Optically Active Co-ordination Compounds. Part 43.[†] Polysulphide Complexes of Platinum(IV)

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Brick-red $[NH_4]_2[Pt(S_5)_3]\cdot 2H_2O$ crystallises from the reaction mixture obtained on adding K_2PtCl_6 to an aqueous ammonium polysulphide solution. Addition of concentrated hydrochloric acid results in the separation of maroon $[NH_4]_2[PtS_{17}]\cdot 2H_2O$. The physical properties (solubility, i.r., Raman, and electronic spectra, *X*-ray powder pattern) of the complexes are described. The $[Pt(S_5)_3]^{2-}$ ion crystallises from solution as the racemate, whereas $[PtS_{17}]^{2-}$ on crystallisation undergoes a second-order asymmetric transformation so that the solid contains an excess of the (−) enantiomer. The $[Pt(S_5)_3]^{2-}$ ion was resolved by forming diastereoisomers with $[RuL_3]^{2+}$ (L = 2,2′-bipyridyl or 1,10-phenanthroline). The circular dichroism spectra of both ions are described. The mechanism of racemisation is discussed.

The reaction of $[PtCl_6]^{2-}$ with ammonium polysulphide was originally investigated by Hofmann and Hochtlen,[1] who isolated $[NH_4]_2[Pt(S_5)_3]\cdot 2H_2O$.[2] Wickenden and Krause[3] reported improved methods of synthesis and, depending on the pH of the solution, obtained either a brick-red or a maroon solid, both of which were said to be $[NH_4]_2[Pt(S_5)_3]$. We are prompted by a recent report[4] to describe our detailed investigation of the system. Our characterisation reveals that two distinct species, containing only platinum and sulphur, can be isolated from the same reaction mixture.

Examples of optically active molecules or ions containing no carbon atoms are extremely rare. Until recently only two authenticated cases existed. These are Werner's[5] 'hexol,' $[Co\{(OH)_2Co(NH_3)_4\}_3]^{6+}$, and *cis*-diaquabis(sulphamato)-rhodate(III).[6] The only recent examples are the heteropolymolybdate ion[7] $[Co_2Mo_{10}O_{34}(OH)_6]^{8-}$ and *cis-cis-cis*-$[Co(NH_3)_2(H_2O)_2(NO_2)_2]^+$.[8]

The other purpose of the present work is to obtain optically active polysulphido-complexes, and we now report the resolution of $[Pt(S_5)_3]^{2-}$ together with a novel asymmetric transformation. A preliminary account[9] of some of this work has already appeared, and a subsequent paper (Part 44 of this series) will give detailed crystallographic results.

Results

Preparation and Characterisation.—Ammonium polysulphide solutions were prepared by bubbling hydrogen sulphide into a slurry of sulphur in concentrated aqueous ammonia solution until all the sulphur had dissolved;[10] this gave a deep red solution. A suspension of K_2PtCl_6 in water was added. The solid dissolved rapidly on mixing and this was accompanied by a noticeable darkening of the solution, indicating that complex formation is rapid. The pH of the reaction mixture at this point was *ca.* 10.4. Two complexes can be isolated depending on the conditions for crystallisation.

Under conditions of slow crystallisation, achieved by storing the reaction mixture at 2—5 °C for several days, well formed brick-red crystals of $[NH_4]_2[Pt(S_5)_3]\cdot 2H_2O$ separate in moderate yield. When the product is induced to crystallise rapidly a different complex, which analyses as $[NH_4]_2[PtS_{17}]\cdot 2H_2O$, is obtained in high yield as maroon microcrystals. This is achieved by adding concentrated hydrochloric acid to the reaction mixture until the pH is *ca.* 9.4.

Both the equilibria that exist in solution and the conditions for the crystallisation of the products are complex. Addition of acid to the reaction mixture will generally produce a precipitate of $[NH_4]_2[PtS_{17}]\cdot 2H_2O$, whereas during slow crystallisation a mixture of brick-red and maroon solids is sometimes formed. In these cases, the brick-red crystals form first while the maroon product crystallises subsequently. Mechanical separation is straightforward.

