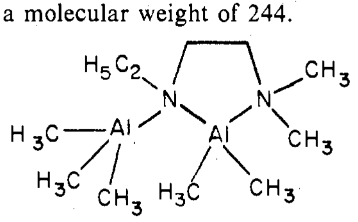
that the $N(CH_3)_2$ lines were also dependent on concentration but integration was more difficult due to solvent side bands and underlying methylene protons. Integration, at various concentrations and temperatures, of the $(CH_3)_2Al$ lines due to the monomer and dimer allowed the relative amounts of monomer and dimer and consequently the equilibrium constants to be calculated. Values of $\Delta H°$ and $\Delta S°$ for the proposed equilibrium were obtained from a plot of log K vs. $1/T°K$. Difficulties of temperature control and the possibility of small amounts of more associated species require these values for K, $\Delta H°$, and $\Delta S°$ be taken as approximations. However, these values are useful in that they do show the interplay between $\Delta H°$ and $T\Delta S°$ for the monomer–dimer equilibrium of this compound and the importance of these factors to chelation in general. If one uses the values determined ($\Delta H° = -39.3$ kJ mol^{-1}; $\Delta S° = 166$ J deg^{-1} mol^{-1}) to calculate $\Delta G°$ for the reaction $2A \rightleftarrows A_2$, the values obtained are as follows: $\Delta G°_{300°K} = +10.5$ kJ mol^{-1}; $\Delta G°_{233°K} = -0.622$ kJ mol^{-1}. These values indicate that it is the large negative entropy associated with the dimer formation that predominates at room temperature to favor the monomeric chelate. As the temperature decreases, this effect becomes less important and enthalpy favors the formation of the dimer.

The chemical properties of the chelate $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$ suggest that it can behave as a very weak Lewis acid and a Lewis base. Dimethylamine reacts to give an equilibrium mixture with the products $[(CH_3)_2AlN(CH_3)_2]_2$ and the dibasic ligand $H(C_2H_5)NC_2H_4N(CH_3)_2$. Trimethylamine, however, does not react with the chelate, possibly due to the entropy effect or to the fact that the ligand nitrogen atoms of the chelate are stronger bases than $N(CH_3)_3$. The competition reaction between the chelate and $N(CH_3)_3$ for trimethylalane suggests that the chelate is a stronger base than $N(CH_3)_3$. Approximately 75% of the $N(CH_3)_3$ was recovered unreacted. The major aluminum-containing product from the competition reaction had a molecular weight in benzene of 287. The following adduct, the most likely potential product, has a molecular weight of 244.



The product, formed by the chelate coming apart and the dimethylamino end of the ligand binding the $Al(CH_3)_3$, would be expected to dimerize through the $N(C_2H_5)$ and form a four-coordinate $Al(CH_3)_2$ group. A mixture of these two species would lead to a molecular weight greater than 244. Dissociation to give the chelate and $Al_2(CH_3)_6$ would give a lower molecular weight. The ^1H NMR spectrum of the adduct in toluene-d_8 shows two or more lines in the Al–CH_3 region and two lines of equal intensity for the $N(CH_3)_2$ protons. These data are not inconsistent with the type of adduct postulated. If the postulated adduct is indeed the product, it provides evidence for the polarization of the Al–N bond and the increased basicity of the nitrogen bound to the aluminum. Considering only steric factors one would have expected the trimethylamine to be a stronger base than the ethylamino group of the chelate toward trimethylalane.

Acknowledgment. We wish to thank the National Science Foundation, Grant No. GP-20200, for financial support of this research.

Registry No. $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$(monomer), 55975-87-6; $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2$(dimer), 55975-89-8; $Al(CH_3)_3$, 75-24-1; $(CH_3)_2AlN(C_2H_5)C_2H_4N(CH_3)_2 \cdot Al(CH_3)_3$, 55975-88-7; $N(CH_3)_2H$, 124-40-3; $[(CH_3)_2AlN(CH_3)_2]_2$, 22450-81-3.

