Conformational rearrangement of 2,6-bis-(1-salicyloylhydrazonoethyl)pyridine (H_4daps) on complexation. Synthesis and X-ray characterisation of H_4daps and its copper helicate complex $[Cu(H_2daps)(H_2O)]_2 \cdot 2CH_3CN$

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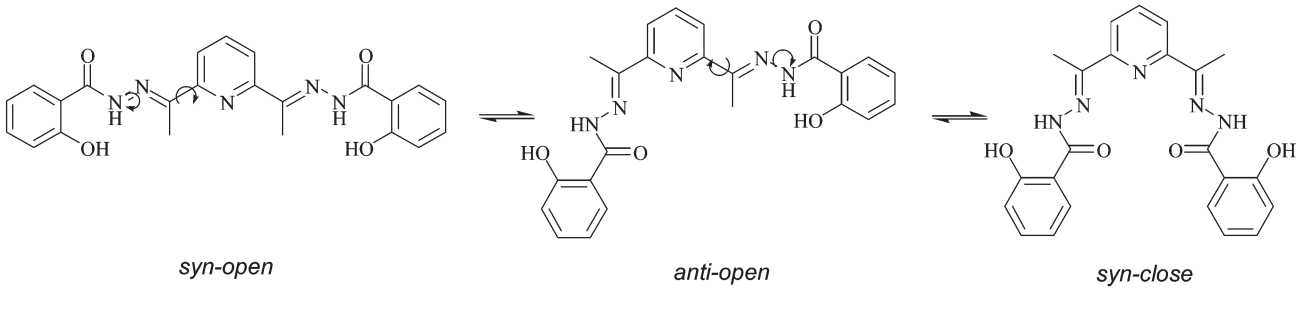
The copper complex of 2,6-bis(1-salicyloylhydrazonoethyl)pyridine, H_4daps, has been prepared by an electrochemical procedure and characterised by elemental analysis, IR, FAB mass spectroscopy, Λ_M, magnetic susceptibility measurements and EPR studies. The molecular structures of the ligand H_4daps (**1**) and its copper complex $[Cu(H_2daps)(H_2O)]_2 \cdot 2CH_3CN$ (**3**) have been determined by X-ray diffraction studies. The ligand shows in the solid state a syn-open conformation that allows it to act as a binucleating ligand, after a conformational change, as is shown by the study of the copper dihelicate **3**. This compound contains the dianionic ligand $[H_2daps]^{2-}$ in an anti-open conformation. The comparative study of this complex, with others previously reported, allows us to confirm that the conformational rearrangement undergone by H_4daps upon complexation depends strongly on the metal nature and its stereochemical preferences.

Introduction

The chelating properties of pentadentate hydrazone derived ligands have been intensively studied in several research fields. The variety of structures observed for metal complexes of this type,[1–6] their pharmacological activity[7–9] and magnetic properties[10–12] make these compounds of special interest. Mono- and polynuclear complexes have been obtained by changing the experimental conditions and the geometry of hydrazone ligands in order to enhance their properties and coordinative ability.[1–15]

Metal complexes with the pentadentate hydrazone Schiff base H_4daps (Scheme 1) have been prepared by chemical methods, yielding a great variety of compounds, depending on the metallic salt used. (a) The use of metal(II) chlorides produced compounds formulated as $[M(H_4daps)Cl_2](solvent)_x$ ($M = Co^{+2}$, Ni^{+2}, Zn^{+2}, Cd^{+2}).[2b] (b) When metal(II) acetates were used the resulting stoichiometries were $[M(H_2daps)](solvent)_x$ ($M = Co^{+2}$, Ni^{+2}, Zn^{+2}, Cd^{+2}).[2b] (c) Different Fe(II) and Fe(III) complexes could be prepared, such as $[Fe(H_4daps)Cl_2](solvent)_x$, $[Fe(H_2daps)Cl](solvent)_x$, $[Fe(H_2daps)(NCS)(OH_2)]$ and $[Fe_2(daps)Cl_2(C_2H_5OH)_2]$.[2d,14](d) When tin organometallic salts were used, a complex with the formula $[SnR_2(daps)]$ was obtained.[2a]

We have been using electrochemical methods of synthesis to obtain neutral complexes derived from the ligand H_4daps, which has been found to be a convenient route for the preparation of neutral Schiff base metal complexes[16] through the oxidation of a metal anode in a solution of a Schiff base bearing weakly acidic groups.[17] As result of this study mononuclear compounds of manganese,[18,19] cobalt[18] and cadmium,[20] as well as dinuclear helical nickel complexes[18,19] have been recently reported by us. These structural studies have allowed us to obtain better knowledge about the influence of factors



Scheme 1 Conformations of H_4daps.

such as metal, pH and solvent to control the nuclearity and helicity in the obtained complexes.[21,22]

However, many questions still remain. The desire for an in-depth understanding of the various factors involved in the self-assembly process[22] has led us to explore the effect of the metal nature and the conformational freedom of the ligand. Having this purpose in mind and using our previous results we have tried to study the conformational changes experimented by the ligand H_4daps upon complexation, as well as its electrochemical interaction with copper. The results are described herein.

Experimental

Materials and methods

All solvents, 2,6-diacetylpyridine and 2-salicyloylhydrazide are commercially available and were used without further purification. Copper metal (Ega Chemie) was used as a *ca.* 2×2 cm^2 plate.

Elemental analyses were performed on a Carlo Erba EA 1108 analyser. The NMR spectra were recorded on a Bruker DPX-250 spectrometer using DMSO-d_6 as solvent. Infrared spectra were registered as KBr pellets on a Bio-Rad FTS 135 spectrophotometer in the range of 4000–600 cm^{-1}. Fast atom bombardment (FAB) mass spectra were obtained on a Kratos MS-50 mass spectrometer, employing Xe atoms at 70 KeV in *m*-nitrobenzylalcohol as a matrix. Conductivities were obtained at 25 °C from 10^{-3} M solutions in DMF on a Crison microCM 2200 conductivimeter. The EPR spectrum of **3** was recorded on a Varian ESR9 spectrometer working at the X-ray frequency (9.225 GHz) equipped with a ^{4}He continuous flow cryostat for low temperature measurements. Room temperature magnetic measurements were performed using a Sherwood Scientific Magnetic susceptibility balance, calibrated using mercury tetrakis(isothiocyanato)cobaltate(II). Variable temperature magnetic measurements were performed with a Cryogenics Squid S600 magnetometer with an applied field of 1 T. The data were corrected for the sample holder contribution and diamagnetism of the sample by use of Pascal's constants.

