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Playing with different metalloligands [NiL] and Hg to [NiL] ratios to tune the nuclearity of Ni(II)–Hg(II) complexes: Formation of di-, tri-, hexaand nona-nuclear Ni–Hg clusters



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ABSTRACT

Five new hetero-metallic nickel(II)-mercury(II) complexes, [(NiL¹)HgCl₂] (1), [(NiL¹)₂HgCl₂] (3), [(NiL¹)₂- $Hg(N_3)_2$ [4), [{(NiL²)₂Hg(N₃)($\mu_{1,1}$ -N₃)}₂] (5) and [{(NiL²)₂Hg(N₃)($\mu_{1,1}$ -N₃)HgCl₂}₂{Hg(N₃)($\mu_{1,1}$ -N₃)}] (6) have been synthesized by reacting metalloligands $[NiL^1]$ or $[NiL^2]$ (where H_2L^1 is N,N-bis(salicylidene)-1,2-ethylenediamine and H_2L^2 is N,N'-bis(salicylidene)-1,3-propanediamine) with HgX₂ (X⁻ = Cl⁻ or N_3^-) at different molar ratios. All five complexes have been characterised by X-ray single-crystal structural, elemental and spectroscopic analyses. In complex 1, the Hg(II) ion is coordinated to two phenoxido oxygen atoms of one [NiL¹] moiety and two terminal chloride ions to form a NiHg dinuclear complex. In the trinuclear complexes 3 and 4, the central Hg(II) ion is coordinated by two terminal [NiL¹] units through two phenoxido oxygens from each and two terminal chloride (in $\mathbf{3}$) or azide (in $\mathbf{4}$) ions. The centrosymmetric hexanuclear complex 5 consists of two trinuclear $[(NiL^2)_2Hg(N_3)(\mu_{1,1}-N_3)]$ units, where the phenoxido bridges connect two terminal Ni(II) atoms of the trinuclear units. In these trinuclear units, one azido ligand adopts a $\mu_{l,1}$ -briding mode between Hg and Ni whereas the other one is terminal. In the nonanuclear complex **6**, two tetranuclear [$\{(NiL^2)_2Hg(N_3)(\mu_{1,1}-N_3)\}HgCl_2$] units are linked to a central Hg(II) positioned on a two fold axis, via chlorido, azido, and phenoxido bridges. The tetranuclear unit is formed by the addition of a HgCl₂ molecule to a trinuclear $[(NiL^2)_2 Hg(N_3)(\mu_{1,1}-N_3)]$ unit, similar to that present in **5**. Complex **5** shows weak ferromagnetic interactions ($J = +2.1 \text{ cm}^{-1}$) between the two octahedral Ni(II) ions through double phenoxido bridges with a Ni–O–Ni bond angle of 95.87(11)°.

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1. Introduction

In recent years, the design and synthesis of high nuclearity metal clusters have become a very popular research topic not only for their unique and attractive structures but also for their diverse applications such as optical materials, magnetic materials and catalysts for organic reactions [1]. Moreover, the introduction of a hetero-metallic centre (M') into the cluster may modify the topologies or may create unusual metal coordination environments that influence the physical properties of the materials [2]. The complex (ML), essentially a metalloligand, has been widely used to synthesize hetero-metallic complexes containing divalent transition metal ions (M) and different hetero-metals (M') [3] because their nuclearity can be sometimes controlled by changing M', the ML:M'

reactant ratios and the counter ions [4]. High coordination numbers of M' enhance the probability of binding to additional ML units and may open up the possibility of building high nuclearity hetero-metallic clusters. In this approach, besides the size and type of M', the M':ML ratio may also play an important role in determining the number of ML complexes that coordinate to M' and, therefore, in the final nuclearity of the hetero-metallic cluster [5]. A third factor playing a key role is the counter-ion when it has a coordinating and/or bridging capacity since it may further increase the nuclearity of the final hetero-metallic cluster [6]. Since the stability of the metalloligand is strongly dependent on the chelating ring size of the ligand moiety [7], we have performed a systematic study to determine the influence of metalloligand with different chelating ring size in the diamine fragments and the M':ML ratios on the nuclearity of the hetero-metallic cluster in a Hg:NiL system containing salen type Schiff base ligands (L). We have selected metalloligands containing Ni(II) and salen type Schiff bases for the following reasons: (i) Ni(II) is capable of forming four, five or



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Scheme 1. Metalloligands [NiL¹] and [NiL²] used in the syntheses.

six coordinated complexes and (ii) the chelating ring size can be modified by simply changing the chain length in the amine. We have chosen Hg(II) as hetero-metal (M') because it may present different coordination numbers and geometries given the lack of energy of stabilization of the crystal field in Hg(II) (d¹⁰ ion) complexes for any geometry with only σ bonds. Finally, we have also included two different counterions (Cl⁻ and N₃⁻) to study the influence of the coordinating/bridging capacity of these ligands into the nuclearity of the final hetero-metallic clusters.

Herein, we report the synthesis and structural characterization of five hetero-metallic Ni(II)–Hg(II) coordination complexes presenting different nuclearities, thanks to the use of different ring sizes in L, M':ML ratios and counter ions. These clusters include: a dinuclear complex [(NiL¹)HgCl₂] (**1**), two trinuclear complexes [(NiL¹)₂HgCl₂] (**3**) and $[(NiL^1)_2Hg(N_3)_2]$ (**4**), a hexanuclear complex $[\{(NiL^2)_2Hg(N_3)\}$ $(\mu_{1,1}-N_3)_2$ (5) and a nonanuclear complex [{ $(NiL^2)_2Hg(N_3)(\mu_{1,1}-N_3)$ $HgCl_{2}{Hg(N_{3})(\mu_{1,1}-N_{3})}$ (6), prepared by reacting HgX_{2} (X = Cl or N_3) with two metalloligands $[NiL^1]$ and $[NiL^2]$ with different ring sizes (Scheme 1) and at different molar ratios (Scheme 2) (H_2L^1 is N,N'-bis(salicylidene)-1,2-ethylenediamine and H_2L^2 is N,N'-bis(salicylidene)-1,3-propanediamine). A careful search in the CCDC database (updated November 2013) shows that among the several thousands of complexes prepared with N,N'-bis(salicylidene)diamine-type Schiff bases, only 25 contain Hg as hetero-metal: three chain complexes (two alternating Cu-Hg [8,9] and one Mn-Hg [10]), three tetranuclear (two Hg₂Cu₂ [11,12] and one Hg₃Cu [13]), five trinuclear (four HgCu₂ [9,11,14] and one HgMn₂ [10]), thirteen dinuclear (six HgNi, [13,15,16] six HgCu [11,13,17–20] and one HgZn [21]) and one mononuclear [22]. Therefore, complexes 5 and 6 are the only known examples presenting nuclearities of six and nine, respectively, in these kind of complexes.

2. Experimental

2.1. Starting materials

Salicylaldehyde, 1,2-ethylenediamine and 1,3-propanediamine were purchased from Lancaster and were of reagent grade. They were used as received.

Caution! Perchlorate and azide salts of metal complexes with organic ligands are potentially explosive. Only a small amount of material should be prepared and it should be handled with care.

