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Inter- and intra-molecular condensation patterns of (en)Pd^{II} with *trans*-$[a_2PtL_2]^{2+}$ (a = am(m)ine, L = 2-aminopyridine): $PtPd_3$ and Pt_2Pd_4 species with multiple amide bridges. Unexpected trapping of a pair of nitrate ions by a Pt_2Pd_4 double cone †

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Reaction of *trans*-$[a_2Pt(Hampy)_2]X_2$ (a = NH_3, **2**; a = $MeNH_2$, **3**; Hampy = 2-aminopyridine; X = NO_3 or ClO_4) with an excess of $[(en)Pd(H_2O)_2]^{2+}$ in aqueous solution leads to two types of condensation products: (i) tetranuclear $PtPd_3$ species, in which the deprotonated "a" ligands (μ-NH_2, μ-MeNH) and the deprotonated amino group of the 2-aminopyridine (ampy) ligands are chelated by two (en)Pd^{II} entities and in addition a single Pd^{II} ion (without en) cross-links the amido functions of ampy in a nearly linear fashion. The four metal ions thus form a diamond arrangement with a short (<2.5 Å) Pt⟶Pd dative bond. (ii) Hexanuclear Pt_2Pd_4 species, in which (en)Pd^{II} moieties bridge exclusively amido groups of four ampy ligands in such a way that an open rectangular box (or double cone) is formed. This allows two nitrate counter ions to become inserted in the cavity of the +8 charged cation. Thus in both cases the ampy ligand acts as a μ_3-ligand, either in an intramolecular or an intermolecular fashion.

Introduction

Following up on extensive work on di- and multi-nuclear complexes derived from *cis*-$[a_2ML_2]$ (a = NH_3 or amine, a_2 = diamine; M = Pt^{II} or Pd^{II}; L = N-heterocycle; charge omitted) and a variety of different (hetero)metal ions,[1,2] we have lately extended these studies to *trans*-$[a_2PtL_2]$ compounds and (hetero)metal entities sufficiently flexible to bridge available donor atoms at the *trans*-positioned ligands L.[3] The heterometals applied displayed either (**i**) linear, (**ii**) distorted tetrahedral, (**iii**) *trans*-square-planar, or (**iv**) square-pyramidal coordination geometries (Chart 1). Among these, the combination of *trans*-$[a_2PtL_2]$ with square-planar Pd^{II} (**iii**) proved of particular interest as a consequence of formation of strong Pt⟶Pd dative bonds.[4–6]

As a further extension of this work we have recently started to combine *trans* and *cis* geometries, hence have reacted *trans*-$[a_2PtL_2]$ compounds with (en)Pd^{II}.[7] In this combination, the *cis* metal entity ((en)Pd^{II}) is incapable of bridging donor sites of the two ligands L in an intramolecular fashion. It is obvious that there are (at least) three alternatives of heterometal binding, which are either monodentate binding of (en)Pd^{II} to L, intramolecular chelation with another ligand in the coordination sphere of Pt^{II}, or intermolecular bridging. Much to our surprise we observed facile intramolecular chelate formation involving L and the am(m)ine ligand "a" at the Pt, hence formation of amido bridges (**v**). At the same time a combination (**vi**) between patterns (**iii**) and (**v**) was realized,[7] which implied that $[(en)Pd(H_2O)_2]^{2+}$ had undergone (partial) dismutation to generate a $[Pd(H_2O)_4]^{2+}$ species. Case (**vi**) was found with a = NH_3 and L = 2-aminopyridine anion (ampy),[7] while (**v**) was realized with L = pyrazolate (pz).[7]

Here we report on our findings that *trans*-$[a_2PtL_2]^{2+}$ (with L = Hampy) and (en)Pd^{II} can also condense in an intermolecular fashion, thereby generating a cage structure (**vii**),

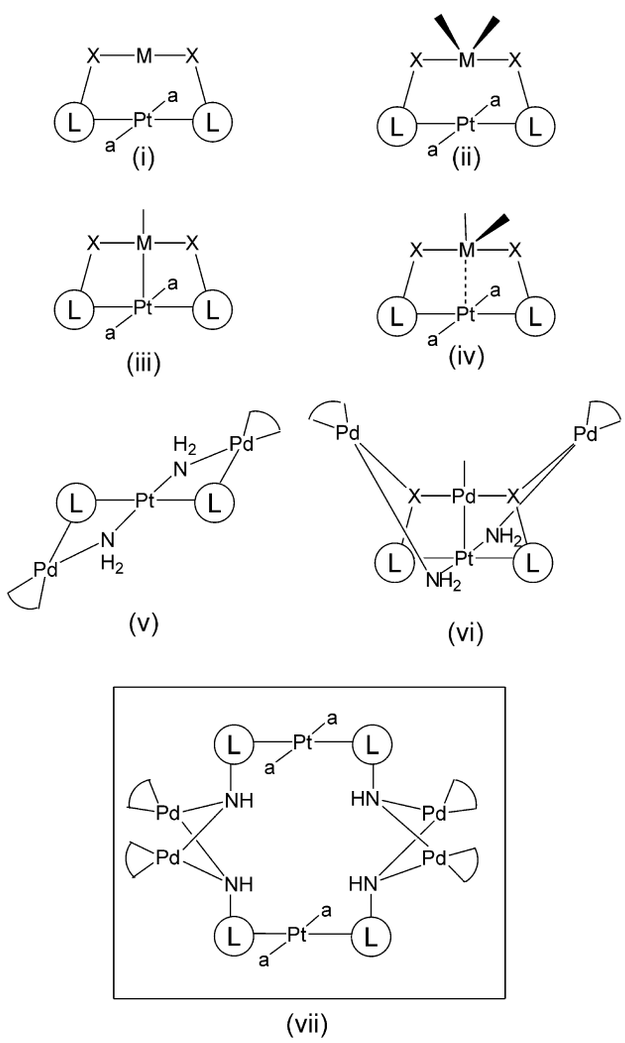

Chart 1

† Electronic supplementary information (ESI) available: ^1H NMR spectra of **2a**, **4a** and **5**; views of the crystal structure of **5**. See http://www.rsc.org/suppdata/dt/b3/b301708g/

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which represents a hybrid between a flat rectangle and an open box, to be also viewed as a double cone. We have previously reported on a structurally related compound, in which the en ligands were replaced by nitrato and aqua ligands.[8] The principal difference between (**vii**) on one hand, and (**v**) as well as (**vi**) on the other is that (en)Pd^{II} condenses with *trans*-[a_2PtL_2] in different ways, inter- and intra-molecularly. The former pattern (**vii**) permits inclusion of two nitrate counter ions.

