

Metal Complexes of a Novel Achiral Symmetric Pentadentate Ligand – Crystal Structures of Monohelical Zinc(II) and Cadmium(II) Complexes

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By both electrochemical synthesis and a traditional chemical procedure the interaction of the pentadentate ligand 2,6-bis{1-[2-(tosylamino)phenylimino]ethyl}pyridine (H₂DAPATs), with Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II} gives rise to neutral mononuclear complexes that have been characterised by elemental analyses, FAB mass spectrometry, IR, ¹H and COSY NMR spectroscopy and magnetic measurements, where appropriate. Recrystallisation of the zinc complex obtained electrochemically yielded single crystals of [Zn(DAPATs)] (1), while recrystallisation of cadmium complexes obtained by both techniques afforded the same structure,

[Cd(DAPATs)(H₂O)] (2). Both 1 and 2 are monohelical single-stranded compounds with different coordination geometries. In the zinc complex, the metal ion assumes a distorted trigonal-bipyramidal geometry involving the N₅ atoms of the dianionic ligand. For cadmium complexes the metal ion is in a distorted pentagonal-pyramidal environment, as the result of coordination to the N₅ ligand donor set and an additional water molecule.

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Introduction

Helical complexes are an active research area in supramolecular chemistry.^[1–5] Nevertheless, predicting the outcome of a self-assembly process is still difficult and dependent upon numerous factors, such as the nature of the metal (coordination numbers and stereochemical preferences), the structure of the ligand, the existence of weak non-covalent interactions, etc.

Most ligands employed in the synthesis of helicates are predominantly benzimidazole,^[6] catecholate^[7] or polypyridine types,^[8] and they usually imply long and complicated synthetic routes. More recently, readily prepared Schiff-base ligands have been used to obtain helical species.^[9,10]

In recent years part of our research program has focused on using pentadentate hydrazone ligands derived from 2,6-diacetylpyridine to produce helical compounds.^[10–12] Previous works have demonstrated that such ligands react with metal chlorides to yield complexes containing the non-deprotonated ligand, while complexes with the bis(deprotonated) ligand could be obtained with metal acetates.^[13,14] We have recently found that pentadentate ligands incorporating a rigid spacer such as pyridine yield dinuclear helical complexes for Ni^[10,11] and Cu^[15] and non-helical mononuclear

complexes for Mn,^[10,11] Co^[10] and Cd^[12] by electrochemical synthesis.

We have also shown that introducing bulky tosyl groups in Schiff-base ligands with different spacers is very useful in obtaining mono- and dihelical species.^[16]

We then wanted to check the effect of the simultaneous presence of a bulky group, such as tosyl, and a rigid spacer, like pyridine, in a pentadentate Schiff-base ligand. Therefore, we have designed the novel pentadentate N₅ ligand 2,6-bis{1-[2-(tosylamino)phenylimino]ethyl}pyridine (H₂DAPATs).

The interaction of H₂DAPATs with Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} and Cd^{II} using electrochemical and chemical procedures was investigated and the results obtained are described herein.

Results and Discussion

Synthesis of the Ligand

The Schiff base H₂DAPATs has been prepared according to a two-step synthetic route (Scheme 1) with an overall yield of 50%. The first step involves the *N*-tosylation of 1,2-diaminobenzene^[17] (I), to obtain 2-(tosylamino)aniline (II). Treatment of II with 2,6-diacetylpyridine in a 1:2 stoichiometric ratio in ethanol under reflux yields the N₅ Schiff-base ligand H₂DAPATs.

The deep yellow powdery solid formed was satisfactorily characterised by elemental analysis, FAB mass spec-

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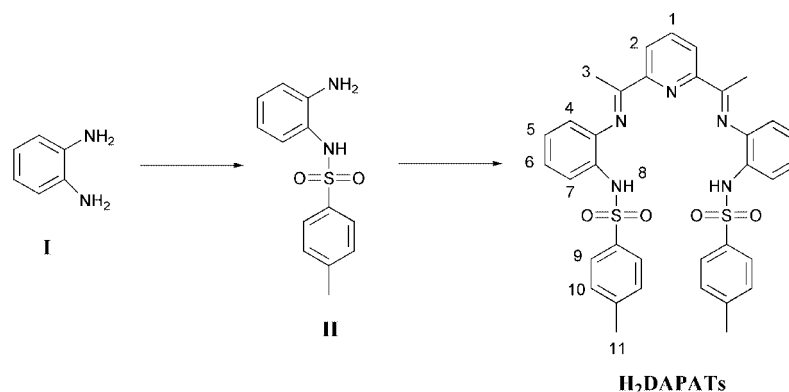
Scheme 1. Synthesis of H₂DAPATs

Table 1. Elemental analysis and selected data for the ligand and its complexes obtained by electrochemical synthesis

Compound	Yield (%)	Colour	C ^[a]	H ^[a]	N ^[a]	S ^[a]	FAB ^[b]	μ ^[c]
H ₂ DAPATs	50	yellow	55.3 (55.4)	5.0 (4.9)	9.0 (9.2)	8.2 (8.4)	652	—
Mn(DAPATs)(H ₂ O) ₃	85	brown	55.1 (55.3)	4.7 (4.9)	9.1 (9.2)	8.5 (8.4)	705	5.6
Fe(DAPATs)(H ₂ O) ₃	55	brown	57.6 (57.8)	4.6 (4.8)	9.7 (9.6)	8.8 (8.8)	706	5.0
Co(DAPATs)(H ₂ O)	95	black	56.3 (56.5)	4.9 (4.7)	9.4 (9.4)	8.6 (8.6)	709	3.9
Ni(DAPATs)(H ₂ O) ₂	85	brown	54.7 (54.8)	4.8 (4.6)	8.0 (8.1)	8.4 (8.1)	709	2.9
Cu(DAPATs)(H ₂ O) ₃	55	black	54.7 (54.8)	4.8 (4.6)	8.0 (8.1)	8.4 (8.1)	713	2.0
Zn(DAPATs)(H ₂ O) ₂	95	orange	56.1 (55.9)	4.9 (4.7)	9.2 (9.3)	8.4 (8.5)	716	—
Cd(DAPATs)(H ₂ O)	95	orange	53.8 (53.9)	4.2 (4.3)	8.8 (9.0)	8.1 (8.2)	765	—

[a] Found (calcd.). [b] amu; peaks corresponding to [ML]⁺. [c] In B.M.