2.2. Synthesis of Schiff base ligands $(H_2L^1 \text{ and } H_2L^2)$ and metalloligands $[NiL^1]$ and $[NiL^2]$

The two di-condensed Schiff base ligands, N,N'-bis(salicylidene)-1,2-ethylenediamine (H_2L^1) and N,N'-bis(salicylidene)-1,3propanediamine (H_2L^2) were prepared by standard methods. 10 mmol of salicylaldehyde (1.04 mL) in methanol (20 mL) were mixed with 5 mmol of the required amine 1,2-ethylenediamine (0.30 mL) or 1,3-propanediamine (0.42 mL) in methanol (20 mL). The resulting solutions were refluxed for *ca*. 2 h and allowed to cool. The yellow precipitate of H_2L^1 was filtered off, washed with methanol and dried in a vacuum desiccator containing anhydrous CaCl₂. On the other hand, the yellow coloured methanolic solution of H_2L^2 was used directly for complex formation. An aqueous solution (20 mL) of Ni(ClO₄)₂·6H₂O (1.820 g, 5 mmol) and 10 mL ammonia solution (20%) were added to a methanolic solution of H_2L^1 or H_2L^2 (5 mmol, 20 mL) to prepare the respective complexes [NiL¹] or [NiL²] as reported earlier [23].

2.3. Synthesis of $[(NiL^1)HgCl_2]$ (1) and $[(NiL^2)HgCl_2]$ (2)

The previously prepared $[NiL^1]$ complex (0.325 g, 1 mmol) was dissolved in methanol (50 mL) and then an aqueous solution (1 mL) of HgCl₂ (0.242 g, 1 mmol) was added to the methanolic solution. The solution was stirred for 1 h at room temperature and filtered off. The filtrate was allowed to stand overnight resulting in the formation of prismatic red X-ray quality single crystals of **1**. Red prismatic-shaped single crystals of complex **2** were obtained in the same manner as for **1**, except that $[NiL^2]$ (0.339 g, 1 mmol) was used in the synthesis instead of $[NiL^1]$. The crystals were washed with a methanol–water mixture (1:1) and dried in a desiccator containing anhydrous CaCl₂, and then characterised by elemental analysis, spectroscopic methods and X-ray diffraction.

Complex **1**: Yield: 0.534 g (89%). *Anal.* Calc. for $C_{16}H_{14}Cl_2HgN_2$ NiO₂: C, 32.22; H, 2.37; N, 4.70. Found: C, 32.49; H, 2.31; N, 4.88%. UV–Vis: λ_{max} (solid, reflectance) = 554 and 413 nm. IR (KBr): ν (C=N) 1619 cm⁻¹.

Complex **2**: Yield: 0.557 g (91%). *Anal.* Calc. for $C_{17}H_{16}Cl_2HgN_2$ NiO₂: C, 33.44; H, 2.64; N, 4.59. Found: C, 33.41; H, 2.55; N, 4.71%. UV–Vis: λ_{max} (solid, reflectance) = 598, 490 and 392 nm. IR (KBr): ν (C=N) 1618 cm⁻¹.

2.4. Synthesis of $[(NiL^1)_2HgCl_2]$ (3)

Complex **3** was prepared by mixing the same components as for **1** but doubling the NiL¹:Hg ratio (2:1 instead of 1:1). The precursor metalloligand [NiL¹] (0.325 g, 1 mmol) was dissolved in methanol (50 mL) and then an aqueous solution (1 mL) of HgCl₂ (0.121 g, 0.5 mmol) was added. The solution was stirred for 1 h at room temperature and filtered off. Brown rhombic shaped X-ray quality



Scheme 2. Synthesis of the complexes 1-6.

single crystals of **3** were obtained by slow evaporation of the filtrate. The crystals were washed with diethyl ether and dried in a desiccator containing anhydrous CaCl₂.

Complex **3**: Yield: 0.394 g, (85%). *Anal.* Calc. for $C_{32}H_{28}Cl_2HgN_4$ Ni₂O₄: C, 41.71; H, 3.06; N, 6.08. Found: C, 41.69; H, 3.18; N, 6.02%. UV–Vis: λ_{max} (solid, reflectance) = 551 and 414 nm. IR (KBr): ν (C=N) 1620 cm⁻¹.

2.5. Synthesis of $[(NiL^1)_2Hg(N_3)_2]$ (**4**) and $[\{(NiL^2)_2Hg(N_3)(\mu_{1,1}-N_3)\}_2]$ (**5**)

The precursor metalloligand [NiL¹] (0.325 g, 1 mmol) was dissolved in methanol (50 mL) and then an aqueous solution (0.5 mL) of HgCl₂ (0.121 g, 0.5 mmol) followed by an aqueous solution (0.5 mL) of sodium azide (0.065 g, 1 mmol) were added to this solution. The mixture was stirred for 1 h at room temperature and filtered off. The filtrate was allowed to stand overnight at open atmosphere resulting in the formation of red prismatic shaped X-ray quality single crystals of **4**. Brown prismatic-shaped single crystals of complex **5** were obtained in the same manner as **4**, except that [NiL²] (0.339 g, 1 mmol) was used in the synthesis instead of [NiL¹]. The crystals were washed with a methanol-water mixture (1:1) and dried in a desiccator containing anhydrous CaCl₂.

Complex **4**: Yield: 0.353 g, (76%) *Anal.* Calc. for $C_{32}H_{28}HgN_{10}Ni_2$ O₄: C, 41.12; H, 3.02; N, 14.99. Found: C, 41.21; H, 3.02; N, 15.11%. UV–Vis: λ_{max} (solid, reflectance) = 552 and 409 nm. IR (KBr): ν (C=N) 1615 and ν (N₃) 2044 cm⁻¹.

Complex **5**: Yield: 0.331 g, (69%) *Anal.* Calc. for $C_{68}H_{64}Hg_2N_{20}$ Ni₄O₈: C, 42.42; H, 3.35; N, 14.55. Found: C, 42.68; H, 3.51; N, 14.69%. λ_{max} (solid, reflectance) = 1028, 568, 410 and 358 nm. IR (KBr): v(C=N) 1616 and $v(N_3)$ 2047 and 2075 cm⁻¹.

2.6. Synthesis of [{(NiL²)₂Hg(N₃)($\mu_{1,1}$ -N₃)HgCl₂}₂{Hg(N₃)($\mu_{1,1}$ -N₃)}] (**6**)

Complex **6** was also prepared by mixing the same components as for **5** but with a greater proportion of HgCl₂. The precursor metalloligand $[NiL^2]$ (0.339 g, 1 mmol) was dissolved in methanol (50 mL) and then an aqueous solution (0.5 mL) of HgCl₂ (0.484 g, 2 mmol) followed by an aqueous solution (0.5 mL) of sodium azide (0.065 g, 1 mmol) were added to this solution. The solution was stirred for 1 h at room temperature and filtered off. Evaporation at room temperature of the filtrate yielded red needle shaped X-ray quality single crystals of **6**. The crystals were washed with a methanol–water mixture (1:1) and dried in a desiccator containing anhydrous CaCl₂.

Complex **6**: Yield: 0.266 g, (38%, calculated based on [NiL²]). Anal. Calc. for $C_{68}H_{64}Cl_4Hg_5N_{26}Ni_4O_8$: C, 29.67; H, 2.34; N, 13.23. Found: C, 29.77; H, 2.31; N, 13.31%. UV–Vis: λ_{max} (solid, reflectance) = 1026, 570, 412 and 360 nm. IR (KBr): ν (C=N) 1617 and ν (N₃) 2050 and 2078 cm⁻¹.

2.7. Physical measurements

Elemental analyses (C, H and N) were performed using a Perkin-Elmer 2400 series II CHN analyzer. IR spectra in KBr pellets (4000–500 cm⁻¹) were recorded using a Perkin-Elmer RXI FT-IR spectrophotometer. Electronic spectra in solid state were recorded in a Hitachi U-3501 spectrophotometer. The magnetic susceptibility measurements were carried out in the temperature range 2– 300 K with an applied magnetic field of 0.1 T on a polycrystalline sample of complex **5** (with a mass of 31.17 mg) with a Quantum Design MPMS-XL-5 SQUID susceptometer. The susceptibility data were corrected for the sample holder previously measured using the same conditions and for the diamagnetic contribution of the salt as deduced by using Pascal's constant tables ($\chi_{dia} = -839 \times 10^{-6} \text{ cm}^3 \text{ mol}^{-1}$) [24].

