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# Synthesis and molecular structure of oxydiacetate complexes of nickel(II) and cobalt(II). Theoretical analysis of the planar and non-planar conformations of oxydiacetate ligand and oxydiacetic acid†

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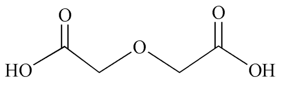
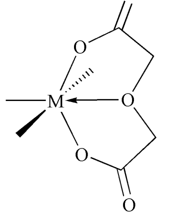
A novel synthetic route to $[Ni(oda)(H_2O)_3]\cdot 1.5H_2O$ **1** and $[Co(oda)(H_2O)_2]\cdot H_2O$ **2** [oda = oxydiacetate, $O(CH_2CO_2^-)_2$] is presented. These complexes react with bidentate N-donor ligands to yield compounds of general formula [M(oda)(N–N)($H_2O$)] (M = Ni, N–N = bipy, **3**; phen, **5**; tmeda, **7**. M = Co, N–N = bipy, **4**; phen, **6**; tmeda, **8**), which can be isolated as crystalline solids with different numbers of hydration water molecules. The molecular structures of the compounds **3** and **4** have been shown by X-ray analysis to crystallize with $2.5H_2O$. In these compounds, the oda ligand adopts a planar, tridentate conformation (*mer*) in binding the octahedral metal centre. By contrast, the recent X-ray characterization of **1** has shown that the oxydiacetate ligand completes the octahedral coordination of the metal in the *fac* arrangement. The DFT method has been adopted to investigate theoretically the flexibility of this ligand. First, calculations have been carried out on the free oxydiacetic acid ($H_2$oda) and its anion. Then, a model of **1** has been studied in order to find the geometric and energetic implications for the alternative oda conformations (*mer* and *fac*) in reaching the octahedral environment about the metal. In general, the geometric parameters are in good agreement with those available from crystal structures. From the energetic viewpoint, the *mer* conformation is favoured by a small energy difference (2.0 kcal $mol^{-1}$). On the other hand, the *fac* conformation in **1** may be justified with the presence of the water hydration molecules (not considered by our model) which may deeply affect the energetics of the overall system by forming strong hydrogen bonds with the oxydiacetate ligand.

The study of the chemical properties of transition metals containing coordinated carboxylate ligands is a subject of continuing interest.[1] Polycarboxylic acids and polycarboxylate ligands are used as linking agents of solid aggregates. The presence of two or more carboxylic or carboxylate groups in different orientations permits the construction of one-, two- or three-dimensional networks that can be reinforced by the presence of intermolecular hydrogen bonds.[2] An example of an acid that contains two carboxylic groups is oxydiacetic acid, **I**, commonly named diglycolic acid.

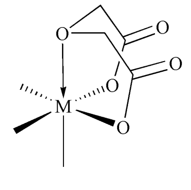


**I**

The corresponding oxydiacetate anion [oda, $O(CH_2CO_2^-)_2$] forms a variety of metal complexes with some important features. In the last few years, the research group of Perec and co-workers have extensively developed this field. For instance, thermal decomposition of the oda complexes affords, under the appropriate conditions, metal oxides.[3] The functionality of oda as a bridging ligand between copper and rare-earth cations has permitted the synthesis of new heterometallic systems[4] of potential relevance for solid state technologies.[5] oda is a versatile ligand capable of adopting several coordination modes in transition metal complexes. In mononuclear compounds, the tridentate *O,O′,O″*-planar coordination mode is the most commonly adopted. This conformation is found in many octahedral complexes (see **II**, *mer* configuration) of the first-[3b,6] and second-row[3a,6d,7] metals, as well as in other non-transition metal complexes.[8] Also, the tridentate planar coordination mode has been found in some lanthanide[4,9] and actinide[10] complexes with high coordination numbers. However, the ligand may lose its overall planar conformation in some cases. For instance, some oda complexes of copper(II)[6a,11] as well as the complex $[Ni(oda)(H_2O)_3]\cdot 1.5H_2O$ **1**, just reported by Perec and co-workers,[12] show a non-planar conformation of the ligand, a *fac* coordination mode in an octahedral environment (see **III**).



**II**



**III**

In this paper, we report the synthesis and characterization of oxydiacetate complexes of nickel(II) and cobalt(II) of general formula [M(oda)(N–N)($H_2O$)] (M = Ni, N–N = bipy, **3**; phen, **5**; tmeda, **7**. M = Co, N–N = bipy, **4**; phen, **6**; tmeda, **8**). In addition, we have performed DFT calculations to compare the relative stabilities of planar (*mer*) and non-planar (*fac*) conformations of the oxydiacetate ligand in six-coordinated complexes. Small energy differences have been computed between

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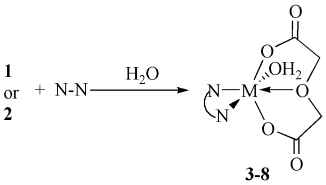
† Electronic supplementary information (ESI) available: table of cartesian coordinates for the optimised structures of the computed models presented in Fig. 2–4. See http://www.rsc.org/suppdata/dt/b2/b201885c/

the two possible isomers of [Ni(oda)$(H_2O)_3$] **1**. Also in order to gain a better picture of the stereochemical and electronic properties of the free oxydiacetic acid and its associated anion, specific DFT calculations have been carried out. The computational results compare well with the available experimental data.

