N3*B*—Ni1*B*—N4*B*—C7*B*	44.6 (8)
N4*B*—Ni1*B*—N3*B*—C5*B*	−35.1 (9)
Ni1*B*—N4*B*—C8*B*—C9*B*	34.7 (11)
N4*B*—C8*B*—C9*B*—N5*B*	−50.7 (13)
Ni1*B*—N5*B*—C9*B*—C8*B*	40.5 (12)
N4*B*—Ni1*B*—N5*B*—C9*B*	−17.0 (9)
N5*B*—Ni1*B*—N4*B*—C8*B*	−9.6 (8)
Ni1*B*—N5*B*—C10*B*—C11*B*	−28.3 (13)
N5*B*—C10*B*—C11*B*—N1*B*	46.2 (14)
Ni1*B*—N1*B*—C11*B*—C10*B*	−39.6 (10)
N5*B*—Ni1*B*—N1*B*—C11*B*	18.4 (7)
N1*B*—Ni1*B*—N5*B*—C10*B*	5.2 (8)

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

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1*A*—H1*A*···O9^{i}	0.91	2.29	3.15 (2)	156.7
N3*A*—H3*A*···O3	0.91	2.33	3.18 (1)	154.5
N4*A*—H4*A*···O2	0.91	2.26	3.11 (1)	155.9
N1*B*—H1*B*···O13	0.91	2.58	3.30 (2)	136.3
N1*B*—H1*B*···O14	0.91	2.35	3.23 (1)	162.6
N2*B*—H2*B*···O10^{ii}	0.91	2.32	3.16 (2)	153.6
N3*B*—H3*B*···O8	0.91	2.58	3.33 (2)	141.2
N5*B*—H5*B*···O4^{iii}	0.91	2.63	3.35 (1)	137.0

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

All H-atom positions were obtained by geometrical calculation and were refined with a riding model.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: *NRCVAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*. 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: TA1177). Services for accessing these data are described at the back of the journal.

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Acta Cryst. (1997). C**53**, 1780–1782

Chloro(1,4,7,11-tetraazacyclotetradecane-*N*,*N*′,*N*″,*N*‴)zinc(II) Perchlorate

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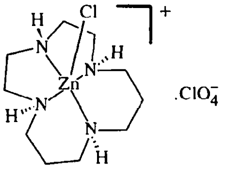
Abstract

In the title compound, $[ZnCl(C_{10}H_{24}N_4)]ClO_4$, the coordination about the Zn^{II} ion is distorted square pyramidal with the four N atoms of the macrocycle in the basal positions and the Cl ion axial. The Zn—Cl and average Zn—N bond lengths are 2.2734 (8) and 2.125 (3) Å, respectively.

Comment

The macrocyclic ligand 1,4,7,11-tetraazacyclotetradecane (isocyclam) is an isomer of 1,4,8,11-tetraazacyclotetradecane (cyclam). The coordination behaviour of cyclam and isocyclam with transition metals has been studied extensively (Boeyens, 1983; Satake *et al.*, 1992; Tahirov *et al.*, 1993, 1995). We report here the structure of [Zn(isocyclam)Cl]ClO_4, (I).



(I)

The Zn^{II} ion is coordinated in a distorted square pyramidal environment, with the four N atoms of the macrocyclic ligand in the basal positions and the Cl axial. The four N atoms form a square plane [the mean deviation is 0.205 (1) Å], with the Zn^{II} ion lying 0.542 (1) Å out of this plane towards the Cl ligand. The perchlorate ion is not coordinated to the metal ion. In the cation, both five-membered chelate rings are *gauche* and both six-membered rings are in chair conformations. The average Zn—N bond length is 2.125 (3) Å, which is longer than that found in $[Zn(cyclam)(ClO_4)_2]$ [2.088 (2) Å; Tyson *et al.*, 1990], but shorter than that in $[Zn(1,4,8,11\text{-tetramethyl-}1,4,8,11\text{-tetraazacyclotetradecane})Cl]^+$ [2.197 (9) Å; Alcock, Herron & Moore, 1978] and similar to that in $[Zn(cyclam)Cl]^+$ [2.13 (1) Å; Alcock, Berry & Moore, 1992]. The Zn—Cl bond length is 2.2734 (8) Å, which is shorter than that in $[Zn(cyclam)Cl]^+$ [2.730 (4) Å; Alcock, Berry & Moore, 1992]. The arrangement of the four chiral N atoms is the same as in $[Ni(isocyclam)]^{2+}$ (planar form) (Boeyens, 1983) and $[Cu(isocyclam)(NCS)]^+$ (Tahirov *et al.*, 1993). Hydrogen bonds among the amido groups and perchlorate groups stabilize the crystal structure.

