in a synergetic fashion with [M(diphosphine)]$^{2+}$ moieties, giving rise to a bifunctional antitumor agent, prompted us to prepare and characterize purine−metal−phosphine complexes. As a continuation of our studies along this line,[4] herein we report on the preparation, characterization, and reactivity of a number of Pt(II) and Pd(II) complexes with 8-thiotheophylline (hereafter H$_2$TT).

Experimental Section

The purine derivative 1,3-methyl-8-thioxanthine (8-thiotheophylline) was prepared according to literature procedures,[5] while bis(diphenylphosphino)methane (dppm) was purchased from Aldrich and used as received. The compounds [PtCl$_2$(dppm)] and [PdCl$_2$(dppm)] were prepared by standard methods.[6] [PtCl$_2$(bipy)] and [PdCl$_2$(bipy)] were prepared by procedures described for the related complexes with ethylenediamine.[7]

Physical Measurements. Microanalyses and IR spectra were obtained as already described.[4] The ^{31}P-NMR spectra were obtained in dimethyl-d_6 sulfoxide (DMSO-d_6) at 298 K on a Bruker AM-300 operating at 121.42 MHz and using H$_3$PO$_4$ (85% (w/w) in D$_2$O) as external standard.

Preparations. [Pt(HTT)$_2$(dppm)] (1). This complex can be prepared by following these methods: (a) To a solution of [PtCl$_4$(NH$_3$)$_2$] (0.282 g, 0.76 mmol) in ethanol (50 mL) was added H$_2$TT (0.424 g, 2.0 mmol). The suspension was stirred until a clear solution was obtained. After filtration of any amount of insoluble material, the resulting orange solution was allowed to stand at room temperature, whereupon the dark-orange product [Pt(HTT)$_2$(NH$_3$)Cl] formed. This complex (0.1 g, 0.15 mmol) and dppm (0.13 g, 0.3 mmol) were stirred

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and heated in ethanol (50 mL) until a clear yellow solution was obtained. This solution, kept at room temperature for several days, gave yellow needlelike crystals of **1**; yield, 70%. (b) To a solution of H_2TT (0.12 g, 0.3 mmol) in 5 mL of water containing 0.3 mmol of NaOH was added a suspension of [$PtCl_2$(dppm)] (0.1 g, 0.15 mmol) in ethanol (50 mL). The reaction mixture was warmed for 15 min to give a light yellow solution from which, after evaporation at room temperature, yellow needlelike crystals of **1** were formed; yield, 80%. Anal. Calcd for $C_{39}H_{36}N_8O_4P_2S_2Pt$: C, 46.75; H, 3.62; N, 11.18; S, 6.40. Found: C, 46.29; H, 3.72; N, 10.99; S, 6.50.

[Pd(HTT)$_2$(dppm)]·4H$_2$O (2). The complex [$PdCl_2$(dppm)] (0.1 g, 0.18 mmol) and H_2TT (0.08 g, 0.36 mmol) were reacted by using the preceding b procedure to yield orange crystals; yield, 75%. Anal. Calcd for $C_{39}H_{44}N_8O_8P_2S_2Pd$: C, 47.54; H, 4.50; N, 11.37; S, 6.51. Found: C, 47.42; H, 4.33; N, 10.91; S, 6.10.

[Pt(μ-TT)(dppm)]$_2$·2DMSO (3). This complex can be obtained by following two different procedures: (a) A suspension of [$PtCl_2$(dppm)] (0.1 g, 0.15 mmol) in ethanol (50 mL) was added to a solution of H_2TT (0.03 g, 0.15 mmol) in 5 mL of water containing 0.3 mmol of NaOH. After the mixture was warmed for 15 min, a yellow light solution was obtained, which, kept at room temperature, yielded a yellow precipitate, which was washed with ethanol and diethyl ether. Recrystallization from DMSO gave yellow crystals; yield, 70%. (b) To a suspension of [$PtCl_2$(dppm)] (0.1 g, 0.15 mmol) in 30 mL of ethanol were added **1** (0.15 g, 0.15 mmol) and NaOH (12 mg, 0.3 mmol). The reaction mixture was heated to reflux for 15 min to give a light yellow solution, which, kept at room temperature, provided a yellow precipitate of **3**. Anal. Calcd for $C_{36}H_{40}N_4O_4P_2S_3Pt$: C, 47.06; H, 3.95; N, 6.46; S, 7.39. Found: C, 47.58; H, 3.88; N, 6.48; S, 7.60.

