

Pentaammine Complexes of Osmium with π -Acceptor Ligands

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Dedicated to Jannik Bjerrum on the occasion of his 70th birthday

A series of pentaammineosmium(III) complexes containing *N*-heterocycles was synthesized by oxidizing dinitrogenpentaammineosmium(II) chloride in triethyl phosphate and adding the desired ligand to the solution. The reduction potentials of the osmium complexes are about 500 mV more negative than those of their ruthenium counterparts. Osmium(II) species were formed from the osmium(III) species by using reducing agents such as zinc amalgam and sodium dithionite. The osmium(II) species are unstable in acidic solutions but are much more stable at high values of pH. The values of pK_a for the deprotonations of the osmium(II) complexes containing protonated pyrazine, pyridazine, and pyrimidine are 7.4, 3.7, and 2.1, respectively, to be compared to 0.6, 2.33 and 1.3 for the monoprotinated forms of the uncoordinated ligands. The enhancement in pK_a , particularly for pyrazinium, is evidence for very strong back-bonding from osmium(II) to the ligand.

The complex pentaamminesulfur dioxide osmium(II) was synthesized by combining aquopentaammineosmium(III) and sodium metabisulfite in aqueous media, saturating with SO_2 and heating the mixture for four hours. The stabilization of the SO_2 form of the ligand by Os(II) is demonstrated by the fact that the complex does not react with hydroxide ion until the pH is raised to 7.0, at which point two hydroxides per complex react.

Back-bonding is prominent in the chemistry of Ru(II) and Os(II), and especially when the ligands complementary to the π acceptor are saturated. For this reason among others the ammine complexes have received special attention. However, because of preparative difficulties, the chemistry of Os(II) amines has not been developed as much as that of the ruthenium analogs. The species $[Ru(NH_3)_5-$

$H_2O]^{2+}$ is a convenient reagent for the preparation of mono π -acid complexes of Ru(II), but the osmium analog is very unstable and rapidly reduces water, so that less direct approaches to the preparation of the Os(II) complexes need to be developed.

The determination of the pK_a of a coordinated ligand such as pyrazinium ion is one way of assessing the back-bonding capacity of a metal center. Magnuson *et al.*¹ discovered a route for the preparation of Os(II) tetraammine complexes, and in the course of their work determined the pK_a for pyrazinium ion coordinated to $Cl(NH_3)_4Os(II)$. The large increase, by about seven units, attending coordination of pyrazinium ion to Os(II) was attributed to back-bonding, but just how much of the effect is assignable to Cl^- itself is not known.

We have continued the investigation into the effects of back-bonding by Os(II), and in this paper, we report the preparation and characterization of a series of pentaammineosmium(II) and (III) complexes of aromatic nitrogen heterocycles. Because of the great utility of the sulfitepentaammineruthenium(II) complex² for the preparation of other complexes in the ruthenium ammine series, the investigation has been extended to include $[(NH_3)_5OsSO_2]^{2+}$.

EXPERIMENTAL SECTION

Materials and Reagents

The preparation of water of high purity, of O_2 free gases, and of the reducing agent Eu^{2+} has been described previously.³ Isonicotinamide was recrystallized from hot water. Deuterium chloride (38% solution in deuterium oxide at 99 atom %, 4

International Chemical and Nuclear) was diluted 1:100 with deuterium oxide (99.8 mol %) for use in near-infrared measurements. The hydrogen form of the cation exchange resin AG 50W-X2 (200–400 mesh) was obtained from Bio Rad and cleaned as described by Deutsch, with the exception that HCl was used in place of HClO_4 .³ SP-Sephadex C-25 from Pharmacia Fine Chemicals, Inc. was used for the cation exchange of weakly colored materials. The Pharmacia catalog (August 1971) states that this resin is stable in the range $2 < \text{pH} < 10$. Because solutions as acidic as 0.5 M HCl were needed, a column containing about 20 ml of wet resin was washed with 50 ml of 0.5 M HCl. Then another 50 ml of 0.5 M HCl was run through the column and collected. The 50 ml of liquid was put into a round-bottomed flask and the volume of liquid was reduced to 1 ml by rotary evaporation. No residue was visible on the sides of the flask. The remaining liquid appeared slightly yellow but the UV spectrum of the liquid showed no absorption peaks. Microanalyses of samples of osmium compounds eluted with 0.1 M to 0.5 M HCl from columns containing the Sephadex resin were no different from those of samples isolated with the Bio Rad resin. It has therefore been assumed that the decomposition of the Sephadex resin was not interfering in separations, and no precautions were taken to exclude decomposition products of the resin from eluted samples. Triethyl phosphate (95 %, Aldrich) was stored over molecular sieves (Linde 3A Union Carbide).

Syntheses

Ammonium hexachloroosmate(IV) was prepared from osmium tetroxide by the procedure of Dwyer and Hogarth.⁴

Dinitrogenpentaammineosmium(II) chloride was prepared by the procedure of Allen and Stevens.⁵

Iodopentaammineosmium(III) iodide was prepared according to the method of Allen and Stevens.⁶

Aquapentaammineosmium(III) was prepared by either of two procedures. The first procedure was adapted from that described by Gulens and Page.⁷ Approximately 100 mg of $[(\text{NH}_3)_5\text{OsN}_2]\text{Cl}_2$ in 3 to 5 ml of 0.1 M HCl was oxidized by a controlled potential electrolysis at a Pt electrode at +400 mV vs. SCE. The solution containing the aquapentaammineosmium(III) species was removed from the electrolysis cell and used for the synthesis of $[(\text{NH}_3)_5\text{OsSO}_2]^{2+}$. In the second method for the preparation of aquapentaammineosmium(III), a solution containing three equivalents of silver trifluoroacetate was added dropwise to a stirred slurry of $[(\text{NH}_3)_5\text{OsN}_2]\text{Cl}_2$ in a small amount of

water. Stirring was continued for ten more minutes and then the silver chloride and silver were removed by filtration and washed with a small amount of water. The aquapentaammineosmium(III) was used as prepared in solution.

