Chemical and Structural Characterization of a Palladium Polysulfide, $(NH_4)_2PdS_{11} \cdot 2H_2O$

P. S. HARADEM. J. L. CRONIN, R. A. KRAUSE and L. KATZ

Department of Chemistry and Institute of Materials Science, University of Connecticut, Storrs, Conn. 06268, U.S.A.

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A reproducible synthesis for $(NH_4)_2PdS_{11} \cdot 2H_2O$ (and the analogous potassium salt) has been devised. Single crystal X-ray studies indicate that Pd atoms are linked via S_6 chains in an extended three-dimensional array; there are no discrete PdS_{11}^{2-} groups. The crystal structure is a composite of different possible linkages in which some chains are apparently aborted, principally at the middle sulfurs of the chains. Sulfur absences reduce the ideal PdS_{12}^{2-} composition to PdS_{11}^{2-}. The structure implies an oxidation state for Pd of +2, which is consistent with the chemical reaction behavior with CN^- in H_2O and DMF. The structure also explains why it is impossible to work with these compounds in solution without degrading them. The crystals have a (statistical) tetragonal symmetry, a = 11.065(12), c = 6.862(15)Å, probable space group P4/mnc, Z = 2. Automated counter methods were used to measure 1800 reflections of which 608 were independent and 243 were considered observed. Structure refinement led to a conventional R of 11.3%. The Pd–S distance of 2.32 Å, S–S distances ranging from 2.01 to 2.06 Å, and S–S–S angles of 106.8 and 108.9° are all consistent with values in known structures. Reaction with CN^- in DMF results in oxidation of the Pd(II) to Pd(IV).

Introduction

The compounds $(NH_4)_2PtS_{15} \cdot 2H_2O$ and $(NH_4)_2$-$PdS_{11} \cdot \frac{1}{2}H_2O$ were first reported at the turn of the century [1, 2]. The first of these was shown to have a structure in which three cis bidentate S_5 ligands are octahedrally coordinated to the platinum ion [3]. However, several efforts in our laboratory to establish the structure of the palladium compound were unsuccessful. In the present paper we describe the chemical characterization of $(NH_4)_2PdS_{11} \cdot 2H_2O$ and the synthesis of $K_2PdS_{11} \cdot xH_2O$. We also offer a structure model for $(NH_4)_2PdS_{11} \cdot 2H_2O$ based on single crystal X-ray diffraction studies.

Experimental

Preparation of $(NH_4)_2PdS_{11} \cdot 2H_2O$

Ammonium polysulfide solution was prepared by adding 35 g elemental sulfur to 100 ml Mallinckrodt $(NH_4)_2S$ solution and stirring for one hour. The excess sulfur, about 5 g, was removed by filtration. Three grams of K_2PdCl_4 in 10.0 ml water was added to the polysulfide solution, immediately forming a black precipitate. After shaking for about two minutes the black material redissolved and the solution was filtered through Celite which had been washed twice with concentrated ammonium hydroxide solution. The filtrate was stoppered and stored at room temperature for three to five days until the solution was noticeably lighter in color and there was considerable precipitate in the flask. This was then filtered and the dark red complex was washed with water, ethanol, ether, carbon disulfide and again with ether and dried *in vacuo* over P_4O_{10} for five hours. This procedure gave the complex with variable amounts of hydration, the most common being the dihydrate. *Anal.* Calcd for $(NH_4)_2$-$PdS_{11} \cdot 2H_2O$: H, 2.27; N, 5.27; Pd, 20.03; S, 66.4. Found: H, 2.35; N, 5.16; Pd, 20.15; S, 66.55. This is a representative analysis; several other preparations were analyzed and gave similar results.

The above procedure was found to give a material with a crystal size that was easily handled and washed. If the storage was at 0 °C the reaction took between twelve and twenty days and the crystal size was rather large, about 0.3 mm in diameter. Analyses proved to be less than reproducible with this size material, possibly because of foreign material occluded within the crystalline matrix. On the other hand, if storage was at higher temperatures, about 35 °C, or if the temperature of the polysulfide solution was above room temperature when the palladium was added, a very fine material, orange in color, was obtained. Again analyses were variable presumably because the material was of very small crystal size and the removal of adsorbed material by washing was unsatisfactory. Because of the insolubility of the complex it could not be recrystallized or purified in any

way after the initial isolation. All the materials produced by this method gave reasonably sharp X-ray powder diffraction patterns indicating that they were crystalline.