2.8. Crystallographic data collection and refinement

4966 and 10884 independent reflection data for **1** and **6** were collected with Cu Ka and Mo Ka radiation, respectively at 150 K using the Oxford Diffraction X-Calibur CCD System. The crystals were positioned at 50 mm from the CCD. For 1, 1450 and for 6, 321 frames were measured with counting times of 1 and 10 s, respectively. Data analyses were carried out with the CRYSALIS program [25]. 3093, 5189, 5904 reflections for 3, 4 and 5 were collected using Mo Ka radiation at 293 K using the Bruker-AXS SMART APEX II diffractometer. The crystals were positioned at 60 mm from the CCD. 360 frames were measured with a counting time of 5 s. All five structures were solved using direct methods with the shelxs97 program [26]. The non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atoms bound to carbon were included in geometric positions and given thermal parameters equivalent to 1.2 times those of the atom to which they were attached. Absorption corrections were carried out using the ABSPACK program [27] for **1** and **6** and SADABS program [28] for 3, 4 and 5. Data collection, structure refinement parameters and crystallographic data for the five complexes are given in Table 1

3. Results and discussion

3.1. Synthesis of the complexes

The Schiff base ligands H_2L^1 and H_2L^2 and their corresponding Ni(II) complexes [NiL¹] and [NiL²] were synthesized using the reported procedure [23]. The [NiL¹] metalloligand on reaction with HgCl₂, in a 1:1 molar ratio, resulted in a hetero-metallic discrete dinuclear complex, [(NiL¹)HgCl₂] (**1**) (Scheme 2). Complex [(NiL²)HgCl₂] (**2**) was synthesized by following a similar procedure to that of **1**, by using $[NiL^2]$ instead of $[NiL^1]$. The structure of **2** has been reported previously by others [15,16], although the influence of the synthetic conditions on the nuclearity of the obtained complex was not studied. Therefore, we include complex 2 in the present study only to establish a relationship between synthetic conditions and the nuclearities and structures of the obtained complexes, but we will not describe the structure in detail. The CIF file obtained by us is given as ESI. Interestingly, when the [NiL¹]:HgCl₂ ratio was increased from 1:1 to 2:1, the trinuclear complex [(NiL¹)₂HgCl₂] (**3**), with a Ni:Hg ratio of 2:1, was obtained. However, for the metalloligand [NiL²], no product other than complex **2** could be isolated when the proportion of [NiL²] is increased from 1:1 to 2:1 or even to 4:1. As expected, the use of N_3^- as co-ligand has led to the preparation of additional complexes with larger nuclearities. Thus, the trinuclear complex $[(NiL^1)_2Hg(N_3)_2]$ (4) was synthesized by mixing [NiL¹], HgCl₂ and NaN₃ in a 2:1:2 molar ratio. Interestingly, when using [NiL²] instead of [NiL¹], the hexanuclear complex $[{(NiL^2)_2Hg(N_3)(\mu_{1,1}-N_3)}_2]$ (5) was obtained by following a similar procedure to that of 4. Furthermore, when the same components i.e., [NiL²], HgCl₂ and NaN₃ were mixed in a 1:2:1 molar ratio i.e., increasing the proportion of HgCl₂, then the nonanuclear complex [{ $(NiL^2)_2$ Hg(N₃)($\mu_{1,1}$ -N₃)HgCl₂}₂{Hg(N₃)($\mu_{1,1}$ -N₃)}] (6) was obtained. It may also be noted that for the [NiL¹] metalloligand, complex **4** was the only product even when the molar ratio of HgCl₂ was increased. Thus a complex equivalent to nona-nuclear species **6** was not formed with L¹. Thus, it can be concluded that the reaction of the [NiL¹] metalloligand with HgCl₂, yields dinuclear (1) and trinuclear (3) complexes by simply increasing the proportion of [NiL¹]. However, for the [NiL²] metalloligand this

Table 1							
Crystal data	and	structure	refinement	of com	plexes 1	l and	3-6.

Complexes	1	3	4	5	6
Formula	C ₁₆ H ₁₄ Cl _{2.25} Hg _{1.13} N ₂ NiO ₂	C32H28Cl2HgN4Ni2O4	C32H28HgN10Ni2O4	C ₆₈ H ₆₄ Hg ₂ N ₂₀ Ni ₄ O ₈	C68H64Cl4Hg5N26Ni4O8
Μ	630.43	921.45	934.65	1925.33	2753.04
Crystal system	triclinic	triclinic	monoclinic	triclinic	monoclinic
Space group	ΡĪ	ΡĪ	Cc	ΡĪ	C2/c
a (Å)	9.2950(6)	8.573(5)	16.354(5)	10.329(5)	40.627(5)
b (Å)	10.0541(7)	9.632(5)	10.684(5)	10.828(5)	9.9391(7)
c (Å)	10.1801(6)	10.677(5)	19.377(5)	15.940(5)	24.408(2)
α (°)	72.156(6)	74.338(5)	90	104.847(5)	90
β(°)	77.803(5)	78.861(5)	105.887(5)	99.058(5)	125.518(16)
γ (°)	86.275(6)	67.585(5)	90	94.813(5)	90
V (Å ³)	885.15(10)	780.7(7)Å	3256(2)	1687.3(12)	8022.0(13)
Ζ	2	1	4	1	2
$D_{\rm calc}$ (g cm ⁻³)	2.365	1.960	1.906	1.895	2.280
μ (mm ⁻¹)	21.771	6.314	5.903	5.699	10.650
F (000)	593	450	1832	948	5192
R _{int}	0.084	0.023	0.025	0.024	0.096
Total reflections	8126	9368	11117	19378	17256
Unique reflections	2486	3093	5189	5904	8775
$I > 2\sigma(I)$	2269	2847	4571	5354	4906
R_1^a $(I > 2\sigma(I))$	0.0549	0.0245	0.0277	0.0260	0.0684
wR_2^{b} (all data)	0.1410	0.0653	0.0553	0.0666	0.1313
Temperature (K)	150	293	293	293	150
Goodness-of-fit (GOF) ^c	1.06	1.08	0.95	1.09	0.93

^a $R_1 = \sum ||F_0| - |F_c|| / \sum |F_0|.$

^b $wR_2(F_o^2) = \sum [w(F_o^2 - F_c^2)^2 / \sum wF_o^4]^{\frac{1}{2}}.$

^c GOF = $\sum [w(F_o^2 - F_c^2)^2 / (N_{obs} - N_{params})]^{\frac{1}{2}}$.

increase has no influence on the final obtained complex and we could isolate only dinuclear complex **2**. On the other hand, the use of N_3^- inverts this tendency and thus, the metalloligand [NiL²] gives rise to high nuclearity (six and nine) complexes by increasing the proportion of HgCl₂ without changing the [NiL²]: N_3^- ratio. In contrast, the reaction of the metalloligand [NiL¹] with HgCl₂ and NaN₃ only gives rise to the trinuclear complex **4** even with high molar ratio of HgCl₂.

3.2. IR spectra and UV–Vis spectra of the complexes

Besides the elemental analysis, all six complexes were initially characterised by IR spectroscopy (Figs. S1–S6). A strong and sharp band due to the azomethine v(C=N) group of the Schiff base appears at 1619, 1618, 1620, 1615, 1616 and 1617 cm⁻¹ for complexes **1–6**, respectively. In addition, the presence of azido ligands in complexes **4–6** is confirmed by the detection of a sharp and strong characteristic stretching band in the 2080–2040 cm⁻¹ region. In case of **4**, a single strong and sharp peak at 2044 cm⁻¹ appeared while there were strong and sharp peaks at 2075 and 2078 cm⁻¹ along with shoulders at 2047 and 2050 cm⁻¹ in the spectra of **5** and **6**. The splitting of the band is indicative of the presence of two different coordinated azide ions in both **5** and **6**, in agreement with their crystal structures.

