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THE PREPARATION AND PROPERTIES OF COMPOUNDS CONTAINING Pt(III)

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CONTENTS

ABBREVIATIONS

dmso	dimethylsulphoxide
en	ethylenediamine
MeC	1-methylcytosine anion
4Mepy	4-methylpyridine
MeU	1-methyluracil anion
pic	picoline
pn	propylenediamine
pop	$P_2O_5H_2^{2-}$
py	pyridine
pyms	pyrimidine-2-thione anion
pyr	α-pyridone anion
pyrl	α-pyrrolidone anion
tn	trimethylenediamine

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A. INTRODUCTION

The aim of this review is to survey the materials coming under the broad heading of platinum(III) compounds. In this context it should be remembered that formal oxidation numbers are essentially a convenience; they do not necessarily provide information on the reactivity/stability of particular compounds but they can provide a useful means of classification. In the following pages we have sought to present information on compounds which have an average platinum oxidation number of (III) (although as in the trihalides they actually contain Pt(II) and Pt(IV)) as well as compounds which contain one or more Pt(III) atoms such as the platinum blues or pure Pt(III) compounds. There are difficulties in deciding whether to classify a compound as Pt(II)–Pt(IV) or Pt(III)–Pt(III) and this subject has been dealt with previously [1,2]. Although mixed valence compounds containing Pt(III) centres are covered we have excluded the partially oxidised one-dimensional compounds such as those based on $Pt(CN)_4^{2-}$ since these types of materials have been thoroughly reviewed elsewhere [3,4]. For convenience we have divided the material in the text into sections dealing with mononuclear compounds, mixed valence Pt(II)–Pt(IV) compounds, binuclear compounds and platinum blues and related systems. It should be noted that the latter section includes binuclear compounds that contain biologically relevant ligands (e.g. α-pyridone, 1-methyluracil). The literature has been reviewed up to 1 June 1984.

B. MIXED VALENCE Pt(II)–Pt(IV) SYSTEM

(i) Trihalides

The chloride, bromide and iodide systems are known and in the cases of chloride and bromide have been fully characterised. The chemistry of the trihalides has a history going back into the 19th century [5] but they have only recently been fully investigated and their structures determined.

The preparations are similar in each case. The tribromide is formed [6] by bromination of the metal in a closed system at 900°C. A temperature gradient of 900–300°C enables transportation of the crystals to the colder zone where they appear as blackish green needles. The trichloride is made [7] in the same manner with a temperature gradient of 600–400°C. The triiodide can be obtained [8] by sealing potassium iodide and iodine in an ampoule together with water and platinum metal. The mixture is heated at 160°C for four days to give black crystals which are washed with water to remove any K_2PtI_6 present.

Much of the early work on the trihalides provided thermodynamic data. For example, Shchukarev et al. [9] studied their heats of formation (eqn. 1). Their thermal stabilities [8] are intermediate between the di- and tetrahalides (eqn. 2).

$$2\ PtX_4 \rightarrow 2\ PtX_3 + X_2 \tag{1}$$

$X = Br\ \Delta H = 20.8$ kcal mol^{-1}

$X = Cl\ \Delta H = 29.1$ kcal mol^{-1}

$$PtI_4 \xrightarrow{220°C} PtI_3 \xrightarrow{310°C} Pt_3I_8 \xrightarrow{370°C} \alpha/\beta\ PtI_2 \xrightarrow{440°C} Pt \tag{2}$$

More recently [10,11] the dissociation pressures of the trihalides and the ability of $PtCl_3$ to form hydrated compounds of the type $PtCl_3 \cdot nH_2O$ ($n = 1$–6) have been reported.

Studies on the magnetic properties of the trihalides were carried out by Syrkin and Belova [12] who measured the magnetic susceptibility of $PtCl_3$ and concluded that the value obtained was appropriate to Pt(II) and Pt(IV) systems and hence showed, for the first time, their mixed valence nature. Several years later Argue and Banewicz [13] showed that PtI_3 exhibits temperature-dependent paramagnetism. This was attributed to impurities rather than the presence of Pt(III) atoms.

The first structure to be determined [6], was that of $PtBr_3$. This consists of Pt_6Br_{12} and $\frac{1}{\infty}(PtBr_2Br_{4/2})$ units. The six platinum atoms of the Pt_6Br_{12} unit form an octahedron with the twelve bromine atoms lying at the edges. In this part of the structure each platinum has a square-planar environment similar to that of $PtBr_2$. The other unit contains platinum atoms surrounded octahedrally by bromine atoms, comparable to PtI_4; each octahedron is distorted and linked to two others via common edges to form an infinite chain. The two types of units are only loosely bonded together allowing the crystals to readily cleave into fibres. Later work showed that $PtCl_3$ has a similar structure [7]. Due to its amorphous nature X-ray work has not been attempted on PtI_3 and its structure is still not established.

Finally, PtI_3 has been studied [14,15] both for its ability to form compounds of the type M_2PtI_5 ($M = Rb, NH_4^+$) and in reactions with pyridine to give typically $PtI_2 \cdot 6$ py and $PtI_2 \cdot 2$ py.

(ii) Amine-halides

Like the trihalides these compounds have a long history. Before the turn of the century both $Pt(NH_3)(en)Br_3$ and $Pt(NH_3)(py)Cl_3$ had been reported [16]. Later work in the 1920's and 30's produced $PtCl_3(en)$ [17] and $Pt(NH_3)_2Cl_3$ [18]. More recent work has expanded the field enormously with many amines and sulphur containing species being used as ligands. The area has been reviewed [19,20] and so only a few remarks are made here for completeness.

The general structure of the compounds is that of a chain of platinum atoms bridged by halide ions. The structure of Pt(en)Br_3 is shown in Fig. 1. As can be seen the compounds consist of two units which contain Pt(II) and Pt(IV) and the formulae should more correctly be written as, for example, [Pt(en)Cl_2][Pt(en)Cl_4]. In this case the two units are the square planar [Pt(en)Cl_2] and the tetragonal bipyramidal [Pt(en)Cl_4]. From the above description it is apparent that the Pt–X distance will vary, in any given compound, depending on the oxidation state of the platinum atom in question; the Pt(IV)–X distance being shorter than the Pt(II)–X distance thus allowing the oxidation state of any particular platinum atom to be judged. Although the platinum atoms can be crystallographically classified as Pt(II) or Pt(IV) the picture is complicated somewhat when the bond distances in a series of related compounds are considered. It can be seen in Table 1 that the Pt–Pt distance depends on the bridging halogen. The Pt(II)–X distances stay roughly constant and so the changes in the Pt–Pt separation can be related to the changes in the Pt(IV)–X bond length. As the Pt(IV)–X distances increases, which it is found to do as the halogen size increases, there is greater overlap of the electronic systems of the metal and the halogen. This can be shown by the variation in colour of the compounds as the halogen is changed; chloro compounds are normally red, bromo compounds a shiny dark green and iodo compounds a golden metallic

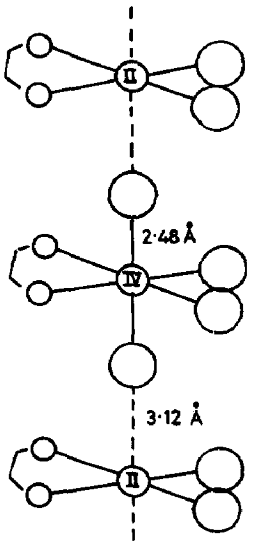


Fig. 1. Columnar structure of [Pt(en)Br_3].

TABLE 1

Pt–Pt and Pt–halide distances (in Å) for some platinum–amine-halides. R is the ratio Pt(IV)–X distance/Pt(II)–X distance

Compound	Pt–Pt	Pt(IV)–X	Pt(II)–X	R
$[Pt(NH_3)_2Cl_2][Pt(NH_3)_2Cl_4]$	5.33	2.03	3.30	0.62
$[Pt(pn)_2][PtCl_2(pn)_2](ClO_4)_4$	5.501	2.326	3.069	0.72
$[Pt(en)_2][PtCl_2(en)_2](ClO_4)_4$	5.403	2.318	3.095	0.74
$[Pt(tn)_2][PtCl_2(tn)_2](BF_4)_4$	5.395	2.299	3.096	0.75
$[Pt(en)Br_2][Pt(en)Br_4]$	5.60	2.48	3.125	0.79
$[Pt(NH_3)_2Br_2][Pt(NH_3)_2Br_4]$	5.53	2.50	3.03	0.83
$[Pt(NH_2C_2H_5)_4][Pt(NH_2C_2H_5)_4Br_2]Br_4 \cdot 4H_2O$	5.586	2.479	3.139	0.79
$[Pt(tn)_2][PtBr_2(tn)_2](ClO_4)_4$	5.501	2.546	2.955	0.86
$[Pt(tn)_2][PtBr_2(tn)_2](BF_4)_4$	5.462	2.541	2.921	0.87
$K_4(PtI_4)(PtI_6)$	5.74	2.74	3.00	0.91
$[Pt(en)_2][PtI_2(en)_2](ClO_4)_4$	5.82	2.726	3.093	0.93

colour. As R (the ratio of the Pt(IV)–X and Pt(II)–X distances) approaches one the metal sites become more difficult to distinguish and thus for compounds like $[Pt(en)_2][Pt(en)_2I_2](ClO)_4$ it may be more appropriate to consider all the platinums as Pt(III). This assertion has been supported by X-ray photoelectron spectroscopy on the series of compounds $[Py(en)_2][Pt(en)_2X_2](ClO_4)_4$ (X = Cl, Br, I). On going from the chloro to the bromo compound the separation of the two sets of Pt 4*f* peaks is reduced whilst in the iodo compound the spectrum is interpreted as indicating almost equivalent platinum atoms [21]. For a more detailed discussion of this area see refs. 19, 20, 22.