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Nitrosodisulfonates and Hydroxylamine-*N*,*N*-disulfonates. IV. Crystal Structure of Sodium Nitrosyl-*N*,*N*-disulfonate Trihydrate

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Received May 7, 1975 AIC50304O

The crystal structure of $Na_3[ON(SO_3)_2]\cdot 3H_2O$ has been determined by Patterson methods and refined by full-matrix least squares to a weighted residue of 0.033 using 928 independent reflections. The crystals are orthorhombic, of space group $Cmc2_1$ with $a = 14.234$ (2) Å, $b = 11.052$ (1) Å, $c = 5.8607$ (5) Å. The $[ON(SO_3)_2]^{3-}$ anion, which contains a crystallographic mirror plane passing through the NO group, has a pyramidal coordination at nitrogen and an N–O bond length of 1.427 Å, both features distinguishing it from the radical nitrosodisulfonate $[ON(SO_3)_2]^{2-}$, where the N–O bond length is 1.28 Å. In the present structure the N–O bond is directed at the centroid of a triangle formed by the three Na atoms, which have coordination numbers of 6, 6, and 7 respectively.

Previous articles[1,2] in this series have discussed the preparation and characterization of a number of alkali metal salts of hydroxylamine-*N*,*N*-disulfonate and related anions. In particular, the crystal structure of a rubidium salt, $Rb_5\{H[ON(SO_3)_2]_2\}\cdot 3H_2O$, was determined[2] and led to the suggestion that in alkaline solution, pH 11–12, at which that salt crystallizes, the $[HON(SO_3)_2]^{2-}$ ion coexists with nitrosyl-*N*,*N*-disulfonate $[ON(SO_3)_2]^{3-}$ in solution. This latter

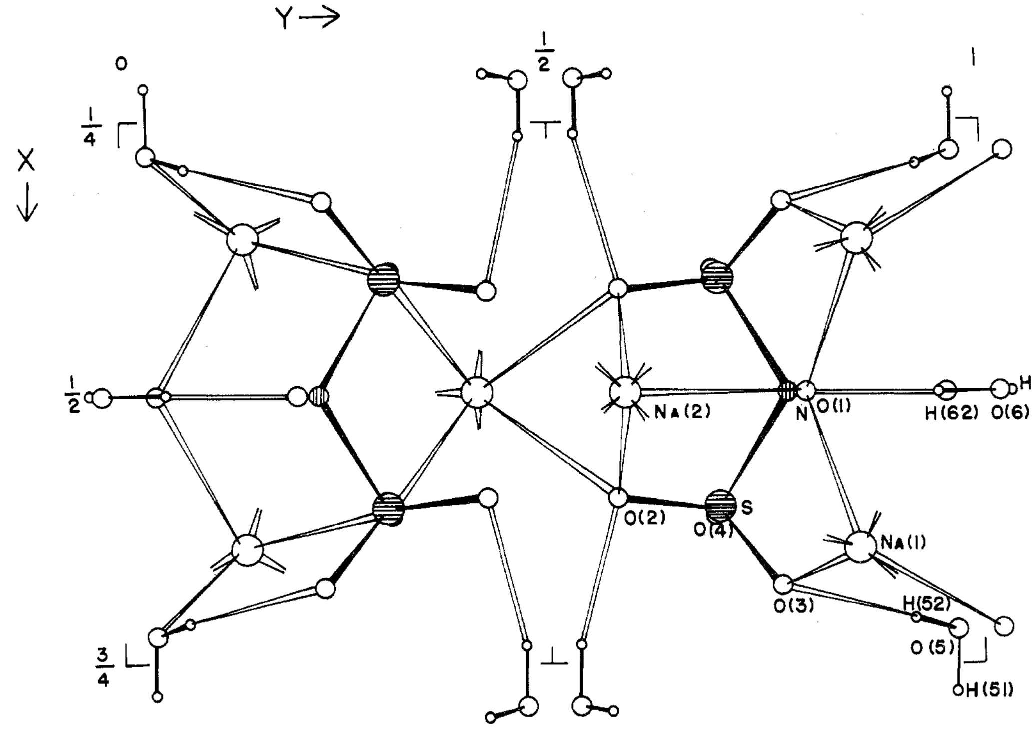

Figure 1. Crystal structure of $Na_3ON(SO_3)_2\cdot 3H_2O$ projected on (001).

