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Structural and Magnetic Characterization of μ-Hydroxo-bis[pentaamminechromium(III)] Chloride Monohydrate, the Acid Rhodo Chloride Complex

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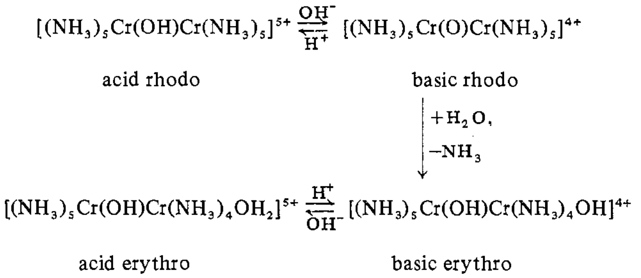
The crystal and molecular structure of μ-hydroxo-bis[pentaamminechromium(III)] chloride monohydrate $[(NH_3)_5Cr\text{-}OH\text{-}Cr(NH_3)_5]Cl_5 \cdot H_2O$ (the acid rhodo chloride) has been determined from three-dimensional X-ray counter data. The material crystallizes in the tetragonal space group $P4_2/mnm$ with four formula units in a cell of dimensions $a = 16.259$ (7) and $c = 7.411$ (7) Å. Least-squares refinement of 228 independent intensities gives a conventional R factor of 0.077. The cation is dimeric, the bridging oxygen atom lying on a site of C_{2v} symmetry with a Cr-O-Cr bridging angle of 165.6 (9)° and a Cr-O distance of 1.94 (1) Å. The coordination around each Cr(III) atom is roughly octahedral. The magnetic susceptibilities of the complex in the temperature range 6.8-300°K have been determined; these data lead to a value of -31.5 cm^{-1} for the singlet-triplet splitting parameter $2J$. Inclusion of biquadratic exchange does not significantly improve the fit of the magnetic data to the theoretical equation.

Introduction

The rhodo and erythro binuclear chromium(III) ammine complexes were first reported by Jorgensen[2] in 1882, and since that time they have been the subject of considerable interest. The acid rhodo salts were formulated by Werner[3] as hydroxo-bridged dimers of the type $[(NH_3)_5Cr\text{-}OH\text{-}Cr(NH_3)_5]X_5$, and this formulation has been confirmed by a variety of more recent evidence.[4-6] All of the members of the rhodo and erythro series contain a single oxygen bridge and undergo the reactions shown in Scheme I.[6]

Scheme I



$$[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+} \underset{H^+}{\overset{OH^-}{\rightleftharpoons}} [(NH_3)_5Cr(O)Cr(NH_3)_5]^{4+}$$

acid rhodo basic rhodo

$$\downarrow +H_2O, -NH_3$$

$$[(NH_3)_5Cr(OH)Cr(NH_3)_4OH_2]^{5+} \underset{OH^-}{\overset{H^+}{\rightleftharpoons}} [(NH_3)_5Cr(OH)Cr(NH_3)_4OH]^{4+}$$

acid erythro basic erythro

The magnetic properties of several salts in these series have been examined in several laboratories.[7-14] The diamagnetic basic rhodo complexes have been shown by X-ray crystallography to contain a linear Cr-O-Cr linkage,[15,16] and preliminary structural data have also been reported on the acid rhodo[15] and acid erythro complexes.[16] Preliminary work in our laboratory on the acid rhodo chloride complex which was completed before the publication of the preliminary structural information, however, suggested to us that Urushiyama, *et al.*,[15] may have incorrectly assigned the space group of this complex as a result of crystallographic twinning, and so we have completed our determination of the structure of the acid rhodo chloride monohydrate. Since some confusion has arisen because of the existence of more than one hydrate of this complex, we have also examined the low-temperature magnetic susceptibility of a crystallographically pure sample of the monohydrate, and we report the results of these crystallographic and magnetic studies herein.

Experimental Section

Collection and Reduction of the X-Ray Data. Red, needle-shaped crystals of $[Cr_2(NH_3)_{10}(OH)]Cl_5 \cdot H_2O$ were prepared by the method of Wilmarth, *et al.*;[5] the formation of the trihydrate was suppressed by careful monitoring of the pH during the recrystallization, and the composition of the complex was confirmed by elemental analysis. *Anal.* Calcd for $Cr_2N_{10}O_2H_{33}Cl_5$: N, 28.79; Cl, 36.43; H, 6.84. Found: N, 28.94; Cl, 36.15; H, 6.98.