Utilizing this procedure but starting with K_2PdCl_6 resulted in the formation of the same complex.

Preparation of $K_2PdS_{11} \cdot xH_2O$

A solution of potassium polysulfide was prepared by adding 96 g K_2S and 120 g sulfur to 300 ml water and stirring. After ten hours the sulfur did not appear to be going into solution so 60 g KOH was added in 20 g increments until the sulfur dissolved yielding a dark red solution approximately 3 M in potassium sulfide. To 100 ml of this solution was added 0.50 g K_2PdCl_4 in 5 ml water. It was stirred for five minutes, filtered and the filtrate stored at room temperature for eleven days. The dark red complex which crystallized was filtered and washed with water, ethanol, ether, carbon disulfide and ether, then dried in vacuo over P_2O_5 for five hours. Anal. Calcd for $K_2PdS_{11} \cdot 2H_2O$: K, 13.64; Pd, 18.56; S, 61.52. Found: K, 13.72; Pd, 18.0; S, 61.3.

Analyses

Microanalyses were performed by Baron Consulting Co., P.O. Box 663, Orange, Ct. 06477. Palladium was determined by us in the following fashion: weighed samples of approximately 0.30 g of the palladium complex were added to 100 ml of water to which 8 g bromine had been added. It was then heated to 100 °C for five hours in order to drive off all bromine and to decompose the hexabromopalladium-(IV) that may have formed during the oxidation at the lower temperature. This solution was cooled in ice water and 8 ml of a 2% solution of dimethylglyoxime in ethanol added. A yellow precipitate formed almost immediately. After digestion for twenty minutes the solution was filtered, washed with ethanol and 0.5 M hydrochloric acid, and dried in an oven at 105 °C for one hour. The precipitate was weighed as $Pd(DMGH)_2$. Six separate determinations on one sample of $(NH_4)_2PdS_{11} \cdot 2H_2O$ averaged 20.03 % Pd (theoretical: 20.03%) with an average deviation of 0.10%.

Reactions of $(NH_4)_2PdS_{11} \cdot 2H_2O$ with KCN

Using the method reported earlier [4] the reaction of the palladium complex with KCN was studied in order to further establish the constitution of the compound. Reactions were followed in water and in dimethylformamide (DMF). For the reaction in water, thirty milliliters of 0.1 M KCN solution was added to the reaction flask and maintained at 68 °C for thirty minutes before the addition of the complex. Weighed samples, approximately 0.1 g of $(NH_4)_2PdS_{11} \cdot 2H_2O$, were added. After the reaction period the flask was put into ice water to cool

and the rate of nitrogen flow increased. When the reaction mixture reached 5 °C (about five minutes), 50 ml of 0.5 M perchloric acid was added slowly and the cyanide and sulfide allowed to distil for one hour. The traps were then titrated potentiometrically with 0.1000 M silver nitrate.

It should be noted that $(NH_4)_2PdS_{11} \cdot 2H_2O$ is insoluble in water; the above reaction was therefore heterogeneous. The results indicated that the reaction needed to be studied in a homogeneous medium. DMF was selected as a solvent because it was found to dissolve the complex at elevated temperatures.

Thirty ml of DMF was heated to 100 °C in the reaction flask. Samples weighing approximately 0.1 g were added and the mixture stirred for ten minutes at which time 30.00 ml of 0.1 M aqueous potassium cyanide was pipetted into the solution. At this point the intense red color of the polysulfide changed to a blue which faded within one minute to a very light yellow. After ten minutes the flask was immersed in ice water, the nitrogen flow was increased and 50.0 ml of 0.5 M perchloric acid added slowly. At the end of one hour the traps and reaction flask were titrated potentiometrically with 0.1000 M silver nitrate solution.

Blank determinations using sodium sulfide in the reaction flask showed that, particularly in DMF, sulfide determinations were consistently low. However, cyanide, thiocyanate, and $Pd(CN)_4^{2-}$ could be determined quite accurately in the DMF reactions as well as in the aqueous system.

