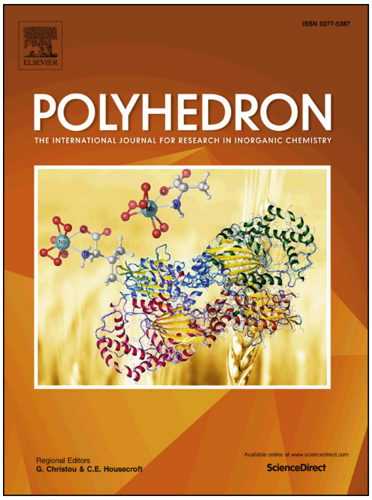

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# New complexes of Ni(II) and Co(III) with a Schiff-base ligand derived from *o*-vanillin. Crystal structure, magnetic and catalytic properties of a dissymmetric binuclear nickel(II) complex

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*Dedicated to Professor Spyros Perlepes, a great scientist and friend*

## ABSTRACT

A binuclear complex, $[Ni_2L_2(NO_3)(H_2O)(CH_3CN)]ClO_4\cdot CH_3CN$ (**1**), has been obtained using a Schiff-base ligand (HL) derived from *o*-vanillin and 4-(2-aminoethyl)morpholine. The crystal structure of **1** has been solved. Both Ni(II) ions are hexacoordinated, but they display different coordination spheres. The exchange interaction between the two nickel ions is antiferromagnetic ($J = -7.9\pm0.2$ cm$^{-1}$; $\boldsymbol{H} = -J\mathbf{S}_1\mathbf{S}_2$), in line with the DFT calculations. Compound **1** was tested as a catalyst in the epoxidation of various olefins. The reaction of the same ligand with a mixture of cobalt(II) perchlorate and nitrate affords a mononuclear Co(III) complex, $[CoL_2(H_2O)]ClO_4\cdot CH_3OH$ (**2**).

**Keywords:** nickel complexes; cobalt complexes; Schiff-base ligands; magnetic properties; catalysis

## 1. Introduction

The interest in the chemistry of oligonuclear complexes of nickel(II) arises from their relevance in molecular magnetism, model bioinorganic chemistry, and catalysis. Numerous binuclear complexes have been synthesized and employed as models for the investigation of the factors governing the nature (ferro- or antiferromagnetic) and strength of the exchange interactions between the Ni(II) ions mediated by various bridges, e. g. phenoxido [1], azido [2], cyanato and thiocyanato [2a,3], carboxylato [4] etc. The magneto-structural correlations have been supported by DFT calculations [1a,b,d]. The bioinorganic chemistry of nickel started with the discovery of urease, an enzyme that catalyzes the hydrolysis of urea [5], the active site containing two nickel ions bridged by one carboxylato and one hydroxido group. This discovery prompted chemists to synthesize model compounds for urease [6], as well as new compounds able to catalyze various reactions, e. g. epoxidation of aliphatic, aromatic, and terminal olefins [7], hydrolysis of esters under ambient conditions [8], oligomerization of ethylene [9], and polymerization of olefins [10].

The Schiff-base ligands derived from *o*-vanillin generate a very rich coordination chemistry [11]. In this paper we report on a new dissymmetric binuclear Ni(II) complex (**1**), which is obtained using a Schiff-base proligand resulted from the condensation reaction between *o*-vanillin and 4-(2-aminoethyl)morpholine (HL). Its spectral, magnetic, and catalytic properties in epoxidation reactions of olefins have been investigated. This ligand was already employed by Mohanta et al. to obtain a binuclear Ni(II) complex with azido bridges [12], by Su et al. to obtain mononuclear complexes of Co(III) [13], and by Dai et al. to obtain a binuclear Cd(II) complex [14]. We also present here the crystal structure of a mononuclear Co(III) complex (**2**), which is obtained by reacting the proligand HL with a mixture of cobalt (II) nitrate and perchlorate.

## 2. Experimental part

### 2.1. Synthesis

All chemicals used for the present study were purchased from commercial sources and used without further purification.

### 2.1.1. Synthesis of $[Ni_2L_2(NO_3)(H_2O)(CH_3CN)]ClO_4\cdot CH_3CN$ **1**

A solution of 45.57 mg 4-(2-aminoethyl)morpholine (0.35 mmol) in 10 mL acetonitrile was added dropwise under continuous stirring to a solution of 53.25 mg *o*-vanillin (0.35 mmol) in 15 mL acetonitrile. The solution rapidly turned from colorless to bright yellow. After 15 minutes, 35.42 mg triethylamine (0.35 mmol) were added in order to deprotonate the Schiff-base ligand. After another 30 minutes, a solution of $Ni(NO_3)_2 \cdot 6H_2O$ (50.89 mg, 0.175 mmol) and $Ni(ClO_4)_2 \cdot 6H_2O$ (64 mg, 0.175 mmol) in 10 mL acetonitrile was added dropwise, the color of the solution changing to dark green. The solution was stirred for another 30 minutes and by slow evaporation of the solution at room temperature, in 10-14 days, dark green rectangular crystals were obtained, suitable for X-Ray diffraction. IR (KBr disk/cm$^{-1}$): 3418(w), 2953(w), 2308(w), 1636(m), 1604(w), 1545(w), 1450(s), 1406(m), 1384(s), 1302(s), 1240(m), 1219(s), 1143(w), 1109(s), 1092(s), 970(w), 927(w), 900(w), 865(w), 786(w), 749(w), 624(m). Elemental analysis: calculated for $C_{32}H_{46}ClN_7Ni_2O_{14}$: C 42.44, H 5.19, N 10.83 %; found: C 42.05, H 5.12, N 10.80 %.

