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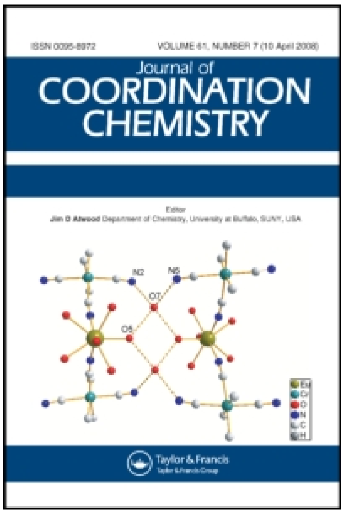

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^{127}I MÖSSBAUER SPECTRA AND X-RAY CRYSTAL STRUCTURES FOR HYPERVALENT IODINE(III) COMPLEX OF HEXAFLUOROCUMYL ALCOHOL AND RELATED 10-I-3 COMPOUNDS

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^{127}I MÖSSBAUER SPECTRA AND X-RAY CRYSTAL STRUCTURES FOR HYPERVALENT IODINE(III) COMPLEX OF HEXAFLUOROCUMYL ALCOHOL AND RELATED 10-I-3 COMPOUNDS[†]

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The crystal structures of 1-chloro-3,3-bis(trifluoromethyl-1λ^3,2(1*H*)-benzoiodoxole (I(hfpp)Cl) and 1-chloro-1λ^3, 2-benzoiodoxole-3(1*H*)-one (I(ba)Cl) are determined. Although the T-shaped molecular structure for I(hfpp)Cl is quite similar to that for I(ba)Cl, the intermolecular interactions including the secondary bondings are significantly different; I(ba)Cl adopts an infinite chain structure with two longer I···O' interactions, whereas I(hfpp)Cl has a dimeric structure with one I···O' secondary bonding. The ^{127}I Mössbauer spectrum for I(hfpp)Cl is quite similar to those of hypervalent iodine(III) compounds having carboxylic and sulfonic ligands and chloride. This shows that the 5p electrons of the iodine(III) atom in I(hfpp)Cl are markedly withdrawn by apical oxygen and chlorine atoms almost equally, suggesting that the alcoholic oxygen atom of the ligand is quite electronegative.

KEYWORDS: hypervalent compound, hexafluorocumyl alcohol, iodine(III) compound, iodine-127 Mössbauer spectra, secondary bonding

INTRODUCTION

1,1,1,3,3,3-Hexafluoro-2-phenylpropan-2-ol (hexafluorocumyl alcohol; HFPP) has been well known as a ligand that stabilizes the hypervalent bonding of heavier main group elements such as silicon, phosphorus, sulphur, antimony and iodine to form stable hypervalent compounds.[1] We have recently elucidated the bonding in the hypervalent antimony complexes of HFPP by ^{121}Sb Mössbauer spectroscopy.[2] To extend our knowledge on the characteristics of HFPP we have studied the hypervalent iodine compound of HFPP. In this report we describe the crystal structure and the ^{127}I Mössbauer spectrum for the 10-I-3[3] HFPP complex of iodine, 1-chloro-3,3-bis(trifluoromethyl)-1λ^3,2(1*H*)-benzoiodoxole (I(hfpp)Cl) together with

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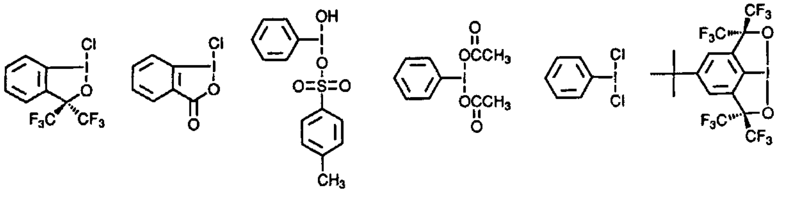
[†] Dedicated to Professor Toschitake Iwamoto, The University of Tokyo, on the occasion of his 60th birthday.

the ^{127}I Mössbauer spectra for related 10-I-3 compounds having ICO_2 and $ICCl_2$ in the coordination sphere. Since only the molecular dimensions have been reported for 1-chloro-1λ^3,2-benzoiodoxole-3(1*H*)-one[4] (I(ba)Cl), to which I(hfpp)Cl has a similar structure, we have also carried out the crystal structure analysis of I(ba)Cl to obtain information on intermolecular interactions.



