Monoclinic
$P2_1/c$
$a = 14.131\,(3)$ Å
$b = 8.281\,(2)$ Å
$c = 15.473\,(3)$ Å
$\beta = 108.36\,(2)^\circ$
$V = 1718.3\,(6)$ Å^3
$Z = 4$
$D_x = 1.370$ Mg m^{-3}
D_m not measured

Cell parameters from 59 reflections
$\theta = 2.5–12.0^\circ$
$\mu = 0.200$ mm^{-1}
$T = 173\,(2)$ K
Tablet
0.6 × 0.3 × 0.1 mm
Colourless

Data collection

Siemens *P*4 diffractometer
ω scans
Absorption correction: none
3015 measured reflections
3005 independent reflections
1515 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.009$

$\theta_{\rm max} = 25^\circ$
$h = -16 \rightarrow 0$
$k = 0 \rightarrow 9$
$l = -17 \rightarrow 17$
3 standard reflections every 247 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.043$
$wR(F^2) = 0.078$
$S = 0.791$
3005 reflections
260 parameters
H-atom treatment: see below
$w = 1/[\sigma^2(F_o^2) + (0.0242P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} = -0.002$
$\Delta\rho_{\rm max} = 0.16$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °)*

C1—C10a	1.537 (3)	C4a—C4b	1.479 (3)
C1—C2	1.571 (3)	C4a—C10a	1.510 (3)
C2—C3	1.540 (3)	C4b—C8a	1.404 (3)
C3—N4	1.264 (3)	C8a—C9	1.508 (3)
C3—C4	1.477 (3)	C9—C10	1.517 (3)
C4—C4a	1.355 (3)	C10—C10a	1.538 (3)
N4—C3—C4	129.0 (2)	C4—C3—C2	114.2 (2)
N4—C3—C2	116.8 (2)		
C10a—C1—C2—C3	−60.9 (2)	C4b—C8a—C9—C10	−17.1 (3)
C1—C2—C3—C4	45.0 (3)	C8a—C9—C10—C10a	47.4 (3)
C2—C3—C4—C4a	−8.4 (4)	C4—C4a—C10a—C1	−5.1 (3)
C3—C4—C4a—C10a	−13.3 (4)	C4b—C4a—C10a—C10	49.9 (3)
C10a—C4a—C4b—C8a	−20.7 (3)	C2—C1—C10a—C4a	41.9 (3)
C4a—C4b—C8a—C9	3.1 (4)	C9—C10—C10a—C4a	−63.7 (3)

The thienyl ring is disordered over two positions (rotated by *ca* 180° about the C4—C11 bond), with occupancies of 0.831 (3) and 0.169 (3). The atoms of the minor component were refined with isotropic displacement parameters. An extensive system of similarity restraints was employed; the final instruction file, including full details of the restraints, is included in the supplementary material. The weak diffraction is accounted for by the disorder. The H atom on N4 was located on a difference map and refined freely. Other H atoms were positioned geometrically and refined using a riding model.

Data collection: *XSCANS* (Fait, 1991). Cell refinement: *XSCANS*. Data reduction: *XSCANS*. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XP* (Siemens, 1994). Software used to prepare material for publication: *SHELXL*93.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1245). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1468-1471

3,3′-[Ethane-1,2-diylbis(aminomethylene)]-bis(pentane-2,4-dione) and the Nickel(II) Complex of a Condensation Product

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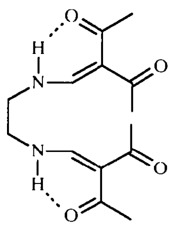
Abstract

3,3′-[Ethane-1,2-diylbis(aminomethylene)]bis(pentane-2,4-dione) [$C_{14}H_{20}N_2O_4$, (1)] displays crystallographic twofold symmetry. The N—H function forms the donor part of a three-centre hydrogen bond, with two oxygen acceptors. [6,13-Diacetyl-5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato(2−)-κ^4N]-nickel(II) bis(deuterochloroform) solvate $\{[Ni(C_{16}H_{22}N_4O_2)].2CDCl_3$, (2)$\}$ is a nickel complex of a condensation product of (1). It displays non-crystallographic inversion symmetry, with square-planar geometry at nickel and Ni—N bond lengths of 1.881 (3) and 1.882 (3) Å to N1 and N8 (with a neighbouring α-methyl group), respectively, and bond lengths of

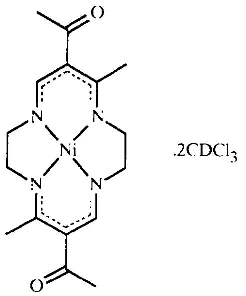
1.835 (3) and 1.839 (3) Å to N4 and N11. Hydrogen bonds are formed from the carbonyl O atoms to the solvent D atoms.

