diastereoisomers and have "common physiological specificity." The diastereoisomer solubility criterion would seem to be unsound as the phenanthroline complex crystallizes as (d-Ni(phen)$_3$)(d-SbOtart)$_2 \cdot 7H_2O$ and the bipyridine complex as (l-Ni(bipy)$_3$)$_3$(d-SbOtart)$_4I_2 \cdot 18H_2O$. Further, the relative solubilities of the possible diastereoisomers depend on the concentration of the resolving agent that has been used.[25] In addition, the assignment of relative configurations based on the common physiological specificity of the complexes is not supported by the literature. Although much has been published on the physiological action of 1,10-phenanthroline and 2,2′-bipyridine complexes, the stated comparison was not found.[26]

Although it was not possible with the present circular dichrograph to study the complete $^3T_{1g}$ band, the highest energy component centered at about 13 kK for the four nickel complexes was found to be positive for the l isomers. By comparison with the circular dichroism of L-tris(l-*trans*-1,2-diaminocyclohexane)-nickel(II) for both this band and the $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ band,[27] it can be concluded that the l isomers have the L configuration.

For *cis*-bis(bidentate) complexes, one of the components with E trigonal parentage generally seems to dominate the circular dichroism spectra in the vicinity of the first ligand field band.[28] The absolute configurations assigned on this basis agree with those from the nonempirical method except for l-Cr(bipy)$_2$(ox)$^+$, which also has an overlapping Cotton effect from a neighboring transition.

Acknowledgments.—The authors gratefully acknowledge financial support from the Australian Research Grants Committee.

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[25] See, for example, A. M. Sargeson in "Chelating Agents and Metal Chelates," F. P. Dwyer and D. P. Mellor Ed., Academic Press, New York, N. Y., 1964, pp 218–220.

[26] For a comprehensive review of the subject see A. Shulman and F. P. Dwyer, ref 25, pp 383–439.

[27] R. S. Treptow, *Inorg. Chem.*, 7, 1229 (1968).

[28] A. J. McCaffery, S. F. Mason, and B. J. Norman, *J. Chem. Soc.*, 5094 (1965).

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Polysulfide Chelates. II. Desulfuration of PtS_{15}^{2-} and the Synthesis of PtS_{10}^{2-} [1a,b]

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A reproducible method for obtaining a high yield of $(NH_4)_2PtS_{15}$ from a polysulfide solution is described. One ligand reaction, the attack of polysulfide chelate rings by cyanide ion, has been investigated in detail. The over-all stoichiometry of this reaction has been shown to be: $PtS_{15}^{2-} + 17CN^- \rightarrow Pt(CN)_4^{2-} + 13SCN^- + 2S^{2-}$. Early in the reaction a new polysulfide chelate, PtS_{10}^{2-}, may be isolated as a tetrapropylammonium salt. This compound has been characterized and compared with $(NH_4)_2PtS_{15}$. The new complex consists of planar platinum(II) surrounded by two pentasulfide chelating ligands. During the course of the cyanide reaction a novel electron transfer occurs reducing platinum(IV) to platinum(II).

Introduction

Polysulfides should be capable of forming a novel class of coordination compounds, complexes in which each chelate ring consists of only one metal ion and several sulfurs. We have reported a method[1a] whereby the polysulfide has been constructed about the metal ion *via* the template effect. One should also be able to utilize polysulfide ions to synthesize such complexes. Several compounds have been reported which probably contain chelating polysulfides but have not been recognized as such. Most recently Köpf, Block, and Schmidt[2] have demonstrated that the compound which they synthesized, $Ti(C_5H_5)_2S_5$, does contain a polysulfide chelate ring.

One of the most interesting polysulfide complexes, $(NH_4)_2PtS_{15}$, was isolated by Hofmann and Höchtlen in 1903.[3] They were aware of the fact that S_5^{2-} groups were probably present, but they did not propose a structure for the compound. Recently, Jones and Katz[4] reported the crystal structure of $(NH_4)_2PtS_{15}$ and confirmed that it does indeed contain pentasulfide chelate rings about platinum(IV).

