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# The Crystal Structure and Conformation of *bis*(*N*-methyl-5-chlorosalicylideneiminato)nickel(II) and *bis*(*N*-ethyl-5-chlorosalicylideneiminato)nickel(II)

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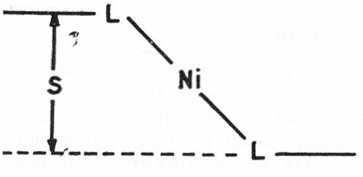
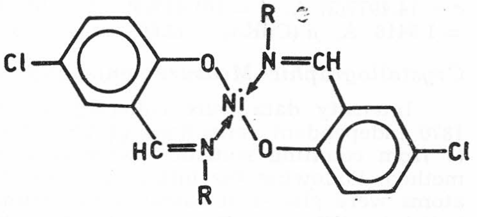
The crystal structures of *bis*(*N*-methyl-5-chlorosalicylideneiminato)nickel(II) (A) and *bis*(*N*-ethyl-5-chlorosalicylideneiminato)nickel(II) (B) have been determined by X-ray structure analysis using heavy atom method and refined by full matrix least-squares procedure to *R* values of 0.044 and 0.040 for (A) and (B), respectively. Both structures have molecular centre of symmetry and the nickel atom in a planar coordination. Molecules of both complex compounds have »stepped« conformation with distinct difference in the step heights: 0.121 and 0.702 Å in (A) and (B), respectively. The Ni—O and Ni—N bond lengths are 1.818 and 1.924 Å in (A), and 1.830 and 1.916 Å in (B).

A feature of the molecular geometry of many salicylideneimine (salim) complexes of divalent copper and nickel is their »stepped« conformation arising from a distinct bend in the otherwise planar molecules along a line joining the two donors within each separate ligand. The step distance *S* (see (a)) is defined as the perpendicular separation between the planes through the chelate ring and/or through the benzene ring atoms.[1] A bend of the opposite



(a)



(A) $R = CH_3$ , (B) $R = C_2H_5$

(b)

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sense in one of the ligands results in an »umbrella-shaped« complex. Both steric[2] and electronic[3] causes have been implicated but crystal forces cannot be overlooked. Although both metals show effect, there are some notable differences between them. Thus, their *bis*(*N*-methylsalicylideneiminato) complexes are isostructural and perfectly planar[4,5] in one crystal form (orthorhombic)* whereas their *N*-ethyl analogues are not.[7,8] Here the Ni(II) complex is stepped whereas both crystalline forms of the copper complex possess tetrahedrally distorted molecules.[9–11] As the first step towards a better understanding of the reasons for these differences in conformation we have determined the structure of *bis*(*N*-methyl-5-chlorosalicylideneiminato)nickel(II) (A) and *bis*(*N*-ethyl-5-chlorosalicylideneiminato)nickel(II) (B) (see formula (b)) so that their overall geometries and, where accuracy allows, details of their bond lengths and the positions of their hydrogen atoms can be compared with earlier work.

## EXPERIMENTAL

### *(A) Ni(*N*-Me-chlorosalim)$_2$*

### *Crystal Data*

$C_{16}H_{14}Cl_2N_2O_2Ni$, fw = 395.92, monoclinic, $C2/c$, $a = 20.490(4)$, $b = 3.957(1)$, $c = 21.477(5)$ Å, $\beta = 114.75(1)^\circ$, $V = 1581.38$ Å$^3$, $Z = 4$, $D_c = 1.663$ g cm$^{-3}$, $\lambda$ (MoK$\alpha$) = 0.7107 Å (graphite monochromator) $\mu$ (MoK$\alpha$) = 14.90 cm$^{-1}$, crystal, dimensions (mm): 0.17 × 0.04 × 0.46.

### *Crystallographic Measurements and Structure Determination*

Intensity data were collected on a Philips PW 1100 diffractometer using $\omega - 2\Theta$ scan technique in the range $4 \leqslant 2\Theta \leqslant 60^\circ$. Out of the total 1247 independent reflections, 1157 with $I \geqslant 3\sigma(I)$ were used in structure refinement. The structure was solved using the heavy atom method. Following the initial refinement hydrogen atoms were placed at calculated positions after appropriate maxima had been noted in difference electron density syntheses. When all had been located, the refinement of the positional and anisotropic thermal parameters proceeded for all non-hydrogen atoms while the hydrogen atom positions were used in the structure factor calculations with fixed isotropic temperature factors (separately for hydrogen atoms belonging to the benzene ring and those belonging to the methyl group). Using full-matrix least-squares procedure the function $\Sigma w (|F_o| - |F_c|)^2$ was minimized. The weighting scheme was $w(F_o) = 0.5331/\sigma^2(F_o) + 0.003874\ F_o^2$. The final $R$ was 0.044 ($R_w = 0.049$).

