

tion of 100-MHz nmr spectra with T. Luisebrink and T. Hirakawa, IBM Research, San Jose, Calif., with D. Falcon, IBM, East Fishkill, N. Y., and disclosure of their results by A. J. Ashe (University of Michigan) and A. Davison (MIT) prior to publication are noted with great appreciation.

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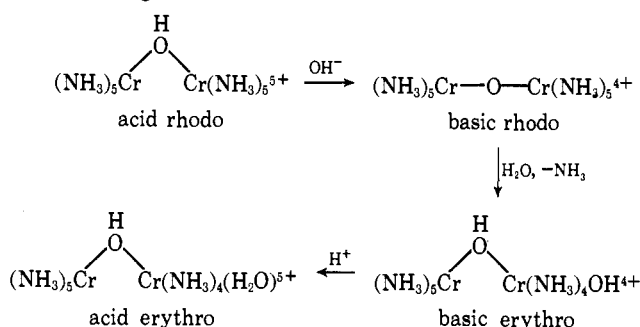
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On the Structures of the Oxo- and Hydroxo-Bridged, Binuclear Chromium(III)-Ammine Complexes. The Rhodo and Erythro Series¹

Sir:

Since their discovery in 1882 by Jorgensen,² the rhodo and erythro series of binuclear ammine complexes of chromium(III) have provided many challenges with regard to the elucidation of their exact constitution, their unusual acid-base isomerization behavior, their reaction kinetics,³⁻⁹ and, more recently, their electronic structures and magnetic properties.¹⁰⁻¹⁴ By now it is well established that these complexes have as a common structural feature a single oxygen bridge, and undergo the following chemical transformations.



To date, evidence for these structural formulations has been mainly chemical and spectroscopic.³⁻¹⁴ X-Ray structural information on these complexes would be useful in confirming their presumed gross molecular structures (*i.e.*, angular about the bridge oxygen in the hydroxo-bridged species and linear in the oxo-bridged species), and in providing detailed bond distance information. The latter should aid in the interpretation of certain features of the magnetic and spectral properties of the complexes which are attributed to

(1) The terminology rhodo and erythro is taken here to refer to the classification of the binuclear chromium(III)-ammine complexes on the basis of the NH_3 ligand-to-Cr atom ratio. For the rhodo series this is 10:2, and for the erythro series 9:2.

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the exchange interaction between the two, spin $3/2$, Cr(III) ions in the dimeric unit.¹⁰⁻¹⁴ An X-ray study could also settle the geometric configuration of the tetraammine unit in the erythro series, which is still in doubt, since both cis and trans isomers are claimed to exist.⁹

The salts of these binuclear complexes have proven difficult to work with crystallographically because of their light and X-ray sensitivity, their unusual hydration problems, and their tendency to form twinned and disordered crystals. Recently, however, we have obtained fairly stable, single crystals of the basic rhodo chloride salt μ -oxo-bis[pentaamminechromium(III)] chloride monohydrate and of the acid erythro chloride salt pentaamminechromium(III)- μ -hydroxo-aquotetraamminechromium(III) chloride monohydrate, and wish to report our structural findings.

In the conversion of the acid rhodo chromium chloride salt $[(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_5]\text{Cl}_5$ to the corresponding erythro series by the addition of base (see above diagram), the solution always goes through a deep blue intermediate color. This intermediate color is presumed to be due to the presence of the oxy-bridged species, $[(\text{NH}_3)_5\text{Cr}(\text{O})\text{Cr}(\text{NH}_3)_5]^{4+}$, which has been most frequently isolated as an unstable perchlorate salt.⁵ We have found that if this transformation is effected by dissolving the acid rhodo chloride in *cold* (5°) $2\text{ N NH}_4\text{OH}$, shortly after dissolution there is a deposition of a quantity of the blue intermediate as a chloride salt. This precipitate can be filtered, washed with alcohol and ether, and air-dried. Examination under a polarizing microscope showed the residue to be composed of well-formed (if small) crystal plates which extinguish along face diagonals and exhibit some dichroism. The crystals were allowed to remain in air for several days and appeared to be quite stable in low humidity. Analytical data and the infrared spectrum⁶ for the compound confirmed its formulation as the oxo-bridged salt, $[\text{Cr}_2\text{O}(\text{NH}_3)_{10}]\text{Cl}_4 \cdot \text{H}_2\text{O}$.

