Binuclear Nickel(II) Complexes Based on Bridging Oxalate and Pseudohalides as Peripheral Ligands: Synthesis, Crystal Structure, DFT Calculations and Magnetic Properties of [{Ni(X)(dien)}$_2$(μ-ox)]·nH$_2$O Complexes (X = N$_3^-$, NCS$^-$, n = 0; NCO$^-$, n = 1)

Iñaki Muga,[a] Juan M. Gutiérrez-Zorrilla,*[a] Pablo Vitoria,[a] Antonio Luque,[a] Maite Insausti,[a] Pascual Román,[a] and Francesc Lloret[b]

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Nickel(II) molecular complexes were obtained by water displacement reactions of [{Ni(dien)(H$_2$O)}$_2$(μ-ox)]Cl$_2$ and the corresponding pseudohalide. The three nickel(II) compounds [{Ni(N$_3$)(dien)}$_2$(μ-ox)] (**1**), [{Ni(NCO)(dien)}$_2$(μ-ox)] · H$_2$O (**2**) and [{Ni(NCS)(dien)}$_2$(μ-ox)] (**3**) are almost isostructural. The structure determinations reveal the presence of a binuclear complex with C_{2h} symmetry, where the oxalate ligand is coordinated in a bis(bidentate) fashion to the twofold related nickel atoms. The distorted octahedral environment of each nickel atom is completed by the three nitrogen atoms of the diethylenetriamine ligand in a *fac* arrangement and one nitrogen atom from a pseudohalide ligand. Magnetic susceptibility data in the temperature range 4.2–300 K shows intramolecular antiferromagnetic coupling.

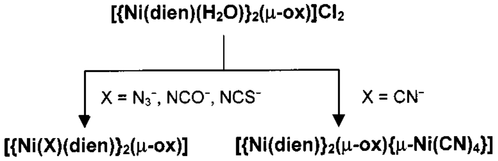
Introduction

The design and synthesis of molecular magnetic compounds has attracted increasing attention over the past two decades or so.[1] A significant amount of magnetostructural research work during the last twenty five years has been devoted to analysing the remarkable ability of the oxalate bridge to mediate exchange coupling between first-row transition metal ions separated by more than 5 Å in both homo- and heteropolynuclear compounds.[2] The simple binuclear geometry involving symmetric, in-plane bridging with a single oxalate ion binding through two oxygen atoms to each of two metal centres has been observed in the chemistry of copper,[3] nickel,[4] and less frequently, the remaining first transition series metal ions.[5] Magnetostructural data of oxalato-bridged Ni^{II} complexes have revealed that J varies from -22 to -39 cm^{-1}.[6] This value is strongly dependent on the nature of the donor atoms in the peripheral ligands. The present contribution is devoted to the analysis of this factor in oxalato-bridged octahedral nickel(II) complexes with an NiN$_4$O$_2$ environment. We have succeeded in synthesising a related series of nickel(II) complexes of general formulation [{Ni(X)(dien)}$_2$(μ-ox)]·nH$_2$O (X = N$_3^-$, NCS$^-$, n = 0; X = NCO$^-$, n = 1). This work has allowed us to study the influence of the water of crystallization on the crystal packing and thermal behaviour of these compounds.

Results and Discussion

Synthesis

In the synthesis of the three molecular compounds, the binuclear complex [{Ni(dien)(H$_2$O)}$_2$(μ-ox)]Cl$_2$[2c] was used as a precursor owing to the lability of its water molecules, which may be substituted by pseudohalide ligands. The preparation of the compound was performed as follows: the sodium or potassium salt of the corresponding pseudohalide dissolved in a small amount of water was added to a hot aqueous solution of [{Ni(dien)(H$_2$O)}$_2$(μ-ox)]Cl$_2$. When we used cyanide as pseudohalide, a neutral trinuclear complex was obtained where the two water molecules were replaced by two cyano groups belonging to a square planar [Ni(CN)$_4$]$^{2-}$ unit,[7] (Scheme 1).



Scheme 1

Description of the Crystal Structures

The three compounds crystallize in the same monoclinic space group $C2/m$ and could be considered almost isostructural. Single crystal structure analyses were performed for the neutral [{Ni(N$_3$)(dien)}$_2$(μ-ox)] (**1**) and [{Ni(NCO)(dien)}$_2$(μ-ox)]·H$_2$O (**2**) complexes. These analyses reveal the presence of a binuclear complex of C_{2h} symmetry, with nickel atoms and pseudohalide ligands contained in the symmetry plane. The twofold axis is defined by the C−C bond of the oxalate ligand which is coordinated in a bis(bidentate) fashion to the twofold related nickel atoms.