### *2.1.2. Synthesis of* $[CoL_2(H_2O)]ClO_4 \cdot CH_3OH$ **2**

A solution of 45.57 mg 4-(2-aminoethyl)morpholine (0.35 mmol) in 10 mL methanol was added dropwise under continuous stirring to a solution of 53.25 mg *o*-vanillin (0.35 mmol) in 15 mL methanol. The solution rapidly turned from colorless to bright yellow. After 15 minutes, 35.42 mg triethylamine (0.35 mmol) were added in order to deprotonate the Schiff-base ligand. After 30 minutes, a solution of $Co(NO_3)_2 \cdot 6H_2O$ (50.93 mg, 0.175 mmol) and $Co(ClO_4)_2 \cdot 6H_2O$ (64.04 mg, 0.175 mmol) in 10 mL methanol was added dropwise, the color of the solution changing to dark brown. The solution was stirred then for 30 minutes and, by slow evaporation at room temperature, dark brown needle-like crystals were obtained. IR (KBr disk/cm$^{-1}$): 3562(w), 3359(w), 2972(w), 2863(w), 2354(w), 2310(w), 1644(m), 1622(s), 1603(m), 1548(w), 1472(m), 1449(m), 1404(w), 1385(w), 1323(s), 1251(s), 1226(s), 1197(w), 1112(s), 1088(s), 1013(m), 974(w), 931(w), 913(w), 861(w), 776(w), 748(m), 737(m), 668(w), 624(w). Elemental analysis: calculated for $C_{29}H_{44}ClN_4CoO_{12}$: C 47.34, H 5.99, N 7.62 %; found: C 47.09, H 8.41, N 6.10 %.

*Caution!* Perchlorate salts are potentially explosive and they should be handled in small quantities. The synthesis was carried out at the mmol scale and the crystals were grown by slow evaporation at room temperature.

### *2.2. Physical measurements*

The IR spectra (KBr pellets) were recorded on a Bruker Tensor 37 spectrophotometer in the 4000-400 $cm^{-1}$ region and the UV-Vis spectra were recorded with a Jasco V-670 spectrophotometer.

Magnetic susceptibility measurements on a polycrystalline sample of **1** were carried out on a Quantum Design SQUID magnetometer in the temperature range 1.9–300 K. The diamagnetic corrections for the compound were estimated using Pascal's constants. The magnetic data were also corrected for diamagnetic contributions of the sample holder.

### *2.3. X-ray crystallographic analysis*

Crystals were measured on STOE IPDS II single crystal diffractometer, using graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods and refined by full-matrix least-squares techniques based on $F^2$. The non-H atoms were refined with anisotropic displacement parameters. The crystallographic data are collected in Table 1.

### *2.4. Computational details*

The DFT calculations for **1** were performed on the geometries obtained from the X-ray crystal structure, without other optimization, using two functionals, UB3LYP [15] and UB3PW91 [16], and two atomic basis sets, LANL2DZ [17] and TZVP [18]. The energies of the Broken Symmetry ($E_{BS}$, $S = 0$) and High Spin ($E_{HS}$, $S = 2$) states were calculated using the procedure of the fragments as implemented in the Gaussian09 program [19] and further checked for their stability.

### *2.5. Catalytic properties*

In a typical experiment, an ampoule was charged with 3-chloroperbenzoic acid (0.1 mmol), olefin (0.035 mmol), and nickel catalyst (compound **1**) dissolved in acetonitrile (2.5, 5.8 or 10 mmol %). The reaction was carried out with stirring at room temperature for different times. The resultant mixture was diluted and analyzed by GC-MS. GC-MS was performed using an Agilent GS-MS turbo system (5975-7820A) model equipped with a HP-5MS capillary column (30 m x 0.25 mm x 0.25 µm), under the following conditions: cyclooctene, styrene, and *trans*-stilbene: 40˚C, ramp 10˚C/min until 250˚C, held 2 min, solvent delay at 0.0-3.0 min. Retention times:

peak at 5.04 min cyclooctene and at 8.20 min epoxide; peak at 4.90 min styrene and at 7.58 min epoxide; peak at 16.17 min *trans*-stilbene and at 16.29 min epoxide. Cyclohexene: 40˚C, ramp 10˚C/min until 250˚C, held 2 min, solvent delay at 3.50-3.65 min. Retention times: peak at 2.53 min cyclohexene and at 4.42 min epoxide. 1-Hexene: 35˚C, ramp 10˚C/min until 250˚C, held 2 min, no solvent delay. Retention times: peak at 2.05 min 1-hexene and at 4.05 min epoxide.

## 3. Results and Discussion

The new compounds have been synthesized *in situ*, following a two-step procedure: in the first step the proligand HL (Scheme 1) was obtained by reacting *o*-vanillin and 4-(2-aminoethyl)morpholine; in the next step, the deprotonated ligand was reacted with a mixture of $Ni(NO_3)_2\cdot 6H_2O$ and $Ni(ClO_4)_2\cdot 6H_2O$ salts for compound **1**, and, respectively, a mixture of $Co(NO_3)_2\cdot 6H_2O$ and $Co(ClO_4)_2\cdot 6H_2O$ for compound **2**.

### *3.1. Spectral properties*

The FTIR spectra of compounds **1** and **2** show the characteristic bands of the azomethine group (1636 $cm^{-1}$ and 1622 $cm^{-1}$ respectively), and the uncoordinated perchlorate ion (1109 and 624 $cm^{-1}$ for **1**, respectively 1112 and 624 $cm^{-1}$ for **2**). In the case of compound **1** the FTIR spectrum also shows the characteristic band of the nitrato ligand (1384 $cm^{-1}$). The diffuse reflectance electronic spectrum of **1** (Figure 1) clearly shows that the Ni(II) ions are hexacoordinated: the two bands with maxima at 878 nm and 594 nm are assigned to the $^3A_2 \rightarrow {}^3T_2$ and $^3A_2 \rightarrow {}^3T_1$ transitions, respectively (assuming the *O* symmetry for the two nickel ions) [20]. The spin forbidden transition, $^3A_2 \rightarrow {}^1E$, is observed at 760 nm.

