Crystallisation Solvent Influence on the Crystal Structures of Mn^{II} and Ni^{II} Complexes with 2,6-bis(1-salicyloylhydrazonoethyl)pyridine, H₄daps

Manuel R. Bermejo*, Antonio Sousa*, Matilde Fondo, Ana M. González, Olga L. Hoyos^a, Rosa Pedrido, Miguel A. Maestro^b, José Mahía^b

Santiago de Compostela/Spain, Departamento de Química Inorgánica, Facultad de Química, Universidad de Santiago de Compostela, E-15706

^a Popayán/Colombia, Departamento de Química, Universidad del Cauca

^b La Coruña/Spain, Servicios Generales de Apoyo a la Investigación, Universidad de La Coruña

Received June 24th, 1999.

Abstract. Neutral manganese and nickel complexes of the empirical formulae $Mn(H_2daps)(H_2O)_{0.5}$ and $Ni(H_2daps) \cdot (H_2O)_{1.5}(CH_3CN)$ have been prepared by electrochemical syntheses. The structures of the complexes formed from solvents with different donor ability were investigated. Recrystallisation of $Mn(H_2daps)(H_2O)_{0.5}$ from pyridine and ethanol yields $[Mn(H_2daps)(py)_2]$ **1** and $[Mn(H_2daps)(C_2H_5OH) \cdot (H_2O)]$ **2**. Slow evaporation of dichloromethane and methanol solutions of $Ni(H_2daps)(H_2O)_{1.5}(CH_3CN)$ allows the isolation of single crystals of $[Ni_2(H_2daps)_2] \cdot CH_2Cl_2$ **4** and

 $[Ni_2(H_2daps)_2(CH_3OH)_2] \cdot 3 CH_3OH \cdot H_2O 5$, suitable for Xray diffraction studies. Recrystallisation of 4 from pyridine yields $[Ni_2(H_2daps)_2(py)_2] \cdot CH_2Cl_2$ 6, previously characterised by us. This study shows the versatility of the H₄daps ligand and the influence that the crystallisation solvent can have on the crystal structure of these complexes.

Keywords: Manganese complexes; Nickel complexes; Helical structures; Schiff bases; Solvent effects

Einfluss des Lösungsmittels auf die Kristallstrukturen der Mn^{II}und Ni^{II}-Komplexe von 2,6-Bis(1-salicyloylhydrazonoethyl)pyridin, H₄daps

Inhaltsübersicht. Mittels Elektrosynthese wurden die neutralen Mangan- und Nickel-Komplexe $Mn(H_2daps) \cdot 0,5 (H_2O)$ und Ni $(H_2daps) \cdot (H_2O) \cdot 1,5 (CH_3CN)$ synthetisiert. An Komplexen, die aus Lösungsmitteln unterschiedlicher Donorstärke auskristallisiert waren, wurden Strukturuntersuchungen durchgeführt. $Mn(H_2daps) \cdot 0,5 (H_2O)$ kristallisiert aus Pyridin bzw. Ethanol als $[Mn(H_2daps)(py)_2]$ **1** bzw. $[Mn(H_2daps) \cdot (C_2H_5OH)(H_2O)]$ **2**, die kristallographisch charakterisiert wurden. Durch langsames Eindunsten der Lösungen von $[\rm Ni(H_2daps)_2] \cdot 1,5 (H_2O) \cdot (\rm CH_3CN)$ in Dichlormethan bzw. Methanol konnten für die Röntgenbeugung geeignete Einkristalle von $[\rm Ni_2(H_2daps)_2] \cdot (\rm CH_2Cl_2)$ 4 und $[\rm Ni_2(H_2daps)_2(\rm CH_3OH)] \cdot 3 (\rm CH_3OH) \cdot (\rm H_2O)$ 5 erhalten werden. Umkristallisieren von 4 aus Pyridin ergab $[\rm Ni_2(H_2daps)_2(py)_2]$ 6, welches wir schon früher charakterisiert hatten. Die Untersuchungen belegen den Einfluss des H_4daps-Liganden und des eingebauten Lösungsmittels auf die Kristallstrukturen der Komplexe.

Introduction

The properties of hydrazone ligands have been largely investigated in the past few years [1–9]. The interest in the co-ordination chemistry of this type of ligand has increased, in part, due to the interesting donor systems which could result. Intense activity has been focussed on this new field in order to design ligands which can control the selective preparation of complicated, organised chemical architectures. The structural characterisation of the resultant complexes has led to

Departamento de Química Inorgánica Facultad de Química Universidad de Santiago de Compostela 15706 Santiago de Compostela, Spain Telephone number: 00-31-(9)81-59 1076 Fax number: 00-31-(9)81-59 75 25

E-mail address: qimb45@uscmail.usc.es

some emerging patterns [6, 7]. However, many questions still remain and the predicted systems are not always obtained.

The desire for an in depth understanding of the rules that lead to helicates and other systems of different nuclearity, together with their pharmacological activity [10–12], as well as their interesting electric and magnetic properties [13–15], makes further investigation into the chemistry of hydrazone ligands even more attractive.

We have recently characterised one manganese and two dinickel complexes containing H_4 daps in its dianionic form [16]. We have found that the manganese complex is a mononuclear compound when it is recrystallised in a donor solvent, such as pyridine. In contrast, the nickel complexes occur as a double helical structure when recrystallised from both dichloromethane and pyridine.

