complex, both of which do not have any tight ion pairs. The longest Ca—O distances of this type are observed for two 8-coordinate complexes $[Ca(NCS)_2(OH_2)(EG4)]$ and $[Ca(NCS)_2(EG5)]$, each of which has two tight ion pairs.

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Mixed Chelate Complexes. III.
Structures of (L-Alaninato)(aqua)(2,2′-bipyridine)copper(II) Nitrate Monohydrate and Aqua(2,2′-bipyridine)(L-tyrosinato)copper(II) Chloride Trihydrate

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Abstract. (I) $[Cu(C_3H_6NO_2)(C_{10}H_8N_2)(H_2O)]$-$NO_3.H_2O$, $M_r = 405.9$, orthorhombic, $P2_12_12_1$, $a = 19.113\,(3)$, $b = 15.079\,(2)$, $c = 5.782\,(1)$ Å, $V = 1666.4\,(8)$ Å^3, $Z = 4$, $D_x = 1.617$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.409$ mm^{-1}, $F(000) = 836.0$, $T = 288$ K, $R = 0.042$ for 1595 reflections. (II) $[Cu(C_9H_{10}NO_3)(C_{10}H_8N_2)(H_2O)]Cl.3H_2O$, $M_r = 507.4$, hexagonal, $P6_1$, $a = 9.307\,(2)$, $c = 44.432$ Å, $V = 3333\,(3)$ Å^3, $Z = 6$, $D_x = 1.516$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 1.188$ mm^{-1}, $F(000) = 1578.0$, $T = 288$ K, $R = 0.053$ for 2048 reflections. In each complex the Cu ion displays a square pyramidal coordination with an apical water molecule. The apical Cu—OH$_2$ bond lengths are 2.230 (4) Å for (I) and 2.308 (6) Å for (II). The results obtained are compared with those for other aminoacidate copper(II) complexes.

Introduction. Compounds with general formula $[Cu(N\text{–}N)(O\text{–}N)]^+$, where (N–N) = 2,2′-bipyridine and (O–N) = alaninato or tyrosinato, have been synthesized and characterized by Ruíz-Ramírez, Martínez & Gasque (1992) who also determined their stability constants potentiometrically. The compounds are obtained from 1:1 mmol solutions of Cu^{II} ion and the (N–N) ligand in water, followed by the

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addition of the L-amino acid; the pH is then increased to 8 by addition of ammonium hydroxide. Concentration of the solution leads to precipitation of the mixed chelate complex. Blue crystals are grown from a water solution. In order to determine the coordination geometry of the Cu$^{\mathrm{II}}$ ions and confirm the chelating scheme, crystal structure determinations have been carried out on the title compounds (I) and (II).

Experimental. A similar method was followed in the determination of both crystal structures (see Table 1). A prismatic crystal was selected and mounted on a Philips PW1100 four-circle diffractometer. Graphite-monochromated Mo $K\alpha$ radiation was used. Cell parameters were determined from 25 reflections ($4 < \theta < 12°$) and refined by least squares. Intensities were collected with ω-scan technique, with scan width 1° and scan speed $0.03°\ \mathrm{s}^{-1}$. 1693 independent reflections were measured for (I); 1595 with $I > 2.5\sigma(I)$. 2127 independent reflections were measured for (II); 2048 with $I > 2.5\sigma(I)$. Three intensities were measured every 2 h as orientation and intensity controls; significant intensity decay was not observed. Lorentz–polarization, but no absorption corrections were made.

In both structures Cu and several C, N and O atoms were located with *MULTAN* (Main, Fiske, Hull, Lessinger, Germain, Declercq & Woolfson, 1984) and the remaining non-H atoms with *DIRDIF* (Beurskens, Bosman, Doesburg, Gould, Van der Hark, Prick, Noordik, Beurskens & Parthasarathi, 1981). Full-matrix least-squares refinement used *SHELX76* (Sheldrick, 1976). The function minimized was $\sum w||F_o| - |F_c||^2$, where $w = \sigma^{-2}(F_o)$. f, f' and f'' were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–100, 149). Final coordinates for (I) and (II) correspond to the enantiomorph which gives the smaller R factor. H-atom positions were computed and refined with an overall isotropic temperature factor, using a riding model. All computing was carried out on an IBM-3083 computer.

