Investigation into Aroylhydrazones as Chelating Agents. Part 8.[1] Synthesis and Spectroscopic Characterization of Complexes of Co, Ni, Cu, Zn, and Cd with 2,6-Diacetylpyridine Bis(salicyloylhydrazone); *X*-Ray Crystal Structure of Dichloro[2,6-diacetylpyridine bis(salicyloylhydrazone)]cadmium(II)–Chloroform–Methanol (1/1/1)†

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Some new metal complexes of 2,6-diacetylpyridine bis(salicyloylhydrazone) (H_2daps) have been prepared from the reaction of the hydrazone with Co, Ni, Cu, Zn, and Cd chlorides and acetates. The chelating behaviour of the hydrazone has been spectroscopically investigated in all compounds by means of i.r. and ^1H n.m.r. techniques. The complex [Cd(H_2daps)Cl_2]·$CHCl_3$·CH_3OH has been subject to an *X*-ray analysis which established a seven-co-ordinate pentagonal-bipyramidal metal environment, with two axial Cl atoms and the H_2daps ligand forming the basal plane.

In the course of our investigations on the chelating properties of 2,6-diacetylpyridine bis(acylhydrazones), obtained from hydrazides of different aromatic and heteroaromatic acids, we have synthesised some complexes of Co, Ni, Cu, Zn, and Cd with 2,6-diacetylpyridine bis(salicyloylhydrazone) (H_2daps), whose ligand behaviour has been previously examined in two complexes, [$SnPr^n_2$(daps)][2] and [Ni(H_2daps)$(OH_2)_2$]$[NO_3]_2$·$1.5H_2O$.[3]

The presence of two OH groups in the aromatic rings of H_2daps favours the formation of intra- and inter-molecular hydrogen bonds; as previously found for the NH_2 groups in H_2dapab [2,6-diacetylpyridine bis(2-aminobenzoylhydrazone)],[4] the OH groups can be in a *syn* position with respect to the O atoms of the CO group or to the N atoms of the hydrazide moiety.

This paper deals with the synthesis and spectroscopic characterization (i.r. and ^1H n.m.r.) of a series of metal complexes obtained from the reaction of H_2daps with Co, Ni, Cu, Zn, and Cd chlorides and acetates. The results of an *X*-ray structural analysis carried out on the complex [Cd(H_2daps)Cl_2]·$CHCl_3$·CH_3OH are also reported.

Experimental

Materials.—2,6-Diacetylpyridine was commercially available (Aldrich) and used without further purification. Organic solvents were purified using published procedures.[5]

Preparations.—2-Hydroxybenzohydrazide was prepared by treating hydrazine with methyl 2-hydroxybenzoate using the published procedure.[6] 2,6-Diacetylpyridine bis(salicyloylhydrazone) (H_2daps) was prepared as previously described.[2] It was isolated as a white powder (yield *ca.* 95%) and purified from ethanol [mass spectrum: *m*/*e* 431 (21.9), 310 (18.8), 162 (78.1), 121 (100.0), 93 (31.3), 65 (79.7%)]. The Co, Ni, Cu, and Zn complexes were prepared by mixing ethanol–water (1:1 v/v) solutions of H_2daps and ethanol solutions of the metal salt (chloride or acetate) in a 1:1 molar ratio. For the Cd salt a mixture of methanol and chloroform (1:1 v/v) was used. In each case the reaction mixture was refluxed for 1 h and then allowed to stand. Precipitation was almost immediate. The compounds were purified by washing with small portions of warm chloroform. Analytical and physical data are listed in Table 1.

Measurements.—Elemental C, H, and N analyses were carried out on Perkin-Elmer model 240 automatic equipment. The metal was determined by atomic absorption spectroscopy on a Perkin-Elmer model 303-HGA 70 instrument. Infrared spectra (4 000—200 cm^{-1}) for KBr discs were recorded on a Perkin-Elmer model 283 B spectrophotometer. The vibrational bands of H_2daps and its metal complexes are reported as SUP 56643. Mass spectra were registered on a Varian CH-5 spectrometer [70 eV (*ca.* 1.12×10^{-17} J)]. ^1H N.m.r. spectra were determined on a Varian EM-360 instrument.

