Untersuchungen an Polyhalogeniden, XXXVI [1].
Zur Kenntnis des Oktaiodid-Ions I_8^{2-}: Darstellung und Kristallstruktur des $[(Crypt\text{-}2.2.2)H_2]I_8$, des $[Ni(phen)_3]I_8 \cdot 2CHCl_3$ und der Bis(N-alkylurotropinium)oktaiodide $(UrR)_2I_8$ mit R = Methyl und Ethyl

Studies on Polyhalides, XXXVI [1].
On the Octaiodide Ion I_8^{2-}: Preparation and Crystal Structure of $[(Crypt\text{-}2.2.2)H_2]I_8$, of $[Ni(phen)_3]I_8 \cdot 2CHCl_3$ and of the (N-alkylurotropinium)octaiodides $(UrR)_2I_8$ with R = methyl and ethyl

Arista Gräfe-Kavoosian, Shida Nafepour, Klaus Nagel, Karl-Friedrich Tebbe*

Institut für Anorganische Chemie der Universität zu Köln, Greinstraße 6, D-50939 Köln

Z. Naturforsch. **53 b,** 641–652 (1998); eingegangen am 2. März 1998

Cryptate, N-Alkyl-Urotropinium Cation, Tris(1,10-phenanthroline)nickel(II), Octaiodide, Crystal Structure

The new compound $[(Crypt\text{-}2.2.2)H_2]I_8$ has been prepared by the reaction of $[(Crypt\text{-}2.2.2)H_2](I_3)_2$ with iodine in methanol. It crystallizes in the orthorhombic space group Pbcn with a = 11.476 (2), b = 13.589 (2), c = 22.888 (2) Å and Z = 4. The crystal structure has been refined to R_F = 0.031 for 1618 reflections. It may be described as a layerlike packing of octaiodide anions I_8^{2-} and diprotonated 2.2.2-Crypt as cations. The non planar octaiodide anion is built up from two triiodide groups and a bridging iodine molecule.

Tris(1,10-phenanthroline)nickel(II) octaiodide bis(chloroform) crystallizes in the monoclinic space group $P2_1/n$ with a = 11.683 (8), b = 21.717 (8), c = 20.752 (5) Å, β = 95.03 (5)° and Z = 4 formula units. The crystal structure has been refined to R_F = 0.058 for 3894 reflections. The structure consists of two chloroform molecules, octahedrally coordinated complex cations $[Ni(phen)_3]^{2+}$ and nonplanar octaiodide anions I_8^{2-} each composed of two asymmetric triiodide units I_3^- weakly associated with an elongated bridging iodine molecule I_2.

The already known structure of bis(N-methylurotropinium) octaiodide, $(UrMe)_2I_8$, has been verified and more accurate crystal data have been collected. The crystal structure has been refined to R_F = 0.045 for 1908 reflections. The compound crystallizes in the monoclinic space group $P2_1/c$ with a = 11.302 (2), b = 9.850 (2), c = 14.188 (2) Å, β = 92.59 (1)° and Z = 2. The anion has the shape of a stretched Z.

The structure of bis(N-ethylurotropinium) octaiodide $(UrEt)_2I_8$ has been determined and a new configuration ($I_3^- \cdot I_5^-$) for octaiodide ions between Z ($I_3^- \cdot I_2 \cdot I_3^-$) and a "broken" configuration (I_3^-, I_5^-) has been observed. The compound crystallizes in the triclinic space group P1 with a = 9.741 (3), b = 11.815 (3), c = 15.426 (3) Å, α = 91.80 (2), β = 107.14 (2), γ = 90.04 (2)° and Z = 2. The crystal structure has been refined to R_F = 0.037 for 3657 reflections.

* Sonderdruckanforderungen an Prof. Dr. K.-F. Tebbe.