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The Structure of Bis(1,2-dihydro-4-phenyl-4*H*-[1,4]oxazino[4,3-*a*]-benzimidazole)dinitratonickel(II) Acetonitrile Solvate, $[Ni(C_{16}H_{14}N_2O)_2(NO_3)_2].CH_3CN$

By Pamela Carr,* Brian Piggott and Helena J. Tinton

Inorganic Chemistry Research Laboratory, School of Natural Sciences, The Hatfield Polytechnic, Hatfield, Herts AL10 9AB, England

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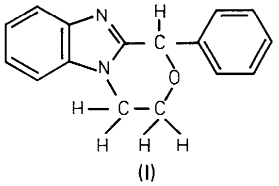
Abstract. $M_r = 724{\cdot}08$, monoclinic, $P2_1$, $a = 10{\cdot}223\,(3)$, $b = 18{\cdot}380\,(5)$, $c = 9{\cdot}495\,(3)$ Å, $\beta = 113{\cdot}58\,(2)°$, $U = 1635{\cdot}1\,(2)$ Å^3, $Z = 2$, $D_m = 1{\cdot}37$ (aq. KI), $D_x = 1{\cdot}35$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 0{\cdot}624$ mm^{-1}, $F(000) = 748$, room temperature, final $R = 0{\cdot}043$ for 1254 reflections. The nickel atom is six coordinate with two *cis* unidentate benzimidazole ligands and two bidentate nitrate groups. The two oxazine rings are in *R* and *S* configurations with pseudo-axial and pseudo-equatorial positioned phenyl substituents, respectively. The octahedral coordination is distorted owing to the small bite angle of the bidentate nitrate ligands.

Introduction. The title compound is one of a number of nickel complexes that we have synthesized as potential models for use in our EXAFS studies of nickel-containing proteins (Hasnain & Piggott, 1983; Alagna, Hasnain, Piggott & Williams, 1984; Diakun, Piggott & Tinton, 1985). One of these complexes with α-(1-propyl-2-benzimidazolyl)benzyl alcohol, which contains a long Ni—O bond (Alagna, Hasnain, Piggott & Williams, 1984), was shown to be a particularly good model for the nickel centre in the enzyme urease. It is thought that some nickel-containing enzymes in the resting state contain a loosely bound water molecule and hence a long Ni—O bond, which is displaced by the substrate during turnover (Dixon, Gazzola, Blakeley & Zerner, 1975). To extend the range of substituted benzimidazole complexes of Ni^{II} with long Ni—O bonds (and possibly loosely bound solvent) a series of 1,2-dihydro-4-phenyl-4*H*-[1,4]oxazino[4,3-*a*]-benzimidazole (POB, I) complexes with Ni^{II} nitrate were synthesized.



(I)

POB being large and unidentate, it was anticipated that the resulting Ni^{II} complex might incorporate a solvent molecule in the first coordination sphere to achieve six coordination and provide us with examples of Ni^{II} complexes with easily displaced solvent molecules.

Three complexes with stoichiometry (i) $Ni(POB)_2(NO_3)_2(CH_3CN)$, (ii) $Ni(POB)_2(NO_3)_2(CHCl_3)$ and (iii) $Ni(POB)_2(NO_3)_2(acetone)_2$ were prepared. We here report the crystal and molecular structure of $Ni(POB)_2(NO_3)_2.CH_3CN$.

Experimental. Green prismatic crystals grown by slow evaporation of 2:1 POB:$Ni(NO_3)_2$ mixture in acetonitrile. Crystal size 0·43 × 0·46 × 0·19 mm, Philips PW 1100 four-circle diffractometer, graphite monochromator, Mo $K\alpha$ radiation; scan conditions as in Lindoy *et al.* (1980) except scan width = 0·8°; lattice parameters determined by least-squares fit of 25 reflections with $\theta = 4$–$6°$; three standard reflections recorded every 3 h, variation ±6%, no evidence for crystal deterioration; 1356 reflections measured at $5 < 2\theta < 50°$, $\pm h, +k, +l$; after averaging, 1254 unique reflections with $I > 3\sigma(I)$; no absorption correction; structure solved by heavy-atom method; hydrogen atoms placed in calculated positions with $d_{\text{C-H}} = 1{\cdot}08$ Å and U_{iso} fixed at 0·05 Å^2 and allowed to ride on associated carbon atoms; refinement by full-matrix least squares with *SHELX* (Sheldrick, 1976) with anisotropic temperature factors for all atoms except hydrogen; refinement based on *F* and 451 parameters, $R = 0{\cdot}043$, $wR = 0{\cdot}048$, unit weights; max. and mean Δ/σ in final cycle 0·08 and 0·013; residual electron density in final difference Fourier map −0·41 to +0·28 e Å^{-3} with major features within 2 Å of Ni atom. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974); correction factors for anomalous dispersion from Cromer & Liberman (1970). Refinement of the alternative enantiomorph gave $R = 0{\cdot}044$, $wR = 0{\cdot}049$.