It would appear that it is the speed of crystallisation that is responsible for the formation of the two complexes. In several cases after the addition of acid the crystallisation was slow and this resulted in a brick-red product. Conversely, a maroon product was in one case obtained when, upon stirring, crystallisation from the untreated reaction mixture was rapid. In all cases, the brick-red product is always $[NH_4]_2[Pt(S_5)_3]\cdot 2H_2O$ and the maroon solid is always $[NH_4]_2[PtS_{17}]\cdot 2H_2O$.

The characterisation of these complexes presents some difficulty in that the only elementary analyses that can be regarded as being definitive are those for platinum and sulphur. This is further complicated by the fact that $[NH_4]_2[Pt(S_5)_3]$ has been reported as being either anhydrous[3] or a dihydrate[1,2]

Table 1. Analytical data and results (%) for $[NH_4]_2[PtS_{15}]\cdot nH_2O$

H	N	Pt	S	Ref.
1.15	3.95	27.4	67.55	Calc. for $n = 0$
1.40	3.85	26.7	65.9	Calc. for $n = 1$
1.60	3.75	26.05	64.3	Calc. for $n = 2$
—	3.85	25.75	64.8	1
		25.85	65.2	
—	3.55	25.95	64.15	2
	3.65	26.0	64.35	
—	3.85	27.2	67.65	2
	3.90	27.6	67.65	
1.45	3.90	27.1	68.3	17
1.40	4.00	27.1	66.9	
1.60	3.70	26.5 ± 0.5[a]	62.8	This work
1.45	3.90			This work
			63.5[b]	This work
			63.9[b]	This work

[a] Residue from thermogram; values varied from 26.0 to 27.1%. [b] By method in text: these analyses were done, on different samples, by Mr. S. H. Mitchell.

[†] Part 42 is R. D. Gillard, J. A. Arce Sagues, D. H. Smalley, and P. A. Williams, *Inorg. Chim. Acta*, 1980, **43**, 211.

Table 2. Electronic and c.d. results[a]

$[NH_4]_2[Pt(S_5)_3]\cdot 2H_2O$				$[NH_4]_2[PtS_{17}]\cdot 2H_2O$			
Electronic[b]		C.d.[c]		Electronic[b]		C.d.	
$\lambda_{max.}$/nm	$10^{-5}\varepsilon$/ dm^2 mol^{-1}	$\lambda_{max.}$/nm	$\Delta\varepsilon$/ dm^2 mol^{-1}	$\lambda_{max.}$/nm	$10^{-5}\varepsilon$/ dm^2 mol^{-1}	$\lambda_{max.}$/nm	$\Delta\varepsilon$/ dm^2 mol^{-1}
390	1.44	392	+550	384	1.49	376	−538
290 (in)	1.69	300	−275	308	1.89	306	+191
250 (in)	1.93	260 (sh)	−174				
210 (sh)	3.78	220	−233	220 (sh)	4.54	215	+705

[a] In water. [b] in = Inflexion, sh = shoulder. [c] In ethanol.

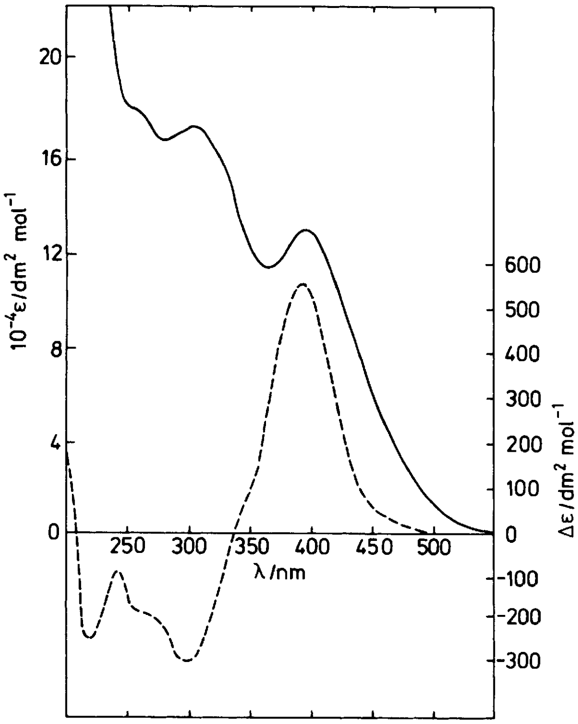

Figure 1. Electronic (——) and c.d. (– – –) spectra of $[NH_4]_2(+)$-$[Pt(S_5)_3]$ in ethanol

(or both!).[11] The elemental analyses (see Table 1) that have been reported by various workers are evenly divided between these two formulations.