Pentaammine(L)osmium(III) complexes, $L = \text{Isonicotinamide, pyridine, pyrazine, pyrimidine and pyridazine}$. Dinitrogenpentaammineosmium(II) chloride (50 mg) and silver tosylate (111 mg) were combined with about 2 ml of triethyl phosphate and stirred for several hours until the mixture was gray and no $[(\text{NH}_3)_5\text{OsN}_2]\text{Cl}_2$ could be seen. The mixture was filtered, and the flask and the solid material were washed with 1 to 2 ml of triethyl phosphate which was then added to the filtrate. About 3 mmol of the heterocycle was added to the solution and the reaction mixture was left at room temperature overnight. The mixture was diluted about 1:3 with water and put on a cation exchange column. AG 50W-X2 could be used for the isonicotinamide and pyrazine complexes, but it was difficult to see the other complexes on this resin so Sephadex was used for them. On AG 50W-X2, the desired complexes were eluted with 3 to 4 M HCl. When Sephadex was used, the complexes moved down the column with 0.3 to 0.4 M HCl. The fractions containing the complexes were rotary evaporated to dryness and the solids were dissolved in 5 M HCl and reprecipitated by adding acetone. The bromide salt of the isonicotinamide complex was made by dissolving the chloride in water and adding solid NaBr until the osmium(III) bromide precipitated from the solution. The hexafluorophosphate salt of the pyridazine complex was made following the procedure for pentaammineisonicotinamideosmium(III) bromide except that NH_4PF_6 was used as precipitant instead of NaBr. The solids were collected, washed with acetone, and dried overnight in a vacuum desiccator. Yields were as follows: pentaammineisonicotinamideosmium(III) chloride, 27 %; pentaamminepyridineosmium(III) chloride, 24 %; pentaamminepyrazineosmium(III) chloride, 27 %; pentaamminepyrimidineosmium(III) chloride, 38 %; pentaamminepyridazineosmium(III) chloride, 33 %.

Pentaamminesulfurdioxideosmium(II) chloride. Dinitrogenpentaammineosmium(II) chloride (100 mg) in 3 to 5 ml of 0.1 M HCl was converted to $[(\text{NH}_3)_5\text{OsH}_2\text{O}]^{3+}$ by one of the two methods described above. Sodium disulfite (140 mg) was added to the solution containing aquapentaammineosmium(III). The reaction mixture was heated at 80 °C and sulfur dioxide was bubbled through it for 4 h. The solution was then diluted 1:4 with water and was put on a column of AG 50W-X2 cation exchange resin. The species $[(\text{NH}_3)_5\text{Os}(\text{SO}_2)]^{2+}$ was eluted with 1 M HCl. The fraction containing the complex was dried by rotary evap-

oration. The solid was dissolved in 5 M HCl, precipitated by adding acetone, and it was collected by filtration, washed with acetone, and dried overnight in a vacuum desiccator (yield, 60%).

When $[(\text{NH}_3)_5\text{OsI}]_2$ was substituted for $[(\text{NH}_3)_5\text{OsH}_2\text{O}]^{3+}$ in the synthesis procedure, some starting material was identified after the usual reaction time, but no $[(\text{NH}_3)_5\text{OsSO}_2]^{2+}$ was detected.

Apparatus and Techniques

Spectra. Ultraviolet (UV) and visible (vis) spectra were recorded on a Cary 15 or a Beckman ACTA MVII spectrophotometer.

Near infrared (NIR) spectra were recorded on a Cary 14 or Beckman ACTA spectrophotometer. Samples were usually dissolved in 0.12 M deuterium chloride and put into cells with a pathlength of 1 mm. A matched cell containing deuterium oxide was placed in the reference beam.

Infrared (IR) spectra were recorded with a Perkin-Elmer 621 grating spectrophotometer with a range of 4000 to 200 cm^{-1} or a Perkin-Elmer 421 grating spectrophotometer with a range of 4000 to 400 cm^{-1} . Samples were prepared in potassium bromide pellets.

Magnetic susceptibility. A magnetic susceptibility measurement was done for the $[(\text{NH}_3)_5\text{Os}(\text{SO}_2)]\text{Cl}_2$ complex with the assistance of Dr. J. Kung. A Faraday electrobalance (Cahn Electrobalance DTL) was used. The sample size was 25.89 mg and the standard was Hg Co(NCS)₄.

Microanalyses. All microanalyses were done by the Stanford Microanalytical Laboratory, Stanford, California. Analysis for oxygen was not done and water of crystallization was included in formulas to improve the fit of the analyses to the calculated values.

Cyclic voltammetry. Cyclic voltammetry measurements were first made with an electrochemical circuit designed and constructed by G. M. Tom,⁸ and later with the following Princeton Applied Research (PAR) equipment: Model 173 Potentiostat and Galvanostat, Model 175 Universal Programmer, and Model 176 Current Follower. The output, a scan of potential vs. current, was recorded on an Omnigraphic 2000 X-Y recorder with types 5 and 6 precision attenuators purchased from Houston Instruments, Texas. The sweep rate was usually 200 mV/s and the work was done at ambient temperatures (about 20 °C).

Reduction potentials are reported as formal values, E_f , and were measured at half the distance between the anodic and cathodic peaks. The diffusion coefficients for the reduced and oxidized species were assumed to be equal. Potentials were measured with respect to SCE (saturated calomel

electrode) and converted to the NHE (normal hydrogen electrode) scale by adding 0.24 V. No corrections were made for junction potentials.

Three types of indicator electrodes were used: a platinum bead sealed in glass was used for positive, a hanging mercury drop electrode for negative potentials, and a carbon paste electrode for both regions. The auxiliary electrode was a piece of platinum wire. The experiments were done in an H-shaped cell that had a fine glass frit dividing the two sides of the cell. The solutions contained at least 0.1 M supporting electrolyte, and the sample was at mM concentrations; the solution was deaerated with argon before measurements were taken. Measurements are estimated to be precise to $\neq 10$ mV.

Determinations of pK_a using cyclic voltammetry. The values of pK_a of the complexes $[(\text{NH}_3)_5\text{OsLH}]^{3+}$, where L = pyrazine, pyridazine, or pyrimidine were determined by using cyclic voltammetry. A cyclic voltammetry cell was used that made feasible continuous measurement of the pH of the solution in the indicator chamber. Both the indicator electrode and the reference electrode were immersed in phosphate buffer. The buffer solution was made from 42.5 ml of 0.20 M disodium hydrogenphosphate and 7.5 ml of 0.20 M sodium dihydrogenphosphate diluted with water to give a total volume of 100 ml and to which enough NaCl was added to make the solution 1 M in NaCl.

