

# Synthesis, structure and magnetic properties of homotrimeric Ni(II) complexes with asymmetric Schiff-base ligands



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## ABSTRACT

By using 1,3-propanediamine, 2-hydroxyacetophenone and salicylaldehyde an asymmetric ONNO type Schiff base, N(hydroxyphenylidene)-N'(2-hydroxyacetophenylidene)-1,3-propanediamine (H<sub>2</sub>metsalpn), has been prepared and isolated. This Schiff base has been reduced yielding N(2-hydroxybenzyl)-N'[1-(2-hydroxyphenyl)ethyl]-1,3-diaminopropane (H<sub>2</sub>metsalpn<sup>H</sup>). These two ligands were used in preparing three trinuclear Ni(II) complexes with *catena*-[Ni<sub>3</sub>] structural motif, where DMF and carboxylato (formate, acetate, benzoate) ligands occur. These complexes were characterized by EA, IR, TG, DTA and MS data. The X-ray diffraction confirms that the Ni(II) central atoms are in a distorted octahedral coordination environment: the terminal centers possess {NiN<sub>2</sub>O<sub>4</sub>} octahedral coordination sphere whereas the very central atom possesses {NiO<sub>6</sub>} chromophore. The coordinated DMF groups are liberated between 140–240 °C. The SQUID magnetometry confirms presence of weak exchange coupling of the antiferromagnetic nature,  $J/hc = -2$  to  $-7$  cm<sup>-1</sup>, with a moderate single-ion anisotropy reflected by the zero-field splitting  $D/hc = +4$  to  $+7$  cm<sup>-1</sup>.

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## 1. Introduction

The ONNO type symmetric Schiff base made of 1,3-propanediamine and salicylaldehyde, N,N'(salicylidene)-1,3-propanediamine, finds applications in the coordination chemistry for about 70 years [1]. From 1990 to today, a few trinuclear complexes of the symmetric Schiff base were reported [2–11]. In the last decade also the complexes of the ONNO type asymmetric Schiff bases were prepared [12–19]. The asymmetric Schiff base complexes are usually obtained by a template synthesis; there are only a few studies on the isolated asymmetric Schiff bases. In the amphyrotic solvents, the Schiff bases can easily be reduced by NaBH<sub>4</sub> to the secondary amines [20–22].

In this study a preparation of the asymmetric Schiff base is described by combining 1,3-propanediamine and two different aldehydes (salicylaldehyde and 2-hydroxyacetophenone) giving rise to N(2-hydroxyphenylidene)-N'(2-hydroxyacetophenylidene)-1,3-propanediamine (H<sub>2</sub>metsalpn). In methanol solution this Schiff base has been reduced by using NaBH<sub>4</sub>, and N(2-hydroxybenzyl)-N'

[(2-hydroxyphenyl)ethyl]-1,3-propanediamine (H<sub>2</sub>metsalpn<sup>H</sup>) has been isolated. These ligands are sketched in Scheme 1.

Using these ligands, the formate, acetate or benzoate anions in presence of DMF (dimethylformamide), trinuclear Ni(II) complexes have been prepared, namely [(Ni metsalpn<sup>H</sup>)<sub>2</sub>Ni(HCOO)<sub>2</sub>(DMF)<sub>2</sub>] (1), [(Nimetsalpn)<sub>2</sub>Ni(ACO)<sub>2</sub>(DMF)<sub>2</sub>] (2), and [(Ni metsalpn)<sub>2</sub>Ni(C<sub>6</sub>H<sub>5</sub>COO)<sub>2</sub>(DMF)<sub>2</sub>] (3). Single-crystal X-ray diffraction confirms their trinuclear structure of the *catena*-[Ni<sub>3</sub>] type. In addition, thermogravimetry and magnetometry have been used in order to characterize thermal and magnetic properties of these species.

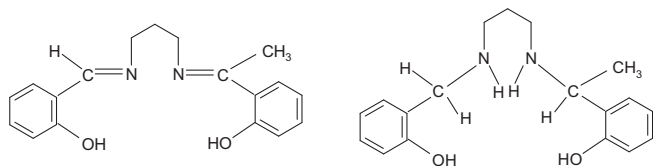
## 2. Experimental

### 2.1. Materials and instruments

All reagents and solvents were purchased from chemical sources and used directly without purification. Elemental C, H and N analysis was performed using Eurovector 1018 apparatus. Ni analysis was conducted using atomic absorption spectrometer (GBC Avanta PM) using the FAAS mode. The mass spectra were obtained by a Shimadzu, 2010 plus with a DI (direct inlet) unit with an electron impact ionizer. The interface temperature of DI

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**Scheme 1.** Sketch of  $H_2metsalpn$  (left) and  $H_2metsalpn^H$  (right) asymmetric Schiff bases.

unit was varied between 40 and 230 °C and the ionization was carried out with electrons of 70 eV energy.

The NMR spectra of the ligands were recorded on a 400 MHz FT-NMR (Varian Mercury) spectrometer using  $d_6$ -DMSO as a solvent. The IR spectra of the complexes and ligand were recorded using Shimadzu Infinity model FTIR spectrometer equipped three reflections ATR attachment.

The thermogravimetric analysis was performed by a Shimadzu DTG-60H apparatus; temperature varied between 30 and 600 °C and scan rate was 10 °C/min under  $N_2$  atmosphere in Pt pans. Calibration of the instrument was done with metallic In and Zn. The stoichiometry of the complexes was estimated using elemental analysis results and with the help of the mass loss data of the coordinated DMF ligands.

The magnetic data was taken with a SQUID apparatus (MPMSXL7, Quantum Design) using the RSO mode of detection. The temperature dependence of the magnetic susceptibility taken at  $B = 0.1$  T has been corrected for the underlying diamagnetism and converted to the effective magnetic moment. The field dependence of the magnetization has been measured at two temperatures:  $T = 2.0$  and  $T = 4.6$  K.