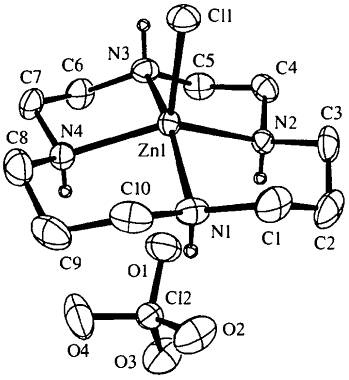


Fig. 1. The structure of the title compound showing 30% probability displacement ellipsoids. Amide H atoms are shown as small circles.

Experimental

The ligand 1,4,7,11-tetraazacyclotetradecane was prepared according to the method of Richman & Atkins (1974). Equimolar quantities of $ZnCl_2$ and the ligand were mixed in aqueous solution and allowed to react for 3 h at room temperature. The resulting solution was dried using a rotary evaporator. The colourless crystals, suitable for crystallographic study, were obtained from a mixture of acetone and 5 *N* $NaClO_4$ at room temperature after several days.

Crystal data

$[ZnCl(C_{10}H_{24}N_4)]ClO_4$
$M_r = 400.61$
Orthorhombic
Pcab
$a = 13.716 (1)$ Å
$b = 14.969 (3)$ Å
$c = 15.925 (1)$ Å
$V = 3269.8 (6)$ Å^3
$Z = 8$
$D_x = 1.628$ Mg m^{-3}
D_m not measured

Mo $K\alpha$ radiation
$\lambda = 0.7107$ Å
Cell parameters from 25 reflections
$\theta = 9.66–28.32°$
$\mu = 1.848$ mm^{-1}
$T = 293 (2)$ K
Pillar
0.32 × 0.28 × 0.26 mm
Colourless

Data collection

Enraf–Nonius CAD-4 diffractometer
$\theta/2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.729$, $T_{max} = 0.895$
4748 measured reflections
4748 independent reflections

3146 reflections with $I > 2\sigma(I)$
$\theta_{max} = 29.89°$
$h = 0 \rightarrow 19$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 22$
3 standard reflections
frequency: 60 min
intensity decay: 1%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.054$
$wR(F^2) = 0.143$
$S = 0.936$
4748 reflections
287 parameters
All H atoms refined
$w = 1/[\sigma^2(F_o^2) + (0.1022P)^2]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = -0.025$

$\Delta\rho_{max} = 0.512$ e Å^{-3}
$\Delta\rho_{min} = -0.386$ e Å^{-3}
Extinction correction: *SHELXL*93 (Sheldrick, 1993)
Extinction coefficient: 0.0067 (6)
Scattering factors from *International Tables for Crystallography* (Vol. C)

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

Zn1—N2	2.084 (3)	Zn1—N3	2.199 (3)
Zn1—N4	2.099 (3)	Zn1—Cl1	2.2734 (8)
Zn1—N1	2.116 (3)		
N2—Zn1—N4	136.71 (11)	N1—Zn1—N3	161.96 (11)
N2—Zn1—N1	91.92 (11)	N2—Zn1—Cl1	108.40 (8)
N4—Zn1—N1	91.75 (12)	N4—Zn1—Cl1	113.51 (8)
N2—Zn1—N3	82.06 (11)	N1—Zn1—Cl1	99.19 (8)
N4—Zn1—N3	81.35 (12)	N3—Zn1—Cl1	98.85 (8)

All H atoms were located from difference Fourier maps and their positional and displacement parameters were refined independently.

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989). Cell refinement: *CAD*-4 *Software* (Enraf–Nonius, 1989). Data reduction: *NRCVAX* (Gabe *et al.*, 1989). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *NRCVAX*. Software used to prepare material for publication: *SHELXL*93.

