The Stereochemistry of Binuclear Complexes of Chromium(III)

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The normal rhodo chromic complex ion, $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$, and the basic rhodo complex ion, $[(NH_3)_5Cr(O)Cr(NH_3)_5]^{4+}$, have both been characterized in terms of their magnetic[1] and spectroscopic[2,3] behaviour, which is at least in part, to be ascribed to the Cr–O–Cr angles in the complex ions. In the present work, in order to establish the stereochemistry of binuclear Cr(III) complexes, the crystals of the rhodo compounds have been subjected to three-dimensional X-ray analysis.

Their crystal data are as follows: normal rhodo chromic chloride, $[(NH_3)_5Cr(OH)Cr(NH_3)_5]Cl_5 \cdot H_2O$-tetragonal, space group $P4_12_12$ (or $P4_32_12$), $a=16.26$, $c=14.80$ Å, $Z=8$, $D_m=1.65$, $D_x=1.65$ g·cm^{-3}; basic rhodo chromic chloride, $[(NH_3)_5Cr(O)Cr(NH_3)_5]Cl_4 \cdot H_2O$-orthorhombic, space group $Pbca$, $a=11.94$, $b=11.71$, $c=13.40$ Å, $Z=4$, $D_m=1.58$, $D_x=1.59$ g·cm^{-3}. Their structures have been solved by the heavy-atom method and refined to $R=0.16$ for the acid rhodo salt, and to $R=0.11$ for the basic rhodo salt, by least-squares analysis based on 1169 and 811 three-dimensional data respectively.

The structures of the complexes are shown in Figs. 1 and 2. In the normal rhodo chromic complex, a bridging oxygen atom is located on the two-fold rotation axis. Approximately, there are two mirror planes, perpendicular to one another, in the complex. Thus, the acid rhodo complex has a quasi-C_{2v} symmetry. The Cr–O–Cr bond angle is 154°. The coordination around the chromium atoms is approximately octahedral, with bond distances of Cr–O 2.00 Å and Cr–N 2.07 Å (average). In the basic rhodo chromic complex, a bridging oxygen atom is situated on the inversion center. Therefore, the complex exactly has a center of symmetry and, accordingly, a linear Cr–O–Cr system. As the complex has approximately a four-fold rotation axis passing through a sequence of the N–Cr–O–Cr–N atoms, it seems reasonable to say that the basic rhodo chromic complex has D_{4h} symmetry. The eight N–Cr–O angles are nearly 90°, and the Cr–N bond distance is 2.11 Å(average). The Cr–O distance is 1.80 Å, which is quite short compared with that in the acid rhodo chromic complex. The linear Cr–O–Cr system and its short bond distance suggest the presence of an extensive π-bonding in this system like that in similar oxo-bridged binuclear complexes, $K_4[Cl_5Ru\text{–}O\text{–}RuCl_5]$ (Ru–O= 1.86 Å)[4] and $K_4[Cl_5Re\text{–}O\text{–}ReCl_5]$ (Re–O= 1.80 Å)[5], both of which have been confirmed to be of D_{4h} symmetry by the X-ray method.

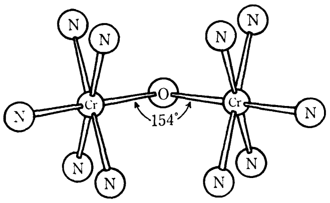

Fig. 1. Perspective drawing of the acid rhodo chromic complex ion, $[(NH_3)_5Cr(OH)Cr(NH_3)_5]^{5+}$.

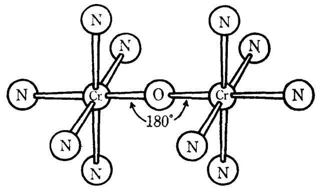

Fig. 2. Perspective drawing of the basic rhodo chromic complex ion, $[(NH_3)_5Cr(O)Cr(NH_3)_5]^{4+}$.

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