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Syntheses, Characterization and X-ray Crystal Structure of Trinuclear Ni^{II}—Na^{I}—Ni^{II} Assembled with Salen-type Schiff Base

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Abstract

The present investigation describes the synthesis and structural study of a metal-zinc ligand $[NiL]\cdot H_2O$, which was used to generate a trinuclear complex formulated as $\{Ni(\mu\text{-}L)Na(\mu\text{-}L)Ni\}\cdot(SCN)_{0.6}\cdot(Cl)_{0.4}$. The title compound crystallizes in the tetragonal space group $I4_1/acd$ with the following unit cell parameters: a = 185403(5) Å, c = 51.925(2) Å, V = 17849.0(3) Å^3, Z = 16, $R1$ = 0.074 and w$R2$ = 0.209. Each organic molecule acts as a hexadentate ligand and bridges Ni(II) and Na(I). For both Ni(II) cations the coordination environment around the metal center can be described as distorted square planar. The Na(I) cation is eight coordinated and the polyhedron around the sodium ions is best described as a distorted square anti-prism. The means planes of the two phenyl rings with a methoxy substituent form a dihedral angle of 3.870(4)°, while the dihedral angle values of these mean planes with the means plane of the central phenyl ring are, respectively, 11.233(4)° and 14.138(3)°. The Zn–Na distance is 3.4285(7) Å. Weak hydrogen bonds involving C—H as donor and Cl, S or O as acceptor are observed.

1. Introduction

Heteronuclear complexes assembled with Schiff bases are widely examined in the past year. Ligands with smaller N_2O_2 and larger O_2O_2 cages are suitable for assembling heteronuclear with a 3d metal ions and a s-, p-, d- or f-block metal ions. Schiff bases with two cavities of different sizes which can accommodate metal ions of different sizes have

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been synthesized using condensation reaction between well-selected keto precursors and diamines [1–3]. Trinuclear complexes formed by two 3d metals with organic ligand in which the 3d metal atom is situated in the smaller N_2O_2 cage and one s-, d- or f-blockmetal ion is coordinated to larger O_2O_2 cage have been reported [4–13]. Two different strategies are developed for preparing heteronuclear complexes. The first method called self-assembly method is widely used to prepare 3d/4f complexes with remarkable properties [14–20]. The second method consists in preparing, in first step, a precursor complex called metalloligand, [13, 21] which is used in a second step as ligand for preparing the heteronuclear complex. Our synthetic approach consists in using a nickel(II)-based metalloligand $[\mathrm{Ni}L]\cdot(\mathrm{H_2O})$ as precursor synthesized from the bi-compartmental Schiff ligand bis(2-hydroxy-3-methoxybenzylidene)-1,2-diaminobenzene. In this article we report a hetero-trinuclear species $\{\mathrm{Ni^{II}}(\mu\text{-}L)\mathrm{Na^{I}}(\mu\text{-}L)\mathrm{Ni^{II}})]\}\cdot(\mathrm{SCN})_{0.6}\cdot(\mathrm{Cl})_{0.4}$ (**2**) obtained using the metalloligand $[\mathrm{Ni}L]\cdot(\mathrm{H_2O})$ (**1**) and NaSCN (Figure 1). The crystal structure and the physico-chemical properties are discussed.

2. Experimental

2.1. Starting materials and instrumentations

o–Vanillin and 1,3–diaminobenzene, nickel chloride dihydrate, and sodium thiocyanate were purchased from Sigma–Aldrich and used as received without further purification. All solvents used were of reagent grade. The ligand bis(2-hydroxy-3-methoxybenzylidene)-1,2-diaminobenzene(H_2L) was synthesized following the reported procedure [22]. Elemental analyses of C, H and N were recorded on a VxRio EL Instrument. Infrared spectra were obtained on an FTIR Spectrum Two of Perkin Elmer spectrometer in the 4000–400 cm^{-1} region. The molar conductance of 1×10^{-3} M in DMSO solutions of the metal complexes was measured at 25 °C using a WTW LF–330 conductivity meter with a WTW conductivity cell. Room temperature magnetic susceptibilities of the powdered samples were measured using a Johnson Mattey scientific magnetic susceptibility balance (Calibrant: $Hg[Co(SCN)_4]$).