^{*} Manuel R. Bermejo

Previous results in the literature seemed to indicate that if a metal ion with a strong ligand field-imposed preference for an octahedral geometry was selected, together with a ligand with a central pyridine unit and two other bidentate domains in each thread was used, a double helicate would result [7]. The only difficulty to get helicates would be to prevent the metal centres from adopting a pentagonal bipyramidal geometry. This could be avoided by introducing bulky substituents on the hydrazone. Thus, it seemed that H₄daps could be an appropriate ligand to obtain helical compounds. An additional complication in these systems, however, is that the solvent of crystallisation appears to play an important role in the preparation of helicates. It has previously been reported that the presence of a good donor solvent could break the pyridine bridges in a double helical complex to give rise to monomeric compounds with a co-ordination number of seven [7].

With these considerations in mind we were interested in checking the effect of the solvent of recrystallisation on the nuclearity of complexes mentioned above. For this reason, we have prepared again the reported manganese and nickel complexes and they were recrystallised in solvents of different donor properties in order to study their behaviour. In this paper we describe the results achieved.

Results and Discussion

 $Mn(H_2daps)(H_2O)_{0.5}$ and $Ni(H_2daps)(H_2O)_{1.5}(CH_3CN)$ have been prepared by means of an electrochemical synthesis, as previously reported [16, 17]. The electrochemical efficiency of the cell is close to 0.5 molF⁻¹ in both cases, which is in accordance with the following mechanism for the reaction:

Cathode: H_4 daps + 2e⁻ \rightarrow $H_2(g) + H_2$ daps²⁻ Anode: H_2 daps²⁻ + M \rightarrow M(H₂daps) + 2e⁻

Manganese complexes. Recrystallisation of $Mn(H_2daps) \cdot (H_2O)_{0.5}$ from pyridine allows the mononuclear complex [Mn(H_2daps)(py)_2] **1** to be isolated, as previously described [16]. It shows a pentagonal bipyramidal geometry, with the ligand H₄daps, acting as a pentadentate donor, occupying the equatorial positions of the

bipyramid, with the apical positions filled with two pyridine molecules. As the pyridine solvent is a good donor, we were interested in knowing if $Mn(H_2daps) \cdot (H_2O)_{0.5}$ could be a helical compound where the pyridine bridges were broken by the presence of pyridine as solvent. For this reason, we tried to recrystallise $Mn(H_2daps)(H_2O)_{0.5}$ from a poorer donor solvent. Unfortunately, this complex is insoluble in non polar or chlorinated solvents such as carbon tetrachloride, chloroform and dichloromethane, but it is sparingly soluble in alcohols. Recrystallisation from ethanol allowed us to isolate crystals of $[Mn(H_2daps) \cdot (C_2H_5OH)(H_2O)]$ **2**, suitable for X-ray diffraction studies.

FAB mass and IR spectra and magnetic measurements

The FAB mass spectrum of **2** shows a peak (Table 1) due to the fragment $[Mn(H_2daps)]^+$ at 485 amu, that indicates co-ordination of the ligand to the metal. No fragments containing ethanol or water could be observed.

The IR spectrum shows a negative shift of 63 cm^{-1} and 62 cm^{-1} of the amide I [ν (CO)] and amide II [δ (NH) + ν (CN)] modes, respectively. This behaviour suggests the participation of the oxygen atoms of both carbonyl CO groups in co-ordination to the metal, in agreement with previous results [18]. The spectrum also shows the absence of the ν (N–H) band, which in the free ligand appears at 3208 cm⁻¹. This is in accordance with the dianionic nature of the ligand. This is further supported by the room temperature magnetic moment of 5.6 B.M., which is consistent with the presence of a magnetically dilute high spin Mn^{II} ion [19].

Crystal structure of $[Mn(H_2daps)(C_2H_5OH)(H_2O)]$ 2

An ORTEP view of the compound is shown in Fig. 1. Experimental details are given in Table 2 and selected bond lengths and angles in Table 3.

The crystal structure of **2** shows the compound to consist of a distorted pentagonal bipyramidal geometry about the manganese ion, with the pentadentate ligand H_2daps^{2-} occupying the equatorial belt of the bipyramid. The pentadentate ligand gives rise to four five-membered chelate rings. Four of the five angles

 Table 1
 Analytical and some selected data for the complexes

Complex	Analysis (%	Analysis (%) ^{a)}		$\mu_{\rm eff}^{\rm b)}$	FAB ^{c)}	Colour
	С	Ν	Н			
Mn(H ₂ daps)(H ₂ O) _{0.5} Ni(H ₂ daps)(H ₂ O) _{1.5} (CH ₃ CN)	56.0(55.9) 53.6(53.9)	14.4(14.2) 15.4(15.1)	3.6(4.0) 4.6(4.5)	5.7 2.9	485 488 976*	Dark orange Yellow brown
$\begin{array}{l} [Mn(H_{2}daps)(C_{2}H_{5}OH)(H_{2}O)] \ \textbf{2} \\ [Ni_{2}(H_{2}daps)_{2}(CH_{3}OH)_{2}] \cdot \ \textbf{3} \ CH_{3}OH \cdot H_{2}O \ \textbf{5} \end{array}$	55.1(54.8) 53.5(53.1)	12.9(12.8) 11.1(11.1)	4.6(4.7) 4.9(5.2)	5.6 2.9	485 488 976*	Dark orange Yellow green

^{a)} Found(calculated); ^{b)} In B.M.; ^{c)} Peaks corresponding to $[ML]^+$ except * that correspond to $[M_2L_2]^+$



Fig. 1 Molecular structure of $[Mn(H_2daps)(C_2H_5OH) \cdot (H_2O)]$ 2 showing the atomic numbering scheme.