C. BINUCLEAR COMPOUNDS

(i) Sulphate bridged species

The first of the compounds in this category was prepared almost eighty years ago [23] by electrolytic dissolution of platinum in sulphuric acid. At that time it was formulated as $KPt(SO_4)_2 \cdot H_2O$, however, in 1976 the binuclear formula $K_2[Pt_2(SO_4)_4(H_2O)_2]$, **1**, was established by X-ray crystallography [24]. The corresponding ammonium salt to **1** was prepared via reaction of $Pt(NH_3)_2(NO_2)_2$ with sulphuric acid [25], the equilibria in eqn. (3) being proposed to account for this reaction.

$$H_2SO_4 + Pt(NH_3)_2(NO_2)_2 \rightleftharpoons [Pt(NH_3)_2(NO_2)(NO_2H)]HSO_4$$

$$[Pt(NH_3)_2(NO_2)(NO_2H)]HSO_4 \rightleftharpoons Pt(NH_3)_2(NO_2H)(SO_4) + HNO_2$$

$$H_2SO_4 + Pt(NH_3)_2(NO_2H)(SO_4) \rightleftharpoons [Pt(NH_3)_2(NO)(SO_4)]HSO_4 + 2\ H^+$$
$$H_2SO_4 + [Pt(NH_3)_2(NO)(SO_4)]HSO_4 \rightleftharpoons 1/2(NH_4)_2[Pt_2(SO_4)_4(H_2O)_2] + NH_4SO_4 \qquad (3)$$

Compound **1** has the typical "lantern" structure which is a familiar feature of many of the binuclear compounds in this review with a Pt–Pt separation of 2.466 Å. Reaction [26] of an aqueous solution of **1** with dmso yields yellow crystalline $K_2[Pt_2(SO_4)_4(dmso)_2]\ 4H_2O$, **2**, which has a Pt–Pt distance of 2.471 Å and the structure shown in Fig. 2. As would be expected by comparison with the reactions of rhodium acetate [43,44] replacement of the axial aquo ligands of **1** is a general reaction. Heating $K_2Pt(NO_2)_4$ in sulphuric acid [27] gives the yellow salt $K_2(H_3O)[Pt_2(SO_4)_4(H_2O)(OH)]$, **3**, which undergoes a wide variety of reactions [28], as shown below (eqn. 4)

$$\mathbf{3} + Cs_2SO_4 \rightarrow Cs_2(H_3O)[Pt_2(SO_4)_4(H_2O)(OH)]$$
$$\mathbf{3} + KOH \rightarrow K_4[Pt_2(SO_4)_4(OH)_2]H_2O$$
$$\mathbf{3} + KCl \rightarrow K_4[Pt_2(SO_4)_4Cl_2]H_2O$$
$$\mathbf{3} + CsBr \rightarrow KCs_3[Pt_2(SO_4)_4Br_2]H_2O$$
$$\mathbf{3} + NH_4OH \rightarrow K_2[Pt_2(SO_4)_4(NH_3)_2]H_2O$$
$$\mathbf{3} + KNO_2 \rightarrow K_4[Pt_2(SO_4)_4(NO_2)_2]H_2O \qquad (4)$$

For all of the eqn. (4) reactions the infra-red spectra of the products reveal

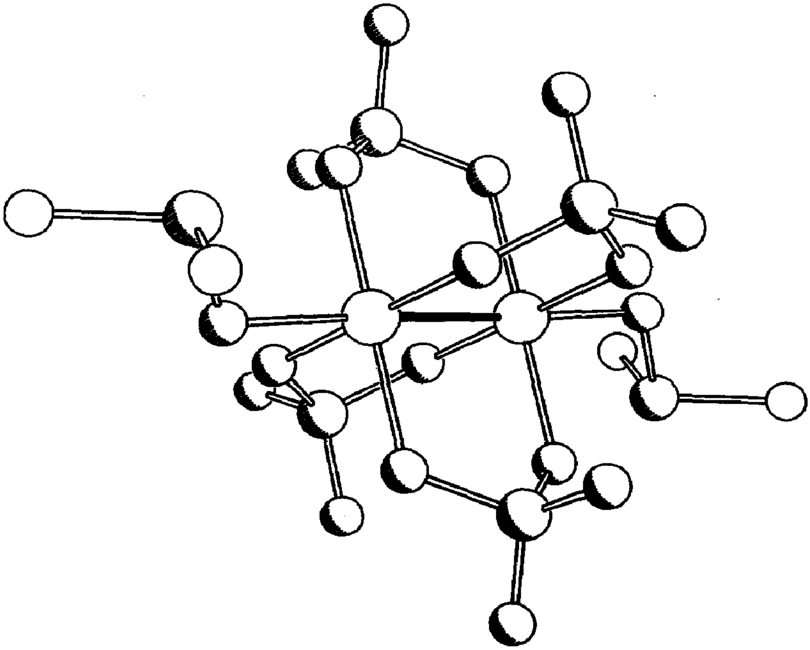


Fig. 2. The crystal structure of the anion in $K_2[Pt_2(SO)_4(dmso)_2]\cdot 4H_2O$ [26].

that the sulphate framework is unchanged with four bands in the range of the ν(SO) vibrations (919, 995, 1150 and 1290 cm^{-1}) and four bands in the sulphate bending region (503, 590, 653 and 677 cm^{-1}) characteristic of bridging sulphato groups. Attempts to cleave the sulphato bridged Pt(III) compounds using potassium chloride or hydrochloric acid result in the formation of K_2PtCl_4 and K_2PtCl_6, whilst potentiometric titration of **3** confirms the average oxidation state of the platinum as (III) [28].

(ii) Phosphate bridged species

It was reported in 1980 that if *cis* or *trans* $Pt(NH_3)_2(NO_2)_2$ is heated with phosphoric acid at 100°C then a mixture of brown, green and blue precipitates is obtained [30]. Compounds formulated as $(NH_4)_2[Pt_2(HPO_4)_4(H_2O)_2]$, **4**, $(NH_4)_2[(H)_4Pt_2(PO_4)_4(H_2O)_2]$, **5**, $(NH_4)_4[(H)_2Pt_2(PO_4)_4(NH_3)_2(H_2O)]$, **6**, and related analogues were isolated from these precipitates, although later work (discussed below) cast doubt on the formulations **5** and **6**.

In 1982 Cotton et al. [29] were able to obtain an X-ray crystal structure of $Na_2[Pt_2(PO_4)_4(H_2O)_2]$, **7** which reveals the expected structure with a Pt–Pt distance of 2.486 Å. Later studies [31] were carried out on the $[Pt_2(HPO_4)_4]^{2-}$ anion. To this end solutions of $[Pt_2(HPO_4)_4]^{2-}$ in phosphoric acid were reacted with methanolic solutions of pyridine and substituted pyridines to give yellow solids of general formula $(BH)_2[Pt_2(HPO_4)_4B_2]$, **8** (B = heteroaromatic ligand). These compounds are air stable, slightly soluble in organic solvents and all have closely similar infrared spectra. The IR and UV/VIS data are consistent with the assumption that the B molecules act as ligands in the axial positions. The compound having B = pyridine, $(pyH)_2[Pt_2(HPO_4)_4(py)_2]$, **9** can be used in a variety of reactions, eqn. (5)

$$\mathbf{9} \xrightarrow[H_2O]{PPh_3} Pt_2(HPO_4)_3(PPh_3)_2(H_2O)_2$$

$$\mathbf{9} \xrightarrow[(2)\ H_2O]{(1)\ PPh_3\ CH_3CO_2H} \quad (1)\ Pt_2(HPO_4)_3(PPh_3)_2(H_2O)_2$$

$$(2)\ Pt(O_2CCH_3)_2(PPh_3)_2$$

$$\mathbf{9} \xrightarrow{CN\text{-}t\text{-}Bu} Pt(CN\text{-}t\text{-}Bu)_2(CN)_2 \qquad (5)$$

Attempts to obtain crystals of **9** suitable for X-ray crystallography were unsuccessful; however, when the filtrate left after isolation of **9** was kept for several days large crystals were obtained. Although similar in colour to **9** X-ray crystallography revealed the presence of only one pyH^+ cation and the product is thus formulated as $(pyH)[Pt_2(H_2PO_4)(HPO_4)_3(py)_2]H_2O$, **10**.

