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Synthesis, characterization and crystal structure of bis(1H-indole-3-ethylene-3′-ethoxysalicylaldimine)nickel(II)

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Abstract

A complex of Ni(II) with the Schiff base 1H-indole-3-ethylene-3′-ethoxysalicylaldimine (3EtOsalTPA) has been prepared and characterized by means of elemental analysis, IR, ^{1}H NMR, electronic spectroscopy, magnetic susceptibility measurements, as well as by X-ray diffraction. The compound crystallizes in the monoclinic system, $P2_1/c$ space group, $Z=2$, cell dimensions: $a=10.794(1)$, $b=10.494(1)$, $c=14.571(1)$ Å; $\beta=98.93(9)°$, $V=1630(1)$ Å^3, final $R=0.056$. The geometry around the Ni atom is square planar with the metal lying on a center of symmetry. There is an intermolecular hydrogen bond between the N atom of the indol group and the phenolic oxygen of the ethoxysalicylaldiminate moiety, through the $-x, y+\frac{1}{2}, -z-\frac{1}{2}$ symmetry operation.

Introduction

In previous reports we have described the synthesis and characterization of Cu(II), Ni(II) and Co(II) complexes with the Schiff base 1H-indole-3-ethylen-salicylaldimine (salTPA) and their 3-methoxy and 5-methoxy derivatives [1–5]. We have prepared a new Ni(II) complex with the ligand bis(1 H-indole-3-ethylene-3′-ethoxysalicylaldimine, Fig. 1. In this paper we describe the results of its structural and spectroscopic study and we discuss them in comparison with those of related compounds to see how the nature and position of the alkoxy group affects its properties.

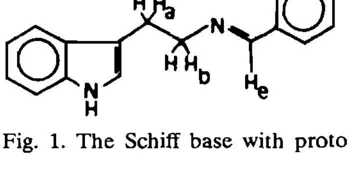

Fig. 1. The Schiff base with proton numbering scheme.

Experimental

Synthesis

3EtOsalTPA was prepared in a similar way to those reported for the syntheses of 3MeOsalTPA and 5MeOsalTPa [1–5]. The yellowish-orange microcrystalline compound was recrystallized twice from ethanol. *Anal.* Calc. for $C_{19}H_{20}N_2O_2$: C, 74.00; H, 6.54; N, 9.08. Found: C, 73.92; H, 6.56; N, 9.03%.

Ni(3EtOsalTPA)$_2$ was prepared as previously reported [1] for the complex Ni(salTPA)$_2$. Green crystals suitable for X-ray diffraction analysis were grown from CH_2Cl_2. *Anal.* Calc. for $NiC_{38}H_{36}N_4O_4$: C, 67.98; H, 5.40; N, 8.34; Ni, 8.72. Found: C, 68.02; H, 5.35; N, 8.37; Ni, 8.57%. Analyses of C, H and N were performed with a Carlo Erba 1106 microanalyzer. Ni was determined by atomic absorption with a Perkin-Elmer 3030 spectrophotometer.

Physical measurements

Infrared spectra were recorded on a Nicolet 5PCFT-IR spectrophotometer using KBr pellets as support, in the 4000–250 cm^{-1} spectral range. ^{1}H NMR spectra were recorded at 297 K on a Bruker WP 250 SI apparatus at 200 MHz, with TMS as internal standard after dilution of the sample in

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$CDCl_3$. Solid state electronic spectra were run on a Beckman DU-2 spectrophotometer after dilution of the sample in $BaSO_4$, in the 400–1000 nm spectral range. Electronic spectra in a chloroform solution of the complex were obtained using a Perkin-Elmer 550S spectrophotometer. Variable temperature (77–297 K) magnetic susceptibility data were collected on powdered samples on a Faraday type microbalance.

Crystallographic data collection and structure determination

Crystal data: $NiC_{38}H_{36}N_4O_4$, $M=671.44$; monoclinic, space group $P2_1/c$, $a=10.794(1)$, $b=10.494(1)$, $c=14.571(1)$ Å, $\beta=98.93(9)°$, $V=1630(1)$ Å^3, $D_m=1.36$ (picnometry), $D_c=1.37$ g cm^{-3}, $Z=2$, $\mu=12.04$ cm^{-1} (Cu Kα), $F(000)=704$.