### *3.2. Description of the crystal structure*

Compound **1** crystalizes in the monoclinic $P2_1/c$ space group. Its structure consists of non-centrosymmetric binuclear cations, uncoordinated perchlorate ions, and solvent molecules. A view of the complex cation is shown in Figure 2. The two anionic Schiff bases act differently as ligands. One of them (A) is coordinated simultaneously to the two Ni(II) ions (chelated with the nitrogen atoms and the phenoxido oxygen to Ni2 and with the methoxy group to Ni1); the other one (B) acts as a NNO tridentate ligand towards Ni1 (the two nitrogen atoms and the phenoxido oxygen), the methoxy group being uncoordinated. The nickel ions are bridged by the phenoxido oxygen atom (from A) and by the bidentate nitrato ligand. Both Ni(II) ions display a pseudo-octahedral stereochemistry. Ni1 is coordinated by the two nitrogen and the terminal phenoxido oxygen atoms from ligand B, two oxygen atoms from the bridging nitrato and phenoxido groups, and by the methoxy oxygen from ligand A. Ni2 is coordinated by two nitrogen atoms arising from the organic ligand A, two oxygen atoms from the bridging nitrato and phenoxido groups, one water molecule, and one acetonitrile molecule. The two Ni–N distances involving the azomethine nitrogen atoms (Ni1–N2 = 1.980(3); Ni2–N3 = 1.987(3) Å) are shorter than those involving the morpholine nitrogen atoms (Ni1–N1 = 2.172(3); Ni2–N4 = 2.271(3) Å). The shortest and longest Ni-O distances involve the terminal phenoxido oxygen atom (Ni1–O8 = 1.983(2) Å) and, respectively, the methoxy oxygen atom (Ni1–O6 = 2.140(2) Å). The intramolecular distance between the nickel ions is 3.514 Å and the value of the bridging angle, Ni1–O4-Ni2, is 117.7º. The shortest intermolecular distance between the nickel ions is 7.514 Å.

Compound **2** crystalizes in the monoclinic $P2_1/n$ space group. Its structure consists of mononuclear cations, uncoordinated perchlorate ions, and solvent molecules. A view of the complex cation is shown in Figure 3. One organic molecule acts as a tridentate chelating ligand (through the two nitrogen atoms and the phenoxido oxygen atom); the other one acts as a bidentate chelating ligand (the nitrogen atom from the azomethine group and the phenoxido oxygen). The cobalt ion displays an octahedral stereochemistry, being coordinated by three nitrogen and two oxygen atoms from the organic ligands and by an aqua ligand. The Co-N and Co-O distances vary between 1.871 and 2.064 Å, confirming the oxidation state of the cobalt ion (+3). The cobalt(III) complex reported by Su et al., [$CoL_2(N_3)$], has a similar structure, but the water molecule is replaced by the monodentate azido ligand [13].

### *3.3 Magnetic properties*

The temperature dependence of the $\chi_M T$ product for compound **1** is shown in Figure 4. The value of $\chi_M T$ at room temperature (2.30 cm$^3$ mol$^{-1}$ K) corresponds to two $S = 1$ uncoupled Ni(II) ions ($g = 2.16$). By decreasing the temperature, $\chi_M T$ decreases slowly down to 80 K, then more and more, reaching 0.10 cm$^3$ mol$^{-1}$ K at 2 K. This behavior suggests the occurrence of an antiferromagnetic coupling of the two Ni(II) ions. The magnetic data have been analyzed using the following Hamiltonian: $\boldsymbol{H} = -J\mathbf{S}_1\mathbf{S}_2$ ($S_1 = S_2 = 1$). The temperature dependence of the molar magnetic susceptibility is then given by eq. (1):

$$\chi_M = \frac{Ng^2\beta^2}{kT} \cdot \frac{2e^x + 10e^{3x}}{1 + 3e^x + 5e^{3x}}, \qquad x = \frac{J}{kT} \tag{1}$$

The best fit to the data is obtained with the following parameters: $J$ = -7.9±0.2 cm$^{-1}$; $g$ = 2.19±0.02. Since the intermolecular distances between the paramagnetic centers are quite large, we did not include a Weiss term in eq. (1).

To our knowledge, except for compound **1,** only one binuclear complex with one phenoxido and one nitrato bridge is described, but its magnetic properties have not been investigated [21a]. The few compounds existing in literature and characterized from the magnetic point of view are bi- and trinuclear species with two phenoxido and one nitrato bridges [21b-d]. In these compounds, the Ni-O(phenoxido)-Ni angles vary between ~93.2º and ~96.9º, smaller than in **1** and favoring a ferromagnetic coupling (accidental orthogonality of the magnetic orbitals). Nanda et al. have shown that, for bis-phenoxido-bridged Ni(II) complexes, values of this angle larger than 97º lead to antiferromagnetic interactions [1g,h]. The value of the Ni-O(phenoxido)-Ni angle in **1** is 117.7º, therefore the antiferromagnetic coupling of the Ni(II) ions is not surprising.

