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Crystal and molecular structures of *N*-(1-adamantyl)pyridinium diiodobromide

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The iodination of *N*-(1-adamantyl)pyridinium bromide with an equimolar amount of molecular iodine yields the salt $C_{15}H_{20}Br_{0.89}I_{2.11}N[C_{15}H_{20}^{+}\cdot 0.41(I_3^-)\cdot 0.30(Br_2I^-)\cdot 0.29(BrI_2^-)]$ and its crystal structure was studied by X-ray diffraction.

Adamantane-containing compounds have been used as antimicrobial and antipsychotic agents.[1–3] To estimate the biological activity and other properties of adamantyl-containing cation iodohalides directly depending on the speciation of iodine in solutions and in a crystal state, the structural features and stability of iodine organic complexes should be studied.[4]

The synthesis and investigation of structural characteristics and thermodynamic stability of nitrogen-containing organic cation iodohalides[5–8] are of considerable current interest due to the unique σ-acceptor properties of the iodine molecule. The synthesis and structure of polyiodide systems, the nature of their chemical bonds, optical magnetic resonance investigations, X-ray diffraction data and conductometric measurements were surveyed.[9]

Quantum-chemical studies and X-ray diffraction analysis can be useful to establish the relative stability of iodohalides in a gas phase and solutions.[10–12] The quantum-chemical calculation data (gas phase, the HW basis set) and spectrophotometric estimation of the stability of N-containing cation iodohalides (N-RPyXI_2, where R = H, Me, Et or Pr and X = Cl, Br or I) in chloroform solutions showed that the ability to retain molecular iodine was related to the nature of the anion.[13–15] For the directed synthesis of N-propylisoquinolinium diiodobromide,[16] we studied the effect of iodine-coordinated solvents on the composition and crystal structure since the disproportionation of unsymmetrical anions (I_2Br^-, I_2Cl^-) gives rise to various compounds. According to X-ray diffraction data for tetraphenylarsonium diiodobromide, a superposition of I_3^- and Br_2I^- was observed with ratios of 0.526 and 0.474, respectively. The formation of the I_3^- and Br_2I^- ions occurs *via* the disproportionation of I_2Br^- under the action of a solvating solvent on crystallization.[17]

For the directed synthesis and characterization of pyridinium interhalide *N*-derivatives we initially performed an *ab initio* quantum-chemical study of the compounds N-RPyXI_2, where R = H, Me, Et or Pr and X = Cl, Br or I. The transition from diiodochloride to triiodide decreased the $RPy^+\cdots XI_2^-$ interaction and increased the ability to retain molecular iodine in the complex. The same sequence in the stability of iodohalides was found in *N*-cetylpyridinium. In chloroform solutions, *N*-cetylpyridinium chloride and bromide coordinate one iodine molecule, and *N*-cetylpyridinium iodide forms stable pentaiodide.[13]

The aim of this work was to synthesize *N*-(1-adamantyl)-pyridinium diiodobromide and to study its molecular and crystal structures in a solid phase and also to estimate the limiting amount of iodine molecules coordinated by *N*-(1-adamantyl)-pyridinium bromide in a chloroform solution and the stability of formed interhalides.

The new salt $C_{15}H_{20}Br_{0.89}I_{2.11}N[C_{15}H_{20}^{+}\cdot 0.41(I_3^-)\cdot 0.30(Br_2I^-)\cdot 0.29(BrI_2^-)]$ **1**[†] was synthesized by the iodination of *N*-(1-adamantyl)pyridinium bromide.

The number of iodine molecules coordinated by *N*-(1-adamantyl)pyridinium bromide and the stability of diiodobromide were determined using the average iodine number function $\bar{n}_{I_2}$ described previously.[18] For this purpose, the spectrophotometric method[‡] was used to study the equilibrium in the organic bromide – molecular iodine system in chloroform. The unbound iodine ($[I_2]$) concentration was calculated from the absorbance at the absorption band maximum (A_{max}) of elemental iodine.

