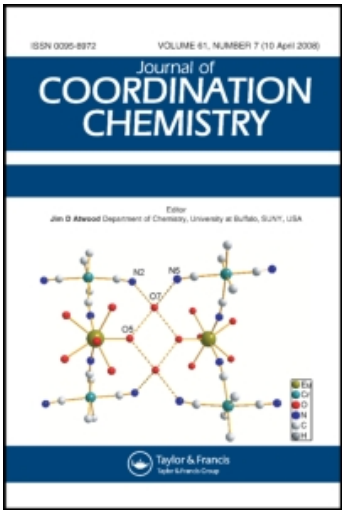

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Crystal structure, electrochemical, and antibacterial activity of the sodium complex formed by *o*-vanillin salicylhydrazone

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The mononuclear sodium(I) complex [NaL(HL)] (**1**) [where HL is $(OH)C_6H_4$–CO–HN–$N{=}CC_6H_3(OMe)(OH)$ synthesized by condensation of *o*-vanillin and salicyloylhydrazine] has been prepared and characterized by IR, elemental analysis, single crystal X-ray diffraction, and cyclic voltammetry. Single crystal X-ray diffraction analysis reveals that NaL(HL) is a neutral complex. Each six-coordinate Na(I) in the unit is linked through O bridges forming a ladder-like arrangement of the 1-D Na(I) double chain. The oxidation–reduction processes have been determined in CH_3CN by cyclic voltammetry. The complex displayed two quasi-reversible reduction couples and one oxidation response between +1.0 and −0.6 V. The trend in the half wave potentials reflects the electronic nature of the hydrazone ligand. The antibacterial activity results show that the complex possesses strong inhibition activity against *Staphyloccus aureus* and *Bacillus subtilis*.

Keywords: Schiff-base complex; Cyclic voltammetry; Crystal structure; Antibacterial activity

1. Introduction

Hydrazones are an important Schiff base which can function as tridentate ligands toward a number of metal cations [1, 2]. Hydrazones are azomethines C=N–N, which are interesting because some play an important role in the treatment of several diseases. Hydrazones and their complexes have gained wide application in industry and in synthetic and analytical chemistry as novel heterogeneous catalysts in oxidation–reduction processes [3–6]. Additionally, hydrazones play an important role in bioinorganic chemistry exhibiting remarkable biological activity, especially against

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Gram-positive bacteria *in vitro*. Some hydrazone derivatives are potential oral drugs to treat genetic disorders like thalassemia [7] and complexes are several fold more potent than the metal free chelate. The biological activities are dependant on their mode of chelation with metal ions. These features include short intramolecular hydrogen bonds and packing configurations. Therefore, studies of the metal complexes are important to explore possible new drugs.

Hydrazone ligands are neutral or monoanionic, bidentate, or tridentate depending on the heterocyclic ring substituents attached to the hydrazone unit and the reaction conditions. Salicyloylhydrazone can coordinate many metal ions and some of its complexes have important material properties [8]. However, few studies have been conducted with the sodium(I) chelated complexes containing tetradentate salicyloylhydrazone. In this study, we report the preparation and characterization of a sodium(I) complex containing the *o*-vanillin salicyloylhydrazone (HL) and describe the IR, electrochemical studies, X-ray crystal structures, and antibacterial activities of this complex.

2. Experimental

2.1. *Materials for synthesis*

Reagents of commercial quality were used without purification. All solvents were dried using standard methods before use.

2.2. *Physical measurements and methods*

C, H, and N microanalyses are conducted on a Perkin Elmer Elemental analyzer. FT-IR spectra were recorded using KBr discs (4000–400 cm^{-1}) on Bruker Tensor 27 instruments. Cyclic voltammograms were performed using 1×10^{-3} M solutions of complex in ethanol using a CHI660B. A three electrode system was composed of a glassy carbon working electrode, a platinum wire auxiliary electrode, and a Ag/AgCl reference electrode.