Table II

Fractional Atomic Coordinates[a]

Atom	x/a	y/b	z/c
S	10196 (4)[b]	19490 (5)	0
Na(1)	14022 (9)	36343 (12)	48992 (36)
Na(2)	0	9436 (14)	48338 (44)
O(1)	0	29192 (28)	30574 (53)
O(2)	9816 (15)	7543 (18)	10784 (44)
O(3)	17497 (16)	27033 (20)	9887 (44)
O(4)	10337 (16)	19121 (21)	−24686 (40)
O(5)	28170 (20)	3186 (24)	31418 (53)
O(6)	0	53819 (36)	19368 (66)
N	0	27166 (31)	6728 (64)

Thermal Parameters[c]

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
S	142 (2)[d]	106 (2)	112 (2)	−21 (2)	−18 (3)	8 (3)
Na(1)	337 (6)	297 (6)	196 (6)	−131 (6)	0 (8)	21 (8)
Na(2)	237 (7)	138 (6)	136 (7)	0	0	−16 (10)
O(1)	321 (15)	187 (13)	49 (9)	0	0	−33 (11)
O(2)	186 (9)	116 (7)	279 (12)	5 (7)	−25 (10)	60 (8)
O(3)	225 (9)	225 (10)	198 (10)	10 (8)	−63 (10)	6 (8)
O(4)	199 (9)	255 (11)	107 (8)	−15 (8)	12 (8)	−27 (8)
O(5)	252 (12)	232 (11)	199 (10)	10 (8)	−42 (10)	−27 (10)
O(6)	351 (18)	163 (12)	160 (14)	0	0	34 (13)
N	200 (15)	105 (12)	93 (12)	0	0	−13 (10)

Hydrogen Atom Coordinates[c]

Atom	x/a	y/b	z/c	B, Å^2
H(51)	230 (3)	20 (5)	287 (11)	3.5 (12)
H(52)	287 (3)	69 (4)	375 (9)	2.0 (11)
H(61)	0	566 (8)	350 (21)	5.6 (23)
H(62)	0	469 (12)	215 (21)	7.3 (31)

[a] $\times 10^5$. [b] Numbers in parentheses are estimated standard deviations. [c] $\times 10^3$. [d] The temperature factor expression is $\exp[-2\pi^2(h^2b_1{}^2U_{11} + \ldots + 2hkb_1b_2U_{12} + \ldots)]$.

Table III. Bond Lengths (Å) and Angles (deg) in $Na_3ON(SO_3)_2\cdot 3H_2O$

Anion Bond Lengths

O(1)–N	1.415 (5)
S–N	1.727 (2)
S–O(2)	1.465 (3)
S–O(3)	1.453 (3)
S–O(4)	1.448 (2)

Anion Bond Angles

O(1)–N–S	107.65 (1)
S–N–S[a]	114.38 (1)
N–S–O(2)	108.27 (1)
N–S–O(3)	103.19 (1)
N–S–O(4)	104.70 (1)
O(2)–S–O(3)	111.81 (1)
O(2)–S–O(4)	113.97 (1)
O(3)–S–O(4)	113.89 (1)

Na–O Lengths

Na(1)–O(1)	2.403 (3)
Na(1)–O(3)	2.560 (3)
Na(1)–O(4)[b]	2.506 (3)
Na(1)–O(5)	2.400 (3)
Na(1)–O(5)[c]	2.487 (4)
Na(1)–O(6)	2.567 (3)
Na(2)–O(1)	2.419 (4)
Na(2)–O(2)	2.451 (3) (twice)
Na(2)–O(2)[d]	2.616 (4) (twice)
Na(2)–O(4)[b]	2.410 (3) (twice)