Unfortunately the hydrogen atoms in **10** were not located in the crystal structure determination. The authors concluded [31] that **10** contains the $[Pt_2(H_2PO_4)(HPO_4)_3(py)_2]^-$ anion, as already stated, because of the observation of only one pyH^+ cation and also because none of the oxygen atoms in the structure have contacts indicative of an H_3O^+ cation. The pattern of P–O distances and O···O contacts is also used to support the proposed presence of a bridging $H_2PO_4^-$ group. It was also proposed that analogues of **10** are present as impurities in all of the preparations of compounds **8** resulting in the microanalyses being low in carbon and high in hydrogen for these latter compounds. Finally, it should be noted that Cotton and co-workers [29,31] did not obtain any compounds of the type **5** or **6** during their studies and in fact they regard the existence of these compounds as being doubtful.

Binuclear Pt(II) species with diphosphite ligands such as $Pt_2(pop)_4^{4-}$ (pop = $P_2O_5H_2^{2-}$) undergo oxidative addition with halogens or methyl iodide to give binuclear Pt(III) compounds, [32,32a,33] (eqn. 6.)

$$K_4[Pt_2(pop)_4]\ 2\ H_2O + CH_3I \rightarrow K_4[Pt_2(pop)_4(CH_3)I]$$

$$K_4[Pt_2(pop)_4]\ 2\ H_2O + X_2 \rightarrow K_4[Pt_2(pop)_4X_2] \qquad (6)$$

The Pt–Pt bond length in $K_4[Pt_2(pop)_4Cl_2]$, **11**, is 2.695 Å, compared with 2.925 Å in the starting material (Fig. 3). The spectral data for the $Pt_2(pop)_4X_4^{4-}$ species are summarised in Table 2. The ^{31}P NMR spectra show single resonances with ^{195}Pt satellites, the chemical shift and $^1J(PtP)$ coupling constant varying with the halogen. Additional lines due to the $^{195}Pt^{195}Pt$ (~ 11%) isotopomer are also observed, the $^2J(PtP)$ coupling showing that binuclear structure is retained in solution. The ^{195}Pt NMR data are consistent with the above interpretation; the spectrum is made up of a quintet of quintets together with signals due to the $^{195}Pt^{195}Pt$ isotopomer again indicating a binuclear structure in solution as well as confirming that the halogens occupy the axial positions. The ^1H NMR of $K_4[Pt_2(pop)_4(CH_3)I]$ consists of a quintet (δ 1.51, $^3J(PH)$ 5.24 Hz) with two sets of ^{195}Pt satellites ($^2J(PtH)$ 52.66 Hz, $^3J(PtH)$ 18.83 Hz) as well as lines due to the $^{195}Pt^{195}Pt$ isotopomer. This data together with ^{13}C, ^{195}Pt and ^{31}P NMR confirms that the methyl and iodo groups are in the axial sites occupied by chloride ions in **11**. The $\nu(Pt–Pt)$ and $\nu(Pt–X)$ vibrations of aqueous solutions of $K_4[Pt_2(pop)_4X_2]$ were obtained by resonance Raman spectroscopy [32,32a]. Increased mixing of halide character into the metal orbitals in the order I > Br > Cl was invoked [32] to explain the changes in $\nu(Pt–Pt)$ frequency and the electronic spectra on going from iodide to chloride, although a later paper [32a] attributes the change in $\nu(Pt–Pt)$ frequency to kinematic coupling between the Pt–Pt and Pt–X stretching

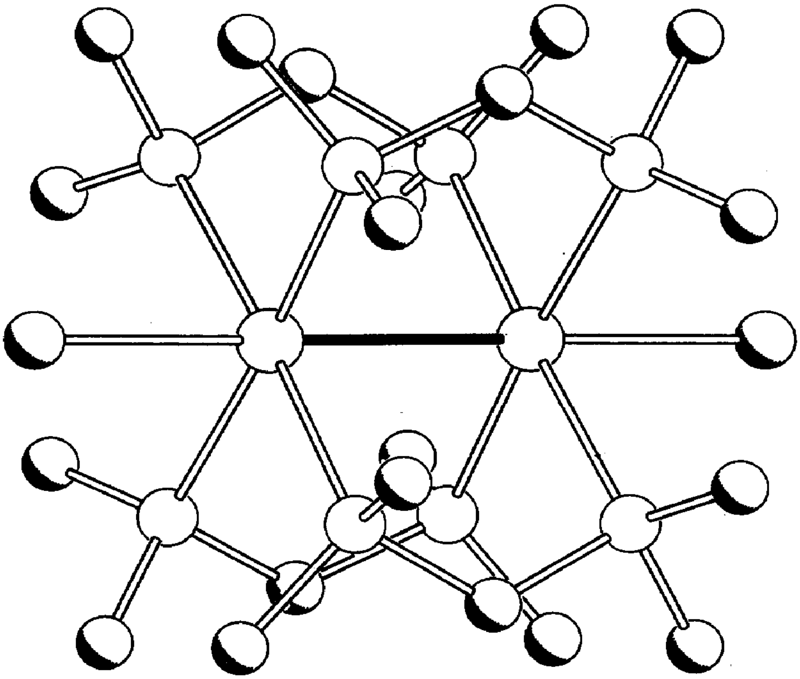


Fig. 3. The crystal structure of the anion in $K_4[Pt_2(pop)_4Cl_2]$ [33].

motions. The visible spectral data were interpreted as follows. Formation of the binuclear Pt(III) species is accompanied by the transfer of two electrons to the incoming halogen. The electronic configuration for the Pt(II)–Pt(II) complex is $(d\sigma)^2(d\sigma^*)^2$ and for the Pt(III)–Pt(III) complex is $d(\sigma)^2$ in accord with the observed reduction in Pt–Pt separation. The higher energy, more intense, components of the electronic spectra are assigned to $d\sigma \rightarrow d\sigma^*$ transitions.

Finally, partial oxidation of $K_4[Pt_2(pop)_4]$ $2H_2O$ using bromine water has been reported [33] to give $K_4[Pt_2(pop)_4Br]$ $3H_2O$, **12**, which has an average oxidation number for platinum of 2.5. Similar reactions give the chloro and iodo species. Interestingly, crystals of **12** have a conductivity of

TABLE 2

NMR data for $K_4[Pt_2(pop)_4X_2]$ compounds

Complex	$\delta^{195}Pt$	$\delta^{31}P$	$^1J(PtP)$ (Hz)	$^2J(PtP)$ (Hz)	Raman (cm^{-1})		UV/VIS (nm)
					ν(Pt–Pt)	ν(PtX)	
$K_4[Pt_2(pop)_4Cl_2]$	−4236	27.96	2085	88	158	304	345, 282
$K_4[Pt_2(pop)_4Br_2]$	−4544	24.01	2100	82	134	222	340, 305
$K_4[Pt_2(pop)_4I_2]$	−5103	18.01	2148	75	100	195	435, 330

$\sim 10^{-3}$ ohm^{-1} cm^{-1}, indicating semiconductor properties. Whatever the halide the compounds exist as golden or copper-bronze metallic-like crystals and have broad absorbances at ca. 600 nm in the solid state which are absent in aqueous solutions. Their aqueous solutions were shown to contain $Pt_2(pop)_4^{4-}$ and $Pt_2(pop)_4X_2^{4-}$ ions by UV/VIS and resonance Raman spectroscopy. The structure of **12** is quite similar to the non-oxidised starting material; the Pt–Pt distance is 2.793 Å in **12** compared with 2.695 Å in **11**. Both compounds can be described in terms of roughly cylindrical $Pt_2(pop)_4^{x-}$ "barrels" held together by strong $K^+ \cdots O^-$ interactions. These barrels are stacked end to end and in **12** bromine atoms connect adjacent $Pt_2(pop)_4^{3-}$ units to provide a pathway for conduction [33].