Discussion. Final atomic coordinates and equivalent isotropic thermal coefficients are given in Table 2.* Table 3 shows selected bond lengths and angles. Figs. 1 and 2 present views of structures (I) and (II), respectively, with atom numbering.

Table 1. *Experimental details*

	(I)	(II)
Crystal size (mm)	0.1 × 0.1 × 0.1	0.1 × 0.1 × 0.15
No. of intensities	1693	2127
θ range (°)	2→25	2→25
Range of h	0→22	−11→11
k	0→17	0→11
l	0→6	0→50
R_{int} (on F)		0.034
No. of intensities with $I > 2.5\sigma(I)$	1595	2048
Weighting scheme $[\sigma^2(F_o) + k\|F_o\|^2]^{-1}$		
k	0.021	0.13
R	0.042	0.053
wR	0.043	0.058
Maximum shift/σ	0.3	0.09
Maximum $\Delta\rho$ (e Å^{-3})	0.3	0.4
Minimum $\Delta\rho$ (e Å^{-3})	−0.4	−0.3

Table 2. *Final atomic coordinates* (×10^4, Cu ×10^5) *and equivalent isotropic thermal coefficients* (Å^2)

$$B_{\mathrm{eq}} = (8\pi^2/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
(I)				
Cu	8888 (3)	6413 (3)	−2789 (11)	2.59 (3)
O(1)	763 (2)	1418 (2)	2410 (7)	3.11 (14)
C(2)	852 (2)	2239 (3)	2009 (8)	2.37 (17)
O(2)	849 (2)	2805 (2)	3560 (7)	3.36 (15)
C(3)	917 (2)	2518 (3)	−541 (8)	2.34 (17)
N(3)	1167 (2)	1751 (3)	−1904 (8)	2.69 (17)
C(4)	1371 (4)	3328 (4)	−924 (12)	3.66 (25)
N(5)	692 (2)	−437 (3)	1571 (8)	2.72 (16)
C(6)	269 (3)	−475 (4)	3409 (10)	3.10 (21)
C(7)	151 (3)	−1252 (3)	4642 (11)	3.34 (20)
C(8)	497 (3)	−2008 (4)	3940 (11)	3.48 (22)
C(9)	935 (3)	−1974 (4)	1990 (12)	3.50 (22)
C(10)	1025 (2)	−1182 (3)	843 (10)	2.56 (18)
C(11)	1470 (2)	−1050 (3)	−1220 (10)	2.73 (19)
C(12)	1890 (3)	−1713 (4)	−2102 (13)	3.90 (25)
C(13)	2311 (3)	−1517 (5)	−4043 (14)	4.79 (31)
C(14)	2283 (3)	−710 (4)	−4997 (12)	4.03 (26)
C(15)	1843 (3)	−71 (4)	−4044 (10)	3.21 (21)
N(16)	1458 (2)	−240 (3)	−2172 (8)	2.68 (16)
O(*W*1)	−193 (2)	588 (3)	−1717 (9)	3.48 (17)
O(*W*2)	6053 (3)	4182 (4)	341 (10)	4.77 (21)
N(21)	2852 (2)	1082 (3)	124 (10)	3.61 (20)
O(22)	2760 (2)	1426 (3)	−1816 (9)	4.55 (21)
O(23)	3435 (3)	784 (5)	626 (13)	7.91 (36)
O(24)	2382 (3)	1085 (5)	1572 (11)	6.46 (28)
(II)				
Cu	72602 (10)	12140 (10)	58945†	2.47 (4)
O(1)	8055 (7)	3536 (6)	5810 (1)	2.79 (22)
C(2)	7571 (9)	3790 (10)	5558 (2)	2.57 (31)
O(2)	8108 (8)	5203 (8)	5448 (2)	3.60 (26)
C(3)	6394 (9)	2293 (9)	5372 (2)	2.67 (30)
N(4)	5612 (8)	825 (8)	5577 (1)	2.62 (26)
C(5)	7363 (11)	1989 (11)	5118 (2)	3.16 (34)
C(6)	8691 (10)	1653 (9)	5225 (2)	2.50 (29)
C(7)	10289 (10)	2898 (11)	5275 (2)	3.32 (34)
C(8)	11517 (10)	2573 (11)	5385 (2)	3.73 (37)
C(9)	11061 (10)	933 (11)	5449 (2)	3.23 (35)
O(9)	12288 (8)	634 (9)	5562 (2)	4.58 (32)
C(10)	9468 (9)	−338 (10)	5402 (2)	2.83 (31)
C(11)	8290 (10)	9 (10)	5289 (2)	2.78 (31)
N(12)	9280 (8)	1818 (9)	6139 (2)	2.81 (26)
C(13)	10418 (11)	3374 (11)	6211 (2)	3.75 (36)
C(14)	11905 (12)	3704 (14)	6355 (2)	4.36 (42)
C(15)	12178 (12)	2396 (15)	6422 (2)	4.69 (48)
C(16)	10952 (12)	778 (13)	6350 (2)	3.99 (44)
C(17)	9513 (10)	510 (11)	6211 (2)	3.00 (33)
C(18)	8127 (11)	−1135 (10)	6126 (2)	2.90 (33)
C(19)	8136 (13)	−2573 (11)	6183 (2)	3.75 (39)
C(20)	6792 (15)	−4040 (12)	6087 (2)	4.51 (47)
C(21)	5482 (13)	−4031 (10)	5931 (2)	4.23 (40)
C(22)	5576 (11)	−2517 (9)	5884 (2)	3.28 (32)
N(23)	6879 (9)	−1084 (8)	5977 (1)	2.84 (27)
Cl	3580 (3)	6300 (2)	1804 (1)	3.57 (8)
O(*W*1)	5420 (8)	1076 (9)	6257 (2)	4.67 (32)
O(*W*2)	8665 (7)	2614 (8)	631 (2)	4.11 (29)
O(*W*3)	447 (9)	6228 (11)	6689 (2)	5.46 (36)
O(*W*4)	7970 (10)	5407 (11)	4566 (2)	5.40 (39)