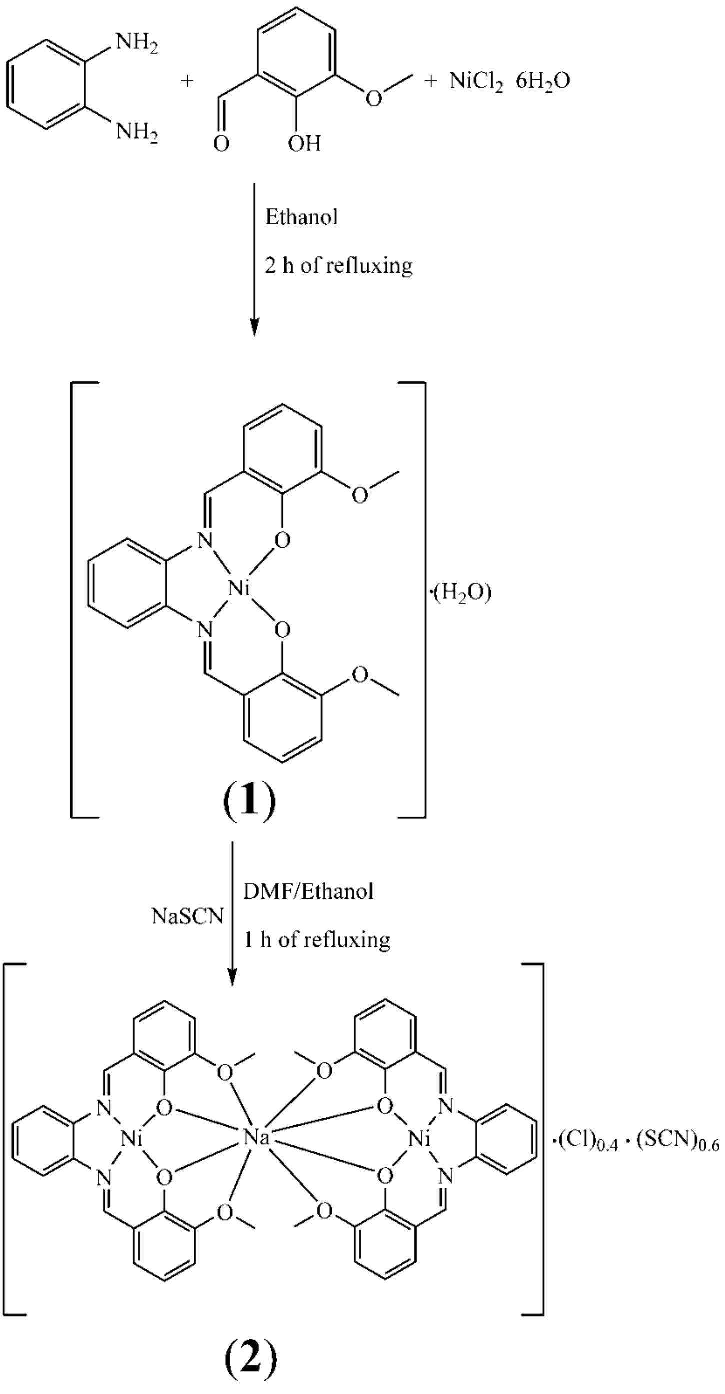

Figure 1. Chemical diagrams for $[Ni(L)]\cdot(H_2O)$ (1) and $\{Ni(\mu\text{-}L)Na(\mu\text{-}L)Ni\}\cdot(SCN)_{0.6}\cdot(Cl)_{0.4}$.

