SbCl₃, BiCl₃ and Na⁺ Complexes of Maleonitrile-Dithiacrown Ethers: Synthesis, Crystal Structures and DEP-MS Experiments

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Z. Naturforsch. 54b, 799–806 (1999); received September 24, 1998

Maleonitrile-Dithiacrown Ether Complexes, Antimony and Bismuth Trichlorides, Sodium, Crystal Structure, DEP-MS

The reactions of MCl₃ (M = Sb, Bi) with maleonitrile-dithia-15-crown-5 (mn-15S₂O₃) and maleonitrile-dithia-18-crown-6 (mn-18S₂O₄) in MeCN yielded the complexes [MCl₃(mn-15S₂O₃)] {M = Sb(1), Bi(2)} and [MCl₃(mn-18S₂O₄)] {M = Sb(3), Bi(4)}, respectively. The pyramidal MCl₃ units are coordinated very weakly to the three oxygen and two sulphur donor atoms of mn-15S₂O₃ in 1 and 2, and to the four oxygen donor atoms of mn-18S₂O₄ in 3 and 4. Both mn-15S₂O₃ complexes, 1 and 2, crystallize isotypically in the monoclinic space group P2(1)/n with four formula units per unit cell, while the isotypic mn-18S₂O₄ complexes, 3 and 4, are triclinic, space group P-1, with two formula units per unit cell. In the SbCl₃ complexes, 1 and 3, the mean contact distances between the Sb centres and the macrocyclic donor atoms are longer than the corresponding distances in their isostructural BiCl₃ analogues, 2 and 4, which may reflect a stereochemical activity of the Sb³⁺ lone pair. Under the conditions of DEP-MS experiments with 1 and 3 the monocationic SbCl₂⁺ complexes [SbCl₂(L)]⁺ (L = mn-15S₂O₃, mn-18S₂O₄) were detected.

NaSbCl₆ and mn-18S₂O₄ in MeCN furnished the 2:1 complex [Na(mn-18S₂O₄)₂]SbCl₆ {(5)SbCl₆}. In the complex cation 5 the sodium atom is coordinated sandwich-like through the eight oxygen atoms of two mn-18S₂O₄ molecules. Compound (5)SbCl₆ crystallize in the triclinic space group P-1 with two formula units per unit cell.

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