[Pd(μ-TT)(dppm)]$_2$·3H$_2$O (4). This complex was prepared either from [$PdCl_2$(dppm)] and H_2TT or from **2** and [$PdCl_2$(dppm)], by using the procedures described for **3**, as orange crystals. Anal. Calcd for $C_{32}H_{34}N_4O_5P_2SPd$: C, 52.79; H, 4.29; N, 7.70; S, 4.40. Found: C, 52.16; H, 4.20; N, 7.58; S, 4.75.

[PtPd(μ-TT)$_2$(dppm)$_2$]·7H$_2$O (5). Complex **1**(0.15 g, 0.15 mmol) and [$PdCl_2$(dppm)] (0.08 g, 0.15 mmol) were reacted in ethanol using the same procedure (b) as that for **3**; yield, 70%. Anal. Calcd for $C_{64}H_{70}N_8O_{11}P_4S_2PdPt$: C, 47.54; H, 4.36; N, 6.93; S, 3.97. Found: C, 48.03; H, 4.18; N, 6.63; S, 3.75.

[Pt$_2$(μ-TT)$_2$(dppm)(bipy)] (6). To a stirred suspension of [Pt(HTT)$_2$(dppm)] (0.15 g, 0.15 mmol) in 50 mL of MeOH/H_2O (80% (w/w)) was added [$PtCl_2$(bipy)] (0.06 g, 0.15 mmol). Then, NaOH (0.30 mmol) was added and the reaction mixture heated to reflux for 15 min; the color of the solution changed from yellow to orange. Evaporation of the resulting solution at room temperature led to an orange powder, which was washed with methanol and diethyl ether; yield, 60%. Anal. Calcd for $C_{49}H_{42}N_{10}O_4P_2S_2Pt_2$: C, 43.56; H, 3.13; N, 10.37; S, 4.75. Found: C, 43.08; H, 2.96; N, 10.85; S, 4.27.

[PtPd(μ-TT)$_2$(dppm)(bipy)] (7). The complexes [Pt(HTT)$_2$(dppm)] (0.15 g, 0.15 mmol) and [$PdCl_2$(bipy)] (0.05 g, 0.15 mmol) were reacted, in MeOH/H_2O, by using the preceding procedure to give an orange powder; yield, 59%. Anal. Calcd for $C_{49}H_{42}N_{10}O_4P_2S_2PdPt$: C, 46.62; H, 3.35; N, 11.09; S, 5.08. Found: C, 46.43; H, 3.85; N, 10.94; S, 5.04.

X-ray Data Collections and Structure Determinations. Single crystal data collections for **3** and **5** were performed at 293 K with a Siemens R3m/V diffractometer using graphite monochromatized Mo Kα (λ = 0.710 69 Å) radiation. The unit cell parameters were calculated by least-squares refinement of 25 well centered reflections in the range $15 < 2\theta < 45°$ for **3** and **5**. The data were collected by the $\omega/2\theta$ scan mode. Intensities of four check reflections measured after every 120 min showed only statistical variation. The data were corrected for Lorentz and polarization effects. Absorption corrections were applied via an empirical Ψ scan. The structures were solved by direct methods and subsequent Fourier syntheses with the SHELXTL/PC V5.0 program.[8] All non-hydrogen atoms were refined anisotropically, and the positions of the hydrogen atoms were calculated with isotropic temperature factors, with the following exceptions: (a) the phenyl rings were refined as a rigid group having a common isotropic temperature factor; (b) for **3**, the DMSO molecules were refined isotropically, having one of them be a disordered sulfur atom; and (c) for **5**, the hydrogen atoms belonging to the water molecules were omitted, while the positions of both metal ions are disordered with Pt and Pd in ca. 50%. Crystal data and structure determination parameters are given in Table 1. Selected atomic coordinates and equivalent isotropic thermal parameters are listed in Table 2.

