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Structure of Triaqua[*N*-(5-bromosalicylidene)-L-tryptophanato]nickel(II) Dihydrate

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Abstract. $[Ni(C_{18}H_{13}BrN_2O_3)(H_2O)_3].2H_2O$, $M_r = 534{\cdot}0$, monoclinic, $P2_1$, $a = 7{\cdot}379\,(1)$, $b = 7{\cdot}636\,(1)$, $c = 19{\cdot}981\,(3)$ Å, $\beta = 99{\cdot}29\,(1)°$, $V = 1111{\cdot}1\,(2)$ Å^3, $D_x = 1{\cdot}59$ g cm^{-3}, $Z = 2$, $F(000) = 544$, Cu $K\alpha$, $\lambda = 1{\cdot}5418$ Å, $\mu = 37{\cdot}7$ cm^{-1}, room temperature. Final $R = 0{\cdot}051$, $wR = 0{\cdot}050$ for 1811 observed reflections. The structure consists of discrete molecules of the complex, with the Ni^{II} ion octahedrally coordinated to one terdentate Schiff-base moiety and three water molecules; there are two additional non-coordinated water molecules in the asymmetric unit. The crystal structure is supported by a network of hydrogen bonds, involving water molecules and the phenolic and carboxylic O atoms.

Introduction. The magnetic properties of complexes of *N*-salicylidene-L-amino acids with transition-metal ions have been extensively investigated by variable-temperature magnetic susceptibility measurements and ESR spectroscopy. These compounds exhibit a wide range of magnetic and spectroscopic properties and have been described as monomers, dimers and polymers. As part of the study initiated to investigate the structural factors which cause such differences, we describe in this paper the preparation and the crystal structure determination of the nickel(II) complex with the Schiff base derived from the condensation of 5-bromosalicylaldehyde and L-tryptophan.

Experimental. All chemicals are reagent grade and were used without further purification. The title compound was prepared by the following method: a solution of the amino acid (0·05 mol) in water (100 ml) was added dropwise and with magnetic stirring to a solution obtained from 5-bromosalicylaldehyde (0·05 mol) and ethanol (400 ml). Nickel(II) acetate tetrahydrate (0·05 mol) was disolved in 200 ml water and slowly added to the Schiff-base solution, and the resulting mixture was refluxed overnight.

A green precipitate was filtered off, washed with ethanol, water and diethyl ether and air dried. The precipitate was redissolved and crystallized as dark

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Table 1. *Fractional atomic coordinates and equivalent isotropic temperature factors* ($Å^2 \times 10^3$) *with e.s.d.'s in parentheses*

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
Ni	0·7264 (1)	0·4380 (2)	0·5994 (1)	342 (3)
Br	1·0806 (1)	0·0000	0·9263 (1)	574 (3)
O1	0·8250 (6)	0·4351 (7)	0·5085 (2)	281 (12)
O2	0·9035 (7)	0·6417 (7)	0·6326 (3)	336 (16)
O3	0·5488 (6)	0·2265 (7)	0·5617 (3)	300 (15)
O4	0·1777 (6)	0·2548 (7)	0·5592 (3)	342 (16)
O5	0·8036 (8)	0·9462 (9)	0·5684 (3)	506 (19)
O20	0·9163 (6)	0·2650 (7)	0·6394 (3)	280 (15)
O21	0·5132 (7)	0·6084 (8)	0·5663 (2)	305 (15)
O23	0·2396 (6)	0·6869 (8)	0·5885 (3)	347 (16)
N12	0·6097 (6)	0·4424 (8)	0·6826 (2)	192 (13)
N2	0·6965 (11)	0·6730 (16)	0·8999 (4)	630 (31)
C1	0·7026 (12)	0·7185 (14)	0·8336 (5)	501 (29)
C3	0·5190 (13)	0·6161 (14)	0·9046 (5)	510 (29)
C4	0·4502 (17)	0·5565 (19)	0·9602 (5)	723 (44)
C5	0·2660 (18)	0·5060 (20)	0·9490 (6)	730 (40)
C6	0·1609 (14)	0·5145 (16)	0·8844 (6)	600 (33)
C7	0·2326 (11)	0·5751 (12)	0·8294 (5)	429 (25)
C8	0·4174 (10)	0·6268 (10)	0·8393 (4)	339 (22)
C9	0·5368 (10)	0·6930 (10)	0·7951 (4)	315 (20)
C10	0·4913 (10)	0·7237 (10)	0·7212 (4)	342 (22)
C11	0·4486 (8)	0·5542 (9)	0·6778 (3)	254 (19)
C13	0·6583 (9)	0·3473 (10)	0·7360 (3)	270 (19)
C14	0·8226 (9)	0·2438 (9)	0·7495 (3)	255 (19)
C15	0·8661 (11)	0·1755 (10)	0·8162 (4)	320 (22)
C16	1·0242 (11)	0·0857 (11)	0·8362 (4)	373 (22)
C17	1·1479 (11)	0·0558 (11)	0·7922 (4)	401 (25)
C18	1·1079 (11)	0·1160 (12)	0·7268 (4)	418 (25)
C19	0·9464 (9)	0·2147 (10)	0·7032 (4)	286 (20)
C22	0·3937 (9)	0·6186 (9)	0·6056 (3)	226 (18)