2.2. Preparation of the metallo-ligand {6,6'–Di–methoxy–2,2'–[1,2–phenylenebis (nitrilomethylidyne)]diphenolato–κ4O,N,N'O'}nickel(II) monohydrate (1)

The compound **1** is obtained following the reported procedure with slight modification [22]. In a round bottomed flask, the ligand (H_2L) (10 mmol, 0.374 g) was dissolved in 5 mL of acetonitrile. A solution of $NiCl_2{\cdot}6H_2O$ (10 mmol, 0.2370 g) in 5 mL of ethanol was added. After two hours under reflux, the brown precipitate was recovered by filtration, washed with ether (2 x 10 mL) and dried in air. The compound was formulated as $[NiL]{\cdot}(H_2O)$. Yield: 83%. Elemental Anal. Found (Calcd.) (%): C, 58.58 (58.53); H, 4.47(4.45); N, 6.21 (6.19). IR (ν, cm^{-1}): [ν(O–H) 3371, ν(OH_2) 851]; 1615ν(C=N); 1586; 1533; 1485; 1460;1248, ν(C–OPh); 1201 ν(C–OMe). Conductance Λ ($S{\cdot}cm^2{\cdot}mol^{-1}$): 3. μ_{eff} (μ_B): 0.

2.3. Preparation of Ni/Na complex : {Ni(μ-L)Na(μ-L)Ni}.(SCN)0.6.(Cl)0.4

To a solution of $[NiL]{\cdot}(H_2O)$ (**1**) (1 mmol, 0.4511 g) in 5 mL of DMF was added a solution of $NaNO_3$ (3 mmol, 0.255 g) in 5 mL of ethanol. The mixture was refluxed for two hours. On cooling yellow solution was filtered. The filtrate was left for slow evaporation. On standing for two weeks, yellow crystals of (**2**) suitable for X-ray diffraction were isolated. Yield: 74 %. Elemental Anal. Found (Calcd.) for $C_{46.6}H_{36}Cl_{0.4}N_{4.6}NaNi_2O_8S_{0.6}$(%) C, 57.10 (57.08); % H, 3.87 (3.85); % N, 6.87 (6.84); % Cl1.51 (1.48); % S2.05 (2.02). IR (ν, cm^{-1}): 3319; 2057; 1606; 1594; 1581; 1543; 1485; 1463; 1242 ; 1192] 749, 487. Conductance Λ ($S{\cdot}cm^2{\cdot}mol^{-1}$): 62.$\mu_{eff}$ (μ_B): 0.

2.4. Crystal structure determination

Crystals suitable for single-crystal X-ray diffraction, of the reported compounds, were grown by slow evaporation of MeOH solution of the complexes. Details of the crystal structure solution and refinement are given in Table 1. Diffraction data were collected using an ENRAF NONIUS Kappa CCD diffractometer with graphite monochromatized MoKα radiation (λ = 0.71073 Å). All data were corrected for Lorentz and polarization effects. No absorption correction was applied. Complex scattering factors were taken from the program package SHELXTL [23]. The structures were solved by direct methods, which revealed the position of all non-hydrogen atoms. All the structures were refined on F^2 by a full-matrix least-squares procedure using anisotropic displacement parameters for all non-hydrogen atoms [24]. The hydrogen atoms of water molecules and NH groups were located in the Fourier difference maps and refined. Others H atoms (CH and CH_3 groups) were geometrically optimized and refined as riding model by AFIX instructions. Molecular graphics were generated using ORTEP [25].

Table 1. Crystal and structure refinement data for $\{Ni(\mu\text{-}L)Na(\mu\text{-}L)Ni\}\cdot(SCN)_{0.6}\cdot(Cl)_{0.4}$.

Chemical formula	$C_{44}H_{36}N_4NaNi_2O_8\cdot 0.4(Cl)\cdot 0.3(C_2N_2S_2)$
Mr	938.20
Crystal system, space group	Tetragonal, $I4_1/acd$
Temperature (K)	140
a (Å)	18.5403 (5)
c (Å)	51.925 (2)
V (Å^3)	17849.0 (13)
Z	16
Radiation type	Mo $K\alpha$
μ (mm^{-1})	0.96
Crystal size (mm)	0.22 × 0.15 × 0.06
T_{min}, T_{max}	0.752, 1.000
No. of measured reflections	28809
No. of independent reflections	4077
No. of observed reflections	3254
R_{int}	0.068
$R[F^2 > 2\sigma(F^2)], wR(F^2)$	0.0741, 0.2085
Indices R (all data)	$R_1 = 0.0896$, $wR_2 = 0.1992$
GOF	1.12
No. of reflections	4077
No. of parameters/restraints	295 / 0
$\Delta\rho_{max}$, $\Delta\rho_{min}$ (e Å^{-3})	1.10, −0.57