Table 2 Crystal data and details of refinement

	2	5
Formula	C25H26MnN5O6	C ₅₁ H ₆₀ N ₁₀ Ni ₂ O ₁₄
M. W.	547.45	1154.51
a (Å)	10.4242(4)	14.360(2)
b (Å)	14.8371(6)	18.208(4)
c (Å)	16.1221(6)	20.870(3)
α (°)	90	90
β(°)	90.697(2)	90
γ (°)	90	90
Z	4	4
$V(Å^3)$	2493.34(17)	5456.7(15)
$Dc (g/cm^3)$	1.458	1.405
Space group	$P2_1/n$	P2 ₁ 2 ₁ 2 ₁
Crystal system	Monoclinic	Orthorhombic
Crystal size (mm)	$0.20 \times 0.10 \times 0.05$	$0.45 \times 0.20 \times 0.15$
θ range (°)	1.87-25.03	1.48-25.05
Scan type	ω scan	ω scan
Reflections collected	10041	13848
No. unique reflections	$4390 (R_{int} = 0.1363)$	9230 ($R_{int} = 0.0709$)
No. variables	343	689
$\mu ({\rm mm}^{-1})$	0.580	0.763
F(000)	1136	2416
Largest Peak and	0.350 and -0.438	1.325 and -0.848
hole/e Å ⁻³		
R	$0.0773 [1837, I > 2\sigma]$	0.0819 [5534, I > 2σ]
R (all data)	0.2052	0.1318
wR2	0.1865	0.2188

Table 3 Selected bond lengths (Å) and angles (°) for $[Mn(H_2daps)(C_2H_5OH)(H_2O)]$ 2

Mn–N1	2.292(5)	N2-Mn-N1	68.7(2)
Mn-N2	2.280(6)	O2S-Mn-N4	89.75(17)
Mn–N4	2.292(5)	O1S-Mn-N4	90.25(18)
Mn-O1	2.227(4)	O1–Mn–O3	84.89(17)
Mn-O3	2.247(5)	O1–Mn–O1S	93.29(17)
Mn-O2S	2.236(6)	O3–Mn–O1S	92.78(18)
Mn-O1S	2.268(5)	O2S-Mn-N2	92.29(19)
		O1S-Mn-N2	86.84(19)
O1-Mn-O2S	87.25(16)	O2S-Mn-N1	92.50(17)
O2S-Mn-O3	88.39(17)	O1S-Mn-N1	86.35(18)
O2S-Mn-O1S	178.75(18)	O1–Mn–N4	154.23(19)
O1-Mn-N2	69.71(18)	O3-Mn-N4	69.43(17)
O3-Mn-N2	154.52(19)	N2-Mn-N4	136.0(2)
O1-Mn-N1	138.35(19)	N1-Mn-N4	67.3(2)
O3-Mn-N1	136.75(18)		

subtended at manganese by adjacent equatorial atoms range from 67.3(2) to $69.71(18)^{\circ}$ while the fifth angle O1-Mn-O3 has a value of 84.89(17)°. This clearly shows the distortion of the polyhedron from ideal geometry (ideal value of $\alpha = 72^{\circ}$). The apical positions are filled by a water and an ethanol molecules, from the crystallisation solvents. The interaxial angle O1S-Mn-O2S is 178.75(18)°, very close to the ideal value of 180°. The structure of this compound is very similar to those previously reported for manganese compounds containing neutral hydrazone ligands [20] and to $[Mn(H_2daps)(py)_2]$ **1**. All bond distances and angles in the two structures are also very similar and in the range of those expected for this type of compound. The planarity of the pentagon formed by the N_3O_2 donor set of the hydrazone is also comparable in both cases but it shows a more planar ligand in 2, maybe as a consequence of the reduced steric bulk of the apical ligands. The maximum deviation from the N₃O₂ calculated least square plane is 0.084 Å in 1, with the manganese atom sitting on the plane, and 0.040 Å for 2, with the manganese atom 0.027 Å above this plane. However, if we compare 1 and 2 some differences are note worthy (see Table 4):

1. Compound **1** has a crystallographic 2-fold axis which bisects the molecule through the Mn and pyridine nitrogen atom of the $[H_2daps]^{2-}$ ligand. This does not occur in compound **2**.

2. The Mn-Npyridine distance is significantly shorter in **2** [M–Npyridine = 2.380(6) Å for **1** and 2.292(5) Å for **2**]. Opposite, the distances Mn–Nimine are slightly longer in **2** [M–Nimine = 2.267(5) Å for **1** and 2.280(6), 2.292(5) Å for **2**]. The different strength of these bonds in both complexes is also reflected in the C–Npyridine and C–Nimine bond lengths. As expected from the above observations, the C–Npyridine bond distances in **1** [1.313(6) Å] are shorter than in **2** [1.333(8) and 1.357(8) Å] and the C–Nimine distances are longer in **1** [1.376(7) Å for **1** and 1.270(7), 1.287(8) Å for **2**]. These latter distances are closer to the ideal value of 1.28 Å for a C–Nimine bond in **2** and seem to indicate a lack of electronic delocalisa-

