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The double helical binuclear copper complex of 6,6'''' dimethyl-4', 4''' diphenyl-quinquepyridine and monohelical cadmium complex of 6,6''''-dimethyl-quinquepyridine. Syntheses, crystal and molecular structure of $[Cu_2(L_2)_2][ClO_4]_3\cdot 2CH_3CN$ and $[CdL_1][ClO_4]_2$

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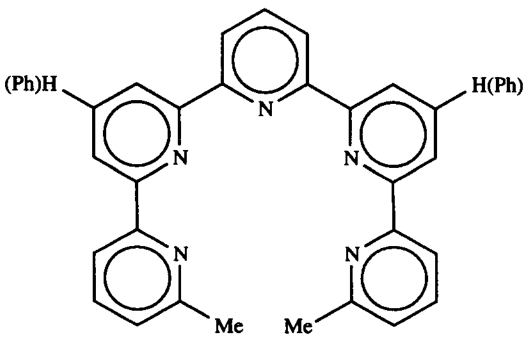
Abstract—The binuclear copper complex of 6,6''''-dimethyl-4',4'''-diphenylquinquepyridine L_2 and the mononuclear cadmium complex of 6,6''''-dimethyl-quinquepyridine L_1 have been prepared by the reaction of L_2 with $Cu(ClO_4)_2\cdot 6H_2O$ and L_1 with $Cd(ClO_4)_2\cdot 2H_2O$, respectively. These complexes were characterized by elemental analysis, IR, ^1H NMR and fast atom bombardment MS spectra. X-ray crystallographic measurement reveals that a Cu^I Cu^{II} mixed valence state copper complex is obtained, in which two ligand molecules self-organized around the Cu^I and Cu^{II} ions to form a double helical configuration. The cadmium complex is mononuclear, has a highly symmetrical configuration and may be regarded as a monohelical compound. © 1997 Elsevier Science Ltd. All rights reserved.

Keywords: double helicate; binuclear copper complex; cadmium complex; synthesis; quinquepyridine; crystal structure.

In recent years the selective and spontaneous assembly of supramolecules by the complexation of polydentate ligands around metal ions has aroused considerable interest of chemists. It has been revealed that in the presence of suitable cations molecular threads can be twisted, self-assembled to form mono-helical [1], double helical [2–5], or trihelical complexes [6]. 4',4''' di-*n*-propyl thio [7] and 4',4''' di-(4-ClC_6H_5) substituted quinquepyridine (qpy) have been reported to react with $CoCl_2$ or $Co(OAc)_2$ respectively to give monohelical complexes [8] under the conditions where qpy forms a double helical complex. In our previous paper, the double helical Ag complexes were obtained by the reaction of 6,6''''-dimethyl and 6,6''''-dimethyl-4'4'''-diphenyl quinquepyridine with silver nitrate and show that the substituents of methyl group have steric effect on the self-assembly of the helix [9]. In the work described in this paper a copper complex of the ligand 6,6''''-dimethyl-4',4'''-diphenyl quinquepyridine and a cadmium complex of ligand 6,6''''-dimethyl-quinquepyridine were prepared and were characterized by elemental analysis, IR, MS and ^1H NMR along with the crystal structure.



$L_1(L_2)$

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EXPERIMENTAL

Microanalyses were performed using a Perkin-Elmer 240 C elemental analyser, metal contents were determined by a J-A 1100 Mark II inductive coupled plasma atomic emission spectrometer. Infrared spectra were recorded on a Nicolet FTIR 170 SX spectrometer. ^1H NMR spectra were measured using Bruker AM-500 and fast bombardment mass spectra on a VG-ZAB-HS spectrometer with 3-nitro benzyl alcohol as supporting matrix.

