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Synthesis and X-ray Structural Studies of some Dinuclear Platinum(III) Complexes of Pyrimidine-2-thione and 2-Thiouracil

DAVID M. L. GOODGAME*, ROBERT W. ROLLINS, ALEXANDRA M. Z. SLAWIN, DAVID J. WILLIAMS and PAULA W. ZARD

Chemistry Department, Imperial College of Science and Technology, London SW7 2AY, U.K.

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Abstract

The dinuclear Pt(III) compounds $[Pt(pymS)_2Cl]_2$ (**A**) (pymS = the anion of pyrimidine-2-thione) and $[Pt(2\text{-}TU)_2I]_2$ (**B**) (2-TU = the anion of 2-thiouracil) have been prepared and their structures determined by X-ray diffraction methods. Compound **A** is monoclinic, space group $P2_1/n$, with $a = 10.404(4)$, $b = 13.345(3)$, $c = 17.522(3)$ Å, $\beta = 103.61(2)°$, $V = 2364$ Å^3, and $Z = 4$; **B** is triclinic, space group $P\bar{1}$, $a = 10.925(13)$, $b = 11.896(4)$, $c = 13.639(6)$ Å, $\alpha = 92.05(3)$, $\beta = 99.74(7)$, $\gamma = 110.28(7)°$, $V = 1630$ Å^3, and $Z = 2$. The halogen atoms occupy the axial positions of the dinuclear unit in which two Pt atoms are bridged by four thione ligands. Compound **A** differs from **B** and from previously reported $[Pt(pymS)_2I]_2$ (**C**) in that in **A** one of the Pt atoms is coordinated to one N atom and three S atoms of the thione bridges, while the other Pt is bonded to three N atoms and one S atom. The Pt–Pt bond length in **A** (2.518(1) Å) is shorter than that (2.554(1) Å) in **C**. $[Pt(pymS)_2Br]_2$ (**D**) has also been isolated and is believed to have a similar structure to **C**. Pt(2-mercapto-4-methylpyrimidinato)$_2$X (X = Cl, I) and $Pt_2(pymS)_5Cl$ were also obtained, but not in suitable crystalline form for X-ray characterisation. Attempts to prepare $Pt_2(pymS)_5Br$ gave crystals which X-ray study showed to be dinuclear $[Pt_2(pymS)_4BrX]$ (**E**), with X corresponding to partial occupancy of one axial position by a $pymS^-$ anion, coordinated by S, and by halide. Crystal data for **E** are: monoclinic, space group $P2_1/n$, $a = 12.632(7)$, $b = 14.302(6)$, $c = 15.109(7)$ Å, $\beta = 91.95(4)°$, $V = 2728$ Å^3, and $Z = 4$. Several Pt(II) complexes with related thiones and some pyrimidine-2-one ligands are briefly reported.

Introduction

During studies of the coordination of pyrimidine-2-thione ligands to metal ions, we observed [1] that the reaction of pyrimidine-2-thione (pymSH) with K_2PtI_4 in aqueous methanol gave a dinuclear Pt(III) complex $[Pt(pymS)_2I]_2$. As Pt(III) complexes are of current interest [2–5], we have studied the reactions of PtX_4^{2-} (X = Cl, Br, I) with a number of ligands related to pymSH in an attempt to extend the number of Pt(III) compounds and to explore the features of the organic ligands favouring the formation of such complexes. We report here some results of this work.

Experimental

Preparations

The ligands used were either commercially available or were synthesized by standard literature methods [6–10]. For preparations involving the $PtBr_4^{2-}$ and PtI_4^{2-} ions, these species were generated *in situ* by mixing the appropriate amounts of K_2PtCl_4 and KBr or KI respectively in the minimum volume of water and stirring for several minutes before use.

$[Pt(pymS)_2Cl]_2$ (A)

A solution of K_2PtCl_4 (0.2 g) in water (2 cm^3) was added to one of pyrimidine-2-thione (0.13 g) in hot ethanol (60 cm^3). A yellow precipitate was immediately formed. On further heating the precipitate redissolved to give a red–orange solution which then afforded red crystals on standing overnight. The crystals were characterized by X-ray diffraction.

A sample of the same stoichiometry, but of insufficient crystal quality for X-ray studies, was obtained from a reaction between K_2PtCl_4 in water and pyrimidine-2-thione in methanol containing an equimolar amount of sodium methoxide. *Anal.* Found: C, 21.55; H, 1.42; N, 12.24. Calc. for $Pt(C_4H_3N_2S)_2Cl$: C, 21.22; H, 1.34; N, 12.38%.

$[Pt(pymS)_2Br]_2$ (D)

This was obtained as a red powder as for the chloride analogue but using K_2PtBr_4. *Anal.* Found: C, 19.54; H, 1.28; N, 11.21. Calc. for $Pt(C_4H_3N_2S)_2$-

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*Author to whom correspondence should be addressed.

Br: C, 19.32; H, 1.22; N, 11.27%. A further preparation in which the mixture was allowed to cool slowly to room temperature gave some red crystals which were studied by X-ray diffraction.

$Pt_2(pymS)_5Cl$

Pyrimidine-2-thione (0.26 g) was dissolved in a methanolic solution of sodium methoxide (0.11 g in 60 cm^3). The solution was warmed and K_2PtCl_4 (0.2 g) in water (2 cm^3) was added. The mixture was heated to boiling and then allowed to stand, when a red powder was obtained. *Anal.* Found: C, 24.90; H, 1.49; N, 14.16; Cl, 2.83. Calc. for $Pt_2(C_4H_3N_2S)_5$-Cl: C, 24.48; H, 1.54; N, 14.28; Cl, 3.61%.

$[Pt_2(pymS)_4Br(Br/pymS)]$ *(E)*

An aqueous solution of K_2PtBr_4 (0.25 mmol in 2 cm^3) was added dropwise to a solution of pyrimidine-2-thione (0.7 mmol) in hot methanol (80 cm^3). The mixture was heated for a few minutes and then allowed to stand at room temperature. The orange–red crystals which formed were characterized by X-ray diffraction (see 'Results and Discussion').

Pt(2-mercapto-4-methylpyrimidinato)₂Cl

K_2PtCl_4 (0.05 g) in water (5 cm^3) was added dropwise to a solution of 2-mercapto-4-methylpyrimidine (0.045 g) in methanol (25 cm^3). After stirring, the orange solution was stored in the dark at room temperature when very small red crystals were obtained. *Anal.* Found: C, 25.65; H, 2.20; N, 11.69; Cl, 6.54. Calc. for $Pt(C_5H_5N_2S)_2Cl$: C, 24.97; H, 2.10; N, 11.65; Cl, 7.37%.

Pt(2-mercapto-4-methylpyrimidinato)₂I

K_2PtI_4 (0.25 mmol) in water (10 cm^3) was added dropwise to a solution of 2-mercapto-4-methylpyrimidine (0.091 g) in ethanol (90 cm^3). The red solution was allowed to stand overnight when a purple solid was formed. *Anal.* Found: C, 21.20; H, 1.87; N, 9.39. Calc. for $Pt(C_5H_5N_2S)_2I$: C, 20.98; H, 1.76; N, 9.79%.

Bis(4,6-dimethyl-2-mercaptopyrimidinato)platinum(II)

This orange–yellow compound precipitated from attempts to prepare Pt(4,6-dimethyl-2-mercaptopyrimidinato)$_2$X (X = Cl, I) following the general procedure outlined above for 2-mercaptopyrimidine and its 4-methyl-analogue. *Anal.* Found for product from K_2PtCl_4: C, 30.66; H, 2.91; N, 11.87. Calc. for $Pt(C_6H_7N_2S)_2$, C, 30.44; H, 2.98; N 11.84%.

