Syntheses, Characterization and X-ray Crystal Structure of Polymeric Heteronuclear Oxo-bridged Fe/Na Assembled with Salen-type Schiff Base and Dicyanamide

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Abstract: Reaction of FeCl₂·4H₂O with 2-((2-((2-hydroxy-3-methoxybenzylideneamino)phenylimino)methyl)-6-methoxyphenol (H₂L) gives the metalloligand [Fe(L)]·(H₂O) (1). Reaction of metalloligand (1) with three fold of sodium dicyanamide Na[N(CN)₂] gives the new tetranuclear compound [{FeIINaI(L)(EtOH)(HN(CN)₂)}(µ-O){FeIII NaI(L)(NO₃)}]ₙ (2) in which one of the two irons is oxidized to +3. Suitable crystals of (2) were grown by slow evaporation of ethanol solution during two weeks. The metalloligand (1) and the tetranuclear (2) complexes are characterized by IR and physical measurement. Spectroscopic evidence indicated that the Schiff base H₂L behave an N₂O₂O'2 coordination tetradentate ligand. The structure of (2) was elucidated by X-ray diffraction analysis. The asymmetric unit of the compound contains two dideprotonated ligand molecules, two iron ions, one hexacoordinated sodium ion, one heptacoordinated sodium ion, one bidentate nitrate group, one monodentate dicyanamide unit, one coordinated ethanol molecule and an O²⁻ ion which acts as a bridge between the FeII and the FeIII of two entities: [FeIII NaI(L)(EtOH)(HN(CN)₂)] and [FeIII NaI(L)(NO₃)]. Bridge Fe—O(µ) bond lengths are 1.7813(14) and 1.7856(13) Å and bridging angle Fe—O—Fe is 144.78(8)°. The second terminal cyano group of the dicyanamide link another molecule complex through the heptacoordinated NaI leading a polymeric structure. Intermolecular hydrogen bond connect the polymeric chains to develop a three dimensional structure.

Keywords: Iron, Metalloligand, O-vanillin, Sodium Dicyanamide

1. Introduction

Bi-compartmental Schiff bases are widely used in the design of homo-polynuclear and hetero-polynuclear complexes owing to their peculiar physicochemical properties [1-5]. This development results in the association of metal ions with different nature and ligands which can yield molecular entities with great interest in the fields of molecular magnetism [6-9], optics [10-12], biology [13], absorption [14], catalysis [15] and luminescence [16, 17]. Hetero-polynuclear complexes with 3d transition metal and 4f lanthanide ions are largely reported in the literature [18-20]. This field has also experienced a renaissance with the synthesis of new hetero-metallic compounds 3d/ns very promising in much domains such as molecular magnetism [1, 2, 5, 21]. In addition, the insertion of diamagnetic metal ions such as alkali ions and lanthanide ions can gave precious information on the relationship magneto-structural of these compounds [3, 22]. However, access to hetero-polynuclear polymers incorporating ns ions and 3d ions with different degrees of oxidation, ie. Sodium (I) and iron (II, III) is a challenge from a synthetic point of view [21, 22]. Systematically, hetero-polymetallic complexes can be obtained according to two different strategies. The self-
assembly method is widely used to prepare 3d/4f complexes [4-7]. Indeed, many hetero-polynuclear complexes with remarkable properties have been obtained by the self-assembly method [8-10]. The metalloligand method, which consists to prepare a complex as a precursor [3, 23] for the second step of the reaction. This last method can be used to prepare discrete or infinite hetero-metallic complexes [11-13].

Our synthetic approach consists in using an iron(II)-based metalloligand [Fe(L)].(H2O) as precursor synthesized from the bi-compartmental Schiff ligand derived from o-vanillin (Hm). In this article we report a hetero-polynuclear species [{FeIINa(L)(EtOH)(HN(CN)}]n (2) obtained using the metalloligand [Fe(L)].(H2O) (1) and Na(N(CN)) (Figure 1). The crystal structure and the physico-chemical properties are discussed.

2.1. General Information

o-Vanillin and 1,3-diaminobenzene, iron chloride tetrahydrate, and sodium dicyanamide were purchased from Sigma-Aldrich and used as received without further purification. All solvents used were of reagent grade. The ligand (H2L) was synthesized following the reported method [24]. Elemental analyses of C, H and N were recorded on a VxRio EL Instrument. Infrared spectra were obtained on a FTIR Spectrum Two of Perkin Elmer in the 4000-400 cm⁻¹ region. The molar conductance of 1×10⁻³ M in DMSO solution 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 Matthey scientific magnetic susceptibility balance (Calibrant: Hg[Co(SCN)4]).

