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A Heteronuclear (Pt, Zn) Complex of 1-Methyluracil with Different Coordination Geometries (Square-planar and Square-pyramidal) of the Two Metals

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Abstract

Reaction of *cis*-$(NH_3)_2Pt(1\text{-}MeU)_2$ (1-MeU = 1-methyluracil anion, $C_5H_5N_2O_2$) with $ZnSO_4 \cdot 7H_2O$ leads to the formation of a dinuclear complex of composition $[(NH_3)_2Pt(C_5H_5N_2O_2)_2Zn(H_2O)_3]SO_4 \cdot 2H_2O$. The compound crystallizes in space group $P2_1/c$ with $a = 10.534(1)$, $b = 17.933(2)$, $c = 11.490(1)$ Å, $\beta = 94.61(1)°$, $Z = 4$. The structure was refined to $R = 0.043$ and $R_w = 0.061$. In this compound, Pt is coordinated through N3 to the 1-MeU ligand, while Zn is bound through the two O4 oxygens and completes its distorted square-pyramidal coordination sphere by three aqua ligands. The positions of the two metals relative to their basal donor atoms and the shortness of the Pt–Zn separation (2.760(1) Å) suggest a bonding interaction between the two metals. Using ^1H NMR spectroscopy, a formation constant of *ca.* 114 l mol^{-1} for the Pt, Zn complex has been estimated.

Introduction

Cis- and *trans*-$(NH_3)_2PtL_1L_2$ complexes (with L_1 = 1-methyluracil, 1-MeU, or 1-methylthymine, 1-MeT, anions coordinated to Pt through N3, and L_2 = 1-MeU, 1-MeT, or other nucleobase) are interesting ligands for metal ions [1]. Depending on the nature of the available metal, any other ligands attached to it, the counter anions present, and the concentration conditions, a variety of homo- and heteronuclear complexes with different stoichiometries and metal geometries are formed [2]. Frequently, rather short distances between the metal centers in these types of complexes are observed. Coordination of additional metal ions to *cis*- and *trans*-$(NH_3)_2PtL_1L_2$ is a consequence of the basicity of the exocyclic oxygens in N3 platinated 1-MeU and 1-MeT [3]. With the coordination geometry of the Pt being square-planar, two different coordination geometries of the entering metal have been observed so far, a distorted tetrahedral with Ag [4], and a square-planar with Pt [5], Mn [6], and Cu [1a]. Once the dinuclear complex is formed, the geometry of a third entering metal appears to be dictated by the geometry of the second metal *i.e.* square-planar, if the second metal is coordinated this way [7], and tetrahedral, if the second metal has a tetrahedral coordination geometry [8].

In continuation of our studies on heteronuclear complex containing different metals bound to a nucleobase, this report is based on the structure of a mixed Pt, Zn complex of 1-methyluracil having one metal (Pt) in a square-planar, and the second one (Zn) in a square-pyramidal coordination geometry.

Experimental

The title compound *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Zn(H_2O)_3]SO_4 \cdot 2H_2O$, $C_{10}H_{26}N_6O_{13}PtSZn$, was prepared as described elsewhere by reaction of $ZnSO_4 \cdot 7H_2O$ and *cis*-$(NH_3)_2Pt(1\text{-}MeU)_2 \cdot 4H_2O$ [2]. A crystal of dimensions 0.2 × 0.2 × 0.3 mm was used for the X-ray measurements (room temperature, graphite monochromator, $\lambda = 0.71069$ Å, Philips PW 1100 single crystal diffractometer).

Crystal Data

Monoclinic, space group $P2_1/c$, $a = 10.534(1)$, $b = 17.933(2)$, $c = 11.490(1)$ Å, $\beta = 94.61(1)°$ (by least-squares from the setting angles of 17 reflections). $D_c = 2.244$ g cm^{-3} for $Z = 4$. Intensities were measured for all ($\pm h$, $+k$, $+l$) reflections between 3 and 46° in 2θ by using $\theta/2\theta$ scans (scan width 1°, 10 s background before and after each scan; $\sigma(I)$ calculated on the basis of counting statistics; 3 check reflections measured every 60 min). The I and $\sigma(I)$ values were corrected for Lp effects and, in a later stage, for absorption by the Walker and Stuart method [9] ($\mu = 74.3$ cm^{-1}). A total of 3013 independent reflections was obtained. Seven reflections

0020-1693/85/$3.30

at low θ, evidently affected by the beam-catcher, were excluded in the following calculations.

