

¹²⁷I Mössbauer Studies of Oxygen-Bonded Iodine Complexes. 1. Tris(carboxylato)iodine(III) Derivatives. Crystal and Molecular Structure of Tris(acetato)iodine(III)

Thomas Birchall,* Christopher S. Frampton, and Pratibha Kapoor

Received April 26, 1988

¹²⁷I Mössbauer spectra have been recorded at 4.2 K for a series of tris(carboxylato)iodine(III) derivatives. The observed Mössbauer parameters appear to be influenced only by the primary bonds to iodine. Details of the preparation of a Mg₃^{127m}TeO₆ source for ¹²⁷I Mössbauer spectroscopy are given. The crystal and molecular structure of tris(acetato)iodine(III), I(O₂CCH₃)₃, has been determined. The crystals are monoclinic, of space group *P*2₁/*c*, with *a* = 6.630 (1) Å, *b* = 8.047 (3) Å, *c* = 18.296 (4) Å, β = 93.82 (2)°, *V* = 974 (1) Å³, *D*_c = 2.07 g cm⁻³ for *Z* = 4, and *R*₁ = 0.0863 (*R*₂ = 0.0982) for 1436 reflections. The geometry about iodine consists of primary bonds to the three acetate groups (I-O = 2.159 (12), 2.023 (15), 2.168 (12) Å) and two strong intramolecular secondary bonds (I...O = 2.463 (13), 2.518 (13) Å) to two of the acetate groups forming a AX₃Y₂E₂ pentagonal-planar arrangement.

Introduction

We have recently reported the crystal structure and ¹²⁷I Mössbauer spectrum of diphenyliodonium-2-carboxylate hydrate¹ in an attempt to gain further information regarding I...O secondary bonding interactions and the interrelationship of the ¹²⁷I Mössbauer parameters with the structure of the molecule and the nature of bonding to iodine. It was found that the Mössbauer parameters appeared to be relatively insensitive to changes in secondary interactions at the iodine nucleus, whereas changes in the primary bonding had a much more significant effect. This trend has also been noted in a separate study of halogeno-iodine compounds.²

Previous ¹²⁷I Mössbauer studies of oxo-iodine compounds are limited,^{1,3,4} and those utilizing the ¹²⁹I isotope⁵ have been restricted to frozen-solution studies due to the instability of the prepared absorbers. In view of the paucity of both ¹²⁷I Mössbauer and X-ray crystallographic data for oxo-iodine compounds, we decided to extend the range of available data for these compounds.

In this paper, the first part of a systematic investigation into the correlation of ¹²⁷I Mössbauer parameters and structure of oxo-iodine compounds, we report the ¹²⁷I Mössbauer parameters, at 4.2 K, for a series of iodine(III) carboxylates and also for that of the analogous trifluoromethanesulfonate. The crystal and molecular structure of tris(acetato)iodine(III) was determined in order to gain further information on the environment of the iodine atom and to probe the nature of any I...O secondary bonding interactions that may be present.

Experimental Section

Preparation of Mg₃^{127m}TeO₆. Mg₃¹²⁶TeO₆ was prepared in a manner similar to that reported by Newnham et al.⁶ ¹²⁶TeO₂ (98% enriched) (0.05 g, 0.310 mmol) and MgO (0.044 g, 1.092 mmol) (15% excess) were finely ground together. The resultant mixture was fired at 900 °C for 24 h in a closed silica crucible. After cooling to room temperature, the sample was reground and annealed at 700 °C for a further 12 h. Previous preparations of this material using TeO₂ containing the natural isotope afforded the X-ray powder diffraction pattern reported for this material.⁷ The prepared Mg₃¹²⁶TeO₆ was pressed into a pellet (6-mm diameter) and was placed in a specially machined graphite capsule. This capsule was irradiated in the graphite reflector elements on the edge of the McMaster reactor core at a nominal neutron flux of 1.5 × 10¹³ cm⁻² s⁻¹ for approximately 2 months. The McMaster University Nuclear Reactor is a 5-MW (thermal) pool-type reactor. The estimated activity of the ^{127m}Te produced is ca. 5 mCi. After irradiation the graphite capsule was contained within a threaded aluminum cell. Apiezon-N grease was applied to the thread of the cell to ensure against leakage.

