Electrochemical Synthesis and X-ray Characterisation of Cadmium Complexes Containing 2,6-Bis(1-salicyloylhydrazonoethyl)pyridine − the Influence of the Supporting Electrolyte on the Nature of the Isolated Compounds

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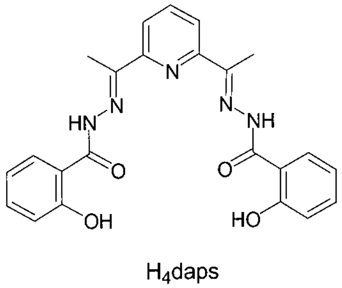
The influence of the supporting electrolyte and the solvent of crystallisation on the nature of cadmium complexes of 2,6-bis(1-salicyloylhydrazonoethyl)pyridine (H_4daps), obtained by an electrochemical procedure, has been investigated. [Cd(H_2daps)(H_2O)$_2$] (**1**), [Cd(H_2daps)(H_2O){(CH_3)$_2$CHOH}] (**2**), [Cd(H_3daps)Cl]·CH_3CN·0.25H_2O (**3**), [Cd(H_3daps)Cl(CH_3OH)]·2H_2O·CH_3OH (**4**), and [Cd(H_2daps)Cl(H_2O)]N(CH_3)$_4$ (**5**), have all been isolated and crystallographically characterised. X-ray diffraction studies show that the cadmium atom in **3** is in an unusual pentagonal pyramidal [CdN_3O_2Cl] geometry, while in the other compounds the cadmium atom is in a bipyramidal pentagonal environment. The organic ligand acts as a pentadentate dianionic ligand in **1**, **2**, and **5**, and as a pentadentate monoanionic ligand in **3** and **4**.

Introduction

The coordination chemistry of hydrazones has been extensively studied. The diversity seen in the structures of their metal complexes,[1−6] their pharmacological activity,[7−9] and magnetic properties[10−12] make these compounds of special interest.

Earlier studies of the coordination chemistry of hydrazone ligands have revealed some interesting aspects, such as their tendency to act as approximately planar pentadentate ligands in most complexes,[1−5,13,14] although an example of tridentate behaviour has recently been reported.[13] Furthermore, these ligands can coordinate in either the neutral,[2b−2d,14] monoanionic,[5,15] dianionic,[2a,16] or tetraanionic[17] form, giving rise to mononuclear or binuclear species. The type of complex obtained seems to be critically dependent on the reaction conditions employed.

We have recently reported that an electrochemical procedure can be used for the isolation of neutral hydrazone complexes that apparently cannot be prepared by other chemical methods.[18] For example, most nickel complexes with hydrazone ligands are mononuclear, while electrochemical synthesis yields a binuclear complex. As a continuation of this work, we have turned our attention to other metals such as cadmium. Although one chemical method for the synthesis of [Cd(H_2daps)(H_2O)] has been described,[2b] we were interested in studying the interaction of cadmium with H_4daps (Scheme 1) under an electrical current in the presence of different supporting electrolytes. The results of this study are described herein.



Scheme 1

Results and Discussion

The reaction of H_4daps with cadmium in an electrochemical cell in the presence of different electrolyte species yields a variety of complexes, as illustrated in Scheme 2. Thus, when a suspension of H_4daps in acetonitrile is electrolysed using [N(CH_3CH_2)$_4$]ClO_4 as the supporting electrolyte, the

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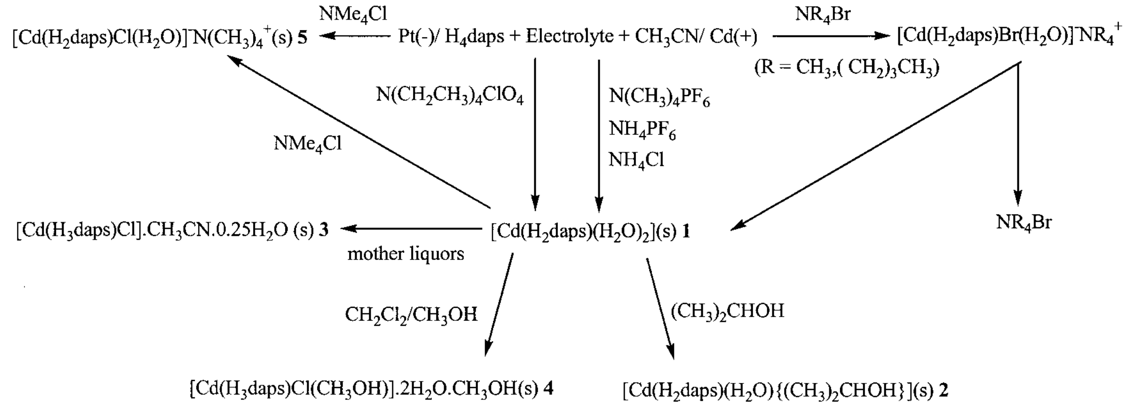


Scheme 2. Routes for the isolation of the metal complexes

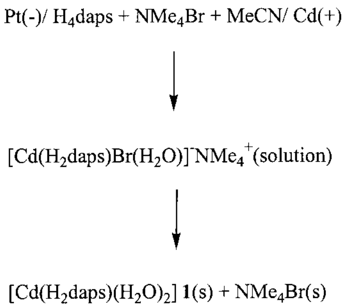
insoluble complex [Cd(H_2daps)(H_2O)$_2$] (**1**) is isolated as the main product. A similar complex, [Cd(H_2daps)(H_2O){(CH_3)$_2$CHOH}] (**2**), has been isolated and crystallographically characterised by recrystallisation of **1** from 2-propanol. Complex **1** is stable in air and thermally stable, melting above 300 °C without decomposition. The compound is insoluble or sparingly soluble in water and common organic solvents, but soluble in polar coordinating solvents such as DMF, DMSO, and pyridine.