The dependence of the average iodine number on unbound iodine concentration allowed us to make a conclusion concerning the mechanism of complex formation and the limiting number of iodine molecules coordinated by the halide molecule in chloroform. The average iodine numbers for compound **1** were $0 < n_{I_2} < 2$. The stability constants of *N*-(1-adamantyl)-pyridinium iodobromide were calculated by equations (1) and (2).

$$\frac{\bar{n}_{I_2}}{(1-\bar{n}_{I_2})[I_2]} = \beta_1 + \beta_2 \frac{(2-\bar{n}_{I_2})[I_2]}{(1-\bar{n}_{I_2})}; \quad (1)$$

$$\bar{n}_{I_2} = \frac{\beta_1[I_2] + 2\beta_2[I_2]^2}{1 + \beta_1[I_2] + \beta_2[I_2]^2}; \quad (2)$$

$\lg\beta_1 = 4.74\pm0.08$; $\lg\beta_2 = 8.27\pm0.07$ [equation (1)]
$\lg\beta_1 = 4.74\pm0.10$; $\lg\beta_2 = 8.27\pm0.08$ [equation (2)]

† *Synthesis of* **1**. *N*-(1-Adamantyl)pyridinium diiodobromide was synthesized by mixing equimolar amounts of solutions of organic cation bromide (CAS #19984-57-7) and iodine in chloroform. After the removal of the solvent at room temperature, dark brown needle crystals were formed. Recrystallization was accomplished by slowly saturating a solution of diiodobromide **1** in chloroform by light petroleum vapour. Mp 127–129 °C. ^{1}H NMR ($CDCl_3$, 250 MHz) δ: 1.87–2.45 (m, 15H, adamantyl), 8.27 (t, 2H, β-H pyridine), 8.55 (t, 1H, γ-H pyridine), 9.15 (d, 2H, α-H pyridine, J_1 5.9 Hz). The coordination of a iodine molecule by halide leads to displacement of α-protons signal position of pyridine ring in ^{1}H NMR spectrum in a strong field by 0.46 ppm. ^{1}H NMR spectra were recorded on a Bruker DPX-250 spectrometer.

‡ Electronic absorption spectra of chloroform solutions with different organic cation bromide concentrations and elemental iodine were recorded on a Specord UV-VIS spectrophotometer in cells with an optical path length of 1.0 (50000–30000 cm^{-1}) or 5.0 cm (30000–14000 cm^{-1}). The initial solutions contained 1.0×10^{-3} mol dm^{-3} of *N*-(1-adamantyl)pyridinium bromide and elemental iodine in chloroform. The concentration of elemental iodine was varied at a constant concentration (5.0×10^{-5} mol dm^{-3}) of organic bromide.

N-(1-Adamantyl)pyridinium bromide coordinates two iodine molecules in chloroform. The presence of polyiodides (diiodobromides) was detected in chloroform solutions, with the triiodide and pentaiodide ions as the predominant species[7,9] but with the I_2Br^- ion only for diiodobromides.[8] A large cation with a high symmetry has been employed to obtain thermally stable iodo-bromide in a chloroform solution.

The molecular and crystal structures of salt **1** were studied by X-ray diffraction.§ The crystal structure of the salt $C_{15}H_{20}Br_{0.89}I_{2.11}N$ is formed by ($C_{15}H_{20}N^+$) cations and the anions I_3^-, Br_2I^- and BrI_2^- disordered at two positions (An1 and An2). The cations and anions form piles of molecules perpendicular to the *a* axes (Figure 1). Pyridine rings have an almost planar configuration with slightly deformed C–C bonds and C(6)–C(10)–C(14) dihedral angle of 169.6°. The basic geometrical parameters of the adamantyl fragment, in particular C–C bond lengths of 1.528(4)–1.541(4) Å are similar to those in *N*-adamantylbenzimidazolium.[19]

The formation of the I_3^- and Br_2I^- ions occurs *via* disproportionation of I_2Br^- under the action of the solvating solvent on crystallization:

$$2CtBrI_2 + Solv = CtBr_2I_{(Solv)} + CtI_{3(Solv)}.$$

The cation–anion pair ($C_{15}H_{20}N^+$)($I_2Br^-/I_3^-/IBr_2^-$) interaction in the crystal was characterized by the formation of I(Br)···H contacts, close to the sum of van der Waals radii of 3.14 Å.[20] The contacts of iodine and bromine atoms with hydrogen atoms up to 3.3 Å are shown in Table 1.