## 2.2. X-ray structure analysis

Single crystals of **1** through **3** were mounted to Xcalibur (TM) single crystal X-ray diffractometer (Oxford Diffraction) with a sapphire CCD detector using Mo  $K\alpha$  radiation ( $\lambda = 0.71073$  Å) operating in the  $\omega/2\theta$  scan mode. The unit-cell dimensions were determined and refined by using the angular settings of 25 automatically centered reflections in  $2.466 \leq \theta \leq 27.817$  range for complex **1**,  $2.74 \leq \theta \leq 26.37$  range for complex **2**,  $2.615 \leq \theta \leq 27.705^\circ$  range for complex **3**. The Data of complex **1** and **2** was collected at  $T = 293$  K and the data of complex **3** at 105 K. The empirical absorption corrections were applied by the semi empirical method via the Crysalis CCD software [23]. Models were obtained from the results of the cell refinement and the data reductions were carried out using the solution software SHELXL97 [24]. The structure of all complexes was solved by direct methods using the SHELXS97 software implemented in the WinGX package [25].

## 2.3. Synthesis of $H_2metsalpn$

The asymmetric Schiff base N-(2-hydroxyphenylidene)-N'-(2-hydroxyacetophenylidene)-1,3-diaminopropane was prepared in MeCN dehydrated by  $CaH_2$  [26]. 1,3-diaminopropane (3.7 g, 0.05 mol) was dissolved in 50 cm<sup>3</sup> of MeCN and temperature was decreased to  $-10$  °C in a salt-ice bath. 2-hydroxyacetophenone (6.80 g, 0.05 mol) was added under stirring for 5 min. This solution was kept in ice-water mixture for 30 min and the temperature was kept under 1 °C. Afterwards, salicylaldehyde (2-hydroxybenzaldehyde) (6.10 g, 0.05 mol) was added to the solution and again the solution was kept in ice-water mixture for 30 min under stirring. This solution was kept in the deep freeze at  $-20$  °C for 12 h. A yellow crystalline substance was obtained, and filtered by vacuum. The filtrate was rinsed with MeCN and Et<sub>2</sub>O and air-dried. This

crystalline product is a mixture of  $H_2metsalpn$  (67%) and bis-N,N'(2-hydroxyacetophenylidene)-1,3-diaminopropane (33%) [26]. For the purification a silica column was used: Merck silica gel 60, 40–63  $\mu m$  with 50 cm height and 2.0 cm diameter; EtAcO:*n*-C<sub>6</sub>H<sub>14</sub> (1:1) was used as a solvent for separation. It was observed that LACH<sub>2</sub> moved rapidly within this solvent. In addition, the ratio of the  $R_f$  value of LACH<sub>2</sub> and  $R_f$  value of  $H_2metsalpn$  was approximately 1:2 (both substances are yellow). The pure compounds were isolated separately by evaporating the solvent from the eluent.  $H_2metsalpn$  was recrystallized from MeCN and its purity was checked by HPLC. Yield: 36–40%, mp 92–93 °C. IR (cm<sup>-1</sup>):  $\nu_{C-H(Ar)}$  3023–3010,  $\nu_{C-H(Aliph)}$  2941–2854,  $\nu_{C=N}$  1631–1624,  $\nu_{C=C(ring)}$  1610,  $\nu_{C-O(Phenol)}$  1278–1159,  $\delta_{C-H(Ar)}$  752.  $\lambda_{max} = 242$  nm,  $\epsilon = 8164$  dm<sup>3</sup> mol<sup>-1</sup> cm<sup>-1</sup> in DMSO. <sup>1</sup>H NMR data in  $d_6$ -CH<sub>3</sub>SOCH<sub>3</sub> ( $\delta$ , ppm): 16.55 (s), 13.47 (s), 8.58 (s), 7.62 (d), 7.45(d), 7.31 (p), 6.88 (t), 6.77 (t), 3.73 (t), 3.66 (t) 2.40 (s), 2.06 (p). <sup>13</sup>C NMR data in  $d_6$ -CH<sub>3</sub>SOCH<sub>3</sub> ( $\delta$ , ppm): 167.70, 164.32, 161.13, 132.86, 132.74, 132.09, 129.21, 119.31, 119.11, 118.97, 118.95, 118.62, 117.13, 117.08, 116.91, 56.46, 46, 33, 14.80. MS ( $m/z$ ): 296 (molecular peak), 175, 162, 148 (base peak), 134, 107, 91, 77. Anal. Calc. for C<sub>18</sub>H<sub>20</sub>N<sub>2</sub>O<sub>2</sub>: C, 72.94; H, 6.80; N, 9.44. Found: C, 73.07; H, 6.23; N, 9.81%.

## 2.4. Preparation of $H_2metsalpn^H$

3.0 g of asymmetric Schiff base  $H_2metsalpn$  was dissolved in 70.0 cm<sup>3</sup> of MeOH by stirring and heating. This solution was heated up to 50 °C and to this solution solid NaBH<sub>4</sub> in small portions was added until colorless under strong mixing [26–29]. After 10 min. of stirring, 300 cm<sup>3</sup> of ice water was added. The final mixture was left to stand for 24 h. After filtration the white precipitate was air-dried. The product  $H_2metsalpn^H$  was recrystallized from MeOH:H<sub>2</sub>O (2:1,v/v). Yield: 54–67 %, mp: 107 °C. IR (cm<sup>-1</sup>):  $\nu_{N-H}$  3307,  $\nu_{C-H(Ar)}$  3041–3014,  $\nu_{C-H(Aliph)}$  2965–2846,  $\nu_{C=C(ring)}$  1610–1588,  $\nu_{C-O(Phenol)}$  1255–1107,  $\delta_{C-H(Ar)}$  752. <sup>1</sup>H NMR data in  $d_6$ -CH<sub>3</sub>SOCH<sub>3</sub> ( $\delta$ , ppm): 7.03 (m), 6.68 (m), 6.30(d), 3.84 (q), 3.78 (s), 2.52(t), 2.36 (m), 1.63 (s), 1.28 (d), 1.27 (d), <sup>13</sup>C NMR data in  $d_6$ -DMSO ( $\delta$ , ppm): 157.49, 157.15, 157.09, 128.40, 127.91, 127.73, 127.52, 124.02, 118.32, 115.75, 115.31, 57.23, 50.63, 46.27,45.03, 28.98, 22.86. MS ( $m/z$ ): 300 (molecular peak), 178, 164, 150 (base peak), 135, 107, 91, 77. Anal. Calc. for C<sub>18</sub>H<sub>24</sub>N<sub>2</sub>O<sub>2</sub>: C, 71.97; H, 8.05; N, 9.32. Found: C, 72.49; H, 7.58; N, 9.24%.