Table 4Comparison of bond lengths (Å) in 1, 2

Distance (Å)	$[Mn(H_2daps)(py)_2]^{a}$	$\begin{array}{l} \left[\text{Mn}(\text{H}_2\text{daps}) \cdot \\ (\text{C}_2\text{H}_5\text{OH})(\text{OH}_2) \right]^{\text{b})} \end{array}$
Mn-Npyridine	2.380(6)	2.292(5)
Mn–Nimine	2.267(5); 2.267(5)	2.280(6); 2.292(5)
Mn–Ocarbonyl	2.243(4); 2.243(4)	2.227(4); 2.247(5)
C-Npyridine	1.313(6); 1.313(6)	1.333(8); 1.357(8)
Cpyridine-Cimine	1.436(7); 1.436(7)	1.470(9); 1.488(9)
C–Nimine	1.376(7); 1.376(7)	1.270(7); 1.287(8)
Nimine-Nhydrazide	1.347(6); 1.347(6)	1.379(7); 1.389(7)
Nhydrazide-Ccarbonyl	1.340(7); 1.340(7)	1.341(8); 1.348(8)
C–Ocarbonyl	1.263(6); 1.263(6)	1.279(8); 1.284(8)
C-Ophenol	1.323(8)	1.316(8); 1.337(8)
Nhydrazide · · · Ophenol	2.499(6); 2.499(6)	2.497(7); 2.545(8)

a) Ref. 16; b) This work

tion in this compound. Longer Nhydrazide-Nimine distances (ca. 1.35 Å for 1 and 1.38 Å for 2) also point to the lower degree of electronic delocalisation in 2. These facts reflect the different donor nature of ethanol and water compared with pyridine.

3. The C–Ophenol bond distances are very similar in both cases (ca. 1.32 Å) and smaller than the ideal value (C–OH = 1.36 Å), indicating some double bond character. This is in agreement with a hydrogen bond between the phenol oxygen and the hydrazide nitrogen atom. This intramolecular hydrogen bond is also suggested by the N···O distances of *ca.* 2.5 Å for **1** and **2** and it is indicative of the dianionic nature of $[H_2daps]^{2-}$. In addition, two hydrogen bonds between the water molecule of one unit and the carbonyl oxygen atoms of one neighbouring molecule are observed in **2** [distances O1···O2S' = 2.731(6) Å and O3···O2S' = 2.771(6) Å]. These interactions lead to a weakly joined dimer that is repeated in the space



Fig. 2 Molecular packing for $[Mn(H_2daps)(C_2H_5OH) \cdot (H_2O)]$ **2** showing the hydrogen bonds between neighbouring units.

(Fig. 2). The molecules are also interacting by π - π stacking between two parallel phenol rings.

The solution of the crystal structure of **2** shows that the different donor ability of ethanol and pyridine does not introduce a change in the nuclearity of the complex but affects the electronic distribution on the hydrazone ligand. From these results, it seems that manganese has a low tendency to form helicate complexes with this class of ligand. In fact, to the best of our knowledge, no helical compounds have been described for manganese complexes containing hydrazone ligands. It, thus, appears that the central atom plays an essential role in the isolation of helicates and that the role of the solvent is secondary.

Nickel complexes. Slow evaporation of a dichloromethane solution of $Ni(H_2daps)(H_2O)_{1.5}(CH_3CN)$ yields $[Ni_2(H_2daps)_2] \cdot CH_2Cl_2$ 4, the structure of which has previously been reported by us [16]. It is a binuclear complex with a distorted octahedral environment around the Ni atoms. Each ligand $[H_2daps]^{2-}$ uses one imine nitrogen atom and one carbonyl oxygen atom of one of its molecular threads to join a nickel centre and then use the same atoms of the second molecular thread to link the second metal centre. The co-ordination number 6 is attained by means of two bridges between the metal centres via the two nitrogen atoms of the central pyridine rings of both hydrazone ligands. Thus, the complex has a double helical structure, in contrast to the mononuclear structure found for the manganese compounds.

It has been previously reported that a binuclear cobalt complex containing qpy (qpy =2,2':6',2":6",2":6"',2"''-quinquepyridine) could be converted to a monomeric species simply by adding a strong donor solvent such as pyridine. We therefore anticipated that addition of pyridine to the binuclear nickel helicate might also result in conversion to a monomeric species [7]. Thus, we tried to react 4 with pyridine in order to obtain the mononuclear $[Ni(H_2daps)(py)_2]$ complex. However, this attempt was unsuccessful and we obtained a different binuclear helical Ni complex, $[Ni_2(H_2daps)_2(py)_2] \cdot CH_2Cl_2$ 6, that we have previously reported [16]. The structure of this compound could be rationalised by breaking the pyridine bridges in complex 4 (Scheme 1). The ligands still use one imine nitrogen atom and one carbonyl oxygen atom of one of its molecular threads to join a nickel centre and the same atoms of the second molecular thread to link the second metal atom. The two pyridine nitrogen atoms of the central rings are now linked to the same metal centre, Ni1, acting as terminal, rather than bridging donors. In the absence of donor solvent molecules this would lead to a co-ordination number of six for one metal centre and to a co-ordination number of four for the other one. Two pyridine molecules from the solvent of crystallisation increase the co-ordination number of the second me-



Scheme 1 Reaction of $[Ni_2(H_2daps)_2] \cdot CH_2Cl_2$ 4 with pyridine to yield $[Ni_2(H_2daps)_2(py)_2] \cdot CH_2Cl_2$ 6.

tal centre, Ni2, to six. This experiment seems to indicate that the solvent of crystallisation can lead to different crystal structures. However we could not convert the dinuclear helicate into a monomer.

In view of this unsuccessful attempt we tried to recrystallise the initial bulk material $Ni(H_2daps)$. $(H_2O)_{1.5}(CH_3CN)$ again, as it was perhaps too difficult to break the helical structure once formed. We knew that when the manganese compound prepared electrochemically was recrystallised from ethanol a mononuclear complex forms. Furthermore, the crystal structure of $[Ni(H_4daps)(H_2O)_2](NO_3)_2$, obtained from an ethanol solution, has been reported [21] and the compound is mononuclear. Therefore, an alcohol seemed to be an appropriate solvent to obtain the desired neutral mononuclear complex $[Ni(H_2daps)L_2]$ (L = solvent).Recrystallisation of $Ni(H_2daps)$. $(H_2O)_{1.5}(CH_3CN)$ from methanol resulted in isolation of single crystals of $[Ni_2(H_2daps)_2(CH_3OH)_2]$. $3 \text{ CH}_3 \text{OH} \cdot \text{H}_2 \text{O}$ 5, suitable for X-ray diffraction studies.

