Binuclear Platinum(II) Complexes bridged by Pyridine-2-thiolate and Related Ligands. Synthesis and Crystal Structure†

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Bis(ethylenediamine)di-μ-pyridine-2-thiolato-diplatinum(II) chloride trihydrate (**1**), bis(ethylenediamine)di-μ-4-methylpyridine-2-thiolato-diplatinum(II) chloride dihydrate (**2**), and di(μ-2-aminoethyl 2-pyridyl sulphide)-bis[chloroplatinum(II)] chloride trihydrate (**3**) were synthesized and their structures investigated by means of *X*-ray crystallography. The binuclear complexes (**1**) and (**2**) have the head-to-head configuration in which planar PtN_2S_2 and PtN_4 co-ordination spheres face one another with Pt ··· Pt distances of 3.083(1) Å in (**1**) and 3.101(1) Å in (**2**). The two co-ordination spheres are slanted against one another and twisted about the Pt ··· Pt axis, the interplanar and the torsion angles being 31.0(3) and 32.6(3)° in (**1**) and 31.9(2) and 34.3(2)° in (**2**). In complex (**3**) two planar PtN_2SCl co-ordination spheres bridged by two pyridine-2-thiol segments have an eclipsed conformation; the interplanar and torsion angles [17.9(4) and 3.4(2)°] are much less than those of (**1**) and (**2**). The complex is of the head-to-tail isomer and has an approximate two-fold axis perpendicular to the Pt ··· Pt axis. The Pt ··· Pt distance is 2.956(1) Å. Both of the head-to-head dimers in (**1**) and (**2**) form a centrosymmetric pair of the dimers in the solid state, the PtN_2S_2 co-ordination planes of the respective dimers being in contact with one another. The interdimer Pt ··· Pt distance is 3.613(1) Å in (**1**) and 3.726(2) Å in (**2**).

The synthesis and structure determination of the very intriguing platinum pyridone blue $[Pt_2(NH_3)_4(C_5H_4NO)_2]_2[NO_3]_5\cdot H_2O$ (C_5H_4NO = 2-pyridonate) by Lippard and co-workers[1] have stimulated study of polynuclear complexes bridged by pyrimidinate or its analogues. In a subsequent study they synthesized the binuclear platinum(II) complexes $[Pt_2(NH_3)_4(C_5H_4NO)_2]^{2+}$[2] and $[Pt_2(en)_2(C_5H_4NO)_2]^{2+}$ (en = ethylenediamine),[3] and showed that these complexes are oxidized to give $[Pt^{III}{}_2X_2(NH_3)_4(C_5H_4NO)_2]^{2+}$[4] and $[Pt^{III}{}_2X_2(en)_2(C_5H_4NO)_2]^{2+}$[5] (X = axial ligand) which have a Pt^{III}–Pt^{III} bond. The $Pt^{II} \cdots Pt^{II}$ and Pt^{III}–Pt^{III} distances in the en complexes are significantly longer than the corresponding distances in the NH_3 complexes.[3,4] The head-to-head to head-to-tail isomerization of $[Pt_2(en)_2(C_5H_4NO)_2]^{2+}$ is much faster than that of $[Pt_2(NH_3)_4(C_5H_4NO)_2]^{2+}$, and $[Pt^{III}{}_2(NO_3)(NO_2)(en)_2(C_5H_4NO)_2]^{2+}$ readily decomposes to $[Pt^{II}{}_2(en)_2(C_5H_4NO)_2]^{2+}$ by loss of the axial ligands.[5] These observations have been rationalized on the basis of the conformational strain in the en complexes of Pt^{II} and Pt^{III} due to the repulsion between the en ligands.

Pyridine-2-thiol (C_5H_5NS) is structurally similar to C_5H_5NO but has sulphur in place of oxygen. The longer N ··· S (2.7 Å) bite compared with the N ··· O bite (2.3 Å) in the latter suggests that C_5H_5NS acts not only as a bridging ligand but also as a chelating ligand for Pt^{2+}. However we found that the reaction of *cis*-$[PtCl_2(NH_3)_2]$ with C_5H_5NS in dioxane affords $[Pt^{II}(C_5H_4NS)_4Pt^{II}]$ in high yield, which abstracts chlorine atoms from chloroform to give $[ClPt^{III}(C_5H_4NS)_4Pt^{III}Cl]$.[6] Attempts have been made to prepare C_5H_4NS-bridged binuclear platinum complexes similar to the C_5H_4NO-bridged complexes of Pt^{II} and Pt^{III}, in order to compare their properties. In addition to C_5H_4NS and 4-MeC_5H_3NS (4-methylpyridine-2-thiolate), we used 2-aminoethyl 2-pyridyl sulphide (aps) as a bridging ligand. A scale model indicates that the three donor atoms of aps are unable to occupy coplanar co-ordination sites, and therefore aps is thought to act as a bi- or poly-nucleating ligand for Pt^{2+} which assumes square-planar co-ordination exclusively.