Table I. Analytical Data

compd	% I		% acid ligand	
	found	calcd	found	calcd
I(O ₂ CCH ₃) ₃	41.46	41.75	57.83	58.22
I(O ₂ CCF ₃) ₃	27.20	27.23	72.16	72.74
I(O ₂ CCH ₂ Cl) ₃	31.59	31.56	68.87	68.83
I(OSO ₂ CF ₃) ₃	22.94	22.13	77.13	77.87

Preparation of the Compounds. Tris(carboxylato)iodine(III) derivatives were prepared by the oxidation of iodine with fuming nitric acid in the presence of the appropriate carboxylic acid and acetic anhydride.⁸

Tris(acetato)iodine(III). A 2.7-mL quantity of fuming nitric acid, 2.5 g (10 mmol) of sublimed iodine, and 3.5 mL (61 mmol) of acetic acid were added to 7 mL of acetic anhydride, which was maintained at -30 °C. The cooling bath was removed after the additions were made, and the contents were then allowed to warm to room temperature. The reaction mixture was stirred for 2 h, during which oxides of nitrogen were evolved and the iodine dissolved completely. All volatiles were removed under vacuum at room temperature. The other tris(carboxylates) were prepared in a similar manner.

Tris(trifluoromethanesulfonato)iodine(III). A 0.5-g (~1-mmol) sample of tris(trifluoroacetato)iodine(III) was dissolved in excess trifluoromethanesulfonic acid. The mixture was stirred for 1 h. All volatiles were removed under vacuum at room temperature.

Analysis. The compounds were analyzed for iodine and acid ligand according to the standard procedures.⁹ See Table I for analytical data.

Materials. Acetic acid (BDH, AnalaR) was refluxed with 2 mol % acetic anhydride (BDH) for 24 h and then distilled. The fraction distilling at 114-115 °C was collected for use. Trifluoroacetic acid (Baker Analyzed) was refluxed with 2 mol % of trifluoroacetic anhydride (BDH) for 8 h and then distilled. The fraction distilling at 72 °C was collected and used. Trifluoromethanesulfonic acid (Aldrich) was refluxed with 2 mol % trifluoromethanesulfonic anhydride (Aldrich) for 4 h and then distilled. The fraction distilling at 161-162 °C was collected for use. Mono- and trichloroacetic acids (Aldrich) were made anhydrous by the addition of their anhydrides (Aldrich). Iodine (BDH, AnalaR) was freshly sublimed before use. Magnesium oxide (BDH, Gold label) was dried at 120 °C for 12 h before use. ¹²⁶TeO₂ (isotopic purity 98%) (Technabexport) was used without further purification.

Mössbauer Spectroscopy. The source of 57.6-keV radiation was Mg₃^{127m}TeO₆. We have previously reported the use of Ca₃^{127m}TeO₆ as a source matrix for ¹²⁷I Mössbauer spectroscopy; however, this source preparation procedure is complicated by the fact that the chemistry has to be performed after the irradiation.¹ The preparation of nonradioactive Mg₃¹²⁶TeO₆ is an experimentally easier procedure, and the material can be repeatedly irradiated to regenerate the ^{127m}Te activity as has been reported for the ¹²⁹I source.¹⁰

With the Mg₃^{127m}TeO₆ source (4.2 K), the spectrum of Cu¹²⁷I (4.2 K) (0.015 g cm⁻² of ¹²⁷I) displayed a perfectly Lorentzian single line with Γ = 3.56 (8) mm s⁻¹. By comparison, this line width is narrower than