Thermogravimetric analysis cannot be used to determine water of crystallisation accurately because of the low decomposition temperature of the complexes. The thermogram of $[NH_4]_2[Pt(S_5)_3]\cdot 2H_2O$ shows that weight loss begins at 85 °C. However, before this can form a plateau that would be indicative of water of crystallisation, decomposition of the complex sets in at 170 °C. Sulphur is rapidly lost in a series of steps to leave at 450 °C a residue of platinum metal. The weight of the residue ($26.5 \pm 0.5\%$) is not considered to be sufficiently reliable to distinguish between the various possible hydrates. The most conclusive proof that the complex crystallises as a dihydrate is the *X*-ray crystal structure determination.[2,12]

The thermogram of $[NH_4]_2[PtS_{17}]\cdot 2H_2O$ is similar but not identical to that of the tris(pentasulphido)-complex. Slow decomposition begins at 70 °C and rapid weight loss begins at 170 °C. The loss of sulphur is more rapid with the platinum residue being formed at 340 °C. The weight of the residue ($24.0 \pm 0.2\%$) is in good agreement with the calculated value (24.0%). However, the existence of lower hydrates cannot be discounted.

To overcome these difficulties in analysis, the tetraethylammonium salts were prepared by metathesis. These salts, which *are* anhydrous, are more thermally stable than the ammonium salts, with the decomposition temperatures for $[NEt_4]_2[Pt(S_5)_3]$ and $[NEt_4]_2[PtS_{17}]$ being 200 and 170 °C respectively. The platinum residues together with the other elemental analyses are fully consistent with these formulations.

Properties.—The complexes $[NH_4]_2[Pt(S_5)_3]\cdot 2H_2O$ and $[NH_4]_2[PtS_{17}]\cdot 2H_2O$ are quite distinct in colour and crystal form.* $[NH_4]_2[Pt(S_5)_3]\cdot 2H_2O$ crystallises as well formed brick-red crystals of moderate size, moderately soluble in water (1.5 g in 100 cm^3 at 18.4 °C); $[NH_4]_2[PtS_{17}]\cdot 2H_2O$ separates as maroon microcrystals that are sparingly soluble in water (0.14 g per 100 cm^3). Both complexes are freely soluble in polar organic solvents.

The electronic spectra of the two complexes in water are similar, but not identical (Table 2, Figures 1 and 2). Although the first maximum for both complexes is at *ca.* 390 nm, the spectrum of $[PtS_{17}]^{2-}$ has a more pronounced tail into the visible region indicative of unresolved transitions at higher wavelength. This tail accounts for the different colours of the complexes.

The far-i.r. and Raman spectra of the complexes are summarised in Table 3. The bands in the i.r. spectrum are all of low intensity whereas those in the Raman spectrum vary from weak to very strong. The vibrational spectrum consists only of Pt–S and S–S modes. An indication of the frequencies of the S–S modes can be obtained from the vibrational spectra of cyclohexasulphur[13] and ionic polysulphides such as K_2S_5.[14] The PtS_5 chelate ring and *cyclo*-hexasulphur[15] both have the chair configuration although the symmetry is different (C_2 and D_{3d} respectively). The i.r. spectrum of S_6 shows two bands at 462 and 312 cm^{-1}, while the Raman spectrum has bands at 471, 449, 262, and 203 cm^{-1}. The vibrational S–S modes are considered by Janz *et al.*[14] to be in the region 400—500 cm^{-1} and the bonding modes between 200 and 300 cm^{-1}. It is not possible to assign the Pt–S modes by inspection with any certainty.

Optical activity. The salt $[NH_4]_2[Pt(S_5)_3]\cdot 2H_2O$ crystallises as the racemate. The $[Pt(S_5)_3]^{2-}$ ion was resolved by forming

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* *X*-Ray powder patterns[12] indicate that $[NH_4]_2[Pt(S_5)_3]\cdot 2H_2O$ crystallises in two forms. One form (say A) corresponds to the structure reported by Jones and Katz.[2] The crystal and molecular structure of the new form (B) have been determined.[12] The unit cell is monoclinic, space group *C*2/*c*, and the cell parameters are: *a* = 16.93, *b* = 8.92, *c* = 27.30 Å, and β = 101.4°. When A and B are crystalline, they are red and very dark red respectively. On grinding, both look orange.

