metal-organic papers

Acetato[μ-10,21-dibutyl-3,6,14,17-tetrazatricyclo-[17.3.1.1^{8,12}]tetracosa-1(23),2,6,8,10,12(24),13,-17,19,21-decaene-23,24-diolato(2−)-$\kappa^4N^3,N^6,O^{23},O^{24}$:$\kappa^4N^{14},N^{17},O^{23},O^{24}$]dinickel(II) perchlorate acetonitrile hemisolvate

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In the title complex, $[Ni_2(C_{28}H_{34}N_4O_3)(CH_3CO_2)]ClO_4 \cdot 0.5CH_3CN$, the macrocyclic ligand shows significant deviations from a planar structure. The coordination polyhedra of the Ni atoms can be described as square planar for one of the atoms and as distorted octahedral for the other. The two Ni atoms are bridged by two phenolate O atoms of the macrocycle with an Ni···Ni distance of 2.9612 (5) Å. The acetonitrile solvent molecule occupies a special position on a twofold axis with the H atoms disordered.

Comment

Schiff base macrocyclic ligands with phenolic O atoms, capable of serving as oxo-bridges, are known to form various types of transition metal complexes. Owing to the short distance between the two metal atoms, these complexes often exhibit special optical, electric and magnetic properties. (Mohanta *et al.*, 1998; Wang *et al.*, 1997). Transition metal complexes involving macrocyclic ligands, synthesized by the cyclocondensation of 2,6-diformyl-4-*R*-phenol and alkyl-enediamine by the stepwise template reaction (*R* = CH₃, *n*-butyl, Cl), have been extensively studied (Thompson *et al.*, 1996; Zhou *et al.*, 2005; Raimondi *et al.*, 2004). However, only a few crystal structures of Ni^II complexes of these ligands have been published (Brooker *et al.*, 2000). We report here the structure of a macrocyclic complex, in which two Ni atoms have significantly different coordination environments, even though they reside in two chemically equivalent macrocyclic cavities.

(I)
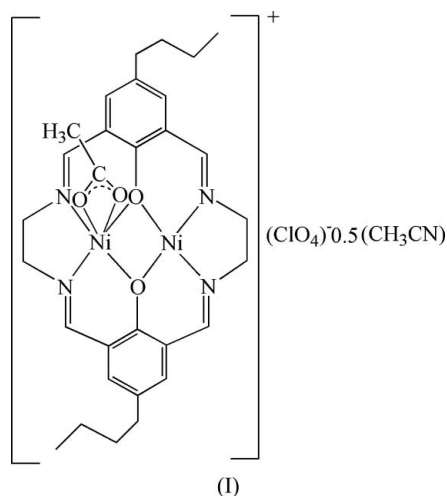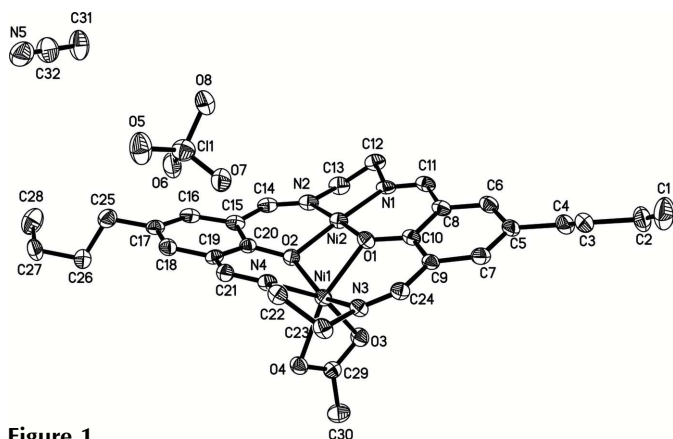
Figure 1
A view of the cation in the structure of the title compound, showing the labeling of the non-H atoms and 30% probability ellipsoids; H atoms have been omitted for clarity.