X-Ray Structure Determination of [Cd(H_2daps)Cl_2]·$CHCl_3$·CH_3OH.—*Crystal data.* $C_{25}H_{26}CdCl_5N_5O_5$, $M = 766.18$, monoclinic, $a = 10.649(5)$, $b = 14.822(5)$, $c = 18.566(8)$ Å, $\beta = 95.24(6)°$, $U = 2\,918(2)$ Å^3 (by least-squares fit to centred angle settings of 30 reflections), space group $P2_1/c$, $Z = 4$, $D_c = 1.744$ g cm^{-3}, $F(000) = 1\,536$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 12.5 cm^{-1}.

Data collection and processing. Intensities were collected on a Siemens AED diffractometer, operating in the θ–2θ scan mode using Nb-filtered Mo-K_α radiation. A total of 4 219 reflections were measured for $5 \leqslant 2\theta \leqslant 45°$ ($\pm h + k + l$), 1 409 of which were considered observed [$I > 3\sigma(I)$]. One standard reflection remeasured every 100 reflections to monitor deterioration and alignment of the crystal showed only slight intensity fluctuation. The reflections were processed with the peak-profile analysis procedure and corrected for Lorentz, polarization and absorption effects.

Structure solution and refinement. The structure was solved by conventional heavy-atom techniques. Initial co-ordinates for the cadmium atom were derived from a Patterson map and the positions of the other non-hydrogen atoms were found by Fourier difference syntheses. Refinement was by full-matrix least squares, minimising the quantity $\Sigma w|\Delta F^2|$. Because of the low number of observed reflections, anisotropic thermal parameters were assigned only to the Cd and Cl atoms as well as to the C atom of the chloroform molecule, the others being refined isotropically. All but two (the hydroxylic ones) of the 21 hydrogen atoms of the hydrazone moiety were included at calculated positions in the last refinement cycle. The hydrogens belonging to the solvent molecules were ignored. The final *R*

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† *Supplementary data available* (No. SUP 56643, 2 pp.): i.r. vibrational bands for H_2daps and its metal complexes. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Physical and analytical data

			Analysis *(%)			
Compound	Colour	M.p. (°C)	C	H	N	M
$[Co(H_2daps)Cl_2]\cdot 4H_2O$	Pale yellow	>300	44.10	4.80	11.35	10.00
			(43.60)	(4.60)	(11.05)	(9.30)
$[Ni(H_2daps)Cl_2]\cdot 4H_2O$	Pale green	295	43.90	4.80	11.50	9.55
			(43.65)	(4.60)	(11.05)	(9.25)
$[Zn(H_2daps)Cl_2]\cdot 4H_2O$	Pale yellow	285	42.95	4.15	10.35	10.55
			(43.20)	(4.55)	(10.95)	(10.20)
$[Cd(H_2daps)Cl_2]\cdot CHCl_3\cdot CH_3OH$	Yellow	>300	38.90	3.70	9.65	15.00
			(39.20)	(3.40)	(9.15)	(14.65)
$[Co(daps)]\cdot 2H_2O$	Orange	>300	53.00	5.00	13.00	11.80
			(52.70)	(4.80)	(13.35)	(11.25)
[Ni(daps)]	Brown-yellow	>300	56.80	4.00	14.70	13.00
			(56.60)	(3.90)	(14.35)	(12.05)
[Cu(daps)]	Brown-yellow	>300	56.15	3.60	13.40	13.20
			(56.05)	(3.90)	(14.20)	(12.90)
[Zn(daps)]	Yellow	>300	56.10	4.10	14.45	13.90
			(55.85)	(3.85)	(14.15)	(13.20)
$[Zn(daps)]\cdot 2H_2O$	Yellow	>300	51.55	4.65	12.10	13.00
			(52.05)	(4.35)	(13.20)	(12.30)
$[Cd(daps)]\cdot H_2O$	Yellow-orange	>300	49.80	3.95	12.60	21.10
			(49.35)	(3.80)	(12.50)	(20.10)