We report here the synthesis and structural features of binuclear $[Pt_2(en)_2(C_5H_4NS)_2]Cl_2\cdot 3H_2O$, $[Pt_2(en)_2(4\text{-}MeC_5H_3NS)_2]Cl_2\cdot 2H_2O$, and $[Pt_2Cl_2(aps)_2]Cl_2\cdot 3H_2O$. A preliminary communication of part of this work has been published.[7]

Experimental

Chemicals.—Pyridine-2-thiol (C_5H_5NS) was purchased from Wako Pure Chemical Industries Ltd. 4-Methylpyridine-2-thiol (4-MeC_5H_4NS) was prepared from 2-amino-4-methylpyridine (Aldrich Chemical Co.) by the literature method.[8] They were recrystallized from benzene. 2-Aminoethyl 2-pyridyl sulphide (aps) was prepared by the reaction of pyridine-2-thiol (13.0 g) with ethyleneimine (5.05 g) in tetrahydrofuran (thf) (200 cm^3) at 50 °C for 48 h and then at boiling point for 4 h. The oily product obtained by evaporation of the solvent was purified by distillation at 98—103 °C (1 mmHg, *ca.* 133 Pa). Yield 10.5 g (58%).

Preparation of the Complexes.—$[Pt_2(en)_2(C_5H_4NS)_2]Cl_2\cdot 3H_2O$ (**1**).[7] A suspension of $[PtCl_2(en)]$ (163 mg, 0.5 mmol) and C_5H_5NS (56 mg, 0.5 mmol) in water (200 cm^3) was stirred at 35 °C, the suspension being kept at pH 9 by addition of 0.1 mol dm^{-3} KOH solution. After an equimolar amount of KOH had been added, the solution was stirred until the pH of the solution became 7, and then rotary evaporated. The yellow residue was washed with methanol. Lemon-yellow crystals were obtained by recrystallization of the methanol-insoluble residue. Yield 141 mg (66%) (Found: C, 19.90; H, 3.10; N, 9.85. Calc. for $C_7H_{15}ClN_3O_{1.5}PtS$: C, 19.65; H, 3.55; N, 9.80%).

$[Pt_2(en)_2(4\text{-}MeC_5H_3NS)_2]Cl_2\cdot 2H_2O$ (**2**). Lemon-yellow

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1989, Issue 1, pp. xvii—xx.

crystals were obtained similarly by using 4-MeC_5H_4NS (63 mg, 0.5 mmol) in place of C_5H_5NS. Yield 152 mg (70%) (Found: C, 21.95; H, 3.55; N, 9.40. Calc. for $C_8H_{16}ClN_3OPtS$: C, 22.20; H, 3.75; N, 9.70%).

$[Pt_2Cl_2(aps)_2]Cl_2 \cdot 3H_2O$ (**3**). *Method* (*a*). A methanol solution of aps (185 mg, 1.20 mmol per 150 cm^3) was added gradually to an aqueous solution of $K_2[PtCl_4]$ (500 mg, 1.20 mmol per 300 cm^3) with stirring at 45 °C. After stirring for 48 h at 45 °C, the white-brown precipitate was filtered off, and then the filtrate was evaporated slowly. Yellow prismatic crystals were obtained by recrystallization of the residue from water. Yield 135 mg (25%) (Found: C, 18.65; H, 2.90; N, 6.20. Calc. for $C_7H_{13}Cl_2N_2O_{1.5}PtS$: C, 18.80; H, 2.95; N, 6.25%).

Method (*b*). A methanol solution of aps (128 mg per 20 cm^3) was added to an aqueous solution of $K_2[PtCl_6]$ (403 mg, 0.83 mmol per 100 cm^3) at 60 °C. To the solution was added dropwise an aqueous solution of hydrazine dihydrochloride (40 mg, 0.38 mmol per 20 cm^3) with stirring. After further stirring for 8 h the white-brown precipitate was filtered off, and then the filtrate was concentrated. Yellow crystals were collected and washed with small amounts of water. Yield 150 mg (40%).

Crystal Structure Determinations.—Crystal data and data collection for $[Pt_2(en)_2(C_5H_4NS)_2]Cl_2 \cdot 3H_2O$ (**1**). $C_{14}H_{30}Cl_2N_6O_3Pt_2S_2$, $M = 855.70$, triclinic, space group $P\bar{1}$, $a = 12.992(2)$, $b = 11.886(2)$, $c = 8.899(2)$ Å, $\alpha = 94.45(2)$, $\beta = 75.29(2)$, $\gamma = 112.77(2)°$, $U = 1\,225.2(3)$ Å^3 (from least-squares treatment of diffractometer angles for 18 automatically centred reflections, $\lambda = 0.710\,69$ Å), $Z = 2$, $D_c = 2.32$ g cm^{-3}, $F(000) = 804$, lemon-yellow crystals, dimensions (distance to faces from centre) 0.023($\bar{1}10$, $1\bar{1}0$) × 0.090(210, $\bar{2}\bar{1}0$) × 0.090(102, $\bar{1}0\bar{2}$) mm, μ(Mo-K_α) = 124.1 cm^{-1}. PW1100 diffractometer, ω—2θ scan with scan width = 1.0 + 0.4 tan θ, scan speed 0.033° s^{-1}, graphite-monochromated Mo-K_α radiation; 4 797 unique reflections ($2.0 \leqslant \theta \leqslant 27.5°$, $\pm h$, $\pm k$, $+l$) giving 3 330 with $I > 3\sigma(I)$. The intensity data were corrected for absorption.[9]

