Inorganic Chemistry
Communication

Inorg. Chem. **2009**, *48*, 9983–9985 **9983**
DOI: 10.1021/ic9015492

Does $[I_3]^+$ Act as an "$[I]^+$" Donor to CH_3CN and N_2O? Structure of $[H_3CCN\text{-}I\text{-}NCCH_3]^+[AsF_6]^-$

Margaret-Jane Crawford, Michael Göbel, Konstantin Karaghiosoff, Thomas M. Klapötke,* and Jan M. Welch

Department of Chemistry and Biochemistry, Ludwig-Maximilian University, Butenandtstrasse 5-13 (Haus D), D-81377 Munich, Germany

Received August 4, 2009

The solid state structure of the $[(CH_3CN)_2I]^+$ cation in $[(CH_3CN)_2I][AsF_6]$ was determined using single crystal X-ray diffraction. The highly reactive cation was prepared by reaction of $[I_3][AsF_6]$ with CH_3CN in liquid SO_2. In the solid state, the CNI backbone consisting of seven atoms is linear and shows a dicoordinate iodine center. The ability of $[I_3][AsF_6]$ to act as a source of "$[I]^+$" to CH_3CN and N_2O is compared, and the computed structures of the $[CH_3CNI]^+$, $[(CH_3CN)_2I]^+$, $[IN_2O]^+$ and $[ION_2]^+$ cations are discussed.

Homopolyatomic halogen cations have been synthesized and isolated in the solid state at room temperature for all of the halogens except fluorine and astatine.[1] Out of the group 17 elements, the largest number of isolated and structurally characterized (X-ray) examples of homopolyatomic cations has been described for iodine, namely $[I_2]^+$,[2a] $[I_3]^+$,[2b] $[I_4]^{2+}$,[2c−e] $[I_5]^+$,[2f] and $[I_{15}]^{3+}$.[2g] The above-mentioned $[I_x]^{y+}$ cations can be prepared by the oxidation of elemental iodine using AsF_5 or SbF_5.[1a] Salts of the "$[I]^+$" cation have so far not been isolated under standard conditions. Although the halogen cations have been of great interest for many years, reports about their reactivity are scarce.

The ability of $[I_3]^+$ salts to act as "$[I]^+$" cation transfer reagents has been previously discussed in the literature;[3] however, the structure of a simple salt formed by the reaction of a nitrile with $[I_3][AsF_6]$ has not been determined. The first reported complex, which had been formed using the isolated salt of a homopolyatomic iodine cation as a reagent and showed the coordination of a neutral nitrogen base to the "$[I]^+$" cation in a 1:1 stoichiometry, was $[H_3CCN\text{-}I]^+[AsF_6]^-$.[4a] This report proposed that under the reaction conditions applied, CH_3CN had effectively displaced I_2 as the better Lewis base to coordinate the $[I]^+$ cation.[5] It was shown that $[I_3][AsF_6]$ was able to react with CH_3CN in liquid SO_2 with the formation of the $[CH_3CNI]^+[AsF_6]^-$ or $[CH_3CN\text{-}I\text{-}NCCH_3]^+[AsF_6]^-$ salts, in addition to I_2, depending on whether a 1:1 or 1:2 ratio of $[I_3]^+[AsF_6]^-$ with CH_3CN in liquid SO_2 was used,[4] and further related salts were reported.[7]

The solid state structures of salts containing $[R\text{-}I\text{-}R]^+$ cations (R = neutral Lewis base with a nitrogen donor atom) have been reported in the literature. These salts all showed a dicoordinate iodonium center. These salts were not prepared using $[I_3]^+[AsF_6]^-$ or $[I_3]^+[SbF_6]^-$ as a starting material and used other sources such as ICl instead.[8] Therefore, the "$[I]^+$" donor properties of isolated $[I]_x^{y+}$ cations (x = 2, 3, 5, y = 1; x = 4, y = 2; x = 15, y = 3) were not investigated. Recently, the use of $[I(py)_2][BF_4]$ as a

---

*E-mail: tmk@cup.uni-muenchen.de.

(1) See for example: (a) Brownridge, S.; Krossing, I.; Passmore, J.; Jenkins, H. D. B.; Roobottom, H. K. *Coord. Chem. Rev.* **2000**, *197*, 397. (b) Gillespie, R. J.; Passmore, J. *Chem. Brit.* **1972**, *8*, 475. (c) Gillespie, R. J. *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 49. (d) Burford, N.; Passmore, J.; Sanders, J. C. P. In *From Atoms to Polymers*; Liebman, J. F., Greenberg, A., Eds.; VCH Verlagsgesellschaft: Weinheim, 1989; p 53. (e) Tornieporth-Oetting, I. C.; Klapötke, T. M. *Heteroatom Chem.* **1993**, *4*, 543 and references cited therein.

