crystal-packing forces than by the basicities of the various sites. A precise crystal structure of free, neutral 8-azaadenine is not available at this time, but the details of the above structures suggest that the site of protonation will be either N(8) or N(9). Nevertheless, all three structures are anomalies according to the rules established for the natural purines, and they do not seem to lend themselves to the creation of a new set of rules for all 8-azapurines.

The 8-aza substitution achieves at least two changes in the purine ring system. First, it provides an additional basic site for potential proton attachment and hydrogen bonding. Second, as a basic site, it is bound to reduce the basicity of the two adjacent sites. This is confirmed by electron density calculations using the CNDO/2 approximation[55] on adenosine[56,57] and 8-azaadenosine.[57] It is this second effect that most likely is responsible for the unruly behavior of metal ion interactions with 8-azapurines. The reduction of basicity at N(9) and N(7) may be sufficient to allow the basic sites on the pyrimidine portion to compete favorably for metal ion coordination. The extent to which 8-aza substitution evens out the basicities of the triazole and pyrimidine nitrogen atoms will vary from purine to purine. Thus, it is unknown whether all 8-azapurines will exhibit similar anomalous behavior with respect to metal ion coordination, and, therefore, it is necessary to study these systems before the utility of their interactions can be evaluated.

Acknowledgment. This research was supported by the University Research Council of The University of North Carolina through Grant No. VC811.

Registry No. Hg(8-AAd)$_2$Cl$_2$, 77495-61-5; Hg(8-AHx$^-$)$_2$(H$_2$O)$_4$, 77495-59-1.

Supplementary Material Available: Listings of atomic thermal parameters and of observed and calculated structure amplitudes (15 pages). Ordering information is given on any current masthead page.

---

(55) Pople, J. A.; Beveridge, D. L. "Approximate Molecular Orbital Theory"; McGraw-Hill: New York, 1970.
(56) Lai, T. F.; Marsh, R. E. *Acta Crystallogr., Sect. B* **1972**, *B28*, 1982.
(57) Singh, P.; Hodgson, D. J. *J. Am. Chem. Soc.* **1977**, *99*, 4807.

Contribution from the Department of Chemistry, The University of North Carolina, Chapel Hill, North Carolina 27514,
and Chemistry Department I, Inorganic Chemistry, H. C. Ørsted Institute,
University of Copenhagen, DK-2100 Copenhagen Ø, Denmark

Synthesis and Structural and Magnetic Characterization of *trans*-Aquatetraamminechromium(III)-μ-hydroxo-pentaamminechromium(III) Chloride Trihydrate [$[(NH_3)_4(H_2O)Cr(OH)Cr(NH_3)_5]Cl_5\cdot 3H_2O$]

SUSAN J. CLINE,[1a,b] JØRGEN GLERUP,*[1b] DEREK J. HODGSON,*[1a] GUNNAR S. JENSEN,[1b]
and ERIK PEDERSEN*[1b]

Received November 11, 1980

The crystal and molecular structure of the dinuclear chromium(III) complex *trans*-aquatetraamminechromium(III)-μ-hydroxo-pentaamminechromium(III) chloride trihydrate (*trans*-$[(NH_3)_4(H_2O)Cr(OH)Cr(NH_3)_5]Cl_5\cdot 3H_2O$) has been determined from three-dimensional single-crystal counter X-ray data. The complex crystallizes in the monoclinic space group $C2/c$ with four formula units in a cell of dimensions a = 23.855 (7) Å, b = 7.387 (3) Å, c = 16.763 (7) Å, and β = 129.8 (1)°. The structure has been refined by full-matrix least-squares methods to a final value of the conventional R factor (on F) of 0.049 on the basis of 1638 independent intensities. The bridging hydroxo group lies on a crystallographic twofold axis, giving rise to a 50/50 disorder of the trans OH$_2$ and NH$_3$ ligand positions. The dinuclear cation is symmetrically bridged by the OH group, with Cr–O distances of 1.983 (1) Å and a bridging Cr–O–Cr angle of 155.1 (3)°. The geometry at each chromium(III) center is roughly octahedral, the ligating atoms being four cis ammine groups (Cr–N distances 2.062 (4)–2.084 (4) Å), the hydroxo bridge, and the disordered trans ligand. The magnetic susceptibility of the complex indicates antiferromagnetic coupling. The susceptibility data were fitted to a model assuming independent triplet, quintet, and septet energies; the results are almost consistent with the Van Vleck expression corrected for biquadratic exchange and lead to a triplet energy of 34.6 cm^{-1}. This triplet–singlet separation is much larger than that found in the related cis complex *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH)]^{4+}$.