## Results and discussion

### Synthesis and characterization of oxydiacetate complexes

Treatment of aerobic aqueous solutions of nickel chloride with a 1 : 1 mixture of $Na_2CO_3$ and oxydiacetic acid $O(CH_2CO_2H)_2$, affords, after the appropriate work-up, green crystals of complex [Ni(oda)$(H_2O)_3$]·1.5$H_2O$ **1** in good yields. The synthesis and characterization of this compound have appeared while this work was already in progress.[12] In particular, the X-ray analysis has shown the complex has the skeletal structure **III**. Consequently, no further experimental details will be provided for **1**, except for the previously unreported effective magnetic moment (3.4 $\mu_B$ at 20 °C), which is consistent with two unpaired electrons for the ground-state configuration. Next, we have prepared the cobalt species [Co(oda)$(H_2O)_2$]·$H_2O$ **2**, by following a modified experimental procedure with respect to that reported by Hatfield and co-workers.[4b] It has been found that, for both **1** and **2**, two coordinated water molecules can be easily displaced by reaction with bidentate N-donor ligands. In fact, the reactions of aqueous solutions of compounds **1** and **2** with 2,2′-bipyridine (bipy), *o*-phenanthroline (phen) and *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) give complexes of general formula [M(oda)(N–N)$(H_2O)$] (M = Ni, N–N = bipy, **3**; phen, **5**; tmeda, **7**. M = Co, N–N = bipy, **4**; phen, **6**; tmeda, **8**) [eqn. (1)].



(1)

**3-8**

All complexes can be isolated as crystalline solids in good yields, while the number of the water molecules of hydration vary case by case. The crystal structure of the nickel complex with *o*-phenanthroline, **5**, is already available in the literature.[12] Complexes **3**–**8** may be dissolved in water but are not soluble in solvents of low polarity. They are stable, both in solution and in the solid state. The effective magnetic moments of the nickel derivatives **3**, **5** and **7** (in the solid state and at room temperature) are in the range of 3.1–3.2 $\mu_B$. These values are consistent with two unpaired electrons in the ground-state configuration. The same values are found in nickel octahedral complexes containing related coordination environments, for example, the pyridine-2,6-dicarboxylato ligand and nitrogen-donor coligands.[13] For the cobalt compounds **4**, **6** and **8**, the value of $\mu_{eff}$ spans between 4.9 and 5.3 $\mu_B$, according to the presence of three unpaired electrons. These data are in agreement with the typical values observed for high-spin cobalt(II) complexes (4.77–5.40 $\mu_B$).[14]

Complexes **3**–**8** display the characteristic IR absorptions of the oxydiacetate ligand. A very strong and broad band at about 1600 $cm^{-1}$ corresponds to the asymmetric vibrations of the carboxylate groups (shifted from the 1734 $cm^{-1}$ value of the oxydiacetic acid) and a strong band at *ca.* 1430 $cm^{-1}$ is assigned to the symmetric vibrations of the $CO_2^-$ groups. The spectra show also broad bands in the normal regions where coordinated and lattice water molecules give absorptions[15] (3600–3200 and 1640–1610 $cm^{-1}$, the latter overlapping the asymmetric vibrations of the carboxylate groups). Besides these absorptions, bands representative of coordinated bipy, phen and tmeda ligands are also observable.[15,16] A special comment must be made with respect to the IR absorption due to the COC stretching in oxydiacetate. With reference to transition metal complexes, on the basis of the computed findings discussed below, we assigned the experimental strong absorption that comes out in the region 1150–1130 $cm^{-1}$ to the asymmetric COC stretching of oxydiacetate ligand. We have found that the position of this IR signal depends on the conformation of the ligand. Thus, for example, planar oxydiacetate ligand in compounds **2**–**8** are characterized by a strong band in the above region. On the contrary, in **1** and in complex [Cu(oda)]·0.5$H_2O$,[11] both with a *fac* disposition, the equivalent absorption is found at lower frequencies, *i.e.* at 1094 and 1112 $cm^{-1}$,[17] respectively. The trend is computationally confirmed (*vide infra*). In conclusion, we suggest that the position of this IR band can be used as a convenient tool to discriminate between planar and non-planar conformations of coordinated oda ligand.

With the aim of synthesizing complexes with two different tridentate ligands, the possible interaction of compounds **1** and **2** with pyridine-2,6-dicarboxylic acid (dipicolinic acid, $H_2$dipic) was attempted. However, the work-up for the corresponding reactions produced the known complexes [Ni(dipic)]·3.5$H_2O$ **9**[13] and [Co(dipic)]·3.5$H_2O$ **10**,[18] in a crystalline form. The compounds were identified by analytical and spectroscopic methods. The displacement reaction of oda by dipic depends on the higher formation constant of dipic transition metal complexes with respect to the oda-derivatives.[19] This effect is known and, for instance, the displacement of oda by iminodiacetate ligand, where one ligand has a saturated oxygen donor and the other a saturated nitrogen, is well established.[20]

### Crystal and molecular structures of 3 and 4

The crystal structures of complexes **3** and **4** have been determined by X-ray diffraction methods. The two compounds are isomorphous also with the equivalent Zn(II) complex, previously reported by Perec *et al.*[3b] (TISBOM CSD[21] refcode). The significant hydrogen bonding network, that involves uncoordinated water molecules, was already illustrated in detail for the Zn structure. Therefore, we only depict (Fig. 1) the structural features of the pseudo-octahedral coordination sphere of the nickel derivative, **3**. The overall geometry of the cobalt analogue **4** is essentially the same except for some minor differences concerning the central oxygen atom (see the comments below). Table 1 allows the direct comparison of the geometrical features of **3** and **4**.