Table 1. Crystal Data and Structure Refinement for **3** and **5**

compd	[$Pt_2(\mu$-TT$)_2$(dppm)$_2$]·2DMSO	[PtPd(μ-TT)$_2$(dppm)$_2$]·7H$_2$O
emp formula	$C_{68}H_{68}N_8O_6S_4P_4Pt_2$	$C_{64}H_{70}N_8O_{11}S_2P_4Pd$ Pt
fw	1735.60	1616.77
cryst syst	triclinic	orthorhombic
space group	$P\bar{1}$	$P2_12_12_1$
unit cell dimens		
a, Å	12.949(3)	16.560(5)
b, Å	13.009(3)	17.063(5)
c, Å	22.980(5)	24.428(5)
α, deg	96.89(3)	90.000(5)
β, deg	103.53(3)	90.000(5)
γ, deg	106.43(3)	90.000(5)
Z	2	4
vol, Å^3	3537.3(14)	6903(3)
dens (calcd), g cm^{-3}	1.630	1.556
abs coeff, mm^{-1}	4.215	2.501
F(000)	1720	3256
cryst size, mm	0.40 × 0.20 × 0.16	0.25 × 0.18 × 0.15
θ range, deg	1.67−20.00	1.67−22.50
limiting indices	$0 \leq h \leq +12$ $-12 \leq k \leq +12$ $-22 \leq l \leq +21$	$-1 \leq h \leq +17$ $-1 \leq k \leq +18$ $-1 \leq l \leq +26$
reflcns collecd	6976	6117
independ reflecns	6597 [*R*(int) = 0.0227]	5848 [*R*(int) = 0.0404]
refinement method	full-matrix least-squares	full-matrix least-squares
data/params	6566/418	5805/446
goodness-of-fit (F^2)	1.038	0.883
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0454$, $R_{w2} = 0.1024$	$R_1 = 0.0420$, $R_{w2} = 0.1071$
R indices (all data)	$R_1 = 0.0595$, $R_{w2} = 0.1175$	$R_1 = 0.0531$, $R_{w2} = 0.1557$
largest peak and hole	1.463 and −0.826 e·A^{-3}	0.839 and −0.665 e·A^{-3}

Results and Discussion

The reaction of *cis*-[M(dppm)Cl_2] (where M = Pd(II) and Pt(II) and dppm = 1,2-bis(diphenylphosphino)methane) with H_2TT and NaOH in ethanol and a 1:2:2 molar ratio leads to complexes **1** and **2**, of empirical formula [M(dppm)(HTT)$_2$]. Interestingly, the platinum(II) complex can also be obtained from the reaction of [Pt(HTT)$_2$][Pt(NH$_3$)(HTT)Cl_2] (prepared by reduction of $K_2[PtCl_6]$ with the ligand itself) with dppm in 1:2 molar ratio (see Scheme 1).

It should be pointed out that H_2TT has two ionizable protons in the imidazole ring (see Scheme 1). When these protons dissociate in basic medium, the sulfur atom must be the most probable binding site, since a soft polarizable metal, such as Pt(II) and Pd(II), shows preference toward the softer S donor over the less polarizable nitrogen donor atom. The second position of coordination must be N(7) rather than N(9) because of the steric hindrance from the N(3)−CH_3 group.

Information about the structure of these mononuclear complexes was derived from the IR and ^{31}P-NMR results, which confirm the *S*(8)-monodentate coordination of the HTT$^-$ anion in **1** and **2**. Thus, the IR spectra show no S−H bands, whereas only one N−H band is observed in the 2800−3200 cm^{-1} region. The ^{31}P-NMR spectra exhibit a single chemical shift (with a pair of ^{195}Pt satellites for the platinum compound), consistent with a square-planar geometry with two equivalent *cis* phosphine moieties.[9] Furthermore, the values of $\delta(^2P)$ are similar to those