(2) (a) Davies, C. G.; Gillespie, R. J.; Ireland, P. R.; Sowa, J. M. *Can. J. Chem.* **1974**, *52*, 2048. (b) Passmore, J.; Sutherland, G.; White, P. S. *Inorg. Chem.* **1981**, *20*, 2169. (c) Gillespie, R. J.; Kapoor, R.; Faggiani, R.; Lock, C. J. L.; Murchie, M.; Passmore, J. *J. Chem. Soc., Chem. Commun.* **1983**, 8. (d) Faggiani, R.; Gillespie, R. J.; Kapoor, R.; Lock, C. J.; Vekris, J. E. *Inorg. Chem.* **1988**, *27*, 4350. (e) Gillespie; Morton, M. J.; Milne, J. B. *Inorg. Chem.* **1968**, *7*, 2221. (f) Apblett, A; Grein, F.; Johnson, J. P.; Passmore, J.; White, P. S. *Inorg. Chem.* **1986**, *25*, 422. (g) Passmore, J.; Taylor, P.; Whidden, T. K.; White, P. S. *Can. J. Chem.* **1979**, *57*, 968.

(3) (a) Klapötke, T. M.; Passmore, J. *Acc. Chem. Res.* **1989**, *22*, 234. (b) Minkwitz, R.; Prenzel, H. *Z. Anorg. Allg. Chem.* **1987**, *548*, 97.

(4) (a) Tornieporth-Oetting, I. C.; Klapötke, T. M.; Passmore, J. *Z. Anorg. Allg. Chem.* **1990**, *586*, 93. (b) X-ray powder diffraction measurements of the $[I_3][AsF_6]$ starting material showed $[I_5][AsF_6]$ impurities were also present.

(5) Klapötke, T. M.; Gowik, P. K. *Chem. Commun.* **1990**, 1433.

(6) Pearson R. G. *J. Am. Chem. Soc.*, **1988**, *110*, 7684 and references cited therein.

(7) (a) Tornieporth-Oetting, I. C.; Klapötke, T. M. *Chem. Ber.* **1991**, *124*, 1571. (b) Broschag, M.; Klapötke, T. M.; Tornieporth-Oetting, I. C. *Inorg. Chim. Acta* **1993**, *205*, 167. (c) Tornieporth-Oetting, I. C.; Klapötke, T. M. *Polyhedron* **1989**, *8*, 2911.

(8) (a) Brock, C. P.; Fu, Y.; Blair, L. K.; Chen, P.; Lovell, M. *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.* **1988**, *C44*, 1582. (b) Hassel, O.; Hope, H. *Acta Chem. Scand.* **1961**, *15*, 407. (c) Jones, C. H. W. *J. Chem. Phys.* **1975**, *62*, 4343. (d) Brayer, G. D.; James, M. N. G. *Acta Crystallogr., Sect. B: Struct. Sci.* **1982**, *B38*, 654. (e) Pritzkow, H. *Acta Crystallogr., Sect. B: Struct. Sci.* **1975**, *B31*, 1505. (f) Batsanov, A. S.; Lightfoot, A. P.; Twiddle, S. J. R.; Whiting, A. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2006**, *E62*, o901. (g) Batsanov, A. S.; Howard, J. A. K.; Lightfoot, A. P.; Twiddle, S. J. R.; Whiting, A. *Eur. J. Org. Chem.* **2005**, 1876. (h) Álvarez-Rúa, C.; García-Granada, S.; Ballesteros, A.; González-Bobes, F.; González, J- M. *Acta Crystallogr., Sect. E: Struct. Rep. Online* **2002**, *E58*, o1381. (i) Grebe-Metz, J.; Weller, F.; Dehnicke, K. *Z. Anorg. Allg. Chem.* **2003**, *629*, 1110.