Comment

We are interested in the synthesis and structure of cyclam-type ligands and their complexes. Raney nickel hydrogenation of macrocyclic phenylenediamine–dicarbonyl condensation products leads to such ligands in high yield and with complete all-*cis* stereoselectivity (König *et al.*, 1996, 1997). In order to extend this synthetic procedure to functionalized condensation products of ethylenediamine and acetylacetone derivatives, we prepared 3,3′-[ethane-1,2-diylbis(aminomethylene)]bis(pentane-2,4-dione), (1), and [6,13-diacetyl-5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,6,11,13-tetraenato(2−)]nickel(II) bis(deuterochloroform) solvate, (2), according to known procedures (Wolf & Jäger, 1966; Jäger, 1968; Douglas, 1978) and crystallized them by slow evaporation from deuterochloroform. Unfortunately, hydrogenation of (2) under the established conditions (König *et al.*, 1996, 1997) gave a mixture of stereoisomers. We present here the structures of (1) and (2); the structure of the tetracyanoquinodimethane (TCNQ) adduct of (2) has been reported previously (Soriano-García *et al.*, 1985), and consists of stacks of alternating molecules of (2) and TCNQ, both with crystallographic inversion symmetry.



(1)



(2)

Compound (1) (Fig. 1) crystallizes with imposed twofold symmetry. Bond lengths and angles are unexceptional. The molecular conformation is defined by the torsion angles N—C7—C7^i—N^i of 46.5 (3)° and C6—N—C7—C7^i of −90.5 (2)° (symmetry code as in Table 1); the region C7—N—C6—C3—C4—O2 displays an extended conformation, and indeed the whole asymmetric unit (excluding H atoms) is coplanar to within 0.06 Å (r.m.s. deviation).

A short intramolecular N—H0···O1 contact is observed (Table 2); the same atoms are involved in an intermolecular contact and the whole system may thus be described as a three-centre hydrogen bond. Additionally, there is a possible intermolecular C—H$_{\mathrm{methyl}}$···O hydrogen bond involving C5 and O2.

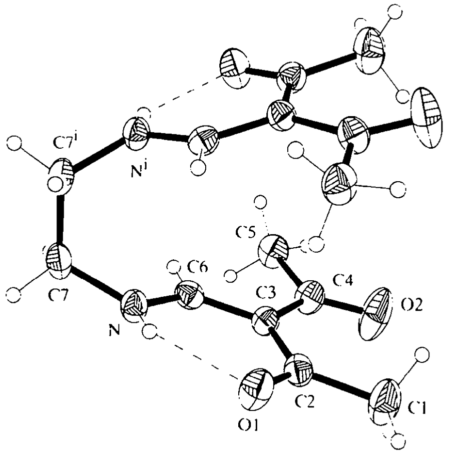


Fig. 1. The molecule of compound (1) in the crystal. Ellipsoids represent 50% probability levels and H-atom radii are arbitrary. Hydrogen bonds are indicated by dashed lines. Only the asymmetric unit is numbered. [Symmetry code: (i) $1 - x, y, \frac{1}{2} - z$.]

The nickel(II) complex, (2) (Fig. 2), possesses no imposed symmetry, but is inversion-symmetric to a good approximation. It displays square-planar geometry at the metal atom, with Ni—N bond lengths of 1.881 (3) and 1.882 (3) Å [1.887 (3) Å; Soriano-García *et al.*, 1985] to N1 and N8 (with a neighbouring α-methyl group), respectively, and bond lengths of 1.835 (3) and 1.839 (3) Å [1.828 (3) Å] to N4 and N11. A search of the Cambridge Structural Database (version of October 1997; Allen & Kennard, 1993) revealed 18 neutral complexes with 14-membered macrocycles involved in square-planar N_4 coordination at nickel, with a mean Ni—N bond length of 1.87 (2) Å.

The macrocyclic ligand is not planar; the Ni and N atoms, together with C5, C7, C12 and C14, are coplanar to within 0.060 Å (r.m.s. deviation). Selected torsion angles associated with the five-membered rings, which display local twofold symmetry, are given in Table 3. Within the immediate metal coordination sphere, the N atoms alternate 0.007 (2) Å above and below their least-squares plane, with the Ni atom lying exactly in the plane [deviation 0.000 (2) Å]. The N atoms display a planar geometry; distortions of bond angles from the ideal value of 120° are attributable to the inherently smaller angles of five-membered rings. Bond lengths indicate extensive delocalization of multiple bonding in the six-membered chelate rings.

The molecular packing is such that the molecules of (2), which are neither stacked nor parallel, occupy the regions $z \simeq 0, \frac{1}{2}, 1$ *etc.*, and the solvent molecules the regions at $z \simeq \frac{1}{4}, \frac{3}{4}$ *etc.* Hydrogen bonds are formed between the carbonyl O atoms and the solvent D atoms (Table 4). There are weak axial contacts from nickel to methyl H atoms [Ni···H19C($-\frac{1}{2}+x, 1-y, z$) 2.79 Å and Ni···H20A($\frac{1}{2}+x, 2-y, z$) 2.82 Å].