The ligands $6,6''''$ dimethyl-$4',4'''$-diphenyl quinquepyridine (L_2) and $6,6''''$-dimethyl quinquepyridine (L_1) were prepared by the reaction of 2,6-bis (1-pyridinio acetyl) pyridine diiodide, 1-($6'$-methyl-$2'$-pyridyl)-3-phenyl-2-propen-1-one and ammonium acetate in glacial acetic acid, and the reaction of 2,6-bis(3-dimethylamino-propanoyl) pyridine dihydrochloride, 2-(6-methyl-2-pyridyl)-2-oxo-1-ethyl pyridinium iodide and ammonium acetate in methanol, respectively [10].

Synthesis of $[Cu_2(L_2)_2][ClO_4]_3 \cdot 2CH_3CN$

To $6,6''''$ dimethyl-$4',4'''$-diphenyl quinquepyridine (L_2) (200 mg, 0.35 mmol) suspended in 25 cm^3 methanol was added $Cu(ClO_4)_2 \cdot 6H_2O$ (132 mg, 0.36 mmol). The mixture was refluxed for 2 h. Accompanying the dissolution of L_2, the copper complex gradually precipitated out and was filtered off, washed several times with methanol and then dried *in vacuo* to give green crystals. Found; C, 56.1; H, 3.6; N, 8.6; Cu, 7.6. Calc. for $C_{78}H_{58}N_{10}O_{16}Cl_4Cu_2$. C, 56.5; H, 3.5; N, 8.4; Cu, 7.6%. *m/z* FAB (based on Cu 63) 1360 $[Cu_2(L_2)_2][ClO_4]$, 1261 $[Cu_2(L_2)_2]$, 630 CuL_2. After recrystallization of the green crystal, brown violet crystals of complex (**1**) (196 mg, 99%) were obtained, Found: C, 59.9; H, 4.1; N, 10.2; Cu, 7.7. Calc. for $C_{82}H_{64}N_{12}O_{12}Cl_3Cu_2$, C, 59.9; H, 3.9; N, 10.2; Cu, 7.7%. IR (KBr) 2248 $\gamma_{C\equiv N}$, 1611, 1568, 1547, 1501, $\gamma_{C=C,C=N}$, 765 697 $\delta_{=CH}$, 1090, 623 $(ClO_4)^-$ cm^{-1}. *m/z* FAB (based on Cu 63) 1461 $[Cu_2(L_2)_2]$ $[ClO_4]_2$, 1360 $[Cu_2(L_2)_2][ClO_4]$, 1262 $[Cu_2(L_2)_2]$, 1198 $[Cu(L_2)_2]$, 630 $Cu(L_2)$.

Synthesis of $(CdL_1)(ClO_4)_2$ (**2**)

To a suspension of L_1 (70 mg 0.17 mmol) in methanol (10 cm^3) was added $Cd(OAc)_2 \cdot 2H_2O$ (160 mg 0.6 mmol) in methanol (5 cm^3). The mixture was heated to reflux until a clear solution was obtained, $NaClO_4 \cdot H_2O$ (87 mg, 0.62 mmol) was added and the mixture was then refluxed for 2 h. After cooling, the precipitate was filtered off, washed several times with methanol and dried *in vacuo* to give yellow crystals of complex **2** (0.113 g, 91%). Found: C, 44.1; H, 3.0; N, 9.8; Cd, 15.6, Calc. for $C_{27}H_{21}$ $CdCl_2N_5O_8$. C, 44.6; H, 2.9; N, 9.6; Cd, 15.5% γ_{max} (KBr) 3100 ($\gamma_{=CH}$), 1598, 1581, 1465 ($\gamma_{C=C,C=N}$), 795 ($\delta_{=CH}$) 1109, 619 (δ_{ClO_4}) cm^{-1}. δ_H (solvent CD_3CN, standard $SiMe_4$): 7.63–7.65 (2H, d, $J = 7.7$ Hz, $H^{5,5''''}$), 8.21–8.23 (2H, t, $J = 7.8$ Hz, $H^{4,4''''}$), 8.48–8.53 (5H, m, $H^{3,3'''',4',4'',4'''}$), 8.61–8.65 (6H, m, $H^{3',3'',3''',5',5'',5'''}$) ppm. *m/z* (FAB): 627 $[CdL_1][ClO_4]$, 528 (CdL_1) and 416 (L_1, base peak).