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Table 2. Selected Atomic Coordinates ($\times 10^4$) and *U*(eq) Parameters (Å^2 $\times$ 10^3) for **3** and **5**

atom	*x*	*y*	*z*	*U*(eq)
	[(dppm)Pt(μ-TT)$_2$Pt(dppm)]·2DMSO			
Pt(1)	1716(1)	4858(1)	3381(1)	36(1)
Pt(2)	1566(1)	3259(1)	1642(1)	35(1)
P(2)	1053(3)	3838(3)	4011(2)	41(1)
P(1)	394(3)	5496(3)	3643(2)	46(1)
P(3)	1892(3)	1673(3)	1377(2)	43(1)
P(4)	−77(2)	2061(2)	1072(2)	39(1)
S(8)	3108(3)	4065(3)	3284(1)	45(1)
C(8)	3676(10)	4614(9)	2721(6)	37(3)
N(7)	3187(7)	4238(8)	2119(4)	36(2)
N(9)	4668(7)	5449(8)	2857(5)	41(3)
C(4)	4748(10)	5604(10)	2292(6)	41(3)
C(5)	3889(10)	4885(10)	1838(6)	38(3)
C(6)	3746(11)	4958(11)	1223(7)	49(3)
O(6)	2985(8)	4397(8)	774(4)	68(3)
N(3)	4630(9)	5827(9)	1140(5)	54(3)
C(3)	4543(14)	5996(13)	515(7)	83(5)
C(2)	5516(12)	6561(11)	1593(7)	51(4)
O(2)	6216(9)	7296(9)	1480(5)	86(3)
N(1)	5589(8)	6433(9)	2179(6)	53(3)
C(1)	6499(12)	7188(12)	2677(7)	81(5)
S(18)	933(3)	4779(2)	1728(1)	42(1)
C(18)	2013(10)	5858(9)	2239(6)	38(3)
N(17)	2256(7)	5967(7)	2861(4)	33(2)
N(19)	2663(8)	6693(8)	2053(5)	40(2)
C(15)	3144(10)	6931(9)	3077(6)	37(3)
C(14)	3357(11)	7335(10)	2587(7)	46(3)
N(13)	4243(9)	8288(9)	2649(6)	56(3)
C(13)	4440(12)	8690(12)	2110(7)	75(5)
C(12)	4911(12)	8831(12)	3229(9)	65(4)
O(12)	5706(9)	9668(9)	3279(6)	103(4)
N(11)	4665(10)	8394(10)	3711(6)	69(3)
C(11)	5390(16)	9000(14)	4313(8)	109(6)
C(16)	3816(11)	7416(11)	3684(7)	54(4)
O(16)	3746(8)	7084(8)	4161(5)	76(3)
C(012)	326(12)	4761(11)	4263(6)	58(4)
C(034)	520(10)	1032(9)	799(6)	48(3)
	[(dppm)Pt(μ-TT)$_2$Pd(dppm)]·7H$_2$O			
Pt(1)	6788(1)	−1202(1)	2928(1)	29(1)
Pd(2)	8484(1)	−2854(1)	2655(1)	29(1)
P(1)	6953(2)	−215(2)	3535(1)	39(1)
P(2)	5974(2)	−1467(2)	3636(1)	38(1)
P(3)	8367(2)	−4183(2)	2638(1)	37(1)
P(4)	9207(2)	−3300(2)	3354(1)	37(1)
N(3)	7853(7)	−2015(7)	556(4)	52(3)
C(2)	8629(11)	−2130(10)	363(6)	65(4)
N(1)	9184(7)	−2435(7)	726(5)	51(3)
C(6)	9060(9)	−2618(7)	1276(5)	42(3)
C(5)	8248(8)	−2471(7)	1443(5)	37(3)
C(4)	7690(8)	−2210(8)	1096(5)	41(3)
N(7)	7872(6)	−2569(6)	1952(3)	33(2)
C(8)	7108(8)	−2326(7)	1869(5)	38(3)
N(9)	6948(7)	−2105(7)	1341(4)	47(3)
C(3)	7238(12)	−1684(14)	183(7)	93(7)
O(2)	8817(8)	−1960(9)	−107(4)	90(4)
C(1)	10016(9)	−2542(10)	507(7)	68(5)
O(6)	9608(6)	−2854(6)	1568(4)	57(3)
S(8)	6396(2)	−2282(2)	2394(1)	45(1)
N(13)	8249(7)	76(6)	1107(4)	45(3)
C(12)	7595(11)	425(9)	880(6)	61(4)
N(11)	6886(7)	404(7)	1172(5)	48(3)
C(16)	6742(9)	−6(8)	1671(5)	50(3)
C(15)	7468(7)	−350(7)	1873(5)	36(3)
C(14)	8181(7)	−295(6)	1600(5)	35(3)
N(17)	7599(6)	−799(5)	2336(4)	34(2)
C(18)	8394(7)	−977(6)	2310(5)	35(3)
N(19)	8776(6)	−689(6)	1865(4)	40(3)
C(13)	8977(10)	25(10)	782(6)	65(5)
O(12)	7623(7)	755(7)	431(4)	75(3)
C(11)	6179(11)	822(11)	942(8)	83(6)
O(16)	6052(6)	−60(6)	1852(4)	64(3)
S(18)	8874(2)	−1553(2)	2812(1)	44(1)
C(012)	6367(8)	−698(8)	4082(5)	44(3)
C(034)	9157(8)	−4334(7)	3159(5)	42(3)