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[a] Departamento de Química Inorgánica, Facultad de Ciencias,
Universidad del País Vasco,
Apartado 644, 48080 Bilbao, Spain
E-mail: qipguloj@lg.ehu.es
[b] Departament de Química Inorgànica, Facultat de Química,
Universitat de València,
Dr. Moliner 50, 46100 Burjassot, València, Spain

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The distorted octahedral environment of each nickel atom is completed by three nitrogen atoms from a diethylenetriamine ligand in a *fac* arrangement and one nitrogen atom from a pseudohalide ligand (Figure 1). The Ni−oxalato−Ni fragments adopt a chair conformation with a Ni−Ni distance of 5.397 Å for **1** and 5.491 Å for **2**. The nickel atoms are displaced by 0.021 Å for **1** and 0.198 Å for **2** out of the oxalate plane towards the N atom of the pseudohalide. The dihedral angle between the oxalato group and the equatorial mean plane is 2.37° for **1** and 3.98° for **2**. Bond lengths and angles involving non-hydrogen atoms are listed in Table 1. The Ni−O (oxalate) distances are 2.081 Å for **1** and 2.108 Å for **2**, whereas the Ni−N bonds vary in the range 2.08−2.16 Å. These distances agree with those observed in other oxalato-bridged nickel(II) complexes.

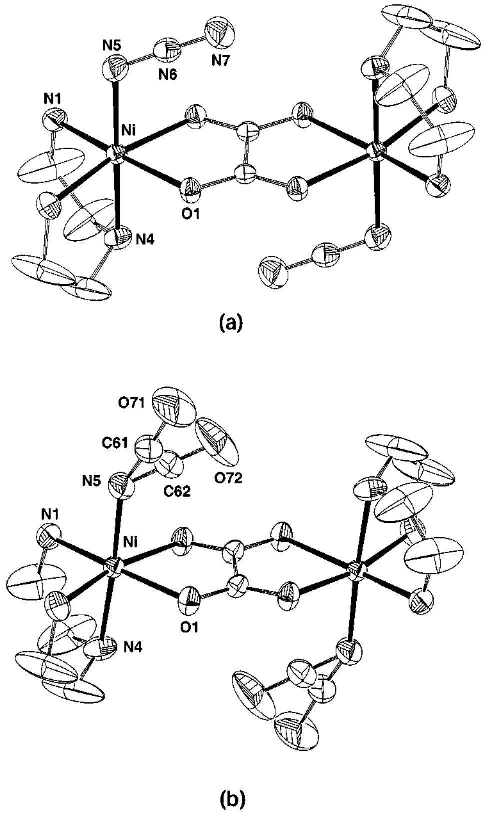


Figure 1. ORTEP views of compound **1** (a) and compound **2** (b) with atom labelling

The thermal analysis of the compound **2** confirms the presence of one water molecule, which is found to be disordered around an inversion centre in the crystal structure determination.

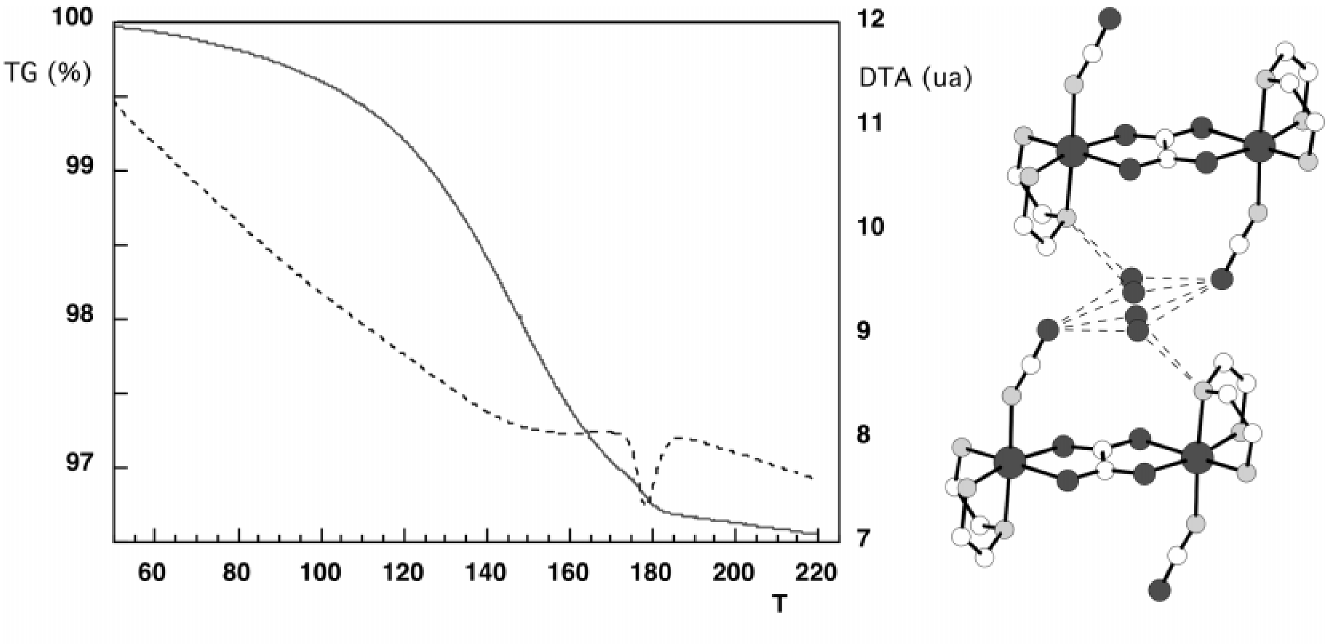
Table 1. Selected experimental and theoretical (obtained using BPW91 optimizations) bond lengths [Å] and angles [°] for compounds **1** and **2**