We are currently investigating the chemistry of this compound in some detail. One aspect of considerable

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[1] (a) For Part I see N. B. Egen and R. A. Krause, *J. Inorg. Nucl. Chem.*, **31**, 127 (1969). (b) Presented in part at the 155th National Meeting of the American Chemical Society, San Francisco, Calif., 1968. (c) From a dissertation submitted to the Graduate School of the University of Connecticut by A. E. W. in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] H. Köpf, B. Block, and M. Schmidt, *Chem. Ber.*, **101**, 272 (1968).

[3] K. A. Hofmann and F. Höchtlen, *ibid.*, **36**, 3090 (1903).

[4] P. E. Jones and L. Katz, *Chem. Commun.*, 842 (1967).

interest to us is the reactions which coordinated polysulfide may undergo. It is well known that cyanide ion readily removes sulfur from sulfur chains with the formation of thiocyanate. Of interest to us, then, is the cyanide degradation of PtS_{15}^{2-}. Quite unexpectedly this reaction led to the isolation of a new platinum(II) polysulfide chelate, PtS_{10}^{2-}. These results are described below.

Experimental Section

All chemicals were of common laboratory grade and were used as supplied.

Preparation of $(NH_4)_2PtS_{15}$.—Hoffman and Höchtlen[3] simply stated that they saturated a 25% $(NH_4)_2S$ solution at 30° with sulfur and then added a 10% solution of platinum chloride until a precipitate formed. After filtering and storing at 5° several days, crystals were obtained. Attempting to follow these directions gave varying results. Two general procedures were devised; they vary in the method of generating the polysulfide solution.

Method A.—The first method was to generate the polysulfide by saturating 100 ml of Mallinckrodt $(NH_4)_2S$ solution with sulfur; of the 40 g added, approximately 30 g dissolved. The remaining sulfur was removed by filtration. Such *in situ* generation probably gave a mixture of polysulfides, but S_5^{2-} was considered to be the most stable polysulfide and undoubtedly predominated. Assuming mainly pentasulfide was formed, approximately 100 mol was available per mole of platinum taken.

To the polysulfide solution 1.00 g of H_2PtCl_6 (40% Pt) in 10 ml of water was added dropwise with vigorous stirring. The resulting mixture was rapidly filtered and the filtrate was stored at 5° for at least 24 hr. The brick red to maroon complex obtained was rapidly washed twice with a small amount of ice water and dried *in vacuo* over P_4O_{10} for 12 hr. It was then washed with CS_2 to remove sulfur and redried under vacuum over P_4O_{10}. This method of drying gave the anhydrous complex in contrast to Hoffman and Höchtlen's dihydrate obtained from drying over H_2SO_4. The compound was prepared 15 times using these directions. *Anal.* Calcd for $(NH_4)_2PtS_{15}$: N, 3.94; Pt, 27.40; S, 67.54. Found: N, 3.86; Pt, 27.22; S, 67.65. This analysis is for a representative compound; a number of others were analyzed and gave similar results.

The principal problem with the above method is that in 11 of the 15 attempts a substantial amount of product precipitated before the initial filtration. Only about a 20% yield was obtained from the second crop. Close to 1 g of solid was obtained in the first precipitate which may not be of very high purity owing to contamination by insoluble platinum sulfides and ammonium salts. (One analysis of this initial precipitate showed it to be of acceptable composition, however.)

Method B.—The second method of generating polysulfide solution was that given by Mills and Robinson[5] for the preparation of $(NH_4)_2S_5$. Forty grams of sulfur was slurried in 100 ml of concentrated NH_3 and the solution was saturated with H_2S until all of the sulfur dissolved. (This solution presumably contains a somewhat greater quantity of pentasulfide than that from method A.) The platinum solution was added dropwise. No product precipitated and the solution was filtered and refrigerated. After 24 hr a maroon solid was isolated, washed with ice water, and dried *in vacuo* over P_4O_{10}. When the product was dry, it was washed with CS_2 and redried. This experiment was repeated 5 times; a sample analysis is given. *Anal.* Calcd for $(NH_4)_2PtS_{15}$: N, 3.94; Pt, 27.40; S, 67.54. Found: N, 3.91; Pt, 27.59; S, 67.65.