I (hfpp)Cl I (ba)Cl PhI (OTs)OH PhI $(OAc)_2$ $PhICl_2$ 1

Scheme 1

EXPERIMENTAL

I(hfpp)Cl,[5] I(ba)Cl,[6] (dichloroiodo)benzene ($PhICl_2$),[7] (bisacetoxyiodo)benzene ($PhI(OAc)_2$),[8] and [hydroxy(tosyloxy)iodo]benzene (PhI(OTs)OH)[9] were prepared according to the literature.

^{127}I Mössbauer spectra

Iodine-127 Mössbauer spectra were measured using an Austin S-600 Mössbauer controller coupled with a Norland-ORTEC IT-5600 multichannel analyser. Both the $Mg_3{}^{127m}TeO_6$ Mössbauer source (1.5 GBq) and samples containing 30 mgI cm^{-2} were kept in a cryostat with a closed-cycle refrigerator. The Mössbauer source was prepared by a high-flux neutron (2×10^{14} cm^{-2} s^{-1}) irradiation of $Mg_3{}^{126}TeO_6$ (189 mg) derived from commercial MgO and enriched ^{126}Te (98.4%, Rare Metallic Corp.) at reactor core of JRR-3M of Japan Atomic Energy Research Institute for 25 days. The 57.6 keV Mössbauer γ-rays were detected by a pure germanium detector. The Doppler velocity of the source was measured with an Austin LC-9 laser interferometer and calibrated by measuring the ^{57}Fe Mössbauer spectrum of an iron foil at 20 K using a ^{57}Co(Rh) source. The ^{127}I Mössbauer spectra were computer-fitted to twelve-line quadropole-split lines using the transmission-integral method.[10] The values of the isomer shift are given relative to KI at 20 K.

Structure Determination

The crystallographic and experimental data are summarized in Table 1. The reflection data were collected on a Rigaku AFC5S diffractometer with graphite monochromated Mo Kα radiation at room temperature using a ω-2θ scan technique. The space groups were determined based on the systematic absences and confirmed by the successful solutions and refinements of the structures. The data were corrected for Lorentz, absorption, and polarization effects.

All calculations were carried out using the TEXSAN[11] software package installed on the diffractometer. The direct method (MITHRIL[12]) with successive Fourier and

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Table 1 Crystallographic and experimental data

Empirical Formula	$C_9H_4IOClF_6$	$C_7H_4O_2ICl$
Formula Weight	404.48	282.46
Crystal System	orthorhombic	monoclinic
Space Group	*Pbca* (No. 61)	$P2_1/c$ (No. 14)
Lattice Parameters: a =	14.328(5)Å	8.526(6)Å
b =	16.526(2)Å	6.295(2)Å
c =	9.806(5)Å	14.877(5)Å
β =		94.09(4)°
U =	2322(2)Å^3	796.5(7)Å^3
Z value	8	4
D_{calc}	2.314 g/cm^3	2.355 g/cm^3
F(000)	1520	528
μ(MoKα)	30.22 cm^{-1}	42.58 cm^{-1}
Crystal Dimensions (mm)	0.40 × 0.40 × 0.15	0.48 × 0.48 × 0.20
No. of Reflections		
Measured	3051	2141
Used (I>3.00σ(I))	1712	1571
No. variables	163	100
Reflection/Parameter Ratio	10.50	15.71
Residuals* R	0.039	0.025
R_w	0.048	0.031
Goodness of Fit Indicator	1.63	1.39
Max Shift/Error in Final Cycle	0.01	0.01
Maximum Peak in Final Diff. Map	0.50 e$^-$/Å^3	0.37 e$^-$/Å^3
Minimum Peak in Final Diff. Map	-1.39 e$^-$/Å^3	-0.70 e$^-$/Å^3
Scan Type	ω-2θ	ω-2θ
Scan Rate	8.0°/min (in omega)	8.0°/min (in omega)
Scan Width	(1.21 + 0.30 *tan*θ)°	(1.73 + 0.30 *tan*θ)°
$2\theta_{max}$	55.1°	55.1°
Function Minimized	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$	$\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2$
Least-squares Weights	$4F_o^2/\sigma^2(F_o^2)$	$4F_o^2/\sigma^2(F_o^2)$

$$* R = \frac{\Sigma \lvert \lvert F_o\rvert - \lvert F_c\rvert \rvert}{\Sigma \lvert F_o\rvert}, \quad R_w = \sqrt{\frac{\Sigma w(\lvert F_o\rvert - \lvert F_c\rvert)^2}{\Sigma w \lvert F_o\rvert^2}}$$

Fourier difference synthesis and full-matrix least-squares refinement were applied for each compound. All the non-H atoms were refined anisotropically and hydrogen atoms were located on calculated positions. Crystallographic diagrams were obtained using the ORTEP[13] program.