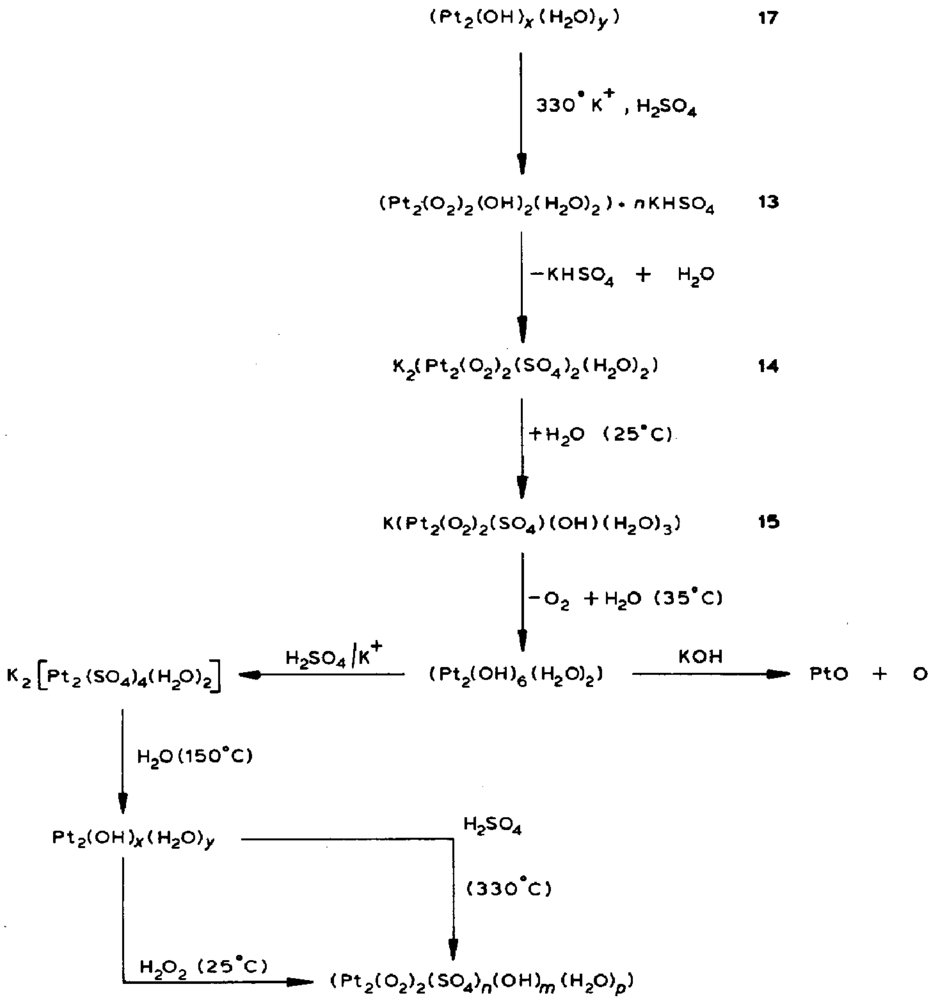
(iii) Hydroxide and peroxide bridged species

The first examples in this class were isolated by Russian workers [27,34] who heated $K_2Pt(NO_2)_4$ in H_2SO_4 at 100°C to give a precipitate formulated as $K_2(H_3O)[Pt_2(SO_4)_4(H_2O)(OH)]$, **3**, as described in section 3(a). If **3** is filtered off and the solution evaporated down and the residue extracted into acetone $[Pt_2(O_2)_2(OH)_2(H_2O)_2]n KHSO_4$, **13**, is claimed as the product. This compound is believed to contain the peroxide species O_2^{2-}. Hydrolysis of **13** with water and treatment with acetic acid gives $K_2[Pt_2(O_2)_2(SO_4)_2(H_2O)_2]$, **14**, when **14** is redissolved in water and treated with more acetic acid $K[Pt_2(O_2)_2(SO_4)(OH)(H_2O)_3]$, **15**, is obtained. The action of water on **15** gives the final hydrolysis product $[Pt_2(OH)_6(H_2O)_2]$, **16**, which can be converted to $K_2[Pt_2(SO_4)_4(H_2O)_2]$ by the action of sulphuric acid [35]. The above compounds are usually violet in colour and potentiometric titrations suggest the oxidation number of (III) for the platinums. The above and further findings are summarised in eqn. (7).

The structures of compounds **13**–**17** are based on the lantern structure and Muraveiskaya et al. [36] give a series of structural equations for several of the reactions. Unfortunately none of the above work has been verified by X-ray crystallographic studies, the structures being inferred from infrared spectroscopy, microanalyses and potentiometric titrations. The existence of hydroxy and peroxy bridged Pt(III) compounds cannot be regarded as established; in this context we note that electrochemical studies on hydroxy bridged Pt(II) compounds gave no indications of Pt(III)-containing species [38].

(iv) Carboxylate bridged species

The first studies on carboxylate bridged Pt(III) compounds were reported



(7)

in 1976 and 1977 [37,39]. Compounds of the type $Pt_2R_4(O_2CR')_2(R^2_2)_2$ (where $R = Ph$, p-tolyl, Me, $R' = Me$, CF_3, $R^2 = Et$, Pr) were prepared almost quantitatively according to reactions of the type shown in eqn. (8)

$$Pt_2R_4(R^2_2S)_2 + 2\ AgO_2CR' \rightarrow Pt_2R_4(O_2CR')_2(R^2_2S)_2 + 2\ Ag$$

$$Pt_2R_4(R^2_2S)_2 + 2\ Hg(O_2CR')_2 \rightarrow Pt_2R_4(O_2CR')_2(R^2_2S)_2 + Hg_2(O_2CR')_2 \quad (8)$$

If *cis*-$PtMe_2(PPhMe_2)_2$ is used in the reaction with $Hg(O_2CR')_2$ then ligand displacement followed by isomerisation results in the formation of *trans*-$PtMe(O_2CR')(PPhMe_2)_2$.

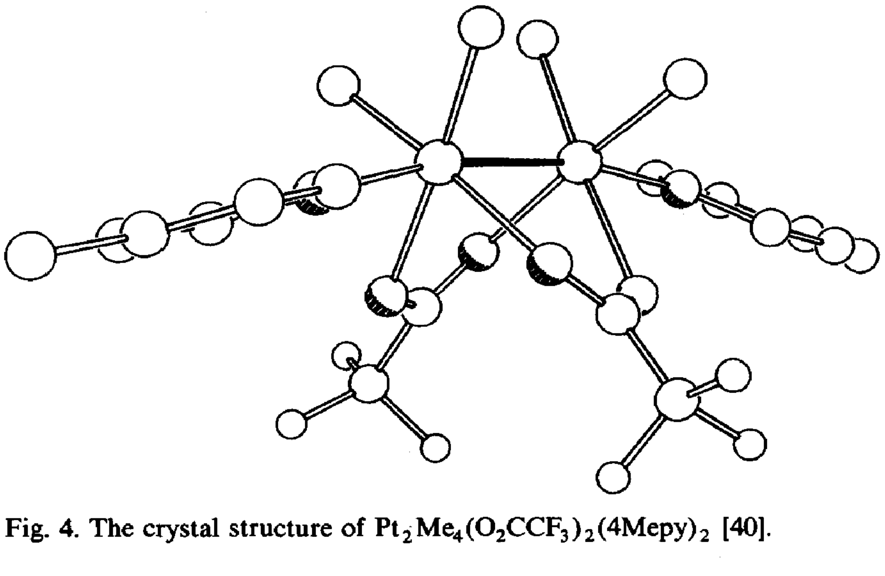


Fig. 4. The crystal structure of $Pt_2Me_4(O_2CCF_3)_2(4Mepy)_2$ [40].