Compounds	**1**		**2**		
Ni environment	Experimental	*BPW91*	Experimental		*BPW91*
Ni1−O1	2.081 (2)	2.029	2.108 (2)		2.036
Ni1−N1	2.079 (2)	2.067	2.082 (2)		2.070
N1−N4	2.106 (3)	2.102	2.122 (4)		2.102
NI1−N5	2.154 (4)	2.004	2.091 (4)		2.001
O1−Ni1−O1′	80.8 (1)	84.4	79.2 (1)		84.0
O1−Ni1−N5	89.3 (1)	91.6	91.9 (1)		92.4
N1−Ni1−N4	83.5 (1)	84.3	83.0 (1)		84.1
N1−Ni1−N5	96.9 (1)	96.8	94.8 (1)		96.4
N4−Ni1−N5	180.0 (1)	178.1	176.5 (2)		179.2
Oxalate ligand					
C1−C1′	1.553 (5)	1.556	1.552 (3)		1.558
C1−O1	1.252 (2)	1.268	1.260 (2)		1.269
N_3^- ligand					
N5−N6	1.179 (4)	1.211			
N6−N7	1.180 (5)	1.188			
Ni1−N5−N6	113.3 (2)	117.0			
N5−N6−N7	178.9 (4)	179.6			
NCO^- ligand			X = 1	X = 2	
N5−C6X			1.126 (7)	1.191 (2)	1.217
C6X−O7X			1.20 (1)	1.20 (3)	1.223
Ni1−N5−C6X			152.0 (6)	121.4 (9)	120.4
N5−N6X−O7X			176 (1)	179 (2)	179.6

The different coordination modes of the pseudohalide ligands are remarkable. In compound **1** the azide ligand coordinates with an Ni−N5−N6 angle of 113.3°, while in compound **2** the cyanate ligand shows two coordination modes, with different values of the Ni−N5−C6 angle, 152.0° (64%) and 121.4° (36%). In order to check if this behaviour is due to electronic or packing effects, theoretical calculations were performed on a mononuclear model compound of general formula $[Ni(X)(NH_3)_3(CH_2O_2)]^+$ where $X = N_3^-$, NCO^-. Both structures were fully optimised and only one minimum was found for each, with a coordination angle of 109.9° for the azide and 124.8° for the cyanate ligand. Both values agree quite well with experimental ones. As there is no energy minimum with (quasi)linear coordination of the cyanate ligand, the experimental value of 152° observed for 64% of the molecules in the crystal must be due to the formation of hydrogen bonds with the water molecule present in compound **2** but absent in compound **1** (vide infra). The water molecule plays an important role in the thermal behaviour of this compound. Just before the end of the dehydration process (210 °C) the heat flow curve shows a sharp endothermic peak superimposed on the broad peak associated with water loss (Figure 2). Preliminary studies indicate a disorder-order phase transition. The loss of the water molecule destabilises the cyanate coordination mode having the higher angle and all cyanate ligands should coordinate with an angle of ≈120°.

Based on the high accuracy of the above-mentioned DFT calculations on model monomers, the geometry of the dimers has been optimized at the same level. The combination of the BPW91 functional with the 6-31G* basis set seems a good choice for studies of coordination compounds.[8] A summary comparison of the experimental and theoretical geometrical parameters is given in Table 1, which show good agreement.

In both compounds the dinuclear units are held together by means of an extensive two-dimensional hydrogen bonding network, involving the amino groups as donors and the oxygen atoms of the oxalate ligand and nitrogen atoms of the pseudohalide ligand as acceptors, such that each dimeric unit is connected to its neighbours through eight N1−H11···O1 and eight N1−H12···N5 hydrogen bonds



(a) (b)

Figure 2. (a) Thermal analysis of the dehydration process and (b) disordered water molecule environment in compound **2**

(Table 2), leading to an infinite two-dimensional arrangement along the *xy* plane (Figure 3). However, they differ in the connections between layers, which in compound **1** are held together through hydrophobic interactions involving the CH_2 groups of dien ligand, but in compound **2** such connections are through hydrogen bonding of the water molecule, the oxygen atom of NCO^- and the secondary nitrogen atom of the dien ligand (Figure 2b). The presence of this water molecule in the structure causes an increase of about 1 Å in the value of the unit cell *c* parameter with respect to that of compound **1**, corresponding with the layer packing direction.

