Related literature. Preparation and chemistry of the title complex are described by Kwiatkowski, Ossowski & Jankowska (1985). The structure of similar Schiff base complexes is described by De Vaira, Orioli & Sacconi (1971), Podlakova, Knižek, Loub & Hašek (1988) and references cited therein.

References

DE VAIRA, M., ORIOLOI, P. L. & SACCONI, L. (1971). *Inorg. Chem.* **10**, 553–558.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JASKÓLSKI, M. (1982). *Collected Abstracts of the Fourth Symposium on Organic Crystal Chemistry*, Poznań, September 1982, edited by Z. KALUSKI, pp. 70–71. Poznań: A. Mickiewicz Univ.

JOHNSON, C. K. (1976). *ORTEPII.* Report ORNL-5138. Oak Ridge National Laboratory, Tennessee, USA.

KWIATKOWSKI, E., OSSOWSKI, T. & JANKOWSKA, A. (1985). *Polyhedron*, **4**, 1191–1196.

LEHMANN, M. S. & LARSEN, F. K. (1974). *Acta Cryst.* A**30**, 580–584.

MOTHERWELL, W. D. S. & CLEGG, W. (1978). *PLUTO.* Program for plotting molecular and crystal structures. Univ. of Cambridge, England.

PODLAKOVA, J., KNIŽEK, K., LOUB, J. & HAŠEK, J. (1988). *Acta Cryst.* C**44**, 631–633.

SHELDRICK, G. M. (1976). *SHELX76.* Program for crystal structure determination. Univ. of Cambridge, England.

SHELDRICK, G. M. (1986). *SHELXS86.* Program for crystal structure solution. Univ. of Göttingen, Federal Republic of Germany.

A Redetermination of the Structures of Bis(salicylideneaminato)nickel(II) and Monoclinic and Orthorhombic Forms of Bis(N-methylsalicylideneaminato)nickel(II)

BY BORIS KAMENAR AND BRANKO KAITNER

Laboratory of General and Inorganic Chemistry, Faculty of Science, The University, PO Box 153, 41001 Zagreb, Yugoslavia

GEORGE FERGUSON*

Department of Chemistry and Biochemistry, University of Guelph, Guelph, Ontario, Canada N1G 2W1

AND T. NEIL WATERS

Massey University, Palmerston North, New Zealand

Abstract. (I): Bis(salicylideneaminato)nickel(II), [Ni(C$_7$H$_6$NO)$_2$], $M_r = 298.97$, monoclinic, $P2_1/c$, $a = 12.959$ (3), $b = 5.848$ (1), $c = 8.147$ (1) Å, $\beta = 95.98$ (1)°, $V = 614.10$ Å^3, $Z = 2$, $D_x = 1.617$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 1.580$ mm^{-1}, $F(000) = 308$, room temperature, final $R = 0.028$ for 1083 reflections. (II): Bis(N-methylsalicylideneaminato)nickel(II), [Ni(C$_8$H$_8$NO)$_2$], $M_r = 327.03$, monoclinic, $P2_1/c$, $a = 12.119$ (6), $b = 7.090$ (2), $c = 8.348$ (1) Å, $\beta = 92.75$ (6)°, $V = 716.47$ Å^3, $Z = 2$, $D_x = 1.516$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 1.289$ mm^{-1}, $F(000) = 340$, room temperature, final $R = 0.029$ for 1195 reflections. (III): Bis(N-methylsalicylideneaminato)nickel(II), [Ni(C$_8$H$_8$NO)$_2$], $M_r = 327.03$, orthorhombic, *Ibam*, $a = 9.189$ (2), $b = 24.331$ (5), $c = 6.600$ (2) Å, $V =$ 1475.61 Å^3, $Z = 4$, $D_x = 1.472$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.7107 Å, $\mu = 1.252$ mm^{-1}, $F(000) = 680$, room temperature, final $R = 0.030$ for 670 reflections. The redeterminations of the title structures based on diffractometer data have yielded more precise structural parameters than the previous photographic results [(I): Stewart & Lingafelter (1959). *Acta Cryst.* **12**, 842–845; (II): Frasson, Panattoni & Sacconi (1959). *J. Phys. Chem.* **63**, 1908–1911; (III): Fox & Lingafelter (1967). *Acta Cryst.* **22**, 943–944] thus extending the data to give a better understanding of the reasons for differences in the molecular conformations of these complexes. All three complexes have molecular centres of symmetry and Ni atoms in a square-planar coordination. Molecule (I) is almost completely planar with the molecular step between planes through the two benzene rings of 0.098 Å, molecule (II) is distinctively 'stepped' (step height of 0.782 Å),

