

part in interligand hydrogen bonds with axial (10–15°) or equatorial (2.5°) sites in the coordination sphere (Szalda *et al.*, 1976a).

The crystal packing of the complexes is shown in Fig. 2. The principal feature is the connection in chains, running along *c*, of the translationally related complexes *via* hydrogen bonds involving the N(9) hydrogen donor atom from a complex and the O(6) exocyclic O atom from a complex at $x, 1-y, \frac{1}{2}+z$ [N(9)···O(6) = 2.75 (2) Å, H(9)···O(6) = 1.83 (16), N(9)–H(9)–O(6) = 150 (14)°]. Van der Waals contacts complete the packing.

References

BATTAGLIA, L. P., BONAMARTINI CORRADI, A., MARCOTRIGIANO, G., MENABUE, L. & PELLACANI, G. C. (1979). *Inorg. Chem.* **18**, 148–152.

BIAGINI CINGI, M., MANOTTI LANFREDI, A. M., TIRIPICCHIO, A. & TIRIPICCHIO CAMELLINI, M. (1979). *Transition Met. Chem.* **4**, 221–224.
 GRIFFITH, E. H. & AMMA, E. L. (1979). *J. Chem. Soc. Chem. Commun.* pp. 322–324.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 KINDBERG, B. L., GRIFFITH, E. A. H., AMMA, E. L. & JONES, E. R. (1976). *Cryst. Struct. Commun.* **5**, 533–538.
 KISTENMACHER, T. J., SZALDA, D. J., CHIANG, C. C. & ROSSI, M. (1978). *Inorg. Chem.* **17**, 2582–2584.
 KISTENMACHER, T. J., SZALDA, D. J. & MARZILLI, L. G. (1975). *Inorg. Chem.* **14**, 1686–1691.
 SHELDRICK, G. M. (1976). *SHELX76*. System of programs for structure determination. Univ. of Cambridge.
 SORREL, T., MARZILLI, L. G. & KISTENMACHER, T. J. (1976). *J. Am. Chem. Soc.* **98**, 2181–2188.
 SZALDA, D. J., KISTENMACHER, T. J. & MARZILLI, L. G. (1976a). *Inorg. Chem.* **15**, 2783–2788.
 SZALDA, D. J., KISTENMACHER, T. J. & MARZILLI, L. G. (1976b). *J. Am. Chem. Soc.* **98**, 8371–8377.

Acta Cryst. (1983). **C39**, 1525–1527

{N-[2-(2-Aminoethylamino)ethyl]salicylideneaminato-O,N,N',N''}nickel(II) Tetraphenylborate, [Ni(C₁₁H₁₆N₃O)] [B(C₆H₅)₄]

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(Received 30 May 1983; accepted 19 July 1983)

Abstract. $M_r = 583.9$, monoclinic, $P2_1/n$, $a = 11.475$ (2), $b = 14.544$ (2), $c = 18.295$ (3) Å, $\beta = 102.7$ (1), $U = 2979$ (1) Å³, $Z = 4$, $D_x = 1.30$ g cm⁻³, $\mu = 6.84$ cm⁻¹, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $F(000) = 1232$, $T = 298$ K. Final $R = 0.086$ and $R_w = 0.084$ for 2593 reflections. The coordination polyhedron around Ni is an irregular square, with the saldien ligand tetradentate to the metal through one O and three N atoms. A short intermolecular contact Ni···O of 3.377 (6) Å indicates partial dimerization of the cation.

Introduction. Metal complexes of Schiff bases have contributed widely to the inorganic chemistry of chelate systems. Particular attention has been paid to the salicylaldimino complexes owing to the electronic and structural similarity between salicylaldehyde and pyridoxal, a very active component of vitamin B₆, which plays an important part in some enzymatic reactions in the presence of metal ions (Snell, Fasella, Bramstein & Rossi Fanelli, 1963). Metal-coordination compounds of Schiff bases received a renewed pronounced impetus since Floriani & Calderazzo (1969) and Crumbliss & Basolo (1970) discovered that

salicylideneamino derivatives of cobalt(II), in the proper conditions, reversibly bind one molecule of O₂ per atom of cobalt, mimicking the naturally occurring system of hæmoglobin.

