Table 2. *Interatomic distances* (Å) *and bond angles* (°) *with e.s.d.'s in parentheses*

	Complex (I)	Complex (II)		Complex (I)	Complex (II)		Complex (I)	Complex (II)
Ni–N	2·050 (2)	2·050 (4)	C(13)–C(14)	1·383 (4)	1·376 (11)	N(21)–C(26)	1·342 (3)	1·330 (6)
Ni–N(11)	2·174 (2)	2·142 (4)	C(13)–C(17)	1·507 (6)	1·535 (9)	C(22)–C(23)	1·379 (3)	1·394 (7)
Ni–N(21)	2·151 (2)	2·113 (4)	C(17)–C(18)	1·421 (8)	1·460 (25)	C(23)–C(24)	1·391 (4)	1·390 (7)
N–C	1·157 (3)	1·158 (6)	C(17)–C(181)	—	1·640 (30)	C(23)–C(27)	1·514 (4)	1·502 (9)
C–S	1·616 (3)	1·616 (5)	C(14)–C(15)	1·383 (4)	1·360 (10)	C(27)–C(28)	1·501 (5)	1·508 (11)
N(11)–C(12)	1·341 (4)	1·330 (6)	C(15)–C(16)	1·366 (4)	1·356 (9)	C(24)–C(25)	1·376 (4)	1·389 (9)
N(11)–C(16)	1·349 (3)	1·340 (8)	N(21)–C(22)	1·347 (3)	1·342 (6)	C(25)–C(26)	1·373 (4)	1·371 (9)
C(12)–C(13)	1·387 (4)	1·408 (8)						
N–Ni–N	180·0 (1)	179·7 (2)	N(11)–C(12)–C(13)	124·4 (3)	124·2 (5)	N(21)–C(22)–C(23)	124·2 (2)	124·0 (5)
Ni–N–C	161·5 (2)	163·2 (4)	C(12)–C(13)–C(14)	117·3 (3)	115·5 (6)	C(22)–C(23)–C(24)	117·4 (2)	117·0 (5)
N–C–S	177·6 (2)	179·1 (5)	C(12)–C(13)–C(17)	120·0 (3)	121·5 (6)	C(22)–C(23)–C(27)	120·4 (2)	121·1 (5)
Ni–N(11)–C(12)	123·4 (2)	120·1 (3)	C(13)–C(17)–C(18)	115·8 (4)	116·1 (10)	C(23)–C(27)–C(28)	111·1 (3)	113·0 (6)
Ni–N(11)–C(16)	119·9 (2)	122·2 (3)	C(13)–C(17)–C(181)	—	105·6 (11)	C(24)–C(23)–C(27)	122·2 (2)	121·8 (5)
Ni–N(21)–C(22)	120·8 (2)	120·5 (3)	C(13)–C(14)–C(15)	119·3 (3)	121·3 (7)	C(23)–C(24)–C(25)	119·1 (3)	119·2 (6)
Ni–N(21)–C(26)	122·3 (2)	122·2 (3)	C(14)–C(13)–C(17)	122·7 (3)	123·0 (7)	C(24)–C(25)–C(26)	119·5 (3)	119·0 (6)
N–Ni–N(11)	90·0 (1)	89·9 (2)	C(14)–C(15)–C(16)	119·5 (3)	118·5 (7)	C(25)–C(26)–N(21)	122·8 (2)	123·4 (5)
N–Ni–N(21)	90·6 (1)	90·5 (2)	C(15)–C(16)–N(11)	122·9 (3)	123·8 (5)	C(26)–N(21)–C(22)	116·9 (2)	117·3 (4)
N(21)–Ni–N(11)	93·1 (1)	90·9 (2)	C(16)–N(11)–C(12)	116·6 (2)	116·7 (4)			