The crystal structure is built of complex cations, perchlorate anions and solvent acetonitrile molecules. The acetonitrile molecule occupies a special position on a twofold axis; the H atoms of the acetonitrile methyl group are disordered. Neither the perchlorate ions nor the acetonitrile molecules participate in coordination of the Ni atoms.

The cation in the crystal structure of the title complex is shown in Fig. 1. The macrocyclic ligand shows significant deviations from planarity, with the two benzene planes forming a dihedral angle of 23.4 (3)°. Atom Ni2 has a slightly distorted square-planar coordination; its deviation from the mean plane of atoms N1, N2, O1 and O2 is 0.001 (3) Å. Coordination of the acetate ligand at atom Ni1 results in a severely distorted octahedral environment; the distortions are obviously due to the effect of the rigid macrocyclic framework, as well as the presence of a four-membered chelate ring formed by the acetate ligand. Even though atoms O1, O2, N3 and N4 are in fact no longer coplanar, the bond angles in the coordination octahedron show considerable deviations from the ideal values, spanning the range 62.66 (8)–111.73 (9)° for *cis*- and being as narrow as 152.02 (9), 155.26 (8) and 155.13 (9)° for *trans*-angles in the octahedron (see Table 1). The difference in coordination polyhedra of Ni1 and Ni2 is also reflected in the differences in bond lengths; the Ni—O and Ni—N bonds involving the square-planar Ni2 atom [1.8364 (19), 1.8461 (19) and 1.822 (2), 1.846 (2) Å, respectively] are significantly shorter than the corresponding Ni—O and Ni—N bonds of the octahedral Ni1 atom [2.024–2.096 and 1.983 (2), 2.018 (2) Å, respectively]. The presence of two bridging phenolic oxo atoms gives rise to a short metal–metal distance, typical for binuclear complexes with macrocyclic phenoxo-bridging ligands [Ni1···Ni2 = 2.9612 (5) Å; Brooker *et al.*, 2000].

Experimental

2,6-Diformyl-4-*n*-butylphenol was prepared using a variant of the method suggested by Taniguchi (1984). *N*,*N*′-bis(3-formyl-5-butyl-salicylidene)ethylenediimine was prepared according to Zhou *et al.*

(2005). The title complex was synthesized by the following procedure: a suspension of *N*,*N*′-bis(3-formyl-5-butylsalicylidene)ethylenedi-imine (0.5 mmol) in 30 ml of absolute methanol was added to a methanol solution of Ni(OAc)$_2$H$_2$O (0.5 mmol). The mixture was stirred at ambient temperature for about 3 h, then triethylamine (5 ml) and a methanol solution (5 ml) containing nickel perchlorate hexahydrate (0.5 mmol) were added, and stirring was continued for about a further 10 h. A methanol solution (10 ml) containing 1,2-ethylenediamine (0.5 mmol) was added dropwise for more than 40 min, and the mixture was refluxed for 1 h to give a red solution. The compound was crystallized by a slow diffusion of ethyl acetate into the mother solution. Red needle-shaped crystals of the title complex suitable for X-ray diffraction precipitated in about a month. The needle crystal used in the experiment was cut (see crystal dimensions in the crystal data), so that the crystal could fit within the X-ray beam.

Crystal data

C$_{30}$H$_{37}$N$_4$Ni$_2$O$_4^+$·ClO$_4^-$·0.5C$_2$H$_3$N	$Z = 8$
$M_r = 755.01$	$D_x = 1.500$ Mg m^{-3}
Monoclinic, $C2/c$	Mo $K\alpha$ radiation
$a = 31.353$ (2) Å	$\mu = 1.26$ mm^{-1}
$b = 11.2316$ (7) Å	$T = 298$ (2) K
$c = 21.2808$ (14) Å	Block cut from needle, red
$\beta = 116.875$ (1)°	$0.30 \times 0.20 \times 0.20$ mm
$V = 6684.6$ (7) Å^3	

