For both compounds, data collection: *EXPOSE* (Stoe & Cie, 1993); cell refinement: *CELL* (Stoe & Cie, 1993); data reduction: *CONVERT* (Stoe & Cie, 1993); program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1985); program(s) used to refine structures: *SHELXL*93; molecular graphics: *ORTEP*II (Johnson, 1976) in *NRCVAX* (Larson *et al.*, 1986); software used to prepare material for publication: *SHELXL*93.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry, distances from the metal centre to the ligand planes and angles between the ligand planes have been deposited with the IUCr (Reference: SK1022). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Diiodobis(nicotinamide-N^1-acetate-O)-zinc(II)

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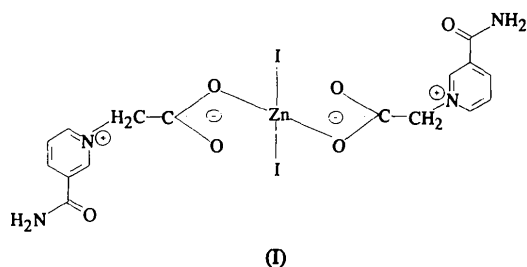
Abstract

In the title compound, $[ZnI_2(C_8H_8N_2O_3)_2]$, the Zn atom, which lies on a twofold axis, exists in a slightly distorted tetrahedral geometry involving two zwitterionic nicotinamide-N^1-acetate substituents [Zn—O1 2.008 (2) Å] and two iodide ligands [Zn—I 2.5848 (3) Å]. Molecules of the complex are connected by intermolecular N—H⋯O hydrogen bonds, with N⋯O distances of 2.965 (3) and 3.133 (3) Å.

Comment

As part of a long-term project involving structural, spectroscopic, thermal and biological activity studies of zinc(II) carboxylates with bioactive N-donor ligands, we have been interested in the product of the reaction between zinc(II) iodoacetate and nicotinamide, *i.e.* diiodobis(nicotinamide-N^1-acetate)zinc(II), (I). We have previously reported the mechanism of the reaction (Zeleňák, Györyová & Císařová, 1995).

(I)

The crystal structure of (I) consists of discrete monomeric units (Fig. 1) with the four-coordinate Zn atom lying on the crystallographic twofold axis. The distorted coordination tetrahedron is formed by two I atoms and two O atoms from the zwitterionic nicotinamide-N^1-acetate ligands. The complexes are linked by intermolecular N—H⋯O hydrogen bonds (Table 3), causing the two N—H distances to be different.

The zwitterionic nicotinamide-N^1-acetate ligands are unidentate with the carboxylate O1 atom bonded to Zn
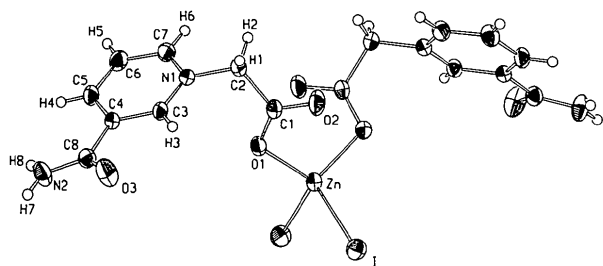
Fig. 1. View of $[ZnI_2(CONH_2C_5H_4N^+CH_2COO^-)_2]$. Displacement ellipsoids are plotted at the 50% probability level.

$[Zn—O1\ 2.008\,(2)\,Å]$ and the carboxylate O2 atom involved in only a weak interaction $[Zn\cdots O2\ 2.878\,(2)\,Å]$. The C1—O1 distance is slightly longer than the C1—O2 distance because of the greater double-bond character in the latter. The N1—C2 bond is synperiplanar to the C1—O1 bond and antiperiplanar to the C1—O2 bond [N1—C2—C1—O1 and N1—C2—C1—O2 are 5.3 (3) and −176.9 (2)°, respectively].

The Zn—O1 bond length is similar to that found in the analogous bromine complex, $[ZnBr_2(CONH_2\text{-}C_5H_4N^+CH_2COO^-)_2]$ [2.005 (2) Å; Zeleňák, Györyová & Císařová, 1995), shorter than that found in $[ZnCl_2\text{-}(CONH_2C_5H_4N^+CH_2COO^-)_2]$ [2.014 (1) Å; Zeleňák, Györyová, Císařová & Loub, 1996) and longer than those found in another complex with a zwitterionic carboxylate ligand, namely, dichlorobis(pyridine betaine)zinc(II) [1.988 (3) and 1.964 (2) Å; Chen & Mak, 1991].