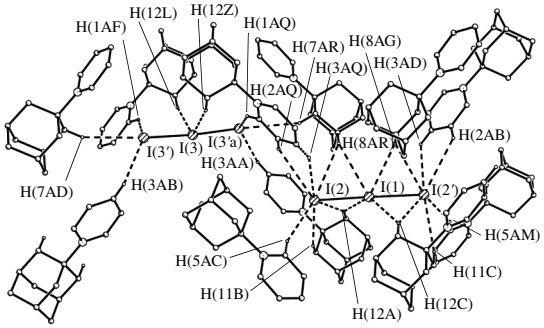

Figure 1 Cation–anion interactions in a crystal of **1**. Atoms of bromine are not specified for simplicity.

§ *X-ray diffraction*. Crystals **1**, $C_{15}H_{20}Br_{0.88}I_{2.13}N$ (M = 553.90), rhombic, at 100 K, space group *Pbcn*, a = 13.1275(11), b = 14.6753(12) and c = 17.8351(15) Å, V = 3435.9(5) Å^3, Z = 8, d_{calc} = 2.142 g cm^{-3}. The experimental set of 29204 reflections was obtained on a Bruker SMART APEX2 diffractometer with a CCD detector at 100(2) K (MoKα radiation, $2\theta_{max}$ = 52°) from a 0.45×0.30×0.15 mm single crystal. The absorption correction (μ = 5.910 mm^{-1}) was used by the SADABS program[21] (transmission coefficients T_{max} and T_{min} were 0.413 and 0.135, respectively). After averaging equivalent reflections, 3378 unique reflections were obtained (R_{int} = 0.0744) and used for structure solution and refinement. The structure was solved by direct methods, all non-hydrogen atoms were refined on F^2_{hkl} in the anisotropical approximation. Atoms of bromine in one independent anion I(2)[Br(2)]–I(1)–I(2a)[Br(2a)] (An1) take one position in the ratio I(2):Br(2) = 0.47:0.53. In the other anion I(3′)[Br(3)]–I(3)–I(3′a)[Br(3a)], atoms I(3′) and Br(3) (An2) disordered on two positions with occupations of 0.65 and 0.35, respectively. The final uncertainty factors were as follows: R_1 = 0.0220 [on F_{hkl} for 2620 reflections with $I > 2\sigma(I)$], wR_2 = 0.0440 (on F^2_{hkl} for all 3378 independent reflections), GOOF = 1.009, 193 refined parameters, the maximum and minimum residual electron density peaks were 0.910 and –0.747 eÅ^{-3}, respectively. All calculations were performed using the SHELXTL PLUS5 programs package.[22]

CCDC 775014 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif. For details, see 'Notice to Authors', *Mendeleev Commun.*, Issue 1, 2010.

Table 1 Interatomic contacts in compound **1**.

Contact	*d*/Å	Contact	*d*/Å
I(1)···H(8)	3.23×2	I(1)···H(12)	3.11×2
I(2)···H(2)	3.28	I(2)···H(3)	3.25
I(2)…H(5)	2.96	I(2)···H(8)	3.26
I(2)···H(11)	3.26	I(2)···H(12)	3.21
I(3)···H(12)	3.05×2	I(3′)···H(1)	2.10
I(3′)···H(3)	3.17	I(3′)···H(7)	3.28
Br(2)···H(2)	3.28	Br(2)···H(3)	3.26
Br(2)···H(5)	2.96	Br(2)···H(8)	3.26
Br(2)···H(11)	3.26	Br(2)···H(12)	3.21
Br(3)···H(1)	3.05	Br(3)···H(3)	3.18
Br(3)···H(7)	3.27		

The coordination capacities of anions An1 and An2 are different. Anion An1 is surrounded by eight cations, at that terminal atoms form the shortest contact (2.96 Å) with the H(5a) atom of the pyridine ring; anion An2 is surrounded only by six cations with the shortest contact (3.05 Å) with the H(12) atom of adamantyl. Note that the basic contacts occur due to the H atoms of pyridine ring, and only hydrogen atoms of the $(CH_2)_3CN$ group of adamantyl substituent links cations and anions in a crystal structure.

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