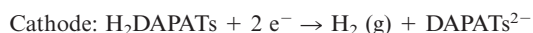
Table 2. Selected IR data [cm⁻¹] for the ligand and its complexes obtained by electrochemical synthesis

Compound	ν(N–H)	ν(C=N)	ν(C–N) _{py}	ν _{as} (SO ₂)	ν _s (SO ₂)
H ₂ DAPATs	3273 m	1627 s	1596 s	1335 s	1167 s
Mn(DAPATs)(H ₂ O) ₃	—	1656 s	1597 s	1335 s	1162 s
Fe(DAPATs)(H ₂ O) ₃	—	1636 s	1596 s	1361 s	1159 s
Co(DAPATs)(H ₂ O)	—	1621 m	1590 s	1374 s	1154 s
Ni(DAPATs)(H ₂ O) ₂	—	1656 m	1588 s	1372 s	1163 s
Cu(DAPATs)(H ₂ O) ₃	—	1621 m	1590 s	1381 s	1138 s
Zn(DAPATs)(H ₂ O) ₂	—	1634 m	1587 s	1370 s	1138 s
Cd(DAPATs)(H ₂ O)	—	1636 s	1586 s	1370 s	1130 s

trometry, IR and ¹H and COSY NMR spectroscopy (Tables 1, 2 and 6).

Synthesis of the Complexes

A series of neutral complexes were obtained by electrochemical oxidation of the corresponding metal anode in the presence of the ligand.^[18] The electrochemical efficiency of the cell was close to 0.5 mol·F⁻¹, which is compatible with the following reaction scheme:



This synthetic procedure allowed us to obtain neutral complexes of the type M(DAPATs)(H₂O)_n with high purity and in very good yield.

These metal compounds were also obtained by a traditional chemical procedure, in which a solution of the ligand was refluxed in the presence of a metal(II) acetate. As the characterisation patterns of these complexes are similar to those obtained by electrochemical synthesis we shall discuss only the latter ones.

Elemental analyses (Table 1) show that metal ions react with the ligand in a molar ratio of 1:1 to afford solvated complexes of the bis(deprotonated) ligand DAPATs²⁻. These neutral complexes are either insoluble or sparingly soluble in water and common organic solvents, but soluble in polar coordinating organic solvents such as DMSO, DMF and pyridine. The powdery complexes appear to be stable both in the solid state and in solution, and all of them melt above 300 °C without decomposition.

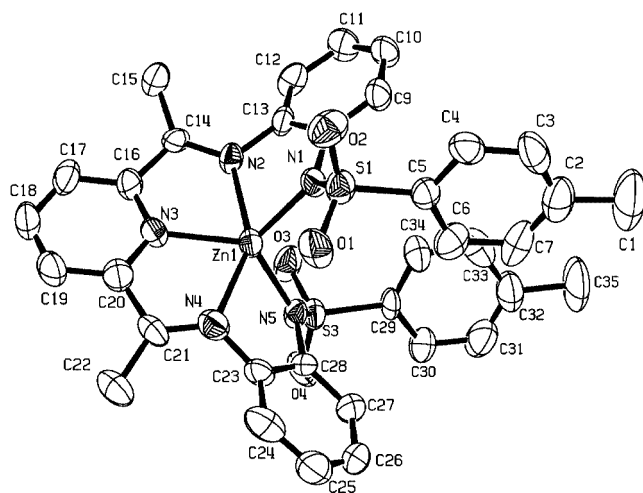
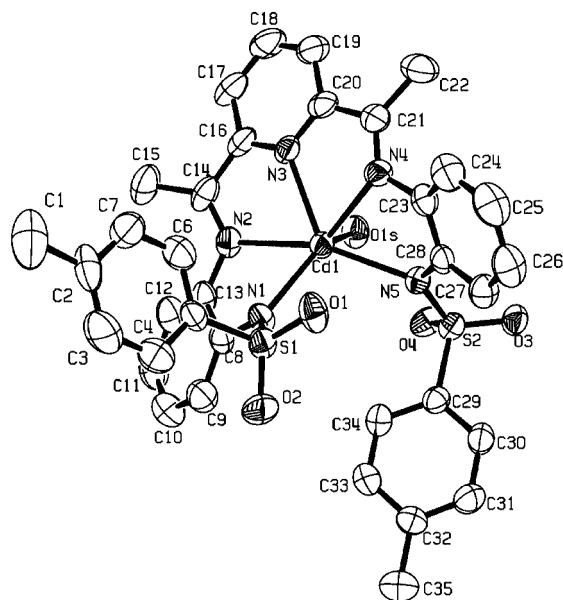
X-ray Studies

The crystal structures of complexes [Zn(DAPATs)] (1) and [Cd(DAPATs)(H₂O)] (2) are shown in Figures 1, 2 and 3. Selected bond lengths and angles are given in Tables 4 and 5. The complexes are considered together here in order to comment on their structural similarities and differences.

They consist of discrete neutral molecules of [Zn(DAPATs)] (1) and [Cd(DAPATs)(H₂O)] (2), the ligand being bis(deprotonated), DAPATs²⁻. In complex 1 all five nitrogen donor atoms of the ligand (two imine, two amide and one pyridine nitrogen atoms) bind to the same zinc ion. No additional ligands are coordinated to the zinc ion, resulting in a coordination number of five and a distorted bipyramidal-trigonal geometry. In this complex the Schiff-base li-

Table 3. Crystal data and structure refinement for **1** and **2**

	[Zn(DAPATs)] (1)	[Cd(DAPATs)(H ₂ O)] (2)
Empirical formula	C ₃₅ H ₃₁ N ₅ O ₄ S ₂ Zn	C ₃₅ H ₃₃ CdN ₅ O ₅ S ₂
Formula mass	715.14	780.18
Temperature [K]	293.0(2)	298.0(2)
Crystal system	triclinic	monoclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> [Å]	9.3474(14)	11.2037(10)
<i>b</i> [Å]	10.8789(14)	10.6130(2)
<i>c</i> [Å]	17.853(3)	28.4432(3)
α [°]	73.691(3)	90
β [°]	84.882(3)	97.46(7)
γ [°]	65.678(3)	90
<i>Z</i>	2	4
Volume [Å ³]	1587.1(4)	3353.41(8)
Absorption coefficient [mm ⁻¹]	0.954	0.826
Crystal size [mm]	0.15 × 0.10 × 0.02	0.24 × 0.20 × 0.14
Reflections collected	10909	17862
Independent reflections	3900 [<i>R</i> (int) = 0.0925]	8197 [<i>R</i> (int) = 0.0824]
Absorption correction	SADABS	SADABS
Data/restraints/parameters	3900/0/424	8197/0/437
Final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)]	<i>R</i> 1 = 0.0432 <i>wR</i> 2 = 0.0821	<i>R</i> 1 = 0.0697 <i>wR</i> 2 = 0.1099
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1343 <i>wR</i> 2 = 0.1368	<i>R</i> 1 = 0.1533 <i>wR</i> 2 = 0.1457