2.2. Synthesis and Characterization of (1) and (2)

In a round bottomed flask, the ligand (H2L) (10 mmol, 0.374 g) was dissolved in 5 mL of acetonitrile. A solution of FeCl3·4H2O (10 mmol, 0.199 g) in 5 mL of methanol 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 [Fe(L)].(H2O). Yield: 80%. Elemental Anal. Found (Calcd.) (%): C, 58.92 (58.95); H, 4.48 (4.50); N, 6.22 (2.25). IR ( , cm⁻¹): ν(O—H) 3343, (OH⁻) 851; 1627 ν(C=N), 1597; ν(C-OPh), 1236; ν(C-OMe), 1201. Conductance ^ (S.cm⁻¹.mol⁻¹): 7. eff (MB): 4.8.

To a solution of [Fe(L)].H2O (1) (1 mmol, 0.43 g) in 5 mL of DMF was added a solution of Na[N(CN)] (3 mmol, 0.261 g) in 5 mL of ethanol. The mixture was refluxed during two hours. On cooling red precipitate, which appears, was recovered by filtration. The filtrate was left for slow evaporation. On standing for two weeks, red crystals of (2) suitable for X-ray diffraction were isolated. Yield: 50%. Elemental Anal. Found (Calcd.) (%): C, 52.51 (52.53); H, 3.92 (3.95); N, 10.19 (10.21). IR ( , cm⁻¹): ν(C=N) = 1599; ν(C-OPh) = 1241; ν(C-OMe) = 1197; ν(C=N): 2250, 2201 et 2142; ν3 (NO3), 1488; ν5 (NO3), 1313, 36 ν2 (NO3) = 1041; ∆ν = 175 cm⁻¹. Conductance ^ (S.cm⁻¹.mol⁻¹) = 5. eff (MB): 5.1.

2.3. 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 [25]. The structures were solved by direct methods, which revealed the position of all non-hydrogen atoms. All the structures were refined as riding model by AFIX instructions. Molecular graphics were generated using ORTEP-3 [27].

3. Results and Discussion

3.1. General Study

The ligand H2L 2-((2-(2-hydroxy-3-methoxybenzylideneamino)phenylimino)methyl)-6-methoxyphenol was prepared by mixing under reflux o-vanillin and 1,2-diamino benzene in molar ratio 2:1 in ethanol, following a reported method [24]. The H2L react

![Figure 1. Chemical diagrams for [Fe(L)].(H2O) (1) and [{FeIINa(L)(EtOH)(HN(CN)}] (2).](image)
with FeCl$_2$·4H$_2$O in methanol to yield [Fe(L)]H$_2$O (1). This metallogligand reacts with sodium thiocyanate in molar ratio 1:3 and the complex formulated as
\[
[\text{Fe}^{II}\text{Na}^{I}(L)(\text{EtOH})(\text{HN(CN)}_2)](\mu-O)[\text{Fe}^{III}\text{Na}^{I}(L)(\text{NO}_3)]_n \text{ (2)}
\]
was afforded after slow evaporation of the filtrate. The IR spectrum of the metallogligand (1) shows an absorption band at 1627 cm$^{-1}$ (1632 cm$^{-1}$ for the free H$_2$L) which is indicative of a coordinated azomethine (C=N). Additional band (C—OPh) pointed at 1236 cm$^{-1}$ corresponds to the deprotonated phenoxy group. The corresponding band in the free ligand appears at 1254 cm$^{-1}$ band. For the complex (2) the (C=N), (C—OPh) and (C—OMe) bands are pointed respectively at 1600 cm$^{-1}$, 1197 cm$^{-1}$ and 1241 cm$^{-1}$. The coordinated dicyanamide group exhibits bands at 2250 cm$^{-1}$, 2201 cm$^{-1}$ and 2142 cm$^{-1}$. The bands at 1488 ($v_1$), 1313 ($v_2$), 1041 ($v_3$) and $v_1 – v_5 = 175$ cm$^{-1}$ are indicative of the presence of a bidentate chelating nitrate group. The molar conductance $\Lambda$ measured in DMF solution are 5 and 7 S cm$^2$ mol$^{-1}$ respectively for (1) and (2) which are indicative of a neutral electrolyte [28]. Magnetic moment at room temperature are 4.8 $\mu_B$ for (1) and 5.1 $\mu_B$ for (2). The magnetic moment value of (1) is close proximity of the spin-only value of 4.9 $\mu_B$ expected for a d$^6$ iron(II) ion [29]. The magnetic moment for complex (2) is considerably smaller than the value of 10 $\mu_B$ expected for the simultaneous presence of one iron(II) and iron(III) ions. These results indicated that there are antiferromagnetic exchange interactions between the d$^6$ iron(II) and d$^5$ iron(III) ions present in the complex via the -oxo bridge [30].

