$S = 1.128$
10035 reflections
587 parameters
H atoms constrained
$w = 1/[\sigma^2(F_o^2) + (0.0143P)^2 + 3.8414P]$
where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

| | | | |
|---|---|---|---|
| Cu—S4 | 2.175 (2) | Cu—S3 | 2.179 (2) |
| Cu—S2 | 2.178 (2) | Cu—S1 | 2.179 (2) |
| S4—Cu—S2 | 178.17 (9) | S3—Cu—S1 | 177.00 (9) |
| S4—Cu—S3 | 92.79 (7) | C1—S1—Cu | 104.6 (2) |
| S2—Cu—S3 | 87.20 (7) | C2—S2—Cu | 103.8 (2) |
| S4—Cu—S1 | 87.18 (7) | C10—S3—Cu | 104.2 (2) |
| S2—Cu—S1 | 92.74 (7) | C9—S4—Cu | 104.3 (2) |

Table 2. *Contact distances (Å)*

| | | | |
|---|---|---|---|
| S1···H3B$^{i}$ | 2.87 | C9···H9B$^{ii}$ | 2.78 |
| S4···H12B$^{ii}$ | 2.94 | C16···H18A$^{iv}$ | 2.79 |
| N1···H9A$^{iii}$ | 2.63 | | |

Symmetry codes: (i) $x, 1+y, z$; (ii) $1-x, 1-y, -z$; (iii) $1-x, 1-y, 1-z$; (iv) $x, 1+y, z-1$.

Data collection: *CAD-4 Software* (Enraf–Nonius, 1989). Cell refinement: *CAD-4 Software*. Data reduction: *MolEN PROCESS* (Fair, 1990). Program(s) used to solve structure: *SHELXS86* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976). Software used to prepare material for publication: *SHELXL93*.

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# A Nickel(II) Compound with a Tetradentate Diamine–Diimine Ligand, (2,4,6,9,11-Pentamethyl-5,8-diazadodeca-4,8-diene-2,11-diamine)nickel(II) Tetrachlorozincate

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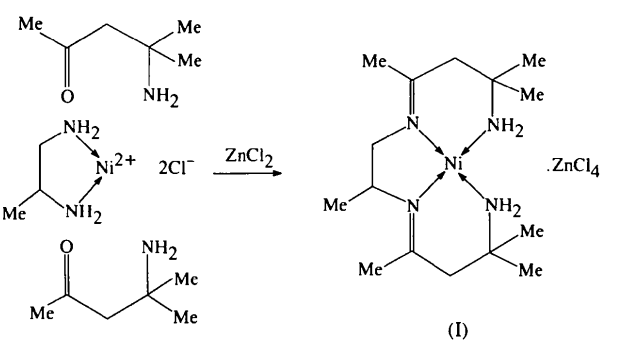
## Abstract

The title compound, $[Ni(C_{15}H_{32}N_4)][ZnCl_4]$, has a tetradentate diamine–diimine ligand in a tetrahedrally twisted square-planar coordination to singlet ground-state nickel(II), with a mean Ni—N distance of 1.909 (3) Å. The cation has approximate mirror symmetry, apart from the axially oriented C6 methyl substituent.

## Comment

Compounds with amine–imine ligands have been prepared by reaction of a variety of amine compounds of copper(II) and nickel(II) with 4-amino-4-methylpentan-2-one (Morgan & Curtis, 1980; Morgan, Martin & Curtis, 1979). The yellow diamagnetic title compound, $[Ni(pnda)][ZnCl_4]$, (I), was prepared by reaction with tris(propane-1,2-diamine)nickel(II) tetrachlorozincate. The structures of (2,4-dimethyl-5,8-diazadec-4-ene-7,10-diamine)copper(II) tetrachlorozincate, formed from (3-azapentane-1,5-diamine)copper(II) (Gladkikh, Curtis & Heath, 1997), $[Cu(pnda)](ClO_4)_2$ and the pentadentate ligand compound (2,4-dimethyl-5,8,11-triazatridec-4-ene-2,13-diamine)copper(II) perchlorate, formed by reaction with 3,6-diazaoctane-1,8-diamine)copper(II) perchlorate (Curtis, Gladkikh & Turnbull, 1997) have been described.




(I)


ISSN 0108-2701 

The presence of the imine groups, C4=N5 and N8=C9, is confirmed by the distances of 1.286 (5) and 1.282 (6) Å, respectively, and the trigonal bond angles about these atoms.

The nickel(II) ion is in a square-planar coordination with the two primary amine (N1 and N12) and two imine N atoms (N5 and N8) of the ligand. The Ni—N distances range from 1.906 (3) to 1.913 (4) Å [mean 1.909 (3) Å] with no significant difference between bonds to the amine and imine N atoms. These values are within the normal range for singlet ground-state nickel, although bonds to imine N atoms are usually *ca* 0.03 Å shorter than those to amine N atoms.