Figure 1. ORTEP view of the crystal structure of [Zn(DAPATs)] (**1**); ellipsoids are drawn at 50% of probability; hydrogen atoms have been omitted for clarityFigure 2. ORTEP view of the crystal structure of [Cd(DAPATs)(H₂O)] (**2**); ellipsoids are drawn at 50% of probability; hydrogen atoms have been omitted for clarity

gand fulfills all the stereochemical requirements of the metal, and subsequently it can be considered a saturated compound.^[4]

However, **2** is an unsaturated compound because the cadmium ion is coordinated to the same five nitrogen donor atoms of the bis(deprotonated) ligand but also needs one additional water molecule, leading to a coordination number of six and to a distorted pentagonal-pyramidal geometry.

This geometry is unusual for cadmium complexes derived from pentadentate Schiff-base ligands because, to the best of our knowledge, only one such cadmium complex with this type of geometry has been previously reported.^[12] In

addition, helicity in cadmium compounds is uncommon – only two monohelical cadmium complexes with Schiff-base ligands have been reported.^[12,19]

For complex **1** the Zn–N_{imine} distances [Zn(1)–N(2) 2.160(6) Å, Zn(1)–N(4) 2.172(7) Å] are of the order of those found for the unique monohelical zinc complex reported with similar geometry,^[20] [Zn(SpyNpy₂)]²⁺. The distance Zn–N_{pyridine} [Zn(1)–N(3) 2.102(7) Å] is shorter than those found for penta-^[21] or heptacoordinated^[13,22] com-

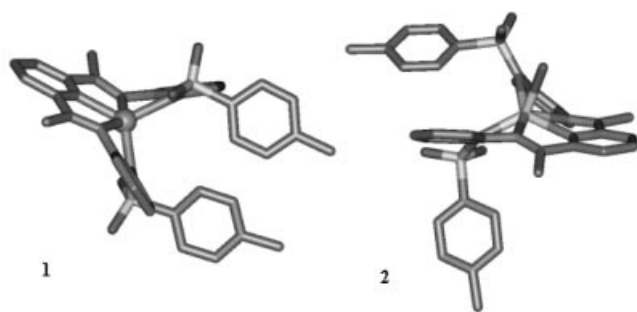


Figure 3. Stick view of [Zn(DAPATs)] (**1**) and [Cd(DAPATs)(H₂O)] (**2**), showing the screwing of the ligand

Table 4. Selected bond lengths [Å] for **1** and **2**

[Zn(DAPATs)] (1)		[Cd(DAPATs)(H ₂ O)] (2)	
Zn(1)–N(5)	2.006(7)	Cd(1)–N(1)	2.237(4)
Zn(1)–N(1)	2.017(6)	Cd(1)–N(5)	2.345(4)
Zn(1)–N(3)	2.102(7)	Cd(1)–N(3)	2.350(5)
Zn(1)–N(2)	2.160(6)	Cd(1)–N(4)	2.360(4)
Zn(1)–N(4)	2.172(7)	Cd(1)–O(1s)	2.377(4)
Zn(1)···O(1)	3.052	Cd(1)–N(2)	2.464(5)
Zn(1)···O(2)	4.147	Cd(1)···O(1)	3.126
Zn(1)···O(3)	3.092	Cd(1)···O(2)	4.475
Zn(1)···O(4)	4.273	Cd(1)···O(3)	4.749
		Cd(1)···O(4)	3.540

Table 5. Selected bond angles [°] for **1** and **2**

[Zn(DAPATs)] (1)		[Cd(DAPATs)(H ₂ O)] (2)	
N(5)–Zn(1)–N(1)	108.9(3)	N(1)–Cd(1)–N(5)	105.3(16)
N(1)–Zn(1)–N(2)	75.9(3)	N(1)–Cd(1)–N(2)	67.7(16)
N(3)–Zn(1)–N(2)	73.3(3)	N(2)–Cd(1)–N(3)	66.8(17)
N(3)–Zn(1)–N(4)	73.7(3)	N(3)–Cd(1)–N(4)	73.7(17)
N(5)–Zn(1)–N(4)	75.4(3)	N(5)–Cd(1)–N(4)	69.4(15)
C(5)–S(1)–N(1)	108.2(4)	N(1)–Cd(1)–O(1s)	125.2(15)
C(29)–N(5)–S(3)	108.4(4)	N(5)–Cd(1)–O(1s)	83.9(14)
		N(3)–Cd(1)–O(1s)	81.5(14)
		N(2)–Cd(1)–O(1s)	81.7(14)
		N(4)–Cd(1)–O(1s)	101.8(14)
		C(5)–S(1)–N(1)	107.0(3)
		C(29)–S(2)–N(5)	111.1(2)

plexes with pentadentate ligands containing Zn–N_{pyridine} bonds.

For complex **2** all Cd–N distances are significantly longer than the corresponding Zn–N distances, and in both complexes M–N_{imine} are longer than M–N_{amide}. In addition, the Cd–N_{pyridine} bond [Cd(1)–N(3) 2.350(5) Å] is shorter than that of the distorted pyramidal-pentagonal cadmium complex with the pentadentate Schiff base H₄daps^[12] [2.403(6) Å], but longer than those found in octahedral complexes with quite similar Schiff-base ligands (ranging from 2.310 to 2.346 Å).^[23–26]

The distance Cd–O(1s) [2.377(4) Å] is of the order of those found for similar cadmium complexes.^[12]

The remaining distances for both compounds are in the usual range for complexes derived from Schiff-base ligands

containing tosyl groups^[16,27,28] and do not merit further analysis.