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Table II. Crystal Data for I(O₂CCH₃)₃

chem formula	C ₆ H ₉ O ₆ I
fw	304.6
system	monoclinic
space group	P2 ₁ /c, No. 14
a, Å	6.630 (1)
b, Å	8.047 (3)
c, Å	18.296 (4)
β, deg	93.82 (2)
V, Å ³	974 (1)
Z	4
D _c , g cm ⁻³	2.07
temp, °C	-60
radiation	λ = 0.71069 (Mo Kα)
μ(Mo Kα), cm ⁻¹	33.31
final R ₁ , R ₂ ^a	0.0863, 0.0982

$$^a R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|; R_2 = (\sum w(|F_o| - |F_c|)^2 / \sum wF_o^2)^{1/2}.$$

the value reported previously for the Ca₃^{127m}TeO₆ source (Γ = 3.75 (6) mm s⁻¹).¹ Hence, it may be concluded that Mg₃TeO₆ also contains Te in a cubic local environment and that the effects of radiation damage to the source matrix are negligible.

The iodine absorbers were pressed into a threaded Kel-F cell under an atmosphere of dry nitrogen to give approximately 0.05 g cm⁻² of ¹²⁷I. ¹²⁷I Mössbauer spectra were recorded with both source and absorber immersed in liquid helium in a cryostat manufactured by Janis Corp. An Elscint MFG-N-5 Mössbauer function generator, an Elscint MDF-N-5 driver/generator, and an Elscint MVT-4 transducer operating in the sinusoidal-waveform mode were used. The transmitted radiation was detected by an Aptec (500 mm² × 10 mm) planar germanium detector, and the pulses were fed through a Canberra 2022 linear amplifier to a CMTE Multichannel Data Processor controlled by an IBM Pc/AT microcomputer. The velocity scale was calibrated with a standard iron-foil absorber and a ⁵⁷Co/Rh source mounted on the reverse end of the transducer. Calibration spectra were thus recorded without interruption of the drive sequence. The calibration spectra were computer-fitted to give a linear velocity scale and folding point.

Folded ¹²⁷I spectra were fitted by using the program GMFP,¹¹ which incorporates full-transmission integral procedures. The source linewidth was arbitrarily set at the natural line width 1.27 mm s⁻¹, the effective recoilless fraction was set equal to that of the previous Ca₃^{127m}TeO₆ source, 0.75 at 4.2 K, and the dimensionless absorber thickness T_a was made a variable parameter of the iterative fitting process. All isomer shifts were referenced to K¹²⁷I at 4.2 K.¹²

X-ray Crystallography. Colorless cylindrical crystals of I(O₂CCH₃)₃ were examined under a polarizing microscope for homogeneity. A well-formed crystal (cylinder, r = 0.15 mm, l = 0.50 mm) was selected and sealed in a Lindemann capillary. Crystal selection, examination, and mounting were all performed under an atmosphere of dry nitrogen; to prevent decomposition it was necessary to maintain the temperature of the crystals below 0 °C during the above procedure. The mounted crystal was rapidly transferred to a Nicolet P3 diffractometer fitted with an LT-1 attachment and cooled to -60 °C. Unit cell parameters were obtained from a least-squares fit of χ, φ, and 2θ for 15 reflections in the range 20° < 2θ < 25° with use of graphite-monochromated Mo Kα radiation (λ = 0.71069 Å). The density was not determined due to the instability of the crystals. Intensities were also recorded on the Nicolet P3 diffractometer with a coupled θ(crystal)-2θ(counter) scan for reflections in the quadrant (h,k,±l) with 2θ ≤ 45°. The methods of selection of scan rates and initial data treatment have been described.^{13,14} Corrections were made for Lorentz-polarization effects but not for absorption. Despite data collection at low temperature, intensity variations occurred in the two standard reflections (monitored every 48 reflections), and the data were adjusted accordingly (maximum rescale factor (on F) 1.984). The variations in intensity were due to decomposition of the crystal, and the data collection was terminated after 1436 reflections had been collected. Systematically absent reflections (95) were excluded, and 178 symmetry-equivalent data were then averaged (R_{int} = 0.0177) to give 1163 unique reflections.