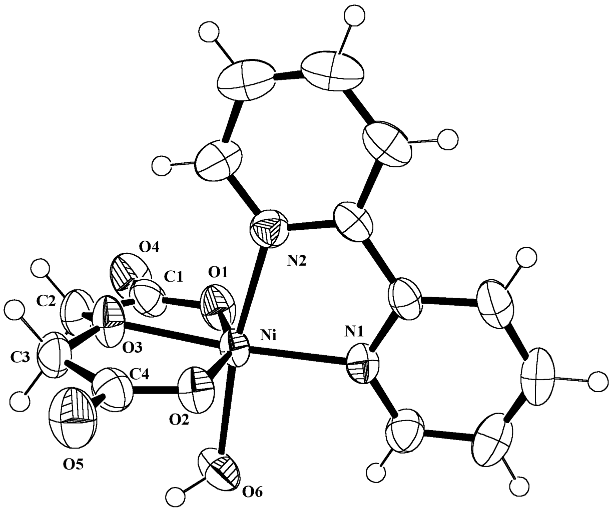


**Fig. 1** ORTEP drawing of the complex [Ni(oda)(bipy)$(H_2O)$] **3** (ellipsoid probability = 50%).

The distortions from the regular octahedral geometry are due to the bites of the ligands 2,2′-bipyridine and oda. The

**Table 1** Selected bond distances (Å) and angles (°) for complexes **3** and **4**

| | **3**(Ni) | **4**(Co) |
|---|---|---|
| M–O1 | 2.055(3) | 2.050(3) |
| M–O2 | 2.054(3) | 2.096(3) |
| M–O3 | 2.042(2) | 2.115(3) |
| M–N1 | 2.046(3) | 2.096(3) |
| M–N2 | 2.067(3) | 2.115(3) |
| M–O6 | 2.057(3) | 2.094 (3) |
| O1–C1 | 1.251(4) | 1.252(4) |
| O4–C1 | 1.239(4) | 1.246(4) |
| C1–C2 | 1.521(5) | 1.516(6) |
| O3–C2 | 1.412(4) | 1.400(5) |
| O3–C3 | 1.412(4) | 1.398(5) |
| C3–C4 | 1.514(5) | 1.512(5) |
| C4–O5 | 1.245(4) | 1.249(5) |
| C4–O2 | 1.256(4) | 1.258(5) |
| O1–M–O2 | 155.7(1) | 149.6(1) |
| O1–M–O3 | 77.8(1) | 75.4(1) |
| O2–M–O3 | 78.1(1) | 74.4(1) |
| O1–M–O6 | 92.3(1) | 97.6(1) |
| O2–M–O6 | 85.9(1) | 86.2(1) |
| O3–M–O6 | 94.3(1) | 92.5(1) |
| N1–M–N2 | 79.3(1) | 77.1(1) |
| O1–M–N1 | 105.6(1) | 108.9(1) |
| O2–M–N1 | 98.7(1) | 101.1(1) |
| O3–M–N1 | 172.8(1) | 173.5(1) |
| O6–M–N1 | 91.9(1) | 91.8(1) |
| O1–M–N2 | 93.8(1) | 92.4(1) |
| O2–M–N2 | 91.6(1) | 89.3(1) |
| O3–M–N2 | 94.3(1) | 98.0(1) |
| O6–M–N2 | 170.4(1) | 167.1(1) |
| C3–O3–C2 | 120.0(3) | 120.6(3) |
| O1–C1–O4 | 124.9(4) | 125.0(4) |
| O1–C1–C2 | 118.6(3) | 118.3(4) |
| O4–C1–C2 | 116.5(3) | 116.7(3) |
| O2–C4–O5 | 124.2(3) | 123.2(3) |
| O2–C4–C3 | 118.8(3) | 118.8(4) |
| O5–C4–C3 | 117.1(3) | 118.0(3) |
| O3–C2–C1 | 107.9(3) | 107.6(3) |
| O3–C3–C4 | 108.5(3) | 107.3(3) |

oxydiacetate ligand, which occupies three adjacent coplanar positions of the octahedron (*mer*), does not permit the attainment of coordination angles of 90° (*cis* donors) or 180° (*trans* donors). Due to the significantly longer M–O3 central bond [2.115(3) Å in **4** *vs*. 2.042(2) Å in **3**], the cobalt complex exhibits smaller O–M–O oda angles by *ca*. 4–5° (see Table 1). While all of the Ni–O and Ni–N distances are similar to those reported for **5** (the complex with *o*-phenanthroline reported by Perec and co-workers),[12] the Co–$O_{water}$ and the two Co–N distances in **4** are 0.04–0.05 Å longer than the corresponding Ni–$O_{water}$ and Ni–N distances in **3**. Most elongated, as mentioned, is the central Co–O3 bond. A more expanded octahedron around the Co(II) ion is somewhat surprising since the atomic and covalent radii of the Co and Ni atoms are essentially equal. Furthermore, since in a high spin octahedral Co(II) complex ($d^7$) one "$t_{2g}$" orbital is only half populated with respect to the Ni(II) ion ($d^8$), a minor repulsion toward one or more filled combinations of the π orbitals at the donor atoms, could be expected.

As a final remark, the atom O3 is more distorted from planarity in **3** than in **4** (sums of the bond angles *ca*. 353° *versus* *ca*. 357°). However, in both cases, the O3 thermal ellipsoids are significantly elongated in the direction perpendicular to the oda plane. This is an indication of some disorder with a pseudo-tetrahedral O3 atom flipping above or below the oda plane.