Crystal data and data collection for $[Pt_2(en)_2(4\text{-}MeC_5H_3NS)_2]Cl_2 \cdot 2H_2O$ (**2**). $C_{16}Cl_2H_{32}N_6O_2Pt_2S_2$, $M = 865.74$, triclinic, space group $P\bar{1}$, $a = 12.221(3)$, $b = 13.898(6)$, $c = 8.974(2)$ Å, $\alpha = 102.98(3)$, $\beta = 92.80(3)$, $\gamma = 63.47(2)°$, $U = 1\,326.5(8)$ Å^3 (from least-squares treatment of diffractometer angles for 16 automatically centred reflections, $\lambda = 0.710\,69$ Å), $Z = 2$, $D_c = 2.17$ g cm^{-3}, $F(000) = 816$, lemon-yellow crystals, dimensions (distance to faces from centre) 0.055(110, $\bar{1}\bar{1}0$) × 0.105($\bar{1}10$, $1\bar{1}0$) × 0.050(001, $00\bar{1}$) mm, μ(Mo-K_α) = 113.2 cm^{-1}. PW1100 diffractometer, ω—2θ scan with scan width = 1.2 + 0.5 tan θ, scan speed 0.050° s^{-1}, graphite-monochromated Mo-K_α radiation; 6 082 unique reflections ($2.0 \leqslant \theta \leqslant 27.5°$, $\pm h$, $+k$, $\pm l$) giving 5 261 with $|F_o| > \sigma(F_o)$. The intensity data were corrected for absorption.[9]

Crystal data and data collection for $[Pt_2Cl_2(aps)_2]Cl_2 \cdot 3H_2O$ (**3**). $C_{14}H_{26}Cl_4N_4O_3Pt_2S_2$, $M = 894.54$, triclinic, space group $P\bar{1}$, $a = 10.653(2)$, $b = 14.931(4)$, $c = 8.281(2)$ Å, $\alpha = 115.27(2)$, $\beta = 93.45(2)$, $\gamma = 90.51(2)°$, $U = 1\,188.1$ Å^3 (from least-squares treatment of diffractometer angles for 16 automatically centred reflections, $\lambda = 0.710\,69$ Å), $Z = 2$, $D_c = 2.50$ g cm^{-3}, $F(000) = 836$, yellow crystals, dimensions (distance to faces from centre) 0.075(110, $\bar{1}\bar{1}0$) × 0.075($\bar{1}10$, $1\bar{1}0$) × 0.075(001, $00\bar{1}$) mm, μ(Mo-K_α) = 130.1 cm^{-1}. PW1100 diffractometer, ω—2θ scan with scan width = 1.2 + 0.5 tan θ, scan speed 0.050° s^{-1}, graphite-monochromated Mo-K_α radiation; 5 444 unique reflections ($2.0 \leqslant \theta \leqslant 27.5°$, $\pm h$, $+k$, $\pm l$) giving 4 637 with $|F_o| > \sigma(F_o)$. The intensity data were corrected for absorption.[9]

Structure analysis and refinement. The crystal structures were solved by the Patterson–Fourier method. The positional and thermal parameters were refined anisotropically for all non-hydrogen atoms by the block-diagonal-matrix least-squares method. Hydrogen atoms of complex (**3**) found from the final difference map were included in the refinement with the same isotropic thermal parameters as the equivalent isotropic thermal parameters of the atoms to which they are bonded. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = \sigma(F_o)^{-2}$ for complex (**1**) and $w = [\sigma(F_o)^2 + 0.000\,80(F_o)^2]^{-\frac{1}{2}}$ for (**2**) and (**3**). Final R and R' $\{= [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}\}$ values were 0.035 and 0.041 for (**1**), 0.034 and 0.049 for (**2**) and 0.032 and 0.043 for (**3**). In the final cycle of the refinement all parameter shifts were less than 0.1σ for all structures. No correction was made for secondary extinction.

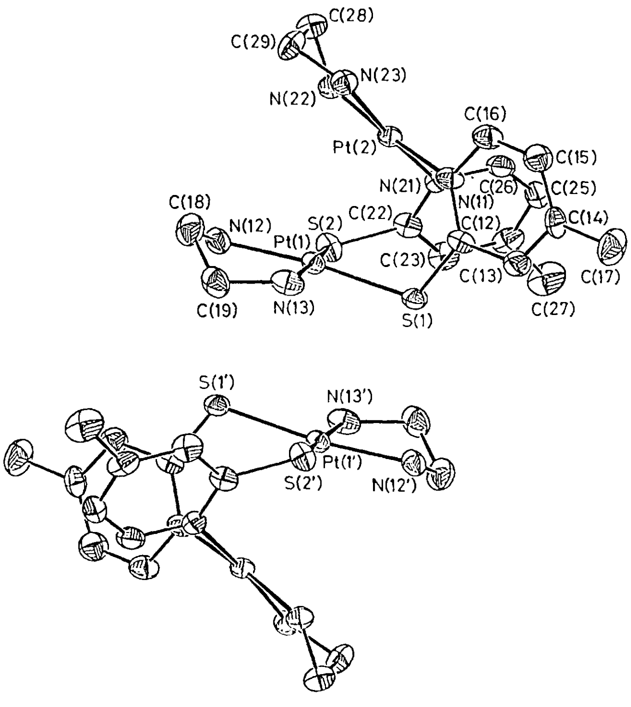

Figure 1. ORTEP diagram of the dimer pair of $[Pt_2(en)_2(4\text{-}MeC_5H_3NS)_2]^{2+}$ (50% probability contours for all atoms)

The atomic scattering factors, with correction for anomalous dispersion of Pt^0, Cl^0, and S, were taken from ref. 10. The computation was carried out by the FACOM 180II-AD computer at Osaka City University, using ORTEP[11] and standard programs in UNICS.[12]

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Electrochemical Measurement.—Cyclic voltammetric measurements were performed with a Yanaco P-1100 system equipped with a Rika Denki RW-201K x-y recorder. The working and the counter electrodes were a glassy carbon disk and a platinum wire.