Solution of the Structure. The coordinates of the iodine atom were found from a three-dimensional Patterson synthesis, and a series of

Table III. Positional Parameters × 10⁴ and U_{iso} × 10³ for I(O₂CCH₃)₃ with Estimated Standard Deviations in Parentheses

atom	x	y	z	U _{iso} , Å ²
I	-398 (2)	8473 (1)	4037 (1)	29.2 ^a
O(11)	2467 (19)	8961 (16)	4630 (6)	29.6
O(12)	1683 (22)	6343 (16)	4696 (7)	42.0
C(11)	2902 (29)	7468 (24)	4881 (9)	31.7
C(12)	4766 (35)	7298 (32)	5408 (11)	56.9
O(21)	-381 (18)	10930 (19)	3959 (6)	38.8
O(22)	1462 (21)	10793 (19)	2967 (7)	47.9
C(21)	645 (34)	11628 (22)	3423 (11)	39.0
C(22)	599 (38)	13470 (24)	3449 (8)	48.3
O(31)	-3099 (19)	8930 (16)	3339 (6)	32.5
O(32)	-3038 (22)	6335 (16)	3660 (7)	42.7
C(31)	-3822 (29)	7475 (24)	3298 (9)	32.4
C(32)	-5773 (33)	7231 (29)	2769 (10)	49.1

$$^a U_{eq} = 1/3(U_{11} + U_{22} + U_{33} + (2 \cos \beta)U_{13}).$$

Table IV. Bond Lengths (Å) and Angles (deg) for I(O₂CCH₃)₃ with Estimated Standard Deviations in Parentheses

(1) Iodine Coordination				
I-O(11)	2.16 (1)	I---O(12)	2.46 (1)	
I-O(21)	2.02 (2)	I---O(22)	3.03 (1)	
I-O(31)	2.17 (1)	I---O(32)	2.52 (1)	
O(11)-I-O(21)	81.1 (5)	C(11)-O(11)-I	100 (1)	
O(11)-I-O(31)	157.8 (5)	C(21)-O(21)-I	117 (1)	
O(21)-I-O(31)	77.2 (5)	C(31)-O(31)-I	98 (1)	
(2) Acetates				
I C(11)-O(11)	1.31 (2)	O(12)-C(11)-O(11)	116 (2)	
C(11)-O(12)	1.25 (2)	C(12)-C(11)-O(11)	117 (2)	
C(11)-C(12)	1.52 (3)	C(12)-C(11)-O(12)	126 (2)	
II C(21)-O(21)	1.34 (2)	O(22)-C(21)-O(21)	124 (2)	
C(21)-O(22)	1.23 (2)	C(22)-C(21)-O(21)	111 (2)	
C(21)-C(22)	1.48 (3)	C(22)-C(21)-C(22)	126 (2)	
III C(31)-O(31)	1.30 (2)	O(32)-C(31)-O(31)	122 (2)	
C(31)-O(32)	1.23 (2)	C(32)-C(31)-O(31)	116 (2)	
C(31)-C(32)	1.58 (3)	C(32)-C(31)-O(32)	123 (2)	

full-matrix least-squares refinements followed by a three-dimensional electron density synthesis revealed all of the non-hydrogen atoms. After refinement the temperature factor of the iodine atom was made anisotropic, and further full-matrix least-squares refinement, which minimized $\sum w(|F_o| - |F_c|)^2$, was terminated when the maximum shift/error reached 0.002. The temperature factors of the carbon and oxygen atoms were left isotropic. No attempt was made to locate the hydrogen atoms. Corrections were made for secondary extinction by the method in SHELX.¹⁵ Throughout the refinement the scattering curves were from ref 16, and anomalous dispersion corrections from ref 17 were applied to the curve for iodine. Crystal data are listed in Table II. The final atom parameters for non-hydrogen atoms are listed in Table III; bond lengths and bond angles are given in Table IV.