The $NiN_4$ group of [Ni(pnda)][$ZnCl_4$] is close to being coplanar [deviations of atoms from the plane being less than 0.06 (1) Å]. [Cu(pnda)]($ClO_4$)$_2$ shows appreciable tetrahedral twisting of this plane, with *trans* N—Cu—N angles of 161.8 (4) and 170.9 (4)°, and displacement from the best $N_4$ plane of ±0.23 (1) Å.

The nickel ion in (I) forms no significant axial interaction, the closest contact being Ni···Cl4($2-x$, $y-\frac{1}{2}$, $\frac{1}{2}-z$) at 3.58 (1) Å. In comparison, [Cu(pnda)]($ClO_4$)$_2$ has one axial interaction with a perchlorate ion with a Cu—O distance of 2.65 (1) Å.

The singlet ground-state nickel(II) ion clearly exerts greater restraint towards coplanarity on the donor atoms of the ligand and has much weaker axial interactions with the anion than the copper(II) ion.

The tetradentate ligand is sterically constrained by the two planar imine groups. The two six-membered amine–imine chelate rings have envelope conformations with atoms Ni, N1, C3, C4, N5 and Ni, N8, C9, C10, N12 coplanar to within ±0.09 (1) Å, with C2 and C11 both displaced from these planes by 0.71 Å. The cation has both trimethyl-substituted amine–imine chelate rings tilted to the same side of the molecular plane, with approximate mirror symmetry, unlike the copper(II) compound which has these rings tilted to opposite sides of the plane with approximate twofold symmetry. The five-membered chelate ring has a *gauche* conformation, with C6 and C7 displaced from the $NiN_2$ plane by 0.44 (1) and −0.18 (1) Å, respectively. Steric interactions between the imine methyl substituent C41 and the propanediamine residue methyl substituent C61 result in a conformation with methyl substituent C61 axially oriented, on the same side of the plane as the other axially oriented methyl substituents, C21 and C111.

The Zn—Cl distances of the tetrachlorozincate ion vary from 2.233 (1) to 2.314 (1) Å, the longest Zn—Cl distance being associated with the Cl atom which forms the strongest hydrogen bond (N1—H1*A*···Cl1). The structure contains centrosymmetric contact groups comprising two complex cations and two complex anions, linked by four symmetrically independent N—H···Cl hydrogen bonds (Table 2). C—H···Cl interactions link these units into layers of self-symmetry $P2_1/c$, parallel to the (100) plane. No specific hydrogen-bonding interactions between these layers are discernable.

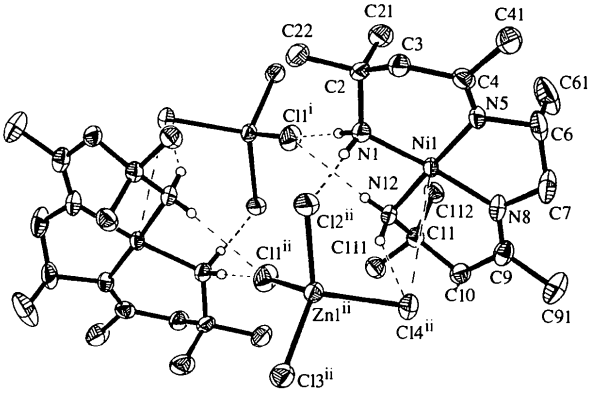



Fig. 1. The complex cation and closest tetrachlorozincate ion, with displacement ellipsoids drawn at the 50% probability level.

## Experimental

Excess 4-amino-4-methylpentan-2-one was added to a methanol solution/suspension of tris(propane-1,2-diamine)-nickel(II) tetrachlorozincate. After 2 d at 308 K, zinc chloride in equimolar proportions was added, followed by propan-2-ol. The yellow crystalline product was filtered off and recrystallized from methanol (Morgan & Curtis, 1980).

*Crystal data*

[$Ni(C_{15}H_{32}N_4)$][$ZnCl_4$]
$M_r$ = 534.33
Monoclinic
$P2_1/c$
$a$ = 9.3718 (14) Å
$b$ = 17.085 (3) Å
$c$ = 14.351 (2) Å
$\beta$ = 95.121 (4)°
$V$ = 2288.7 (6) Å$^3$
$Z$ = 4
$D_x$ = 1.551 Mg m$^{-3}$
$D_m$ not measured

Mo $K\alpha$ radiation
$\lambda$ = 0.71073 Å
Cell parameters from 5419 reflections
$\theta$ = 2.18–28.02°
$\mu$ = 2.344 mm$^{-1}$
$T$ = 160 (2) K
Needle
0.30 × 0.08 × 0.04 mm
Yellow

*Data collection*

Siemens SMART CCD diffractometer
$\omega$ rotation scans with narrow frames
Absorption correction: semi-empirical from $\psi$ scans (*SHELXTL/PC*; Sheldrick, 1994)
$T_{min}$ = 0.641, $T_{max}$ = 0.911