### *(B) Ni(*N*-Et-5-chlorosalim)$_2$*

### *Crystal Data*

$C_{18}H_{18}Cl_2N_2O_2Ni$, fw = 423.97, monoclinic, $P2_1/n$, $a = 11.9452(6)$, $b = 5.3660(2)$, $c = 14.4977(3)$ Å, $\beta = 101.417(3)^\circ$, $V = 910.885$ Å$^3$, $Z = 2$, $D_c = 1.497$ g cm$^{-3}$, $\lambda$ (CuK$\alpha$) = 1.5418 Å, $\mu$ (CuK$\alpha$) = 42.66 cm$^{-1}$, crystal dimensions (mm): 0.39 × 0.20 × 0.20.

### *Crystallographic Measurements and Structure Solution*

Intensity data were collected on an Enraf-Nonius CAD-4 diffractometer for 1870 independent reflections of $2\Theta \leqslant 150^\circ$. After processing, 1244 data of $I \geqslant 3\sigma(I)$ ($\sigma$ from counting statistics) were used to solve the structure by the heavy atom method. Following the initial refinement of non-hydrogen atom positions, hydrogen atoms were placed at calculated coordinates after corresponding maxima had been noted in difference Fourier syntheses. When all had been located, the refinement of the positional and anisotropic thermal parameters proceeded for all other atoms. Using full-matrix least-squares programme the conventional $R$ factor fell to 0.040 ($R_w = 0.053$). The function minimized was $\Sigma w (|F_o| - |F_c|)^2$ with $w = 1/\sigma^2(F_o)$. The refined coordinates for both structures are listed in Table I. The temperature

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* The monoclinic form of Ni (*N*-Me-salim)$_2$ has a stepped conformation with $S = 0.797$ Å.[6,7]

TABLE I

*Positional Parameters with Standard Deviations in Parentheses*

| | (A) Ni (*N*-Me-5-chlorosalim)$_2$ | | | (B) Ni (*N*-Et-5-chlorosalim)$_2$ | | |
|---|---|---|---|---|---|---|
| Atom | *x/a* | *y/b* | z/c | *x/a* | *y/b* | *z/c* |
| Ni | 0.25 | 0.25 | 0 | 1.0 | 0 | 0 |
| Cl | 0.0839(1) | —0.1785(4) | 0.2265(1) | 0.85484(7) | 0.3648(2) | 0.43789(5) |
| O | 0.1663(2) | 0.2657(8) | 0.0101(2) | 0.9945(1) | —0.1192(1) | 0.1173(1) |
| N | 0.3000(2) | 0.0146(9) | 0.0853(2) | 0.8896(2) | 0.2546(5) | 0.0075(2) |
| C(1) | 0.2004(2) | —0.0012(10) | 0.1193(2) | 0.8990(2) | 0.2188(6) | 0.1757(2) |
| C(2) | 0.1508(2) | 0.1636(10) | 0.0601(2) | 0.9626(2) | —0.0039(6) | 0.1872(2) |
| C(3) | 0.0810(2) | 0.2139(12) | 0.0550(3) | 0.9894(3) | —0.1083(6) | 0.2778(2) |
| C(4) | 0.0618(2) | 0.1173(13) | 0.1054(3) | 0.9571(3) | 0.0023(7) | 0.3530(2) |
| C(5) | 0.1111(2) | —0.0420(12) | 0.1637(2) | 0.8950(2) | 0.2233(7) | 0.3408(2) |
| C(6) | 0.1797(2) | —0.1082(12) | 0.1704(2) | 0.8652(2) | 0.3290(6) | 0.2534(2) |
| C(7) | 0.2720(2) | —0.0674(10) | 0.1274(2) | 0.8622(3) | 0.3272(6) | 0.0845(2) |
| C(8) | 0.3758(2) | —0.0897(12) | 0.1068(2) | 0.8281(3) | 0.3818(7) | —0.0794(2) |
| C(9) | | | | 0.7442(3) | 0.2047(11) | —0.1375(3) |
| H(3) | 0.042 | 0.333 | 0.010 | 1.035 | —0.268 | 0.289 |
| H(4) | 0.008 | 0.165 | 0.100 | 0.977 | —0.075 | 0.414 |
| H(6) | 0.217 | —0.242 | 0.215 | 0.817 | 0.477 | 0.246 |
| H(7) | 0.307 | —0.200 | 0.174 | 0.807 | 0.464 | 0.078 |
| H(81) | 0.394 | —0.010 | 0.069 | 0.785 | 0.528 | —0.065 |
| H(82) | 0.380 | —0.361 | 0.112 | 0.881 | 0.445 | —0.116 |
| H(83) | 0.409 | 0.027 | 0.155 | | | |
| H(91) | | | | 0.707 | 0.283 | —0.195 |
| H(92) | | | | 0.692 | 0.283 | —0.103 |
| H(93) | | | | 0.788 | 0.066 | —0.155 |

factors, structure factor amplitudes and thermal parameters for both compounds are part of supplementary material available from the authors.

