Contents lists available at ScienceDirect







journal homepage: www.elsevier.com/locate/inoche

Unique example of a trigonal dodecahedral Na⁺ in a compartmental Schiff base N,N'-(1,2-Phenylene)-bis(3-methoxysalicylideneimine)

Mithun Das ^a, Sudipta Chatterjee ^b, Shouvik Chattopadhyay ^{a,*}

^a Department of Chemistry, Inorganic Section, Jadavpur University, Kolkata 700 032, India

^b Department of Chemistry, Serampore College, Serampore, Hooghly-712201, India

ARTICLE INFO

Article history: Received 17 March 2011 Accepted 12 May 2011 Available online 20 May 2011

Keywords: Nickel(II) Sodium Compartmental Schiff base Crystal structure

ABSTRACT

A unique heteronuclear Schiff base compound, $[(NiL)Na(NiL)]ClO_4$ (1), derived from the compartmental Schiff base ligand N,N'-(1,2-Phenylene)-bis(3-methoxysalicylideneimine) (H₂L) has been prepared and its molecular structure has been elucidated on the basis of X-ray crystallography. The compound contains an octa-coordinated Na⁺ in trigonal dodecahedral geometry and two terminal square planar Ni(II).

© 2011 Elsevier B.V. All rights reserved.

The synthesis of hetero-nuclear compounds continues to be an intensive and challenging area of investigation since long. Among the many interesting aspects of these species, most important are their electrochemical and magnetic properties. On the other hand, recent developments in the field of supramolecular chemistry have shown that small building blocks can lead, through self-assembly processes, to large, well-defined structures, which are held together by noncovalent interactions such as hydrogen bonds [1,2] and metal-ligand coordination [3-7]. In this field, coordination supramolecular chemistry has progressed remarkably and important achievements have been made in the design and preparation of multidentate ligands capable of participating in complicated molecular structures upon complexation, in predetermined manners, with transition metals [8,9]. The family of salen ligands provides good examples of these types of ligands which coordinate to various kinds of transition and typical metals in a tetradentate fashion to give stable compounds, some of which are used as catalysts for organic reactions [10-12], models of reaction centers of metalloenzymes[13,14], nonlinear optical materials[15,16], and building blocks for interlocked molecules [17].

In recent years, the multi-nucleating properties of the compartmental Schiff base ligand, H_2L [=N,N'-(1,2-Phenylene)-bis(3-methoxysalicylideneimine)], obtained by the condensation of 3-methoxysalicylaldehyde and o-phenylenediamine, have been used to prepare discrete heterodinuclear 3d/alkali-metal and 3d/4f metal compounds, where the 3d ion is coordinated by the

E-mail address: shouvik.chem@gmail.com (S. Chattopadhyay).

 N_2O_2 compartment and the alkali-metal or the 4f metal ions by the O_2O_2 compartment of the ligand without exception. The isolated compounds were formulated as LMM/X [18] or LMLnX[19–25], where L stands for the ligand, M for the 3d ion (mainly Zn(II) and Cu(II)), M[/] for alkali metals, Ln for the 4f metals, and X for the anionic species [26,27]. To the best of our knowledge, there are no reports on the preparation of trinuclear cationic $M_2M^/$ compound with a ClO_4^- as the counter ion. In the present paper, we report the facile synthesis, characterisation, redox behavior and magnetic property of a trinuclear compound, [(NiL)Na(NiL)]ClO₄ (1).

Compound **1** was readily obtained by refluxing H_2L with Ni(ClO₄)₂ and NaClO₄ in methanol [28]. X-ray quality dark red single crystals of **1** were obtained from DMF solution by slow evaporation at room temperature [29]. The ligand was prepared by the 1:2 condensation of the o-phenylenediamine with 3-methoxysalicylaldehyde in methanol following the literature method [30]. The ligand was then made to react with a mixture of Ni(ClO₄)₂ and NaClO₄ to prepare trinuclear compound 1 (Scheme 1). In absence of NaClO₄, a different compound [NiL] was formed, the structure of which was reported elsewhere [31]. The same ligand when made to react with CuCl₂ and NaCl, Na⁺ was found to be hexa-coordinated by the O_2O_2 compartment of the ligand, chloride ion and a solvent molecule, CH₃OH [18]. However, no crystal structure was reported where the ligand was utilised to form trinuclear compound. All the preparations, reported in the literature, were carried out at room temperature by simple stirring, whereas we prepared compound 1 by refluxing. The elevated temperature might provide the energy to overcome the activation barrier for preparing a compound with trigonal dodecahedron Na⁺ coordinated by eight O atoms of two NiL fragments, thus producing the first trinuclear Ni-Na-Ni compound with this ligand.