A more recent application of Schiff bases derived from polyfunctional diprimary amines concerns the synthesis of compartmental ligands capable of forming homo- and heterobinuclear complexes (Costes, Cros, Darbien & Laurent, 1982). The synthesis of 'half-units', that is of non-symmetrical Schiff bases, seems to be of great potential usefulness in providing a facile extension to the available range of compartmental ligands (Bett, Fenton & Tate, 1981). We have recently described the copper(II)-template non-symmetrical synthesis of diethylenetriamine with salicylaldehyde within the coordination sphere of the metal (Rotondo & Cusmano Priolo, 1982). The crystal structure determination of the resulting copper(II) cationic derivative demonstrated the tetradentate behaviour of the 'half-unit' in a square-pyramidal complex whose apical position was occupied by a water molecule (Cusmano Priolo, Rotondo, Rizzardi, Bruno & Bombieri, 1983). We now report the result concerning the crystal structure of the same monoimine with nickel(II). In the present case the hydrophobic nature of the bulky tetraphenylborate

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counter ion preserves the metal from coordination of solvent molecules, and a square-planar arrangement of the ligand about the central ion is expected.

Experimental. 1 mmol of Ni(NO₃)₂·6H₂O dissolved in 10 ml of H₂O was added to 1 mmol of bis(salicylaldehyde)nickel(II) dihydrate suspended in 10 ml of methanol; to the resulting solution was added dropwise a solution of 1.2 mmol of dien dissolved in 10 ml of MeOH; the reaction mixture was allowed to stand for several days at room temperature. The addition of sodium tetraphenylborate to the solution yielded precipitation of the title compound as a yellow powder; the crude material was redissolved in boiling methanol; slow evaporation of the solvent from the ensuing filtrate led to the formation of orange crystals of the compound. The analytical data (%) with calculated values in parentheses and the characteristic IR bands (cm⁻¹) of this compound are: C 72.33 (71.98), H 6.18 (6.17), N 7.20 (7.20); $\nu(\text{NH})$ 3350–3200(br), $\nu(\text{C}=\text{N})$ imino 1620.

Prismatic crystal, 0.15 × 0.10 × 0.08 mm, 20 reflections with $7 \leq \theta \leq 10^\circ$ used for measuring lattice parameters; two standard reflections measured every 120 min, no significant intensity variation; 4645 independent reflections collected on a Siemens–Stoe four-circle diffractometer ($3 \leq \theta < 25^\circ$; $-13 \leq h \leq 13$, $0 \leq k \leq 17$, $0 \leq l \leq 20$) with ω/θ scan mode, 2593 with $I \geq 2.50\sigma(I)$, Lp correction, absorption ignored; structure solved by Patterson and Fourier methods and refined by full-matrix least-squares techniques, H atoms [except those belonging to N(2), C(1), C(3), C(4) because of a conformational disorder encountered in this part of the molecule] introduced at calculated positions (C–H 0.95 Å) with isotropic $U = 7 \times 10^{-2} \text{ \AA}^2$, anisotropic temperature factors assigned to the non-hydrogen atoms except for the carbons of the B(C₆H₅)₄ moiety; phenyl rings refined as rigid groups (D_{6h} symmetry, C–C 1.395 Å, C–C–C 120°), $\sum(w|F_o| - |F_c|)^2$ minimized with $w = 7.3006 [\sigma^2(F_o) + 25.3 \times 10^{-5} (F_o)^2]^{-1}$ used in the last refinement cycles, final $R = 0.086$ and $R_w = 0.084$, atomic scattering factors (corrected for anomalous dispersion of Ni) taken from *International Tables for X-ray Crystallography* (1974); final $\Delta\rho$ excursions $< 0.4 \text{ e \AA}^{-3}$; computations carried out using the *SHELX* system (Sheldrick, 1976) on an IBM 4331 computer.*

Discussion. Table 1 shows atomic parameters, Table 2 distances and angles. Fig. 1 shows a perspective view of the unit-cell contents with the four complex cations and the four tetraphenylborate anions, while Fig. 2 gives the

asymmetric units with the atom-numbering scheme as viewed down **c**. In the cation the Ni atom exhibits a square-planar geometry being coordinated to three nitrogens and one oxygen of the saldien ligand. The Ni atom is coplanar [0.009 (2) Å] with the basal plane; the deviations of the four donor atoms from their weighted mean plane are in the range 0.015 (5)–0.043 (9) Å; other significant displacements from this plane are C(1)–0.300 (14), C(2)–0.033 (11), C(3)–0.165 (12), C(4)–0.060 (14), C(5)–0.201 (9), C(6)–0.228 (9) and C(11)–0.195 (7) Å indicating a non-planarity of the saldien moiety. The large thermal parameters of C(1), N(2), C(3), C(4) in the chelate pentaatomic rings N(1)–Ni–N(2) and N(2)–Ni–N(3) suggest for them a flexible conformation. In any case the average conformation of the saldien ligand is very close to that adopted in the analogous copper derivative (Cusmano Priolo *et al.*, 1983) [rings: N(3)–Ni–N(2) envelope; N(2)–Ni–N(1) envelope]. The torsion angles N(2)–C(1)–C(2)–N(3) and N(2)–C(3)–C(4)–N(1)