### 3.2. Crystal Structure

The polymer formulated as
\[
[\text{Fe}^{III}\text{Na}^{I}(L)(\text{EtOH})(\text{HN(CN)}_2)](\mu-O)[\text{Fe}^{III}\text{Na}^{I}(L)(\text{NO}_3)]_n \text{ (2)}
\]
crystallizes in the triclinic system with a space group P-1. The crystal data collection and refinement are reported in Table 1. The ORTEP diagram of the structure of the heteronuclear polymer complex is illustrated in Figure 2. Selected bonds lengths and angles are listed in Table 2.

**Figure 2.** Crystal structure of the tetranuclear complex (2). H atoms are omitted for clarity. The labelling scheme of C atoms in the ligand are not shown for clarity.

The oxo-bridged complex displays a structure constructed from two entities [Fe$^{III}$Na$^{I}$(L)(EtOH)(HN(CN)$_2$)] and [Fe$^{II}$Na$^{I}$(L)(NO$_3$)] bridged by an O$^{2-}$ ion, giving rise to a heterotetranuclear neutral complex. These motifs are connected through the Na atoms to each other by protonated dicyanamide which acts as spacer via their two terminal nitrogen atoms. As shown in Figure 2, the asymmetric unit of the compound is made up of two dideprotonated chelating ligand molecule, two pentacoordinated iron atoms, one hexacoordinated sodium atom, one heptacoordinated Na atom, one bidentate nitrate group, one monodentate dicyanamide unit, one coordinated ethanol molecule and an O$^{2-}$ ion. The twice deprotonated Schiff base molecule (L$^{2-}$) is a donor of N$_2$O$_2$O$^-$ ion. The arrangement of these atoms leads to the formation of one internal inner N$_2$O$_2$ and one outer inner O$_2$O$^-$ ion. The iron ion atom being smaller than the sodium ion is located in the smaller cavity N$_2$O$^-$ and the sodium ion is located in the larger compartment O$_2$O$^-$ of the ligand. Each iron atom (Fe1 and Fe2) atom is pentacoordinated in a N$_2$O$_2$ inner by two azomethine atoms and two phenolate oxygen.
atoms and are bridged by one dianionic oxygen atom (O$_2^-$). The two sodium atoms are differently coordinated. The two sodium atoms of the complex (Na3 and Na4) are situated in the O$_2$O$_2'$ inner from the metalloligand (two phenolate oxygen atoms and two methoxy oxygen atoms). Additionally, two oxygen atoms from a bidentate nitrate moiety and one nitrogen atom (N66) from a dicyanamide group of another complex molecule coordinate the Na3 atom, resulting in a heptacoordinated Na3 atom. One nitrogen atom from a dicyanamide group and one oxygen atom from a coordinated ethanol molecule coordinated also the Na4 atom, resulting in a hexacoordinated sodium atom.

The environment around each pentacoordinated iron atom is determined using the Addison [31] parameter ($\tau$) which is calculated with the following formula $\tau = (\beta - \alpha) / 60$ (where $\alpha$ and $\beta$ are the values of the largest bond angles around the iron atom). When $\tau = 0$, the geometry is a pyramid with a perfect square base; $\tau = 1$ indicates a perfect trigonal bipyramid geometry. The trigonality indices $\tau$ values of the Fe1 and the Fe2 are respectively 0.013 and 0.029. These values are indicative of a slightly distorted square pyramidal around each iron atom. The distortion is greater around Fe2 atom. For Fe1 and Fe2 atoms, the basal planes are defined by the atoms [N12, N19, O27, O32] for Fe1 and [O60, O57, N40, N47] for Fe2. The two pyramids share one vertex occupied by the oxygen atom O61 that is on the axial positions of the two square pyramids (Figure 3). The Fe1—Fe2 distance is 3.3998(5) Å.