O–H· · ·O Lengths

O(5)–H(51)· · ·O(2)	2.91
O(5)–H(52)· · ·O(3)[e]	2.81
O(6)–H(61)· · ·O(6)[f]	3.05
O(6)–H(62)· · ·O(1)	2.80

[a] $\bar{x}, y, z$. [b] $x, y, 1 + z$. [c] $x, 1 - y, 1/2 + z$. [d] $x, \bar{y}, 1/2 + z$. [e] $1/2 - x, 1/2 - y, 1/2 + z$. [f] $x, 1 - y, z - 1/2$.

species was particularly interesting because it differs only by one electron from the radical nitrosodisulfonate anion, $[ON(SO_3)_2]^{2-}$, of Fremy's salt.[3] The X-ray diffraction study reported here was performed on crystals grown from a solution containing sodium hydroxide, crystals which proved to be the previously reported trihydrate,[4] and confirms the formulation of this species and of its sodium salt.

Experimental Section

A spherical crystal fragment of $Na_3[ON(SO_3)_2]\cdot 3H_2O$, of radius 0.025 cm, was used for data collection. The crystal was first placed on a Buerger precession camera, to determine space group and approximate lattice constants. The systematic extinctions found were $h + k = 2n + 1$ for hkl and $l = 2n + 1$ for $h0l$, showing the space group to be one of $Cmcm$, $Cmc2_1$ or $C2cm$. A positive piezoelectric test rules out the first named of these.

The crystal was then transferred to a Picker FACS-I automated diffractometer equipped with a highly oriented graphite monochromator. The lattice constants were determined by a least-squares fit to the positions of 12 reflections with 2θ values between 35 and 50° as observed using Mo Kα_1 radiation, wavelength 0.70926 Å. The lattice constants determined in this way were a = 14.234 (2) Å, b = 11.052 (1) Å, c = 5.8607 (5) Å, and V = 921.94 Å^3 at 22°. Assuming four formula units per cell and a formula weight of 313.1, the calculated density is 2.256 g cm^{-3} while the measured value is 2.25 g cm^{-3} obtained by pycnometry. The linear absorption coefficient

