

“Ligands-with-Benefits”: Naphthalene-Substituted Schiff Bases Yielding New Ni^{II} Metal Clusters with Ferromagnetic and Emissive Properties and Undergoing Exciting Transformations

Panagiota S. Perlepe,[†] Luís Cunha-Silva,[‡] Kevin J. Gagnon,[§] Simon J. Teat,[§] Christos Lampropoulos,[⊥] Albert Escuer,^{||} and Theodoros C. Stamatatos^{*,†}

[†]Department of Chemistry, Brock University, St. Catharines, Ontario L2S 3A1, Canada

[‡]REQUIMTE/LAQV and Department of Chemistry and Biochemistry, Faculty of Sciences, University of Porto, 4169-007 Porto, Portugal

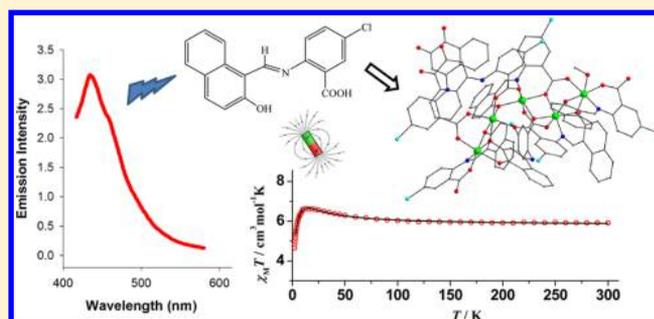
[§]Advanced Light Source, Lawrence Berkeley National Laboratory, 1 Cyclotron Road, Berkeley, California 94720, United States

[⊥]Department of Chemistry, University of North Florida, Jacksonville, Florida 32224, United States

^{||}Departament de Química Inorgànica and Institut de Nanociència i Nanotecnologia, Universitat de Barcelona, Diagonal 645, 08028 Barcelona, Spain

S Supporting Information

ABSTRACT: The initial employment of the fluorescent bridging ligand *N*-naphthalidene-2-amino-5-chlorobenzoic acid (nacbH₂) in metal cluster chemistry has led to new Ni₁₂ (1) and Ni₅ (2) clusters with wheel-like and molecular-chain topologies, respectively. The doubly-deprotonated nacb²⁻ ligands were found to adopt four different coordination modes within 1 and 2. The nature of the ligand has also allowed unexpected organic transformations to occur and ferromagnetic and emission behaviors to emerge. The combined work demonstrates the ability of some “ligands-with-benefits” to yield beautiful structures with exciting topologies and interesting physicochemical properties.



INTRODUCTION

The choice of a organic chelating/bridging ligand is currently one of the most appealing challenges toward the synthesis of new polynuclear 3d metal complexes with diverse physical properties, such as magnetic,¹ optical,² conductive,³ catalytic,⁴ and a combination of properties (i.e., photomagnetic⁵ and multiferroics⁶). The nature, stereoconfiguration, and electronic properties of the organic chelate are very crucial characteristics and can affect the chemical identities and properties of the resulting polymetallic species.⁷ In particular, the type and number of donor atoms (i.e., O and/or N) can facilitate the formation of high-nuclearity metal complexes with moderate-to-high oxidation states (i.e., Mn^{III}, Ni^{II}, etc.), nanoscale dimensions, and beautiful topologies.⁸ In addition, the bridging donor atoms of a chelate ligand dictate not only the topology and coordination preferences of the metal ions but also the nature and strength of the intramolecular magnetic exchange interactions. In an ideal case, ferromagnetic and high-spin molecules may result from the accidental orthogonality of the interacting magnetic orbitals of two or more metal ions via the unoccupied orbital(s) of the donor atom.⁹

Apart from the bridging part, the remaining scaffold of an organic chelate is also of importance; aromatic and

polyaromatic chelates are known to (i) enhance the solubility of the metal cluster compounds in solution and subsequently make their crystallization feasible, (ii) provide a rigid, protective “shell” between neighboring molecules in the crystal, (iii) promote energy-transfer effects and act as efficient “antennas” in order to enhance the complexes’ optical response,² and (iv) undergo unusual and unpredicted metal-ion-assisted transformations that lead to new organic groups with different properties than the parent ones.⁴

For all of the above reasons, and more, we have recently started a research program aimed at the exploration of Schiff base chelates, which are based on the *N*-salicylidene-*o*-aminophenol (saphH₂; Scheme 1) scaffold, in Ni^{II} cluster chemistry as a means of obtaining nanosized molecular materials with primarily interesting magnetic properties. Thus, the replacement of the –OH group of the *o*-aminophenol moiety with a carboxylate (–CO₂H) functionality, in conjunction with the addition of a chloro group in place of a phenyl H atom at the 5 position, produced the new ligand *N*-salicylidene-2-amino-5-chlorobenzoic acid (sacbH₂; Scheme

Received: October 28, 2015

Published: January 20, 2016

Scheme 1. Structural Formulas and Abbreviations of the Ligands Discussed in the Text^a



^aThe blue coloration illustrates the different substituents of the three ligands.

1).¹⁰ The latter was proven to be an extremely versatile and capable tetradentate bridging ligand, yielding novel Ni^{II} clusters with record nuclearities (i.e., Ni₂₆¹¹) and unprecedented structural topologies (i.e., Ni₁₁¹² and Ni₁₈¹¹ molecular chains). However, the magnetic properties of Ni^{II}/sacb²⁻ complexes were rather trivial, dominated by antiferromagnetic exchange interactions, and the optical response of these compounds was negligible, most likely because of quenching effects from the paramagnetic metal ions and/or insufficient energy transfer from the ligand.^{11,12}

On the basis of these findings and by following a more rational synthetic approach toward the preparation of Ni^{II} clusters with new motifs and additionally interesting magnetic and emission properties, we decided to replace the phenyl ring of the *N*-salicylidene moiety with a naphthalene one. The resulting ligand *N*-naphthalidene-2-amino-5-chlorobenzoic acid (nacbH₂; Scheme 1) is still tetradentate as sacbH₂ but undoubtedly more rigid and sterically demanding than sacbH₂, thus presaging the isolation of new Ni^{II} clusters. The similarities between the two ligands would also allow for a structural comparison between the sacb²⁻- and nacb²⁻-related coordination compounds. More delighting though with nacbH₂ is the presence of the naphthalene substituent, a well-known fluorescent group,¹³ which could open new prospects in the field of optics and particularly in the properties of Ni^{II} metal clusters.

We here report our first results from the initial employment of nacbH₂ in Ni^{II} coordination chemistry, which led us to two new Ni₁₂ and Ni₅ clusters with interesting molecular topologies, ferromagnetic and emissive behaviors, and an exciting nacbH₂ to LH₂ ligand transformation, where LH₂ is 5-chloro-2-[(3-hydroxy-4-oxo-1,4-dihydronaphthalen-1-yl)amino]benzoic acid.

EXPERIMENTAL SECTION

Syntheses. All manipulations were performed under aerobic conditions using chemicals and solvents as received. *N*-Naphthalidene-2-amino-5-chlorobenzoic acid (nacbH₂) was prepared in a manner similar to that of *N*-salicylidene-2-amino-5-chlorobenzoic acid (sacbH₂).^{11,12} **Safety note!** Perchlorate salts are potentially explosive; such compounds should be synthesized and used in small quantities and treated with utmost care at all times.