The sample was put in the indicator compartment and the solution there was then titrated with HCl or NaOH. A cyclic voltammetry scan was made after each addition of acid or base and the pH of the solution was also determined.

The plot of E_f vs. pH shows a line of slope -60 mV intersecting with a line of zero slope. The former describes the half-reaction $\text{Os(III)} + \text{H}^+ + e^- \rightleftharpoons \text{Os(II)H}^+$, and the latter, the half reaction $\text{Os(III)} + e^- \rightleftharpoons \text{Os(II)}$. At the point of intersection $[\text{Os(II)}] = [\text{Os(III)}] = [\text{Os(II)H}^+]$, and it follows from the Nernst equation that there the pH equals the pK_a of the osmium(II) complex.

Determination of the pK_a of $[(\text{NH}_3)_5\text{Os}(\text{SO}_2)]\text{Cl}_2$. A concentrated solution of $[(\text{NH}_3)_5\text{Os}(\text{SO}_2)]\text{Cl}_2$ in 0.1 M HCl was deaerated with argon. The absorbance of the complex at 530 nm was used to determine the concentration. Buffer solutions were made by mixing the components of citrate or phosphate buffers to get a pH value slightly greater than that desired for an absorption measurement. A known volume of the buffer was deaerated with argon in a Zwickel flask⁹ for 15 min. A known amount of the $[(\text{NH}_3)_5\text{Os}(\text{SO}_2)]\text{Cl}_2$ solution was added and the absorbance at 530 nm was recorded immediately. Reproducibility was estimated to be ± 0.01 of an absorbance unit. The pK_a was set equal to the value of the pH at the

absorbance midway between the limiting values at high and at low pH. The error limits associated with this method are estimated to be ± 0.5 pH units.

Measurement of molar absorptivities. A circulator described by Clarke¹⁰ was used for measuring the molar absorptivities in the UV-vis range in basic solutions for the Os(II) complexes containing nitrogen heterocycles. The circulator moved solutions between a cell inside the spectrophotometer and a small flask on the outside. The flask had an inlet for argon and could accommodate a pH electrode. The Os(III) form of the complex was dissolved in 0.10 M HCl and the solution was put into the circulator. A spectrum was taken to determine the concentration of the osmium complex. The solution was then made basic by adding sodium bicarbonate, the reducing agent was introduced, and the spectrum of the osmium(II) species was recorded.

Spectrophotometric work on the isonicotinamide complex in 0.1 M HCl was done by reducing the solution rapidly with Eu^{2+} and immediately recording the spectrum. The reducing power of the pentaamminepyridineosmium(II) complex made it necessary to resort to $\text{Na}_2\text{S}_2\text{O}_4$ as the reducing agent. When zinc amalgam was used in the basic solution, band maxima appeared but altered in intensity randomly with time, perhaps due to oxygen leaking into the system. The molar absorptivities for the pyrazine complex in acid were estimated by measuring the absorption immediately after the bands began to lose intensity.

RESULTS

Pentaammineosmium(III) complexes with aromatic nitrogen heterocycles

Microanalyses on the compounds which were prepared are summarized in Table 1.

The easily distinguishable features of the absorption spectra are outlined in Table 3, and by way of illustration, the spectrum in the UV for $[(\text{NH}_3)_5\text{Os pyrazine}]^{3+}$ is shown in Fig. 1 and the absorption in the near infrared for $[(\text{NH}_3)_5\text{Os isonicotinamide}]^{3+}$ in Fig. 2.

It will be noticed in Fig. 1 that the long-wave length portion of the lowest energy band in the UV is unsymmetrical, indicating that there is an additional, unresolved band in this region. This feature is common to all the spectra, and the much weaker absorption at >400 nm to all but that of the pyridine complex.

Table 1. Microanalyses for the pentaammineosmium complexes containing nitrogen-heterocycles.

$[(\text{NH}_3)_5\text{Os isonicotinamide}]\text{Br}_3 \cdot 2\text{H}_2\text{O}$
Calc: C 10.7; N 14.6; H 3.7.
Found: C 10.3; N 14.3; H 3.5.

$[(\text{NH}_3)_5\text{Os isonicotinamide}]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$
Calc: C 13.3; N 18.2; H 4.7.
Found: C 12.7; N 17.7; H 4.3.

$[(\text{NH}_3)_5\text{Os pyridine}]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$
Calc: C 12.1; N 16.9; H 4.9.
Found:^a C 12.4; N 16.4; H 4.7.

$[(\text{NH}_3)_5\text{Os pyrazine}]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$
Calc: C 9.7; N 19.7; H 4.7; Cl 21.4.
Found: C 9.8; N 19.8; H 4.6; Cl 20.7.

$[(\text{NH}_3)_5\text{Os pyridazine}](\text{PF}_6)_3$
Calc: C 6.1; N 12.4; H 2.4; F 43.3.
Found: C 6.3; N 12.0; H 2.6; F 42.6.

$[(\text{NH}_3)_5\text{Os pyrimidine}]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$
Calc: C 9.7; N 19.7; H 4.7; Cl 21.4.
Found: C 9.8; N 19.4; H 4.5; Cl 21.4.

^a Average of two analyses.

The IR spectra of the pentaammineosmium(III) complexes containing aromatic nitrogen heterocycles were taken,¹¹ cf. Table 2. They display peaks attributable to coordinated ammonia and the heterocycles, and the spectra resemble those of the related chlorotetraammineosmium(II) compounds.¹

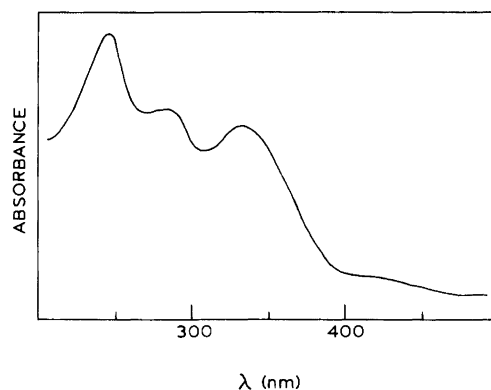


Fig. 1. Absorption spectrum in UV-visible of $[(\text{NH}_3)_5\text{Os pyrazine}]\text{Cl}_3$ in 0.10 M HCl (see Table 3 for molar absorptivities).