Table 3. Far-i.r. and Raman results[a] for the polysulphide complexes

K_2S_5[b]		$[Pt(S_5)_3]^{2-}$			$[PtS_{17}]^{2-}$		
		NEt_4^+	NH_4^+		NH_4^+		NEt_4^+
I.r.	Raman	I.r.	I.r.	Raman[c]	I.r.	Raman[c]	I.r.
			536w				
494	496m	502wm	500wm	498m	538w	494s	498wm
481	485w			490m	495wm	486s	
				464s		472s	472wm
		455wm	457w	459s	475wm	443 (sh)	
	432s			430vw	440w	440m	440w
416		423w	424w	425 (sh)	424w	426ms	422w
				326vs	331 (sh)	329vs	330 (sh)
					319wm	317ms	319wm
		306wm	306wm	306s	314wm	309s	315 (?)
				296s	307wm	305 (sh)	307wm
				292 (sh)	294wm	292s	293wm
		285wm	284wm	284s	285w	281 (sh)	284w
270	268w	272wm	272 (sh)	273m	264wm	263w	264 (sh)
					260wm	261w	259wm
	252m			237ms	*ca.* 250w	250w	*ca.* 250wm
				224m		229s	
				212m			
				204m		202ms	
	172m			172 (sh)			
				165m			
				149ms		142s	
						135s	
				127s		124s	

[a] All values are given in cm^{-1}; s = strong, m = medium, w = weak, v = very, and sh = shoulder. [b] G. J. Janz, J. W. Coutts, J. R. Downey, jun., and E. Roduner, *Inorg. Chem.*, 1976, **15**, 1755. [c] Recorded at 80 K with 647.1 nm radiation.

diastereoisomers with $[RuL_3]^{2+}$ [L = 2,2′-bipyridyl (bipy) or 1,10-phenanthroline (phen)]. Thus, addition of $(-)[Ru(bipy)_3][ClO_4]_2$ to a solution of $[NH_4]_2[Pt(S_5)_3]$ in acetone results in the precipitation of $(-)[Ru(bipy)_3](-)[Pt(S_5)_3]$ leaving the *dextro* enantiomer of the anion in solution. The circular dichroism (c.d.) spectrum of $(+)[Pt(S_5)_3]^{2-}$ in ethanol is shown in Figure 1 (see also Table 2). The maxima compare favourably with those in the electronic spectrum. Resolution with $[Ru(phen)_3][ClO_4]_2$ was not as effective, the best $\Delta\varepsilon$ value at 392 nm being 80 dm^2 mol^{-1}. As above, $(-)[Ru(phen)_3]^{2+}$ precipitates $(-)[Pt(S_5)_3]^{2-}$.

Circular dichroism* (see Figure 2) and polarimetric measurements on solutions of $[NH_4]_2[PtS_{17}]\cdot 2H_2O$ show that the solids that crystallise from the reaction mixture are optically active. All samples that have been crystallised so far show optical activity with the *laevo* enantiomer in excess. However, the optical activity is not the same for each sample. The chiroptical properties of a representative number of samples are summarised in Table 4. Sample 2 shows the greatest optical activity and we assume that it contains the pure *laevo* enantiomer, while the other samples consist of mixtures of both *dextro* and *laevo* enantiomers.

All samples of $[NH_4]_2[PtS_{17}]\cdot 2H_2O$ have the same *X*-ray powder pattern (Table 5) and the same solubility in water, suggesting that a spontaneous resolution occurs when the crystals form. If the compound crystallised as separate crystals of the racemate and the *laevo* enantiomer, the solubility and the