Synthesis of nacbH₂. The organic ligand 2-[[[(2-hydroxy-1-naphthalenyl)methylene]amino]-5-chlorobenzoic acid or, for simplicity, nacbH₂ was prepared in quantitative yield (~93%) by the condensation reaction of 2-amino-5-chlorobenzoic acid (8.58 g, 50 mmol) with 2-hydroxy-1-naphthaldehyde (8.61 g, 50 mmol) in a molar ratio of 1:1 in 100 mL of refluxing methanol (MeOH; Scheme S1). The reaction was stirred under reflux for 2 h and then cooled to room temperature, during which time an orange microcrystalline solid had appeared. The orange solid was collected by filtration, dried under vacuum, and analyzed as solvent-free. Elem anal. Calcd for nacbH₂: C, 66.37; H, 3.66; N, 5.08. Found: C, 66.46; H, 3.76; N, 4.89. Selected IR data (ATR): $\nu = 3561$ (mb), 3010 (m), 1586 (s), 1543 (s), 1475 (m), 1408 (m), 1361 (s), 1306 (m), 1265 (m), 1231 (w), 1168 (m), 1134

(w), 1111 (m), 1064 (w), 1027 (w), 972 (s), 886 (w), 866 (s), 834 (m), 815 (s), 744 (s), 704 (m), 656 (w), 629 (m), 591 (m), 559 (m), 498 (vs), 437 (m). ¹H NMR (DMSO-*d*₆, ppm): 15.10 (s, 1H, -OH), 13.20 (s, 1H, -COOH), 9.39 (s, 1H, -CH=N), 6.83–8.42 (m, 9H, 9-ArH). ¹³C NMR (DMSO-*d*₆, ppm): 115.8, 116.9, 118.4, 124.4, 126.3, 127.9, 128.7, 131.4, 132.1, 133.0, 138.2, 138.7, 150.4, 162.9, 193.7.

(NHET₃)₂[Ni₁₂(nacb)₁₂(H₂O)₄](ClO₄) (1). To a stirred orange suspension of nacbH₂ (0.07 g, 0.2 mmol) in acetonitrile (MeCN; 20 mL) was added triethylamine (NEt₃; 56 μ L, 0.4 mmol). The resulting yellow solution was stirred for 5 min, during which time solid Ni(ClO₄)₂·6H₂O (0.07 g, 0.2 mmol) was added and the color of the solution changed to orange-red. Additional stirring for 20 min did not alter the color or form of the solution. The latter was then filtered, and the filtrate was layered with diethyl ether to afford after 5 days yellow blocks of 1. The crystals were collected by filtration, washed with cold MeCN (2 \times 2 mL), and dried under vacuum. The yield was 35%. Elem anal. Calcd for 1·3H₂O (*M*_w = 4916.94 g mol⁻¹): C, 54.23; H, 3.07; N, 3.70. Found: C, 54.35; H, 3.16; N, 3.62. Selected IR data (ATR): $\nu = 2973$ (w), 1582 (s), 1553 (vs), 1535 (vs), 1473 (m), 1449 (m), 1427 (s), 1382 (s), 1339 (vs), 1249 (m), 1216 (m), 1179 (m), 1152 (m), 1112 (m), 1089 (w), 1037 (m), 984 (m), 960 (m), 885 (s), 814 (s), 770 (m), 741 (s), 632 (m), 552 (m), 509 (m), 454 (m).

(NHET₃)₂[Ni₅(nacb)₄(L)(LH)₂(MeOH)] (2). This complex was prepared in the exact same manner as complex 1, but using MeOH (20 mL) in place of MeCN, under the same aerobic conditions. After 7 days, X-ray-quality dark-red platelike crystals of 2 were collected by filtration, washed with cold MeOH (2 \times 2 mL), and dried in air. The yield was 50% based on the total available Ni. Elem anal. Calcd for the solvent-free 2 (*M*_w = 2807.04 g mol⁻¹): C, 58.19; H, 3.77; N, 4.49. Found: C, 58.35; H, 3.83; N, 4.27. Selected IR data (ATR): $\nu = 2981$ (m), 1695 (m), 1574 (vs), 1534 (vs), 1481 (m), 1450 (m), 1404 (s), 1355 (s), 1261 (m), 1217 (m), 1180 (m), 1156 (m), 1111 (mb), 977 (m), 887 (m), 824 (m), 775 (m), 742 (m), 620 (m), 569 (m), 507 (w), 454 (m). The IR band at ~ 1700 cm⁻¹ indicates the presence of a quinone-type C=O double bond in the structure of 2.

X-ray Crystallography. Data for complex 1 were collected on beamline 11.3.1 at the Advanced Light Source, Lawrence Berkeley National Laboratory. Samples were mounted on MiTeGen kapton loops and placed in a 100(2) K nitrogen cold stream provided by an Oxford Cryostream 700 Plus low-temperature apparatus on the goniometer head of a Bruker D8 diffractometer equipped with a PHOTON100 CMOS detector operating in shutterless mode. Diffraction data were collected using synchrotron radiation monochromated using silicon(111) to a wavelength of 0.7749(1) Å. An approximate full-sphere of data was collected using a combination of ϕ and ω scans with scan speeds of 1 s per 4 deg for the ϕ scans and 1 and 3 s per 1 deg for the ω scans at $2\theta = 0$ and -45° , respectively. The structures were solved by intrinsic phasing (SHELXT) and refined by full-matrix least squares on *F*² (SHELXL-2014). All non-H atoms were refined anisotropically. H atoms were geometrically calculated and refined as riding atoms. The H atoms on the water molecules were found in the difference map, and their distances were fixed and allowed to refine with a riding model. The triethylammonium and perchlorate ions were severely disordered and have been heavily constrained and modeled as such. H positions were calculated on all atoms in these disorder models and included in the molecular formula. There exist a large number of solvent molecules including diethyl ether, acetonitrile (MeCN), and water. Because of the positional and occupancy disorder of these solvents, stable refinements could not be achieved, and as such, the density was treated using SQUEEZE,¹⁴ as implemented in the software package PLATON.^{15,16}

Crystalline material of complex 2 was manually harvested, and a selected single crystal was mounted on a cryoloop using adequate oil.¹⁷ Diffraction data were collected on a Bruker X8 Kappa APEX II charge-coupled-device area-detector diffractometer controlled by the APEX2 software package (Mo *K* α graphite-monochromated radiation, $\lambda = 0.71073$ Å)¹⁸ and equipped with an Oxford Cryosystems series 700 cryostream monitored remotely with the software interface Cryopad.¹⁹ Images were processed with the software SAINT+,²⁰ and the

absorption effects were corrected by the multiscan method implemented in SADABS.²¹ The structure was solved using the algorithm implemented in SHELXT-2014^{22,23} and refined by successive full-matrix least-squares cycles on F^2 using the latest SHELXL-v.2014.^{22,24} All of the non-H atoms were successfully refined using anisotropic displacement parameters, except the H atoms of one Et_3NH^+ cation, which were only refined with isotropic parameters. H atoms bonded to C atoms were placed at their idealized positions using appropriate *HFIX* instructions in SHELXL: 43 for the aromatic C atoms, 137 for the terminal CH_3 groups, 23 for the CH_2 groups, and 13 for the CH groups. All of these atoms were included in subsequent refinement cycles in a riding-motion approximation with isotropic thermal displacement parameters (U_{iso}) fixed at 1.2 or $1.5 \times U_{\text{eq}}$ of the relative atom. Although the H atoms of the NH groups in the $\text{LH}^-/\text{L}^{2-}$ ligands, as well as those of the Et_3NH^+ cation, were neither located from difference Fourier maps nor positioned in calculated positions and refined with isotropic parameters, they were included in the molecular formula of the complex. Substantial electron density was found on the diffraction data, almost certainly because of disordered lattice solvate molecules occupying the spaces created by the packing arrangement of the complexes. Our efforts to locate, model, and refine properly these residues were unsuccessful, while the search for the total potential solvent area using the software package PLATON^{15,16} confirmed the existence of cavities with a potential solvent-accessible void volume. Consequently, the original data set was treated with SQUEEZE¹⁴ to minimize the contribution from these highly disordered molecules, and the calculated solvent-free reflection list was then used for the final refinement of the structure. The last difference Fourier map of the crystal structure of **2** revealed the highest peak ($4.406 \text{ e } \text{\AA}^{-3}$) located at 1.29 \AA from C11, and it reflects the structural disorder of one of the Et_3NH^+ cations, which was not possible to model.