Dichlorobis(1-methyl-2-mercaptopyrimidine)platinum(II)

K_2PtCl_4 (0.103 g) in water (15 cm^3) was added to a solution of 1-methyl-2-mercaptopyrimidine (0.063 g) in dichloromethane (15 cm^3). The mixture was shaken and left in the dark at room temperature overnight. The yellow precipitate was collected, washed with water (2 × 5 cm^3) and then ethanol (5 cm^3) and air-dried (65% yield). *Anal.* Found: C, 23.09; H, 2.21; N, 10.52. Calc. for $Pt(C_5H_6N_2S)_2Cl_2$: C, 23.17; H, 2.33; N, 10.81%.

Di-iodo(1-methyl-2-mercaptopyrimidine)platinum(II)

This orange–yellow complex was obtained in 68% yield by the addition of K_2PtI_4 (0.5 mmol) in water (5 cm^3) to a solution of 1-methyl-2-mercaptopyrimidine (0.139 g, 1.1 mmol) in methanol (25 cm^3). *Anal.* Found: C, 11.07; H, 1.09; N, 4.98. Calc. for $Pt(C_5H_6N_2S)I_2$: C, 10.44; H, 1.05; N, 4.87%.

[Pt(2-thiouracilato)₂I]₂ (B)

An aqueous solution of K_2PtI_4 was added dropwise and with stirring to a hot methanolic solution of 2-thiouracil (2:1 thiouracil: Pt mole ratio). Dark blue–purple crystals of the complex separated on storage at *ca.* 0 °C. *Anal.* Found: C, 16.94; H. 0.99; N, 9.52; S, 11.81. Calc. for $Pt(C_4H_3N_2OS)_2I$: C, 16.78; H, 1.05; N, 9.71; S, 11.11%.

Pt(2-mercaptopyridine)(2-mercaptopyridinato)Cl

Reaction between K_2PtCl_4 (0.1 g) and 2-mercaptopyridine (0.05 g) in 1:1 ethanol/water (10 cm^3) gave a yellow precipitate. *Anal.* Found: C, 26.47; H, 1.67; N, 6.05. Calc. for $PtC_{10}H_9N_2S_2Cl$: C, 26.58; H, 2.01; N, 6.20%.

Pt(2-mercaptopyridine)(2-mercaptopyridinato)Br

An aqueous solution of K_2PtCl_4 (0.06 g) and KBr (0.086 g) was added slowly to a methanolic solution of 2-mercaptopyridine (0.032 g). A yellow solid precipitated. *Anal.* Found: C, 23.47; H, 1.81; N, 5.80. Calc. for $PtC_{10}H_9N_2S_2Br$: C, 24.20; H, 1.83; N, 5.65%.

Product of the reaction between K_2PtI_4 and 2-mercaptopyridine

An analogous reaction between K_2PtI_4 and 2-mercaptopyridine in aqueous methanol gave an initial yellow precipitate which quickly redissolved with the formation of a green solid on standing overnight. *Anal.* Found: C, 21.49; H, 1.58; N, 4.93. Calc. for $PtC_{10}H_8N_2S_2I$: C, 22.15; H, 1.49; N, 5.17. Calc. for $PtC_{10}H_9N_2S_2I$: C, 22.11; H, 1.67; N, 5.16%.

Dichlorobis(2-mercaptothiazoline)platinum(II)

Bright yellow solid from the addition of K_2-$PtCl_4$ (0.1 g) in water (5 cm^3) to 2-mercaptothiazoline (0.056 g) in hot ethanol (25 cm^3). *Anal.* Found: C, 14.64; H, 1.85; N, 5.50. Calc. for $Pt(C_3H_5NS_2)_2$-Cl_2: C, 14.29; H, 2.00; N, 5.56%.

TABLE I. Some Pyrimidine-2-one Complexes of type PtL$_2$X$_2$ (X = Cl, I)

Complex	Found (%)			Calculated (%)		
	C	H	N	C	H	N
Pt(pyrimidine-2-one)$_2$Cl$_2$	20.78	1.74	11.75	20.97	1.76	12.23
Pt(pyrimidine-2-one)$_2$I$_2$	14.84	1.32	8.65	14.99	1.26	8.74
Pt(1-methyl-pyrimidine-2-one)$_2$Cl$_2$	24.44	2.45	11.05	24.70	2.49	11.52
Pt(1-methyl-pyrimidine-2-one)$_2$I$_2$	17.76	1.90	8.25	17.95	1.81	8.37
Pt(4,6-dimethyl-pyrimidine-2-one)$_2$Cl$_2$	27.66	3.08	10.36	28.03	3.14	10.89

TABLE II. Summary of Crystal Data and Data Collection Parameters

	A	B	E
Formula	$C_{16}H_{12}N_8S_4Pt_2Cl_2$	$C_{16}H_{12}N_8O_4S_4Pt_2I_2$	$(C_4H_3N_2S)_{4.8}Br_{1.2}Pt_2$[b]
Molecular weight	905.7	1152.6	1019.6
Crystal system	monoclinic	triclinic	monoclinic
Space group	$P2_1/n$	$P\bar{1}$	$P2_1/n$
a (Å)	10.404(4)	10.925(13)	12.632(7)
b (Å)	13.345(3)	11.896(4)	14.302(6)
c (Å)	17.522(3)	13.639(6)	15.109(7)
α (°)	90	92.05(3)	90
β (°)	103.61(2)	99.74(7)	91.95(4)
γ (°)	90	110.28(7)	90
Cell volume (Å^3)	2364	1630	2728
Z	4	2	4
ρ_{calc} (g cm^{-3})	2.54	2.35	2.48
μ (cm^{-1})	277	337	249
Radiation	Cu Kα	Cu Kα	Cu Kα
Crystal dimensions (mm)	0.17 × 0.10 × 0.13	0.18 × 0.30 × 0.23	0.21 × 0.20 × 0.17
Unique reflections measured	2433	4132	2177
2θ range (°)	100	116	100
Reflections considered observed $\lvert F_o \rvert > 3\sigma(\lvert F_o \rvert)$	2227	3399	2482
Weight (G)[a]	0.00057	0.00010	0.00030
Number of parameters varied	290	326	344
R	0.038	0.101	0.089
R_w	0.039	0.097	0.088
Absorption correction	empirical	empirical	empirical[c]

[a] $w^{-1} = \sigma^2(F) + GF^2$. [b] Fractional values because of mixed metal/ligand stoichiometries. [c] Both numerical and empirical absorption corrections were carried out. Despite the crystal having well defined and easily indexed faces the empirically corrected data refined better. This was probably due to the presence of internal defects in the crystal as evidenced by a noticeable opaqueness of the sample.

Pyrimidine-2-one complexes of type PtL$_2$X$_2$ (X = Cl, I)

The complexes listed in Table I all precipitated on mixing the stoichiometric amounts of PtX$_4^{2-}$ (X = Cl, I) and the appropriate pyrimidine-2-one ligand in water. They are all yellow.

X-ray Studies

A summary of the crystal data and of the data collection and refinement parameters for compounds **A**, **B** and **E** is given in Table II.

Intensity data were measured with graphite monochromated Cu Kα radiation using ω-scans on a Nicolet R3m/Eclipse S140 diffractometer system. The data were corrected for Lorentz and polarization factors.