## 2.5. Preparation of $[(Ni\ metsalpn^H)_2Ni(HCOO)_2(DMF)_2]$ (**1**)

0.300 g (0.001 mol) of the reduced asymmetric Schiff base  $H_2metsalpn^H$  was dissolved in 40.0 cm<sup>3</sup> of DMF by heating. The temperature was raised up to 95 to 110 °C. To this solution, added were the solution of 0.237 g (0.0015 mol) NiCl<sub>2</sub>·6H<sub>2</sub>O salt in 10 cm<sup>3</sup> MeOH : DMF (50/50, v/v) and the solution of 0.070 g (0.001 mol) NaHCOO in MeOH : DMF (50/50, v/v), and the solution of 0.28 g Et<sub>3</sub>N in 5 cm<sup>3</sup> MeOH. The final mixture was allowed left to stand for 4–5 days. The formed crystalline complex was separated by vacuum filtration and air dried. Yield: 27%, IR (cm<sup>-1</sup>):  $\nu_{N-H}$  3279, 3047–3020,  $\nu_{C-H(Aliph)}$  2966–2849,  $\nu_{C=O(DMF)}$  1648,  $\nu_{C=O(formate)}$  1635,  $\nu_{C=C(ring)}$  1597–1591,  $\nu_{C-O(Phenol)}$  1195,  $\delta_{C-H(Ar)}$  756. MS ( $m/z$ ): 356 (base peak). Anal. Calc. for C<sub>44</sub>H<sub>58</sub>N<sub>6</sub>Ni<sub>3</sub>O<sub>10</sub>: C, 52.36; H, 5.99; N, 8.32; Ni, 17.45. Found: C, 52.83; H, 5.66; N, 7.91; Ni, 18.11%.

## 2.6. Preparation of $[(Ni\ metsalpn)_2Ni(AcO)_2(DMF)_2]$ (**2**)

0.296 g (0.001 mol) of the asymmetric Schiff base,  $H_2metsalpn$  was dissolved in 50.0 cm<sup>3</sup> of DMF by heating. This solution was heated up to 110 °C and then the solution of 0.375 g (0.0015 mol) of Ni(AcO)<sub>2</sub>·4H<sub>2</sub>O in 10 cm<sup>3</sup> of MeOH : DMF (50/50, v/v) was added.

The final mixture was left to stand for 4 days. The formed crystalline complex was filtered by vacuum filtration, washed with EtOH and dried in air. Yield: 23%, IR ( $\text{cm}^{-1}$ ): 3053–3026,  $\nu_{\text{C-H(Aliph)}}$  2934–2847,  $\nu_{\text{C=O(DMF)}}$  1670,  $\nu_{\text{C=O(Acetate)}}$  1641,  $\nu_{\text{C=N}}$  1616,  $\nu_{\text{C=C(ring)}}$  1583,  $\nu_{\text{C-O(Phenol)}}$  1257,  $\delta_{\text{C-H(Ar)}}$  750. MS ( $m/z$ ): 356 (base peak). Anal. Calc. for  $\text{C}_{46}\text{H}_{56}\text{N}_6\text{Ni}_3\text{O}_{10}$ : C, 53.69; H, 5.48; N, 8.16; Ni, 17.11. Found: C, 53.04; H, 5.21; N, 7.84; Ni, 17.95%.

### 2.7. Preparation of $[\{\text{Ni metsalpn}\}_2\text{Ni}(\text{C}_6\text{H}_5\text{COO})_2(\text{DMF})_2] \text{ (3)}$

0.296 g (0.001 mol) of the asymmetric Schiff base,  $\text{H}_2\text{metsalpn}$  was dissolved in  $50.0 \text{ cm}^3$  of DMF by heating. Temperature was raised up to  $115^\circ\text{C}$ . This solution was combined with the solution of 0.237 g (0.0015 mol) of  $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$  salt in  $10 \text{ cm}^3$  of MeOH:DMF (50/50, v/v) and the solution of 0.432 g (0.003 mol) of  $\text{NaC}_6\text{H}_5\text{COO}$  in  $10 \text{ cm}^3$  of MeOH :  $\text{H}_2\text{O}$  (50/50, v/v); the mixture was mixed for 10 min and then left to stay for 2 days. The formed crystalline complex was separated by vacuum filtration and air dried. Yield: 46 %, IR ( $\text{cm}^{-1}$ ): 3051–3017,  $\nu_{\text{C-H(Aliph)}}$  2939–2853,  $\nu_{\text{C=O(DMF)}}$  1647,  $\nu_{\text{C=O(benzoate)}}$  1633,  $\nu_{\text{C=N}}$  1626,  $\nu_{\text{C=C(ring)}}$  1595,  $\nu_{\text{C-O(Phenol)}}$  1195,  $\delta_{\text{C-H(Ar)}}$  740. MS ( $m/z$ ): 356 (base peak). Anal. Calc. for  $\text{C}_{56}\text{H}_{60}\text{N}_6\text{Ni}_3\text{O}_{10}$ : C, 58.32; H, 5.24; N, 7.28; Ni, 15.27. Found C, 57.81; H, 4.97; N, 7.16; Ni, 14.51%.

## 3. Results and discussion

### 3.1. Crystal and molecular structure

The molecular structures obtained by the X-ray diffraction analysis are shown in Fig. 1 as Pluton drawing. The crystal data, data collection and refinement parameters are given in Table 1. Selected bond lengths and angles are listed in Table 2.

In all three complexes, the central and terminal Ni(II) ions are in a distorted octahedral environment. The very central Ni(II) ions possess the  $\{\text{NiO}_6\}$  octahedral coordination sphere formed of the phenolic oxygens of the two ligands and the oxygen atoms of the carboxylato bridges. The terminal Ni(II) ions have the  $\{\text{NiN}_2\text{O}_4\}$  coordination sphere formed of the phenolic oxygens of the two ligands and nitrogen atoms, one carboxylato bridge oxygen and the oxygen atom of the DMF molecule.