Results and Discussion

Structure. The geometry about the trivalent iodine is the familiar distorted T-shaped (AX₃E₂) arrangement with three primary bonds to the acetate groups I-III [I-O(11) = 2.159 (12), I-O(21) = 2.023 (15), I-O(31) = 2.168(12) Å]. The corresponding O-I-O bond angles are O(11)-I-O(21) = 81.5 (5), O(21)-I-O(31) = 77.2 (5), and O(11)-I-O(31) = 157.8 (5)°. The coordination about the iodine is completed by two longer I---O intramolecular secondary bonds from acetates I and III [I---O(12) = 2.463 (13), I---O(32) = 2.518 (13) Å]. These oxygens cap two XEE faces (for notation see ref 18) of the trigonal bipyramid, forming an AX₃Y₂E₂ pentagonal-planar arrangement (Figure 1). The maximum displacement of any of the IO₅ atoms from the mean plane is 0.169 Å. Acetate II is oriented such that it is almost perpendicular to the IO₅ pentagonal plane with a

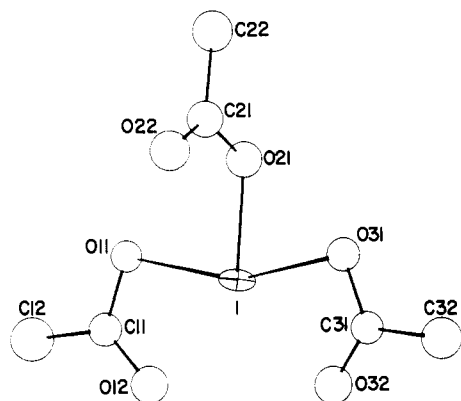
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Table V. ^{127}I Mössbauer Data for Tris(carboxylato)iodine(III) Derivatives

compound	δ , mm s $^{-1}$ ^a	$e^2q^{127}Q_8/h$, MHz	Γ , mm s $^{-1}$	η	T_a ^b	ψ^2	ref
$\text{I}(\text{O}_2\text{CCH}_3)_3$	-1.83 (3)	+3419 (16)	1.73 (8)	0.07 (3)	0.63 (2)	1.22	<i>h</i>
$\text{I}(\text{O}_2\text{CCH}_3)_3$	-1.24 (5)	+3412 (20)		0.11 (3)			5 ^c
$\text{I}(\text{O}_2\text{CCF}_3)_3$	-1.60 (3)	+3540 (18)	1.63 (9)	0.00 ^d	0.87 (4)	0.96	<i>h</i>
$\text{I}(\text{O}_2\text{CCH}_2\text{Cl})_3$	-1.75 (3)	+3501 (15)	1.90 (7)	0.00 ^d	0.85 (3)	0.96	<i>h</i>
$\text{I}(\text{O}_2\text{CCCl}_3)_3$ ^e	-1.75 (3)	+3549 (20)	2.78 (5)	0.00 ^d	1.75 (4)	2.16	<i>h</i>
$\text{I}(\text{OSO}_2\text{CF}_3)_3$	-1.74 (3)	+3680 (14)	1.72 (7)	0.16 (1)	1.28 (4)	1.19	<i>h</i>
I_2Cl_6	-1.41 (3)	+3028 (19)	2.68 (15)	0.09 (3)	0.44 (1)	1.28	2
$\text{KICl}_4 \cdot \text{H}_2\text{O}$	-1.48 (4)	+3139 (24)	2.61 (12)	0.00 ^d	1.40 (5)	1.33	2
$\text{I}(\text{Ph})(\text{PhCO}_2)$	-0.50 (3)	+1914 (6)	1.50 (4)	0.499 (6)			1
$\text{PhI}(\text{OAc})_2$	-0.87 (1)	+2507 (6)	1.53 (4)	0.79 (1)			4
KI	0		2.23 (2)		0.28 (2)	0.71	<i>h</i>
KI ^e	-0.56 (6)		2.23 (2)		0.28 (2)	0.71	<i>h</i>
CuI	0.97 (2)		2.91 (8)		1.48 (7)	0.83	<i>h</i>
CuI ^{e,f}	0.97 (2)		3.56 (8)			0.83	<i>h</i>