All three structures were solved by the heavy-atom method and their non-hydrogen atoms were refined anisotropically. All hydrogen atom positions were idealized, C–H = 0.96 Å, assigned isotropic thermal parameters, U(H) = 1.2U_{eq} (C), and allowed to ride on their parent carbons. In **E** a ΔF map revealed the presence of a partial occupancy pymS$^-$ anion in one of the terminal positions superimposed upon the halogen atom. Refinement indicated the relative occupancies to be 80% and 20% respectively.

Refinements were by block-cascade full-matrix least-squares. Computations were carried out using the SHELXTL program system [11]. Fractional coordinates for the non-hydrogen atoms in **A**, **B** and **E** are given in Tables III, IV and V respectively. Tables VI, VII, and VIII give the respective bond lengths and angles.

TABLE III. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for **A**

Atom	*x*	*y*	*z*	U^a
Pt(1)	2702(1)	2510(1)	4295(1)	55(1)
Pt(2)	373(1)	1844(1)	3974(1)	51(1)
Cl(1)	4940(3)	3193(3)	4595(2)	74(1)
Cl(2)	−1901(3)	1183(2)	3658(2)	67(1)
N(1)	3398(8)	1038(7)	4173(5)	55(4)
C(2)	2647(13)	216(9)	4269(6)	62(5)
S(2)	1128(3)	309(2)	4479(2)	60(1)
N(3)	3107(10)	−713(8)	4232(6)	70(4)
C(4)	4235(13)	−847(10)	4059(9)	82(6)
C(5)	4996(13)	−59(11)	3901(7)	77(5)
C(6)	4495(13)	881(10)	3960(7)	67(5)
N(11)	630(9)	1362(7)	2903(5)	56(3)
C(12)	1454(12)	1847(9)	2516(7)	61(5)
S(12)	2486(4)	2795(3)	2949(2)	69(1)
N(13)	1496(12)	1608(10)	1793(6)	81(5)
C(14)	834(15)	799(12)	1482(8)	85(6)
C(15)	114(15)	221(12)	1868(8)	84(6)
C(16)	34(14)	535(10)	2579(7)	74(5)
N(21)	−284(9)	3254(7)	3511(5)	57(4)
C(22)	346(13)	4112(9)	3805(7)	64(5)
S(22)	1898(3)	4091(2)	4439(2)	69(1)
N(23)	−180(11)	5015(8)	3615(7)	86(5)
C(24)	−1298(16)	5080(12)	3088(9)	104(7)
C(25)	−1913(15)	4251(11)	2673(8)	86(6)
C(26)	−1363(14)	3322(10)	2923(7)	76(5)
N(31)	169(10)	2308(7)	5058(5)	57(4)
C(32)	1216(13)	2305(9)	5698(7)	62(5)
S(32)	2837(3)	2234(3)	5630(2)	67(1)
N(33)	1036(12)	2408(8)	6427(6)	72(5)
C(34)	−145(18)	2575(11)	6517(9)	82(7)
C(35)	−1246(15)	2675(10)	5910(9)	74(6)
C(36)	−1065(14)	2502(9)	5161(8)	67(5)

^{a}Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE IV. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for **B**

Atom	*x*	*y*	*z*	U^a
Pt(1)	4902(2)	2993(1)	1622(1)	57(1)
Pt(2)	2408(2)	2113(1)	1574(1)	54(1)
I(1)	7499(3)	3988(2)	1328(2)	86(1)
I(2)	−250(3)	882(2)	1590(2)	72(1)
N(1)	5084(31)	1328(22)	1987(23)	67(13)
C(2)	4020(34)	339(27)	1765(26)	59(15)
S(2)	2472(10)	222(7)	1249(7)	64(4)
N(3)	4185(30)	−737(24)	1905(21)	59(13)
C(4)	5465(33)	−859(37)	2288(27)	62(17)
O(4)	5452(27)	−1882(21)	2382(20)	74(13)
C(5)	6454(44)	229(32)	2573(34)	86(20)
C(6)	6326(34)	1314(32)	2455(30)	65(16)
N(11)	5202(30)	3546(26)	3080(25)	69(14)
C(12)	4397(40)	3006(31)	3702(26)	60(16)
S(12)	2827(11)	1928(8)	3247(7)	71(4)
N(13)	4705(34)	3291(26)	4689(23)	72(15)
C(14)	5845(55)	4163(45)	5205(38)	102(25)
O(14)	6008(37)	4310(34)	6167(24)	123(20)
C(15)	6684(48)	4782(40)	4572(36)	98(23)
C(16)	6391(40)	4459(34)	3598(34)	79(20)
N(21)	2090(30)	2347(21)	46(21)	57(12)
C(22)	2940(47)	2318(30)	−553(30)	74(20)
S(22)	4500(10)	2294(8)	−37(7)	65(4)
N(23)	2654(31)	2368(25)	−1510(19)	62(13)
C(24)	1521(45)	2478(37)	−1995(28)	73(20)
O(24)	1327(33)	2521(33)	−2904(23)	108(18)
C(25)	627(41)	2539(33)	−1404(28)	70(18)
C(26)	913(44)	2493(32)	−387(32)	76(19)
N(31)	2282(37)	3815(22)	1862(21)	78(15)
C(32)	3317(32)	4800(32)	1664(26)	58(16)
S(32)	4706(10)	4793(7)	1235(8)	68(4)
N(33)	3213(34)	5890(24)	1691(26)	78(15)
C(34)	2200(52)	6145(37)	2016(39)	101(25)
O(34)	2216(30)	7179(22)	2063(32)	122(19)
C(35)	1284(39)	5088(29)	2295(38)	90(21)
C(36)	1304(50)	4020(38)	2244(33)	89(24)

^{a}Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

TABLE V. Atom Coordinates (×10^4) and Temperature Factors (Å^2 × 10^3) for **E**

Atom	*x*	*y*	*z*	U^a
Br(1)	−2759(3)	1502(2)	3829(2)	72(1)
Pt(1)	−1062(1)	1823(1)	2929(1)	50(1)
Pt(2)	617(1)	2275(1)	2137(1)	50(1)
S(52)	2299(4)	2475(4)	1350(4)	64(2)
N(11)	758(20)	3541(14)	2815(18)	68(7)
C(12)	258(27)	3572(20)	3696(18)	69(7)
S(12)	−514(6)	2753(5)	4108(5)	61(3)
N(13)	434(20)	4383(19)	4163(17)	70(7)
C(14)	977(25)	5068(22)	3855(25)	77(8)
C(15)	1375(24)	5052(22)	3043(24)	77(8)
C(16)	1234(23)	4261(20)	2587(21)	65(7)
N(21)	−292(18)	2993(15)	1166(13)	52(6)
C(22)	−1312(23)	3352(18)	1340(22)	65(7)
S(22)	−1921(6)	3076(5)	2303(5)	57(2)
N(23)	−1817(20)	3915(17)	798(18)	73(7)
C(24)	−1406(28)	4137(22)	45(22)	78(8)
C(25)	−457(23)	3802(22)	−204(24)	77(8)
C(26)	76(26)	3208(22)	401(21)	72(7)
N(31)	−1527(17)	994(15)	1846(14)	54(6)

(continued)