Syntheses

Ligand preparation. 2,6-Bis(1-salicyloylhydrazonoethyl)pyridine, H_4daps, was synthesised as previously described[2a] and satisfactorily characterised by elemental analysis, IR, FAB mass spectrometry and ^{1}H NMR spectroscopy. Recrystallisation of the obtained powder in DMSO yields pale yellow crystals of H_4daps (**1**) suitable for X-ray diffraction studies. Yield 90%; m. p. 234 °C. Anal. found: C, 64.1; H, 4.8; N, 16.1; $C_{23}H_{21}N_5O_4$ requires: C, 64.0; H, 4.9; N, 16.2. FAB-MS: m/z 454 (100%). ^{1}H NMR (DMSO-d_6): δ 2.50 (s, 6H), 7.01 (t, 2H, 7.3Hz), 7.05 (d, 2H, 7.3Hz), 7.44 (t, 2H, 8.2 Hz), 7.96 (t, 1H, 7.3Hz), 8.01 (d, 2H; 8.2 Hz), 8.16 (d, 2H; 7.3 Hz), 11.50 (br s, 2H), 11.84 (br s, 2H). IR (cm^{-1}): ν(OH) = 3400 (m), ν(NH) = 3208 (m), ν(amide I) = 1655 (s), ν(amide II) = 1559 (s).

Synthesis of Cu(H_2daps)(H_2O). Cu(H_2daps)(H_2O) (**2**) was obtained by an electrochemical synthesis.[23,24] The cell can be represented as Pt(−) | H_4daps + MeCN | Cu(+). To a suspension of H_4daps (0.108 g, 2.5×10^{-4} mol) in acetonitrile (80 cm^3), a small amount of tetraethylammonium perchlorate was added as supporting electrolyte. The resulting mixture was electrolysed at 10 mA and 12 V for 1 h 20 min. The green-yellow powder obtained was washed with diethyl ether and dried under vacuum. Slow evaporation of the solvent from the mother liquors of the electrochemical experiment led to the isolation of green-yellow crystals of [Cu(H_2daps)(H_2O)]$_2$·2CH_3CN (**3**), suitable for a crystallographic study. **2**: yield 90 %; m. p. > 300 °C. Anal. found: C, 54.1; H, 4.2; N, 13.8; $C_{23}H_{21}N_5O_5Cu$ requires: C, 54.1; H, 4.1; N, 13.7. FAB-MS: m/z 493–495 (100%). IR (cm^{-1}): ν(OH) = 3435 (m), ν(amide I) = 1621 (s), ν(amide II) = 1513 (s). Λ_M = 2.46 Ω^{-1} cm^2 mol^{-1}; μ(B. M.) = 1.91.

Caution! Perchlorate salts are potentially explosive and should therefore be handled with the appropriate care.

Crystallographic measurements

Table 1 provides a summary of the crystal data, data collection and refinement parameters.

Crystals of **1** suitable for X-ray diffraction studies were grown as previously described. Data were collected at room temperature on a MACH3 Enraf Nonius diffractometer, using graphite-monochromated Cu-Kα radiation (λ = 1.54180 Å) from a fine-focus sealed tube source. Single crystals of **3** were grown as described above. Data were collected at room temperature on a Siemens CCD diffractometer, using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) from a fine-focus sealed tube source. The structures were solved by direct methods and refined by full-matrix least-squares based on F^2 using SHELX-97 software.[25] All non-hydrogen atoms were anisotropically refined. All hydrogen atoms were included in the model at geometrically calculated positions and refined using a riding model. Molecular graphics are represented by Ortep-3 for Windows.[26]†

Results and discussion

Synthesis

The Schiff base H_4daps (Fig. 1) has been prepared as previously described[2a] and satisfactorily characterised by elemental analysis, FAB mass spectrometry and IR and ^{1}H NMR spectroscopy.

The reaction of H_4daps with copper in an electrochemical cell in the presence of an electrolyte species yields the neutral complex Cu(H_2daps)(H_2O) (**2**). The electrochemical efficiency of the cell (0.47 mol·F^{-1}) is in accordance with the following reaction mechanism:

$$\text{Cathode}: \ H_4\text{daps} + 2e^- \rightarrow H_2(g) + H_2\text{daps}^{2-}$$

$$\text{Anode}: \ H_2\text{daps}^{2-} + Cu \rightarrow Cu(H_2\text{daps}) + 2e^-$$

The complex seems to be 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. Its molar conductivity in DMF is consistent with the non-electrolyte nature of this compound.[27]

Slow evaporation of the solvent from the mother liquors obtained following this electrochemical reaction allowed us to isolate cross-shaped crystals of [Cu(H_2daps)(H_2O)]$_2$·2CH_3CN (**3**), which has also been crystallographically characterised.

IR and FAB mass spectroscopy

The IR spectrum of the complex Cu(H_2daps)(H_2O) (**2**) shows a negative shift of the bands amide I [ν(CO)] and amide II [δ(NH) + ν(CN)] of 34 and 46 cm^{-1}, respectively. This behaviour is indicative of ligand coordination to the metal centre and is compatible with participation of the oxygen atoms of both carbonyl CO groups, in agreement with previous

† CCDC reference numbers 209560 and 209561. See http://www.rsc.org/suppdata/nj/b3/b305354g/ for crystallographic data in .cif or other electronic format.

Table 1 Crystal and structure refinement of H_4daps (**1**) and [Cu(H_2daps)(H_2O)]$_2$·2CH_3CN (**3**)

	1	**3**
Empirical formula	$C_{23}H_{21}N_5O_4$	$C_{50}H_{48}Cu_2N_{12}O_{10}$
Formula weight	431.45	1104.08
Crystal system	Orthorhombic	Monoclinic
a/Å	13.302(4)	23.936(4)
b/Å	14.540(2)	14.650(2)
c/Å	22.451(8)	18.069(3)
α/°	90.00	90.00
β/°	90.00	129.566(3)
γ/°	90.00	90.00
U/Å^3	4342(2)	4884.5(13)
T/K	293(2)	293(2)
Space group	*Pbca*	*C*2/*c*
Z	8	4
μ(Mo-Kα)/mm^{-1}	0.767	0.944
Reflections collected	3286	16 673
Independent reflections	2896	3683
R_{int}	0.0	0.079
R_1 [$I > 2\sigma(I)$]	0.0650	0.1120
wR_2 [$I > 2\sigma(I)$]	0.1120	0.1665
R_1 (all data)	0.2753	0.1456
wR_2 (all data)	0.1604	0.1986

results.[14,18–20] 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 in Cu(H_2daps)(H_2O). Furthermore, the presence of a broad band assigned to ν(OH) is in agreement with the hydrate nature of the solid complex **2**.