Experimental

Starting materials and syntheses

2-Aminopyridine (Hampy) was of commercial origin. The following compounds were prepared as reported: *trans*-a_2PtCl_2 (a=NH_3,[9] $MeNH_2$ [10]),(en)$PdCl_2$,[11] *trans*-[$(MeNH_2)_2$Pt(Hampy)$_2$]-[X]$_2$ (X = NO_3 **3a**, ClO_4 **3b**),[8] *trans*-[Pt(μ-NH_2)$_2$(ampy-N^1,N^2,$N^{2'}$)$_2$}{(en)Pd}$_2$Pd(H_2O)][NO_3]$_4$·2H_2O **4a**,[7] *trans*-[Pt-(μ-NH_2)$_2$(ampy-N^1,N^2,$N^{2'}$)$_2$}{(en)Pd}$_2$PdCl][NO_3]$_3$·1.3H_2O **4b**,[7] *trans*-[Pt(μ-NH_2)$_2$(ampy-N^1,N^2,$N^{2'}$)$_2$}{(en)Pd}$_2$PdBr]Br[NO_3]$_2$·4.6H_2O **4c**.[7]

***trans*-[$(NH_3)_2$Pt(Hampy-N^1)Cl]X (X = NO_3 1a, ClO_4 1b).** *trans*-$(NH_3)_2PtCl_2$ and $AgClO_4$ (2 mmol each) were stirred in water (25 ml) for 5 h at 50 °C, then the mixture was cooled, filtered from AgCl, and Hampy (2 mmol) was added. The solution was kept at 50–60 °C for 2 d, then $NaClO_4$ (6 mmol) was added, and the solution cooled to 4 °C for 2.5 d. After filtration of a precipitate consisting of the 1 : 2 complex, the filtrate was evaporated to a small volume (4 ml) and **1b** allowed to crystallise (40% yield). **1a** was obtained by passing an aqueous solution of **1b** over an anion exchange column in its NO_3^- form (60% yield based on **1b**). (Found **1a**: C, 14.4; H, 2.8; N, 16.8%. Calc. for $C_5H_{12}N_5O_3Pt$: C, 14.3; H, 2.9; N, 16.6%. Found **1b**: C, 13.0; H, 2.9; N, 12.0%. Calc. for $C_5H_{12}N_4O_4Cl_2Pt$: C, 13.1; H, 2.6; N, 12.2%). ^{1}H NMR (D_2O, pD 5): δ 8.23 (d, H(6), ^3J(^{195}Pt–^{1}H) = 35 Hz), 7.57 (t, H(4)), 6.78 (d, H(3)), 6.69 (t, H(5)).

***trans*-[$(NH_3)_2$Pt(Hampy-N^1)$_2$][NO_3]$_2$ 2a.** *trans*-$(NH_3)_2PtCl_2$ (2 mmol) and $AgNO_3$ (4 mmol) were stirred in water (50 ml) for 2 d at 40 °C. After cooling and filtration of AgCl, Hampy (4 mmol) was added and the mixture kept at 60 °C for 1 d. The solution was then concentrated by rotary evaporation to one third of the original volume and allowed to stand at 4 °C for 2 d. Crystals of **2a** were then filtered off (76% yield). (Found: C, 22.2; H, 3.6; N, 20.6 %. Calc. for $C_{10}H_{18}N_8O_6Pt$: C, 22.2; H, 3.4; N, 20.7%). ^{1}H NMR (D_2O, pD 6.5): δ 8.29 (d, H(6), ^3J(^{195}Pt–^{1}H) = 33 Hz), 7.67 (t, H(4)), 6.79 (m, H(3)/H(5)).

[*trans*-{$(MeNH_2)_2$Pt(ampy-N^1,N^2,$N^{2'}$)$_2$}$_2$}{(en)Pd}$_4$][NO_3]$_8$·5H_2O 5. (en)$PdCl_2$ (4 mmol) and $AgNO_3$ (8 mmol) were mixed in water (50 ml) and AgCl was filtered off after a few hours of stirring at room temperature. The pH of the solution was 3.4. The solution was combined with an aqueous solution of **3a** (2 mmol, 40 ml), the pH of which had been raised from 6.7 to 12.2 by means of 1 M NaOH. After mixing, the resulting pH (3.9) was adjusted to 7.7 by addition of more NaOH. Within 24 h at room temperature (stoppered flask), the solution had changed color from yellow to orange. At that point the solution was rotary evaporated (30 °C) to a volume of 10 ml and the compound allowed to crystallise. Within 8 d, two fractions of orange crystals of **5** were harvested (21% yield). (Found: C, 17.8; H, 3.7; N, 18.1%. Calc. for $C_{32}H_{82}N_{28}O_{29}Pt_2Pd$: C, 18.0; H, 3.9; N, 18.3%). ^{1}H NMR shifts of **5** (D_2O, pD 8): δ 9.01 (d, H(6)), 8.52 (d, H(3)), 8.14 (t, H(4)), 7.35 (t, H(5)), 2.56 (m, en-CH_2), 2.07 (s, *Me*NH_2) (see ESI †). Brown needles of **6** were obtained in low yield during later fractions of crystallisation. **6** has only been characterised by an incomplete X-ray analysis (*cf*. text). ^{1}H NMR shifts of **6** (D_2O, pD 7): δ 8.57 (d, H(6)), 7.95 (t, H(4)), 7.29 (t, H(3),H(5)), 2.78 (s, en-CH_2), 2.12 (d, *Me*NH).

Spectroscopic and other measurements

Proton NMR spectra were recorded on Bruker AC200 and DRX400 FT spectrometers in D_2O solutions using sodium 3,3,3-trimethylpropanesulfonate as internal reference. Values of pD (D_2O solutions) were determined by use of a glass electrode and addition of 0.4 units to the pH meter reading (uncorrected pH*). D_2O solutions of NaOD and DNO_3 were applied to adjust pD values.

The association constants of the halogen-capped complexes derived from **4a** were determined from the concentration dependence of the H(6) resonance of the ampy ligands. 20 mM aqueous solutions of **4a** were mixed with equimolar amounts of NaCl, KBr and KI, respectively, and the solutions then successively diluted. The data points of δ H(6) were fitted with a non-linear least-squares program after Newton–Gauss, similar to a procedure described in the literature.[12] Three independent experiments were carried out for each combination, from which the weighted mean K values were obtained.

The potentiometric titration of **4a** was carried out on a Metrohm Titroprocessor 686 by titrating an acidified solution of **4a** with 0.01 M NaOH. The pK_a value was estimated from the pH reached when 50% of the aqua ligand was neutralized.

^{195} Pt NMR spectra were recorded on a Bruker AC200 spectrometer at a frequency of 42.998 MHz with Na_2PtCl_6 as external reference.

X-Ray crystallography

Intensity data of **1a**, **1b**, and **5** were collected on an Enraf-Nonius KappaCCD[13] (graphite-monochromator). Structures were solved by standard Patterson methods[14] and refined by full-matrix least squares based on F^2 using the SHELXTL-PLUS[15] and SHELXL-93 programs.[16] The positions of all non-hydrogen atoms were deduced from difference Fourier maps and were refined anisotropically. Exceptions are the disordered oxygen atoms of the perchlorate anion in **1b** and of one of the nitrate ions as well as one of the water molecules in **5**, which were refined isotropically.

Crystal data for **3a** were collected on a Nicolet R3m/V single diffractometer at room temperature using graphite-monochromated Mo-Kα radiation (λ = 0.71069 Å). Unit cell parameters were obtained from least-squares fit with 50 randomly selected reflections in the range 14.0 < 2θ < 29.8°. Intensity data were collected at variable scan speed (3–15° min^{-1} in ω) using an ω/2θ scan technique. An empirical absorption correction *via* ψ-scans was applied. The structure was solved by conventional Patterson methods and subsequent Fourier syntheses and refined by full-matrix least squares on F^2 using the SHELXTL PLUS and SHELXL-93 programs.[15,16] Hydrogen atoms were generated geometrically and given isotropic thermal parameters equivalent to 1.2 times those of the atom to which they were attached.