The coordination polyhedra are much distorted. In **1**, three angles along the *trans* coordinate are  $\text{O4-Ni-O5} = 174.28(10)$ ,  $\text{O1-Ni-N2} = 172.81(10)$ , and  $\text{N1-Ni-O2} = 172.72(10)$  deg. In **2**, these angles amount to  $175.6(4)$ ,  $173.2(5)$ , and  $171.9(5)$  deg, whereas in **3**, they are  $175.8(5)$ ,  $171.1(6)$ , and  $170.0(5)$  deg, respectively. There is no angle in these polyhedra that exceed  $177^\circ$ . Bond lengths are dispersed more homogeneously. In both three complexes, the chemical bonds between the very central Ni(II) ion and the donor oxygen atoms are approximately  $2.00 \text{ \AA}$ . In all three complexes only the Ni–O5 bond length (to the DMF ligand) exceeds  $2.15 \text{ \AA}$ .

The ligand in the complex **1** is a kind of the asymmetric Schiff base and possesses the phenol-amine structure. The ligands in the complexes **2** and **3** have the phenol-imine structures. Owing to these reason, the conformation of the six-membered chelate ring that occurs in **1** is closer to the chair conformation. The chelate rings in **2** and **3** are further from the chair conformation. In **1** the six-membered chelate ring is formed of  $\text{NiN1C8C9C10N2}$  atoms; the angle between the  $\text{C8N1N2C9}$  and  $\text{C8C9C10}$  planes is ca  $72^\circ$  deg and the angle between the  $\text{C8N1N2C9}$  and  $\text{N1NiN2}$  planes is  $37^\circ$  deg. On the other hand, for the phenol-imine ligands in **2** these angles are  $65$  and  $23^\circ$  deg, whereas in **3** they are  $84$  and  $26^\circ$  deg, respectively. Notice, the imine nitrogen atom in **2** and **3** possesses a double bond and it is harder for it to fit into the chair conformation. In **1** the amine N-atom is  $\text{sp}^3$  hybridized that is more

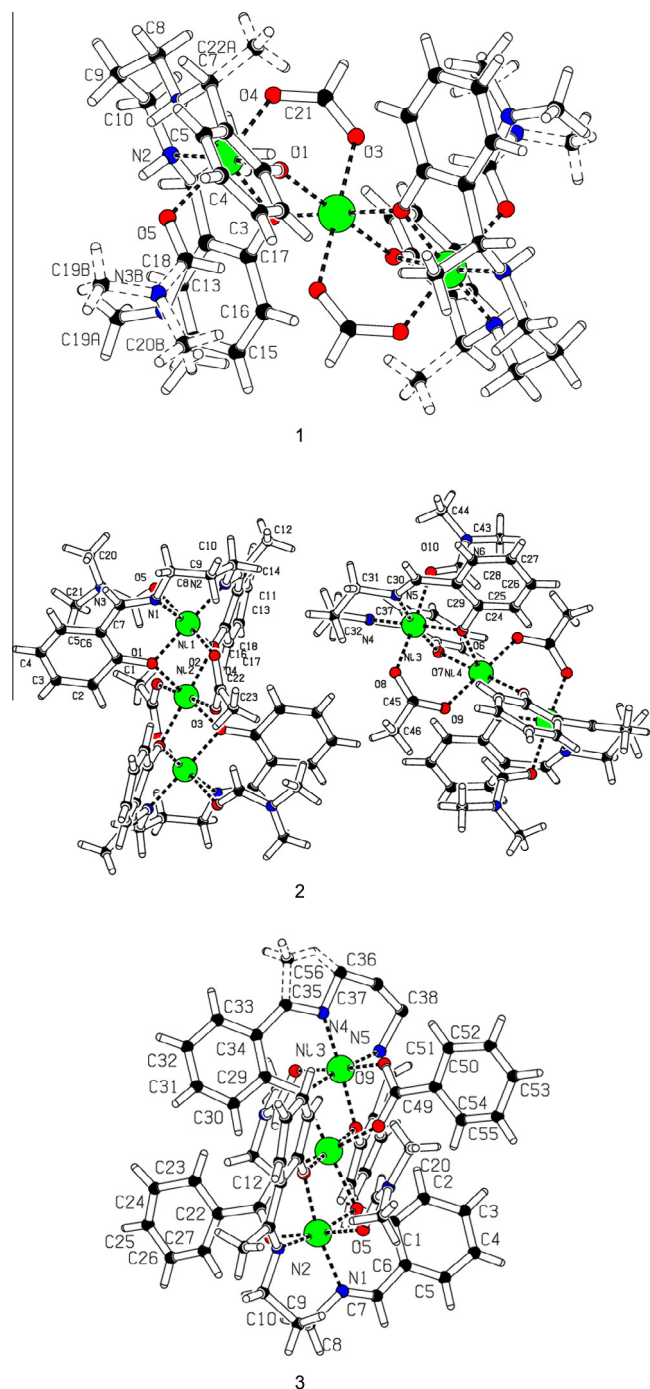


Fig. 1. The Pluton drawing of the complexes **1** through **3**.

appropriate in forming the chair conformation. These data match the literature sources on Schiff-base complexes [27,28]. In the ligands of this study there is one methyl group that creates an asymmetry and this causes that the chelate rings are more distorted manifesting itself mostly in the torsion angles  $\phi$ . In **2** the torsion angles (in deg) within the six-membered chelate ring are  $\phi(\text{N1NiN2C10}) = 35$ ,  $\phi(\text{N2NiN1C8}) = 19$ ,  $\phi(\text{C8C9C10N2}) = 56$ , and  $\phi(\text{C10C9C8N1}) = 74^\circ$  deg. In **3** these values are found as  $25$ ,  $27$ ,  $81$  and  $87^\circ$ . In the reduced ligand  $\text{SALLACH}_2^{\text{H}}$  the nitrogen and carbon atoms within the chelate rings are  $\text{sp}^3$  hybridized and the torsion angles amount to  $39$ ,  $35$ ,  $70$  and  $74^\circ$  deg that are nearer to the ideal chair conformation [28].