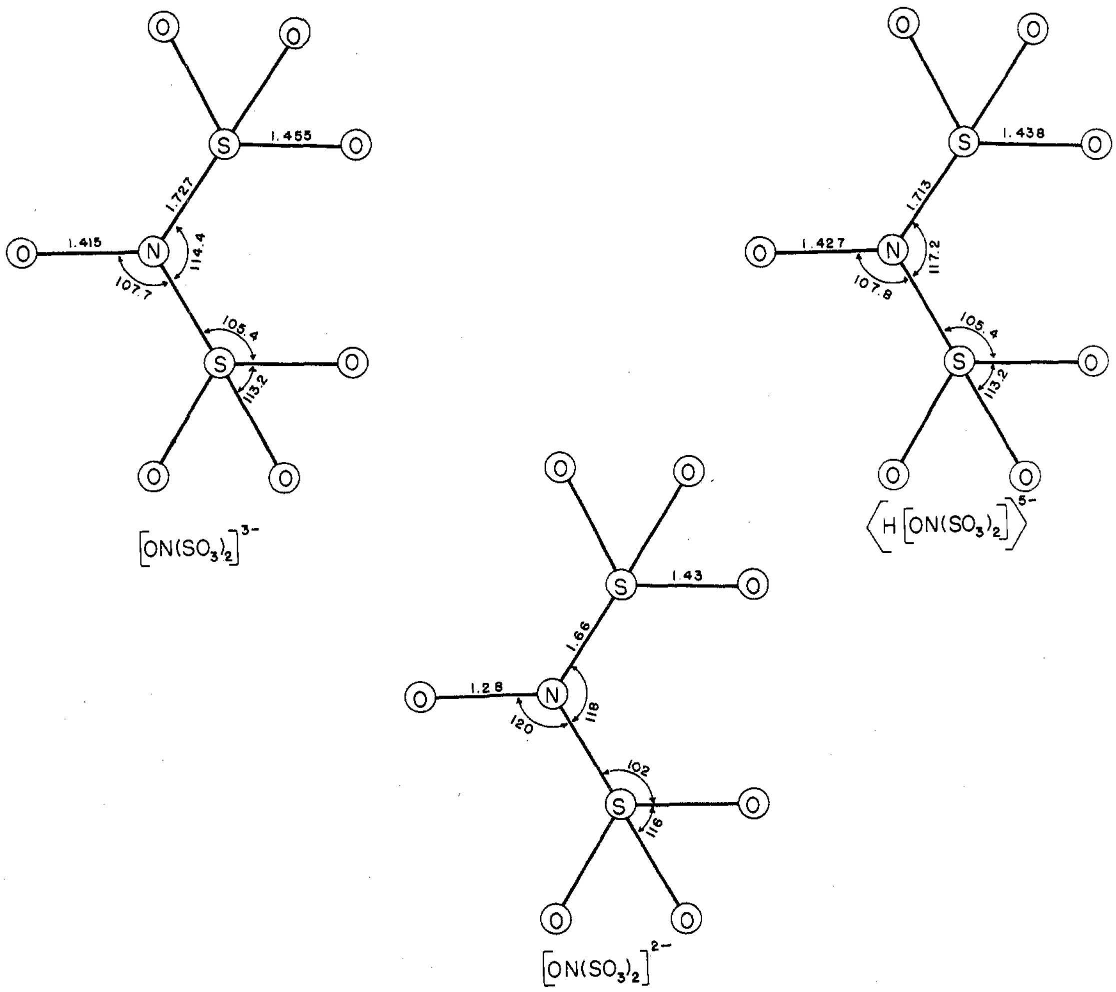

Figure 2. Average bond lengths (Å) and angles (deg) in nitrosyl-*N*,*N*-disulfonate and related species.

for Mo Kα radiation is 7.62 cm^{-1}. A total of 928 data were collected between 5 and 65° in 2θ, using the θ–2θ scan mode. The intensities of three standard reflections were unchanged throughout the period of data collection.

The data were then reduced to observed structure factors by standard methods. The polarization factor used was $(\cos^2 2\theta_m + \cos^2 2\theta_s)/(2 \sin \theta_s)$, where θ_m and θ_s are the monochromator and sample Bragg angles, respectively. The scattering factors were calculated from the series coefficients given by Cromer and Mann.[5]

Considering the expected chemical structure of the anion in this compound, both the space groups experimentally possible would require the anion to contain a crystallographic mirror plane. In $C2cm$ the parallel mirror planes in the structure would lie 2.9 Å apart. No chemically reasonable structure could be based on this arrangement, and therefore $Cmc2_1$ was tentatively chosen as the space group, an assumption borne out by the subsequent solution of the three-dimensional Patterson function.

Interpretation of the Patterson function initially gave the S and Na atom positions. Since these heavy atoms all lie in planes at z = 0 and 1/2 (assuming the origin is fixed in the polar space group $Cmc2_1$ by setting z(S) equal to zero), it was then necessary to introduce some of the light atoms into the structure factor calculations, in order to phase reflections with odd l. Further examination of the Patterson function showed peaks in the vicinity of the origin arising from the tetrahedral group around the S atom. These showed the tetrahedron to be oriented with a threefold axis parallel to c and a mirror plane perpendicular to a. Trial structure factor calculations with the two possible alternative arrangements of the tetrahedron, arrangements which are related by reflection in a plane through the central S atom perpendicular to b, showed which of these was correct. The water oxygen atoms were then located by difference Fourier synthesis.[6] The positions of these atoms were first refined by full-matrix least-squares using individual isotropic temperature factors, with all weights set at unity. The temperature factors were next allowed to vary anisotropically. Following this a further difference synthesis showed the positions of the hydrogen atoms in the structure. Their positions were also refined, using isotropic temperature factors only.

