New Hydrogen Peroxide Adducts of Alkali Metal Tetracyanoplatinates

\(A_2[Pt(CN)_4] \cdot H_2O_2\) \((A = K, Rb, Cs)\)

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Dedicated to Professor Otto J. Scherer on the occasion of his 75th birthday

The title compounds have been synthesized by adding hydrogen peroxide to an aqueous solution of \(A_2[Pt(CN)_4]\) \((A = K, Rb, Cs)\). They grow as yellow needles after concentrating and cooling to 4 °C. The structures were elucidated from single crystal analysis. The isostructural compounds crystallize monoclinically, in space group \(C2/c\) with \(Z = 4\). K\(_2\)Pt(CN)\(_4\)·H\(_2\)O\(_2\): \(a = 13.3751(7), b = 11.2713(6), c = 6.5461(3) \text{ Å}, \beta = 105.432(1)^\circ, V = 951.3(3) \text{ Å}^3\). Rb\(_2\)Pt(CN)\(_4\)·H\(_2\)O\(_2\): \(a = 13.6103(2), b = 11.6759(1), c = 6.5683(7) \text{ Å}, \beta = 106.588(2)^\circ, V = 1000.3(2) \text{ Å}^3\). Cs\(_2\)Pt(CN)\(_4\)·H\(_2\)O\(_2\): \(a = 13.9569(2), b = 12.2023(2), c = 6.5857(9) \text{ Å}, \beta = 107.590(3)^\circ, V = 1069.1(2) \text{ Å}^3\). As a remarkable feature, the hydrogen bonds O–H···N vary significantly with the cation size: in the Cs compound the O–H bonds are weakest, and the N···H interactions are strongest. All three compounds were characterized by differential thermal analysis, thermogravimetry and infrared spectroscopy.

Key words: Crystal Structure, Alkali Metal Tetracyanoplatinate, Hydrogen Peroxide, Infrared Spectroscopy