The complex obtained this way was invariably amorphous, in contrast to that from method A, which gave fine crystals that had an X-ray powder pattern.

Aside from the sulfur content, the only difference between the solutions of polysulfide from the two methods was their pH. The solution from the $(NH_4)_2S$ method (method A) contained little excess ammonia and had an initial pH of 8.7. After adding the H_2PtCl_6 and removing the initial precipitate, the pH of the mother liquor dropped to 8.3. The solution generated from H_2S and NH_3 (method B), however, had a pH of 10.4. After adding the platinum, the pH dropped to 10.1.

It was felt that control of the pH could correct the problems of both methods A and B. An experiment was run in which method B directions for the generation of $(NH_4)_2S_5$ were followed; the platinum was added as usual, and the solution was filtered. At this point concentrated HCl was added dropwise with stirring while the pH was monitored (pH meter). Owing to the high NH_3 concentration, the solution was well buffered and the pH changed very slowly. Precipitation started at about pH 9.8. After 7.0 ml of acid was added, considerable red precipitate was present and the pH registered 9.3. The mixture was allowed to digest and finish precipitating at 5° for 48 hr. The $(NH_4)_2PtS_{15}$, obtained in 90% yield, was crystalline. *Anal.* Calcd for $(NH_4)_2PtS_{15}$: N, 3.94; Pt, 27.40; S, 67.54. Found: N, 3.56; Pt, 25.41; S, 67.67.

Attempted Synthesis of $(NH_4)_2PtS_{10}$.—The platinum(II) analog of $(NH_4)_2PtS_{15}$ was sought by a comparable route. $(NH_4)_2S_5$ was generated by the Mallinckrodt $(NH_4)_2S$ route (method A). A solution of 1.00 g of K_2PtCl_4 (0.00240 mol) in 10 ml water was added dropwise. No precipitation occurred and the solution was stoppered and refrigerated overnight. Fine orange-red crystals were obtained, washed with ice water, dried *in vacuo* over P_4O_{10}, rewashed with CS_2, and redried. *Anal.* Calcd for $(NH_4)_2PtS_{10}$: N, 5.08; Pt, 35.40; S, 58.17. Calcd for $(NH_4)_2PtS_{15}$: N, 3.93; Pt, 27.40; S, 67.54. Found: N, 3.73; Pt, 27.88; S, 66.95. This compound is obviously the platinum(IV) complex and not the desired platinum(II) compound.

Synthesis of $[(C_3H_7)_4N]_2PtS_{10}$.—One gram of $(NH_4)_2PtS_{15}$ was slurried in 75 ml of water and was warmed to 70° to effect solution. Then 1.37 g of solid KCN was added to the warm solution. The color immediately darkened. The reaction was allowed to proceed for 2 min and then suction filtered. A solution of 1.00 g of $(C_3H_7)_4NBr$ in 10 ml of water was immediately added to the filtrate; a red-orange precipitate formed at once. The precipitate was cooled 0.5 hr in ice and then filtered, washed with water, and dried *in vacuo* over P_4O_{10}; yield, 1.02 g, 82%. *Anal.* Calcd for $[(C_3H_7)_4N]_2PtS_{10}$: C, 32.25; H, 6.31; N, 3.16; Pt, 21.98; S, 36.08. Found: C, 32.28; H, 6.71; N, 3.23; Pt, 21.05; S, 36.81.