Introduction

The magnetic properties of dimeric transition-metal complexes have been shown to be dependent upon their structures. For the cases of complexes of the formulation $[M(L)OH]_2^{n+}$, where M is Cu(II) and L is a bidentate ligand, the magnetic exchange parameter, J, varies linearly[2] with the Cu–O–Cu bridging angle, Φ. In the case where M is Cr(III), the correlation between the structural and magnetic properties of the analogous complexes $[M(L)_2OH]_2^{n+}$ still exists,[3-8] but the exact nature of the variation of J with Φ is more difficult to discern.[7,8] So that a larger range in the bridging angle, Φ, can be obtained, the singly bridged rhodo and erythro chromium dimers, first reported by Jørgensen in 1882, are being examined structurally, magnetically, and spectroscopically.[9-21]

---

(1) (a) The University of North Carolina. (b) H. C. Ørsted Institute, University of Copenhagen.
(2) Hodgson, D. J. *Prog. Inorg. Chem.* **1975**, *19*, 173 and references therein. Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107.
(3) Scaringe, R. P.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chim. Acta*, **1977**, *22*, 175; *Inorg. Chem.* **1977**, *16*, 1601.
(4) Josephsen, J.; Pedersen, E. *Inorg. Chem.* **1977**, *16*, 2523.
(5) Scaringe, R. P.; Singh, P.; Eckberg, R. P.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1975**, *14*, 1127.
(6) Cline, S. J.; Scaringe, R. P.; Hatfield, W. E.; Hodgson, D. J. *J. Chem. Soc., Dalton Trans.* **1977**, 1662.
(7) Cline, S. J.; Kallesøe, S.; Pedersen, E.; Hodgson, D. J. *Inorg. Chem.* **1979**, *18*, 796.
(8) Michelsen, K.; Pedersen, E. *Acta Chem. Scand., Ser. A* **1978**, *A32*, 847.
(9) Veal, J. T.; Jeter, D. Y.; Hempel, J. C.; Eckberg, R. P.; Hatfield, W. E.; Hodgson, D. J. *Inorg. Chem.* **1973**, *12*, 2928.
(10) Engel, P.; Güdel, H. U. *Inorg. Chem.* **1977**, *16*, 1589.
(11) Urishiyama, A.; Nomura, T.; Nakahara, M. *Bull. Chem. Soc. Jpn.* **1970**, *43*, 3971.
(12) Yevitz, M.; Stanko, J. A. *J. Am. Chem. Soc.* **1971**, *93*, 1512.

0020-1669/81/1320-2229$01.25/0

These complexes, which are bridged by a single hydroxyl moiety, have Cr–O–Cr bridging angles ranging from 166° in the acid rhodo case[9] to 135.4° in the ethylenediamine complex $[(en)_2(OH)CrOHCr(en)_2OH](ClO_4)_3{\cdot}H_2O$.[15] There are, however, insufficient magnetic and structural data on these singly bridged dimers to demonstrate the existence and/or nature of the dependence of J on Φ. Consequently, we are continuing our investigations on these systems; the synthesis and structural and magnetic properties of one such complex, *trans*-aquatetraamminechromium(III)-μ-hydroxy-pentaamminechromium(III) pentachloride trihydrate (*trans*-$[(NH_3)_4(H_2O)Cr(OH)Cr(NH_3)_5]Cl_5{\cdot}3H_2O$) are reported here. Unlike the cis isomer, this trans complex has not been reported before.

Experimental Section

Materials. Pentaamminechromium(III)-μ-hydroxo-*trans*-chlorotetraamminechromium(III) chloride, hereinafter called trans-chloro erythro, was prepared as described in the literature.[20]

Analyses. The chromium analyses were performed with the use of a Perkin-Elmer 403 atomic absorption spectrophotometer. Ammonia and halogens were determined by standard procedures.

Synthesis. *trans*-$[(H_2O)(NH_3)_4Cr(OH)Cr(NH_3)_5](NO_3)_5{\cdot}2H_2O$. Mercury(II) acetate (50 g) was dissolved in 200 mL of water containing 20 mL of acetic acid. The solution was cooled in ice, and 25 g of crude trans-chloro erythro was added in small portions with magnetic stirring. After 25 min, the solution was filtered and nitric acid (100 mL, 7 M) was added dropwise to yield 30 g of the crude product. The product was recrystallized by dissolving it in the dilute nitric acid (1200 mL, 0.01 M) at 30 °C and precipitating by the dropwise addition of concentrated nitric acid (50 mL); the yield of recrystallized product was 25.7 g. After one recrystallization, the product does not contain any mercury(II) chloride contaminant; this is essential for the subsequent synthesis of the chloride salt. Anal. Calcd for $[Cr_2(NH_3)_9(OH)(H_2O)](NO_3)_5{\cdot}2H_2O$: Cr, 16.29; NH_3, 24.01; N, 30.72. Found: Cr, 16.38; NH_3, 23.94; N, 30.66.

***trans*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH_2)]Cl_5{\cdot}4H_2O$.** The nitrate salt from the previous synthesis (vide supra, 18 g) was dissolved in dilute hydrochloric acid (900 mL, 0.01 M) at 25 °C. The solution was filtered and cooled in ice, and concentrated hydrochloric acid (300 mL) was added dropwise. The product was washed with ethanol, yielding 15 g of crude product. The product was recrystallized by dissolving it in hydrochloric acid (450 mL, 0.01 M), filtering, and reprecipitating it by dropwise addition of concentratd hydrochloric acid (100 mL) under cooling; yield, 12 g of brick red crystals. Anal. Calcd for $[Cr_2(NH_3)_9(OH)(H_2O)]Cl_5{\cdot}4H_2O$: Cr, 19.20; N, 23.27; Cl, 32.73. Found: Cr, 19.26; N, 23.31; Cl, 32.96. Several different preparations have yielded compounds which have been analyzed to have 3.5–4.0 mol water; moreover, on the basis of the subsequent crystal structure analysis (vide infra), it appears that upon prolonged standing the crystals may lose enough water to produce a trihydrate.