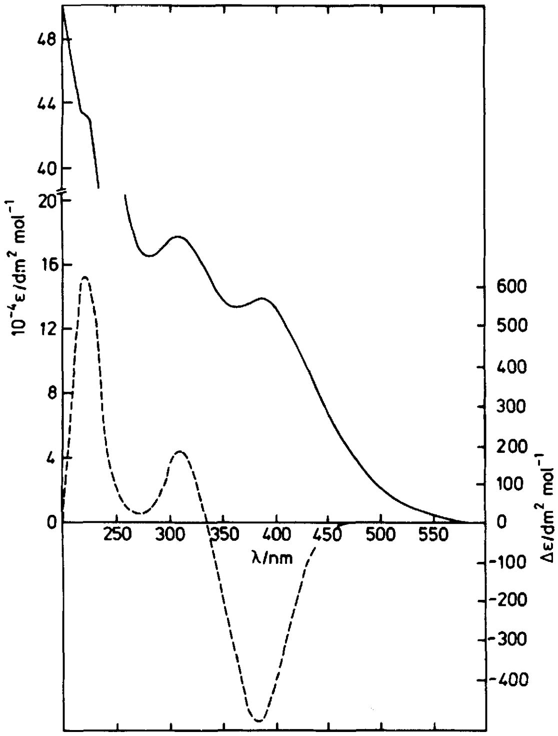

Figure 2. Electronic (——) and c.d. (– – –) spectra of $[NH_4]_2(-)$-$[PtS_{17}]$ in water

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* In a previous communication[9] the circular dichroism spectrum which was shown for $[Pt(S_5)_3]^{2-}$ is actually that of $[PtS_{17}]^{2-}$.

Table 4. Chiroptical properties of $[NH_4]_2[PtS_{17}]\cdot 2H_2O$ in water

Sample	$-\alpha_{546.1}/^\circ$	$-\Delta\varepsilon$(376 nm)/ dm^2 mol^{-1}
1	360	107
2	1 910	538
3	800	
4	1 660	
5	630	
6		269
7		216
8		314

Table 5. *X*-Ray powder pattern[a] for $[NH_4]_2[PtS_{17}]\cdot 2H_2O$

d/Å	Relative intensity[b]	d/Å	Relative intensity[b]
8.51	s	3.62	m
6.42	vs	3.47	ms
5.64	wm	3.21	w
5.37	vw	3.06	s
4.91	w	2.92	vw
4.71	vw	2.84	w
4.38	vw	2.80	w
4.25	w	2.69	w
3.90	wm		

[a] Copper K_α radiation (λ = 1.5418 Å). [b] w = Weak, m = medium, s = strong, and v = very.

powder pattern should show some variation between the different samples, since the solubility of racemic crystals differs from that of the pure enantiomer. Moreover, the simplicity of the powder pattern suggests a single lattice type.

The mechanism of the spontaneous asymmetric transformation leading to an excess of $(-)[PtS_{17}]^{2-}$ should be related to the mechanism of racemisation. Solutions of $[Pt(S_5)_3]^{2-}$ and $[PtS_{17}]^{2-}$ in water are stable in the dark, but slowly deposit sulphur and form platinum(II) species on exposure to light. In the case of the former complex, the product is $[Pt(S_5)_2]^{2-}$, whereas the product for the latter complex has not yet been characterised. However, the optical activity of solutions of $[PtS_{17}]^{2-}$ is unaffected by the presence of the platinum(II) reduction product. Similarly, addition of $[NEt_4]_2[Pt(S_5)_2]$ to $[NH_4]_2[PtS_{17}]$ in acetonitrile causes no change in the c.d. spectrum, indicating the absence of any Pt^{II}—Pt^{IV} interchange like that observed[16] with halogeno-complexes.

Treatment of $[Pt(S_5)_3]^{2-}$ with sodium sulphide causes a rapid reduction to $[Pt(S_5)_2]^{2-}$,[17] but on similar treatment with sodium polysulphide solution the complex remains unaltered. Indeed, the reaction of K_2PtCl_4 with a polysulphide solution results[3] in oxidation to $[Pt(S_5)_3]^{2-}$.

Treatment of $[PtS_{17}]^{2-}$ with an aqueous sodium polysulphide solution results in a very rapid decrease in the optical activity, although the complex is still in the +4 oxidation state. Thus, even when working as rapidly as possible, the complex has completely racemised by the time the solutions have been introduced into the spectrometer.

Although the platinum(IV) polysulphido-complexes are inert with respect to substitution and racemisation, the presence of a mixture of polysulphides brings about lability. This can occur either by reduction to platinum(II) and reoxidation to platinum(IV) or by nucleophilic attack on the ligand.[17] A further example of this lability can be seen in the reaction mixture where the formation of $[Pt(S_5)_3]^{2-}$ from $[PtCl_6]^{2-}$ occurs on mixing.