Besides these intermolecular hydrogen bonds, two intramolecular N4−H41···N7 interactions are also present in compound **1**.

Magnetic Properties

The molar magnetic susceptibility, χ_M, vs. temperature curves for compounds **1−3** are depicted in Figure 4. The susceptibility curve for these complexes increases when the compound is cooled until a maximum is reached (T_{max} = 46.4, 42.0 and 48.7 K, for **1−3**, respectively) and then decreases very quickly. The ground state of nickel(II) ion in an octahedral environment is orbitally nondegenerate, and as such, it is possible to represent the intradimer magnetic interaction, *J*, with the isotropic spin Hamiltonian $H = -JS_A{\cdot}S_B$. The molar magnetic susceptibility for a nickel(II) dimer (local spins $S_A = S_B = 1$) may be expressed by Equation 1, where *N*, β, *k*, *g* and *T* have their usual meaning.

$$\chi_M = \frac{2N\beta^2 g^2}{kT} \times \frac{\exp(J/kT) + 5\exp(3J/kT)}{1 + 3\exp(J/kT) + 5\exp(3J/kT)}$$

Table 2. Hydrogen bonding contacts

Type	D−H [Å]	D···A [Å]	H···A [Å]	<D−H···A [°]
Compound **1**				
N1−H11···N5[a][b]	0.91 (5)	3.130 (4)	2.28 (5)	155 (4)
N1−H12···O1[c]	0.83 (4)	3.062 (3)	2.23 (5)	172 (4)
N4−H41···N7[d][e](intra)	0.91 (5)	3.130 (4)	2.28 (5)	155 (4)
N4−H41···N7 (BPW91)	*1.04*	*3.25*	*2.22*	*175.4*
Compound **2**				
N1−H11···N5[a][b]	0.87 (8)	3.267 (4)	2.49 (9)	149 (8)
N1−H12···O1[c]	0.89 (4)	3.060 (3)	2.19 (5)	168 (8)
N4−H41···Ow1[f]	0.80 (9)	2.97 (2)	2.25 (9)	149.2 (5)
Ow1···O71[d][e]		2.68 (2)		
Ow1···O71[g][h]		2.89 (2)		
Ow1···O72[g][h]		2.73 (3)		

Symmetry codes: [a] 1 − *x*, −*y*, −*z*. − [b] 1 − *x*, *y*, −*z*. − [c] 1/2 − *x*, 1/2 − *y*, −*z*. − [d] −*x*, −*y*, −*z*. − [e] −*x*, *y*, −*z*. − [f] *x*, −*y*, *z*. − [g] *x*, *y*, 1 + *z*. − [h] *x*, −*y*, 1 + *z*.