Magnetic Measurements. The magnetic susceptibility of powdered samples (containing 3.5 mol of H_2O/dimer) was measured by the Faraday method at a field strength of 12 000 Oe in the temperature range 2–296 K. Data below 13 K were rejected from the fitting procedure (vide infra) since preliminary fits suggested that impurities present in the sample did not adhere to the Curie law and were, therefore, difficult to account for. Data above 240 K were rejected because at this temperature, under the evacuated conditions of our instrument, the sample tends to lose water. Preliminary descriptions of the instrument are found elsewhere.[4,16]

X-ray Data Collection. Red crystals of the title complex were assigned to the monoclinic system on the basis of Weissenberg and precession photography; the observed systematic absence of hkl for $h + k$ odd and $h0l$ for l odd suggest that the space group is either $C2/c$ or Cc. The cell constants, obtained by least-squares procedures, are $a = 23.855$ (7) Å, $b = 7.387$ (3) Å, $c = 16.763$ (7) Å, and $\beta = 129.8$ (1)°. The observed density of 1.53 (1) g cm^{-3} (flotation in methylene chloride and bromoform) is consistent with the density of 1.532 g cm^{-3} calculated for four dimeric units in the cell. Thus, in the centrosymmetric space group $C2/c$, the cations would be constrained to lie on an inversion center or a twofold axis, both of which require some form of disorder; in the space group Cc, however, no crystallographic symmetry is imposed on the complex.

Table I. Cell Constants Observed for $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5{\cdot}3H_2O$ and $[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH_2)]Cl_5{\cdot}3H_2O$

	$[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$		*trans*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4OH_2]^{5+}$	
	single crystal[a]	powder	single crystal	powder
a, Å	23.656 (9)	23.60 (4)	23.855 (7)	23.81 (4)
b, Å	7.36 (1)	7.41 (2)	7.387 (3)	7.37 (8)
c, Å	16.718 (8)	16.74 (4)	16.763 (7)	16.78 (4)
β, deg	128.1 (1)	127.9 (3)	129.8 (1)	130.0 (3)
V, Å^3	2.30×10^3	2.31×10^3	2.269×10^3	2.26×10^3

[a] Data from ref 10.

At this stage it was apparent that the cell constants and space group observed here are very similar to those reported by Engel and Güdel[10] for the symmetric acid rhodo complex $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5{\cdot}3H_2O$; the only difference between the two complexes, of course, is the substitution of one aqua ligand for an ammine ligand. We consequently synthesized both complexes and compared their cell constants by the powder method. The results of these studies are summarized in Table I. It is apparent that there are small but significant differences between the cell constants obtained for the two complexes, and that these differences are consistent despite the use of two different techniques (single crystal and powder diffraction) involving three sets of workers in three different countries. In this context, since it is difficult to distinguish between the rhodo and the *trans*-aqua erythro complex crystallographically, we note here a reaction which unambiguously allows the differentiation between them. The rhodo complex reacts in basic solution as follows: $[(NH_3)_5CrOCr(NH_3)_5]^{4+} + H_2O \rightarrow$ *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH)]^{4+} + NH_3$ with a half-life of 44 s.[21] The trans-aqua complex, however, reacts in basic solution under similar conditions with a half-life of approximately 2 s. We are confident, therefore, that the crystal which we studied is the same as the bulk sample and that this sample is indeed the trans-aqua complex rather than the rhodo complex.

Diffraction data were collected from a crystal of dimensions of 0.11 mm, 0.12 mm, 0.12 mm, 0.32 mm in the [100], [201], [101], and [010] directions, respectively, mounted normal to (010). The data were collected on a Picker FACS-1 four-circle automatic diffractometer equipped with a graphite monochromator and Mo Kα (0.7093 Å) radiation. The data were collected by the θ–2θ scan technique.

A unique data set having $4° \leq 2\theta \leq 52°$ was gathered; a total of 2223 intensities was recorded. The intensities of three standards, measured after every 75 reflections, showed no systematic decline as a function of exposure time.

Data processing was carried out as described by Ibers and coworkers.[22] The data were corrected for Lorentz–polarization effects and absorption. The attenuation coefficient for this complex with Mo Kα radiation is 15.58 cm^{-1}, and for the sample chosen the transmission coefficients ranged from 0.83 to 0.87 with an average value of 0.85. Of the 2223 independent reflections collected, only 1638 had intensities greater than three times their estimated standard deviations; only these reflections were used in the subsequent structure analysis and refinement.