Results of the cyanide reactions are given in Tables I and II.

Crystal data

The crystals examined for X-ray studies were of two habits, small parallelepipeds and near spheres with one flattened side. Except for one crystal which was unfortunately lost, none of the crystals examined gave generally sharp diffraction maxima, but the spherical crystals gave the better diffraction patterns. The flattened side was an accident of growth and not crystallographically significant. Since these crystals resembled spherulites, their relatively better single crystal patterns surprised us. Small face development could be seen on these crystals when examined under sufficient magnification. The X-ray data were obtained from crystals of this habit.

The primary data crystal resembled a hemisphere with a diameter of about 0.25 mm. From precession photographs all crystals examined appeared to be tetragonal, Laue group 4/mmm. There were no systematic absences among the general reflections, h0l reflections were observed only for h + l = 2n, hhl reflections only for l = 2n. The space groups consistent with the above are P4nc (No. 104) and P4/mnc (No. 128). Both were tried, as well as a number of

TABLE I. Reaction of $(NH_4)_2PdS_{11} \cdot 2H_2O$ with KCN in Water at 68 °C.

Run	Mol CN⁻	Mol SCN⁻	Mol Complex[a]
1	12.79	8.56	0.84
2	12.64	9.18	1.06
3	12.60	8.57	0.95
4	12.82	9.20	1.29

Avg.: 12.59 CN⁻: 8.75 SCN⁻: 1.00 complex

[a]$Pd(CN)_4^{2-}$ after reaction.

TABLE II. Reaction of $(NH_4)_2PdS_{11} \cdot 2H_2O$ with KCN in DMF at 100 °C.

Run	Mol CN⁻	Mol SCN⁻	Mol Complex
1	13.92	8.05	0.99
2	13.95	8.07	1.00
3	13.97	8.07	1.02
4	13.95	7.98	1.03

Avg.: 13.81 CN⁻: 7.96 SCN⁻: 1.00 complex

others, in our efforts to deduce the structure. Unit cell dimensions are $a = 11.065(12)$ and $c = 6.862(15)$ Å. The observed density is 2.09 g/cm³; the calculated density for $(NH_4)_2PdS_{11} \cdot 2H_2O$ with Z = 2 is 2.10 g/cm³. Intensities were measured with a Picker automated diffractometer using the $\theta-2\theta$ scan technique and Zr filtered Mo radiation. Of the roughly 1800 reflections measured to $2\theta = 60°$, 608 were independent and 243 were greater than 3σ and were considered observed $(\sigma = [TC + 0.25t^2BG + (0.04I)^2]^{1/2}$ where TC = total counts, t = time to scan peak, BG = background count, I = peak count corrected for background). As can be seen from these numbers, the fraction of reflections which were weak was unusually high; indeed a number of "observed" reflections were only slightly above the 3σ threshold. Undoubtedly a larger crystal would have helped. The only compensation was that an absorption correction was not considered necessary.

Structure Determination

It was soon determined that the Pd atoms were at 000 and ½½½. With only Pd in the cell, R was about 55%. The positions of four S atoms about each Pd were also indicated on Patterson maps and difference Fourier maps. Inclusion of these eight S atoms reduced R to about 42%. At this point the remainder of the problem should have been straightforward, but the addition of more S atoms only succeeded in reducing R to about 39% and the problem appeared to

be at a dead end. Since the symmetry requirements on the Pd complex seemed improbably high (4 in P4nc, 4/m in P4/mnc) a number of attempts were made in less symmetric space groups, but the R factor always remained above 35%. A significant improvement was finally obtained in P4nc by considering hk0 data only. The projection obtained on refining a model with Pd atoms at 0, 0 and ½, ½ and S atoms at about 0.15, 0.15; 0, 0.38; 0.32, 0 resulted in an R of 15.6%. Then holding x and y coordinates fixed in the initial stages, including water and ammonium ion positions, allowing for anisotropic thermal motion for Pd and S and a partially disordered arrangement for one third of the S atoms, resulted in R = 14.5% for the three dimensional data. A second data set which had been collected earlier with a different crystal of $(NH_4)_2PdS_{11} \cdot 2H_2O$ was also tested with the same model and gave about the same result (R = 15.7%).

