

Crystal Engineering towards Design of Macrocyclic Coordination Compounds: Crystal Structure of Rubidium Tetrachloro- and Tetracyanoaurate(III) Complexes with 18-Crown-6

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The new macrocyclic complexes of composition Rb(18-crown-6)AuX₄ (X = Cl (**1**) and CN (**2**)) have been prepared and characterized by X-ray crystallography (**1**: monoclinic, space group P2₁/n, with $a = 8.747(1)$, $b = 8.366(1)$, $c = 15.404(1)$ Å; $\beta = 104.37(1)^\circ$, $V = 1092.0(3)$ Å³, $Z = 2$; final $R1 = 0.025$ for 2030 independent reflections used; **2**: monoclinic, space group P2₁/c, with $a = 14.765(3)$, $b = 17.134(3)$, $c = 8.855(2)$ Å; $\beta = 90.20(1)^\circ$, $V = 2240.2(8)$ Å³, $Z = 4$; final $R1 = 0.080$ for 2034 independent reflections used). Both structures consist of Rb(18-crown-6)⁺ cations (A) and complex aurate(III) anions AuX₄⁻ (B). Complex **1** has a linear polymeric array -A-B-A-B- (Rb-Cl 3.604(3), 3.654(3) Å) with the rubidium ions disordered 0.276(2) Å above and below the crown ether plane (Rb-O 2.819(5)-2.884(5) Å, av. 2.846(5) Å). The positioning of the rubidium atom away from the center of the 18-crown-6 is effected by the packing of the Rb(18-crown-6)⁺ and AuCl₄⁻ moieties, and by the resemblance in the charge and symmetry of the cationic and anionic parts of the structure. Complex **2** has a zig-zag polymeric array -A-B-A-B- (Rb-N 2.92(2), 2.94(1) Å) with orthogonal disposition of Rb(18-crown-6)⁺ and Au(CN)₄⁻ planes. The rubidium atom is situated 0.90(2) Å above the mean plane of the macrocyclic oxygen atoms (Rb-O 2.93(5)-3.15(4) Å) and adopts a typical “sunrise coordination”.

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