Table 1. Atomic coordinates ($\times 10^4$), equivalent isotropic and isotropic U ($\text{\AA}^2 \times 10^3$) for non-hydrogen atoms with e.s.d.'s in parentheses

$$U_{\text{eq}} = \frac{1}{3} \sum_i \sum_j U_i a_i^* a_j^* \mathbf{a}_i \cdot \mathbf{a}_j. \text{ An asterisk indicates a } U_{\text{eq}} \text{ value.}$$

| | <i>x</i> | <i>y</i> | <i>z</i> | $U_{\text{eq}}/U_{\text{iso}}$ |
|-------|-----------|-----------|----------|--------------------------------|
| Ni | 224 (1) | 366 (1) | 1012 (1) | 62.0 (5)* |
| N(1) | –1373 (6) | 140 (5) | 931 (5) | 73 (3)* |
| N(2) | –109 (7) | 1608 (5) | 1175 (5) | 88 (4)* |
| C(1) | 848 (9) | 2105 (8) | 1492 (8) | 132 (7)* |
| C(3) | –1314 (9) | 1715 (8) | 1254 (7) | 101 (6)* |
| C(4) | –2115 (9) | 990 (7) | 975 (8) | 115 (6)* |
| N(3) | 1860 (5) | 741 (5) | 1168 (4) | 53 (3)* |
| O(1) | 635 (5) | –794 (4) | 843 (3) | 53 (2)* |
| C(2) | 1977 (8) | 1750 (6) | 1337 (6) | 73 (4)* |
| C(5) | –1869 (7) | –649 (7) | 872 (5) | 67 (4)* |
| C(6) | –1295 (8) | –1482 (6) | 781 (5) | 55 (4)* |
| C(7) | –1949 (8) | –2293 (8) | 714 (6) | 74 (4)* |
| C(8) | –1464 (9) | –3123 (7) | 628 (6) | 78 (5)* |
| C(9) | –245 (11) | –3172 (7) | 656 (6) | 83 (5)* |
| C(10) | 438 (8) | –2397 (7) | 734 (5) | 65 (4)* |
| C(11) | –26 (7) | –1528 (7) | 814 (4) | 49 (4)* |
| B | 4905 (7) | –481 (6) | 2334 (6) | 48 (4)* |
| C(21) | 6024 (5) | –497 (4) | 3105 (3) | 45 (2) |
| C(22) | 7188 (5) | –385 (4) | 3008 (3) | 63 (2) |
| C(23) | 8147 (5) | –415 (4) | 3626 (3) | 77 (3) |
| C(24) | 7942 (5) | –558 (4) | 4342 (3) | 81 (3) |
| C(25) | 6778 (5) | –670 (4) | 4439 (3) | 76 (3) |
| C(26) | 5819 (5) | –640 (4) | 3820 (3) | 54 (2) |
| C(31) | 5087 (4) | 454 (3) | 1817 (3) | 44 (2) |
| C(32) | 4733 (4) | 453 (3) | 1037 (3) | 43 (2) |
| C(33) | 4800 (4) | 1259 (3) | 635 (3) | 55 (2) |
| C(34) | 5222 (4) | 2067 (3) | 1014 (3) | 61 (2) |
| C(35) | 5577 (4) | 2068 (3) | 1793 (3) | 55 (2) |
| C(36) | 5509 (4) | 1262 (3) | 2195 (3) | 52 (2) |
| C(41) | 3596 (4) | –368 (3) | 2609 (3) | 48 (2) |
| C(42) | 3403 (4) | 461 (3) | 2948 (3) | 59 (2) |
| C(43) | 2355 (4) | 593 (3) | 3203 (3) | 79 (3) |
| C(44) | 1500 (4) | –103 (3) | 3118 (3) | 82 (3) |
| C(45) | 1693 (4) | –932 (3) | 2780 (3) | 78 (3) |
| C(46) | 2740 (4) | –1064 (3) | 2525 (3) | 52 (2) |
| C(51) | 4930 (4) | –1470 (3) | 1841 (3) | 43 (2) |
| C(52) | 3995 (4) | –1666 (3) | 1233 (3) | 48 (2) |
| C(53) | 4010 (4) | –2476 (3) | 827 (3) | 57 (2) |
| C(54) | 4961 (4) | –3090 (3) | 1029 (3) | 65 (3) |
| C(55) | 5896 (4) | –2894 (3) | 1637 (3) | 59 (2) |
| C(56) | 5880 (4) | –2084 (3) | 2043 (3) | 55 (2) |