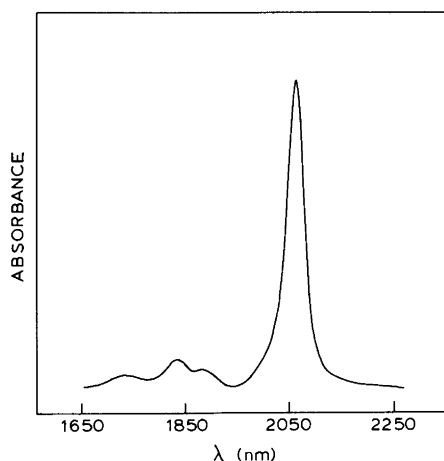


Fig. 2. Near infrared absorption spectrum of $[(\text{NH}_3)_5\text{Os isonicotinamide}]\text{Cl}_3$ in 0.12 M DCl in D_2O (see Table 3 for molar absorptivities).

The E_f values were determined by cyclic voltammetry and are listed in Table 3. The couples, except that for $[(\text{NH}_3)_5\text{Os}(\text{pyrazine})]^{3+,2+}$, are reversible. The $[(\text{NH}_3)_5\text{Os}(\text{pyrazine})]^{3+,2+}$ couple is quasi-reversible at pH 1. In this case, the anodic to cathodic current ratio is close to 1 but as the scan rate increases, so does the peak to peak separation. The couple becomes reversible in more basic media. The values of E_f for the three azine complexes are pH dependent in the lower range; E_f increased by 60 mV for each unit decrease in pH.

Pentaammineosmium(II) complexes with aromatic nitrogen heterocycles

The pentaammineosmium(II) complexes containing aromatic nitrogen heterocycles were prepared by reducing the pentaammineosmium(III) complexes. The reduction behavior of the pentaammineosmium(III) compounds containing nitrogen heterocycles has been only partially examined. The cyclic voltammetry experiments indicate that in both acidic and basic media the first event in the reduction of the osmium complexes is the addition of an electron to the metal center. In basic solutions the pentaammineOs(II) complexes appear to be stable as long as air or other oxidants are excluded, but in acidic solution, contact with excess reducing agent can lead to ligand reduction.

Table 2. Electronic spectra of pentaammineosmium(III) complexes.

Medium	$\lambda(\text{nm})$	$\epsilon(\text{M}^{-1} \text{cm}^{-1})$
L = pyrazine		
0.1 M HCl	246	1.9×10^3
	282	1.5×10^3
	329	1.4×10^3
0.12 M DCl/ D_2O	1748	~ 12
	1802	~ 8
	1905	~ 4
	2075	~ 40
L = isonicotinamide		
0.1 M HCl	238	5.0×10^3
	264 (sh)	
	289	3.6×10^3
0.12 M DCl/ D_2O	1730	~ 4
	1831	~ 7
	1831	~ 7
	1886	~ 5
	2064	62
L = pyridine		
0.1 M HCl	234	4.5×10^3
	266	4.3×10^3
	290 (sh)	2.5×10^3
0.12 M DCl/ D_2O	2065	50
	1930	< 10
	1840 ?	< 10
	1750	< 10
L = pyridazine		
0.1 M HCl	225 (sh)	3×10^3
	256	2.5×10^3
	305	3.0×10^3
	420 (sh)	4×10^2
0.12 M DCl/ D_2O	1744	10
	1837	14
	1898	11
	2082	51
	2151	11
L = pyrimidine		
0.1 M HCl	228	5.1×10^3
	290	2.8×10^3
0.12 M DCl/ D_2O	1750	< 10
	1840(?)	< 10
	2073	42

Thus, when the pyrazine complex was reduced with zinc amalgam in 0.1 M HCl, the solution first changed from yellow to orange and then became colorless. After exposure to air, the colorless solution displayed absorption only at about 270

Table 3. E_f for $(\text{NH}_3)_5\text{Os(III)L} \rightarrow (\text{NH}_3)_5\text{Os(II)L}$.

L	Conditions	E_f (mV)
Isonicotinamide	0.1 N HCl	-240 ^a
Pyrazine	pH ~9	-90 ^b
	sodium acetate	
Pyridazine	pH ~9	-210 ^b
	sodium acetate	
Pyrimidine	pH ~9	-260 ^b
	sodium acetate	
Pyridine	0.1 N HCl	-395 ^a

^a Independent of pH. ^b Invariant for $\text{pH} > \text{pK}_a$ of Os(II) complex.

nm, and cyclic voltammetry using a carbon paste electrode showed a reduction wave at about -900 mV vs. SCE. It is apparent that the original complex was not regenerated by exposure to O_2 , and the negative value of the reduction potential suggests that much of the unsaturation has been removed from the pyrazine when the complex is left in contact with zinc.

When zinc amalgam was used to reduce pentaamminepyridazineosmium(III) in 0.1 M HCl, an orange species appeared initially, following which all absorption at wavelength greater than 200 nm disappeared. On adding an equivalent of Eu^{2+} to a solution of the osmium(III) pyridazine complex, again in acid, the solution first turned orange and then became purple (λ_{max} at 585 nm).

Reduction of $[(\text{NH}_3)_5\text{Os isonicotinamide}]^{3+}$ with zinc amalgam in 0.10 M HCl initially produced a pink species, undoubtedly the corresponding Os(II) complex, but on continued action by the reducing

Table 4. Electronic spectra of pentaammineosmium-(II)(L) complexes.

L	Medium	λ (nm)	ϵ ($\text{M}^{-1} \text{cm}^{-1}$)
Isonicotinamide	0.1 M HCl	508	1.7×10^4
		768	3×10^3
	pH 9.6 (HCO_3^-)	244 (sh)	5.6×10^3
		508	1.5×10^4
Pyridine	pH 8 (HCO_3^-)	430	1.1×10^4
		553	3.5×10^3
Pyrazine	0.1 M HCl	266	2.4×10^3
		428	4.0×10^3
	pH 9 (HCO_3^-)	460	7.3×10^3
Pyrimidine	pH 9 (HCO_3^-)	250 (sh)	5.7×10^3
		458	8.6×10^3
		663	2.1×10^3
Pyridazine	pH 9 (HCO_3^-)	470	5.8×10^3

agent, the solution turned green. On exposure to air, the green solution became yellow. The yellow species was elutable from Sephadex resin with 0.30 to 0.40 M HCl. The atom ratio of C:N:H in the chloride salt recovered from the eluate was found by microanalysis to be 6.00:6.70:23.5. The carbonyl stretch was not observed in the infra-red spectrum of the solid and cyclic voltammetry on the solution showed that the prolonged exposure to the reducing agent had produced a species which had a reduction potential ca. 80 mV more negative than the starting material, but also revealed a small set of waves,

Table 5. pK_a measurements.