1,3 angles in (I) are 75·8 (1) and 60·0 (1)°, while in (II) they are 55·0 (1) and 44·6 (1)°, respectively; 2,3 angles are 80·3 (1) (I) or 75·3 (1)° (II). The torsion angles (atoms defining the torsion angles are Ni, N, C and S) are 3·4 (1) and 15·2 (7)° for (I) and (II), respectively. The different arrangement of 3-Etpy and NCS ligands for complexes (I) and (II) can be assumed to be a consequence of the different mode of complex-molecule formation [*i.e.* of the different sequence of ligand bonding upon the formation of the complex molecules (I) and (II)]: as the bulky 3-Etpy ligands are bonding to the N^{II} atom in the presence of NCS groups in ethanolic solution (see *Experimental*) forming complex (I), they can occupy only the positions and Ni–N distances allowed by the NCS groups. On the other hand, upon formation of complex (II) the 3-Etpy formerly added to the aqueous Ni^{II} solution {$[Ni(H_2O)_6]^{2+}$ cations} can occupy the advantageous orientation in the presence of small H_2O ligands, forming the $[Ni(H_2O)_2(3\text{-Etpy})_4]^{2+}$ cation with the shorter Ni–N distances in comparison with those found for complex (I) (Table 2). The additional NCS^- bonding to this cation (KSCN added) allows only forced orientation of these groups (Fig. 2). The differences in the molecular structure lead to the different packing of the complex molecules [the higher density of complex (I)].

The structural differences of complexes (I) and (II) correspond to their spectral properties, *e.g.* the 10 D_q values of 10 200 cm^{-1} for complex (I) (blue) and 10 650 cm^{-1} for complex (II) (violet) (obtained from the electronic spectra) are in agreement with the differences in Ni–N(3-Etpy) interatomic distances of both complexes.

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Structure of Diacetato(*m*-tolyl)iodine(III)

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Abstract. $[I(C_2H_3O_2)_2(C_7H_7)]$, $M_r = 336{\cdot}1$, orthorhombic, *Pbca*, $a = 9{\cdot}254$ (2), $b = 14{\cdot}109$ (3), $c = 19{\cdot}400$ (3) Å, $V = 2532{\cdot}9$ Å^3, $Z = 8$, $D_x = 1{\cdot}763$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71069 Å, $\mu = 2{\cdot}56$ mm^{-1}, $F(000) = 1312$, $T = 294$ K. Final $R = 0{\cdot}050$ for 1663 unique observed reflections. The characteristic T-shaped coordination geometry of dsp^3-hybridized trivalent iodine compounds [I–O, 2·13 (1), 2·15 (1) Å; I–C, 2·11 (1) Å] is the main conformational feature of the molecule. This is complemented by two equal intramolecular I···O contacts of 2·86 (1) Å which may be considered as secondary bonds so that

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the overall coordination geometry of iodine can be described as pentagonal planar.

Introduction. In the course of a study of various hypervalent iodine compounds, aimed at the elucidation of the nature of I^{III} bonds in them and the correlation between their structure and their chemical reactivity and physical–chemical properties, the crystal structures of some members of the group $(m\text{-}XC_6H_4)I(OCOR)_2$ (X: CH_3, NO_2; R: CH_3, CF_3) were required in order to obtain the necessary quantitative structural information. We now report the structure of the title compound (MTID hereafter).

Experimental. Transparent colourless crystals, 0·60 × 0·44 × 0·40 mm, m.p. 421–422 K; computer-controlled PW 1100 four-circle single-crystal diffractometer, graphite-monochromated Mo $K\alpha$, ω-scan mode; cell parameters and e.s.d.'s by least-squares analysis of measured θ angles of the 115 strongest reflections; space group *Pbca* from systematic absences; three standard reflections per 90 min without significant intensity variation; 3582 measured unique reflections, $\theta = 3$–$30°$, max. *hkl*: 12,19,24, 1663 observed reflections with $I_o > 2\sigma(I_o)$; no absorption correction; I atom located by Patterson synthesis, remaining non-H atoms by Fourier synthesis; 'blocked-cascade' full-matrix least squares using F with *SHELX76* (Sheldrick, 1976) and *SHELXTL* (Sheldrick, 1981); H atoms at calculated positions (very close to those from a difference Fourier map) and riding on the corresponding C atoms to which they are bonded, with isotropic temperature factors refined; $w = 1/[\sigma^2(F_o) + 0{\cdot}002F_o^2]$; $R = 0{\cdot}050$, $wR = 0{\cdot}062$, $S = 1{\cdot}04$, $(\Delta/\sigma)_{\text{max}} = 0{\cdot}262$, $(\Delta/\sigma)_{\text{mean}} = 0{\cdot}034$, $\Delta\rho = -1{\cdot}10$ to $1{\cdot}54$ e Å^{-3} in region of I atom (next-highest peak 0·44 e Å^{-3}); atomic scattering factors from *International Tables for X-ray Crystallography* (1974).