### *3.4. DFT calculations*

The $J$ value for compound **1** can be calculated according to the eqs. (2-4) [22], using the energy values for the high ($E_{\mathrm{HS}}$) and low spin states ($E_{\mathrm{BS}}$ - Broken Symmetry):

$$J = 2(E_{\mathrm{BS}} - E_{\mathrm{HS}})/S^2_{\mathrm{max}} \tag{2}$$

$$J = 2(E_{\mathrm{BS}} - E_{\mathrm{HS}})/(\langle S^2\rangle_{\mathrm{HS}} - \langle S^2\rangle_{\mathrm{BS}}) \tag{3}$$

$$J = 2(E_{\mathrm{BS}} - E_{\mathrm{HS}})/S(S+1) \tag{4}$$

In eq. (2), $\langle S^2\rangle_{\mathrm{HS}}$ and $\langle S^2\rangle_{\mathrm{BS}}$ are the expectation values of the spin-squared operator in the two states, HS and BS respectively. In our case, $S_1 = S_2 = 1$, $S = S_{\mathrm{max}} = S_1 + S_2 = 2$. The calculated $J$ values, using the three formulas, are gathered in Table 4. Both functionals and basis sets led to similar $J$ values, in a qualitative agreement with the experimental one; a comparison of the values calculated by the three equations shows that eq. (4) predicts the lowest $J$ value, which is close to the experimental one. In the BS state, regardless of the method used, the positive and negative spin densities are concentrated on the two paramagnetic Ni(II) ions and on their close surroundings, as can be seen in Figure 5; for example, at the UB3LYP/TZVP level, the values are (+1.646) and (-1.661) respectively.

### *3.5. Catalytic properties*

The catalytic epoxidation of various olefins was performed with MCPBA (3-chloroperbenzoic acid) in the presence of Ni-complex (compound **1**) under mild conditions [7,23-25]. The oxidant MCPBA was added to a mixture of olefin, catalyst, and acetonitrile. Blank runs (in the absence of catalyst) provided almost negligible conversions. The results of the epoxidation reactions are summarized in Table 5. Quantitative conversions were obtained for cyclic olefins, such as cyclohexene and cyclooctene (entries 1-2) in very mild conditions: room temperature, short times (5-10 min) and 1 mol %, under milder conditions than those in literature [7,23]. In addition, the epoxides were the only products obtained, no by-products were detected, therefore free radical oxidation reactions were not involved in this epoxidation [23,26,27]. Terminal olefins are substrates difficult to oxidize [28], even in harder conditions: 60 min and 10 mol %, a low conversion (entry 3) was obtained.

Styrene was oxidized to its corresponding epoxide with good conversions (68 and 93 %, entries 4 and 5, respectively). In terms of selectivity, styrene oxide is the major product (≈ 90%), some amounts of others products being also obtained: benzaldehyde (4.0%) and phenylacetaldehyde (≈ 6%). *Trans*-stilbene was converted to *trans*-stilbene oxide (46 and 49%, entries 6 and 7, respectively) and benzaldehyde (4.51 and 6.73%, entries 6 and 7, respectively), but 2-phenylacetophenone was not detected; for olefins containing aromatic rings, the substrates produced aldehyde and ketone, but our catalyst, in the case of *trans*-stilbene, is more selective than others [7,23]. Formation of aldehydes and ketones indicates that the reaction mechanism implies nickel(III)-oxo or peroxyl radical intermediates [23,28], and the presence of chlorobenzene supports this proposal. A higher amount of catalyst has a major influence for styrene (68 *vs.* 93%, entries 4 and 5, respectively) but not for *trans*-stilbene (41 *vs* 46%, entries 6 and 7, respectively). The reason may be that because of the bulky steric hindrance of the phenyl group, it is unfavourable for the alkene to access the active nickel centre.

**4. Conclusions.** In conclusion, we described herein two new complexes of Ni(II) and Co(III) with a Schiff-base ligand derived from *o*-vanillin. The nickel derivative is a rare example of dissymmetric binuclear complex, featuring one phenoxido and one nitrato bridges. The exchange interaction between the nickel(II) ions was found moderately strong antiferromagnetic, in line with DFT calculations. This compound acts as an efficient catalyst in epoxidation reactions of olefins.

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## 6. Supplementary material

CCDC 1826839 and 1839534 contain the supplementary crystallographic data for **1** and **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

## REFERENCES

[1] (a) H. Sakiyama, Y. Chiba, K. Tone, M. Yamasaki, M. Mikuriya, J. Krzystek, A. Ozarowski, Inorg. Chem. 56 (2017) 138.

(b) M. Mondal. S. Giri, P. M. Guha, A. Ghosh, Dalton Trans. 46 (2017) 697.

(c) P. Ghorai, A. Chakraborty, A. Panja, T. K. Mondal, A. Saha, RSC Adv. 6 (2016) 36020.

(d) R. Biswas, S. Giri, S. K. Saha, A. Ghosh, Eur. J. Inorg. Chem. (2012) 2916.

(e) X.-He Bu, M. Du, L. Zhang, D.-Z. Liao, J.-K. Tang, R.-H. Zhang, M. Shionoya, J. Chem. Soc., Dalton Trans. (2001) 593.

(f) S. Naiya, M.G.B. Drew, C. Estarellas, A. Frontera, A. Ghosh, Inorg. Chim. Acta 363 (2010) 3904.

(g) K. K. Nanda, L. K. Thompson, J. N. Bridson, K. Nag, J. Chem. Soc., Chem. Commun. (1994) 1337.

(h) K. K. Nanda, R. Das, L. K. Thompson, K. Venkatsubramanian, P. Paul, K. Nag, Inorg. Chem. 33 (1994) 1188.

[2] (a) A. Panja, N. Ch. Jana, S. Adak, P. Brandão, Dlhàň, J. Titiš, R. Boča, New J. Chem. 41 (2017) 3143.

(b) M. Č. Romanović, B. R. Cobeljić , A. Pevec, I. Turel, V. Spasojević, A. A. Tsaturyan, I. N. Shcherbakov, K. K. Andelković, M. Milenković, D. Radanović, M. R. Milenković, Polyhedron 128 (2017) 30.

[3] A. Das, K. Bhattacharya, S. Giri, A. Ghosh, Polyhedron 134 (2017) 295.

[4] K. Rühlig, A. Abylaikhan, A. Aliabadi, V. Kataev, S. Liebing, S. Schwalbe, K. Trepte, C. Ludt, J. Kortus, B. Büchner, T. Rüffer, H. Lang, Dalton Trans. 46 (2017) 3963.