## Theoretical analysis

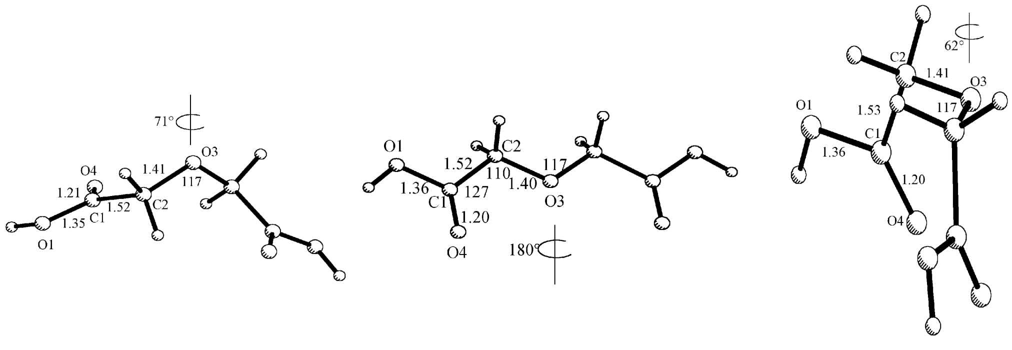
A series of DFT calculations have been carried out with the goal of better understanding the bonding capabilities of the oxydiacetate ligand toward transition metal ions. To the best of our knowledge no theoretical study of this ligand has been tackled before. Since the ligand has an intrinsic flexibility that leads eventually to the formation of different conformational isomers, we have first analysed in detail the stereochemistry of both the oxydiacetic acid and its associated dianion. Subsequently, we have performed calculations on the two conformational isomers of the complex [Ni(oda)$(H_2O)_3$] having the arrangements depicted in **II** and **III**, respectively.

### Conformations of the free oxydiacetic acid and of the oxydiacetate dianion

In the crystal structure of oxydiacetic acid,[22] **I**, the molecule has crystallographic $C_2$ symmetry with the twofold axis passing through the central oxygen atom. The dihedral angle between the planes defined by the two halves of oda is *ca*. 70°. A similar folding (close to 70°) occurs also in two crystal structures (TUFLUB[9k] and VARQOU[9l] refcodes) in which the acid is present as a solvate molecule. In another case, with $H_2$oda being also a solvate molecule (CEVSIF[9o] refcode), an almost planar conformation is found with the angle between the planes being *ca*. 12°. The symmetry is not too far from $C_{2v}$. Thus, small energy differences between the two conformations may be anticipated. The hypothesis is confirmed by DFT calculations of the oxydiacetic acid with imposed $C_{2v}$ and $C_2$ symmetries, respectively. Moreover, a third conformation with symmetry $C_s$ has also been calculated. The latter is not observed experimentally for the free acid but it is related to the geometry found in the *fac* oda-complexes (**III**). The three optimised structures of $H_2$oda are shown in Fig. 2. All of them are stationary points on the potential energy surface (PES) as confirmed by the calculations of the frequencies. The reproducibility of the experimental geometry is satisfactory by considering that the calculations are carried out for the molecule in the gas phase. In this respect, it is worth mentioning that a significant amount of intermolecular hydrogen bonding may occur in the crystalline environment. Only the computed C–O(H) bond appears somewhat overestimated in all cases (*ca*. 1.35 Å *vs*. the experimental value of *ca*. 1.30 Å) while the remaining distances agree within 0.02 Å. No significant variation (0.01 Å) in bond distances occurs in going from one conformation to the other. Furthermore, the COC bond angle remains constant in all the geometries. Energetically, the $C_2$ conformer is the most stable one, in agreement with the structure found for the single, not solvated, molecule.[22] However, the other conformers are not much destabilized, the $C_{2v}$ and the $C_s$ ones lying higher in energy by 4.2 and 6.6 kcal $mol^{-1}$, respectively. In spite of the small destabilization, the $C_s$ structure has never been reported whereas, as mentioned, an almost planar geometry is found when the oxydiacetic acid acts as solvate molecule.[9o] In this case, the environment may compensate for the loss of conformational energy.

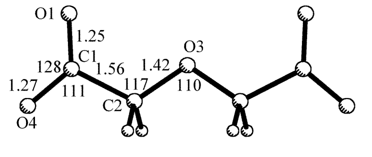
The free associated base of the oxydiacetic acid has been structurally characterized as the counterion of the hexakis(imidazole)nickel(II) cation[23] as well as of the 3-oxapentane-1,5-diammonium cation.[24] The oda anion is close to planarity in the former structure (COCC torsion angle of *ca*. 15°) and it is practically planar in the two structures available for the latter salt (different solvate molecules are present in these cases). Accordingly, we have carried out DFT calculations for the oxydiacetate anion only in the planar conformation, namely with a fixed $C_{2v}$ symmetry. In Fig. 3 the optimised geometry is compared with that found for the anion of the 3-oxapentane-1,5-diammonium salt.[24] The agreement is satisfactory as the bond distances agree within 0.05 Å and the largest deviation of bond angles are 4°.