† Coordinate fixed to define origin for non-centrosymmetric structure.

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* Lists of structure factors, anisotropic thermal parameters, bond distances and angles involving H atoms and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55079 (20 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU0253]

Table 3. *Bond lengths* (Å) *and bond angles* (°)

(I)

O(1)—Cu	1.962 (4)	C(8)—C(7)	1.378 (8)
C(2)—Cu	2.749 (5)	C(9)—C(8)	1.406 (8)
N(3)—Cu	1.991 (4)	C(10)—C(9)	1.376 (7)
N(5)—Cu	1.982 (4)	C(11)—C(10)	1.479 (8)
N(16)—Cu	2.037 (4)	C(12)—C(11)	1.380 (8)
O(*W*1)—Cu	2.230 (4)	N(16)—C(11)	1.340 (6)
C(2)—O(1)	1.270 (6)	C(13)—C(12)	1.412 (10)
O(2)—C(2)	1.238 (6)	C(14)—C(13)	1.337 (10)
C(3)—C(2)	1.538 (6)	C(15)—C(14)	1.393 (8)
N(3)—C(3)	1.479 (6)	N(16)—C(15)	1.333 (7)
C(4)—C(3)	1.515 (7)	O(22)—N(21)	1.248 (8)
C(6)—N(5)	1.337 (7)	O(23)—N(21)	1.236 (7)
C(10)—N(5)	1.359 (6)	O(24)—N(21)	1.228 (7)
C(7)—C(6)	1.390 (7)		