Slow evaporation of the solvents from the mother liquors obtained following this electrochemical reaction allows the isolation of [Cd(H_3daps)Cl]·CH_3CN·0.25H_2O (**3**) as a secondary product, which has also been crystallographically characterised. It is clear that the chlorine ligand could only have come from the electrochemical reduction of the tetraethylammonium perchlorate used as the supporting electrolyte, as there is no other chlorine source in the reaction medium. This type of behaviour has been reported previously.[19]

Recrystallisation of **1** from CH_2Cl_2/CH_3OH yields a complex with the molecular formula [Cd(H_3daps)Cl(CH_3OH)]·2H_2O·CH_3OH (**4**). In this case, there are two possible sources of the chlorine ligand: (a) a slight impurity in **1**, arising from the reduction of the perchlorate electrolyte, or (b) the chlorine could have come from the dichloromethane used as solvent.

In an attempt to discern between these two possibilities, the perchlorate was replaced by a chlorine-free electrolyte, such as [N(CH_3CH_2)$_4$]PF_6. The electrochemical synthesis performed under these conditions again yielded complex **1**. Recrystallisation of the resulting powder from purified CH_2Cl_2/CH_3OH led to compound **4**, which was crystallographically characterised. This result demonstrates that the dichloromethane is the chlorine source. In view of this evidence, it was envisaged that electrolytes such as NH_4Cl or N(CH_3)$_4$Cl might produce the same result. Therefore, the electrochemical synthesis in the presence of these chloride salts was investigated. Surprisingly, it was found that these two electrolytes play different roles in the reactions. NH_4Cl acts as a simple current carrier and leads to the isolation of the insoluble complex **1**, while the use of N(CH_3)$_4$Cl produces the soluble complex [Cd(H_2daps)Cl(H_2O)]N(CH_3)$_4$ (**5**). Compound **5** was also obtained when a suspension of **1** in acetonitrile was treated with a stoichiometric amount of N(CH_3)$_4$Cl.

These results indicate that the cadmium centre is susceptible to nucleophilic attack, yielding ionic complexes. To verify this, the aforementioned electrochemical reaction was performed in the presence of other electrolytes, such as NH_4PF_6, N(CH_3)$_4$Br, or N($CH_2CH_2CH_2CH_3$)$_4$Br. In the case of NH_4PF_6, the reaction yielded **1**, as one would expect in view of the poor nucleophilicity of PF_6^-. The use of the bromide electrolytes led to transparent yellow acetonitrile solutions, rather than to the insoluble complex **1**. When the solutions were left to stand, two different compounds could be identified. Thus, when N(CH_3)$_4$Br was used, **1** and N(CH_3)$_4$Br were identified by X-ray diffraction studies. A possible explanation for this could be the formation of [Cd(H_2daps)Br(H_2O)]NR_4, which reorganises when the solution is concentrated to give the final products **1** and NR_4Br, as shown in Scheme 3.



Scheme 3

Complexes **1** and **4** show very low conductivities in DMF (5.46 and 10.97 Ω^{-1} cm^2 mol^{-1}, respectively), in agreement with their nonelectrolyte natures.[20] This indicates that the chlorine ligand is coordinated to the metal in complex **4** and that it remains coordinated even after dissolution in a donor solvent. The conductivity of complex **5** in DMF (84.1 Ω^1 cm^2 mol^{-1}) is in the expected range for 1:1 electrolytes, in accordance with the proposed formulation.

X-ray Diffraction Studies

Pentagonal Bipyramidal Complexes [Cd(H_2daps)(H_2O)$_2$] (1), [Cd(H_2daps)(H_2O){$(CH_3)_2CHOH$}] (2), [Cd(H_3daps)Cl(CH_3OH)]·$2H_2O$·CH_3OH (4), and [Cd(H_2daps)Cl(H_2O)]N$(CH_3)_4$ (5)

ORTEP views of **1**, **2**, **4**, and **5** are shown in Figures 1 to 4. Experimental details are given in Table 1 and selected bond lengths and angles are shown in Table 2.

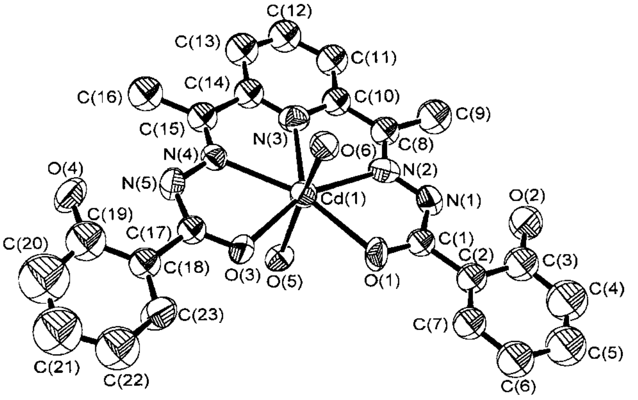


Figure 1. An ORTEP view of [Cd(H_2daps)(H_2O)$_2$] (**1**) showing the atomic numbering scheme; ellipsoids are drawn at a 50% probability level

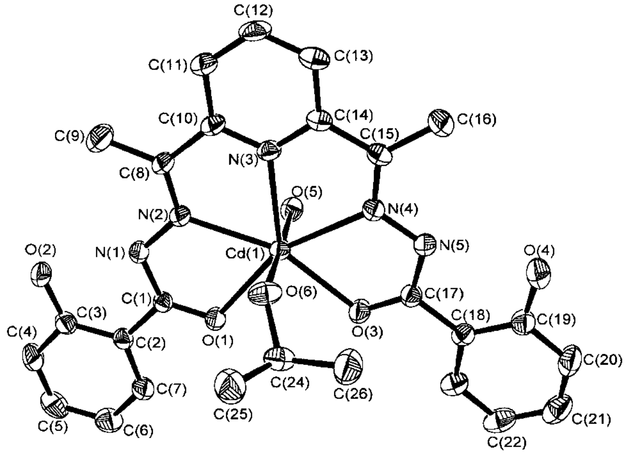


Figure 2. An ORTEP view of [Cd(H_2daps)(H_2O){$(CH_3)_2CHOH$}] (**2**) showing the atomic numbering scheme; ellipsoids are drawn at a 50% probability level