As is the case for sulphate and phosphate bridged compounds, and for rhodium carboxylates [43,44], the most widely reported reaction of the carboxylate compounds is ligand displacement. For example, pyridine or picoline react according to eqn. (9). In the case

$$Pt_2Me_4(O_2CR')_2(R^2_2S)_2 + 2\ py \rightarrow Pt_2Me_4(O_2CR')_2(py)_2 + 2\ R^2_2S \qquad (9)$$

where $R' = CF_3$ the amine complex reacts (eqn. 10) with $Hg(O_2CCF_3)_2$ to give a product with one vacant axial site [39]. An X-ray crystal structure of $Pt_2Me_4(O_2CCF_3)_2(4\text{-}Mepy)_2$ (4-Mepy = 4-methyl pyridine), **18**, (Fig. 4) revealed the expected structure with a Pt–Pt distance of 2.557 Å [40]. The Pt–Pt bondlength in **18** is rather long when compared with that seen for the sulphate bridged complex $K_2[Pt(SO_4)_4(H_2O)_2]$, **1**, (Pt–Pt 2.466 Å). This difference has been accounted for by arguing that the aquo ligands in **1** have a weaker *trans* effect than the pyridine in **18**. It was also suggested that the four methyl groups in **18** have a steric influence on the bond length. Steric effects are also believed to be responsible for the non-linearity in the N–Pt–Pt–N fragment of **18** which deviates from linearity by 26°.

$$[Pt_2Me_4(O_2CCF_3)_2L_2] + Hg(O_2CCF_3)_2 \rightarrow 2[Pt_2Me_4(O_2CCF_3)_2L] + L_2Hg(O_2CCF_3)_2 \qquad (10)$$

The majority of the compounds mentioned above have NMR properties which are consistent with the crystal structure of **18**. Thus, in the ^1H NMR the signal arising from the Pt–Me groups is (in most cases) a singlet with platinum satellites ($^2J(PtH) = 80$ Hz) consistent with *cis* methyl groups. However, the room temperature spectra of $Pt_2Me_4(O_2CCF_3)_2(pic)$ has two inequivalent sets of Pt–Me signals (^{1}H and ^{13}C NMR) as do the spectra of $Pt_2Me_4(OAc)_2P(OMe)_3$. This is interpreted as good evidence for the proposed structures having one vacant axial site.

Compounds of the type $Pt_2Me_4(O_2CR)_2(EPh_3)_2$ (R = Me, CF_3; E = P, As, Sb) have been prepared by addition of two moles of donor ligand to one mole of $Pt_2Me_4(O_2CR)_2(R_2S)_2$. The stability in solution of these complexes is found to be in the order Sb > As > P and OAc > O_2CCF_3. If only one equivalent of suitable donor ligand per molecule is added then asymmetric compounds are produced (eqn. 11)

$$Pt_2R_4(OAc)_2(Et_2S)_2 + L \rightarrow Pt_2R_4(OAc)_2L + 2\ Et_2S \qquad (11)$$

where L = PEt_3 or $P(OMe)_3$ and R = Me, Ph or *para*-tolyl. ^{31}P NMR confirms that the structures are asymmetric; one main signal together with two sets of ^{195}Pt satellites due to direct and long range coupling being observed.

The above asymmetric compounds are considered to be of special interest for a number of reasons. Firstly, the high upfield chemical shift of the phosphorus in $Pt_2R_4(OAc)_2(PEt_3)$. In these compounds the phosphorus resonance is at higher field than in the free ligand in contrast to the normal observation upon complexation when a downfield shift is observed. Secondly, the value of ^1J(PtP) (of the order of 2500 Hz) indicates a *trans* effect of the *trans* platinum comparable to a tertiary phosphine. Thirdly, the preparative results may also indicate that the *trans* influence of the phosphine and the platinum could be additive since attempts to substitute the vacant site in these complexes invariably failed.

Rudyi et al. [41,42] reported the preparation of $Pt_2(OAc)_6$, **19**, eqn. (12)

$$K_2Pt(OH)_6 \xrightarrow[H_3CCO_2H]{HCO_2H} Pt_2(OAc)_6\ (50\%\ \text{yield}) \qquad (12)$$

Further reduction of **19** with excess formic acid results in a polymeric compound of approximate formula $Pt_2(OAc)_5$ which is believed to consist of $Pt_2(OAc)_4$ and $Pt_2(OAc)_6$ units.

Finally, Bellitto et al. [45] have recently reported the synthesis of some thioacetate bridged compounds, $Pt_2(CH_3CS_2)_4X_2$, **20** (eqn. 13), as well as the preparation of a mixed valence compound $Pt_2(CH_3CS_2)_4I$, **21**, by two different routes, eqns. (14).

$$Pt_2(CH_3CS_2)_4 + X_2 \rightarrow Pt_2(CH_3CS_2)_4X_2\ (X = Cl, Br, I) \qquad (13)$$

$$\left.\begin{aligned} &Pt_2(CH_3CS_2)_4 + \tfrac{1}{2}I_2 \rightarrow Pt_2(CH_3CS_2)_4I \\ &Pt_2(CH_3CS_2)_4 + Pt_2(CH_3CS_2)_4I_2 \rightarrow Pt_2(CH_3CS_2)_4I \end{aligned}\right. \qquad (14)$$

This latter compound consists (from X-ray crystallography, Fig. 5) of linear chains of $[Pt_2(CH_3CS_2)_4]^+$ cations bridged by iodide ions in a similar

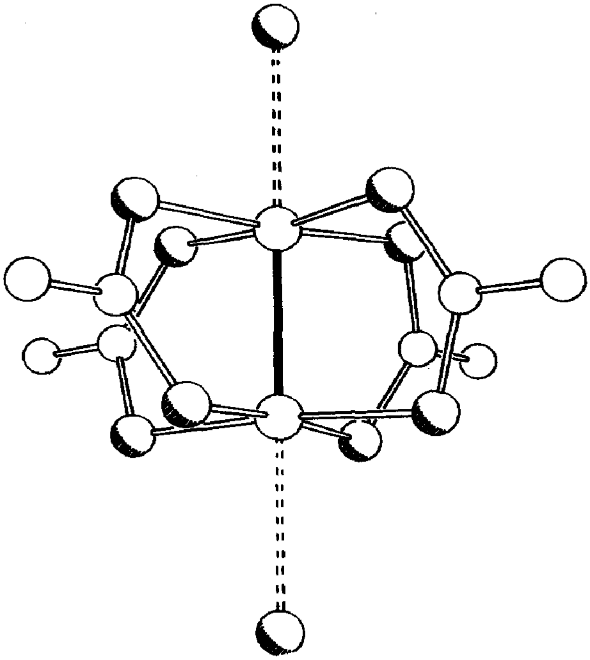


Fig. 5. The crystal structure of $Pt_2(CH_3CS_2)_4I$ [45].

manner to the pop compounds, **12**, discussed earlier. Compounds **20** and **21** were studied by a number of techniques. X-ray photoelectron spectroscopy showed the expected shift in the Pt 4*f* binding energies to higher energy relative to the Pt(II) starting material. The conductivity of pressed discs of **21** is around 5×10^{-3} ohm^{-1} cm^{-1}, which compares with **12**. As expected, **21** has an axial EPR spectrum and exhibits a low energy absorption in the near IR in the solid state.

TABLE 3

Pt–Pt separations in binuclear Pt(III)–Pt(III) compounds. Compounds marked * have average Pt oxidation state of 2.5

Compound	Pt–Pt distance (Å)	Ref.
$K_2[Pt_2(SO_4)_4(H_2O)]$	2.466	24
$K_2[Pt_2(SO_4)_4(dmso)_2]4H_2O$	2.471	26
$Na_2[Pt_2(PO_4)_4(H_2O)]$	2.486	29
$[pyH][Pt_2(H_2PO_4)(HPO_4)_3(py)_2]H_2O$	2.494	31
$K_4[Pt_2(pop)_4Cl_2]$	2.695	32
$K_4[Pt_2(pop)_4Br]3H_2O$ *	2.793	33
$Pt_2Me_4(O_2CCF_3)_2(4Mepy)_2$	2.557	40
$Pt_2(CH_3CS_2)_4I$ *	2.677	45

Table 3 gives the Pt–Pt separations in binuclear Pt(III)–Pt(III) compounds.