A green crystal of approximate dimension 0.2×0.5×0.6 mm was mounted on a four circle computer-controlled Siemens AED diffractometer and data collected with the w:θ scan mode, using graphite monochromated Cu Kα radiation ($\lambda=1.5418$ Å). Cell constants were determined by least-squares refinement of the setting angles of 28 reflections in the range $20 \leqslant 2\theta \leqslant 40°$. Of the 2048 independent reflections with $3 \leqslant 2\theta \leqslant 120°$, 1844 were considered observed with $I \geqslant 2\sigma(I)$; index range *h* 0, 11; *k* 0, 11; *l* 1, 16. Two standard reflections measured every 60 min showed no intensity decay.

The structure was solved by the heavy-atom method and successive Fourier syntheses [6]. In the course of the isotropic least-squares refinement, an empirical absorption correction was carried out with the DIFABS program [7]. All the hydrogen atoms were located on a difference Fourier synthesis map. Refinement with anisotropic thermal parameters for non-hydrogen atoms, isotropic for the hydrogen atom and the methyl of the ethoxy moiety as a rigid group converged to a standard crystallographic residual of $R=0.056$ [8], unit weights, *F* minimized. The highest peak in the final difference Fourier synthesis map showed a density of 0.44 e Å^{-3}. Scattering factors were taken from standard tables [9]. Bond angles and distances, torsion angles and mean least-squares planes were calculated with the PARST package of programs [10].

Results and discussion

Final values of the positional non-hydrogen atoms are given in Table 1 with the atom-numbering scheme reported in Fig. 2. Interatomic angles and bond

TABLE 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å^2) with e.s.d.s. in parentheses

Atom	*x/a*	*y/b*	*z/c*	B_{eq}[a]
Ni	0.0	0.0	0.0	2.7(1)
O20	−0.1657(3)	0.0145(3)	0.0149(2)	3.3(2)
O21	−0.3667(3)	−0.0304(4)	0.0896(3)	4.4(2)
N12	0.0100(4)	0.1771(4)	−0.0232(3)	2.8(2)
N2	0.2321(5)	0.3537(5)	−0.3464(4)	4.6(3)
C1	0.1482(6)	0.3638(6)	−0.2848(4)	3.9(3)
C3	0.2522(5)	0.2264(6)	−0.3607(4)	3.6(3)
C4	0.3252(6)	0.1636(10)	−0.4187(5)	5.3(4)
C5	0.3262(7)	0.0320(9)	−0.4167(6)	6.5(5)
C6	0.2574(7)	−0.0364(8)	−0.3611(6)	5.6(4)
C7	0.1873(6)	0.0238(6)	−0.3046(5)	4.3(3)
C8	0.1834(5)	0.1572(5)	−0.3036(4)	3.0(2)
C9	0.1185(5)	0.2467(5)	−0.2545(4)	3.3(3)
C10	0.0318(6)	0.2142(7)	−0.1866(4)	4.0(3)
C11	0.0942(6)	0.2279(5)	−0.0865(4)	3.2(3)
C13	−0.0562(5)	0.2606(5)	0.0128(4)	3.2(3)
C14	−0.1597(5)	0.2347(5)	0.0611(4)	3.1(3)
C15	−0.2135(6)	0.3332(6)	0.1061(4)	4.3(3)
C16	−0.3187(6)	0.3123(6)	0.1456(4)	4.6(3)
C17	−0.3724(6)	0.1908(6)	0.1408(4)	4.5(3)
C18	−0.3219(5)	0.0925(5)	0.0964(4)	3.4(3)
C19	−0.2119(4)	0.1113(5)	0.0572(3)	2.7(2)
C22	−0.4702(5)	−0.0600(7)	0.1373(4)	5.1(3)
C23	−0.4907(6)	−0.2015(7)	0.1295(5)	6.3(4)

[a] $B_{eq}=(1/3)$ sum $(b_{ij}A^*_iA^*_jA_iA_j \cos(A_iA_j))$.

TABLE 2. Bond distances (Å), bond angles (°) and selected torsion angles (°) and planes

