(7) W. Hieber and G. Braun, *Z. Naturforsch., B*, **14**, 132 (1959).
(8) M. Tsutsui and C. P. Hrung, *J. Am. Chem. Soc.*, **95**, 5777 (1973).
(9) M. Tsutsui and C. P. Hrung, *Chem. Lett.*, 941 (1973).
(10) D. G. Eakins, D. G. Humphreys, and C. E. Mellish, *J. Chem. Soc.*, 6012 (1963).
(11) F. A. Cotton and W. F. Bratton, *J. Am. Chem. Soc.*, **87**, 921 (1965).
(12) (a) W. K. Bratton and F. A. Cotton, *Inorg. Chem.*, **9**, 789 (1970); (b) F. A. Cotton and L. W. Shive, *ibid.*, **14**, 2032 (1975).
(13) (a) M. B. Cingi, D. A. Clemente, L. Magon, and U. Mazzi, *Inorg. Chim. Acta*, **13**, 47 (1975); (b) G. Bandoli, D. A. Clemente, and U. Mazzi, *J. Chem. Soc., Dalton Trans.*, 125 (1976).
(14) A. A. Orio, B. J. Chanstain, and H. B. Gray, *Inorg. Chim. Acta*, **3**, 8 (1969).
(15) D. D. Titus, A. A. Orio, R. E. Marsh, and H. B. Gray, *Chem. Commun.*, 322 (1971).
(16) A. Bertacco, U. Mazzi, and A. A. Orio, *Inorg. Chem.*, **11**, 2547 (1972).
(17) E. Bordignon, U. Croatto, U. Mazzi, and A. A. Orio, *Inorg. Chem.*, **13**, 935 (1974).
(18) G. Bandoli, D. A. Clemente, U. Mazzi, and E. Tondello, *Cryst. Struct. Commun.*, **3**, 293 (1974).
(19) G. A. Mazzocchin, F. Magno, U. Mazzi, and R. Portanova, *Inorg. Chim. Acta*, **9**, 263 (1974).
(20) R. Rabinowitz and J. Pellon, *J. Org. Chem.*, **26**, 4623 (1961).
(21) (a) D. F. Evans, *J. Chem. Soc.*, 2003 (1959); (b) R. A. Bailey, *J. Chem. Educ.*, **49**, 297 (1972).
(22) D. N. Figgis and J. Lewis, "Modern Coordination Chemistry", J. Lewis and R. G. Wilkins, Ed., Interscience, New York, N.Y., 1960, p 403.
(23) G. A. Mazzocchin, U. Mazzi, R. Portanova, and O. Traverso, *J. Inorg. Nucl. Chem.*, **36**, 3783 (1974).
(24) Throughout this paper, estimated standard deviations for the last significant figures are in parentheses.
(25) "International Tables for X-Ray Crystallography", Vol. 1, Kynoch Press, Birmingham, England, 1962.
(26) The space group originally reported[18] is $P2_1/b$, but, following a referee's suggestion, we have changed it into the standard setting $P2_1/c$.
(27) W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **22**, 457 (1967).
(28) G. Bandoli, C. Panattoni, D. A. Clemente, E. Tondello, A. Dondoni, and A. Mangini, *J. Chem. Soc. B*, 1407 (1971).
(29) The absorption program was written by D. A. Clemente using the *m*-point Gaussian integration formula. The program is mainly in FORTRAN IV, but the computation of optical pathway for each ray inside the crystal (usually ten FORTRAN statements) is written in COMPASS (CDC 7600). With only this small variation the execution time is reduced to one-third with respect to the all-FORTRAN program.
(30) S. J. La Placa and J. A. Ibers, *Acta Crystallogr.*, **18**, 511 (1965).
(31) D. T. Cromer and J. T. Waber, *Acta Crystallogr.*, **18**, 104 (1965); D. T. Cromer, *ibid.*, **18**, 17 (1965).
(32) Supplementary material.
(33) "X-Ray 70 System of Programs", Technical Report TR 6 46, University of Maryland.
(34) D. M. Adams, "Metal-Ligand and Relative Vibrations", E. Arnold, London, 1965.
(35) J. Lewis, R. S. Nyholm, and G. A. Rodley, *J. Chem. Soc.*, 1483 (1965).
(36) L. J. Guggenberger, *Inorg. Chem.*, **12**, 1317 (1973).
(37) B. R. Davis and J. A. Ibers, *Inorg. Chem.*, **10**, 578 (1971).
(38) M. Mercer, *J. Chem. Soc., Dalton Trans.*, 1637 (1974).
(39) V. G. Albano and P. L. Bellon, *J. Organomet. Chem.*, **37**, 151 (1972).
(40) E. M. Shustorovich, M. A. Porai-Koshits, and Yu. A. Buslaev, *Coord. Chem. Rev.*, **17**, 1 (1975).
(41) M. Elder, J. E. Fergusson, G. J. Gainsford, J. H. Hickford, and B. R. Penfold, *J. Chem. Soc., Dalton Trans.*, 1423 (1967).
(42) M. Elder and B. R. Penfold, *Inorg. Chem.*, **5**, 1197 (1966).
(43) M. A. Bennett, G. B. Robertson, and J. M. Rosalky, *Acta Crystallogr., Sect. A*, **31**, S136 (1975).
(44) L. Pauling, "The Nature of the Chemical Bond", 3d ed, Cornell University Press, Ithaca, N.Y., 1960, p 255.