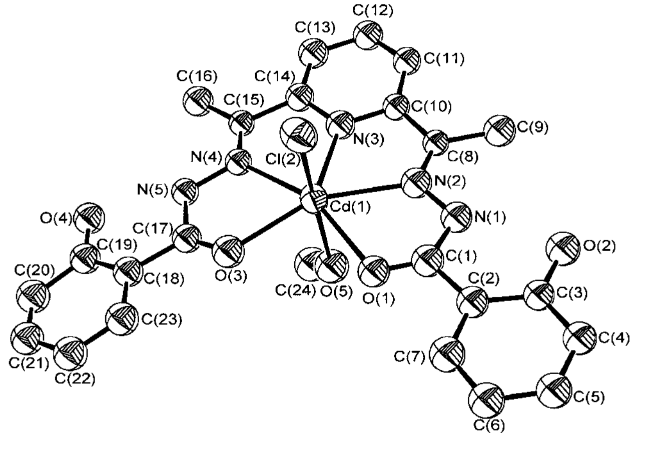


Figure 3. Molecular structure of [Cd(H_3daps)-Cl(CH_3OH)]·$2H_2O$·CH_3OH (**4**) showing the atomic numbering scheme; solvent molecules are omitted for clarity; ellipsoids are drawn at a 30% probability level

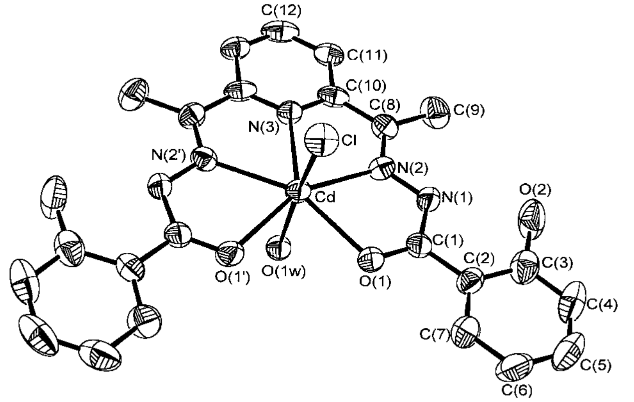


Figure 4. An ORTEP view of [Cd(H_2daps)Cl(OH_2)]N$(CH_3)_4$ (**5**) showing the complex anion; the N$(CH_3)_4^+$ cation is omitted for clarity; ellipsoids are drawn at a 50% probability level

X-ray quality crystals of complex **4** proved to be extremely unstable under X-ray irradiation and we were unable to prevent them from decomposing (standard decay = 38%). This is the reason for the rather poor resolution of the structure. Therefore, only the general structural aspects will be discussed.

All the compounds are noncentrosymmetric, with the exception of **5**, which has a twofold crystallographic axis and hence the two halves of the hydrazone ligand are symmetry related. Complexes **1**, **2**, and **4** are neutral, while **5**, containing the [Cd(H_2daps)Cl(H_2O)]$^-$ anion, is ionic. This is remarkable, as all the previously reported ionic complexes derived from H_4daps or similar hydrazones contain a positively charged metallic fragment.

All the compounds exhibit a distorted pentagonal-bipyramidal environment around the Cd atom, with the hydrazone ligand being pentadentate. The N_3O_2 donor set of the dianionic (**1**, **2**, and **5**) or monoanionic (**4**) hydrazone occupies the equatorial plane of the bipyramid, while solvent molecules and/or chlorine atoms occupy the apical positions. All the distances around the cadmium atom are in the expected ranges for heptacoordinated cadmium,[21,22] although the interaxial and equatorial angles around the metal (Table 2) differ from the ideal values of 180° and 72°, respectively, for a pentagonal bipyramidal arrangement. Four of the five equatorial angles are smaller than the ideal value and the fifth $O_{carbonyl}-Cd-O_{carbonyl}$ angle is greater. These angles show the degree of distortion from the ideal polyhedron.

The N_3O_2 donor set is nearly planar in all cases, with the ionic complex **5** showing the least deviation from the N_3O_2 least-squares calculated plane (maximum deviation of any atom in **5**: 0.014 Å, with the cadmium atom lying 0.2251 Å below the plane).

Table 1. Crystal data and structure refinement for **1−5**

	1	**2**	**3**	**4**	**5**
Empirical formula	$C_{23}H_{19}N_5O_6Cd$	$C_{26}H_{29}N_5O_6Cd$	$C_{25}H_{23}N_6O_{4.25}CdCl$	$C_{25}H_{20}N_5O_8CdCl$	$C_{27}H_{33}N_6O_5CdCl$
Molecular weight	573.83	619.94	623.34	665.29	669.44
Crystal system	Tetragonal	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
a (Å)	11.382(2)	10.556	11.556(3)	22.03(3)	11.7752(11)
b (Å)	11.382(2)	16.127	12.829(7)	7.531(5)	14.023(3)
c (Å)	35.874(3)	16.171	35.773(3)	36.66(3)	17.6946(8)
α (°)	90	90	90	90	90
β (°)	90	90.47	98.61(1)	97.73(8)	90
γ (°)	90	90	90	90	90
Volume ($Å^3$)	4647(1)	2582.1	5243(2)	6028(9)	2921.7(8)
Temperature (K)	296(1)	293(2)	296(1)	293(2)	293(2)
Space group	$P4_12_12$ (No. 92)	$P21/n$ (No. 14)	$C2/c$ (No. 15)	$C2/c$ (No. 15)	$Pnnm$
Z	8	4	8	8	4
Absorption coeff. (cm^{-1})	79.63	8.97	79.75	70.73	8.86
Reflections collected	2630	36217	5962	2211	3102
Independent reflections	2630	4306 [R(int) = 0.048]	5670 [R(int) = 0.039]	2107 [R(int) = 0.050]	3102
Final R indices [$I > 2\sigma(I)$] $R1$	0.0542	0.0291	0.0574	0.0994	0.0461
R indices (all data)	0.1120	0.0433	0.1477	0.2050	0.1910