TABLE V. *(continued)*

Atom	x	y	z	U^a
C(32)	−765(27)	562(18)	1310(17)	64(7)
S(32)	488(6)	910(5)	1340(5)	64(3)
N(33)	−1064(21)	−85(17)	757(18)	73(7)
C(34)	−2064(26)	−347(22)	646(18)	69(7)
C(35)	−2819(33)	57(24)	1032(23)	91(8)
C(36)	−2551(30)	750(26)	1693(20)	83(8)
N(41)	−287(17)	653(13)	3451(12)	43(6)
C(42)	818(23)	610(22)	3564(21)	65(7)
S(42)	1603(6)	1527(5)	3231(5)	57(2)
N(43)	1343(20)	−83(16)	3983(15)	59(6)
C(44)	728(23)	−788(20)	4243(17)	55(7)
C(45)	−308(22)	−826(22)	4097(19)	63(7)
C(46)	−765(23)	−66(18)	3715(17)	51(7)
C(52)	3254(26)	2737(26)	2100(24)	116(8)
N(53)	4206(22)	2391(23)	1931(23)	98(8)
C(54)	5010(31)	2492(35)	2496(27)	187(9)
C(55)	4996(23)	2992(24)	3275(29)	69(8)
C(56)	3985(21)	3312(28)	3409(27)	103(8)
N(51)	3124(26)	3159(23)	2903(21)	95(8)

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

Results and Discussion

Our aims in this work were: (1) to determine whether the formation of binuclear Pt(III) complexes of type $[PtL_2X]_2$ analogous to $[Pt(pymS)_2I]_2$ was limited to X = I, or whether other anions could occupy the terminal positions; (2) to vary the potentially bridging ligand to see what other molecules containing the N–C–S arrangement present in pyrimidine-2-thione formed such complexes; and (3) to compare the behaviour of analogous ligands in which the exocyclic sulphur atom is replaced by oxygen. We have concentrated on attempting to obtain compounds in crystalline form suitable for X-ray diffraction studies, because of the difficulty in making an unambiguous characterization of compounds of this type by other, less direct methods. In many cases the ligands studied gave only Pt(II) complexes when reacted with PtX_4^{2-}. Some of these are briefly described here, for comparison with those systems which gave Pt(III) complexes, but their properties were not studied in detail, nor was any attempt made to survey the full range of such Pt(II) complexes with the ligands used.

TABLE VI. Bond Lengths (Å) and Angles (deg) for A

Pt(1)–Pt(2)	2.518(1)	Pt(1)–Cl(1)	2.440(3)
Pt(1)–N(1)	2.121(10)	Pt(1)–S(12)	2.346(3)
Pt(1)–S(22)	2.306(3)	Pt(1)–S(32)	2.339(3)
Pt(2)–Cl(2)	2.463(3)	Pt(2)–S(2)	2.295(3)
Pt(2)–N(11)	2.059(9)	Pt(2)–N(21)	2.099(9)
Pt(2)–N(31)	2.055(10)	N(1)–C(2)	1.379(16)
N(1)–C(6)	1.300(17)	C(2)–S(2)	1.710(14)
C(2)–N(3)	1.336(16)	N(3)–C(4)	1.292(19)
C(4)–C(5)	1.383(21)	C(5)–C(6)	1.371(20)
N(11)–C(12)	1.374(17)	N(11)–C(16)	1.327(16)
C(12)–S(12)	1.717(12)	C(12)–N(13)	1.317(17)
N(13)–C(14)	1.327(20)	C(14)–C(15)	1.361(23)
C(15)–C(16)	1.335(20)	N(21)–C(22)	1.359(15)
N(21)–C(26)	1.337(15)	C(22)–S(22)	1.732(12)
C(22)–N(23)	1.334(16)	N(23)–C(24)	1.305(18)
C(24)–C(25)	1.395(20)	C(25)–C(26)	1.392(19)
N(31)–C(32)	1.368(14)	N(31)–C(36)	1.363(18)
C(32)–S(32)	1.722(15)	C(32)–N(33)	1.340(18)
N(33)–C(34)	1.295(23)	C(34)–C(35)	1.374(20)
C(35)–C(36)	1.389(22)		
Pt(2)–Pt(1)–Cl(1)	178.7(1)	Pt(2)–Pt(1)–N(1)	89.1(2)
Cl(1)–Pt(1)–N(1)	92.1(2)	Pt(2)–Pt(1)–S(12)	88.5(1)
Cl(1)–Pt(1)–S(12)	91.0(1)	N(1)–Pt(1)–S(12)	90.2(3)
Pt(2)–Pt(1)–S(22)	89.6(1)	Cl(1)–Pt(1)–S(22)	89.2(1)
N(1)–Pt(1)–S(22)	178.4(3)	S(12)–Pt(1)–S(22)	90.6(1)
Pt(2)–Pt(1)–S(32)	89.8(1)	Cl(1)–Pt(1)–S(32)	90.8(1)
N(1)–Pt(1)–S(32)	90.8(3)	S(12)–Pt(1)–S(32)	178.0(1)
S(22)–Pt(1)–S(32)	88.4(1)	Pt(1)–Pt(2)–Cl(2)	179.7(1)
Pt(1)–Pt(2)–S(2)	90.2(1)	Cl(2)–Pt(2)–S(2)	89.5(1)
Pt(1)–Pt(2)–N(11)	89.4(3)	Cl(2)–Pt(2)–N(11)	90.4(3)

(continued)

TABLE VI. *(continued)*

S(2)–Pt(2)–N(11)	88.1(3)	Pt(1)–Pt(2)–N(21)	88.8(3)
Cl(2)–Pt(2)–N(21)	91.5(3)	S(2)–Pt(2)–N(21)	179.0(3)
N(11)–Pt(2)–N(21)	91.6(4)	Pt(1)–Pt(2)–N(31)	89.4(3)
Cl(2)–Pt(2)–N(31)	90.8(3)	S(2)–Pt(2)–N(31)	90.7(3)
N(11)–Pt(2)–N(31)	178.3(4)	N(21)–Pt(2)–N(31)	89.5(4)
Pt(1)–N(1)–C(2)	120.5(8)	Pt(1)–N(1)–C(6)	121.5(8)
C(2)–N(1)–C(6)	117.9(11)	N(1)–C(2)–S(2)	123.1(9)
N(1)–C(2)–N(3)	120.9(12)	S(2)–C(2)–N(3)	115.9(9)
Pt(2)–S(2)–C(2)	103.4(4)	C(2)–N(3)–C(4)	119.6(12)
N(3)–C(4)–C(5)	122.4(13)	C(4)–C(5)–C(6)	115.8(13)
N(1)–C(6)–C(5)	123.0(13)	Pt(2)–N(11)–C(12)	122.3(7)
Pt(2)–N(11)–C(16)	120.1(9)	C(12)–N(11)–C(16)	117.6(11)
N(11)–C(12)–S(12)	121.7(9)	N(11)–C(12)–N(13)	121.9(11)
S(12)–C(12)–N(13)	116.4(10)	Pt(1)–S(12)–C(12)	103.1(4)
C(12)–N(13)–C(14)	117.3(13)	N(13)–C(14)–C(15)	123.4(14)
C(14)–C(15)–C(16)	116.7(14)	N(11)–C(16)–C(15)	122.3(14)
Pt(2)–N(21)–C(22)	121.6(7)	Pt(2)–N(21)–C(26)	119.8(8)
C(22)–N(21)–C(26)	118.5(10)	N(21)–C(22)–S(22)	121.6(9)
N(21)–C(22)–N(23)	122.2(10)	S(22)–C(22)–N(23)	116.2(9)
Pt(1)–S(22)–C(22)	104.6(4)	C(22)–N(23)–C(24)	118.8(11)
N(23)–C(24)–C(25)	122.6(14)	C(24)–C(25)–C(26)	116.0(12)
N(21)–C(26)–C(25)	120.8(12)	Pt(2)–N(31)–C(32)	121.5(9)
Pt(2)–N(31)–C(36)	119.0(7)	C(32)–N(31)–C(36)	119.0(11)
N(31)–C(32)–S(32)	123.1(10)	N(31)–C(32)–N(33)	121.3(13)
S(32)–C(32)–N(33)	115.5(9)	Pt(1)–S(32)–C(32)	103.4(4)
C(32)–N(33)–C(34)	118.9(11)	N(33)–C(34)–C(35)	124.3(15)
C(34)–C(35)–C(36)	116.2(15)	N(31)–C(36)–C(35)	119.9(11)