The structure was solved by Patterson and difference Fourier techniques. The Pt, Zn, and S atoms were refined with anisotropic temperature factors, the other non-hydrogen atoms with isotropic temperature factors. Hydrogen atoms were not considered at any stage. Final parameters are listed in Table I. $R = 0.043$, $R_w(F) = 0.061$ (3006 observations, 144 parameters). Scattering factors for neutral atoms were taken from Cromer and Mann [10]; $\Delta f'$ and $\Delta f''$ corrections were applied [11], and the SHELX-76 program package [12] was used for the calculations.

The formation constant K of the 1:1-Pt, Zn complex was estimated using ^1H NMR spectroscopy (Jeol JNM-FX 60, D_2O, 30 °C, $[N(CH_3)_4]BF_4$ as internal reference). To a solution of *cis*-$(NH_3)_2Pt(1\text{-}MeU)_2$ (0.025 M Pt) increasing amounts of solid $ZnSO_4 \cdot 7H_2O$ were added, and the downfield shifts of the 1-MeU resonances were measured. Since the pD of the mixtures were in the range 6–4, no protonation of 1-MeU ligands took place. The 1-MeU resonances showed a very slight concentration dependency (upfield shifts of 0.7–1 Hz when going from 0.003 to 0.05 M) which was not, however, considered in the determination of K. The NMR data were analyzed for seven different mixtures containing a threefold to ninefold excess of Zn over Pt with the assumption that, under these conditions, only the Pt, Zn complex is formed and amounts of Pt_2, Zn are negligeable. This assumption seems to be justified considering the fact that, on a preparative scale, a 1:1-mixture of *cis*-$(NH_3)_2Pt(1\text{-}MeU)_2$ and $ZnSO_4$ gives the Pt, Zn complex as a 65% yield, at least [2].

TABLE I. Atomic Parameters for *cis*-$[(NH_3)_2Pt(1\text{-}MeU)_2Zn(H_2O)_3]SO_4 \cdot 2H_2O$[a].

Atom	x	y	z	U
Pt1	0.3545(1)	0.0668(1)	0.1226(1)	0.017(1)
Zn1	0.1735(1)	0.1226(1)	0.2601(1)	0.024(1)
N10	0.2539(7)	−0.0194(4)	0.0443(6)	0.027(2)
N11	0.3093(7)	0.1287(4)	−0.0242(7)	0.029(2)
O20	0.0240(7)	0.0701(3)	0.1576(7)	0.039(2)
O21	0.0563(7)	0.1534(4)	0.3850(7)	0.047(2)
O22	0.1390(6)	0.2150(4)	0.1516(6)	0.039(1)
N1a	0.6545(7)	0.2195(4)	0.1793(6)	0.029(2)
C1a′	0.7717(11)	0.2332(7)	0.1210(11)	0.055(3)
C2a	0.5708(8)	0.1674(4)	0.1323(7)	0.024(2)
O2a′	0.5906(6)	0.1341(3)	0.0423(6)	0.034(1)
N3a	0.4625(6)	0.1524(4)	0.1924(6)	0.019(1)
C4a	0.4340(8)	0.1914(5)	0.2884(8)	0.026(2)
O4a′	0.3352(6)	0.1769(3)	0.3358(6)	0.034(1)
C5a	0.5271(9)	0.2439(5)	0.3346(8)	0.033(2)
C6a	0.6334(10)	0.2556(6)	0.2803(9)	0.041(2)
N1b	0.5475(7)	−0.0821(5)	0.3559(7)	0.032(2)
C1b′	0.6655(12)	−0.1215(7)	0.3651(10)	0.054(3)
C2b	0.5129(8)	−0.0358(5)	0.2683(8)	0.029(2)
O2b′	0.5864(6)	−0.0266(4)	0.1903(6)	0.038(2)
N3b	0.3997(6)	0.0002(3)	0.2652(6)	0.020(1)
C4b	0.3193(8)	−0.0104(5)	0.3484(8)	0.027(2)
O4b′	0.2134(6)	0.0250(3)	0.3459(5)	0.032(1)
C5b	0.3501(10)	−0.0620(5)	0.4433(10)	0.037(2)
C6b	0.4659(10)	−0.0949(6)	0.4415(10)	0.047(2)
S1	−0.0096(2)	0.3553(1)	0.3576(2)	0.025(2)
O30	−0.0039(8)	0.2941(5)	0.4394(8)	0.060(2)
O31	0.0677(7)	0.3392(4)	0.2614(7)	0.053(2)
O32	0.0422(7)	0.4224(4)	0.4215(6)	0.042(2)
O33	−0.1385(8)	0.3699(4)	0.3162(7)	0.055(2)
O40	0.0009(10)	−0.0695(5)	0.4322(9)	0.068(3)
O41	0.7810(18)	0.0705(9)	0.2992(17)	0.147(6)