Information concerning crystallographic data collection and structure refinement details is summarized in Table 1. Crystallographic data (excluding structure factors) for the structures of complexes **1** and **2** (Supporting Information) have been deposited with the Cambridge Crystallographic Data Centre (CCDC) as supplementary publication numbers CCDC 1426684 (**1**) and 1422591 (**2**). Copies of these data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 2EZ, U.K. [Fax (+44) 1223 336033], online via www.ccdc.cam.ac.uk/data_request/cif, or by emailing data_request@ccdc.cam.ac.uk.

Physical Measurements. IR spectra were recorded in the solid state on a Bruker Fourier transform infrared spectrometer (Alpha platinum ATR single reflection) in the $4000\text{--}450 \text{ cm}^{-1}$ range. NMR spectra were recorded on a Bruker 300 MHz spectrometer at the Chemistry Department, Brock University. All chemical shifts are referenced to tetramethylsilane [$\text{Si}(\text{CH}_3)_4$] or a residual non-deuterated solvent. Data for proton spectra are reported as follows: chemical shift multiplicity [singlet (s) and multiplet (m)]. Elemental analyses (C, H, and N) were performed on a PerkinElmer 2400 series II analyzer. Excitation and emission spectra were recorded in the solid state using a PTI FeliX32 spectrofluorometer. Magnetic susceptibility studies were performed at the Chemistry Department, University of Barcelona, on a DSMS Quantum Design magnetometer. Pascal's constants were used to estimate the diamagnetic correction, which was subtracted from the experimental susceptibility to give the molar paramagnetic susceptibility (χ_{M}).²⁵

RESULTS AND DISCUSSION

Synthesis of Ni^{II} Clusters and Organic Ligand Transformations. In order to solely assess the coordination and bridging affinity of nacbH_2 , we have avoided the use of any additional bridging groups such as carboxylates and/or pseudohalides. Thus, the reaction between $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$, nacbH_2 , and NEt_3 in a 1:1:2 molar ratio in MeCN gave yellow crystals of **1** in 35% yield. Although the mechanism of cluster formation is very difficult to be predicted or explained, it is

Table 1. Crystallographic Data for Complexes **1** and **2**

parameter	1	2
formula ^a	$\text{C}_{222}\text{H}_{144}\text{Cl}_{13}\text{N}_{13}\text{O}_{44}\text{Ni}_{12}$	$\text{C}_{136}\text{H}_{105}\text{Ni}_5\text{O}_{25}\text{N}_9\text{Cl}_7$
fw/g mol ⁻¹	4862.86	2806.98
cryst type	yellow block	red plate
cryst size/mm ³	$0.15 \times 0.08 \times 0.06$	$0.64 \times 0.21 \times 0.03$
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
<i>a</i> /Å	16.9856(6)	18.010(4)
<i>b</i> /Å	25.1456(11)	18.427(4)
<i>c</i> /Å	32.8854(13)	22.874(5)
α /deg	72.694(2)	103.960(9)
β /deg	84.405(2)	91.535(9)
γ /deg	83.388(2)	92.898(10)
<i>V</i> /Å ³	13291.1(9)	7351(3)
<i>Z</i>	2	2
<i>T</i> /K	100(2)	150(2)
<i>D_c</i> /g cm ⁻³	1.215	1.268
μ /mm ⁻¹	1.290	0.822
θ range/deg	2.171–28.967	3.638–25.027
index ranges	$-21 \leq h \leq 21, -31 \leq k \leq 31, -41 \leq l \leq 41$	$-21 \leq h \leq 21, -21 \leq k \leq 21, -27 \leq l \leq 26$
reflns collected	175095	141055
indep reflns	54164 ($R_{\text{int}} = 0.0514$)	25733 ($R_{\text{int}} = 0.0308$)
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^b	$R1 = 0.0516, wR2 = 0.1186$	$R1 = 0.0528, wR2 = 0.1454$
final <i>R</i> indices (all data)	$R1 = 0.0802, wR2 = 0.1306$	$R1 = 0.0590, wR2 = 0.1506$
$(\Delta\rho)_{\text{max,min}}/\text{e } \text{\AA}^{-3}$	2.452, -1.227	4.406, -0.773

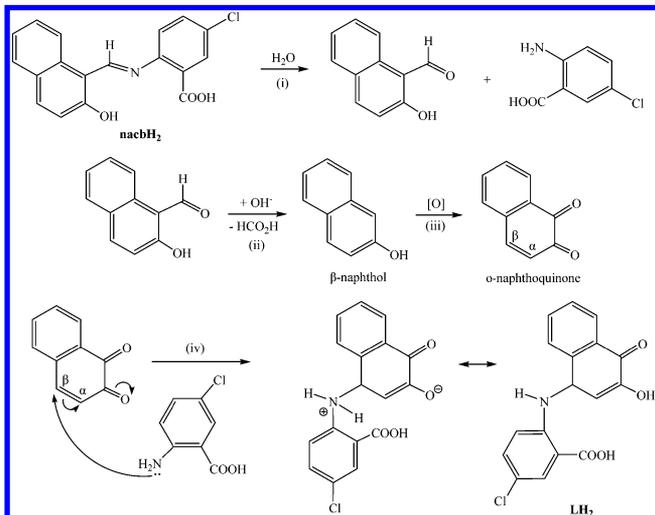
^aExcluding lattice solvate molecules. ^b $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$. $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (ap)^2 + bp]$, where $p = [\max(F_o^2, 0) + 2F_c^2]/3$.

known that the volatility, polarity, rigidity, and coordination affinity of reaction solvent(s) are some of the features that affect the identity of the resulting product(s). To that end, the exact same aerobic reaction, but in solvent MeOH instead of MeCN, led to the isolation of dark-red crystals of **2** in 50% yield.

The new bridging ligand LH_2 (and its anions $\text{L}^{2-}/\text{LH}^-$) resulted from a complicated and unexpected metal-assisted organic transformation of nacbH_2 , further highlighting the rich reactivity chemistry of Schiff bases bearing naphthalene groups. Note that this is the first report of LH_2 in both organic and inorganic chemistry. A proposed mechanism of LH_2 formation is shown in Scheme 2 and most likely includes (i) hydrolysis of nacbH_2 to the original precursors 2-hydroxy-1-naphthaldehyde and 2-amino-5-chlorobenzoic acid,²⁶ (ii) decarbonylation of 2-hydroxy-1-naphthaldehyde to yield β -naphthol with the subsequent release of HCO_2H ,²⁷ (iii) oxidation of β -naphthol from atmospheric O_2 to the corresponding *o*-naphthoquinone,²⁸ and (iv) Michael addition of the NH_2 group of 2-amino-5-chlorobenzoic acid to the β -C atom of naphthoquinone;²⁹ the resulting LH_2 group could also be in resonance with other quinone/semiquinone-type products in solution. It is worth mentioning that the dark-red crystals of **2**, opposite to the yellow-green crystals of **1**, are indicative of the formation of a new ligand with a different chromophore than nacbH_2 ; crystalline (arylamino)naphthoquinones are known dyes with intense-red coloration.³⁰

Description of Structures. Complex **1** comprises 12 Ni^{II} atoms linked by the carboxylate and naphthoxido O atoms of

Scheme 2. Proposed Simplified Mechanism That Leads to LH₂ and Subsequently to the Coordinated, upon Deprotonation, LH⁻ and L²⁻ Groups in Complex 2^a



^aThe Ni²⁺ ions possibly stabilize some of the intermediate products and undoubtedly the final compound 2 (vide infra).