Physical Measurements.—Electronic spectra were run on a Cary 14 spectrophotometer equipped with a high-intensity visible source. A 3.07×10^{-3} *M* solution of $(NH_4)_2PtS_{15}$ in water was run from 200 to 1200 mμ. Between 190 and 600 mμ a 3.07×10^{-5} *M* solution was scanned, and the peak locations and intensities were calculated from this curve. $[(C_3H_7)_4N]_2PtS_{10}$ was made up to 1.00×10^{-3} *M* in spectrograde acetonitrile and its spectrum was recorded against acetonitrile in the reference compartment between 200 and 1000 mμ. Dilutions were made up to 3.00×10^{-4} and 3.00×10^{-5} *M*, and they were scanned between 200 and 600 mμ to obtain the reported spectra.

For the spectrum of $(NH_4)_2S_5$ this compound was generated as in method A (above) to give an approximately 2 *M* solution of S_5^{2-} on the basis of sulfur dissolved. The solution was diluted with concentrated aqueous NH_3 to 10^{-4} and 10^{-2} *M* to obtain the spectrum.

An infrared spectrum of $[(C_3H_7)_4N]_2PtS_{10}$ was run as a mineral oil mull on NaCl plates between 2 and 16 μ on a Perkin-Elmer Infracord instrument, Model 137. In the 11–35-μ region, a Beckman IR 5A CsBr instrument was used to scan mineral oil mulls of both compounds, supported between CsBr plates.

Conductivity was run on a 1.0×10^{-3} *M* solution of $[(C_3H_7)_4N]_2PtS_{10}$ in acetonitrile. A molar conductance of 239 mhos (25°) verified the 2:1 electrolyte nature of this compound.

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(5) H. Mills and P. L. Robinson, *J. Chem. Soc.*, 2326 (1928).

Analyses were performed by Galbraith Laboratories, Knoxville, Tenn. It was requested that they analyze sulfur by the Carius method and, for $(NH_4)_2PtS_{15}$, nitrogen by the Dumas method. Kjeldahl analyses for nitrogen gave low results.

Stoichiometry of the Cyanide Reaction.—The following experiments were designed so that a 20:1 mole ratio of cyanide to complex was used.

Reaction of $(NH_4)_2PtS_{15}$ with CN^- at 67°.—In order to maintain a constant temperature for these reactions, a refluxing solvent bath was used around the reaction flask. A reactor was constructed from a 200-ml, three-necked, round-bottomed flask. To the outside of this flask was fused a Pyrex jacket to contain the refluxing thermostating liquid. A Ŧ neck for a condenser connection was added to the jacket.

One neck of the inside flask was outfitted with a sintered-glass gas dispersion stick reaching the bottom of the flask; this was used as an N_2 inlet. Into a second neck was placed a connecting tube to conduct the N_2 effluent through a trap containing NaOH solution. The center neck was stoppered and used for access to the flask during the addition of complex; later in the reaction the stopper was removed and a pressure compensation addition funnel was placed in the neck.

A mixture of hexane isomers (boiling range 67–69°) was selected as the thermostat liquid. Approximately 200 ml of hexane was placed in the jacket (this quantity brought the level of the bath above the level of the contents of the reaction flask), and a condenser was added to the port in the jacket. The reaction flask assembly was placed on a hot plate and the hexane was brought to relux. In this apparatus, the reflux temperature was 67° and remained so for several hours. In case any fractionation of the hexane isomers occurred on prolonged refluxing, a fresh charge was used for each experiment.

At the start of each run, 20.00 ml of a standardized solution of KCN (0.14 *M*) was pipetted into the interior flask. A 0.1-g sample of $(NH_4)_2PtS_{15}$ (actual weights ranged from 0.1000 to 0.1036 g) was placed in a vial; 8.12 ml of water was pipetted into the vial with the complex. This container was placed upright in the reaction flask; thus the complex was not in contact with the cyanide. A gentle N_2 flow was started through the apparatus and conducted into a trap containing 200 ml of 0.1 *M* NaOH.

The contents of the reactor were allowed to preheat 1 hr after the hexane in the outer jacket started refluxing. At this time the inner flask contents were at 67°; the two reactants were mixed by shaking the entire apparatus.