Acid	Conditions	pK_a	Ref.
$[(\text{NH}_3)_5\text{Os pyrazine H}]^{3+}$	HCl, Na_2HPO_4	7.4	
$\text{cis}-[(\text{NH}_3)_4\text{ClOs pyrazine H}]^{2+}$	HCl	7.6	1
$[(\text{NH}_3)_5\text{Os pyridazine H}]^{3+}$	HCl, Na_2HPO_4	3.7	
$[(\text{NH}_3)_5\text{Os pyrimidine H}]^{3+}$	HCl, Na_2HPO_4	2.1	
$[(\text{NH}_3)_5\text{Ru pyrazine H}]^{3+}$	HClO_4	2.5	19
$[(\text{NH}_3)_5\text{Ru pyridazine H}]^{3+}$	HCl	0.03	19
$[(\text{NH}_3)_5\text{Ru pyrimidine H}]^{3+}$	HCl	0.00	19
[Pyrazine H] ⁺		0.6	19
[Pyridazine H] ⁺		2.33	19
[Pyrimidine H] ⁺		1.3	19
$[(\text{NH}_3)_5\text{Ru pyrazine H}]^{4+}$	HClO_4	-0.8	19

90 mV still more negative. That some unsaturation has been lost from the ligand is indicated by the fact that the absorption in the visible has changed from 508 and 768 characteristic of the isonicotinamide complex (*cf.* Table 4) to 453 and 625 nm, but the NMR spectrum showed that the ring retained its aromatic character. It is apparent from these observations that the amide group has been reduced. That it has been replaced by a carbinol function is suggested by the remaining data, except for the microanalysis, which is more nearly compatible with an amine having been produced. At any rate, the instability of the ligand when it is coordinated to Os(II) in acid solution is demonstrated.

Features of the electronic spectra of the pentaammineosmium(II) species that were investigated are summarized in Table 4. The study was not complete: little work was done at wavelengths longer than 700 nm, and the reducing agents and solution media usually had interfering absorption in the UV region.

Although the Os(II) pentaammine complexes are not stable in acidic media, it was possible to determine the pK_a 's of the complexes containing azine ligands by cyclic voltammetry as described in the experimental section. The pK_a values are listed in Table 5.

Pentaamminesulfur dioxide osmium(II) Chloride.

The microanalysis on the title compound was as follows: $[(NH_3)_5OsSO_2]Cl_2$ Calc: H 3.7; Cl 17.3; N 17.1; S 7.8. Found: H 3.7; Cl 17.4; N 16.9; S 7.0. The solid was stable to oxidation, but in acidic solution ($pH < 1$), the complex was subject to slow oxidation in air over a period of two to three days. As the solution was made more basic, the rate of oxidation increased and at a pH around 7, oxidation was evident within one or two minutes after addition of the complex to the solvent.

A second reaction occurred in the range pH 3–10 in air or under argon forming a product which was purple in acidic solutions and green in basic solutions. Along with the formation of the purple species, there was a decrease in the pH of the solutions. The purple species moved with 4 M HCl on an AG 50W-X2 cation exchange resin column. The IR spectrum of the solid obtained from the eluate was too complex to yield useful structural information.

The magnetic susceptibility of $[(NH_3)_5OsSO_2]Cl_2$ was measured as $(0.00 \pm 0.73) \times 10^{-6} \text{ cm}^3/\text{g}$ and

is consistent with the expected low spin d^6 electronic structure.

The sulfur dioxide complex is magenta in acidic and colorless in basic solutions. The UV-vis spectrum of $[(NH_3)_5Os(SO_2)]^{2+}$ in 0.10 M HCl has the following features: $\lambda_{\text{max}} = 254 \text{ nm}$ (sh) ($\epsilon = 2.6 \times 10^3 \text{ M}^{-1} \text{ cm}^{-1}$), 281 (3.6×10^3), 530 (1.0×10^2). At $pH > 7$ no absorption bands are exhibited in the UV-vis spectrum at wavelengths longer than 200 nm. The change in absorbance at $\lambda = 530$ with pH was determined. The only endpoint observed was at pH 7. Determination of the endpoint does not answer the question of whether the net change at the endpoint is $[(NH_3)_5OsSO_2]^{2+} + OH^- = [(NH_3)_5OsSO_3H]^+$ or $[(NH_3)_5OsSO_2]^{2+} + 2 OH^- = [(NH_3)_5OsSO_3] + H_2O$. If it is assumed that of the three forms of the complex only $[(NH_3)_5OsSO_2]^{2+}$ is colored, the two possibilities can easily be distinguished. If the first equation describes the net change, then one equivalent of OH^- per mol should discharge the color, while if the reaction obeys the second equation, the absorbance corresponding to the magenta color should decrease to one-half the original value. The change in color following the addition of slightly more than one mol of OH^- per mol of complex in two successive portions was noted. The first addition of NaOH caused the partial loss of the magenta color of the solution, but the resulting solution was still intensely magenta in color. Addition of the second aliquot of NaOH resulted in the complete disappearance of the magenta color. Because the first aliquot did not discharge the color, it was concluded that the conversion of the sulfur dioxide directly to sulfite (SO_3^{2-}) was observed during the titration. No difference in the absorbance in the UV-vis region was measured after the sulfur dioxide complex was rapidly converted to the sulfite form and back again to the sulfur dioxide species.

The IR spectrum of the $[(NH_3)_5OsSO_2]Cl_2$ complex exhibits absorptions at 1110 (strong), 1235 (strong), 1300 (weak), 1340 (medium), and 1360 cm^{-1} (medium). Following the assignments given in Refs. 12 and 13, for ruthenium sulfur dioxide complexes, the absorption at 110 cm^{-1} is assigned to the symmetric S=O stretch. The absorption at 1235 cm^{-1} is due to one of the asymmetric S=O stretches. The absorptions assigned to S=O stretches in ruthenium compounds are usually strong, which would make it unlikely that the weak absorption at 1300 cm^{-1} is the result of an

S=O stretch. One of the absorption bands, 1340 or 1360 cm^{-1} , is probably due to an ammine band, and the other band can be attributed to the second S=O asymmetric stretch.