[5] N. E. Dixon, C. Gazzola, R. Blakeley, B. Zerner, J. Am. Chem. Soc. 97 (1975) 4131.

[6] See, for example: (a) D. Volkmer, B. Hommerich, K. Griesar, W. Haase, B. Krebs, Inorg. Chem. 35 (1996) 3792.

(b) S. B. Jadner, H. Schwöppe, H. Nimir, A. Rampel, D. A Brown, B. Krebs, Inorg. Chim. Acta 340 (2002) 181.

(c) H. Carlson, M. Haukka, A Bousseksou, J.-M. Latour, E. Nordlander, Inorg. Chem. 43 (2004) 8252.

[7] A. R. Jeong, J. W. Shin, J. H. Jeong, K. H. Bok, C. Kim, D. Jeong, J. Cho, S. Hayami, K. S. Min, Chem.-Eur. J. 23 (2017) 3023.

[8] S. K. Barman, F. Lloret, R. Mukherjee, Inorg. Chem. 55 (2016) 12696.

[9] (a) A. Kermagoret, P. Braunstein, Organometallics 27 (2008) 88.
(b) F. Speiser, P. Braunstein, Inorg. Chem. 43 (2004) 4234.

[10] D. Zhang, G. X. Jin, Organometallics, 22 (2003) 2851.

[11] M. Andruh, Dalton Trans. 44 (2015) 16633.

[12] S. Sasmal, S. Hazra, P. Kundu, S. Dutta, G. Rajaraman, E. C. Sañudo, S. Mohanta, Inorg. Chem. 50 (2011) 7257.

[13] P. Wang, Q. L. Li, Q. Ruan, Y. Q. Su, Russ. J. Coord. Chem. 37 (2011) 935.

[14] C.-H. Dai, F.-L. Mao, J. Coord. Chem. 42 (2012) 537.

[15] A. D. Becke, J. Chem. Phys. 98 (1993) 5648.

[16] Y. Wang, J.P. Perdew, Phys. Rev. B 44 (1991) 13298

[17] P. J. Hay, W.R. Wadt, J. Chem. Phys. 82 (1985) 270.

[18] F. Weigend, R. Ahlrichs, PhysChemChemPhys. 7 (2005) 3297.

[19] M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, O. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, D. J. Fox, GAUSSIAN 09, Revision C.01, Gaussian, Inc.,Wallingford CT, 2009.

[20] A. B. P. Lever, Inorganic Electronic Spectroscopy, Elsevier, Amsterdam, 1984.

[21] (a) R. Sanyal, X. Zhang, P. Chakraborty, F. A. Mautner, C. Zhao, D. Das, RSC Adv. 6 (2016) 73534.

(b) T. Chattopadhyay, M. Mukherjee, A. Mondal, P. Maiti, A. Banerjee K.S. Banu, S. Bhattacharya, B. Roy, D. J. Chattopadhyay, T. K.Mondal, M. Nethaji, . Zangrando, D. Das, Inorg. Chem. 49 (2010) 3121.

(c) M. Dieng, O. Diouf, M. Gaye, A. Salam Sall, P. Perez-Lourido, L. Valencia, A. Caneschi, L. Sorace, Inorg. Chim. Acta 394 (2013) 741.

(d) S.-Y. Zhang, B. Xu, L. Zheng, W. Chen, Y. Li, W. Li, Inorg. Chim. Acta 367 (2011) 44.

[22] (a) L. Noodleman, J. Chem. Phys. 74 (1981) 5737.

(b) E. Ruiz, J. Cano, S. Alvarez, P. Alemany, J. Comput. Chem. 20 (1999) 1391.

(c) M. Shoji, K. Koizumi, Y. Kitagawa, T. Kawakami, S. Yamanaka, M. Okumura, K. Yamaguchi, Chem. Phys. Lett. 432 (2006) 343.

[23] K. H. Bok, M. M. Lee, G. R. You, H. M. Ahn, K. Y. Ryu, S.-J. Kim, Y. Kim, C. Kim, Chem. Eur. J. 23 (2017) 3117.

[24] M. Sankaralingam, P. Vadivule, E. Suresh, M. Palaniandavar, Inorg. Chem. Acta 407 (2013) 98.

[25] M. Sankaralingam, M. Balamurugan, M. Palaniandavar, P. Vadivelu, C. H. Suresh, Chem. Eur. J. 20 (2014) 11346.

[26] T. K. M. Shing, Y. Y. Yeung, P. L. Su, Org. Lett. 8 (2006) 3149.

[27] M. Sankaralingam, P. Vadivelu, M. Palaniandavar, Dalton Trans. 46 (2017) 7181.

[28] (a) I. García-Bosch, X. Ribas, M. Costas, Adv. Synth. Catal. 351 (2009) 348.

(b) S. Taktak, W. Ye, A. M. Herrera, E. V. Rybak-Akimova, Inorg. Chem. 46 (2007) 2929.

(c) E. Hao, Z. Wang, L. Jiao, S. Wang, Dalton Trans. 39 (2010) 2660.

(d) H .K. Kwong, P. K. Lo, K. C. Lau, T. C. Lau, Chem. Commun. 47 (2011) 4273.

(e) S. Y. Lee, N. Kim, M. M. Lee, Y. D. Jo, J. M. Bae, M. Y. Hyun, S. Yoon, C. Kim, Dalton Trans. 45 (2016) 1727.