All the complexes are sparingly soluble in organic solvents like methanol, acetonitrile etc. Therefore, the UV–Vis spectra of the complexes are recorded in the solid state and their solid state diffuse reflectance spectra are shown in Fig. 1. The electronic spectra of complexes **1**, **3** and **4** containing H_2L^1 ligand are very similar, showing a broad absorption band centred at 413, 414 and 409 nm, respectively, attributed to ligand-to-metal charge transfer transitions. Besides this band, a broad absorption band (v_1) is observed in the visible region at 554, 551 and 552 nm for **1**, **3** and **4**, respectively (compared to 555 nm in the non-coordinated metalloligand [NiL¹]). This band is typical of d–d transitions of Ni(II) ions with a square planar environment. The electronic spectra of nickel(II) complexes with square planar geometry are



Fig. 1. Electronic spectra of the metalloligands and complexes in the solid state.

expected to exhibit absorption bands near 610 (v_1) and 500 nm (v_2) corresponding to the spin allowed d-d transitions ${}^{l}B_{lg} \leftarrow {}^{l}A_{g}$ and ${}^{1}B_{3g} \leftarrow {}^{1}A_{g}$, respectively [29]. Here, the v_{2} band cannot be located presumably because it overlaps with charge transfer bands. On the other hand, the spectra of complexes 5 and 6, containing the H_2L^2 ligand, are different from their mononuclear precursor [NiL²]. The [NiL²] shows band maxima (v_1) at 623 nm along with a less intense shoulder (v_2) at 500 nm, assigned to d-d transitions of Ni(II) ions with a square planar environment. However, both 5 and **6** exhibit a distinct band at 568 and 570 nm, respectively, which can be assigned to the spin-allowed d-d transition ${}^{3}T_{1g}$ $(F) \leftarrow {}^{3}A_{2g}$. In addition, they show a well-separated broad band at 1028 and 1026 nm, respectively, due to the transition ${}^{3}T_{2g} \leftarrow {}^{3}A_{2g}$ for octahedral Ni(II) geometry [30], in agreement with the structural data (see below). Moreover, complexes **5** and **6** show a sharp single absorption band near 358 and 360 nm, respectively, attributed to ligand-to-metal charge transfer transitions.

3.3. Description of the structures of the complexes

All six structures contain either L^1 or L^2 , the latter having an extra methylene moiety. The dinuclear structure of $[(NiL^1)HgCl_2]$



Fig. 2. The structure of **1** with ellipsoids at 30% probability. An additional [HgCl] moiety with 25% occupancy is not shown. The structure of **2** with an additional methylene moiety is similar.

Table 2	
Bond distances (Å) and angles (°) for complex 1 .	

Hg(1)-Cl(1)	2.320(3)	Ni(1)-O(11)	1.862(8)
Hg(1)-Cl(2)	2.325(3)	Ni(1)-O(30)	1.858(7)
Hg(1) - O(11)	2.523(7)	Ni(1)-N(19)	1.848(9)
Hg(1)-O(30)	2.488(7)	Ni(1)-N(22)	1.837(9)
Cl(1)-Hg(1)-Cl(2)	158.16(12)	O(11)-Ni(1)-O(30)	83.3(3)
Cl(1)-Hg(1)-O(30)	99.9(2)	O(11)-Ni(1)-N(22)	178.6(4)
Cl(2)-Hg(1)-O(30)	101.3(2)	O(11)-Ni(1)-N(19)	94.1(4)
Cl(1)-Hg(1)-O(11)	101.2(2)	O(30)-Ni(1)-N(22)	95.3(4)
Cl(2)-Hg(1)-O(11)	94.1(2)	O(30)-Ni(1)-N(19)	177.4(4)
O(11)-Hg(1)-O(30)	59.1(2)	N(22)-Ni(1)-N(19)	87.3(4)

(1) is shown in Fig. 2 together with the atomic numbering scheme in the coordination spheres. Bond lengths and angles in the metal coordination sphere are given in Table 2. The structure of **2** with an additional methylene moiety is equivalent.

The nickel atom has a four coordinate square planar environment formed by the four donor atoms of the tetradentate Schiff base ligand (L¹). Bond lengths from nickel are 1.837(9), 1.848(9) Å to nitrogen and 1.858(7), 1.862(8) Å to oxygen. The four donor atoms are planar with a root mean squared (r.m.s.) deviation of 0.008 Å, the nickel being 0.001(5) Å away from the equatorial plane. The two oxygen atoms also coordinate the mercury atom which completes its highly distorted tetrahedral coordination with two chlorine atoms. The distortions from the regular tetrahedral geometry are clearly shown by the small O–Hg–O bond angle of $59.1(2)^{\circ}$, the large Cl–Hg–Cl angle of $158.16(12)^{\circ}$ and by the shorter Hg–Cl bond lengths of 2.320(3) and 2.325(3) Å compared to Hg–O of 2.488(7) and 2.523(7) Å (Table 2).

Apart from the complex, the structure contains two residual peaks of high electron density. These were refined as Hg(2) in a centrosymmetric position and Cl(3) in a general position, with population parameters of 0.25. The resulting geometry around Hg(2) is approximately square planar, the metal being bound weakly to Cl(2) at 2.787(4) Å which bridges to Hg(1) and strongly to Cl(3) at 2.242(11) Å.

In the structure, there is an inter-molecular π - π stacking between the two phenyl rings (symmetry: 1 - x, 1 - y, 1 - z) with a centroid Cg···Cg distance of 3.665(8) Å. Additionally, there is a weak C20–H20B···O30 hydrogen bonding interaction between the phenoxido oxygen atom, O30 and the methylene hydrogen atom (H20B) of an adjacent molecule (1 - x, 2 - y, 1 - z) with distance of O30···C20 3.292(18) Å and C20–H20B···O30 angle of 144°. These interactions generate polymeric chains as depicted in Fig. 3.

Complexes $[(NiL^1)_2HgCl_2]$ (3) and $[(NiL^1)_2Hg(N_3)_2]$ (4), both containing L¹ are trinuclear and very similar. The main differences are that 3 contains an crystallographic inversion centre while 4 does not, although its structure is closely centrosymmetric, and 3 contains chloride ions and 4 azide ions. In both structures the Hg atom presents an octahedral geometry with two axial short bonds to two mutually *trans* anions (Cl⁻ or N₃⁻) and four long equatorial bonds from the four oxygen atoms from the two [NiL¹] metalloligands. The structures of 3 and 4 are shown in Fig. 4 together with the atomic numbering schemes. Bond lengths and angles in the metal coordination spheres are given in Tables 3 and 4, respectively.

In **3**, the axial Hg(1)–Cl(1) distance is 2.303(2) Å and the weak equatorial bonds to the oxygen atoms O(11) and O(30) are 2.827(3) and 2.834(3) Å. These oxygen atoms bridge the Hg and Ni metals. The nickel atom has the expected four-coordinate square planar structure with Ni–O bond lengths of 1.844(3) and 1.847(3) Å and Ni–N bond lengths of 1.847(3) and 1.856(3) Å. The r.m.s deviation for the four donor atoms is 0.006 Å, with the Ni(1) atom 0.001(2) Å away from the plane.

The structure of **4** shows a similar Ni₂Hg trinuclear unit. The Hg also presents a compressed octahedral geometry with two short bonds to the two *trans*-azide anions with Hg(1)–N(1) 2.067(10) Å and Hg(1)–N(4) 2.054(9) Å and four longer bonds to the oxygen atoms of two [NiL¹] metalloligands with Hg–O bond lengths in the range 2.736(5)–2.842(5) Å. These four oxygen are almost coplanar, with a r.m.s. deviation of 0.036 Å, being the Hg atom 0.030(3) Å away from the plane. These oxygen atoms bridge the Hg atom to a nickel atom. The nickel atoms are four coordinate square planar being bound to the four donor atoms of the ligands with r.m.s. deviations of the four donor atoms of 0.060 and 0.045 Å, being Ni(2) and Ni(3) 0.009(3) and 0.008(3) Å away from their respective planes, which form a dihedral angle of 6.1(4)°.

