O(4)—Nd—O(5)	139.1 (2)	O(3)—Nd—O(141)	63.1 (2)
O(3)—Nd—O(5)	75.5 (2)	O(3)—Nd—O(4)	141.5 (2)
O(2)—Nd—O(81)	62.6 (2)	O(1)—Nd—O(21)	63.8 (2)
Complex (II)			
Er—O(1)	2.253 (5)	Er—O(2)	2.224 (5)
Er—O(3)	2.264 (6)	Er—O(4)	2.346 (5)
Er—O(5)	2.302 (6)	Er—O(6)	2.265 (6)
Er—O(21)	2.749 (7)	Er—O(81)	2.636 (7)
Er—O(141)	2.600 (5)		
O(4)—Er—O(5)	141.1 (2)	O(3)—Er—O(141)	65.6 (2)
O(3)—Er—O(5)	75.9 (2)	O(3)—Er—O(4)	137.0 (2)
O(2)—Er—O(81)	66.1 (2)	O(1)—Er—O(21)	63.0 (2)

Table 4. *Summary of the structural parameters* (Å, °) *for the picrate and trans*-1,4-*dithiane S,S'-dioxide ligands in complexes* (I) *and* (II)

	(I)	(II)
Picrate		
C_{sp^2}—O	1.266 (8)	1.263 (6)
C_{sp^2}—N	1.46 (1)	1.47 (1)
N—O	1.21 (1)	1.21 (1)
C_{sp^2}—C_{sp^2}	1.395 (9)	1.39 (1)
C—C—C	119.9 (7)	120.0 (8)
O—C—C	123.2 (7)	123.9 (7)
O—N—C	118.9 (8)	118.6 (8)
N—C—C	118.6 (7)	118.0 (7)
O—N—O	122.2 (8)	122.7 (8)
trans-1,4-Dithiane *S,S'*-dioxide		
S—O	1.513 (6)	1.511 (6)
C_{sp^3}—S	1.788 (9)	1.795 (9)
C_{sp^3}—C_{sp^3}	1.54 (1)	1.53 (1)
O—S—C	105.6 (4)	105.0 (4)
C—S—C	98.1 (4)	98.3 (4)

The space groups for the Nd and Er complexes were determined unambiguously, from the systematic absences, to be $P2_1/c$ (No. 14). In both the Nd and Er compounds, the H-atom contributions were introduced in calculated positions (C—H = 0.98 Å, U_{iso} = 0.07 Å^2) For both compounds, Enraf–Nonius CAD-4 software was used for data collection and cell refinement. Data reduction was acheived using *MolEN* (Fair, 1990). Structure solution and refinement were performed using *SHELX*76 (Sheldrick, 1976) and molecular graphics were produced using *ORTEP*II (Johnson, 1976).

One of us (JDA) is much indebted to Conselho Nacional de Desenvolvimento Cientìfico e Tecnològico (CNPq) for a fellowship at the University of Milan. The authors are grateful to CNPq, FAPESP (Fundaçào de Amparo à Pesquisa do Estado de São Paulo) and PADCT–FINEP (Plano de Apoio de Desenvolvimento Cientifico e Tecnològico-Financiadora de Estudos e Projetos) for financial support.

Lists of structure factors for both complexes, anisotropic displacement parameters, H-atom coordinates and complete geometry for complex (I) have been deposited with the IUCr (Reference: NA1059). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Ayala, J. D., Zinner, L. B., Vicentini, G., Del Pra, A. & Bombieri, G. (1993). *Inorg. Chim. Acta*, **211**, 161–166.
Herbstein, F. H. & Kaftory, M. (1976). *Acta Cryst.* B**32**, 387–396.
Johnson, C. K. (1976). *ORTEP*II. Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.
Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.
Nardelli, M., Pelizzi, G., Vitali, F., Bordi, F., Plazzi, P. V. & Vitali, T. (1987). *Acta Cryst.* C**43**, 507–514.
Shearer, H. M. M. (1959). *J. Chem. Soc.* 1394–1397.
Sheldrick, G. M. (1976). *SHELX*76. *Program for Crystal Structure Determination.* Univ. of Cambridge, England.