**Table 1**. Crystallographic data, details of data collection and structure refinement parameters for **1** and **2**.

| Compound | **1** | **2** |
|---|---|---|
| Chemical formula | $C_{32}H_{46}Ni_2N_7O_{14}Cl$ | $C_{29}H_{44}CoN_4O_{12}Cl$ |
| M (g mol$^{-1}$) | 905.63 | 735.06 |
| Temperature (K) | 200(2) | 173(2) |
| Wavelength (Å) | 0.71073 | 0.71073 |
| Crystal system | *monoclinic* | *monoclinic* |
| Space group | $P\ 2_1/c$ | $P\ 2_1/n$ |
| $a$ (Å) | 10.1085(2) | 17.3009(10) |
| $b$ (Å) | 33.0735(3) | 10.5552(4) |
| $c$ (Å) | 11.9323(4) | 18.0734(12) |
| $\alpha$ (°) | 90 | 90 |
| $\beta$ (°) | 108.497(5) | 103.793(5) |
| $\gamma$ (°) | 90 | 90 |
| $V$ (Å$^3$) | 3783.16(18) | 3205.3(3) |
| $Z$ | 4 | 4 |
| $D_c$ (g cm$^{-3}$) | 1.590 | 1.523 |
| $\mu$ (mm$^{-1}$) | 1.143 | 0.689 |
| $F(0\ 0\ 0)$ | 1888 | 1544 |
| Goodness-of-fit (GOF) on $F^2$ | 0.981 | 0.805 |
| Final $R_1$, $wR_2$ [$I > 2\sigma(I)$] | 0.0433, 0.1110 | 0.0522, 0.1257 |
| $R_1$, $wR_2$ (all data) | 0.0587, 0.1216 | 0.0834, 0.1437 |
| Largest difference in peak and hole (e Å$^{-3}$) | 0.447, -0.639 | 0.728, -0.592 |

**Table 2**. Selected bond lengths (Å) and angles (°) for **1**

| Bond lengths | | Bond angles | |
|---|---|---|---|
| Ni1 - O2 | 2.089(2) | Ni1 - O4 - Ni2 | 117.73(10) |
| Ni1 - O4 | 2.059(2) | N1 - Ni1 - N2 | 83.90(11) |
| Ni1 - O6 | 2.140(2) | N1 - Ni1 - O2 | 94.27(10) |
| Ni1 - O8 | 1.983(2) | N1 - Ni1 - O4 | 100.32(10) |
| Ni1 - N1 | 2.172(3) | N1 - Ni1 - O6 | 89.27(10) |
| Ni1 - N2 | 1.980(3) | N1 - Ni1 - O8 | 175.02(10) |
| Ni2 - O1 | 2.081(2) | N2 - Ni1 - O2 | 85.74(10) |
| Ni2 - O4 | 2.048(2) | N2 - Ni1 - O4 | 169.51(10) |
| Ni2 - O5 | 2.070(2) | N2 - Ni1 - O6 | 92.95(10) |
| Ni2 - N3 | 1.987(3) | N2 - Ni1 - O8 | 91.12(10) |
| Ni2 - N4 | 2.271(3) | O2 - Ni1 - O4 | 103.40(9) |
| Ni2 - N5 | 2.080(3) | O2 - Ni1 - O6 | 176.07(9) |
| | | O2 - Ni1 - O8 | 85.44(10) |
| | | O4 - Ni1 - O6 | 77.59(9) |
| | | O4 - Ni1 - O8 | 84.58(9) |
| | | O6 - Ni1 - O8 | 90.88(10) |
| | | O1 - Ni2 - O4 | 91.34(9) |
| | | O1 - Ni2 - O5 | 86.51(9) |
| | | O1 - Ni2 - N3 | 175.98(10) |
| | | O1 - Ni2 - N4 | 94.23(10) |
| | | O1 - Ni2 - N5 | 83.03(10) |
| | | O4 - Ni2 - O5 | 86.62(9) |
| | | O4 - Ni2 - N3 | 91.65(10) |
| | | O4 - Ni2 - N4 | 173.14(10) |
| | | O4 - Ni2 - N5 | 88.16(10) |
| | | O5 - Ni2 - N3 | 96.34(11) |
| | | O5 - Ni2 - N4 | 97.69(10) |
| | | O5 - Ni2 - N5 | 168.19(11) |
| | | N3 - Ni2 - N4 | 82.60(11) |
| | | N3 - Ni2 - N5 | 94.39(11) |
| | | N4 - Ni2 - N5 | 88.56(11) |

**Table 3**. Selected bond lengths (Å) and angles (°) for **2**

| Bond lengths | | Bond angles | |
|---|---|---|---|
| Co1 – N1 | 1.902(3) | O2 – Co1 – O5 | 91.77(10) |
| Co1 – N2 | 2.064(3) | O2 – Co1 – N1 | 94.66(10) |
| Co1 – N3 | 1.953(2) | O5 – Co1 – N1 | 84.38(11) |
| Co1 – O2 | 1.871(2) | O2 – Co1 – O7 | 88.32(10) |
| Co1 – O5 | 1.874(2) | O5 – Co1 – O7 | 173.75(10) |
| Co1 – O7 | 1.943(3) | N1 – Co1 – O7 | 89.39(11) |
| | | O2 – Co1 – N3 | 85.02(10) |
| | | O5 – Co1 – N3 | 94.68(11) |
| | | N1 – Co1 – N3 | 179.00(11) |
| | | O7 – Co1 – N3 | 91.55(11) |
| | | O2 – Co1 – N2 | 179.78(11) |
| | | O5 – Co1 – N2 | 88.03(10) |
| | | N1 – Co1 – N2 | 85.23(11) |
| | | O7 – Co1 – N2 | 91.87(10) |
| | | N3 – Co1 – N2 | 95.09(10) |