The four bond angles N–Zn–N formed by the four chelate rings are close to 75°. The fifth one, N(5)–Zn(1)–N(1), is 108.9(3)°. These values explain the distorted trigonal-bipyramidal geometry adopted in **1**. In complex **2** the distortion from the ideal geometry is clearly shown by the angles between water, cadmium and the donor set of the ligand (Table 5). Four of the five angles subtended at Cd by adjacent equatorial atoms are slightly smaller than those of an ideal pentagonal-pyramidal arrangement, being close to 70°, while the fifth, N(1)–Cd(1)–N(5) is 105.33(16)°. Moreover three bond angles O(1s)–Cd(1)–N are in the range 81–84° while the other two are in the range 101–125°, reinforcing the highly distorted pyramidal-pentagonal geometry adopted by **2**.

The bond angles C(5)–S(1)–N(1) and C(29)–S(3)–N(5) are quite similar for the zinc complex [108.2(4) and 108.7(4)°, respectively]; both tosyl groups adopt a similar conformation (Figure 3). Nevertheless, in the cadmium complex these angles, C(5)–S(1)–N(1) and C(29)–S(2)–N(5), are slightly different [107.0(3) and 111.1(2)°, respectively], causing an *anti* orientation of the tosyl groups to reduce the steric hindrance.

Why do zinc and cadmium complexes show different coordination numbers and geometries? We suggest that two factors could be responsible:

i. Steric hindrance of the bulky tosyl groups.

The pentadentate dianionic ligand, DAPATs^{2–}, is wrapped around the metal ions to afford a helical arrangement in both complexes. This screwed disposition of the ligand seems to be clearly favoured by the two terminal bulky tosyl groups. The steric hindrance these groups induce appears to provoke a twisting of the Schiff base to minimise the sterically unfavourable interactions.

Therefore, a rigid spacer such as pyridine, containing a donor atom, and the torsion around the C=N bonds will allow the imine nitrogen atoms to be quite close (ca. 4.2 Å for **1** and 4.4 Å for **2**) and coordinate to the same metal centre. This permits the five nitrogen atoms to bind to the same metal centre, leading to the isolation of mononuclear single-stranded helical complexes.

ii. Closeness of the tosyl oxygen atoms to the metal centre.

For **1**, one oxygen atom of each tosyl group, O(1) and O(3), seems to weakly interact with the metal ion [distances O(1)···Zn(1) 3.052 Å and O(3)···Zn(1) 3.092 Å]. These Zn···O distances are too long to be true coordinated bonds, but could be considered as secondary intramolecular interactions that could be responsible for the distorted trigonal-bipyramidal disposition around the metal centre, instead of the usual bipyramidal-pentagonal or pyramidal-pentagonal geometries, because these oxygen atoms avoid coordinating additional donor ligands in the apical positions.

In complex **2** the bigger cadmium ion leads to longer metal–donor distances, in general, and in Cd–O_{tosyl} especially. Thus, only one oxygen atom of one tosyl group, O(1) could weakly interact with the cadmium ion [distance

Cd(1)⋯O(1) 3.126 Å], while in the other tosyl group both oxygen atoms are too far to interact with the cadmium ion [Cd(1)⋯O(4) 3.540 Å, Cd(1)⋯O(3) 4.749 Å]. Such a situation affords an easy entrance and binding for a new additional ligand such as water, increasing the coordination number to six.

Thus, the different monohelical dispositions of these two complexes can be attributed to the tosyl groups, which show different spatial orientations (Figure 3). In the zinc complex the angle between the benzene rings of the tosyl groups is 11.75°. This nearly parallel orientation for the terminal tosyl aromatic rings is unusual for complexes with Schiff-base ligands containing these bulky groups. It can be explained by the lack of superposition of the tosyl groups, which avoid the unfavourable steric interactions.

In the cadmium complex the angle between the benzene rings is 47.60°, yielding a spatial conformation quite similar to that of other monohelical complexes derived from tetradentate Schiff bases containing tosyl groups.^[16]

The DAPATs²⁻ thread forms four five-membered chelate rings around the metal centres. The angles between adjacent calculated chelate planes (36.65 and 37.76° for **1**; 29.48 and 26.10° for **2**) confirm the different twisting degree of the ligand for both complexes. The smaller degree of twisting for the cadmium complex is also confirmed by the angles formed between the benzyldiene rings (63.45° for **1** and 37.21° for **2**).

If the tosyl groups are not considered, we can clearly observe that the wrapping angle is less than 360°, and slightly higher for the zinc complex than for the cadmium (287° for **1** and 274° for **2**). All these considerations agree with the ionic radius of the metals, as expected. The size of the cadmium ion forces the N₅ donor set of the ligand to deviate from planarity when it surrounds this metal, resulting a smaller twisting degree.

[Zn(DAPATs)] crystallises in the achiral space group *P* $\bar{1}$ and [Cd(DAPATs)(H₂O)] in *P*(2)₁/*c*, so that both right- (*P*) and left-handed (*M*) helices^[4] can be simultaneously observed (in 50% yields) in their unit cells. Helicates obtained from ligands not containing chiral groups usually crystallise as racemic mixtures and self-recognition is not a very common process.

Finally, no face-to-face π -stacking interactions between the terminal tosyl aromatic rings can be identified in either complex.

FAB Mass and IR Spectra

All the FAB mass spectra show peaks due to the fragments [M(DAPATs)]⁺, indicating ligand coordination to the metal centres (Table 1). No additional peaks appear, suggesting that the complexes are mononuclear.

The IR spectra of the complexes (Table 2) show a strong band between 1621 and 1656 cm⁻¹ attributable to ν (C=N). This band appears 6 cm⁻¹ shifted to lower energy from that in cobalt and copper complexes. With manganese, iron, nickel, zinc and cadmium complexes the ν (C=N) band is shifted to higher wavenumbers (7–29 cm⁻¹), indicating a slight shift of charge towards the CN group on coordination. However, the ν (C–N)_{py} stretching frequency is not shifted for manganese and iron complexes and is slightly shifted to lower energy (6–10 cm⁻¹) for the other compounds. This behaviour is compatible with the participation of both imine and amide nitrogen atoms in the coordination to the metal centres. Additionally, two bands in the ranges 1335–1381 and 1130–1167 cm⁻¹ are assigned to the asymmetric and symmetric vibration modes of SO₂ groups, respectively.^[29,30]

Furthermore, no bands around 3270 cm⁻¹ are seen, indicating the deprotonation of the NH groups, and therefore the dianionic character of the ligand.

Finally, the ν (O–H) bands around 3400 cm⁻¹ agree with the hydrate nature of these complexes.