TABLE VII. Bond Lengths (Å) and Angles (deg) for **B**

Pt(1)–Pt(2)	2.546(2)	Pt(1)–I(1)	2.776(4)
Pt(1)–N(1)	2.127(29)	Pt(1)–N(11)	2.007(34)
Pt(1)–S(22)	2.298(10)	Pt(1)–S(32)	2.295(10)
Pt(2)–1(2)	2.766(3)	Pt(2)–S(2)	2.304(10)
Pt(2)–S(12)	2.284(10)	Pt(2)–N(21)	2.099(28)
Pt(2)–N(31)	2.104(32)	N(1)–C(2)	1.317(36)
N(1)–C(6)	1.404(50)	C(2)–S(2)	1.673(38)
C(2)–N(3)	1.369(48)	N(3)–C(4)	1.465(52)
C(4)–O(4)	1.224(53)	C(4)–C(5)	1.359(47)
C(5)–C(6)	1.358(60)	N(11)–C(12)	1.343(52)
N(11)–C(16)	1.422(42)	C(12)–S(12)	1.741(34)
C(12)–N(13)	1.332(46)	N(13)–C(14)	1.370(50)
C(14)–O(14)	1.292(61)	C(14)–C(15)	1.404(74)
C(15)–C(16)	1.323(66)	N(21)–C(22)	1.345(62)
N(21)–C(26)	1.391(58)	C(22)–S(22)	1.741(51)
C(22)–N(23)	1.298(48)	N(23)–C(24)	1.352(59)
C(24)–O(24)	1.228(49)	C(24)–C(25)	1.386(68)
C(25)–C(26)	1.377(57)	N(31)–C(32)	1.391(43)
N(31)–C(36)	1.353(72)	C(32)–S(32)	1.719(41)
C(32)–N(33)	1.340(52)	N(33)–C(34)	1.380(74)
C(34)–O(34)	1.223(56)	C(34)–C(35)	1.420(57)
C(35)–C(36)	1.278(62)		
Pt(2)–Pt(1)–I(1)	170.2(1)	Pt(2)–Pt(1)–N(1)	90.6(9)
I(1)–Pt(1)–N(1)	93.7(9)	Pt(2)–Pt(1)–N(11)	89.7(9)
I(1)–Pt(1)–N(11)	99.1(9)	N(1)–Pt(1)–N(11)	90.5(13)
Pt(2)–Pt(1)–S(22)	88.7(3)	I(1)–Pt(1)–S(22)	82.7(3)
N(1)–Pt(1)–S(22)	88.1(9)	N(11)–Pt(1)–S(22)	177.9(9)

(continued)

TABLE VII. *(continued)*

Pt(2)–Pt(1)–S(32)	89.4(3)	I(1)–Pt(1)–S(32)	86.3(3)
N(1)–Pt(1)–S(32)	179.8(9)	N(11)–Pt(1)–S(32)	89.3(10)
S(22)–Pt(1)–S(32)	92.1(4)	Pt(1)–Pt(2)–I(2)	172.5(1)
Pt(1)–Pt(2)–S(2)	88.7(3)	I(2)–Pt(2)–S(2)	84.5(3)
Pt(1)–Pt(2)–S(12)	89.4(3)	I(2)–Pt(2)–S(12)	87.3(3)
S(2)–Pt(2)–S(12)	89.3(4)	Pt(1)–Pt(2)–N(21)	88.8(8)
I(2)–Pt(2)–N(21)	94.7(8)	S(2)–Pt(2)–N(21)	92.0(8)
S(12)–Pt(2)–N(21)	177.7(5)	Pt(1)–Pt(2)–N(31)	93.1(10)
I(2)–Pt(2)–N(31)	93.7(10)	S(2)–Pt(2)–N(31)	178.2(10)
S(12)–Pt(2)–N(31)	91.0(8)	N(21)–Pt(2)–N(31)	87.8(11)
Pt(1)–N(1)–C(2)	118.5(27)	Pt(1)–N(1)–C(6)	119.3(20)
C(2)–N(1)–C(6)	122.1(31)	N(1)–C(2)–S(2)	127.5(29)
N(1)–C(2)–N(3)	117.6(34)	S(2)–C(2)–N(3)	114.8(21)
Pt(2)–S(2)–C(2)	104.8(12)	C(2)–N(3)–C(4)	124.3(27)
N(3)–C(4)–O(4)	116.7(28)	N(3)–C(4)–C(5)	111.9(39)
O(4)–C(4)–C(5)	131.0(39)	C(4)–C(5)–C(6)	125.2(42)
N(1)–C(6)–C(5)	118.1(29)	Pt(1)–N(11)–C(12)	124.4(21)
Pt(1)–N(11)–C(16)	123.0(29)	C(12)–N(11)–C(16)	112.0(33)
N(11)–C(12)–S(12)	121.2(25)	N(11)–C(12)–N(13)	123.2(30)
S(12)–C(12)–N(13)	115.6(29)	Pt(2)–S(12)–C(12)	105.1(13)
C(12)–N(13)–C(14)	125.8(38)	N(13)–C(14)–O(14)	118.2(44)
N(13)–C(14)–C(15)	112.5(41)	O(14)–C(14)–C(15)	129.3(42)
C(14)–C(15)–C(16)	120.9(37)	N(11)–C(16)–C(15)	125.3(40)
Pt(2)–N(21)–C(22)	123.6(27)	Pt(2)–N(21)–C(26)	118.7(28)
C(22)–N(21)–C(26)	117.7(34)	N(21)–C(22)–S(22)	119.8(29)
N(21)–C(22)–N(23)	121.5(43)	S(22)–C(22)–N(23)	118.6(38)
Pt(1)–S(22)–C(22)	106.1(15)	C(22)–N(23)–C(24)	124.6(40)
N(23)–C(24)–O(24)	120.6(45)	N(23)–C(24)–C(25)	115.9(34)
O(24)–C(24)–C(25)	123.5(46)	C(24)–C(25)–C(26)	120.4(42)
N(21)–C(26)–C(25)	119.8(43)	Pt(2)–N(31)–C(32)	116.3(30)
Pt(2)–N(31)–C(36)	125.4(24)	C(32)–N(31)–C(36)	118.3(33)
N(31)–C(32)–S(32)	127.5(32)	N(31)–C(32)–N(33)	119.6(37)
S(32)–C(32)–N(33)	112.5(26)	Pt(1)–S(32)–C(32)	104.7(13)
C(32)–N(33)–C(34)	124.1(33)	N(33)–C(34)–O(34)	119.9(41)
N(33)–C(34)–C(35)	110.3(41)	O(34)–C(34)–C(35)	129.7(56)
C(34)–C(35)–C(36)	128.1(50)	N(31)–C(36)–C(35)	118.7(41)