**Table 1**  
Data collection and crystal data for **1** through **3**.

| Compound                                        | <b>1</b>                                                                       | <b>2</b>                                                                       | <b>3</b>                                                                       |
|-------------------------------------------------|--------------------------------------------------------------------------------|--------------------------------------------------------------------------------|--------------------------------------------------------------------------------|
| Empirical formula                               | C <sub>44</sub> H <sub>58</sub> N <sub>6</sub> Ni <sub>3</sub> O <sub>10</sub> | C <sub>46</sub> H <sub>56</sub> N <sub>6</sub> Ni <sub>3</sub> O <sub>10</sub> | C <sub>56</sub> H <sub>60</sub> N <sub>6</sub> Ni <sub>3</sub> O <sub>10</sub> |
| Formula weight (g mol <sup>-1</sup> )           | 1007.09                                                                        | 1029.10                                                                        | 1153.23                                                                        |
| T (K)                                           | 293(2)                                                                         | 293(2)                                                                         | 105(2)                                                                         |
| Crystal size (mm)                               | 0.30 × 0.22 × 0.12                                                             | 0.28 × 0.16 × 0.04                                                             | 0.30 × 0.12 × 0.08                                                             |
| Crystal system                                  | monoclinic                                                                     | triclinic                                                                      | triclinic                                                                      |
| Space group                                     | P2 <sub>1</sub> /c                                                             | P $\bar{1}$                                                                    | P $\bar{1}$                                                                    |
| a (Å)                                           | 10.3856(4)                                                                     | 10.9416(9)                                                                     | 10.9177(6)                                                                     |
| b (Å)                                           | 16.0360(7)                                                                     | 12.3770(10)                                                                    | 11.3010(6)                                                                     |
| c (Å)                                           | 14.2395(6)                                                                     | 18.623(2)                                                                      | 11.6251(7)                                                                     |
| $\alpha$ (°)                                    | 90.00                                                                          | 75.863(8)                                                                      | 76.722(5)                                                                      |
| $\beta$ (°)                                     | 92.083(4)                                                                      | 85.947(8)                                                                      | 68.174(6)                                                                      |
| $\gamma$ (°)                                    | 90.00                                                                          | 76.710(8)                                                                      | 89.648(6)                                                                      |
| V (Å <sup>3</sup> )                             | 2369.93(17)                                                                    | 2379.8(4)                                                                      | 1290.91(13)                                                                    |
| Z                                               | 2                                                                              | 2                                                                              | 1                                                                              |
| Calc. density (g cm <sup>-3</sup> )             | 1.411                                                                          | 1.436                                                                          | 1.483                                                                          |
| $\mu$ (mm <sup>-1</sup> )                       | 1.240                                                                          | 1.237                                                                          | 1.149                                                                          |
| F(000)                                          | 1056                                                                           | 1076                                                                           | 602                                                                            |
| T <sub>min</sub> –T <sub>max</sub>              | 0.7073–0.8654                                                                  | 0.7233–0.9522                                                                  | 0.7243–0.9137                                                                  |
| $\theta$ Range (°)                              | 2.466–27.817                                                                   | 2.74–26.37                                                                     | 2.615–27.705                                                                   |
| Index ranges                                    | –12 ≤ h ≤ 6, –17 ≤ k ≤ 20, –16 ≤ l ≤ 17                                        | –12 ≤ h ≤ 13, –15 ≤ k ≤ 15, –23 ≤ l ≤ 22                                       | –13 ≤ h ≤ 13, –13 ≤ k ≤ 14, –8 ≤ l ≤ 14                                        |
| Reflections collected                           | 4783                                                                           | 9600                                                                           | 9259                                                                           |
| Reflections unique                              | 3390                                                                           | 4316                                                                           | 4516                                                                           |
| R <sub>1</sub> , wR <sub>2</sub> (2 $\sigma$ )  | 0.0478, 0.0901                                                                 | 0.1335, 0.4075                                                                 | 0.0594, 0.1482                                                                 |
| R <sub>1</sub> , wR <sub>2</sub> (all)          | 0.0788, 0.0805                                                                 | 0.2417, 0.3516                                                                 | 0.0931, 0.1261                                                                 |
| Data/parameters                                 | 3390/336                                                                       | 4316/584                                                                       | 4516/678                                                                       |
| GOOF of F <sup>2</sup>                          | 1.071                                                                          | 1.039                                                                          | 0.994                                                                          |
| Largest difference peak hole /e Å <sup>-3</sup> | 0.325/–0.258                                                                   | 1.481/–0.644                                                                   | 1.229/–1.139                                                                   |
| CCDC number                                     | 993122                                                                         | 993123                                                                         | 993124                                                                         |

**Table 2**  
Selected bond lengths in the coordination spheres of the complexes.<sup>a</sup>

| <b>1</b> |             | <b>2, unit-a</b> |              | <b>2, unit-b</b> |              | <b>3</b> |              |
|----------|-------------|------------------|--------------|------------------|--------------|----------|--------------|
| Ni1–N1   | 2.086(3)    | Ni1–N1           | 2.051(12)    | Ni3–N4           | 2.042(13)    | Ni1–N1   | 2.093(13)    |
| Ni1–N2   | 2.080(3)    | Ni1–N2           | 2.015(11)    | Ni3–N5           | 2.045(11)    | Ni1–N2   | 2.003(17)    |
| Ni1–O1   | 2.040(2)    | Ni1–O1           | 1.996(9)     | Ni3–O6           | 2.003(10)    | Ni1–O1   | 2.042(9)     |
| Ni1–O2   | 2.028(2)    | Ni1–O2           | 1.985(9)     | Ni3–O7           | 2.005(9)     | Ni1–O2   | 2.040(13)    |
| Ni1–O4   | 2.041(2), c | Ni1–O4           | 2.086(10), c | Ni3–O8           | 2.069(11), c | Ni1–O5   | 2.164(11)    |
| Ni1–O5   | 2.168(2)    | Ni1–O5           | 2.252(11)    | Ni3–O10          | 2.214(13)    | Ni1–O6   | 2.080(11), c |
| Ni2–O1   | 2.044(2)    | Ni2–O1           | 2.109(9)     | Ni4–O6           | 2.086(9)     | Ni2–O1   | 2.098(11)    |
| Ni2–O2   | 2.046(2)    | Ni2–O2           | 2.080(8)     | Ni4–O7           | 2.102(8)     | Ni2–O3   | 2.076(11)    |
| Ni2–O3   | 2.114(2), c | Ni2–O3           | 2.068(10), c | Ni4–O9           | 2.059(11), c | Ni2–O2   | 2.037(11)    |
|          |             |                  |              |                  |              | Ni2–O4   | 2.080(9)     |
| N1–H1A   | 0.86(3)     |                  |              |                  |              | Ni2–O7   | 2.038(11), c |
| N2–H2A   | 0.85(3)     |                  |              |                  |              | Ni2–O8   | 2.048(10), c |
|          |             |                  |              |                  |              | Ni3–N4   | 1.973(17)    |
|          |             |                  |              |                  |              | Ni3–N5   | 1.992(14)    |
|          |             |                  |              |                  |              | Ni3–O3   | 1.924(11)    |
|          |             |                  |              |                  |              | Ni3–O4   | 2.011(12)    |
|          |             |                  |              |                  |              | Ni3–O9   | 2.064(12), c |
|          |             |                  |              |                  |              | Ni3–O10  | 2.168(13)    |

<sup>a</sup> c – carboxylato oxygen atom.