Magnetic Characterisation

Magnetic measurements were performed at room temperature for all paramagnetic complexes. Their magnetic moments are close to those expected for magnetically dilute M^{II} ions, confirming the oxidation state II for the central atom and, therefore, that the ligands are dianionic.

¹H NMR Spectroscopy

The ¹H NMR spectra of the zinc and cadmium complexes were recorded in [D₆]DMSO at room temperature and CD₃CN at low temperatures (273 and 233 K). Selected ¹H NMR data are shown in Table 6. The room-temperature spectra were totally assigned by COSY experiments. The spectra do not show significant changes with temperature, being quite similar to those recorded at room temperature. All spectra show a single set of signals that could be completely assigned. This seems to indicate a single species in

Table 6. Selected ¹H NMR spectroscopic data for the ligand H₂DAPATs and its diamagnetic complexes (in ppm)

Compound	H1	H2	H3	H4	H5	H6	H7	H8	H9	H10	H11
H ₂ DAPATs	8.09 (t, 1 H)	8.31 (d, 2 H)	2.06 (s, 6 H)	6.75 (d, 2 H)	7.10 (t, 2 H)	7.09 (t, 2 H)	7.32 (d, 2 H)	9.34 (s, 2 H)	7.56 (d, 4 H)	7.21 (d, 4 H)	2.31 (s, 6 H)
Zn(DAPATs)(H ₂ O) ₂	8.57 (t, 1 H)	8.47 (d, 2 H)	2.60 (s, 6 H)	7.31 (m, 2 H)	7.19 (t, 2 H)	7.28 (m, 2 H)	7.48 (d, 2 H)	—	7.36 (d, 4 H)	7.09 (d, 4 H)	2.20 (s, 6 H)
Cd(DAPATs)(H ₂ O)	8.50 (t, 1 H)	8.37 (d, 2 H)	2.48 (s, 6 H)	7.23–7.12 (m, 2 H)	7.23–7.12 (m, 2 H)	6.88 (t, 2 H)	7.23–7.12 (m, 2 H)	—	7.64 (d, 4 H)	7.03 (d, 4 H)	2.24 (s, 6 H)

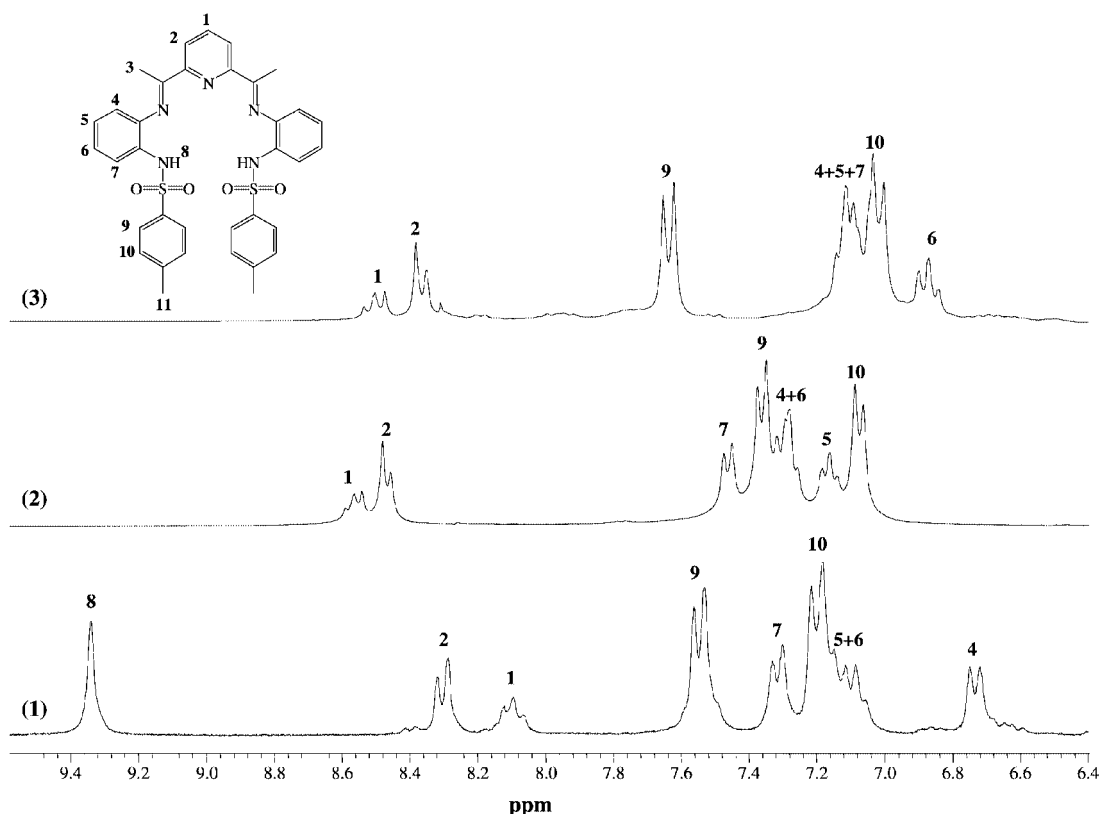


Figure 4. ^1H NMR spectra in $[\text{D}_6]\text{DMSO}$ at room temperature for: (1) H_2DAPATs , (2) $\text{Zn}(\text{DAPATs})(\text{H}_2\text{O})_2$ and (3) $\text{Cd}(\text{DAPATs})(\text{H}_2\text{O})_2$

solution. Comparison of the ^1H NMR spectrum of the free ligand with those of the complexes (Figure 4) shows some interesting aspects:

- The NH (H8) protons present in the free ligand disappear for both complexes, in agreement with the bis(deprotonation) of the ligand.

- The aromatic proton signals of the pyridine ring are shifted downfield, and the displacements are higher for the zinc complex. The spectra show that complexation through the $\text{N}_{\text{pyridine}}$ atom affects the environments of the H1 and H2 atoms, and these signals appear with their positions exchanged with respect to the free ligand.

- The aromatic proton signals of the tosyl groups also shift on complexation, but the displacements differ for the zinc and cadmium complexes. For the zinc complex the H9 and H10 signals are shifted upfield, whilst in the cadmium compound the H10 signal is shifted upfield and the H9 signal is shifted downfield. This could be attributed to an interaction between the tosyl groups and the metal centres, as the solid-state X-ray structures of **1** and **2** seem to confirm.