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Di-μ-acetato-bis[dicarbonyl(pyrazole)-ruthenium(I)] and Di-μ-acetato-bis-[dicarbonyl(3,5-dimethylpyrazole)-ruthenium(I)]†

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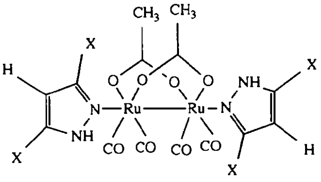
Abstract

The crystal structures of the title compounds, [$Ru_2(C_2H_3O_2)_2(C_3H_4N_2)_2(CO)_4$], (1), and [$Ru_2(C_2H_3O_2)_2(C_5H_8N_2)_2(CO)_4$], (2), have been determined. The octahedral coordination about the Ru$^{\rm I}$ ion is slightly distorted in (1) and more distorted in (2), with the two O atoms and two C atoms in the equatorial positions, and one N atom and another Ru ion in the axial positions. Compound (2) has mirror symmetry.

Comment

Diruthenium(I) carbonyl complexes are either involved as the active intermediates in homogeneously catalyzed reactions or catalytic precursors for the carbonylation of amines, the hydrogenation of carboxylic acids, and the addition of acetic acid to alkynes (Suss-Fink *et al.*, 1985; Matteoli *et al.*, 1985; Frediani *et al.*, 1995). The main purpose of this study is to explore the synthesis and reactivity of some diruthenium(I)–carbonyl complexes containing the μ-acetato linkage. Here, the crystal structures of di-μ-acetato-bis[dicarbonyl(pyrazole)ruthenium(I)] {[$Ru_2(\mu$-$O_2CMe)_2(HPz)_2(CO)_4$], (1)} and di-μ-acetato-bis[dicarbonyl(3,5-dimethylpyrazole)ruthenium(I)] {[$Ru_2(\mu$-$O_2CMe)_2(HPz')_2(CO)_4$], (2), where HPz is pyrazole and HPz′ is 3,5-dimethylpyrazole} are presented.



(1) X=H (2) X=CH_3

Compound (2) has a mirror plane passing through the μ-acetato groups and bisecting the Ru—Ru bond. In compound (1), both Ru$^{\rm I}$ ions have distorted octahedral geometry, coordinated by two O atoms of μ-acetato groups and two C atoms of carbonyl groups in the equatorial positions, and the pyrazole N atom and another Ru ion are in the axial positions, whereas in (2), the Ru$^{\rm I}$ atom has a more distorted octahedral geometry, because the O4—C11—Ru1 system is not linear [O4—C11—Ru1 171 (2)°] and also, there is a non-bonded interaction between the O2 and C11 atoms. All the bond lengths and angles are normal with respect to related compounds in the literature. The Ru—Ru bond length is 2.675 (1) and 2.682 (1) Å in compounds (1) and (2), respectively, shorter than that in [$Ru_2(\mu$-$Pz')(\mu$-$O_2CMe)(CO)_4(PPh_3)_2$] [2.726 (1) Å] and [$Ru_2(\mu$-$Pz')_2(CO)_2(\mu_1,\eta^2$-dppm$)_2$] [2.738 (1) Å], and similar to that in [$Ru_2(\mu$-$Pz')(\mu$-$O_2CMe)(CO)_4(HPz')_2$] [2.682 (1) Å] and [$Ru_2(\mu$-$Pz')(\mu$-$CO)_2(CO)_2(\mu_1,\eta^2$-phen$)_2]^+$ [2.685 (1) Å; Shiu *et al.*, 1996]. The pyrazole moieties in (1) and (2) are planar to within 0.005 (2) and 0.014 (6) Å, respectively. Both crystal structures are stabilized by a three-dimensional network of N—H···O hydrogen bonds.

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† Alternative names: di(μ-acetato-1:2κ^2O:O')tetracarbonyl-1κ^2C,2κ^2C-bis(pyrazole)-1κN^2,2κN^2-diruthenium(I)(*Ru*—*Ru*) and di(μ-acetato-1:2κ^2O:O')tetracarbonyl-1κ^2C,2κ^2C-bis(3,5-dimethylpyrazole)-1κN^2,2κN^2-diruthenium(I)(*Ru*—*Ru*).