Scheme 1

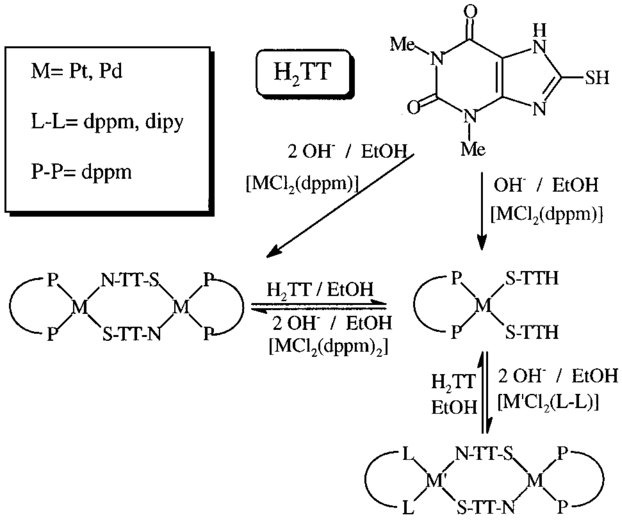

Table 3. Phosphorus-31 NMR Data[a]

compound	δ_A	δ_X	^1J_A	^1J_X	^2J
[Pt(HTT)$_2$(dppm)] **(1)**		−42.7		2683	
[Pd(HTT)$_2$(dppm)] **(2)**		−32.1			
[Pt(μ-TT)(dppm)]$_2$ **(3)**	−53.2	−46.0	2830	2430	68
[Pd(μ-TT)(dppm)]$_2$ **(4)**	−39.9	−31.5			97
[(dppm)Pt(μ-TT)$_2$Pd(dppm)] **(5)**	−40.3	−32.0	2839	2428	68
	−53.1	−45.8			97
[(dppm)Pt(μ-TT)$_2$Pt(bipy)] **(6)**	−52.9	−46.3	2820	2428	69
[(dppm)Pt(μ-TT)$_2$Pd(bipy)] **(7)**	−53.2	−45.9	2832	2428	69

[a] DMSO-d_6 solutions, external reference 85% H_3PO_4.

found for other M(dppm)(dithiolates) (M = Pd and Pt).[10] In view of all this, the compounds should be formulated as *cis*-[M(dppm)(HTT-*S*(8))$_2$].

On reacting *cis*-[M(dppm)Cl$_2$] with Na$_2$TT (prepared *in situ* from the reaction of H_2TT and NaOH) in ethanol and 1:1 molar ratio, the dinuclear complexes **3** and **4**, of empirical formula [M(TT)(dppm)], are obtained. The IR spectra show neither N−H nor S−H bands, suggesting the coordination of the anion in bidentate fashion. Clear evidence for this mode of coordination can be derived from the ^{31}P-NMR spectra (Table 3), since they consists of AX doublets with $^2J_{PP_{cis}}$ coupling that is appropriate to Pt(II) and Pd(II) complexes[10] (Figure 1). In the case of the platinum complex (**3**), satellites due to $^1J_{PtP}$ couplings with ^{195}Pt are also apparent (Figure 1b). The two ^1J values, which are in the usual range for Pt(II), are quite different, with the larger value being assigned to the phosphorous *trans* to nitrogen on the basis of the Pt−P bond distances in [Pt(μ-TT)(dppm)]$_2$, the shorter distance being associated with the larger coupling constant. The S,N-coordinated TT^{2-} ligand would act in either chelate or bridging mode to form mononuclear or oligomeric species, respectively. Nevertheless, because of geometric requirements, the latter coordination mode is generally favored over the former.[4c] The results of the X-ray structure determination for [Pt(μ-TT)(dppm)]$_2$·2DMSO reveals the coordination mode expected from the spectroscopic data. The structure consists of dinuclear [Pt(μ-TT)(dppm)]$_2$ molecules, having a pseudo-2-fold axis perpendicular to that defined by the platinum atoms (see Figure 2), and two DMSO crystal solvent molecules. The two halves of the dinuclear units are chemically but not crystallographically equivalent. Inside the dinuclear molecule, the two platinum atoms are bibridged by