Acta Cryst. (1994). C**50**, 1461–1464

A Novel Inorganic/Organic Macrocycle Involving a Binuclear Zn^{II} Complex of Tetra(2′-pyridyl)pyrazine (TPPZ): Bis[$Zn_2(\mu$-TPPZ)$H_2OCl(\mu$-$ZnCl_4)(\mu$-$ZnCl_2)(\mu$-$ZnCl_3H_2O)$]

MARION GRAF AND HELEN STOECKLI-EVANS

Institut de Chimie, Université de Neuchâtel, Avenue de Bellevaux 51, CH-2000 Neuchâtel, Switzerland

(*Received* 28 *September* 1993; *accepted* 18 *January* 1994)

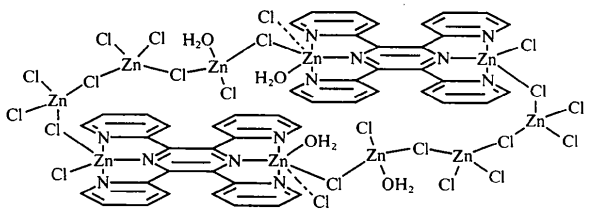
Abstract

The macrocycle, *cyclo*-tetraaqua-1κO,2κO,6κO,7κO-octa-μ-chloro-1:2κ^2Cl;2:3κ^2Cl;3:4κ^2Cl;4:5κ^2Cl;6:7-κ^2Cl;7:8κ^2Cl;8:9κ^2Cl;9:10κ^2Cl-dodecachloro-2κCl,-3κ^2Cl,4κ^2Cl,5κCl,7κCl,8κ^2Cl,9κ^2Cl,10κCl-bis[μ-2,3,5,6-tetra(2-pyridyl)pyrazine]-1$\kappa^3N^{1,2,6}$:10$\kappa^3N^{3,4,5}$;-5$\kappa^3N^{1,2,6}$:6$\kappa^3N^{3,4,5}$-decazinc, $[Zn_5Cl_{10}(C_{24}H_{16}N_6)(H_2O)_2]_2$, is composed of two twisted binuclear Zn^{II} complexes of the ligand tetra(2′-pyridyl)pyrazine connected end to end by two chains of three Cl···Zn···Cl bridging units.

Comment

The ligand tetra(2′-pyridyl)pyrazine (TPPZ) was originally synthesized by Goodwin & Lions (1959). It was thought unlikely that it would act as a bis(tridentate) ligand owing to the steric repulsions between adjacent coplanar pyridine rings. However, binuclear complexes have been prepared with Ru^{II} (Thummel & Chirayil, 1988; Ruminski, Kipling, Cockcroft & Chase, 1989), Cu^{II} (Escuer, Comas, Ribas, Vicente, Solans, Zanchini & Gatteschi, 1989) and Rh^{II} (Ruminski & Letner, 1989). Recently Arana & Abruna (1993) prepared a series of monometallic and homo- and hetero-, bi- and trimetallic complexes of Ru^{II} and Os^{II}. We have shown, crystallographically, that TPPZ forms both mononuclear complexes with Cu^{II} and Zn^{II} (Graf, Greaves & Stoeckli-

Evans, 1993) and Co^{III} and Ni^{II} (Graf & Stoeckli-Evans, 1994), and binuclear complexes with Cu^{II} (Graf, Greaves & Stoeckli-Evans, 1993) and Zn^{II} and Ni^{II} (Graf & Stoeckli-Evans, 1994). The title compound, (I), was produced quite unexpectedly during an attempt to convert a mononuclear zinc perchlorate complex of TPPZ into a binuclear complex.



(I)