The calculation of the oxydiacetate anion is particularly helpful for comparing computed and experimental IR spectra. The information may be also extended to interpret some of the IR bands observed in the oxydiacetate-metal complexes. In

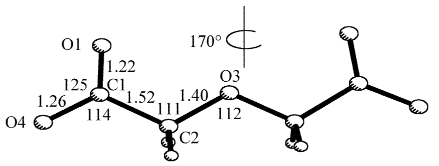


**symmetry $C_2$** **symmetry $C_{2v}$** **symmetry $C_s$**

**Fig. 2** Selected structural parameters (bond distances in Å and angles in °) of the optimised geometries of three conformations of the oxydiacetic acid molecule.



**symmetry $C_{2v}$**



**experimental**

**Fig. 3** Selected structural parameters (bond distances in Å and angles in °) of the optimised geometry of the oxydiacetate anion and, for comparison, those of the molecular structure XELJUT (CCDC refcode).[24]

particular, the aqueous solutions containing oxydiacetate salts[8a] show bands at *ca.* 1130 and 1050 cm$^{-1}$. These frequencies were assigned to the asymmetric and symmetric COC stretching vibrations, respectively. The symmetric absorption appears at lower frequency and its intensity is weaker (*i.e.*, 1412 *vs.* 1597 cm$^{-1}$ for sodium oxydiacetate solutions).[8a] We find the corresponding $CO_2$ bands in the computed spectrum at 1364 and 1668 cm$^{-1}$, respectively. Also, the computed COC stretching vibrations (1110, asym stretching, and 1056 cm$^{-1}$, sym stretching) fit particularly well with the experimental values (1129 and 1052 cm$^{-1}$ for sodium oxydiacetate solutions).[8a] Moreover, the computed asym/sym signal ratio is 5 and confirms the assignment of the strong absorption to the COC asymmetric stretching vibration.

### Alternative conformations of the oxydiacetate ligand in [Ni(oda)($H_2O$)$_3$]

The flexibility of oda in coordinating a transition metal centre has also been tested computationally. In particular, the complex **1** uniquely exhibits the *fac* conformation of oda in an experimental structure,[12] whereas in many other cases (including the present structures **3** and **4**) the ligand prefers a planar conformation. Thus, for the species [Ni(oda)($H_2O$)$_3$] not only the experimentally observed *fac* conformation has been reproduced but also the alternative *mer* conformation. Fig. 4 presents the computed geometries of the latter models and, for a direct comparison, that of the X-ray structure (QAVBOE refcode). In particular, there is a satisfactory agreement between the Ni(oda) moiety of the latter structure and the computed *fac* isomer. Even the amount of folding of the oda ligand about the Ni–O3 bonds is very well matched (122 *vs.* 124°).

In contrast, all of computed Ni–O$_{water}$ bonds are significantly elongated (by 0.07 and 0.13 Å, for the apical and the equatorial coordination sites, respectively). Most likely, this is because the strong hydrogen bonding established between the coordinated $H_2O$ molecules and other solvent molecules are neglected by the gas-phase calculation. The Ni(oda) moiety in the unobserved *mer* isomer can be conveniently compared with that of the present complex **3** (see Table 1) or that of the analogous complex **5**[12] (QAVBUK refcode). Thus, it is evident that, while the central Ni–O3 distance is well reproduced, the length of two lateral Ni–O bonds is underestimated by the calculations (1.98 *vs. ca.* 2.05 Å). This is likely a consequence of a more puckered oda conformation in the calculated structure. In fact, although the pyramidality of the O3 atom is slightly larger than in complex **3** (sum of the bond angles = 347 *vs.* 353°), the computed model shows larger torsions at the C–C bonds (16 *vs.* 8°). In comparing these results, it is hard to say whether the presence of two water molecules in place of another chelate ligand (bipy) may be responsible for the conformational difference.

In the *fac*, as well as in the *mer* conformer, the three Ni–O$_{water}$ bond lengths are overestimated (by *ca.* 0.1 Å). It is however noteworthy that, in any case, the Ni–O$_{water}$ values of both the computed isomers are within the range of experimental bond distances (1.96–2.34 Å) as determined from a CSD search[21] carried out over 629 samples.

A remarkable difference between computed *mer* and *fac* conformers is the *ca.* 0.11 Å elongation of the Ni–O3 bond in the latter. Although such a pair of isomers is not available experimentally, the trend is confirmed by the comparison of the same distances in *fac* complex **1** and the *mer* complexes **3** or **5**[12] [2.130(3) Å *vs.* 2.042(2) and 2.050(4) Å]. An intuitive rationalization of the trend is provided by a qualitative FMO analysis at the EHMO level and its pictorial representation.[25] In the *mer* isomer, the Ni–O3 bond originates from the interaction of a *in-plane* oxygen lone pair with the σ hybrid of a d$^8$-ML$_5$ fragment. The same bond in the *fac* isomer is due to the interaction of an oxygen lone pair with an equivalent hybrid. It appears that the directionality of the lone pair is much better suited for maximum overlap, in the former case. Probably for this reason, the *mer* isomer is calculated (DFT level) to be *ca.* 2.0 kcal mol$^{-1}$ more stable than the *fac* isomer. On the other hand, the energy difference is small and it may not be excluded that the *fac* geometry, experimentally found in **1**, is favoured by the presence of additional water molecules capable of forming strong hydrogen bonds with the oxydiacetate ligand. An extended model could be tested computationally by using the positions of the extra $H_2O$ molecules available from the X-ray data of **1**.[12] On the other hand, the analogous structural information is not available for the *mer* isomer. For this reason, we did not pursue any further the search for the most stable conformer based on the larger thermodynamic stabilization. Moreover, since the latter energy term is in any case small, it