* Calculated values are given in parentheses.

and R' values were 0.0673 and 0.0813 respectively with an observations:variables ratio of 7.7:1. Weights were assigned according to the formula $w = 1.1056/[\sigma^2(F_o) + 0.001\,757\,F_o^2]$. The largest peak of the final ΔF map was of height 0.34 e $Å^{-3}$ and was close to the metal atom.

Neutral-atom scattering factors were used and the effects of anomalous dispersion were included in F_c. Computation used the SHELX 76[7] program system on a GOULD-SEL 32/77 computer. Other programs employed were ASSORB,[8] PARST,[9] and PLUTO.[10]

The final fractional atomic co-ordinates of the non-hydrogen atoms are listed in Table 2 and selected bond distances and angles are in Table 3.

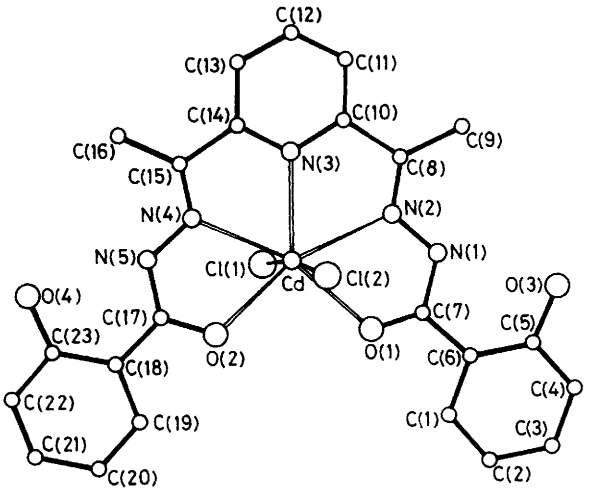


Figure 1. Molecular structure of $[Cd(H_2daps)Cl_2]\cdot CHCl_3\cdot CH_3OH$ showing the atomic numbering scheme

Results and Discussion

All the complexes were isolated in high yields and are stable both in the solid state and in solution. Elemental analyses established a 1:1 metal:ligand stoicheiometry. Complexes [M(daps)] are hydrated when M = Co or Cd and anhydrous when M = Ni or Cu. In the case of Zn both anhydrous and hydrated complexes are isolated. Moreover, the complexes [M(daps)] are less soluble in the common solvents and melt at higher temperatures than the compounds $[M(H_2daps)Cl_2]\cdot nH_2O$ (n = 4, M = Co, Ni, or Zn) (Table 1).

X-Ray Crystal Structure of $[Cd(H_2daps)Cl_2]\cdot CHCl_3\cdot CH_3OH$.—The crystal structure consists of $Cd(H_2daps)Cl_2$ units and solvating chloroform and methanol molecules. The geometry and atomic labelling scheme are illustrated in Figure 1 and the crystal packing in Figure 2. The cadmium atom is seven-co-ordinate and is in a slightly distorted pentagonal bipyramidal environment with H_2daps forming the basal plane, while the two chloride ions are axial. The girdle is markedly flat, with no atom being more than 0.007 Å from the weighted least-square plane; the Cd atom is exactly in this plane. The observed Cd–O and Cd–N bond distances are comparable to those in other seven-co-ordinate pentagonal-bipyramidal cadmium complexes,[11] whereas the Cd–Cl bond distances (mean 2.588 Å) are longer than that (2.425 Å) found for non-bridging Cl in the only known example of a seven-co-ordinate Cd complex, $CdCl_2\cdot CH_3O(CH_2CH_2O)_4CH_3$ (2/1 complex).[12] Of the five interior angles in the pentagon four are between 65.5(6) and 67.4(6)°, thus only slightly narrower than the ideal 72°, while the fifth, involving the two O atoms, is considerably greater [94.2(5)°]. The axial to axial angle deviates significantly from linearity, amounting to 170.4(2)°. The angles between equatorial and axial ligands are close to 90°, ranging from 85.1(4) to 96.6(5)°.