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38747 (18 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

of the two ethylene bridges are $-25(1)$ and $21(1)^\circ$ respectively. The corresponding C—C lengths are $1.48(1)$ and $1.42(1)$ Å. It is a general feature of salen complexes that the ethylene bridges deviate slightly from the $M-N-N$ plane (Bresciani-Pahor, Calligaris, Delise, Nardin, Randaccio, Zotti, Facchinetti & Floriani, 1976) and there is a shortening of the C—C distances, but in our case the short values could be attributable to the thermal motion in the crystal.

As in the analogous copper complex with the same saldien ligand (Cusmano Priolo *et al.*, 1983) the three $M-N$ are not equivalent, the two Ni—N(amine) bond distances [Ni—N(2) $1.884(7)$ Å and Ni—N(3) $1.915(6)$ Å] are comparable and longer with respect to the third [Ni—N(1) $1.835(7)$ Å], which has a value near to that in [*N,N'*-ethylenebis(salicylideneamino)]nickel(II) [Ni—N $1.848(5)$ Å (Bresciani-Pahor *et al.*, 1976)]. An examination of the crystal packing, Fig. 1, shows that the pairs of cations, related through inversion centres, are close and the Ni atom of one unit lies approximately above the O atom of the centrosymmetric adjacent unit; the intermolecular Ni...O contact, $3.377(6)$ Å, indicates a kind of partial dimerization of the compound [the Ni...Ni separation is $3.778(3)$ Å]. Analogous features have been reported in ethylmethylglyoximatonicel(II) (Bowers, Banks & Jacobson, 1972) where two adjacent molecules are separated by a distance of 3.286 Å and in Ni(salen) (Shkol'nikova, Yutal, Shugam & Voblikova, 1970) with a Ni...Ni separation of $3.21(1)$ Å.

Table 2. Bond distances (Å) and angles ($^\circ$) with *e.s.d.'s* in parentheses

| | | | |
|------------------|------------|------------------|------------|
| Ni—N(1) | 1.835 (7) | C(7)—C(6) | 1.390 (11) |
| Ni—N(2) | 1.884 (7) | C(7)—C(8) | 1.353 (12) |
| Ni—N(3) | 1.915 (6) | C(8)—C(9) | 1.390 (13) |
| Ni—O(1) | 1.797 (5) | C(9)—C(10) | 1.362 (12) |
| C(4)—N(1) | 1.514 (11) | C(10)—C(11) | 1.392 (11) |
| C(5)—N(1) | 1.275 (10) | C(11)—C(6) | 1.445 (10) |
| C(1)—N(2) | 1.336 (11) | B—C(21) | 1.686 (11) |
| C(3)—N(2) | 1.430 (11) | B—C(31) | 1.697 (10) |
| C(1)—C(2) | 1.478 (13) | B—C(41) | 1.693 (10) |
| C(4)—C(3) | 1.418 (13) | B—C(51) | 1.701 (10) |
| N(3)—C(2) | 1.498 (10) | | |
| O(1)—C(11) | 1.304 (9) | | |
| C(5)—C(6) | 1.406 (11) | | |
| N(2)—Ni—N(1) | 87.2 (3) | C(3)—N(2)—Ni | 110.8 (6) |
| N(2)—Ni—N(3) | 86.0 (3) | C(3)—N(2)—C(1) | 128.2 (9) |
| O(1)—Ni—N(1) | 96.4 (3) | C(2)—C(1)—N(2) | 113.6 (9) |
| O(1)—Ni—N(3) | 90.5 (3) | C(4)—C(3)—N(2) | 116.6 (9) |
| C(4)—N(1)—Ni | 114.3 (6) | C(3)—C(4)—N(1) | 107.4 (8) |
| C(5)—N(1)—Ni | 126.0 (6) | C(2)—N(3)—Ni | 110.5 (5) |
| C(5)—N(1)—C(4) | 119.6 (7) | C(11)—O(1)—Ni | 127.1 (5) |
| C(1)—N(2)—Ni | 114.2 (7) | N(3)—C(2)—C(1) | 109.8 (7) |
| C(6)—C(5)—N(1) | 125.0 (8) | C(10)—C(11)—C(6) | 116.3 (8) |
| C(11)—C(6)—C(5) | 121.8 (9) | C(6)—C(11)—O(1) | 122.4 (8) |
| C(11)—C(6)—C(7) | 119.0 (8) | C(10)—C(11)—O(1) | 121.0 (8) |
| C(7)—C(6)—C(5) | 118.9 (8) | C(21)—B—C(41) | 108.4 (6) |
| C(8)—C(7)—C(6) | 122.7 (8) | C(41)—B—C(31) | 108.3 (5) |
| C(9)—C(8)—C(7) | 118.5 (9) | C(51)—B—C(21) | 109.4 (5) |
| C(10)—C(9)—C(8) | 120.9 (9) | C(51)—B—C(31) | 111.3 (6) |
| C(11)—C(10)—C(9) | 122.5 (9) | C(21)—B—C(31) | 108.3 (6) |
| | | C(41)—B—C(51) | 110.0 (5) |