Electrochemical measurements were performed at 25 ± 1 °C. The sample solutions (*ca.* 0.2 mmol dm^{-3}) containing 0.1 mol dm^{-3} KNO_3 as supporting electrolyte were deoxygenated with a stream of nitrogen. All potentials reported here are relative to the silver–silver chloride reference electrode.

Results and Discussion

Structure.—X-Ray structure analysis disclosed that the reaction of $[PtCl_2(en)]$ with C_5H_4NS or 4-MeC_5H_3NS selectively affords the head-to-head isomer of binuclear $[(en)Pt(C_5H_4NS$ or $4\text{-}MeC_5H_3NS)_2Pt(en)]^{2+}$ (Figure 1), and that the sole crystalline product from the reaction of $K_2[PtCl_4]$ with aps

Table 1. Positional parameters

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
(*a*) $[Pt_2(en)_2(C_5H_4NS)_2]Cl_2\cdot 3H_2O$							
Pt(1)	0.858 38(4)	0.885 98(4)	0.076 6(1)	S(2)	0.882 1(3)	0.911 1(3)	0.326 1(4)
Pt(2)	0.696 22(4)	0.639 97(4)	0.243 3(1)	N(12)	0.771 5(9)	1.005 2(9)	0.114(1)
N(11)	0.778 6(8)	0.560 7(8)	0.065(1)	C(18)	0.714(1)	0.992(1)	−0.017(2)
C(12)	0.888 6(9)	0.616(1)	−0.015(1)	C(19)	0.798(1)	0.987(1)	−0.167(2)
C(13)	0.944(1)	0.549(1)	−0.119(1)	N(13)	0.839 9(9)	0.887(1)	−0.149(1)
C(14)	0.883(1)	0.427(1)	−0.136(2)	N(22)	0.601 1(8)	0.703 9(9)	0.424(1)
C(15)	0.768(1)	0.370(1)	−0.059(2)	C(28)	0.477(1)	0.647(1)	0.414(2)
C(16)	0.721(1)	0.440(1)	0.043(2)	C(29)	0.479(1)	0.657(1)	0.246(2)
S(1)	0.969 9(3)	0.771 4(3)	0.000 9(4)	N(23)	0.559 4(8)	0.602 5(9)	0.148(1)
N(21)	0.820 9(8)	0.667 2(9)	0.358(1)	Cl(1)	0.390 1(3)	0.324 1(3)	0.218 5(4)
C(22)	0.889(1)	0.780(1)	0.393(1)	Cl(2)	0.353 1(5)	0.880 4(4)	0.337 2(6)
C(23)	0.971(1)	0.795(1)	0.477(1)	O(1)	0.542(1)	1.156(1)	0.207(2)
C(24)	0.974(1)	0.691(1)	0.540(2)	O(2)	0.597 8(9)	0.940 0(9)	0.394(1)
C(25)	0.899(1)	0.576(1)	0.506(2)	O(3)	0.759(1)	1.262(1)	0.325(2)
C(26)	0.825(1)	0.566(1)	0.413(1)				
(*b*) $[Pt_2(en)_2(4\text{-}MeC_5H_3NS)_2]Cl_2\cdot 2H_2O$							
Pt(1)	0.102 92(2)	0.350 95(2)	0.421 96(3)	C(27)	0.268(1)	0.558 6(7)	−0.096(1)
Pt(2)	0.348 68(2)	0.180 80(2)	0.242 73(2)	S(2)	0.075 4(1)	0.371 5(2)	0.174 6(2)
N(11)	0.426 2(5)	0.252 0(4)	0.410 5(6)	N(12)	−0.013 2(5)	0.277 3(5)	0.400 2(7)
C(12)	0.371 7(6)	0.359 1(5)	0.484 5(8)	C(18)	0.002 8(8)	0.223 2(7)	0.533(1)
C(13)	0.445 3(6)	0.405 9(6)	0.568 9(8)	C(19)	0.005 3(7)	0.304 2(7)	0.676 0(9)
C(14)	0.566 9(6)	0.342 4(6)	0.585 9(8)	N(13)	0.103 1(6)	0.337 5(5)	0.649 7(6)
C(15)	0.615 8(7)	0.229 2(6)	0.517 8(9)	N(22)	0.284 0(5)	0.098 3(4)	0.072 0(6)
C(16)	0.547 1(6)	0.187 4(6)	0.429 9(8)	C(28)	0.345 7(7)	−0.021 1(6)	0.082 7(8)
C(17)	0.642 8(9)	0.391 7(8)	0.680(1)	C(29)	0.336 8(7)	−0.022 9(6)	0.249 7(9)
S(1)	0.217 7(1)	0.446 2(1)	0.477 1(2)	N(23)	0.388 0(5)	0.049 7(5)	0.338 3(7)
N(21)	0.319 5(5)	0.300 1(4)	0.129 6(6)	Cl(1)	0.675 3(2)	0.883 4(2)	0.282 7(2)
C(22)	0.204 0(6)	0.373 7(5)	0.105 6(7)	Cl(2)	0.878 6(2)	0.140 8(2)	0.844 4(3)