green crystals from a mixture of dimethylformamide:ethanol (1:1). Anal. calc. for $Ni(C_{18}H_{13}BrN_2O_8)$: C 40·48, H 2·44, N 5·25 and Ni 11·0%. Found: C 40·50, H 2·42, N 5·18 and Ni 10·99%.

Data were collected with a four-circle computer-controlled Siemens AED diffractometer using graphite-monochromated Cu $K\alpha$ radiation; crystal dimensions 0·4 × 0·6 × 0·8 mm. Lattice parameters and their e.s.d.'s were derived from least-squares refinement of the setting angles of 28 reflections in the range $20 < 2\theta < 40°$. Crystal stability was confirmed by the constancy of two standard reflections (211 and 124) measured every hour. Of 2038 measured reflections, ω/θ scan mode, in the range $3 < 2\theta < 122°$ ($0 \leq h \leq 8$, $0 \leq k \leq 8$, $-22 \leq l \leq 22$), 1811 with $I \geq 2\sigma(I)$ were considered as observed, after correction for Lp factors, and used in the solution and refinement of the structure. An empirical absorption correction (*DIFABS*; Walker & Stuart, 1983) was performed on the isotropic model (correction range 0·57 to 1·87). The structure was solved by Patterson and Fourier methods (*SHELXS*86; Sheldrick, 1986) and refined on ΔF by full-matrix least squares (*XRAY*80; Stewart, Machin, Dickinson, Ammon, Heck & Flack, 1980), with anisotropic thermal parameters for all non-H atoms. The H atoms bound to C atoms were placed in calculated positions (C—H distance 1·00 Å) (*HSEARCH*; Fayos & Martinez-Ripoll, 1980) and included in the last refinement as a fixed isotropic contribution, with thermal parameters set to B_{eq} of the parent atoms. A weighting scheme was chosen to obtain flat dependence of $\langle \Delta^2 F \rangle$ *versus* $\langle F_o \rangle$ and $\langle \sin\theta/\lambda \rangle$ (*PESOS*; Martinez-Ripoll & Fayos, 1980). 270 parameters. The final discrepancy indices are $R = 0·051$ and $wR = 0·050$. Maximum Δ/σ in final refinement cycle was 0·005, maximum electron density in final difference Fourier synthesis 0·53 e $Å^{-3}$. Scattering factors from *International Tables for X-ray Crystallography* (1974).

Table 2. *Bond distances* (Å), *bond angles* (°) *and selected torsion angles* (°) *with e.s.d.'s in parentheses*