Ni–O20	1.841(3)	Ni–N12	1.895(4)
O20–C19	1.325(6)	O21–C22	1.438(7)
N12–C11	1.490(8)	N12–C13	1.292(7)
N2–C1	1.375(9)	N2–C3	1.375(8)
N2–H2	0.914(81)	C1–C9	1.361(8)
C3–C4	1.406(10)	C3–C8	1.401(9)
C4–C5	1.381(14)	C5–C6	1.382(12)
C6–C7	1.358(11)	C7–C8	1.401(8)
C8–C9	1.428(8)	C9–C10	1.503(9)
C10–C11	1.516(8)	C13–C14	1.436(8)
C14–C15	1.398(9)	C14–C19	1.410(7)
C15–C16	1.368(10)	C16–C17	1.398(9)
C17–C18	1.375(9)	C18–C19	1.409(8)
C22–C23	1.503(10)		
O20–Ni–N12	91.3(2)	Ni–O20–C19	124.1(3)
C18–O21–C22	117.3(5)	Ni–N12–C13	122.8(4)
Ni–N12–C11	121.2(3)	C11–N12–C13	115.9(4)
C1–N2–C3	108.0(5)	N2–C1–C9	110.8(5)
N2–C3–C8	107.6(5)	N2–C3–C4	131.5(6)
C4–C3–C8	120.8(6)	C3–C4–C5	117.3(6)
C4–C5–C6	121.9(8)	C5–C6–C7	121.0(8)
C6–C7–C8	119.5(7)	C3–C8–C7	119.5(5)
C7–C8–C9	132.9(5)	C3–C8–C9	107.6(5)
C1–C9–C8	105.8(5)	C8–C9–C10	125.8(5)
C1–C9–C10	128.4(5)	C9–C10–C11	112.5(5)
N12–C11–C10	109.8(5)	N12–C13–C14	126.3(5)
C13–C14–C19	119.4(5)	C13–C14–C15	120.1(5)
C15–C14–C19	120.4(5)	C14–C15–C16	120.7(6)
C15–C16–C17	119.3(6)	C16–C17–C18	121.1(5)
O21–C18–C17	125.2(5)	C17–C18–C19	120.4(5)
O21–C18–C19	114.3(4)	C14–C19–C18	118.0(5)
O20–C19–C18	118.9(5)	O20–C19–C14	123.1(4)
O21–C22–C23	107.0(5)		
O20–Ni–N12–C13	30.3(4)	N12–Ni–O20–C19	−38.7(4)
Ni–O20–C19–C14	27.6(6)	Ni–N12–C13–C14	−11.2(8)
N12–C13–C14–C19	−12.0(9)	C13–C14–C19–O20	3.8(8)

Planes with deviations (Å): 1: C13 0.01, C14 −0.02, C19 0.01, O20 −0.00, N12 −0.15, Ni −0.77; 2: C14 0.01, C15 0.00, C16 −0.00, C17 −0.00, C18 0.01, C19 −0.01, C13 0.14, O20 0.01, Ni −0.64.

lengths, and some selected torsion angles and planes are listed in Table 2.

The Ni atom is lying on a center of symmetry and is four coordinated to the phenolic oxygen atoms and iminic nitrogen atoms of two different Schiff base units which are related through the center of symmetry. The geometry around the metal is square planar. However, the Ni—O, 1.841(3) Å and Ni—N, 1.895(4) Å bond distances together with the N—Ni—O angle (91.3(2)°) within the same ligand unit, show a slightly rhombohedral distortion. The six-membered chelate ring, is observed puckered as shown by the O20—Ni—N12—C13, 30.3(5)° and C19—O20—Ni—N12, −38.7(4)° torsion angles. In the related compounds [2, 11–13] the equivalent rings are nearly planar, this structural difference probably due to the accommodation of the larger ethoxy groups present in our compound, in order to avoid steric hindrance. The planar indolic moiety (maximum deviation from the mean least-squares plane is −0.015(6) Å for N2), is connected, through the C10—C11 bond, in an antiperiplanar fashion to the chelate ring, as indicated by the C9—C10—C11—N12 torsion angle −172.0(5)°.

The crystalline structure can be described in terms of chains of complex units along the *c* crystallographic axis. The complex units in the chains are held together by intermolecular hydrogen bonds, Fig. 3. Each hydrogen bond is formed between the nitrogen atom of the indolic group and the phenolic oxygen atom

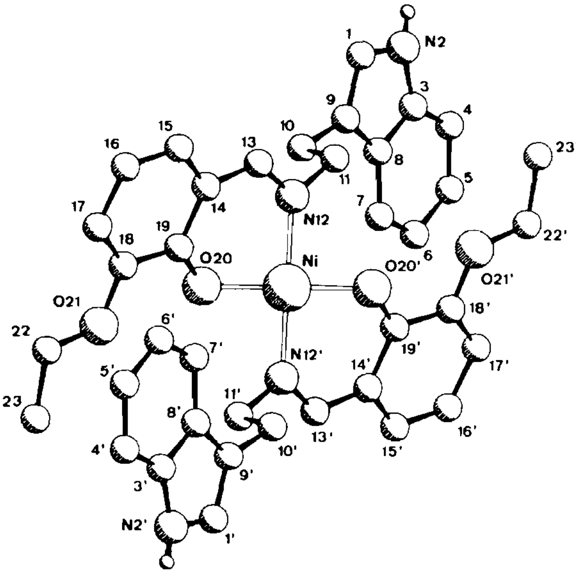

Fig. 2. Pluto drawing showing the atom-numbering scheme for $Ni(3EtOsalTPA)_2$.