Discussion. Final positional parameters and equivalent isotropic temperature coefficients for the non-H atoms are given in Table 1.* Interatomic distances and angles are given in Table 2. An *ORTEP*II (Johnson, 1976) view of the MTID molecule is shown in Fig. 1. The primary geometry of the I atom is the expected T-shaped geometry of *dsp*^{3}-hybridized trivalent iodine compounds. Moreover, there are two weak intramolecular I···O contacts [I···O(3) = 2·858 (6), I···O(4) = 2·863 (6) Å] which involve the carbonyl O atoms of the acetate groups and are significantly

Table 1. *Atom coordinates* (×10^4, *for* I ×10^5) *and equivalent isotropic temperature factors* (Å^2 ×10^3)

	x	y	z	U_{eq}*
I	11846 (5)	11919 (4)	2187 (2)	43
O(1)	3364 (6)	1032 (5)	−112 (3)	60
O(2)	−749 (6)	1319 (4)	822 (3)	56
O(3)	2374 (6)	1106 (5)	−1139 (3)	71
O(4)	−1758 (6)	1451 (5)	−197 (3)	63
C(1)	2124 (8)	1015 (6)	1204 (4)	49
C(2)	2998 (8)	1746 (7)	1441 (4)	54
C(3)	3641 (8)	1641 (8)	2077 (5)	70
C(4)	3336 (9)	825 (7)	2459 (5)	71
C(5)	2439 (9)	130 (7)	2211 (4)	69
C(6)	1810 (9)	214 (7)	1564 (4)	57
C(7)	3437 (8)	1045 (6)	−786 (4)	50
C(8)	4963 (8)	923 (7)	−1069 (5)	72
C(9)	−1884 (8)	1408 (6)	412 (4)	46
C(10)	−3268 (8)	1475 (7)	799 (5)	60
C(11)	4588 (11)	2413 (7)	2378 (6)	95

* U_{eq} defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 2. *Bond lengths* (Å) *and angles* (°)

I–O(1)	2·128 (7)	I–O(2)	2·146 (7)
I–C(1)	2·114 (9)	O(1)–C(7)	1·31 (1)
O(2)–C(9)	1·32 (1)	O(3)–C(7)	1·20 (1)
O(4)–C(9)	1·19 (1)	C(1)–C(2)	1·39 (1)
C(1)–C(6)	1·36 (1)	C(2)–C(3)	1·38 (1)
C(3)–C(4)	1·40 (1)	C(3)–C(11)	1·52 (1)
C(4)–C(5)	1·37 (1)	C(5)–C(6)	1·39 (1)
C(7)–C(8)	1·53 (1)	C(9)–C(10)	1·48 (1)
I···O(3)	2·858 (6)	I···O(4)	2·863 (6)

O(1)–I–O(2)	164·4 (2)	O(1)–I–C(1)	82·5 (3)
O(2)–I–C(1)	81·9 (3)	I–O(1)–C(7)	110·4 (5)
I–O(2)–C(9)	110·0 (5)	I–C(1)–C(2)	116·8 (6)
I–C(1)–C(6)	118·4 (6)	C(2)–C(1)–C(6)	124·9 (7)
C(1)–C(2)–C(3)	117·8 (8)	C(2)–C(3)–C(4)	118·5 (9)
C(2)–C(3)–C(11)	121·1 (9)	C(4)–C(3)–C(11)	120·3 (8)
C(3)–C(4)–C(5)	121·6 (8)	C(4)–C(5)–C(6)	120·6 (8)
C(1)–C(6)–C(5)	116·5 (8)	O(1)–C(7)–O(3)	121·9 (7)
O(1)–C(7)–C(8)	114·0 (7)	O(3)–C(7)–C(8)	124·0 (7)
O(2)–C(9)–O(4)	121·6 (7)	O(2)–C(9)–C(10)	112·7 (7)
O(4)–C(9)–C(10)	125·6 (7)	O(1)–I···O(3)	49·7 (2)
O(2)–I···O(4)	49·6 (2)	O(3)···I···O(4)	96·4 (2)

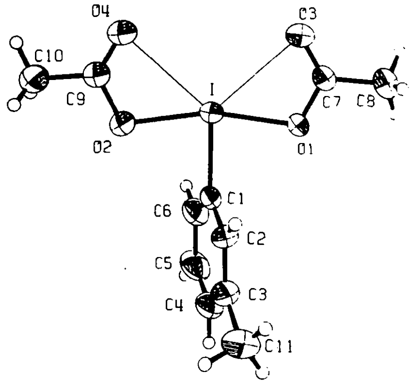

Fig. 1. *ORTEP*II drawing of the MTID molecule. Thermal ellipsoids are drawn at 50% probability level; isotropic H thermal parameters are represented by spheres of arbitrary size.