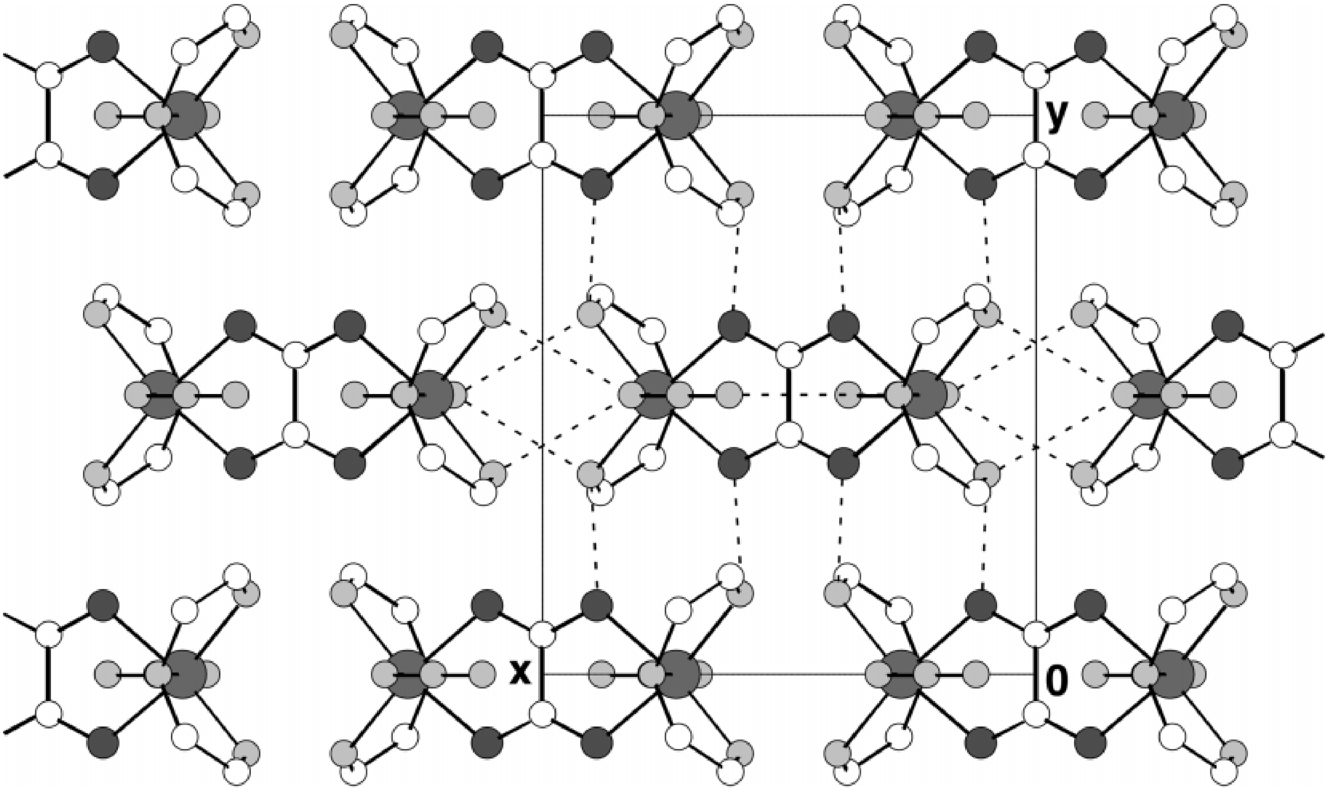


Figure 3. Two dimensional arrangement along the *xy* plane; dotted lines mean all hydrogen bonds of one binuclear unit

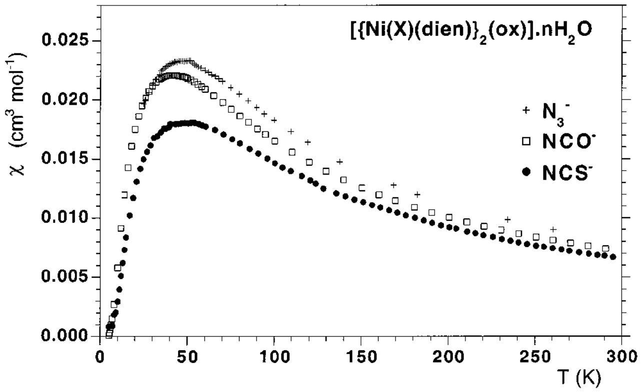


Figure 4. Thermal dependence of the molar magnetic susceptibility for compounds **1−3**

Although nickel(II) with axial symmetry can have a large zero-field splitting *D*, the magnetic behaviour of nickel(II) dimers closely follows Equation 1 when a relatively strong antiferromagnetic interaction is operative.[9] This is the case for complexes **1−3** where least-squares analysis of the experimental data with Equation 1 leads to $J = -31.4\ \mathrm{cm}^{-1}$, $g = 2.25$ and $R = 1{\cdot}10^{-4}$ for **1**; $J = -28.5\ \mathrm{cm}^{-1}$, $g = 2.14$ and $R = 5{\cdot}10^{-5}$ for **2**; $J = -33.0\ \mathrm{cm}^{-1}$, $g = 2.08$ and $R = 1.6{\cdot}10^{-5}$ for **3**. *R* is the agreement factor defined as $R = \Sigma(\chi_M^{obs} - \chi_M^{calc})^2/\Sigma(\chi_M^{obs})^2$. Previously reported *J* values for μ-oxalato bridged nickel(II) binuclear complexes are close to those of compounds **1−3**. This information is summarized in Table 3 for dinuclear Ni^{II}-oxalato systems in an NiO_2N_4 environment. It is well known that structural distortions (distance Ni−O$_{ox}$, bite angle O−Ni−O, deviation from the planarity of the nickel ion respect to mean plane of the oxalate bridging ligand) can play a key role in the fine-tuning of exchange coupling and the influence of apical pseudohalide ligands on the *J* values is similar in the three compounds since all are N-donor ligands.

A graphical representation of the four DFT magnetic orbitals of compound **2** is given in Figure 5, with those for compound **1** being very similar. As expected for the case of octahedral nickel centres, the unpaired electrons are mainly located in the d_{z^2} and d_{xy} orbitals, with a noticeable contribution to the d_{z^2} magnetic orbital of the pseudohalide orbital.