Precession and Weissenberg photography indicated that the material belongs to the tetragonal system, but examination of the crystals on the diffractometer demonstrated that all but the smallest crystals were twinned. The systematic absences observed for the crystals which showed no evidence of twinning are $0kl$ for $k + l$ even, which suggest that the space group is either $P4_2/mnm$ (D_{4h}^{14}), $P\bar{4}n2$ (D_{2d}^{8}), or $P4_2nm$ (C_{4v}^{4}). $P\bar{4}n2$ was eliminated on the basis of the vector distribution in the Patterson function (*vide infra*). An attempt, at a late stage in the refinement, to refine the structure in space group $P4_2nm$ was unsuccessful, and so the centrosymmetric space group $P4_2/mnm$ is taken as the correct choice; this assignment is also consistent with the results of a Wilson plot. The cell constants, obtained by the least-squares procedure by Busing and Levy[17] at 25° with the wavelength assumed as $\lambda(\text{Mo } K\alpha_1) = 0.7093$ Å, are $a = 16.259$ (7) and $c = 7.411$ (7) Å. The density of 1.649 g cm^{-3} calculated for four dimeric formula units in this cell is in acceptable agreement with the value of 1.63 g cm^{-3} observed by flotation in carbon tetrachloride-diiodomethane solution. Hence, the dimer is constrained to have either mm (C_{2v}), $\bar{4}$ (S_4), or $2/m$ (C_{2h}) symmetry. This space group assignment differs from that reported by Urushiyama, *et al.*,[15] who give the space group as $P4_12_12$ (D_4^{4}) or $P4_32_12$ (D_4^{8}) and the cell constants as $a = 16.26$ and $c = 14.80$ Å, with eight dimers in the cell.[15] We find that some of our films of larger crystals, which were later found to be twinned, could also be interpreted in terms of this space group assignment. Hence, we believe that the crystal used in

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the study of Urushiyama, *et al.*,[15] may have been twinned and that this may explain why their data were not refined below a conventional R factor of 0.16.

The crystal specimen which was chosen for data collection was a rectangular needle of dimensions 0.17 × 0.002 × 0.002 cm, with the needle axis parallel to the c axis. The crystal was mounted roughly parallel to the needle axis, with the goniometer head readjusted to avoid multiple reflections.[18] The crystal mosaicity was checked in the usual way,[19] the average width at half-height for the ω scans of several strong peaks being 0.15°. While this value is larger than we would normally consider desirable, the peaks were single and symmetric; we examined 27 crystals without finding any whose ω scans were superior to those of the sample chosen. The intensity data were collected in the manner previously described,[20] using Mo Kα radiation. Two forms (hkl) and (khl) of the data were collected out to a value of $2\theta = 45°$, a total of 896 intensities being recorded. Few of the intensities in the region $2\theta > 40°$ were above background, and we found no intensities above background at values of $2\theta > 45°$.

The data were processed by the method of Corfield, Doedens, and Ibers,[21] using our program DATPRC.[20] The value of p in the expression[22]

$$\sigma(I) = [C + 0.25(t_s/t_b)^2(B_H + B_L) + (pI)^2]^{1/2}$$

where the symbols have their usual meanings[23] was chosen as 0.05. In view of the minute size of the specimen, no absorption correction was applied. Of the 896 data recorded, only 368 exceeded three times their estimated standard deviations, and after averaging of equivalent forms this led to 184 independent intensities. There were 228 independent intensities greater than twice their estimated standard deviations, and these data were used in the structure analysis.