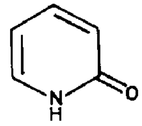
D. PLATINUM BLUES AND RELATED COMPOUNDS

(i) Platinum blues

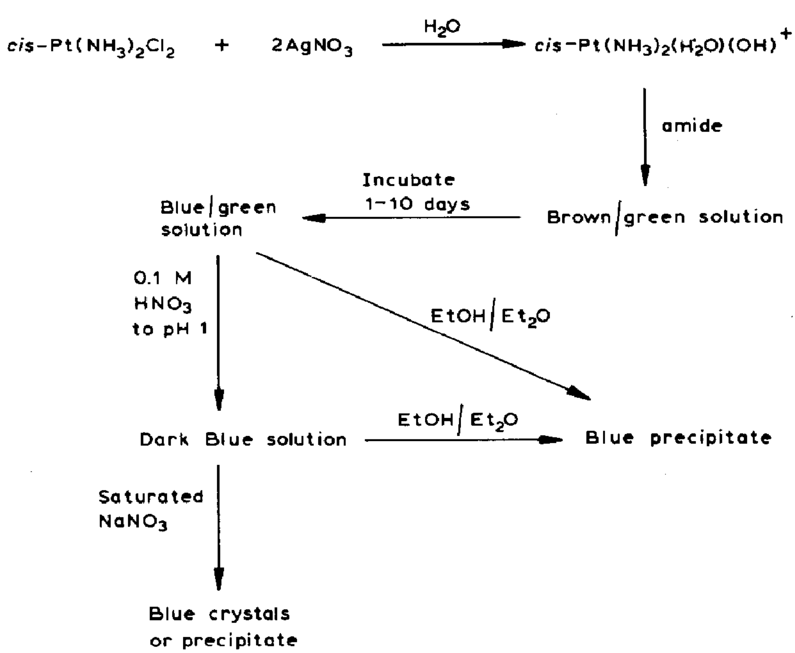
The first of these compounds was reported in 1908 by Hofmann and Bugge [46] from the reaction of $Pt(CH_3CN)_2Cl_2$ with K_2PtCl_4. The resulting product, called by them "Platinblau" was characterised by elemental analyses and freezing point depression. It was assigned the formula $Pt(CH_3CONH)_2 \cdot H_2O$ and assumed to have a square-planar structure. Over fifty years later Gillard and Wilkinson [47] suggested that Platinblau was actually a polymer. Contrary to this Brown et al. [48,49] studied the reaction of trimethylacetamide with $Pt(CH_3CN)_2Cl_2$ and concluded that the product was a monomeric Pt(IV) complex with bidentate amidate ligands.

Although these early papers are of interest historically, the major activity in this area came about as a result of the discovery of the powerful anti-tumour activity of platinum blues prepared from *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ and pyrimidines [50–52]. Like the discovery of the first platinum anti-cancer drug, *cis*-$Pt(NH_3)_2Cl_2$, the preparation of the first platinum pyrimidine blue was serendipitous. Rosenberg and co-workers [50] were investigating the reactions of a number of platinum compounds with polynucleotides as part of their studies on mechanisms of anti-cancer activity of *cis*-$Pt(NH_3)_2Cl_2$. They observed that when *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ was incubated for several days at pH 7 and 37°C with polyuracil, blue products were formed. It was soon established that similar reactions occur with thymine, uracil and a wide variety of substituted pyrimidines. Many of these blue products have high anti-tumour activity as well as low renal toxicity.

In the ten years since the first report on pyrimidine blues a large number of platinum blues have been synthesised but unfortunately very few of the compounds have been amenable to complete characterisation. The first major exception to this remark was α-pyridone blue, **22**, which was prepared and thoroughly investigated by Barton et al. [53–57]. Since this is the archetype with which other platinum blues are compared it is worth describing its properties in detail. The preparative route to **22** as well as the alternative routes used for other blues is shown in eqn. (15).



α-pyridone



(15)

X-ray crystallography showed the crystal structure of **22** (Fig. 6) to be a dimer of binuclear $[(NH_3)_2Pt(pyr)_2Pt(NH_3)_2]$ units with an overall charge for the Pt_4 unit of $+5$, resulting in an average oxidation state for the platinums of 2.25. The effective magnetic moment of **22** is 1.81 μ [54], which is higher than the value of 1.73 μ expected from the spin-only formula, indicating the presence of spin–orbit coupling. The Weiss constant is low, and thus there are no long-range interactions in the solid state. The magnetic properties are consistent with the presence of one unpaired electron per four platinum atoms. Electron paramagnetic resonance studies on single crystals of **22** gave g_{xx} 2.307, g_{yy} 2.455 and g_{zz} 1.975 whilst aqueous solutions [55] exhibit $g_{\perp}$ 2.38 and $g_{\parallel}$ 1.976. At low ionic strengths hyperfine splitting is observed due to the interaction of the unpaired electron with the ^{195}Pt atoms, assuming the presence of two inequivalent types of platinums. The g values are considered to be appropriate to a model for the electronic structure of the Pt_4 unit which has a dz^2 hole state along the mean axis of the platinum chain. The visible spectrum of **22** is characterised by a broad transition around 680 nm [55], with the extinction coefficient being a sensitive function of the anion present. The relationship between the visible spectrum and the EPR signal was demonstrated by the concurrent loss of both when a solution of **22** was oxidised using Ce(IV), an endpoint being reached when 0.77 equivalents of Ce(IV) per platinum have been consumed. This evidence

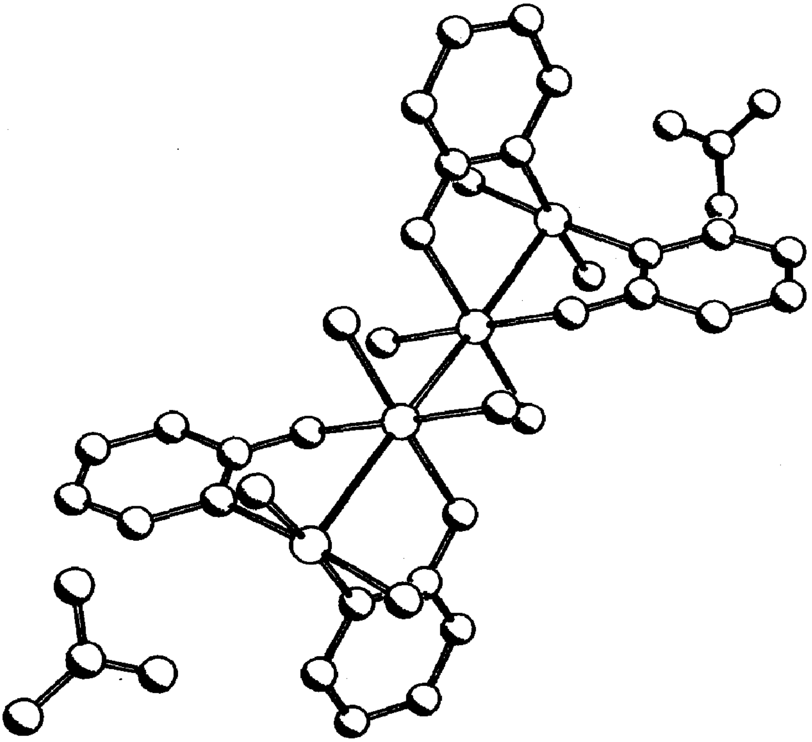
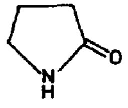


Fig. 6. The crystal structure of α-pyridone blue (**22**), showing axial NO_3^- groups only [54].

supports the proposed formal oxidation state for the platinum atoms of 2.25, with the endpoint for the titration being assumed to be Pt(III) species. Finally, it is of interest to establish if the average oxidation state is localised (3 × Pt(II) and 1 × Pt(III) or delocalised, 4 × Pt(2.25)). X-ray photoelectron spectroscopy showed that the platinum oxidation state is close to 2 with all of the platinums being equivalent [58].

The visible EPR and XPS studies described above mean that **22** is very well characterised and since many of the spectroscopic studies were carried out in comparison with pyrimidine blues it has been possible to draw the conclusion that **22** is the archetypal blue, but a rider might be added that since α-pyridone does not have the exocyclic groups of the pyrimidines it is possible that other forms (e.g., longer chains held together by H-bonds) do exist in the latter types of compounds. The anti-cancer activity of **22** has, surprisingly, not been discussed.



α-pyrrolidone

Closely related to **22** are compounds based upon α-pyrrolidone.

Matsumoto et al. [59,60] obtained the tan coloured $[Pt_4(NH_3)_8(pyrl)_4](NO_3)_6 \cdot 2\,H_2O$, **23** which has an analogous structure to **22** except that there is an average oxidation state of 2.5, rather than 2.25 in **22**. This difference in oxidation state is reflected in the Pt–Pt distances. In the pyridone compound the separations are 2.774 and 2.877 Å whilst in the pyrrolidone case the distances are 2.702 and 2.709 Å. More recently [61] a green α-pyrrolidone compound which contains a mixture of Pt_4^{5+} and Pt_4^{6+} cations was isolated and characterised by X-ray crystallography and magnetic susceptibility measurements.

Much of the remaining work published on platinum blues consists of preparations and identification by UV/VIS, IR and EPR spectroscopies. These techniques often, by themselves, do not enable the structures to be established and generally there is a reliance upon spectroscopic comparison with the crystallographically identified compounds already outlined. Blues have been prepared using: phthalimide [62], phosphate [63], tryptophan [64], glutamine [65], succinamic acid [66], 1-methyl-hydantoin [67], 1-methylnicotinamide [68,69], oxamic acid [70,71], asparagine [72] and trimethylacetamide [73]. Nucleotides and nucleosides also provide many examples: UMP, CMP [74], cytidine [75], uracils [76–79] and cytosine [80]. Some of the above compounds used K_2PtCl_4 rather than *cis*-$Pt(NH_3)_2(H_2O)_2^{2+}$ as starting material [65,66,67,68,70,75]; equally, it is possible to replace the ammine group by another primary amine [81].