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(10) (a) Bates, P. A.; Hursthouse, M. B.; Kelly, P. F.; Woolins, J. D. *J. Chem. Soc., Dalton Trans.* **1986**, 2367. (b) Verkade, J. G.; Fazlur-Rahman, A. K. *Inorg. Chem.* **1992**, *31*, 5331.

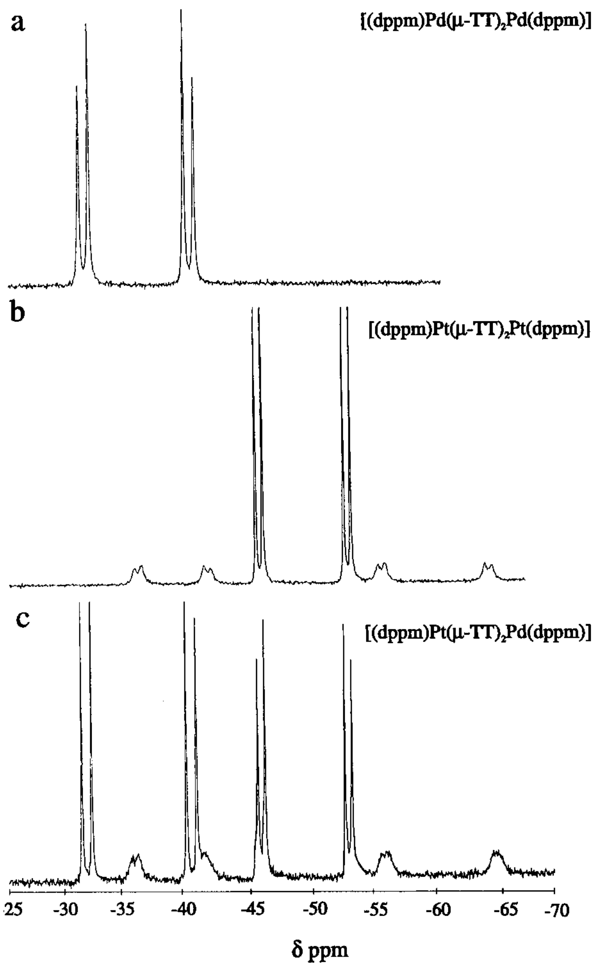

Figure 1. ^{31}P-NMR spectra: (a) [Pd(μ-TT)(dppm)]$_2$·3H$_2$O (**4**), (b) [Pt(μ-TT)(dppm)]$_2$·2DMSO (**3**), and (c) [(dppm)Pt(μ-TT)$_2$Pd(dppm)]·7H$_2$O (**5**).

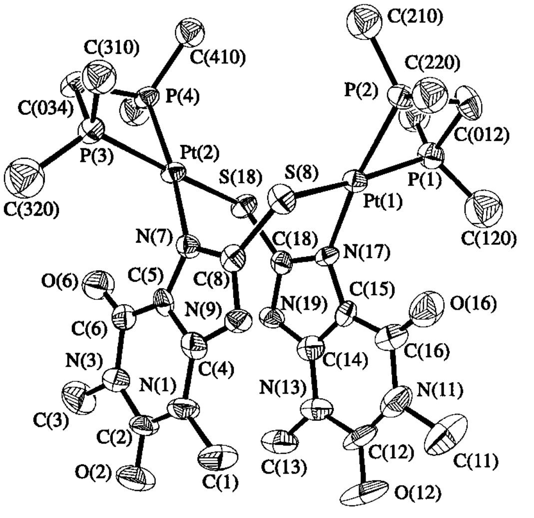

Figure 2. View of the dinuclear unit of **3**. Hydrogen atoms, solvent molecules, and phenyl rings have been omitted for clarity.