Discussion

Both maroon and brick-red solids were also obtained by Wickenden and Krause,[3,4] who characterised both of them as $[NH_4]_2[PtS_{15}]$. When they used ammonium sulphide to prepare the reaction mixture (pH = 8.7) the colour of the product varied from brick-red to maroon. Moreover, in some preparations the product tended to crystallise rapidly (colour not specified). These observations are consistent with the formulation of $[NH_4]_2[PtS_{17}]$. From a more basic reaction mixture (pH = 10.4) a maroon solid, said to be amorphous, was obtained. Addition of acid to this reaction mixture gave a red precipitate in high yield. However, the elemental analyses reported for this solid (N, 3.55; Pt, 25.4; S, 67.7%) suggest the formation of $[NH_4]_2[PtS_{17}]$. These colours are opposite to those obtained in this work.

The ion $[PtS_{15}]^{2-}$ contains* three pentasulphido-chelate rings,[2,11,12] each ring being analogous to *cyclo*-hexasulphur. In the case of $[PtS_{17}]^{2-}$ the structure cannot yet be assigned from the spectroscopic results; two leading possibilities are $[Pt(S_5)_2(S_7)]^{2-}$ or $[Pt(S_5)(S_6)_2]^{2-}$. Using the previous analogy, both *cyclo*-heptasulphur[18,19] and *cyclo*-octasulphur[20] are known together with derivatives such as S_7NH.[21]

Complexes containing polysulphido-chelates with more than five sulphur atoms are not yet known. Tetrasulphido-chelates are present in complexes such as $[M(S_4)(cp)_2]$ (cp = η^5-cyclopentadienyl, M = Mo[22] or W[23]), $[Pt(S_4)(PPh_3)_2]$,[24] $[Mo_2S_{10}]^{2-}$,[25] and $[MoS(S_4)_2]^{2-}$.[26] The only known[27] trisulphido-complex is $[\{Ti(S_3)(cp)_2\}_2]$ which contains an eight-membered ring, while a large number of disulphido-complexes have been reported.[28] The complex $[NH_4]_2[PdS_{11}]\cdot 2H_2O$ contains bridging hexasulphido-ligands, resulting in a three-dimensional lattice.[29]

The equilibria in aqueous polysulphide solutions as a function of pH and sulphur content have been investigated by several workers.[30–33] Giggenbach[31] reported that in the region pH 9—10 the predominant species is the tetrasulphide ion with only minor amounts of the pentasulphide ion. A decrease in pH results in an increase in the average chain length. At near neutral pH in highly concentrated solutions species with more than five sulphur atoms are thought to exist.[32]

Thus, it appears that the platinum atom selects the appropriate chain length for co-ordination even if that species is present in only small amounts. The addition of acid to the reaction mixture will give rise to longer chain-length species favouring the formation of $[PtS_{17}]^{2-}$. The rate of rearrangement of the various polysulphide species as a result of a change in pH has been shown to be high.[33] Further, the rate of formation and racemisation of the platinum complexes in a polysulphide medium is rapid. Both these criteria are necessary both for the formation and the asymmetric transformation of $[PtS_{17}]^{2-}$.

The results here include, for the $[PtS_{15}]^{2-}$ ion, the first inorganic optically active species with a third-row transition element as centre, the first with only two elements (Pt and S) present, and the first with six-membered chelate rings. As for the $[PtS_{17}]^{2-}$ ion, this is the first spontaneous occurrence of optical activity in a purely inorganic ion, and as for the salt $[NH_4]_2[PtS_{17}]\cdot 2H_2O$, this is the first spontaneous occurrence of optical activity in a purely inorganic salt.

Experimental

General.—All preparations and reactions were carried out in vessels open to the air and shielded from direct light. All

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* In the salts obtained so far; other isomers will probably be found.

compounds and solutions were stored in the dark. Solvents were of analytical grade purity.