12 nacb²⁻ ligands to form a puckered wheel of virtual D₄ point group symmetry (Figures 1 and S1). The void space at the

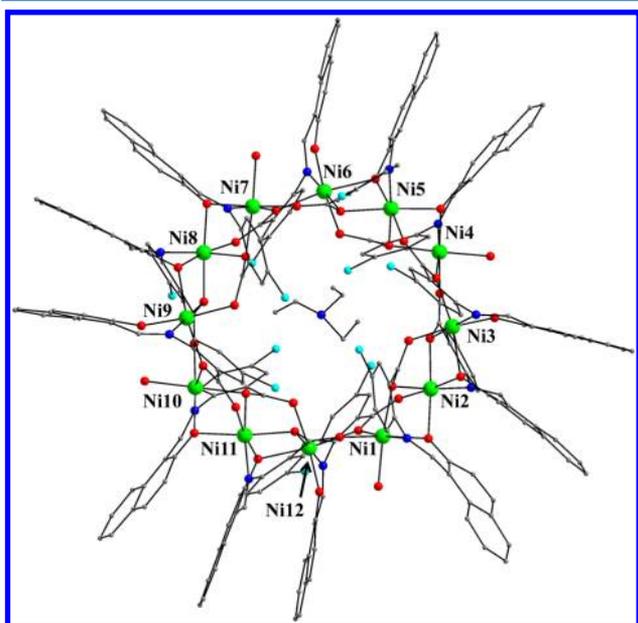


Figure 1. Partially labeled structure of the cation of 1. All H atoms are omitted for clarity. Color scheme: Ni^{II}, green; O, red; N, blue; C, dark gray; Cl, cyan.

central hole of the wheel is occupied by a NH₄⁺ cation, and the overall charge of the Ni₁₂ cluster is counterbalanced by a ClO₄⁻ anion. Four nacb²⁻ groups bind in an $\eta^1:\eta^1:\eta^2:\eta^1:\mu_3$ mode (Figure 2), bridging solely through the carboxylate O atoms, in a manner similar to how sacb²⁻ binds in all of the previously reported cluster compounds. The remaining eight nacb²⁻ ligands adopt the $\eta^2:\eta^1:\eta^2:\eta^1:\mu_3$ mode (Figure 2), with the two “pockets” of each ligand chelating a Ni^{II} atom and both the carboxylate and naphthoxido O atoms participating in the bridging of two additional metal ions. This unique coordination

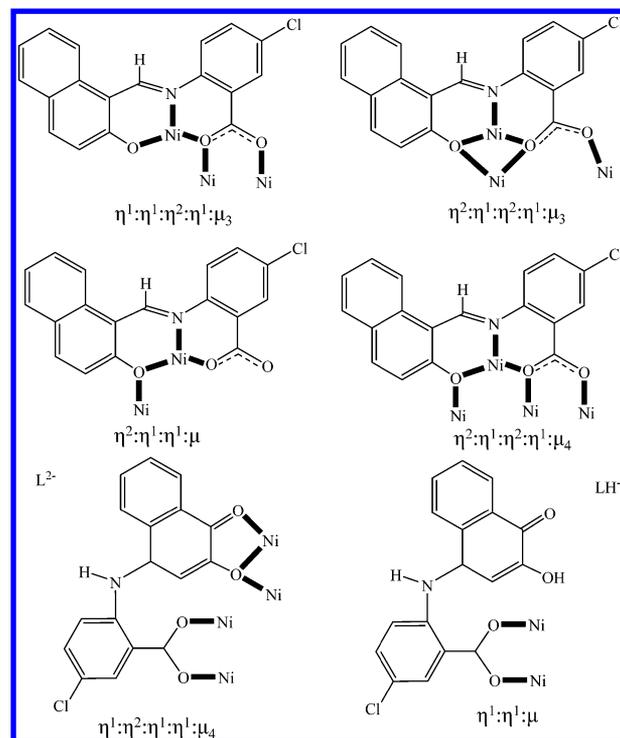


Figure 2. Crystallographically established coordination modes of all organic ligands present in complexes 1 (top) and 2 (middle and bottom).

mode, responsible for the formation and stabilization of the Ni₁₂ wheel, is unprecedented in Ni^{II}/nacb²⁻ chemistry.^{10–12}

We have thus tried to understand the reasons of such coordination differences, which would also allow us to tentatively interpret the structural variations between the Ni^{II}/nacb²⁻ and Ni^{II}/sacb²⁻ products (Figure S2). In all of the reported Ni^{II}/sacb²⁻ compounds,^{10–12} the ligand’s phenyl rings are arranged in an average angle of $\sim 47^\circ$ from each other. However, the analogous average angle between the naphthalene and phenyl rings of nacb²⁻-related products is $\sim 34^\circ$, significantly smaller than that of sacb²⁻. Consequently, the aromatic rings of sacb²⁻ show a higher degree of rotation about the imino “axle” compared to the naphthalene–benzene pair of nacb²⁻, allowing sacb²⁻ to have a greater flexibility and thus yield a variety of different Ni^{II} products. In contrast, the smaller angles between the aromatic rings of nacb²⁻ allow the donor atoms of the ligand to interact differently with the metal ions and consequently stabilize compounds with topologies different from those seen in Ni^{II}/sacb²⁻ products.^{10–12}

Hence, the complete core of 1 (including only the doubly bridging monatomic groups) is [Ni₁₂(μ -OR)₂₀]⁴⁺ (Figure 3) and can be conveniently described as four bent Ni₃ units (Ni1–Ni2–Ni3, Ni4–Ni5–Ni6, etc.; Figure S3) linked at each end by a μ -OR⁻ group (O8, O17, O26, and O35) from a nacb²⁻ ligand. All Ni^{II} atoms are six-coordinate with distorted octahedral geometries. The coordination spheres of Ni-(1,4,7,10) are completed by a terminal H₂O molecule; the latter are all strongly hydrogen-bonded to the nonbridging phenoxido O atoms of nacb²⁻. Finally, a space-filling representation (Figure S4) shows the nanoscale dimensions of 1, with a diameter of ~ 25 Å and a central hole of ~ 7 Å diameter; note that the polar surface area of NH₄⁺ is ~ 3.3 Å², justifying its accommodation in the void space of the Ni₁₂ wheel. Complex 1 is only the third Ni₁₂ wheel-like cluster

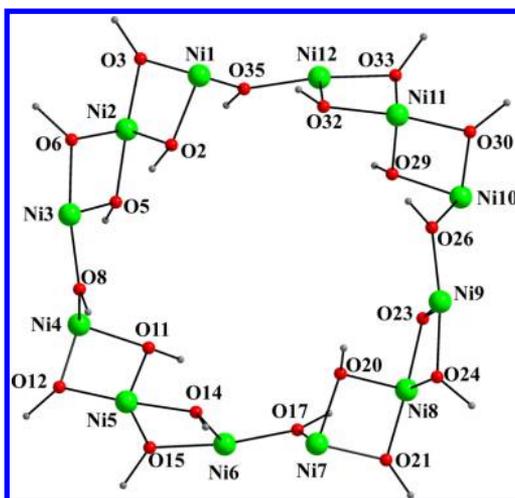


Figure 3. Complete $[\text{Ni}_{12}(\mu\text{-OR})_{20}]^{4+}$ core of **1**. Bond angles (deg): Ni1–O2–Ni2 = 92.6(9); Ni1–O3–Ni2 = 94.7(9); Ni1–O35–Ni12 = 116.9(1); Ni2–O5–Ni3 = 95.1(9); Ni2–O6–Ni3 = 97.7(1); Ni3–O8–Ni4 = 116.0(1); Ni4–O11–Ni5 = 92.9(1); Ni4–O12–Ni5 = 95.3(1); Ni5–O14–Ni6 = 96.2(9); Ni5–O15–Ni6 = 96.8(1); Ni6–O17–Ni7 = 116.0(1); Ni7–O20–Ni8 = 91.3(9); Ni7–O21–Ni8 = 95.1(1); Ni8–O23–Ni9 = 95.8(9); Ni8–O24–Ni9 = 96.9(9); Ni9–O26–Ni10 = 117.3(1); Ni10–O29–Ni11 = 91.4(9); Ni10–O30–Ni11 = 94.4(9); Ni11–O32–Ni12 = 96.1(9); Ni11–O33–Ni12 = 95.7(9).

reported in the literature to date, with the two previous ones possessing $S = 12^{31}$ and 0^{32} spin ground states.