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Crystal Structure of $[(NH_3)_5RuSSRu(NH_3)_5]Cl_4\cdot 2H_2O$. A Structural Trans Effect and Evidence for a Supersulfide S_2^- Bridge

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Received August 20, 1976 AIC606268

The structure of $[(NH_3)_5RuSSRu(NH_3)_5]Cl_4\cdot 2H_2O$ has been determined using single-crystal x-ray diffraction. The crystal is of the orthorhombic class, space group *Pnma*, with unit cell constants $a = 11.673$ (2), $b = 7.216$ (1), and $c = 25.782$ (4) Å. The reflection data measured on an automated diffractometer have been refined by least-squares to $R_1 = 0.024$ and $R_2 = 0.033$. The dimeric cation contains two pentaammineruthenium moieties joined in a rigorously trans conformation by a two sulfur atom bridge. Evidence is adduced for the formulation of the bridging species as a supersulfide ion, S_2^-. A trans effect of 0.058 (9) Å is observed with the trans Ru–N bonds lengthened relative to the cis Ru–N bonds.

Introduction

Taube and co-workers[2] have reported the synthesis and characterization of a dimeric cation which they postulate to be $[(NH_3)_5RuSSRu(NH_3)_5]^{4+}$, two pentaammineruthenium groups joined by a two sulfur atom bridge. The electronic structure of the RuSSRu core may be described as two ruthenium(II) atoms bridged by a singlet disulfur, two ruthenium(III) atoms bridged by a disulfide ion, S_2^{2-}, one ruthenium(III) and one ruthenium(II) atom bridged by a supersulfide ion, S_2^-, or some hybrid combination of these, where each formulation is expected to lead to a rather different structure. Siebert and Thym[3] have reported the synthesis of $[(CN)_5CoSSCo(CN)_5]^{6-}$ and also proposed a two sulfur atom bridge. Recently, Sykes[4] and co-workers have described the preparation of $[(H_2O)_5CrSSCr(H_2O)_5]^{4+}$. In an effort to further characterize the geometrical and electronic structures of this class of complexes and also to examine whether the coordinated sulfur atom of the bridge causes a structural trans effect similar to those we have investigated in $[(NH_3)_5CoX]^{n+}$ complexes,[5] we have determined the single-crystal structure of $[(NH_3)_5RuSSRu(NH_3)_5]Cl_4\cdot 2H_2O$ and report it here.

Experimental Section

Preparation and Crystallization of $[(NH_3)_5RuSSRu(NH_3)_5]Cl_4\cdot 2H_2O$, I. The trans chloro complex $[Cl(NH_3)_4RuSSRu(NH_3)_4Cl]Cl_2$, prepared according to method 2 of Brulet, Isied, and Taube,[2,6] was converted to I by warming in a solution of 3 N NH_3 and 0.6 N NH_4Cl. Solid was obtained on addition of ethanol with sufficient aqueous ammonia added to give an indication of pH ~9 on test paper. Recrystallization of I was effected by dissolving the solid in a solution of 3 N NH_3 and 0.6 N NH_4Cl at room temperature and then adding ethanol/NH_3 solution. Some difficulty was encountered in growing crystals suitable for x-ray diffraction. If crystallization was rapid, the resultant crystals were too small; if crystallization took more than 1 day, decomposition took place and the crystals were of poor quality. The visible–UV absorption spectrum of I dissolved in 3 N NH_3/0.6 N NH_4Cl and measured on a Cary 14 spectrophotometer is essentially the same as that reported previously.

