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 $Z = 4$. $K_2Pt(CN)_4 \cdot H_2O_2$: a = 13.3751(7), b = 11.2713(6), c = 6.5461(3) Å, β = 105.432(1)°, V = 951.3(3) Å^3. $Rb_2Pt(CN)_4 \cdot H_2O_2$: a = 13.6103(2), b = 11.6759(1), c = 6.5683(7) Å, β = 106.588(2)°, V = 1000.3(2) Å^3. $Cs_2Pt(CN)_4 \cdot H_2O_2$: a = 13.9569(2), b = 12.2023(2), c = 6.5857(9) Å, β = 107.590(3)°, V = 1069.1(2) 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