![Figure 3. Plot showing the coordination sphere of the two iron atoms in the crystal.](image)

### Table 1. Crystal data, X-ray data collection, data reduction and structure refinement for (2).

| Crystal data | Value |
|--------------|-------|
| Chemical formula | C$_{48}$H$_{43}$Fe$_2$N$_8$Na$_2$O$_{13}$ |
| $M_r$ | 1088.59 |
| Crystal system, space group | Triclinic, P-1 |
| Temperature (K) | 293 |
| $a$, $b$, $c$ (Å) | 13.39754 (16), 13.98896 (16), 14.2041 (3) |
| $\beta$, $\gamma$, $\alpha$ (°) | 74.4737 (15); 67.6043 (15); 72.7787 (10) |
| $V$ (Å$^3$) | 2314.53 (7) |
| $Z$ | 2 |
| Calculated density (g·cm$^{-3}$) | 1.562 |
| F (000) | 1120 |
| Radiation type | $\mu = 0.71073$ Å |
| $\mu$ (mm$^{-1}$) | 0.72 |
| Crystal size (mm) | 0.32 × 0.09 × 0.08 |
| Data collection | XtaLAB AFC12 (RCD3): Kappa single |
| Diffractometer | Multi-scan |
| Absorption correction | 0.893; 1.000 |
| $h$ | -19→18 |
| $k$ | -20→20 |
| $l$ | -20→20 |
| No. of measured, independent and observed [I > 2σ(I)] reflections | 57221, 13219, 11414 |
| $R_{int}$ | 0.030 |
| Refinement | $R(I^2 > 2\sigma(I^2))$, wR(I$^2$), S |
| | 0.044, 0.128, 1.06 |
Table 2. Selected bond lengths [Å] and angles (°) for the complex 2.

| Bond | Bond lengths [Å] | Bond | Bond angles (°) |
|------|-----------------|------|----------------|
| Fe1—O32 | 1.9164 (13) | O32—Fe1—O27 | 84.79 (6) |
| Fe1—O27 | 1.9249 (13) | O32—Fe1—N19 | 144.23 (6) |
| Fe1—O61 | 1.7813 (14) | O32—Fe1—N12 | 87.95 (6) |
| Fe1—N19 | 2.0891 (15) | O27—Fe1—N19 | 87.15 (6) |
| Fe1—N12 | 2.0790 (15) | O27—Fe1—N12 | 143.46 (6) |
| Na3—O27 | 2.4307 (15) | N12—Fe1—N19 | 78.18 (6) |
| Na3—O28 | 2.6470 (17) | O32—Na3—O27 | 84.79 (5) |
| Fe2—O57 | 1.9200 (13) | O27—Na3—N66' | 93.81 (6) |
| Fe2—O60 | 1.9254 (13) | O32—Na3—N66' | 101.78 (7) |
| Fe2—O61 | 1.7856 (13) | Fe1—O61—Fe2 | 144.78 (8) |
| Fe2—N40 | 2.0989 (15) | O57—Fe2—O60 | 85.50 (6) |
| Fe2—N47 | 2.0855 (16) | O57—Fe2—N40 | 142.60 (6) |
| Na4—O35 | 2.6007 (18) | N47—Fe2—N40 | 77.46 (6) |
| Na4—O57 | 2.3849 (16) | O60—Fe2—N40 | 87.75 (6) |
| Na3—O30 | 2.5662 (17) | O60—Fe2—N47 | 144.32 (6) |
| Na3—O32 | 2.4133 (15) | O57—Fe2—N47 | 86.99 (6) |
| Na3—O62 | 2.4435 (18) | O60—Na4—O57 | 66.52 (5) |
| Na3—O65 | 2.5402 (19) | N70—Na4—O57 | 120.85 (8) |
| Na3—N66' | 2.453 (2) | N70—Na4—O60 | 121.54 (8) |
| Na4—O58 | 2.7189 (18) | Fe1—O61—Fe2 | 144.78 (8) |
| Na4—O60 | 2.3746 (16) | O57—Fe2—O60 | 85.50 (6) |
| Na4—O71 | 2.280 (2) | O57—Fe2—N40 | 142.60 (6) |
| Na4—N70 | 2.372 (2) | N47—Fe2—N40 | 77.46 (6) |

Symmetry Codes: (i) x, y, z=1.