The IR spectrum (Nujol mull, KBr plates, Perkin-Elmer 337) exhibits a relatively sharp water stretching band at 3400 cm^{-1}, several ill-defined N–H stretches between 3270 and 3130 cm^{-1}, and bands at 1610, 1290, 1280, 1250, 1235, and 790 cm^{-1} in close parallel to those for a sample of $[(NH_3)_5RuS]_2Br_4$ provided by C. Kuehn and H. Taube. An additional band was observed at 1265 cm^{-1} for I. The Raman spectrum of a crystalline sample of I was run by L. J. Basile of Argonne National Laboratory. With excitation at 488 nm, a single relatively sharp band which has been attributed to the S–S stretch is observed at 514 ± 2 cm^{-1}. This band is absent from the IR spectrum.

X-Ray Characterization. Preliminary precession photographs (Cu, $K\alpha$ radiation) were taken of a crystal of $[(NH_3)_5RuSSRu(NH_3)_5]Br_4 \cdot 2H_2O$ supplied by Kuehn and Taube. Systematic absences are as follows: $0kl$ for $k + l$ odd and $hk0$ for h odd. These lead to two possible orthorhombic space groups:[7] $Pnma\text{-}D_{2h}^{16}$ (No. 62, centric) or $Pn2_1a\text{-}C_{2v}^{9}$ (No. 33, acentric). Approximate cell constants are $a = 11.74$ (3), $b = 7.39$ (1), and $c = 26.7$ (1) Å.

Since none of the bromide crystals were suitable for intensity data collection, we prepared the chloride salt, I (see above). A dark green parallelepiped of I with approximate dimensions 0.06 × 0.10 × 0.28 mm was mounted on a glass fiber such that the long dimension was parallel to the fiber axis. Precession photographs (Cu, $K\alpha$ radiation) of the $hk0$, hkl, $hk2$, $0kl$, and $1kl$ layers indicated the crystal was of the orthorhombic class. Systematic absences ($0kl$ for $k + l$ odd, $hk0$ for h odd) lead to the same choices for space groups as for the bromide salt, $Pnma$ or $Pn2_1a$. Unit cell constants and intensity data were obtained in the usual manner[8] with a Syntex $P\bar{1}$ diffractometer (Mo $K\alpha$ radiation) equipped with a graphite crystal monochromator. The unit cell constants for $[(NH_3)_5RuSSRu(NH_3)_5]Cl_4 \cdot 2H_2O$ are $a = 11.673$ (2), $b = 7.216$ (1), and $c = 25.782$ (4) Å. All measurements were made at 22 (3) °C. Density measurements made by neutral buoyancy techniques in $CHCl_3/CHBr_3$ ($d_{measd} = 1.90$ (3) g cm^{-3}, $d_{calcd} = 1.88$ g cm^{-3}) indicated $Z = 4$. Crystal quality and correctness of indexing were checked by taking oscillation photographs (±14°) about each of the crystal axes.

Intensity measurements for 2287 unique reflections in the sphere $2\theta < 52°$ were made as previously described.[8] The θ–2θ scan was from 1° below to 1° above the reflection in 2θ. Scan rates varied from 0.5 to 8.0°/min depending on reflection intensity. Four standard reflections were used to check stability and to account for long-term drift. The drift correction varied from 1.018 to 0.977. Absorption corrections were applied since μ, the linear absorption coefficient, was 20.6 cm^{-1}. The calculated transmission coefficients varied from 0.780 to 0.862. Of the 2287 unique reflections 2048 had $I > 2\sigma(I)$, where the Ibers ignorance factor,[9] p, was set to 0.03. All reflections were used in subsequent refinement.