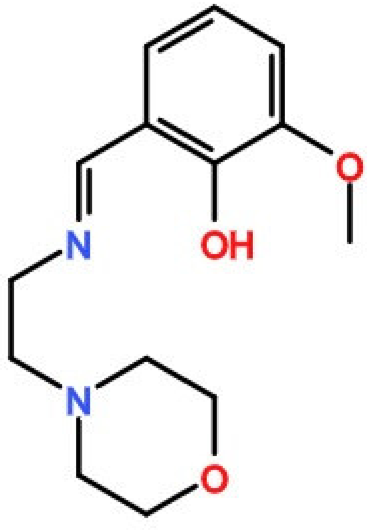
**Table 4**. Exchange coupling constants (cm$^{-1}$) for compound **1**

| Functional | Atomic Basis Set | $(E_{HS} - E_{BS})$ (Ha) | $(E_{HS} - E_{BS})$ (cm$^{-1}$) | *J* (eq.2) | *J* (eq.3) | *J* (eq.4) |
|---|---|---|---|---|---|---|
| UB3LYP | Landl2dz | -0.0001013 | -22.22473376 | -11.11 | -11.11 | -7.41 |
| UB3LYP | TZVP | -0.0001046 | -22.94873792 | -11.47 | -11.47 | -7.65 |
| UB3PW91 | Landl2dz | -0.0001018 | -22.33443136 | -11.17 | -11.17 | -7.44 |
| UB3PW91 | TZVP | -0.0001034 | -22.68546368 | -11.34 | -11.34 | -7.56 |

**Table 5.** Epoxidation of olefins by MCPBA with complex **1** as a catalyst.[a]

| Entry | Olefin | Catal. (mmol %) | Time (min) | Conv.[b] (%) | Selec. (%) | |
|---|---|---|---|---|---|---|
| **1** | Cyclooctene | 1 | 10 | 98.5 | Epoxide | |
| **2** | Cyclohexene | 1 | 5 | 100 | Epoxide | |
| **3** | 1-hexene | 10 | 60 | 16 | Epoxide | |
| **4** | Styrene | 2.5 | 60 | 68 | Epoxide<br>Benzaldehyde<br>Phenylacetaldehyde | 90.65<br>5.35<br>4.00 |
| **5** | | 5.7 | 60 | 93 | Epoxide<br>Benzaldehyde<br>Phenylacetaldehyde | 90.00<br>6.00<br>4.00 |
| **6** | *Trans*-stilbene | 2.5 | 60 | 46 | Epoxide<br>Benzaldehyde | 95.49<br>4.51 |
| **7** | | 5.7 | 60 | 49 | Epoxide<br>Benzaldehyde | 92.70<br>7.30 |

[a] Reactions conditions: MCPBA (0.1 mmol), olefin (0.035 mmol) and nickel catalyst dissolved in acetonitrile (2.5, 5.8 or 10 mmol %). [b] Based on olefins.



**Scheme 1**. Structure of the Schiff-base proligand, HL.

## CAPTION TO THE FIGURES

**Figure 1**. Diffuse reflectance spectrum of **1**.

**Figure 2**. Perspective view of the binuclear complex cation in crystal **1**. Hydrogen atoms have been omitted for clarity.

**Figure 3**. Perspective view of the mononuclear complex cation in crystal **2**. Hydrogen atoms have been omitted for clarity.

