Crystal Structure and NQR Studies of Compounds (RH)[ZnBr₃(R)], (RH)₂[ZnBr₄] and [ZnBr₂(R)₂] (R = Py, n-MePy; n = 2, 3, 4); on the Dominant Stability of the Monoanionic Complexes over the Dianionic and Neutral Species

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Z. Naturforsch. 2011, 66b, 27–35; received August 27, 2010

The monoanionic complexes (C₅H₅NH)[ZnBr₃(C₅H₅N)] (1) and (n-CH₃C₅H₄NH)[ZnBr₃(n-CH₃C₅H₄N)] (n = 2 (2), 3 (3), 4 (4)) were prepared by crystallization from ethanol solutions through redistribution reactions between the corresponding dianionic complexes (C₅H₅NH)₂[ZnBr₄] (5) and (n-CH₃C₅H₄NH)₂[ZnBr₄] (n = 2, 3 (6), 4 (7)) and the neutral complexes [ZnBr₂(C₅H₅N)₂] (10) and [ZnBr₂(n-CH₃C₅H₄N)₂] (n = 2 (8), 3, 4 (9)). The crystal structures of 1, 4, 9, and 10 were determined; 1: triclinic, P ̅1, a = 7.6957(5), b = 7.7975(4), c = 12.4768(8) Å, α = 90.857(5), β = 95.917(5), γ = 107.899(6)°, Z = 2, 150 K; 4: monoclinic, P ̅2₁/c, a = 14.8369(6), b = 13.9504(5), c = 8.0041(3) Å, β = 96.318(4)°, Z = 4, 299 K; 9: monoclinic, P ̅2₁/c, a = 14.2883(5), b = 8.0269(3), c = 13.6031(5) Å, β = 100.581(4)°, Z = 4, 150 K; 10: monoclinic, P ̅2₁/c, a = 8.7388(5), b = 17.9730(10), c = 8.5452(5) Å, β = 100.024(6)°, Z = 4, 300 K. The cation and anion are paired up via bifurcated hydrogen bonds in the structure of 1 and via a normal N–H···Br hydrogen bond in the structure of 4.

8¹Br NQR resonance lines coinciding in number with the Br atoms in the chemical formulae were observed for the compounds 1–5 and 7–9 throughout the temperature range from 77 to ca. 320 K. The comparison between the net charges on the Br atoms obtained by the Townes-Daily analysis or by the Mulliken population analysis seems to indicate that the formation of the intermolecular N–H···Br hydrogen bonds and the π–π and the CH₃–π interactions in the crystal structures of the monoanionic complexes are the driving forces to the redistribution reactions.

Key words: Zinc(II) Bromide Complexes, 8¹Br NQR, Crystal Structure, Intermolecular Interactions