Table 2. Selected bond lengths [Å] and angles [deg.] for $[Cd(H_2daps)(H_2O)_2]$ (**1**), $[Cd(H_2daps)(H_2O)\{(CH_3)_2CHOH\}]$ (**2**), $[Cd(H_3daps)Cl(CH_3OH)]\cdot 2H_2O\cdot CH_3OH$ (**4**), and $[Cd(H_2daps)Cl(OH_2)]N(CH_3)_4$ (**5**)

	1	**2**	**4**	**5**[a]
Cd(1)−O(1)	2.328(9)	2.3494(18)	2.438(17)	2.349(4)
Cd(1)−O(3)	2.346(10)	2.3334(18)	2.299(19)	−
Cd(1)−O(5)	2.382(7)	2.370(2)	2.36(2)	2.452(5)
Cd(1)−O(6)	2.362(8)	2.395(2)	−	−
Cd(1)−N(2)	2.362(10)	2.353(2)	2.39(2)	2.348(5)
Cd(1)−N(3)	2.359(9)	2.371(2)	2.43(2)	2.411(6)
Cd(1)−N(4)	2.347(10)	2.345(2)	2.42(2)	−
Cd(1)−Cl	−	−	2.559(8)	2.556(2)
O(1)−Cd(1)−O(3)	89.7(3)	89.83(6)	91.5(7)	89.98(19)
O(1)−Cd(1)−N(2)	67.7(3)	67.67(7)	64.7(8)	67.13(14)
O(3)−Cd(1)−N(4)	68.6(3)	67.79(7)	70.4(7)	−
N(2)−Cd(1)−N(3)	67.6(4)	67.36(7)	68.2(9)	66.92(10)
N(3)−Cd(1)−N(4)	66.4(4)	67.49(7)	63.7(8)	−
O(5)−Cd(1)−O(6)	164.5(3)	178.76(8)	−	−
O(5)−Cd(1)−Cl			168.7(5)	171.70(14)

[a] For **5**: O(5) = O(1w), O(3) = O(1′), and N(4) = N(2′).

In **1**, **2**, and **4**, the $C-O_{phenol}$ distances are noticeably shorter than the ideal value of 1.36 Å, indicating some double character for this bond. This is consistent with the participation of the phenol oxygen atom in hydrogen-bonding interactions. In the case of complexes **1** and **4**, the hydrogen atoms bonded to oxygen were not included as they could not be unequivocally defined; they could not be located by difference Fourier methods and have more than one possibility for hydrogen bonding. However, the hydrogen atoms attached to oxygen could be located for **2** and **5**. Both complexes feature two types of hydrogen bond: intramolecular between the phenol oxygen and the hydrazide nitrogen atoms [O(2)···N(1) = 2.509(3) Å and O(4)···N(5) = 2.538(3) Å in **2**; O(2)···N(1) ≈ 2.516 Å in **5**], and intermolecular, involving solvent molecules. Thus, in complex **2**, the water molecule establishes two hydrogen bonds with the carbonyl oxygen atoms of another unit [O(5)···O(1′) = 2.781(3) Å and O(5)·O(3′) = 2.753(3) Å] and vice versa. The 2-propanol molecule also interacts through hydrogen bonding with a phenol oxygen atom of another unit [O(6)···O(2′′) = 2.815(3) Å]. These contacts lead to shorter and longer Cd···Cd distances [Cd(1)···Cd(1′) = 5.1125(5) Å and Cd(1)···Cd(1′′) = 8.981(5) Å].

In complex **5**, the water molecule of one unit establishes hydrogen bonds with the two carbonyl oxygen atoms of a neighbouring unit [O(1w)···O(1) distance ≈ 2.758 Å] and vice versa. Thus, two complex molecules interact through four hydrogen bonds, the shortest Cd···Cd distance being ca. 5.264 Å, with the structure resembling a weakly joined dimer (Figure 5).

Pentagonal Pyramidal Complex $[Cd(H_3daps)Cl]\cdot CH_3CN\cdot 0.25H_2O$ (3)

The X-ray crystal structure of **3** is shown in Figure 6 and selected bond lengths and angles are given in Table 3.

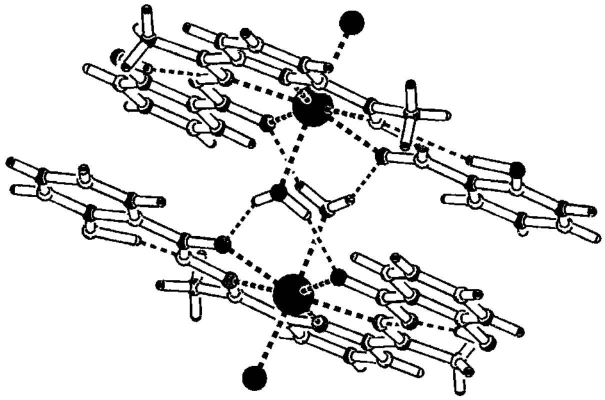


Figure 5. Part of the unit cell of **5** showing the association between two $[Cd(H_2daps)Cl(H_2O)]^-$ anions through hydrogen bonding

The crystal structure consists of discrete $[Cd(H_3daps)Cl]$ molecules with acetonitrile and disordered water in the unit

