Di-μ-bromo-2κ²Br:2′κ²Br-bis[bis(μ-acetylacetonato-1κO:2κO′)bromo-2κBr-bis(tetrahydrofuran-1κO)cadmium(II)nickel(II)]

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The title compound, $[Cd_2Ni_2Br_4(C_5H_7O_2)_4(C_4H_8O)_4]$, is a tetranuclear coordination compound with two Ni and two Cd centres. The Ni atoms are octahedrally surrounded by two tetrahydrofuran ligands in *trans* positions and two acetylacetonate ligands. One O atom of each acetylacetonate ligand acts as a bridging atom to a Cd atom. The two Cd atoms are bridged by two Br ligands and each of them bears one additional Br substituent. The molecule is located on a crystallographic centre of inversion.

Comment

The addition of transition metal complexes, *e.g.* nickel(II) and iron(III) compounds, has been shown to enhance reaction rates and selectivity of cross-coupling reactions of carbonic acid derivatives with Grignard reagents (Fiandanese *et al.*, 1983; Cason & Kraus, 1961). Sobota *et al.* (1984) were able to isolate and structurally characterize a dinuclear compound, $[(THF)_4Mg(\mu\text{-}Cl)_2FeCl_2]$ (THF is tetrahydrofuran), from the reaction of $MgCl_2$ and $FeCl_3$ in THF, and could also demonstrate that it plays a crucial role in the catalytic cycle of the cross-coupling reaction. The addition of $Fe(acac)_3$ (acac is acetylacetonate) or $Ni(acac)_2$ turned out to be a more efficient way of achieving a catalytic cross-coupling reaction with carbonic acid derivatives (Fiandanese *et al.*, 1984; Cardellicchio *et al.*, 1987; Hayashi *et al.*, 1980, 1981). The reaction of Grignard reagents with $Fe(acac)_3$ produces dinuclear complexes of the form $[(THF)_2Mg(\mu\text{-}acac)_2FeCl_2]$ and treatment of Grignard reagents with $Ni(acac)_2$ results in the formation of the nickel analogue, $[(THF)_2Mg(\mu\text{-}acac)_2NiX_2]$. In both compounds, the acac ligands act as bridges (Döring *et al.*, 1989). Similar ligand-exchange processes on the basis of salicylideneiminate complexes have been studied in detail by Floriani and co-workers (Solari *et al.*, 1990). One of the major reasons for the observed ligand exchange is presumably the preference of magnesium for an octahedral coordination mode, compared with the more flexible transition metal ions. Therefore, the question concerning the coordination chemistry of transition metal acetylacetonates in reactions with Zn, Cd or Hg salts arose. The latter metals, due to the filled *d* orbitals, show a somewhat related chemistry to the alkaline earth metals, although preferring tetrahedral coordination.

In principle, acac ligands should also be able to act as bridging ligands towards group 12 metal halides. The molecular structures of related compounds based mainly on salicylideneiminates have been described in the literature for Zn (Atakol, Ercan *et al.*, 1999; Atakol *et al.*, 2000, 2003; Tatar, 2002; Arıcı *et al.*, 1999, 2001; Elmali & Elerman, 2003; Tatar *et al.*, 1999, 2002; Solari *et al.*, 1990; Weiss *et al.*, 1998; Svoboda *et al.*, 2001; Ercan, Arici, Akay *et al.*, 1999; Ercan, Arici, Ülkü *et*

al., 1999; Ülkü *et al.*, 2003), Cd (Nesterov *et al.*, 2004; Müller & Thewalt, 1997) and Hg (Atakol, Arici *et al.*, 1999; Kaynak *et al.*, 1999; Colon *et al.*, 2004). By analogy with the published results, the reaction of Ni(acac)$_2$ with zinc halides in THF leads to the formation of the dinuclear compounds [(THF)$_2$Ni(μ-acac)$_2$ZnX$_2$] (Hahn, 1997). Thus, in contrast with magnesium halides or Grignard reagents, no ligand-exchange reaction is observed and each metal retains the preferred ligand geometry. The title compound, (I), was isolated from a reaction of Ni(acac)$_2$ and CdBr$_2$ in THF. Due to the low solubility of cadmium halides in organic solvents, the yields are quite low and the reaction had to be carried out at boiling temperature for several hours.
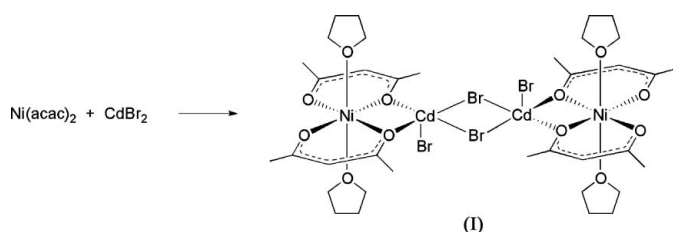
Fig. 1 shows the molecular structure of (I), and selected bond lengths and angles are summarized in Table 1. The Ni centres are octahedrally coordinated by two acac ligands and two THF molecules each. The bond lengths and angles are very close to those observed for the parent compound, [Ni(THF)$_2$(acac)$_2$] (Wolski, 1992). The only differences result from the coordination of the Cd atoms by the O atoms of the acac ligands. This leads to a smaller O1—Ni1—O3 angle, whereas the other O—Ni—O angles of the acac ligands are slightly larger than in [Ni(THF)$_2$(acac)$_2$].