* E-mail address: CHMFERG@UOGUELPH

Table 1. *Details of data collection and refinement for* (I), (II) *and* (III)

		(I)	(II)	(III)
Crystal form and size (mm)		Dark red prism	Green prism	Dark red prism
		0·38 × 0·20 × 0·20	0·38 × 0·40 × 0·08	0·28 × 0·38 × 0·48
Diffractometer		Enraf–Nonius CAD-4	Philips PW1100	Philips PW1100
Radiation		Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Reflections for cell constants		25	16	17
		$(8 < \theta < 16°)$	$(2\theta \geq 10°)$	$(2\theta \geq 12°)$
Scan speed (° s^{-1})		0·05	0·04	0·04
Scan width (°)		0·6	1·6	1·6
Scan mode		θ–2θ	θ–2θ	θ–2θ
$2\theta_{max}$ (°)		54	54	54
Range of indices	h	0–16	−16–16	0–12
	k	0–7	0–9	0–34
	l	−10–10	0–11	0–8
Standard reflections		313	40$\bar{2}$	280
		21$\bar{3}$	021	262
		42$\bar{2}$	120	$\bar{2}$62
Intensity variation (%)		0·7	0·7	2·3
Max. and min. transmission factors		0·770, 0·723	—	0·816, 0·676
R		0·028	0·029	0·030
wR		0·039	0·029	0·037
Weighting scheme		$w = 1/[\sigma^2(F_o) + g(F_o)^2]$	$w = 1$	$w = k/[\sigma^2(F_o) + g(F_o)^2]$
		$g = 0·04$		$k = 1·0, g = 0·0015$
Independent measured reflections		1341	1533	827
Observed reflections [$I \geq 3\sigma(I)$]		1083	1195	670
Refined parameters		88	108	72
Max. Δ/σ		0·010	0·004	0·136
Max. and min. $\Delta\rho$ features (e Å^{-3})		±0·40	0·26, −0·21	0·27, −0·62

while molecule (III) is strictly planar having mirror-plane symmetry. Such different conformations are also due to the close intramolecular approaches of the O atoms $(-x, -y, -z)$ to the H atom attached to N in (I) or to the methyl H atoms in (II) and (III). These contacts are 2·34 Å in (I), 2·32 Å in (II) and 2·47 Å in (III). The Ni—O bond lengths are almost the same in all three structures being 1·840 (1) Å in (I), 1·835 (2) Å in (II) and 1·830 (2) Å in (III), while Ni—N distances are significantly different amounting to 1·852 (2), 1·907 (2) and 1·926 (3) Å in (I), (II) and (III), respectively.

Experimental. Crystals were prepared as reported in the previous papers. Crystal dimensions and data collection procedures are given in Table 1. Structures were solved by the heavy-atom method. Refinement was by full-matrix least-squares method, with anisotropic thermal parameters for non-H atoms. The function minimized was $w(|F_o| - |F_c|)^2$, with weighting schemes given in Table 1. Absorption corrections were applied [(I): *SDP-Plus*; B. A. Frenz & Associates, Inc., 1984; (III): Harkema, 1978]. Difference Fourier maps showed maxima in positions consistent with the expected locations of H atoms; in the final cycles of refinements H atoms were positioned on geometrical grounds [C—H, N—H 0·95 Å in (I) and 1·08 Å in (II) and (III)] and included (as riding atoms) in the structure-factor calculations with an overall isotropic temperature factor. All calculations were performed with *SDP-Plus* for (I), and *SHELX76* (Sheldrick, 1976) and *CSU – Crystal Structure Utility* program (Vickovič, 1988) for (II) and (III). Scattering factors and anomalous-dispersion corrections were from *Interna-*