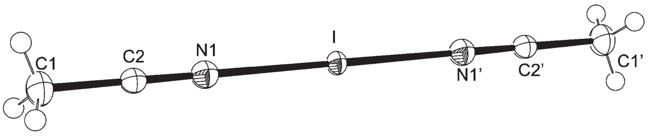

Figure 1. ORTEP representation of the structure of the $[CH_3CN\text{-}I\text{-}NCCH_3]^+$ cation in **1** in the crystalline state. The thermal displacement ellipsoids are shown at the 50% probability level.

useful reagent in organic synthesis has received considerable attention.[9]

The synthesis of the $[CH_3CN\text{-}I\text{-}NCCH_3]^+$ cation in the $[MoF_6]^-$ and $[UF_6]^-$ salts has already been reported via the reaction of I_2 with the corresponding MF_6 (M = Mo, U) in CH_3CN solution.[10] Although no solid state X-ray structure determination was reported of these salts, a linear backbone of the non-hydrogen atoms was proposed based on low temperature Raman and EXAFS spectroscopy.[10a−c] A first determination of the structure of the $[I(NCMe)_2]^+$ cation using K-edge extended X-ray absorption fine structure (EXAFS) revealed an I−N bond length of 2.17 ± 0.03 Å[10c] which is in reasonable agreement with our reported value of 2.198(3) Å.

In related work, *Roesky* and *co-workers* reported the synthesis and structures of $[AsF_6]^-$ or $[SbF_6]^-$ salts containing complexes of Ag^+ coordinated to the nitrogen atoms of Lewis bases such as ClCN, HCN and $(CN)_2$ forming linear cations in the complexes $[Ag(NCCl)_2]^+[SbF_6]^-$,[11a] $[Ag(NCH)_2]^+$ $[SbF_6]^-$,[11b] and $[Ag\{(CN)_2\}_2]_n[AsF_6]_n$.[11c]

In this report, the structure of the salt $[CH_3CN\text{-}I\text{-}NCCH_3]\text{-}[AsF_6]$ (**1**), containing the dicoordinate iodine cation $[CH_3CN\text{-}I\text{-}NCCH_3]^+$ is reported for the first time using single crystal X-ray diffraction. The cation in **1** may be viewed as resulting from the complexation of a hypothetical "$[I]^+$" (from $[I_3]^+$) by two molecules of CH_3CN acting as Lewis bases.[4b]

1 was prepared using a slight modification of the literature procedure.[4a] Two equivalents of CH_3CN were reacted with one equivalent of $[I_3][AsF_6]$ in liquid SO_2, and after filtering off the I_2 formed, the volatile material of the colorless filtrate was slowly removed. This resulted in the formation of colorless, highly air sensitive crystals of **1** which were suitable for single crystal X-ray diffraction.[12]

Bis-(acetonitrile)-iodonium-(I)-hexafluoroarsenate, $[CH_3\text{-}CN\text{-}I\text{-}NCCH_3]^+[AsF_6]^-$ (**1**), crystallizes in the cubic space group $Pa\overline{3}$(#205) and shows a NaCl-like face centered cubic lattice. The arsenic atoms of the anions (O_h symmetry) are arranged in a cubic close-packing (corresponding to the chloride anions in sodium chloride), whereas the iodine atoms of the cations (D_{3d} symmetry) are arranged in the octahedral gaps (corresponding to the sodium cations in the crystal structure of sodium chloride)[13] (Figure 2). The bis-(acetonitrile)-iodonium-(I)-cation shows a linear coordination of two CH_3CN molecules to the iodine center (Figure 1). The N−I bond lengths in **1** (d(N−I) = 2.198(3) Å) are in good agreement with the value reported for the $[(C_5H_5N)_2I]^+$ cation (2.16(10) Å)[8b] but are shorter than the average N−I bond lengths reported for the solid state structures of other $[R\text{-}I\text{-}R]^+$ cations (R = neutral Lewis base with nitrogen donor atom): for example, d(N−I) = 2.29 Å in $[(C_7H_{13}N)_2I][BF_4]$,[8a] 2.29 Å (average) in $[(2,4,6\text{-}Me_3py)_2I]\text{-}[ClO_4]$,[8d] and 2.30 Å in $[(Hexamethylenetetramine)_2I][I_3]$).[8e]

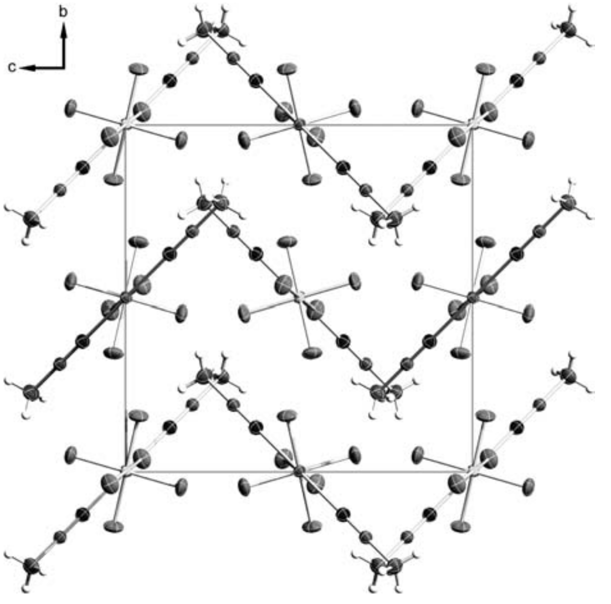

Figure 2. ORTEP representation of the cubic unit cell of **1**. The thermal displacement ellipsoids are shown at the 50% probability level.