[a] For Pt, Zn, and S the equivalent isotropic temperature factors are listed. They were calculated from the U_{ij} values by $U_{eq} = 1/3\Sigma_{ij}U_{ij}a_i^*a_j^*a_i \times a_j$.

The equation of Wang and Li [13]:

$$\frac{M_0}{\nu - \nu_f} = \frac{1}{\nu_c - \nu_f}(L_0 + M_0 - ML) + \frac{1}{K(\nu_c - \nu_f)} \qquad (1)$$

for 1:1-complex formation with M_0 and L_0 being the initial concentrations of Zn(II) and *cis*-$(NH_3)_2Pt(1\text{-}MeU)_2$, respectively, ML, the equilibrium concentration of the Pt, Zn complex, ν the observed frequency of the proton under consideration, ν_f and ν_c the frequencies of free *cis*-$(NH_3)_2Pt(1\text{-}MeU)_2$ and Pt, Zn, respectively, was used for the determination of K.

Data were analyzed as outlined by Kan and Li [14] with ν_c taken as the frequency at which Zn(II) no longer affects the 1-MeU resonances (>10-fold excess of Zn over Pt, *c.f.* Table IV). Substituting ML in (1) by:

$$ML = \frac{\nu - \nu_f}{\nu_c - \nu_f} L_0$$

and replacing $\nu - \nu_f$ by $\Delta\delta$, and $\nu_c - \nu_f$ by Δ_{max}, plots of $M_0/\Delta\delta$ *vs.* $(L_0 + M_0 - (\Delta\delta/\Delta_{max})L_0)$ gave straight lines both for H5 and H6. From the intercepts obtained by linear regression (5.639×10^{-4} for H5 and 6.7849×10^{-4} for H6) K values of 114.4 l mol^{-1} (H5) and 113.4 l mol^{-1} (H6) were found.

Results and Discussion

Atomic coordinates and temperature factors of the title compound *cis*-$[(NH_3)_2Pt(C_5H_5N_2O_2)_2Zn(H_2O)_3]SO_4 \cdot 2H_2O$ are listed in Table I. Interatomic distances and angles are given in Table II and conformational parameters in Table III. The cation, which is shown in Fig. 1, consists of a *cis*-diammineplatinum(II) and a triaquazinc(II) unit linked by two 1-methyluracilato ligands through N3 (Pt) and O4 (Zn). The Pt–Zn distance within the cation is 2.760(1) Å, thus comparable to Pt–Cu (2.765(3) Å) in the corresponding mixed Pt, Cu complex [1a], and

TABLE II. Interatomic Distances (Å) and Angles (deg).