Crystal structure determination

A single crystal of (**1**) was obtained as a brown violet block by slow diffusion of diethyl ether vapour into an acetonitrile solution of the green copper complex. A light yellow monoclinic crystal of the (**2**) was obtained by the same method. A single crystal of (**1**) with dimension of 0.28 × 0.44 × 0.44 mm was sealed in a thin wall glass capillary tube and mounted on a R3M/E four circle diffractometer with graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). Cell parameters were obtained by least squares method using 25 reflections in the range of $4.10 \leqslant 2\theta \leqslant 20.14°$. The positions of the two copper ions in (**1**) were obtained by direct methods. Successive Fourier syntheses provided the coordinates of all non-hydrogen atoms. A final refinement by block diagonal matrix least squares method with anisotropic thermal parameters for non-hydrogen atoms was converged to R 0.0612 and R_w 0.0557; all hydrogen atoms were obtained from theoretical calculations. All calculations (structure analysis and refinement of least squares) were performed on a Eclipse/S140 computer using SHELXTL program system [11]. Crystallographic data for complex (**1**) are summarized in Table 1.

The approximate position of the Cd ion in (**2**) was obtained from the Patterson map. All the non-hydrogen atoms in (**2**) were identified in the Fourier map. These atoms were all refined anisotropically. The hydrogen atoms were placed in calculated positions and allowed to ride on the atoms to which they are bonded and were assigned isotropic thermal parameters which were not refined. Weighting schemes based on counting statistics were applied to data sets. Atomic scattering factors were taken from [12]. The crystallographic data of (**2**) is shown in Table 1.

Additional materials are available from the Cambridge Crystallographic Data Centre including atomic coordinates, thermal parameters and all bond lengths and bond angles.

RESULTS AND DISCUSSION

Complex (**1**)

A comparison of the IR spectrum of (**1**) with that of the ligand L_2 which contains electron withdrawing phenyl groups shows that after L_2 was coordinated with Cu ions, the electronic charge moves only slightly from pyridine ring to the metal ions, hence $\gamma_{=CH}$, $\gamma_{C=C,C=N}$ and $\delta_{=CH}$ bands undergo slight bathochromic shifts ($\Delta\gamma_{=CH}5$, $\Delta\gamma_{C=C,C=N}3$, $\Delta\delta_{=CH}$ 3 cm^{-1}). A small sharp band at 2248 cm^{-1} is assigned to the

Table 1. Crystallographic data for the complexes (**1**) and (**2**)

Formula	$[Cu_2(C_{39}H_{29}N_5)_2]^{3+}(ClO_4)_3^- \cdot 2CH_3CN$	$[Cd(C_{27}H_{21}N_5)^{2+}](ClO_4)_2^-$
fw	1642.9	726.8
Crystal size (mm)	0.28 × 0.44 × 0.44	0.12 × 0.26 × 0.34
Crystal system	monoclinic	monoclinic
Space group	$P2_1/N$	$C2/c$
a (Å)	14.234(3)	15.817(5)
b (Å)	22.954(6)	13.098(5)
c (Å)	23.198(8)	15.586(5)
α (°)	90.00(0)	90.00(0)
β (°)	101.51(2)	118.80(2)
γ (°)	90.00(0)	90.00
V (Å^3)	7427(3)	2832(2)
T (K)	294	293
Z	4	4
d_{cal} (g cm^{-3})	1.47	1.704
μ (M_0-K)(cm^{-1})	7.52	5.10
F (000)	3379	728
2θ range (°)	2–46	40.0–50.0
Reflections collected	11464	2938
Independent reflections	11290	2614
Observed reflections	$5970(I \geqslant 4\sigma(I))$	$1795(F \geqslant 4\sigma(F))$
R	0.0612	0.0447
R_w	0.0557	0.0533
Weighting scheme	$W^{-1} = (\sigma^2$ $(F) + 0.00015(F)^2)/1 - \exp(-5(\sin\theta/\lambda)^2)$	$W^{-1} = \sigma^2(F) + 0.0014(F)^2$