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

|	x	y	z	B_{eq}*
(I)				
Ni	0	0	0	2·853 (6)
O	966 (1)	1567 (3)	1386 (2)	3·62 (3)
N	862 (1)	−2476 (3)	−242 (2)	3·30 (3)
C1	2380 (1)	−1122 (3)	1410 (2)	2·79 (4)
C2	1927 (1)	974 (4)	1856 (2)	2·77 (3)
C3	2544 (2)	2475 (4)	2882 (2)	3·25 (4)
C4	3558 (2)	1957 (4)	3434 (3)	3·71 (4)
C5	4002 (2)	−93 (4)	2989 (3)	4·03 (5)
C6	3420 (2)	−1590 (4)	1992 (3)	3·50 (4)
C7	1810 (1)	−2763 (3)	382 (3)	3·02 (4)
(II)				
Ni	0	0	0	2·669 (8)
O	986 (2)	885 (3)	1559 (3)	3·81 (5)
N	1145 (2)	−549 (3)	−1419 (3)	2·96 (5)
C1	2651 (2)	−438 (4)	611 (4)	3·29 (6)
C2	2031 (2)	457 (4)	1773 (3)	3·20 (6)
C3	2578 (3)	953 (5)	3263 (4)	3·82 (7)
C4	3675 (3)	530 (5)	3536 (4)	4·60 (9)
C5	4278 (3)	−406 (6)	2404 (5)	5·05 (10)
C6	3768 (3)	−865 (6)	937 (4)	4·37 (9)
C7	2168 (3)	−773 (5)	−980 (4)	3·32 (7)
C8	879 (3)	−731 (6)	−3162 (4)	3·85 (7)
(III)				
Ni	0	0	0	3·458 (12)
O	1678 (3)	405 (1)	0	4·61 (5)
N	−1227 (3)	642 (1)	0	3·84 (5)
C1	739 (4)	1319 (2)	0	4·08 (7)
C2	1868 (4)	940 (1)	0	3·89 (7)
C3	3316 (4)	1139 (2)	0	5·24 (8)
C4	3591 (5)	1697 (2)	0	6·11 (10)
C5	2442 (6)	2079 (2)	0	6·71 (11)
C6	1054 (5)	1884 (1)	0	5·53 (10)
C7	−772 (4)	1138 (1)	0	3·84 (7)
C8	−2833 (4)	581 (2)	0	4·66 (8)

* Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $\frac{4}{3}[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab\cos\gamma B(1,2) + ac\cos\beta B(1,3) + bc\cos\alpha B(2,3)]$.

tional Tables for X-ray Crystallography (1974). Calculations were carried out on a PDP11/73 for (I) and on a UNIVAC 1110 computer for (II) and (III).

Table 3. *Bond distances* (Å) *and angles* (°)

	(I)	(II)	(III)
Ni—O	1·840 (1)	1·835 (2)	1·830 (2)
Ni—N	1·852 (2)	1·907 (2)	1·926 (3)
O—C2	1·312 (2)	1·305 (3)	1·313 (4)
N—C7	1·291 (2)	1·285 (4)	1·278 (4)
N—C8	—	1·481 (4)	1·484 (5)
C1—C2	1·423 (3)	1·407 (4)	1·389 (5)
C1—C6	1·408 (3)	1·400 (4)	1·404 (5)
C1—C7	1·428 (3)	1·445 (4)	1·457 (5)
C2—C3	1·403 (3)	1·426 (4)	1·416 (5)
C3—C4	1·377 (3)	1·371 (5)	1·379 (5)
C4—C5	1·394 (3)	1·391 (5)	1·407 (7)
C5—C6	1·367 (3)	1·384 (5)	1·361 (6)
O—Ni—N	94·33 (7)	92·4 (1)	93·23 (9)
O—Ni—Nⁱ	85·67 (7)	87·6 (1)	86·76 (9)
Ni—O—C2	127·8 (1)	127·7 (2)	130·2 (2)
Ni—N—C7	128·3 (1)	124·7 (2)	125·1 (2)
Ni—N—C8	—	119·8 (2)	120·1 (2)
C7—N—C8	—	115·5 (3)	114·8 (3)
C2—C1—C6	119·2 (2)	120·5 (3)	119·8 (3)
C2—C1—C7	121·8 (2)	120·1 (3)	120·7 (3)
C6—C1—C7	119·0 (2)	119·2 (3)	119·5 (3)
O—C2—C1	123·9 (2)	123·9 (3)	124·1 (3)
O—C2—C3	118·3 (2)	118·0 (3)	117·7 (3)
C1—C2—C3	117·8 (2)	118·1 (3)	118·3 (3)
C2—C3—C4	121·5 (2)	119·8 (3)	120·6 (4)
C3—C4—C5	120·7 (2)	121·9 (3)	120·8 (4)
C4—C5—C6	119·2 (2)	119·1 (3)	118·2 (4)
C1—C6—C5	121·7 (2)	120·5 (3)	122·3 (4)
N—C7—C1	123·8 (2)	125·8 (3)	126·6 (3)