Space group P4/mnc was tried when it was noticed that all of the sulfur sites used in P4nc could be accommodated in three independent positions instead of four (the intensity statistics suggested a centrosymmetric space group, but with the heaviest atoms in special positions necessarily related by a center not much importance was attached to these statistics). Large values for U_{33} however suggested that all of the S atoms were disordered; for only one of the S positions was it possible to refine z and U_{33} simultaneously because of large parameter interaction. The water and ammonium ions form four-membered rings between the palladium atoms in the c direction. The symmetry does not allow for distinguishing between a water molecule and an ammonium ion, a distinction which is difficult to make even in ordered structures. The distance within the four membered rings are good hydrogen bonded distances. A final conventional R of 11.3% (weighted R = 13.5%) was obtained with unit weights for $F_{obs} \leq 36$ and $36/F_{obs}$ for $F_{obs} > 36$. Neutral atom form factors were used [5] and calculations were made with "X-Ray 70" [6]. Atomic parameters are listed in Table III, bond lengths and angles in Table IV, and observed and calculated structure factors in Table V.

Discussion

A reproducible synthesis for $(NH_4)_2PdS_{11} \cdot 2H_2O$ has been devised, further improving the original directions of Hoffman and Höchtlen. We have also been able to prepare the analogous potassium salt. It has been impossible to work with the compounds in solution without degrading them; the reason for this is now apparent from the X-ray structural results. Lack of any chelate rings, but instead linking of palladiums through polysulfide chains, accounts for the solubility properties.

TABLE III. Atomic Parameters[a] for $(NH_4)_2PdS_{11} \cdot 2H_2O$, Space Group P4/mnc (No. 128).

Atom	Position	Pop. Par.	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Pd	2a	1.0	0	0	0	281(15)	281	1249(55)	0	0	0
S1	16i	0.50	1481(8)	1483(8)	231(42)	309(47)	341(47)	1475(128)	−39(29)	−431(106)	268(111)
S2	16i	0.50(2)	3157(9)	799(9)	496(26)	326(47)	440(51)	1455(227)	22(39)	−78(79)	27(90)
S3	16i	0.41(2)	46(12)	3878(10)	1892(26)	276(53)	284(49)	1499(186)	51(62)	−206(122)	−64(65)
O[b]	16i	0.50	3420(26)	4124(28)	444(56)	802(116)					

[a]Position and thermal parameters have been multiplied by 10^4. [b]H_2O or NH_4^+. Isotropic thermal parameter.

TABLE IV. Interatomic Distances and Angles, $(NH_4)_2PdS_{11} \cdot 2H_2O$.

Pd–S1	2.32(1) Å 4x	Pd–S1–S2	111.0(4)°
S1–S2	2.06(1)	S1–S2–S3	108.9(4)
S2–S3	2.05(2)	S2–S3–S3	106.8(8)
S3–S3	2.01(2)	S1–Pd–S1	89.7(3)[a]
O1–O1	2.83(4)	S1–Pd–S1	90.3(3)[b]
	2.89(4)		
S1–O1	3.35(4)		
S1–S1	3.28(1)		
S3–S3	2.48(2)[c]		
	1.88(2)[c]		

[a]Both sulfurs above or both below the palladium. [b]One sulfur above, one below the palladium. [c]Non bonded; positions not occupied simultaneously.

In describing the crystal structure one notes that splitting the sulfur atom positions makes it possible to pick out eight S_6 chains extending from each Pd to its eight Pd neighbors. The Pd–S distance (about 2.32Å) and the S–S distances (about 2.05Å) as well as the S–S–S angles are all reasonable. However, it is of course not possible to have eight sulfur chains attached to each palladium atom. The roughly 50% occupancy of the sulfur positions, a value confirmed by least squares refinement of population parameters, implies a random arrangement of four S_6 chains to each Pd. With eight equivalent nearest neighbor Pd atoms, such randomness would be expected. A simple picture for the structure involves four different structures related to each other by four-fold symmetry. For each, Pd is surrounded in a square planar arrangement by S, and a slight tilt from the *c* direction of the normal to this plane allows for easy linkage via S_6 chains to two Pd atoms at z + ½ and two at z − ½. Ninety degree rotations of this model produce the composite deduced from the X-ray evidence. The high symmetry of the result is thus statistical and perhaps accounts for the nearly spherical habit of the crystals. In addition one can assume two more structures, one with a palladium in the plane of the upper set of four sulfurs and the S chains extending to the Pd atoms at z + ½, the other with a palladium in the plane of the lower set of four sulfurs and the S chains extending to Pd atoms at z − ½. Each of these structures would have four-fold symmetry; together they would produce 4/m symmetry. The composite of these structures could be represented by Pd atoms only at 000 and ½½½ but with large thermal motion in the *c* direction, as we have done.