$\gamma_{C\equiv N}$ stretching, the vibration of the perchlorate ion appears as a single band around 1090 and 623 cm^{-1}, implying that the ion is not coordinated to the copper ions. The FAB mass spectrum of the green crystal complex exhibits peaks at 1360, 1261 and 630 which may be assigned to $[Cu_2(L_2)_2][ClO_4]$, $[Cu_2(L_2)_2]$ and $Cu(L_2)$, respectively. Combined with elemental analysis data, this is consistent with a formulation of $[Cu_2(C_{39}H_{29}N_5)_2]^{4+}[ClO_4]_4^-$ containing two Cu^{II} copper ions. The FAB mass spectrum of the brown violet copper complex (**1**) exhibits peaks at 1461, 1360, 1262, 1198 and 631 which may be assigned to $[Cu_2(L_2)_2][ClO_4]_2$, $[Cu_2(L_2)_2][ClO_4]$, $[Cu_2(L_2)_2]$, $[Cu(L_2)_2]$ and $Cu(L_2)$, respectively. These observations are consistent with a formula of $[[Cu_2(C_{39}H_{29}N_5)_2]^{3+}[ClO_4]_3^-] \cdot 2CH_3CN$, which is a bicopper complex in which one of the Cu^{II} ions in the original green crystal complex is reduced to Cu^I in the course of recrystallization.

The structure of the cation $[Cu_2(L_2)]^{3+}$ in (**1**) and labelling scheme of atoms and planes are shown in Fig. 1. Bond lengths between Cu and donor nitrogen atoms and bond angles in (**1**) are shown in Table 2.

The crystal structure of the complexes shows that the ligand molecules in (**1**) adopt a double helical configuration about the two copper atoms. In (**1**), Cu_2 is hexa-coordinated and is bonded to the nitrogen atoms of the terpyridine portion of each ligand molecule (rings 3–5, rings C–E). The bond lengths of Cu_2—N_3, Cu_2—N_5, Cu_2—N_8, Cu_2—N_{10} are in the range 2.239–2.329 Å, while the bond lengths of Cu_2—N_4 (1.950 Å) and Cu_2—N_9 (1.966 Å) are rather shorter. Hence Cu_2 exhibit a compressed octahedral geometry, due to restricted bite of the bipyridine portion of each ligand molecule; this is nicely reflected in the three *trans* angles N(3)—Cu(2)—N(5), N(8)—Cu(2)—N(10) and N(4)—Cu(2)—N(9) [154.7, 154 and 178° which reflect the meridional octahedron structure]. Cu_1 is four-coordinated and is bound to the two remaining pyridine nitrogen atoms of each ligand molecule. The bond lengths of Cu_1—N_1, Cu_1—N_2, Cu_1—N_7, and Cu_1—N_6 are almost the same. The angles of N(1)—Cu(1)—N(2), N(6)—Cu(1)—N(7), N(6)—Cu(1)—N(2), are 81.7, 81.3, 121.9° respectively, therefore, the geometry of Cu_1 may be regarded as being distorted tetrahedron. The two Cu atoms have different oxidation states, the first being +2 and the second +1. The different geometries have been found in the Cu complex of unsubstituted quinquepyridine (**3**) [3]. The bond distance of Cu(1)—Cu(2) is 3.953 Å showing that no interaction of metal-to-metal ions are observed.