The FAB mass spectrum of Cu(H_2daps)(H_2O) shows peaks at m/z 488–494, related to the fragment [CuL]$^+$, indicating coordination of the ligand to the metal.

X-Ray diffraction studies

Crystal structure of H_4daps (1). An ORTEP view of the crystal structure of H_4daps (**1**) is shown in Fig. 1. Selected bond distances and angles are given in Table 2. To our knowledge, only one X-ray structure of a neutral uncoordinated pentadentate hydrazone ligand derived from diacetylpyridine has been previously reported, that of 2,6-diacetylpyridinebis(picolinoylhydrazone), H_2DIP.[28]

The crystal structure reveals that H_4daps exists as discrete molecules. The salicyloyl units adopt a syn-open conformation (see Scheme 1) in order to minimise unfavourable electronic interactions between the two phenol groups.[29] As expected, this disposition is conditioned by the presence of intramolecular hydrogen bonds between the phenol hydrogen atoms and the amide nitrogen atoms, with the distances N(1)···O(1) and N(5)···O(4) being 2.618(7) and 2.629(3) Å, respectively (see Fig. 2). Consequently, O(4)–C(19)–C(18)–C(17)–N(5)–H(5A) and O(1)–C(1)–C(6)–C(7)–N(1)–H(1) form two almost perfectly planar six-membered rings, with deviations from planarity of 0.0458 and 0.0246 Å, respectively.[30]

Significant intermolecular interactions *via* hydrogen bonds can be also observed between the phenolic oxygen atoms O(1) and O(4) of one molecule and the amido oxygen atoms O(2c) and O(3d) of a neighbouring molecule [O(1)···O(2c) = 2.586(6) Å and O(4)···O(3d) = 2.608(6) Å]. The bond angles around the imine nitrogen atoms [N(1)–N(2)–C(8) = 115.6° and N(5)–N(4)–C(15) = 115.9°] are slightly smaller than those expected for atoms with sp^2 character. Other bond lengths and angles are typical[31] and similar to those found for the related structure of the ligand H_2DIP, suggesting a partial conjugation, mainly in the central part of this ligand.

The conformation of the free ligand in the solid state is of particular interest in relation to that required in a metal complex. So, the study of the crystal structure of H_4daps allowed us to investigate the conformational changes experienced by this ligand upon coordination. Thus, it seems clear that the syn-open conformation found for H_4daps in the solid state (Scheme 1 and Fig. 1) is not suitable for direct coordination of the N_3O_2 donor set to the same metal ion. A significant rearrangement of the molecule structure must occur for the mononuclear complexation found in the manganese, cobalt and cadmium compounds.[18–20] Both molecular threads are almost planar in these cases, with a syn-close conformation for the ligand (Scheme 1) as a result of similar twisting around the C–C bonds adjacent to the pyridine ring. The metal will be coordinated to the [ONNNO] donor set of [H_2daps]$^{2-}$, leading to more-or-less distorted bipyramidal pentagonal or pyramidal pentagonal geometries.[18–20]

To achieve the coordinative disposition of H_4daps found in the helical nickel dimers[18,19] a similar conformational change is necessary, but only in one of its arms, resulting in an anti-open conformation for the ligand (Scheme 1). Each nickel centre will be coordinated to two [ONN] or [ONN] + [NO] donor sets corresponding to two different [H_2daps]$^{2-}$ units, yielding a bishelical complex.

Crystal structure of [Cu(H_2daps)(H_2O)]$_2$·2CH_3CN (3). The crystal structure of [Cu(H_2daps)(H_2O)]$_2$·2CH_3CN (**3**) is shown in Fig. 3, together with the atom numbering scheme. Main bond distances and angles are given in Table 3.

This compound is a bishelical copper complex solvated with two acetonitrile molecules. The [H_2daps]$^{2-}$ ligand spans both metal atoms and each copper atom is in a distorted octahedral environment [CuN_3O_3]. The environments for both copper atoms are identical, arising from coordination of each copper

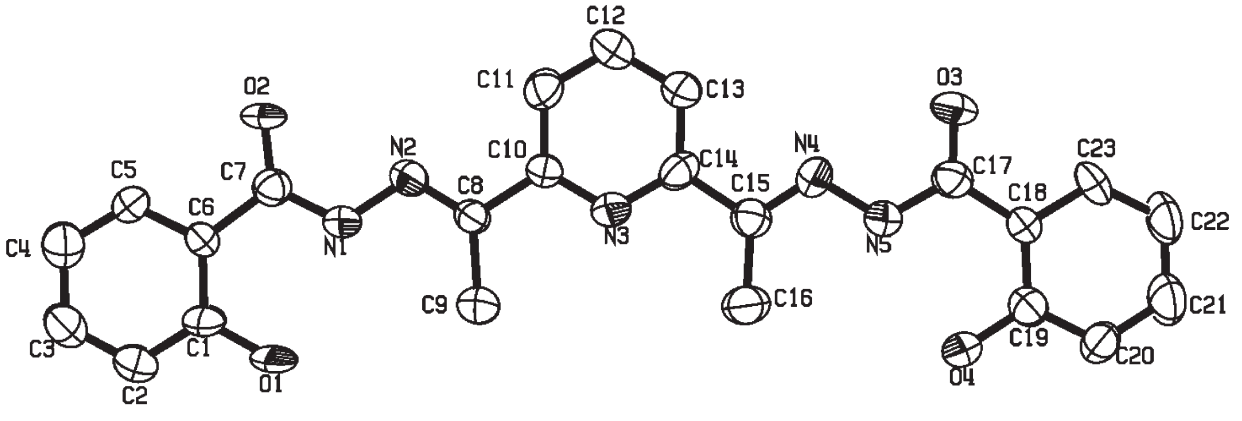


Fig. 1 Molecular structure of H_4daps (**1**) showing the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level.