Crystal data collection for **3b** was carried out at 293(3) K using Mo-Kα radiation (λ = 0.71073 Å) on a Nonius DIP-1030H system (30 frames, exposure time of 20 min each with a rotation of 6° about φ, detector being at 80 mm from the crystal). Cell refinement, indexing and scaling of the data set were performed using programs Mosflm and Scala.[17] The contribution of hydrogen atoms at calculated positions were included in final cycles of refinements. The structures were solved by Patterson and Fourier analyses and refined by the full-matrix least-squares method based on F^2 with all observed reflections.[18] The perchlorate anion was found disordered over two orientations (occupancies of 0.56/0.44) about a Cl–O bond. All the calculations were performed using the WinGX System, Ver 1.64.[19]

Relevant crystal data and data collection parameters are summarised in Table 1.

CCDC reference numbers 203709–203713.

Table 1 Crystallographic data for compounds **1a**, **1b**, **3a**, **3b** and **5**

	1a	**1b**	**3a**	**3b**	**5**
Formula	$C_5H_{12}N_5O_3PtCl$	$C_5H_{12}N_4O_4PtCl_2$	$C_{12}H_{22}N_8O_6Pt$	$C_{12}H_{22}Cl_2N_6O_8Pt$	$C_{32}H_{82}N_{28}O_{29}Pt_2Pd_4$
M_w	420.74	458.18	569.44	644.35	2139.04
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	$P2_1/c$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
Unit cell dimensions:					
a/Å	11.811(2)	8.830(2)	8.013(2)	9.394(1)	11.447(2)
b/Å	8.233(2)	14.135(3)	9.394(2)	11.127(1)	13.201(3)
c/Å	11.746(2)	10.635(2)	12.320(3)	10.174(1)	13.673(3)
α/°					108.51(3)
β/°	97.46(3)	113.97(3)	91.27(2)	98.71(1)	103.75(3)
γ/°					110.50(3)
V/Å^3	1132.5(4)	1212.9(4)	927.1(4)	1051.2(2)	1687.7(6)
Z	4	4	2	2	1
T/K	293	293	293	293	293
$\lambda_{Mo\text{-}K\alpha}$/Å	0.71069	0.71069	0.71069	0.71073	0.71069
μ/mm^{-1}	12.623	12.014	7.62	6.980	5.270
Ind. reflns. (R_{int})	3976 (0.047)	3787 (0.074)	1775 (0.048)	2575 (0.0383)	5905 (0.042)
Obsd. reflns. [$I > 2\sigma(I)$]	1645	1501	917	1863	4461
$R1$ [$I > 2\sigma(I)$][a]	0.0241	0.0328	0.028	0.0377	0.0323
wR_2 [$I > 2\sigma(I)$][b]	0.0553	0.0732	0.074	0.0953	0.0695

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma w(F_o^2)^2]^{1/2}$.

See http://www.rsc.org/suppdata/dt/b3/b301708g/ for crystallographic data in CIF or other electronic format.

Results and discussion

2-Aminopyridine as ligand

2-Aminopyridine (Hampy) and its substituted derivatives are widely used ligands in coordination chemistry. Metal coordination can take place at either the endocyclic pyridine-N atom [20–24] or the exocyclic amino group,[25] even in equilibrium,[26] or simultaneously through both sites in a chelating [27–29] or bridging mode [30–33] as demonstrated in the selected examples given in the references. Although the pK_a value of the exocyclic amino group is high (23.5,[34] 27.7 [35]), metal binding to the free electron pair at the exocyclic amino group causes a dramatic increase in acidity of these protons. As a consequence, the amide formation is facile and enables a second metal to bind to this site. In combination with the endocyclic N atoms, μ_3-binding of the ampy ligand is possible, as indeed observed in trinuclear clusters of Ru and Os, with the exocyclic amido group spanning two metal centers.[36–38]

Simple 1 : 1 and 1 : 2 complexes of *trans*-a$_2$Pt^{II}

Reactions of *trans*-$(NH_3)_2PtCl_2$ with Hampy leads to *trans*-[$(NH_3)_2$Pt(Hampy-N^1)Cl]Cl **1** and *trans*-[$(NH_3)_2$Pt(Hampy-N^1)$_2$]Cl$_2$ **2**. Anion exchange generates other salts, *e.g.* nitrates (**1a**, **2a**) or perchlorate (**1b**). X-Ray crystal structures of the nitrate and perchlorate salts of the 1 : 1 complex have been solved: *trans*-[$(NH_3)_2$Pt(Hampy-N^1)Cl]X (X = NO_3, **1a**, and ClO_4, **1b**). The cations of both compounds are rather similar (Fig. 1 for **1a**), without significant differences in geometries, except for the dihedral angle between the Pt coordination plane and the plane of the heterocycle (80.0(2)° in **1a**, 67.1(2)° in **1b**). Pt coordination is *via* the endocyclic N donor atom. In both compounds, all potential H bonding sites of the cation – NH_3 groups, chloro ligand, the exocyclic amino group of Hampy – are involved in hydrogen bonding with oxygen atoms of the anions. In general, these H bonds are longer than 3 Å, with one exception (N(10) ··· O(22) in **1b**, 2.80(4) Å).

Of the 1 : 2 complexes, X-ray crystal structure analyses were performed for two different salts of the methylamine analogue, *trans*-[$(MeNH_2)_2$Pt(Hampy-N^1)$_2$]X$_2$, with X = NO_3, **3a**, and X = ClO_4, **3b**. The cation of **3a** is shown in Fig. 2. The cation of **3b** is closely similar (Table 2). In both compounds the two

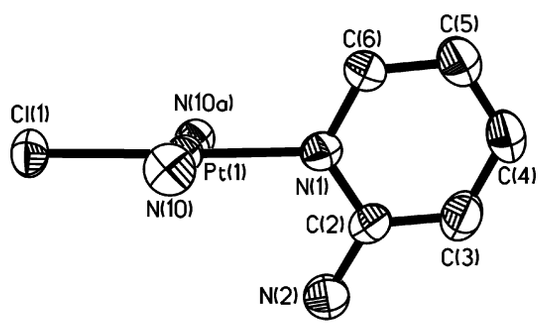

Fig. 1 View of cation of *trans*-[$(NH_3)_2$Pt(Hampy)Cl]NO_3 **1a** with atom numbering scheme. The cation of the ClO_4 salt **1b** is rather similar and not shown.

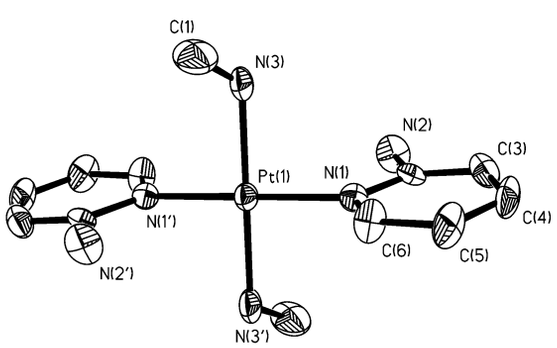

Fig. 2 View of cation of *trans*-[$(MeNH_2)_2$Pt(Hampy)$_2$][NO_3]$_2$ **3a** with atom numbering scheme. The equivalent atoms with additional labels (′) are generated by the symmetry operation $-x$, $-y$, $-z$. The cation of the ClO_4 salt **3b** is rather similar and not shown.

aminopyridine ligands adopt a *head–tail* orientation, with Pt sitting on a center of symmetry. The Hampy ligands in **3a** and **3b**, which are coplanar to each other, form dihedral angles of 79.8(4)° (**3a**) and 85.9(2)° (**3b**) with the metal coordination plane. The cations form stacks along the *x*-axis. There are multiple intermolecular hydrogen bonds involving oxygen atoms of the anions on one hand and the NH_2 groups of the Hampy ligands as well as those of the methylamine ligands on the other. Hydrogen bond lengths are not unusual.