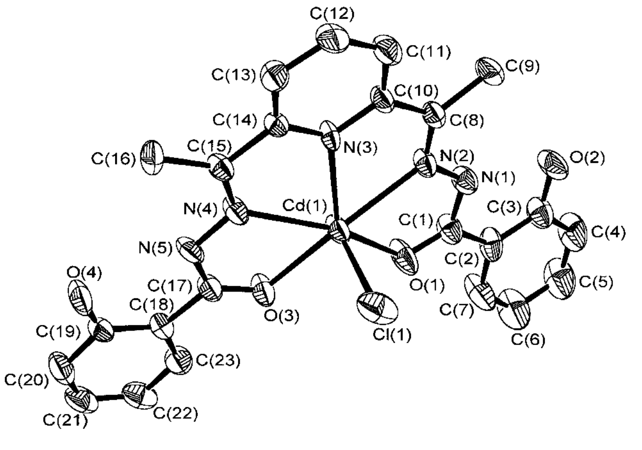


Figure 6. Molecular structure of [Cd(H_3daps)Cl]·CH_3CN·0.25H_2O (**3**); solvent molecules are omitted for clarity; ellipsoids are drawn at a 50% probability level

Table 3. Selected bond lengths [Å] and angles [deg] for [Cd(H_3daps)Cl]·CH_3CN·0.25H_2O (**3**)

Cd(1)−Cl(1)	2.497(3)	O(3)−Cd(1)−N(2)	152.0(2)
Cd(1)−O(1)	2.344(5)	O(3)−Cd(1)−N(3)	131.6(2)
Cd(1)−O(3)	2.374(4)	O(3)−Cd(1)−N(4)	68.0(2)
Cd(1)−N(2)	2.392(5)	N(2)−Cd(1)−N(3)	65.3(2)
Cd(1)−N(3)	2.403(6)	N(2)−Cd(1)−N(4)	129.3(2)
Cd(1)−N(4)	2.370(6)	N(3)−Cd(1)−N(4)	65.1(2)
		Cl(1)−Cd(1)−O(1)	95.6(2)
O(1)−Cd(1)−O(3)	89.2(2)	Cl(1)−Cd(1)−O(3)	97.1(1)
O(1)−Cd(1)−N(2)	67.9(2)	Cl(1)−Cd(1)−N(2)	100.8(2)
O(1)−Cd(1)−N(3)	132.4(2)	Cl(1)−Cd(1)−N(3)	101.1(1)
O(1)−Cd(1)−N(4)	154.3(2)	Cl(1)−Cd(1)−N(4)	98.7(2)

cell, these having occupancies of 0.25. The terminal carbon atom of the acetonitrile molecule is disordered over two sites with occupancies of 0.65 and 0.35.

The metal atom is in a hexacoordinate environment [CdN_3O_2Cl]. The seventh position is unoccupied, despite of the presence of acetonitrile in the unit cell. The Cd···N(6) distance, 2.739(10) Å, is too long to be considered a true coordinated bond and may be viewed as a secondary intramolecular interaction. Thus, the environment of the metal atom can be described as distorted pentagonal pyramidal, with the chlorine atom at the apex and the base formed by the N_3O_2 donor set of the pentadentate monoanionic [H_3daps]$^-$ ligand. The distortion from ideal geometry is clearly shown by the angles between chlorine, cadmium, and the donor set of the hydrazone ligand (Table 3). Moreover, four of the five angles subtended at Cd by adjacent equatorial atoms are slightly smaller than the value for an ideal pentagonal pyramidal arrangement, ranging from 65.1(2)° to 68.0(2)°, while the fifth angle, O(1)−Cd−O(3), is 89.2(2)°. The distortion of the polyhedron is further reinforced by the deviation of the donor set of the hydrazone ligand and the Cd atom from planarity. The maximum deviation from the N_3O_2 least-squares calculated plane is 0.044 Å, with the Cd atom lying 0.348 Å above this plane, giving rise to an "umbrella-like" distortion.

All the cadmium−donor distances are similar to those found in **1−3** and **5**, and the C−O_{phenol} bond lengths (ca. 1.32 Å) also suggest hydrogen-bonding interactions. The short distances between phenol oxygen atoms of adjacent units [O(2)O(2′) = 2.446(9) Å and O(4)···O(4″) = 2.505(9) Å] and the disposition of the molecules in the unit cell seem to indicate that every molecule establishes two intermolecular hydrogen bonds with neighbouring units. Thus, the unit cell shows a zigzag chain disposition of the molecules, with wide channels between layers of these chains (Figure 7).