The macrocycle possess C_i symmetry and is composed of two highly twisted binuclear Zn^{II} complexes of TPPZ linked end to end by three Cl···Zn···Cl bridges (Fig. 1). The central pyrazine ring is twisted by 11.6 (3)° {this is the dihedral angle between planes *C'* [N(1), C(1), C(2)] and *C''* [N(4^v), C(13), C(14)]} as can be seen more clearly in Fig. 2. Such deformations have been observed previously (Graf *et al.*, 1993, and references therein). The central Zn—N(pyrazine) distance [average value 2.134 (2) Å] is very slightly longer than the terminal Zn—N(pyridine) distance [average value 2.115 (2) Å]. The same trend has been observed in the binuclear zinc complex (Graf & Stoeckli-Evans, 1994) but the opposite was observed for the mononuclear zinc complex (Graf *et al.*, 1993) and a zinc terpyridyl complex (Vlasse, Rojo & Beltran-Porter, 1983). In the binuclear complex of the macrocycle (Fig. 2) atom Zn(1) has trigonal bipyrimidal coordination and lies in the plane of atoms N(1), O(*W*1) and Cl(1) with atoms N(2) and N(3) displaced from the best plane by 2.024 (4) and −2.059 (4) Å, respectively. In the case of atom Zn(5), which also has trigonal bipyrimidal coordination, the Zn atom lies in the plane of atoms N(4), Cl(7) and Cl(10) with atoms N(5) and N(6) displaced by −2.048 (4) and 2.048 (4) Å, respectively, from this best plane. Pyridine rings *A* [N(2), C(3), C(4), C(5), C(6), C(7)] and *B* [N(3), C(8), C(9), C(10), C(11), C(12)], which are coordinated to Zn(1), are inclined to each other by 7.72 (17)°, while pyridine rings *D* [N(5), C(15), C(16), C(17), C(18), C(19)] and *E* [N(6), C(20), C(21), C(22), C(23), C(24)], coordinated to Zn(5), are inclined to each other by 12.19 (18)°. Pyridine rings diagonally opposite each other, *A* and *D*, and *B* and *E*, are inclined by 48.61 (18) and 35.00 (16)°, respectively. Adjacent rings *A* and *E* are inclined by 41.56 (16)° and adjacent rings *B* and *D* by 41.20 (18)°.

The Zn(1) atom is linked to Zn(5^i) by three Cl···Zn···Cl bridges. The average Zn···Cl bridging distance is 2.3239 (4) Å, which is slightly longer than the

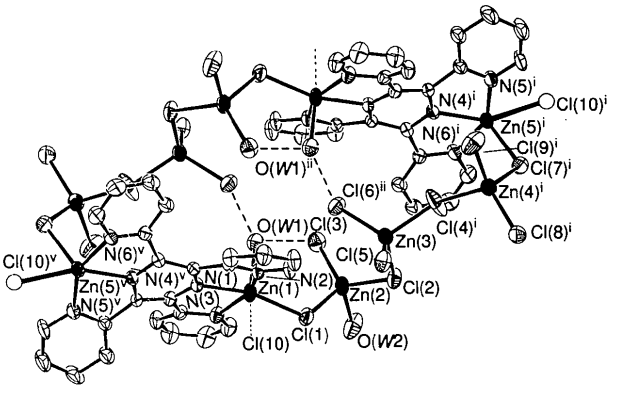


Fig. 1. Perspective view of the macrocycle showing part of the numbering scheme. Displacement ellipsoids are drawn at 50% probability. H atoms have been omitted for clarity. (See Table 2 for symmetry codes.)

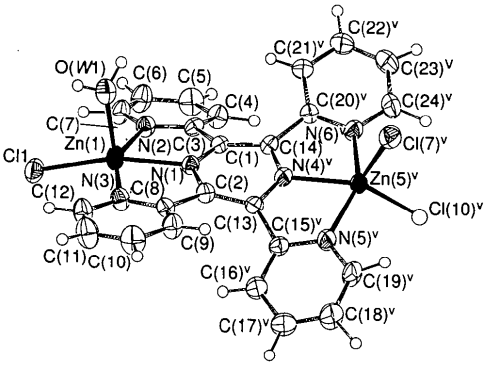


Fig. 2. Perspective view of the binuclear complex showing the numbering scheme. Displacement ellipsoids are drawn at 50% probability. (See Table 2 for symmetry codes.)

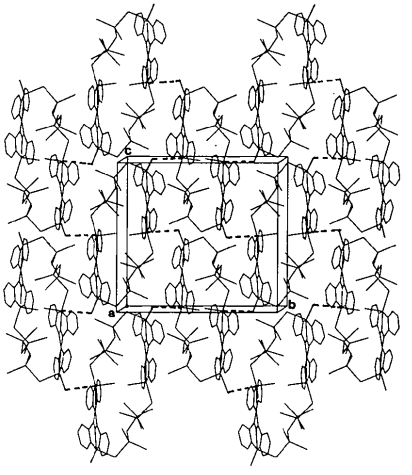


Fig. 3. Crystal packing showing the Zn(5)—Cl(10)···Zn(1) bridging bond (dashed line) linking the macrocycles.