C(2)—Cu—O(1)	24.8 (1)	C(4)—C(3)—N(3)	111.6 (4)
N(3)—Cu—O(1)	84.5 (2)	C(3)—N(3)—Cu	108.7 (3)
N(3)—Cu—C(2)	59.8 (2)	C(6)—N(5)—Cu	125.4 (4)
N(5)—Cu—O(1)	92.2 (2)	C(10)—N(5)—Cu	115.0 (3)
N(5)—Cu—C(2)	117.0 (2)	C(10)—N(5)—C(6)	119.6 (4)
N(5)—Cu—N(3)	174.0 (2)	C(7)—C(6)—N(5)	122.8 (5)
N(16)—Cu—O(1)	151.8 (2)	C(8)—C(7)—C(6)	117.9 (5)
N(16)—Cu—C(2)	147.6 (1)	C(9)—C(8)—C(7)	119.4 (5)
N(16)—Cu—N(3)	98.8 (2)	C(10)—C(9)—C(8)	119.5 (5)
N(16)—Cu—N(5)	81.8 (2)	C(9)—C(10)—N(5)	120.7 (5)
O(*W*1)—Cu—O(1)	101.8 (2)	C(11)—C(10)—N(5)	114.1 (4)
O(*W*1)—Cu—C(2)	100.8 (1)	C(11)—C(10)—C(9)	125.3 (4)
O(*W*1)—Cu—N(3)	95.8 (2)	C(12)—C(11)—C(10)	122.3 (5)
O(*W*1)—Cu—N(5)	89.7 (2)	N(16)—C(11)—C(10)	116.4 (4)
O(*W*1)—Cu—N(16)	105.7 (2)	N(16)—C(11)—C(12)	121.3 (5)
C(2)—O(1)—Cu	114.9 (3)	C(13)—C(12)—C(11)	118.2 (6)
O(1)—C(2)—Cu	40.3 (2)	C(14)—C(13)—C(12)	119.7 (6)
O(2)—C(2)—Cu	162.3 (3)	C(15)—C(14)—C(13)	119.3 (6)
O(2)—C(2)—O(1)	122.6 (5)	N(16)—C(15)—C(14)	121.5 (6)
C(3)—C(2)—Cu	77.1 (2)	C(11)—N(16)—Cu	112.5 (3)
C(3)—C(2)—O(1)	116.9 (4)	C(15)—N(16)—Cu	127.4 (4)
C(3)—C(2)—O(2)	120.4 (4)	C(15)—N(16)—C(11)	119.9 (4)
N(3)—C(3)—C(2)	108.8 (4)	O(23)—N(21)—O(22)	119.3 (6)
C(4)—C(3)—C(2)	114.0 (4)	O(24)—N(21)—O(22)	120.5 (5)
		O(24)—N(21)—O(23)	120.1 (6)

(II)

O(1)—Cu	1.939 (5)	C(10)—C(9)	1.375 (11)
N(4)—Cu	1.978 (6)	C(11)—C(10)	1.383 (11)
N(12)—Cu	1.994 (6)	C(13)—N(12)	1.337 (11)
N(23)—Cu	2.018 (6)	C(17)—N(12)	1.376 (11)
O(*W*1)—Cu	2.308 (6)	C(14)—C(13)	1.413 (13)
C(2)—O(1)	1.271 (9)	C(15)—C(14)	1.395 (15)
O(2)—C(2)	1.250 (10)	C(16)—C(15)	1.398 (15)
C(3)—C(2)	1.516 (10)	C(17)—C(16)	1.379 (12)
N(4)—C(3)	1.496 (10)	C(18)—C(17)	1.475 (12)
C(5)—C(3)	1.556 (11)	C(19)—C(18)	1.366 (11)
C(6)—C(5)	1.495 (11)	N(23)—C(18)	1.357 (10)
C(7)—C(6)	1.372 (11)	C(20)—C(19)	1.379 (15)
C(11)—C(6)	1.411 (11)	C(21)—C(20)	1.408 (16)
C(8)—C(7)	1.407 (12)	C(22)—C(21)	1.383 (13)
C(9)—C(8)	1.394 (13)	N(23)—C(22)	1.343 (10)
O(9)—C(9)	1.397 (11)		