Solution and Refinement of the Structure. The structure was solved in the space group Cc by direct methods[23] with use of the multiple solution program MULTAN.[24] The chosen solution provided an E map

---

(13) Hodgson, D. J.; Pedersen, E. *Inorg. Chem.* **1980**, *19*, 3116.
(14) Kaas, K. *Acta Crystallogr., Sect. B* **1979**, *B35*, 596.
(15) Kaas, K. *Acta Crystallogr., Sect. B* **1979**, *B35*, 1603.
(16) Pedersen, E. *Acta Chem. Scand.* **1972**, *26*, 333 and references therein.
(17) Glerup, J. *Acta Chem. Scand.* **1972**, *26*, 3775.
(18) Furrer, A.; Güdel, H. U. *Phys. Rev. Lett.* **1977**, *39*, 65.
(19) Dubicki, L. *Aust. J. Chem.* **1972**, *25*, 739. Ferguson, J.; Güdel, H. U. *Ibid.* **1973**, *26*, 505. Ferguson, J.; Güdel, H. U.; Puza, M. *Ibid.* **1973**, *26*, 513.
(20) Linhard, M.; Weigel, M. *Z. Anorg. Allg. Chem.* **1959**, *299*, 15.
(21) Schwarzenbach, G.; Magyar, B. *Helv. Chim. Acta* **1962**, *168*, 1425.
(22) Corfield, P. W. R.; Doedens, R. J.; Ibers, J. A. *Inorg.Chem.* **1967**, *6*, 197.
(23) Hauptman, H.; Karle, J. American Crystallographic Association, Monograph No. 3, 1953.

Table II. Positional Parameters in *trans*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4OH_2]Cl_5 \cdot 3H_2O$

atom	x	y	z
Cr	0.40823 (4)	0.02376 (9)	0.10919 (5)
Cl(1)	0.39480 (8)	0.10811 (28)	0.34879 (11)
Cl(2)	$^1/_2$	0.49838 (25)	$^1/_4$
Cl(3)	0.70413 (7)	0.54023 (20)	0.54755 (11)
O(1)	$^1/_2$	0.0816 (6)	$^1/_4$
N(1)	0.4594 (2)	−0.1691 (6)	0.0865 (3)
N(2)	0.3786 (2)	−0.1678 (6)	0.1657 (3)
N(3)	0.4316 (2)	0.2145 (6)	0.0425 (3)
N(4)	0.3527 (2)	0.2149 (6)	0.1255 (3)
ON[a]	0.3109 (2)	−0.0290 (6)	−0.0377 (3)
O(2)[b]	0.2366 (3)	0.3154 (10)	0.2162 (4)
O(3)[c]	0.3906 (7)	0.4031 (11)	−0.1646 (9)
HO(1)[d]	$^1/_2$	0.2082	$^1/_4$
H1N1	0.4724	−0.1162	0.0480
H2N1	0.5052	−0.2100	0.1456
H3N1	0.4323	−0.2613	0.0526
H1N2	0.3827	−0.1104	0.2133
H2N2	0.3426	−0.2136	0.1212
H3N2	0.4176	−0.2519	0.1967
H1N3	0.4191	0.1790	−0.0115
H2N3	0.4743	0.2478	0.0809
H3N3	0.3982	0.3068	0.0210
H1N4	0.3744	0.2278	0.1880
H2N4	0.3096	0.1917	0.0868
H3N4	0.3621	0.3284	0.1068

[a] Position occupied by disordered trans oxygen and nitrogen atoms; see text. [b] Occupancy factor 0.90. [c] Occupancy factor 0.60. [d] Hydrogen atom coordinates were not refined.

which revealed all the nonhydrogen atoms except two ligating nitrogen atoms and the solvent water oxygen atoms in the top 27 peaks. Isotropic least-squares refinement of these atoms (with all nonbridging ligating atoms assigned as nitrogen) gave values of the conventional agreement factors $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(F_o)^2]^{1/2}$ of 0.190 and 0.249, respectively. All least-squares refinements were carried out on F, the function minimized being $\sum w(|F_o| - |F_c|)^2$, where the weighting factor w was taken as $4F_o^2/\sigma^2(F_o^2)$. In calculations of F_c, the atomic scattering factors for nonhydrogen atoms were taken from ref 25 while those for hydrogen were from Stewart et al.[26] The remaining nonhydrogen atoms were located in the subsequent difference Fourier map. After including these positions in the least-squares calculation, the values of R_1 and R_2 were reduced to 0.109 and 0.149, respectively. The trans-ligating atom with the smaller thermal parameter was reassigned as oxygen, and anisotropic refinement lowered the values of R_1 and R_2 to 0.052 and 0.066, respectively.

In subsequent Fourier maps, one hydrogen atom was located on each nitrogen atom and the coordinated water oxygen atom. The other hydrogen atoms on these atoms were placed in calculated positions based on N–H and O–H bond lengths of 0.90 and 0.95 Å[27] and tetrahedral geometry. The position of the bridging hydroxyl hydrogen atom was found in a difference Fourier map. None of the solvent hydrogen atoms were located. The found and calculated hydrogen atom positions were included (B = 5.0 Å^2) but not refined in subsequent least-squares iterations. A cycle of least squares, which involved 1638 observations and 189 variables, converged to values of 0.047 and 0.058 for R_1 and R_2, respectively. No positional parameter shifted more than 0.9 times its estimated standard deviation which was taken as evidence of convergence.