- The aromatic proton signals of the benzylidene rings also appear to show different behaviour on complexation. In the zinc complex the H5 signal moves its position slightly while the H4, H6 and H7 signals are shifted downfield, with the H4 and H6 signals overlapped. With the cadmium complex the H4, H5 and H7 signals are completely overlapped. The H5 signal does not show significant changes in its position, while the H6 and H7 signals are shifted upfield and the H4 signal is strongly shifted downfield.

- Finally, in both complexes the methyl proton signals corresponding to tosyl and acetyl groups are shifted slightly downfield.

Comparison of the ^1H NMR spectra of zinc and cadmium complexes suggests that the tosyl groups adopt different spatial orientations in each complex, as the X-ray structures confirm, because of the size of the metal ions and their different geometrical preferences.

From the characterisation techniques employed in this work, some general points can be made. All complexes seem to be mononuclear, as FAB mass spectrometry suggests. The magnetic studies, the similar IR patterns and X-ray results agree with the coordination of the N_5 donor set of the ligand to the metal centres. In addition ^1H NMR studies, and other data, indicate that the solid-state structures of **1** and **2** are retained in solution.

Conclusion

The novel potentially dianionic and pentadentate Schiff-base ligand H_2DAPATs readily stabilises neutral mononuclear complexes of Mn^{II} , Fe^{II} , Co^{II} , Ni^{II} , Cu^{II} , Zn^{II} and Cd^{II} formed by either an electrochemical method or a traditional chemical procedure. The electrosynthesis is both simpler and shorter.

The rigid spacer in this ligand, such as pyridine, and the bulky terminal groups, such as tosyl, favour the formation of monohelical single-stranded compounds.

It thus seems that careful design of the ligand is useful in controlling the selective formation of monohelical complexes.

Experimental Section

General: Elemental analyses were performed with a Carlo Erba EA 1108 analyser. NMR spectra were recorded with Bruker DPX-250 and AMX-500 spectrometers with $[D_6]DMSO$ (296 K) and CD_3CN (273 and 233 K) as solvents. Infrared spectra were registered as KBr pellets with a Bio-Rad FTS 135 spectrophotometer in the range 4000–600 cm^{-1} . Fast atom bombardment (FAB) mass spectra were obtained with a Kratos MS-50 mass spectrometer, employing Xe atoms at 70 keV in *m*-nitrobenzyl alcohol as matrix. Room-temperature magnetic susceptibilities were measured using a Digital Measurement system MSB-MKI, calibrated by using tetrakis(isothiocyanato)cobaltate(II).

Syntheses: All solvents, 2,6-diacetylpyridine, 1,2-diaminobenzene, tosyl chloride and M^{II} acetates are commercially available and were used without further purification. Metals (Ega Chemie) were used as ca. $2 \times 2 \text{ cm}^2$ plates and were cleaned of oxides in dilute hydrochloric acid prior to electrolysis. 2-(Tosylamino)aniline was prepared and characterised according to a method previously reported^[17] (Scheme 1).

Ligand Synthesis: $H_2DAPATs$ has been prepared by condensation of 2,6-diacetylpyridine (2 g, 12.3 mmol) with 2-(tosylamino)aniline (6.4 g, 24.6 mmol) in ethanol (250 cm^3). The solution was heated under reflux over a 5-h period, concentrated with a Dean–Stark trap to ca. 30 mL and cooled during 12 h (4 °C). The yellow precipitate that then formed was collected by filtration and purified by Soxhlet extraction (with EtOH as solvent) over a period of 12 h. The resulting solid was finally washed with diethyl ether (3 $\times$ 10 mL) and dried in vacuo.

Metal Complexes Syntheses: All complexes have been obtained by two methods: an electrochemical synthesis^[18] and a traditional chemical procedure.

Electrochemical Synthesis: A warm acetone suspension of $H_2DAPATs$, containing tetramethylammonium perchlorate (about 10 mg) as supporting electrolyte, was electrolysed using a platinum wire as the cathode and a metal plate as anode. The cell can be summarised as: $Pt(-) | H_2DAPATs + MeCOMe | M(+)$, where $M = Mn, Fe, Co, Ni, Cu, Zn$ and Cd . The synthesis is typified by the preparation of $Zn(DAPATs)(H_2O)_2$: A suspension of the ligand $H_2DAPATs$ (0.2 g, 0.46 mmol) in warm acetone (80 mL), containing tetramethylammonium perchlorate (10 mg), and using a zinc plate as anode, was electrolysed for 2.5 h using a current of 10 mA. **Caution:** Although no problems have been encountered in our experiments, all perchlorate compounds are potentially explosive, and should be handled in small quantities and with great care! The resulting orange solid was washed with diethyl ether and dried in vacuo. Slow diffusion of diethyl ether into a dichloromethane/acetone solution of $Zn(DAPATs)(H_2O)_2$ yielded orange crystals of $[Zn(DAPATs)]$ (**1**) suitable for X-ray diffraction studies. The other complexes were obtained by the same method, using the appropriate metal anode. Orange prismatic crystals of $[Cd(DAPATs)(H_2O)]$ (**2**), suitable for single X-ray diffraction studies, were obtained by slow concentration of acetone solutions containing $Cd(DAPATs)(H_2O)$.

Chemical Synthesis: Complexes were obtained by refluxing the ligand and the appropriate metal(II) acetate hydrate in ethanol. A typical preparation is outlined below.

$Cd(DAPATs)(H_2O)$: A mixture of $H_2DAPATs$ (0.2 g, 0.31 mmol) and $Cd(C_2H_3O_2)_2 \cdot 2H_2O$ (0.08 g, 0.31 mmol) in ethanol (60 mL) was refluxed for 3 h to afford a black suspension. Filtration followed by washing with diethyl ether and drying in vacuo yielded an orange powdery solid. Recrystallisation of $Cd(DAPATs)(H_2O)$ complex in DMSO yielded $[Cd(DAPATs)(H_2O)]$ (**2**).