C(23)	0.188 7(7)	0.457 3(6)	0.028 0(8)	O(1)	0.048 4(6)	0.104 1(5)	0.124 4(7)
C(24)	0.289 2(7)	0.461 9(6)	−0.025 9(7)	O(2)*	0.159(1)	0.982 2(8)	0.713(1)
C(25)	0.404 5(6)	0.385 6(6)	−0.002 3(9)	O(3)*	0.728(1)	0.230 5(9)	0.188(1)
C(26)	0.417 3(6)	0.306 7(5)	0.074 9(8)				
(*c*) $[Pt_2Cl_2(aps)_2]Cl_2\cdot 3H_2O$							
Pt(1)	0.376 84(2)	0.240 59(2)	0.093 30(3)	Cl(4)	0.568 1(2)	0.608 1(1)	0.270 0(3)
Pt(2)	0.166 91(2)	0.198 41(2)	0.271 36(3)	H[C(13)]	0.559(10)	0.153(8)	0.592(14)
Cl(1)	0.405 9(2)	0.089 3(1)	−0.144 0(2)	H[C(14)]	0.758(11)	0.164(9)	0.542(15)
Cl(2)	−0.005 0(2)	0.211 5(1)	0.101 7(2)	H[C(15)]	0.795(11)	0.218(9)	0.306(15)
N(11)	0.497 2(5)	0.205 0(4)	0.257 7(7)	H[C(16)]	0.640(11)	0.239(9)	0.146(15)
C(12)	0.473 0(6)	0.180 3(4)	0.391 0(8)	H(1)[C(18)]	0.210(11)	0.012(8)	0.378(14)
C(13)	0.563 8(6)	0.161 5(5)	0.495 0(9)	H(2)[C(18)]	0.351(11)	0.003(8)	0.395(14)
C(14)	0.689 5(8)	0.171 2(6)	0.468(1)	H(1)[C(19)]	0.256(11)	−0.062(8)	0.109(14)
C(15)	0.717 5(7)	0.196 2(6)	0.333(1)	H(2)[C(19)]	0.346(10)	0.013(8)	0.071(14)
C(16)	0.620 5(7)	0.214 9(6)	0.232(1)	H(1)[N(12)]	0.081(10)	0.033(8)	0.140(14)
S(1)	0.314 7(1)	0.170 2(1)	0.448 4(2)	H(2)[N(12)]	0.162(10)	0.028(8)	−0.024(14)
C(18)	0.292 6(7)	0.035 4(5)	0.353(1)	H[C(23)]	0.279(11)	0.582(8)	0.551(15)
C(19)	0.263 9(7)	−0.004 9(5)	0.155(1)	H[C(24)]	0.136(11)	0.622(9)	0.773(15)
N(12)	0.157 9(5)	0.049 4(4)	0.117 6(7)	H[C(25)]	0.008(11)	0.480(9)	0.735(15)
N(21)	0.164 5(5)	0.348 6(4)	0.436 4(7)	H[C(26)]	0.016(10)	0.313(8)	0.561(14)
C(22)	0.239 2(6)	0.419 6(4)	0.441 2(8)	H(1)[C(28)]	0.360(10)	0.449(8)	0.078(14)
C(23)	0.229 7(8)	0.518 1(5)	0.560 1(9)	H(2)[C(28)]	0.278(10)	0.513(8)	0.223(14)
C(24)	0.136 4(8)	0.543 3(5)	0.682(1)	H(1)[C(29)]	0.163(10)	0.403(8)	−0.074(14)
C(25)	0.060 8(8)	0.467 7(6)	0.681 5(9)	H(2)[C(29)]	0.135(10)	0.367(8)	0.077(14)
C(26)	0.073 6(6)	0.372 1(5)	0.556 6(9)	H(1)[N(22)]	0.330(10)	0.286(8)	−0.158(14)
S(2)	0.367 1(2)	0.398 8(1)	0.299 7(2)	H(2)[N(22)]	0.199(10)	0.240(8)	−0.167(14)
C(28)	0.299 7(7)	0.449 5(5)	0.148(1)	H1[O(1)]	0.592(12)	0.364(9)	−0.051(17)
C(29)	0.205 8(7)	0.376 0(5)	0.014 9(9)	H2[O(1)]	0.624(12)	0.447(9)	0.092(16)
N(22)	0.268 5(5)	0.280 4(4)	−0.074 9(7)	H1[O(2)]	0.914(11)	−0.063(9)	0.243(15)
O(1)	0.631 2(6)	0.375 1(4)	0.016 3(8)	H2[O(2)]	0.959(11)	0.048(9)	0.332(15)
O(2)	0.937 0(6)	0.004 9(4)	0.251 4(7)	H1[O(3)]	0.908(14)	0.316(11)	0.840(19)
O(3)	0.871 9(8)	0.368 6(5)	0.859(1)	H2[O(3)]	0.822(14)	0.335(11)	0.836(19)
Cl(3)	0.978 8(2)	0.833 8(1)	0.365 8(2)				

* Occupancy factor of 0.5.

comprises the head-to-tail isomer of $[Pt_2Cl_2(aps)_2]^{2+}$. The white-brown insoluble material obtained during the preparation was found to be amorphous by means of *X*-ray diffraction. It presumably consists of aps-bridged platinum(II) oligomers with diverse degrees of polymerization. As the platinum(II) dimers (**1**)—(**3**) involve similar ligand segments, a common atom