The crystal structure of **2** consists of $[\text{Ni}_5(\text{nacb})_4(\text{L})(\text{LH})_2(\text{MeOH})]^{2-}$ anions (Figure 4) counterbalanced by

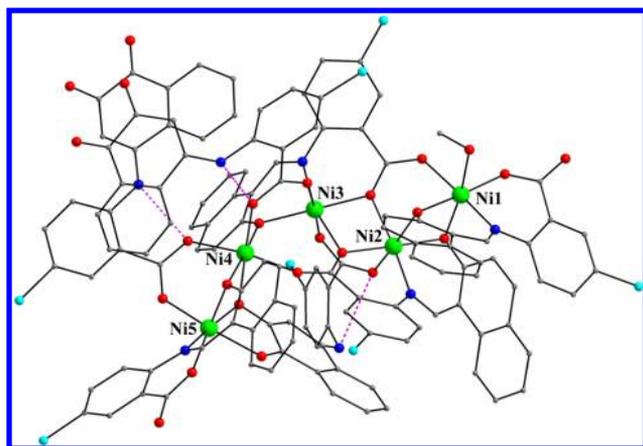


Figure 4. Partially labeled structure of the $[\text{Ni}_5(\text{nacb})_4(\text{L})(\text{LH})_2(\text{MeOH})]^{2-}$ anion of **2**. The purple dashed lines indicate the three strong intramolecular hydrogen bonds between the N–H groups and carboxylate O atoms of the three $\text{L}^{2-}/\text{LH}^-$ ligands.

NH_4Et_3^+ cations; the latter will not be further discussed. The Ni_5 anion comprises a nonlinear, zigzag array of five Ni^{II} atoms (av. Ni–Ni–Ni angle = 125.5°) linked together through the naphthoxido (O1, O6, O10, and O13), naphthoquinonato (O25), and carboxylate (O2, O3, O8, O9, O16, O17, O18, O19, O22, and O23) functionalities of two $\eta^2:\eta^1:\eta^1:\mu$ and $\eta^2:\eta^1:\eta^2:\eta^1:\mu_4$ nacb^{2-} ligands, as well as two $\eta^1:\eta^1:\mu$ LH^- and an $\eta^1:\eta^2:\eta^1:\eta^1:\mu_4$ L^{2-} groups (Figure 2). Thus, the overall core of **2**, including the triatomic carboxylate bridges, is $[\text{Ni}_5(\mu\text{-OR})_5(\mu_3\text{-O}_2\text{CR})_2(\mu\text{-O}_2\text{CR})_3]$ (Figure 5), with peripheral ligation

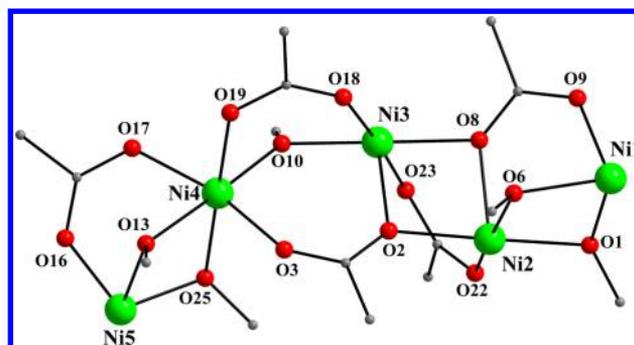


Figure 5. Complete zigzag core of complex **2**. Bond angles (deg): Ni1–O1–Ni2 = 95.4(1); Ni1–O6–Ni2 = 94.3(1); Ni2–O8–Ni3 = 97.2(1); Ni2–O2–Ni3 = 98.1(1); Ni3–O10–Ni4 = 110.1(1); Ni4–O13–Ni5 = 92.3(1); Ni4–O25–Ni5 = 94.3(1).

provided by the chelating parts of the ligands and a terminal MeOH molecule on Ni1. None of the Ni–O–Ni–O rhombus is planar but instead quite distorted; the average torsion angle is 16.8° . The Ni^{II} atoms are all six-coordinate with distorted octahedral geometries. The differences between the C...O bond lengths (C=O = 1.21(1)–1.23(1) Å versus C–O = 1.25(1)–1.33(1) Å) in the coordinated $\text{L}^{2-}/\text{LH}^-$ ligands are indicative of a hydroquinone-type unit rather than a pure quinone or catechol.³³ Although there are many Ni_5 clusters reported to date, most of them consist of either fused Ni_3 triangular units or strictly linear, Ni–Ni-bonded species. Complex **2** is the sixth Ni_5 cluster with a zigzag “molecular chain” structure reported to date albeit the first nonoximate one.³⁴

Solid-State Magnetic Susceptibility Studies. Variable-temperature (2.0–300 K range), direct-current (dc) magnetic susceptibility measurements were performed on freshly prepared microcrystalline solids of **1**·3H₂O and **2**; a dc field of 0.3 T was applied from 30 to 300 K, and a weak dc field of 0.03 T was used from 2 to 30 K to avoid saturation effects. The data are shown as $\chi_M T$ versus T plots in Figure 6. For the Ni_{12} wheel, the $\chi_M T$ product steadily decreases with decreasing T , from a value of $13.60 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 300 K to $4.07 \text{ cm}^3 \text{ mol}^{-1} \text{ K}$ at 2 K; such behavior is consistent with the presence of predominant antiferromagnetic exchange interactions between

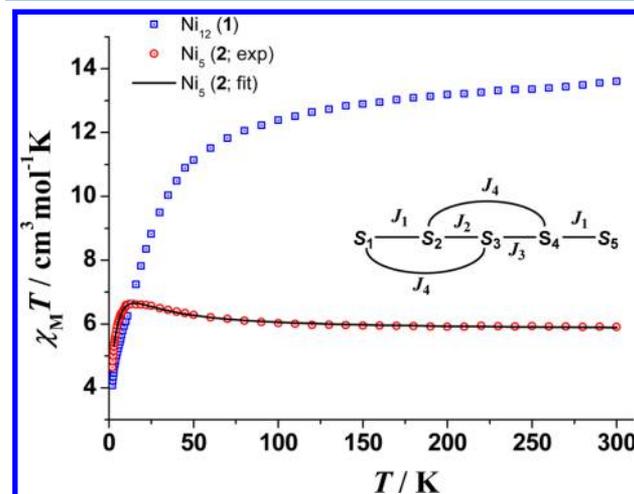


Figure 6. $\chi_M T$ versus T plots of **1**·3H₂O and **2**. The solid line is the fit of the data; see the text for the fit parameters. (inset) J -coupling scheme employed for the elucidation of magnetic exchange interactions in **2**.

the 12 Ni^{II} atoms. Because of the size, shape, and low symmetry of **1**, a fit of the experimental data to a theoretical model ($H = -2J_{ij}\hat{S}_i\cdot\hat{S}_j$, convention) turned out to be unsuccessful. Undoubtedly, **1** possesses a small ground-state spin value, if not zero. Magnetostructural correlations on complex **1** failed to rationalize, even tentatively, any other than an $S = 0$ spin ground-state value. An $S = 0$ spin ground state may result from the antiferromagnetic interactions between the four bent Ni₃ units within **1**, promoted by the μ -OR⁻ groups; the Ni–O–Ni bond angles for the latter monatomic bridges span the range 116.0–117.3°, clearly suggesting antiferromagnetic interactions between the Ni1⋯Ni12, Ni9⋯Ni10, Ni6⋯Ni7, and Ni3⋯Ni4 pairs. The two previously reported [Ni₁₂(chp)₁₂(O₂CMe)₁₂(thf)₆(H₂O)₆]³¹ and [Ni₁₂(C₁₃H₉N₃O₂)₁₂(MeOH)₁₂]³² wheel-like complexes are ferromagnetically and antiferromagnetically coupled with $S = 12$ and 0 spin ground states, respectively. This is due to the Ni–O–Ni angles in the former case, which fall into the 95.7–97.4° range, and the large Ni–N–N–Ni torsion angles for the latter case.