The coordination pattern of Pt^{II} in **3** is maintained in aqueous solution, as evident from coupling of the ^{195}Pt isotope with H(6) of the Hampy ligands (^3J = 32 Hz) (see ESI †). The ^{195} Pt

Table 2 Selected distances (Å) and angles (°) for **1a**, **1b**, **3a** and **3b**

	1a	**1b**
Pt(1)–N(1)	2.022(5)	2.024(8)
Pt(1)–N(10)	2.039(5)	2.040(8)
Pt(1)–N(10a)	2.041(5)	2.041(8)
Pt(1)–Cl(1)	2.296(2)	2.290(3)
C(2)–N(2)	1.333(8)	1.338(12)
N(1)–Pt(1)–N(10)	91.0(2)	91.4(3)
N(1)–Pt(1)–Cl(1)	178.7(1)	179.6(2)
Pt plane/Hampy plane	80.0(2)	67.1(2)
	3a	**3b**
Pt(1)–N(1)	2.060(9)	2.035(4)
Pt(1)–N(3)	2.064(13)	2.060(6)
N(3)–C(1)	1.51(2)	1.461(8)
C(2)–N(2)	1.36(2)	1.349(8)
N(1)–Pt(1)–N(3)	88.0(4)	89.9(2)
Pt plane/Hampy plane	79.8(4)	85.9(2)

NMR chemical shift of **3** (−2681 ppm, D_2O) is consistent with a PtN_4 environment.[39] Separate signals for *head–tail* and *head–head* rotamers are neither detected in ^{1}H nor in ^{195} Pt NMR spectra at ambient temperature. The resonances are insensitive to pH, even up to pH* 14, meaning that the pK_a of the exocyclic amino group of Hampy is (expectedly) well above 14 in the N(1) platinated complex.

Reaction of 1 : 2 complex 2a with (en)Pd^{II}

Reaction of an aqueous solution of *trans*-[$(NH_3)_2$Pt(Hampy-N^1)$_2$][NO_3]$_2$ **2a** with two equiv. of [(en)Pd$(H_2O)_2]^{2+}$ and adjustment of the pH to 8–9 has previously been shown to lead to the tetranuclear $PtPd_3$ species *trans*-[Pt(μ-NH_2)$_2$(ampy-N^1,N^2,$N^{2'}$)$_2${(en)Pd}$_2$Pd(H_2O)][NO_3]$_4$·2H_2O **4a**.[7] Depending on the presence of other anions, derivatives of **4a** can be prepared and crystallised, *e.g.* with Cl^-, **4b** and Br^-, **4c**.[7] Selected structural data of **4a**–**4c** are compiled in Table 3, and the cation of **4b** is presented in Fig. 3. In all these complexes, a Pd^{II} ion is inserted between two deprotonated exocyclic amide donors of the two heterocycles, and in addition two (en)Pd^{II} moieties bridge the exocyclic amide group of the amidinate ligand with a NH_2 ligand at the Pt^{II} . The cations are chiral. The four metal ions form a diamond with sides of *ca.* 3 Å and *ca*. 3.45 Å and diagonals of *ca*. 2.45–2.49 Å, depending on the axial ligand at Pd(1) (Table 3), and *ca*. 5.85 Å. The short Pt(1) ··· Pd(1) distance is clearly indicative of a dative bond from the filled d_{z^2} orbital of Pt^{II} into the empty $d_{x^2-y^2}$ orbital of Pd.[4–6]

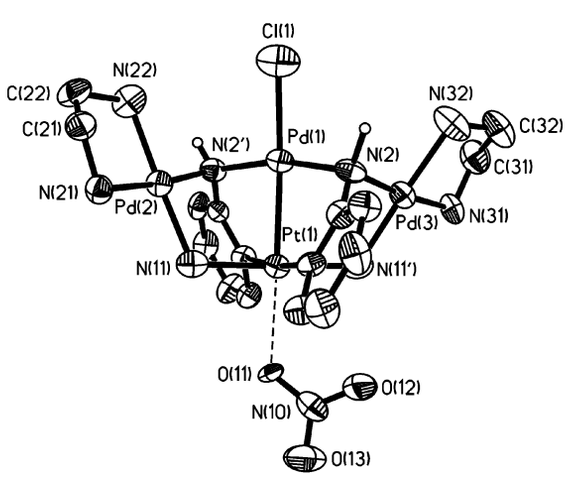

Fig. 3 Cation of **4b**, and weakly bonded nitrate with atom numbering scheme.

Table 3 Selected distances (Å) and angles (°) for **4a**,, **4b**, and **4c**

	4a	**4b**	**4c**
Pt(1)–Pd(1)	2.450(1)	2.477(1)	2.492(1)
Pt(1)–Pd(2)	3.422(1)	3.372(2)	3.405(2)
Pt(1)–Pd(3)	3.445(1)	3.430(1)	3.415(2)
Pd(1)–Pd(2)	2.971(1)	2.891(1)	2.932(2)
Pd(1)–Pd(3)	3.030(1)	3.025(2)	3.016(2)
Pd(1)–X[a]	2.084(5)	2.336(3)	2.490(2)
Pt(1)–Y[b]	2.425(5)	2.523(6)	2.808(2)
Pt(1)–N(1)	2.026(5)	1.998(6)	2.023(9)
Pt(1)–N(1′)	2.016(5)	2.023(6)	2.050(9)
Pt(1)–N(11)	2.038(6)	2.063(7)	2.035(9)
Pt(1)–N(11′)	2.041(6)	2.050(7)	2.051(9)
Pd(1)–N(2)	2.049(6)	2.084(6)	2.063(9)
Pd(1)–N(2′)	2.024(6)	2.098(6)	2.035(9)
Pd(2)–N(11)	2.039(6)	2.016(7)	2.036(9)
N(1′)–Pt(1)–N(1)	175.1(2)	172.5(3)	171.8(4)
N(11′)–Pt(1)–N(11)	175.3(3)	178.0(3)	178.0(4)
N(2′)–Pd(1)–N(2)	168.0(2)	167.1(3)	166.0(5)
N(2′)–Pd(2)–N(11)	91.9(2)	92.4(3)	91.4(4)
N(2)–Pd(3)–N(11′)	91.7(2)	92.3(3)	90.8(4)
Pd(2)–N(11′)–Pt(1)	114.1(3)	111.5(3)	112.9(4)
Pd(1)–Pt(1)–N(1)–C(2)	–22.3(5)	–20.9(6)	–24.7(8)
N(21)–C(21)–C(22)–N(22)	–51.9(9)	–53.4(9)	44(2)
ampy 1/Pt(1)N_4	67.2(2)	65.6(2)	63.6(3)
ampy 1/ampy 2	42.3(2)	49.5(4)	53.6(5)
Pd(2)N_4/Pd(3)N_4	63.0(2)	51.6(2)	52.1(3)
Pd(1)N_2Pt(1)X[a]/Pt(1)N_4	89.0(1)	89.4(1)	86.4(3)

[a] Axial ligand at Pd(1), *e.g.* OH_2 in **4a**, Cl in **4b**, Br in **4c**. [b] Axial ligand at Pt(1), *viz*. ONO_2 in **4a**, **4b** and Br in **4c**.