The ideal formula from the above is $(NH_4)_2PdS_{12} \cdot 2H_2O$ rather than $(NH_4)_2PdS_{11} \cdot 2H_2O$. A possible way to account for a reduced sulfur content is to assume reduced population parameters for the three

TABLE V. Observed and calculated structure factors. The columns are k, $10F_o$, $10F_c$.

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  0,K,0      11  508  541      0,K,1      8  191  156  14  242  228  10  428  425   6  630  694    7,K,3        4,K,4        3,K,5
            13  196  220                  9  171 -137          12  218  199   8  222  247
  2 1025  987 15  175  176   1  963 1370  10  679  686   1,K,2       5,K,2       12  215  222   8  253  233   4  323  340   4  183  171
  4  583 -475                3  763  756  12  224  250              5  342  336  14  208  190    8,K,3        8  136  106  10  238  168
  6 1381 1138     4,K,0      5  337  297              1  977 1181   7  304  267              9  118  118   10  186  195    4,K,5
  8  633  569                7  921  861     4,K,1      2  239 -303   9  268  231    2,K,3                  5,K,4
 10  346  362   4  622  643  9  245  235              3  269  342             3  419  478    0,K,4                  5  117  108
 12  437  466   5  308 -264 13  519  554   5  635  582   5  268  304  11  148  150   4  112   70              5  243  219
 14  264  292   6  318 -264 15  178  194   6  247 -218   6   97  -65              5  169  155   0  659  695   7  156  148     5,K,5
                7  271  288              9  305  294   7  818  837    6,K,2        7  230  222   2  192  195    6,K,4
   1,K,0        8  305  315     1,K,1     10  184  193   9  393  411              9  354  356   6  297  354              6  130  120
               10  448  469              11  341  372  13  260  270   6  362  322             11  129  142   8  173  172    6,K,5
  1  528  393                2  126  139                           8  362  337  13  116   20              1,K,4
  2  662 -532     5,K,0      3  658 -606     5,K,1      2  256  313  12  259  244              3,K,3                  7  136  119
  3  290  311                4  256  247              4  787  819  14  259  285              4  561  582   2  336  346    7,K,4
  4  122   90   5 1390 1230  5  369 -343   6  614  518                           7,K,2       10  274  283   2  103  -57              0,K,6
  5  517  434   6  142  -87  6  977  943   7  101   62   3  168  222                         12  181  125   5  163  186    7,K,4
  6  103 -111   7  597  575  7  302  286   8  677  641   4  787  819   7  532  488   5  134 -137   7  251  270   7  231  227   0  179  125
  7  718  750   8  104  -90  9  366  370   9  160 -161   5  118  108   9  141  134              9  117   97    8,K,4      6  140  102
 10  185  224   9  279  287 10  141  169  10  234  235   6  636  598              4,K,3                  8  151  163    1,K,6
 13  319  384  11  332  349 12  163  172  12  123  100   8  148  155    8,K,2                  2,K,4        0,K,5
               13  180  186                           9  174 -196              8  255  217   5  325  325              1  108   65
   2,K,0                       2,K,1                   10  251  244              7  164  151   2  258  228              2,K,6
                 6,K,0                   7  492  466  12  179  166    9,K,2       9  419  403   3   92   46   1  218  209
  2  599  533               3 1478 1255  11  184  190                           11  334  311   4  264  264   3  127  131   2  129   93
  3  411  325   7  103   57  4  286  288  13  211  255    3,K,2       9  293  313              6  203  193   7  216  206    3,K,6
  4  800  688   8  559  567  5  711  640              3  763  883              5,K,3        8  136  148  13  154  139
  5  135  130  14  218  227  6  179 -166    7,K,1      4  309  342    0,K,3                  6  223  241   0,K,5        3  198  119
  6  816  735                7  450  420              5  121  152              6  146  152   1,K,5        9  141   62
  8  535  505     7,K,0      9  439  419   8  506  506   7  132 -128   1  492  583              3,K,4        6  118  108    0,K,7
  9  360 -353               11  175  187              9  440  428   7  359  389   6,K,3                  8  126  108
 10  515  535   7  448  462 12  151 -147    8,K,1     11  331  332   9  130  128              3  422  437   1,K,5        5  111   33
                5  117 -110 13  130  157              4,K,2      13  168  192   7  396  395   5  200  195   2,K,5
   3,K,0       11  120  132 15  157  118   9  120  129                           9  130  124   9  166  206              3,K,7
                                                     4 1169 1146    1,K,3      11  134  137  11  151  172  11  151  172
  3 2443 1870     8,K,0       3,K,1       0,K,2      5  162 -157   2  301  344  13  179  155                  2,K,5        9  124   11
  4  793  669               4 1014  958              6  264  244   3  175 -227                              3  227  204
  5 1046  847   8  667  650  5  187 -172   4  277 -258   7  177  164   4  430  507                          5  155  154
  6  144 -112  10  196  197  6  238 -211   6  666  671   8  258  265   5  133 -157                         11  126   71
  7  113 -112              7  302  284  12  301  297
  9  410  401
 10  151  147
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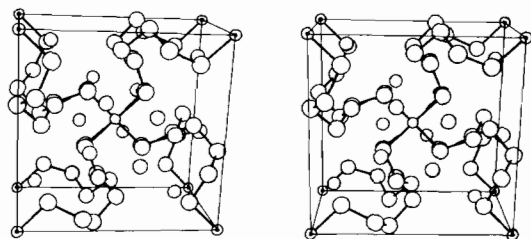