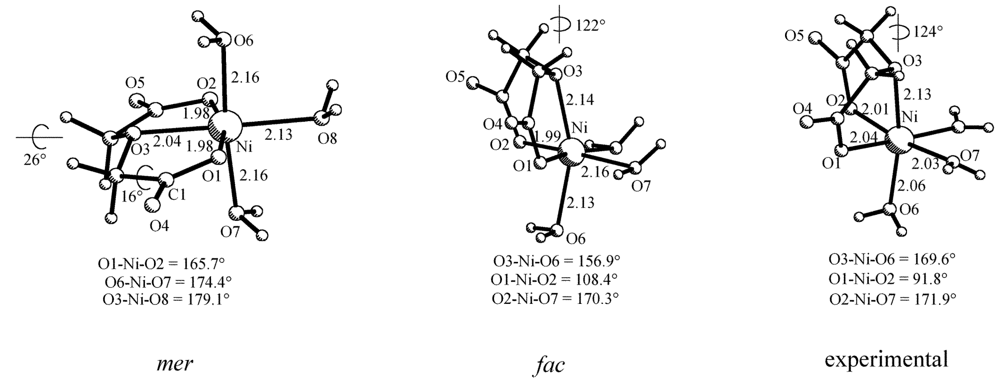


**Fig. 4** Selected structural parameters (bond distances in Å and angles in °) of the optimised geometries of *mer* and *fac* isomers of [Ni(oda)($H_2O$)$_3$] **1** and, for comparison, those of its molecular structure.[12]

may be overwhelmed by entropic factors that are certainly quite important for multi-molecular aggregates such as the present ones.

Finally, it is noteworthy that the calculated IR spectra of the *mer* and *fac* conformers differ for having the COC asymmetric stretching frequencies centred at 1083 and 1058 $cm^{-1}$, respectively. Although the latter values do not perfectly match the experimental ones (for example: 1137 $cm^{-1}$ for **3** and 1094 $cm^{-1}$ for **1**, respectively), their difference supports our previous suggestion that *mer* or *fac* conformations of the oda ligand in transition metal complexes can be discriminated on the basis of IR spectra. Namely, an active IR band in the region around 1100 $cm^{-1}$ or lower diagnoses the presence of the *fac* arrangement whereas higher frequencies are expected for the *mer* arrangement.

## Experimental

All preparations and other operations were carried out under aerobic conditions. Microanalyses (C, H, N) were carried out by the Microanalytical Service of the Instituto de Investigaciones Químicas (CSIC). Infrared spectra were recorded on a Perkin-Elmer Model 883 spectrophotometer (Nujol emulsion in NaCl plates). Magnetic moments were measured in the solid state with a Sherwood Scientific (Cambridge Research Laboratory) magnetic balance. Oxydiacetic acid and other chemicals were obtained from commercial sources and were used without further purification. The experimental procedures for the synthesis of complexes **1** and **2** have been included here because they are somewhat different with respect to those reported in the bibliography.[4b,12]

### Syntheses

**[Ni(oda)($H_2O$)$_3$]·1.5$H_2O$ 1.** To a solution of $O(CH_2CO_2H)_2$ (0.4 g, 3 mmol) in water (20 ml) was added $Na_2CO_3$ (0.32 g, 3 mmol). The mixture was stirred until the evolution of $CO_2$ ceased and then added onto a solution of $NiCl_2{\cdot}6H_2O$ (0.71 g, 3 mmol) in water (25 ml). The resulting solution was stirred for a few minutes and then concentrated. Acetone was added and the solution was kept at room temperature overnight. Green needle crystals of **1** were formed, filtered off, washed with acetone and diethyl ether and air dried (0.69 g, 85%). IR and analytical data are in agreement with those previously reported.[12] $\mu_{eff} = 3.4\ \mu_B$ at 20 °C.

**[Co(oda)($H_2O$)$_2$]·$H_2O$ 2.** $Na_2CO_3$ (1.27 g, 12 mmol) dissolved in 15 ml of water was added slowly to a solution of $O(CH_2CO_2H)_2$ (1.61 g, 12 mmol) in 15 ml of water. This was added onto a 20 ml water solution of $CoCl_2{\cdot}6H_2O$ (2.85 g, 12 mmol). The resulting solution was stirred for a few minutes. Addition of 30 ml of acetone gave maroon crystals of **2** after standing the mixture for 12 h at room temperature, which were collected by filtration, washed with acetone and diethyl ether and dried in air (80% yield after two crops). IR ($cm^{-1}$): 3500–3000 vbr, 1670 sh, 1628 vs, 1591 vs, 1472 m, 1449 m, 1431 s, 1408 m, 1385 w, 1358 m, 1316 s, 1243 w, 1146 vs, 1054 s, 940 s, 839 m, 742 s, 673 w. $\mu_{eff} = 5.0\ \mu_B$ at 24 °C. (Found: C, 19.59; H, 4.04. $C_4H_{10}O_8Co$ requires C, 19.60; H, 4.08%).