Table 2 Selected bond distances (Å) and angles (°) for **1**

C(19)–O(4)	1.355(7)	C(1)–O(1)–H(1A)	109.5
N(4)–N(5)	1.374(6)	C(7)–N(1)–N(2)	120.6(6)
C(1)–O(1)	1.370(7)	C(19)–O(4)–H(4A)	109.5
N(1)–N(2)	1.373(6)	C(17)–N(5)–N(4)	119.1(6)
C(7)–O(2)	1.230(7)	N(2)–C(8)–C(10)	116.6(6)
C(17)–O(3)	1.225(8)	N(4)–C(15)–C(14)	113.7(7)
C(8)–N(2)	1.277(7)	N(5)–C(17)–H(5A)	120.4
C(15)–N(4)	1.300(7)	N(5)–N(4)–H(5A)	120.4
C(10)–N(3)	1.328(7)	H(1)–N(1)–C(7)	119.7
C(14)–N(3)	1.344(7)	H(1)–N(1)–N(2)	119.7
C(8)–C(10)	1.465(8)	N(1)–N(2)–C(8)	115.5(6)
C(15)–C(14)	1.473(8)	N(5)–N(4)–C(15)	116.0(6)

D–H···A	D–H	H···A	D···A	D–H···A
N(1)–H(1)···O(1)	0.8608	1.9223	2.618(7)	136.99
O(1)–H(1A)···O(2)^{i}	0.8188	1.8087	2.586(6)	157.97
O(4)–H(4A)···O(3)^{ii}	0.8198	1.7897	2.608(6)	175.27
N(5)–H(5A)···O(4)	0.8601	1.9532	2.629(3)	134.48

Symmetry transformations used to generate equivalent atoms: (i) $1/2+x$, y, $1/2-z$; (ii) $1/2+x$, $3/2-y$, $-z$.

atom to the pyridine nitrogen atom, one imine nitrogen atom and one carbonyl oxygen atom of one $[H_2daps]^{2-}$ moiety and one imine nitrogen atom and one carbonyl oxygen atom of the second $[H_2daps]^{2-}$ unit. One water molecule from the solvent completes the coordination sphere of the metal centres.

It is important to note that the coordination mode of the ligand in this complex is quite different to that found in the three dinuclear complexes previously described by us with H_4daps: $[Ni(H_2daps)]_2{\cdot}2CH_2Cl_2$[18] (**4**), $[Ni(H_2daps)(py)]_2{\cdot}CH_2Cl_2$[18] (**5**) and $[Ni(H_2daps)(MeOH)]_2{\cdot}3CH_3OH{\cdot}H_2O$[19] (**6**). In **4** each ligand uses one imine nitrogen atom and one carbonyl oxygen atom to bind one nickel centre, with both pyridine nitrogen atoms acting as bridges between the two nickel atoms and resulting in similar octahedral environments for both metals. In **5** and **6** each nickel centre has a different environment. One of them arises from coordination of one nickel atom to the pyridine nitrogen atom, one imine nitrogen atom and one carbonyl oxygen atom of both $[H_2daps]^{2-}$ ligands, while the other environment comes from the coordination of the metal centre to one imine nitrogen and one carbonyl oxygen of both $[H_2daps]^{2-}$ moieties, as well as to the donor atoms of two pyridine molecules (in the case of **5**) or to two methanol molecules (in the case of **6**).

The coordination mode found in $[Cu(H_2daps)(H_2O)]_2{\cdot}2CH_3CN$ (**3**) produces three five-membered chelate rings and a distorted octahedral geometry around each copper atom. The Cu···Cu separation is 4.73 Å. This intermetallic distance

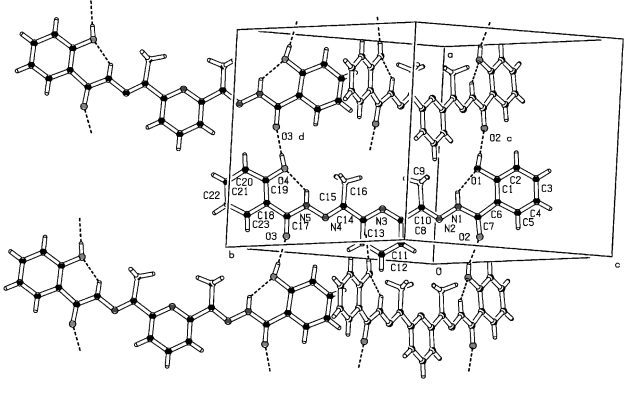


Fig. 2 Intermolecular O–H···O and intramolecular O–H···N hydrogen bonds for H_4daps (**1**).

is shorter than the distance found in complexes derived from ligands containing rigid spacers[32] and also shorter than that found for copper(II) dihelicates with ligands containing longer and flexible spacers.[33] It is interesting to note that the Cu···Cu distance is on the order of the Ni···Ni distance found in **5** and **6**[18,19] and longer than the corresponding one in **4**, where two pyridine bridges bring the metal centres closer together.[19]

The $Cu–N_{pyridine}$ bond lengths (*ca.* 2.14 Å) are longer than the $Cu–N_{imine}$ bonds (*ca.* 1.98 Å) corresponding to the same ligand arm, but they are on the order of the $Cu–N_{imine}$ distances of the other ligand arm. A similar situation occurs with both $Cu–O_{carbonyl}$ lengths: one of them is similar to the Cu–O distance corresponding to the coordinated water molecules while the other is shorter, probably due to steric hindrance.

The $C–O_{phenol}$ distances of *ca.* 1.33 Å are shorter than the ideal value for the C–O bond in phenols (1.362 Å).[30] These data and the $N_{amide}···O_{phenol}$ distances of *ca.* 2.5 Å indicate the presence of an intramolecular hydrogen bond between the phenol oxygen and the amide nitrogen atoms, as well as intermolecular hydrogen bonds between the phenol and the carbonyl oxygen atoms belonging to neighbouring molecules. Such a situation has been found in the free ligand in the solid state, but now it is accentuated because the ligand is doubly deprotonated in the complex.

To the best of our knowledge, **3** is the first dicopper bishelical compound with hydrazone ligands derived from diacetylpyridine (dap), so no direct comparison with similar complexes can be made. However, if we compare this binuclear compound **3** with other copper complexes derived from similar pentadentate ligands, such as the monomers $[Cu(dapsc)(Cl)(H_2O)]{\cdot}Cl{\cdot}2H_2O$[34] and $[Cu(dapsox)(H_2O)]{\cdot}H_2O$,[35] the dimer $[Cu_2(dapsc)(Cl)_2(H_2O)]$[36] and the tetramers[37a] $\{[Cu_2(DIP)Cl_2](H_2O)\}_2$, $[Cu_2(dappc)(H_2O)_3]_2^{4+}$, $[Cu_2(dappc)(H_2O)_2(ClO_4)]_2^{2+}$ and $\{[Cu_2(dapip')(H_2O)Br_2]\}_2{\cdot}2H_2O$,[37b] we can conclude that the bond distances and angles are quite similar and in the range of those expected for complexes containing hydrazone ligands (Table 4). The comparison of **3** with the compounds mentioned above reveals some general trends that will now be described.