FAB mass and IR spectra and magnetic measurements

The FAB mass spectrum of **5** shows a peak assigned to the fragment $[Ni(H_2daps)]^+$ at 488 amu and a second peak, due to the fragment $[Ni(H_2daps)]_2^+$, at 976 amu. This latter peak was previously observed for the bulk material Ni(H₂daps)(H₂O)_{1,5}(CH₃CN). This is in direct contrast to the behaviour of the mononuclear non helical Mn(H₂daps)(H₂O)_{0.5}, which shows no fragments relating to $[Mn(H_2daps)]_2^+$. Therefore it seems that this technique is useful in distinguishing between the presence of mononuclear and dinuclear species.

The IR spectrum also indicates the co-ordination of the ligand to the metal. The bands due to the amide I $[\nu(CO)]$ and amide II $[\delta(NH) + \nu(CN)]$ modes undergo negative shifts of 56 cm⁻¹ and 67 cm⁻¹, respectively, in agreement with the co-ordination of the oxygen atoms of both carbonyl CO groups to the nickel atom. Additionally, the absence of the band at 3208 cm⁻¹, assigned in the free ligand to $\nu(N-H)$, is in accordance with the dianionic character of both H₄daps ligands. The dianionic nature of the ligands is also supported by the magnetic moment of the compound at room temperature (2.9 B.M.), which is in the expected range for Ni(II) in an octahedral environment [16, 22].

Crystal structure of $[Ni_2(H_2daps)_2(CH_3OH)_2] \cdot 3 CH_3OH \cdot H_2O$ 5

An ORTEP view of the structure is shown in Fig. 3. Experimental details are presented in Table 2 and selected bond distances and angles in Table 5.

The compound is a binuclear nickel complex, with the $[H_2daps]^{2-}$ ligands spanning both metal centres. Each ligand uses one imine nitrogen atom (N2, N7), the pyridine nitrogen (N1, N6) atom and one carbonyl oxygen atom (O1, O5) to coordinate to one nickel centre, leading to a co-ordination number of six around Ni1. The remaining imine nitrogen (N4, N9) and carbonyl oxygen (O3, O7) atoms of both $[H_2 daps]^{2-}$ moieties are used to bind the second nickel atom. Two methanol molecules from the solvent of crystallisation complete the co-ordination sphere of this second metal centre (Ni2). Thus, the structure could be related to that found for 6. The environment of both metals could be described as distorted octahedral, as found for $[Ni_2(H_2daps)_2(py)_2] \cdot CH_2Cl_2$, with comparable Ni1...Ni2 distances (ca. 4.5 Å). However, in complex 6 both metal centres are surrounded by an N_4O_2 donor set while in 5 one of the nickel atoms is in a N_4O_2 and the other one in a N_2O_4 environment, due to the replacement of two nitrogen donors (pyridine) by oxygen donor ligands (methanol). The presence of methanol leads to a higher degree of hydrogen bonding in 5. The co-ordinated solvent molecules interact with methanol solvates [distances $O1S \cdots O4S = 2.744(12) \text{ Å}, O2S \cdots O5S = 2.718(11) \text{ Å}].$ A further intramolecular hydrogen bonding interaction is observed between one phenol oxygen atom (O4) and a solvent methanol molecule [distance $O4 \cdots O3S = 2.742(12) A$]. Moreover, intermolecular hydrogen bonds are established between the carbonyl oxygen atoms linked to Ni1 and two different methanol molecules from two neighbouring asymmetric



Fig. 3 An ORTEP view of the crystal structure of $[Ni_2(H_2daps)_2(CH_3OH)_2] \cdot 3 CH_3OH \cdot H_2O$ **5**. Thermal ellipsoids are drawn at the 30% probability level. Lattice CH₃OH and H₂O are not depicted.

Table 5 Selected bond lengths (Å) and angles (°) for $[Ni_2(H_2daps)_2(CH_3OH)_2] \cdot 3 CH_3OH \cdot H_2O 5$

Ni1-O1	2.106(6)	Ni2-O3	2.026(6)
Ni1-O5	2.145(7)	Ni2–O7	2.016(7)
Ni1-N1	2.155(7)	Ni2–O1S	2.127(7)
Ni1-N2	1.995(7)	Ni2–O2S	2.111(7)
Ni1-N6	2.147(7)	Ni2–N4	2.096(7)
Ni1-N7	1.999(7)	Ni2–N9	2.104(7)
Ni1 · · · Ni2	4.372(10)		
N2-Ni1-N1	77.0(3)	N4-Ni2-O1S	164.3(3)
N2-Ni1-N6	107.0(3)	N4-Ni2-O2S	84.2(3)
N2-Ni1-O1	77.2(3)	N4-Ni2-N9	106.7(3)
N2-Ni1-O5	98.1(3)	N9-Ni2-O2S	164.2(3)
N7-Ni1-O5	76.4(3)	N9-Ni2-O1S	84.6(3)
N7-Ni1-O1	91.9(3)	N9-Ni2-O3	106.3(3)
N7-Ni1-N1	113.6(3)	O1S-Ni2-O2S	87.2(3)
N7-Ni1-N6	77.5(3)	O3-Ni2-N4	77.9(3)
N7-Ni1-N2	167.5(3)	O3-Ni2-O1S	88.5(3)
O1-Ni1-O5	94.0(3)	O3-Ni2-O2S	86.8(3)
O1-Ni1-N1	154.1(3)	O7-Ni2-N4	103.9(3)
O1-Ni1-N6	84.9(3)	O7-Ni2-N9	77.3(3)
O5-Ni1-N1	87.7(3)	O7-Ni2-O3	175.4(3)
O5-Ni1-N6	153.9(3)	O7-Ni2-O2S	89.1(3)
N1-Ni1-N6	104.5(3)	O7-Ni2-O1S	89.1(3)

units [distances $O1 \cdots O4S' = 2.889(11) \text{ Å}, O5 \cdots O5S'' = 2.810(11) \text{ Å}].$