^{*} Corresponding author. Tel.: +91 9903756480.

^{1387-7003/\$ –} see front matter 0 2011 Elsevier B.V. All rights reserved. doi:10.1016/j.inoche.2011.05.009

Elemental analysis (carbon, hydrogen and nitrogen) was performed using a Perkin-Elmer 240C elemental analyzer. IR spectrum in KBr (4500–500 cm⁻¹) was recorded using a Perkin-Elmer RXI FT-IR spectrophotometer. Electronic spectrum in DMF (800–200 nm) was recorded in a Hitachi U-3501 spectrophotometer. The magnetic susceptibility measurement was done with an EG & PAR vibrating sample magnetometer, model 155 at room temperature and diamagnetic corrections were made using Pascal's constants. Electrochemical measurement was performed in DMF solution under a dry nitrogen atmosphere in conventional three electrode configurations using Pt disk working electrode, Pt auxiliary electrode and Ag/AgCl reference electrode, with TBAP (Tetrabutylammonium Perchlorate) as supporting electrolyte in the potential range from -2 to 2 V and uncorrected for junction contribution. The value for the Fc–Fc⁺ couple under our conditions is 0.39 V.

In the IR spectrum of compound **1**, a distinct band due to the azomethine (C=N) group at 1613 cm⁻¹ is customarily noticed [32–34]. The sharp, strong, single peak at 1092 cm⁻¹ gives evidence for the presence of ionic perchlorate in it [35]. The electronic spectrum shows that absorption bands of **1** occur below 486 nm. Lack of any electronic transition at longer wavelengths indicates a large crystal-field splitting and is consistent with the square planar geometry of Ni (II) [36]. Room temperature magnetic susceptibility measurement shows that the trinuclear compound is diamagnetic, thereby indicating the presence of magnetically non-coupled square planar Ni(II).

The trinuclear structure of **1**, as shown in Fig. 1, contains a sodium and two nickel atoms in an approximately linear arrangement. A central Na^+ core is linked to two neutral NiL via four phenolate O



Fig. 1. ORTEP3 diagram of compound **1** with 30% ellipsoid probability. Hydrogen atoms and perchlorate are not shown for clarity. Selected bond distances (Å): Ni(1)-O(2) 1.843(10), Ni(1)-O(3) 1.857(8), Ni(1)-N(1) 1.848(14), Ni(1)-N(2) 1.843(12), Ni(2)-O(6) 1.853(10), Ni(2)-O(7) 1.837(10), Ni(2)-N(3) 1.856(18), Ni(2)-N(4) 1.826(15), Na (1)-O(1) 2.526(12), Na(1)-O(2) 2.543(10), Na(1)-O(3) 2.554(11), Na(1)-O(4) 2.561 (12), Na(1)-O(5) 2.507(12), Na(1)-O(6) 2.528(12), Na(1)-O(7) 2.524(10), and Na (1)-O(8) 2.530(11). Bond angles are given in Supplementary Tables S1 and S2.

atoms and four methoxy O atoms from salen-type Schiff base ligand (H₂L). The Na⁺ is eight-coordinated in trigonal-dodecahedron geometry (Fig. 2), which is rarely scarce except for Na⁺ coordinated with adequate crown ether ligands. The Na-O(phenolate) distances are 2.528(12), 2.524(10), 2.543(10), and 2.554(11) Å; and the distances of Na-O(methoxy) are larger than that of Na-O(phenolate) distances. The dihedral angle between the mean planes passing through [O(1)-O(2)-O(3)-O(4)] and [O(5)-O(6)-O(7)-O(8)] is 72.87°, suggesting that the two sets of salen-type Schiff base ligands



Scheme 1. Synthetic routine of complex 1.