two μ-TT ligands, in a head to tail arrangement, with Pt−N bond distances of 2.057 and 2.075 Å and Pt−S bond lengths of 2.356 and 2.349 Å. It should be noted that cleavage of a Pt−S(8) bond in the mononuclear precursor [Pt(HTT-*S*(8))$_2$(dppm)] is needed to give a head to tail arrangement of the purine ligands in the dinuclear complex; however, this process should be very rapid since it has not been detected by NMR spectroscopy. The square-planar coordination of the Pt(II) atom is completed by a chelate dppm ligand, the platinum atoms being deviated from the mean coordination plane by 0.0807 and 0.0851 Å. The P−Pt bond distances *trans* to nitrogen (2.235 and 2.236 Å) are shorter than those *trans* to sulfur (2.262 and 2.270 Å), as expected. Owing to the geometric requirements of the chelate dppm ligand some of the coordination bond angles considerably differ from the ideal value of 90°. The Pt···Pt distance (4.212 Å) is much longer than the sum of the van der Waals radii, so that the metal−metal interaction can be discarded. As the N···S bite distance in the TT^{2-} ligand is not much different from those observed for other S,N-bridging ligands in dinuclear platinum(II) complexes with metal−metal interaction,[11] the steric repulsions between the bulky dppm ligands must be the main factor precluding metal−metal interaction in this compound. Owing to these interligand steric repulsion within the molecules the coordination planes splay apart by a dihedral angle of 69.2°.

Table 4. Selected Bond Lengths (Å) and Angles (deg) for **3** and **5**

[(dppm)Pt(μ-TT)$_2$Pt(dppm)]·2DMSO		[(dppm)Pt(μ-TT)$_2$Pd(dppm)]·7H$_2$O	
Pt(1)−N(17)	2.057(9)	Pt(1)−N(17)^a	2.090(10)
Pt(1)−P(2)	2.235(3)	Pt(1)−P(2)	2.238(3)
Pt(1)−P(1)	2.270(3)	Pt(1)−P(1)	2.259(3)
Pt(1)−S(8)	2.356(3)	Pt(1)−S(8)	2.349(3)
Pt(2)−N(7)	2.075(9)	Pd(2)−N(7)^a	2.052(9)
Pt(2)−P(4)	2.236(3)	Pd(2)−P(4)	2.221(3)
Pt(2)−P(3)	2.262(3)	Pd(2)−P(3)	2.277(3)
Pt(2)−S(18)	2.349(3)	Pd(2)−S(18)	2.343(3)
C(8)−N(7)	1.344(14)	C(8)−N(7)	1.35(2)
C(8)−N(9)	1.366(14)	C(8)−N(9)	1.37(2)
S(8)−C(8)	1.760(12)	C(8)−S(8)	1.742(13)
S(18)−C(18)	1.741(12)	C(18)−S(18)	1.761(12)
C(18)−N(19)	1.355(14)	C(18)−N(19)	1.35(2)
C(18)−N(17)	1.370(14)	C(18)−N(17)	1.35(2)
N(17)−Pt(1)−P(2)	171.8(3)	N(17)−Pt(1)−P(2)	171.1(3)
N(17)−Pt(1)−P(1)	99.2(3)	N(17)−Pt(1)−P(1)	97.5(3)
P(2)−Pt(1)−P(1)	73.35(12)	P(2)−Pt(1)−P(1)	73.53(12)
N(17)−Pt(1)−S(8)	90.8(2)	N(17)−Pt(1)−S(8)	92.9(3)
P(2)−Pt(1)−S(8)	96.37(11)	P(2)−Pt(1)−S(8)	96.00(12)
P(1)−Pt(1)−S(8)	168.91(11)	P(1)−Pd(1)−S(8)	169.15(12)
N(7)−Pt(2)−P(4)	172.5(3)	N(7)−Pd(2)−P(4)	172.3(3)
N(7)−Pt(2)−P(3)	99.6(3)	N(7)−Pd(2)−P(3)	100.3(3)
P(4)−Pt(2)−P(3)	73.35(12)	P(4)−Pd(2)−P(3)	73.64(12)
N(7)−Pt(2)−S(18)	90.5(3)	N(7)−Pd(2)−S(18)	92.8(3)
P(4)−Pt(2)−S(18)	96.28(11)	P(4)−Pd(2)−S(18)	92.91(12)
P(3)−Pt(2)−S(18)	168.26(11)	P(3)−Pd(2)−S(18)	165.97(12)
N(7)−C(8)−S(8)	123.2(9)	N(7)−C(8)−S(8)	122.6(10)
N(17)−C(18)−S(18)	123.7(9)	N(17)−C(18)−S(18)	122.1(9)
P(1)−C(012)−P(2)	94.8(6)	P(1)−C(012)−P(2)	94.3(6)
P(4)−C(034)−P(3)	93.5(5)	P(4)−C(034)−P(3)	94.4(6)