non-bridging Zn—Cl distances which have an average value of 2.208 (6) Å. The macrocycles are linked to one another by a longer Zn—Cl···Zn bridging bond [2.806 (1) Å], involving the Zn(1) and Zn(5) atoms of the binuclear complex and the Cl(10) atom, which is directly coordinated to atom Zn(5) of a symmetry-related molecule (Fig. 3). There are two coordinated water molecules in the asymmetric half of the macrocycle; one to Zn(1) [Zn(1)—O(W1) 2.090 (4) Å] and the other to a bridging Zn atom [Zn(2)–O(W2) 2.004 (5) Å]. There are two intramolecular hydrogen bonds involving water O(W1) and atoms Cl(3) and Cl(6). A third hydrogen bond links the macrocycles and involves water O(W2) and a Cl(10) atom of a symmetry-related molecule.

Experimental

The title compound was prepared in the following manner. $Zn(ClO_4)_2$ (68.3 mg, 0.26 mmol) and TPPZ (100 mg, 0.26 mmol) were dissolved in 30 ml of an ethanol/water (1:1) mixture and stirred at 363 K for 1 h. The solution was allowed to stand for 3 d. The yellow precipitate which formed was filtered off and dried. It was identified as the mononuclear complex $[Zn(TPPZ)(H_2O)_2](ClO_4)_2$. 50 mg of this complex was dissolved in 15 ml of an ethanol/water (1:1) mixture and stirred with 2.03 g of $ZnCl_2$ at 363 K for 1 h. The colour changed to deep yellow. After several days the white precipitate that had formed was filtered off. The filtrate was allowed to stand in a closed crystallizer for 2 months. Deep yellow crystals of the title compound were obtained.

Crystal data

$[Zn_5Cl_{10}(C_{24}H_{16}N_6)(H_2O)_2]$
M_r = 1105.88
Monoclinic
$P2_1/c$
a = 12.826 (1) Å
b = 17.739 (1) Å
c = 16.422 (2) Å
β = 95.11 (1)°
V = 3721.5 (7) Å^3
Z = 4
D_x = 1.974 Mg m^{-3}
Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 22 reflections
θ = 14.00–20.00°
μ = 4.02 mm^{-1}
T = 293 K
Biprism
0.53 × 0.46 × 0.34 mm
Deep yellow

Data collection

Stoe AED-2 four-circle diffractometer
ω/θ scans
Absorption correction: empirical (*EMPIR*; Stoe & Cie, 1989)
T_{min} = 0.173, T_{max} = 0.276
6559 measured reflections
6559 independent reflections
5133 observed reflections [$I > 2.0\sigma(I)$]
θ_{max} = 25.01°
$h = -15 \rightarrow 15$
$k = 0 \rightarrow 21$
$l = 0 \rightarrow 19$
2 standard reflections
frequency: 60 min
intensity variation: 2.5%

Refinement

Refinement on F
R = 0.037
wR = 0.055
S = 1.08
5133 reflections
504 parameters
H atoms isotropic
$w = 1/[\sigma^2(F) + 0.0020F^2]$
$(\Delta/\sigma)_{max}$ = 0.333
$\Delta\rho_{max}$ = 1.23 e Å^{-3}
$\Delta\rho_{min}$ = −0.88 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV, Table 2.2B)

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

$U_{eq} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$.