TABLE VIII. Bond Lengths (Å) and Angles (deg) for E

Br(1)–Pt(1)	2.617(4)	Pt(1)–Pt(2)	2.553(2)
Pt(1)–S(12)	2.310(7)	Pt(1)–S(22)	2.283(7)
Pt(1)–N(31)	2.089(22)	Pt(1)–N(41)	2.082(19)
Pt(2)–S(52)	2.486(6)	Pt(2)–N(11)	2.085(22)
Pt(2)–N(21)	2.101(21)	Pt(2)–S(32)	2.296(8)
Pt(2)–S(42)	2.298(7)	S(52)–C(52)	1.669(34)
N(11)–C(12)	1.494(40)	N(11)–C(16)	1.246(37)
C(12)–S(12)	1.659(32)	C(12)–N(13)	1.372(39)
N(13)–C(14)	1.292(42)	C(14)–C(15)	1.341(52)
C(15)–C(16)	1.334(44)	N(21)–C(22)	1.421(37)
N(21)–C(26)	1.297(38)	C(22)–S(22)	1.715(34)
C(22)–N(23)	1.299(39)	N(23)–C(24)	1.307(43)
C(24)–C(25)	1.355(47)	C(25)–C(26)	1.403(46)
N(31)–C(32)	1.420(38)	N(31)–C(36)	1.353(44)
C(32)–S(32)	1.659(34)	C(32)–N(33)	1.295(37)
N(33)–C(34)	1.323(41)	C(34)–C(35)	1.274(50)
C(35)–C(36)	1.439(49)	N(41)–C(42)	1.401(35)
N(41)–C(46)	1.264(33)	C(42)–S(42)	1.730(31)

(continued)

TABLE VIII. *(continued)*

C(42)–N(43)	1.340(38)	N(43)–C(44)	1.341(37)
C(44)–C(45)	1.320(41)	C(45)–C(46)	1.351(40)
C(52)–N(53)	1.333(45)	C(52)–N(51)	1.370(49)
N(53)–C(54)	1.312(49)	C(54)–C(55)	1.378(60)
C(55)–C(56)	1.378(42)	C(56)–N(51)	1.326(45)
Br(1)–Pt(1)–Pt(2)	174.7(1)	Br(1)–Pt(1)–S(12)	86.0(2)
Pt(2)–Pt(1)–S(12)	89.1(2)	Br(1)–Pt(1)–S(22)	88.1(2)
Pt(2)–Pt(1)–S(22)	89.9(2)	S(12)–Pt(1)–S(22)	89.6(3)
Br(1)–Pt(1)–N(31)	95.4(6)	Pt(2)–Pt(1)–N(31)	89.6(6)
S(12)–Pt(1)–N(31)	178.6(6)	S(22)–Pt(1)–N(31)	90.2(6)
Br(1)–Pt(1)–N(41)	92.6(6)	Pt(2)–Pt(1)–N(41)	89.6(6)
S(12)–Pt(1)–N(41)	92.6(6)	S(22)–Pt(1)–N(41)	177.7(6)
N(31)–Pt(1)–N(41)	87.5(8)	Pt(1)–Pt(2)–S(52)	172.0(1)
Pt(1)–Pt(2)–N(11)	92.8(7)	S(52)–Pt(2)–N(11)	94.3(7)
Pt(1)–Pt(2)–N(21)	90.5(6)	S(52)–Pt(2)–N(21)	93.7(6)
N(11)–Pt(2)–N(21)	87.4(9)	Pt(1)–Pt(2)–S(32)	89.2(2)
S(52)–Pt(2)–S(32)	83.9(2)	N(11)–Pt(2)–S(32)	177.6(7)
N(21)–Pt(2)–S(32)	91.2(6)	Pt(1)–Pt(2)–S(42)	89.1(2)
S(52)–Pt(2)–S(42)	86.9(2)	N(11)–Pt(2)–S(42)	90.9(7)
N(21)–Pt(2)–S(42)	178.2(6)	S(32)–Pt(2)–S(42)	90.5(3)
Pt(2)–S(52)–C(52)	108.1(13)	Pt(2)–N(11)–C(12)	115.6(17)
Pt(2)–N(11)–C(16)	128.0(23)	C(12)–N(11)–C(16)	116.4(25)
N(11)–C(12) -S(12)	125.8(21)	N(11)–C(12)–N(13)	114.7(25)
S(12)–C(12)–N(13)	119.5(22)	Pt(1)–S(12)–C(12)	106.4(10)
C(12)–N(13)–C(14)	122.3(28)	N(13)–C(14)–C(15)	122.5(31)
C(14)–C(15)–C(16)	116.1(30)	N(11)–C(16)–C(15)	128.0(32)
Pt(2)–N(21)–C(22)	121.7(18)	Pt(2)–N(21)–C(26)	122.4(20)
C(22)–N(21)–C(26)	115.7(25)	N(21)–C(22)–S(22)	120.6(21)
N(21)–C(22)–N(23)	122.4(28)	S(22)–C(22)–N(23)	116.9(23)
Pt(1)–S(22)–C(22)	108.2(10)	C(22)–N(23)–C(24)	119.9(28)
N(23)–C(24)–C(25)	122.5(31)	C(24)–C(25)–C(26)	116.3(31)
N(21)–C(26)–C(25)	123.1(30)	Pt(1)–N(31)–C(32)	121.1(18)
Pt(1)–N(31)–C(36)	121.5(19)	C(32)–N(31)–C(36)	116.9(24)
N(31)–C(32)–S(32)	121.2(20)	N(31)–C(32)–N(33)	119.4(29)
S(32)–C(32)–N(33)	119.3(24)	Pt(2)–S(32)–C(32)	108.6(10)
C(32)–N(33)–C(34)	122.7(29)	N(33)–C(34)–C(35)	122.7(31)
C(34)–C(35)–C(36)	117.9(35)	N(31)–C(36)–C(35)	119.9(32)
Pt(1)–N(41)–C(42)	122.4(17)	Pt(1)–N(41)–C(46)	123.3(19)
C(42)–N(41)–C(46)	114.3(23)	N(41)–C(42)–S(42)	120.6(21)
N(41)–C(42)–N(43)	124.4(26)	S(42)–C(42)–N(43)	114.8(21)
Pt(2)–S(42)–C(42)	105.1(10)	C(42)–N(43)–C(44)	114.3(25)
N(43)–C(44)–C(45)	124.3(27)	C(44)–C(45)–C(46)	116.4(28)
N(41)–C(46)–C(45)	126.0(27)	S(52)–C(52)–N(53)	115.0(28)
S(52)–C(52)–N(51)	126.4(27)	N(53)–C(52)–N(51)	118.0(31)
C(52)–N(53)–C(54)	121.2(36)	N(53)–C(54)–C(55)	125.5(38)
C(54)–C(55)–C(56)	109.7(33)	C(55)–C(56)–N(51)	127.3(38)
C(52)–N(51)–C(56)	117.5(32)		

Reaction of pyrimidine-2-thione with $PtCl_4^{2-}$ and $PtBr_4^{2-}$ in aqueous ethanol or methanol, following the general procedure used for $[Pt(pymS)_2I]_2$ [1] gave red compounds of stoichiometry $Pt(pymS)_2X$ (X = Cl or Br).

Structures of $[Pt(pymS)_2X]_2$ (X = Cl, Br)

In the case of the chloride, the crystals were of adequate quality for X-ray diffraction study. This confirmed (Fig. 1) that $[Pt(pymS)_2Cl]_2$ is a dinuclear Pt(III) complex formed by four pyrimidine-2-thionato-bridges with chlorine atoms in the terminal positions of the dinuclear unit.