Discussion. Final atomic coordinates with their e.s.d.'s and equivalent isotropic temperature factors for the non-hydrogen atoms are given in Table 1. Bond lengths

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* To whom correspondence should be addressed.

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Table 1. *Final atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å^2 $\times 10^3$)

$$U_{\rm eq} = \tfrac{1}{3}\textstyle\sum_i\sum_j U_{ij}a^*_i a^*_j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
Ni	−2693 (1)	−2500	−2348 (2)	31 (1)
O(1)	−4437 (8)	−2829 (5)	−4329 (10)	49 (5)
O(2)	−2325 (8)	−3075 (5)	−4034 (10)	50 (5)
O(3)	−4126 (11)	−3514 (7)	−6014 (12)	81 (7)
O(4)	−3106 (8)	−1413 (5)	−3265 (10)	49 (5)
O(5)	−3832 (8)	−1809 (4)	−1533 (10)	40 (4)
O(6)	−4303 (10)	−688 (6)	−2382 (14)	87 (7)
O(7)	−5438 (8)	−3535 (5)	249 (9)	42 (5)
O(8)	1031 (7)	−2475 (7)	3158 (8)	60 (5)
N(1)	−3646 (13)	−3166 (6)	−4873 (13)	44 (6)
N(2)	−3757 (10)	−1286 (6)	−2391 (13)	46 (6)
N(3)	−2715 (9)	−3447 (5)	−1285 (11)	38 (5)
N(4)	−3191 (9)	−4287 (5)	195 (11)	38 (5)
N(5)	−635 (8)	−2193 (5)	−998 (9)	28 (4)
N(6)	1619 (8)	−2185 (5)	702 (10)	33 (5)
C(1)	3644 (11)	3700 (7)	−725 (14)	37 (6)
C(2)	−5121 (10)	−3391 (6)	−1072 (12)	30 (6)
C(3)	−6257 (10)	−3746 (6)	−2490 (14)	35 (6)
C(4)	−5996 (15)	−4229 (8)	−3408 (15)	56 (8)
C(5)	−7086 (17)	−4528 (8)	−4693 (17)	66 (9)
C(6)	−8483 (15)	−4281 (10)	−5029 (16)	70 (9)
C(7)	−8771 (14)	−3788 (8)	−4134 (15)	55 (8)
C(8)	−7697 (14)	−3493 (9)	−2930 (16)	47 (8)
C(9)	−5365 (12)	−4277 (8)	617 (16)	56 (8)
C(10)	−3869 (13)	−4592 (8)	1154 (14)	53 (8)
C(11)	−1836 (13)	−4449 (7)	241 (15)	46 (7)
C(12)	−882 (11)	−5019 (7)	1037 (14)	40 (6)
C(13)	386 (13)	−5001 (8)	825 (15)	51 (7)
C(14)	669 (13)	−4520 (8)	−91 (16)	51 (8)
C(15)	−296 (12)	−3968 (7)	−895 (15)	49 (7)
C(16)	−1575 (11)	−3952 (7)	−678 (13)	35 (6)
C(17)	185 (10)	−2324 (6)	429 (11)	30 (6)
C(18)	−187 (10)	−2533 (9)	1715 (11)	38 (5)
C(19)	−1305 (11)	−2043 (7)	1893 (13)	37 (7)
C(20)	−1245 (12)	−1304 (7)	1846 (14)	41 (7)
C(21)	−2171 (14)	−864 (8)	2174 (17)	62 (9)
C(22)	−3218 (14)	−1197 (8)	2515 (16)	61 (8)
C(23)	−3325 (14)	−1922 (8)	2565 (15)	57 (7)
C(24)	−2401 (12)	−2375 (9)	2239 (14)	50 (7)
C(25)	2238 (13)	−2831 (9)	3072 (16)	62 (8)
C(26)	2826 (10)	−2371 (8)	2142 (13)	41 (6)
C(27)	1694 (10)	−1992 (6)	−622 (13)	29 (6)
C(28)	2818 (12)	−1772 (7)	−1010 (16)	48 (7)
C(29)	2470 (12)	−1593 (8)	−2513 (17)	47 (8)
C(30)	1100 (13)	−1625 (7)	−3647 (15)	51 (7)
C(31)	−31 (13)	−1806 (7)	−3230 (14)	46 (7)
C(32)	260 (10)	−1983 (6)	−1744 (12)	30 (6)
Solvate molecule				
N(7)	−6754 (27)	−589 (14)	−7317 (39)	168 (21)
C(33)	−7231 (28)	−336 (12)	−6513 (34)	108 (17)
C(34)	−7900 (25)	−44 (11)	−5550 (22)	119 (15)