3. Result and Discussion

3.1. General study

The metallo ligand [Ni(L)]·H_2O (**1**) was synthesized by mixing the ligand H_2L and $NiCl_2·6H_2O$ in acetonitrile under reflux. The resulting [Ni(L)]·H_2O (**1**) was reacted with sodium nitrate and ammonium thiocyanate in molar ratio 1:3:3to yield a trinuclear complex formulated as {Ni(μ-L)Na(μ-L)Ni}·(C_2N_2S)·(Cl) (**2**) after slow evaporation of the filtrate. The IR spectrum of the ligand is compared to the spectrum of the metalloligand. The band due to the $\nu_{C=N}$ with appears at 1632 cm^{-1}in the spectrum of the ligand is shifted to low frequency in the spectrum of the metalloligand and appears at 1615 cm^{-1}. This fact indicates the involvement of the azomethine nitrogen atom to the coordination to the Ni(II) cation. The involvement of the phenoxy oxygen atom to the coordination is assumed by shift of the $\nu_{C—O(phenolic)}$ which is pointed at 1248 cm^{-1}in the spectrum of H_2L and at 1242 cm^{-1}in the spectrum of [Ni(L)]·H_2O. The methoxy oxygen atoms remain uncoordinated as attested by the non-shift of its band pointed in both spectra at 1201 cm^{-1}. The band at 3319 cm^{-1} in the metalloligand spectrum is due to the free water molecule. Upon reaction of the metalloligand with Na(I) cation the resulting compound gives a FTIR spectrum which is similar to the spectrum of the metalloligand. All band are slightly shifted to low frequencies. Shifted. The band due to the $\nu_{C—O(methyl)}$ is shifted from 1201 cm^{-1}in the spectrum of (**1**) to 1192 cm^{-1}in the spectrum of (**2**) indicating the involvement of the methoxy oxygen atom to the coordination to the Na(I). New sharp bands appear at 2057 cm^{-1}, 749 cm^{-1} and 487 cm^{-1} and are attributed, respectively, to ν_{as}(CN), ν_s(CS) and δ(SCN) of the uncoordinated thiocyanate moiety [26] present in the trinuclear compound. The molar conductance in DMF of compound **1** is 3 $S·cm^2·mol^{-1}$, while the conductance of **2** is 62 $S·cm^2·mol^{-1}$. These values indicate that the compound **1** is a neutral electrolyte while the compound **2** is 1:1 electrolyte [27]. Both NiL and {Ni(μ-L)Na(μ-L)Ni}·$(SCN)_{0.6}$·$(Cl)_{0.4}$ showed diamagnetism, indicating that the compounds assume a square planar geometry around Ni(II), as expected for a Ni(II) d^8 species [28].