	x	y	z	U_{eq}
Zn(1)	0.27462 (4)	0.35793 (3)	0.00264 (3)	0.0348 (3)
Zn(2)	0.28555 (4)	0.41010 (3)	−0.23566 (3)	0.0383 (3)
Zn(3)	0.58030 (4)	0.39535 (3)	−0.21160 (3)	0.0368 (3)
Zn(4)	0.16050 (4)	−0.07265 (3)	−0.13691 (3)	0.0376 (3)
Zn(5)	0.22582 (4)	0.13229 (3)	−0.08296 (3)	0.0328 (3)
Cl(1)	0.27699 (11)	0.32002 (7)	−0.13470 (7)	0.0446 (7)
Cl(2)	0.42721 (9)	0.37561 (8)	−0.30065 (7)	0.0446 (6)
Cl(3)	0.25679 (10)	0.52665 (7)	−0.19991 (8)	0.0494 (6)
Cl(4)	0.31728 (14)	−0.05040 (10)	−0.19635 (14)	0.0841 (11)
Cl(5)	0.65178 (10)	0.29217 (7)	−0.15813 (7)	0.0459 (6)
Cl(6)	0.47197 (10)	0.52040 (7)	0.12253 (7)	0.0455 (6)
Cl(7)	0.19085 (10)	0.01321 (7)	−0.03006 (7)	0.0440 (6)
Cl(8)	0.15067 (11)	−0.18622 (7)	−0.08395 (8)	0.0497 (7)
Cl(9)	0.03313 (12)	−0.03646 (10)	−0.22899 (11)	0.0714 (9)
Cl(10)	0.22843 (9)	0.20616 (6)	0.03152 (7)	0.0382 (6)
O(W1)	0.3038 (3)	0.47257 (20)	−0.01422 (24)	0.0419 (18)
O(W2)	0.1648 (4)	0.3771 (4)	−0.3133 (3)	0.072 (3)
N(1)	0.2613 (3)	0.36137 (19)	0.13049 (20)	0.0271 (17)
N(2)	0.4261 (3)	0.33353 (21)	0.05421 (22)	0.0311 (18)
N(3)	0.1125 (3)	0.37351 (21)	0.01151 (23)	0.0344 (18)
N(4)	0.2436 (3)	0.14010 (20)	−0.21131 (20)	0.0287 (17)
N(5)	0.0741 (3)	0.15848 (23)	−0.13709 (23)	0.0366 (19)
N(6)	0.3902 (3)	0.12540 (21)	−0.09267 (22)	0.0338 (19)
C(1)	0.3486 (3)	0.35369 (22)	0.17941 (24)	0.0261 (18)
C(2)	0.1652 (3)	0.36539 (23)	0.1556 (3)	0.0285 (19)
C(3)	0.4406 (3)	0.32995 (23)	0.1360 (3)	0.0274 (19)
C(4)	0.5301 (4)	0.3000 (3)	0.1760 (3)	0.0382 (23)
C(5)	0.6113 (4)	0.2769 (3)	0.1312 (3)	0.046 (3)
C(6)	0.5991 (4)	0.2844 (3)	0.0467 (3)	0.044 (3)
C(7)	0.5041 (4)	0.3120 (3)	0.0111 (3)	0.0377 (23)
C(8)	0.0812 (3)	0.38133 (24)	0.0885 (3)	0.0296 (19)
C(9)	−0.0188 (4)	0.4053 (3)	0.1003 (3)	0.039 (3)
C(10)	−0.0902 (4)	0.4154 (3)	0.0335 (3)	0.050 (3)
C(11)	−0.0597 (4)	0.4051 (3)	−0.0441 (4)	0.052 (3)
C(12)	0.0425 (4)	0.3854 (3)	−0.0522 (3)	0.044 (3)
C(13)	0.1567 (3)	0.35251 (23)	0.23887 (25)	0.0272 (18)
C(14)	0.3401 (3)	0.36485 (22)	0.26443 (25)	0.0271 (18)
C(15)	0.0643 (3)	0.17096 (25)	−0.2184 (3)	0.0306 (21)
C(16)	−0.0205 (4)	0.2075 (3)	−0.2564 (3)	0.044 (3)
C(17)	−0.1019 (4)	0.2280 (4)	−0.2096 (4)	0.060 (4)
C(18)	−0.0960 (4)	0.2088 (4)	−0.1286 (4)	0.061 (4)
C(19)	−0.0045 (4)	0.1766 (4)	−0.0939 (3)	0.052 (3)
C(20)	0.4232 (3)	0.11743 (23)	−0.1679 (3)	0.0289 (20)
C(21)	0.5210 (4)	0.0891 (3)	−0.1800 (3)	0.0353 (24)
C(22)	0.5906 (4)	0.0754 (3)	−0.1126 (3)	0.042 (3)
C(23)	0.5592 (4)	0.0875 (3)	−0.0358 (3)	0.048 (3)
C(24)	0.4571 (4)	0.1119 (3)	−0.0288 (3)	0.046 (3)