The H-bonding and C-H \cdots π interactions in complexes **3** and **4** give rise to a 2D supramolecular network (Fig. 5 for 3 and Fig. S7 for 4). In both complexes, H-bonding interactions are formed between the phenoxido oxygen atoms and the methylene hydrogen atom of an adjacent molecule (2 - x, 1 - y, -z for 3 and x, 1 + y, z for 34) with dimensions $0 \cdots C 3.272(6)$ and 3.452(9) Å and $C-H \cdots O$ angles of 143° and 161°, respectively. Moreover, a trinuclear unit of complex 4 interacts with other trinuclear unit via two additional H-bonding between nitrogen atoms of azido ligands and iminic hydrogen atoms with dimensions N···C 3.466(12) and 3.447(13) Å and C-H...N angles of 151° and 176°. Besides these H-bonding interactions two adjacent trinuclear units establish C–H \cdots π interactions between the methylene hydrogen atoms of one trinuclear unit and the centroid of a phenyl ring of other trinuclear units (symmetry 1 - x, 1 - y, -z for **3** and -1/2 + x, 1/2 + y, z for **4**) with distances of 2.59 (3) Å for **3** and 2.52(1) Å for **4**.

Complex [{(NiL²)₂Hg(N₃)₂]₂] (**5**) is a centrosymmetric hexanuclear cluster formed by two symmetry related Ni₂Hg units. Fig. 6 shows the structure of complex **5** together with the atomic numbering scheme. Selected bond lengths and angles are summarized in Table 4. As in **4**, the Hg atoms present a compressed octahedral geometry with two strongly bound *trans*-azide ligands Hg–N(1) and Hg–N(4) at 2.063(4) and 2.093(4) Å, respectively. The equatorial plane is formed by four oxygen atoms with longer bond lengths: Hg–O(61) 2.548 (3) Å, Hg–O(11) 2.719(3) Å, Hg–O(31) 2.733(3) Å and Hg–O(41) 2.964(3) Å. The four oxygen atoms are



Fig. 3. The 1D chain formed in 1 through H-bonds and intermolecular $\pi \cdots \pi$ interactions. Other H-atoms have been removed for clarity. Distances in Å.



Fig. 4. Left: The centrosymmetric structure of 3 with ellipsoids at 50% probability. Right: The structure of 4 with ellipsoids at 30% probability. The weak Hg...O interactions are shown as open bonds in both cases.

Table 3Bond distances (Å) and angles (°) for complex 3.

Hg(1)-Cl(1)	2.303(2)	Ni(1)-O(11)	1.844(3)
Hg(1)-O(11)	2.827(3)	Ni(1)-N(19)	1.847(3)
Hg(1)-O(30)	2.834(3)	Ni(1)-N(22)	1.856(3)
Cl(1)-Hg(1)-O(11)	86.82(6)	Ni(1)-O(30)	1.847(3)
Cl(1)-Hg(1)-O(30)	86.79(7)	O(11)-Ni(1)-O(30)	85.09(11)
O(11)-Hg(1)-O(30)	52.32(8)	O(11)-Ni(1)-N(22)	179.44(13)
		O(11)-Ni(1)-N(19)	94.60(13)
		O(30)-Ni(1)-N(22)	94.43(13)
		O(30)-Ni(1)-N(19)	179.46(14)
		N(22)-Ni(1)-N(19)	85.89(15)

almost planar with a r.m.s. deviation of 0.001 Å, with the Hg(1) atom 0.310(2) Å from the plane directed towards N(1) from the more strongly bound azide.

Ni(2) has a square planar geometry formed by the four donor atoms of the L² ligand showing a r.m.s. deviation of 0.034 Å, being the Ni(2) atom 0.001(2) Å away from the plane. Bond lengths are Ni(2)–O = 1.852(3) and 1.869(3) Å and Ni(2)–N = 1.894(4) and 1.917(4) Å. In contrast, Ni(3) presents an octahedral geometry formed by four donor atoms from one L² ligand in the equatorial plane with a $\mu_{1,1}$ -N₃ ligand and an oxygen atom from another L² ligand in the axial positions with Ni(3)–N(4) 2.291(4) Å and Ni(3)–O(41) 2.132(3) Å. Each of these axial atoms connects Ni(3) to a Hg(1) atom whereas the two O(41) atoms form a double oxido bridge connecting both Ni(3) atoms (with a Ni(3)–O(41)–Ni(3)

bond angle of $84.13(11)^\circ$). The r.m.s. deviation of the four equatorial atoms is 0.088 Å, with the Ni(3) atom 0.061(2) Å away from the plane. The bond lengths are Ni(3)–O 2.052(3) and 1.999(3) Å and Ni(3)–N = 2.027(3) and 2.054(4) Å, all longer than those observed for the square planar Ni(2) atom, as a consequence of the extra coordination of the two axial ligands in Ni(3). The two equatorial planes around Ni(2) and Ni(3) form a dihedral angle of $46.0(1)^\circ$.

In the structure, there is an intra-molecular π - π stacking between the two phenyl rings (symmetry: -x, -y, 2 - z) with a centroid Cg...Cg distance of 3.784(3) Å. The non classical hydrogen bonding interactions [C26–H26···N3 (-1 - x, -1 - y, 1 - z) and C56–H56···N3 (1 + x, y, z) with dimensions N···C 3.292(18) and 3.421(8) Å, respectively] are also present.

The molecular structure of complex **6** contains a nonanuclear unit $[\{(NiL^2)_2Hg(N_3)(\mu_{1,1}-N_3)HgCl_2\}_2\{Hg(N_3)(\mu_{1,1}-N_3)\}]$ with C_2 symmetry formed by two tetrameric Ni_2Hg_2 units connected through a Hg(3) atom located on the C_2 axis. The structure of **6** is shown in Fig. 7 together with the atomic numbering scheme. Dimensions in the metal coordination sphere are given in Table 5. The central mercury atom Hg(3) occupies a 2-fold axis and presents a highly distorted octahedral geometry formed by two short mutually *trans* azide ligands with dimensions Hg(3)–N(4) 2.042(11) Å, N(4)–Hg(3)–N(4) 159.6(7)° two mutually *cis*-O atoms Hg(3)–O(61) 2.679(9) Å, O(61)–Hg(3)–O(61) 142.6(3)°) and two mutually *cis*-Cl atoms Hg(3)–Cl(2) 3.081(4) Å, Cl(2)–Hg(3)–Cl(2) 74.8(1)°). Hg(2) also presents a very distorted octahedral geometry formed by two *trans*-azide ligands with dimensions Hg(2)–N(1) 2.101(13) Å,

Table 4	
Bond distances (Å) and angles (°) for complexes 4	and 5 .