^a Values relative to K^{127}I at 4.2 K. ^b Dimensionless absorber thickness (see ref 10). ^c Values converted from ^{129}I data. ^d Parameter fixed in fitting procedure. ^e Value relative to $\text{Mg}_3^{127\text{m}}\text{TeO}_6$ source. ^f Lorentzian fitting approximation. ^g Frozen-solution spectrum. ^h This work.

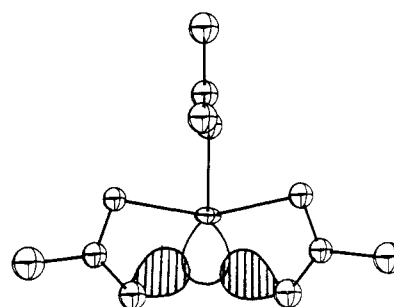
**Figure 1.** View of the molecule, showing the atom-numbering scheme.

dihedral angle between their least-squares mean planes of 87.9°.

The I...O(22) intramolecular contact [3.027 (14) Å] is such that it bisects the EE edge of the trigonal bipyramid. This distance is significantly longer than the two secondary bonds from acetates I and III but is still less than the sum of the van der Waals radii (3.55 Å). Thus, the overall geometry of the iodine may be described as $\text{AX}_3\text{Y}_2\text{Y}'\text{E}_2$.

With use of the bond valence parameters reported by Altermatt and Brown,¹⁹ it is possible to calculate bond valences for both the primary and secondary bonds present in this structure and hence assign coordination modes for the three acetate groups. (For a review of carboxylate coordination modes see ref 20.) The primary bonds between iodine and acetates I-III have bond valences of 0.687, 0.992, and 0.670, respectively. The corresponding values for the secondary bonds are 0.301, 0.066, and 0.260. The overall bond valence sum of 2.976 is close to the assigned oxidation state of the iodine nucleus, i.e., +3. Thus, the coordination mode of acetates I and III may be best described as being anisobidentate, whereas that for acetate II is unidentate. Further evidence in support of this assignment may be found from an examination of the I-O-C bond angles. For acetates I and III the I-O-C bond angles are 100.1 (8) and 98.3 (8)°, respectively. The corresponding angle for acetate II is 116.5 (8)°. The increase in the I-O-C bond angle for acetate II is due to its unidentate mode of binding. This carboxylate group is prevented from being bidentate because of a steric interaction between O(22) and one of the iodine lone pairs.

A pentagonal-planar arrangement of primary and secondary bonds has been observed for a number of iodine(III) oxo compounds, for examples $\text{C}_6\text{H}_5\text{I}(\text{O}_2\text{CR})_2$ derivatives where R = CH_3 ,^{21,22} CHCl_2 ,²¹ and CF_3 ,²³ and also for the μ -oxo compounds

**Figure 2.** Secondary bonding model for $\text{I}(\text{O}_2\text{CCH}_3)_3$.²¹

$[\text{C}_6\text{H}_5\text{I}(\text{O}_2\text{CCF}_3)]_2\text{O}^{24}$ and $[\text{C}_6\text{H}_5\text{I}(\text{NO}_3)]_2\text{O}^{25}$ The I...O secondary bonding distances in these structures lie in the range of 2.817–3.133 Å and are consequently much weaker than those observed in the structure reported here.