An important difference between **5** and **6** is that $[Ni_2(H_2daps)_2(py)_2] \cdot CH_2Cl_2$ is symmetrically related (space group C2/c), with the nickel atoms located in a crystallographic two fold axis. This does not occur in complex **5**, leading to a less symmetrical compound. However all the bond distances and angles are comparable between the complexes and are in the range of those expected for Ni complexes with hydrazone ligands [16, 21, 23].

In spite of the marked similarities between **5** and **6**, some differences can be seen (see Table 6):

1. The Ni2–Nimine distances are clearly shorter for **5** [2.096(7) and 2.104(7)] than for **6** [2.148(12) Å].

2. The Ni1–Ocarbonyl distances are significantly different in 5 [2.106(6) Å and 2.145(7) Å] while they are equal in 6 [2.120(10) Å]. This leads to a more distorted environment around Ni1 in 5. However, no significant differences are observed for the distances Ni2–Ocarbonyl for 5 or for 6, the standard deviations in bond lengths are taking in account. The Nimine-Nhydrazine bonds are also equal for 6 while in 5 one of the Nimine-Nhydrazine bond length is shorter than the other one for one $[H_2daps]^{2-}$ ligand [N2-N3 = 1.370(11) Å and N4-N5 = 1.427(10) Å], thelonger distance corresponding to the thread around Ni2. In addition, the Nhydrazine-Ccarbonyl bonds are also more asymmetrical in 5. One of the bonds in each ligand is significantly longer [1.315(12) Å and 1.366(12) Å; 1.322(12) Å and 1.409(12) Å] and again this corresponds to the thread around Ni2. All these seem to be, newly, an effect of the higher electronegativity of the oxygen atom in methanol compared with the nitrogen atom in pyridine.

The comparison of the crystal structure of 4, 5 and 6, as well as the experimental conditions in which they were obtained, allow us to draw some conclusions. It seems that Ni has a high preference for an octahedral environment and a great tendency to form helicates with appropriate hydrazone ligands. Thus, the solvent of crystallisation does not seem to be able to reverse this tendency although it can change the structure of the helicate. The presence of a very poor donor solvent, such as dichloromethane, force the central pyridine ring

Table 6Comparison of bond lengths (Å) in **5** and **6**

Distance (Å)	$[\mathrm{Ni}_2(\mathrm{H}_2\mathrm{daps})_2(\mathrm{py})_2]^{a)}$	$\begin{array}{c} [\mathrm{Ni}_2(\mathrm{H}_2\mathrm{daps})_2 \cdot \\ (\mathrm{CH}_3\mathrm{OH})_2]^{\mathrm{b})} \end{array}$
Ni1–Npyridine	2.175(11); 2.175(11)	2.147(7); 2.155(7)
Ni1–Nimine	1.990(12); 1.990(12)	1.995(7); 1.999(7)
Ni2–Nimine	2.148(12); 2.148(12)	2.096(7); 2.104(7)
Ni1–Ocarbonyl	2.120(10); 2.120(10)	2.106(6); 2.145(7)
Ni2–Ocarbonyl	2.036(10); 2.036(10)	2.016(6); 2.026(6)
Ni1···Ni2	4.51(2)	4.372(10)
C–Npyridine	1.36(2); 1.34(2)	1.357(11); 1.368(11)
	1.36(2); 1.34(2)	1.343(11); 1.351(11)
Cpyridine–Cimine	1.50(2); 1.44(2)	1.501(13); 1.520(13)
	1.50(2); 1.44(2)	1.488(13); 1.495(12)
C–Nimine	1.30(2); 1.30(2)	1.269(12); 1.275(12)
	1.30(2); 1.30(2)	1.269(11); 1.290(11)
Nimine–Nhydrazine	1.39(2); 1.39(2)	1.370(11); 1.427(10)
-	1.39(2); 1.39(2)	1.368(11); 1.390(10)
Nhydrazine–Ccarbonyl	1.35(2); 1.34(2)	1.315(12); 1.409(12)
	1.35(2); 1.34(2)	1.322(12); 1.366(12)
C–Ocarbonyl	1.28(2); 1.25(2)	1.241(10); 1.285(11)
	1.28(2); 1.25(2)	1.248(10); 1.286(11)
C–Ophenol	1.34(2); 1.27(2)	1.351(14); 1.370(14)
-	1.34(2); 1.27(2)	1.358(12); 1.359(13)
Nhydrazine · · · Ophenol	2.56(2); 2.56(2)	2.505(10); 2.540(10)
		2.569(12); 2.569(12)

^{a)} Ref. 16; ^{b)} This work

of the hydrazone ligand to act as a bridge, in order to satisfy the desire for a co-ordination number of six around the nickel atoms. The addition of a stronger donor solvent, such as methanol, can satisfy the co-ordination number six of both metals, without the need for formation of pyridine bridges, by co-ordination to the metal centre itself. However, the solvent is not able to force the nickel atom to attain a co-ordination number of seven and, thus, to lead to the isolation of the monomer. Similarly, a strong donor solvent such as pyridine, leads to the same situation: a co-ordination number of six around each metal centre is attained without necessity of central pyridine bridges, but this does not convert the helicate into a mononuclear complex.