Symmetry code: (i) −x, −y, −z.
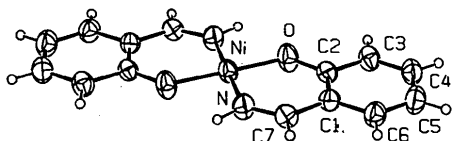
(I)
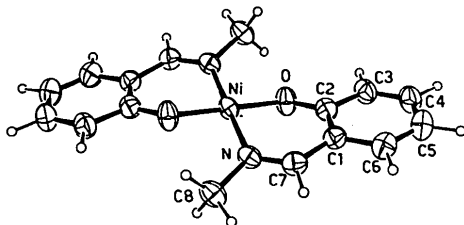
(II)
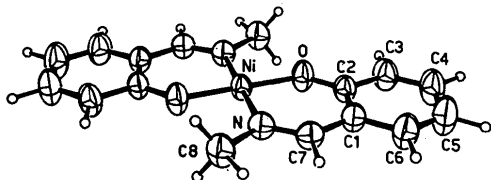
(III)

Fig. 1. An *ORTEP* (Johnson, 1971) view of the molecular structures of (I), (II) and (III) showing the atom-numbering schemes. Ellipsoids are at 50% probability level.

Table 2 contains final atomic parameters.* Bond lengths and bond angles are given in Table 3. The structures are illustrated in Fig. 1.

Related literature. The Ni-atom coordination as well as the molecular conformations of the bis(*N*-*R*-salicylideneaminato)nickel(II) complexes depend upon the N atom and benzene-ring substituents. Both tetrahedral (Fox, Orioli, Lingafelter & Sacconi, 1964; Braun & Lingafelter, 1967; Castellano, Hodder, Prout & Sadler, 1971) and square-planar coordinations of the Ni atoms have been found. Square-planar complexes may have either strictly planar or 'stepped' conformation (Braun & Lingafelter, 1966; Shkol'nikova, Knyazeva & Voblikova, 1967; Maslen & Waters, 1975; Tamura, Ogawa, Takeuchi & Yamada, 1979; Bhatia, Bindlish, Saini & Jain, 1981; Bhatia, Syal, Kashyap, Jain & Brown, 1983; Jones, Waters, Kaitner & Kamenar, 1986; Fernández, Rosales, Toscano & Tapia T., 1986; Ravikumar, Rajan, Rajaram, Ramalingam & Natarajan, 1986; Britton & Pignolet, 1989; Kamenar, Kaitner, Stefanović & Waters, 1990).

---

* Lists of structure factors, anisotropic thermal parameters, H-atom coordinates, least-squares planes and torsion angles have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52865 (33 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

B. A. FRENZ & ASSOCIATES, INC. (1984). *SDP-Plus Structure Determination Package.* College Station, Texas 77840, USA.

BHATIA, S. C., BINDLISH, J. M., SAINI, A. R. & JAIN, P. C. (1981). *J. Chem. Soc. Dalton Trans.* pp. 1773–1779.

BHATIA, S. C., SYAL, V. K., KASHYAP, R. P., JAIN, P. C. & BROWN, C. J. (1983). *Acta Cryst.* C39, 199–200.

BRAUN, R. L. & LINGAFELTER, E. C. (1966). *Acta Cryst.* 21, 546–553.

BRAUN, R. L. & LINGAFELTER, E. C. (1967). *Acta Cryst.* 22, 780–787.

BRITTON, D. & PIGNOLET, L. H. (1989). *Acta Cryst.* C45, 819–821.

CASTELLANO, E. E., HODDER, O. J. R., PROUT, C. K. & SADLER, P. J. (1971). *J. Chem. Soc. A*, pp. 2620–2627.

FERNÁNDEZ, J. M., ROSALES, M. J., TOSCANO, R. A. & TAPIA T., R. G. (1986). *Acta Cryst.* C42, 1313–1316.

FOX, M. R. & LINGAFELTER, E. C. (1967). *Acta Cryst.* 22, 943–944.

FOX, M. R., ORIOLI, P. L., LINGAFELTER, E. C. & SACCONI, L. (1964). *Acta Cryst.* 17, 1159–1166.

FRASSON, E., PANATTONI, C. & SACCONI, L. (1959). *J. Phys. Chem.* 63, 1908–1911.

HARKEMA, S. (1978). *ACXR. Absorption Correction Program for use with a PW1100 Diffractometer.* Twente Univ. of Technology, The Netherlands.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JOHNSON, C. K. (1971). *ORTEPII*. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.

JONES, T. C., WATERS, T. N., KAITNER, B. & KAMENAR, B. (1986). *Croat. Chem. Acta*, **59**, 825–831.