X-ray Crystallographic Studies: Crystals of **1** and **2**, suitable for X-ray diffraction studies, were grown as described above. Data were collected with a Smart CCD-1000 Bruker diffractometer, using graphite-monochromated $Mo-K_{\alpha}$ radiation ($\lambda = 0.71073 \text{ \AA}$) from a fine focus sealed tube source. The structures were solved by direct methods^[31] and DIRDIF-99.2 for Windows and finally refined by full-matrix least squares based on F^2 . An empirical absorption correction was applied using SADABS.^[32] All non-hydrogen atoms were anisotropically refined, and all hydrogen atoms were included in the model at geometrically calculated positions. CCDC-203518 (**1**) and -203519 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: (internat.) + 44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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- [1] J. M. Lehn, *Supramolecular Chemistry – Concepts and Perspectives*, VCH, Weinheim, 1995.
- [2] [2a] E. C. Constable in *Comprehensive Supramolecular Chemistry*, vol. 9 (Eds.: J. P. Sauvage, M. W. Hosseini); Pergamon Press, Oxford, 1996, p. 213–252. [2b] E. C. Constable, C. E. Housecroft, M. Neuburger, D. Phillips, P. R. Raithby, E. Schofield, E. Sparr, D. A. Tocher, M. Zehnder, Y. Zimmermann, *J. Chem. Soc., Dalton Trans.* **2000**, 2219–2228.
- [3] D. Philp, J. F. Stoddart, *Angew. Chem. Int. Ed. Engl.* **1996**, 35, 1155–1196.
- [4] C. Piguet, G. Bernardinelli, G. Hopfgartner, *Chem. Rev.* **1997**, 97, 2005–2062.
- [5] G. F. Swiegers, T. J. Maleftse, *Chem. Rev.* **2000**, 100, 3483–3537.
- [6] [6a] C. Piguet, G. Bernardinelli, J. C. G. Bünzli, S. Petoud, G. Hopfgartner, *J. Chem. Soc., Chem. Commun.* **1995**, 2575–2576. [6b] N. Martin, J. C. G. Bünzli, C. Piguet, V. McKee, G. Hopfgartner, *Inorg. Chem.* **1998**, 37, 577–589. [6c] C. Piguet, C. Edler, S. Rigault, G. Bernardinelli, J. C. G. Bünzli, G. G. Hopfgartner, *J. Chem. Soc., Dalton Trans.* **2000**, 3999–4006.
- [7] [7a] C. Piguet, G. Bernardinelli, B. Bocquet, A. Quattropiani, A. F. Williams, *J. Am. Chem. Soc.* **1992**, 114, 7440–7451. [7b] E. J. Enemark, T. D. P. Stack, *Angew. Chem. Int. Ed. Engl.* **1995**, 34, 996–998. [7c] B. Kersting, M. Meyer, R. E. Meyers, K. N. Raymond, *J. Am. Chem. Soc.* **1996**, 118, 7221–7222. [7d] M. Albrecht, R. Fröhlich, *J. Am. Chem. Soc.* **1997**, 119, 1656–1661.
- [8] [8a] E. C. Constable, A. J. Edwards, P. R. Raithby, J. V. Walker, *Angew. Chem. Int. Ed. Engl.* **1993**, 32, 1465–1466. [8b] E. C. Constable, S. M. Elder, M. J. Hannon, A. Martin, P. R. Raithby, D. A. Tocher, *J. Chem. Soc., Dalton Trans.* **1996**, 2423–2433. [8c] R. Chotalia, E. C. Constable, M. Neuburger, D. R. Smith, M. Zehnder, *J. Chem. Soc., Dalton Trans.* **1996**, 4207–4216. [8d] E. C. Constable, F. Heirlitzner, M. Neuburger, M. Zehnder, *J. Am. Chem. Soc.* **1997**, 119, 5606–5617. [8e] M. J. Hannon, C. L. Painting, W. Errington, *Chem. Commun.* **1997**, 1805–1806. [8f] G. Baum, E. C. Constable, D. Fenske, C. E.