## DESCRIPTION OF THE STRUCTURES AND DISCUSSION

### *(A) Ni(*N*-Me-5-chlorosalim)*$_2$

The nickel atoms are required to be at the centres of symmetry and the bonds around the nickel atom are in a *trans*-planar arrangement (Figure 1).

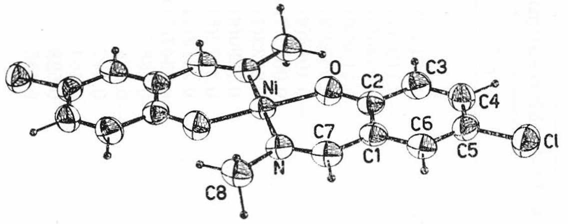

Figure 1. A perspective ORTEP drawing of the *bis*(*N*-methyl-5-chlorosalycilidene-iminato)nickel(II) molecule with the atom numbering scheme.

The molecule appears to differ in having a shorter Ni—O bond of 1.818(3) Å as compared to 1.830(2) Å in the ethyl analogue and, indeed, all the bonds in the chelate ring appear alternately shorter or longer than those in the analogue (Table II). It is likely, therefore, that some electron redistribution does occur with a change in substituent at nitrogen, which may account for the close approximation to the overall planarity found in this molecule. While the molecular step, as measured by the perpendicular distance between planes of best fit through the two benzene rings, is 0.702 Å in the ethyl derivative, it is only 0.121 Å here. In this respect, the complex is similar to the orthorhombic form of *bis*(*N*-methylsalicylideneiminato)nickel (II), which does not show a »stepped« conformation.[5]

The benzene ring shows the usual feature of having three consecutive longer (C(6) to C(3)) and three shorter bonds (C(3) to C(6)), similarly as in the *N*-ethyl analogue. Such shortening and lengthening of C—C bonds within the benzene ring is often found also in the salicylideneiminato complexes of copper(II).[3,12]

There are no significant interactions between neighbouring molecules, the closest contacts are between Cl . . . $C(7)^{I}$ and Cl . . . $C(8)^{I}$ and they amount to 3.629 and 3.697 Å, respectively ($I = 1/2 - x,\ 1/2 - y,\ 1/2 - z$). However, there is a close intramolecular approach (2.446 Å) between one methyl hydrogen atom (H(81)) and the oxygen atom of the other ligand.

### *(B) Ni(*N*-Et-5-chlorosalim)*$_2$

In this structure also the Ni atoms occupy the symmetry centres, thus realizing a *trans*-planar arrangement around the Ni atom (Figure 2). Bond lengths and angles appear normal, the benzene ring showing the pattern of three shorter and three longer bonds, as it has been pointed out in the previous example of the methyl analogue. Two of the bonds, C(3)—C(4) of 1.363(3) and C(5)—C(6) of 1.369(3) Å, are so much shorter as to suggest a significant quinonoid character in the ring. Compared to the non-chloro derivative parent

TABLE II

*Bond Lengths and Angles in* bis(N-*methyl-5-chlorosalicylideneiminato)nickel(II) (A) and* bis(N-*ethyl-5-chlorosalicylideneiminato)nickel(II) (B)*