Solution and Refinement of Structure. The statistical distribution[10] of the derived E values suggested a centrosymmetric electron density, favoring the space group $Pnma$. With $Z = 4$, halves of the dimeric cation are required to be related either by a center of symmetry or a mirror plane. A solution, determined from a Patterson map, had two ruthenium atoms and two sulfur atoms in the mirror plane. A first electron density map based on these positions clearly indicated the positions of the chlorine atoms and a subsequent map showed the nitrogen atom positions as well. Least-squares refinement of these atom positions and associated isotropic thermal parameters yielded $R_1 = 0.09$.[11] The addition of two oxygen atoms from water molecules and continued refinement of the other nonhydrogen atoms with anisotropic thermal parameters gave $R_1 = 0.055$. A difference electron density map indicated positions for the hydrogen atoms of the ammonia ligands and one of the water molecules. The same map indicated a disorder and/or partial occupancy problem with the second water molecule. The hydrogen atoms were added to the calculation at their indicated positions and assigned arbitrary isotropic temperature parameters,[12] $U = 0.05$ Å^2. A model which allowed refinement of a partial occupancy parameter for the second oxygen atom, anisotropic thermal parameters for all nonhydrogen atoms, and positional parameters for all atoms, including hydrogen, was refined to convergence, yielding $R_1 = 0.028$ and $R_2 = 0.039$. A difference electron density map indicated significant unaccounted electron density about 0.6 Å from the second oxygen atom. A new model was refined to convergence. The second oxygen atom was replaced by two partial atoms, O(2) and O(3), with variable occupancy factors and isotropic temperature parameters. No hydrogen atoms were located near O(2) and O(3). This model gave $R_1 = 0.024$ and $R_2 = 0.033$. The occupancy factors obtained in the refinement were 0.56 (1) and 0.48 (1). It is the latter model in which 2287 reflections were used to refine 162 parameters which we discuss below. In the final cycle of refinement no parameter varied by more than 0.7 times its estimated standard deviation and the average shift was 0.02 times the respective estimated standard deviation. A final difference electron density map had six peaks within 1.0 Å of either one of the two ruthenium atoms or Cl(1) with $^1/_{14}$th the height of an average nitrogen atom on the same scale. The remaining peaks were less than $^1/_{21}$st the height of a nitrogen peak. Groups of reflections ordered on $|F_o|$ and $(\sin\theta)/\lambda$ were examined to look for systematic errors in the model. No significant disagreement was found. The neutral-atom scattering factors of Cromer[13] were used for Ru, S, Cl, O and N. Those of Stewart[14] were used for H. Corrections for anomalous dispersion[15] were made as follows: Ru, $\Delta f' = -1.2$, $\Delta f'' = 1.1$; Cl, $\Delta f' = 0.1$, $\Delta f'' = 0.2$; S, $\Delta f' = 0.1$, $\Delta f'' = 0.2$. A compilation of $|F_o|$ and F_c is available in Table A.[16]

Table I. Fractional Atomic Positional Parameters[a, b]

Atom	x	y	z
Ru(1)	0.626 66 (2)	$^1/_4$[c]	−0.171 89 (1)
Ru(2)	0.244 24 (2)	$^1/_4$	0.050 39 (1)
Cl(1)	0.759 53 (12)	$^3/_4$	0.244 82 (5)
Cl(2)	0.134 78 (8)	$^3/_4$	−0.030 16 (4)
Cl(3)	0.491 09 (9)	$^1/_4$	0.321 33 (4)
Cl(4)	0.464 97 (9)	$^1/_4$	−0.089 00 (4)
S(1)	0.518 98 (7)	$^1/_4$	0.102 29 (3)
S(2)	0.350 40 (8)	$^1/_4$	0.120 68 (4)
N(1)	0.737 0 (3)	$^1/_4$	0.240 1 (1)
N(2)	0.134 1 (3)	$^1/_4$	−0.018 2 (1)
N(3)	0.529 7 (2)	0.4620 (4)	0.208 1 (1)
N(4)	0.735 0 (2)	0.456 4 (4)	0.140 2 (1)
N(5)	0.134 4 (2)	0.4597 (4)	0.080 9 (1)
N(6)	0.344 9 (2)	0.4608 (3)	0.015 1 (1)
O(1)	0.277 0 (4)	$^3/_4$	0.132 4 (2)
O(2)[d]	0.458 6 (9)	$^3/_4$	0.357 6 (5)
O(3)[d]	0.481 9 (22)	$^3/_4$	0.335 8 (22)

[a] The estimated errors in the last digit are given in parentheses. This form is used throughout. [b] The numbering scheme for the dimeric cation is shown in Figure 1. [c] These coordinates, given as integer fractions, are for atoms constrained to lie in the mirror plane and thus have no associated errors. [d] Disordered oxygen atoms: O(2) has a population parameter of 0.56 (2) and O(3) has a population parameter of 0.48 (2).

Table II. Rms Displacements (Å)

Atom	⊥[a]	∥ min	∥ max
Ru(1)	0.167	0.150	0.160
Ru(2)	0.162	0.141	0.163
Cl(1)	0.228	0.223	0.304
Cl(2)	0.199	0.185	0.198
Cl(3)	0.380	0.180	0.199
Cl(4)	0.182	0.194	0.223
S(1)	0.185	0.156	0.172
S(2)	0.199	0.160	0.171
N(1)	0.250	0.177	0.200
N(2)	0.228	0.176	0.211
O(1)	0.233	0.230	0.260
O(2)[b]	0.275	0.275	0.275
O(3)[b]	0.419	0.419	0.419
Atom	Min	Mean	Max
N(3)	0.192	0.199	0.214
N(4)	0.184	0.196	0.211
N(5)	0.174	0.204	0.213
N(6)	0.171	0.174	0.202

[a] These displacements (⊥) are perpendicular to the crystallographic mirror plane. Those given as ∥ lie in the mirror plane due to symmetry constraints. [b] These disordered atoms were only refined isotropically.