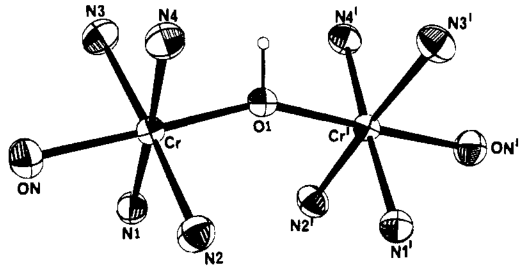

Figure 1. View of the binuclear *trans*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH_2)]^{5+}$ cation. The atom labeled "ON" is the 50/50 disordered OH_2/NH_3 trans ligand. Thermal parameters are drawn at the 40% probability level, except for that of the hydrogen atom on the bridge which is of arbitrary size. Other hydrogen atoms are omitted for clarity.

Table III. Interatomic Distances (Å) in *trans*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4OH_2]Cl_5 \cdot 3H_2O$

Cr–Cr'	3.873 (2)	N(2)–H1N2	0.85
Cr–O(1)	1.983 (1)	N(2)–H2N2	0.77
Cr–N(1)	2.064 (4)	N(2)–H3N2	0.95
Cr–N(2)	2.062 (4)	N(3)–H1N3	0.79
Cr–N(3)	2.084 (4)	N(3)–H2N3	0.82
Cr–N(4)	2.070 (4)	N(3)–H3N3	0.93
Cr–ON	2.071 (4)	N(4)–H1N4	0.82
N(1)–H1N1[a]	0.96	N(4)–H2N4	0.81
N(1)–H2N1	0.94	N(4)–H3N4	0.97
N(1)–H3N1	0.86	O(1)–HO(1)	0.93

[a] Hydrogen atom coordinates were not refined.

Table IV. Selected Bond Angles (Deg) in *trans*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4OH_2]Cl_5 \cdot 3H_2O$

O(1)–Cr–N(1)	92.0 (1)	N(1)–Cr–ON	89.8 (2)
O(1)–Cr–N(2)	92.4 (1)	N(2)–Cr–N(3)	176.2 (1)
O(1)–Cr–N(3)	91.3 (2)	N(2)–Cr–N(4)	88.3 (2)
O(1)–Cr–N(4)	90.5 (1)	N(2)–Cr–ON	87.9 (2)
O(1)–Cr–ON	178.1 (3)	N(3)–Cr–N(4)	91.3 (2)
N(1)–Cr–N(2)	91.6 (2)	N(3)–Cr–ON	88.3 (2)
N(1)–Cr–N(3)	88.6 (2)	N(4)–Cr–ON	87.7 (2)
N(1)–Cr–N(4)	177.5 (4)	Cr–O(1)–Cr'	155.1 (3)

At this stage, the model was checked to see whether the space group could be $C2/c$; such a calculation was deemed particularly significant since Engel and Güdel[10] had reported that the symmetric acid rhodo complex (see Table I) crystallizes in the centrosymmetric space group and also because the model showed a tendency to oscillate.[28] It was also noteworthy that one of the cis Cr–N bond lengths was in very poor agreement with the others. Since the centrosymmetric space group requries some disorder, the trans-ligating atom was entered as a 50/50 mixture of oxygen and nitrogen, and no hydrogen atoms were associated with it. The occupancy factors of the water molecules were also tested by allowing them to vary subject to the constraint that the total occupancy was 1.50 (i.e., that there were three water molecules per dinuclear cation). This model refined to values of R_1 and R_2 of 0.049 and 0.063, respectively, with use of 1638 observations and 102 variables. No parameter underwent a final shift of more than 0.4σ, which was taken as evidence of convergence. Application of an R factor ratio test of the type described by Hamilton[29] was inconclusive. The centrosymmetric, disordered model was chosen because the derived parameters were more self-consistent and because there was no compelling mathematical reason for adopting the noncentrosymmetric model. A final difference Fourier was featureless, with no peak higher than 0.16 e Å^{-3}.

The positional parameters derived from the final least-squares cycle, along with their standard deviations as estimated from the inverse matrix, are listed in Table II. A table of observed and calculated structure amplitudes is available as supplementary material.

Description of the Structure

The structure consists of *trans*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4OH_2]^{5+}$ cations, chloride anions, and water molecules which are hydrogen bonded to each other. A view of the cation

---

(24) Main, P.; Woolfson, M. M.; Germain, G. "MULTAN: A Computer Program for the Automatic Solution of Crystal Structures"; University of York: York, England, 1971.

(25) "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(26) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(27) Churchill, M. R. *Inorg. Chem.* **1973**, *12*, 1213.

(28) Similar effects are often observed in nearly centrosymmetric structures. See for example: Veal, J. T.; Hodgson, D. J. *Acta Crystallogr., Sect. B* **1972**, *B28*, 3525.

(29) Hamilton, W. C. *Acta Crystallogr.* **1965**, *18*, 502.