Solution of the Structure. The locations of the one independent chromium atom and the bridging oxygen atom were determined by means of a three-dimensional Patterson function. The oxygen atom was found to lie on a special position with site symmetry mm (C_{2v}), while the chromium atom has site symmetry m (C_s). Three cycles of least-squares refinement of these positions were run. All least-squares refinements were carried out on F, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$ with the weights w being assigned as $4F_o^2/\sigma^2(F_o^2)$. The atomic scattering factors for Cr and Cl were taken from Cromer and Waber,[24] those for N and O from Ibers,[25] and that for H from Stewart, Davidson, and Simpson.[26] The effects of the anomalous dispersion of Cr and Cl were included in F_c,[27] the values of $\Delta f'$ and $\Delta f''$ being taken from Cromer.[28]

After three cycles of least-squares refinement the usual agreement factors $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$ and $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w(F_o)^2]^{1/2}$ were 0.542 and 0.558, respectively. The remaining atoms in the cation (excluding hydrogen atoms) were located in a difference Fourier synthesis, and isotropic refinement yielded values of 0.297 and 0.314 for R_1 and R_2. Examination of a subsequent difference Fourier map led us to conclude that the anions and the water molecules were disordered. Several possible disorder models were examined, with only one giving good agreement; this accepted model leads to threefold disorder of the water molecules and to six independent chlorine positions, of which only two are fully occupied while the other four are half occupied. Two cycles of refinement of these parameters with Cr and N atoms refined anisotropically and Cl and O atoms refined isotropically gave values of 0.066 and 0.063 for R_1 and R_2 for the 184 independent data greater than three times their estimated standard deviations. The hydrogen atom on the bridging oxygen atom was located in a difference Fourier map, and although its location could not be refined and is clearly imprecise, inclusion of its contribution with an isotropic thermal parameter assigned as 6.5 Å^2 further reduced the agreement factors to 0.061 and 0.056. Attempts to locate the ammine hydrogen atoms were unsuccessful, and we believe that there may be disorder of the ammine groups also. Inclusion of the 44 additional data whose intensities were greater than twice their estimated standard deviations led to increased values of 0.077 and 0.065 for R_1 and R_2 but also reduced the estimated standard deviations of the atomic parameters. The small number of independent data which were available did not justify the anisotropic refinement of any other atoms. In the final cycle of least-squares calculation there were 228 data and 51 variables; if all atoms were refined anisotropically there would have been 69 variables, which we judged to be unjustifiable. The thermal parameters of atoms O(2) and O(3) are clearly unsatisfactorily high and may indicate some minor error in the occupancies assigned to these water oxygen atoms. The apparently large thermal parameters for atom N(3) may suggest the existence of some slight disorder in the position of this atom relative to the mirror plane. Attempts at more clearly defining these areas were again hampered by the lack of available data.

In the final cycle of least-squares refinement, the greatest shift of any atomic parameter was 0.32 times its estimated standard deviation, which is taken as evidence that the refinement had converged. The value of R_2 showed no dependence on sin θ or on $|F_o|$, which suggests that our choice of $p = 0.05$ is acceptable. Examination of the final values of $|F_c|$ and $|F_o|$ suggests to us that no correction for secondary extinction is necessary. The positional and thermal parameters derived from the last cycle of least-squares refinement, along with their associated standard deviations as estimated from the inverse matrix, are presented in Tables I and II. A table of observed and calculated structure amplitudes is available.[29]

Results

Description of the Structure. The structure consists of discrete dimeric $[Cr_2(NH_3)_{10}OH]^{5+}$ cations which are well separated from the Cl^- anions and the water molecules. The geometry of the cation is shown in Figure 1. The bridging oxygen atom lies on a site of C_{2v} (mm) symmetry, while the chromium atoms and some of the nitrogen atoms [N(3)] sit on sites of C_s (m) symmetry. The coordination around each chromium atom is roughly octahedral with no angle deviating from that expected for octahedral geometry by more than 3°. The internuclear distances and angles in the cation are shown in Table III; the closest approach of an anion or solvent molecule to the cation is a O(3)· · ·N(1) separation of 2.85 Å, and there are no other contacts of less than 3.18 Å. Since both the water molecules O(3) and the hydrogen atoms on the ammine nitrogen atoms appear to be disordered, it seems unlikely that this O(3)· · ·N(1) contact is the result of intermolecular hydrogen bonding.