The mean bond distance Fe—N of 2.0882 Å is comparable to the distances found for the complexes [( - O)(Fe(vanophen))₃]·2H₂O (H₂vanophen is (N,N’-(1,2-phenylene)-bis(3-methoxysalicylideneimine)) and [( - O)(Fe(naphophen))₃]·2CH₃Cl₂ (H₂naphophen is (N,N’-bis(2-hydroxy-1-naphthaldehyde)-1,2-phenylenediammine)) [32]. The mean bond distance Fe—O(phenoxo) is 1.9250 Å, which is shorter than the mean bond distance Fe—O (bridge) of 1.7835 Å. These values are comparable to those reported for [H₃Fe(nophen)]Cl. The mean bond distance Fe—N of 2.0882 Å is comparable to the following values: Fe—N = 1.9164 (13) —1.9254 (13) Å while the Fe-Nimine bond distances are the longest [2.0989 (15) —2.0790 (15) Å]. These values are close to those reported in a heteronuclear complex formulated as [NaFe₆(sae)₆(MeO)₆]·(N(CN)₂)(H₂O) [34] where the Schiff-based ligand H₃sae is salicylidene-2-ethanolamine. The Na-O bonded distances are the longest in the structure [2.5662 (17) —2.7189 (18) Å].

Each organic ligand hosts one sodium (I) ion in its O₂O’₂ open site and one iron atom in the adjacent Na₂O₂ iminic inner. The two ions, in close proximity to each other (Fe1···Na3 = 3.432 Å, Fe2···Na4 = 3.352 Å), share two bridging phenolate oxygen atoms of the organic ligand. The Na4 ion exhibits a distorted 6-fold coordination, involving four O atoms of the organic ligand, one additional coordinated C₂H₄OH molecule and one nitrogen atom of the dicyanamide group. The Na3 ion has a 7-fold coordination involving four O atoms of the organic ligand, two O atoms from a bidentate chelating nitrate groups and one nitrogen atom of the dicyanamide group of another molecule.

The environment around the 6-fold sodium atom Na4 can be described as a distorted pyramidal pentagon while the geometry of the 7-fold sodium atom Na3 is best described as a distorted bipyramidal pentagon (Figure 4). The basal angles for both geometries are in the range [60-90°]. These values deviate from the value of the ideal angle for a regular pentagon (72°) and the sum of the equatorial angles around Na3 and Na4 are respectively 358.15° and 355.86°. The apical position for the pentagon pyramid around Na4 is occupied by N70, N66 and O62 occupy the axial positions.
for the severely distorted pentagonal bipyramid geometry around Na3 with the angle value of 145.62(7)°.

The hydrogen bonding geometry of the compound is listed in Table 3. Intermolecular hydrogen bond C45—H45···O65\textsuperscript{i}, C24—H24···O68\textsuperscript{ii} and intramolecular hydrogen bond C29—H29C···O65, O71—H71···O62 has been observed. In crystal, C—H···O and O—H···O hydrogen bonds link the molecules. The structure consists of several chains superimposed on each other. These chains are linked by inter and intramolecular bonds which ensure the cohesion and stability of the polymer as shown in Figure 5.

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

| D—H···A  | D—H  | H···A  | D···A  | D—H···A |
|----------|-------|--------|--------|---------|
| C45—H45—O65\textsuperscript{i} | 0.93  | 2.49   | 3.067 (3) | 119.9   |
| O71—H71—O62  | 0.871 (9) | 1.96 (2) | 2.761 (3) | 152 (3) |
| C24—H24—N68\textsuperscript{ii} | 0.93  | 2.49   | 3.392 (3) | 164.5   |
| C29—H29C—O65 | 0.96  | 2.64   | 3.416 (4) | 138.1   |

Symmetry codes: (i) x+1, y, z; (ii) −x, −y+2, −z+1.

4. Conclusion

In summary, we have successfully synthesized and studied the hetero tetranuclear complex containing two natrium (I), one iron (II) and iron (III) ions. A suitable crystal of the complex was obtained by slow evaporation of ethanol solution of the compound for two weeks. Infrared spectra of the compound and the metalloligand were discussed in this paper. Crystal data, X-ray data collection, data reduction and structure refinement are studied. The heteronuclear complex crystallizes in the triclinic system with a space group P-1. The two square pyramidal environments of the iron (II) and iron (III) ions share one vertex. The environment around the 6-fold sodium atom Na4 can be described as a distorted pyramidal pentagon while the geometry of the 7-fold sodium atom Na3 is best described as a distorted bipyramidal pentagon.

Supplementary Materials

CCDC-1978558 contains the supplementary crystallographic data for this paper. These data can be
obtained free of charge from the Cambridge Crystallographic data Center via www.ccdc.cam.ac.uk/data_request/cif.

Conflicts of Interest

The authors declare that they have no competing interests.

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