

Supporting Information:

Figure S1

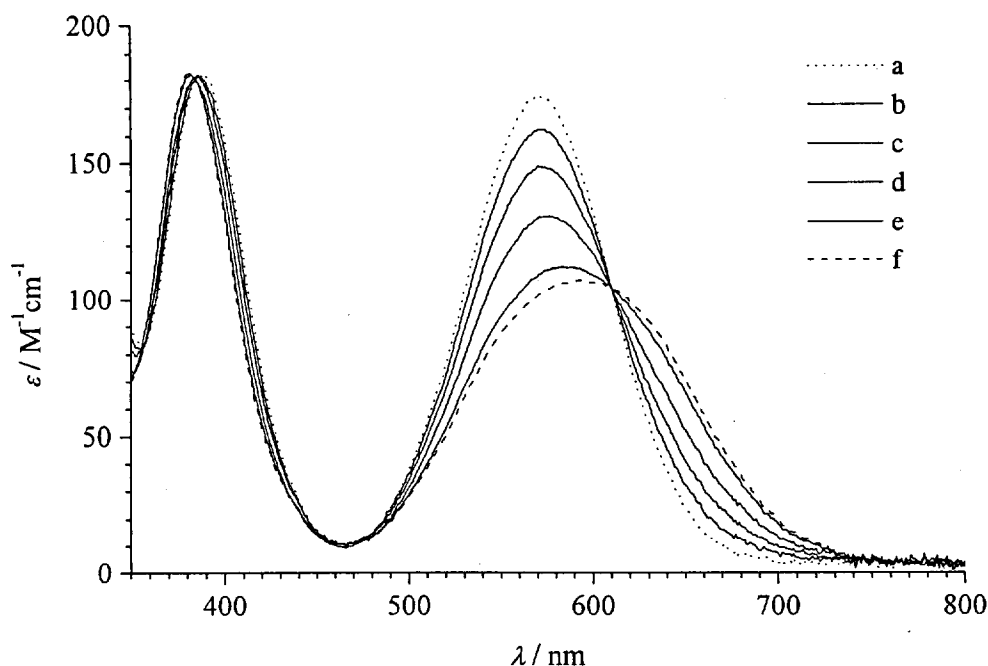


Figure Captions

Figure S1: Variation at 25 °C with acid concentration of the optical spectra of solutions of the $[\text{Co}([\text{3}^5]\text{adz})(\text{CO}_3)]\text{ClO}_4$ salt (**1c**), $I = 5.0 \text{ M}$ ($\text{CF}_3\text{SO}_3\text{H} / \text{CF}_3\text{SO}_3\text{Na}$). From these spectra K_a was determined to $0.54(2) \text{ M}^{-1}$ at 25 °C. **a:** 5.0 M $\text{CF}_3\text{SO}_3\text{Na}$. **b:** 0.1 M $\text{CF}_3\text{SO}_3\text{H} / 4.9 \text{ M}$ $\text{CF}_3\text{SO}_3\text{Na}$. **c:** 0.3 M $\text{CF}_3\text{SO}_3\text{H} / 4.7 \text{ M}$ $\text{CF}_3\text{SO}_3\text{Na}$. **d:** 0.9 M $\text{CF}_3\text{SO}_3\text{H} / 4.1 \text{ M}$ $\text{CF}_3\text{SO}_3\text{Na}$. **e:** 5.0 M $\text{CF}_3\text{SO}_3\text{H}$. **f:** calculated spectrum for the $[\text{Co}([\text{3}^5]\text{adz})(\text{HCO}_3)]^{2+}$ ion (**2**).

Figure S2: View of the cation in $[\text{Co}([\text{3}^5]\text{adz})(\text{SO}_4)]\text{AsF}_6 \cdot \text{H}_2\text{O}$ (**3a**).

Appendix S1:

X-ray Crystal Structures of $[\text{Co}([\text{3}^5]\text{adz})(\text{SO}_4)]\text{AsF}_6 \cdot \text{H}_2\text{O}$ (**3a**).

Crystal data for the compound are listed in Table 1.

Compound **3a** consists of $[\text{Co}([\text{3}^5]\text{adz})(\text{SO}_4)]^+$ and AsF_6^- ions and one water molecule. Bond lengths and angles of the coordination sphere around the cobalt ion are listed in Table 2. The SO_4^{2-} ligand is coordinated as bidentates giving a *cis* configuration as found in the nickel complexes with the ligand $[\text{2}^4.\text{3}^1]\text{adamanzane}$,²⁶ and with $[\text{3}^5]\text{adamanzane}$.²⁵ In the present structure, the angles around the cobalt ion show substantial distortions with respect to those of a regular octahedron. This is mainly due to the very small angle O(1)-Co-O(2) of $72.56(13)^\circ$. As a consequence, the SO_4^{2-} is distorted from regular tetrahedral symmetry, the O(1)-S-O(1)ⁱ (ⁱ = $x, \frac{1}{2} - y, z$) being $99.0(2)^\circ$. These value is similar to that found in $[(\text{trpn})\text{Co}(\eta^2\text{-SO}_4)]\text{ClO}_4 \cdot \text{H}_2\text{O}$.⁶⁰

As found in $[(\text{trpn})\text{Co}(\eta^2\text{-SO}_4)]\text{ClO}_4 \cdot \text{H}_2\text{O}$ ⁶⁰ the S-O bonds in $[\text{Co}([\text{3}^5]\text{adz})(\text{SO}_4)]\text{AsF}_6 \cdot \text{H}_2\text{O}$ (**3a**) are shorter to the non-coordinating oxygens (1.436(4) and 1.449(4) Å) than to the coordinated oxygens (1.515(2) Å).

In the present three structures the Co-N bonds are similar and so are the Co-O bond lengths.

In the sulphato compound (**3a**) the two rings containing N(1) are in a chair conformation, the two rings involving N(3) are in a twist-boat form, whereas the fifth ring is in a half-chair conformation.

The N(2)⋯N(4) distance between the bridgehead nitrogen atoms is 3.211(5) Å (here it is the N(2)⋯N(2)ⁱ distance, (ⁱ = $x, \frac{1}{2} - y, z$)). The N(1)⋯N(3) distance is 4.023(5) Å. The hydrogen atoms attached to N(1) and N(3) are in the structure oriented away from the inorganic ligand. The hydrogen atom at N(1) is involved in a hydrogen bond with O(2) ($\frac{1}{2} + x, \frac{1}{2} - y, \frac{3}{2} - z$) of 2.981(5) Å (D⋯A), and between the hydrogen atom H(1Ow) attached to Ow and O(3) ($1 + x, y, z$) there is a hydrogen bond of 2.682(7) Å (D⋯A).