N(4)—Cu—O(1)	84.0 (2)	C(10)—C(9)—C(8)	121.2 (8)
N(12)—Cu—O(1)	90.6 (3)	C(10)—C(9)—O(9)	121.4 (8)
N(12)—Cu—N(4)	167.3 (3)	C(11)—C(10)—C(9)	119.6 (8)
N(23)—Cu—O(1)	169.4 (3)	C(10)—C(11)—C(6)	121.0 (7)
N(23)—Cu—N(4)	103.1 (3)	C(13)—N(12)—Cu	124.0 (6)
N(23)—Cu—N(12)	80.8 (3)	C(17)—N(12)—Cu	114.9 (5)
O(*W*1)—Cu—O(1)	93.3 (3)	C(17)—N(12)—C(13)	120.9 (7)
O(*W*1)—Cu—N(4)	90.1 (3)	C(14)—C(13)—N(12)	120.2 (9)
O(*W*1)—Cu—N(12)	101.8 (3)	C(15)—C(14)—C(13)	119.6 (9)
O(*W*1)—Cu—N(23)	94.7 (3)	C(16)—C(15)—C(14)	119.0 (8)
C(2)—O(1)—Cu	113.9 (5)	C(17)—C(16)—C(15)	119.5 (9)
O(2)—C(2)—O(1)	123.3 (7)	C(16)—C(17)—N(12)	120.8 (8)
C(3)—C(2)—O(1)	118.0 (7)	C(18)—C(17)—N(12)	114.5 (7)
C(3)—C(2)—O(2)	118.5 (7)	C(18)—C(17)—C(16)	124.6 (8)
N(4)—C(3)—C(2)	107.7 (6)	C(19)—C(18)—C(17)	122.6 (8)
C(5)—C(3)—C(2)	110.2 (6)	N(23)—C(18)—C(17)	114.1 (7)
C(5)—C(3)—N(4)	109.7 (6)	N(23)—C(18)—C(19)	123.3 (8)
C(3)—N(4)—Cu	106.8 (4)	C(20)—C(19)—C(18)	117.8 (9)
C(6)—C(5)—C(3)	115.0 (6)	C(21)—C(20)—C(19)	120.4 (9)
C(7)—C(6)—C(5)	122.4 (7)	C(22)—C(21)—C(20)	117.9 (9)
C(11)—C(6)—C(5)	119.5 (7)	N(23)—C(22)—C(21)	122.0 (9)
C(11)—C(6)—C(7)	118.1 (7)	C(18)—N(23)—Cu	115.2 (5)
C(8)—C(7)—C(6)	122.0 (8)	C(22)—N(23)—Cu	126.1 (6)
C(9)—C(8)—C(7)	118.1 (8)	C(22)—N(23)—C(18)	118.6 (7)
O(9)—C(9)—C(8)	117.4 (7)		

The Cu ion displays a square pyramidal coordination in both structures, being linked to O and N atoms of the aminoacidate ligand and two N atoms of the bipyridine ligand in the basal plane, and an O atom of a water molecule in the apical site.

The four basal or equatorial atoms are in a more or less puckered plane [average deviations from the mean plane defined by these four atoms are ±0.1907 (7) Å for (I) and ±0.040 (2) Å for (II), while the Cu ion is 0.289 (4) and 0.165 (6) Å, for (I) and (II) respectively, out of this plane].

The average Cu—N(ar) bond length is 2.00 (2) Å, which is similar to those observed in related complexes (Aoki & Yamasaky, 1980; Solans, Ruíz-Ramírez, Gasque & Briansó, 1987; Solans, Ruíz-Ramírez, Martínez, Gasque & Briansó, 1988; Solans, Aguiló, Gleizest, Faus, Julve & Verdaguer, 1990; Antolini, Marcotrigiano, Menabue & Pellacani, 1983; Solans, Ruíz-Ramírez, Martínez, Gasque & Moreno-Esparza, 1992). The Cu—O(1)(carboxylate) bond lengths are longer than comparable values (Solans, Ruíz-Ramírez, Martínez, Gasque & Briansó, 1988; Antolini, Marcotrigiano, Menabue & Pellacani, 1983) whereas the Cu—N(aminoacidate) bonds are shorter than those previously observed (Solans, Ruíz-Ramírez, Martínez, Gasque & Moreno-Esparza, 1991).