In 0.1 M HCl, the cyclic voltammogram of $[(\text{NH}_3)_5\text{OsSO}_2]^{2+}$ displays an irreversible reduction wave at +90 mV *vs.* NHE. In 0.1 M NaOH, the cyclic voltammogram displays a couple at -235 mV *vs.* NHE. The couple appears to be reversible but it is difficult to establish the reversibility with certainty because there is an irreversible oxidation wave nearby at a somewhat more positive potential.

An attempt was made to synthesize the osmium analog of $[(\text{NH}_3)_5\text{RuSSRu}(\text{NH}_3)_5]^{4+}$. The ruthenium species has been synthesized in a variety of ways; one of the first useful methods involved reduction of $[(\text{NH}_3)_5\text{RuSO}_2]^{2+}$.^{14,12} Some $[(\text{NH}_3)_5\text{OsSO}_2]\text{Cl}_2$ was dissolved in 0.1 M HCl and a few pieces of zinc amalgam were added. The solution was stirred in air for several hours until it became blue. The zinc amalgam was removed whereupon the solution gradually turned from blue to purple. A purple band was eluted with 4 M HCl from a column of AG 50W-X2 cation exchange resin. The purple species was isolated as a chloride salt. The microanalysis was as follows: Found: H 3.7; N 16.9; S 7.7; Cl 19.3. Ratio S:Cl:N:H is 1:2.3:5.0:15. The UV-visible spectrum shows maxima at 265, 470, and 560 nm in 0.1 M HCl. The compound is green in basic solution with λ_{max} at 310 nm and 667 nm at pH ~9. The change of color from purple to green does not require O_2 . When cyclic voltammetry was done in 0.1 M HCl with a carbon paste indicator electrode, a reversible couple was recorded at +315 mV *vs.* NHE. Potassium hydroxide was added until the solution turned green and then it was rescanned. An irreversible oxidation wave was observed at -140 mV. During an attempt to do a spectrophotometric acid-base titration under argon, it was observed that the green form did not revert back to the purple from upon reacidification. However, the solution did change to purple after it was exposed to air. It was also observed that a plot of E_f *vs.* pH in the range 0.78 to 2.90 gave a slope of about 30 mV, and the peak to peak separation of the waves in the cyclic voltammograms was 60 mV, indicating that one electron is absorbed for two protons. The ruthenium disulfur complex does not display this sort of pH dependent behavior.^{12,14} No further work was done on the reduction product of

$[(\text{NH}_3)_5\text{OsSO}_2]\text{Cl}_2$.

The $[(\text{NH}_3)_5\text{OsSO}_2]\text{Cl}_2$ complex is readily oxidized with H_2O_2 (oxidation occurs immediately upon mixing). When the oxidation was done by adding rapidly an excess of 30% H_2O_2 (about 0.5 ml 30% H_2O_2 was added to ~50 mg $[(\text{NH}_3)_5\text{OsSO}_2]^{2+}$ in ~3 ml of 0.1 M HCl), two yellow bands could be eluted from a Sephadex cation exchange column. One band was eluted with 0.1 M HCl and the second band with 0.3 M HCl. If the H_2O_2 was diluted (to ~0.03%) and added dropwise until the pink color just disappeared from the solution, only traces of the second band could be seen on the cation exchange column. The eluate containing the first band was dried by rotary evaporation. The solid was dissolved in 5 M HCl and reprecipitated by the addition of acetone. The solid was collected by filtration, washed with acetone, and dried in a vacuum desiccator. A microanalysis for sulfur gave the sulfur content as 6.2% (the material was probably impure). Because the material is probably not pure, the absorption spectra is not reported in detail, but it sufficed to show that the Os(II)- SO_2 complex was not being dealt with. The cyclic voltammogram of the material from the first band in 0.1 M NaOH is identical with that of $[(\text{NH}_3)_5\text{OsSO}_2]^{2+}$ in 0.1 M NaOH. A dilute solution of Eu^{2+} in 0.1 M HCl was added dropwise to a solution of material from the first band in 0.1 M HCl until a pink color developed. The pink solution absorbed at 530 nm, as does $[(\text{NH}_3)_5\text{OsSO}_2]^{2+}$ in 0.1 M HCl. From the evidence cited, it is likely that oxidation as described produces the sulfite complex of Os(III). This behavior is in marked contrast to that of the Ru(II)- SO_2 complex, which is oxidized to the Ru(III) sulfato complex under the same conditions.

A microanalysis of material isolated from the second band gave the following values: H 3.06; C 0; Cl 27.56; N 18.76; S 0. The analysis is rather close to that of $[(\text{NH}_3)_5\text{OsCl}]\text{Cl}_2$ which has the following calculated values: H 3.96; Cl 27.86; N 18.35. However, the calculated H value is too high in comparison with that found for the oxidized material, and two other discrepancies are apparent. The chloropentaammine complex has λ_{max} at 244 nm ($\epsilon=200 \text{ M}^{-1} \text{ cm}^{-1}$) and 267 (2.01×10^3). The oxidation product has λ_{max} in H_2O at 238 and 270 (sh) nm with the shoulder at 270 nm having about half the intensity of the peak at 238 nm. The second difference is that the IR spectrum of the oxidation product has a strong,

sharp band at 1090 cm^{-1} that is absent from the IR spectrum of the chloropentaammine complex. Osmium nitrido complexes display a strong band in the range 1020 to 1100 cm^{-1} that is assigned to an $\text{Os}\equiv\text{N}$ stretch.¹⁵ The IR spectrum of the complex $[\text{NH}_3)_4\text{ClOs(N)OsCl}(\text{NH}_3)_4]\text{Cl}_3$ displays an absorption at 1104 cm^{-1} and the UV spectrum shows bands at 242 nm and 265 (sh) nm .¹⁶ However, the calculated values for analysis are the following: H 3.41; Cl 25.04; N 17.81. The second band of oxidized material is tentatively identified as $[(\text{NH}_3)_4\text{ClOsN}]\text{Cl}_2$, which, it will be noted, has an analysis close to that of $[(\text{NH}_3)_5\text{OsCl}]\text{Cl}_2$, apart from H content.