Table 2. Selected bond distances (Å) and angles (°) of $[Pt_2(en)_2(C_5H_4NS)_2]Cl_2 \cdot 3H_2O$ (**1**), $[Pt_2(en)_2(4\text{-}MeC_5H_3NS)_2]Cl_2 \cdot 2H_2O$ (**2**), and $[Pt_2Cl_2(aps)_2]Cl_2 \cdot 3H_2O$ (**3**)

	(**1**)	(**2**)	(**3**)
Pt(1) ••• Pt(2)	3.083(1)	3.101(1)	2.956(1)
Pt(1) ••• Pt(1′)	3.613(1)	3.726(2)	
Pt(1)–N(11)			2.050(6)
Pt(1)–N(12)	2.089(13)	2.068(8)	
Pt(1)–N(13)	2.081(11)	2.093(6)	
Pt(1)–N(22)			2.038(7)
Pt(1)–S(1)	2.302(4)	2.294(2)	
Pt(1)–S(2)	2.299(4)	2.291(2)	2.257(2)
Pt(1)–Cl(1)			2.314(1)
Pt(2)–N(11)	2.059(10)	2.042(6)	
Pt(2)–N(12)			2.036(5)
Pt(2)–N(21)	2.041(11)	2.024(7)	2.070(5)
Pt(2)–N(22)	2.053(10)	2.047(6)	
Pt(2)–N(23)	2.040(12)	2.041(7)	
Pt(2)–S(1)			2.251(2)
Pt(1)–Cl(2)			2.301(2)
C(12)–S(1)	1.749(11)	1.732(6)	1.801(7)
C(22)–S(2)	1.756(16)	1.733(9)	1.793(7)
C(18)–S(1)			1.828(7)
C(28)–S(2)			1.835(9)
S(1)–Pt(1)–S(2)	94.8(1)	94.6(1)	
N(11)–Pt(1)–S(2)			92.5(1)
N(22)–Pt(1)–S(2)			86.9(1)
N(22)–Pt(1)–Cl(1)			89.3(1)
N(11)–Pt(1)–Cl(1)			90.7(1)
N(12)–Pt(1)–N(13)	83.1(5)	83.3(3)	
N(11)–Pt(2)–N(21)	90.0(4)	89.2(3)	
N(21)–Pt(2)–S(1)			93.7(2)
N(12)–Pt(2)–S(1)			87.0(2)
N(12)–Pt(2)–Cl(2)			88.6(2)
N(21)–Pt(2)–Cl(2)			90.2(2)
N(22)–Pt(2)–N(23)	83.7(4)	83.7(3)	
S(1)–C(12)–N(11)	123.2(9)	123.8(6)	121.8(5)
S(2)–C(22)–N(21)	120.9(11)	121.5(6)	123.4(4)
C(12)–S(1)–C(18)			100.1(3)
C(22)–S(2)–C(28)			98.9(3)
Pt(2)–N(11)–C(12)	123.9(7)	124.2(4)	
Pt(1)–N(11)–C(12)			130.1(4)
Pt(1)–N(12)–C(18)	108.2(8)	108.2(5)	
Pt(2)–N(12)–C(19)			114.7(4)
Pt(1)–N(13)–C(19)	109.6(8)	108.6(5)	
Pt(2)–N(21)–C(22)	122.4(10)	121.7(6)	128.3(4)
Pt(2)–N(22)–C(28)	107.8(8)	106.4(4)	
Pt(1)–N(22)–C(29)			114.6(4)
Pt(2)–N(23)–C(29)	109.5(8)	110.6(5)	
Pt(1)–S(1)–C(12)	112.9(5)	112.0(3)	
Pt(2)–S(1)–C(18)			97.8(3)
Pt(2)–S(1)–C(12)			113.5(3)
Pt(1)–S(2)–C(22)	110.4(4)	108.6(2)	114.0(2)
Pt(1)–S(2)–C(28)			97.1(2)
Torsion angles			
S(1)–Pt(1)–Pt(2)–N(11)	36.4(3)	30.1(2)	
S(2)–Pt(1)–Pt(2)–N(21)	28.7(3)	38.3(2)	3.9(2)
N(11)–Pt(1)–Pt(2)–S(1)			2.8(2)

numbering was used. Atomic co-ordinates are listed in Table 1, selected bond lengths and angles in Table 2.

The structures of the C_5H_4NS and $4\text{-}MeC_5H_3NS$ dimers are very similar and resemble that of the head-to-head isomer of $[Pt_2(en)_2(C_5H_4NO)_2]^{2+}$.[3] The $[Pt_2Cl_2(aps)_2]^{2+}$ has an approximate two-fold axis perpendicular to the Pt ••• Pt axis, thus having configurational dissymmetry. Racemic compound (**3**) was actually resolved into $(+)^{CD}_{400}$- and $(-)^{CD}_{400}$-$[Pt_2Cl_2(aps)_2][ClO_4]_2$ *via* di-μ-(+)-tartrato(4−)-bis-antimonate(III)