Conclusions

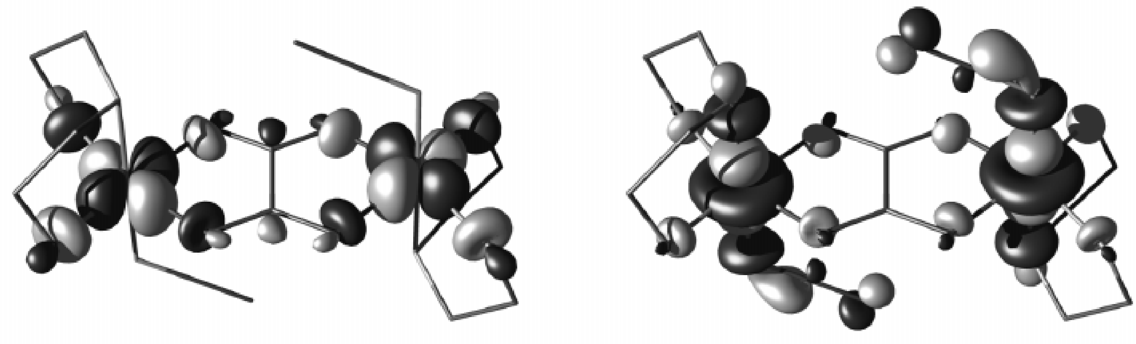
The reaction between pseudohalogen species and the cationic complex $[\{Ni(dien)(H_2O)\}_2(\mu\text{-ox})]^{2+}$ results in water displacement when the pseudohalides are N_3^-, NCO^-, and NCS^-, leading to the corresponding neutral binuclear complexes. However, in the case of cyanide anion, the trinuclear species $[\{Ni(dien)\}_2(\mu\text{-ox})\{\mu\text{-}Ni(CN)_4\}]$ is obtained due to the high stability of the $[Ni(CN)_4]^{2-}$ complex which is initially formed when the cyanide salt is added. The tetracyanonickelate(II) acts a template for the formation of the trinuclear unit.

The three compounds are almost isostructural, but differ in the degree of hydration. Compound **2** is monohydrated

Table 3. Selected magnetostructural parameters [Å,°] for dinuclear nickel(II) oxalato systems in an NiO_2N_4 environment

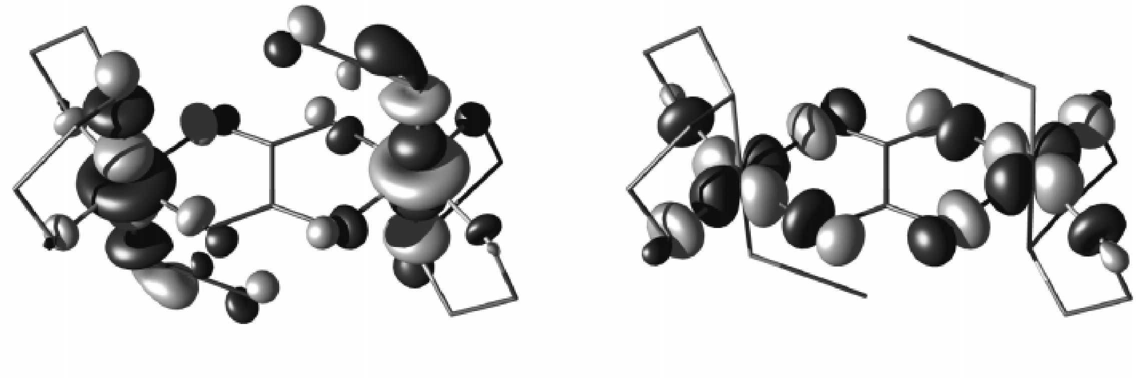
Compound[a]	$-J$[b]	g	d(Ni−O)[c]	d(Ni−N_{eq})[d]	D(Ni−N_{ap})[e]	d(Ni···Ni)[f]	O−Ni−O[g]	h(Ni)[h]	ref.
[{Ni(cth)}$_2$(μ-ox)](ClO$_4$)$_2$	36.8	2.19							[4a]
[{Ni(trien)}$_2$(μ-ox)](ClO$_4$)$_2$	35.2	2.20							[4a]
[{Ni(en)$_2$}$_2$(μ-ox)](ClO$_4$)$_2$	36.8	2.27	2.091 / 2.093	2.12	2.15	5.488	81.05	0.106	[5d]
[{Ni(en)$_2$}$_2$(μ-ox)](NO$_3$)$_2$	32.0	2.19	2.094 / 2.098	2.09	2.10	5.420	79.71	0.037	[3a]
[{Ni(tn)$_2$}$_2$(μ-ox)](ClO$_4$)$_2$	36.4	2.18	2.080−2.162	2.09	2.09	5.481 / 5.492	78.05−79.33	0.032−0.101	[4g]
[{Ni(cyclam)}$_2$(μ-ox)](NO$_3$)$_2$	39.0	2.33	2.070 / 2.071	2.09	2.10	5.395	80.75	0.040	[4f]
[{Ni(cyclen)}$_2$(μ-ox)](NO$_3$)$_2$	35.0	2.15							[4j]
[{Ni(Me$_2$cyclen)}$_2$(μ-ox)](ClO$_4$)$_2$	34.0	2.30	2.095 / 2.102	2.05	2.15	5.465	79.28	0.021	[4j]
[{Ni(323-tet)}$_2$(μ-ox)](ClO$_4$)$_2$	28.9	2.17	2.115 / 2.124	2.11	2.11	5.506	78.88	0.073	[4m]
[{Ni(tren)$_2$}$_2$(μ-ox)](ClO$_4$)$_2$	28.8	2.16	2.050 / 2.112	2.07	2.13	5.413	80.43	0.044	[4p]
[{Ni(dien)$_2$}$_2$(μ-ox){μ-Ni(CN)$_4$}]	31.2	2.15	2.088	2.08	2.09	5.324	80.30	0.391	[7]
[{Ni(N$_3$)(dien)$_2$}$_2$(μ-ox)]	31.4	2.25	2.081	2.08	2.13	5.397	80.77	0.021	Compound **1**
[{Ni(NCO)(dien)$_2$}$_2$(μ-ox)]	28.5	2.14	2.108	2.08	2.11	5.491	79.18	0.198	Compound **2**
[{Ni(NCS)(dien)$_2$}$_2$(μ-ox)]	33.0	2.08							Compound **3**