2.3. *Preparation of o-vanillin salicylhydrazone ligand (HL)*

The hydrazone ligand $C_{15}H_{14}N_2O_4$ was obtained by condensation of 1 mol of *o*-vanillic with 1 mol of salicyloylhydrazine in ethanol [9]. The product was isolated, recrystallized from ethanol, and dried *in vacuo* to give the pure compound in 78.5% yield, m.p. 185°C. Calcd for $C_{15}H_{14}N_2O_4$: C, 62.93; H, 4.92; N, 9.78. Found: C, 63.42; H, 5.04; N, 10.12. IR spectra (KBr, 4000–400 cm^{-1} selected): 3046 (s, νO–H), 1650 (s, νC=O), 1579 (m, νC=N), 1235 (m, νPh–O), 1218 (m, νC–O–C).

2.4. *Synthesis of NaL (HL)*

To a boiling solution of NaN_3 (0.065 g, 0.1 mmol) in ethanol (30 cm^3), an ethanolic solution of *o*-vanillin salicylhydrazone HL (0.0286 g, 0.2 mmol) in ethanol (30 cm^3) was

added slowly with constant stirring and the mixture was refluxed for 4 h. The resulting brown solution was cooled to room temperature and allowed to stand for 1 week during which brown crystals formed. The crystals were filtered off, washed with cold ethanol, and dried in air. m.p. 215°C. IR spectra (KBr, 4000–400 cm^{-1} selected): 3082 (s, νO–H), 1623 (s, νC=O), 1577 (m, νC=N), 1258 (s, νC–O–C or νPh–O), 465(m, νNa–O). Elemental analysis found: C, 60.39; H, 4.85; N, 9.33. Calcd for $C_{30}H_{27}N_4NaO_8$: C, 60.60; H, 4.58; N, 9.42%.

2.5. *X-ray structure determination*

X-ray diffraction data were collected on a Bruker Smart Apex CCD diffractometer ($\lambda = 0.71073$ Å) at 295 K. The intensity data were corrected for Lorentz and polarization effects and empirical absorption corrections were also applied [10]. The structure was solved by direct methods [11] and refined by full-matrix least-squares with anisotropic temperature factors for non-hydrogen atoms. H1B was located by difference Fourier map, and the other hydrogen atoms were located by HYDROGEN program and added to the structure factor calculation, but their positions were not refined. Further details are given in table 1.

2.6. *Biological activity*

Antibacterial activity of the ligand and the metal complex were examined by agar diffusion method [12]. The minimum inhibitory concentration of the ligand and complex were ascertained using different bacteria. The concentration of the drug solution was maintained to be 200 μg mL^{-1} in DMF. One day prior to the test, the bacteria were inoculated in a nutrient broth (inoculation medium) and kept in an incubator at 37°C for 48 h.

Table 1. Crystallographic data for NaL(HL).

Empirical formula	$C_{30}H_{27}N_4NaO_8$
Formula weight	594.53
Temperature (K)	293(2)
Wavelength (Å)	0.71073
Crystal system	Monoclinic
Space group (Å, °)	*P*2/*c*
a	14.59(3)
b	6.127(8)
c	17.55(3)
α	90.00
β	114.17(12)
γ	90.00
Volume, *Z*	1432(4), 2
Calculated density (g cm^{-3})	1.384
Absorption coefficient	0.114
F(000)	616
θ range for data collection	1.53–25.00
Data/restraints/parameters	2524/0/201
Goodness-of-fit on F^2	1.094
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0578$, $wR_2 = 0.1393$
R indices (all data)	$R_1 = 0.0765$, $wR_2 = 0.1517$
Largest different peak and hole	0.499/−0.257

3. Results and discussion

3.1. *Crystal structure*

The structure for NaL(HL) is illustrated in figures 1 and 2 show the ladder-like arrangement of the double chain propagated along the crystallographic *b*-axis; selected bond lengths and angles are collected in table 2.