RESULTS AND DISCUSSION

The atomic coordinates for I(hfpp)Cl and I(ba)Cl are summarized in Table 2 and selected bond distances and angles are in Table 3. Our lattice parameters and bond distances for I(ba)Cl coincided with the reported values.[4]

The molecular structure of I(hfpp)Cl is the well-known T-shaped one with three primary bonds as shown in Fig. 1(a). The molecule is essentially planar, the dihedral angle between ICClO least-squared plane and phenyl ring being 6.0°. The coordination geometry around the iodine atom in I(hfpp)Cl is quite close to that in I(ba)Cl.

A wide range of I-O bond lengths has been reported for 10-I-3 compounds.[9,14–19] The I-O distances in I(hfpp)Cl and I(ba)Cl are comparable to those in $PhI(OAc)_2$

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Table 2 Positional parameters and estimated standard deviations

atom	*x/a*	*y/b*	*z/c*	B_{eq}
I(hfpp)Cl				
I(1)	0.46743(3)	0.12946(2)	0.01723(5)	3.04(2)
Cl(1)	0.3761(2)	0.2445(1)	-0.0627(3)	5.9(1)
F(1)	0.7118(3)	-0.0440(3)	0.1353(6)	5.0(3)
F(2)	0.7742(4)	0.0415(3)	0.2694(7)	6.7(3)
F(3)	0.7491(4)	0.0724(3)	0.0622(7)	6.7(3)
F(4)	0.6266(4)	0.0529(3)	0.4442(5)	5.5(3)
F(5)	0.5800(4)	-0.0501(3)	0.3306(5)	5.6(3)
F(6)	0.4916(4)	0.0556(3)	0.3531(6)	6.1(3)
O(1)	0.5595(4)	0.0420(3)	0.0975(5)	3.3(2)
C(1)	0.5565(5)	0.2026(4)	0.1356(8)	2.9(3)
C(2)	0.6194(5)	0.1601(4)	0.2121(7)	2.7(3)
C(3)	0.6806(6)	0.2029(4)	0.2950(8)	3.4(4)
C(4)	0.6786(7)	0.2864(5)	0.2949(9)	4.1(4)
C(5)	0.6158(7)	0.3267(4)	0.2145(9)	3.9(4)
C(6)	0.5533(6)	0.2867(4)	0.1332(8)	3.4(4)
C(7)	0.7151(6)	0.0345(4)	0.166(1)	3.9(4)
C(8)	0.6163(5)	0.0672(4)	0.2004(7)	2.8(3)
C(9)	0.5787(7)	0.0308(5)	0.3346(9)	3.9(4)
H(1)	0.7236	0.1749	0.3517	4.1
H(2)	0.7209	0.3160	0.3506	5.0
H(3)	0.6156	0.3842	0.2153	4.7
H(4)	0.5098	0.3150	0.0778	4.1
I(ba)Cl				
I(1)	0.79147(3)	0.19415(4)	0.68355(2)	3.35(1)
Cl(1)	0.6087(1)	0.4913(2)	0.65076(8)	4.52(5)
O(1)	0.9340(3)	-0.0762(5)	0.6942(2)	4.3(1)
O(2)	1.0199(4)	-0.3499(5)	0.6205(2)	4.7(1)
C(1)	0.7526(4)	0.0693(5)	0.5530(2)	2.8(1)
C(2)	0.6598(5)	0.1595(6)	0.4842(3)	3.3(1)
C(3)	0.6491(5)	0.0538(7)	0.4022(3)	3.8(2)
C(4)	0.7294(5)	-0.1331(7)	0.3910(3)	4.1(2)
C(5)	0.8229(5)	-0.2198(6)	0.4608(3)	3.8(2)
C(6)	0.8364(4)	-0.1160(6)	0.5434(3)	3.0(1)
C(7)	0.9373(5)	-0.1943(6)	0.6214(3)	3.6(2)
H(1)	0.6054	0.2891	0.4923	4.0
H(2)	0.5852	0.1110	0.3531	4.6
H(3)	0.7201	-0.2031	0.3343	4.9
H(4)	0.8776	-0.3491	0.4526	4.6