The ^{1}H NMR spectrum of **4a** in D_2O (ESI†) consists of multiplets of the aromatic ampy resonances in the low field region (D_2O pD 6.4, δ, 8.45 (H6), 7.84 H(4), 7.15 H(3)/H(5)), a multiplet due to the en resonances at around 2.8 ppm as well as a broad singlet with unresolved ^{195} Pt satellites (*ca*. 45 Hz) at 2.05 ppm. The latter is assigned to the μ-NH_2 protons, in agreement with literature data.[40] Surprisingly, isotopic exchange of these protons in D_2O is very slow at ambient temperature (days). The proton of the exocyclic amido group of ampy is not observed due to rapid exchange. Of the aromatic ampy resonances, H(6) is readily identified because of Pt coupling ($^3J(^{195}$ Pt–^{1}H(6)) = 29 Hz). As compared to the starting compound *trans*-[$(NH_3)_2$Pt(Hampy-N^1)$_2$]$^{2+}$ **2**,[8] all three sets of aromatic protons are downfield shifted. The ^{195}Pt resonance of **4a**, which is observed at −1265 ppm, is shifted to lower field by more than 1400 ppm relative to **2**.

Formation of **4a** from **2a** and an excess of [(en)Pd$(D_2O)_2]^{2+}$ (four-fold) was also followed by ^{1}H NMR spectroscopy with pD adjusted to 8–9. It was evident that the product is formed virtually quantitatively, *viz*. no resonances due to **2a** remain after two days. At present we are unable to tell in which sequence the Pd^{II} entities attach to **2a**. A feasible way of generation of a [Pd$(D_2O)_4]^{2+}$ species and its hydrolysis products, respectively, would be a dismutation reaction of [(en)Pd$(D_2O)_2]^{2+}$ into [$(en)_2$Pd]$^{2+}$ and [Pd$(D_2O)_4]^{2+}$, but the number of en resonance in the 2.4–2.8 ppm range does not permit an unambiguous answer.

Complex **4a** is stable in aqueous solution at least up to pD 13. In acidic medium (pD < 2, HCl) gradual decomposition is observed. The axial ligand in **4a** deprotonates with a pK_a of *ca*. 6, as determined by potentiometric titration. This value is close to expectations.[41] Addition of different salts (NaCl, KBr, KI, $NaNO_2$) to an aqueous solution of **4a** leads to changes in chemical shifts of the ampy resonances, notably for the H(6) signal, and also of the ^{195}Pt chemical shifts (Table 4).

Qualitatively, trends in relative shifts for the halogen species relative to the aqua/hydroxo species **4a** are similar as in previously studied 1-methylcytosinato complexes containing Pt⟶Pd bonds,[5,6] but the shift range is quite different. By means

Table 4 Chemical shifts [ppm] of ampy-H(6) and ^{195}Pt resonances of **4a** in the presence of other ligands X

X	δ(H(6))	δ(^{195}Pt)	pD
NO_2^-	8.23		7.4
H_2O	8.45	−1265	6.0
Cl^-	8.78	−1197	7.2
Br^-	8.89	−1132	7.2
I^-	9.12	−1073	7.3

of a ^{1}H NMR dilution experiment, stabilities of the complexes with axial Cl^-, Br^- and I^- ligands were determined and found to be 122(5) l mol^{-1} for the Cl^- species, 116(12) l mol^{-1} for the Br^-, and 201(8) l mol^{-1} for the I^- derivative of **4a**.

Reaction of 1 : 2 complex 3a with (en)Pd^{II}

When we carried out reactions of $[(en)Pd(H_2O)_2]^{2+}$ with *trans*-$[(MeNH_2)_2Pt(Hampy\text{-}N^1)_2][NO_3]_2$ **3a** instead of the NH_3 compound **2a**, we expected to isolate compounds analogous to **4**. Indeed, ^{1}H NMR spectroscopy revealed formation of one or possibly two new species with chemical shifts close to those of **4a** as major species. However, the compound isolated in moderate yield and fully characterised proved to be a hexanuclear Pt_2Pd_4 complex of completely different composition: [*trans*-$\{(MeNH_2)_2Pt(ampy\text{-}N^1,N^2,N^{2'})_2\}_2\{(en)Pd\}_4][NO_3]_8\cdot 5H_2O$ **5**. Its resonances (*cf.* ESI †) were unambiguously identified in the ^{1}H NMR spectra of reaction mixtures (H(6) and H(4) resonances of **5** do not interfere with any of the other resonances), but the intensities are considerably lower than those assigned to **6**, the analogue/s of **4**. Nevertheless this major solution species **6** could be isolated in low yield only. At present we have only preliminary X-ray data on **6**, which unambiguously confirm the tetranuclear $PtPd_3$ structure as seen in **4**, with μ-NH_2 ligands replaced by μ-MeNH. The problem arises from the uncertain nature of the axial ligand at Pd(1) and its origin. It is possible, that formation of **5** is favored by high concentration, hence that **5** is formed to an appreciable extent only during the crystallisation process. We have tried to verify this assumption by means of ^{1}H NMR spectroscopy, but conclusive evidence was not found, possibly due to the narrow concentration range studied.

Description of Pt_2Pd_4 complex 5

In the following, only **5** will be further discussed. The cation of **5** is depicted in Fig. 4. Pt is cross-linking two ampy ligands *via* endocyclic N(1) and N(1′) sites, while (en)Pd^{II} moieties are bridging exocyclic amido functions N(2) and N(2′) two-fold. As

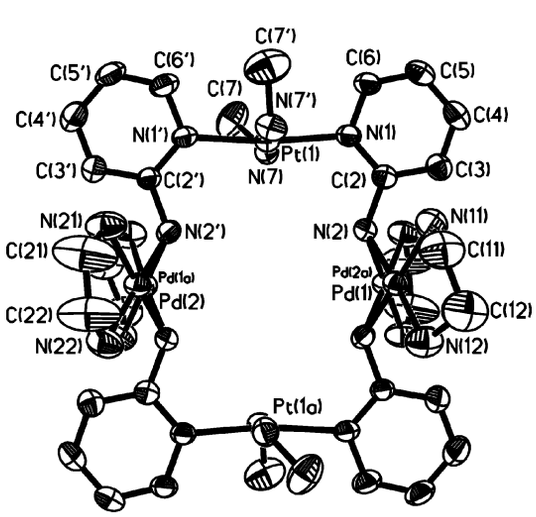

Fig. 4 View of cation of *trans*-$\{(MeNH_2)_2Pt(ampy)_2\}_2\{Pd(en)\}_4]$-$[NO_3]_8\cdot 5H_2O$ **5** with atom numbering scheme. Metal ions labelled with (a) are generated by the symmetry operation $-x+2, -y+2, -z+1$.