The Cr-N distances of 2.07 (2), 2.09 (2), and 2.15 (2) Å are consistent with the mean values of 2.063 Å in di-μ-hydroxo-tetraglycinatodichromium(III),[30] $[Cr(gly)_2OH]_2$, 2.068 Å in tris(glycinato)chromium(III) hydrate,[31] $Cr(gly)_3 \cdot H_2O$, 2.075 and 2.081 Å in two different salts of tris(ethylenediamine)chromium(III),[32,33] and 2.116 Å in the basic rhodo chloride complex.[16] The Cr-N(3) bond length of 2.15 (2) Å trans to the bridging oxygen may be significantly longer than the average value of 2.08 (1) Å of the cis Cr-N bond lengths; this lengthening of the bond trans to the bridge is not unexpected, and may explain why it is possible to remove one ammine from this system to form the erythro complexes,[6] but was not observed in the basic rhodo complex.[16] The

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Table I. Positional Parameters for $[(NH_3)_5CrOHCr(NH_3)_5]Cl_5 \cdot H_2O$

Atom	Occupancy (atom/cell)	Wyckoff notation	*x*	*y*	*z*
Cr	8	8i	0.2421 (3)	0.0745 (3)	0.0000
N(1)	16	16k	0.1909 (10)	−0.0023 (10)	0.1969 (24)
N(2)	16	16k	0.1442 (10)	0.2972 (9)	0.2008 (28)
N(3)	8	8i	0.3485 (15)	−0.0042 (14)	0.0000
O(1)	4	4f	0.1478 (13)	0.1478 (13)	0.0000
O(2)	1	2b	0.0000	0.0000	0.5000
O(3)	2	8j	0.3102 (75)	0.3102 (75)	0.3842 (36)
O(4)	1	4f	0.4488 (66)	0.4488 (66)	0.0000
C(11)	4	8i	0.4995 (15)	0.1350 (18)	0.0000
C(12)	4	8i	0.3472 (20)	−0.0075 (18)	0.5000
C(13)	4	4f	0.3106 (8)	0.3106 (8)	0.5000
C(14)	4	4f	0.1348 (6)	0.1348 (6)	0.5000
C(15)	2	4f	0.3274 (8)	0.3274 (8)	0.0000
C(16)	2	4e	0.5000	0.5000	0.4343 (33)
H(B1)[a]	4	4f	0.1190	0.1190	0.0000

[a] The coordinates of the hydrogen atom were not refined.

Table II. Thermal Parameters of $[(NH_3)_5CrOHCr(NH_3)_5]Cl_5 \cdot H_2O$

Atom	β_{11}[a] or *B*, Å^2	β_{22}	β_{33}
Cr	0.0016 (1)	0.0016 (1)	0.0148 (10)
N(1)	0.0055 (9)	0.0035 (9)	0.0196 (61)
N(2)	0.0053 (11)	0.0045 (10)	0.0211 (66)
N(3)	0.0031 (8)	0.0031 (8)	0.1266 (289)
O(1)	3.85 (8)		
O(2)	12.3 (44)		
O(3)	13.8 (54)		
O(4)	6.5 (40)		
C(11)	2.7 (8)		
C(12)	4.7 (11)		
C(13)	6.1 (4)		
C(14)	4.8 (3)		
C(15)	2.8 (5)		
C(16)	3.6 (5)		
H(B1)	6.5		

Atom	β_{12}	β_{13}	β_{23}
Cr	0.0004 (2)	0.0000	0.0000
N(1)	−0.0012 (7)	0.0045 (17)	0.0004 (19)
N(2)	−0.0023 (6)	0.0006 (20)	−0.0025 (17)
N(3)	0.0023 (11)	0.0000	0.0000

[a] The form of anisotropic thermal ellipsoid is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)]$.

Table III. Intramolecular Distances and Angles in $(NH_3)_5Cr(OH)Cr(NH_3)_5{}^{5+}$

Atoms	Distance, Å	Atoms	Angle, deg
Cr–Cr	3.852 (9)	Cr–O–Cr	165.6 (9)
Cr–O(1)	1.941 (16)	O–Cr–N(1)	93.0 (6)
Cr–N(1)	2.093 (16)	O–Cr–N(2)	90.4 (6)
Cr–N(2)	2.073 (18)	O–Cr–N(3)	178.7 (10)
Cr–N(3)	2.152 (22)	N(1)–Cr–N(3)	88.0 (8)
O–H[a]	0.66	N(1)–Cr–N(2)	89.8 (6)
		N(2)–Cr–N(3)	88.7 (7)

[a] O–H bond distance not refined, located from difference Fourier map.

large estimated standard deviations on our parameters, which are due to the limited number of data obtainable from so small a crystal, make quantitative comparisons of these bond lengths hazardous.