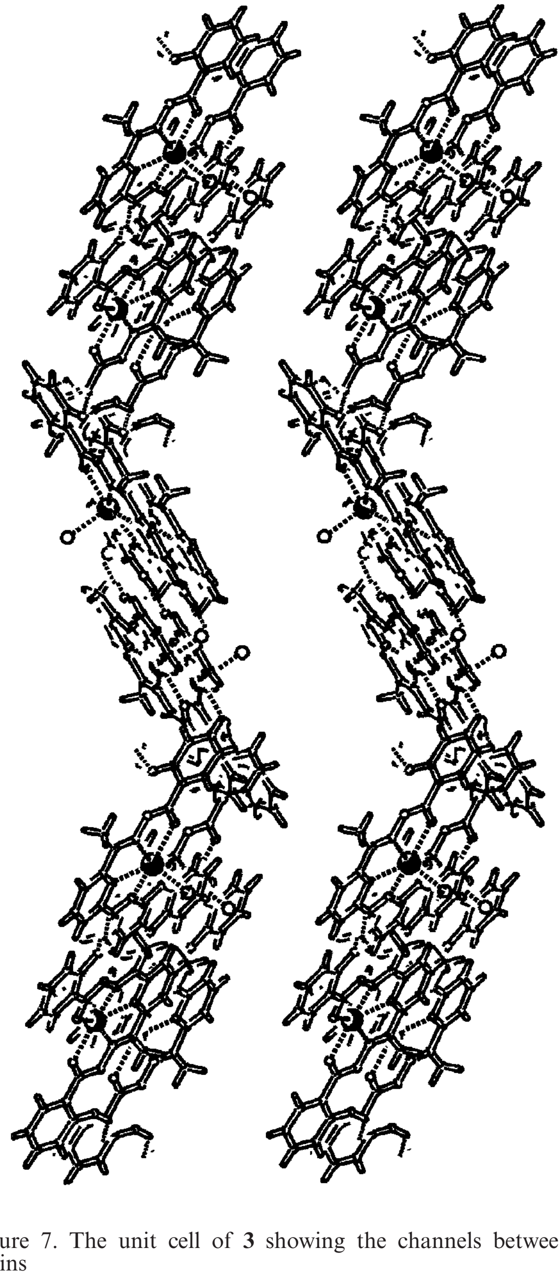


Figure 7. The unit cell of **3** showing the channels between the chains

It should be noted that the crystal structure of [Cd(H_4daps)Cl_2], containing H_4daps as a neutral ligand, has been described previously.[2b] In this case, the complex has a pentagonal-bipyramidal geometry, characteristic of mononuclear compounds containing pentadentate hy-

Table 4. Comparison of bond lengths (Å) in **1−5** and similar related complexes

	1	**2**	**3**	**4**	**5**	**Cd(H$_4$daps)Cl$_2$** [a]
Cd−O$_{carbonyl}$	2.328(9)	2.3334(18)	2.344(5)	2.299(19)	2.349(4)	2.33(1)
	2.346(8)	2.3494(18)	2.374(4)	2.438(17)		2.35(1)
Cd−N$_{imine}$	2.347(10)	2.345(2)	2.370(6)	2.39(3)	2.348(5)	2.40(2)
	2.362(10)	2.353(2)	2.392(5)	2.42(2)		2.41(2)
Cd−N$_{pyridine}$	2.359(9)	2.371(2)	2.403(6)	2.43(2)	2.411(6)	2.42(2)
Cd−O$_{water}$	2.362(8)	2.370(2)	−	−	2.452(5)	−
	2.382(7)					
Cd−Cl	−	−	2.497(3)	2.559(8)	2.556(2)	2.565(7)
C−O$_{phenol}$	1.297(14)	1.343(4)	1.315(9)	1.27(3)	1.367(8)	1.36(2)
	1.319(17)	1.350(4)	1.325(9)	1.32(3)		1.36(2)
C−O$_{carbonyl}$	1.258(14)	1.267(3)	1.237(7)	1.18(3)	1.254(3)	1.20(2)
	1.273(14)	1.271(3)	1.241(7)	1.26(3)		1.27(2)
C−N$_{imime}$	1.283(15)	1.285(3)	1.260(8)	1.24(3)	1.309(6)	1.25(3)
	1.290(15)	1.286(3)	1.265(8)	1.28(3)		1.29(3)
O$_{phenol}$···N$_{hydrazine}$	2.485	2.503(3)	2.525	2.526	2.516(5)	2.67(2)
	2.494	2.538(3)	2.541	2.556		2.71(2)
Shortest Cd···Cd	5.258	5.1125(5)	8.225	8.216	5.264	

[a] See ref.[2b]

drazone ligands, as observed for **1**, **2**, **4**, and **5**. However, the geometry of **3** is quite unexpected, especially considering the presence of a possible donor molecule (acetonitrile) in the unit cell. The pentagonal pyramidal geometry is very unusual and, to the best of our knowledge, no other complexes containing hydrazone ligands have been reported with this structure. Some hydrazone complexes having the metal atom in a hexacoordinate environment have been published.[3,6,18,23−25] In all these cases, the metal atom resides in a distorted octahedral environment. On the other hand, although some examples of complexes with a pentagonal pyramidal geometry have been reported, mainly for metals of the s- or p-blocks,[26,27] to the best of our knowledge no cadmium complexes showing this type of geometry have hitherto been reported.

A comparison of the cadmium complexes described herein with [Cd(H$_4$daps)Cl$_2$] reveals some general trends (Table 4):

(i) Cadmium complexes with H$_4$daps contain the hydrazone ligand acting in a pentadentate manner and show a high preference for pentagonal-bipyramidal geometry.

(ii) The Cd−O$_{carbonyl}$ distances are more symmetric in those complexes in which the ligand is dianionic (**1**, **2**, **5**) or neutral {[Cd(H$_4$daps)Cl$_2$]} than in those in which the ligand is monoanionic (**3**, **4**).

(iii) The Cd−Cl distance in **3** is significantly shorter than those in **4**, **5**, and [Cd(H$_4$daps)Cl$_2$]. This reflects the lower coordination number for **3**.

(iv) The Cd−O$_{water}$ distances in **1** and **2** are markedly shorter than those in **4**. This may be attributed to the stronger "*trans* effect" of the chlorine ligand. This pattern was also observed in previously reported pentagonal-bipyramidal cadmium complexes.[22]

(v) The C−O$_{phenol}$ distances seem to reflect the deprotonation of the ligand in neutral complexes. Thus, complexes **1** to **4** show C−O$_{phenol}$ distances that are shorter than the ideal value. However, anionic complexes do not seem to follow this pattern, as the C−O$_{phenol}$ distance in **5** [1.367(8) Å] is typical of a single C−O bond.

(vi) A comparison of complexes **1** to **5** shows that when cadmium is coordinated by water, the shortest Cd···Cd distances have a lower value (ca. 5.26 Å for **1** and **5**; 5.11 Å for **2**) than in the remaining cases (ca. 8.2 Å for **3** and **4**).