3.2. Structure description of the complex{Ni(μ-L)Na(μ-L)Ni}.(SCN)0.6.(Cl)0.4

The detailed crystallographic data for the compound is listed in Table 1. Selected interatomic distances and angles are shown in Table 2. The compound crystallizes in the tetragonal system with the space group *I*4_1/*acd*. The crystal structure of the complex is shown in Figure2 and comprises two Ni(II) cation, one Na(I) cation, two di-negative ligand, one free chloride anion and one free thiocyanate anion. Each ligand acts as bridge between one Ni(II) cation and the Na(I). The Ni(II) is coordinated to the ligand through two azomethine nitrogen atoms and two phenoxo oxygen atoms. These two phenoxo oxygen atoms link the Na(II) cation which is also coordinated to two methoxy oxygen atoms. Thus, the two Ni(II) ions are tetracoordinated while the Na(I) is octacoordinated. In the trinuclear complex, both Ni ions are situated in an N_2O_2 environment which can be characterized by tetragonality parameter: $\tau_4 = (360 - \alpha - \beta) / 141$: α and β are the two largest angles around the central atom; $\tau_4 = 0$ designates a perfect square planar geometry and $t_4 = 1$ gives a perfect tetrahedron) [29]. The $\tau_4$value of 0.0094 is indicative of a slightly distorted square planar geometry around the Ni atoms. The Ni—O [1.852(4)Å and 1.845(4) Å] and Ni—N [1.850(5) Å and 1.853(5) Å] are comparable to the Ni—O and Ni—N bonds lengths reported for the metalloligand complex [30]. The Na(I) cation is situated in an O_8 environment. The environment around the Na(I) is best described as a distorted square-antiprism (Figure 3). The two square faces are occupied, respectively, by two phenoxo oxygen atoms of the same ligand and two methoxy oxygen atoms from two different ligand molecules: O2, O3, O1 and O1^{i} and O2^{i}, O3^{i}O4 and O4^{i}. The bonds lengths of Na—$O_{phenoxo}$ [2.396(4) Å and 2.389(4) Å] are shorter than the distances Na—$O_{methoxy}$ [2.538(4) Å and 2.554(4) Å]. These values are comparable to those reported for the complex [Zn(μ-*L*)Na(NO_3)(EtOH)] [11]. The dihedral angle between the two phenyl rings (C2—C7 and C9—C14) with methoxy group is 3.870(4)°,while these rings form with the central phenyl ring (C16—C21) dihedral angles of 11.1233(4)° and 14.138(3)°, respectively. Each ligand form with the Ni(II) two six membered rings of type NiOCCCN with bites angles of 95.39(18)° [N1—Ni1—O2] and 95.31(19)° [O3—Ni1—N2]. These two rings form a dihedral angle of 8.580(3)°. The means planes occupied by the atoms of the two metalloligand a not quite perpendicular with dihedral angle of 79.16(1)°. Additionally, each ligand form two five membered rings of type NaOCCO with Na(I) with bite angles of 63.70(13)° [O2—Na1—O1] and 63.74(13)° [O3—Na1—O4]. The two NaOCCO rings form dihedral angles of 3.432(3)°. These facts are indicative of that the ligands molecule are twisted. The positive charge of the two Ni(II) cations and the Na(I) cation are balanced by the two dideprotonated ligand L^{2-}, 0.4 chloride anion (Cl^-) and 0.6 thiocyanate (SCN^-) anion. The Ni—Na distance is 3.4285(7) Å. The hydrogen bonding geometry of the compound is listed in Table 3. In tramolecular hydrogen bond C15—H15···Cl1,C13—H13···Cl1 resulting in a *S*(7) ring and C22—H22B···S1has been observed. Intermolecular hydrogen bond C22—H22C···O3^i(i = −x+1/2, y, −z+1) link the molecules to form sheets parallel to the *b* axis. The chloride anions are located in the empty space between the sheets (Figure 4, Table 3).

Table 2. Selected geometric parameters (Å, °).

Bond	Distance	Bond	Angle
Ni1—Na1	3.4285 (7)	O2—Ni1—N2	178.56 (19)
Ni1—O2	1.852 (4)	O3—Ni1—N1	177.21 (19)
Ni1—O3	1.845 (4)	O3—Ni1—O2	83.30 (16)
Ni1—N1	1.850 (5)	O2^i—Na1—O1	79.41 (15)
Ni1—N2	1.853 (5)	O3—Ni1—N2	95.31 (19)
Na1—O2	2.398 (4)	N1—Ni1—O2	95.39 (18)
Na1—O2^i	2.398 (4)	N1—Ni1—N2	86.0 (2)
Na1—O3	2.396 (4)	O2^i—Na1—O2	128.8 (2)
Na1—O3i	2.396 (4)	O2^i—Na1—O4	95.74 (13)
Na1—O4	2.538 (4)	O2—Na1—O4	125.31 (13)
Na1—O4^i	2.538 (4)	O3—Na1—O2^i	139.72 (13)
Na1—O1	2.554 (4)	O3—Na1—O3^i	141.0 (2)
Na1—O1^i	2.554 (4)	O3^i—Na1—O1^i	125.36 (13)

Symmetry code: (i) −x+1/2, y, −z+1.