Table V. Probable A-H· · ·B Hydrogen Bonds in *trans*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4OH_2]Cl_5 \cdot 3H_2O$

A	H	B[a]	A· · ·B, Å	H· · ·B, Å	A-H· · ·B, deg
O(1)	HO(1)	Cl(2)	3.078 (5)	2.14	180
N(2)	H1N2	Cl(1)	3.494 (5)	2.65	172
N(2)	H3N2	$Cl(2)^{I}$	3.350 (5)	2.41	170
N(3)	H3N3	$Cl(3)^{II}$	3.506 (5)	2.58	174
N(4)	H1N4	Cl(1)	3.291 (5)	2.57	147
N(4)	H3N4	$Cl(3)^{II}$	3.316 (5)	2.53	138

[a] Symmetry operations are denoted by Roman superscripts: I, $x, 1-y, z$; II, $1-x, y, \frac{1}{2}-z$.

is given in Figure 1. The bond lengths and bond angles in the cation are listed in Tables III and IV. The geometry around the chromium(III) centers is roughly octahedral, the ligating atoms being the oxygen atom O(1) of the bridging hydroxyl group, four cis nitrogen atoms, and the disordered trans ligand. The four Cr–N distances lie in the range 2.062 (4)–2.084 (4) Å with an average value of 2.070 (9) Å. These bond lengths are comparable to those of 2.081 (9)–2.091 (9) Å in $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$,[10] 2.055 (11)–2.111 (10) Å in *cis*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4OH]^{4+}$,[13] 2.080 (6)–2.081 (7) Å in $[Cr(en)_2OH]_2^{4+}$,[6] and the values of 2.05–2.15 Å reported for a variety of other complexes containing Cr^{III}–N bonds.[5,9,14,15]

The bridging Cr–OH–Cr unit is constrained to be planar. The Cr–O(1) bond length of 1.983 (1) Å is very similar to the values of 1.986 (4)–1.990(4) Å reported for the ethylenediamine analogues.[14,15] The bridging Cr–O(1)–Cr angle, Φ, of 155.1 (3)° is similar to the values of 154–166° reported[9–11] for the corresponding angle in the symmetric rhodo ion $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$ but is significantly larger than the values of 135.4 (2)° in $[(HO)(en)_2Cr(OH)Cr(en)_2(OH)]^{3+}$ [15] and 142.8° in *cis*-$[(HO)(NH_3)_4Cr(OH)Cr(NH_3)_5]^{4+}$.[13] The hydrogen atom (HO1) on the bridging hydroxyl group is constrained to lie in the plane of the bridge; it is noteworthy that in the cis-hydroxo complex[13] this atom is apparently 0.48 Å from the bridging plane. The Cr–Cr′ separation of 3.873 (2) Å is similar to the values reported for the acid rhodo complex[9,10] but larger than that in the ethylenediamine complex.[15]

There is an extensive network of hydrogen bonding in the crystals; a list of probable hydrogen bonds is collected in Table V. The bridging hydroxyl group apparently forms a strong hydrogen bond to Cl(2), with O···Cl and H···Cl separations of 3.078 (5) and 2.14 Å, respectively, and an O–H···Cl angle of 180°. Since we were unable to locate the hydrogen atoms on the solvent water moelcules, it is difficult to discuss the hydrogen bonding of these molecules.

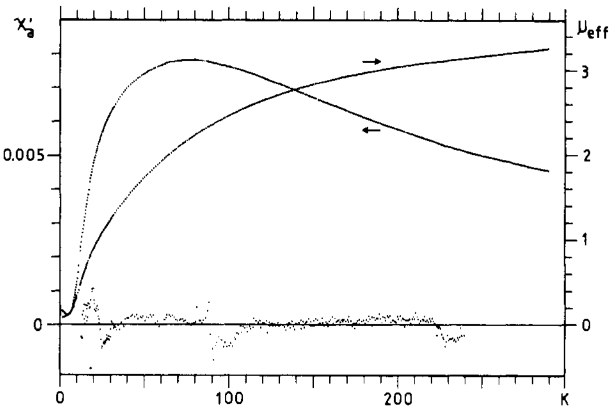

Figure 2. Magnetic susceptibility per chromium (left scale, cgs units) and effective magnetic moment (right scale, Bohr magnetons) of *trans*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(OH_2)]Cl_5 \cdot 3H_2O$. The lower (almost random) distribution of dots around the abscissa indicates the corresponding values of $(X_{obsd} - X_{calcd}) \times 25$. X_{calcd} refers to the parameters of model 3 in Table VI.

Table VI. Parameters Derived from Magnetic Susceptibility Data

parameter	model 1[a]	model 2[a]	model 3[a]
J, cm^{-1}	36.09 (9)	33.30 (10)	
j, cm^{-1}		0.293 (10)	
$E(1)$, cm^{-1}	36.09 (9)[b]	35.20 (10)[b]	34.64 (6)
$E(2)$, cm^{-1}	108.3 (3)[b]	103.9 (3)[b]	103.4 (1)
$E(3)$, cm^{-1}	216.5 (5)[b]	202.4 (6)[b]	198.7 (5)
g	2.106 (6)	1.998 (4)	1.981 (4)
f[c]	298	297	296
var/f	7.3	1.8	1.16
% monomer	0.43 (3)	0.15 (2)	0.02 (2)

[a] See text for description of the three models used. [b] Calculated from the derived parameter(s) for comparison with other models. [c] The number of degrees of freedom in the calculation; this is simply the number of data minus the number of variables.