In contrast, for the Ni₅ complex (**2**), the $\chi_M T$ product steadily increases from 5.90 cm³ mol⁻¹ K at 300 K to a value of 6.65 cm³ mol⁻¹ K at 13 K and then decreases rapidly to a value of 4.64 cm³ mol⁻¹ K at 2 K. The data and shape of the plot indicate predominant ferromagnetic exchange interactions between the metal centers. However, the fact that the magnetic susceptibility does not reach a value of ~15 cm³ mol⁻¹ K, expected for an $S = 5$ system (with $g \approx 2$), is suggestive of the copresence of competing antiferromagnetic interactions within **2**. In any case and for any sign, the magnetic interactions in **2** should be weak.

Despite the relatively low nuclearity of **2**, the fit of the magnetic data was rather challenging because of the low symmetry of the complex and the fact that most of the superexchange pathways consist of countercomplementary carboxylate–alkoxido bridges, with the Ni–O–Ni bond angles close to the ferromagnetic/antiferromagnetic border. The interactions between Ni1⋯Ni2 and Ni4⋯Ni5 can be considered very similar (J_1) because they result from the same bridges with very close bond and torsion angles. However, the remaining superexchange pathways are clearly different from each other (J_2 – J_4) and cannot be further simplified to reduce the total number of coupling constants. On the basis of Figure 6 (inset), the applied Heisenberg spin Hamiltonian for **2** is

$$H = -J_1(\hat{S}_1\cdot\hat{S}_2 + \hat{S}_4\cdot\hat{S}_5) - J_2(\hat{S}_2\cdot\hat{S}_3) - J_3(\hat{S}_3\cdot\hat{S}_4) - J_4(\hat{S}_1\cdot\hat{S}_3 + \hat{S}_2\cdot\hat{S}_4)$$

The PHI program³⁵ was used to fit the susceptibility and magnetization data of **2**. An excellent fit (solid line in Figure 6) was obtained with the following parameters: $J_1 = +7.6$ cm⁻¹, $J_2 = -8.4$ cm⁻¹, $J_3 = +2.1$ cm⁻¹, $J_4 = +2.4$ cm⁻¹, and $g = 2.15$. To evaluate the reliability of the obtained J_{ij} parameters, we performed a systematic set of fits including a D term or assuming a simpler, linear magnetic structure, excluding the J_4 parameter, which accounts for the interaction mediated by the syn–anti carboxylate moiety of nacb²⁻ and is much smaller than J_2 . In all cases, the sign and magnitude of the remaining J_1 – J_3 interactions were practically unaltered. Obviously, the absolute values of the coupling constants are poorly reliable, but they agree with the expected values that can be envisaged from the structural data. In particular, the smaller Ni–O–Ni

bond angles (related to J_1) promote weak ferromagnetic interactions, whereas the larger Ni–O–Ni bond angles (110.1°, related to J_2) propagate weak antiferromagnetic interactions; finally, the intermediate Ni–O–Ni bond angles and the syn–anti carboxylate bridges (corresponding to J_3 and J_4 , respectively) promote very weak interactions. As a result of the above-reported J values, the ground state cannot be strictly defined, with four consecutive spin states, $S = 3, 2, 1$ and 4, in a short range of less than 3 cm⁻¹, further justifying the shape and value of magnetization, as shown in Figure 7.

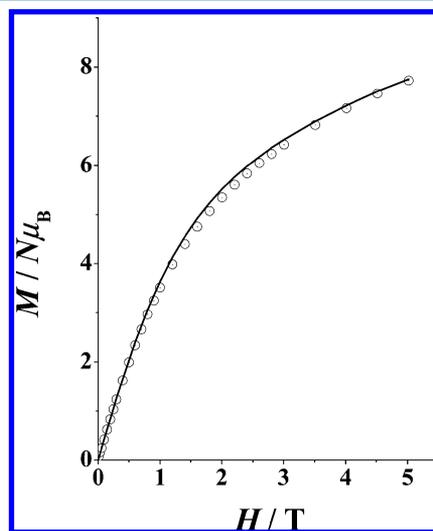


Figure 7. Plot of magnetization (M) versus field (H) for complex **2** at 2 K. The solid line is the fit of the data obtained by using the J coupling constants discussed in the text.

Four different Ni₅ compounds with a zigzag topology have been structurally and magnetically characterized to date. The ferromagnetically coupled complex [Ni₅{pyCOpyC(O)(OMe)py}₂(O₂CMe)₄(N₃)₄(MeOH)₂] has an $S = 5$ spin ground state in line with the presence of end-on bridging azides and alkoxido groups with Ni–O–Ni angles close to 95°. ^{34a} For the [Ni₅(Hpyaox)₄(pyaox)₂L₂](ClO₄)₂ complex, ^{34b} where H₂pyaox is the pyridine-2-amidoxime ligand and L is 2-[(2-aminoethyl)amino]ethanol, the overall weak ferromagnetic behavior is due to the particular Ni–N–O–Ni torsion angles, which result in different signs and magnitudes for the Ni⋯Ni magnetic exchange interactions. Complex [Ni₅(3-Cl-BzO)₄(6-mepao)₄(6-mepaoH)₂(N₃)₂], where 6-mepaoH is the 6-methylpyridine-2-carbaldehydeoxime ligand and 3-Cl-BzO⁻ is the 3-chlorobenzoate anion, ^{34c} has an $S = 3$ ground state that arises from the combination of antiferromagnetic and ferromagnetic exchange interactions via the triple carboxylate–oximate–oxo bridge, the single oximate bridge, and finally the interaction involving the end-on azido bridges. Finally, complex [Ni₅(RCO₂)₂(dapdo)₂(dapdoH)₂(N(CN)₂)₂(MeOH)₂] (R = various) comprises three paramagnetic Ni^{II} centers and two square-planar and diamagnetic Ni^{II} atoms bridged together by the anionic forms of the organic chelate 2,6-diacetylpyridine dioxime (dapdoH₂). ^{34e} The compound is antiferromagnetically coupled because of the large Ni–O–N–Ni torsion angles.