The Cu–OW bond distance in **3** [2.148(5) Å] is slightly shorter than in most aqua complexes of Cu(II) (the average value is 2.186 Å). This seems to be not very common among the complexes of acylhydrazones with diacetylpyridine because this bond distance is notably longer for $[Cu(dapsc)(Cl)(H_2O)]{\cdot}Cl{\cdot}2H_2O$[34] [2.269(5) Å] and $[Cu(dapsox)(H_2O)]{\cdot}H_2O$[35] [2.300(2) Å], both monomers with different coordination numbers and geometries for copper, and also for $[Cu_2(dapsc)(Cl)_2(H_2O)]$[36] [2.393(8) Å]. This compound is a dinuclear single-stranded one, due to the hydroxylation of the methyl groups of diacetylpyridine, which increases the donor atom number of one of the strands, making possible the coordination of a second copper atom.

The mentioned tetranuclear complexes contain two non-crossed ligand units, so they are better considered as box-like compounds. The four nuclearity reached in these compounds is due to the use of sixth and seventh donor atoms, pyridine nitrogen atoms in this case, to coordinate two copper atoms into the internal compartments of both ligands, allowing the two carbonyl oxygens to be coordinated to the third and fourth copper atoms, respectively. This situation does not occur in **3** as the sixth and seventh donor atoms are hydroxyl groups that must be deprotonated for coordination. The tetradeprotonation of H_4daps has not been possible under usual chemical and electrochemical synthesis conditions and only one complex containing $[daps]^{4-}$ has been previously reported.[14]

The Cu···Cu separation in the dinuclear helicate **3** is 4.732 Å. The only comparable Cu···Cu distances in the related tetramers[37] involves the copper atoms coordinated to $N_{pyridine}$ of diacetylpyridine. These distances, in the range of 3.849–4.538 Å, are shorter in all cases, as a result of a high degree of

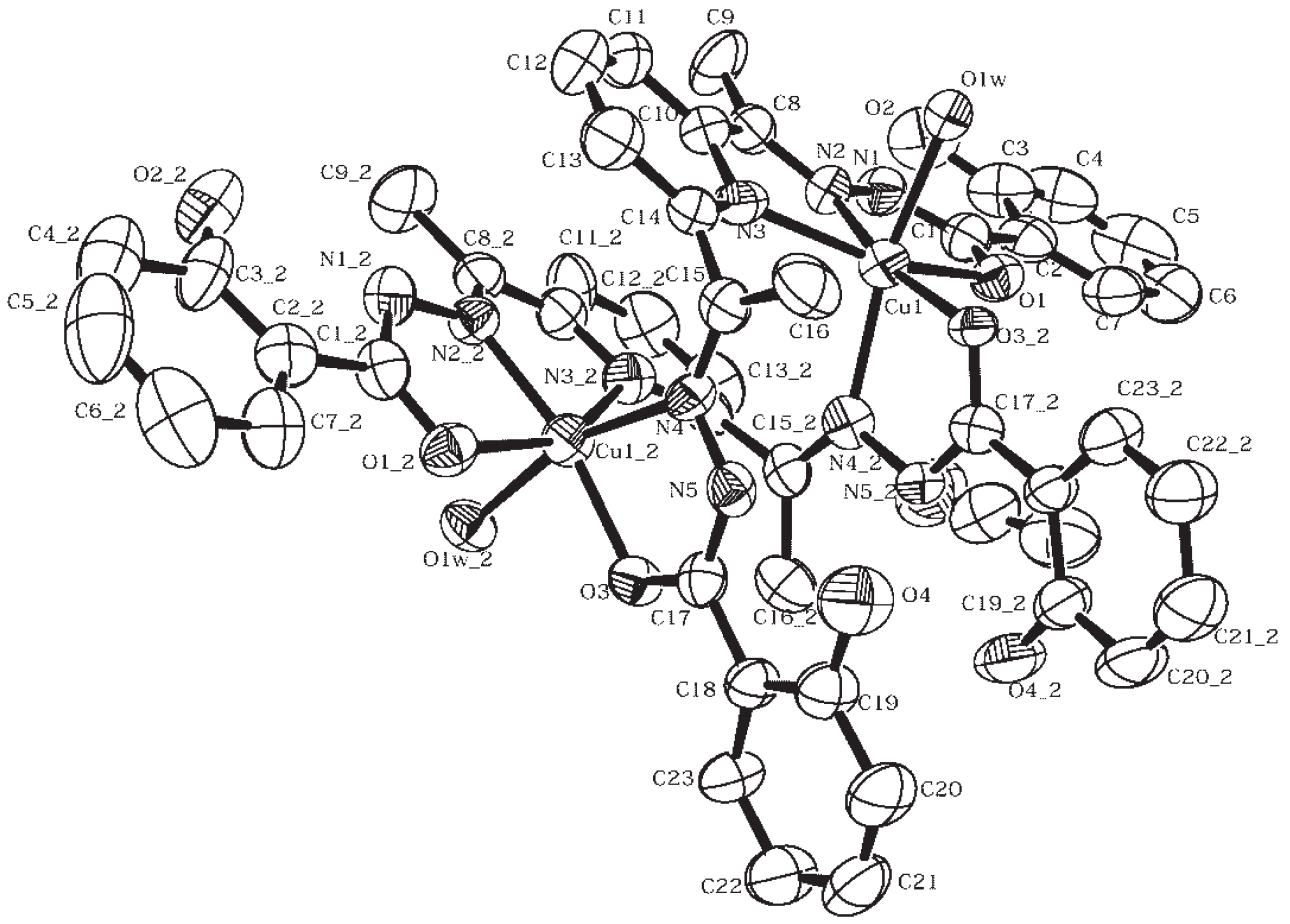


Fig. 3 Molecular structure of $[Cu(H_2daps)(H_2O)]_2 \cdot 2CH_3CN$ (**3**) showing the atomic numbering scheme. Thermal ellipsoids are drawn at the 50% probability level. Lattice CH_3CN are not depicted. Hydrogen atoms are omitted for clarity. Symmetry operation to generate _2 atoms: $2-x, y, 3/2-z$.

closeness of the binding threads in the ligand units to form the tetranuclear clusters.

Finally, we must indicate that the unit cell of complex **3** shows a *grid-shaped* network architecture (Fig. 4) with wide channels. The size of these channels offers an appreciable potential for guest molecule uptake. The formation of this type of porous metal-organic compound demonstrates that this aspect of crystal engineering has many potential implications for material science as new candidates for catalysis or separation process.