Table 5 Selected distances (Å) and angles (°) for **5**

Pt(1)–N(1)	2.025(5)	N(1)–Pt(1)–N(1′)	172.6(2)
Pt(1)–N(1′)	2.037(5)	N(1)–Pt(1)–N(7′)	90.1(2)
Pt(1)–N(7)	2.052(5)	N(1′)–Pt(1)–N(7′)	90.0(2)
Pt(1)–N(7′)	2.050(5)	N(1)–Pt(1)–N(7)	87.7(2)
N(7)–C(7)	1.469(8)	N(1′)–Pt(1)–N(7)	92.0(2)
N(7′)–C(7′)	1.458(8)	N(7′)–Pt(1)–N(7)	177.1(2)
Pd(1)–N(11)	2.041(5)	N(11)–Pd(1)–N(2)	98.3(2)
Pd(1)–N(12)	2.062(5)	N(11)–Pd(1)–N(12)	82.4(2)
Pd(1)–N(2)	2.056(5)	N(2)–Pd(1)–N(12)	176.4(2)
Pd(1)–N(2′)[a]	2.068(5)	N(11)–Pd(1)–N(2′)[a]	177.7(2)
Pd(2)–N(21)	2.040(5)	N(2)–Pd(1)–N(2′)[a]	79.7(2)
Pd(2)–N(22)	2.035(5)	N(12)–Pd(1)–N(2′)[a]	99.7(2)
Pd(2)–N(2′)	2.073(5)	N(22)–Pd(2)–N(21)	82.0(2)
Pd(2)–N(2)[a]	2.069(5)	N(22)–Pd(2)–N(2)[a]	99.5(2)
N(10)–O(11)	1.226(6)	N(21)–Pd(2)–N(2)[a]	178.4(2)
N(10)–O(12)	1.253(7)	N(22)–Pd(2)–N(2′)	178.7(2)
N(10)–O(13)	1.210(7)	N(21)–Pd(2)–N(2′)	99.3(2)
Pt(1)–Pt(1)[a]	7.053(3)	N(2)[a]–Pd(2)–N(2′)	79.3(2)
Pd(1)–Pd(2)	6.151(2)	O(11)–N(10)–O(12)	120.5(6)
Pd(2)–Pd(1)[a]	2.904(1)	O(11)–N(10)–O(13)	121.0(6)
N(2)–N(2′)	4.859(7)	O(12)–N(10)–O(13)	118.5(6)
		Pt(1)N_4/ampy (N1)	88.8(2)
		Pt(1)N_4/ampy (N1′)	84.7(2)
		ampy (N1)/ampy (N1′)	6.7(2)
		Pd(1)N_4/Pd(2)[a]N_4	136.6(2)
		Pd(2)N_4/ampy (N1′)	66.5(2)

[a] Symmetry operation $-x+2, -y+2, -z+1$.

far as the overall appearance is concerned, **5** is similar to a compound reported by us some time ago, in which the en ligands at the Pd atoms are replaced by monodentate nitrato ligands and water molecules.[8] Consequently, the previously described cation and that of **5** differ markedly in their charges in the solid state, which are +2 and +8, respectively. The four heterocyclic rings, including the exocyclic N atoms, and the two Pt atoms of **5** are close to coplanar, while the Pd atoms are pairwise above and below this plane, by 1.45 Å, as are the methylamine ligands of the Pt atoms (Pt(1)–N(7) 2.05 Å). Salient structural features are listed in Table 5. The Pt(1) ··· Pt(1a) distance is 7.053(3) Å, Pd ··· Pd separations are 6.151(2) Å (Pd(1) ··· Pd(2)) as well as 2.904(1) Å (Pd(1) ··· Pd(2a)), and N(2) ··· N(2′) distances are 4.859(7) Å. The rectangle is "walled" by the four (en)Pd^{II} moieties at the long sides of the rectangle and by the $MeNH_2$ ligands at the short sides. Since the (en)Pd^{II} units, like the methyl substituents of the methylamine ligands, are tilted away from the central cavity, the cation can be regarded as having the appearance of a double cone. The maximum height of the complex, as calculated by distances between CH_2 groups of the en ligands, is 8.16(1) Å (av. C(12) ··· C(21) and C(11) ··· C(22)). Two exocyclic amido nitrogens of the ampy ligands and two Pds form four-membered Pd_2N_2 rings, which are not planar, however, but folded along the N–N vector (ESI †), as seen in related cases.[42–44] In **5** the angle between the two triangular halves of the ring is 132.0(2)°. As a consequence, the two metal centers get quite close, 2.904(1) Å, closer than in planar Pd_2N_2 rings, *e.g.* 3.063(1) Å.[45]

A fascinating feature of the solid-state structure of **5** is the close association of two of the eight counter ions with the cation. As shown in Fig. 5, two nitrate anions penetrate from either side of the open rectangular box into the cavity and are in a way "captured". They are held by four bifurcated hydrogen bonds extending from the amido protons at the exocyclic N(2) and N(2′) groups of the ampy ligands to O(11) (3.12(1)–3.20(1) Å) and by H bonds between the methylamine ligands N(7) and N(7′) and the two other oxygen atoms O(12) and O(13) of the nitrates (2.88(1) Å each). Moreover, O(12) forms a weak hydrogen bond with the water molecule O(3wa), 3.28(5) Å, while O(13) is within reach of C(21)H_2 of an en ligand of an adjacent cation. In addition, O(11) is halfway between Pd(1) and Pd(2) (3.078(5) and 3.075(5) Å), hence each nitrate is sandwiched between two (en)Pd^{II} units. It is obvious that the O(11) oxygen

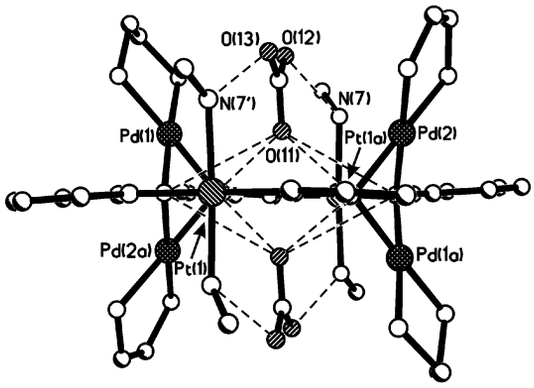

Fig. 5 Cation **5** with two inserted NO_3^- anions.

atoms are in axial positions of these Pd atoms. The structure data provide no evidence for a pyramidalization of the Pd coordination sphere, however, which could be expected if O(11) acted as a Lewis base.[46] A space filling model reveals that the nitrates fit snugly into the opening of the rectangular box (Fig. 6). The O(11) atoms of the two "captured" nitrate ions at either side of the $Pt_2(ampy)_4$ plane are remarkably close, 3.03 Å, but of course still further apart than in $[O_2NO \cdots H \cdots ONO_2]^-$, where this distance is 2.45 Å.[47]

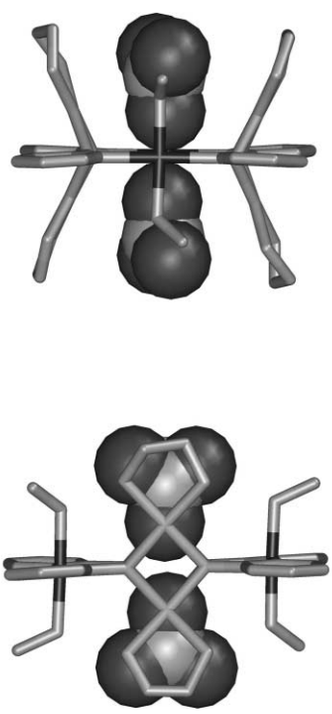

Fig. 6 Partial space filling representation of "captured" nitrates: (a) view along the Pt–Pt vector; (b) view perpendicular to Pd atoms.

