A Pentagonal Bipyramidal Indium(III) Complex: Synthesis and Characterization of Diaqua(2,6-diacetylpyridinedisemicarbazone)indium(III) Hydroxide Dinitrate

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Seven coordination is still a relatively rare coordination number [1, 2]. In fact for many ions there are either no known examples or at best only one or two. The group IIIA elements Ga, In, and Tl have no examples of complexes with a coordination number of seven. Our success in synthesizing and characterizing complexes with a pentagonal bipyramidal geometry using planar pentadentate ligands [3, 4] prompted us to investigate the group IIIA ions Ga, In and Tl. We now wish to report our synthesis and characterization of the first pentagonal bipyrimidal complex of In(III), the diaqua(2,6-diacetylpyridinedisemicarbazone)indium(III) cation.

Hydrated indium nitrate in a minimum amount of water was added to a slurry of the ligand DAPSC, 2,6-diacetylpyridinedisemicarbazone in 50 ml of ethanol. The suspension was heated to about 50 °C with stirring. After about 30 min, water was added slowly until the suspension cleared. Then the solution was filtered and cooled. Evaporation of the filtrate gave pale yellow crystals suitable for diffraction studies.

Crystal Data: $\text{In(DAPSC)(H}_2\text{O)}_2{}^{3+}\cdot 2\text{NO}_3{}^{-}\cdot\text{OH}^{-}$, $C_{11}H_{20}N_9O_{11}In$, M = 569.15, monoclinic, $P2_1/n$, a = 11.750(7), b = 14.762(10), c = 12.029(9) Å, β = 105.81(5)°, V = 2008 Å^3, Z = 4, D_m = 1.88, D_c = 1.883 g cm^{-3}, crystal size 0.31 × 0.31 × 0.14 mm. A P$\bar{1}$ diffractometer, a variable scan technique (1 to 24°/min), and graphite monochromatized MoKα radiation (0.70926 Å) were used to measure the intensity data. The complex is isomorphous with the corresponding Sc(III) complex [5], and the Sc coordinates were used for the starting parameters for the least-squares refinement. A difference Fourier synthesis after the anisotropic refinement was used to locate all the hydrogen atoms which were included in subsequent calculations. The final $R = \Sigma|\Delta F|/\Sigma/F_{\text{obs}}$ value was 0.052.

The pentagonal bipyramidal cation $\text{In(DAPSC)(H}_2\text{O)}_2{}^{3+}$ is shown in Fig. 1, together with the atomic numbering and thermal ellipsoids. The ligand and metal ion deviate only slightly from planarity. The two semicarbazone side arms are twisted by 1.5 and 2.1° relative to the plane of the pyridine ring. The deviations from the plane defined by In, N(1), N(2), N(5), O(1), and O(2) range from −0.017 to 0.030 Å. The In^{3+} and Sc^{3+} complexes with DAPSC have some of the smallest deviations from planarity that we have found in the first row DAPSC complexes that we have studied.

The average In–O distance of 2.164(36) Å is surprisingly close to the value of 2.132(8) Å found in the octahedral $\text{In(acetylacetonato)}_3$ and related complexes [6]. In fact the axial In–O distances of 2.134 and 2.154 Å are slightly shorter than the distances observed in the five coordinate $\text{InCl}_3\ (\text{hexamethylphosphoramide})_2$ complex of 2.175(10) and 2.185(11) Å [7]. However, the In–N distances average 2.280(28) Å which appears to be longer than expected on the basis of the In–O distances. A complete analysis of the distances in In(III) complexes is in progress and will be presented in more detail in a future publication.

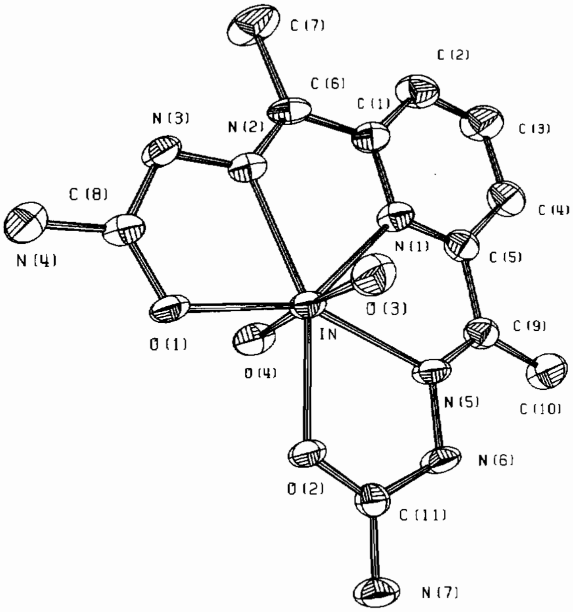

Fig. 1. An ORTEP drawing of the pentagonal bipyramidal diaqua(2,6-diacetylpyridinedisemicarbazone)indium(III) cation. Pertinent distances (±0.005 Å) involving the In atom are: N(1) 2.272, N(2) 2.257, N(5) 2.310, O(1) 2.151, O(2) 2.216, O(3) 2.135, and O(4) 2.154. The angles (±0.2°) around the In atom are: N(1)–N(2) 70.2, N(1)–N(5) 67.3, N(2)–O(1) 71.3, N(5)–O(2) 69.2, O(1)–O(2) 82.0 and O(3)–O(4) 174.7.

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