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

Cu(1)–N(2)	1.975(6)	O(3)–Cu(1)–O(1)	94.8(2)
Cu(1)–O(3)	1.997(5)	N(4)–Cu(1)–O(1)	91.6(2)
Cu(1)–N(4)	2.107(6)	N(2)–Cu(1)–N(3)	77.1(3)
Cu(1)–O(1)	2.124(6)	O(3)–Cu(1)–N(3)	111.0(3)
Cu(1)–N(3)	2.133(7)	N(4)–Cu(1)–N(3)	100.8(2)
Cu(1)–O(1W)	2.134(7)	O(1)–Cu(1)–N(3)	153.2(2)
N(2)–Cu(1)–O(3)	167.6(2)	N(2)–Cu(1)–O(1W)	85.1(3)
N(2)–Cu(1)–N(4)	111.0(3)	O(3)–Cu(1)–O(1W)	86.3(3)
O(3)–Cu(1)–N(4)	77.4(2)	N(4)–Cu(1)–O(1W)	163.8(3)
N(2)–Cu(1)–O(1)	76.3(2)	O(1)–Cu(1)–O(1W)	90.3(3)

D–H···A	D–H	H···A	D···A	D–H···A
O(1W)–H(1WA)···O(1)^{i}	0.77(6)	2.57(8)	2.842(12)	103(6)
O(1W)–H(1WA)···O(3)^{ii}	0.77(6)	2.15(6)	2.786(11)	158(7)
O(2)–H(2)···N(1)	1.08(19)	1.54(15)	2.542(12)	153.19
O(1W)–H(1WB)···O(1)^{i}	0.69(9)	2.33(9)	2.842(12)	133(7)
O(4)–H(4A)···N(5)	1.12(9)	1.75(11)	2.558(10)	124(10)

Symmetry transformations used to generate equivalent atoms: (i) $3/2-x, 1/2-y, 1-z$; (ii) $-1/2+x, 1/2-y, -1/2+z$.

Magnetic measurements

The copper compound shows a magnetic moment value per atom very close to that expected for magnetically dilute M(II) ions at room temperature. This confirms the +2 oxidation state of the copper centres and supports the double deprotonation of H_4daps. In agreement with the large distance between the centres and the absence of any suitable exchange path, no appreciable interaction is observed between Cu(II) ions. Finally, only a broad and partially resolved feature was observed by X-band EPR, interpreted on the basis of g values of $g// = 2.24$, $g = 2.11$, which are in the expected range for the given coordination environment of the Cu(II) ions.

Conformational study of H_4daps in its metallic complexes

The structural study of the ligand H_4daps offers three possible conformers (Scheme 1), suggesting the possibility of very versatile behaviour, in spite of the syn-open conformer that is the most stable in the solid state. Why does the ligand H_4daps adopt a different conformation in the metallic complexes? Unfortunately, this question still remains unclear but the comparative study of the complexes prepared for us with the ligand H_4daps can shed some light..

The coordinating behaviour of H_4daps towards Mn,[18,19] Co,[18] Ni,[18,19] Cu and Cd[20] in related complexes is similar, acting as dianionic and pentadentate. The comparison between the structural disposition of free H_4daps and its complexed

Table 4 Comparison of bond lengths (Å) in **3** and similar related complexes

	[Cu(dapsc)(Cl)(H_2O)]·Cl·2H_2O [34]	[Cu(dapsox)(H_2O)]·(H_2O)[35]	[Cu_2(dapsc)Cl_2(H_2O)][36]	[Cu_2(dapip')(H_2O)Br]$_2$·2H_2O[37b]	**3** (This work)
Cu1–$N_{pyridine}$	1.978(4)	1.957(2)	1.976(7)	2.078(13)	2.138(7)
Cu2–$N_{pyridine}$	–	–	–	1.992(11)	2.138(7)
Cu1–N_{imine}	2.107(4)	1.909(3)	1.948(8)	1.925(14)	1.976(6)
	2.068(5)	1.986(3)			2.110(6)
Cu2–N_{imine}	–	–	1.945(8)	1.958(13)	1.976(6)
					2.110(6)
Cu1–$O_{carbonyl}$	2.351(4), 2.330(4)	1.993(2)	2.023(6)	1.999(10)	1.999(5)
					2.124(6)
Cu2–$O_{carbonyl}$	–	–	1.945(6)	–	1.999(5)
					2.124(6)
Cu1–Cu2	–	–	–	4.370(3)	4.732(5)
				5.040(4)	
				4.219(3)	
Cu–OW	2.269(5)	2.300(2)	2.393(8)	–	2.148(5)
C–$N_{pyridine}$	1.351(6)	1.339(4)	–	–	1.358(10)
	1.321(7)	1.348(5)			1.337(10)
$C_{pyridine}$–C_{imine}	1.463(8)	1.486(5)	–	1.49(2)	1.432(12)
	1.495(8)	1.472(5)		1.50(2)	1.495(11)
C–N_{imine}	1.297(7)	1.290(5)	–	1.30(2)	1.305 (10)
	1.304(8)	1.296(5)		1.28(2)	1.264(9)
N_{imine}–$N_{hydrazine}$	1.352(7)	1.368(4)	–	1.32(2)	1.383(9)
	1.381(6)	1.383(4)		1.42(2)	1.390(8)
$N_{hydrazine}$–$C_{carbonyl}$	1.387(7)	1.349(4)	–	1.33(2)	1.327(10)
	1.374(8)	1.320(4)		1.33(2)	1.312(9)
C–$O_{carbonyl}$	1.235(7)	1.224(5)	–	1.26(2)	1.289(9)
	1.220(8)	1.214(4)		1.22(2)	1.277(9)
		1.252(4)			
		1.238(5)			

forms reveals that no significant differences are observed in the bond distances and angles. It seems that these parameters are little influenced by coordination to the metal ions.

In all cases Mn and Co complexes[18,19] show a more-or-less distorted bipyramidal pentagonal structure, with $[H_2daps]^{2-}$ occupying the equatorial plane in a syn-close conformation and with additional ligands in apical positions. A particular case are the Cd complexes, in which $[H_2daps]^{2-}$ uses again the syn-close conformation, but with a very different environment around the metal centre.[20] The geometry around Cd is dependent on the methods used to obtain the different complexes. The geometries vary from the usual pentagonal bipyramidal structure to a distorted pentagonal pyramidal one. In Ni[18,19] and Cu complexes the most interesting feature is the octahedral environment around each metal centre and the double helical structures. In these complexes $[H_2daps]^{2-}$ acts as an anti-open conformer but with clear differences in the form to use both binding domains. In these complexes both ligand arms are not planar due to a different helical twisting about the C–C bond adjacent to the pyridine ring. This allows each thread of $[H_2daps]^{2-}$ to be coordinated to different metal ions, so that $[H_2daps]^{2-}$ is then acting as a dinucleating ligand.