KAMENAR, B., KAITNER, B., STEFANOVIĆ, A. & WATERS, T. N. (1990). *Acta Cryst.* C46, 1923–1925.

MASLEN, H. S. & WATERS, T. N. (1975). *Coord. Chem. Rev.* **17**, 137–176.

RAVIKUMAR, K., RAJAN, S. S., RAJARAM, V., RAMALINGAM, S. K. & NATARAJAN, S. (1986). *Z. Kristallogr.* **175**, 117–123.

SHELDRICK, G. M. (1976). *SHELX*76. Program for crystal structure determination. Univ. of Cambridge, England.

SHKOL'NIKOVA, L. M., KNYAZEVA, A. N. & VOBLIKOVA, V. A. (1967). *Zh. Strukt. Khim.* **8**, 94–99.

STEWART, J. M. & LINGAFELTER, E. C. (1959). *Acta Cryst.* **12**, 842–845.

TAMURA, H., OGAWA, K., TAKEUCHI, A. & YAMADA, S. (1979). *Bull. Chem. Soc. Jpn*, **52**, 3522–3527.

VICKOVIĆ, I. (1988). *J. Appl. Cryst.* **21**, 987–990.

Structure of Bis(*N*-methyl-5-nitrosalicylideneaminato)nickel(II)

BY BORIS KAMENAR, BRANKO KAITNER AND ALEKSANDAR STEFANOVIĆ

Laboratory of General and Inorganic Chemistry, Faculty of Science, The University, PO Box 153, 41001 Zagreb, Yugoslavia

AND T. NEIL WATERS

Massey University, Palmerston North, New Zealand

Abstract. [Ni($C_8H_7N_2O_3$)$_2$], $M_r = 417.00$, monoclinic, $P2_1/n$, $a = 20.500$ (4), $b = 10.266$ (3), $c = 3.824$ (1) Å, $\beta = 92.93$ (2)°, $V = 803.67$ Å^3, $Z = 2$, $D_m = 1.73$ (by flotation), $D_x = 1.72$ g cm^{-3}, $\lambda(Cu\ K\alpha) = 1.5418$ Å, $\mu = 21.21$ cm^{-1}, $F(000) = 428$, room temperature, final $R = 0.036$ for 1244 observed unique reflections. The title complex has a molecular centre of symmetry and the Ni atom is in square-planar coordination. The molecule has a stepped conformation with a step height of 0.136 Å, measured by the perpendicular distance between planes of best fit through the two benzene rings. The close intramolecular approaches between O(1′) (−x, −y, −z) and H(81) and H(82) atoms of the methyl group [2.445 and 2.470 Å] possibly influence the conformation of the complex molecule. The Ni—O and Ni—N bond lengths are 1.826 (2) and 1.924 (2) Å, respectively. Within the benzene system, three consecutive bonds are longer [C(6)—C(1) 1.400 (3), C(1)—C(2) 1.411 (3), C(2)—C(3) 1.419 (3) Å] and three shorter [C(3)—C(4) 1.368 (4), C(4)—C(5) 1.396 (4), C(5)—C(6) 1.377 (4) Å]. The two distinctly shorter bonds [C(3)—C(4) and C(5)—C(6)] suggest a quinonoid character of the ring.

Experimental. Crystals obtained by slow evaporation of dimethyformamide solution. Crystal dimensions and data collection procedure are given in Table 1. The structure was solved by the heavy-atom method and refined by a full-matrix least-squares procedure using anisotropic temperature factors for all non-hydrogen atoms. Function minimized $\Sigma w(|F_o| - |F_c|)^2$ with weighting scheme given in Table 1. No absorption correction applied. At an intermediate stage in the refinement, difference maps showed peaks at the expected locations of H atoms. In the final rounds of calculations they were positioned on geometrical grounds (C—H = 1.08 Å) and included in the structure factor calculations. Structure solution and refinement performed with modified *SHELX*76 (Sheldrick, 1976), molecular geometry calculations with *CSU – Crystal Structure Utility* program (Vicković, 1988). Anomalous-scattering factors from *International Tables for X-ray Crystallography* (1974). All calculations carried out on IBM PC/AT-compatible microcomputer (microprocessor 80386/20 MHz and mathematical coprocessor 80387). Final atomic coordinates are given in Table 2,* the bond lengths and angles in Table 3. The structure is shown in Fig. 1.

Related literature. The structures of a number of the bis(*N-R*-salicylideneaminato)nickel(II) complexes reported so far showed that the coordination around