Each Cd atom is coordinated by three Br ligands, one adopting an η^1-binding mode, whereas the other Br atoms are in a bridging position, thus producing a tetranuclear dimeric structure. The centre of the Cd$_2$Br$_2$ ring is located on a crystallographic centre of inversion. The Cd—Br bonds in the four-membered ring are slightly different [2.717 (1) and 2.691 (3) Å] and the η^1-coordinated Br atom shows a much shorter Cd—Br bond [2.533 (2) Å]. The Cd atoms are therefore pentacoordinated and the coordination is best described as square-pyramidal, with the base formed by atoms Br1/Br1A/O1/O3 ($\tau = 0.28$), taking into account the criteria of Addison *et al.* (1984) for the distinction between a square-pyramidal *versus* a trigonal–bipyramidal ligand environment. Nevertheless, the Cd atoms are situated 0.845 (2) Å above the square plane consisting of atoms Br1/Br1A/O1/O3.

In contrast with related zinc compounds, the Ni—O—Cd—O ring is not planar in (I), showing an angle of 21.3 (2)° between the planes Ni/O1/O3 and Cd/O1/O3. The angle between the least-squares plane through Ni—O1—O3—Cd and the planar central Cd$_2$Br$_2$ ring measures 118.15 (8)°.

A tetranuclear arrangement similar to the observed [Ni-(μ-acac)$_2$Cd(μ-Br)$_2$Cd(μ-acac)$_2$Ni] arrangement has only once been observed, for a mixed Cu–Hg compound with a salicylideneiminate ligand (Ercan *et al.*, 2002). Nevertheless, in
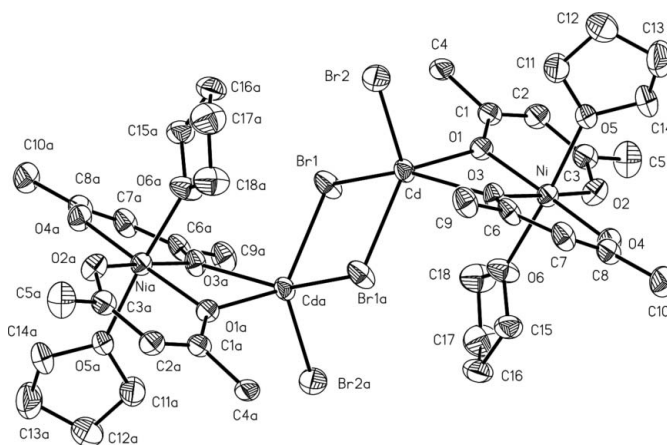

Figure 1
The molecular structure of (I). H atoms have been omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level. Atoms with the suffix 'a' are generated by the symmetry operator ($-x$, $1 - y$, $-z$).

that structure the Hg—Cl bonds are nearly identical (2.321 and 2.332 Å) and the second bridging Cl atom is only very weakly bound to mercury (3.301 Å). Corresponding to this sterically more relaxed structure, the angle between the least-squares planes Cu1/O1/O2/Hg1 and Hg1/Cl1/Cl1A/Hg1A measures 91.1°.

Experimental

A sample of Ni(acac)$_2$ (1 g, 3.9 mmol) was refluxed for 8 h with CdBr$_2$ (1.06 g) in anhydrous tetrahydrofuran (THF; 40 ml) under an argon atmosphere. Due to the low solubility of CdBr$_2$ under the reaction conditions, the percentage conversion was low. The solution was filtered over kieselguhr to separate unreacted CdBr$_2$. The THF was evaporated until only 3 ml was left and the resulting solution was layered with *n*-hexane. After 1–2 d, light-blue crystals of the title compound, (I), were obtained (yield 0.37 g, 10%). Elemental analysis for C$_{36}$H$_{60}$O$_{12}$Ni$_2$Cd$_2$Br$_4$, found (calculated): C 31.56 (32.11), H 4.38 (4.49), Br 23.36 (23.73), Ni 8.20 (8.72), Cd 15.87% (16.69%). IR (Nujol, 298 K, cm^{-1}): 1585 ($\nu_{C=O}$), 1514 (δ_{CH_3}).