(2.153(5), 2.159(5) Å)[14] and PhI $(O_2CCF_3)_2$, (2.138(5), 2.186(3) Å)[15] and endocyclic I-O distances in 10-*tert*-butyl-3,3,6,6-tetrakis(trifluoromethyl)-4,5,6-benzo-$1\lambda^3$-ioda-2,8-dioxa-bicyclo[3,3,1]octane (**1**; 2.113(3), 2.077(3) Å)[16] and 1-(*tert*-butylperoxy)-$1\lambda^3$,2-benziodoxol-3(1*H*)-one (2.181(5) Å)[17] but shorter than the endocyclic I-O lengths in 1-hydroxy-$1\lambda^3$,2-benziodoxole-3(1*H*)-one (2.30(5) Å)[18] and 1-hydroxy-3-methyl-$1\lambda^3$,2,3-benziodoxaphosphole-3(1*H*)-one (2.286 Å).[19] The endocyclic I-O distances for I(hfpp)Cl and I(ba)Cl are also shorter than those for the iodine(V) complexes of these ligands; $[IO_2(hfpp)]^-$ (2.296(7) Å)[20] and [IO(ba)OH] (2.324(3) Å).[21]

The I-Cl bond length is close to that of $PhICl_2$ (2.45(2) Å)[22] and 1,2-dichloro-$1\lambda^3$,2-benziodazalin-3(1*H*)-one (2.52 Å).[4] The I-C bond length is also comparable to

Table 3 Selected bond distances (Å) and angles (°) in I(hfpp)Cl and I(ba)Cl.

(a) I(hfpp)Cl			
I(1)-Cl(1)	2.438(2)	I(1)-O(1)	2.110(5)
I(1)-C(1)	2.105(7)	I(1)-O(1)^{i}	3.073(5)
O(1)-C(8)	1.361(8)	C(1)-C(2)	1.37(1)
C(2)-C(8)	1.540(9)		
Cl(1)-I(1)-O(1)	172.0(1)	Cl(1)-I(1)-C(1)	93.2(2)
Cl(1)-I(1)-O(1)^{i}	122.3(1)	O(1)-I(1)-C(1)	78.9(2)
O(1)-I(1)-O(1)^{i}	65.4(2)	I(1)-O(1)-C(8)	116.2(4)
I(1)-C(1)-C(2)	114.1(5)	I(1)-C(1)-C(6)	123.0(6)
C(1)-C(2)-C(8)	116.9(7)	O(1)-C(8)-C(2)	112.2(6)
Symmetry operation; i: $(-x + 1, -y, -z)$			
(b) I(ba)Cl			
I(1)-Cl(1)	2.461(1)	I(1)-O(1)	2.091(3)
I(1)-C(1)	2.100(4)	I(1)-O(1)^{i}	3.205(3)
I(1)-O(2)^{i}	3.239(4)	O(1)-C(7)	1.316(5)
O(2)-C(7)	1.207(5)	C(1)-C(6)	1.381(5)
C(6)-C(7)	1.479(5)		
Cl(1)-I(1)-O(1)	171.96(8)	Cl(1)-I(1)-C(1)	92.6(1)
Cl(1)-I(1)-O(1)^{i}	101.30(7)	Cl(1)-I(1)-O(2)^{i}	120.68(7)
O(1)-I(1)-C(1)	79.5(1)	O(1)-I(1)-O(1)^{i}	85.82(6)
O(1)-I(1)-O(2)^{i}	120.68(7)	O(1)^{i}-I(1)-O(1)^{i}	39.84(8)
I(1)-O(1)-C(7)	116.4(2)	I(1)-C(1)-C(6)	111.3(2)
C(1)-C(6)-C(7)	118.5(3)	O(1)-C(7)-O(2)	120.9(4)
O(1)-C(7)-C(6)	114.4(3)	O(2)-C(7)-C(6)	124.7(4)
Symmetry operation; i: $(-x + 2, y - 1/2, -z + 3/2)$			

those in organoiodine(III) compounds having ICO_2 or $ICCl_2$ as the coordination sphere.