Magnetic Properties. The average magnetic susceptibility and effective magnetic moment of polycrystalline samples of *trans*-$[(NH_3)_5Cr(OH)Cr(NH_3)_4(H_2O)]Cl_5 \cdot 3.5H_2O$ as functions of temperature are shown in Figure 2. The susceptibility data were fitted to expression 1 where the quantities E_i are

$$\chi_A' = -\frac{N}{H}\frac{\sum_i\left(\frac{\partial E_i}{\partial H}\right)\exp(-E_i/kT)}{\sum_i \exp(-E_i/kT)} \qquad (1)$$

the energies of the 16 components of the ground-state manifold. The fitting was accomplished with use of three different models for the exchange Hamiltonian. In the first (model 1) we assumed the simple Van Vleck Hamiltonian

$$\mathcal{H} = J\vec{S}_1 \cdot \vec{S}_2 \qquad (2)$$

in which the only exchange variable is J and in which the triplet, quintet, and septet energies are J, $3J$, and $6J$, respectively. In the second model (model 2), we expanded the Hamiltonian to include a biquadratic exchange term of the type

$$\mathcal{H} = J\vec{S}_1 \cdot \vec{S}_2 + j(\vec{S}_1 \cdot \vec{S}_2)^2 \qquad (3)$$

where the variable magnetic parameters are now J and j and the triplet, quintet, and septet energies are given by $(J + 6.5j)$, $(3J + 13.5j)$ and $(6J + 9.0j)$, respectively. Finally, in model 3, we used the generalized Hamiltonian

$$H = E(S') + g\beta M_{S'} \qquad (4)$$

where $\vec{S}' = \vec{S}_1 + \vec{S}_2$ and (consequently) S' can have the values 0–3. This Hamiltonian implies independent energies of the triplet, quintet, and septet states, and the absence of any zero-field splitting within these levels; it merely assumes, as do the earlier models, an isotropic Zeeman effect. In model 3, therefore, the variable magnetic parameters are $E(1)$, $E(2)$, $E(3)$, the energies of the triplet, quintet, and septet states. In all three models, in addition to the magnetic parameters noted, we varied the isotropic g value, a temperature-independent susceptibility term, and a term which allows for the presence of a small quantity of monomeric impurity (assumed to obey the Curie law).

The results of the data fitting to these three models are displayed in Table VI. It is apparent that the magnetic susceptibility of the complex is relatively poorly described by the simple Van Vleck model (model 1) since the variance per degree of freedom (var/f) is high (7.3) and the derived g value of 2.106 (6) is entirely unreasonable for a d^3 ion. Inclusion of biquadratic exchange (model 2) leads to a marked improvement in the fit (var/f = 1.8). This model gives g = 1.998

(4), $J = 33.30$ (10) cm^{-1}, and $j = 0.293$ (10) cm^{-1}, leading to triplet, quintet, and septet energies of 35.20 (10), 103.9 (3), and 202.4 (6) cm^{-1}, respectively. Application of model 3 significantly improves the fit, the value of var/f reducing to 1.16. The ratio of the fitting parameters (var/f) for models 2 and 3 (1.8/1.6) is 1.55, which is at the 99.95% fractile of the V^2 distribution; i.e., the improvement brought about by the inclusion of the additional variable is significant at the 99.95% confidence level. This model (model 3) gives $g = 1.981$ (4) and $E(1) = 34.64$ (6), $E(2) = 103.4$ (1), and $E(3) = 198.7$ (5) cm^{-1}.

The results obtained here for this trans erythro complex can be compared with those reported for other monol dimers of this general type. The singlet–triplet splitting in the presnt complex (approximately 35 cm^{-1}) is considerably larger than that of approximately 21 cm^{-1} reported[13] for two salts of the cis complex $[(NH_3)_5Cr(OH)Cr(NH_3)_4OH]^{4+}$ and is also larger than the value of approximately 31 cm^{-1} reported[9,10] for the symmetric rhodo complex $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$. It is apparent that the difference between the magnetic properties of the present complex and those of the cis hydroxo complex may be explained in part by the increased value of the bridging Cr–O–Cr angle (Φ) from 142.8° in the cis hydroxo complex to 155.1° in the present complex. It is also noteworthy, however, that in the present case the bridging hydrogen atom is in the bridging plane, at least on a time average, while in the cis hydroxo complex it lies approximately 0.5 Å above the plane.[13] As will be demonstrated in a future publication from our laboratories and has been suggested in some earlier papers,[2,4,8,17] both of these parameters are of importance in determining the magnitude of the magnetic interaction.

Acknowledgment. We are very grateful to Mrs. Solveig Kallesøe, who collected the susceptibility data. S.J.C. gratefully acknowledges the receipt of a NATO postdoctoral fellowship. This research was also supported by the Scientific Affairs Division, North Atlantic Treaty Organization (NATO), through Grant No. 1318 (to D.J.H., J.G., and E.P.), by the donors of the Petroleum Research Fund, administered by the American Chemical Society (to D.J.H.), and by the Danish National Science Research Council through Grant Nos. 511-742, 511-3993, and 511-10516 (to E.P.).