At this point, we must note that $[Ni(H_4daps) \cdot (H_2O)_2](NO_3)_2$ was previously reported [21] as a mononuclear complex with a pentagonal bipyramidal geometry. Thus, if this has been obtained from an ethanol solution, it seems that there are more factors involved in obtaining helical arrays than the metal, the ligand and the solvent itself. The charge on the ligand seems to be essential in same cases. But, why the neutral ligand H₄daps can easier afford a co-ordination number seven for the nickel centre than the bisdeprotonated ligand? This question still remains unclear but it is the only reasonable difference which can explain the different structures observed in **5** and the related monomer $[Ni(H_4daps)(H_2O)_2](NO_3)_2$.

Conclusions

From the experimental results previously reported by us [16] and others [20, 21, 23] and reported herein by us, we can conclude:

1. Nickel(II) has a higher preference for an octahedral environment than manganese(II), favouring the formation of helicates with appropriate pentadentate hydrazone ligands. Thus, selection of the right ligand and the metal seems to be the first step in the isolation of helical structures.

2. The charge of a pentadentate hydrazone ligand seems to play an active role in the isolation of helicates containing metals with a high preference for an octahedral environment.

3. The solvent of crystallisation can change the structure of one helicate complex. However the rules that govern this change are still unclear. Although it has been reported that a mononuclear cobalt complex could be obtained from a double helical compound in the presence of a donor solvent, the helicates derived from Ni and H_4 daps do not become mononuclear compounds by influence of the crystallisation solvent.

Experimental Section

General: All solvents, 2,6-diacetylpyridine and salicylhydrazide are commercially available and they were used without further purification. Metals (Ega Chemie) were used as *ca*. $2 \times 2 \text{ cm}^2$ plates. Elemental analyses were performed on a Carlo Erba EA 1108 analyser. NMR spectra were recorded on a Bruker WM-250 spectrometer using DMSO-d₆ as solvent. Infrared spectra were recorded as KBr pellets on a Bio-Rad FTS 135 spectrophotometer in the range 4000–600 cm⁻¹. Fast atom bombardment mass spectra (FAB) were obtained on a Kratos MS-50 mass spectrometer, employing Xe atoms at 70 KeV in *m*-nitrobenzylalcohol as a matrix. Room-temperature magnetic susceptibilities were measured using a Digital Measurement system MSB-MKI, calibrated using tetrakis(isothiocyanato)cobaltate(II).

Preparation: 2,6-bis(1-salicyloylhydrazonoethyl)pyridine,

 H_4 daps, was prepared as previously described [2]. The purity of the ligand was checked by ¹H NMR and IR spectroscopy. The yield was almost quantitative.

¹H NMR(250 MHz, DMSO-d₆): $\delta = 2.50$ (s, 6 H), 6.97–8.17 (m, 11 H), 11.51 (s, b, 2 H), 11.80 (b, 2 H) ppm.

IR (KBr): v(NH) 3208 cm⁻¹.

Mn(H₂daps)(H₂O)_{0.5} and Ni(H₂daps)(H₂O)_{1.5}(CH₃CN): The complexes Mn(H₂daps)(H₂O)_{0.5} and Ni(H₂daps)(H₂O)_{1.5} · (CH₃CN) were obtained using an electrochemical procedure [16, 17].

An acetonitrile solution of the ligand containing about 10 mg of tetramethylammonium perchlorate, as supporting electrolyte, was electrolysed using a platinum wire as the cathode and a metal plate as the anode. The cell can be summarised as:

 $Pt_{(-)}|H_4daps + MeCN|M_{(+)}$, where M stands for the metal.

The synthesis of $Mn(H_2daps)(H_2O)_{0.5}$ and $Ni(H_2daps) \cdot (H_2O)_{1,5}(CH_3CN)$ is typified by the preparation of $Mn(H_2daps)(H_2O)_{0.5}$: A suspension of the ligand (0.2 g, 0.464 mmol) in acetonitrile (80 mL), containing tetramethyl-ammonium perchlorate (ca. 10 mg), was electrolysed for 2.5 h. using a current of 10 mA. Concentration of the resulting solution to a third of its initial volume yielded a solid that was washed with diethyl ether and dried under vacuum. Analytical and some selected data are given in Table 1.

Diffusion of dichloromethane into a pyridine solution containing $Mn(H_2daps)(H_2O)_{0.5}$, yields crystals of $[Mn(H_2daps) \cdot (py)_2]$ **1**, previously reported [16]. Slow evaporation of an ethanol solution of $Mn(H_2daps)(H_2O)_{0.5}$ allows the isolation of crystals of $[Mn(H_2daps)(C_2H_5OH)(H_2O)]$ **2**, suitable for X-ray diffraction studies.

 $Ni(H_2daps)(H_2O)_{1.5}(CH_3CN)$ was obtained by the same electrochemical procedure. Its crystallisation from dichloromethane/hexane and from methanol produced crystals of $[Ni_2(H_2daps)_2] \cdot CH_2Cl_2$ **4**, as previously described [16] and $[Ni_2(H_2daps)(CH_3OH)_2] \cdot 3 CH_3OH \cdot H_2O$ **5**, respectively, also suitable for X-ray diffraction.

Yellow crystals of $[Ni_2(H_2daps)_2(py)_2] \cdot CH_2Cl_2$ 6, suitable for single-crystal X-ray studies, were obtained by diffusion of dichloromethane into a pyridine solution of $[Ni_2(H_2daps)_2] \cdot CH_2Cl_2$ [16].

Crystallographic measurements. Crystal data and details of refinement are given in Table 2.