It is worthwhile to compare the I−N bond lengths observed in **1** with those reported for IN_3 in the crystalline state,[14] since the latter shows a polymeric structure with a linear N−I−N bridge. The I−N bond lengths observed for **1** (2.198(3) Å) are considerably shorter than those observed for IN_3 in the solid state (d(N−I) = 2.264(23), 2.30(3) Å),[14] although dicoordinate iodine atoms are present in both compounds. The structural parameters for the CH_3CN groups in **1** (d(C−C) = 1.453(6) Å, d(C−N) = 1.142(4) Å, ∠(CCN) = 180.0(4)°) show no significant differences in comparison with the single crystal structures of the α- and β-polymorphs of acetonitrile reported previously in the literature (d(C−C) = 1.448(6) Å (α-CH_3CN), 1.436(12) Å (β-CH_3CN); d(C−N) = 1.141(5) Å (α-CH_3CN), 1.149(12) Å (β-CH_3CN); ∠(CCN) = 179.3(4)° (α-CH_3CN), 178.9(12)° (β-CH_3CN)).[15] In addition, the experimentally determined structural parameters for the $[I(NCCH_3)_2]^+$ cation in **1** in the crystalline state are found to be in good agreement with

---

(9) See for example: Fañanás, F. J.; Álvarez-Pérez; M.; Rodríguez, F. *Chem. Eur. J.* **2005**, *11*, 5938 and references cited therein.

(10) (a) Anderson, G. M.; Winfield, J. M. *Dalton Trans.* **1986**, 337. (b) Anderson, G. M.; Fraser, I. F.; Winfield, J. M. *J. Fluor. Chem.* **1983**, *23*, 403. (c) Garner, C. D.; McGgee, L.; Steel, A.; Winfield, J. M. *J. Fluorine Chem.* **1994**, *69*, 73.

(11) (a) Roesky, H. W.; Schimkowiak, J.; Jones, P. G.; Noltemeyer, M.; Sheldrick, G. M. *Dalton Trans.* **1988**, 2507. (b) Jones, P. G.; Roesky, H. W.; Schimkowiak, J. *Chem. Commun.* **1988**, 730. (c) Roesky, H. W.; Hofmann, H.; Schimkowiak, J.; Jones, P. G.; Meyer-Bäse, K.; Sheldrick, G. *Angew. Chem., Int. Ed.* **1985**, *24*, 417.

(12) $^{14}N\{^1H\}$ NMR (RT, SO_2, 28.9 MHz, rel. to $MeNO_2$, δ/ppm): −260 (s, $\nu 1/2$ = 1037 Hz). ^{19}F NMR (RT, SO_2, 376.5 MHz, rel. to $CFCl_3$, δ/ppm): −58.1 (q, $^1J_{As\text{-}F}$ = 933 Hz, AsF_6^-).

(13) Crystallographic data collection for 1: $C_4H_6As_1F_6I_1N_2$, fw = 397.92, crystal size, 0.1 × 0.1 × 0.1 mm, cubic ($Pa\overline{3}$(#205)), $a = b = c$ = 10.10870(10) Å, V = 1032.966(18) Å^3, Z = 4, T = 100(2) K, R_1 [*all data*] = 0.0289, wR_2 [*all data*] = 0.0355, R_1 [I > 2σ(I)] = 0.0143, wR_2 [I > 2σ(I)] = 0.0320, S = 0.877. CCDC 643230.

(14) Buzek, P.; Klapötke, T. M.; von Rague Schleyer, P.; Tornieporth-Oetting, I. C.; White, P. S. *Angew. Chem., Int. Ed.* **1993**, *32*, 275.

(15) Enjalbert, R.; Galy, J. *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, *B58*, 1005.