Ni—O*W*1	2·063 (5)	Ni—O*W*2	2·071 (5)
Ni—O*W*3	2·139 (5)	Ni—O20	1·996 (5)
Ni—O21	2·066 (5)	Ni—N12	1·993 (5)
Br—C16	1·897 (8)	O20—C19	1·314 (9)
O21—C22	1·275 (9)	O23—C22	1·247 (8)
N12—C11	1·454 (8)	N12—C13	1·292 (8)
N2—C1	1·378 (13)	N2—C3	1·398 (13)
C1—C9	1·350 (11)	C3—C4	1·370 (15)
C3—C8	1·398 (11)	C4—C5	1·396 (18)
C5—C6	1·396 (15)	C6—C7	1·375 (15)
C7—C8	1·403 (11)	C8—C9	1·436 (11)
C9—C10	1·479 (11)	C10—C11	1·562 (10)
C11—C22	1·517 (9)	C13—C14	1·436 (10)
C14—C15	1·419 (10)	C14—C19	1·419 (11)
C15—C16	1·357 (11)	C16—C17	1·384 (12)
C17—C18	1·373 (12)	C18—C19	1·424 (11)

O21—Ni—N12	81·2 (2)	O20—Ni—N12	92·7 (2)
O20—Ni—O21	173·6 (2)	O*W*3—Ni—N12	89·1 (2)
O*W*3—Ni—O21	88·4 (2)	O*W*3—Ni—O20	89·6 (2)
O*W*2—Ni—N12	93·2 (2)	O*W*2—Ni—O21	92·2 (2)
O*W*2—Ni—O20	90·2 (2)	O*W*2—Ni—O*W*3	177·7 (2)
O*W*1—Ni—N12	175·1 (2)	O*W*1—Ni—O21	94·8 (2)
O*W*1—Ni—O20	91·2 (2)	O*W*1—Ni—O*W*3	88·0 (2)
O*W*1—Ni—O*W*2	89·7 (2)	Ni—O20—C19	125·4 (5)
Ni—O21—C22	114·1 (4)	Ni—N12—C13	125·4 (4)
Ni—N12—C11	114·4 (4)	C11—N12—C13	120·0 (5)
C1—N2—C3	108·6 (8)	N2—C1—C9	110·2 (8)
N2—C3—C8	106·6 (8)	N2—C3—C4	129·1 (9)
C4—C3—C8	124·2 (9)	C3—C4—C5	116·2 (9)
C4—C5—C6	121·1 (11)	C5—C6—C7	121·8 (10)
C6—C7—C8	118·2 (8)	C3—C8—C7	118·6 (7)
C7—C8—C9	133·7 (7)	C3—C8—C9	107·7 (7)
C1—C9—C8	106·9 (7)	C8—C9—C10	127·3 (7)
C1—C9—C10	125·8 (7)	C9—C10—C11	114·6 (6)
N12—C11—C10	111·1 (5)	C10—C11—C22	105·0 (5)
N12—C11—C22	110·1 (5)	N12—C13—C14	125·3 (6)
C13—C14—C19	125·2 (6)	C13—C14—C15	115·8 (6)
C15—C14—C19	118·9 (6)	C14—C15—C16	121·0 (7)
Br—C16—C15	120·0 (6)	C15—C16—C17	121·4 (7)
Br—C16—C17	118·6 (6)	C16—C17—C18	119·2 (8)
C17—C18—C19	122·1 (7)	C14—C19—C18	117·4 (6)
O20—C19—C18	118·5 (6)	O20—C19—C14	124·1 (6)
O23—C22—C11	119·2 (6)	O21—C22—C11	117·5 (6)
O21—C22—O23	123·2 (6)		

O20—Ni—N12—C13	−3·2 (6)	O21—Ni—N12—C11	−0·2 (4)
N12—Ni—O20—C19	−9·6 (6)	N12—Ni—O21—C22	−10·1 (5)
Ni—O20—C19—C14	15·3 (10)	Ni—O21—C22—C11	18·1 (7)
Ni—N12—C13—C14	11·1 (10)	Ni—N12—C11—C22	8·5 (6)
N12—C13—C14—C19	−7·4 (12)	N12—C11—C22—O21	−17·8 (8)
C13—C14—C19—O20	−7·1 (12)		

Discussion. The atomic positional and equivalent isotropic thermal parameters are listed in Table 1.* Bond lengths and angles are given in Table 2. The

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* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52799 (17 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

correct enantiomer is shown in Fig. 1 together with the atomic numbering system; the absolute configu ation is fixed by the *S* configuration at the C11 carbon of the L-amino-acid moiety. Fig. 2 shows the packing of the molecules in the unit cell.