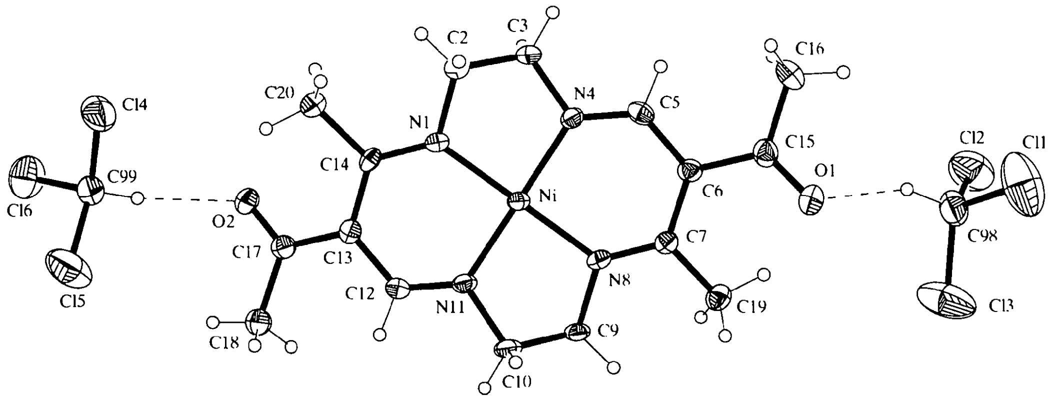


Fig. 2. The formula unit of compound (2) in the crystal. Ellipsoids represent 50% probability levels and H-atom radii are arbitrary. One H atom is wholly eclipsed by C9. Hydrogen bonds are indicated by dashed lines.

Experimental

Compounds (1) and (2) were prepared according to known procedures (Wolf & Jäger, 1966; Jäger, 1968; Douglas, 1978) and crystallized by slow evaporation from deuterochloroform.

Compound (1)

Crystal data

$C_{14}H_{20}N_2O_4$
$M_r = 280.32$
Monoclinic
$C2/c$
$a = 13.756\ (2)$ Å
$b = 8.9663\ (14)$ Å
$c = 11.6831\ (18)$ Å
$\beta = 99.828\ (10)°$
$V = 1419.8\ (4)$ Å^3
$Z = 4$
$D_x = 1.311$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 62 reflections
$\theta = 5.5–11.9°$
$\mu = 0.097$ mm^{-1}
$T = 173\ (2)$ K
Needle
$0.80 \times 0.12 \times 0.12$ mm
Colourless

Data collection

Siemens $P4$ diffractometer
ω scans
Absorption correction: none
1316 measured reflections
1249 independent reflections
841 reflections with $I > 2\sigma(I)$
$R_{\rm int} = 0.014$

$\theta_{\rm max} = 25°$
$h = -16 \rightarrow 16$
$k = -10 \rightarrow 0$
$l = 0 \rightarrow 13$
3 standard reflections every 247 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.040$
$wR(F^2) = 0.093$
$S = 0.909$
1249 reflections
97 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.052P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\rm max} < 0.001$
$\Delta\rho_{\rm max} = 0.19$ e Å^{-3}
$\Delta\rho_{\rm min} = -0.19$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

Table 1. *Selected geometric parameters (Å, °) for (1)*

N—C6	1.320 (2)	N—C7	1.451 (2)
C6—N—C7	120.46 (15)	N—C7—C7$^{\rm i}$	111.54 (11)
C6—N—C7—C7$^{\rm i}$	−90.5 (2)	N—C7—C7$^{\rm i}$—N$^{\rm i}$	46.5 (3)

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

Table 2. *Hydrogen-bonding geometry (Å, °) for (1)*

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
N—H0$\cdots$O1	0.91 (2)	1.97 (2)	2.638 (2)	129.1 (16)
N—H0$\cdots$O1$^{\rm i}$	0.91 (2)	2.36 (2)	3.070 (2)	135.6 (16)
C5—H5$C\cdots$O2$^{\rm ii}$	0.98	2.54	3.482 (2)	161.5

Symmetry codes: (i) $1 - x, 1 - y, 1 - z$; (ii) $\frac{3}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

Compound (2)

Crystal data

$[Ni(C_{16}H_{22}N_4O_2)].2CDCl_3$
$M_r = 601.83$
Orthorhombic
$Pca2_1$
$a = 8.542\ (3)$ Å
$b = 9.406\ (3)$ Å
$c = 30.213\ (8)$ Å
$V = 2427.3\ (13)$ Å^3
$Z = 4$
$D_x = 1.641$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 60 reflections
$\theta = 5.9–12.5°$
$\mu = 1.484$ mm^{-1}
$T = 173\ (2)$ K
Prism
$0.60 \times 0.45 \times 0.25$ mm
Red