14 058 measured reflections
5243 independent reflections
3746 reflections with $I > 2\sigma(I)$
$R_{int}$ = 0.061
$\theta_{max}$ = 28.47°
$h$ = −12 → 12
$k$ = −12 → 21
$l$ = −19 → 18

*Refinement*

Refinement on $F^2$
$R[F^2 > 2\sigma(F^2)]$ = 0.047
$wR(F^2)$ = 0.109

$(\Delta/\sigma)_{max}$ = 0.001
$\Delta\rho_{max}$ = 0.694 e Å$^{-3}$
$\Delta\rho_{min}$ = −0.634 e Å$^{-3}$

$S$ = 1.082
5241 reflections
246 parameters
Only coordinates of H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.0375P)^2 + 3.3856P]$ where $P = (F_o^2 + 2F_c^2)/3$
Extinction correction: *SHELXL*93
Extinction coefficient: 0.0017 (3)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

| | | | |
|---|---|---|---|
| Ni1—N8 | 1.906 (3) | N1—C2 | 1.505 (5) |
| Ni1—N5 | 1.906 (3) | C4—N5 | 1.286 (5) |
| Ni1—N1 | 1.911 (3) | N8—C9 | 1.282 (6) |
| Ni1—N12 | 1.913 (4) | | |
| N8—Ni1—N5 | 86.6 (2) | C4—N5—C6 | 120.8 (4) |
| N8—Ni1—N1 | 173.3 (2) | C4—N5—Ni1 | 130.4 (3) |
| N5—Ni1—N1 | 93.5 (2) | C6—N5—Ni1 | 108.8 (3) |
| N8—Ni1—N12 | 91.9 (2) | C9—N8—C7 | 118.0 (4) |
| N5—Ni1—N12 | 178.4 (2) | C9—N8—Ni1 | 130.1 (3) |
| N1—Ni1—N12 | 88.0 (2) | C7—N8—Ni1 | 110.2 (3) |
| C2—N1—Ni1 | 120.2 (3) | N8—C9—C10 | 121.8 (4) |
| N5—C4—C3 | 120.6 (4) | C11—N12—Ni1 | 118.7 (3) |

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

| *D*—H···*A* | *D*—H | H···*A* | *D*···*A* | *D*—H···*A* |
|---|---|---|---|---|
| N1—H1*A*···Cl1$^{i}$ | 0.92 (5) | 2.48 (5) | 3.401 (4) | 174 (4) |
| N1—H1*B*···Cl2$^{ii}$ | 0.91 (5) | 2.50 (4) | 3.389 (4) | 167 (4) |
| N12—H12*A*···Cl1$^{i}$ | 0.79 (5) | 2.64 (5) | 3.426 (4) | 177 (4) |
| N12—H12*B*···Cl4$^{ii}$ | 0.83 (5) | 2.59 (4) | 3.306 (4) | 145 (4) |

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

Neutral atom-scattering factors were from Ibers & Hamilton (1992). Non-H atom parameters were refined anisotropically. Atoms H1*A*, H1*B*, H12*A* and H12*B* were located from difference maps, other H-atom positions were calculated and parameters were refined in isotropic approximation.

Data collection: *SMART* (Siemens, 1995). Cell refinement: local programs. Data reduction: *SAINT* (Siemens, 1995). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *XPMA* (Zsolnai, 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: SK1009). Services for accessing these data are described at the back of the journal.

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# Accurate Redeterminations of 1,1′-Dibenzoylferrocene and (4-Nitrophenyl)ferrocene

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## Abstract

In the solid state, molecules of 1,1′-dibenzoylferrocene, $[Fe(C_{12}H_9O)_2]$, (I), are linked to form infinite chains in the [100] direction *via* (cyclopentadienyl)C—H···O hydrogen bonds [C···O 3.354 (4) Å]. In the structure of (4-nitrophenyl)ferrocene, $[Fe(C_5H_5)(C_{11}H_8NO_2)]$, (II), there are no C—H···O hydrogen bonds and molecules are separated by normal van der Waals distances. For earlier determinations see Struchkov [*Dokl. Akad. Nauk SSSR* (1956), **110**, 67–70] for (I) and Roberts *et al.* [*J. Chem. Soc. Dalton Trans.* (1988), pp. 1549–1556] for (II).


## Comment

The structure of 1,1′-dibenzoylferrocene, $[Fe(C_5H_4CO\text{-}Ph)_2]$, (I), was reported many years ago (Struchkov, 1956) and there are a number of reasons why this structure should be redetermined to modern standards. First, the unit cell was described as monoclinic ($P2_1/n$), but with $\beta$ = 90 (1)°; secondly, there are no coordinate data for this compound in the Cambridge Structural Database (Allen & Kennard, 1993) or indeed in the original publication, although uncertainties on the C—C bond lengths are quoted, all in the range 0.03–0.05 Å (Struchkov, 1956); thirdly, the illustrations in the original report suggest the possibility that the molecules are close to having twofold rotational symmetry, and finally, the original report appeared long