Description of the Structure.

Atomic positional parameters for the nonhydrogen atoms are presented in Table I, whereas those for the hydrogen atoms are to be found in Table B.[16] The refined thermal parameters are given in Table C[16] and the derived root-mean-square displacements for nonhydrogen atoms are located in Table II and illustrated in Figure 1. Bond lengths and bond angles not involving hydrogen atoms have been gathered in Table III and those involving hydrogen atoms are in Table D.[16]

The structure of the dimeric cation is illustrated in Figure 1. Each ruthenium atom is coordinated to five ammonia

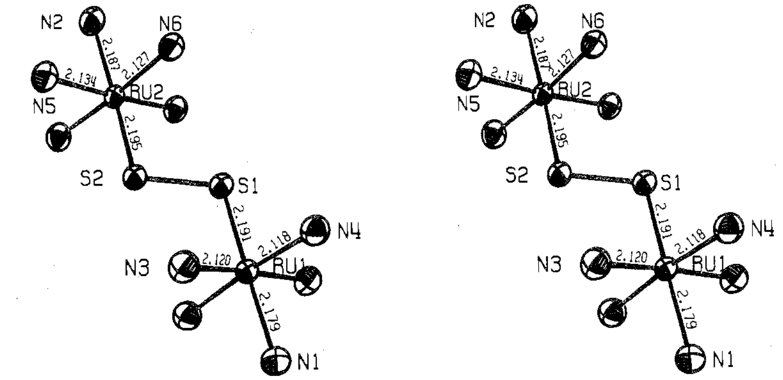


Figure 1. Stereoscopic view of the dimeric cation $[(NH_3)_5RuSSRu(NH_3)_5]^{4+}$.

Table III. Bond Lengths (Å) and Bond Angles (deg)

	Lengths		
Ru(1)-S(1)	2.191 (1)	Ru(2)-S(2)	2.195 (1)
Ru(1)-N(1)	2.179 (4)	Ru(2)-N(2)	2.187 (4)
Ru(1)-N(3)	2.120 (3)	Ru(2)-N(5)	2.134 (3)
Ru(1)-N(4)	2.118 (3)	Ru(2)-N(6)	2.127 (2)
S(1)-S(2)	2.014 (1)		
	Angles		
Ru(1)-S(1)-S(2)	111.46 (4)	Ru(2)-S(2)-S(1)	110.82 (4)
N(1)-Ru(1)-N(3)	87.7 (1)	N(2)-Ru(2)-N(5)	86.8 (1)
N(1)-Ru(1)-N(4)	87.6 (1)	N(2)-Ru(2)-N(6)	88.8 (1)
		Av N(trans)-Ru-N(cis	87.7 (8)
S(1)-Ru(1)-N(3)	93.1 (1)	S(2)-Ru(2)-N(5)	92.0 (1)
S(1)-Ru(1)-N(4)	91.5 (1)	S(2)-Ru(2)-N(6)	91.5 (1)
		Av S-Ru-N(cis)	92.0 (7)
N(3)-Ru(1)-N(4)	88.9 (1)	N(5)-Ru(2)-N(6)	89.0 (1)
N(3)-Ru(1)-N(3)[a]	92.4 (1)	N(5)-Ru(2)-N(5)[a]	90.4 (1)
N(4)-Ru(1)-N(4)[a]	89.4 (1)	N(6)-Ru(2)-N(6)[a]	91.3 (1)

[a] These atoms were generated by $x, {}^1/_2 - y, z$.

Table IV. Possible Hydrogen Bonds[a]