The X-ray structure determination shows that the complex crystallizes in a $P2/c$ space group with two units of NaL (HL) per unit cell. The sodium(I) coordination sphere is NaO_6. Each Na(I) lies on an inversion center and is defined by six oxygens from four different ligands in a distorted octahedron. Phenolic hydroxyl is not deprotonated and the title complex is electronically neutral. 2-Hydroxy-3-methoxybenzaldehyde-salicyloylhydrazine (HL) is a tridentate bridging ligand and is approximately planar, with a mean deviation of non-H atoms from the plane of 0.0749 Å. Methoxy and phenolic oxygen of each ligand are attached to Na in the form of O,O′-μ coordination whereas carbonylic oxygen is in the form of O-μ coordination. The Na(I) atoms are linked by six O in the EO [13–15] fashion with a ladder-like arrangement of the 1-D Na(I) double chain, with a Na···Na separation of 6.127 Å. The Na–O bond lengths span the range 2.285(3)–2.481(5) Å within the sodium octahedron, and have a mean value of 2.383 Å, similar to previously observed [16–18] (table 2).

In the coordination chain, Na(I) atoms are linked forming a ladder-like double chain. In particular, neighboring L molecule share H1B to form a hydrogen bond along *a*-axis [O1···H1B···O1B = 2.435(3) Å, H1B atom was located in difference maps]. The 1-D chains link into a 2-D supramolecular network with several strong hydrogen bonds.

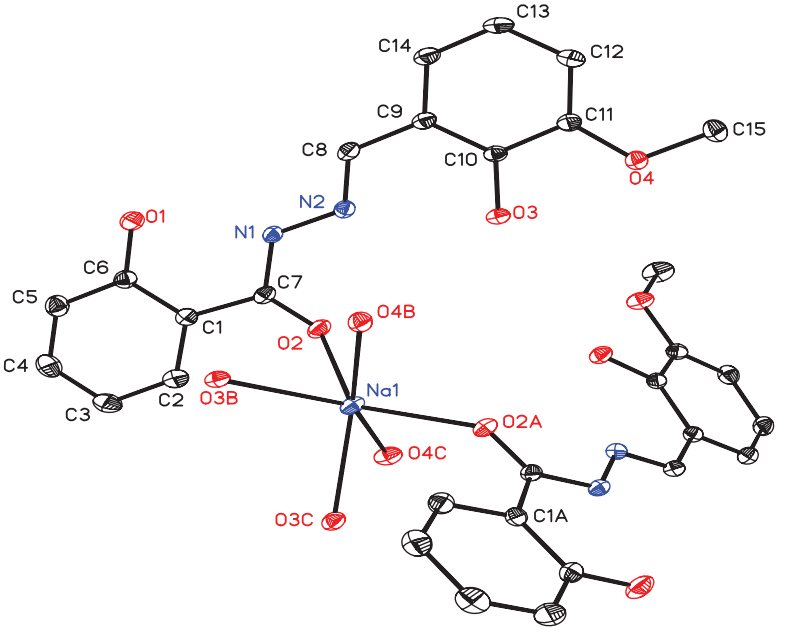

Figure 1. Perspective view with atom labeling of **1** (H atoms omitted for clarity). A: $-x$, y, $0.5-z$; B: x, $-y$, z; C: $-x$, $1-y$, $0.5-z$.