A secondary bonding model to account for the pentagonal-planar geometry found in these complexes has been proposed by Alcock et al.,²¹ by considering the overlap of the σ^* orbital of the "equatorial" primary bond with two lone pairs from the uncoordinated oxygens (see Figure 2).

Although this secondary model would account for the pentagonal-planar geometry found in the present structure, it would be anticipated that, by donation of electron density from the oxygen lone pairs to the vacant σ^* orbital, the corresponding I-O primary bond should be weakened slightly. It is, however, the shortest and hence the strongest of the three primary bonds in the present structure and is also the shortest yet reported for an I-O carboxylate bond.

Previous workers,²¹ in their studies of organoiodine(III), IRX_2 , compounds, have observed an important empirical correlation in that the effect of changing from halogenoiodine(III) to oxoiodine(III) compounds always produces a conversion from square-planar to pentagonal-planar coordination. From the evidence of the work presented here, this correlation can now be extended to include IX_3 compounds, where the square-planar geometry found for the I_2X_6 compound with X = Cl²⁶ is changed to the pentagonal-planar coordination found in $\text{I}(\text{O}_2\text{CCH}_3)_3$.

The present structure may be compared to that of the tris(*O*-ethyl xanthato)tellurate(II) anion in which the tellurium atom is in a similar pentagonal-planar arrangement.²⁷ The geometry of this anion was explained in terms of the VSEPR theory as a

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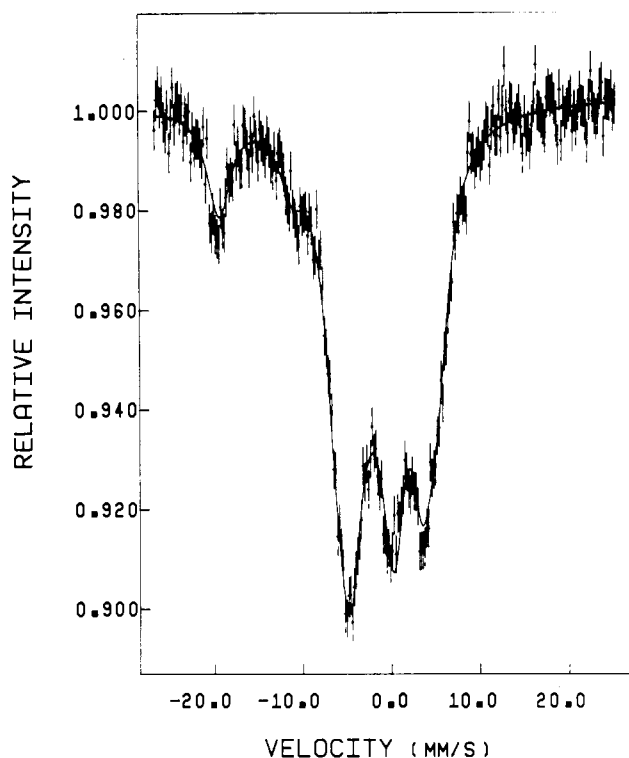


Figure 3. ¹²⁷I Mössbauer spectrum of $I(O_2CCF_3)_3$ measured at 4.2 K. The solid line is the best fit to the data.

pentagonal-bipyramidal, AX_5E_2 , arrangement with axial lone pairs. However, this structure shows similar trends in variation of bond lengths/bond angles as the present structure and therefore is probably better described as having an $AX_3Y_2E_2$ geometry.

The crystal packing appears to be determined only by van der Waals forces, and the absence of any intermolecular secondary I...O bonding is unexpected. However, this is similar to the situation found for diphenyliodonium-2-carboxylate hydrate¹ and bis(4-hydroxy-3-methylphenyl)tellurium(IV) dichloride,²⁸ where hydrogen bonds rather than secondary bonds determine the crystal packing.