**[M(oda)(bipy)($H_2O$)]·2.5$H_2O$ (M = Ni, 3; Co, 4).** An aqueous solution (40 ml) of **1** (0.142 g, 0.54 mmol) was added to a solution of bipy (0.085 g, 0.54 mmol) in 40 ml of water. The mixture, that turned blue immediately, was stirred for a few minutes, concentrated to a volume of about 40 ml and was poured onto a crystallization dish. Slow evaporation of water resulted in the formation of blue crystals of [Ni(oda)(bipy)($H_2O$)]·2.5$H_2O$ **3** which were collected by filtration, washed with water, acetone and diethyl ether and dried in air (0.2 g, 90% yield). IR ($cm^{-1}$): 3616 s, 3400–3000 vbr, 1605 vs, 1450 s, 1426 m, 1380 s, 1353 w, 1311 s, 1256 w, 1243 w, 1187 m, 1164 m, 1137 s, 1073 m, 1050 m, 1031 s, 981 w, 926 s, 884 w, 774 m, 743 m, 728 m, 660 w, 641 w. $\mu_{eff} = 3.2\ \mu_B$ at 23 °C. (Found: C, 40.94; H, 4.46; N, 7.00. $C_{14}H_{19}N_2O_{8.5}Ni$ requires C, 41.0; H, 4.63; N, 6.83%).

Following a similar synthetic procedure as described above, but using **2** (2.8 g, 12 mmol) as starting material, the compound [Co(oda)(bipy)($H_2O$)]·2.5$H_2O$ **4** was obtained as maroon crystals in 76% yield. IR ($cm^{-1}$): 3625 s, 3400–3000 vbr, 1660 sh, 1605 vs, 1450 s, 1426 s, 1385 s, 1357 m, 1311 s, 1256 w, 1243 w, 1187 m, 1164 m, 1151 s, 1073 m, 1050 m, 1041 m, 1027 m, 1013 m, 981 w, 930 s, 907 w, 774 m, 742 m, 728 w, 660 w, 637 w. $\mu_{eff} = 5.0\ \mu_B$ at 22 °C. (Found: C, 40.93; H, 4.72; N, 7.09. $C_{14}H_{19}N_2CoO_{8.5}$ requires C, 41; H, 4.63; N, 6.83%).

**[M(oda)(phen)($H_2O$)]·$x$$H_2O$ (M = Ni, 5; $x$ = 1.5. M = Co, 6; $x$ = 2).** The synthesis of complex **5** is similar to that reported in the bibliography,[12] the IR properties are identical. **5** has a $\mu_{eff}$ in the solid state of 3.2 $\mu_B$ at 22 °C. (Found: C, 46.0; H, 4.0; N, 6.9. $C_{16}H_{17}O_{7.5}N_2Ni$ requires C, 46.2; H, 4.1; N, 6.7%).

A solution containing 0.30 g (1.9 mmol) of *o*-phenanthroline in 20 ml of hot water was added to a solution of **2** (0.51 g, 1.9 mmol) in 15 ml of water. The resulting solution was stirred for a few minutes. The compound [Co(oda)(phen)($H_2O$)]·2$H_2O$ **6** crystallized upon evaporation of the solvent at room temperature after a few days. The crystals were filtered off, washed with water and acetone and dried in air (0.59 g, 57% yield). IR ($cm^{-1}$): 3500–3000 vbr, 1656 sh, 1610 vs, 1523 m, 1500 w, 1467 s, 1431 s, 1357 m, 1316 m, 1243 w, 1220 w, 1132 vs, 1036 s, 981 w, 925 s, 875 m, 857 s, 792 m, 737 s, 673 w, 650 w. $\mu_{eff} = 5.3\ \mu_B$ at 25 °C. (Found: C, 44.85; H, 4.10; N, 6.87. $C_{16}H_{18}O_8N_2Co$ requires C, 45.18; H, 4.23; N, 6.59%).

**[M(oda)(tmeda)($H_2O$)]·2$H_2O$ (M = Ni, 7; Co, 8).** 1 mmol (151 μl) of tmeda was syringed to a solution containing 0.26 g (1 mmol) of **1** dissolved in 20 ml of water. The resulting solution was stirred for a few minutes. The Ni(II) compound crystallized as blue turquoise crystals upon evaporation of the solvent at room temperature after a few days. The crystals were filtered off, washed with acetone and diethyl ether and dried in air. Yield 0.30 g (82%). IR (cm$^{-1}$): 3500–3000 vbr, 1671 s, 1606 vs, 1467 vs, 1432 s, 1387 s, 1357 m, 1312 s, 1257 w, 1207 w, 1133 vs, 1053 s, 1033 s, 1013 m, 963 s, 928 s, 888 w, 814 s, 779 w, 734 s, 619 m. $\mu_{eff} = 3.1\ \mu_B$ at 22°C. (Found: C, 33.29; H, 7.11; N, 7.96. $C_{10}H_{26}N_2O_8Ni$ requires C, 33.27; H, 7.20; N, 7.76%).

Following a similar synthetic procedure as described above, but using **2** (0.23 g, 1 mmol) as starting material, was obtained the compound **8** as pink crystals in 80% yield. IR (cm$^{-1}$): 3500–3000 vbr, 1671 s, 1611 vs, 1472 s, 1432 s, 1387 s, 1357 m, 1312 s, 1257 w, 1207 w, 1138 vs, 1053 s, 1033 s, 1018 m, 958 s, 928 s, 809 s, 774 w, 729 s, 619 m. $\mu_{eff} = 4.9\ \mu_B$ at 22.5 °C. (Found: C, 33.22; H, 7.06; N, 7.83. $C_{10}H_{26}N_2O_8Co$ requires C, 33.25; H,7.20; N, 7.76%).