Solid-State Emission Studies. The use of metal complexes in the design of luminescent-responsive probes has attracted interest over the last years because they can offer

improved photophysical responses over the pure organic fluorophores.² Thus, in order to gain any possible access to additional physical properties for **1** and **2** and to compare the optical potency of nacbH_2 versus sacbH_2 , we decided to perform solid-state photoluminescence studies on all compounds at room temperature. The free ligand nacbH_2 is a promising “antenna” group with a pronounced ability for promoting energy-transfer effects. Upon maximum excitation at 349 nm, nacbH_2 exhibits a strong emission in the 380–420 nm visible range with two clear maxima at 391 and 410 nm and a weak shoulder at 482 nm (Figure 8). The two maxima are

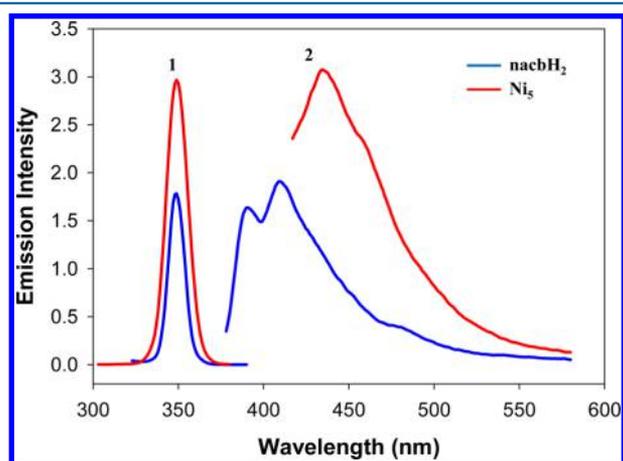


Figure 8. Excitation (1) and emission (2) spectra of nacbH_2 (blue lines) and complex **2** (red lines) in the solid state and at room temperature.

probably due to the presence of two different aromatic groups (naphthalene and benzene) within the same molecule;³⁶ the emission at ~ 390 nm is characteristic of the naphthalene functional group.¹³ The optical response of nacbH_2 in various solutions and different concentrations is exactly the same as that reported in the solid state. The free ligand sacbH_2 has shown a similar emission, albeit with only one emission band at 415 nm, further supporting the fact that the phenyl emission on this class of Schiff base ligands appears at ~ 410 nm.¹¹

Although there has been no emission detected for any $\text{Ni}^{\text{II}}/\text{sacb}^{2-}$ complex reported to date,^{11,12} most likely because of inefficient energy transfer from the ligand and/or quenching effects,³⁷ this turned out not to be the case for complex **2**. In contrast to the high-nuclearity Ni_{12} , which shows no emission at room temperature, complex **2** exhibits a strong blue-centered emission at 435 nm, upon maximum excitation at 352 nm (Figure 8). The emission of **2** is slightly red-shifted with respect to the free ligand nacbH_2 and more intense; the observed and enhanced intensity can be tentatively assigned to the coordination of nacb^{2-} and $\text{L}^{2-}/\text{LH}^-$ ligands to the metal centers. There is no convincing evidence that complexes **1** and **2** retain their structures in solution, and therefore we have not pursued any emission studies in solution.

It is known that the deprotonation and coordination of a ligand to a metal ion increase the rigidity of the organic molecule and consequently reduce the loss of energy via vibrational motions.³⁸ Red shift of the emission maximum can be normally observed for the most fluorescent compounds in the solid state probably because of the π - π -stacking interactions of the aromatic rings in the molecules.³⁹ Given the complexity of **2** and the number of metal ions and ligands

present, among other structural perturbations, a detailed analysis of the photophysical energy-transfer mechanism and the type of emission is not feasible. Undoubtedly, though, the structural characteristics of nacbH_2 , and particularly the presence of the naphthalene substituent, have turned this group into a more liable to optical activity ligand than sacbH_2 .

CONCLUSIONS

In conclusion, we have herein reported a new naphthalene-substituted Schiff base ligand that not only leads to Ni^{II} clusters with unprecedented topologies and beautiful structures but also contributes to the observation of interesting physicochemical properties, such as ferromagnetic coupling and optical emission, as well as unforeseen organic transformations assisted by the presence of 3d metal ions. Attempts to rationalize the structural and physicochemical differences between the metal clusters obtained with the related sacbH_2 ligand were tried out, and these were ascribed to the special steric and electronic properties of nacbH_2 . Finally, these first findings highlight the importance of selecting an appropriate chelating/bridging “ligand with benefits” for the synthesis of new molecule-based materials with multiple properties.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorgchem.5b02492.

Various structural and magnetism figures (PDF)

Crystallographic data in CIF format (CIF)

Crystallographic data in CIF format (CIF)

AUTHOR INFORMATION

Corresponding Author

*E-mail: tstamatatos@brocku.ca.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This work was supported by Brock University, NSERC-DG, and ERA (to T.C.S), the Alexander S. Onassis Public Benefit Foundation (graduate scholarship to P.S.P.), Fundação para a Ciência e a Tecnologia (Portugal), which funded REQUIMTE/LAQUV (UID/QUI/50006/2013), and CICYT (Project CTQ2012-30662 to A.E). The Advanced Light Source was supported by The Director, Office of Science, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract DE-AC02-05CH11231. We also thank Professor Dionyssios Papaioannou (Chemistry Department, University of Patras, Patras, Greece) for assistance with the proposed mechanism for the formation of $\text{L}^{2-}/\text{LH}^-$ groups in complex **2**. C.L. acknowledges support through the Cottrell College Science Award from the Research Corporation for Science Advancement and the Dreyfus Foundation.

REFERENCES

- (1) (a) Brechin, E. K. *Chem. Commun.* **2005**, 5141–5143. (b) Aromí, G.; Brechin, E. K. *Struct. Bonding (Berlin)* **2006**, *122*, 1–67. (c) Tasiopoulos, A. J.; Perlepes, S. P. *Dalton Trans.* **2008**, 5537–5555. (d) Stamatatos, Th. C.; Efthymiou, C. G.; Stoumpos, C. C.; Perlepes, S. P. *Eur. J. Inorg. Chem.* **2009**, 2009, 3361–3391. (e) Milios,