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

Zn(1)—Cl(1)	2.3563 (12)	N(4)—C(14^{iv})	1.337 (5)
Zn(1)—Cl(10)	2.8061 (13)	N(5)—C(15)	1.348 (6)
Zn(1)—O(W1)	2.090 (4)	N(5)—C(19)	1.324 (6)
Zn(1)—N(1)	2.123 (3)	N(6)—C(20)	1.349 (6)
Zn(1)—N(2)	2.094 (4)	N(6)—C(24)	1.317 (6)
Zn(1)—N(3)	2.116 (4)	C(1)—C(3)	1.493 (6)
Zn(2)—Cl(1)	2.3122 (13)	C(1)—C(14)	1.424 (6)
Zn(2)—Cl(2)	2.2716 (13)	C(2)—C(8)	1.497 (6)
Zn(2)—Cl(3)	2.1895 (14)	C(2)—C(13)	1.400 (6)
Zn(2)—O(W2)	2.004 (5)	C(3)—C(4)	1.377 (6)
Zn(3)—Cl(2)	2.3675 (13)	C(4)—C(5)	1.389 (7)
Zn(3)—Cl(4^{i})	2.3003 (15)	C(5)—C(6)	1.389 (7)
Zn(3)—Cl(5)	2.1950 (13)	C(6)—C(7)	1.393 (7)
Zn(3)—Cl(6^{ii})	2.2353 (13)	C(8)—C(9)	1.382 (6)

Zn(4)—Cl(4)	2.3456 (15)	C(9)—C(10)	1.377 (7)
Zn(4)—Cl(7)	2.3299 (13)	C(10)—C(11)	1.378 (8)
Zn(4)—Cl(8)	2.2024 (14)	C(11)—C(12)	1.374 (8)
Zn(4)—Cl(9)	2.2198 (15)	C(13)—N(4^{v})	1.329 (5)
Zn(5)—Cl(7)	2.3426 (13)	C(13)—C(15^{v})	1.490 (6)
Zn(5)—Cl(10)	2.2894 (12)	C(14)—N(4^{v})	1.337 (5)
Zn(5)—N(4)	2.145 (3)	C(14)—C(20^{v})	1.503 (6)
Zn(5)—N(5)	2.117 (4)	C(15)—C(13^{iv})	1.490 (6)
Zn(5)—N(6)	2.132 (4)	C(15)—C(16)	1.368 (6)
Cl(4)—Zn(3^{iii})	2.3003 (15)	C(16)—C(17)	1.399 (7)
Cl(6)—Zn(3^{ii})	2.2353 (13)	C(17)—C(18)	1.368 (9)
N(1)—C(1)	1.326 (5)	C(18)—C(19)	1.382 (8)
N(1)—C(2)	1.336 (5)	C(20)—C(14^{iv})	1.503 (6)
N(2)—C(3)	1.341 (5)	C(20)—C(21)	1.382 (6)
N(2)—C(7)	1.332 (6)	C(21)—C(22)	1.380 (7)
N(3)—C(8)	1.367 (6)	C(22)—C(23)	1.374 (8)
N(3)—C(12)	1.333 (6)	C(23)—C(24)	1.394 (8)
N(4)—C(13^{iv})	1.329 (5)		