(a) Pt, Zn coordination spheres

Pt1–Zn1	2.760(1)	Zn1–Pt1–N10	99.7(2)
Pt1–N10	2.041(7)	Zn1–Pt1–N11	98.6(2)
Pt1–N11	2.044(7)	Zn1–Pt1–N3a	83.8(2)
Pt1–N3a	2.037(6)	Zn1–Pt1–N3b	83.2(2)
Pt1–N3b	2.052(6)	N10–Pt1–N11	88.2(3)
Zn1–O20	2.111(7)	N10–Pt1–N3a	176.3(3)
Zn1–O21	2.044(8)	N10–Pt1–N3b	89.5(3)
Zn1–O22	2.089(7)	N11–Pt1–N3a	90.0(3)
Zn1–O4a′	2.090(6)	N11–Pt1–N3b	177.3(3)
Zn1–O4b′	2.036(6)	N3a–Pt1–N3b	92.2(2)
		Pt1–Zn1–O20	92.2(2)
		Pt1–Zn1–O21	169.9(2)
		Pt1–Zn1–O22	92.4(2)
		Pt1–Zn1–O4a′	80.2(2)
		Pt1–Zn1–O4b′	80.8(2)
		O20–Zn1–O21	92.7(3)
		O20–Zn1–O22	86.2(3)
		O20–Zn1–O4a′	170.6(3)
		O20–Zn1–O4b′	90.2(3)
		O21–Zn1–O22	96.8(3)
		O21–Zn1–O4a′	95.7(3)
		O21–Zn1–O4b′	90.3(3)
		O22–Zn1–O4a′	88.6(2)
		O22–Zn1–O4b′	172.2(3)
		O4a′–Zn1–O4b′	94.0(2)

(b) 1-Methyluracilato ligands

N1a–C1a′	1.472(14)	C1a′–N1a–C6a	120.6(8)
N1a–C2a	1.366(11)	C1a′–N1a–C2a	118.2(8)
C2a–O2a′	1.225(11)	C6a–N1a–C2a	121.2(8)
C2a–N3a	1.406(11)	O2a′–C2a–N1a	121.2(8)
N3a–C4a	1.360(11)	O2a′–C2a–N3a	121.4(8)
C4a–O4a′	1.241(11)	N1a–C2a–N3a	117.4(7)
C4a–C5a	1.430(13)	Pt1–N3a–C2a	113.6(5)
C5a–C6a	1.341(14)	Pt1–N3a–C4a	123.7(5)
C6a–N1a	1.363(13)	C2–N3a–C4a	122.7(7)
N1b–C1b′	1.427(15)	O4a′–C4a–N3a	119.7(8)
N1b–C2b	1.332(12)	O4a′–C4a–C5a	123.4(8)
C2b–O2b′	1.241(11)	N3a–C4a–C5a	116.7(7)
C2b–N3b	1.354(11)	Zn1–O4a–C4a	126.8(6)
N3b–C4b	1.341(11)	C4a–C5a–C6a	120.2(9)
C4b–O4b′	1.282(11)	C5a–C6a–N1a	121.4(9)
C4b–C5b	1.447(14)	C1b′–N1b–C6b	117.1(9)
C5b–C6b	1.356(15)	C1b′–N1b–C2b	123.3(8)
C6b–N1b	1.377(13)	C6b–N1b–C2b	119.6(8)
		O2b′–C2b–N1b	118.7(8)
		O2b′–C2b–N3b	121.1(8)
		N1b–C2b–N3b	120.3(8)
		Pt1–N3b–C2b	116.5(5)
		Pt1–N3b–C4b	122.1(5)
		C2b–N3b–C4b	121.3(7)
		O4b′–C4b–N3b	120.9(8)
		O4b′–C4b–C5b	118.4(8)
		N3b–C4b–C5b	120.8(8)
		Zn1–O4b′–C4b	125.6(5)
		C4b–C5b–C6b	114.4(9)
		C5b–C6b–N1b	123.6(10)

TABLE II *(continued)*

(c) SO$_4$-anion

S1–O30	1.443(9)	O30–S1–O31	110.3(5)
S1–O31	1.455(8)	O30–S1–O32	107.4(4)
S1–O32	1.489(7)	O30–S1–O33	110.2(5)
S1–O33	1.426(8)	O31–S1–O32	109.2(4)
		O31–S1–O33	111.0(5)
		O32–S1–O33	108.5(4)

(d) Possible hydrogen bonding interactions (≤3.4 Å)[a]