 $[Mn(H_2daps)(C_2H_5OH)(H_2O)]$ 2 and $[Ni_2(H_2daps)_2 \cdot (CH_3OH)_2] \cdot 3 CH_3OH \cdot H_2O$ 5. Block like orange crystals of 2 and block yellow-green crystals of 5 were obtained as described above. Data were collected at 298 K using a Siemens CCD diffractometer employing graphite-monochro-

mated Mo–K α ($\lambda = 0.71073$ Å) radiation, using the ω scan mode. The structures were solved by direct methods and refined by full matrix least squares [24–26]. An absorption correction (Sadabs) was applied. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were included in calculated positions except those attached to the water oxygen atom in **2**. These were located in an electronic density map and isotropically refined.

Acknowledgements: We thank to Xunta de Galicia for financial support (XUGA 20901B 97).

References

- [1] D. Wester, G. J. Palenik, Inorg. Chem. 1976, 15, 755.
- [2] C. Pelizzi, G. Pelizzi, J. Chem. Soc., Dalton Trans. 1980, 1970.
- [3] C. Pelizzi, G. Pelizzi, F. Vitali, J. Chem. Soc., Dalton Trans. 1987, 177.
- [4] C. Carini, G. Pelizzi, P. Tarasconi, C. Pelizzi, K. C. Molloy, P. C. Waterfield, J. Chem. Soc., Dalton Trans. 1989, 289.
- [5] A. Bonardi, C. Carini, C. Merlo, C. Pelizzi, G. Pelizzi, P. Tarasconi, F. Vitali, F. Cavatorta, J. Chem. Soc., Dalton Trans. 1990, 2771.
- [6] E. C. Constable, Tetrahedron 1992, 48, 10013.
- [7] E. C. Constable, in: Comprehensive Supramolecular Chemistry, J. L. Atwood, J. E. D. Davies, D. D. McNicol, F. Vögtle, J. P. Sauvage, M. W. Hosseini (eds), Vol. 9, Pergamon, Oxford, 1996, p. 213.
- [8] K. Andjelkovic, Y. Ivanovic, S. R. Niketic, B. Prelesnik, V. M. Leovac, *Polyhedron* 1997, 16, 4221.
- [9] S. Abram, C. Maichle-Mössmer, U. Abram, *Polyhedron* 1998, 17, 131.
- [10] M. Carcelli, P. Mazza, C. Pelizzi, G. Pelizzi, F. Zani, J. Inorg. Biochem. 1995, 57, 43 and references therein.
- [11] A. Bacchi, A. Bonardi, M. Carcelli, P. Mazza, P. Pelagatti, C. Pelizzi, G. Pelizzi, C. Solinas, F. Zani, J. Inorg. Biochem. 1998, 69, 101.

- [12] A. R. Todeschini, A. L. P. De Miranda, K. C. M. Da Silva, S. C. Parrini, E. J. Barreiro, *Eur. J. Med. Chem.* **1998**, *33*, 189.
- [13] O. Kahn, Angew. Chem., Int. Ed. Engl. 1985, 24, 834.
- [14] J. M. Williams, M. A. Beno, K. D. Carlson, U. Geiser, H. C. J. Kao, A. M. Kini, L. C. Porter, A. J. Schultz, R. J. Thorn, H. H. Wang, M.-H. Wanyho, M. Evain, Acc. Chem. Res. 1988, 21, 1.
- [15] R. Sumita, D. D. Mishra, R. V. Maurya, N. Nageswara, *Polyhedron* **1997**, *16*, 1825.
- [16] M. R. Bermejo, M. Fondo, A. M. González, O. L. Hoyos, A. Sousa, C. A. McAuliffe, W. Hussain, R. G. Pritchard, V. M. Novotorsev, J. Chem. Soc., Dalton Trans. 1999, 2211.
- [17] J. Romero, J. A. García-Vázquez, M. L. Durán, A. Castiñeiras, A. Sousa, A. D. Garnovskii, D. A. Garnovskii, *Acta Chem. Scand.* **1997**, *51*, 672.
- [18] A. Bonardi, C. Merlo, C. Pelizzi, G. Pelizzi, P. Tarasconi, F. Cavatorta, J. Chem. Soc., Dalton Trans. 1991, 1063.
- [19] J. Sanmartín, M. R. Bermejo, A. Sousa, M. Fondo, E. Gómez-Fórneas, C. A. McAuliffe, *Acta Chem. Scand.* 1997, 51, 59.
- [20] C. Pelizzi, G. Pelizzi, G. Predieri, S. Resola, J. Chem. Soc., Dalton Trans. 1982, 1342.
- [21] C. Pelizzi, G. Pelizzi, S. Porretta, F. Vitali, Acta Crystallogr., Sect. C, 1986, 42, 1131.
- [22] D. Volkmer, B. Hommerich, K. Griesar, W. Haase, B. Krebs, *Inorg. Chem.* **1996**, *35*, 3792.
- [23] G. Paolucci, S. Stelluto, S. Sitran, D. Ajo, F. Benetollo, A. Polo, G. Bombieri, *Inorg. Chim. Acta* 1992, 57, 153.
- [24] G. M. Sheldrick, SHELXS-86, in *Crystallographic Computing*, G. M. Sheldrick, C. Krueger, R. Goddard (eds), Oxford University Press, **1985**, p. 175.
- [25] G. M. Sheldrick, *Program for the refinement of crystal structures*, University of Göttingen, Germany, **1993**.
- [26] G. M. Sheldrick, SHELX97 Programs for Crystal Structure Analysis, Institut f
 ür Anorganische Chemie der Universität G
 öttingen, Germany, 1998.