In the series of complexes of the type $[ZnX_2(CONH_2\text{-}C_5H_4N^+CH_2COO^-)_2]$, where X = Cl (Zeleňák, Györyová, Císařová & Loub, 1996), Br (Zeleňák, Györyová & Císařová, 1995) and I (the title compound), the Zn—X bond distance increases from Cl to I [2.245 (1) for Cl, 2.381 (1) for Br and 2.5848 (3) Å for I], which is in good agreement with the increase in the covalent radius of the halogen atom. Comparison of the X—Zn—X' and O1—Zn—O1$'$ angles shows two trends. Whereas the X—Zn—X' angles decrease with an increase in the covalent radius of the halogen ligand [107.52 (3) for Cl, 105.9 (1) for Br and 104.29 (2)° for I], the O1—Zn—O1$'$ angles show the contrary trend [106.44 (8) for Cl, 107.8 (1) for Br and 109.24 (9)° for I].

Experimental

The synthesis of the title compound was carried out by reaction of zinc(II) iodoacetate and nicotinamide (molar ratio 1:2) in water at 313 K. The reaction mixture was filtered and then allowed to evaporate slowly at room temperature. After several days, pale yellow crystals were isolated.

Crystal data

$[ZnI_2(C_8H_8N_2O_3)_2]$
$M_r = 679.50$

Mo $K\alpha$ radiation
$\lambda = 0.71069$ Å

Monoclinic
$C2/c$
$a = 14.0585\,(9)$ Å
$b = 7.6504\,(4)$ Å
$c = 18.6550\,(10)$ Å
$\beta = 93.599\,(6)°$
$V = 2002.4\,(2)$ Å^3
$Z = 4$
$D_x = 2.254$ Mg m^{-3}
D_m not measured

Cell parameters from 25 reflections
$\theta = 18–19°$
$\mu = 4.352$ mm^{-1}
$T = 293\,(2)$ K
Hexagon
$0.46 \times 0.38 \times 0.35$ mm
Pale yellow

Data collection

CAD-4-MACHIII-PC diffractometer
ω–2θ scans
Absorption correction: analytical (AGNOSTIC; Templeton & Templeton, 1978)
$T_{min} = 0.210$, $T_{max} = 0.314$
4190 measured reflections
2179 independent reflections

2089 observed reflections
$[I > 4\sigma(I)]$
$R_{int} = 0.0257$
$\theta_{max} = 26.97°$
$h = -17 \rightarrow 17$
$k = 0 \rightarrow 9$
$l = -23 \rightarrow 23$
3 standard reflections
frequency: 60 min
intensity decay: 1%

Refinement

Refinement on F^2
$R(F) = 0.0208$
$wR(F^2) = 0.0537$
$S = 1.113$
2179 reflections
165 parameters
All H-atom parameters refined
$w = 1/[\sigma^2(F_o^2) + (0.0269P)^2 + 2.666P]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.001$

$\Delta\rho_{max} = 0.630$ e Å^{-3}
$\Delta\rho_{min} = -0.851$ e Å^{-3}
Extinction correction: SHELXL93 (Sheldrick, 1993)
Extinction coefficient: 0.0053 (2)
Atomic scattering factors from International Tables for Crystallography (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å^2)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^* a_j^* a_i.a_j.$$

	x	y	z	U_{eq}
I	0.110842 (11)	0.02424 (2)	0.184401 (8)	0.03125 (9)
Zn	0	0.23157 (5)	1/4	0.02342 (11)
O1	0.07358 (12)	0.3835 (2)	0.32160 (9)	0.0269 (3)
O2	0.1140 (2)	0.5363 (3)	0.22642 (10)	0.0386 (4)
N1	0.12293 (14)	0.6505 (2)	0.41525 (10)	0.0239 (4)
C1	0.1048 (2)	0.5192 (3)	0.29097 (13)	0.0236 (4)
C2	0.1299 (2)	0.6788 (3)	0.33743 (12)	0.0277 (5)
C3	0.1904 (2)	0.5543 (3)	0.45152 (12)	0.0229 (4)
C4	0.1876 (2)	0.5271 (3)	0.52449 (12)	0.0224 (4)
C8	0.2694 (2)	0.4224 (3)	0.55921 (13)	0.0264 (4)
C6	0.0452 (2)	0.7006 (3)	0.52204 (13)	0.0307 (5)
C5	0.1136 (2)	0.6005 (3)	0.56022 (12)	0.0263 (5)
C7	0.0514 (2)	0.7234 (3)	0.44947 (14)	0.0290 (5)
O3	0.33721 (13)	0.3877 (3)	0.52403 (11)	0.0436 (5)
N2	0.2631 (2)	0.3747 (3)	0.62698 (12)	0.0364 (5)

Table 2. *Selected geometric parameters (Å, °)*

I—Zn	2.5848 (3)	C3—C4	1.380 (3)
Zn—O1	2.008 (2)	C4—C5	1.389 (3)
O1—C1	1.276 (3)	C4—C8	1.514 (3)