[a] Positions of Pt(1) and Pd(2) are both occupied by Pt and Pd ions at *ca.* 50%.

Finally, bond distances and angles in the thiotheophyllinato ligand do not significantly differ from those observed for other complexes also containing this S,N-bridging ligand.[4] The nine atoms of the purine system are almost coplanar as expected.

It should be noted that the reaction of [M(μ-TT)(dppm)]$_2$ with H$_2$TT in ethanol and a 1:1 molar ratio leads to the mononuclear complexes [M(HTT)$_2$(dppm)]. Noteworthy, the dinuclear complexes can be re-formed by reacting the latter with *cis*-[M(dppm)Cl$_2$] and NaOH in 1:1:2 molar ratio (see Scheme 1). This reaction may be monitored by ^{31}P{^{1}H}-NMR spectroscopy in DMSO-d_6. In the absence of base, the spectrum of the crude reaction mixture, which does not change with time, indicates an equilibrium between the reagents and the dinuclear compound **3**. It is noticeable that no other compounds are present. The equilibrium is pushed to the formation of **3** when NaOH is added to the crude reaction mixture. On the other hand, when NaOH is added to a solution of **1**, no reaction was seen, which indicates

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(11) Umakoshi, K.; Kinoshita, I.; Ichimura, A.; Ooi, S. *Inorg. Chem.* **1987**, *26*, 3351.

that, for the formation of **3**, both **1** and [M(dppm)Cl_2] are needed. This fact prompted us to explore the reactions between the mononuclear complexes and [M(L-L)Cl_2] (M = Pt(II) and Pd(II), and L-L = dppm and 2,2′-bipyridine) in order to obtain homo- and heterodinuclear complexes. Following this procedure we have succeeded in obtaining the complexes [(dppm)Pt(μ-TT)$_2$M(L-L)] (**5**−**7**). The IR spectra of these complexes are very similar to, almost identical with, those of **3** and **4**, thus suggesting the same *S*(8),*N*(7)-bridging mode in all of them. This is supported by the crystal structure results for **5**. The structure of this compound consists of dinuclear [(dppm)Pt(μ-TT)$_2$Pd(dppm)] units and seven lattice crystal water molecules. The dinuclear entities are almost superimposable to those of **3** (Table 4), by which the structure of the dinuclear unit of **5** can be seen as that of **3** with an isomorphic substitution of one of the Pt(II) ions by a Pd(II) ion, the metal ions being disordered in both positions by *ca.* 50%. Nevertheless, some minor differences are found for the relative positions of the purine ligands which are attributed to the existence on an extended hydrogen bond network involving the seven water molecules and the heteroatoms of the purines. In this complex the Pt···Pd distance of 4.034 Å is shorter by *ca.* 0.2 Å than that of **3** as a consequence of a decrease in the dihedral angle between the coordination planes (65.9°). Remaining bond distances and angles fall well within their usual range and do not deserve further comments. In good accord with the structure the ^{31}P-NMR spectrum of **5** exhibits two groups of AX doublets (Figure 1c), arising from the Pd(II) and the Pt(II) fragments of the dinuclear molecule, respectively. The spectra of **6** and **7** are very similar to that of **3**, as expected.

In view of the ability of the H_2TT ligand to form homo- and heterodinuclear complexes, we have decided to extend our work by using other M(II) pairs and/or less sterically hindered ligands which might allow the metal−metal interaction. Work along this line is in progress.

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Supporting Information Available: Full listings of crystal data and structure refinement, fractional atomic coordinates, thermal parameters, and bond lengths and angles (23 pages). Ordering information is given on any current masthead page.

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