Although the molecular geometry for I(hfpp)Cl is quite similar to that for I(ba)Cl as discussed above, the intermolecular interactions with the neighboring molecules are significantly different. The coordination about iodine for I(hfpp)Cl is completed by one longer I-O intermolecular secondary bond(I···O(1)’ = 3.073(5) Å), resulting in a centrosymmetical dimeric structure (Fig. 1(a)). Such a dimeric structure has been reported for **1** having a couple of I···O contacts of 3.000(3) Å,[16] shorter than the sum of van der Waals radii (3.55 Å). The O(1)’ atom lies almost on the ICClO plane (distance from the mean ICClO plane (Δd) is 0.358 Å), forming an $AX_3X^{long}E_2$ geometry, where E denotes the lone pair. On the other hand, I(ba)Cl has two longer intermolecular I···O’ interactions (I···O(1)’ = 3.205(3) and I···O(2)’ = 3.239(4) Å) forming an infinite chain structure (Fig. 1(b)). One of the adjacent oxygen atoms (O(2)’) is on the ICClO plane (Δd = 0.050 Å), but the other (O(1)’) is located above the plane by 1.961 Å. Thus the overall geometry is described as $AX_3X^{long}{}_2E_2$.

The ^{127}I Mössbauer spectra for I(hfpp)Cl and I(ba)Cl are shown in Fig. 2 and Mössbauer parameters are listed in Table 4 together with data for related iodine(III) compounds. Each compound has a large quadrupole coupling constant (e^2qQ) and an asymmetry parameter (η). The large positive values of e^2qQ, thus negative eq (since $eQ < 0$), suggest that one of the lone pairs points along the out-of-plane direction (z axis). The large values of η indicate that there is large inbalance in the electron density distribution in the xy plane; *i.e.*, the valence electrons are withdrawn significantly by the electronegative oxygen and chlorine atoms.

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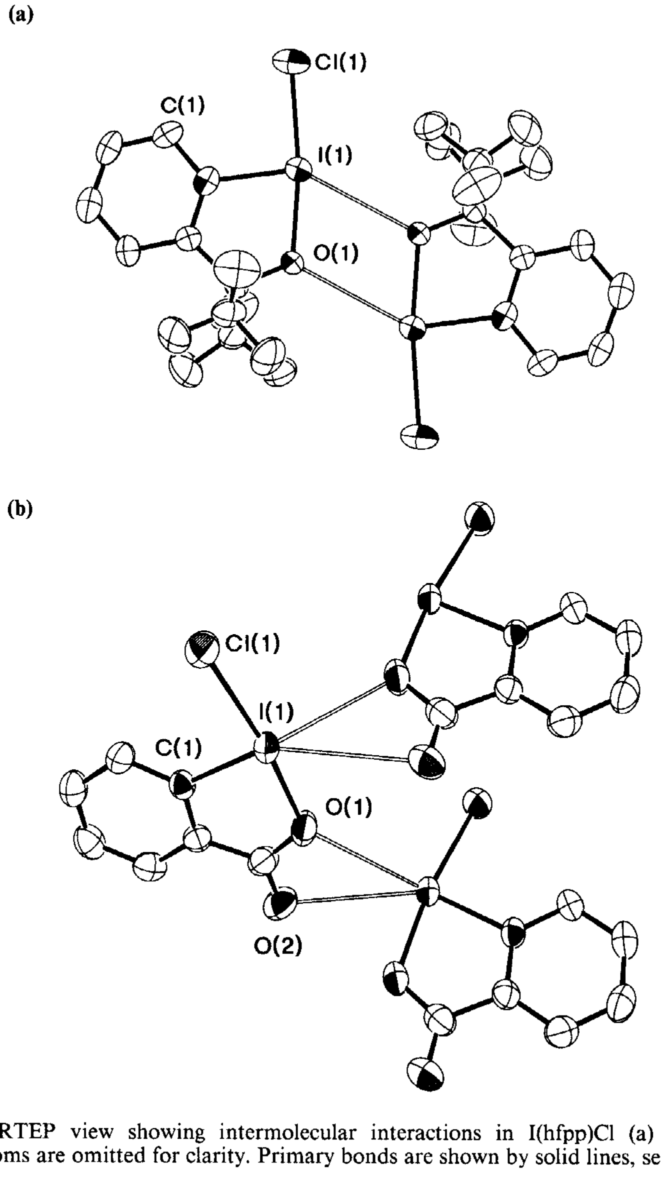