Figure 1. Stereo view of the unit cell contents (down *c*) showing possible Pd to Pd linkages via S_6 chains. Pd atoms are shown as small circles, S atoms as large circles, NH_4^+ and H_2O as intermediate (non-bonded) circles.

Figure 2. Stereo view of a contributing structure. Pd atoms are shown as small circles, S atoms as large circles, NH_4^+ and H_2O as intermediate (non-bonded) circles. The *c* axis is vertical.

16-fold sulfur positions. To this end the population parameters for S1, S2 and S3 were assumed to be 0.50, 046, and 0.42, which would result in 22 S atoms/cell rather than the ideal 24. Such reduction is plausible if one assumes that the sulfur chains build outward from the palladium atoms; the fact that close approaches make half the possible chains incompatible with the other half would result in aborting chain growth in a number of instances. Thus one might expect a reduced population for S3 and possibly for S2. On refinement of the sulfur population parameters with that for S1 fixed at 0.50, the population parameter for S2 converged to 0.50 also, but that of S3 converged to 0.41. The loss of sulfur would thus appear to be entirely at the S3 position. With a total of 8 S1, 8 S2, and 6.6 S3 in the cell, the polysulfide composition would be $PdS_{11.3}$, which is reasonably close to the PdS_{11} composition obtained from chemical analysis.
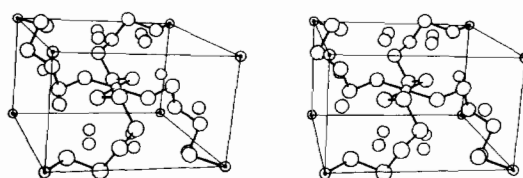
On the basis of the ideal formula with two $S_6^=$ chains per palladium ion, the oxidation state for palladium is +2. This is the most important valency for palladium and thus it differs from platinum for which the tetravalent state is as important [7]. The valency observations are consistent with the complex sulfides formed, *i.e.*, $(NH_4)_2PdS_{11} \cdot 2H_2O$ and $(NH_4)_2PtS_{15} \cdot 2H_2O$, involving transition metal oxidation states of +2 and +4 respectively. The two structures differ in an important way. The complex sulfide of palladium results in a three dimensional palladium–sulfur network with discrete $(NH_4^+)_2$-$(H_2O)_2$ rings interspersed; the complex sulfide of platinum results in discrete $PtS_{15}^=$ units held in a matrix of extended hydrogen bonded NH_4^+–H_2O chains.