IR and ^{1}H NMR Spectroscopy and Mass Spectrometry

The IR spectra of **1**, **4**, and **5** show a negative shift of the amide I and amide II bands, by 39−52 cm^{-1} and 59−64 cm^{-1}, respectively, compared with the values found in free H$_4$daps (see Exp. Sect.). This behaviour is indicative of the coordination of the ligand to the metal through the oxygen atoms of both carbonyl groups in all cases.[2] The spectra also show the absence of the ν(N−H) band for **1** and **5**, which appears at 3208 cm^{-1} in the free ligand. This situation is in accordance with the dianionic nature of the ligand in these cases. However, the IR spectrum of complex **4** features bands at 3200 and 3060 cm^{-1}, indicating that the hydrazide nitrogen atoms are not fully deprotonated.

The ^{1}H NMR spectra of **1** and **5** in [D$_6$]DMSO (see Exp. Sect.) show the absence of a resonance due to the NH protons, which appears at $\delta = 11.8$ in the free ligand.[2] This is in agreement with the bis-deprotonation of the ligand. In the case of complex **4**, the resonance of the NH group is not observed either, in spite of the monoanionic nature of the ligand. This can be attributed to the fact that the hydrogen atom is in rapid exchange between the two nitrogen atoms. The signal due to the OH groups is strongly downfield shifted in each case (from $\delta = 11.51$ to ca. $\delta = 14.5$). This behaviour has been observed previously and was attributed to the participation of the OH groups in strong hydrogen bonds.[2b]

The ES mass spectra of **1**, **4**, and **5** are consistent with the isotopic simulated pattern, with peaks of maximum intensity at $m/z = 544$ attributable to the fragment [CdL]$^+$, confirming the coordination of the ligand to the metal. In addition, it was possible to observe peaks at $m/z = 579$ for **4** and **5**, corresponding to the binding of the chlorine to the cadmium atom.

Conclusion

Electrolysis of a suspension of H_4daps in acetonitrile using a cadmium anode yields [Cd(H_2daps)(H_2O)$_2$] (**1**) as the major product. Recrystallisation of this complex from 2-propanol gives [Cd(H_2daps)(H_2O){$(CH_3)_2CHOH$}] (**2**). Concomitant reduction of the perchlorate electrolyte during the electrochemical process produces [Cd(H_3daps)Cl]·CH_3CN·0.25H_2O (**3**) as a by-product. [Cd(H_3daps)Cl(CH_3OH)]·2H_2O·CH_3OH (**4**) and [Cd(H_2daps)Cl(H_2O)]N$(CH_3)_4$ (**5**) show that dichloromethane and tetramethylammonium chloride can also act as sources of chlorine. The five compounds are all monomers, but have different geometries. Complexes **1**, **2**, **4**, and **5** have pentagonal-bipyramidal environments, but **3** is a pentagonal-pyramidal complex and is, to the best of our knowledge, the first characterised example of an H_4daps metal complex showing this type of geometry. Therefore, this work further emphasises the variety of molecular structures that hydrazone ligands can produce. Moreover, the ability of H_4daps to behave as an anionic ligand has been demonstrated: monoanionic and dianionic forms are found in different complexes containing the same metal atom.

Experimental Section

General Remarks: Elemental analyses (C, H N) were performed on a Carlo Erba EA 1108 analyser. NMR spectra were recorded on a Bruker WM-250 spectrometer with samples in [D_6]DMSO solution. Infrared spectra were recorded from samples in KBr pellets on a Bio-Rad FTS 135 spectrophotometer in the range 4000−600 cm^{-1}. Electrospray mass spectra were obtained on a Hewlett−Packard LC/MS spectrometer, using methanol as solvent. Conductivities of 10^{-3} M solutions in DMF were measured using a Crison microCM 2200 conductivimeter.

Syntheses: All solvents, 2,6-diacetylpyridine, and salicyl hydrazide are commercially available and were used without further purification. Cadmium (Ega Chemie) was used in the form of ca. 2 × 2 cm^2 plates.

2,6-Bis(1-salicyloylhydrazonoethyl)pyridine (H_4daps) was synthesized as described previously[2a] and was satisfactorily characterised by elemental analysis, IR and ^{1}H NMR spectroscopy.

Syntheses of the Complexes: [Cd(H_2daps)(H_2O)$_2$] (**1**) was obtained by electrochemical synthesis. A suspension of H_4daps (0.108 g, 2.5 × 10^{-4} mol) in acetonitrile (80 mL) containing tetraethylammonium perchlorate (ca. 10 mg) as a current carrier was electrolysed at 10 mA, 12 V for 1 h 20 min, using a platinum wire as the cathode and a cadmium plate as the anode. The cell system can be represented as Pt(−)/MeCN + H_4daps/Cd(+). At the end of the experiment, the insoluble yellow powder deposited was collected by filtration, washed with diethyl ether, and dried in air. Recrystallisation of the compound from CH_3CN and 2-propanol yielded crystals of [Cd(H_2daps)(H_2O)$_2$] (**1**) and [Cd(H_2daps)(H_2O){$(CH_3)_2CHOH$}] (**2**), respectively, which were both suitable for X-ray diffraction studies.

Cd(H_2daps)(H_2O)$_2$: Yield: 85%. $C_{23}H_{23}N_5O_6Cd$ (577.4): calcd. C 47.8, H 4.0, N 12.1; found C 48.0, H 3.9, N 12.1. ES-MS (amu): $m/z = 544$ [ML]$^+$. Λ (Ω^{-1} cm^2 mol^{-1}) = 5.46. IR (KBr): $\tilde{\nu} = 1617$ ν(am$_1$), 1530 ν(am$_2$), 3400 cm^{-1} ν(OH). ^{1}H NMR (250 MHz, [D_6]DMSO): $\delta = 14.65$ (s, 2 H, OH), 6.83−8.15 (m, 11 H, H$_{arom}$), 2.45 (s, 6 H, CH_3).

Slow evaporation of the solvent from the mother liquor obtained following the electrochemical experiment led to the isolation of yellow crystals of [Cd(H_3daps)Cl]CH_3CN·0.25H_2O (**3**), which were also suitable for X-ray diffraction analysis.