Fig. 2. Trigonal dodecahedral geometry of Na⁺ in compound 1.

are almost orthogonal. Both the Ni atoms are four-coordinated in an approximately square-planar geometry constructed by two imine N atoms and two phenolate O atoms. Sum of the different angles around the Ni atoms is almost 360° [360.07 for Ni(1) and 360.1 for Ni(2)] indicating very slightly distorted square-planar geometry around the Ni atoms. The distortion may conveniently be measured by the trans angles that are ideally 180° for a square-planar compound and 109.5° in a tetrahedral compound. The trans angles are found to be 177.1(6) {O(2)-Ni(1)-N(1)}, 176.1(6) {N(2)-Ni(1)-O(2)}, 174.9(6) {O(6)-Ni (2)-N(4)} and 177.7(8) {O(7)-Ni(2)-N(3)}. Deviations of the coordinating atoms O(2), O(3), N(1) and N(2) for Ni(1) fragment from the least-square mean plane through them are -0.039(10), 0.040(9), 0.039(15), and -0.040(13) Å respectively. For Ni(2) fragment, deviations of the coordinating atoms O(6), O(7), N(3) and N(4) from the least-square mean plane through them are -0.049(11), 0.049(10), 0.05(2), and -0.048(17) Å respectively. The intramolecular separations between Ni(1)····Ni(2) is 7.18 Å, whereas Ni (1) · · · Na(1) and Ni(2) · · · Na(1) separations are 3.614 Å and 3.601 Å respectively. None of these distances are sufficiently short to imply any metal-metal bonding or to allow intra-metal spin exchange through mutual interaction. The {Ni(1)-O(2)-Na(1)}, {Ni(1)-O(3)-Na(1), {Ni(2)-O(6)-Na(1)} and {Ni(2)-O(7)-Na(1)} angles are 110.0(5), 109.0(4), 109.6(5) and 110.4(5) respectively.

Compound 1 shows one quasi reversible Ni(III)/Ni(II) couple at $E_{1/2} = 1.17$ (vs. Ag/AgCl) which corresponds to the first electron abstraction from the compound and is consistent with [NiL]⁺/[NiL] couple. The reversible Ni(II)/Ni(I) couple at $E_{1/2} = -1.11$ can be assigned to the electron addition to Ni(II) compound to form Ni(I) species. The $E_{1/2}$ and ΔE_p values for these redox couples are given in the Supplementary Table S3. It has been observed that no well defined oxidative or reductive responses could be observed on running further in the positive or negative potential. The single-electron nature of the voltammograms has been confirmed by the comparison of current heights for the compounds and that of a simple $[Fe(bipy)_3]^{2+}$ compound under identical conditions [37]. The criteria of reversibility were checked by observing constancy of peak-peak separation $(\Delta E_{\rm p}\!=\!E_{\rm pa}$ - $E_{\rm pc})$ and the ratio of peak heights $(i_{\rm pa}\!/i_{\rm pc}\!\sim\!1)$ with variation of scan rates [38]. The results of cyclic voltammetry also closely resemble that of the similar reported compounds, which serve as further evidences for similar structural and electronic properties [39]. All the redox signals remain virtually invariant under different scan rates $(0.01-1.0 \text{ Vs}^{-1})$ in the temperature range 300–280 K. Solvent dependent shift and change in electrochemical reversibility of redox couples are not noteworthy.

The isolation and crystal structure determination of the trinuclear compound, [(NiL)Na(NiL)]ClO₄, unambiguously show for the first

time that the salen type compartmental Schiff base N,N'-(1,2-Phenylene)-bis(3-methoxysalicylideneimine), which was hitherto used to prepare dinuclear compounds only, can also be used to synthesise trinuclear compounds as well. Such bonding mode was unprecedented for the ligand. Thus it opens up new possibilities for the synthesis of such type of compounds.

Acknowledgements

This work was supported by the University Grants Commission, CAS-UGC, New Delhi.

Appendix A. Supplementary material

Crystallographic data for the analysis have been deposited with the Cambridge Crystallographic data Centre, CCDC No 805837. The data can be obtained free of charge from CCDC via www.ccdc.cam.ac. uk/data_request/cif. Supplementary data to this article can be found online at doi:10.1016/j.inoche.2011.05.009.