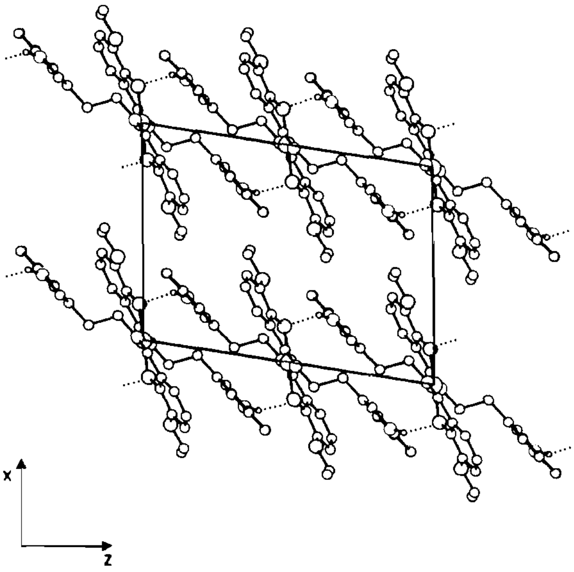

Fig. 3. Crystalline structure showing the chains of complex units along the *c* crystallographic axis.

of the ethoxysalicylaldiminate moiety, through the symmetry operation $-x, y+\frac{1}{2}, -z-\frac{1}{2}$; the N—O bond distance is 2.974(6) Å and the N—H—O angle is 151.6(67)°.

Infrared, ^1H NMR and electronic spectroscopies

The IR spectrum of $Ni(3EtOsalTPA)_2$ shows the indole NH signal split into two bands at 3420 and 3300 cm^{-1}. This splitting is attributed to intermolecular hydrogen interactions associated with the indolic NH [1–4], and is consistent with the data revealed by the structural analysis. The free 3EtOsalTPA ligand spectrum exhibits bands at 2960 and 2920 cm^{-1} which are assigned to intramolecular hydrogen interactions between the iminic nitrogen and the phenolic oxygen atom [1–3]. The band at 1630 cm^{-1} in the free ligand spectrum, assignable to CN stretching vibrations of an imonium-type group ($-C{=}N^+-H$), shows an approximate downward shift of 30 cm^{-1} in the spectrum of the complex which can be related to the coordination of the N atom with the metal [1, 2]. Bands at 576, 553, 509 and 300 cm^{-1} in the spectrum of the complex can be attributed to Ni—N and Ni—O coupled vibrations [1, 2].

The ^1H NMR spectrum of the free ligand shows a resonance at 14.16 ppm due to the presence in solution of intramolecular hydrogen interactions between iminic nitrogen and phenolic oxygen atoms (H_f in Fig. 1). For related salTPA [1], 3-MeOsalTPA and 5-MeOsalTPA [2] ligands the equivalent resonances are observed at 10.85, 14.16 and 13.18 ppm, respectively. In the spectrum of the complex this signal disappears as a result of the proton substitution by the Ni atom. The resonances for the H_b and H_e protons (Fig. 1) which for the free ligand appear at 3.90 (triplet) and 8.00 (singlet) ppm, respectively are shifted for the complex to 4.11 (triplet) and 8.13 (singlet) ppm, as a result of the coordination of the iminic nitrogen to the metal.

The electronic spectrum in the solid state shows a band around 615 nm, whilst the spectrum in chloroform solution exhibits a band at 620 nm ($\epsilon = 0.80 \times 10^2$ mol^{-1} cm^{-1}). This band is assignable to the $^1A_{1g} \rightarrow {}^1B_{1g}$ transition and is similar to those observed for related complexes with planar coordination geometries such as $Ni(salTPA)_2$ [1] and $Ni(3\text{-}MeOsalTPA)_2$ [2].

Variable temperature (77–300 K) magnetic susceptibility measurements indicate a diamagnetic behavior which is consistent with a tetracoordinated planar complex.

Supplementary material

Lists of positional and atomic thermal parameters, least-squares mean planes and observed and calculated structure factors are available from the authors on request.

Acknowledgements

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