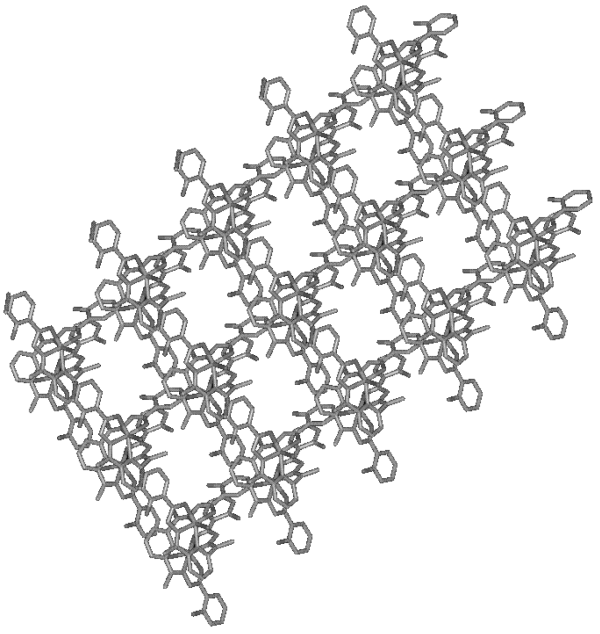


Fig. 4 The unit cell of [Cu(H_2daps)(H_2O)]$_2$·2CH_3CN (**3**), showing the grid-shaped network formed.

This comparative study seems to indicate that the nature of the metal is an important factor in the obtention of helical complexes with the ligand H_4daps, because the electronic and coordinative requirements of the metal determine the existence of a specific conformer of $[H_2daps]^{2-}$ in these complexes. The existence of conformational freedom in the ligand clearly favours the formation of helicates, but only with some metals, demonstrating that both factors are acting in an interactive way.

Conclusions

The experimental results reported herein and the previous work allow us to draw the following conclusions.

The electrochemical synthetic methodology is again shown to be an appropriate and simple way to prepare neutral metal(II) complexes of hydrazone ligands, with high purity and very good yield.

Manganese, cobalt and cadmium neutral complexes obtained by this electrochemical procedure are monomer compounds with bipyramidal or pyramidal pentagonal geometries, while nickel and copper are bishelical dimers. It seems that the

geometrical and/or chemical preferences of the metal play a more important role than the ligand design for the production of dihelicates. Metals with a high preference for an octahedral environment, like nickel and copper, yield dihelicates only when the hydrazone ligand is doubly deprotonated.

The structure of the ligand H_4daps allows us to understand the conformational changes experienced by this ligand to produce monohelical or bishelical compounds. The versatility of this ligand suggests using it as a cheap precursor with selected metals, to obtain helical and other supramolecular species.