O2—C1	1.226 (3)	C8—O3	1.220 (3)
N1—C7	1.346 (3)	C8—N2	1.324 (3)
N1—C3	1.348 (3)	C6—C7	1.373 (4)
N1—C2	1.477 (3)	C6—C5	1.390 (3)
C1—C2	1.526 (3)		
O1—Zn—O1^i	109.24 (9)	N1—C2—C1	114.4 (2)
O1—Zn—I	111.68 (5)	N1—C3—C4	121.0 (2)
O1—Zn—I^i	109.94 (5)	C3—C4—C5	118.7 (2)
I—Zn—I^i	104.29 (2)	C3—C4—C8	115.7 (2)
C1—O1—Zn	110.52 (14)	C5—C4—C8	125.5 (2)
C7—N1—C3	120.7 (2)	O3—C8—N2	123.7 (2)
C7—N1—C2	120.2 (2)	O3—C8—C4	118.9 (2)
C3—N1—C2	119.0 (2)	N2—C8—C4	117.4 (2)
O2—C1—O1	125.9 (2)	C7—C6—C5	119.3 (2)
O2—C1—C2	115.9 (2)	C4—C5—C6	119.5 (2)
O1—C1—C2	118.1 (2)	N1—C7—C6	120.7 (2)

Symmetry code: (i) $-x, y, \frac{1}{2} - z$.

Table 3. Hydrogen-bonding geometry (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
N2—H8···O2^i	0.76 (4)	2.22 (4)	2.965 (3)	167 (4)
N2—H7···O1^{ii}	0.83 (3)	2.32 (4)	3.133 (3)	166 (3)

Symmetry codes: (i) $x, 1 - y, \frac{1}{2} + z$; (ii) $\frac{1}{2} - x, \frac{1}{2} - y, 1 - z$.

The Zn and I atoms were located from Patterson synthesis and the remaining non-H atoms were located from weighted Fourier syntheses. Anisotropic displacement parameters were refined for all non-H atoms. All H atoms were located from difference syntheses and allowed to refine freely with individual isotropic displacement parameters.

Data collection: *CAD-4-PC* (Enraf–Nonius, 1993). Cell refinement: *CAD-4-PC*. Data reduction: *CADRED* in *CAD-4-PC*. Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEP* (Johnson, 1965). Software used to prepare material for publication: *SHELXL93*.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and torsion angles have been deposited with the IUCr (Reference: JZ1127). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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trans-2,2,4,4-Tetrafluoro-1,3-diphenyl-1,3-diphosphetanediyl-1,3-bis[pentacarbonylchromium(0)]

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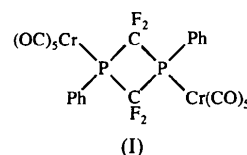
Abstract

The title compound, $[Cr_2(CO)_{10}(C_{14}H_{10}F_4P_2)]$, displays inversion symmetry. The P—CF$_2$ bond is somewhat lengthened on complexation and the phenyl–diphosphetane interplanar angle reduced from 89.15 (6)° in the free ligand to 61.4 (1)° in the complex. The P—Cr bond is short [2.3149 (6) Å].

Comment

We recently reported the preparation and structure of *trans*-2,2,4,4-tetrafluoro-1,3-diphenyl-1,3-diphosphetane (Fild, Jones, Ruhnau & Thöne, 1994). Here we extend our studies to the structure of its 1,3-bis[pentacarbonylchromium(0)] complex, (I).

(I)

The title complex crystallizes with inversion symmetry (as does the free ligand) and the central four-membered diphosphetane ring is thus exactly planar (Fig. 1). The P—CF$_2$ bond is significantly lengthened on complexation, with values of 1.9089 (14) and 1.9065 (13) Å [1.8932 and 1.8886 (14) Å for the free ligand, hereafter in square brackets]. In previous papers, we suggested that P—C$_{halide}$ bonds are systematically lengthened with respect to non-halogenated systems (Jones & Bembenek, 1996, and references therein), but here the long bonds may at least in part be attributed to the diphosphetane ring system, for which a search of the Cambridge Structural Database (Allen & Kennard, 1993) gave a mean P—C bond length of 1.881 Å (sample e.s.d. 0.017 Å for 29 values).

Other bond lengths and angles in the diphosphetane ring are scarcely altered on complexation; P—C$_{Ph}$ 1.8146 (14) Å [1.8161 (14) Å], P—CF$_2$—P 97.43 (6)° [98.20 (6)°] and CF$_2$—P—CF$_2$ 82.57 (6)° [81.80 (6)°]. The conformation, however, shows a major difference,

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