Drawings of the unit cell contents are given in Figures 1 and 2, of the S_6 chain in Figure 3; these drawings were prepared using ORTEP [8].

A survey of the literature leads to the following observations. An *ordered* tetragonal structure with
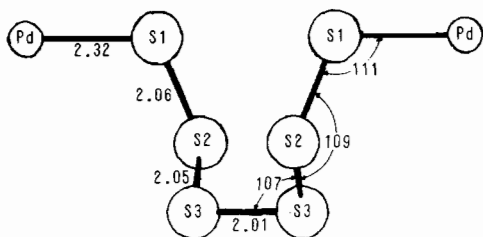
Figure 3. Portion of structure showing S_6 chain connecting two Pd atoms.

palladium atoms at 000 and ½½½ should have led to a rapid deduction of the detailed structure, since problems of similar complexity posed no particular problems [9, 10]. Other examples could of course be cited. Among other structures which can be viewed as composites of domain structures are the tetragonal sodium tungsten bronzes, Na_xWO_3 [11]. Tetragonal palladium complexes with at least some disorder present in the structure are $Pd(NH_3)_4Cl_2 \cdot H_2O$ in which the water molecule appears to be disordered [12] and $Pd(C_2H_3N_2O_2)I$ in which there are linear, probably disordered iodine chains [13]. Most of our conclusions are not without precedent, but the disordered model leaves some doubt about the best way to view the result. Except for U_{33} and z for S1 and S2, for which large interaction prevented simultaneous refinement, all the parameters could be refined simultaneously and convergence (maximum shift to error ratio less than 0.1) was attained.

Despite the difficulties arising from the statistical nature of the composite structure, the bond lengths and angles found are quite reasonable. The S–S bond lengths range from 2.01 to 2.06 Å, and the angles are 106.8 and 108.9°. In Na_2S_4 [14] the bond lengths are 2.07 and 2.06Å, the bond angle 109.8°. In $BaS_4 \cdot H_2O$ [15] the bond length range is 2.062 to 2.079 Å and the bond angles are 104.0 and 104.3°. In Tl_2S_5 [16], the bond length range is 2.06 to 2.16 Å, and the angle range is 107.6 to 108.8°. In Cs_2S_6 [17, 18], the bond length range is 2.02 to 2.11 Å, the angle range is 108.1 to 109.5°. Thus the values found in the present case are quite consistent with other results. The close sulfur to water molecule approach, 3.35 Å, is also about the same as the shortest such distance noted in $BaS_4 \cdot H_2O$ [15], 3.37 Å.

All of the chemical evidence indicates the correctness of the PdS_{11}^{2-} formula. Analyses for palladium give excellent agreement with the formula $(NH_4)_2$-$PdS_{11} \cdot 2H_2O$; microanalyses for nitrogen, hydrogen and sulfur are also in agreement. Reactions with cyanide ion in both water and DMF lend further support to this formulation.

Although the cyanide reaction in water is heterogeneous, the results still suggest a reaction stoichiometry and indicate the correctness of the PdS_{11}^{2-} formula. The X-ray data show the presence of planar

palladium(II) and polysulfide chains; this leads us to anticipate a reaction stoichiometry with cyanide as depicted in eq. (1).
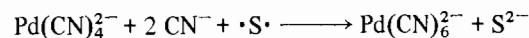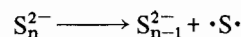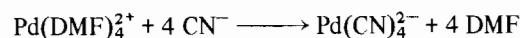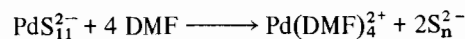
$$PdS_{11}^{2-} + 13\ CN^- \longrightarrow Pd(CN)_4^{2-} + 9\ SCN^- + 2\ S^{2-} \quad (1)$$
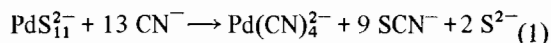
Observed values of 12.6 CN^- and 8.8 SCN^- per palladium are not inconsistent with this reaction.