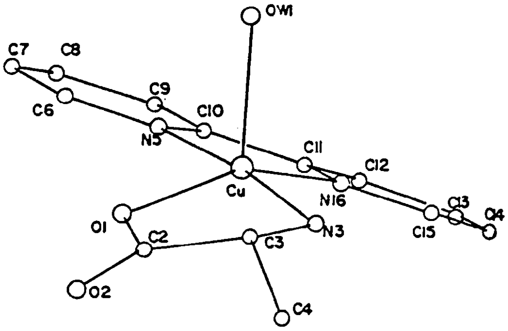

Fig. 1. A molecular view of complex (I).

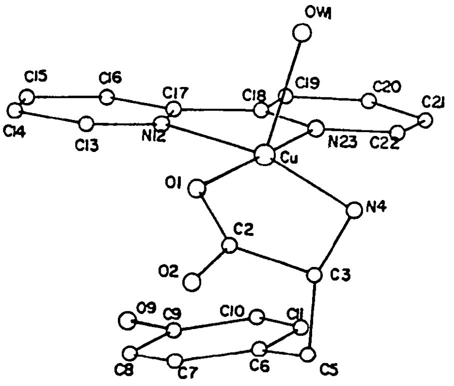

Fig. 2. A molecular view of complex (II).

The five-membered ring Cu, O, C, C, N has a skew-envelope form, where the atom out of the plane defined by the remaining four atoms differs in every compound. It is C(3) for (I) and N(4) for (II).

The Cu—O(*W*1)(aqua) apical bond length alters from 2.23 (4) Å in (I) to 2.308 (6) Å in (II). Values of 2.24 (1) and 2.368 (5) Å are reported for aqua(1,10-phenanthroline)(L-phenylalaninato)copper(II) nitrate monohydrate (Solans, Ruíz-Ramírez, Martínez, Gasque & Briansó, 1988) and aqua(aspartato)(2,2′-bipyridine)copper(II) trihydrate (Antolini, Marcotrigiano, Menabue & Pellacani, 1983), respectively.

The N(3)—Cu—O(1) bond angle is 84.5 (2)° for (I) and the N(4)—Cu—O(1) bond angle is 84.0 (2)° for (II); these angles correlate with the mean metal–ligand bond lengths (1.976 and 1.959 Å respectively). This correlation is based on the constancy of the O(1)···N(3) distances (average 2.66 Å). The mean donor–metal distance increases linearly from 2.0 to 2.5 Å as the interionic angle decreases from 84 to 64° (Freeman, 1967).

In (I) the water molecule coordinated to the Cu is hydrogen bonded to another water molecule and to atom O(2) of an alaninate ligand in a neighbouring complex. This second hydrogen bond is to a chloride ion in (II).

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4-Iodo-2,2,6,6-tetramethylheptane-3,5-dione

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Abstract. $C_{11}H_{19}IO_2$, $M_r = 310.18$, monoclinic, $P2_1/c$, $a = 9.188$ (3), $b = 14.229$ (2), $c = 10.628$ (12), $\beta = 104.74$ (6)°, $V = 1344$ (3) Å^3, $Z = 4$, $D_x = 1.53$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.71069 Å, $\mu = 2.34$ mm^{-1}, $F(000) = 616$, $T = 250$ K, $R = 0.039$ for 1562 unique reflexions [$I > 3\sigma(I)$]. The title compound was prepared as stable single crystals (m.p. 343 K) by the action of iodine on 2,2,6,6-tetramethylheptane-3,5-dione in ether. The molecule is highly dissymmetric with the carbonyl groups non-coplanar. Infrared (both for the solid state and CCl_4 solution) and nuclear magnetic resonance (for CCl_4 solution) spectra were also recorded.

Introduction. The preparation of 4-iodo-2,2,6,6-tetramethylheptane-3,5-dione (Ithd) was first reported by Schoppee & Stevenson (1972) with iodine chloride as an iodination agent. In the course of research on new ligands for volatile metal-organic componds, we incidentally obtained an iodinated compound by reacting iodine with 2,2,6,6-tetramethylheptane-3,5-dione (Hthd). It proved to be

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