Focusing our attention at the hydrazone moiety, we see that the present investigation supports the consideration that this type of ligand upon co-ordination maintains preferentially an approximately planar configuration leaving the two axial positions available for two other ligands, usually water molecules or inorganic anions. In $[Cd(H_2daps)Cl_2]\cdot CHCl_3\cdot$

Table 2. Fractional atomic co-ordinates ($\times 10^4$) for the non-hydrogen atoms

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cd	2 131(2)	7 800(1)	923(1)	C(6)	548(15)	6 331(9)	−1 097(6)
Cl(1)	−147(6)	7 749(4)	1 266(3)	C(7)	1 044(21)	6 987(14)	−550(11)
Cl(2)	4 406(6)	7 563(4)	538(3)	C(8)	1 418(22)	9 337(15)	−332(12)
Cl(3)	3 532(8)	3 531(5)	1 368(4)	C(9)	989(19)	9 768(13)	−1 035(10)
Cl(4)	2 301(8)	3 496(5)	−50(4)	C(10)	1 854(21)	9 899(15)	320(12)
Cl(5)	3 533(9)	5 114(5)	501(5)	C(11)	1 895(21)	10 815(14)	291(12)
O(1)	1 490(14)	6 746(10)	35(8)	C(12)	2 357(24)	11 237(16)	888(14)
O(2)	2 694(13)	6 707(9)	1 811(8)	C(13)	2 667(23)	10 789(16)	1 522(14)
O(3)	184(14)	7 367(9)	−2 094(7)	C(14)	2 562(22)	9 839(16)	1 533(13)
O(4)	3 826(14)	7 320(9)	3 949(7)	C(15)	2 905(24)	9 278(16)	2 198(13)
O(5)	3 954(25)	2 890(18)	7 963(13)	C(16)	3 278(24)	9 706(16)	2 895(12)
N(1)	974(15)	7 890(11)	−730(8)	C(17)	3 163(22)	6 964(14)	2 432(12)
N(2)	1 388(17)	8 476(11)	−219(9)	C(18)	3 568(15)	6 287(9)	2 951(6)
N(3)	2 184(20)	9 434(10)	930(11)	C(19)	3 623(15)	5 405(9)	2 695(6)
N(4)	2 912(17)	8 455(11)	2 060(9)	C(20)	4 028(15)	4 710(9)	3 166(6)
N(5)	3 209(16)	7 845(12)	2 586(9)	C(21)	4 378(15)	4 897(9)	3 892(6)
C(1)	494(15)	5 452(9)	−837(6)	C(22)	4 323(15)	5 779(9)	4 148(6)
C(2)	32(15)	4 760(9)	−1 295(6)	C(23)	3 918(15)	6 473(9)	3 677(6)
C(3)	−376(15)	4 948(9)	−2 014(6)	C(24)	3 601(31)	3 949(17)	511(15)
C(4)	−322(15)	5 827(9)	−2 274(6)	C(25)	2 868(31)	2 698(21)	8 137(16)
C(5)	140(15)	6 519(9)	−1 816(6)				

Table 3. Selected bond distances (Å) and angles (°)