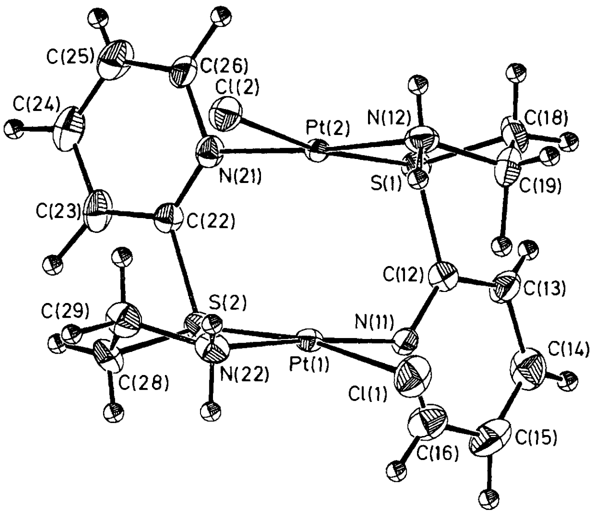

Figure 2. ORTEP diagram of $[Pt_2Cl_2(aps)_2]^{2+}$. Thermal ellipsoids are drawn at the 50% probability level

salt. Although the C_5H_4NS and $4\text{-}MeC_5H_3NS$ dimers are asymmetric in the solid state, the two co-ordination spheres in the dimer presumably undergo rapid thermal oscillation about the Pt ••• Pt axis and each ethylenediamine ligand undergoes rapid conformational $\lambda \longleftrightarrow \delta$ interconversion in solution.

The Pt ••• Pt distances in the C_5H_4NS and $4\text{-}MeC_5H_3NS$ dimers are *ca.* 0.1 Å longer than that in $[Pt_2(en)_2(C_5H_4NO)_2]^{2+}$ [2.992(1) Å]. The Pt atoms deviate from the co-ordination plane towards one another; the deviation from the [2S, 2N] plane is 0.103(3) Å for complex (**1**) and 0.098(2) Å for (**2**), and that from [4N] plane is 0.085(5) Å for (**1**) and 0.076(3) Å for (**2**). These values are comparable to those in the C_5H_4NO analogue (0.090 and 0.091 Å).[3] The [4N] co-ordination square is slanted against the [2S, 2N] square, the interplanar angle (τ) being 31.0(3)° in (**1**) and 31.9(2)° in (**2**). Moreover, the former (or latter) is rotated about the Pt ••• Pt axis from the eclipsed disposition. The mean value (ω) of the S–Pt–Pt–N torsion angles (Table 2) is 32.6° in (**1**) and 34.3° in (**2**). The values of ω and τ are significantly larger and less respectively than the corresponding ones in the C_5H_4NO dimer (ω = 24.9 and τ = 39.6°).[3] The longer N ••• S (2.7 Å) than the N ••• O bite (2.3 Å) in C_5H_4NO may be, at least, responsible for the decrease in τ, since the Pt ••• Pt distances in (**1**) and (**2**) are not much different from that in the C_5H_4NO dimer. The conformations of the en ligand in complexes (**1**) and (**2**) are $\lambda\lambda$ (or $\delta\delta$) and differ from that in the C_5H_4NO dimer ($\lambda\delta$). The larger ω than that of the C_5H_4NO dimer may arise from greater inter-ligand repulsion between $\lambda \longleftrightarrow \lambda$ (or $\delta \longleftrightarrow \delta$) than that between $\lambda \longleftrightarrow \delta$ rings.

The Pt ••• Pt distance in the aps-bridged dimer is 0.13—0.15 Å shorter than, and τ [17.9(4)°] and ω [3.4(2)°] much less than, the corresponding values in (**1**) and (**2**); the aps dimer thus has an eclipsed conformation with regard to the disposition of the co-ordination squares. A scale model indicates that twisting two co-ordination squares about the Pt ••• Pt axis gives rise to a considerable strain in Pt–en segments of the dimer. The very small ω is responsible for the small τ, since τ decreases with decrease of ω when the Pt ••• Pt distance is held constant. Inversion of the $\overline{\mathrm{Pt{-}S{-}CH_2{-}CH_2{-}NH_2}}$ ring conformation in one co-ordination sphere accompanies a rotation of another sphere about the Pt ••• Pt axis along with the inversion of another ring conformation, in order to keep bond angles about the S atom invariable. The ring inversion thus results in an increase of ω. However, the rotation places the Cl atom just below or above the S–CH_2–CH_2–NH_2 segment and gives rise to a significant repulsion between the Cl atom and the atoms of the segment. Thus the molecular conformation shown in Figure 2 must be the most stable one of the possible conformers.

The Pt–S (thioether) bond is *ca.* 0.04 Å shorter than the Pt–S (thiolate) bond, the length of which is comparable to that of $[Pt_2(4\text{-}MeC_5H_3NS)_4]$.[6] The C–S bond lengths of the C_5H_4NS and 4-MeC_5H_3NS ligands are *ca.* 0.06 Å shorter than that of the pyridine-2-thiol segment of the aps ligand and seem to have a partial double bond character. The Pt–N (*trans* to S) bond is 0.02—0.05 Å longer than the Pt–N (*trans* to pyridine N) bond in complexes (**1**) and (**2**). Thus the S atom of the C_5H_4NS or 4-MeC_5H_3NS exhibits a significant *trans* influence, but that of aps shows no appreciable *trans* influence, since the Pt–Cl (*trans* to the thioether S) bond is similar in length to the Pt–Cl bond of $K_2[PtCl_4]$.[13]