The Cr–O separation of 1.94 (2) Å is similar to the values of 1.962–1.967 Å in $Cr(gly)_3 \cdot H_2O$,[31] 1.966–1.968 Å in $[Cr(gly)_2OH]_2$,[30] 1.951 Å in tris(acetylacetonato)chromium(III),[34] and 1.955 Å in bis(μ-diphenylphosphinato)-acetylacetonatochromium(III)[35] but is significantly longer than the values of 1.821 (3)[16] and 1.80 Å[15] reported for the basic rhodo complex. This lengthening of the Cr–O bond in the acid rhodo relative to the basic rhodo value is presumably due to the nonlinearity of the Cr–O–Cr moiety in the acid complex which reduces the possibility of extensive π bonding in the system; short M–O bonds of lengths 1.86 and 1.80 Å have been observed in $[Ru_2Cl_{10}O]_2{}^{2-}$ and $[Re_2Cl_{10}O]_2{}^{2-}$, both of which have linear[36,37] M–O–M linkages. The Cr–O–Cr angle of 166 (1)° and Cr–Cr separation of 3.852 (9) Å found here are significantly different from the values of 154° and 3.90 Å reported by Urushiyama, *et al.*[15] This difference in these parameters may be explained by our suggestion (*vide supra*) that the crystal used in the previous analysis may have been twinned.

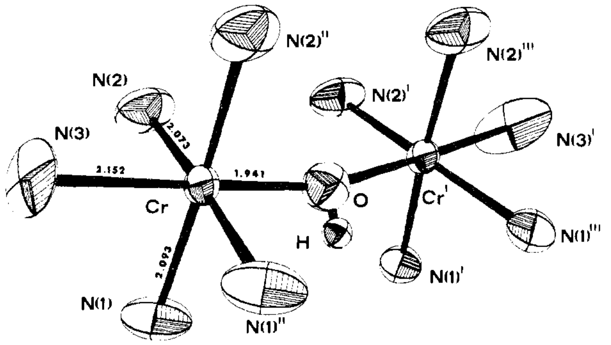

Figure 1. View of the $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$ cation. The thermal ellipsoids are drawn at the 40% probability level.

Electron Paramagnetic Resonance. Epr measurements were carried out at X band on a Varian spectrometer, Model 4502. Field positions were calibrated with a proton nmr probe and microwave frequencies were monitored with a digital counter. Thin-walled quartz tubes were used as sample containers. The room temperature epr spectrum of a powdered sample of $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5 \cdot H_2O$ consists of a symmetrical peak, ~400 G in width and centered at $g = 1.99$, which shows a weak broad shoulder in the field range between 625 and 1250 G. The height of the shoulder is approximately $^1/_{100}$ that of the peak to peak height of the major feature of the spectrum. Assuming that the Zeeman interaction dominates the zero-field splitting,[38] the observed line width of the major feature corresponds to a zero-field parameter $D = 0.018$ cm^{-1} ($\Delta H \simeq 2D/g\beta$).

Magnetic Susceptibility. The magnetic susceptibilities of a

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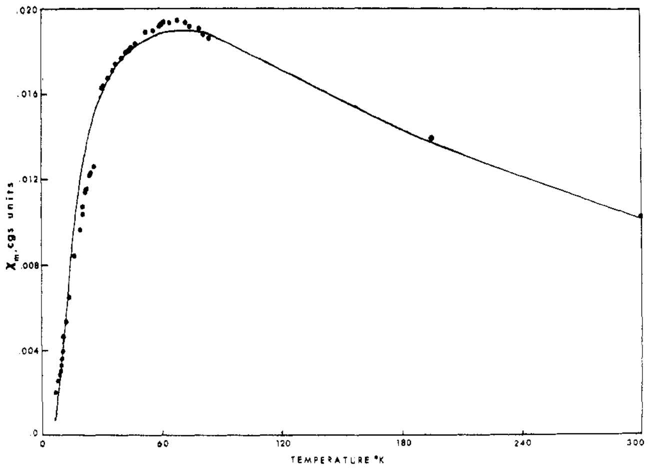