### 3.2. Thermal properties

The distortion caused by the methyl groups probably reflects itself to the thermal stabilities of the complexes examined by thermogravimetry (the recorded TG and DTA curves are deposited as Supplementary Information). The TG curves show the mass loss associated with liberation of DMF groups embodied in the complexes **2** and **3**. In **2** the theoretical mass loss of DMF molecules is 14.1% as compared to the experimental value of 13.7 ± 0.6%. In **3** the expected mass loss is 12.7% that matches the experimental data of 12.4 ± 0.3%. In both complexes DMF ligands are liberated at 140 °C. Thermal decomposition of similar trinuclear complexes is reported elsewhere [30]; however, those ligands were symmetric Schiff bases and the decomposition of their complexes starts with liberation of DMF.

In **1** the DMF ligands are untouched up to 225 °C when 46.5 ± 1.2% mass loss has been observed, associated with an

endothermic peak on the DTA curve. The theoretical mass of DMF ligands in **1** is only 14.5% so that a fragmentation of the complex probably occurs. This is the principal difference with respect to **2** and **3** where a two-step process is evidenced: liberation of DMF, and then an exothermic decomposition at ca 320 °C. The nature of these differences lies in stability intermediates and it is mostly determined by donor properties of H<sub>2</sub>metsalpn and H<sub>2</sub>metsalpn<sup>H</sup> ligands, respectively. Similar observations can be found in literature [31].

### 3.3. Magnetic properties

The complex **1** behaves magnetically as an assembly of three *s* = 1 units in an antiferromagnetic interaction and with some zero-field splitting (Fig. 2). The effective magnetic moment adopts at the room temperature a value of  $\mu_{\text{eff}} = 5.45 \mu_{\text{B}}$  that decrease gradually down to 50 K (5.15  $\mu_{\text{B}}$ ); then it decreases more

progressively and at the lowest temperature of the data taking (1.9 K) it adopts a value of  $\mu_{\text{eff}} = 2.34 \mu_B$ . The room-temperature value yields an estimate of  $\mu_{\text{eff}}/\mu_B = g_{\text{av}}[3s(s+1)]^{1/2} = 5.14$  for three uncoupled  $s = 1$  units with  $g_{\text{av}} = 2.1$ .

The magnetization per formula unit  $M_1 = M_{\text{mol}}/N_A\mu_B = g_{\text{av}}S$ , however, is only  $M_1 = 4.19$  at  $B = 7$  T and  $T = 2.0$  K; this is a fingerprint of a sizable single-ion anisotropy reflected into the axial zero-field splitting (ZFS) parameter  $D$ . Even better evidence for a sizable ZFS is seen when the magnetization is plotted vs the reduced field  $B/T$ : the divergence is evident.

The susceptibility and magnetization data sets have been fitted simultaneously by applying an error functional  $F = R(\chi) \times R(M)$  that accounts uniformly for the susceptibility and magnetization data. The calculated values have been reconstructed by considering the spin Hamiltonian [32]

$$\hat{H}_a = -J(\vec{S}_1 \cdot \vec{S}_2 + \vec{S}_2 \cdot \vec{S}_3) \hbar^{-2} + \sum_{A=1}^3 \mu_B B g_A \hbar^{-1} \hat{S}_{Aa} + \sum_{A=1}^3 D(\hat{S}_{Az}^2 - \hat{S}_A^2/3) \hbar^{-2} \quad (1)$$

for  $a = z, x$ . The susceptibility data were corrected for the molecular-field correction ( $zj$ ) and eventually for the temperature-independent magnetism ( $\chi_{\text{TIM}}$ ) as follows  $\chi_{\text{corr}} = \chi_{\text{mol}}/[1 - (zj/N_A\mu_0\mu_B^2)\chi_{\text{mol}}] + \chi_{\text{TIM}}$ . The latter term accounts to the uncompensated underlying diamagnetism and the temperature-independent paramagnetism, along with the signal of the sample holder.

The optimization routine converged to the following set of magnetic parameters for **1**:  $J/hc = -2.10 \text{ cm}^{-1}$ ,  $g_{\text{av}} = 2.031$ ,  $D/hc = +5.71 \text{ cm}^{-1}$ ,  $(zj)/hc = -0.079 \text{ cm}^{-1}$ ,  $\chi_{\text{TIM}} \sim 7 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$ ; the discrepancy factors  $R(\chi) = 0.033$  and  $R(M) = 0.025$ . The sign of the  $D$ -parameter is consistent with an elongated tetragonal bipyramid which matches the structural data for the central Ni(II) atom: the axial distance is Ni–O = 2.114, whereas the equatorial ones are 2.044 and 2.040 Å, respectively.

The magnetic data for the complex **2** are essentially analogous to those of the complex **1** (Fig. 3). The fitting procedure gave the following set of magnetic parameters:  $J/hc = -2.67 \text{ cm}^{-1}$ ,  $g_{\text{av}} = 2.023$ ,  $D/hc = +4.06 \text{ cm}^{-1}$ ,  $(zj)/hc = -0.091 \text{ cm}^{-1}$ ,  $\chi_{\text{TIM}} \sim 7 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$ ;  $R(\chi) = 0.036$  and  $R(M) = 0.036$ .