A–H–B	A· · ·B, Å	∠ at H, deg
O(1)· · ·H(51)–N(5)	2.99	168
O(1)· · ·H(51)[b]–N(5)[b]	2.99	168
O(1)–H(71)· · ·Cl(4)	3.21	176
O(1)–H(72)· · ·Cl(1)	3.17	175
Cl(1)· · ·?[c]–O(3)	3.33	
Cl(1)· · ·H(41)–N(4)	3.44	133
Cl(2)· · ·H(63)–N(6)	3.43	164
Cl(2)· · ·H(63)[b]–N(6)[b]	3.43	164
Cl(2)· · ·H(22)[d]–N(2)[d]	3.38	174
Cl(3)· · ·H(32)–N(3)	3.33	166
Cl(3)· · ·H(32)[e]–N(3)[e]	3.33	166
Cl(3)· · ·H(53)[f]–N(5)[f]	3.38	171
Cl(3)· · ·H(53)[g]–N(5)[g]	3.38	171
Cl(4)· · ·H(61)–N(6)	3.39	164
Cl(4)· · ·H(61)[e]–N(6)[e]	3.39	164
Cl(4)· · ·H(43)[h]–N(4)[h]	3.42	162
Cl(4)· · ·H(43)[i]–N(4)[i]	2.42	162

[a] Tabulated if N· · ·O < 3.0 Å, O· · ·Cl < 3.3 Å, or N· · ·Cl < 3.45 Å and angle at H atom > 130°. [b] $x, 1{}^1/_2 - y, z$. [c] Hydrogen atom not found. [d] $-x, 1 - y, -z$. [e] $x, {}^1/_2 - y, z$. [f] ${}^1/_2 + x, {}^1/_2 - y, {}^1/_2 - z$. [g] ${}^1/_2 + x, y, {}^1/_2 - z$. [h] $1 - x, 1 - y, -z$. [i] $1 - x, -{}^1/_2 + y, -z$.

molecules and a sulfur atom to complete the octahedral coordination. The RuSSRu linkage is a trans planar arrangement. Crystallographic symmetry requires these atoms and the trans ammonia molecules to lie in a mirror plane. The remaining four ammonia molecules on each ruthenium atom occur in pairs related by the mirror. There is a significant structural trans effect in that the average Ru–N (trans) distance, 2.183 (6) Å, is 0.058 (9) Å longer than the average Ru–N (cis) distance of 2.125 (7) Å. The dimeric cations are surrounded by chloride ions and water molecules which form a hydrogen-bonding network. The list of hydrogen bonds is presented in Table IV.

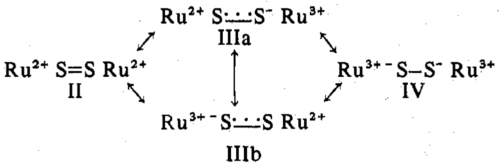
Discussion

Cation Conformation and Environment. This crystal structure clearly substantiates the formulation by Taube and co-workers that $[(NH_3)_5RuSSRu(NH_3)_5]^{4+}$ contains two pentaammineruthenium moieties joined by a free-standing bridge consisting of two sulfur atoms. The crystal symmetry is such that the RuSSRu dihedral angle is exactly 180°. The implications of this trans geometry for the electronic structure of the RuSSRu linkage are discussed in detail below. There are two possible conformations of the pentaammineruthenium moiety consistent with the requirement that the RuSSRu linkage lie in the crystallographic mirror plane: first, that with two of the cis ammonia molecules in the mirror plane and the other two perpendicular to it; second, that conformation rotated 45° about the Ru–S bond, such that the mirror plane passes between pairs of cis ammonia molecules. The former is an eclipsed conformation with respect to the S–S bond and the latter is staggered. The choice of the staggered conformation here results in minimal steric interaction and is identical with the conformation found[17] for the structure of $[(NH_3)_5CoOOCo(NH_3)_5]^{5+}$. The dimeric cation is nearly centrosymmetric although one end [S(1), Ru(1), N(1), N(3), N(4)] appears to have all bonds slightly shorter than the other. (Δ_{av} = 0.008 (4) Å). The root-mean-square displacements of the nitrogen atoms are relatively small and do not appear significantly different at opposite ends of the cation. The only apparent difference in the environments of the two ends of the dimeric cation is that the disordered water molecule is near the "expanded" end, approximately 3.4 Å from N(2) along the extension of the Ru(2)–N(2) bond.

The difference in the hydrogen bonding involving the two water molecules is striking. Four hydrogen bonds are evident around O(1). Two utilize the hydrogen atoms of the water molecule to bind chloride ions and the other two utilize electron pairs on oxygen to bind to the hydrogen atoms of ammonia molecules. The closest contact involving the disordered water molecule is O(2)···N(2) of 3.38 Å and since this contact is along the direction of the N(2)–Ru(2) bond, no hydrogen bond can be formed. Thus, the disordered water molecule merely fills a cavity in the structure without participating in significant hydrogen bonding.