(*a*) Co-ordination polyhedron			
Cd–Cl(1)	2.565(7)	Cd–Cl(2)	2.611(7)
Cd–O(1)	2.33(1)	Cd–O(2)	2.35(1)
Cd–N(2)	2.41(2)	Cd–N(4)	2.40(2)
Cd–N(3)	2.42(2)		
O(1)–Cd–N(2)	66.7(6)	O(2)–Cd–N(4)	67.4(6)
N(2)–Cd–N(3)	66.1(6)	N(4)–Cd–N(3)	65.5(6)
O(1)–Cd–O(2)	94.2(5)	Cl(1)–Cd–Cl(2)	170.4(2)
(*b*) Hydrazone moiety			
N(3)–C(10)	1.34(3)	N(3)–C(14)	1.30(3)
C(10)–C(8)	1.51(3)	C(14)–C(15)	1.50(3)
C(8)–C(9)	1.49(3)	C(15)–C(16)	1.46(3)
C(8)–N(2)	1.29(3)	C(15)–N(4)	1.25(3)
N(2)–N(1)	1.33(2)	N(5)–N(4)	1.35(2)
N(1)–C(7)	1.38(2)	N(5)–C(17)	1.34(3)
C(7)–O(1)	1.20(2)	C(17)–O(2)	1.27(2)
C(7)–C(6)	1.47(2)	C(17)–C(18)	1.43(2)
O(3)–C(5)	1.36(2)	O(4)–C(23)	1.36(2)
Cd–N(3)–C(10)	120(1)	Cd–N(3)–C(14)	118(1)
N(3)–C(10)–C(8)	115(2)	N(3)–C(14)–C(15)	119(2)
C(10)–C(8)–C(9)	121(2)	C(14)–C(15)–C(16)	121(2)
C(9)–C(8)–N(2)	124(2)	C(16)–C(15)–N(4)	127(2)
C(10)–C(8)–N(2)	115(2)	C(14)–C(15)–N(4)	112(2)
Cd–N(2)–N(1)	115(1)	Cd–N(4)–N(5)	114(1)
Cd–N(2)–C(8)	123(1)	Cd–N(4)–C(15)	125(2)
C(8)–N(2)–N(1)	123(2)	C(15)–N(4)–N(5)	121(2)
N(2)–N(1)–C(7)	117(2)	N(4)–N(5)–C(17)	120(2)
N(1)–C(7)–O(1)	121(2)	N(5)–C(17)–O(2)	119(2)
Cd–O(1)–C(7)	120(1)	Cd–O(2)–C(17)	119(1)
(*c*) Chloroform molecule			
C(24)–Cl(3)	1.72(3)	C(24)–Cl(4)	1.78(3)
C(24)–Cl(5)	1.73(3)		
Cl(3)–C(24)–Cl(4)	108(2)	Cl(3)–C(24)–Cl(5)	111(2)
Cl(4)–C(24)–Cl(5)	110(2)		
(*d*) Methanol molecule			
C(25)–O(5)	1.26(4)		

CH_3OH, H_2daps co-ordinates in its neutral form through three N and two O atoms giving rise to four planar five-membered chelate rings. Structural features in the ligand are closely in accord with those reported for the same ligand in two other metal complexes, *i.e.* [SnPr$^n{}_2$(daps)][2] and [Ni(H_2daps)-(OH_2)$_2$][NO_3]$_2$·1.5H_2O,[3] with the following significant exceptions: (*i*) in the tin complex the hydrazone is di-deprotonated and (*ii*) in the nickel complex H_2daps is bound to the Ni^{II} ion in an unsymmetrical quinquedentate manner, this being associated with the non-equivalence of the two Ni–O bonds, which differ by a significant 0.38 Å.

The hydrogen atoms on the hydrazide nitrogens are directed towards the adjacent hydroxyl oxygens, to which they form intramolecular hydrogen bonds [N(1)···O(3) 2.71(2) and N(5)···O(4) 2.67(2) Å]. Moreover, even if there was no evidence in the ΔF map for the two hydrogens of the OH groups, the structure contains two short O···Cl contacts which can be considered as intermolecular hydrogen bonds [O(3)···Cl(1) (at x, $\frac{3}{2} - y$, $z - \frac{1}{2}$) 3.04(1) and O(4)···Cl(2) (at x, $\frac{3}{2} - y$, $z + \frac{1}{2}$) 2.96(1) Å].