DISCUSSION

Complexes of N-Heterocycles. In trying to understand the spectra of the Os(III) complexes, it will simplify matters to dispose of the most obvious features first. In each case but one, the highest energy band can reasonably be assigned as a ligand $\pi^*\leftarrow\pi$ transition. The bands as determined in this and related work are catalogued in the following (where the units are not otherwise specified, they should be read as $\text{cm}^{-1}\times 10^3$; the data for the tetraammines are taken from Ref. 1). For pyrazine: on $(\text{NH}_3)_5\text{Os(III)}$, 40.6; on $\text{Cl}(\text{NH}_3)_4\text{Os(III)}$, 40.0; on $\text{Br}(\text{NH}_3)_4\text{Os(III)}$, 39.8; on $\text{Cl}(\text{NH}_3)_4\text{Os(II)}$, 39.6; on $\text{N}_2(\text{NH}_3)_4\text{Os(II)}$, 40.2; free, 38.3.¹⁷

For pyrazinium ion: on $(\text{NH}_3)_5\text{Os(II)}$, 37.6; on $\text{Cl}(\text{NH}_3)_4\text{Os(II)}$, 37.5; on $\text{N}_2(\text{NH}_3)_4\text{Os(II)}$, 37.3, free, 37.5.¹⁸ For methylpyrazinium ion on $\text{Cl}(\text{NH}_3)_4\text{Os(III)}$, 36.3, on $\text{N}_2(\text{NH}_3)_4\text{Os(II)}$, 37.0.

For pyridine on $(\text{NH}_3)_5\text{Os(III)}$, (42.7); on $(\text{NH}_3)_5\text{Ru(III)}$,¹⁹ 39.5; on $(\text{NH}_3)_5\text{Ru(II)}$, 40.9;¹⁹ free, 39.5;¹⁷ protonated, 39.3.¹⁹

For isonicotinamide on $(\text{NH}_3)_5\text{Os(III)}$, 42.1; on $(\text{NH}_3)_5\text{Os(II)}$, 41.0; on $\text{N}_2(\text{NH}_3)_4\text{Os(II)}$, 41.6 (sh).

For isonicotinic acid: on $\text{Cl}(\text{NH}_3)_4\text{Os(III)}$, 39.2; on $\text{Cl}(\text{NH}_3)_4\text{Os(II)}$, 38.2; on $\text{N}_2(\text{NH}_3)_4\text{Os(II)}$, 39.7.

For pyrimidine: on $(\text{NH}_3)_5\text{Os(III)}$, 43.8; on $(\text{NH}_3)_5\text{Os(II)}$, 40.0; free,¹⁷ 41.2; protonated 41.2.

For pyridazine: on $(\text{NH}_3)_5\text{Os(III)}$, 44.0; free, 40.6;¹⁷ protonated, 42.2.

Coordination of the azines by metal ions shifts the $\pi^*\leftarrow\pi$ absorption to higher energies, the shift being greater for Os(III) than for Os(II). By contrast, the transition for pyridine is less sensitive to the state of coordination than it is for the azines. In view of the insensitivity of the $\pi^*\leftarrow\pi$ transition in

pyridine to the state of coordination shown by the other cases, it is unreasonable to assign the band 42.7 in the Os(III) complex of pyridine to $\pi^*\leftarrow\pi$, and the band proper to it is probably buried in the long wave length shoulder of the highest energy absorption.

A striking feature of the Os(III) spectra is this: after the band ascribable to the $\pi^*\leftarrow\pi$ transition is set aside, two prominent ones remain, separated by a constant (within the limits of accuracy of the measurements) energy interval. Thus, for pyrazine on $(\text{NH}_3)_5\text{Os(III)}$, we have 35.4, 30.4 ($\Delta=5.0$); on $\text{Cl}(\text{NH}_3)_4\text{Os(III)}$, 34.9, 28.7 ($\Delta=6.2$); on $\text{Br}(\text{NH}_3)_4\text{Os(III)}$, 34.8, 28.4 ($\Delta=6.4$). For isonicotinamide on $(\text{NH}_3)_5\text{Os(III)}$, there is a band at 34.6 and a shoulder at longer wave length which is not well resolved. For isonicotinic acid on $\text{Cl}(\text{NH}_3)_4\text{Os(III)}$, 34.8, 29.6 ($\Delta=5.2$). For pyridazine on $(\text{NH}_3)_5\text{Os(III)}$, 39.0, 32.8 ($\Delta=6.2$). The resolution of the two bands in question from that ascribable to $\pi^*\leftarrow\pi$ is least satisfactory for the ligands which are the weakest π acids, namely pyridine and pyrimidine. If the arguments presented earlier for pyridine are accepted, and we count 42.7 and 37.6 as related to the bands under consideration, we have $\Delta=5.0$. For pyrimidine, the band of intermediate energy seems to be buried in the long wave-length shoulder of the $\pi^*\leftarrow\pi$ transition.

Focussing attention on the band of lower energy which in each case but one is well resolved, for $(\text{NH}_3)_5\text{Os(III)}$ these decrease in energy in the following order: py (37.6); pyrimidine (34.7); pyridazine (32.2); pyrazine (30.4). This order is consistent with metal to ligand charge transfer as the origin of the absorption in question and this conclusion obviously applies than also to the higher energy member of the pair. The assignment as MLCT is supported by considering the data for $\text{Cl}(\text{NH}_3)_4\text{Os(III)}$.¹ The lowest energy bands decrease in order as follows: isonicotinic acid (29.6); pyrazine (28.7); methyl pyrazinium ion (21.9). For the latter there is also a band at 26.7 — note again the interval close to 5.0.

The splitting of the MLCT bands can reasonably be ascribed to spin orbit coupling. Because an electron is missing from the πd set for Os(III), the intra-subconfiguration transitions should be directly observable. The data summarized in Table 2 show that the region at $5\times 10^3\text{ cm}^{-1}$ and somewhat higher (the energy interval for the splittings in the UV) is rich in transitions. Absorption in the near IR is not observed for the Os(II) complex, nor is it

expected in the basis of the assignment made. It has been reported for Os(IV) salts, and the spectra have been accounted for successfully by invoking spin orbit coupling.²⁰

Additional bands can be noticed for some of the Os(III) complexes as shoulders on the long wavelength side of the bands already considered. These may be ligand transitions – each of the azines shows weak absorption at energies lower than the $\pi^* \leftarrow \pi$ transitions – but because the energy maxima are not defined by our data, we have made no efforts to assign them.