Structural Trans Effect. Taube and co-workers in their original report noted a kinetic trans effect was present in the dimeric cation, $[(NH_3)_5RuSSRu(NH_3)_5^{4+}$. There is also a ground-state structural trans effect present in this structure. The average trans Ru–N distance is 2.183 (6) Å whereas the average cis Ru–N distance is 2.125 (7) Å, yielding Δ = 0.058 (9) Å. This structural trans effect is essentially the same as that reported by March and Ferguson,[18] Δ = 0.052 (9) Å, for the sulfur-bound (dimethyl sulfoxide)pentaammineruthenium(II) hexafluorophosphate. These trans effects are in the range 0.04–0.06 Å, which we have found for $[A_5CoX]^{n+}$ where A represents an amine ligand and X is a thiol,[8] selenol,[5] or sulfur-bound sulfinic acid[19] ligand. The trans effect found here is significantly less than that[20] found in the structure of $[(NH_3)_5CoSo_3]^+$, 0.089 (4) Å; the sulfito complex also appears to have a larger kinetic trans effect.[21]

Electronic Structure of the RuSSRu Core. There are several possible formulations for this, viz.



Of relevance to these formulations, the following observations have been made by Taube[2] and co-workers or in this study: (a) the dimeric cation (bromide salt) exhibits a temperature-independent paramagnetism of 0.45 μ_B/dimer; (b) no ESR signal is observed from frozen solutions of $[Cl(NH_3)_4RuSSRu(NH_3)_4Cl]Cl_2$; (c) the S–S stretching frequencies of the bromide and chloride salts are, respectively, 519 (3) and 514 (2) cm^{-1} (the bromide and chloride salts are apparently isostructural—see Experimental Section); (d) the dimeric cation has a rigorously trans conformation; (e) the S–S distance is 2.024 (1) Å; (f) the cis Ru–N distance averages 2.125 (7) Å.

We believe that formalism IIIa,b is the most apt description of the RuSSRu core with perhaps some smaller contribution from IV and essentially no contribution from II. The magnetic data and lack of an ESR signal argue against formulation IV where the expected magnetic susceptibility would be ~2.0 μ_B/ruthenium atom. Either magnetic exchange phenomena involving IIIa and IIIb or formulation II involving ground-state singlet disulfur are compatible with the observations. The S–S stretching frequencies appear to exclude II as a significant contributor, since ν(S–S) in compounds containing S═S double bonds is reported[22] at ~700 cm^{-1}. Van Wart and Scheraga[23] have recently shown that for alkyl disulfides ν(S–S) is strongly dependent on the X–S–S–X dihedral angle. For the dihedral angle of 180° found here a value of ~485 cm^{-1} would be expected. Thus, the stretching frequencies favor an admixture of IIIa,b and IV, where the partial π bonding leads to ν(S–S) ~515 cm^{-1}. The trans conformation may be taken as evidence against the disulfide formulation, IV. Hordvik[24] has shown that for a large number of disulfide structures the X–S–S–X dihedral angles cluster around 90°. It should be noted, however, that Schaefer and co-workers[17] have concluded that, for the analogous peroxide and superoxide cobalt complexes, the conformation is largely determined by crystal-packing forces, although the "superoxides "prefer" the planar configuration". An S–S bond length–bond order relation for cis S–S linkages (i.e., X–S–S–X dihedral angle of 0°) has been suggested by Hordvik. This should be equally applicable in terms of π overlaps etc. to the trans case.[25] A π-bond order of 0.4 is predicted in this case, or 80% IIIa,b and 20% IV. The S–S distance found here is the same as that in $[(C_5H_5)Fe(SC_2H_5)S]_2$, 2.023 (3) Å, which is said to contain a cis supersulfide linkage[26] between iron atoms. The same type of analysis may be made on the basis of the cis Ru–N average distance of 2.125 (7) Å. Stynes and Ibers[27] have reported Ru^{III}–N = 2.104 (4) Å and Ru^{II}–N = 2.144 (4) Å for the hexaammines. Assuming a linear change in bond length with ruthenium oxidation state, this leads to a formulation of 100% IIIa,b. However, the pentaammineruthenium(II) dimethyl sulfoxide complex exhibits[18] a slightly longer cis Ru–N distance, 2.155 (5) Å. Using the latter distance for cis Ru^{II}–N and assuming a decrease of 0.040 Å on going to cis Ru^{III}–N lead to a prediction of 50% IIIa,b and 50% IV. Thus, it appears, based on all of the evidence cited above, that a formulation of 75% IIIa,b and 25% IV is most probable.

Acknowledgment. Acknowledgment is made to the University Research Council of the University of Cincinnati for partial support of this work. We thank Professor H. Taube for bringing this problem to our attention and subsequent discussions.