A crystal of dimensions $0.08 \times 0.10 \times 0.14$ mm was mounted on a quartz fiber and precession photographs showed the compound to crystallize in the orthorhombic system. The absences $h0l$ for l odd, $0kl$ for k odd, and $hk0$ for h odd uniquely identified the space group as D_{2h}^{15} - $Pbca$ (no. 61). Unit cell dimensions from a least-squares refinement of 2θ angles of eight reflections are $a = 11.65$ (1), $b = 13.67$ (1), and $c = 12.08$ (2) Å. An experimental density of 1.553 g cm^{-3} (by floatation in a CCl_4 -*n*-hexane mixture) agrees with a calculated value of 1.554 g cm^{-3} based upon *four* formula units per cell. Since the general positions of this space group are eightfold, the dimeric cation is required to possess a center of symmetry in the crystal.

A total of 1085 independent reflections up to $2\theta = 106^\circ$ were collected by the θ - 2θ scan technique on a Syntex computer-controlled diffractometer, using Ni-filtered $\text{Cu K}\alpha$ radiation (λ 1.5418 Å). Of these, 547 having $I \geq 3\sigma(I)$ were corrected for Lorentz and polarization effects and for a slight falloff in intensity during data collection, and were used in the structure solution. The chromium atoms were readily located from a Patterson map and the remaining atoms by successive difference Fourier maps. The structure has been refined by the least-squares method employing anisotropic thermal parameters for all atoms and in-

cluding anomalous dispersion effects.¹⁵ The value at the present time for the conventional R factor, $\Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, is 0.063, and the error in an observation of unit weight, $[\Sigma w(|F_o| - |F_c|)^2 / (\text{NO} - \text{NV})]^{1/2}$, is 3.11. The only peculiarity in the location of any of the atoms in the cell concerns the water molecules of hydration which occur in a set of half-occupied eightfold general positions.

A view of the structure of the oxo-bridged dimer, $[(\text{NH}_3)_5\text{Cr}-\text{O}-\text{Cr}(\text{NH}_3)_5]^{4+}$, in the crystal is shown in Figure 1. Significant structural features of the complex are a linear (180°) Cr-O-Cr' bond angle, an eclipsed configuration (required by symmetry) of the two pentaammine units, and a rather short Cr-O bond distance of $1.821 \pm 0.003 \text{ \AA}$. The Cr-Cr distance is $3.642 \pm 0.001 \text{ \AA}$. These features are entirely consistent with the weak paramagnetism of the complex,¹¹⁻¹³ which can imply either a strong antiferromagnetic superexchange coupling of the three unpaired electrons on each chromium ion center ($J/k > 200^\circ$) or, alternatively, a pairing of chromium electrons through the formation of a system of π molecular orbitals involving the Cr $d\pi$ and bridging O $p\pi$ orbitals. In either description, the coupling is enhanced by the linear configuration of the three atoms. The Cr-N distances in the complex range from 2.098 to 2.136 \AA (with esd's of $\pm 0.010 \text{ \AA}$) and do not reflect any significant trans influence from the implied strong Cr-O bridge bond. This seems surprising in view of the kinetic evidence,^{6,16} which shows this complex to rapidly lose an ammonia ligand to form the basic erythro complex (see diagram above), thus suggesting strong activation of one of the ammine ligands.

In contrast to the oxo-bridged species, the binuclear acid rhodo, acid erythro, and basic erythro complexes, which presumably contain a bridging hydroxo ligand, exhibit electronic spectral and magnetic properties characteristic of weakly interacting mononuclear species.¹⁰⁻¹⁴ We have examined crystallographically the acid rhodo salts $[(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_5]\text{Cl}_5 \cdot x\text{H}_2\text{O}$, where $x = 1$ or 3, and the acid erythro salts $[(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})]\text{X}_5 \cdot \text{H}_2\text{O}$, where $\text{X} = \text{Cl}$ or Br . Each of these has presented some insurmountable difficulty to a complete structural solution. To date the maximum information has been obtained from the acid erythro chloride salt which grows as large, red, twinned orthorhombic plates. The cell information and probable space group are $a = 17.702 (9)$, $b = 10.698 (7)$, $c = 10.522 (7) \text{ \AA}$, $D_2^3-C222_1$, $Z = 4$, $D_m = 1.61$, $D_c = 1.630 \text{ g cm}^{-3}$. In the crystal the dimeric complex has a disordered orientation with respect to one of the twofold axes of the cell, and we have been unable to refine the structure below an R factor of 0.29. However, even at this stage two structural features are clear: (1) the $[(\text{NH}_3)_5\text{Cr}(\text{OH})\text{Cr}(\text{NH}_3)_4(\text{H}_2\text{O})]^{3+}$ cation has a bent Cr-O-Cr linkage with an exceptionally strained angle of $168 \pm 5^\circ$; (2) the Cr-Cr distance of $3.91 \pm 0.05 \text{ \AA}$ is significantly increased compared to that of the oxo-bridged dimer. In two recent structural determinations^{17,18} of hydroxo-bridged tetranuclear