- Housecroft, T. Kulke, M. Neuburger, M. Zehnder, *J. Chem. Soc., Dalton Trans.* **2000**, 945–959. ^[8g] N. W. Alcock, P. R. Barker, J. M. Haider, M. J. Hannon, C. L. Painting, Z. Pikramenou, E. A. Plummer, K. Rissanen, P. Saarenketo, *J. Chem. Soc., Dalton Trans.* **2000**, 1447–1461. ^[8h] C. B. Smith, E. C. Constable, C. E. Housecroft, B. Kariuki, *Chem. Commun.* **2002**, 2068–2069.
- ^[9] ^[9a] G. C. Van Stein, G. Van Koten, K. Vrieze, C. Brevard, A. L. Spek, *J. Am. Chem. Soc.* **1984**, *106*, 4486–4492. ^[9b] M. J. Hannon, C. L. Painting, W. Errington, *Chem. Commun.* **1997**, 307–308. ^[9c] M. J. Hannon, C. L. Painting, A. Jackson, J. Hamblin, W. Errington, *Chem. Commun.* **1997**, 1807–1808. ^[9d] M. J. Hannon, S. Bunce, A. J. Clarke, N. W. Alcock, *Angew. Chem. Int. Ed.* **1999**, *38*, 1277–1278. ^[9e] V. Amendola, L. Fabbrizzi, L. Linati, C. Mangano, P. Pallavicini, V. Pedrazzini, M. Zema, *Chem. Eur. J.* **1999**, *5*, 3679–3688. ^[9f] N. Yoshida, K. Ichikawa, M. Shiro, *J. Chem. Soc., Perkin Trans.* **2000**, 17–26. ^[9g] J. Sanmartín, M. R. Bermejo, A. M. García-Deibe, A. L. Llamas-Saiz, *Chem. Commun.* **2000**, 795–796. ^[9h] L. J. Chidls, N. W. Alcock, M. J. Hannon, *Angew. Chem. Int. Ed.* **2001**, *40*, 1079–1081. ^[9i] M. J. Hannon, P. C. Mayers, P. C. Taylor, *Angew. Chem. Int. Ed.* **2001**, *40*, 1081–1082. ^[9j] J. Hamblin, L. J. Chidls, N. W. Alcock, M. J. Hannon, *J. Chem. Soc., Dalton Trans.* **2002**, 164–169.
- ^[10] M. R. Bermejo, M. Fondo, A. M. González, O. L. Hoyos, A. Sousa, C. A. McAuliffe, W. Hussain, R. Pritchard, V. M. Novotorsev, *J. Chem. Soc., Dalton Trans.* **1999**, 2211–2217.
- ^[11] M. R. Bermejo, A. Sousa, M. Fondo, A. M. González, O. L. Hoyos, R. Pedrido, M. Maestro, J. Mahía, *Z. Anorg. Allg. Chem.* **2000**, *626*, 506–513.
- ^[12] M. Fondo, A. Sousa, M. R. Bermejo, A. García-Deibe, A. Sousa-Pedrares, O. L. Hoyos, M. Helliwell, *Eur. J. Inorg. Chem.* **2002**, 703–710.
- ^[13] ^[13a] M. Carcelli, P. Mazza, C. Pelizzi, G. Pelizzi, F. Zani, *J. Inorg. Biochem.* **1995**, *57*, 43–62 and references therein. ^[13b] A. Bacchi, A. Bonardi, M. Carcelli, P. Mazza, P. Pelagatti, C. Pelizzi, G. Pelizzi, C. Solinas, F. Zani, *J. Inorg. Biochem.* **1998**, *69*, 101–112.
- ^[14] A. Bino, N. Cohen, *Inorg. Chim. Acta* **1993**, *210*, 11–16.
- ^[15] R. Pedrido, PhD Thesis, University of Santiago de Compostela, **2002**.
- ^[16] ^[16a] M. Vázquez, M. R. Bermejo, M. Fondo, A. M. González, J. Mahía, L. Sorace, D. Gatteschi, *Eur. J. Inorg. Chem.* **2001**, 1863–1868. ^[16b] M. Vázquez, M. R. Bermejo, M. Fondo, A. García-Deibe, A. M. González, R. Pedrido, *Eur. J. Inorg. Chem.* **2002**, 465–472. ^[16c] M. Vázquez, M. R. Bermejo, J. Sanmartín, A. M. García-Deibe, C. Lodeiro, J. Mahía, *J. Chem. Soc., Dalton Trans.* **2002**, 870–877. ^[16d] M. Vázquez, M. R. Bermejo, M. Fondo, A. M. García-Deibe, A. M. González, R. Pedrido, J. Sanmartín, *Z. Anorg. Allg. Chem.* **2002**, *628*, 1068–1074. ^[16e] M. R. Bermejo, M. Vázquez, J. Sanmartín, A. M. García-Deibe, M. Fondo, C. Lodeiro, *New J. Chem.* **2002**, *26*, 1365–1370. ^[16f] M. R. Bermejo, J. Sanmartín, A. M. García-Deibe, M. Fondo, F. Novio, D. Navarro, *Inorg. Chim. Acta* **2003**, *347*, 53–60. ^[16g] M. Vázquez, M. R. Bermejo, M. Fondo, A. M. García-Deibe, J. Sanmartín, R. Pedrido, L. Sorace, D. Gatteschi, *Eur. J. Inorg. Chem.* **2003**, 1128–1135.
- ^[17] W. U. Malik, T. C. Sharma, *J. Ind. Chem. Soc.* **1970**, *47*, 167–168.
- ^[18] C. Oldham, D. G. Tuck, *J. Chem. Educ.* **1982**, *59*, 420–421.
- ^[19] N. Beynek, M. McPartlin, B. P. Murphy, I. J. Scowen, *Polyhedron* **1998**, *17*, 2137–2140.
- ^[20] T. Adatia, N. Beynek, B. P. Murphy, *Polyhedron* **1995**, *14*, 335–338.
- ^[21] E. Amadei, M. Carcelli, S. Ianelli, P. Cozzini, P. Pelagatti, C. Pelizzi, *J. Chem. Soc., Dalton Trans.* **1998**, 1025–1029.
- ^[22] S. Ianelli, G. Minardi, G. Pelizzi, L. Reverberi, C. Solinas, P. Tarasconi, *J. Chem. Soc., Dalton Trans.* **1991**, 2113–2120.
- ^[23] ^[23a] B. Cingi, A. G. Manfredotti, C. Guastini, A. Mussatti, M. Nardelli, *Gazz. Chim. Ital.* **1971**, *101*, 315. ^[23b] J. Casabó, J. Colomer, A. Lobet, F. Teixidor, E. Molins, C. Miratvitlles, *Polyhedron* **1989**, *8*, 2743–2747.
- ^[24] K. Linoh, K. L. Nagel, I. Lange, O. Moers, A. Blaschette, P. G. Jones, *Z. Anorg. Allg. Chem.* **1997**, *623*, 1175–1182.
- ^[25] W. Dai, H. Hu, X. Wei, S. Zhu, D. Wang, K. Yu, N. Kent, X. Kou, *Polyhedron* **1997**, *16*, 2059–2065.
- ^[26] S. Cabaleiro, E. Vázquez-López, J. Castro, J. A. García-Vázquez, J. Romero, A. Sousa, *Inorg. Chim. Acta* **1999**, *294*, 87–94.
- ^[27] ^[27a] J. Romero, J. A. García-Vázquez, M. L. Durán, A. Castiñeiras, A. Sousa, A. D. Garnovskii, D. A. Garnovskii, *Acta Chem. Scand.* **1997**, *51*, 672–675. ^[27b] J. A. García-Vázquez, J. Romero, M. L. Durán, A. Sousa, A. D. Garnovskii, A. S. Burlov, D. A. Garnovskii, *Polyhedron* **1998**, *17*, 1547–1552. ^[27c] M. L. Durán, J. A. García-Vázquez, C. Gómez, A. Sousa-Pedrares, J. Romero, A. Sousa, *Eur. J. Inorg. Chem.* **2002**, 2348–2354.
- ^[28] ^[28a] M. R. Bermejo, A. Sousa, M. Fondo, M. Helliwell, *New J. Chem.* **2000**, *24*, 33–38. ^[28b] A. Sousa, M. R. Bermejo, M. Fondo, A. García-Deibe, A. Sousa-Pedrares, O. Piro, *New J. Chem.* **2001**, *25*, 647–654.
- ^[29] M. Morioka, M. Kato, H. Yoshida, T. Ogata, *Heterocycles* **1997**, *45*, 1173–1181.
- ^[30] K. Nakamoto in *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, John Wiley & Sons, New York, **1997**.
- ^[31] ^[31a] G. M. Sheldrick, *SHELX-97 (SHELXS 97 and SHELXL 97)*, Programs for Crystal Structure Analyses, University of Göttingen, Germany, **1998**. ^[31b] DIRDIF-99.2 for Windows: L. J. Farrugia, *J. Appl. Crystallogr.* **1999**, *32*, 837–838.
- ^[32] G. M. Sheldrick, *SADABS, Program for Scaling and Correction of Area Detector Data*, University of Göttingen, Germany, **1996**.

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