The observed and calculated structure factors are listed in Table I.[7] The final conventional R factor is 0.025, and the final weighted least-squares residual R, that is $[\Sigma w(|F_o| - |F_c|)^2/w|F_o^2]^{1/2}$, is 0.033. The final positional and thermal parameters are given in Table II.

Results and Discussion

The structure contains the isolated discrete nitrosyl-*N*,*N*-disulfonate ion, $[ON(SO_3)_2]^{3-}$, previously postulated to exist in alkaline solution.[2] The anion contains a crystallographic mirror plane of symmetry, which passes through the nitrosyl group. One of the three sodium atoms in the formula unit, as well as one of the three water molecules, also lies on this mirror plane. An overall view of the structure is given in Figure 1.

Of the three sodium atoms in the formula unit, two are six-coordinate with a distorted octahedral geometry, while the other is seven-coordinate, the coordination polyhedron approximating a trigonal prism with one rectangular face capped. The three sodium atoms form an equilateral triangle, and the N–O bond of the anion points directly at the centroid of this triangle, so that O(1) is coordinated to all three sodium atoms. Each sodium atom in the triangle also shares one other oxygen with a neighboring sodium atom in the triangle. An alternative description of this effect is that the three coordination polyhedra of the sodium atoms share edges radiating from O(1). The ionic bonding links the structure into sheets perpendicular to b; the only interaction between the sheets is hydrogen bonding, and the crystals show a pronounced cleavage perpendicular to b. Bond lengths and angles within these coordination

Table IV. Bond Strength Sums for $Na_3ON(SO_3)_2 \cdot 3H_2O$

	Na(1)	Na(2)	S	H(51)	H(52)	H(61)	H(62)	Total
O(1)	0.19^a	0.18					0.19	0.75^c
O(2)		0.17^b 0.12^b	1.51	0.16				1.96
O(3)	0.13		1.54		0.18			1.85
O(4)	0.15	0.18^b	1.58					1.91
O(5)	0.19 0.15			0.84	0.82			2.00
O(6)	0.13^a					0.86 0.14	0.81	2.07
Total	0.94	1.12	4.63^c	1.00^d	1.00^d	1.00^d	1.00^d	

[a] Occurs twice in horizontal sum. [b] Occurs twice in vertical sum. [c] Bond to nitrogen ignored. [d] Assumed.

polyhedra are contained in Table III.

The three water molecules in the formula unit are located in the vicinity of one of the glide planes in the structure. The operation of this glide plane generates a continuous ribbon three water molecules wide which runs through the structure in the *c* direction. One hydrogen atom per formula unit is involved in hydrogen bonding within this ribbon; the others are in bonds to the neighboring anions, two of the five being to other sheets. Details of these hydrogen bonds are contained in Table III.

Bond lengths and bond angles within the anion are also given in Table III and are illustrated in Figure 2, along with some averaged molecular geometries for the related species $\{H[ON(SO_3)_2]_2\}^{5-}$ in its rubidium salt and the anion of Fremy's salt, $[ON(SO_3)_2]^{2-}$, determined by Howie et al.[3] It shows that the bond lengths and overall geometry of the isolated nitrosyl-*N*,*N*-disulfonate anion are not significantly different from those of the corresponding moiety in its rubidium acid salt, while the nitrosodisulfonate anion, differing only by one electron, has a markedly shorter N–O distance and a nearly planar conformation at nitrogen.

Bond strength sums were calculated using the formula and constants of Brown and Shannon.[8] The results are given in Table IV. The hydrogen atom positions were assumed to give a bond strength sum of 1.00 around the hydrogen atom, assuming a straight-line O–H···O conformation. The large contribution of 0.75 valence unit to O(1) due to bonds external to the anion illustrates its strongly basic nature and is therefore consistent with the formation of the symmetric dimeric species $\{H[ON(SO_3)_2]_2\}^{5-}$ in other salts. The unusually low bond strength totals for O(2) to O(4), the sulfonate oxygen atoms, may be related to the low thermal motion in this structure compared to many of those used by Brown and Shannon to determine their S–O curve.