(15) Calculated and observed structure factors are deposited as Document No. NAPS-01345 with the ASIS National Auxilliary Publication Service, c/o CCM Information Corp., 909 3rd Ave., New York, N. Y. 10022. A copy may be secured by citing the document number and by remitting \$2.00 for microfiche and \$5.00 for photocopies.

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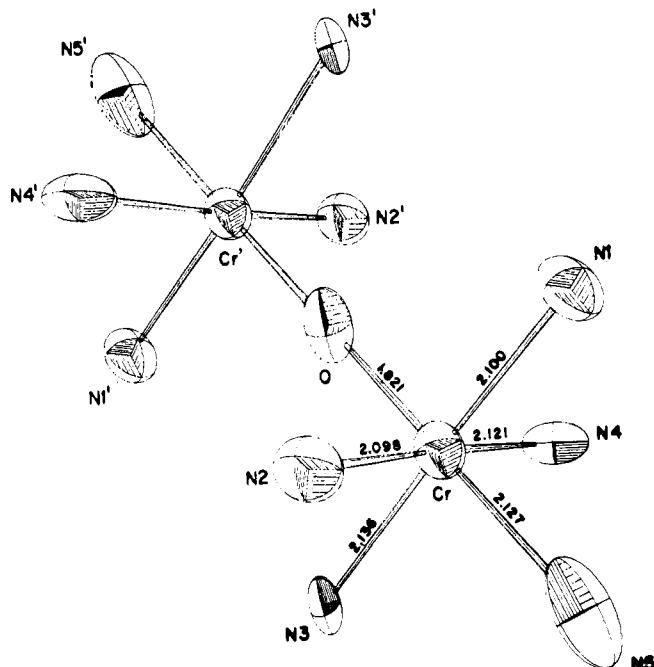


Figure 1. A view of the $[(\text{NH}_3)_5\text{CrOCr}(\text{NH}_3)_5]^{4+}$ cation. The atoms are represented by ellipsoids whose principal axes and sizes were derived from the final values of the anisotropic temperature parameters. Independent distances between bonded atoms are indicated in ångströms. Values for bond angles not shown are 180.0° for Cr-O-Cr', 179.4° for O-Cr-N₅, and range from 90.8 to 92.6° for O-Cr-N₁₋₄. (Esd's of distances are $\pm 0.010 \text{ \AA}$, and for angles, $\pm 0.4^\circ$, except for Cr-O-Cr' which is symmetry determined.)

chromium(III) complexes, the largest Cr-O-Cr bridge angle found was 133° ; however, these were dihydroxo-bridged species. A more reasonable analog to the single-bridged dimer would probably be the μ -amido-bis(pentaamminecobalt(III)) ion which also has the rather strained bridge angle, Co-N-Co, of 153° .¹⁹

In order to strengthen these preliminary findings, we are presently examining other salts of these complexes in hopes of obtaining more suitable crystals.²⁰

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(20) NOTE ADDED IN PROOF. Since this paper was submitted, a report [A. Urushiyama, T. Nomura, and M. Nakahara, *Bull. Chem. Soc. Jap.*, **43**, 3971 (1970)] of a similar structural investigation of these complexes has appeared. The results of the above authors on the oxo-bridged, basic rhodo complex are in essential agreement with those we report here. In addition, however, they were able to refine the structure of a salt of the hydroxo-bridged, acid rhodo complex to a greater extent than we achieved on the acid erythro complex. They also find a bent Cr-O-Cr linkage and an increased Cr-Cr distance in the rhodo complex.

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Behavior of Bent Vinyl Cations Generated by Solvolysis of Cyclic Trifluoromethanesulfonates

Sir:

According to *ab initio* molecular orbital calculations, vinyl cations prefer a linear structure which can be