	4	5		4	5
	x = 0, y = 2	x = 1, y = 3		x = 0, y = 2	x = 1, y = 3
Hg(1)-N(1)	2.067(10)	2.063(4)	Ni(2)-N(19)	1.824(6)	1.917(4)
Hg(1)–N(4)	2.054(9)	2.093(4)	Ni(2)-N(2y)	1.819(9)	1.894(4)
Hg(1)-O(11)	2.768(5)	2.719(3)	Ni(2)-O(11)	1.851(5)	1.852(3)
Hg(1)-O(3x)	2.842(5)	2.733(3)	Ni(2) - O(3x)	1.853(5)	1.869(3)
Hg(1)-O(41)	2.841(5)	2.964(3)	N(19)-Ni(2)-N(2y)	85.1(4)	96.15(18)
Hg(1)-O(6x)	2.736(5)	2.548(3)	N(19)-Ni(2)-O(11)	95.0(3)	91.67(16)
N(1)-Hg(1)-N(4)	177.4(5)	167.10(16)	N(19)-Ni(2)-O(3x)	176.8(3)	170.63(16)
N(1)-Hg(1)-O(6x)	92.7(2)	100.15(16)	N(2y)-Ni(2)-O(11)	175.7(3)	171.88(16)
N(1)-Hg(1)-O(11)	87.6(3)	93.06(16)	N(2y)-Ni(2)-O(3x)	94.4(3)	92.99(16)
N(1)-Hg(1)-O(41)	89.1(3)	99.14(14)	O(11)-Ni(2)-O(3x)	85.7(2)	79.23(13)
N(1)-Hg(1)-O(3x)	88.4(3)	93.53(14)	Ni(3)–N(5y)	1.844(5)	2.054(4)
N(4)-Hg(1)-O(6x)	88.5(2)	73.73(13)	Ni(3)-N(49)	1.850(7)	2.027(3)
N(4)-Hg(1)-O(11)	91.3(2)	95.76(13)	Ni(3)-O(41)	1.845(4)	2.052(3)
N(4)-Hg(1)-O(41)	89.8(3)	67.96(11)	Ni(3)-O(6x)	1.855(4)	1.999(3)
N(4)-Hg(1)-O(3x)	92.8(3)	99.32(12)	Ni(3)-N(4)		2.291(4)
O(11)-Hg(1)-O(3x)	53.37(15)	51.63(9)	Ni(3)-O(41) ^a		2.132(3)
O(3x)-Hg(1)-O(41)	176.13(14)	166.20(9)	N(49) - Ni(3) - N(5y)	86.9(3)	97.10(14)
O(41)-Hg(1)-O(6x)	53.47(13)	58.90(8)	N(49)-Ni(3)-O(41)	94.2(2)	91.19(12)
O(6x)-Hg(1)-O(11)	177.06(17)	161.08(10)	N(49) - Ni(3) - O(6x)	176.7(3)	169.11(13)
O(3x) - Hg(1) - O(6x)	123.71(14)	113.54(9)	N(5y)-Ni(3)-O(41)	177.5(2)	174.39(12)
O(11)-Hg(1)-O(41)	129.46(13)	132.34(8)	N(5y) - Ni(3) - O(6x)	93.6(2)	89.85(13)
			O(41) - Ni(3) - O(6x)	85.5(2)	84.88(11)
			O(61)-Ni(3)-N(4)		96.62(11)
			N(49)-Ni(3)-N(4)		89.39(14)
			O(41)-Ni(3)-N(4)		84.20(12)
			N(53)-Ni(3)-N(4)		96.94(14)
			$O(41)^{a}-Ni(3)-N(4)$		168.30(12)
			O(41) ^a -Ni(3)-O(61)		96.62(11)
			O(41) ^a -Ni(3)-N(49)		91.19(12)
			$O(41)^{a}-Ni(3)-O(41)$		84.13(11)
			$O(41)^{a}-Ni(3)-N(53)$		94.59(12)

^a = symmetry element -x, -y, 2 - z.



Fig. 5. The 2D supramolecular network of 3 formed by the H-bonds and intermolecular C-H···π interactions. Other H-atoms have been removed for clarity. Distance in Å.

Hg(2)-N(7) 2.088(13) Å and $N(1)-Hg(2)-N(7) = 165.8(5)^{\circ}$, three O atoms Hg(2)-O(11) 2.601(9) Å, Hg(2)-O(31) 2.488(8) Å and Hg(2)-O(41) 2.855(9) Å with O-Hg(2)-O bond angles in the range 57.9(2)-148.8(2)^{\circ} and one Cl atom Hg(2)-Cl(1) 3.212(9) Å). Hg(1) presents a distorted tetrahedral geometry, similar to that observed in **1**. The distortions in the tetrahedron are clearly observed in the

bond angles, ranging from $O(41)-Hg(1)-O(61) = 68.9(2)^{\circ}$ to $Cl(1)-Hg(1)-Cl(2) = 154.7(1)^{\circ}$. In contrast, the Hg(1)-Cl bond lengths at 2.332(4), 2.339(5) Å are quite similar to Hg(1)-O bond lengths at 2.390(7), 2.418(10) Å.

The two nickel atoms, Ni(4) and Ni(5) are both bound to the four donor atoms of a L^2 ligand although Ni(4) is square planar



Fig. 6. The centrosymmetric structure of 5 with ellipsoids at 20% probability. Weak interactions to Hg(1) are shown as open bonds.



Fig. 7. The structure of 6 with ellipsoids at 30% probability. Weak interactions from Hg(2) and Hg(3) to oxygen are shown as open bonds. Hg(3) occupies a centre of symmetry.

whereas Ni(5) presents a regular octahedral environment with two additional axial *trans*-N₃ ligands with bond lengths of 2.125(12) and 2.186(14) Å). As a consequence, the equatorial bond lengths around Ni(4) (in the range 1.851(8)–1.869(10) Å) are significantly shorter than those around Ni(5) (in the range Ni–N = 2.020(10)–2.045(12) Å). The two equatorial planes form a dihedral angle of $50.5(3)^\circ$. The r.m.s. deviations of the four donor atoms are 0.189 and 0.109 Å, with the Ni(4) and Ni(5) atoms 0.002(6) and 0.011(6) Å away from their respective planes.

3.4. Magnetic properties

Complexes **1–4** contain only diamagnetic Hg(II) cations and square planar Ni(II) ions, whereas complex **6** only contains two isolated octahedral Ni(II) ions and, therefore, it is not expected to

show any magnetic coupling. A priori, the only complex that may present a magnetic coupling between paramagnetic Ni(II) centres is complex **5** since it presents two octahedral Ni(II) ions with a double oxido bridge (inset in Fig. 8). Accordingly, we have only measured the magnetic properties of complex **5**. The $\chi_m T$ product for complex **5** (χ_m = molar magnetic susceptibility per Ni₄Hg₂ complex) shows a room temperature value of ca. 2.35 cm³ K mol⁻¹ (Fig. 8), which is the expected value for two isolated S = 1 Ni(II) ions. When the sample is cooled down, $\chi_m T$ smoothly increases, reaching a maximum of ca. 3.30 cm³ K mol⁻¹ at ca. 9 K (inset in Fig. 8). Below ca. 9 K $\chi_m T$ sharply decreases and reaches a value of ca. 1.4 cm³ K mol⁻¹ at 2 K. This behaviour suggests the presence of ferromagnetic interactions between the two octahedral Ni(II) ions that account for the increase in $\chi_m T$ as *T* decreases. The sharp decrease at very low temperatures has to be attributed to the

Table 5Bond distances (Å) and angles (°) for complex 6.