and angles are given in Table 2.* Fig. 1 shows the molecular conformation and numbering scheme.

As expected for octahedral coordination the two *cis* bidentate nitrates are mutually perpendicular, thus leaving the two bulky POB ligands very close. The bite angles of the nitrates, 60·8 (3) and 62·2 (4)°, are unexceptional and compare favourably with bidentate nitrates of other octahedral nickel complexes as do the Ni–O bond lengths (Butcher, O'Connor & Sinn, 1981).

The Ni–N bond lengths of 2·06 (1) and 2·02 (1) Å are slightly longer than those recorded for tetrahedral Ni(POB)$_2$Cl$_2$ (Piggott & Skapski, 1983) [1·992 (4) and 2·002 (5) Å], this feature presumably being due to the increase in coordination number. Owing to the small bite angle of the bidentate nitrate ligands, several of the bond angles around the Ni are larger than expected for

Table 2. *Interatomic distances* (Å) *and angles* (°)

Ni–O(1)	2·10 (1)	C(3)–C(4)	1·34 (2)
Ni–O(2)	2·07 (1)	C(3)–C(8)	1·44 (2)
Ni–O(4)	2·15 (1)	C(4)–C(5)	1·39 (2)
Ni–O(5)	2·07 (1)	C(5)–C(6)	1·41 (2)
Ni–N(3)	2·02 (1)	C(6)–C(7)	1·35 (2)
Ni–N(5)	2·06 (1)	C(7)–C(8)	1·34 (2)
O(1)–N(1)	1·28 (2)	C(9)–C(10)	1·52 (2)
O(2)–N(1)	1·28 (1)	C(11)–C(12)	1·42 (2)
O(3)–N(1)	1·18 (2)	C(11)–C(16)	1·36 (2)
O(4)–N(2)	1·28 (2)	C(12)–C(13)	1·39 (2)
O(5)–N(2)	1·28 (2)	C(13)–C(14)	1·35 (2)
O(6)–N(2)	1·23 (2)	C(14)–C(15)	1·41 (2)
O(7)–C(2)	1·44 (2)	C(15)–C(16)	1·40 (2)
O(7)–C(9)	1·40 (2)	C(17)–C(18)	1·47 (2)
O(8)–C(18)	1·44 (1)	C(18)–C(19)	1·52 (2)
O(8)–C(25)	1·43 (2)	C(19)–C(20)	1·36 (2)
N(3)–C(1)	1·34 (2)	C(19)–C(24)	1·42 (2)
N(3)–C(16)	1·42 (1)	C(20)–C(21)	1·37 (2)
N(4)–C(1)	1·35 (2)	C(21)–C(22)	1·38 (2)
N(4)–C(10)	1·46 (2)	C(22)–C(23)	1·34 (2)
N(4)–C(11)	1·40 (2)	C(23)–C(24)	1·38 (2)
N(5)–C(17)	1·30 (1)	C(25)–C(26)	1·51 (2)
N(5)–C(32)	1·42 (2)	C(27)–C(28)	1·40 (2)
N(6)–C(17)	1·41 (1)	C(27)–C(32)	1·43 (1)
N(6)–C(26)	1·47 (1)	C(28)–C(29)	1·37 (2)
N(6)–C(27)	1·34 (2)	C(29)–C(30)	1·39 (2)
C(1)–C(2)	1·52 (2)	C(30)–C(31)	1·40 (2)
C(2)–C(3)	1·53 (1)	C(31)–C(32)	1·36 (2)
O(1)–Ni–O(2)	60·8 (3)	C(2)–C(3)–C(8)	117 (1)
O(1)–Ni–O(4)	86·9 (3)	C(4)–C(3)–C(8)	118 (1)
O(1)–Ni–O(5)	96·2 (3)	C(3)–C(4)–C(5)	122 (1)