Slow recrystallisation of **1**, by diffusion of diethyl ether into a solution in dichloromethane/methanol, yielded crystals of [Cd(H_3daps)Cl(CH_3OH)]·2H_2O·CH_3OH (**4**), which loses solvent to generate Cd(H_3daps)Cl(H_2O)$_2$. Yield: 42%. $C_{23}H_{24}N_5O_6ClCd$ (613.9): calcd. C 44.9, H 3.9, N 11.4; found C 44.9, H 3.3, N 11.2. − ES-MS (amu): $m/z = 544$ [ML]$^+$, 579 [MLCl]$^+$. Λ (Ω^{-1} cm^2 mol^{-1}) = 10.97. IR (KBr): $\tilde{\nu} = 1595$ ν(am$_1$), 1530 ν(am$_2$), 3417 cm^{-1} ν(OH). ^{1}H NMR (250 MHz, [D_6]DMSO): $\delta = 14.45$ (s, 2 H, OH), 6.60−8.10 (m, 11 H, H$_{arom}$), 2.47 (s, 6 H, CH_3).

Compound **1** was also obtained when [N$(CH_2CH_3)_4$]PF$_6$, NH$_4$PF$_6$, or NH$_4$Cl was used as the supporting electrolyte instead of [N$(CH_2CH_3)_4$]ClO$_4$.

[Cd(H_2daps)Cl(H_2O)]N$(CH_3)_4$ (**5**) was obtained by two different methods:

Method A. Electrochemical Method: A suspension of H_4daps (0.108 g, 2.5 × 10^{-4} mol) in acetonitrile containing tetramethylammonium chloride (27.4 mg) was electrolysed at 10 mA, 9 V for 1 h 20 min, using a platinum wire as the cathode and a cadmium plate as the anode. Slow evaporation of the solvent from the resultant yellow solution yielded crystals of [Cd(H_2daps)Cl(H_2O)]N$(CH_3)_4$ (**5**), which proved suitable for X-ray diffraction studies. Yield: 76%. $C_{27}H_{33}N_6O_5ClCd$ (669.44): calcd. C 48.4, H 4.9, N 12.5; found C 47.2, H 4.0, N 12.1. ES-MS (amu): $m/z = 544$ [ML]$^+$, 579 [MLCl]$^+$. − Λ (Ω^{-1} cm^2 mol^{-1}) = 84.1. IR (KBr): $\tilde{\nu} = 1598$ ν(am$_1$), 1530 ν(am$_2$), 3321 cm^{-1} ν(OH). ^{1}H NMR (250 MHz, [D_6]DMSO): $\delta =$ 14.63 (s, 2 H, OH), 6.78−8.20 (m, 11 H, H$_{arom}$), 2.45 (s, 6 H, CH_3), 3.36 [s, 12 H, N$(CH_3)_4$].

Method B. Chemical Method: Tetramethylammonium chloride (0.025 g, 2.3 × 10^{-4} mol) was added to a suspension of H_4daps (0.1 g, 2.3 × 10^{-4} mol) in acetonitrile. The suspension was stirred at room temperature until a yellow solution was obtained (ca. 1 h). The volume of the solution was reduced to ca. 10 mL, whereupon a yellow solid precipitated. This solid was collected by filtration, washed with diethyl ether, and dried in air.

X-ray Crystallographic Study: Crystal data and details of the refinement are given in Table 1.

[Cd(H_2daps)(H_2O)$_2$] (1), [Cd(H_3daps)Cl]·'CH_3CN·0.25H_2O (3), and [Cd(H_3daps)Cl(CH_3OH)]·2H_2O·CH_3OH (4): Orange plate, orange prismatic, and yellow tabular crystals of **1**, **3**, and **4**, respectively, suitable for single-crystal X-ray studies, were obtained as described previously. The crystals were mounted on a glass fibre. Data were collected at 296 K on a Rigaku AFC5R diffractometer, employing graphite-monochromated Cu-K_α radiation ($\lambda = 1.54178$ Å) and a rotating anode generator. The structures were solved by and expanded using Fourier techniques.[28] An empirical absorption correction based on azimuthal scans of several reflections was applied for **1** and **3**. The data were corrected for Lorentz and polarisation effects. Some non-hydrogen atoms were refined anisotropically, while the rest were refined isotropically. The data for **1** and **4** were of rather low quality, hence only the Cd, N and O atoms were refined anisotropically in order to maintain a reasonable data-to-parameter ratio. Hydrogen atoms bonded to carbon were included in the structure factor calculation in idealised positions, but were not refined. Hydrogens attached to oxygen could not be located in the Fourier map and were not included (**1** and **4**) or were included with occupancies of 0.5 and refined isotropically (**3**), with the bond lengths restrained to 0.82 Å. All calculations were performed using the teXsan crystallographic software package from Molecular Structure Corporation.[29]

$[Cd(H_2daps)(H_2O)\{(CH_3)_2CHOH\}]$ (2) and $[Cd(H_2daps)Cl(H_2O)]$-$N(CH_3)_4$ (5): Yellow block and plate crystals of **2** and **5**, respectively, were obtained as detailed above. Data were collected using a CAD4 diffractometer or a Rigaku RAXIS diffractometer at 293(2) K employing Mo-K_α radiation (λ = 0.71073 Å). An absorption correction based on φ-scans was applied for **5**. Non-hydrogen atoms were refined anisotropically. Hydrogens attached to carbon atoms were included in idealised positions, but were not refined. Hydrogens bonded to oxygen atoms were located in the Fourier map and were refined isotropically. Data processing and computation were carried out using the SHELX-97 (**2** and **5**) program package[28] and the teXsan crystallographic software package (**2**).[29]

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-159081 (**1**), -159082 (**2**, -15983 (**3**), -15984 (**4**), -15985 (**5**). Copies of the data can be obtained free of charge on application to the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax: (internat.) +44-(0)1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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