O21–O30	2.69	Zn1–O21–O30	126
O22–O31	2.70	Zn1–O22–O31	115
O2b′–O41	2.90	C2b–O2b′–O41	103
O4b′–O40	3.04	C4b–O4b′–O40	112
O20–O41^{i}	3.14	Zn1–O20–O41^{i}	108
O21–O41^{i}	3.34	Zn1–O21–O41^{i}	103
N10–O2a′^{ii}	2.86	Pt1–N10–O2a′^{ii}	114
N11–O2b′^{ii}	2.92	Pt1–N11–O2b′^{ii}	97
O21–O40^{iii}	2.69	Zn1–O21–O40^{iii}	126
O40–O40^{iii}	2.94		
N10–O32^{iv}	3.08	Pt1–N10–O32^{iv}	96
N11–O32^{iv}	2.98	Pt1–N11–O32^{iv}	99
O20–O32^{iv}	2.74	Zn1–O20–O32^{iv}	115
O22–O30^{iv}	2.77	Zn1–O22–O30^{iv}	122
O31–O40^{v}	2.81	S1–O31–O40^{v}	112
O32–N10^{v}	3.34	S1–O32–N10^{v}	90
O32–O20^{v}	2.87	S1–O32–O20^{v}	121
O33–N10^{v}	2.88	S1–O33–N10^{v}	112

[a] Symmetry operations: i = $-1 + x, y, z$; ii = $1 - x, -y, -z$; iii = $-x, -y, 1 - z$; iv = $x, 0.5 - y, -0.5 + z$; v = $-x, 0.5 + y, 0.5 - z$.

TABLE III. Conformational Paramaters.

(a) Deviations (in Å) of atoms from best planes[a].

N$_4$ coordination plane of Pt1 (plane I):

N10*	N11*	N3a*	N3b*	Pt1	Zn1
0.016	−0.016	0.016	−0.016	−0.042	−2.750

O$_4$ coordination plane of Zn1 (plane II):

O4a′*	O4b′*	O20*	O22*	Zn1	Pt1
−0.010	0.010	−0.010	0.010	0.139	−2.592

1-Me-Ua plane (plane III):

N1a*	C2a*	N3a*	C4a*	C5a*	C6a*
−0.016	−0.012	0.035	−0.029	0.001	0.021
C1a′	O2a′	O4a′	Pt1	Zn1	
0.006	−0.025	−0.019	0.221	−0.515	

1-Me-Ub plane (plane IV):

N1b*	C2b*	N3b*	C4b*	C5b*	C6b*
0.010	−0.011	−0.001	0.012	−0.012	0.002
C1b′	O2b′	O4b′	Pt1	Zn1	
0.008	−0.040	0.048	−0.108	0.707	

(b) Dihedral angles

plane I/plane II	19.3°	plane I/plane III	67.3°
plane III/plane IV	94.3°	plane I/plane IV	81.3°

(continued overleaf)

TABLE III *(continued)*

(c) Torsional angles	
N10–Pt1–Zn1–O20	19.7°
N11–Pt1–Zn1–O22	16.3°

[a] Equations of the planes refer to the a b c basis.

Plane I: $8.912x - 6.093y - 5.488z - 2.121 = 0$

Plane II: $-6.859x + 5.933y + 8.425z - 1.589 = 0$

Plane III: $4.602x - 12.772y + 5.889z - 1.280 = 0$

Plane IV: $4.043x + 13.495y + 5.775z - 3.151 = 0$.

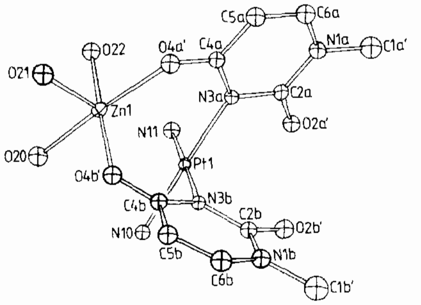

Fig. 1. Molecular cation *cis*-$[(NH_3)_2Pt(C_5H_5N_2O_2)_2Zn(H_2O)_3]^{2+}$.

to Pt–Mn (2.704(1) Å) in the mixed Pt_2, Mn complex [6]. This intermetallic distance is intermediate between the very short distance of 2.681(1) Å observed in a trinuclear Pt_2, Cu complex containing 1-MeU and 1-methylcytosine as bridging ligands [1b] and the considerably longer distances of 2.85–2.95 Å found in dinuclear Pt complexes [5] as well as in mixed Pt, Ag complexes [8].