O(1)–Ni–N(3)	91·4 (3)	C(4)–C(5)–C(6)	117 (2)
O(1)–Ni–N(5)	158·2 (4)	C(5)–C(6)–C(7)	122 (1)
O(2)–Ni–O(4)	103·1 (4)	C(6)–C(7)–C(8)	120 (1)
O(2)–Ni–O(5)	154·6 (3)	C(3)–C(8)–C(7)	121 (1)
O(2)–Ni–N(3)	89·4 (4)	O(7)–C(9)–C(10)	114 (1)
O(2)–Ni–N(5)	99·5 (3)	N(4)–C(10)–C(9)	108 (1)
O(4)–Ni–O(5)	62·2 (4)	N(4)–C(11)–C(12)	129 (1)
O(4)–Ni–N(3)	164·6 (4)	N(4)–C(11)–C(16)	106 (1)
O(4)–Ni–N(5)	89·1 (3)	C(12)–C(11)–C(16)	124 (1)
O(5)–Ni–N(3)	102·8 (4)	C(11)–C(12)–C(13)	113 (1)
O(5)–Ni–N(5)	100·8 (3)	C(12)–C(13)–C(14)	124 (1)
N(3)–Ni–N(5)	98·0 (3)	C(13)–C(14)–C(15)	123 (1)
Ni–O(1)–N(1)	93 (1)	C(14)–C(15)–C(16)	115 (1)
Ni–O(2)–N(1)	94 (1)	N(3)–C(16)–C(11)	111 (1)
Ni–O(4)–N(2)	89 (1)	N(3)–C(16)–C(15)	128 (1)
Ni–O(5)–N(2)	92 (1)	C(11)–C(16)–C(15)	121 (1)
C(2)–O(7)–C(9)	113 (1)	N(5)–C(17)–N(6)	111 (1)
C(18)–O(8)–C(25)	110 (1)	N(5)–C(17)–C(18)	130 (1)
O(1)–N(1)–O(2)	112 (1)	N(6)–C(17)–C(18)	119 (1)
O(1)–N(1)–O(3)	122 (1)	O(8)–C(18)–C(17)	111 (1)
O(2)–N(1)–O(3)	126 (1)	O(8)–C(18)–C(19)	105 (1)
O(4)–N(2)–O(5)	117 (1)	C(17)–C(18)–C(19)	113 (1)
O(4)–N(2)–O(6)	122 (1)	C(18)–C(19)–C(20)	123 (1)
O(5)–N(2)–O(6)	122 (1)	C(18)–C(19)–C(24)	118 (1)
Ni–N(3)–C(1)	130 (1)	C(20)–C(19)–C(24)	119 (1)
Ni–N(3)–C(16)	127 (1)	C(19)–C(20)–C(21)	123 (1)
C(1)–N(3)–C(16)	102 (1)	C(20)–C(21)–C(22)	118 (1)
C(1)–N(4)–C(10)	126 (1)	C(21)–C(22)–C(23)	122 (2)
C(1)–N(4)–C(11)	106 (1)	C(22)–C(23)–C(24)	121 (2)
C(10)–N(4)–C(11)	128 (1)	C(19)–C(24)–C(23)	118 (1)
Ni–N(5)–C(17)	132 (1)	O(8)–C(25)–C(26)	109 (1)
Ni–N(5)–C(32)	118 (1)	N(6)–C(26)–C(25)	107 (1)
C(17)–N(5)–C(32)	107 (1)	N(6)–C(27)–C(28)	133 (1)
C(17)–N(6)–C(26)	124 (1)	N(6)–C(27)–C(32)	106 (1)
C(17)–N(6)–C(27)	109 (1)	C(28)–C(27)–C(32)	121 (1)
C(26)–N(6)–C(27)	126 (1)	C(27)–C(28)–C(29)	117 (1)
N(3)–C(1)–N(4)	115 (1)	C(28)–C(29)–C(30)	124 (1)
N(3)–C(1)–C(2)	126 (1)	C(29)–C(30)–C(31)	119 (1)
N(4)–C(1)–C(2)	120 (1)	C(30)–C(31)–C(32)	119 (1)
O(7)–C(2)–C(1)	107 (1)	N(5)–C(32)–C(27)	108 (1)
O(7)–C(2)–C(3)	109 (1)	N(5)–C(32)–C(31)	132 (1)
C(1)–C(2)–C(3)	112 (1)	C(27)–C(32)–C(31)	121 (1)
C(2)–C(3)–C(4)	125 (1)		
Solvate molecule			
N(7)–C(33)	1·16 (5)	N(7)–C(33)–C(34)	177 (3)
C(33)–C(34)	1·45 (4)		