Most of the compounds mentioned above were characterised by EPR measurements with $g_\parallel \sim 2$, $g_\perp \sim 2.4$, Table 4. Visible spectra usually have a strong absorbance at 600–700 nm. The most striking feature is that although the EPR and UV/VIS spectra are fairly similar, greatly differing average oxidation states for platinum are claimed with anything from 2.1 to 3.75 being estimated. These results underline the difficulty in this area, with many

TABLE 4

Typical EPR data for platinum blues

Ligand	$g_\perp$	$g_\parallel$	Ref.
α-Pyridone	2.380	1.976	54
Asparagine	2.39	1.97	72
Guanosine/1-methylnicotinamide	2.418	1.979	69
Glutamine	2.44	1.99	65
6-Methyluracil			
type O	2.394	1.991	76
type R	2.375	1.983	76
Cytosine	2.394	1.970	77
Thymine	2.378	1.995	77
1-Methyluracil	2.275	1.948	97

problems in assessing purity of products and obtaining reproducible properties.

Surprisingly, there is a recent paper by Zaki et al. [82] which reports reproducible microanalyses for uracil, thymine and cytosine blues prepared by the conventional method. Zaki et al. also report the visible spectra of aqueous solutions of platinum uracil and platinum cytosine blues which in their studies seem little affected by time, a result in contrast to earlier reports [83] and our own studies [84].

One particularly interesting route to platinum 1-methyluracil blue was recently reported by Lippert and Neugebauer [85]. They reacted the 1-methyluracil bridged head to head compound $[Pt_2(NH_3)_4(MeU)_2](NO_3)_2H_2O$ with silver nitrate to give the heterometallic $Ag[Pt(NH_3)_2(MeU)]_4(NO_3)_54H_2O$, **24**, which consists of two Pt_2 units bridged by a Ag^+ ion. When **24** is left to stand in solution a microcrystalline compound which analyses as $[Pt(NH_3)_2(MeU)]_4(NO_3)_55H_2O$ is obtained. This compound is believed to be the 1-methyluracil analogue of **22**.

A number of workers have carried out physical measurements on the blues. Electron paramagnetic resonance studies have already been mentioned and a selection of typical results is shown in Table 4. An extended X-ray absorption fine structure study [86] on platinum uridine blue gave the Pt–Pt separation as 2.93 Å, whilst Fourier analysis of the powder X-ray pattern of platinum acetamide blue gave a Pt–Pt separation of 2.76 Å [87]. Gel chromatography and mass spectroscopic studies on platinum thymine blue [88] indicate a mixture of molecular weights from 3000–1000; HPLC studies [89] supports the idea that this blue, at least, is a mixture of species of different chain length. X-ray photoelectron spectra have been measured for α-pyridone and acetamide blues [56] as well as succinamic acid [66] and oxamic acid [90] blues. The latter two papers interpret the broadness of the Pt $4f$ lines as being indicative of localised Pt(IV)–Pt(II) or Pt(III)–Pt(II) systems whereas Barton et al. [56], although observing broad signals for platinum acetamide blue, were able to obtain cleaner spectra after purification. The α-pyridone blue samples always gave a signal attributable to a single delocalised average oxidation state for the platinum. It may be that the broadness of some XPS spectra [66,90] is due to the presence of impurities.

The question of localised versus delocalised structures has been discussed for phthalimide blue [62]. Using the Hush model, calculations tend to the conclusion that this blue is class II–class III borderline with extensive delocalisation but inequivalent metal centres. However, it should be noted that the authors could not explain the temperature sensitivity of the visible spectra and that the Hush model has severe limitations for extensively delocalised systems. Further studies on the electronic spectrum of α-pyridone blue were recently reported [91].

The interactions of blues with biologically relevant molecules (DNA, lysozyme, etc.) have been reported on [84,92,93].

(ii) Binuclear compounds related to the platinum blues

Binuclear Pt(III) compounds with pyridimine or α-pyridone ligands may be prepared by oxidation of either platinum blues or Pt(II)–Pt(II) species. Thus, when α-pyridone blue is treated with nitric acid red-orange crystals are obtained; identified by X-ray crystallography as head to head, *cis*$[(H_2O)(NH_3)_2Pt(pyr)_2Pt(NH_3)_2(NO_3)](NO_3)_3 2H_2O$, **25** [94,95] with a Pt–Pt bond distance of 2.539 Å. Oxidation of the head to head α-pyridone Pt(II)–Pt(II) species using nitric or nitrous acid [95,96] gives similar Pt(III)–Pt(III) cations to **25**, with axial nitrato and nitrito ligands, respectively. In the nitrito complex the Pt–Pt bond length of 2.575 Å is 0.028 Å longer than in the analogous nitrate species. This difference in bond length is attributed to the difference in donor strengths of the two axial ligands rather than any crystal packing properties. The Pt–O bond to the nitrato ligands in $[(NO_3)(NH_3)_2Pt(pyr)_2Pt(NH_3)_2(NO_3)](NO_3)_2H_2O$ is 0.16 Å longer than in $Pt(NH_3)_2(NO_3)_2$. Similarly, the Pt–N bond to the nitrito ligands in $[(NO_2)(NH_3)_2Pt(pyr)_2Pt(NH_3)_2(NO_2)](NO_3)_2H_2O$ is 0.2 Å longer than in mononuclear platinum compounds. This effect is regarded as being due to the mutual *trans* influence in the Pt–Pt and Pt–L bonds and is compared to similar effects in related rhodium complexes [96,96a].

The head to tail isomer of **25** has been prepared by oxidation of the head to tail Pt(II)–Pt(II) species using nitric acid [95]. The Pt–Pt distance is very similar in the head to head and head to tail cases with the latter being 0.0067 Å longer. Electrochemical studies [94,95] on both isomers reveal similar cyclic voltammograms for the two systems with only single waves being observed in each case. However, from cyclic voltametry experiments at various scan rates, it was suggested that the removal of the second electron was less difficult than removal of the first, eqn. (16), in the head to tail case. On the other hand, for the head to head isomer, the reverse situation is thought to be the case [94,95]. This conclusion has led to experiments on the head to head 1-methyluracil complex $[(NH_3)_2Pt(MeU)Pt(NH_3)_2](NO_3)_2$, **26**, which was observed to have a doublet in CV studies with a separation for the anodic peaks of 160 mV. Controlled potential coulometry was used to produce both the mixed valence $[(NH_3)_2Pt(MeU)_2Pt(NH_3)_2](ClO_4)_3$ and the Pt(III)–Pt(III) complex $[(NH_3)_2Pt(MeU)_2Pt(NH_3)_2](NO_3)_4$ [97]. The head to tail isomer of the latter compound has also been produced by oxidation of Pt(II)–Pt(II) compared using nitric/nitrous acid mixtures [98].

$$\mathrm{Pt(II)–Pt(II)} \rightleftharpoons \mathrm{Pt(II)–Pt(III)} \rightleftharpoons \mathrm{Pt(III)–Pt(III)} \qquad (16)$$

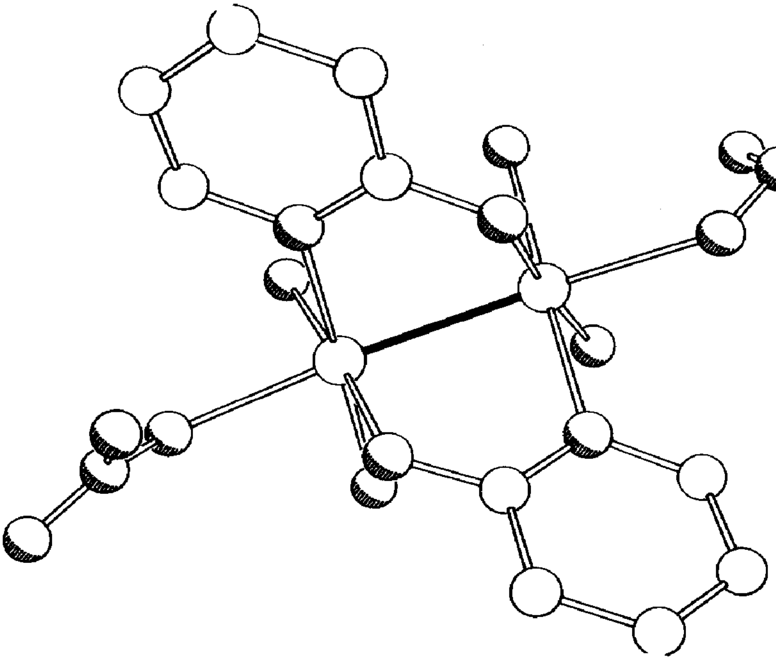


Fig. 7. The crystal structure of the cation in head to tail $[(NO_3)(NH_3)_2Pt(pyr)_2Pt(NH_3)_2(NO_3)](NO_3)_2\frac{1}{2}H_2O$ [95].