Figure 1 ORTEP view showing intermolecular interactions in I(hfpp)Cl (a) and I(ba)Cl (b). Hydrogen atoms are omitted for clarity. Primary bonds are shown by solid lines, secondary bonds by open lines.

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The estimated valence electron populations for iodine and charge on it (Z_I) are also listed in Table 4. The values were derived from the Mössbauer parameters by the Townes-Dailey and the Perlow-Perlow treatment assuming that the $5p_z$ orbital is filled by the lone pair electrons. The procedure for the calculation is described elsewhere.[23] The *x* and *y* axes are adopted to the direction of I-C and Cl-I-O (or O-I-O, Cl-O-Cl) bond, respectively.

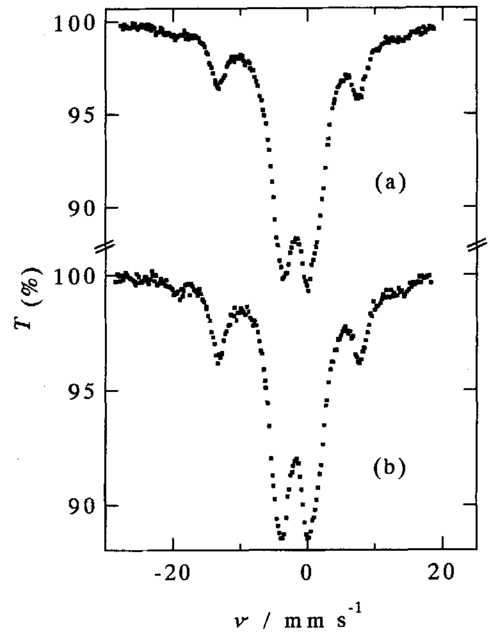

Figure 2 ^{127}I Mössbauer spectra for I(hfpp)Cl (a) and I(ba)Cl (b) at 20 K.

Table 4 Iodine-127 Mössbauer parameters at 20 K and valence electron populations for hypervalent iodine(III) compounds

compound	δ* (mm s^{-1})	e^2qQ (mm s^{-1})	(GHz)	η	N_s	N_x	N_y	N_z	N_{total}	Z_I
I(hfpp)Cl	-0.89	54.7	2.54	0.77	1.93	1.18	0.61	2.00	5.71	+1.29
I(ba)Cl	-1.03	54.5	2.53	0.81	1.98	1.19	0.60	2.00	5.77	+1.23
PhI(OTs)OH	-0.82	53.7	2.49	0.74	1.91	1.18	0.64	2.00	5.74	+1.26
PhI(OAc)$_2$	-0.94	54.4	2.53	0.83	1.95	1.20	0.59	2.00	5.74	+1.26
PhICl$_2$	-0.87	54.0	2.51	0.75	1.93	1.18	0.63	2.00	5.74	+1.26

* Values of isomer shift are given relative to KI at 20 K.

The effective charge on the iodine atom is about +1.2 for each compound, showing the validity of the 3-center-4-electron bonding model that requires positive charge on the central atom. The value of 5s population (N_s) for each iodine(III) compound indicates that the 5s orbital is almost filled, showing little contribution of the 5s orbital to the bonding. The population of I(hfpp)Cl is closed to that of I(ba)Cl though the bond lengths and number of intermolecular secondary bonding interactions are different between them. This suggests that such secondary bonding is too weak to significantly effect the electronic state of the iodine atom. This is in accordance with the ^{127}I Mössbauer spectroscopic observation for $Ph_2I^+ \cdots X^-$ (X = Cl, Br) interactions in $(Ph_2I)_2X_2$.[23,24]

The population of the 5p$_y$ orbital (N_y) for I(hfpp)Cl is quite close to that of PhI(OTs)OH, PhI(OAc)$_2$ and PhICl$_2$; the alcoholic oxygen atom of HFPP becomes electronegative to the same extent as the oxygen atom of both the acetate and