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* Lists of structure factors, anisotropic thermal parameters and calculated hydrogen-atom positions have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39921 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

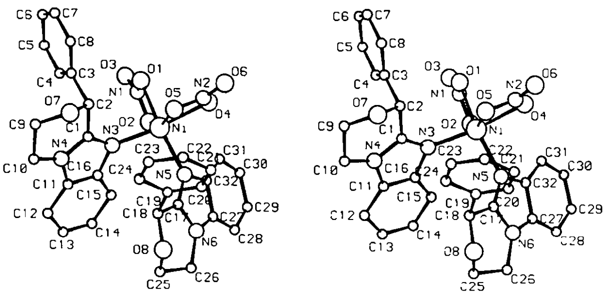

Fig. 1. Stereoscopic view of the complex.

regular octahedral coordination. In fact, the N(3)—Ni—N(5) angle of 98·0 (3)° approaches that of 98·5 (2)° found in the distorted tetrahedral $Ni(POB)_2Cl_2$ complex. The benzimidazole portions of both POB ligands are planar, the dihedral angle between them being 44·8 (3)°.

The oxazine rings are in essentially similar conformations with chiral centres at C(2) and C(18). In the POB ligand with chiral centre C(2) the phenyl substituent is in the pseudo-axial position resulting in *R* chirality, whereas in the other POB ligand this substituent is in the pseudo-equatorial position conferring *S* chirality on C(18) – see Fig. 1. This contrasts with the $Ni(POB)_2Cl_2$ compound where although both oxazine rings are still in similar conformations they now have identical configurations with the phenyl substituents pseudo-equatorial in both. Inspection of a model of the present complex demonstrates that intramolecular steric hindrance causes the oxazine ring and substituents to occupy the aforementioned conformations. An example of this is the phenyl group in POB 1 in the pseudo-axial position, which is very nearly parallel [8·8 (6)°] to the NO_3 group 1 [N(1)O(1)-O(2)O(3)]: however, if it were in the pseudo-equatorial position as in POB 2 it would come into close contact with nitrate group 1. We can see that the close proximity of the two bulky POB ligands has caused significant conformational changes.

The complex crystallizes with one molecule of solvent, CH_3CN. The solvent molecule is not coordinated in any way and controlled heating at 330 K resulted in complete solvent removal. There are no unusual intermolecular contacts.

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The Structure of Bis[(*R*,*S*)-*N*,*N'*-bis(5-methyl-2-thienylmethylene)-1,2-cyclohexanediamine]copper(I) Trifluoromethanesulfonate, $C_{36}H_{44}CuN_4S_4^+.CF_3SO_3^-$

BY A. L. SPEK AND A. J. M. DUISENBERG

Vakgroep Algemene Chemie, afdeling Kristal-en Structuurchemie, Universiteit van Utrecht, Padualaan 8,
3508 *TB Utrecht, The Netherlands*

AND G. C. VAN STEIN AND G. VAN KOTEN

Laboratorium voor Anorganische Chemie, Universiteit van Amsterdam, Nieuwe Achtergracht 166,
1018 *WV Amsterdam, The Netherlands*

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Abstract. $M_r = 873{\cdot}65$, monoclinic, $P2_1/c$, $a = 13{\cdot}948\ (3)$, $b = 19{\cdot}338\ (6)$, $c = 19{\cdot}811\ (3)$ Å, $\beta = 126{\cdot}35\ (2)°$, $V = 4304\ (2)$ Å^3, $Z = 4$, $D_m = 1{\cdot}347$, $D_x = 1{\cdot}348$ g cm^{-3}, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 33{\cdot}3$ cm^{-1}, $F(000) = 1816$, $T = 295$ K, final $R = 0{\cdot}086$ for 2985 unique observed reflections with $I > 2{\cdot}5\sigma(I)$.