When the reaction had run the prescribed length of time, the condenser was removed, the hot hexane was siphoned out of the jacket, and ice-cold hexane was immediately poured in. When the jacket was filled with cold hexane, timing of the reaction was stopped. The reactor was packed into ice and allowed to cool 7 min. This served to quench the reaction; at room temperature and below, the reaction proceeded very slowly.

After cooling, the flask was taken from the ice and the cold hexane was removed. The N_2 flow was stepped up as briskly as the NaOH trap could accommodate; then the reactor was opened and an addition funnel containing 50 ml of 0.5 *M* $HClO_4$ was inserted. After 5 min the acid was added. Outgassing was continued 45 min; at the end of this time the NaOH flask contained the unreacted cyanide and any sulfide that had been generated.

Several runs were made adding dry $(NH_4)_2PtS_{15}$ to the preheated cyanide solution and 8.12 ml of water to keep the concentration effects the same. The remainder of the procedure was carried out as above. This variation did not influence the results.

Procedure for Isolating $[(C_3H_7)_4N]_2PtS_{10}$.—This experiment was conducted to determine if the initial reaction product was identical with that obtained under the high concentration and less rigorously controlled preparative conditions described above. The equipment was modified slightly in this reaction: no N_2 was used so that the inlet stick and outlet tube were removed. Two necks of the reaction flask were stoppered and a thermometer was inserted loosely in the other. Hexane was refluxed in the jacket as described previously; after 15 min the cyanide solution had reached 66°. At this time 0.1003 g of $(NH_4)_2PtS_{15}$ was added, the timing was started, and the reactor was shaken to complete the dissolution of complex. The reaction was allowed to proceed for 10 min.

At the end of 10 min, the hot hexane was siphoned off and the flask contents were poured into a prechilled beaker in an ice bath. This solution was stored in the ice bath while more product was prepared. A total of 0.50 g of $(NH_4)_2PtS_{15}$ was allowed to react in this manner.

The solution was filtered and 0.80 g of $(C_3H_7)_4NBr$ in 4 ml of water was filtered into it. An orange precipitate formed immediately; it was cooled in ice for 10 min, filtered, washed twice with cold water, and dried *in vacuo* over P_4O_{10}; yield, 0.39 g, 62%. *Anal.* Calcd for $[(C_3H_7)_4N]_2PtS_{10}$: C, 32.25; H, 6.31; N, 3.16; Pt, 21.98; S, 36.08. Found: C, 32.29; H, 6.49; N, 3.29; Pt, 21.80; S, 36.35.

Reaction at 25°.—Runs at this temperature were conducted in a three-necked, round-bottomed flask in a water bath at 25 ± 1°. Since the reaction was so slow at this temperature, it was felt that this crude temperature control was of no consequence.

The basic difference in procedure from that described above was the method of quenching the reaction. The addition funnel was installed immediately after the complex was introduced, and at the conclusion of the prescribed time, the $HClO_4$ was added. Outgassing was started immediately after the acid was added. In all of these runs the complex was added dry to 20.00 ml of KCN solution and 8.12 ml of water which had equilibrated in the bath for 15 min. The amount of water added to the KCN solution was that necessary to give the same concentration as that in the 67° experiments.

Analytical Procedure.—At the conclusion of the outgassing step, any unreacted cyanide and the sulfide had been swept into the NaOH flask; the thiocyanate and complex were still in the reaction flask. Both flasks were titrated potentiometrically with 0.1000 *M* $AgNO_3$ using a silver–silver sulfide electrode and a saturated calomel electrode. The calomel electrode was placed in a cup with a sintered-glass bottom which contained 0.1 *M* KNO_3. This was placed in the solution to be titrated and prevented chloride from appearing in the titration curve.