The chloride is not, however, isostructural with the iodide. In the latter, each platinum atom is bonded to 2N and 2S atoms arranged in *cis*-geometry. This contrasts with the chloride where the Pt atoms have inequivalent donor atom sets: Pt(1) is bonded to three sulphur atoms and one nitrogen atom, whereas Pt(2) is bonded to three nitrogens and one

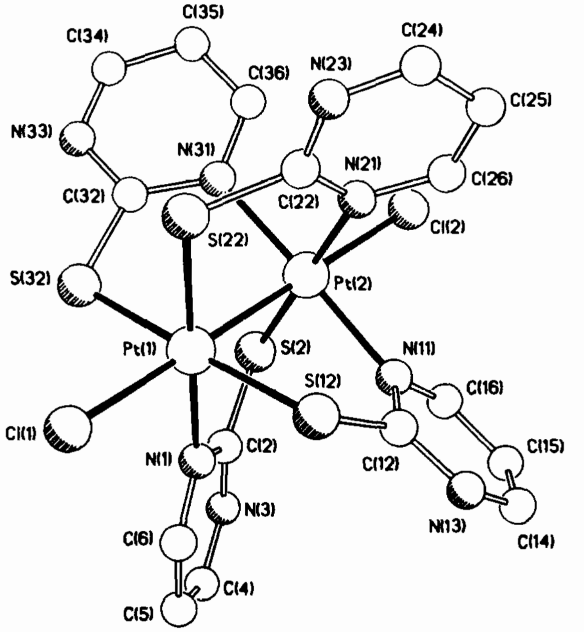

Fig. 1. Molecular structure of [Pt(pymS)$_2$Cl]$_2$, giving the crystallographic numbering scheme.

sulphur. The PtS$_3$N unit is rotated by ~29° relative to the PtN$_3$S unit about the Pt–Pt bond.

The Pt(1)–S bonds are, on average, longer (2.306(3)–2.346(3), mean 2.33 Å) than the Pt(2)–S(2) bond (2.295(3) Å). The shortest Pt(1)–S bond (2.306 Å) is that to S(22), which is *trans* to N(1). Pt(1)–N(1) (2.121(10) Å) is longer than the three Pt(2)–N bonds (2.055(10)–2.099(9), mean 2.07 Å), the longest Pt(2)–N being that to N(21), which is *trans* to Pt(2)–S(2). Pt(1), which has the longer Pt–S and Pt–N bonds, has a shorter Pt–Cl bond (2.440(3) Å) than Pt(2)–Cl(2) (2.463(3) Å).

The bond angles about each Pt atom do not differ appreciably from 90°, the biggest deviation being for Cl(1)–Pt(1)–N(1) (92.1(2)°). Each platinum atom is raised slightly (0.03 and 0.02 Å for Pt(1) and Pt(2) respectively) above its S$_3$N or N$_3$S donor atom set towards the coordinated chlorine atom.

Comparisons between the details of the geometry of [Pt(pymS)$_2$Cl]$_2$ and [Pt(pymS)$_2$I]$_2$ are complicated by the differences in the orientation of one of the bridging ligands. It is difficult, therefore, to assess whether the shortening in the Pt–Pt bond (2.518(1) Å in the chloride *cf.* 2.554(1) Å in the iodide, Table VI) arises from the replacement of iodide by chloride in the terminal positions, as found for [Pt$_2$(P$_2$O$_5$H$_2$)$_4$X$_2$] [12], or from the change in the bridge orientation. One noticeable difference is the near linearity of the Cl–Pt–Pt–Cl chain (Pt(1)–Pt(2)–Cl(2) = 179.7(1)°; Pt(2)–Pt(1)–Cl(1) = 178.7(1)°) compared with I–Pt–Pt–I in the iodide (Pt–Pt–I = 173.8(1)° and 172.6(1)° [1]). The Pt–S bonds (mean 2.294 Å) and Pt–N bonds (mean 2.109 Å) in the iodide are, within statistical significance, the same as the Pt(2)–S(2) (2.295 Å) and Pt(1)–N(1) (2.121 Å) bonds in the chloride. The Pt–Cl bond lengths (2.440(3) and 2.463(3) Å) are very similar to those found for axial Pt–Cl bonds in other Pt(III) complexes [12, 13]. The lengthening in such bonds, as compared to the Pt–Cl bonds in mononuclear complexes of Pt(II) and Pt(IV) or to equatorial Pt–Cl bonds in dinuclear Pt(III) compounds (e.g., 2.285 and 2.296 Å for equatorial Pt–Cl in [Cl(NH$_3$)$_2$Pt(1-MeU)$_2$-PtCl$_3$]·2H$_2$O [13]), is generally attributed to the high *trans*-influence of the Pt–Pt bond.

In the case of [Pt(pymS)$_2$Br]$_2$ the crystals were of poor quality and, although X-ray diffraction data were measured and indicate a dinuclear structure similar to the iodide, a satisfactorily refined structure has not yet been obtained.

Compounds Containing >2pymS$^-$ per Pt

When pyrimidine-2-thione was reacted with PtCl$_4^{2-}$ using an excess over a 2:1 mole ratio of pymS: Pt a red compound analysing as Pt$_2$(pymS)$_5$Cl was obtained, but not in crystalline form suitable for X-ray studies.

Reaction of PtBr$_4^{2-}$ with an excess of pymSH gave a few orange–red crystals which were studied by X-ray diffraction. This showed that the product had a dinuclear structure Pt$_2$(pymS)$_4$BrX, with X corresponding to both pymS$^-$, coordinated by S, and halide, (Fig. 2), with estimated relative occupancies of 80% and 20% respectively. In other words, the crystals which formed represented a co-crystallisation of Pt$_2$(pymS)$_5$Br and the dihalide. Although the accuracy of the determination was inevitably limited by this partial site occupancy, the following features of the structure may be noted.

The Pt–Pt distance (2.554(1) Å) is the same as that found in [Pt(pymS)$_2$I]$_2$, but the Pt–Br bond (2.617(3) Å) is intermediate between Pt–Cl and Pt–I in [Pt(pymS)$_2$X]$_2$ (X = Cl, I). The Pt–N bond lengths (2.08–2.11(2) Å) are similar to those in [Pt(pymS)$_2$X]$_2$ (X = Cl, I). The two PtS$_2$N$_2$ units are rotated by ~25.5° relative to each other.

In view of the above results it seems possible that a platinum(III) complex Pt$_2$(pymS)$_6$ with four bridging and two terminal pyrimidine-2-thionato-ligands might be obtained. Attempts to prepare such a compound gave a red product with C, H, and N analyses near those required for the stoichiometry Pt(pymS)$_3$, but the crystals have so far proved unsuitable for X-ray diffraction studies so we were unable to confirm the true nature of the compound. (Continued efforts to obtain good crystals are in progress).