Hg(1)-Cl(1)	2.332(5)	O(11)-Ni(4)-O(31)	83.3(4)
Hg(1)-Cl(2)	2.339(5)	O(11)-Ni(4)-N(19)	94.6(4)
Hg(1)-O(41)	2.390(7)	O(11)-Ni(4)-N(23)	167.0(5)
Hg(1)-O(61)	2.418(10)	O(31)-Ni(4)-N(19)	168.2(5)
Cl(1)-Hg(1)-Cl(2)	154.69(13)	O(31)-Ni(4)-N(23)	92.2(4)
Cl(1)-Hg(1)-O(41)	93.7(3)	N(19)-Ni(4)-N(23)	92.2(5)
Cl(2)-Hg(1)-O(41)	109.7(3)	Ni(5)-O(41)	2.020(10)
Cl(1)-Hg(1)-O(61)	105.6(2)	Ni(5)-O(61)	2.028(8)
Cl(2)-Hg(1)-O(61)	92.2(2)	Ni(5)-N(49)	2.039(9)
O(41)-Hg(1)-O(61)	68.8(3)	Ni(5)-N(53)	2.045(12)
Hg(2)-N(1)	2.101(13)	Ni(5)-N(1)	2.125(12)
Hg(2)-N(7)	2.088(13)	Ni(5)-N(4)	2.186(14)
Hg(2)-O(31)	2.488(9)	O(41)-Ni(5)-O(61)	84.4(3)
Hg(2)-O(11)	2.602(9)	O(41)-Ni(5)-N(49)	90.1(4)
N(1)-Hg(2)-N(7)	165.8(5)	O(61)-Ni(5)-N(49)	170.9(4)
N(1)-Hg(2)-O(31)	92.1(4)	O(41)-Ni(5)-N(53)	170.7(3)
N(7)-Hg(2)-O(11)	101.1(4)	O(61)-Ni(5)-N(53)	88.7(4)
N(7)-Hg(2)-O(31)	102.0(4)	N(49)-Ni(5)-N(53)	97.6(4)
N(1)-Hg(2)-O(11)	86.9(4)	O(41)-Ni(5)-N(1)	84.4(4)
O(11)-Hg(2)-O(31)	57.8(3)	O(61)-Ni(5)-N(1)	92.6(4)
Hg(3)-N(4)	2.042(11)	N(49)-Ni(5)-N(1)	94.0(5)
$N(4)-Hg(3)-N(4)^{a}$	159.6(7)	N(53)-Ni(5)-N(1)	89.8(5)
Ni(4)-O(11)	1.851(8)	O(41)-Ni(5)-N(4)	89.6(5)
Ni(4)-O(31)	1.852(9)	O(61)-Ni(5)-N(4)	83.3(4)
Ni(4)-N(19)	1.862(12)	N(49)-Ni(5)-N(4)	89.5(4)
Ni(4)-N(23)	1.869(10)	N(53)-Ni(5)-N(4)	95.7(5)
		N(1)-Ni(5)-N(4)	173.0(5)

^a Symmetry element 1 - x, y, 1.5 - z.



Fig. 8. Thermal variation of $\chi_m T$ per Ni₄Hg₂ unit in complex **5**. Solid line represents the best fit to the model (see text).

presence of a zero field splitting (ZFS) in the resulting S = 2 ground state of the dimer. Accordingly, we have fitted the magnetic properties of complex **5** with a simple S = 1 dimer model including ZFS [31]. This model reproduces very satisfactorily the magnetic properties of **5** with g = 2.132, $J = +2.1 \text{ cm}^{-1}$ and $|D| = 8.5 \text{ cm}^{-1}$ (the Hamiltonian is written as $-JS_1S_2$). Note that the sign of D cannot be determined from powder magnetic measurements and also that this high D value could include an antiferromagnetic inter-dimer coupling through a quite short inter-dimer π - π stacking observed in complex **5** along the [101] direction.

As already mentioned, a close inspection at the X-ray structure of **5**, shows that the two Ni(3) ions are connected through a double oxido bridge with Ni(3)–O(41) bond lengths of 2.052(3) and 2.132(3) Å and a Ni(3)–O(41)–Ni(3) bond angle of 95.87(11)°. This Ni–O–Ni bond angle is below 98–99° and therefore, ferromagnetic interactions are to be expected [32–34]. In fact, the observed weak ferromagnetic coupling constant is very close to those observed in other systems with similar double oxido bridges connecting Ni(II) ions [35–38].

4. Conclusions

In the present paper, using two related metalloligands [NiL¹] and $[NiL^2]$ (where H₂L¹ is N.N'-bis(salicylidene)-1.2-ethylenediamine and H_2L^2 is N,N'-bis(salicylidene)-1,3-propanediamine) we have shown that it is possible to synthesise up to six different Ni(II)-Hg(II) hetero-metallic complexes of nuclearities from two to nine, by simply changing the reactant ratios and the counter anions. Both metalloligands [NiL¹] and [NiL²] react with HgCl₂ to produce dinuclear complexes namely 1 and 2. However, when the proportion of HgCl₂ is decreased only [NiL¹] yields a trinuclear complex, namely **3**. On the other hand, when Cl⁻ ion is replaced by N₃, only trinuclear complexes are formed for both ligands; for [NiL¹] it remains as a discrete molecule (**4**) but for [NiL²], terminal nickel atoms of two trinuclear units join together via phenoxido bridges to form a hexanuclear species (5). On increasing the proportion of HgCl₂, [NiL²] even yields an unprecedented nonanuclear complex (6). Complexes 5 and 6 are the only known examples of nuclearities higher than four in discrete hetero-metallic clusters containing Hg(II). The double phenoxido bridged Ni(II) dimer in complex 5 is ferromagnetically coupled as expected from the Ni-O-Ni bond angle. All these results demonstrate the possibility to create novel complexes with different nuclearities by playing not only with the metal to ligand ratio and/or the presence of different terminal or bridging co-ligands but also with the size of the chelating ring in the precursor complexes used as ligands. This strategy is now being used to combine other magnetic metal atoms, mainly lanthanides, in order to prepare novel polynuclear complexes with interesting magnetic properties including single molecules magnets.

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Appendix A. Supplementary data

CCDC 1005578–1005583 contain the supplementary crystallographic data in CIF format for **1–6**, respectively. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/ retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk. Supplementary data associated with this article can be found, in the online version, at http://dx.doi.org/10.1016/j.poly.2014.11.025.

References

- (a) V. Balzani, S. Campagna (Eds.), Photochemistry and Photophysics of Coordination Compounds II, Springer, Berlin, 2007;
 - (b) R. Bagai, G. Christou, Chem. Soc. Rev. 38 (2009) 1011;
 - (c) D. Gatteschi, R. Sessoli, Angew. Chem., Int. Ed. 42 (2003) 268;
 - (d) M. Shibasaki, Y. Yamamoto (Eds.), Multimetallic Catalysts in Organic Synthesis, Wiley-VCH, Weinheim, Germany, 2004;
 - (e) M. Yamamura, H. Miyazaki, M. Iida, S. Akine, T. Nabeshima, Inorg. Chem. 50 (2011) 5315;
 - (f) A. Mishra, A.J. Tasiopoulos, W. Wernsdorfer, K.A. Abboud, G. Christou, Inorg. Chem. 46 (2007) 3105.