Now turning to the results in DMF, a very interesting reaction occurs. The observed stoichiometry of 13.8 CN^- and 8.0 SCN^- per palladium suggests that the metal ion is being oxidized, as depicted in eq. (2)

$$PdS_{11}^{2-} + 14\ CN^- \longrightarrow Pd(CN)_6^{2-} + 8\ SCN^- + 3\ S^{2-} \quad (2)$$
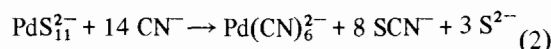
No other explanation is consistent with the facts: six more cyanides required than the eight thiocyanates produced, and a starting complex containing palladium(II). The increased coordination number of palladium(IV) requires more cyanide. The conversion of a neutral sulfur radical into a sulfide (on oxidizing the palladium(II)) generates less thiocyanate than in the aqueous reaction.

Giggenbach [19] has studied the blue solutions of sodium tetrasulfide in DMF and proposed the presence of a sulfur radical anion. We feel that this would be an effective oxidant for the palladium(II), particularly in the presence of cyanide. The sequence of steps occurring may be:

$$PdS_{11}^{2-} + 4\ DMF \longrightarrow Pd(DMF)_4^{2+} + 2S_n^{2-}$$

$$Pd(DMF)_4^{2+} + 4\ CN^- \longrightarrow Pd(CN)_4^{2-} + 4\ DMF$$

$$S_n^{2-} \longrightarrow S_{n-1}^{2-} + \cdot S\cdot$$

$$Pd(CN)_4^{2-} + 2\ CN^- + \cdot S\cdot \longrightarrow Pd(CN)_6^{2-} + S^{2-}$$

The cyanide reactions also aid in establishing the correctness of the average formula, PdS_{11}^{2-}. In water, nearly the theoretical number of thiocyanates are generated in the reaction (8.75 *vs.* 9). While this agreement is not perfect it must be emphasized that this is most likely a lower limit due to the heterogeneous nature of the reaction. In the homogeneous reaction in DMF we observe 8 thiocyanates produced and 8 required (with the added assumption that one sulfur is an oxidizing agent). We feel that the observed stoichiometry in DMF is good evidence for the correctness of the average formula, PdS_{11}^{2-}.

Few palladium(IV) complexes are known. The present work suggests the interesting prospect of preparing these in DMF, perhaps using polysulfides as oxidizing agents.

Acknowledgments

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References

1 K. A. Hofmann and F. Höchtlen, *Ber. dtsch. Chem. Ges., 36,* 3090 (1903).
2 *Id., ibid., 37,* 245 (1904).
3 P. E. Jones and L. Katz, *Acta Cryst., B25,* 745 (1969).
4 A. E. Wickenden and R. A. Krause, *Inorg. Chem., 8,* 779 (1969).
5 D. T. Cromer and J. T. Waber, *Acta Cryst., 18,* 104 (1965).
6 J. M. Stewart, F. A. Kundell, and J. C. Baldwin, eds., "The X-Ray System", Computer Science Center, University of Maryland, College Park (1970).
7 N. V. Sidgwick, "The Chemical Elements and Their Compounds", Vol. II, Oxford University Press, p. 1558 (1950).
8 C. K. Johnson, ORTEP, Oak Ridge National Laboratory, (1965).
9 A. Karipides and D. A. Haller, *Acta Cryst., B28,* 2889 (1972).
10 A. Karipides and K. Wolfe, *Acta Cryst., B31,* 605 (1975).
11 F. Takusagawa and R. A. Jacobson, *J. Solid State Chem., 18,* 163 (1976).
12 J. D. Bell, J. C. Bowles, H. J. Cumming, D. Hall and R. V. Holland, *Acta Cryst., B32, 634* (1976).
13 H. Endres, H. J. Keller, R. Lehmann, and J. Weiss, *Acta Cryst., B32,* 627 (1976).
14 R. Tegman, *Acta Cryst., B29,* 1463 (1973).
15 S. C. Abrahams and J. L. Bernstein, *Acta Cryst., B25,* 2365 (1969).
16 B. Leclerc and T. S. Kabré, *Acta Cryst., B31,* 1675 (1975).
17 S. C. Abrahams and E. Grison, *Acta Cryst., 6,* 206 (1953).
18 A. Hordvik and E. Sletten, *Acta Chem. Scand., 22,* 3029 (1968).
19 W. Giggenbach, *J. Inorg. Nucl. Chem., 30,* 3189 (1968).