References

- [1] J.A. Zerkowski, C.T. Seto, G.M. Whitesides, J. Am. Chem. Soc. 114 (1992) 5473-5475.
- [2] J.-M. Lehn, M. Mascal, A. DeCian, J. Fischer, J. Chem. Soc., Perkin Trans. 2 (1992) 461–467.
- [3] E.C. Constable, A.M.W.C. Thompson, J. Chem. Soc., Dalton Trans. (1992) 3467–3475.
- [4] R. Krämer, J.-M. Lehn, A. Marquis- Rigault, Proc. Natl. Acad. Sci. 90 (1993) 5394–5398.
- [5] E. He, C.N. Moorefield, G.R. Newkome, Chem. Rev. 99 (1999) 1689–1746.
- [6] L. Brunsveld, B.J.B. Folmer, R.P. Sijbesma, E.W. Meijer, Chem. Rev. 101 (2001) 4071–4098.
- [7] B.G.G. Lohmeijer, U.S. Schubert, Angew. Chem. Int. Ed. 41 (2002) 3825-3829.
- [8] J.-P. Sauvage, M.W. Hosseini, in: J.-M. Lehn (Ed.), Comprehensive Supramolecular Chemistry, vol. 9, Pergamon, Oxford, 1995.
- [9] B.J. Holliday, C.A. Mirkin, Angew. Chem. Int. Ed. 40 (2001) 2022-2043.
- [10] E.N. Jacobsen, in: I. Ojima (Ed.), Catalytic Asymmetric Synthesis, VCH, New York, 1993.
- [11] T. Katsuki, Coord. Chem. Rev. 140 (1995) 189-214.
- [12] E.N. Jacobsen, Acc. Chem. Res. 33 (2000) 421-431.
- [13] T.-T. Tsou, M. Loots, J. Halpern, J. Am. Chem. Soc. 104 (1982) 623-624.
- [14] M.F. Summers, L.G. Marzilli, N. Bresciani-Pahor, L. Randaccio, J. Am. Chem. Soc. 106 (1984) 4478–4485.
- [15] S. Di Bella, I. Fragala`, Synth. Met. 115 (2000) 191-196.
- [16] P.G. Lacroix, Eur. J. Inorg. Chem. (2001) 339-348.
- [17] I. Yoon, M. Narita, T. Shimizu, M. Asakawa, J. Am. Chem. Soc. 126 (2004) 16740-16741.
- [18] J. Bian, Acta Crystallogr., Sect. E 64 (2008) m625.
- [19] X. Yang, R.A. Jones, Q. Wu, M.M. Oye, W.-K. Lo, W.-K. Wong, A.L. Holmes, Polyhedron 25 (2006) 271–278.
- [20] W.-K. Wong, X. Yang, R.A. Jones, J.H. Rivers, V. Lynch, W.-K. Lo, D. Xiao, M.M. Oye, A.L. Holmes, Inorg. Chem. 45 (2006) 4340–4345.
- [21] W.-K. Lo, W.-K. Wong, W.-Y. Wong, J. Guo, K.-T. Yeung, Y.-K. Cheng, X. Yang, R.A. Jones, Inorg. Chem. 45 (2006) 9315–9325.
- [22] W.-Y. Bi, X.-Q. Lu, W.-L. Cai, J.-R. Song, W.-K. Wong, X.-P. Yang, R.A. Jones, Z. Anorg. Allg. Chem. 634 (2008) 1795–1800.
- [23] W.-Y. Bi, X.-Q. Lu, W.-L. Chai, W.-J. Jin, J.-R. Song, W.-K. Wong, Inorg. Chem. Commun. 11 (2008) 1316–1319.
- [24] H. Wang, D. Zhang, L. Tian, L.-F. Zhang, Acta Crystallogr., Sect. E 64 (2008) m1460.
- [25] H. Wang, D. Zhang, L.-F. Zhang, Acta Crystallogr., Sect. E 64 (2008) m1408-m1409.
- [26] J.-P. Costes, F. Dahan, A. Dupuis, J.-P. Laurent, Inorg. Chem. 36 (1997) 3429-3433.
- [27] J.-P. Costes, F. Dahan, J.-P. Laurent, Inorg. Chem. 33 (1994) 2738-2742.
- [28] The ligand, H₂L, was synthesised by refluxing a methanol solution of ophenylenediamine (108 mg, 1 mmol) and 3-methoxysalicylaldehyde (304 mg, 2 mmol) in 1:2 molar ratios for 1 h. It was then used directly without further purification. To prepare compound **1**, a methanol solution (10 ml) containing Ni (ClO₄)₂:6H₂O (365 mg, 1 mmol) and NaClO₄ (230 mg, 1 mmol) was added to a methanol solution (20 ml) of the ligand, H₂L (1 mmol) in refluxing condition. Red crystalline compound started to separate from the solution after about 15 min. All the starting materials were commercially available, reagent grade, and used as purchased without further purification. *Caution!* Although no problems were encountered in this work, perchlorate salts containing organic ligands are potentially explosive. Only a small amount of the material should be prepared and it should be handled with care. Yield: 330 mg (66.8%, based on Ni(II) salt). Anal. Calcd. (%) for C4₄H₃₆N₄Ni₂NaO₁₂Cl: C, 53.46; H, 3.67; N, 5.67. Found: C, 53.4; H, 3.7; N, 5.7. UV–Vis, λ_{max} (mm), (ε_{max} (dm³ mol⁻¹ cm⁻¹)) (DMF), 486 (1293), Magnetic moment diamagnetic.
- [29] Single crystals having suitable dimensions for compound 1 were used for data collection using a 'Bruker SMART APEX II' diffractometer equipped with graphite-