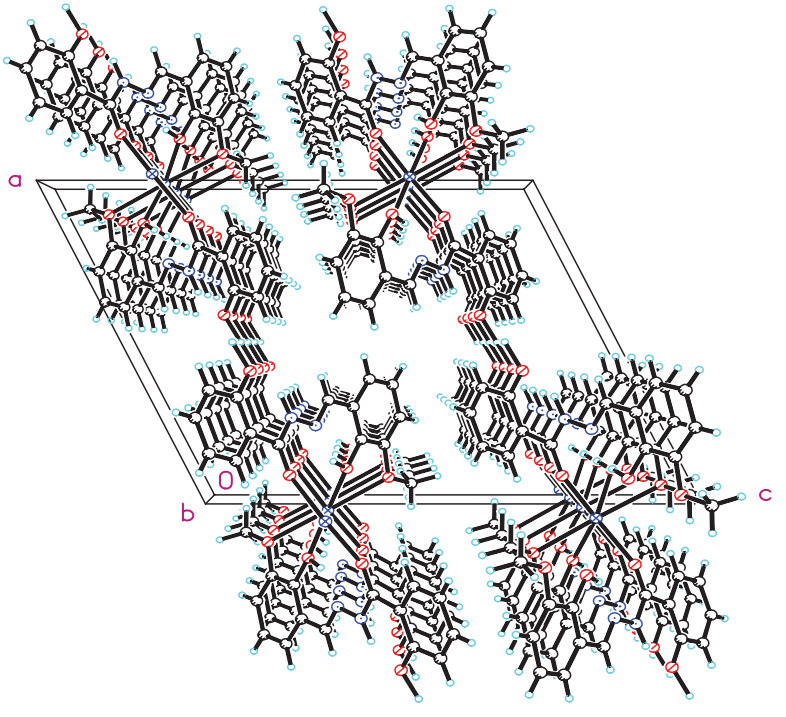

Figure 2. The 2-D framework constructed by NaL(HL).

Table 2. Selected bond lengths (Å) and angles (°).

Na(1)–O(2)	2.283(3)	Na(1)–O(3A)	2.475(4)
Na(1)–O(4A)	2.477(5)	C(15)–O(4)–Na(1A)	120.86(16)
O(2 A)–Na(1)–O(2C)	125.38(14)	O(2)–Na(1)–O(3B)	85.54(14)
O(2A)–Na(1)–O(3B)	133.11(10)	O(3B)–Na(1)–O(3A)	97.39(16)
O(2)–Na(1)–O(4B)	81.94(14)	O(3B)–Na(1)–O(4B)	63.31(11)
O(3C)–Na(1)–O(4B)	135.29(9)	O(2)–Na(1)–O(4B)	87.64(14)
O(4A)–Na(1)–O(4B)	157.15(11)	C(10)–O(3)–Na(1A)	110.53(17)

Symmetry codes: A: $-x$, y, $-z+1/2$; B: x, $y+1$, z; C: $-x$, $y+1$, $-z+1/2$.

H(1A) attached to N1 also participates in one weak intramolecular hydrogen bonding with O1 with distance N1···H1A···O1 of 2.573(4) Å.

3.2. *IR spectra*

The IR spectra of sodium(I) complex were analyzed in comparison with that of the free ligand LH, in the region 4000–400 cm^{-1}. The IR spectrum of the hydrazone shows an intense strong band at 1650 cm^{-1} due to ν(C=O); a shift of 27 to 1623 cm^{-1} indicates coordination of the carbonyl oxygen to metal ion. A strong band in the 1231–1240 cm^{-1} range (1235 cm^{-1}) in the Schiff base has been assigned to Ph–O stretch. The band is strongly affected by chelation through the phenolic oxygen atom of the salicyloylhydrazone shifting to higher frequency in the 1258 cm^{-1} range, implying coordination

of phenolic oxygen with the metal ion [19]. The band at 1577 cm^{-1} due to ν(C=N) in the complex does not shift, suggesting that azomethine nitrogen is not coordinated to sodium. The band at 1218–1222 cm^{-1} in free ligand can be attributed to ν(C–O–C), also shifted to 1258 cm^{-1}, indicating linkage between the metal ion and O of methoxy. The ν(O–H) broad band at 3046 cm^{-1} for the ligand is shifted significantly to lower frequency 3082 cm^{-1} in the complex from O···H···O hydrogen bonding [20]. The ligand coordination to the metal center is substantiated by a band for the complex at 460–470 cm^{-1}, attributable to ν(Na–O). These data give evidence for coordination of the Schiff-base ligand to the sodium(I) via three oxygens.