[a] Abbreviations used: cth = 2,4,4,9,9,11-hexamethyl-1,5,8,12-tetraazacyclotetradecane; trien = triethylenetetramine; en = ethylenediamine; tn = 1,3-diaminopropane; cyclam = 1,4,8,11-tetraazacyclotetradecane; cyclen = 1,4,7,10-tetraazacyclododecane; Me$_2$cyclen = 1,7-dimethyl-1,4,7,10-tetraazacyclododecane, 323-tet = *N,N′*-bis(3-aminopropyl)-1,2-ethenediamine; tren = tris(2-aminoethyl)amine; dien = diethylenetriamine. − [b] J in cm^{-1}. − [c] d(Ni−O): distance Ni−O(oxalato). − [d] d(Ni−N_{eq}): mean distance Ni−N(equatorial). − [e] d(Ni−N_{ap}): mean distance Ni−N(apical). − [f] d(Ni···Ni): nickel−nickel separation across the oxalato ligand. − [g] O−Ni−O: bite angle. − [h] h(Ni): metal height from the oxalato mean plane.



MO 128 (a_u, -0.0760)

MO 129 (a_g, -0.0650)



MO 130 (b_u, - 0.0614)

MO 131 (b_g, -0.0601)

Figure 5. Magnetic orbitals for compound **2** (symmetry, energy)

but compound **1** and **3** are anhydrous. Although the dinuclear units in both compounds are held together by means of an extensive two-dimensional hydrogen bonding network, they differ in the connection between layers. In anhydrous compound **1** the layers are held together through hydrophobic interactions, but in hydrated compound **2** such connections are via hydrogen bonding involving the water molecule. This fact confirms that hydrogen bonds of type O−H···O are stronger than possible O−H···N or O−H···S ones, and are strong enough to force 64% of NCO^- ligands to adopt a coordination fashion which according to the DFT calculations is less stable.

DFT calculations on the binuclear complexes confirm the nature of the magnetic orbital previously reported in these kinds of compounds,[2c] although the energetic order is different.

Experimental Section

General: Microanalyses of carbon, nitrogen, hydrogen, and sulfur were performed on a LECO CHNS-932 analyser. −IR: NICOLET 740 FT-IR. − TG: SETARAM TAG 24 S16. The thermal experiments were performed in synthetic dry air atmosphere (100 mL·min^{-1}) and a heating rate of 2 °C·min^{-1} in the temperature range 25−250 °C. All chemicals were procured commercially and used without subsequent purification.

Synthesis of [{Ni(N_3)(dien)}$_2$(μ-ox)] (1): Obtained from [{Ni(dien)(H_2O)}$_2$(μ-ox)]Cl_2 (0.360 g, 0.707 mmol) in water (40 mL) and NaN_3 (0.114 g, 2.25 mmol) in water (5 mL), as blue crystals in 60% yield (0.210 g, 0.424 mmol). − $C_{10}H_{26}N_{12}Ni_2O_4$ (495.80): calcd. C 24.23; H 5.29; N 33.90; found C 24.2; H 5.4; N 34.0. − IR (KBr): ṽ = 2036 cm^{-1} (N_3^-).