In the titration of the pot contents from the short runs, the silver salt of the complex precipitated before the AgSCN; as the degradation reaction neared completion, the complex was titrated last. In the early time periods some complex appeared to be precipitated by the acid. This solid was slow in coming to equilibrium with the Ag^+ titrant; thus the titration curves are sometimes difficult to interpret.

When the base flask solution was titrated, the sulfide precipitated first, followed by the cyanide. There was no ambiguity in interpreting these curves.

The analytical procedure was tested in known solutions and found to give satisfactory results.

The cyanide solution was standardized by titration with 0.1000 *M* $AgNO_3$ until turbidity was reached (Liebig method). Standardization was repeated at approximately 1-week intervals. Several samples were also standardized potentiometrically; results were within 0.0016 *M*. The Liebig values were used in the calculations.

Standard silver solutions were made from direct weight of reagent grade solid $AgNO_3$.

Results and Discussion

The method reported by Hofmann and Höchtlen for the synthesis of $(NH_4)_2PtS_{15}$ we have found to yield somewhat erratic results. Slight modifications lead to a much more reproducible synthesis. Two distinct forms of the compound (both anhydrous) are prepared through the two different procedures we have devised. Both have the same composition; however, that from the more basic solution (method B) does not give an X-ray powder pattern while that from method A does. These compounds appear to be otherwise identical. If acid is added to the solution generated in method B so that the pH approaches that of method A, immediate precipitation occurs. A crystalline form of $(NH_4)_2PtS_{15}$ of acceptable analysis is isolated in high yield following this procedure.

We attempted to prepare the platinum(II) analog, $(NH_4)_2PtS_{10}$, in the same fashion. However, only $(NH_4)_2PtS_{15}$, the platinum(IV) complex, was isolated. Examination of the few available oxidation potentials[6] indicates that under the concentrations employed oxidation to platinum(IV) is indeed favored. It was through an entirely unexpected route that the PtS_{10}^{2-} ion was isolated. Cyanide attack of the first polysulfide chelate ring in PtS_{15}^{2-} leads to electron transfer along with desulfuration. The platinum(II) complex is isolated (in high yield) as a tetrapropylammonium salt from a reaction mixture consisting of cyanide ion and PtS_{15}^{2-}. Analytical data leave no question regarding the composition of this substance. The molar conductance (in acetonitrile) indicates this compound to be a uni-divalent electrolyte as expected.

Examination of the infrared spectra of these compounds in the CsBr region lends support to the formulation of PtS_{10}^{2-} as a planar platinum(II) complex. The salient features of the spectra are listed in Table I.

TABLE I

FAR-INFRARED SPECTRA OF PtS_{15}^{2-} AND PtS_{10}^{2-}

Compd	Freq,[a] cm⁻¹		
$(NH_4)_2PtS_{15}$	586 m, b	490 w 450 w	294 sh 286
$[(C_3H_7)_4N]_2PtS_{15}$[b]			297 m 286
$[(C_3H_7)_4N]_2PtS_{10}$[b]		455 m 438 m	304 sh 290 m

[a] Abbreviations: m, medium; b, broad; sh, shoulder; w, weak.
[b] $(C_3H_7)_4N^+$ bands removed.

The simplest spectrum to assign is that of $(NH_4)_2PtS_{15}$. Two weak bands at 490 and 450 cm⁻¹ are assigned as S–S modes. This designation is undoubtedly correct as the S–S mode has been located in a wide variety of compounds. Representative values are 450 cm⁻¹ in S_8,[7] 490 cm⁻¹ in $(C_7H_7)_2S_4$, and 460–470 cm⁻¹ in $(C_5H_5)_2TiS_5$.[2] A broad shoulder at 294 cm⁻¹ in the spectrum of PtS_{15}^{2-} is considered to be a Pt–S stretch. The broad, weak band at 568 cm⁻¹ in the ammonium salt of PtS_{15}^{2-} is assigned as an NH_4^+ mode since this band disappears in the tetrapropylammonium salt.