Cl(1)—Zn(1)—Cl(10)	84.77 (4)	C(3)—N(2)—C(7)	118.3 (4)
Cl(1)—Zn(1)—O(*W*1)	97.66 (11)	Zn(1)—N(3)—C(8)	116.6 (3)
Cl(1)—Zn(1)—N(1)	164.60 (10)	Zn(1)—N(3)—C(12)	124.3 (3)
Cl(1)—Zn(1)—N(2)	103.74 (10)	C(8)—N(3)—C(12)	118.5 (4)
Cl(1)—Zn(1)—N(3)	101.52 (11)	Zn(5)—N(4)—C(13^{iv})	117.0 (3)
Cl(10)—Zn(1)—O(*W*1)	176.98 (11)	Zn(5)—N(4)—C(14^{iv})	118.1 (3)
Cl(10)—Zn(1)—N(1)	79.84 (10)	C(13^{iv})—N(4)—C(14^{iv})	124.8 (4)
Cl(10)—Zn(1)—N(2)	86.30 (11)	Zn(5)—N(5)—C(15)	117.0 (3)
Cl(10)—Zn(1)—N(3)	83.69 (11)	Zn(5)—N(5)—C(19)	123.0 (3)
O(*W*1)—Zn(1)—N(1)	97.71 (14)	C(15)—N(5)—C(19)	118.8 (4)
O(*W*1)—Zn(1)—N(2)	94.84 (15)	Zn(5)—N(6)—C(20)	117.9 (3)
O(*W*1)—Zn(1)—N(3)	94.04 (14)	Zn(5)—N(6)—C(24)	122.0 (3)
N(1)—Zn(1)—N(2)	76.08 (13)	C(20)—N(6)—C(24)	118.4 (4)
N(1)—Zn(1)—N(3)	76.22 (14)	N(1)—C(1)—C(3)	113.6 (3)
N(2)—Zn(1)—N(3)	151.79 (14)	N(1)—C(1)—C(14)	116.5 (4)
Cl(1)—Zn(2)—Cl(2)	104.00 (5)	C(3)—C(1)—C(14)	129.8 (4)
Cl(1)—Zn(2)—Cl(3)	116.13 (5)	N(1)—C(2)—C(8)	114.0 (4)
Cl(1)—Zn(2)—O(*W*2)	99.85 (19)	N(1)—C(2)—C(13)	116.6 (4)
Cl(2)—Zn(2)—Cl(3)	122.77 (6)	C(8)—C(2)—C(13)	129.4 (4)
Cl(2)—Zn(2)—O(*W*2)	103.14 (14)	N(2)—C(3)—C(1)	114.8 (4)
Cl(3)—Zn(2)—O(*W*2)	107.92 (17)	N(2)—C(3)—C(4)	122.1 (4)
Cl(2)—Zn(3)—Cl(4^{i})	98.43 (7)	C(1)—C(3)—C(4)	122.8 (4)
Cl(2)—Zn(3)—Cl(5)	114.69 (5)	C(3)—C(4)—C(5)	119.6 (4)
Cl(2)—Zn(3)—Cl(6^{ii})	102.86 (5)	C(4)—C(5)—C(6)	118.6 (4)
Cl(4^{i})—Zn(3)—Cl(5)	111.66 (6)	C(5)—C(6)—C(7)	118.0 (4)
Cl(4^{i})—Zn(3)—Cl(6^{ii})	111.86 (7)	N(2)—C(7)—C(6)	123.2 (4)
Cl(5)—Zn(3)—Cl(6^{ii})	115.77 (5)	N(3)—C(8)—C(2)	114.2 (4)
Cl(4)—Zn(4)—Cl(7)	96.40 (6)	N(3)—C(8)—C(9)	120.9 (4)
Cl(4)—Zn(4)—Cl(8)	113.56 (7)	C(2)—C(8)—C(9)	124.9 (4)
Cl(4)—Zn(4)—Cl(9)	105.90 (8)	C(8)—C(9)—C(10)	119.3 (5)
Cl(7)—Zn(4)—Cl(8)	108.19 (5)	C(9)—C(10)—C(11)	119.7 (5)
Cl(7)—Zn(4)—Cl(9)	112.79 (7)	C(10)—C(11)—C(12)	118.4 (5)
Cl(8)—Zn(4)—Cl(9)	117.97 (6)	N(3)—C(12)—C(11)	123.0 (5)
Cl(7)—Zn(5)—Cl(10)	101.59 (4)	N(4^{v})—C(13)—C(2)	116.8 (4)
Cl(7)—Zn(5)—N(4)	117.60 (10)	N(4^{v})—C(13)—C(15^{v})	113.3 (4)
Cl(7)—Zn(5)—N(5)	98.89 (12)	C(2)—C(13)—C(15^{v})	129.8 (4)
Cl(7)—Zn(5)—N(6)	101.49 (11)	N(4^{v})—C(14)—C(1)	115.9 (4)
Cl(10)—Zn(5)—N(4)	140.81 (10)	N(4^{v})—C(14)—C(20^{v})	114.1 (4)
Cl(10)—Zn(5)—N(5)	99.49 (11)	C(1)—C(14)—C(20^{v})	130.0 (4)
Cl(10)—Zn(5)—N(6)	98.74 (10)	N(5)—C(15)—C(13^{iv})	114.4 (4)
N(4)—Zn(5)—N(5)	75.36 (14)	N(5)—C(15)—C(16)	122.0 (4)
N(4)—Zn(5)—N(6)	74.80 (13)	C(13^{iv})—C(15)—C(16)	123.4 (4)
N(5)—Zn(5)—N(6)	149.20 (14)	C(15)—C(16)—C(17)	118.3 (5)
Zn(1)—Cl(1)—Zn(2)	119.64 (5)	C(16)—C(17)—C(18)	119.3 (5)
Zn(2)—Cl(2)—Zn(3)	108.90 (5)	C(17)—C(18)—C(19)	118.4 (5)
Zn(3^{iii})—Cl(4)—Zn(4)	139.82 (8)	N(5)—C(19)—C(18)	122.6 (5)
Zn(4)—Cl(7)—Zn(5)	109.57 (5)	N(6)—C(20)—C(14^{iv})	113.3 (4)
Zn(1)—Cl(10)—Zn(5)	113.46 (4)	N(6)—C(20)—C(21)	122.2 (4)
Zn(1)—N(1)—C(1)	117.3 (3)	C(14^{iv})—C(20)—C(21)	124.3 (4)
Zn(1)—N(1)—C(2)	117.7 (3)	C(20)—C(21)—C(22)	118.7 (4)
C(1)—N(1)—C(2)	124.8 (4)	C(21)—C(22)—C(23)	119.1 (5)
Zn(1)—N(2)—C(3)	117.1 (3)	C(22)—C(23)—C(24)	118.6 (5)
Zn(1)—N(2)—C(7)	123.9 (3)	N(6)—C(24)—C(23)	122.8 (5)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O(*W*1)—H(*AW*1)···Cl(3)	0.80 (6)	2.41 (6)	3.202 (4)	168 (6)
O(*W*1)—H(*BW*1)···Cl(6)	0.94 (8)	2.23 (8)	3.091 (4)	151 (7)
O(*W*2)—H(*BW*2)···Cl(10^{iv})	0.75 (7)	2.37 (7)	3.116 (5)	168 (7)