Mössbauer Spectroscopy. ¹²⁷I Mössbauer data obtained for the tris(carboxylato)iodine(III) complexes are summarized in Table V; literature data for some related compounds are also included in the table. For $I(O_2CCH_3)_3$, our data are in good agreement with the values reported by Jones⁵ considering that (a) the latter data were recorded on a frozen-solution sample and (b) errors were involved in converting the ¹²⁹I Mössbauer data into their ¹²⁷I equivalents. A representative spectrum of the series, that of $I(O_2CCF_3)_3$, is shown in Figure 3, with the line due to the $^{5/2}(\text{ground}) \rightarrow ^{7/2}(\text{excited})$ transition being well resolved at high negative velocity.²⁹ The spectra for the other compounds studied in this work are similar and indicate that the sign of the quadrupole

coupling constant, $e^2q^{127}Q_0/h$, is positive for all of them, this being expected for a central iodine nucleus bound to three carboxylate groups in the xy plane with the two nonbonding pairs of electrons axially disposed to one another along the internuclear z axis.

Examination of the data in Table V reveals that the magnitude of the quadrupole coupling constant appears to be only slightly influenced by the electronegativity of the carboxylate group bound to the iodine nucleus; an increase in ligand electronegativity gives a small increase in the value of $e^2q^{127}Q_0/h$. A much more dramatic effect is shown, however, when the number and type of ligand that is primarily bonded to the iodine(III) nucleus are varied. For example, as the series $I(O_2CCH_3)_3$, $(C_6H_5)I(O_2CCH_3)_2$, $C_6H_5Ic_6H_4CO_2 \cdot H_2O$ is traversed, i.e. systematically decreasing the number of iodine-oxygen bonds, we see a concomitant decrease in the magnitude of $e^2q^{127}Q_0/h$ from $\sim +3400$ to $\sim +1900$ MHz. In this series the primary bond from iodine to oxygen is much more electronegative than the iodine-carbon bonds and consequently withdraws more charge from the iodine nucleus in the xy plane, hence increasing the value of the quadrupole coupling constant.

The above trend is also apparent in the asymmetry parameter values recorded for these compounds. The η values of the tris(carboxylato)iodine(III) species are all ca. 0.0, indicating approximately equal withdrawal of electron density in the x and y directions by the carboxylate groups. The mono- and diorgano species have much larger values of η , thus reflecting the difference in relative electronegativities of the carbon and oxygen atoms.

The chemical isomer shifts of all the compounds studied are more negative than that of KI, which was used as the reference material. This implies that the total s -electron density at the iodine nucleus in these compounds is greater than in the iodide ion, since $\delta R/R$ has been shown to be negative for ¹²⁷I.²⁹ As with the quadrupole coupling constants, the isomer shift values also appear to be dominated by the primary bonds to iodine, the isomer shifts becoming more positive as the number of iodine-oxygen bonds present within the compound are decreased. The values of δ for the tris(carboxylato)iodine(III) species are the lowest yet recorded for an iodine(III) compound. This suggests that the bonding in these compounds is predominantly p in character with very little or no s participation at all. The more electronegative iodine-oxygen bond results in the withdrawal of more p electrons from the central iodine nucleus, which in turn reduces the shielding effect on the s electrons, giving a more negative isomer shift. The range of isomer shifts within the series is small (-1.83 to -1.60 mm s^{-1}); one might have expected the isomer shift to become more negative as the ligand electronegativity is increased; however, it appears that the opposite is true with the trifluoroacetate derivative giving the more positive value of δ .

Acknowledgment. We thank the Natural Sciences and Engineering Research Council of Canada for providing an operating grant, Dr. J. W. Harvey and M. P. Butler and the McMaster Nuclear Reactor Facility for help with neutron irradiations, and R. Faggiani for technical assistance.

Supplementary Material Available: Tables SI and SII, listing full crystal data and details of mean planes, and Figure SI, showing a stereoscopic view of the crystal packing down b (4 pages); a table of calculated and observed structure factors (5 pages). Ordering information is given on any current masthead page.

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