Comparison of the $[(C_3H_7)_4N]_2PtS_{10}$ spectrum with the spectra of a number of other tetrapropylammonium salts made it possible to subtract out the bands due to the cation in $[(C_3H_7)_4N]_2PtS_{10}$. A tetrapropylammonium band centered at 478 cm⁻¹ obscures the high-energy S–S stretch. A band much too intense for a S–S mode is present at 455 cm⁻¹ so that the lower energy S–S mode is also hidden. Fujita and Nakamoto have carried out a normal-coordinate analysis of the chelate ring of the dithiooxalatoplatinum(II) complex.[8] Their calculations allow them to assign a pair of bands at 436 and 422 cm⁻¹ and another band at 322 cm⁻¹ as the Pt–S stretching modes. By comparison with the platinum(II) dithiooxalate, it is easy to assign the double-peaked band at 455 and 438 cm⁻¹ and the band and shoulder at 290 and 304 cm⁻¹ in PtS_{10}^{2-} as the analogous Pt–S modes of the platinum(II) pentasulfide complex. PtS_{15}^{2-}, which has pseudo-O_h symmetry, is of higher symmetry than PtS_{10}^{2-} (pseudo-D_{4h}), so it is not surprising to observe less splitting in the octahedral complex.

The electronic spectra of these compounds are tabulated in Table II. Most probably, the bands observed in PtS_{15}^{2-} and PtS_{10}^{2-} are primarily of the charge-transfer type on the ligands. Because of the shift from free S_5^{2-} ion, it is obvious that the metal ion influences these charge-transfer spectra. However, the principal usefulness of this data is simply to illustrate further the difference between PtS_{10}^{2-} and PtS_{15}^{2-}.

TABLE II

ELECTRONIC SPECTRA OF PtS_{15}^{2-} AND PtS_{10}^{2-}

Compd	λ, mμ	$\bar{\nu}$, cm⁻¹	ε, M^{-1} cm⁻¹
$[(C_3H_7)_4N]_2PtS_{10}$	<200	>50,000	$>4 \times 10^4$
	233	42,900	2.6×10^4
	476	21,000	2.4×10^3
$(NH_4)_2PtS_{15}$	<190	>52,600	$>3 \times 10^4$
	290	34,500	1.7×10^4
	390	25,500	1.4×10^4
$(NH_4)_2S_5$	<215	>46,500	$>1 \times 10^5$
	250	40,000	3×10^3
	375	26,700	1×10^2

In an effort to learn more about the chemistry of polysulfide chelates, we are currently investigating various ligand reactions of these compounds. The cyanide degradation of sulfur chains is well known and should prove to be of interest in this respect. Data obtained from the series of stoichiometry runs are summarized in Table III. If one plots the SCN⁻ formed *vs.* the CN⁻ consumed, the data at both 25 and 67° fall on the same line, indicating that the same series of reactions is occurring in both cases. When the reaction is allowed to run to completion, the stoichiometry which best fits the data is

$$PtS_{15}^{2-} + 17CN^- \rightarrow Pt(CN)_4^{2-} + 13SCN^- + 2S^{2-}$$

Reduction of platinum(IV) has been confirmed by the isolation of a platinum(II) intermediate during the early stages of the reaction. Under the identical conditions of the stoichiometry determinations, at a point when the reaction had produced five thiocyanates, $[(C_3H_7)_4N]_2PtS_{10}$ (described above) was isolated. No

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(6) W. M. Latimer, "Oxidation Potentials," 2nd ed. Prentice-Hall, Inc., New York, N. Y., 1952.

(7) K. Nakomoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963.

(8) J. Fujita and K. Nakamoto, *Bull. Chem. Soc. Japan*, **37**, 528 (1964).