Both solvent molecules are subject to relatively large thermal motion due to the absence of significant close interactions with other species, the shortest contacts being Cl(5)···O(1) (at x, y, z) 3.31(2), O(5)···Cl(2) (at $1 - x$, $1 - y$, $1 - z$) 3.22(2), and C(25)···Cl(1) (at $\bar{x}$, $1 - y$, $1 - z$) 3.26(3) Å.

Infrared Spectra.—The hydrated nature of some of the complexes is confirmed by the presence of strong and broad absorptions in the 3 500 cm^{-1} region, whereas in the anhydrous complexes [M(daps)] the disappearance of ν(NH) bands is in agreement with the deprotonated nature of the ligand.

In the complexes [M(H_2daps)Cl_2]·$n$$H_2O$ the amide I [ν(CO)] and amide II bands [δ(NH) + ν(CN)] undergo negative shifts of 10—35 and 15—30 cm^{-1} respectively.[13] It can be noted that a high shift of the amide I band gives a corresponding low shift of the amide II.

In the complexes [M(daps)] a strong negative shift of the amide I band (Δν = 35—60 cm^{-1}) is observed as a consequence of the deprotonated nature of the ligand and of the co-ordination to the metal;[1,14] the loss of the hydrogen atom in both NH groups produces the appearance of a new band (at *ca.* 1 515 cm^{-1}) at a lower frequency with respect to those of the amide II bands.[15]

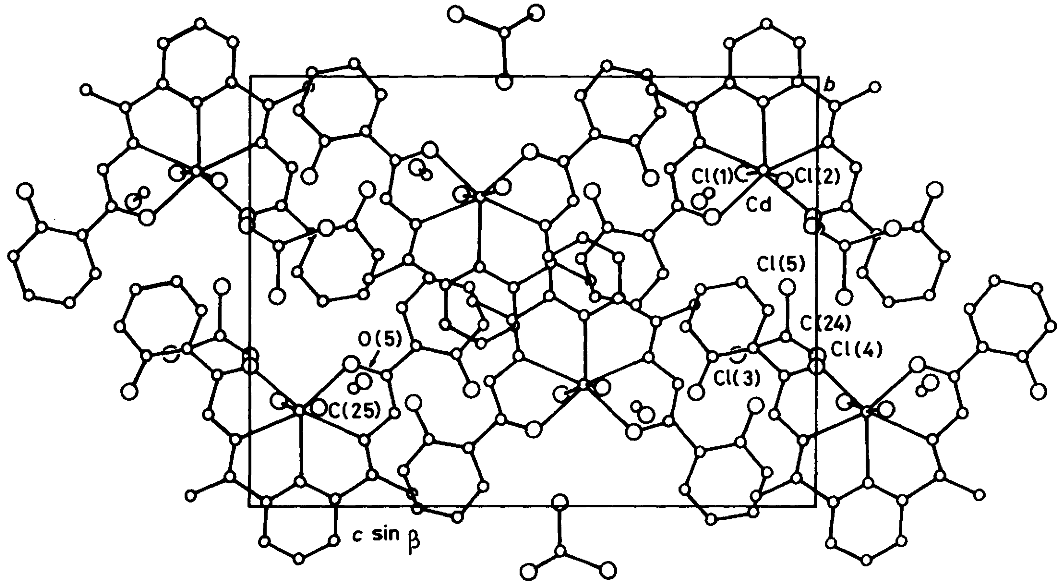


Figure 2. Packing diagram of $[Cd(H_2daps)Cl_2]\cdot CHCl_3\cdot CH_3OH$ viewed down *a*

Table 4. Selected chemical shift data (in p.p.m. from $SiMe_4$) in $(CD_3)_2SO$ solution