Both C_5H_4NS and 4-MeC_5H_3NS dimers were found to exist as dimer pairs in the crystal (Figure 1), though the pair of the former is environmentally different from that of the latter. Each pair has an inversion centre at the midpoint of Pt(1) ··· Pt(1′). Similar dimer pairs were also found in the crystal structures of the head-to-head isomers of $[Pt_2(NH_3)_4(C_5H_4NO)_2]_2[NO_3]_4$[2] and $[Pt_2(en)_2(C_5H_4NO)_2]_2[NO_3]_4$.[3] In these compounds two dimers are linked together by four NH ··· O hydrogen bonds between the $O_2Pt(NH_3$ or $NH_2)_2$ co-ordination halves of the dimers. The inter-dimer Pt ··· Pt distances in complexes (**1**) and (**2**) are *ca.* 0.4—0.5 Å longer than that of $[Pt_2(en)_2(C_5H_4NO)_2]_2{}^{4+}$. The inter-dimer N(12) ··· S(1′) and N(13) ··· S(2′) distances [3.34 and 3.51(1) Å] in (**1**), which has a shorter inter-dimer distance than that of (**2**), indicate that there is no strong NH ··· S interaction and that N–H(equatorial) does not participate in NH ··· S bonding. Therefore, instead of hydrogen bonding, a charge transfer from the filled d_{σ^*} orbital on one dimer to the vacant p_σ orbital of the other may play a major role in the dimer-pair formation in (**1**) and (**2**).[14]

As described above, reaction of $[PtCl_2(en)]$ with C_5H_5NS (or 4-MeC_5H_4NS) at pH 9 selectively gives the head-to-head isomer of $[Pt_2(en)_2(C_5H_4NS$ or 4-$MeC_5H_3NS)_2]^{2+}$. No head-to-tail isomer was detected, though both isomers are expected to be produced in equal amounts on statistical grounds. The reaction of $[PtCl_2(en)]$ with C_5H_4NS may afford, at first, an intermediate $[PtCl(en)(C_5H_4NS')]$ (C_5H_4NS' = unidentate pyridinethiolate ligated to or capable of ligation to Pt *via* S atom), since the chloro ligand in the platinum(II) complex is known to be readily replaced by a stronger nucleophile such as C_5H_4NS'. The intermediate may react further with either (i) $C_5H_4NS^-$ to give $[Pt(en)(C_5H_4NS')_2]$ or (ii) $[PtCl_2(en)]$ to give $[(en)ClPt(C_5H_4NS)PtCl(en)]^+$ and these processes predominate over (iii) $2[PtCl(en)(C_5H_4NS')] \longrightarrow [Pt_2(en)_2(C_5H_4NS)_2]Cl_2$, since the last process selectively produces the head-to-tail isomer. While $[Pt(en)(C_5H_4NS')_2]$ selectively gives the head-to-head isomer by reaction with $[PtCl_2(en)]$, the reaction of $[(en)ClPt(C_5H_4NS)PtCl(en)]^+$ with $C_5H_4NS^-$ affords equal amounts of the head-to-head and the head-to-tail isomers. Thus process (i) seems to prevail over (ii).

The complexes $[Pt_2(en)_2(C_5H_4NS)_2]Cl_2$ (**1**) and $[Pt_2Cl_2(aps)_2]Cl_2$ (**3**) show irreversible oxidation and reduction waves at +0.77 and +0.55 V and at +1.20 and +0.86 V respectively. The perchlorates of these compounds, however, show no oxidation nor reduction waves in the 0 to +1.5 V range. We have shown that the electrochemical behaviour of $[Pt^{II}{}_2(C_5H_4NS)_4]$ in the presence of chloride ions is identical with that of $[Pt^{III}{}_2Cl_2(C_5H_4NS)_4]$, and interpreted the redox processes as follows. Two-electron oxidation of $[Pt_2(C_5H_4NS)_4]$ affords $[Pt_2(C_5H_4NS)_4(dmf)_2]^{2+}$ the dimethylformamide (dmf) ligands of which are immediately replaced by chloride to give $[Pt_2Cl_2(C_5H_4NS)_4]$, which loses the chloro ligands upon electrode reduction giving $[Pt_2(C_5H_4NS)_4]$.[6] On the other hand, $[Pt_2(NH_3)_4(C_5H_4NO)_2]^{2+}$ and $[Pt_2(en)_2(C_5H_4NO)_2]^{2+}$ are oxidized by nitric acid to give the corresponding platinum(III) complexes in the presence of an appropriate anion capable of ligation at the axial sites of the Pt^{III}–Pt^{III} bond. Indeed the C_5H_4NO-bridged platinum(III) complexes structurally characterized so far have nitrato, a nitro, halogeno, or aqua ligand at the axial position.[4,5] The complex $[Pt_2(NH_3)_4(C_5H_4NO)_2]^{2+}$ shows a reversible cyclic voltammogram in aqueous solution corresponding to $Pt^{II}Pt^{II} \rightleftharpoons Pt^{III}Pt^{II} \rightleftharpoons Pt^{III}Pt^{III}$ in the presence of nitrate anions as a supporting electrolyte. These facts indicate the necessity of axial ligands for the stabilization of Pt^{III}. Although we have not yet identified the oxidized species in the cyclic voltammograms of complexes (**1**) and (**3**), the fact that the perchlorates show no oxidation or reduction wave in the 0 to +1.5 V range indicates that the perchlorate and nitrate (supporting electrolyte) anions as well as water molecules do not appear to serve as axial ligands for C_5H_4NS-bridged platinum(III) species.

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