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* Lists of structure factors, anisotropic thermal parameters, coordinates and isotropic temperature factors for H atoms and least-squares-planes' calculations have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 42951 (20 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

shorter than 3·46 Å, the sum of the van der Waals radii of O and I (Bondi, 1964). They may be considered as secondary bonds (Alcock, 1972) so that the overall coordination geometry of iodine can be described as planar pentagonal. The T-shaped group, I, O(1), O(2), C(1), is planar to within 0·007 (7) Å with O(3) and O(4) at distances 0·158 (6) and 0·078 (7) Å from the mean plane. The dihedral angles between this plane and the planes of the acetoxy groups involving O(3) and O(4) are 4·3 (3) and 2·9 (3)°, respectively. The conformational details given so far are comparable with those for (phenyl)bis(trifluoroacetato)iodine(III) (FAIB hereafter) (Stergioudis, Kokkou, Bozopoulos & Rentzeperis, 1984; Alcock, Harrison & Howes, 1984) and those for bis(dichloroacetato)(phenyl)iodine(III) (PICA hereafter) (Alcock, Countryman, Esperas & Sawyer, 1979), and agree very well with those for diacetato(phenyl)iodine(III) (PID hereafter) (Alcock *et al.*, 1979). A comparison of FAIB and PICA with PID shows that secondary I···O bonding is very sensitive to the nature of the ligands. In going from PID to PICA or to FAIB considerable distortion of the overall planar-pentagonal coordination of the I atom occurs, *i.e.* deviations from planarity, appearance of a third weaker intermolecular I···O secondary bond and weakening of the existing intramolecular ones. In the present case the substitution of an *m*-tolyl for a phenyl group does not affect the I···O secondary bonding so that the planar-pentagonal coordination of I is preserved. However, the two I···O secondary bonds are essentially equal (difference 0·8σ) while those in PID [2·850 (5), 2·817 (6) Å] are unequal with a difference of 4·24σ. Also, the dihedral angles formed by the T group and the planar benzene ring [68·4 (2) in MTID, 74·43° in PID] differ significantly.

Fig. 2 shows the molecular packing of MTID in the unit cell. There are no intermolecular hydrogen bonds. The smallest intermolecular separations are: H(C4)···O(2) (at $\frac{1}{2}+x, y, \frac{1}{2}-z$) = 2·64 and H3(C10)···O(3) (at $-\frac{1}{2}+x, \frac{1}{2}-y, -z$) = 2·75 Å.

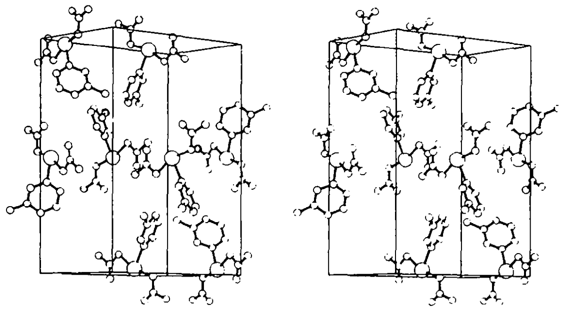

Fig. 2. Stereo plot of the unit cell viewed along [110]. The origin is in the upper front corner of the base of the outline, the *a* axis to the left and the *b* axis to the right. The *c* axis is vertical.

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3,3-Bis(methylnitraminomethyl)oxetane (I) and 3,3-Bis(nitratomethyl)oxetane (II)

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Abstract. (I): $C_7H_{14}N_4O_5$, $M_r = 234\cdot21$, monoclinic, $P2_1/c$, $a = 14\cdot106\ (4)$, $b = 6\cdot472\ (2)$, $c = 11\cdot963\ (3)$ Å, $\beta = 99\cdot50\ (3)°$, $V = 1077\cdot2\ (6)$ Å^3, $Z = 4$, $D_x = 1\cdot444$ Mg m^{-3}, $\lambda(\text{Mo}\ K\alpha) = 0\cdot71069$ Å, $\mu = 0\cdot115$ mm^{-1}, $F(000) = 496$, $T = 295$ K, final $R = 0\cdot049$, $wR = 0\cdot057$ for 1815 independent observed