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References

1 D. Wester and G. J. Palenik, *Inorg. Chem.*, 1976, **15**, 755.
2 (*a*) C. Pelizzi and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 1980, 1970; (*b*) C. Pelizzi, G. Pelizzi and F. Vitali, *J. Chem. Soc., Dalton Trans.*, 1987, 177; (*c*) C. Carini, G. Pelizzi, P. Tarasconi, C. Pelizzi, K. C. Molloy and P. C. Waterfield, *J. Chem. Soc., Dalton Trans.*, 1989, 289; (*d*) A. Bonardi, C. Carini, C. Merlo, C. Pelizzi, G. Pelizzi, P. Tarasconi, F. Vitali and F. Cavatorta, *J. Chem. Soc., Dalton Trans.*, 1990, 2771.
3 E. C. Constable, in *Comprehensive Supramolecular Chemistry*, eds. J. L. Atwood, J. E. D. Davies, D. D. McNicol, F. Vögtle, J. P. Sauvage and M. W. Hosseini, Pergamon, Oxford, 1996, vol. 9, p. 213.
4 K. Andjelkovic, Y. Ivanovic, S. R. Niketic, B. Prelesnik and V. M. Leovac, *Polyhedron*, 1997, **16**, 4221.
5 S. Abram, C. Maichle-Mössmer and U. Abram, *Polyhedron*, 1998, **17**, 131.
6 G. Paolucci, S. Stelluto, S. Sitran, D. Ajo, F. Benetollo, A. Polo and G. Bombieri, *Inorg. Chim. Acta*, 1992, **193**, 57.
7 M. Carcelli, P. Mazza, C. Pelizzi, G. Pelizzi and F. Zani, *J. Inorg. Biochem.*, 1995, **57**, 43 and references therein.
8 A. Bacchi, A. Bonardi, M. Carcelli, P. Mazza, P. Pelagatti, C. Pelizzi, G. Pelizzi, C. Solinas and F. Zani, *J. Inorg. Biochem.*, 1998, **69**, 101.
9 A. R. Todeschini, A. L. P. De Miranda, K. C. M. Da Silva, S. C. Parrini and E. J. Barreiro, *Eur. J. Med. Chem.*, 1998, **33**, 189.
10 O. Kahn, *Angew. Chem., Int. Ed. Engl.*, 1985, **24**, 834.
11 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 and M. Evain, *Acc. Chem. Res.*, 1988, **21**, 1.
12 S. Rao, D. D. Mishra, R. V. Maurya and N. Nageswara, *Polyhedron*, 1997, **16**, 1825.
13 C. Pelizzi, G. Pelizzi, S. Porretta and F. Vitali, *Acta Crystallogr. Sect. C*, 1986, **1131**, C42.
14 A. Bonardi, C. Merlo, C. Pelizzi, G. Pelizzi, P. Tarasconi and F. Cavatorta, *J. Chem. Soc., Dalton Trans.*, 1991, 1063.
15 M. Carcelli, S. Ianelli, P. Pelagatti and G. Pelizzi, *Inorg. Chim. Acta*, 1999, **292**, 121.
16 (*a*) O. L. Hoyos, M. R. Bermejo, M. Fondo, A. García-Deibe, A. M. González, M. Maneiro and R. Pedrido, *J. Chem. Soc., Dalton Trans.*, 2000, 3122; (*b*) M. R. Bermejo, A. M. González, M. Fondo, A. García-Deibe, M. Maneiro, J. Sanmartín, O. L. Hoyos and M. Watkinson, *New. J. Chem.*, 2000, **24**, 235; (*c*) M. Vázquez, M. R. Bermejo, M. Fondo, A. M. González, J. Mahía, L. Sorace and D. Gatteschi, *Eur. J. Inorg. Chem.*, 2001, 1863; (*d*) M. Vázquez, M. R. Bermejo, M. Fondo, A. García-Deibe, A. M. González and R. Pedrido, *Eur. J. Inorg. Chem.*, 2002, 465; (*e*) M. Vázquez, M. R. Bermejo, M. Fondo, A. M. García-Deibe, A. M. González, R. Pedrido and J. Sanmartín, *Z. Anorg. Allg. Chem.*, 2002, **628**, 1068; (*f*) M. Vázquez, M. R. Bermejo, J. Sanmartín, A. García-Deibe, C. Lodeiro and J. Mahía, *J. Chem. Soc., Dalton Trans.*, 2002, 870; (*g*) M. R. Bermejo, M. Vázquez, J. Sanmartín, A. M. García-Deibe, M. Fondo and C. Lodeiro, *New J. Chem.*, 2002, **26**, 1365.
17 (*a*) M. L. Durán, J. A. García-Vázquez, J. Romero, A. Castiñeiras, A. Sousa, A. D. Garnovskii and D. A. Garnovskii, *Polyhedron*, 1997, **16**, 1707; (*b*) J. A. García-Vázquez, J. Romero, M. L. Durán, A. Sousa, A. D. Garnovskii, A. S. Burlov and D. A. Garnovskii, *Polyhedron*, 1998, **17**, 1547.
18 M. R. Bermejo, M. Fondo, A. M. González, O. L. Hoyos, A. Sousa, C. A. McAuliffe, W. Hussain, R. G. Pritchard and V. M. Novotorsev, *J. Chem. Soc., Dalton Trans.*, 1999, 2211.
19 M. R. Bermejo, A. Sousa, M. Fondo, A. M. González, O. L. Hoyos, R. Pedrido, M. A. Maestro and J. Mahía, *Z. Anorg. Allg. Chem.*, 2000, **626**, 506.
20 M. Fondo, A. Sousa, M. R. Bermejo, A. García-Deibe, A. Sousa-Pedrares, O. L. Hoyos and M. Helliwell, *Eur. J. Inorg. Chem.*, 2002, 703.
21 (*a*) A. Bino and N. Cohen, *Inorg. Chim. Acta*, 1993, **210**, 11; (*b*) G. Paolucci, S. Stelluto, S. Sitran, D. Ajo, F. Benetollo, A. Polo and G. Bombieri, *Inorg. Chim. Acta*, 1992, **57**, 193; (*c*) E. C. Constable and J. M. Holmes, *Inorg. Chim. Acta*, 1987, **126**, 187; (*d*) E. C. Constable, J. M. Holmes and P. R. Raithby, *Polyhedron*, 1991, **10**, 127.
22 (*a*) J.-M. Lehn, *Supramolecular Chemistry-Concepts and Perspectives*, VCH, Weinheim, 1995; (*b*) E. C. Constable, C. E. Housecroft, M. Neuburger, D. Phillips, P. R. Raithby, E. Schofield, E. Sparr, D. A. Tocher, M. Zehnder and Y. Zimmermann, *J. Chem. Soc., Dalton Trans.*, 2000, 2219; (*c*) D. Philp and J. F. Stoddart, *Angew. Chem., Int. Ed. Engl.*, 1996, **35**, 1155; (*d*) C. Piguet, G. Bernardinelli and G. Hopfgartner, *Chem. Rev.*, 1997, **97**, 2005; (*e*) G. F. Swiegers and T. J. Maleftse, *Chem. Rev.*, 2000, **100**, 3483.
23 C. Oldham and D. G. Tuck, *J. Chem. Educ.*, 1982, **59**, 420.
24 (*a*) A. Sousa, M. R. Bermejo, M. Fondo, A. García-Deibe, A. Sousa-Pedrares and O. Piro, *New J. Chem.*, 2001, **25**, 647 and references therein.
25 G. M. Sheldrick, *SHELXS-97, Program for solution of crystal structures*, University of Göttingen, Germany, 1997; G. M. Sheldrick, *SHELXL-97, Program for refinement of crystal structures*, University of Göttingen, Germany, 1997.
26 L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565.
27 W. I. Geary, *Coord. Chem. Rev.*, 1997, **7**, 81.
28 C. Pelizzi and G. Pelizzi, *Acta Crystallogr, Sect. B.*, 1979, **126**, 35.
29 N. Yoshida, H. Oshio and T. Ito, *Chem. Commun.*, 1998, 63.
30 F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1–S19.
31 J. M. Fernández, F. Del Río-Portilla, B. Quiroz-García, R. A. Toscano and R. Salcedo, *J. Mol. Struc.*, 2001, **561**, 197 and references therein.
32 (*a*) W. Dai, H. Hu, X. Wei, S. Zhu, D. Wang, K. Yu, N. Kent and X. Kou, *Polyhedron*, 1997, **16**, 2059; (*b*) H.-L. Zhu, Y.-X. Tong and X.-M. Cheng, *J. Chem. Soc., Dalton Trans.*, 2000, 4182.
33 (*a*) P. E. Kruger, N. Martin and M. Nieuwenhuyzen, *J. Chem. Soc., Dalton Trans.*, 2001, 1066; (*b*) B. J. McNelis, L. C. Nathan and C. J. Clark, *J. Chem. Soc., Dalton Trans.*, 1999, 1831; (*c*) M. Shu, W. Sun, C. Duan, Y. Fu, W. Zhang and W. Tang, *J. Chem. Soc., Dalton Trans.*, 1999, 729.
34 G. J. Palenik, A. E. Koziol, M. Gawron and R. C. Palenik, *Acta Crystallogr., Sect. B.*, 1988, **44**, 85.
35 K. Andjelković, S. R. Ivanović, S. R. Niketić, B. Prelesnik and V. M. Leovac, *Polyhedron*, 1997, **24**, 4221.
36 A. E. Koziol, R. C. Palenik and G. J. Palenik, *J. Chem. Soc., Chem. Commun.*, 1989, 650.
37 (*a*) A. Mangia, C. Pelizzi and G. Pelizzi, *Acta Crystallogr., Sect. B*, 1974, **2146**, 30; (*b*) A. Bonardi, S. Ianelli, C. Pelizzi and G. Pelizzi, *Inorg. Chim. Acta*, 1991, **187**, 167.