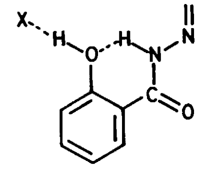
	CH_3	Aryl H	NH	OH
H_2daps	2.5	6.8—8.2	11.5	11.4
$[Zn(H_2daps)Cl_2]\cdot 4H_2O$	2.5	6.8—8.2	11.5	11.4
$[Zn(daps)]\cdot 2H_2O$	2.5	6.8—8.2	—	14.4
H_2dapb	2.6	7.4—8.2	10.9	—
$[Zn(H_2dapb)Cl_2]\cdot 3H_2O$	2.5	7.3—8.1	10.8	—
H_2dapt	2.5	7.2—8.2	11.0	—
$[Zn(H_2dapt)Cl_2]\cdot 4H_2O$	2.5	7.0—8.2	10.9	—
$[Zn(dapt)]$	2.5	6.8—8.0	—	—
H_2dapab*	2.5	6.8—8.2	10.6	—

* The signal due to the NH_2 group falls at 6.2 p.p.m.

It is noteworthy that the amide I band is split into two for the three (M = Co, Zn, or Cd) hydrated complexes; this fact could be explained as the effect of a different structural situation for the CO groups in the co-ordination to the metal as a consequence of a probable hydrogen bond involving one CO group and a water molecule.

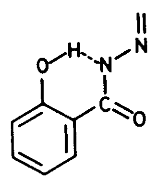
^1H *N.M.R. Spectra*.—The ^1H n.m.r. chemical shifts of H_2daps, $[Zn(H_2daps)Cl_2]\cdot 4H_2O$, and $[Zn(daps)]\cdot 2H_2O$ are reported in Table 4 together with values of other 2,6-diacetylpyridine bis(acylhydrazones) and related zinc complexes.

With the exception of the aryl or heteroaryl functional groups belonging to the original hydrazides, structural analogies are suggested for all free hydrazones. The signals relating to the amidic NH groups fall in the range 10.6—11.0 p.p.m. for H_2dapb [2,6-diacetylpyridine bis(2-benzoylhydrazone)], H_2dapt [2,6-diacetylpyridine bis(2-thenoylhydrazone)], and H_2dapab, while in the spectrum of H_2daps the signal is shifted downfield to 11.5 p.p.m. and overlaps almost perfectly with the signal due to the protons of the OH groups. On this basis it is reasonable to consider that both the NH and OH groups are involved in the formation of hydrogen bonds, as previously found for other similar systems.[3,16,17] As already found for H_2daps, in the spectrum of $[Zn(H_2daps)Cl_2]\cdot 4H_2O$ the resonance of the NH protons falls at a higher δ value with respect to the other complexes and again overlaps with the OH signal. In contrast, in $[Zn(daps)]\cdot 2H_2O$ the signal of the OH group is strongly shifted downfield (to 14.4 p.p.m.) in agreement with a higher association[2] of hydrogen bonds involving the OH groups. Only in this case is a change in chemical environment of the protons in the co-ordination observed. In fact, in H_2daps and in $[Zn(H_2daps)Cl_2]\cdot 4H_2O$ each OH group is probably involved in two H bonds, one intramolecular with an amidic nitrogen atom and the other intermolecular with a solvent molecule (or with a donor atom of a neighbour ligand molecule) (see below).



X = O, N, or Cl

The deprotonation of the NH groups in $[Zn(daps)]\cdot 2H_2O$ can produce inversion in the position of the hydrogen atoms of the OH groups; accordingly, intramolecular H bonds with the deprotonated N-amidic atoms can be formed (see below).



Conclusions

The *X*-ray data and i.r. assignments confirm for H_2daps the strong co-ordinating properties that this type of ligand shows towards transition-metal ions.

As regards the $[M(H_2daps)Cl_2]$ complexes, the similar spectroscopic pattern shown by the Co, Ni, Zn, and Cd derivatives indicates that an ONNNO-quinquedentate H_2daps, as found from the *X*-ray study of the cadmium complex, is also present in the other three compounds.

A lower symmetry stereochemistry should be present in the anhydrous [M(daps)] complexes. The versatile co-ordinating behaviour of this type of ligand,[1,2,14] mainly due to the presence of different donor atoms, suggested an expansion of our work either to asymmetric bis(acylhydrazones) or to bimetallic (homo- and hetero-nuclear) complexes.[18] Work in this research field is now in progress.

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