I_{16}^{4-} Ions in Crystalline (Theobromine)$_2$.H_2I_8; *X*-Ray Structure of (Theobromine)$_2$.H_2I_8

By Frank H. Herbstein* and Moshe Kapon
(*Department of Chemistry, Technion–Israel Institute of Technology, Haifa, Israel*)

Summary Crystal structure analysis shows that (theobromine)$_2$.H_2I_8 is a polyiodide salt composed of alternating cationic and anionic layers; the former consist of hydrogen-bonded protonated theobromine species and the latter of I_{16}^{4-} polyiodide ions.

Although the polyiodide ions studied so far have many geometrical features in common, their structures all differ in detail. The anion in (theobromine)$_2$.H_2I_8, first prepared by Jorgensen[1] and later by Shaw,[2] fits into this overall pattern; furthermore it occurs as essentially discrete I_{16}^{4-} units and is thus the largest discrete polyiodide anion investigated until now.

The dark blue needle-shaped crystals are triclinic, $a = 14{\cdot}47(1)$, $b = 14{\cdot}07(1)$, $c = 7{\cdot}75(1)$ Å, $\alpha = 91{\cdot}2$, $\beta = 100{\cdot}8$, $\gamma = 91{\cdot}2°$, space group $P\bar{1}$ (from structure analysis), $D_m = 2{\cdot}92$ g cm^{-3}, $D_c = 2{\cdot}95$ g cm^{-3}, $Z = 2$ ($C_{14}H_{18}N_8O_4I_8$ units). Intensities of 4200 reflections were measured on a Stoe semi-automatic Weissenberg diffractometer using graphite-monochromated Mo-K_α radiation. The structure was solved by the Patterson method and refined by least-squares (anisotropic temperature factors for iodine atoms and isotropic temperature factors for other atoms; hydrogen atoms were not considered). The current R-factor is 11% (goodness of fit = 0·96), and the e.s.d.s. of I–I and C–C distances are *ca.* 0·003 and *ca.* 0·05 Å respectively.

There are alternating cationic and anionic layers stacked along the c-axis; a rather similar arrangement is found in (phenacetin)$_2$.HI$_5$.[3] The cationic layer consists of theobromine molecules protonated at N(9) and hydrogen-bonded to one another in both [100] and [010] directions; the anionic layers consist of S-shaped centrosymmetric $I_{16}{}^{4-}$ units. Their detailed structure is shown in the Figure. (Theobromine)$_2$.H$_2$I$_8$ is thus a polyiodide salt and should be formulated explicitly as $(H^+C_7H_8N_4O_2)_4.(I_3{}^-.I_2.I_3{}^-.I_3{}^-.I_2.I_3{}^-)$. The shortest distance between adjacent $I_{16}{}^{4-}$ units is 3·84 Å, similar to that found in the tri-iodide chains in (benzamide)$_2$.HI$_3$;[4] the other interionic distances are typical van der Waals contacts. However, the distance of 3·84 Å represents an interaction sufficiently weak, in our view, for the $I_{16}{}^{4-}$ species to be considered as discrete polyiodide anions.

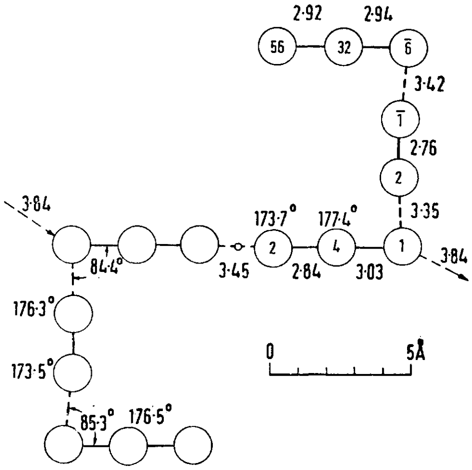

FIGURE. The centrosymmetric $I_{16}{}^{4-}$ ion is shown in projection on (001). The best plane has been calculated through the central I_2--$I_3{}^-$--$I_3{}^-$--I_2 unit and the deviations of all the iodine atoms from this plane are given in units of 10^{-2} Å. The direction of the shortest interionic vector of 3·84 Å is shown.

Financial support from the Deutsche Forschungsgemeinschaft is gratefully acknowledged.

(*Received, 2nd June* 1975; *Com.* 620.)

---

[1] S. M. Jorgensen, *Ber.*, 1869, **2**, 460.
[2] G. E. Shaw, *J. Chem. Soc.*, 1896, **69**, 102.
[3] F. H. Herbstein and M. Kapon, *Nature Phys. Sci.*, 1972, **239**, 153.
[4] J. M. Reddy, K. Knox, and M. B. Robin, *J. Chem. Phys.*, 1964, **40**, 1082.