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tosylate ions and as the chlorine atom. This would result from the two trifluoromethyl groups. However, it is in contrast to the results for the antimony(V) complexes of HFPP in which the oxygen atoms of HFPP attracts much less of the 5p electrons of antimony(V) atom than does the chlorine atom.[2]

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References

1. J.C. Martin, *Science,* **221**, 509 (1983); E.F. Perozzi, R.S. Michalak, G.D. Figuly, W.H. Stevenson III, D.B. Dess, M.R. Ross and J.C. Martin, *J. Org. Chem.*, **46**, 1049 (1981); Y. Yamamoto, H. Fujikawa, H. Fujishima and K.-y. Akiba, *J. Amer. Chem. Soc.*, **111**, 2276 (1989).
2. M. Takeda, M. Takahashi, Y. Yanagida, S. Kojima and K.-y. Akiba, *Chem. Lett.*, 2037 (1993).
3. The *N-X-L* designation has been proposed: *X*, central atom; *N*, the number of formal valence-shell electrons about an *X*; *L*, the number of ligands. See: C.W. Perkins, J.C. Martin, A.J. Arduengo, III, W. Lau, A. Alegria, J.K. Kochi, *J. Amer. Chem. Soc.*, 1980, **102**, 753.
4. K. Prout, N.M. Stevens, A. Code, V. Tazzoli, R.A. Shaw and T. Demir, *Z. Naturforsch.*, **31b**, 687 (1976).
5. E.F. Perrozi, R.S. Michalak, G.D. Figuly, W.H. Stevenson III, D.B. Dess, M.R. Ross, and J.C. Martin, *J. Amer. Chem. Soc.*, **46**, 1049 (1981).
6. R.L. Amey and J.C. Martin, *J. Org. Chem.*, **44**, 1779 (1979).
7. H.J. Lucas and E.R. Kennedy, *Org. Synth.*, **III**, 482 (1955).
8. J.G. Sharefkin and H. Saltzman, *Org. Synth.*, **V**, 660 (1973).
9. G.K. Koser, R.H. Wettach, J.M. Troup and B.A. Frenz, *J. Org. Chem.*, **41**, 3609 (1976).
10. G.K. Shenoy, J.M. Friedt, H. Maletta and S.L. Ruby, in *Mössbauer Effect Methodology*, eds, I.J. Gruverman, C.W. Seidel and D.K. Dieterly, Vol. 9 (Plenum Press, New York, 1974) p. 277.
11. TEXSAN Structure Analysis, Molecular Structure Corporation, Houston, TX (1987).
12. G.J. Gilmore, *J. Appl. Crystallogr.*, **17**, 42 (1984).
13. C.K. Johnson, ORTEP II, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN (1976).
14. N.W. Alcock, R.M. Countryman, S. Esperas and J.F. Sawyer, *J. Chem. Soc, Dalton Trans.*, 854 (1979).
15. N.W. Alcock, W.D. Harrison and C. Howes, *J. Chem. Soc., Dalton Trans.*, 1709 (1984).
16. T.T. Nguyen, S.R. Wilson and J.C. Martin, *J. Amer. Chem. Soc.*, **108**, 3803 (1986).
17. M. Ochiai, T. Ito, Y. Masaki and M. Shiro, *J. Amer. Chem. Soc.*, **114**, 6269 (1992).
18. E. Shefter and W. Wolf, *Nature*, **203**, 512 (1964); *J. Pharm. Sci.*, **54**, 104 (1965).
19. T.M. Balthazor, J.A. Miles and B.R. Stults, *J. Org. Chem.*, **43**, 4538 (1978).
20. D.B. Dess and J.C. Martin, *J. Amer. Chem. Soc.*, **113**, 7277 (1991).
21. J.Z. Gougoutas, *Cryst. Struct. Commun.*, **10**, 489 (1981).
22. E.M. Archer and T.G.D. van Schalwyk, *Acta Crystallogr.*, **6**, 88 (1953).
23. H. Ikezawa, M. Takahashi, M. Takeda, T. Takano and Y. Ito, *Bull. Chem. Soc. Jpn.*, **66**, 1959 (1993).
24. T. Birchall and R.D. Myers, *J. Chem. Soc., Dalton Trans.*, 1060 (1980).

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