Table III[a]

Summary of the Stoichiometry of the Reaction of PtS_{15}^{2-} with CN^-

Time	CN^- used, mol	SCN^- found, mol	S^{2-} found, mol	Δ $[CN]-[SCN^-]$, mol
		67°		
6.7 min	6.5	5.6	0.4	0.9
11.9 min	8.4	7.2	0.5	1.2
20.1 min	11.1	9.6	0.7	1.5
39.6 min	13.5	11.4	1.1	2.1
61.4 min	14.9	12.0	1.3	2.9
125.6 min	16.3	12.8	1.5	3.5
12.5 hr	17.0	12.9	1.5	4.1
		25°		
1 hr	2.3	2.1	0.04	+0.2
2 hr	4.0	4.2	0.05	−0.2
4 hr	7.8	7.4	0.5	0.4
6 hr	9.5	8.6	0.7	0.9
12 hr	12.5	9.6	1.0	2.9
24 hr	14.9	11.7	1.2	3.2
52 hr	15.9	12.5	1.5	3.4

[a] All data normalized to 1 mol of $(NH_4)_2PtS_{15}$.

Table IV

Yields of PtS_{10}^{2-}

Time, min	% yield	Method
2	82	*a*
3	71	*a*
10	62	*b*

[a] Using 1 g of $(NH_4)_2PtS_{15}$ in 75 ml of water, heating to 70° to dissolve, and adding solid KCN. [b] Using 0.1 g of $(NH_4)_2PtS_{15}$ in 8 ml of water, thermostating at 67°, and adding KCN as 20 ml of 0.13 *M* solution.

water, cyanide, or thiocyanate could be detected in the infrared spectrum of this compound, giving additional verification of its composition. Furthermore, the isolation of this platinum(II) complex at this point in the reaction demonstrates that the reduction of platinum(IV) is concurrent with attack on the first chelate ring.

In order to determine the extent of the platinum reduced, an independent series of preparative reactions was run for varying lengths of time and $[(C_3H_7)_4N]_2PtS_{10}$ was isolated. Yields of these reactions are summarized in Table IV. Over 80% of the initial platinum(IV) can be obtained as the platinum(II) complex. This implies all of the platinum, not just a small fraction, undergoes reduction.

Thirteen thiocyanates are produced in this reaction; however, only twelve can result from the nonoxidative degradation of three pentasulfides. This evidence pinpoints a sulfide species as the reducing agent. The extra mole of thiocyanate is produced by cyanide attack on the elemental sulfur formed from quantitative reduction of platinum(IV).

If all of the sulfide from the degradation of the first chelate ring is converted to thiocyanate, no sulfide should be found during the early stages of the reaction. Indeed, the stoichiometric data show that not until the other chelate rings are attacked does sulfide production become appreciable.

In view of the ready oxidation of platinum(II) in pentasulfide medium, the reduction which accompanies the cyanide degradation of the first ring in PtS_{15}^{2-} was unexpected. However, an unusual type of electron-transfer process can be envisioned for the reduction of platinum(IV) by a coordinated sulfide or polysulfide ion. The oxidizing and reducing agents are already in the form of an activated complex, and no bridge or outer-sphere complex formation is necessary to initiate the electron transfer. This ready-made pathway undoubtedly encourages rapid movement of electrons onto the metal. Nucleophilic attack by cyanide on the sulfur chelate ring simply triggers the electron-transfer process and reduction of platinum(IV) occurs.

The Δ column in Table III shows the difference between CN^- used and SCN^- found, which is a measure of the uptake of cyanide ion by platinum. In agreement with the other data it can be seen that there is no coordination of CN^- during the early stages of the reaction, when the first chelate ring is being degraded and reduction occurs. While the second and third rings are attacked, a gradual uptake of cyanide is observed.

The ultimate product of this reaction is the $Pt(CN)_4^{2-}$ ion. Several attempts were made to isolate this ion from the solution at the end of the reaction. These were all unsuccessful owing to the known appreciable solubility of salts of this compound. As the reaction is run for extended periods, the intense red-orange color associated with the PtS_{10}^{2-} fades to colorless, as is $Pt(CN)_4^{2-}$. Even though no final product was isolated, the stoichiometric data and properties of the solution indicate $Pt(CN)_4^{2-}$ to be the final product.

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