Physical Measurements.—Infrared spectra were recorded for Nujol mulls or in acetone solution between caesium iodide plates on a Perkin-Elmer 457 spectrometer and were calibrated with the pure rotation spectrum of water vapour.[34] Raman spectra were run as 2% solids in potassium bromide discs at 80 K using a low-temperature cell on a Spex 1401 spectrometer. The incident radiation was at 647.1 nm with a laser power of 200 mW and a slit width of $\leqslant 5$ cm^{-1}. Electronic spectra were obtained on a Beckman DK-2A ratio-recording spectrophotometer and were calibrated with a holmium oxide filter. Circular dichroism spectra were recorded on a Jobin Yvon CNRS-Roussel-Jouan Dichrographe III spectrophotometer. *X*-Ray powder patterns were recorded on a Nonius Guinier–de Wolfe camera with Cu-K_α radiation and were calibrated with α-alumina.[35]

Thermogravimetric analyses were obtained with a Stanton Redcroft TG750 thermogravimetric balance in a dynamic atmosphere of air (flow rate 25 cm^3 min^{-1}) at a heating rate of 5 °C min^{-1}. Both powdered and crystalline samples between 5 and 10 mg in weight were used. The loss of volatile substances was complete by 450 °C and the crucible was heated to 900 °C to obtain the platinum residue. Elementary microanalyses (C, H, and N) were carried out by the Microanalytical Service, Department of Chemistry, University College, Cardiff. Sulphur analyses were by CHN Analyses Ltd., Leicester.

Reagents.—Laboratory grade reagents were used without further purification; $RuCl_3{\cdot}nH_2O$ and K_2PtCl_6 were purchased from Johnson Matthey. The complexes $[RuL_3]^{2+}$ (L = bipy or phen) were prepared from $RuCl_3{\cdot}nH_2O$ by the method of Liu, *et al.*[36] $[Ru(phen)_3]^{2+}$ was resolved with sodium antimonyl (+)tartrate according to the method of Dwyer and Gyarfas,[37] $[Ru(bipy)_3]^{2+}$ by fractional crystallisation of the double salt $[Ru(bipy)_3]_3I_2[(SbO)\{O_2CCH(OH)CH(OH)CO_2\}]_4{\cdot}18H_2O$.[38] The (+) and (−) enantiomers were converted into the corresponding perchlorate salts which were recrystallised from acetone–ethanol.

$[NH_4]_2[Pt(S_5)_3]{\cdot}2H_2O$. Hydrogen sulphide was bubbled into a slurry of sulphur (40 °C) in concentrated ammonia solution (100 cm^3) with stirring until the dissolution of sulphur was complete. A suspension of K_2PtCl_6 (1.0 g) in water (*ca.*10 cm^3) was added to the deep red solution with vigorous stirring. The solution was filtered and stored at *ca.* 5 °C for several days. The brick-red crystals (*ca.* 0.8 g, 50%) were collected, washed with ice-water (three times), and dried *in vacuo* over silica gel. The crystals were washed with carbon disulphide (three times) and redried. A further crop of crystals (0.3 g) was obtained on storing the filtrate in the refrigerator. The compound is moderately soluble in water and very soluble in polar organic solvents.

$[NH_4]_2[PtS_{17}]{\cdot}2H_2O$. A filtered reaction mixture, prepared (as described above) by adding K_2PtCl_6 (1.0 g) to an ammonium polysulphide solution, was placed in a bath of cold water. Concentrated hydrochloric acid (10—20 cm^3) was added at a moderate rate with vigorous stirring until the pH of the mixture was *ca.* 9.4 (some elemental sulphur usually precipitates). The mixture was stored at *ca.* 5 °C for several hours. The solid was removed by filtration, washed with ice–water (three times), dried over silica gel, and washed free of sulphur with carbon disulphide to give maroon microcrystals of $[NH_4]_2[PtS_{17}]{\cdot}2H_2O$ (1.1 g) (Found: H, 1.5; N, 3.9; Pt, 24.0; S, 66.6. $H_{12}N_2O_2PtS_{17}$ requires H, 1.5; N, 3.5; Pt, 24.0; S, 67.1%). The compound is sparingly soluble in water and very soluble in polar organic solvents.

$[NEt_4]_2[Pt(S_5)_3]$. A dilute solution of NEt_4Br in water was added dropwise with stirring to a solution of $[NH_4]_2[Pt(S_5)_3]{\cdot}2H_2O$ (100 mg) in water (8 cm^3) until precipitation was complete. The mixture was left for 30 min and the orange solid (90 mg, 75%) was collected by filtration, washed twice with cold water, and dried *in vacuo* (Found: C, 19.8; H, 4.2; Pt, 21.3; S, 50.9. $C_{16}H_{40}N_2PtS_{15}$ requires C, 20.5; H, 4.3; Pt, 20.8; S, 51.4%).