Pt exhibits a square-planar coordination geometry, but it is slightly (0.042 Å) out of the best plane, directed towards the Zn, very similar to the corresponding diplatinum(II) complexes of 1-methylthymine and 1-methyluracil [5]. The coordination geometry of Zn is that of a distorted square pyramid with three aqua groups and two O4 oxygens of the 1-MeU ligands pointing towards the vertices. Zn is out of the basal plane defined by the two O4 oxygens and the water oxygens O20 and O22 by 0.139 Å in a direction pointing away from Pt. Although the number of known examples of Zn compounds having a square-pyramidal coordination geometry is very limited [15, 16], it is evident that the observed deviation of Zn in the compound described herein is remarkably small (*c.f.* 0.41 Å in a mono-aqua-bis-(acetylacetonato) [15] and 0.34 Å in an aqua-bis-(salicylidene) complex [16]). This fact, together with the slight movement of the Pt towards the Zn, may be indicative of a bonding interaction between Pt and Zn. It should be pointed out that a similar short distance (2.772(3) Å), between a Pt(II) and Ag(I) in a tetranuclear Pt_2, Ag_2 complex, has been interpreted as a 'Pt–Ag bond of considerable strength' [17]. On the other hand, the 2.760(1) Å distance between the two metal centers in the title compound is still considerably longer than in related diplatinum(III) complexes (around 2.60 Å [18]).

The Pt coordination plane and the basal plane of the pyramid containing the Zn are tilted by an angle of 19.3° and at the same time twisted about the Pt–Zn vector by 17.5° (av), very similar to those found in the majority of related diplatinum(II) complexes (*c.f.* discussion in Ref. [15a]). Resulting from the tilting of Pt and Zn planes, the Pt–Zn and Zn–OH_2(21) are not colinear but form an angle of 170° about the Zn.

The 1-MeU rings are not perfectly planar (Table III). In particular, the deviations of the endocyclic atoms of ring *a*, N3 (+0.035 Å), C4 (–0.029 Å), and the respective direction, combined with the substantial deviation of Pt (+0.221 Å) from the best plane of the ring, indicate a shift of N3 from pure sp^2 hybridization towards sp^3 hybridization. Both 1-MeU rings are, roughly, at right angles (94.3°), relative to each other, but have different inclinations with respect to the Pt coordination plane (67.3° and 81.3°).

The geometry of the sulphate ion is normal. As shown in Table II, section d, there is extensive hydrogen bonding in the crystal, involving aqua, NH_3, and exocyclic O2 oxygens of the cation as well as sulphate oxygens and lattice water. There are no unusually short interactions.

In the ^1H NMR spectrum there is fast exchange between free and coordinated Zn as evident from single signals of the 1-MeU resonances. The formation constant *K* for the reaction:

$$(NH_3)_2Pt(1\text{-}MeU)_2 + [Zn(H_2O)_x]^{2+} \longrightarrow$$
$$[(NH_3)_2Pt(1\text{-}MeU)_2Zn(H_2O)_3]^{2+} + (x-3)H_2O$$

was estimated using ^1H NMR spectroscopy as described under 'Experimental'. Addition of $ZnSO_4$ to an aqueous solution of *cis*-$(NH_3)_2Pt(1\text{-}MeU)_2$ resulted in downfield shifts of all three 1-MeU resonances with the relative effects being $H5 > H6 \gg CH_3$. In Table IV, the changes in chemical shifts are listed as a function of added $ZnSO_4$. *K* values of 114.4 and 113.4 l mol^{-1} were obtained using shifts of H5 and H6 resonances, respectively. The determination of *K* from NMR data is based on the assumption that the diamagnetic, anisotropic effects due to intracomplex base overlap are comparable in *cis*-$(NH_3)_2Pt(1\text{-}MeU)_2$ and in the Pt, Zn derivative, hence reorientation of the 1-MeU ligands (presumably interchanging between head–tail and head–head in *cis*-$(NH_3)_2Pt(1\text{-}MeU)_2$, yet locked in head–head orientation in the Pt, Zn complex) does not effect the protons at C5 and C6 greatly. We cannot, at present, be certain that this is indeed the case and therefore should consider this data to be of a preliminary nature.