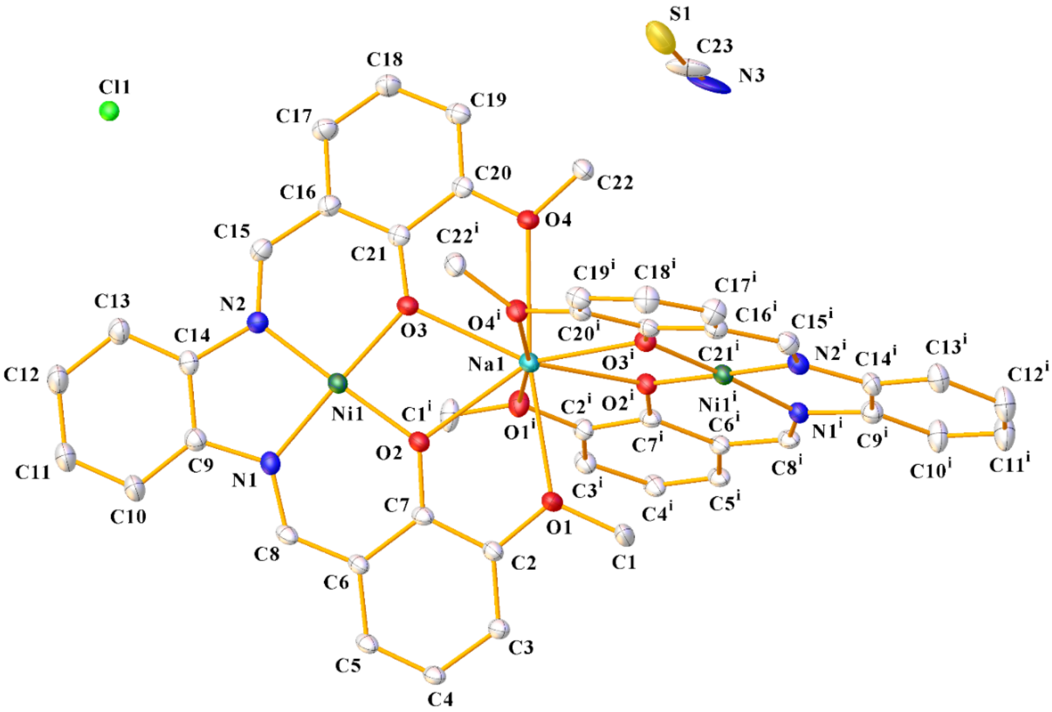

Figure 2. Crystal structure of the trinuclear complex (**2**).

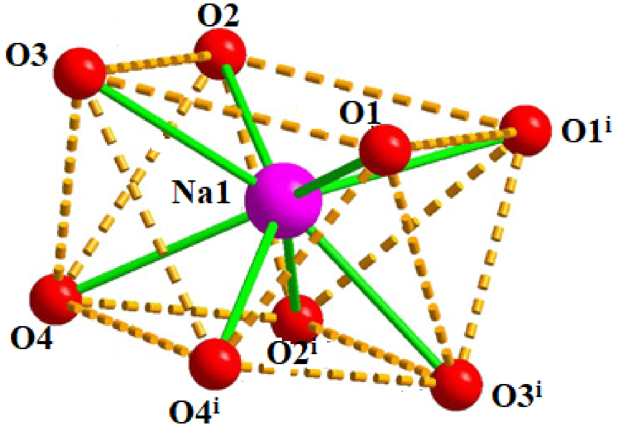

Figure 3. Plot showing the coordination sphere of the sodium ion in the crystal.

Table 3. Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
C15—H15···Cl1	0.95	2.76	3.640(6)	155.2
C22—H22B···S1	0.98	2.78	3.758(7)	172.2
C22—H22C···O3^{i}	0.98	2.59	3.363(7)	135.8
C13—H13···Cl1	0.95	2.96	3.895(7)	168.6

Symmetry code: (i) −x+1/2, y, −z+1.