**Figure 4**. $\chi_M T$ vs. $T$ curve for compound **1**.

**Figure 5.** Spin density in the BS state of complex **1** (isosurface cutoff value = 0.001).

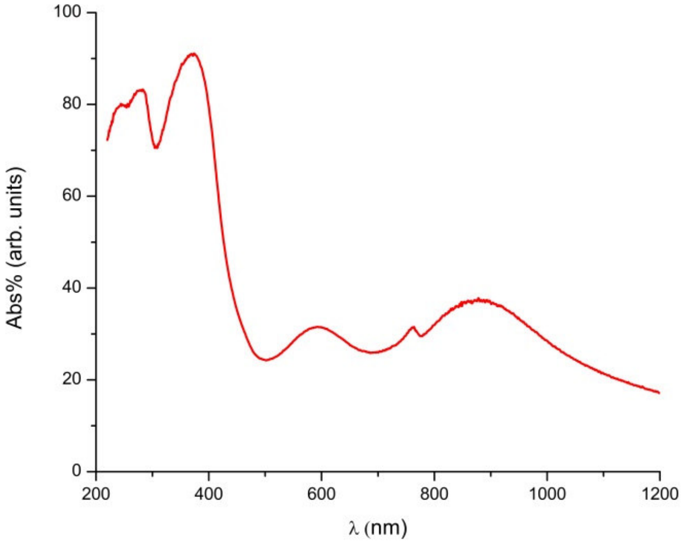


Figure 1

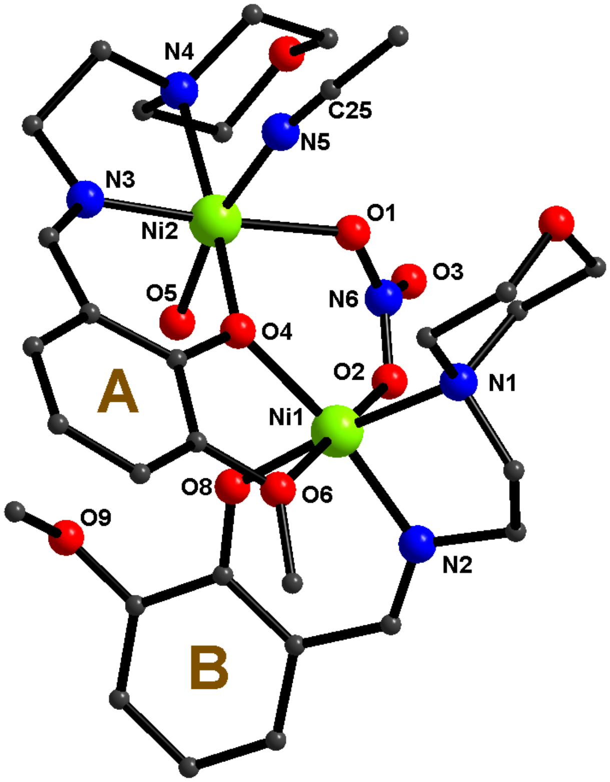


Figure 2

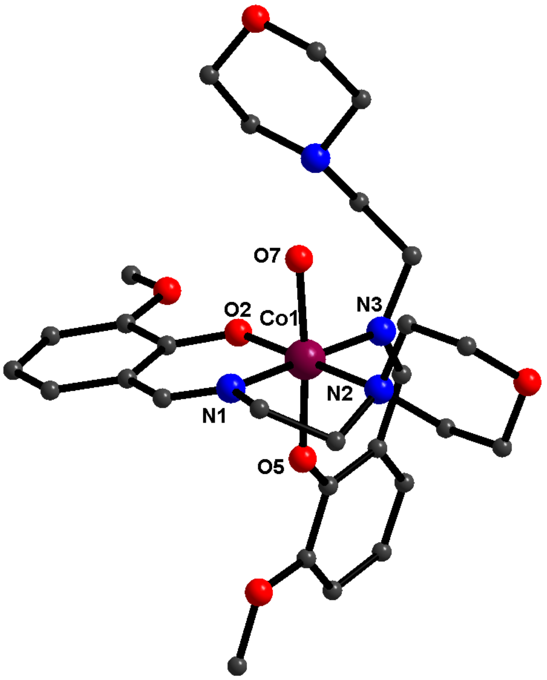


Figure 3

Figure 3

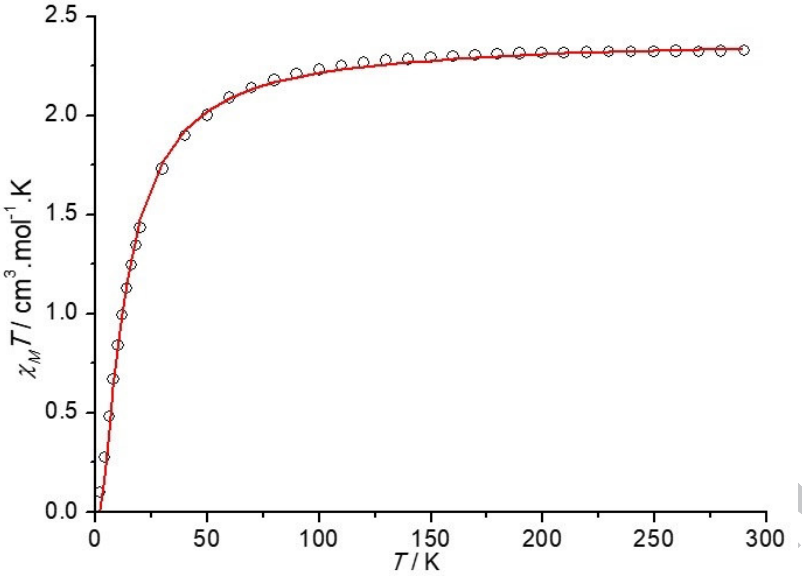


Figure 4

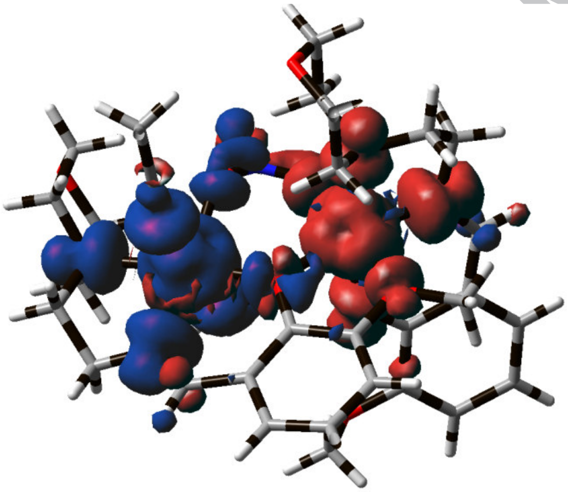
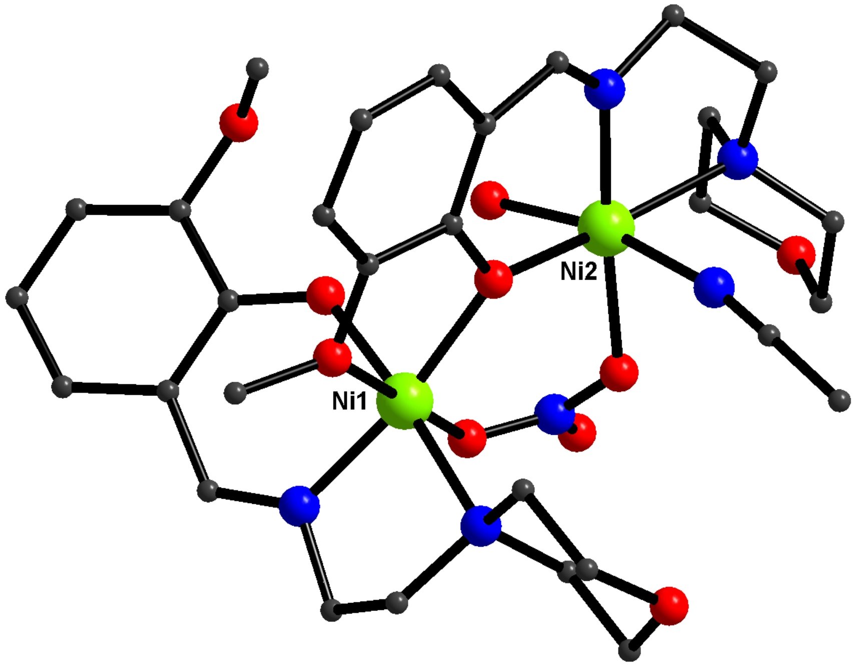


Figure 5



## GRAPHICAL ABSTRACT

**SYNOPSIS TOC**

A novel dissymmetric binuclear Ni(II) complex has been obtained using a Schiff-base ligand derived from *o*-vanillin. Its magnetic, spectroscopic and catalytic properties have been investigated