Registry No. $Na_3[ON(SO_3)_2] \cdot 3H_2O$, 55904-77-3.

Supplementary Material Available. Table I, containing the observed and calculated structure factors, will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Business Office, Books and Journals Division, American Chemical Society, 1155 16th St., N.W. Washington, D.C. 20036. Remit check or money order for \$4.00 for photocopy or \$2.50 for microfiche, referring to code number AIC50304O-10-75.

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Outer-Sphere One-Equivalent Changes in the Vanadium(II) Reductions of Hexachloroplatinate(IV) and Chloropentaammineplatinum(IV)

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Received February 20, 1975 AIC501358

The V^{2+} reductions of $PtCl_6^{2-}$ and $Pt(NH_3)_5Cl^{3+}$, $2V^{II} + Pt^{IV} \rightarrow 2V^{III} + Pt^{II}$, have been studied in aqueous perchloric acid solutions, $I = 1.0$ *M* ($LiClO_4$). No VO^{2+} is generated in the initial redox steps, and a reaction sequence, (i) and (ii),

$$V^{II} + Pt^{IV} \rightarrow V^{III} + Pt^{III} \tag{i}$$

$$V^{II} + Pt^{III} \xrightarrow{\text{fast}} V^{III} + Pt^{II} \tag{ii}$$

involving 1-equiv changes, is consistent with all observations. Both reactions are independent of $[H^+]$ in the range 0.10–1.00 *M*. At 25° the rate constant for the reaction of $PtCl_6^{2-}$ is $3.36\ (\pm 0.13) \times 10^4\ M^{-1}\ sec^{-1}$ ($\Delta H^{\ddagger} = 4.6 \pm 0.2$ kcal mol^{-1}, $\Delta S^{\ddagger} = -22.4 \pm 0.7$ cal K^{-1} mol^{-1}), and for $Pt(NH_3)_5Cl^{3+}$ it is $1.15 \pm 0.10\ M^{-1}\ sec^{-1}$ ($\Delta H^{\ddagger} = 9.9 \pm 0.5$ kcal mol^{-1}, $\Delta S^{\ddagger} = -25.1 \pm 1.7$ cal K^{-1} mol^{-1}). The V^{2+} reduction of $PtCl_6^{2-}$ is too fast for an inner-sphere process to occur. A rate constant of $110 \pm 10\ M^{-1}\ sec^{-1}$ has been obtained for the $Ru(NH_3)_6^{2+}$ reduction of $Pt(NH_3)_5Cl^{3+}$ at 25°, $I = 0.1$ *M* ($LiClO_4$), and using a linear correlation of data for other V^{2+} and $Ru(NH_3)_6^{2+}$ reductions, an outer-sphere mechanism is also assigned to the V^{2+} reduction of $Pt(NH_3)_5Cl^{3+}$. The Cr^{2+} reduction of $Pt(NH_3)_5Cl^{3+}$ has previously been studied, and evidence has been obtained for a two-electron inner-sphere process. Reasons for this different behavior of Cr^{2+} and V^{2+} are considered.

Introduction

It has been demonstrated that the V^{2+} reduction of mercury(II) proceeds by concurrent 1- and 2-equiv paths.[1] Since the vanadium(III) reduction of mercury(II) is known to be slow,[2] the 2-equiv change must occur within the lifetime of a single binuclear adduct. The Cr^{2+} reduction of mercury(II) on the other hand proceeds solely by 1-equiv reactions.[3] Beattie and Basolo[4] have concluded that the Cr^{2+} reduction of $Pt(NH_3)_5Cl^{3+}$ proceeds via a 2-equiv change with intermediate formation of chromium(IV). Since vanadium(IV) is generally easier to generate than chromium(IV), it seemed likely that the V^{2+} reductions of $PtCl_6^{2-}$ and $Pt(NH_3)_5Cl^{3+}$ would