Synthesis and *X*-Ray Characterization of the Novel Pentagonal Bipyramidal Chromium Complex, Diaqua-(2,6-diacetylpyridine bis-semicarbazone)-chromium(III) Hydroxide Dinitrate Monohydrate

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Summary The first pentagonal bipyramidal chromium(III) complex has been prepared and characterized, suggesting that seven-co-ordination may not be as rare as previously assumed and may also be the geometry of intermediates in octahedral substitution reactions.

SEVEN-CO-ORDINATION is extremely rare in first-row transition metal complexes. In fact, the first pentagonal bipyramidal (PBP) complexes of the M^{II} ions (M = Mn—Zn) were prepared only recently using planar pentadentate ligands derived from 2,6-diacetylpyridine and either semicarbazide[1,2] or pyridylhydrazine.[3] In addition, a pentadentate macrocycle was shown to give PBP complexes with Mn^{II} and Zn^{II}.[4] We now report the synthesis and characterization of the first PBP complex of Cr^{III}. Our results suggest that PBP complexes may be synthesized for a much larger variety of metal ions than previously believed possible. Also, the existence of stable PBP complexes of Cr^{III} and other transition metals suggests that PBP complexes are reasonable intermediates in S_N2 type reactions of octahedral molecules.

Chromium nitrate in ethanol–benzene was heated and stirred with an equimolar amount of 2,6-diacetylpyridine bis-semicarbazone (dapsc), until a clear green-black solution was obtained. After cooling and standing, the crude product slowly came out of solution. Recrystallization from aqueous ethanol gave brown crystals whose i.r. spectrum was similar to that of other dapsc complexes.[5]

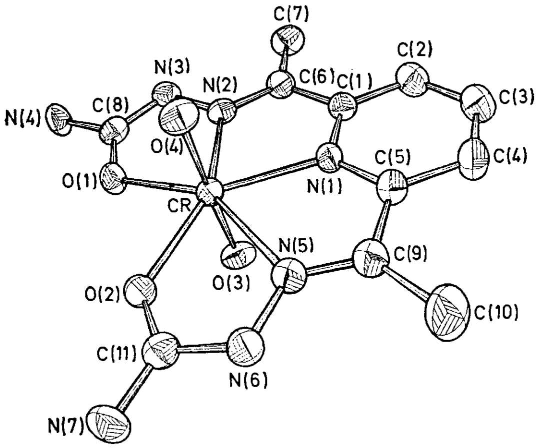

Figure. An ORTEP drawing of the diaqua-(2,6-diacetylpyridine bis-semicarbazone)chromium(III) cation showing the pentagonal bipyramidal geometry. Pertinent distances and angles are: Cr–N(1), 2·177(3); Cr–N(5), 2·023(3); Cr–N(2), 2·397(4); Cr–O(2), 1·979(3); Cr–O(1), 2·173(3); Cr–O(3), 1·978(3); and Cr–O(4), 1·953(3) Å; ∠ N(1)–Cr–N(5), 74·5(1); N(5)–Cr–O(2), 76·6(1); O(1)–Cr–O(2), 76·4(1); O(1)–Cr–N(2), 66·6(1), and N(2)–Cr–N(1), 66·2(1)°.

The magnetic moment was determined by the n.m.r. shift method to be 4·05 ± 0·03 Bohr magnetons which corresponds to 3·17 unpaired electrons.[6] The i.r. and magnetic data were in agreement with the formulation of a high-spin Cr^{III} PBP complex. An *X*-ray crystal structure study of the brown product was undertaken.

Crystal data: $C_{11}H_{22}CrN_9O_{12}$, $[Cr(dapsc)(OH_2)_2]^{+3}(NO_3^-)_2(OH^-),H_2O$ $M = 524{\cdot}34$, monoclinic, space group $P2_1/n$, $a = 8{\cdot}621(2)$, $b = 13{\cdot}854(5)$, $c = 17{\cdot}467(6)$ Å, $\beta = 90{\cdot}33(3)°$ $D_m = 1{\cdot}67$ g cm^{-3}, $Z = 4$, $D_c = 1{\cdot}669$ g cm^{-3}. The intensity data were measured using a Syntex P$\bar{1}$ diffractometer with a variable-speed scan technique, with graphite-monochromatized Mo-K_α radiation. The structure was solved by the heavy-atom method and refined by least-squares techniques to a final R value of 0·045 for the 1982 reflections used in the analysis.

The Figure clearly shows the PBP nature of the complex. The small deviations of the five donor atoms from planarity (in Å × 10^3) are −24 for N(1), −23 for N(5), +61 for N(2), +60 for O(2), and −75 for O(1). These deviations result in part from steric interactions and tend to increase the nonbonded contacts between the oxygen atoms.

The three Cr–N distances are not equal [Cr–N(1), 2·177(3); Cr–N(5), 2·023(3); Cr–N(2), 2·397(4) Å] but the average value of 2·20 Å is identical to the average Fe–N distance of 2·20 Å found in the $[Fe(dapsc)Cl_2]^+$ cation.[5] The asymmetry in the Fe and Cr compounds is puzzling since other PBP complexes with dapsc such as $[M(dapsc)(Cl)(H_2O)]^+$ with M = Mn, Fe, Co, or Zn are reasonably symmetrical.[1,2,5] Whether the smaller size of the +3 ions or the spin state is responsible for the inequality of the M–N distances cannot be decided at the moment, but further studies are in progress.

The appearance of the hydroxide ion was unexpected but not unreasonable considering the starting materials, $[Cr(NO_3)_3],9H_2O$, the solvents used, and the propensity of Cr^{III} to form hydroxo-species.[7] There is extensive hydrogen bonding in the crystal involving virtually all the hydrogen atoms located in the difference Fourier synthesis.

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