The magnetic properties of the complex **3** are displayed in Fig. 4. The set of magnetic parameters reads:  $J/hc = -7.14 \text{ cm}^{-1}$ ,  $g_{\text{av}} = 2.250$ ,  $D/hc = +6.89 \text{ cm}^{-1}$ ,  $(zj)/hc = -0.095 \text{ cm}^{-1}$ ,  $\chi_{\text{TIM}} \sim 3.4 \times 10^{-9} \text{ m}^3 \text{ mol}^{-1}$ ;  $R(\chi) = 0.0087$  and  $R(M) = 0.014$ . Notice the

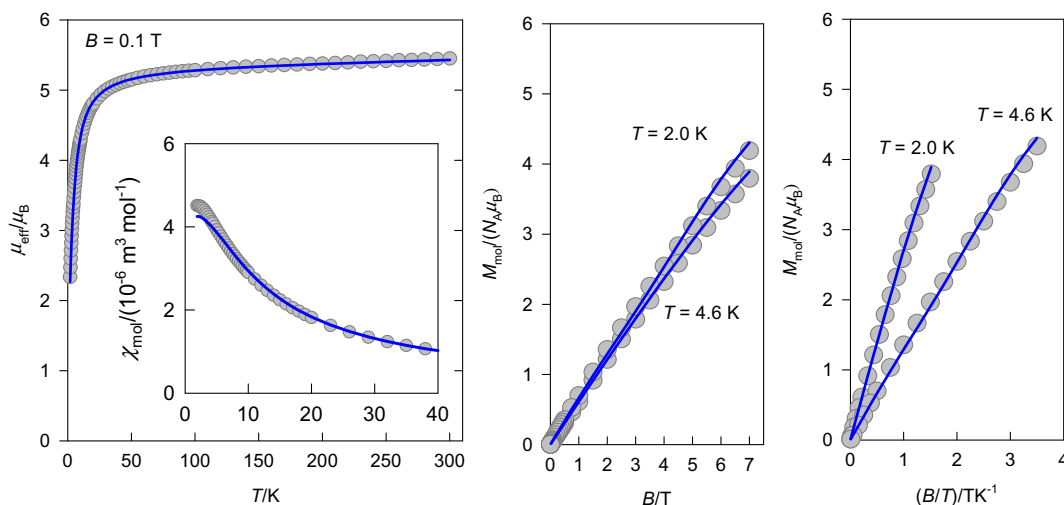
existence of a non-symmetric chromophore of the central Ni(II) atom with *trans*-pairs of Ni–O distances: axial (2.037, 2.048), equatorial (2.037, 2.079) and (2.076, 2.098) Å. This may be the source of an enlarged magnetic anisotropy measured by the axial zero-field splitting parameter  $D$ . As a consequence, the magnetization function is far from its saturation value ( $M_1 \sim 6$ ). There is some intermolecular contact between the aromatic rings of neighboring trinuclear units ( $C \cdots C = 3.58$  Å, see Fig. S2); this probably manifests itself in an enhancement of the molecular-field correction ( $zj$ ).

The model Hamiltonian [32] applied for the data analysis assumes the anisotropic  $g$ -factor; however, in order to avoid overparametrization, it was ignored and only the isotropic value has been considered. For the same reason the asymmetric exchange parameter  $D_{\text{Ni–Ni}}$  was also neglected and the Ni(II) centers were considered equivalent either.

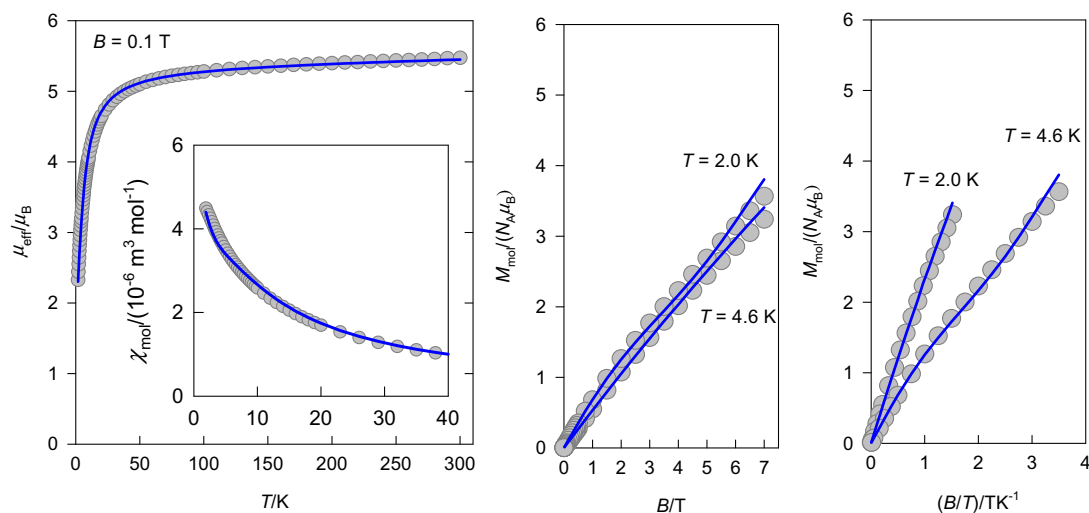
The presence of the non-zero  $D$ -value is a characteristic feature of the Ni(II) complexes that are not strictly octahedral. In mononuclear Ni(II) complexes this parameter varies between  $-7 \text{ cm}^{-1}$  (for compressed tetragonal bipyramid) to  $+7 \text{ cm}^{-1}$  (for an elongated bipyramid) [33]. This was the basis for the formulation of the first magnetostructural  $D$ -correlation in metal complexes [34]. In dinuclear and trinuclear complexes also the exchange interaction is in the play. Therefore, in the case of  $J < 0$  a reliable determination of the  $D$ -parameter is problematic when only the susceptibility data is treated. When also the magnetization is involved into the data analysis, the determination of the  $D$ -value is reliable. However, in the case of  $|D|/hc < 2 \text{ cm}^{-1}$  the reconstructed magnetic data is almost insensitive to the sign of the  $D$ -parameter. In such a case the only way is to utilize the electron spin resonance (high-field/high-frequency ESR, syn. EPR, EMR) [35].

It might be noticed that for an analogous *catena*-[Ni<sub>3</sub>] complex bridged by  $\text{NO}_2^-$  unit (**4**) the following set of magnetic parameters was reported [10]:  $J/hc = -12.5 \text{ cm}^{-1}$ ,  $g_{\text{pz}} = 2.114$ ,  $g_{\text{px}} = 2.150$ ,  $g_{\text{c}} = 2.244$ ,  $|D_p|/hc = +5.7 \text{ cm}^{-1}$  (the peripheral centre is labeled as  $p$ , the very central as  $c$ ).