Data collection

Siemens $P4$ diffractometer
ω scans
Absorption correction: ψ scans (*XEMP*; Siemens, 1994*a*)
$T_{\rm min} = 0.526$, $T_{\rm max} = 0.690$
4120 measured reflections
3996 independent reflections
3587 reflections with $I > 2\sigma(I)$

$R_{\rm int} = 0.024$
$\theta_{\rm max} = 25.48°$
$h = 0 \rightarrow 10$
$k = -11 \rightarrow 11$
$l = -35 \rightarrow 36$
3 standard reflections every 247 reflections intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.031$
$wR(F^2) = 0.069$
$S = 1.055$
3996 reflections
285 parameters
H atoms: see below
$w = 1/[\sigma^2(F_o^2) + (0.0271P)^2 + 2.643P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 0.48$ e Å^{-3}
$\Delta\rho_{\min} = -0.33$ e Å^{-3}
Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)
Absolute structure: Flack (1983)
Flack parameter = 0.422 (16)

Table 3. *Selected geometric parameters (Å, °) for (2)*

Ni—N4	1.835 (3)	Ni—N1	1.881 (3)
Ni—N11	1.839 (3)	Ni—N8	1.882 (3)
N4—Ni—N11	179.42 (16)	C5—N4—C3	120.4 (3)
N4—Ni—N1	87.35 (12)	C5—N4—Ni	126.8 (3)
N11—Ni—N1	92.22 (13)	C3—N4—Ni	112.8 (2)
N4—Ni—N8	92.84 (12)	C7—N8—C9	120.3 (3)
N11—Ni—N8	87.58 (13)	C7—N8—Ni	129.5 (2)
N1—Ni—N8	179.54 (14)	C9—N8—Ni	109.8 (2)
C14—N1—C2	119.9 (3)	C12—N11—C10	120.2 (3)
C14—N1—Ni	129.5 (2)	C12—N11—Ni	127.6 (3)
C2—N1—Ni	110.3 (2)	C10—N11—Ni	112.1 (2)
N4—Ni—N1—C2	−14.9 (2)	Ni—N4—C3—C2	31.5 (4)
N1—Ni—N4—C3	−9.8 (3)	N1—C2—C3—N4	−41.7 (4)
N11—Ni—N8—C9	13.2 (2)	C7—N8—C9—C10	151.3 (3)
N8—Ni—N11—C10	12.5 (3)	Ni—N8—C9—C10	−34.9 (3)
C14—N1—C2—C3	−151.5 (3)	C12—N11—C10—C9	143.3 (3)
Ni—N1—C2—C3	34.8 (3)	Ni—N11—C10—C9	−34.7 (3)
C5—N4—C3—C2	−147.5 (3)	N8—C9—C10—N11	43.9 (4)

Table 4. *Hydrogen-bonding geometry (Å, °) for (2)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C98—D98···O1	1.00	2.33	3.206 (6)	146.2
C99—D99···O2	1.00	2.14	3.094 (5)	159.7

H atoms were located from ΔF syntheses and refined with NH free, rigid methyls and other H atoms riding. For compound (2), which crystallizes in a polar space group, the origin was fixed according to the method of Flack & Schwarzenbach (1988). The structure was refined as a racemic twin with components 0.422 (16) and 0.578 (16), utilizing 1739 Friedel pairs, which were adequate to define the Flack (1983) parameter; no further Friedel opposites were measured as the nozzle of the low-temperature device obscured most of those remaining.

For both compounds, data collection: *XSCANS* (Fait, 1991); cell refinement: *XSCANS*; data reduction: *XSCANS*; program(s) used to solve structures: *SHELXS*86 (Sheldrick, 1990); program(s) used to refine structures: *SHELXL*97 (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1994*b*); software used to prepare material for publication: *SHELXL*97.

We thank the Fonds der Chemischen Industrie for financial support and Mr A. Weinkauf for technical assistance.

Supplementary data for this paper are available from the IUCr electronic archives (Reference: BM1271). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1998). C**54**, 1471–1473

1,2:4,5-Di-*O*-isopropylidenegalactitol†

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Abstract

The title compound, $C_{12}H_{22}O_6$, is composed of two isopropylidene rings, one with approximate *m* symmetry and the other with approximate C_2 symmetry, joined by an extended backbone. Hydrogen bonds connect the molecules into ribbons parallel to the *y* axis.

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† IUPAC name: (2,2-dimethyl-1,3-dioxolan-4-yl)(5-hydroxymethyl-2,2-dimethyl-1,3-dioxolan-4-yl)methanol.

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