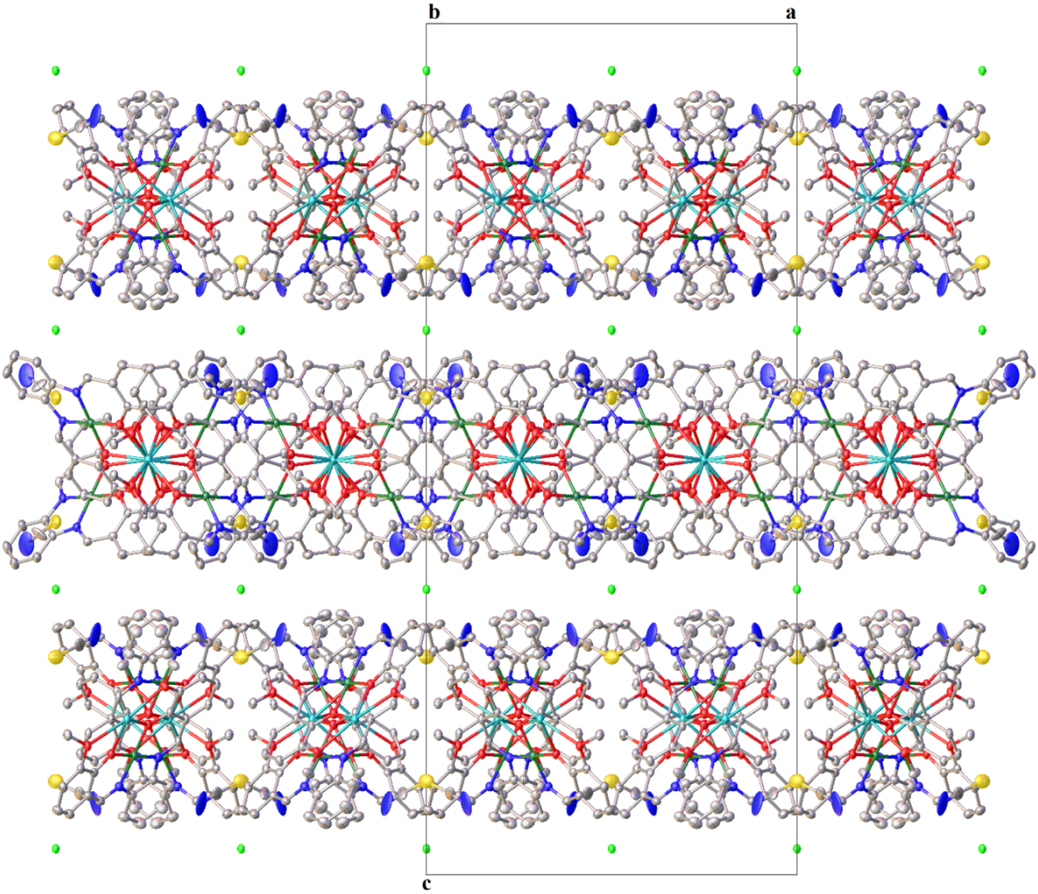

Figure 4. View of the title complex along the b axis showing the sheets formed by hydrogen bonding. The sheets separated by chloride anion.

4. Conclusion

In this work, we have successfully synthesized a trinuclear compound formulated as $\{Ni(\mu\text{-}L)Na(\mu\text{-}L)Ni\}\cdot(SCN)_{0.6}\cdot(Cl)_{0.4}$(**2**) using the metalloligand $[NiL]\cdot(H_2O)$(**1**) firstly isolated. Suitable crystal for X-ray analyzes was obtained by slow evaporation of methanol solution of **2** for few days. The metalloligand and the complex are studied by FTIR, room temperature magnetic moment measurement and conductance measurement. X-ray data collection, data reduction and structure refinement of complex **2** revealed the structure of the trinuclear complex. The two Ni(II) ions tetracoordinated and are situated in square planar environment defined by O_2O_2 cavity and the Na(I) which is octacoordinated is situated in a square antiprism environment define by a O_8 inner. Weak inter and intra molecular hydrogen bonds consolidate the structure.

5. Supporting Information

CCDC-2255666 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge via https://www.ccdc.cam.ac.uk/structures/, or by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033.

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