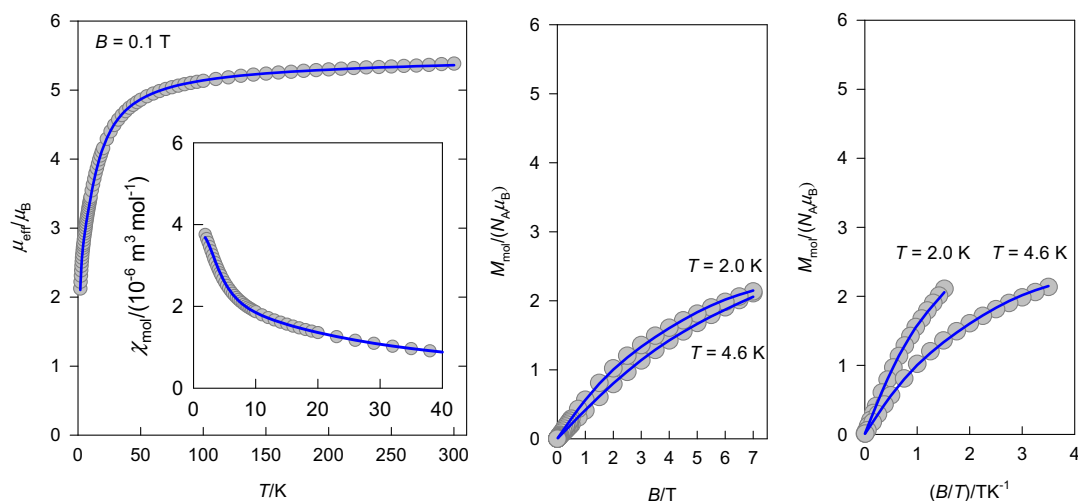
According to Table 3, the  $D$ -parameter in the complexes under study is positive which is implied by the distortion of the octahedron towards to an elongated tetragonal bipyramid. In **1** the very central Ni2 atom lies in the centre of the elongated tetragonal bipyramid, as four equatorial Ni–O distances average to  $R_e = 2.045$  Å and two axial distances (to the formate ligands) are longer,  $R_a = 2.114$  Å. Then the distortion parameter is  $\delta = R_a - R_e = 0.069$  Å and the magnetostructural  $D$ -correlation



**Fig. 2.** Magnetic functions per formula unit for the complex **1**. Left – temperature dependence of the effective magnetic moment, centre – field dependence of the magnetization, right – magnetization vs reduced field. Lines – fitted.



**Fig. 3.** Magnetic functions per formula unit for the complex **2**. Left – temperature dependence of the effective magnetic moment, right- field dependence of the magnetization. Lines – fitted.



**Fig. 4.** Magnetic functions per formula unit for the complex **3**. Left – temperature dependence of the effective magnetic moment, right- field dependence of the magnetization. Lines – fitted.

**Table 3**  
Magnetic parameters for *catena*-[Ni<sub>3</sub>] complexes.

| Complex                                                              | Ni–O(Ph)–Ni /deg          | $J/hc$ (cm <sup>−1</sup> ) | $g$                 | $D/hc$ (cm <sup>−1</sup> ) | Ref.      |
|----------------------------------------------------------------------|---------------------------|----------------------------|---------------------|----------------------------|-----------|
| <b>1</b>                                                             | 96.54, 96.86              | −2.10                      | 2.031               | 5.71                       | this work |
| <b>2</b>                                                             | 96.25, 96.86              | −2.67                      | 2.023               | 4.06                       | this work |
|                                                                      | 95.57, 96.79              |                            |                     |                            |           |
| <b>3</b>                                                             | 95.14, 97.10              | −7.14                      | 2.250               | 6.89                       | this work |
|                                                                      | 96.54, 99.45              |                            |                     |                            |           |
| <b>4</b>                                                             | 94.67, 95.38 <sup>a</sup> | −12.5                      | 2.114, 2.150, 2.244 | +5.7                       | [10]      |
| [Ni <sub>2</sub> (HL <sup>1</sup> ) <sub>4</sub> (H <sub>2</sub> O)] | 92.57, 92.86              | 2.46                       | 2.091               | −2.11                      | [36]      |
| [Ni <sub>2</sub> (HL <sup>2</sup> ) <sub>4</sub> (H <sub>2</sub> O)] | 92.50                     | 1.89                       | 2.12                | −3.56                      | [36]      |
| [Ni <sub>2</sub> (HL <sup>3</sup> ) <sub>4</sub> (H <sub>2</sub> O)] | 93.26, 92.81              | 1.73                       | 2.10                | −3.84                      | [36]      |

<sup>a</sup> Cobalt analogue [5].

predicts  $D/hc = +4.1$  cm<sup>−1</sup>. A similar analysis for the peripheral Ni<sub>2</sub> centers is complicated by the fact that the Ni1–N1 and Ni1–N2 bonds are *cis*-positioned. In **2** there are two different molecular units and **3** is not centrosymmetric so that the prediction of the D-parameter from metal–ligand distances remains unmodeled.

Table 3 brings also an information about the relationship between the bonding angle Ni–O(Ph)–O and the exchange coupling constant. For bonding angles 95–99 deg the coupling is of a weak antiferromagnetic nature. In analogous complexes possessing a bit lower bonding angle the exchange coupling switches to the weakly ferromagnetic one.

#### 4. Conclusions

ONNO type Schiff base has been prepared and isolated by using 2-hydroxybenzaldehyde, 2-hydroxyacetophenone and ethylenediamine. This species has been reduced yielding ONNO type phenol-amine ligand. Asymmetric Schiff bases and the reduced ligand were used in preparing three *catena*-[Ni<sub>3</sub>] complexes which were characterized by X-ray diffraction. The X-ray diffraction confirms that the Ni(II) are in a distorted octahedral coordination environment: the terminal centers possess distorted octahedral coordination sphere {NiN<sub>2</sub>O<sub>4</sub>} whereas the very central atom possesses {NiO<sub>6</sub>} chromophore. In Schiff-base complexes the coordinated DMF ligands leave the bulk powder at about 140 °C. After leaving the DMF molecules, trinuclear Ni(II) complexes decompose in an exothermic way. The SQUID magnetization data is compatible with exchange coupling of an antiferromagnetic nature operating along with a moderate zero-field splitting.

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#### Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ica.2014.07.020>.

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