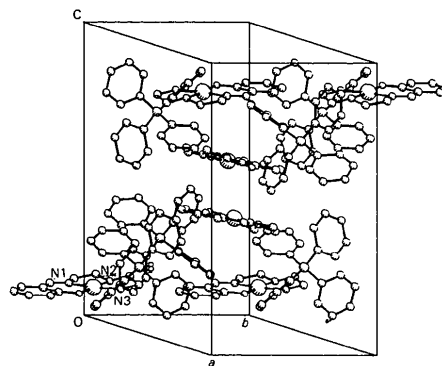


Fig. 1. Perspective view of the unit-cell contents.

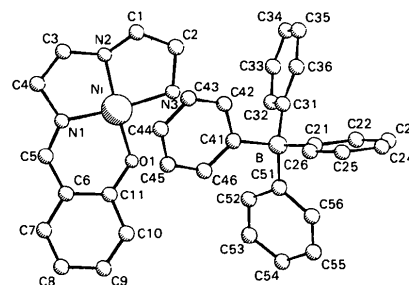


Fig. 2. The asymmetric units as viewed down *c*.

Bond lengths and angles in the tetraphenylborate anion are in the usual ranges.

References

- BETT, G., FENTON, D. E. & TATE, J. R. (1981). *Inorg. Chim. Acta*, **54**, 101–102.
- BOWERS, R. H., BANKS, C. V. & JACOBSON, R. A. (1972). *Acta Cryst.* **B28**, 2318–2322.
- BRESCIANI-PAHOR, N., CALLIGARIS, M., DELISE, P., NARDIN, G., RANDACCIO, L., ZOTTI, E., FACCHINETTI, G. & FLORIANI, C. (1976). *J. Chem. Soc. Dalton. Trans.* pp. 2310–2316.
- COSTES, J. P., CROSS, G., DARBIEN, M. H. & LAURENT, J. P. (1982). *Inorg. Chim. Acta*, **60**, 111–114.
- CRUMBLISS, L. & BASOLO, F. (1970). *J. Am. Chem. Soc.* **92**, 55–60.
- CUSMANO PRIOLO, F., ROTONDO, E., RIZZARDI, G., BRUNO, G. & BOMBIERI, G., (1983). *Acta Cryst.* **C39**, 550–552.
- FLORIANI, C. & CALDERAZZO, F. (1969). *J. Chem. Soc. A*, pp. 1946–1953.
- International Tables for X-ray Crystallography* (1974). Vol. IV. Birmingham: Kynoch Press.
- ROTONDO, E. & CUSMANO PRIOLO, F. (1982). *J. Chem. Soc. Dalton Trans.* pp. 1825–1828.
- SHELDRICK, G. M. (1976). *SHELX 76*. Program for crystal structure determination. Univ. of Cambridge, England.
- SHKOL'NIKOVA, L. M., YUTAL, E. M., SHUGAM, E. A. & VOBLIKOVA, V. A. (1970). *Zh. Strukt. Khim.* **11**, 886–890.
- SNELL, E. E., FASELLA, P. M., BRAMESTEIN, A. & ROSSI FANELLI, A. (1963). *Chemical and Biological Aspects of Pyridoxal Catalysis*. New York: Macmillan.