Table 1. Selected Experimentally Determined (X-ray Diffraction)[13] Structure Parameters for $[(CH_3CN)_2I]^+$ in **1**, As Well As Calculated (B3LYP Level of Theory)[16] Structure Parameters for the $[CH_3CNI]^+$ and $[CH_3CN\text{-}I\text{-}NCCH_3]^+$ Cations

structural parameter d/Å, ∠/°	$[CH_3CNI]^+$ calc	$[(CH_3CN)_2I]^+$ calc	$[(CH_3CN)_2I]^+$ exp (X-ray)
I−N	1.988	2.226	2.198(3)
N−C	1.147	1.145	1.142(4)
C−C	1.439	1.446	1.453(6)
C−C−N	180	180	180.0(4)
C−N−I	180	180	180.0(3)
N−I−N'	180	180	180[a]

[a] The $[(CH_3CN)_2I]^+$ cation is centrosymmetric.

the calculated (B3LYP,[16] D_{3d} symmetry) gas phase values (Table 1).

As was previously mentioned, the reactivity of $[I_3][AsF_6]$ toward only a few other Lewis bases with nitrogen donor atoms has previously been reported in the literature. Using weak Lewis bases such as CF_3CN, C_5F_5N, and BrCN, no reaction was observed under the conditions used.[7a] Attempts to prepare the related $[IN_2O]^+[AsF_6]^-$ salt (**2**) have so far been unsuccessful, with no reaction being observed to occur between $[I_3][AsF_6]$ and N_2O in liquid SO_2 at room temperature under the conditions applied.[17]

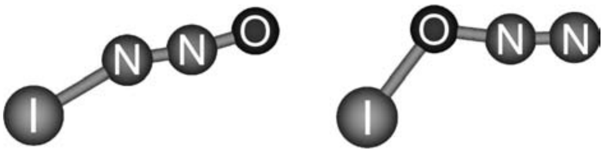

Figure 3. Optimized (B3LYP level of theory) gas phase structures of the (left) $[IN_2O]^+$ (**2a**) (C_s symmetry) and (right) $[ION_2]^+$ (**2b**) (C_s symmetry) isomers.[16]

Table 2. Selected Calculated (B3LYP Level of Theory) Structure Parameters for **2a** and **2b**[16]

structural parameter d/Å, ∠/°	$[IN_2O]^+$ (**2a**)	$[ION_2]^+$ (**2b**)
I−N	2.024	-
N−N	1.128	1.106
N−O	1.150	1.239
O−I	-	2.154
I−N−N	160.2	-
N−N−O	175.7	174.7
N−O−I	-	118.2

The gas phase structures of two possible isomers at the B3LYP level of theory were calculated as described in the Supporting Information,[16] and the optimized structures for the $[IN_2O]^+$ (**2a**) and $[ION_2]^+$ (**2b**) cations are shown in Figure 3, and a comparison of the calculated gas phase structure parameters for **2a** and **2b** is given in Table 2. From the calculations at the B3LYP level of theory, the $[ION_2]^+$ cation **2b** is 8.5 kcal mol^{-1} higher in energy than **2a** in the gas phase at this level of theory.

Acknowledgment. This work was funded by Ludwig-Maximilian University, the Gesellschaft Deutscher Chemiker (GDCh), and the Deutsche Forschungsgemeinschaft (KL 636/6-1, 6-2, CR 138/2-1). The Cusanuswerk is thanked for the award of a scholarship to M. G. Prof. J. Evers and Mr. G. Oehlinger are thanked for X-ray powder diffraction measurements.

Supporting Information Available: Crystallographic file in CIF format for compound **1** as well as details of the computed structures and computed vibrational data for $[CH_3CNI]^+$, $[(CH_3CN)_2I]^+$, $[IN_2O]^+$, and $[ION_2]^+$. This material is available free of charge via the Internet at http://pubs.acs.org.

---

(16) The structure and frequency calculations were performed with Becke's B3 three parameter hybrid functional using the LYP correlation functional (B3LYP). For all H, C, N, and O a correlation consistent polarized triple-ζ basis set was used (cc- pVTZ). For I an energy consistent multielectron Wood-Boring pseudopotential (ECP-46-MWB) treating 46 core electrons was used. The valence electrons of iodine were calculated with a basis set using the following contraction: (16s12p4d2f)/[3s3p2d2f]. Further details and the literature citations for the computational section are given in the Supporting Information.

(17) Attempted preparation of $[IN_2O]^+[AsF_6]^-$: In a two-bulb vessel in the glovebox, 0.570 g (1.0 mmol) of $[I_3][AsF_6]$ solid and a stirrer bar were added. Using a Monel vacuum line, approximately 5.0 mL of predried (CaH_2, distillation) SO_2 were condensed in at −196 °C, followed by 1.0 mmol (0.044 g) N_2O. The reaction vessel was allowed to slowly warm to room temperature whereby a chocolate brown solution was observed and stirred at this temperature overnight. No change in the contents of the reaction vessel or the precipitation of elemental iodine were observed, indicating that no reaction had occurred.