The structure consist of discrete molecules of the complex with the metal octahedrally coordinated by one terdentate Schiff-base moiety and three water molecules. The atoms N12, O20 and O21 of the terdentate Schiff base and the water molecule O*W*1 are in the equatorial plane [largest deviation from N12, O20, O21, O*W*1 mean plane −0·008 (6) Å for N12]. The Ni^{II} ion is 0·045 (1) Å out of this plane, while the water molecules O*W*2 and O*W*3 occupy the apical sites. Distances from the central metal ion to the donor atoms are in the broad range 1·992 (5) to 2·070 (6) Å. The metal—carboxylic oxygen bond distance [2·065 (6) Å] is longer than the metal—phenolic oxygen distance [1·998 (5) Å]. This result is similar to those described in the literature for bis(pyridoxylidene-DL-valinato)nickel(II) [2·14 (1) and 2·03 (1) Å and 2·18 (1) and 2·02 (1) Å], and bis(pyridoxylidene-L-valinato)zinc(II) [2·16 (3) and 2·02 (3) Å] (Capasso, Giordano, Mattia, Mazzarella & Ropamonti, 1974).

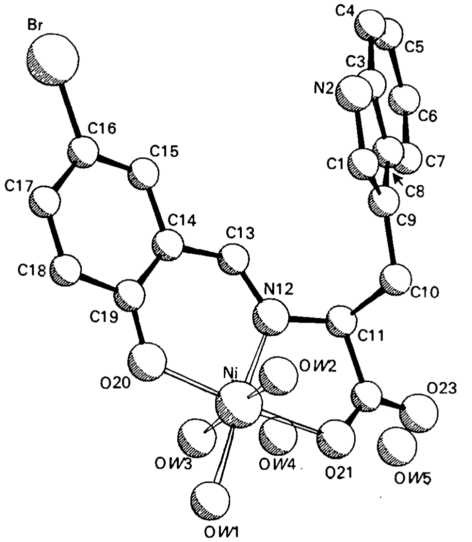

Fig. 1. Perspective view of the correct enantiomer of the title compound with the atomic labelling scheme.

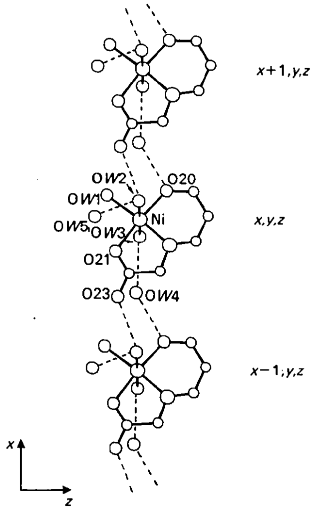

Fig. 2. Molecular packing of the structure along **a**.

Table 3. *Hydrogen-bond geometry*

X···*Y*	Symmetry operation	*X*···*Y* (Å)
O*W*1···O23	$-x+1, y-\frac{1}{2}-z, +1$	2·698 (8)
O*W*2···O23	$x+1, y, z$	2·784 (8)
O*W*3···O21	$-x+1, y-\frac{1}{2}, -z+1$	2·680 (7)
O*W*4···O20	$x-1, y, z$	2·702 (8)
O*W*1···O4	$-x+1, y+\frac{1}{2}, -z+1$	2·790 (8)
O*W*2···O*W*5	x, y, z	2·699 (9)
O*W*3···O*W*4	x, y, z	2·740 (7)

The five- and six-membered chelate rings are almost coplanar; the dihedral angle between the least-squares planes (Ni, N12, C13, C14, C19, O20) and (Ni, N12, C11, C22, O21) being 2·2 (1)°. The five-membered chelate ring is an envelope with C22 [−0·117 (7) Å] out of the plane defined by the remaining four atoms. The deviations of the atoms in the six-membered chelate ring (Ni—N12—C13—C14—C19—O20) from the best plane are in the range −0·063 (5) Å for O20 to 0·092 (8) Å for C19.

Fig. 2 shows a view of part of the crystal structure of the title compound. The discrete units are held together through a network of hydrogen bonds involving water molecules and the phenolic and carboxylic oxygens. Hydrogen-bond lengths are reported in Table 3.

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