- C. J.; Winpenny, R. E. P. *Struct. Bonding (Berlin, Ger.)* **2014**, *164*, 1–109.
- (2) Bünzli, J.- C. G.; Eliseeva, S. V. *Chem. Sci.* **2013**, *4*, 1939–1949.
- (3) (a) Jo, M. H.; Grose, J. E.; Baheti, K.; Deshmukh, M. M.; Sokol, J. J.; Rumberger, E. M.; Hendrickson, D. N.; Long, J. R.; Park, H.; Ralph, D. C. *Nano Lett.* **2006**, *6*, 2014–2020. (b) Coronado, E.; Marti-Gastaldo, C.; Tatay, S. *Appl. Surf. Sci.* **2007**, *254*, 225–235.
- (4) For representative examples, see: (a) Schmidt, S.; Prodius, D.; Mereacre, V.; Kostakis, G. E.; Powell, A. K. *Chem. Commun.* **2013**, *49*, 1696–1698. (b) Brunet, G.; Habib, F.; Cook, C.; Pathmalingam, T.; Loiseau, F.; Korobkov, I.; Burchell, T. J.; Beauchemin, A. M.; Murugesu, M. *Chem. Commun.* **2012**, *48*, 1287–1289. (c) Blackman, A. *Eur. J. Inorg. Chem.* **2008**, *2008*, 2633–2647. (d) Chesman, A. S. R.; Turner, D. R.; Moubaraki, B.; Murray, K. S.; Deacon, G. B.; Batten, S. R. *Eur. J. Inorg. Chem.* **2010**, *2010*, 59–73.
- (5) For example, see: Ababei, R.; Pichon, C.; Roubeau, O.; Li, Y.- G.; Bréfuel, N.; Buisson, L.; Guionneau, P.; Mathonière, C.; Clérac, R. *J. Am. Chem. Soc.* **2013**, *135*, 14840–14853.
- (6) Long, J.; Rouquette, J.; Thibaud, J. M.; Ferreira, R. A. S.; Carlos, L. D.; Donnadiou, B.; Vieru, V.; Chibotaru, L. F.; Konczewicz, L.; Haines, J.; Guari, Y.; Larionova, J. *Angew. Chem., Int. Ed.* **2015**, *54*, 2236–2240.
- (7) (a) Winpenny, R. E. P. *Adv. Inorg. Chem.* **2001**, *52*, 1–111. (b) Winpenny, R. E. P. *J. Chem. Soc., Dalton Trans.* **2002**, 1–10.
- (8) For representative examples, see: (a) Tasiopoulos, A. J.; Vinslava, A.; Wernsdorfer, W.; Abboud, K. A.; Christou, G. *Angew. Chem., Int. Ed.* **2004**, *43*, 2117–2121. (b) Whitehead, G. F. S.; Moro, F.; Timco, G. A.; Wernsdorfer, W.; Teat, S. J.; Winpenny, R. E. P. *Angew. Chem.* **2013**, *125*, 10116–10119. (c) Scott, R. T. W.; Parsons, S.; Murugesu, M.; Wernsdorfer, W.; Christou, G.; Brechin, E. K. *Angew. Chem., Int. Ed.* **2005**, *44*, 6540–6543. (d) Manoli, M.; Inglis, R.; Manos, M. J.; Nastopoulos, V.; Wernsdorfer, W.; Brechin, E. K.; Tasiopoulos, A. J. *Angew. Chem., Int. Ed.* **2011**, *50*, 4441–4444.
- (9) (a) Kahn, O. *Molecular Magnetism*; VCH Publishers: New York, 1993. (b) Benelli, C.; Gatteschi, D. *Chem. Rev.* **2002**, *102*, 2369–2388.
- (10) Perlepe, P. S.; Athanasopoulou, A. A.; Alexopoulou, K. I.; Raptopoulou, C. P.; Psycharis, V.; Escuer, A.; Perlepes, S. P.; Stamatatos, Th. C. *Dalton Trans.* **2014**, *43*, 16605–16609.
- (11) Athanasopoulou, A. A.; Raptopoulou, C. P.; Escuer, A.; Stamatatos, Th. C. *RSC Adv.* **2014**, *4*, 12680–12684.
- (12) Athanasopoulou, A. A.; Pilkington, M.; Raptopoulou, C. P.; Escuer, A.; Stamatatos, Th. C. *Chem. Commun.* **2014**, *50*, 14942–14945.
- (13) Alexandropoulos, D. I.; Mowson, A. M.; Pilkington, M.; Bekiari, V.; Christou, G.; Stamatatos, Th. C. *Dalton Trans.* **2014**, *43*, 1965–1969.
- (14) Van der Sluis, P.; Spek, A. L. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **1990**, *46*, 194.
- (15) Spek, A. L. *Acta Cryst. A* **1990**, *46*, C34.
- (16) Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.
- (17) Kottke, T.; Stalke, D. *J. Appl. Crystallogr.* **1993**, *26*, 615.
- (18) APEX2, *Data Collection Software*, version 2012.4; Bruker AXS: Delft, The Netherlands, 2012.
- (19) Cryopad, *Remote monitoring and control*, version 1.451; Oxford Cryosystems: Oxford, U.K., 2006.
- (20) SAINT+, *Data Integration Engine* version 8.27b; Bruker AXS: Madison, WI, 1997–2012.
- (21) Sheldrick, G. M. *SADABS 2012/1, Bruker AXS Area Detector Scaling and Absorption Correction Program*; Bruker AXS: Madison, WI, 2012.
- (22) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112.
- (23) Sheldrick, G. M. *SHELXT, Program for Crystal Structure Solution*, version 2014/3; University of Göttingen: Göttingen, Germany, 2014.
- (24) Sheldrick, G. M. *SHELXL, Program for Crystal Structure Refinement*; University of Göttingen: Göttingen, Germany, 2014.
- (25) Bain, G. A.; Berry, J. F. *J. Chem. Educ.* **2008**, *85*, 532–536.
- (26) Cordes, E. H.; Jencks, W. P. *J. Am. Chem. Soc.* **1963**, *85*, 2843–2848.
- (27) Ukhin, L. Y.; Morkovnik, Z. S.; Philipenko, O. S.; Aldoshin, S. M.; Shishkin, O. V. *Mendeleev Commun.* **1997**, *7*, 153–154.
- (28) Denisova, A. N.; Denisov, E. T.; Metelitsa, D. I. *Bull. Acad. Sci. USSR, Div. Chem. Sci.* **1969**, *18*, 1537–1542.
- (29) Chatfield, D. C.; Augsten, A.; D’Cunha, C.; Lewandowska, E.; Wnuk, S. F. *Eur. J. Org. Chem.* **2004**, *2004*, 313–322.
- (30) (a) Gornostaev, L. M.; Lyashchenko, T. A.; Arnold, E. V. *Chem. Heterocycl. Compd.* **2014**, *49*, 1827–1830. (b) Harmon, R. E.; Phipps, L. M.; Howell, J. A.; Gupta, S. K. *Tetrahedron* **1969**, *25*, 5807–5813.
- (31) (a) Blake, A. J.; Grant, C. M.; Parsons, S.; Rawson, J. M.; Winpenny, R. E. P. *J. Chem. Soc., Chem. Commun.* **1994**, 2363–2364. (b) Andres, H.; Basler, R.; Blake, A. J.; Cadiou, C.; Chaboussant, G.; Grant, C. M.; Güdel, H.- U.; Murrie, M.; Parsons, S.; Paulsen, C.; Semadini, F.; Villar, V.; Wernsdorfer, W.; Winpenny, R. E. P. *Chem. - Eur. J.* **2002**, *8*, 4867–4876.
- (32) Bai, Y.; Dang, D.; Duan, C.; Song, Y.; Meng, Q. *Inorg. Chem.* **2005**, *44*, 5972–5974.
- (33) (a) Grillo, V. A.; Hanson, G. R.; Wang, D.; Hambley, T. W.; Gahan, L. R.; Murray, K. S.; Moubaraki, B.; Hawkins, C. J. *Inorg. Chem.* **1996**, *35*, 3568–3576. (b) Boudalis, A. K.; Dahan, F.; Bousseksou, A.; Tuchagues, J.- P.; Perlepes, S. P. *Dalton Trans.* **2003**, 3411–3418.
- (34) (a) Boudalis, A. K.; Pissas, M.; Raptopoulou, C. P.; Psycharis, V.; Abarca, B.; Ballesteros, R. *Inorg. Chem.* **2008**, *47*, 10674–10681. (b) An, G.- Y.; Wang, H.- B.; Cui, A.- L.; Kou, H.- Z. *New J. Chem.* **2014**, *38*, 5037–5042. (c) Escuer, A.; Vlahopoulou, G.; Mautner, F. A. *Dalton Trans.* **2011**, *40*, 10109–10116. (d) Perivolaris, A.; Stoumpos, C. C.; Karpinska, J.; Ryder, A. G.; Frost, J. M.; Mason, K.; Prescimone, A.; Slawin, A. M. Z.; Kessler, V. G.; Mathieson, J. S.; Cronin, L.; Brechin, E. K.; Papaefstathiou, G. S. *Inorg. Chem. Front.* **2014**, *1*, 487–494. (e) Escuer, A.; Esteban, J.; Roubeau, O. *Inorg. Chem.* **2011**, *50*, 8893–8901.
- (35) Chilton, N. F.; Anderson, R. P.; Turner, L. D.; Soncini, A.; Murray, K. S. *J. Comput. Chem.* **2013**, *34*, 1164–1175.
- (36) Fleischauer, P. D.; Fleischauer, P. *Chem. Rev.* **1970**, *70*, 199–230.
- (37) Bünzli, J.- C. G.; Piguet, C. *Chem. Soc. Rev.* **2005**, *34*, 1048–1077.
- (38) (a) Lehn, J.- M. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1304–1319. (b) Binnemans, K. *Chem. Rev.* **2009**, *109*, 4283–4374. (c) Chia, Y. Y.; Tay, M. G. *Dalton Trans.* **2014**, *43*, 13159–13168.
- (39) Barwiolek, M.; Szlyk, E.; Muziol, T. M.; Lis, T. *Dalton Trans.* **2011**, *40*, 11012–11022.