Cations of **5** are lined up along the *x*-axis in a stair-case fashion and connected by a network of H bonds involving nitrate anions, water molecules, NH_2 groups of $MeNH_2$, and en ligands (both CH_2 and NH_2 groups). A stereoview representation is provided in the ESI, † and a simplified picture is given in Fig. 7. The cations are parallel but displaced by *ca.* 3 Å in such a way that the en ligands of the neighbouring cations are roughly underneath the "captured" nitrate and capable of interacting with O(13) of the latter in a weak H bond with $C(21)H_2$ (3.28(5) Å). The shortest intercationic Pt ··· Pt distances are 11.447(2) Å ($x + 1$, y, z) and 13.947(5) Å ($-x + 3$, $-y + 2$, $-z + 1$). The closest intermolecular distance between oxygen atoms of the "captured" nitrate ions is 5.60(1) Å (O(13) ··· O(13*), $-x + 3$, $-y + 2$, $-z + 1$). Thus distances between "captured" nitrates

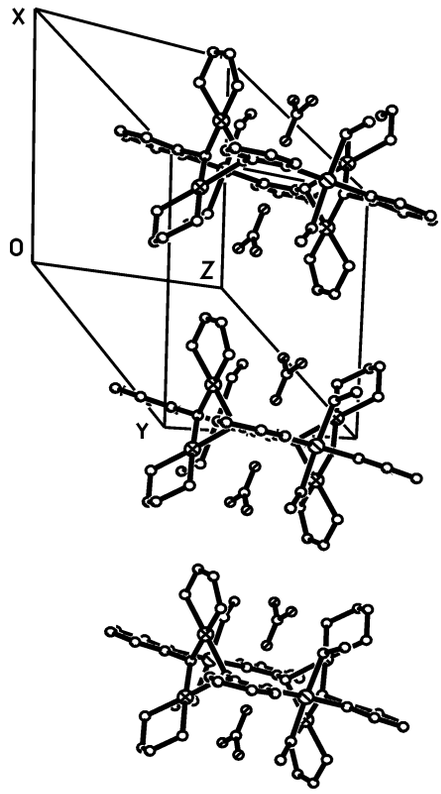

Fig. 7 Stacking of cations of **5** with "captured" nitrates. Individual cations are strongly associated *via* a complex network of H bonds not shown here. A detailed stereo view, which includes H bonding interactions as well as water molecules and other counter ions, is provided in the ESI †.

alternate between short and long. A view along the *x*-axis reveals the line up of these nitrate anions (ESI †).

The association of two nitrate ions with cation **5** suggests that it might be possible to substitute the NO_3^- ion by other planar oxo anions. We have modelled the interaction of oxalate anions with cation **5** and find that three of the four oxygen atoms of oxalate can favourably interact through H bonding with the cation, involving the four NH protons of the ampy, NH_2 of the methylamine ligands as well as $N(12)H_2$ and $N(21)H_2$ of the en ligands. Again, one of the oxygen atoms of the oxalate would be halfway between two Pd atoms. Preliminary ^1H NMR titration experiments indeed suggest that oxalate interacts with NH_2 of the $MeNH_2$ ligands in a concentration-dependent manner. Further work is required to substantiate this finding.

Summary

The solid-state structures of compounds **4** and **5**, which were obtained from the two simple components *trans*-$[a_2Pt(Hampy\text{-}N^1)_2]^{2+}$ and $[(en)Pd(H_2O)_2]^{2+}$, provide a wealth of interesting features. First, they demonstrate that the 2-aminopyridine ligand, following single deprotonation at the exocyclic amino group, hence formation of an amido ligand, can act as a tridentate ligand. Bridging of three metal centers may either occur in an intramolecular fashion (**4**) or an intermolecular manner (**5**). At least with the *trans*-$(MeNH_2)_2Pt^{II}$ system, both options are realized simultaneously (**5**, **6**). The stoichiometries and structures of **4** and **5** are markedly different. Second, in **4** not only amide bridge formation of the amidopyridine ligand is observed, as in **5**, but also NH_2 bridges originating from the ammonia ligands of Pt^{II} are formed. Reactions leading to these NH_2 bridges take place under rather mild reaction conditions. They are of potential relevance also to the coordination chemistry of the antitumor agent Cisplatin as well as its inactive (or:

less active) *trans* isomer, although such a possibility hitherto neither has been anticipated nor even discussed. We note, however, that we have evidence now, that *cis*-$(NH_3)_2Pt^{II}$ compounds indeed are capable of forming μ-NH_2 species in water under mild conditions.[48] Formation of **4** furthermore reveals that loss of even the chelating en ligand from $(en)Pd^{II}$ is facile, not just of am(m)ine ligands bonded in a monodentate fashion.[49] Third, the double-cone structure and the high positive charge of cation **5** make it a preorganized host for two nitrate anions, and possibly for other flat oxo anions as well. The binding pattern appears to be determined by electrostatics and hydrogen bonding, but possibly also favourably reinforced by interactions of one of the nitrate oxygen atoms with two Pd^{II} ions. The fact that the two Pd atoms are located approximately perpendicular to the plane of the nitrate anion makes this situation special. It is certainly different from scenarios seen in other metal containing nitrate hosts,[50–52] and differs also from a host–guest complex in which two stacked nitrate anions are encapsulated in a metal free bicyclic cage.[53] It is, however, remotely reminiscent of nitrate binding in a bicyclic cyclophane host, although in this case the anion is fully sandwiched between two aromatic rings.[54] Finally, the arrangement of cations **5** along the *x*-axis in the solid state, and their tight association *via* H bonding interactions communicated by water molecules as well as other nitrate ions, make **5** a model for an artificial anion channel of nitrate. It thus adds to examples of similar metal containing anion pore structures[55] or fragments thereof.[56]