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

Data collection: *DIF*4 (Stoe & Cie, 1988). Cell refinement: *DIF*4. Data reduction: *NRCVAX DATRD*2 (Gabe, Le Page, Charland, Lee & White, 1989). Program(s) used to solve structure: *NRCVAX SOLVER*. Program(s) used to refine structure: *NRCVAX LSTSQ*. Molecular graphics: *PLUTO* (Motherwell & Clegg, 1978) and *PLATON* (Spek, 1990). Software used to prepare material for publication: *NRCVAX TABLES*.

We wish to thank the Swiss National Science Foundation for financial support.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: AL1077). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Arana, C. R. & Abruna, H. D. (1993). *Inorg. Chem.* **21**, 194–203.

Escuer, A., Comas, T., Ribas, J., Vicente, R., Solans, X., Zanchini, C. & Gatteschi, D. (1989). *Inorg. Chim. Acta*, **162**, 97–103.

Gabe, E. J., Le Page, Y., Charland, J.-P., Lee, F. L. & White, P. S. (1989). *J. Appl. Cryst.* **22**, 384–387.

Goodwin, H. A. & Lions, F. (1959). *J. Am. Chem. Soc.* **81**, 6415–6422.

Graf, M., Greaves, B. & Stoeckli-Evans, H. (1993). *Inorg. Chim. Acta*, **204**, 239–246.

Graf, M. & Stoeckli-Evans, H. (1994). In preparation.

Motherwell, W. D. S. & Clegg, W. (1978). *PLUTO. Program for Plotting Molecular and Crystal Structures*. Univ. of Cambridge, England.

Ruminski, R. R., Kipling, T., Cockcroft, T. & Chase, C. (1989). *Inorg. Chem.* **28**, 370–373.

Ruminski, R. R. & Letner, C. (1989). *Inorg. Chim. Acta*, **162**, 175–177.

Spek, A. L. (1990). *Acta Cryst.* A**46**, C-34.

Stoe & Cie (1988). *DIF*4. *Diffractometer Control Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.

Stoe & Cie (1989). *EMPIR. Empirical Absorption Correction Program*. Version 1.2. Stoe & Cie, Darmstadt, Germany.

Thummel, R. P. & Chirayil, S. (1989). *Inorg. Chim. Acta*, **154**, 77–81.

Vlasse, M., Rojo, T. & Beltran-Porter, D. (1983). *Acta Cryst.* C**39**, 560–563.