**[M(dipic)]·3.5H$_2$O (M = Ni, 9; Co, 10).** A solution of pyridine-2,6-dicarboxylic acid (0.17 g, 1 mmol) in water was added to an aqueous solution of **1** (0.26 g, 1 mmol). After stirring a few minutes, the mixture was concentrated. Compound **9** was obtained as green crystals upon slow evaporation of the solvent at room temperature. Yield 0.18 g (63%). IR (cm$^{-1}$): 3500–3000 vbr, 1619 vs, 1582 s, 1458 s, 1435 s, 1399 s, 1384 s, 1293 s, 1197 m, 1160 w, 1086 s, 1050 m, 1013 w, 926 w, 861 w, 834 w, 820 w, 770 s, 742 s, 728 s, 701 m. (Found: C, 29.12; H, 3.49; N, 5.17. $C_7H_{10}NO_{7.5}Ni$ requires C, 29.29; H, 3.48; N, 4.88%).

Violet crystals of complex **10** were obtained following the same method. Yield 0.19 g (66%). IR (cm$^{-1}$): 3500–3000 vbr, 1619 vs, 1582 sh, 1463 vs, 1385 s, 1293 s, 1210 w, 1197 m, 1160 w, 1082 s, 1041 m, 1013 w, 949 w, 990 m, 862 m, 820 w, 770 s, 728 s, 701 w, 683 w, 669 w. (Found: C, 29.41; H, 3.46; N, 5.00. $C_7H_{10}NO_{7.5}Co$ requires C, 29.27; H, 3.48; N, 4.88%).

### Crystallography

A summary of the crystal data and structural refinement of the compounds is given in Table 2. Well-formed crystals of **3** (blue) and **4** (maroon) were mounted on an Enraf-Nonius CAD4 diffractometer equipped with a graphite monochromator and Mo-Kα radiation ($\lambda = 0.71073$ Å). In both cases, the cell dimensions were refined by least-squares refinement of 25 reflections in the $2\theta$ range of 10–20°. The intensity data were corrected for Lorentz and polarization effects. No absorption correction was applied in view of the tiny size of the crystals and of the small values of the absorption coefficients. In any case, three standard reflections were monitored every two hours during data collection and minimum decay was observed. Atomic scattering factors are those reported by Cromer and Waber.[26] The structure of **3** was solved by direct methods using the SIR97[27] package of programs, while that of the isomorphous compound **4** was refined by starting from the final coordinates of **3**. Refinements were made by full matrix least-squares on all $F^2$ data using SHELXL97.[28] At a later stage of refinement hydrogen atoms were introduced at calculated positions except for those of the $H_2O$ molecules that were found in the $\Delta F$ maps and refined. Anisotropic thermal parameters were allotted to only the non-hydrogen atoms. The methylenic H atoms were all assigned a unique isotropic temperature factor and also the aromatic H atoms of 2,2′-bipyridine were treated in an analogous manner. No unusual trend in $\Delta F$ *vs.* $F_o$ or $(\sin\theta)/\lambda$ was observed. A final difference synthesis showed no significant electron density residues.

It must be mentioned at this point that, while space group of **3** was unambiguously assigned as *Fdd*2, the compound **4** showed a few observed reflections that should be systematically absent. The situation is similar to that reported also for the isomorphous Zn complex,[3b] for which the *Fdd*2 space group was eventually selected after several attempts of refinement with lower symmetry space groups. In our case, during the refinement of **4**, the SHELX program warned that the structure may be affected by twinning. Accordingly, the TWIN directive was successfully applied with a final reduction of the *R* factor by a few decimals. Tracks of some disorder remain, especially in the regions of the O3 atom with a significantly elongated thermal ellipsoid (see the section Crystal and molecular structures of **3** and **4**).

**Table 2** Crystallographic data for complexes **3** and **4**

| | **3**(Ni) | **4**(Co) |
|---|---|---|
| Formula | $C_{14}H_{19}N_2O_{8.5}Ni_1$ | $C_{14}H_{19}N_2O_{8.5}Co_1$ |
| $M$ | 410.02 | 410.24 |
| Crystal system | Orthorhombic | Orthorhombic |
| Space group | *Fdd*2 (no. 43) | *Fdd*2 (no. 43) |
| $T$/K | 293(2) | 293(2) |
| $a$/Å | 13.560(5) | 13.646(6) |
| $b$/Å | 47.533(5) | 47.908(9) |
| $c$/Å | 10.781(5) | 10.752(4) |
| $U$/Å$^3$ | 6949(4) | 7029(4) |
| $Z$ | 16 | 16 |
| $D_c$/g cm$^{-3}$ | 1.57 | 1.55 |
| $\mu$(Mo-Kα)/mm$^{-1}$ | 1.17 | 1.02 |
| $F$(000) | 3408 | 3392 |
| Unique reflections, $I \geq 2\sigma(I)$ | 2862 | 1627 |
| $R$ | 0.028 | 0.030 |
| $wR2$ | 0.077 | 0.072 |

The molecular drawing of Fig. 1 has been made by using the program ORTEP-III for Windows.[29] All of the crystallographic computational work was performed by using the user-friendly graphic interface of WINGX.[30] Crystallographic data for complexes **3** and **4** are given in Table 2.

CCDC reference numbers 180037 and 180038.

See http://www.rsc.org/suppdata/dt/b2/b201885c/ for crystallographic data in CIF or other electronic format.

### Computational details

The DFT calculations were carried out with the Gaussian 98[31] package. All of the computations were performed with the hybrid B3LYP density functional[32] and the basis set was 6-31G(d,p) for all atoms. The effective core potential (LANL2DZ) has been used for the nickel metal.[33]

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