$[NEt_4]_2[PtS_{17}]$. The method is the same as that for $[NEt_4]_2[Pt(S_5)_3]$, except that a mixture of water (5 cm^3) and methanol (10 cm^3) was used to dissolve $[NH_4]_2[PtS_{17}]{\cdot}2H_2O$. Yield 92 mg (70%) of an orange-red powder (Found: C, 19.2; H, 4.2; Pt, 19.6; S, 54.3. $C_{16}H_{40}N_2PtS_{17}$ requires C, 19.2; H, 4.0; Pt, 19.5; S, 54.5%).

These NEt_4^+ salts are soluble in methanol, acetone, and acetonitrile and sparingly soluble in water.

$[NEt_4]_2[Pt(S_5)_2]$. The complex was prepared by the method of Schmidt and Hoffmann[17] using $[NH_4]_2[Pt(S_5)_3]{\cdot}2H_2O$ (125 mg) and $Na_2SO_3{\cdot}7H_2O$ (480 mg) and stirring for 3.5 min (yield 100 mg, 77%) (Found: C, 23.5; H, 5.2; N, 3.4; Pt, 24.7. Calc. for $C_{16}H_{40}N_2PtS_{10}$: C, 24.8; H, 5.2; N, 3.6; Pt, 25.1%). The compound is soluble in acetone and very soluble in acetonitrile.

Resolution of $[Pt(S_5)_3]^{2-}$.—(*a*) *With* $[Ru(bipy)_3]^{2+}$. A solution of $(-)[Ru(bipy)_3][ClO_4]_2$ (51.0 mg, 6.6×10^{-2} mmol) in acetone (14 cm^3) was added dropwise with stirring to a solution of $[NH_4]_2[Pt(S_5)_3]{\cdot}2H_2O$ (100 mg, 0.13 mmol) in acetone (4 cm^3). The orange-red precipitate of $(-)[Ru(bipy)_3](-)[Pt(S_5)_3]$ was collected, washed with acetone, water, and acetone, and dried *in vacuo* (Found: C, 29.4; H, 2.0; N, 7.1. $C_{30}H_{24}N_6PtRuS_{15}$ requires C, 28.9; H, 1.9; N, 6.7%). The salt $[NH_4]_2(+)[Pt(S_5)_3]$ was recovered by evaporating the filtrate to dryness. The mixed salt $[Ru(bipy)_3][Pt(S_5)_3]$ is insoluble.

(*b*) *With* $[Ru(phen)_3]^{2+}$. The procedure is identical to that described in (*a*), but gives only a partial resolution (Found: C, 30.7; H, 1.8; N, 6.3. $C_{36}H_{24}N_6PtRuS_{15}$ requires C, 32.8; H, 1.8; N, 6.4%).

Analysis for Sulphur (*see Table* 1).—Initially, the method of Feher and Berthold[39] for analysis of alkali polysulphides, expressed by equation (1), was followed, but during the titration

$$S_x^{2-} + (2x - 2)OH^- + (3x + 1)H_2O_2 \longrightarrow xSO_4^{2-} + 4xH_2O \qquad (1)$$

of residual hydroxide with 0.1 mol dm^{-3} HCl using phenolphthalein the end-point was not sharp. Our method utilised the above reaction, and additionally precipitated the product sulphate with barium chloride.

Approximately 30—40 mg of $[NH_4]_2[PtS_{15}]{\cdot}nH_2O$ was dissolved in 0.1 mol dm^{-3} NaOH (15 cm^3) and excess of H_2O_2 ('100 volume,' *ca.* 2 cm^3) added. Decolourisation begins almost immediately. The solution was left to stand for several hours (final pale yellow solution), excess of H_2O_2 was evaporated off (steam-bath), and then acidified with HCl. A slight excess of barium chloride was added to the hot solution which was digested for about 30 min before filtering off $BaSO_4$ (pure white precipitate). Typical results were: 0.0389 (0.0352) g compound gave 0.1796 (0.1641) g $BaSO_4$ corresponding to 63.5 (63.9)% S.

Acknowledgements

We thank Mr. Mitchell for recording the *X*-ray powder patterns and for some sulphur analyses and Dr. L. Ferris for the Raman spectra.

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Received 22*nd March* 1984; *Paper* 4/469