1997

monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 150(2) K. The molecular structure was solved by direct method and refinement by full-matrix least squares on F^2 using the SHELX-97 package [40]. Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. Empirical absorption corrections were carried out with the *ABSPACK* program [41]. The structure was refined on F^2 using *SHELX*-97 [40] to R1 = 0.0502, and wR2 = 0.1227, for 6689 reflections with $I > 2\sigma(I)$. Crystal data for 1: Formula C₄₄H₃₆ClN₄NaNi₂O₁₂. Formula Weight 988.59, Crystal system Monoclinic, Space group *P*2₁/*c*, a(Å) = 11.971(4), b(Å) = 18.218(5), c(Å) = 19.054(6), β(deg) = 91.890(5), Z = 4, d_{calc}(g cm⁻³) = 1.581, *F*(000) = 2032, Total Reflections 9827, Unique Reflections 7918, Observed data [I>2 σ (I)] 6689, R1 = 0.0502

- [30] S. Chattopadhyay, G. Bocelli, A. Musatti, A. Ghosh, Inorg. Chem. Commun. 9 (2006) 1053–1057.
- [31] H. Wang, S.-L. Li, D.-X. Liu, X.-G. Cui, X.-Y. Li, Z.-H. Yang, Acta Chim. Sinica 52 (1994) 676–682.

- [32] S. Chattopadhyay, M.G.B. Drew, A. Ghosh, Eur. J. Inorg. Chem. (2008) 1693-1701.
- [33] S. Chattopadhyay, P. Chakraborty, M.G.B. Drew, A. Ghosh, Inorg. Chim. Acta 362 (2009) 502–508.
- [34] P. Bhowmik, S. Chattopadhyay, M.G.B. Drew, C. Diaz, A. Ghosh, Polyhedron 29 (2010) 2637–2642.
- [35] K. Nakamoto, Infrared Spectra of Inorganic Compounds, Wiley, New York, 1970, pp. 242–243.
- [36] S. Chattopadhyay, M.S. Ray, S. Chaudhuri, G. Mukhopadhyay, G. Bocelli, A. Cantoni, A. Ghosh, Inorg. Chim. Acta 359 (2006) 1367–1375.
- [37] K. Mitra, S. Biswas, C.R. Lucas, B. Adhikary, Inorg. Chim. Acta 2006 (1997) 359.
 [38] D.H. Evans, K.M. O'Connell, R.A. Petersen, M.J. Kelly, J. Chem. Educ. 60 (1983) 290–293.
- [39] S. Chattopadhyay, M.G.B. Drew, A. Ghosh, Polyhedron 26 (2007) 3513-3522.
- [40] G.M. Sheldrick, SHELXS-97 and SHELXL-97, University of Göttingen, Germany,
- [41] ABSPACK, version 1, Oxford Diffraction, Abingdon, 2005.