Complexes with other Pyrimidine-2-thiones and Related Ligands

As well as establishing that analogues of [Pt(pymS)$_2$I]$_2$ with anions other than I$^-$ in the axial posi-

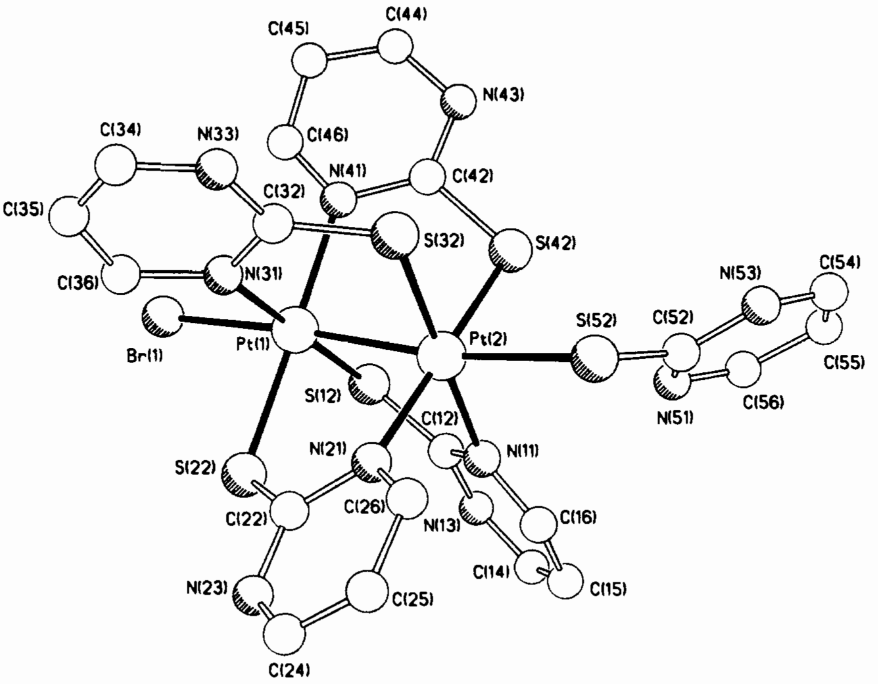

Fig. 2. Molecular structure of $Pt_2(pymS)_4Br(pymS/Br)$, giving the crystallographic numbering scheme.

tions could be obtained, we were also interested in examining the effect of substituents on the pyrimidine ring on the formation of dinuclear Pt(III) complexes of this type.

Reaction of PtX_4^{2-} (X = Cl, I) with 4-methylpyrimidine-2-thione (4-mepymSH) gave red $Pt(4\text{-}mepymS)_2Cl$ and purple $Pt(4\text{-}mepymS)_2I$ respectively, but the compounds were not obtained in a form suitable for single crystal X-ray studies. The reaction of PtI_4^{2-} with 2-thiouracil (2-TUH) gave blue–purple $Pt(2\text{-}TU)_2I$. This formed triclinic crystals which, though subject to cracking and decrepitation, gave a fragment which, after coating, proved adequate to define the main geometry. This structural result (Fig. 3) confirmed the formation of a dinuclear geometry analogous to $[Pt(pymS)_2I]_2$, with the bridging 2-thiouracilato-ligands arranged so that each Pt atom is bonded to 2S and 2N atoms in *cis*-dispositions. The molecule has approximate, non-crystallographic C_2 symmetry.

The Pt–Pt and Pt–I bond lengths (Table VIII) are, within statistical significance, the same as those in the pyrimidine-2-thione analogue. The PtN_2S_2 planes again are not eclipsed; there is a ~25° twist about the Pt–Pt axis. The I–Pt–Pt–I chain is non-linear (Pt–Pt–I = 170.2 and 172.5°).

When 4,6-dimethylpyrimidine-2-thione (Me_2pymSH) and *N*-methyl-pyrimidine-2-thione (*N*-MepymSH) were used as potential bridging ligands in analogous reactions with PtX_4^{2-} (X = Cl or I) yellow or orange yellow Pt(II) compouds were obtained. In the case of *N*-methylpyrimidine-2-thione the compounds were $Pt(N\text{-}mepymSH)_2Cl_2$ and $Pt(N\text{-}mepymSH)I_2$, but with Me_2pymSH the inner complex $Pt(Me_2pymS)_2$ was formed from both $PtCl_4^{2-}$ or PtI_4^{2-}. Crystallographic studies on $Pt(Me_2pymS)_2$ [14] confirmed its formulation as a planar, inner complex, but, although refinement in space group *C2/m* reached

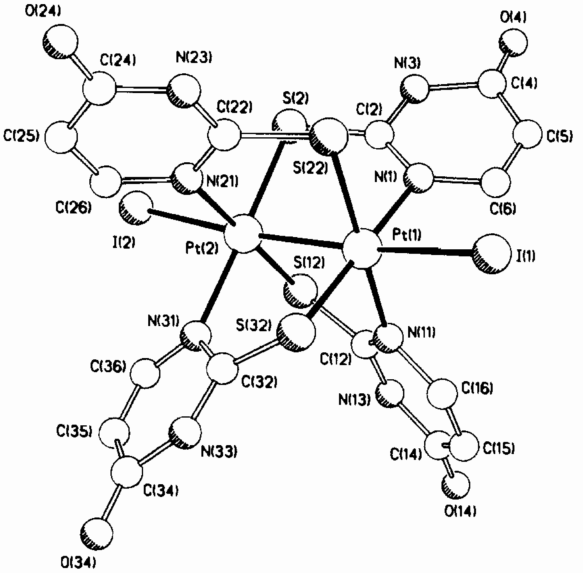

Fig. 3. Molecular structure of $[Pt(2\text{-}TU)_2I]_2$, giving the crystallographic numbering scheme.

$R = 0.016$, disorder precluded assignment of *cis*- or *trans*-geometry [14]*.

Reaction of pyridine-2-thione (pySH) with PtX_4^{2-} (X = Cl, Br) gave yellow platinum(II) complexes of composition Pt(pySH)(pyS)X. When PtI_4^{2-} was employed, an initial yellow precipitate quickly redissolved with the formation of a dark green solid of composition Pt(pySH)(pyS)I or Pt(pyS)$_2$I but the compound was insufficiently crystalline for proper characterisation by X-ray diffraction.

Yellow Pt(II) complexes of stoichiometry PtL_2X_2 were formed by 2-mercapto-thiazoline and by pyrimidine-2-one, 1-methylpyrimidine-2-one, and 4,6-dimethylpyrimidine-2-one (see Table I).

The results of this work show that the formation of dinuclear Pt(III) species, analogous to [Pt(pymS)$_2$-I]$_2$ by direct reaction of pymSH with PX_4^{2-} in air can be extended to anions, X^-, other than iodide. As may be seen from the 'space-filling' drawing of [Pt(2-TU)$_2$I]$_2$ in Fig. 4, the axial positions in such compounds are quite open and there are no significant steric constraints to the binding of ligands in terminal positions. Substituted pyrimidine thiones can also form the bridging groups, provided the substituents do not offer steric hindrance in the axial positions of [PtL$_2$X]$_2$, as with 4,6-dimethylpyrimidine-2-thione, or replace the ionizable proton on N(1).

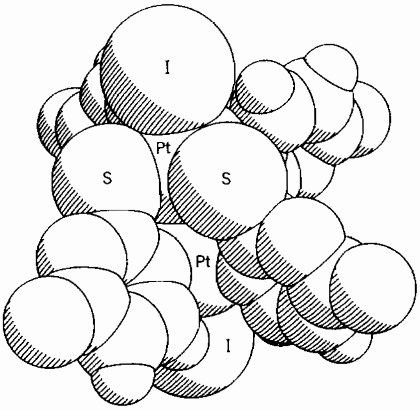

Fig. 4. Space filling representation of [Pt(2-TU)$_2$I]$_2$ illustrating the sterically unhindered axial positions.

The use of pyrimidine-2-one, in which the sulphur atom of pymSH is replaced by oxygen, does not give analogous Pt(III) compounds, at least under the same experimental conditions. Dinuclear platinum(III) complexes involving N–O bridging units are well-established, but are prepared by alternative synthetic strategies, usually involving the use of oxidising agents, such as concentrated nitric acid [13].

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*Crystallographic details are given in the *Ph.D. Thesis* of R. W. Rollins.