3.3. *Cyclic voltammetry*

The redox properties of the complex in acetonitrile have been investigated by cyclic voltammetry using glassy carbon as the working electrode, [*n*-Bu_4N]Br as supporting electrolyte, and platinum wire as the auxiliary electrode. The cyclic voltammetry of Na(I) complex and 2-hydroxy-3-methoxybenzaldehyde-salicyloylhydrazine are almost the same, displaying three responses in the potential range between +1.0 and −0.6 V. The complex shows one oxidation and two reduction responses on the anodic and cathodic sides, respectively (figure 3). The oxidation–reduction couples observed in the range 0.6–0.8 V (Epa = 0.684 V, Epc = 0.603 V) are assigned to the oxidation of hydroxyl and reduction of ketone of ligand, respectively. This oxidation is quasi-reversible for NaL(HL) with peak to peak separations of 81 mV. The complex exhibits an irreversible reduction process at −0.18 V, which is assigned to the reduction of azomethine group of ligand.

3.4. In-vitro *antimicrobial activity*

The *in-vitro* antibacterial and antifungal activities of HL and NaHL(L) were performed against *Staphyloccus aureus*, *Bacillus subtilis Cohn*, *Diplococcus pneumoniae*

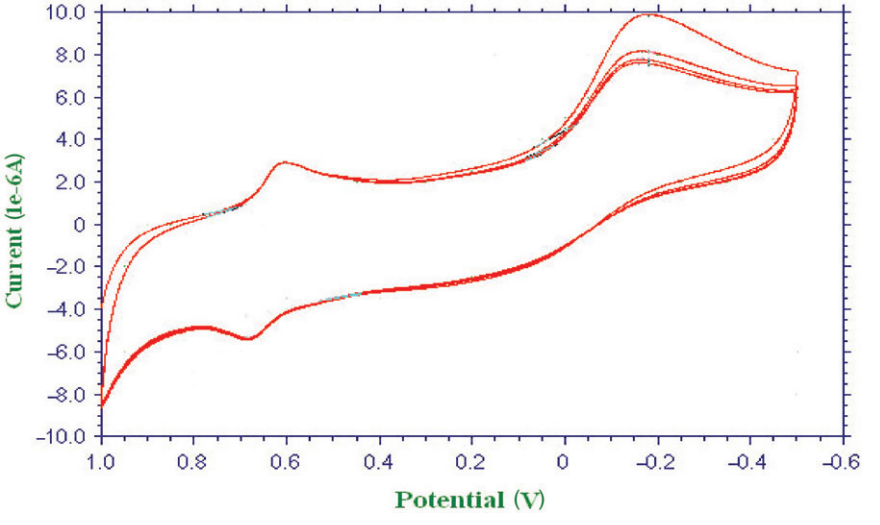

Figure 3. Cyclic voltammogram of NaL(HL).

Table 3. Antibacterial activity of NaL(HL) and ligand (ring of antibacterial diameter millimeter).

Test organisms	*Escherischia coli*	*Staphyloccus aureus*	AS 2,300	*Diplococcus pneumoniae*	*Bacillus subtilis*	ATCC 10231
L	9	15	9	9	20	9
NaL(HL)	9	17	9	9	22	9

(Gram-positive), *Escherischia coli* (Gram-negative), and against the fungi, viz *A. fumigatus*, *C. Albicans*, *C. albicans* (ATCC 10231), *Hansenula anomala* (AS2, 300). The bacteria were cultured in nutrient agar medium. Whatmann filter paper discs (diameter 9.0 mm, solvent used was DMF) were sterilized by dry heat at 140°C for 1 h and saturated with the solution of test compound (concentration: 250 $\mu g\,mL^{-1}$). These discs were air-dried at room temperature to remove solvent, which might interfere with the determination. The obtained results are summarized in table 3.

The antibacterial results show that the ligand and complex possess strong inhibition activity against *S. aureus* and *B. subtilis* NaL(HL) exhibited no distinctly higher biological activity compared with HL *o*-vanillin salicylhydrazone.

Supplementary material

CCDC 699842 contains the supplementary crystallographic data for **1**. The data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: (+44)1223-336-033 or Email: deposit@ccdc.cam.ac.uk).

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