TABLE IV. Downfield Shifts of H5 and H6 Resonances of *cis*-$(NH_3)_2Pt(1\text{-}MeU)_2$ in the Presence of $ZnSO_4$.

[Zn] mol l^{-1}	$[(NH_3)_2Pt(1\text{-}MeU)_2]$ mol l^{-1}	Δ H5[a] (Hz)	Δ H6[a] (Hz)
0.075	0.025	13.7	11.6
0.100	0.025	14.0	12.0
0.125	0.025	14.6	12.3
0.150	0.025	14.5	12.6
0.175	0.025	14.9	12.8
0.200	0.025	15.0	12.8
0.225	0.025	15.1	12.8
⋮	⋮	⋮	⋮
>0.3	0.025	15.5	13.0

[a] Downfield shifts relative to 0.025 M *cis*-$(NH_3)_2Pt(1\text{-}MeU)_2$ in the absence of $ZnSO_4$; error ±0.2 Hz.

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Note Added in Proof

Using a non-linear least squares method (courtesy of Professor R. B. Martin, University of Virginia, Charlottesville, U.S.A.), a stability constant of 120 M^{-1} was obtained for the PtZn species on the basis of the NMR shifts listed above. Considering a larger Zn concentration range, more (27) data points, and both formation of the Pt_2Zn and the PtZn species, log K values were obtained of 2.9 for Pt_2Zn and 1.9 for PtZn. We believe that these data are more reliable than the former.

References

1 (a) D. Neugebauer and B. Lippert, *J. Am. Chem. Soc., 104*, 6596 (1982); (b) B. Lippert, U. Thewalt, H. Schöll-

2 D. M. L. Goodgame, R. W. Rollins and B. Lippert, *Polyhedron, 4*, 829 (1985).

3 B. Lippert, *Inorg. Chim. Acta, 55*, 5 (1981).

4 B. Lippert and D. Neugebauer, *Inorg. Chim. Acta, 46*, 171 (1980).

5 (a) H. Schöllhorn, U. Thewalt and B. Lippert, *Inorg. Chim. Acta, 93*, 19 (1984); (b) B. Lippert, D. Neugebauer and G. Raudaschl, *Inorg. Chim. Acta, 78*, 161 (1983).

6 (a) B. Lippert and U. Schubert, *Inorg. Chim. Acta, 56*, 15 (1981); (b) D. M. L. Goodgame, R. W. Rollins and B. Lippert, *Inorg. Chim. Acta, 66*, L59 (1982).

7 B. Lippert and D. Neugebauer, *Inorg. Chem., 21*, 451 (1982).

8 H. Schöllhorn, U. Thewalt and B. Lippert, *Chem. Commun.*, 769 (1984).

9 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A:, 39*, 158 (1983).

10 D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect. A:, 24*, 321 (1968).

11 D. T. Cromer and D. Liberman, *J. Chem. Phys., 53*, 1891 (1970).

12 G. M. Sheldrick, 'SHELX-76', Program System, University of Cambridge, 1976.

13 S. M. Wang and N. C. Li, *J. Am. Chem. Soc., 90*, 5069 (1968).

14 L. S. Kan and N. C. Li, *J. Am. Chem. Soc., 92*, 4823 (1970).

15 H. Montgomery and E. C. Lingafelter, *Acta Crystallogr., 16*, 748 (1963).

16 D. Hall and F. H. Moore, *J. Chem. Soc. A:*, 1822 (1966).

17 R. Uson, J. Forniés, M. Tomás, F. A. Cotton and L. R. Falvello, *J. Am. Chem. Soc., 106*, 2482 (1984).

18 (a) B. Lippert, H. Schöllhorn and U. Thewalt, *Z. Naturforsch., Teil B:, 38*, 1441 (1983); (b) B. Lippert, unpublished results.