Registry No. I, 61951-00-6; $[(NH_3)_5RuSSRu(NH_3)_5]Br_4$, 42720-73-0.

Supplementary Material Available: Tables A–D, listing structure factor amplitudes, H atom positional parameters, anisotropic thermal parameters of nonhydrogen atoms, and H–X bond lengths and angles (11 pages). Ordering information is given on any current masthead page.

References and Notes

(1) Presented at the 169th National Meeting of the American Chemical Society, Philadelphia, Pa., April 7, 1975; see Abstracts No. INOR 78.
(2) C. R. Brulet, S. S. Isied, and H. Taube, *J. Am. Chem. Soc.*, **95**, 4758 (1973).
(3) V. H. Siebert and S. Thym, *Z. Anorg. Allg. Chem.*, **399**, 107 (1973).
(4) T. Ramasami, R. S. Taylor, and A. G. Sykes, *J. Chem. Soc., Chem. Commun.*, 383 (1976).
(5) C. A. Stein, P. E. Ellis, Jr., R. C. Elder, and E. Deutsch, *Inorg. Chem.*, **15**, 1618 (1976), and references therein.
(6) Note should be taken that an improved synthesis has been published: C. G. Kuehn and H. Taube, *J. Am. Chem. Soc.*, **98**, 689 (1976).
(7) "International Tables for X-Ray Crystallography", Vol. 1, 2d ed, Kynoch Press, Birmingham, England, 1965.
(8) R. C. Elder, L. R. Florian, R. E. Lake, and A. M. Yacynych, *Inorg. Chem.*, **12**, 2690 (1973).
(9) P. W. R. Corfield, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 197 (1967).
(10) All computations were performed using a local version of X-RAY67: J. M. Stewart, University of Maryland, crystallographic computer system.
(11) $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_o|)^2/\sum w(F_o)^2]^{1/2}$.
(12) The form of the isotropic temperature parameters is $\exp(-8\pi^2 U(\sin^2\theta)/\lambda^2)$.
(13) D. T. Cromer and J. B. Mann, *Acta Crystallogr., Sect A*, **24**, 321 (1968).
(14) R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, **42**, 3175 (1965).
(15) "International Tables for X-Ray Crystallography", Vol. 3, Kynoch Press, Birmingham, England, 1962, p 215.
(16) Supplementary material.
(17) W. P. Schaefer and R. E. Marsh, *Acta Crystallogr.*, **21**, 735 (1966); F. R. Fronczek, W. P. Schaefer, and R. E. Marsh, *Acta Crystallogr., Sect. B*, **30**, 117 (1974); F. R. Fronczek and W. P. Schaefer, *Inorg. Chim. Acta*, **9**, 143 (1974); J. R. Fritch, G. G. Cristoph, and W. P. Schaefer, *Inorg. Chem.*, **12**, 2170 (1973); F. R. Fronczek, W. P. Schaefer, and R. E. Marsh, *ibid.*, **14**, 611 (1975).
(18) F. C. March and G. Ferguson, *Can. J. Chem.*, **49**, 3590 (1971).
(19) B. A. Lange, K. Libson, E. Deutsch, and R. C. Elder, *Inorg. Chem.*, **15**, 2985 (1976).
(20) R. C. Elder and M. Trkula, *J. Am. Chem. Soc.*, **96**, 2635 (1974).
(21) J. Halpern, R. A. Palmer, and L. M. Blakely, *J. Am. Chem. Soc.*, **88**, 2877 (1966).
(22) A. J. Banister, L. F. Moore, and J. S. Padley, *Inorg. Sulphur Chem.*, Chapter 5 (1968).
(23) H. E. Van Wart and H. A. Scheraga, *J. Phys. Chem.*, **80**, 1812 (1976).
(24) A. Hordvik, *Acta Chem. Scand.*, **20**, 1885 (1966).
(25) Note for example that the O–O bond length found for the superoxide is 1.31 Å whether found in the trans[17] singly bridged $[(NH_3)_5CoOOCo(NH_3)_5]^{5+}$ or in the cis doubly bridged $[(NH_3)_4Co(\mu\text{-}O_2)(\mu\text{-}NH_2)Co(NH_3)_4]^{4+}$: G. G. Christoph, R. E. Marsh, and W. P. Schaefer, *Inorg. Chem.*, **8**, 292 (1969).
(26) A. Terzis and R. Rivest, *Inorg. Chem.*, **12**, 2132 (1973).
(27) H. C. Stynes and J. A. Ibers, *Inorg. Chem.*, **10**, 2304 (1971).