Crystal data

[Cd$_2$Ni$_2$Br$_4$(C$_5$H$_7$O$_2$)$_4$(C$_4$H$_8$O)$_4$]	$D_x = 1.830$ Mg m^{-3}
$M_r = 1346.68$	Mo $K\alpha$ radiation
Monoclinic, $P2_1/n$	Cell parameters from 25
$a = 10.143$ (3) Å	reflections
$b = 11.378$ (12) Å	$\theta = 18.7$–25.8°
$c = 21.483$ (2) Å	$\mu = 4.94$ mm^{-1}
$\beta = 99.66$ (3)°	$T = 173$ (2) K
$V = 2444$ (3) Å^3	Block, light blue
$Z = 2$	$0.06 \times 0.03 \times 0.02$ mm

Data collection

Enraf–Nonius CAD-4	$R_{int} = 0.058$
diffractometer	$\theta_{max} = 27.4°$
$\omega/2\theta$ scans	$h = -13 \rightarrow 12$
Absorption correction: ψ scan	$k = 0 \rightarrow 14$
(North *et al.*, 1968)	$l = 0 \rightarrow 27$
$T_{min} = 0.768$, $T_{max} = 0.906$	3 standard reflections
5686 measured reflections	frequency: 600 min
5544 independent reflections	intensity decay: 2.4%
4378 reflections with $I > 2\sigma(I)$	

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.1177P)^2$
$R[F^2 > 2\sigma(F^2)] = 0.067$	$+ 10.9432P]$
$wR(F^2) = 0.195$	where $P = (F_o^2 + 2F_c^2)/3$
$S = 1.12$	$(\Delta/\sigma)_{max} = 0.001$
5544 reflections	$\Delta\rho_{max} = 3.91$ e Å^{-3}
257 parameters	$\Delta\rho_{min} = -2.02$ e Å^{-3}
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Cd—O1	2.301 (5)	Ni—O2	1.979 (5)
Cd—O3	2.333 (5)	Ni—O4	1.988 (5)
Cd—Br2	2.5328 (15)	Ni—O3	2.002 (5)
Cd—Br1^i	2.691 (3)	Ni—O1	2.013 (5)
Cd—Br1	2.7168 (12)	Ni—O6	2.096 (6)
Cd—Ni	3.3450 (11)	Ni—O5	2.118 (6)
O1—Cd—O3	69.99 (17)	O4—Ni—O1	175.3 (2)
O1—Cd—Br2	108.36 (14)	O3—Ni—O1	82.9 (2)
O3—Cd—Br2	102.37 (14)	O2—Ni—O6	91.5 (2)
O1—Cd—Br1^i	131.14 (13)	O4—Ni—O6	93.3 (2)
O3—Cd—Br1^i	88.02 (13)	O3—Ni—O6	87.0 (2)
Br2—Cd—Br1^i	118.97 (5)	O1—Ni—O6	86.9 (2)
O1—Cd—Br1	92.36 (12)	O2—Ni—O5	91.3 (2)
O3—Cd—Br1	148.11 (13)	O4—Ni—O5	89.9 (2)
Br2—Cd—Br1	108.47 (4)	O3—Ni—O5	89.8 (2)
Br1^i—Cd—Br1	84.17 (5)	O1—Ni—O5	89.6 (2)
O1—Cd—Ni	36.13 (12)	O6—Ni—O5	175.6 (2)
O3—Cd—Ni	36.03 (12)	O2—Ni—Cd	131.70 (15)
Br2—Cd—Ni	118.19 (5)	O4—Ni—Cd	133.30 (15)
Br1^i—Cd—Ni	105.10 (3)	O3—Ni—Cd	43.25 (14)
Br1—Cd—Ni	117.52 (3)	O1—Ni—Cd	42.38 (14)
Cd^i—Br1—Cd	95.84 (5)	O6—Ni—Cd	74.10 (18)
O2—Ni—O4	92.5 (2)	O5—Ni—Cd	101.49 (15)
O2—Ni—O3	174.9 (2)	Ni—O1—Cd	101.5 (2)
O4—Ni—O3	92.4 (2)	Ni—O3—Cd	100.7 (2)
O2—Ni—O1	92.2 (2)		

Symmetry code: (i) $-x, -y + 1, -z$.

All H atoms were ideally positioned, with C—H distances in the range 0.95–0.99 Å, and refined using a riding model with fixed individual displacement parameters [$U_{iso}(H) = 1.2U_{eq}(C)$, or $1.5U_{eq}(C_{methyl})$]. The methyl groups were allowed to rotate but not to tip. The highest electron-density peak and deepest hole are located 0.90 Å from atom Br1 and 0.95 Å from atom Cd, respectively. the

Data collection: *CAD-4 EXPRESS* (Enraf–Nonius, 1994); cell refinement: *SET4* (de Boer & Duisenberg, 1984); data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1990); software used to prepare material for publication: *SHELXL97*.

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