| Bond Lengths (Å) | (A) | (B) |
|---|---|---|
| Ni—O | 1.818(3) | 1.830(2) |
| Ni—N | 1.924(3) | 1.916(2) |
| Cl—C(5) | 1.748(5) | 1.748(2) |
| O—C(2) | 1.305(6) | 1.306(3) |
| N—C(7) | 1.299(6) | 1.284(3) |
| N—C(8) | 1.482(5) | 1.492(3) |
| C(1)—C(2) | 1.411(6) | 1.409(3) |
| C(1)—C(6) | 1.379(6) | 1.400(3) |
| C(1)—C(7) | 1.428(5) | 1.433(3) |
| C(2)—C(3) | 1.403(6) | 1.405(3) |
| C(3)—C(4) | 1.353(7) | 1.363(3) |
| C(4)—C(5) | 1.387(7) | 1.391(4) |
| C(5)—C(6) | 1.377(6) | 1.369(3) |
| C(8)—C(9) | | 1.511(5) |
| Bond Angles (°) | | |
| O—Ni—N | 93.20(10) | 92.58(7) |
| O—Ni—N$^{\text{II}}$ | 86.80(10) | 87.42(7) |
| Ni—O—C(2) | 130.9(3) | 128.7(2) |
| Ni—N—C(7) | 124.8(3) | 124.2(2) |
| Ni—N—C(8) | 120.1(3) | 120.5(2) |
| C(7)—N—C(8) | 115.1(3) | 115.3(1) |
| C(2)—C(1)—C(6) | 120.5(4) | 119.9(2) |
| C(2)—C(1)—C(7) | 120.7(4) | 120.9(2) |
| C(6)—C(1)—C(7) | 118.8(4) | 119.2(2) |
| O—C(2)—C(3) | 118.9(4) | 119.3(2) |
| C(1)—C(2)—O | 123.6(4) | 123.0(2) |
| C(1)—C(2)—C(3) | 117.5(4) | 117.7(2) |
| C(2)—C(3)—C(4) | 121.7(4) | 121.8(2) |
| C(3)—C(4)—C(5) | 120.3(4) | 119.8(2) |
| Cl—C(5)—C(4) | 119.3(4) | 119.5(2) |
| Cl—C(5)—C(6) | 120.1(4) | 120.2(2) |
| C(4)—C(5)—C(6) | 120.5(4) | 120.4(2) |
| C(1)—C(6)—C(5) | 119.5(4) | 120.4(2) |
| C(1)—C(7)—N | 126.9(4) | 126.5(2) |
| N—C(8)—C(9) | | 110.2(3) |

II = —*x*, —*y*, —*z*.

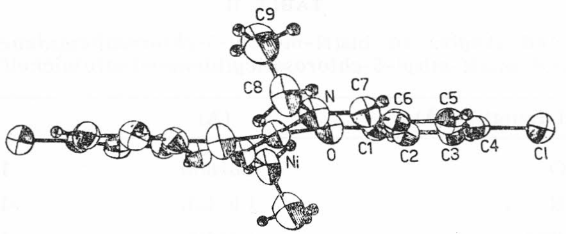

Figure 2. An ORTEP drawing of the *bis*(*N*-ethyl-5-chlorosalicylideneiminato)nickel--(II) molecule with the atom numbering scheme. The coordination plane is viewed edgewise.

complex[7,8] the two compounds are similar, exhibiting the same sort of molecular step. In the chloro derivative, this is smaller in terms of the deviation of the nickel atom from the plane of best fit through a benzene ring being 0.351 Å compared with 0.524 Å. This gives an overall step height of 0.702 Å compared with 1.048 Å. The deviations of the chelate ring atoms in the chloro derivative are 0.017 Å gor O, 0.023 Å for N, and 0.075 Å for C(7), showing that the folding or stepping takes place almost entirely at the donors. The corresponding figures for the parent complex are 0.0, 0.07 and 0.08 Å.

There are no significant intermolecular contacts but, as it can be inferred from Figure 2, there is a very close approach of one hydrogen of the methylene group (C(8)) to the oxygen of the other ligand. This distance is 2.298 Å (cf. 2.60 Å, the sum of van der Waals radii)[13] and is one of the factors connected with the conformation of these molecules, which needs to be assessed as more and accurate structural determinations become available.

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## SAŽETAK

### Kristalna struktura i konformacija *bis*(*N*-metil-5-klorosalicilideniminato)nikla(II) i *bis*(*N*-etil-5-klorosalicilideniminato)nikla(II)

*Tony C. Jones, T. Neil Waters, Branko Kaitner i Boris Kamenar*

Kristalne strukture *bis*(*N*-metil-5-klorosalicilideniminato)-nikla(II) (A) i *bis*(*N*-etil-5-klorosalicilideniminato)nikla(II) (B) određene su rentgenskom strukturnom analizom (metodom teškog atoma) i utočnjene metodom najmanjih kvadrata do vrijednosti $R = 0{,}044$ za (A) i $R = 0{,}040$ za (B). Obje su strukture centrosimetrične, s atomom nikla u planarnoj koordinaciji. Molekule oba kompleksna spoja imaju »stepeničastu« konformaciju s izrazitom razlikom u visini stepenice: 0,121 Å u slučaju strukture (A) i 0,702 Å u slučaju (B). Duljine veza Ni—O i Ni—N iznose 1,818 Å i 1,924 Å u (A) te 1,830 Å i 1,916 Å u (B).