In the earlier paper,¹ the middle transition of three often noted for Os(III) complexes in the UV was interpreted as arising from halide to metal charge transfer. That this isn't the sole origin of the band in question is demonstrated by our results for complexes of the pentaammine series. However, such a transition is expected, and it seems to be exposed in the spectrum of the methyl pyrazinium complex of $\text{Cl}(\text{NH}_3)_4\text{Os(III)}$.¹ In this case, MLCT is shifted to low energies, 26.7 and 21.9, and this leaves a shoulder at 31.3 on the $\pi^* \leftarrow \pi$ band which may indeed be $\text{Os(III)} \leftarrow \text{Cl}^-$ in origin.

In the present work the observations on the spectra of Os(II) ammine complexes are considerably extended, but we have nothing to add by way of interpretation beyond that introduced in the earlier paper.¹ The absorption maxima for pyrazine corresponding to the $\pi d - \pi^*$ transitions on $(\text{NH}_3)_5\text{Os(II)}$ and $\text{Cl}(\text{NH}_3)_4\text{Os(II)}$ are virtually identical and the same is true for the protonated form. Thus the remarkable effect, namely that protonation shifts the $\pi d - \pi^*$ absorption to higher energies, as reported for the chlorotetraammine case, is reproduced for the pentaammine. Also, the feature that second bands may appear at lower energy and intensity than the major $\pi d - \pi^*$ transition is reproduced in some of the new systems – for pyridine on $(\text{NH}_3)_5\text{Os(II)}$, bands at 23.3 and 18.1; for isonicotinamide, at 19.7 and 13.1; for pyrimidine at 21.9 and 15.1. There is no reason to set aside the interpretation of the origin of the weaker band advanced earlier,¹ namely as arising from the $d_{xy} - \pi^*$ transition (z axis directed toward N -heterocyclic). In contrast to the splitting of band pairs observed in the Os(III) spectra, this is not constant for the Os(II) spectra. While the separations are rather constant for the data just cited, for pyrazine on $\text{Cl}(\text{NH}_3)_4\text{Os(II)}$, the interval is 8.4 and for pyrazinium ion on the same center it is 14.5.¹

As to the chemistry of the species, we note

that the earlier conclusions about the effect of back-bonding based on the behavior of the pyrazinium complex of $\text{Cl}(\text{NH}_3)_4\text{Os(II)}$ are not materially altered by our work with the pentaammine. As before, coordination of Os(II) to pyrazinium ion raises the $\text{p}K_a$, 6.8 units as compared to 7.0 for the tetraammine, and, as before, protonation of coordinated pyrazine shifts $\pi d - \pi^*$ absorption to higher energy. This is in contrast to the behavior of pyrazinium ion on Ru(II),¹⁹ or on Os(II) when a strong π acceptor such as dinitrogen is an auxiliary ligand.¹ We subscribe to the suggestions made earlier by way of interpretation.

Finally, it is worth noting the Os(II) complexes of the N -heterocyclic ligands constitute a series of very strong outer-sphere reducing agents with graduated values of E_r . Unfortunately, their utility in acidic solution is limited by the instability to ligand reduction. This sensitivity to self-reduction should be considered in the context of the observation²¹ that coordination of pyrazine to Ru(II) greatly diminishes the rate at which it is attacked by external reducing agents. The two sets of observations are not really in conflict; analysis of the $\pi d - \pi^*$ spectra for the Os(II) complexes shows that there is a great deal of charge transfer from Os(II) to the ligand. This facilitates protonation of the ligand leading to net reduction. The capacity for back-bonding and reducing power are related. A maximum in stabilization to reduction is expected as the back-bonding capacity of the metal ion increases, and when charge transfer exceeds this maximum, instability to internal oxidation reduction ensues.

$[(\text{NH}_3)_5\text{OsSO}_2]^{2+}$. The most striking feature of the chemistry of the sulfur dioxide complexes of Os(II) encountered in this work is the enormous stabilization by the metal ion of the SO_2 form of the ligand. Conversion to the sulfite form does not occur until the pH is raised to 7, and in this pH region two hydroxide ions per molecule of coordinated sulfur dioxide are consumed. This behavior can be understood qualitatively if, as is altogether reasonable, SO_2 is a much stronger π acid than is HSO_3^- or SO_3^{2-} . Since at the neutralization point ($\text{pH}=7$) SO_2 is transformed directly to SO_3^{2-} , $\sqrt{K_1 K_2} = 10^7$. If $\text{p}K_2$ for $[(\text{NH}_3)_5\text{OsSO}_2]^{2+}$ is assumed to be the same as for $[(\text{NH}_3)_5\text{RuSO}_2]^{2+}$, namely 5, then $\text{p}K_1$ for the Os(II) complex is 9. Note that for $[(\text{NH}_3)_5\text{RuSO}_2]^{2+}$, $\text{p}K_1 = 2.15 \pm 0.1$ and for the free ligand, $\text{p}K_1$ and $\text{p}K_2$ are 1.76 and 7.21, respectively. As in the case of pyrazinium ion,

the quantitative difference between Os(II) and Ru(II) in acting on a π acceptor is very striking.

Though the chemistry of S(IV) on Os(II) (and Os(III)) has not been at all thoroughly explored, enough has been done to reveal important differences from that described for Ru(II). Prominent among them is the color: the species $(\text{NH}_3)_5\text{RuSO}_2^{2+}$ shows bands at 225(sh) ($\epsilon=1.1 \times 10^3$) and 288 (4.0×10^3) but no absorption at lower wave-length sufficient to impart color to solutions at ordinary concentrations. The bands in the UV for the Os(II) complex: 254 (sh) (2.6×10^3) and 281 (3.6×10^3) are presumably related to those reported for the Ru(II) complex, but the analog of the band for the former at 530 nm has not been reported for the latter. Other significant differences are the following: labilization of the *trans* position in either the 2+ or 3+ state is less pronounced in the Os than Ru complexes; the chemistry of the reduction of coordinated SO_2 is much more complex for Os(II) than for Ru(II); and, finally, oxidation of the coordinated ligand is much more difficult for Os than for the Ru complex. On the matter of reduction of coordinated SO_2 , it seems likely on the basis of our experience that the species which are formed are not limited to S_2^- as the bridging unit, and that bridging disulfur units carrying one or two oxygen atoms are also featured. Further work on the system is certain to be rewarding.

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