Figure 2. The temperature dependence of the magnetic susceptibility of $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5 \cdot H_2O$. The experimental data are shown as dots and the best fit to the dimer ($S = {}^3/_2 - {}^3/_2$) equation without biquadratic exchange is displayed as the full line. The best fit including biquadratic exchange may be superimposed on the full line shown.

powdered sample of the dimer were determined in the temperature range 6.8–84°K using a Foner-type vibrating sample magnetometer[39] and at 195 and 300°K using a Faraday balance.[40] All vibrating sample magnetometer measurements were made at a field strength of 10,000 G with temperatures measured by a calibrated gallium arsenide diode. Mercury tetrathiocyanatocobaltate(II) was used as a susceptibility standard in all cases.[41] Susceptibilities were corrected for the diamagnetism of substituent atoms using Pascal's constants and for the TIP of chromium (estimated to be 62 × 10^{-6} cgsu per chromium atom).

Experimental results showed a maximum at 68°K in the magnetic susceptibility of the dimer which is indicative of antiferromagnetic exchange coupling. As shown in Figure 2, the experimental data closely conform to the values of χ_m *vs.* temperature calculated according to eq 1[42]

$$\chi_m = \frac{Ng^2\beta^2}{kT}\left[\frac{2\exp(2J/kT) + 10\exp(6J/kT) + 28\exp(12J/kT)}{1 + 3\exp(2J/kT) + 5\exp(6J/kT) + 7\exp(12J/kT)}\right] \quad (1)$$

where J is the exchange coupling constant of two atoms of a dimer each with $S = {}^3/_2$, and where χ_m is the calculated susceptibility of the dimer. In this case, the best linear least-squares fit of experimental data to the above theoretical expression gives the parameter $2J$ a value of -31.5 cm^{-1} when $g = 1.99$ (*vide supra*).

Our investigation of the magnetic behavior of the dimer also included study of the possibility of biquadratic exchange interactions affecting the observed susceptibilities. Including biquadratic exchange in the Hamiltonian results in the general expression

$$\mathcal{H}_c = -2J(S_1 \cdot S_2) - j(S_1 \cdot S_2)^2 \quad (2)$$

where j is the biquadratic exchange parameter.[43] The expanded expression for χ_m using the additional term in the Hamiltonian is the following.[44]

$$\chi_m = \frac{Ng^2\beta^2}{kT} \times \left\{\frac{2\exp[(2J - 6.5j)kT] + 10\exp[(6J - 13.5j)/kT] + 28\exp[(12J - 9j)/kT]}{1.0 + 3\exp[(2J - 6.5j)/kT] + 5\exp[(6J - 13.5j)/kT] + 7\exp[(12J - 9j)/kT]}\right\} \quad (3)$$

The linear least-squares best fit results in $2J = -29.6$ cm^{-1} and $j = +0.55$ cm^{-1} with $g = 1.99$. This result is very close to that obtained without use of the biquadratic exchange term; indeed, the two plots are nearly indistinguishable.

We therefore conclude that the $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5 \cdot H_2O$ dimer exhibits an antiferromagnetic exchange interaction with $2J \sim -32$ cm^{-1}. Second-order exchange interactions are of very minor importance in describing the magnetic behavior of the substance. This is not the case, however, for the compounds $[(NH_3)_5Cr(OH)Cr(NH_3)_4OH]Cl_4 \cdot H_2O$ and $[(NH_3)_5Cr(OH)Cr(NH_3)_5]_2Cl_3(ClO_4)_7 \cdot H_2O$.[12] It is not possible at this time to identify those factors which determine the necessity for biquadratic exchange.

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Registry No. $[(NH_3)_5CrOHCr(NH_3)_5]Cl_5 \cdot H_2O$, 15629-41-1.

Supplementary Material Available. A listing of structure factor amplitudes 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, 20× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for \$3.00 for photocopy or \$2.00 for microfiche, referring to code number INORG-73-2928.

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