Synthesis of [{Ni(NCO)(dien)}$_2$(μ-ox)]·H_2O (2): [{Ni(dien)(H_2O)}$_2$(μ-ox)]Cl_2 (0.231 g, 0.448 mmol) in water (70 mL) and NaNCO (0.110 g, 1.69 mmol), as blue crystals in 55% yield (0.120 g, 0.244 mmol). $C_{12}H_{26}N_8Ni_2O_6\cdot H_2O$ (513.81): calcd. C 28.05; H 5.49; N 21.81; found C 28.1; H 5.6; N 21.9. − IR (KBr): ṽ = 2210, 2169 cm^{-1} (NCO^-).

Synthesis of [{Ni(NCS)(dien)}$_2$(μ-ox)] (3): [{Ni(dien)(H_2O)}$_2$(μ-ox)]Cl_2 (0.230 g, 0.440 mmol) in water (50 mL) and KSCN (0.115 g, 1.18 mmol), as blue spherulites in 75% yield (0.174 g, 0.330 mmol). − $C_{12}H_{26}N_8Ni_2O_4S_2$ (527.91): calcd. C 27.30; H 4.96; N 21.23; found C 27.3; H 4.96; N 21.23. − IR (KBr): ṽ = 2049 cm^{-1} (NCS^-).

Magnetic Susceptibility Measurements: Magnetic susceptibility measurements were carried out on polycrystalline samples in the temperature range 4.2−300 K, with a pendulum type susceptometer/magnetometer (Manicsd DSM8) equipped with a helium continuous flow cryostat. The diamagnetic contribution was calculated from Pascal's constants.

X-ray Crystallographic Studies: Data collection for the prismatic blue single crystals of **1** and **2** was performed on an Enraf−Nonius CAD4 and a Philips PW1100 diffractometer, respectively, with graphite monochromated Mo-K_α radiation (λ = 0.71069 Å). Intensities were collected by the ω-2θ scan technique. A Lorentz-polarization (Lp) correction was applied. The experimental details and crystal data are listed in Table 4. The atomic scattering factors were taken from the International Tables for X-ray Crystallography.[10] The structures were solved by direct methods (DIRDIF92[11]). The non-hydrogen atoms were anisotropically refined by the full-matrix least-squares method. In compound **2**, C

Table 4. Crystallographic data for [{Ni(N_3)(dien)}$_2$(μ-ox)] (**1**), [{Ni(NCO)(dien)}$_2$(μ-ox)]·H_2O (**2**) and [{Ni(NCS)(dien)}$_2$(μ-ox)] (**3**)

Compound	1	2	3
Formula	$C_{10}H_{26}N_{12}Ni_2O_4$	$C_{12}H_{26}N_8Ni_2O_6 \cdot H_2O$	$C_{12}H_{26}N_8Ni_2O_4S_2$
Formula weight	495.80	513.81	527.91
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C 2/m*	*C 2/m*	*C 2/m*
a [Å]	9.681 (4)	9.911 (2)	9.606 (1)
b [Å]	10.938 (3)	10.787 (2)	10.631 (1)
c [Å]	9.050 (2)	9.978 (2)	10.175 (1)
β [°]	92.90 (2)	96.97 (2)	98.55 (2)
V [Å^3]	957.2 (5)	1058.9 (4)	1027.6 (2)
Z	2	2	2
$D_{calcd.}$ [g/cm^3]	1.728	1.608	1.706
Crystal source	H_2O	H_2O	
Crystal size [mm]	0.70×0.50×0.25	0.60×0.50×0.20	
Diffractometer	Enraf Nonius CAD 4	Philips PW 1100	Stoe Darmstad
Radiation	Mo-K_α	Mo-K_α	Cu-$K_{\alpha1}$
μ [mm^{-1}]	2.021	1.829	
θ limits [°]	2−30	2−35	2.5−35
h, *k*, *l* range	0−13	−15−15	
	0−15	0−17	
	−12−12	0−16	
No. of unique reflns.	1457	2424	
No. of obsd. data	1358 [$I > 3\sigma(I)$]	2137 [$I > 3\sigma(I)$]	100
No. of parameters	83	104	
R_1 (obsd. rflns)	0.043	0.051	
wR_2 (all rflns)	0.058	0.066	
$\Delta\rho_{max}/\Delta\rho_{min}$ [e/A^3]	+0.8 / −0.5	+0.9 / −0.9	
R_p			0.217
R_{wp}			0.229
R_{Bragg}			0.060
R_F			0.034

and O pseudohalide atoms were found to be distributed over two positions. Hydrogen atoms bonded to nitrogen atoms were located in a difference Fourier synthesis and refined isotropically. Most calculations were performed using XRAY76 System.[12]

For compound **3** the powder X-ray diffraction pattern was collected on a STOE diffractometer using Cu-$K_{\alpha 1}$ radiation (λ = 1.54059 Å). Data were collected by scanning in the 2θ range 5−70° with increments of 0.02°. The structure was refined by the Rietveld method using the FULLPROF program.[13]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-140558 (**1**), -140559 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (E-mail: deposit@ccdc.cam.ac.uk).

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