Registry No. *trans*-$[(NH_3)_4(H_2O)Cr(OH)Cr(NH_3)_5]Cl_5 \cdot 3H_2O$, 77550-02-8; *trans*-$[(H_2O(NH_3)_4Cr(OH)Cr(NH_3)_5](NO_3)_5$, 77550-03-9; *trans*-chloro erythro, 77550-04-0.

Supplementary Material Available: A list of observed and calculated structure amplitudes (electrons × 10) (10 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry,
Wayne State University, Detroit, Michigan 48202

Oxidation–Reduction Reactions of Complexes with Macrocyclic Ligands. Role of Intermediates in Reactions of μ-Peroxo-dicobalt Complexes[1]

CHUNG-LAI WONG and JOHN F. ENDICOTT*

Received August 19, 1980

The $[H_2OCo([14]aneN_4)]_2O_2^{4+}$ complex decomposes slowly in acidic aqueous solution. The solutions of this μ-peroxo complex have both oxidizing and reducing properties. The rates of oxidation *and* reduction reactions approach limiting first-order behavior for large concentrations of the counterreagent. The limiting first-order rate constants depend on the anionic composition of the medium but are otherwise independent of the counterreagent. This behavior is attributed to rate-limiting homolytic dissociation of the μ-peroxo complex, with the reactive intermediate species being $Co([14]aneN_4)(OH_2)_2^{2+}$ and $Co([14]aneN_4)(OH_2)O_2^{2+}$. It is further proposed that the same kind of intermediates mediate the decomposition of $[H_2OCo([14]aneN_4)]_2O_2^{4+}$. More specifically, in acidic chloride solutions the decomposition products of the μ-peroxo complex were found to be $Co([14]aneN_4)Cl_2^+$ and $Co([14]aneN_4)Cl(O_2H)^+$ in about a 1:0.8 ratio. This suggests an inner-sphere (Cl^--bridged) attack of $Co([14]aneN_4)(OH_2)_2^{2+}$ on $[ClCo([14]aneN_4)]_2O_2^{2+}$. The relative inertness of the μ-peroxo moiety probably arises from a combination of thermodynamic and intrinsic barriers to electron transfer.

Introduction

Transition-metal complexes play crucial roles in mediating the utilization of molecular oxygen by many biological and synthetic systems.[2] Very often the initial uptake of dioxygen can be described by the two steps

$$ML^{n+} + O_2 \rightleftarrows O_2ML^{n+} \qquad k_1, k_{-1}, K_1 \tag{1}$$

$$O_2ML^{n+} + ML^{n+} \rightleftarrows LMO_2ML^{2n+} \qquad k_2, k_{-2}, K_2 \tag{2}$$

The second step is frequently described as "irreversible". Owing in part to the complications introduced by this second step, the role, if any, of the O_2ML^{n+} dioxygen adduct in metal-mediated oxidations and oxygenations has proved difficult to elucidate.

Cobalt(II) complexes are well-known for their reactivity toward dioxygen,[2] and cobalt-mediated oxidations (or oxygenations) are varied and generally complex. However, it is possible to minimize those complexities attributable to variations in the coordination sphere of the metal by use of macrocyclic ligand complexes. This approach is particularly advantageous for 14-membered macrocyclic N_4 ligands since the cobalt(II) complexes tend to be low spin and can persist for hours in acidic aqueous media. This contrasts markedly

---

[1] Partial support of this research by the National Institutes of Health (Grant AM 14341) is gratefully acknowledged.

[2] For reviews see: (a) Taube, H. *J. Gen. Physiol.* **1965**, *49*, 29. (b) Wilkins, R. G. *Adv. Chem. Ser.* **1971**, *No. 100*, 111. (c) Schultz, J., Cameron, B. F., Eds. "The Molecular Basis for Electron Transport"; Academic Press: New York, 1972. (d) Bennett, L. E. *Prog. Inorg. Chem.* **1973**, *18*, 1. (e) Valentine, J. *Chem. Rev.* **1973**, *73*, 235. (f) Basolo, F.; Hoffman, B. M.; Ibers, J. A. *Acc. Chem. Res.* **1975**, *8*, 384. (g) Vaska, L. *Ibid.* **1976**, *9*, 175. (h) McLendon, G.; Martel, A. E. *Coord. Chem. Rev.* **1976**, *18*, 125. (i) Dunford, H. B.; Stillman, J. S. *Ibid.* **1976**. (j) Jones, R. D.; Summerville, D. A.; Basolo, F. *Chem. Rev.* **1979**, *79*, 139. (k) Fee, J. A.; Valentine, J. S. In "Superoxide and Superoxide Dismutases"; Michelson, A. M., McCord, J. M., Fridovich, I., Eds.; Academic Press: New York, 1977; p 19. (l) Collman, J. P. *Acc. Chem. Res.* **1977**, *10*, 235. (m) Lever, A. B. P.; Gray, H. B. *Ibid.* **1978**, *11*, 348. (n) Fidovich, I. *Science* **1978**, *201*, 875. (o) Bielski, B. H. J. *Photochem. Photobiol.* **1978**, *28*, 645.