TABLE 5

Pt–Pt separations and formal oxidation states for platinum blues and related compounds

Compound	Average formal oxidation state	Pt–Pt distance (Å)	Ref.
α-Pyridone blue:			
cis-$[(NH_3)_2Pt(pyr)_2Pt(NH_3)_2]_2(NO_3)_5 \cdot H_2O$	2.25	2.774, 2.877	54
α-Pyrrolidine tan:			
cis-$[(NH_3)_2Pt(pyrl)_2Pt(NH_3)_2]_2(NO_3)_6 \cdot 2H_2O$	2.5	2.702, 2.709	59, 60
Platinum uridine blue	–	2.93 [a]	86
Platinum acetamide blue	–	2.73 [b]	87
cis-$[(H_2O)(NH_3)_2Pt(pyr)_2Pt(NH_3)_2(NO_3)](NO_3)_3 \cdot 2H_2O$			
head to head isomer	3	2.539	94, 95
head to tail isomer	3	2.546	94, 95
cis-$[(NO_3)(NH_3)_2Pt(pyr)_2Pt(NH_3)_2(NO_3)](NO_3)_2H_2O$	3	2.541	96
cis-$[(NO_2)(NH_3)_2Pt(pyr)_2Pt(NH_3)_2(NO_2)](NO_2)_2H_2O$	3	2.575	96
cis-$[Cl(NH_3)_2Pt(pyr)_2Pt(NH_3)_2Cl](NO_3)_2$	3	2.568	96a
cis-$[Br(NH_3)_2Pt(pyr)_2Pt(NH_3)_2Br](NO_3)_2\frac{1}{2}H_2O$	3	2.582	96a
cis-$[(H_2O)(NH_3)_2Pt(MeU)_2Pt(NH_3)_2(NO_2)](NO_3)_3 \cdot 5H_2O$ (head to tail isomer)	3	2.574	98
$(H_5O_2)[(NO_2)(NH_3)_2Pt(MeC)_2Pt(NH_3)_2(NO_2)](NO_3)_2$ (head to tail isomer)	2.5 [c]	2.548	99
$[Pt(pyms)_2I]_2$	3	2.554	100

[a] From EXAFS data. [b] From powder X-ray data. [c] See text.

Related to the compounds mentioned above is a 1-methylcytosine species reported by Faggiani et al. [99]. They reacted $Pt(NH_3)_2(NO_3)_2$ with 1-methylcytosine and, together with a number of other products, obtained a binuclear compound which was formulated as a Pt(2.5) compound, head to tail *cis* $(H_5O_2)[(NH_3)_2(NO_2)Pt(MeC)_2Pt(NH_3)_2(NO_2)](NO_3)_2$, **27**, on the basis of X-ray crystallography. The Pt–Pt separation in **27** is 2.548 Å, close to that seen for Pt(III)–Pt(III) species and so some workers [94,96] have questioned the formulation of this compound.

Finally, in this section, an unusually facile synthesis of a binuclear Pt(III)–Pt(III) pyrimidine-2-thione complex was recently reported by Goodgame et al. [100] who reacted K_2PtI_4 with a methanolic solution of the ligand. If air is excluded a simple Pt(II) complex is obtained but on standing in air red $[Pt(pyms)_2I]_2$, **28**, separates. The crystal structure of **28** shows it to be bridged by four pyrimidine-thione ligands with axial iodo groups and a Pt–Pt distance of 2.554 Å.

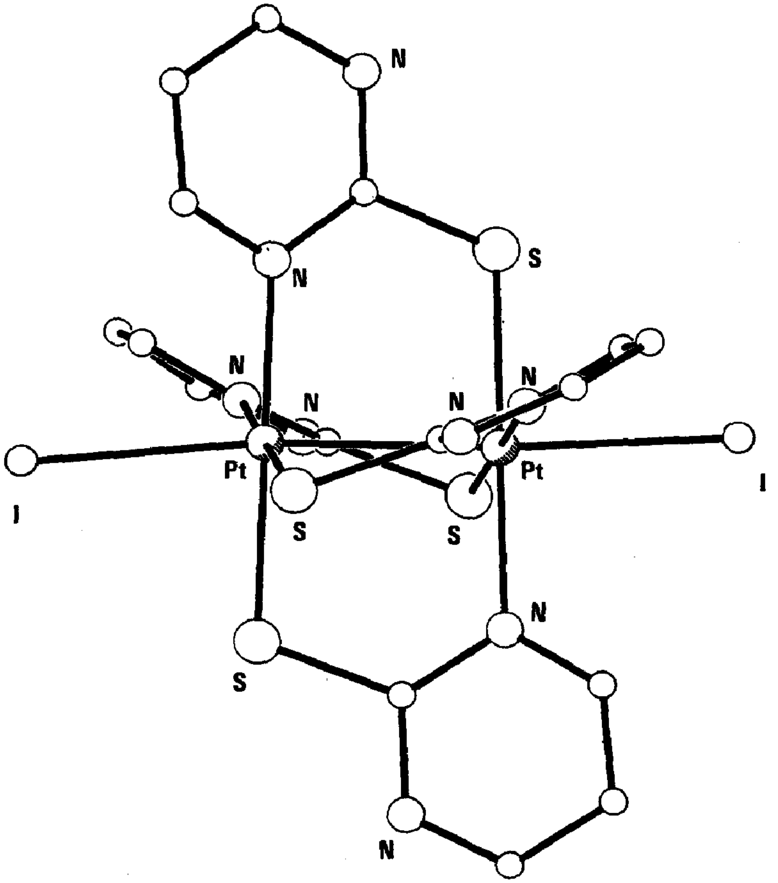
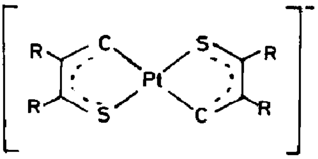
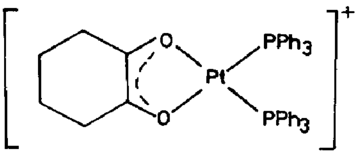


Fig. 8. The crystal structure of $[Pt(pyms)_2I]_2$ [100].

Until very recently there were no examples of mononuclear Pt(III) compounds although there are complexes which could formally be written as containing Pt(III). For example, the anions **29** [101–103] and the cation **30**



29 R = Ph,CN,CF$_3$



30

[104,105]. However, in both of these examples it was concluded that the unpaired electron resides in the π orbitals of the aromatic system with platinum being present as Pt(II). There are examples of mononuclear blue platinum compounds such as the tetraazabutadiene complex [Pt(1,4(4-$NO_2C_6H_4)_2N_4(CHC(PEt_3)HCH_2CH{=}CHCH_2CH_2)(PEt_3)$] but the colour in this complex was attributed to charge transfer transition and not to the presence of any unusual platinum oxidation states [106].

Muraveiskaya et al. [107] have claimed the preparation of $Pt(NH_3)_2(SCN)_2I$ **29**, eqn. (17),

$$cis\text{-}Pt(NH_3)_2(SCN)_2 + \tfrac{1}{2}I_2 \xrightarrow{BuOH} cis\ Pt(NH_3)_2(SCN)_2I \qquad (17)$$

However, the evidence for the formulation of **29** is very sparse. Microanalysis data and the observation of a broad EPR signal, ($g_{eff} = 2.18$) together with the colour of the compound ("marsh green") could be rationalised on the basis of a binuclear (or larger) structure.

The only fully characterised compound was reported by Uson et al. in 1984 [108], eqn. (18),

$$[NBu_4]_2[Pt(C_6Cl_5)_4] + \tfrac{1}{2}X_2 \rightarrow [nBu_4][Pt(C_6Cl_5)_4]\ (\mathbf{30}) \qquad (18)$$

X = Cl, Br yield = 90%; X = I yield 60%. Compound **30** is deep blue and air and moisture stable at room temperature. In acetone solution it behaves as a 1 : 1 electrolyte whilst its IR spectrum shows the absorptions due to C_6Cl_5 increased 10–15 cm^{-1} in frequency relative to the Pt(II) parent. The crystal structure of **30** shows it to be square planar with almost identical geometry to the Pt(II) parent. The $[Pt(C_6Cl_5)_4]^-$ anions are widely separated, the closest Pt–Pt distance being 9.7 Å. The stability of the complex is attributed to the unique C_6Cl_5 ligand.

ACKNOWLEDGEMENT

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