- (a) M.G.F. Vaz, L.M.M. Pinheiro, H.O. Stumpf, A.F.C. Alcantara, S. Golhen, L. Ouahab, O. Cador, C. Mathonière, O. Kahn, Chem. Eur. J. 5 (1999) 1486;
 (b) R. Gheorghe, P. Cucos, M. Andruh, J.-P. Costes, B. Donnadieu, S. Shova, Chem. Eur. J. 12 (2006) 187.
- [3] (a) L.K. Das, M.G.B. Drew, A. Ghosh, Inorg. Chim. Acta 394 (2013) 247;
 - (b) S. Biswas, A. Ghosh, Polyhedron 30 (2011) 676;
 - (c) S. Biswas, A. Ghosh, Indian J. Chem. Sec. A 50A (2011) 1356;
 (d) S. Ghosh, S. Mukherjee, P. Seth, P.S. Mukherjee, A. Ghosh, Dalton Trans. 42
 - (d) 5. Ghosh, 5. Mukherjee, P. Seth, P.S. Mukherjee, A. Ghosh, Datton Hans, 42 (2013) 13554;
 - (e) J.M. Epstein, B.N. Figgis, A.H. White, A.C. Willis, J. Chem. Soc., Dalton Trans. (1974) 1954;
 - (f) P. Seth, L.K. Das, M.G.B. Drew, A. Ghosh, Eur. J. Inorg. Chem. (2012) 2232; (g) G.A. Brewer, E. Sinn, Inorg. Chim. Acta 134 (1987) 13;
 - (h) A. Bencini, C. Benelli, A. Caneschi, R.L. Carlin, A. Dei, D. Gatteschi, J. Am. Chem. Soc. 107 (1985) 8128.
- [4] (a) M. Knorr, F. Guyon, A. Khatyr, C. Strohmann, M. Allain, S.M. Aly, A. Lapprand, D. Fortin, P.D. Harvey, Inorg. Chem. 51 (2012) 9917;
 - (b) L.K. Das, A. Ghosh, CrystEngComm 15 (2013) 9444;
 - (c) L.K. Das, A.M. Kirillov, A. Ghosh, CrystEngComm 16 (2014) 3029;
 - (d) L.K. Das, A. Biswas, C.J. Gómez-García, M.G.B. Drew, A. Ghosh, Inorg. Chem. 53 (2014) 434;
 - (e) S. Ghosh, S. Biswas, A. Bauzá, M. Barceló-Oliver, A. Frontera, A. Ghosh, Inorg. Chem. 52 (2013) 7508.
- [5] (a) S. Biswas, S. Naiya, M.G.B. Drew, C. Estarellas, A. Frontera, A. Ghosh, Inorg. Chim. Acta 366 (2011) 219;
- (b) S. Biswas, S. Naiya, C.J. Gómez-García, A. Ghosh, Dalton Trans. 41 (2012) 462;
- (c) S. Biswas, A. Ghosh, Polyhedron 65 (2013) 322.
- [6] (a) R. Kurtaran, K.C. Emregul, C. Arici, F. Ercan, V.J. Catalano, O. Atakol, Synth. React. Inorg. Met.-Org. Chem. 33 (2003) 281;
 - (b) X.-H. Bu, M. Du, L Zhang, D.-Z. Liao, J.-K. Tang, R.-H. Zhang, M. Shionoya, J. Chem. Soc., Dalton Trans. (2001) 593;
 - (c) H. Adams, N.A. Bailey, P. Bertrand, C.O.R. de Barbarin, D.E. Fenton, S. Gou, J. Chem. Soc., Dalton Trans. (1995) 275.
- [7] (a) R.P. John, K. Lee, B.J. Kim, B.J. Suh, H. Rhee, M.S. Lah, Inorg. Chem. 44 (2005) 7109,
- (b) R.D. Hancock, J. Chem. Educ. 69 (1992) 615.
- [8] R. Gheorghe, J. Costes, S. Shova, M. Andruh, Rev. Roum. Chim. 52 (2007) 753.
- [9] L.K. Das, R.M. Kadam, A. Bauza, A. Frontera, A. Ghosh, Inorg. Chem. 51 (2012) 12407.
- [10] H. Miyasaka, N. Matsumoto, Chem. Lett. (1997) 427.
- [11] S. Biswas, R. Saha, A. Ghosh, Organometallics 31 (2012) 3844.
- [12] I. Ercan, F. Ercan, C. Arici, O. Atakol, Acta Crystallogr., Sect. C 58 (2002) m137.
- [13] E.C. Constable, G. Zhang, C.E. Housecroft, J.A. Zampese, Dalton Trans. 39 (2010) 1941.
- [14] L.T. Yildirim, R. Kurtaran, H. Namli, A.D. Azaz, O. Atakol, Polyhedron 26 (2007) 4187.

- [15] D. Karmakar, M. Fleck, R. Saha, M. Layek, S. Kumar, D. Bandyopadhyay, Polyhedron 49 (2013) 93.
- [16] C. Arici, D. Ulku, O. Atakol, M.N. Tahir, Cryst. Res. Tech. 41 (2006) 204.
- [17] O. Atakol, C. Arici, M.N. Tahir, A. Kenar, D. Ulku, Acta Crystallogr., Sect. C 55 (1999) 1416.
- [18] F.B. Kaynak, D. Ulku, O. Atakol, S. Durmus, Acta Crystallogr., Sect. C 55 (1999) 1784.
- [19] M. Nayak, S. Sarkar, S. Hazra, H.A. Sparkes, J.A.K. Howard, S. Mohanta, CrystEngComm 13 (2011) 124.
- [20] M.L. Colon, S.Y. Qian, D. Vanderveer, X.R. Bu, Inorg. Chim. Acta 357 (2004) 83.
- [21] C. Arici, D. Ulku, O. Atakol, M. Aksu, Cryst. Res. Tech. 37 (2002) 520.
- [22] J. Lee, J.Y. Lee, J. Seo, S.Y. Lee, H.J. Kim, S. Park, K. Park, L.F. Lindoy, S.S. Lee, Polyhedron 27 (2008) 3004.
- [23] (a) O. Atakol, H. Nazir, C. Arici, S. Durmus, I. Svoboda, H. Fuess, Inorg. Chim. Acta 342 (2003) 295;
 - (b) X.-L. Cheng, S. Gao, L.-H. Huo, S.W. Ng, Acta Crystallogr., Sect. E, Online 61 (2005) m385.
- [24] G.A. Bain, J.F. Berry, J. Chem. Educ. 85 (2008) 532.
- [25] CRYSALIS, Oxford Diffraction Ltd., Abingdon, U.K., 2006.
- [26] G.M. Sheldrick, SHELXS 97 and SHELXL 97, programs for crystallographic solution and refinement, Acta Crystallogr., Sect. A 64 (2008) 112.
- [27] ABSPACK, Oxford Diffraction Ltd, Oxford, U.K., 2005.
- [28] SAINT, Version 6.02, SADABS, Version 2.03, Bruker AXS Inc., Madison, WI, 2002.
 [29] (a) J. Ferguson, J. Chem. Phys. 34 (1961) 611;
- (b) M.P. Sigalas, C.A. Tsipis, Inorg. Chem. 25 (1986) 1875.
- [30] (a) M. Dey, C.P. Rao, P.K. Saarenketo, K. Rissanen, Inorg. Chem. Commun. 5 (2002) 924;
- (b) S. Banerjee, M.G.B. Drew, C.-Z. Lu, J. Tercero, C. Diaz, A. Ghosh, Eur. J. Inorg. Chem. (2005) 2376.
- [31] A. Ginsberg, R. Brookes, R. Martin, R. Sherwood, Inorg. Chem. 11 (1972) 2884.
 [32] (a) M.A. Halcrow, J. Sun, J.C. Huffman, G. Christou, Inorg. Chem. 34 (1995) 4167:
 - (b) R. Biswas, P. Kar, Y. Song, A. Ghosh, Dalton Trans. 40 (2011) 5324;
- (c) R. Biswas, S. Giri, S.K. Saha, A. Ghosh, Eur. J. Inorg. Chem. (2012) 2916.
 [33] C.J. Gómez-García, E. Coronado, L. Ouahab, Angew. Chem., Int. Ed. 31 (1992)
- 649. [34] J.M. Clemente-Juan, B. Chansou, B. Donnadieu, J. Tuchagues, Inorg. Chem. 39
- (2000) 5515. [35] R. Modak, Y. Sikdar, S. Mandal, C.J. Gómez-García, S. Benmansour, S. Chatterjee,
- S. Goswami, Polyhedron 70 (2014) 155. [36] J.M. Clemente-Juan, E. Coronado, J.R. Galan-Mascaros, C.J. Gómez-García, Inorg.
- Chem. 38 (1999) 55.
- [37] C.J. Gómez-García, J.J. Borrasalmenar, E. Coronado, L. Ouahab, Inorg. Chem. 33 (1994) 4016.
- [38] S. Saha, S. Pal, C.J. Gómez-García, J.M. Clemente-Juan, K. Harms, H.P. Nayek, Polyhedron 74 (2014) 1.