Data collection

Bruker SMART APEX CCD area-detector diffractometer	28559 measured reflections
φ and ω scans	6572 independent reflections
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	5169 reflections with $I > 2\sigma(I)$
$T_{min} = 0.703$, $T_{max} = 0.786$	$R_{int} = 0.048$
	$\theta_{max} = 26.0°$

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.05P)^2 + 1.55P]$
$R[F^2 > 2\sigma(F^2)] = 0.045$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.101$	$(\Delta/\sigma)_{max} < 0.001$
$S = 1.06$	$\Delta\rho_{max} = 0.26$ e Å^{-3}
6572 reflections	$\Delta\rho_{min} = -0.40$ e Å^{-3}
425 parameters	
H-atom parameters constrained	

Table 1
Selected geometric parameters (Å, °).

Ni1—Ni2	2.9612 (5)	Ni1—N4	2.018 (2)
Ni1—O1	2.0692 (19)	Ni2—O1	1.8461 (19)
Ni1—O2	2.0245 (18)	Ni2—O2	1.8364 (19)
Ni1—O3	2.096 (2)	Ni2—N1	1.822 (2)
Ni1—O4	2.091 (2)	Ni2—N2	1.846 (2)
Ni1—N3	1.983 (2)		
N3—Ni1—N4	82.82 (9)	O2—Ni1—O3	96.38 (8)
N3—Ni1—O2	152.02 (9)	O1—Ni1—O3	92.68 (8)
N4—Ni1—O2	86.43 (8)	O4—Ni1—O3	62.66 (8)
N3—Ni1—O1	86.43 (9)	N1—Ni2—O2	177.19 (9)
N4—Ni1—O1	111.73 (9)	N1—Ni2—O1	95.92 (10)
O2—Ni1—O1	73.70 (8)	O2—Ni2—O1	83.63 (8)
N3—Ni1—O4	100.88 (9)	N1—Ni2—N2	88.27 (11)
N4—Ni1—O4	92.72 (9)	O2—Ni2—N2	92.31 (9)
O2—Ni1—O4	105.39 (8)	O1—Ni2—N2	175.13 (10)
O1—Ni1—O4	155.26 (8)	Ni2—O1—Ni1	98.12 (9)
N3—Ni1—O3	104.18 (9)	Ni2—O2—Ni1	100.05 (9)
N4—Ni1—O3	155.13 (9)		

All H atoms were placed in calculated positions (C—H = 0.93–0.97 Å) and included in the refinement in the riding-model approximation with $U_{iso}(H) = 1.2U_{eq}$(carrier atom) ($1.5U_{eq}$ for methyl H atoms). The H atoms of the acetonitrile molecule (H31A, H31B, and H31C) are disordered over two positions related by a twofold axis.

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

References

Brooker, S., Croucher, P. D., Davidson, T. C. & Smith, P. D. (2000). *Polyhedron*, **19**, 1887–1894.

Bruker (2000). *SMART* (Version 6.22), *SAINT* (Version 6.22), *SADABS* (Version 2.03) and *SHELXTL* (Version 6.10). Bruker AXS Inc., Madison, Wisconsin, USA.

Mohanta, S., Baitalik, S., Dutta, S. K. & Adhikary, B. (1998). *Polyhedron*, **17**, 2669–2677.

Raimondi, A. C., De Souza, V. R., Toma, H. E., Mangrich, A. S., Hasegawa, T. & Nunes, F. S. (2004). *Polyhedron*, **23**, 2069–2074.

Taniguchi, S. (1984). *Bull. Chem. Soc. Jpn*, **57**, 2683–2689.

Thompson, I. K., Mandal, S. K., Tandon, S. S., Bridson, J. N. & Park, M. K. (1996). *Inorg. Chem.* **35**, 3117–3125.

Wang, Z., Reibenspies, J. & Martell, A. E. (1997). *Inorg. Chem.* **36**, 629–636.

Zhou, H., Peng, Z. H., Pan, Z. Q., Liu, B. & Liu, Y. Q. (2005). *J. Coord. Chem.* **58**, 443–451.