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References

1 B. Lippert, *Coord. Chem. Rev.*, 1999, **182**, 263.
2 E. Zangrando, F. Pichierri, L. Randaccio and B. Lippert, *Coord. Chem. Rev.*, 1996, **156**, 275.
3 B. Lippert, *Met. Ions Biol. Syst.*, 1996, **33**, 105.
4 C. Mealli, F. Pichierri, L. Randaccio, E. Zangrando, M. Krumm, D. Holthenrich and B. Lippert, *Inorg. Chem.*, 1995, **34**, 3418.
5 F. Pichierri, E. Chiarpairn, E. Zangrando, L. Randaccio, D. Holthenrich and B. Lippert, *Inorg. Chim. Acta*, 1997, **264**, 109.
6 M. Krumm, E. Zangrando, L. Randaccio, S. Menzer and B. Lippert, *Inorg. Chem.*, 1993, **32**, 700.
7 A. Schneider, E. Freisinger, B. Beck and B. Lippert, *J. Chem. Soc., Dalton Trans.*, 2000, 837.
8 H. Rauter, I. Mutikainen, M. Blomberg, C. J. L. Lock, P. Amo-Ochoa, E. Freisinger, L. Randaccio, E. Zangrando, E. Chiarparin and B. Lippert, *Angew. Chem., Int. Ed.*, 1997, **36**, 1296.
9 G. B. Kauffman and D. O. Cowan, *Inorg. Synth.*, 1963, **7**, 239.
10 J. Arpalahti, B. Lippert, H. Schöllhorn and U. Thewalt, *Inorg. Chim. Acta*, 1988, **153**, 45.
11 J. McCormick, E. N. Jayner jr. and R. I. Kaplan, *Inorg. Synth.*, 1972, **13**, 216.
12 K. H. Scheller, F. Hofstetter, P. R. Mitchell, B. Prijs and H. Sigel, *J. Am. Chem. Soc.*, 1981, **103**, 247.
13 NONIUS BV, Röntgenweg 1, P.O. Box 811, 2600 AV Delft, Netherlands.
14 G. M. Sheldrick, *Acta Crystallogr., Sect. A*, 1990, **46**, 467.
15 G. M. Sheldrick, SHELXTL-PLUS (VMS), Siemens Analytical X-Ray Instruments, Inc., Madison, WI, 1990.
16 G. M. Sheldrick, SHELXL-93, Program for crystal structure refinement, University of Göttingen, Germany, 1993.
17 Collaborative Computational Project, *Acta Crystallogr., Sect. D*, 1994, **50**, 760.
18 G. M. Sheldrick, Programs of Structure Analysis, University of Göttingen, Germany, 1998.
19 L. J. Farrugia, *J. Appl. Crystallogr.*, 1999, **32**, 837.
20 O. Krizanovic, M. Sabat, R. Beyerle-Pfnür and B. Lippert, *J. Am. Chem. Soc.*, 1993, **115**, 5538.
21 J. H. K. Yip, R. Feng and J. J. Vittal, *Inorg. Chem.*, 1999, **38**, 3586.
22 M. C. Navarro Ranninger, S. Martinez-Carrera and S. Garcia-Blanco, *Acta Crystallogr., Sect. C*, 1985, **41**, 21.
23 E. Uhlig and M. Mädler, *Z. Anorg. Allg. Chem.*, 1965, **338**, 199.
24 S. Haghighi, C. A. McAuliffe, W. E. Hill, H. H. Kohl and M. E. Friedman, *Inorg. Chim. Acta*, 1980, **43**, 113.
25 N. Al Obaidi, T. A. Hamor, C. J. Jones, J. A. Mc Cleverty and K. Paxton, *J. Chem. Soc., Dalton Trans.*, 1987, 1063.
26 L. G. Marzilli, M. F. Summers, E. Zangrando, N. Bresciani-Pahor and L. Randaccio, *J. Am. Chem. Soc.*, 1986, **108**, 4830.
27 A. Spannenberg, P. Arndt and R. Kempe, *Angew. Chem., Int. Ed.*, 1998, **37**, 832.
28 R. Kempe and P. Arndt, *Inorg. Chem.*, 1996, **35**, 2644.
29 M. J. Calhorda, M. A. A. F. de C. T. Carrondo, R. Gomes da Costa, A. R. Dias, M. T. L. S. Duarte and M. B. Hursthouse, *J. Organomet. Chem.*, 1987, **320**, 53.
30 F. A. Cotton and A. Yokochi, *Inorg. Chem.*, 1998, **37**, 2723.
31 Y. Li, B. Han, K. M. Kadish and J. L. Bear, *Inorg. Chem.*, 1993, **32**, 4175.
32 J. L. Bear, C.-L. Yao, F. J. Capdevielle and K. M. Kadish, *Inorg. Chem.*, 1988, **27.**
33 A. R. Chakravarty, F. A. Cotton and D. A. Tocher, *Inorg. Chem.*, 1984, **23**, 4693.
34 R. Stewart and M. G. Harris, *J. Org. Chem.*, 1978, **43**, 3123.
35 F. G. Bordwell, D. L. Singer and A. V. Satish, *J. Am. Chem. Soc.*, 1993, **115**, 3543.
36 J. A. Cabeza, I. del Rio, A. Llamazares and V. Riera, *Inorg. Chem.*, 1995, **34**, 1620.
37 P. L. Andreu, J. A. Cabeza, A. Llamazares and V. Riera, *J. Organomet. Chem.*, 1992, **434**, 123.
38 A. J. Deeming, R. Peters, M. B. Hursthouse and J. D. J. Backer-Dirks, *J. Chem. Soc., Dalton Trans.*, 1982, 1205.
39 P. S. Pregosin, *Annu. Rep. NMR Spectrosc.*, 1986, 285.
40 J. J. Li, W. Li, A. J. James, T. Holbert, T. P. Sharp and P. R. Sharp, *Inorg. Chem.*, 1999, **38**, 1563.
41 R. B. Martin, *Cisplatin-Chemistry and Biochemistry of a Leading Anticancer Drug*, ed. B. Lippert, VHCA Zürich and Wiley-VCH Weinheim, 1999, p. 183 and references therein.
42 J. Ruiz, M. T. Martinez, C. Vicente, G. Garcia, G. Lopez, P. A. Chaloner and P. B. Hitchock, *Organometallics*, 1993, **12**, 4321.
43 S. Park, A. L. Rheingold and D. M. Roundhill, *Organometallics*, 1991, **10**, 615.
44 C. Tejel, M. A. Ciriano, M. Bordonaba, J. A. Lopez, F. J. Lahoz and L. A. Oro, *Chem. Eur. J.*, 2002, **8**, 3128.
45 M. Kita and M. Nonoyama, *Polyhedron*, 1993, **12**, 1027.
46 G. Aullón and S. Alvarez, *Inorg. Chem.*, 1996, **35**, 3137.
47 A. F. Wells, *Structural Inorganic Chemistry*, Clarendon Press, Oxford, 5th edn., 1984, p. 821.
48 G. Kampf, A. Schneider, M. Willermann and B. Lippert, to be submitted.
49 T. G. Appleton, J. R. Hall, S. F. Ralph and C. S. M. Thompson, *Aust. J. Chem.*, 1988, **41**, 1425.
50 R.-D. Schnebeck, E. Freisinger and B. Lippert, *Angew. Chem., Int. Ed.*, 1999, **38**, 168.
51 R.-D. Schnebeck, E. Freisinger, F. Glahé and B. Lippert, *J. Am. Chem. Soc.*, 2000, **122**, 1381.
52 A. D. Cutland, R. G. Malkani, J. W. Kampf and V. L. Pecoraro, *Angew. Chem., Int. Ed.*, 2000, **39**, 2689.
53 S. Mason, T. Clifford, L. Seib, K. Kuczera and K. Browman-James, *J. Am. Chem. Soc.*, 1998, **120**, 8899.
54 A. P. Bisson, V. M. Lynch, M.-K. C. Monahan and E. V. Anslyn, *Angew. Chem., Int. Ed. Engl.*, 1997, **36**, 2340.
55 R.-D. Schnebeck, E. Freisinger and B. Lippert, *Chem. Commun.*, 1999, 675.
56 Z. Qin, M. C. Jennings and R. J. Puddephatt, *Chem. Commun.*, 2001, 2676.