In (1) the helical structure is achieved by a series of twists about interannular C—C bonds between two pyridine rings. The twist angles between pyridine planes in the two ligand molecules are illustrated in Table 3.

The twist angles between pyridine rings in each ligand molecule are different from that of the unsubstituted quinquepyridine in the binuclear copper complex (**3**), especially the major twist (133.9°, 129.6°) occurs between the bipyridine and terpyridine portions of the molecule (ring 2 to 3, ring B to C). Within the bipyridine unit and terpyridine unit, the deviations

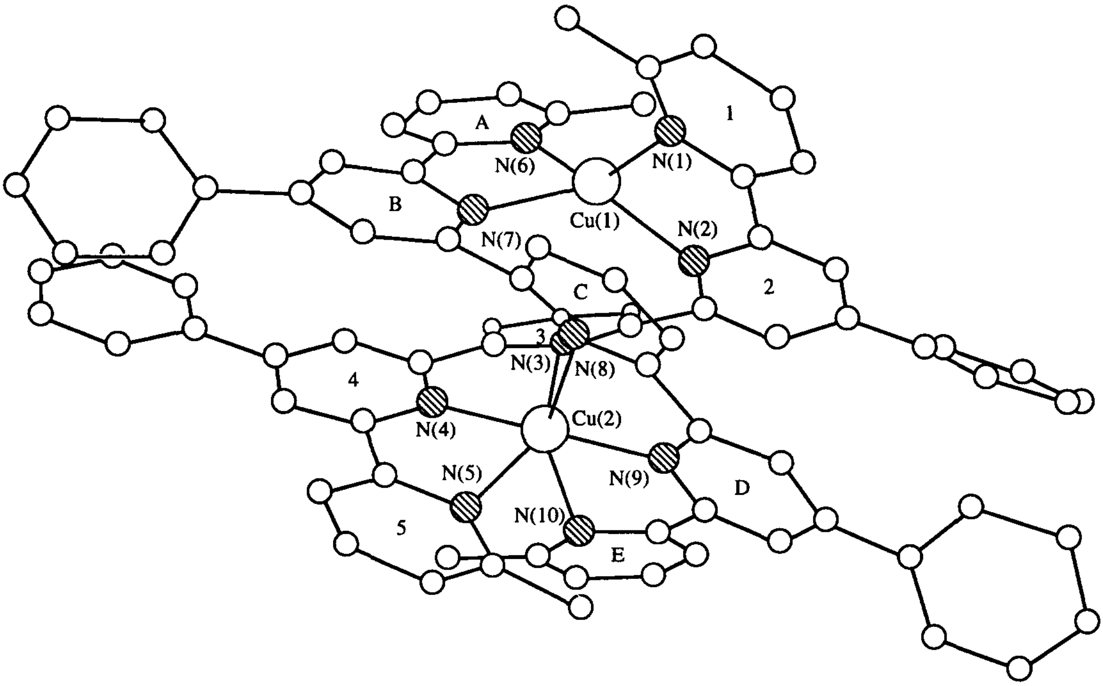

Fig. 1. The molecular structure of complex (**1**) with atom numbering scheme.

of the pyridine rings from coplanarity during the coordination are not very large (twist angles for the former are 19.6°, 15.5° and for the latter are 22.4°, 14.2° and 8.3°, 28.5° respectively). Therefore it appears, that the metal ions induce the two strands of quinquepyridine to self-assemble to a double helical binuclear complex.

These twist angles between pyridine ring 2 to 3 and ring B to C are greater than the unsubstituted quinquepyridine in complex 3 [3]. This is probably due to the steric influence of the phenyl groups attached on the para positions of pyridine rings 2 and 4 in each ligand and very similar to the 4′,4‴-dimethylthio quinquepyridine [13].

The double helical arrangement is emphasized in the space filling diagram presented in Fig. 2.

There are no significant interactions between perchlorate anions and CH_3CN molecules with the cations.

From the present results and literature, it can be deduced that to construct a double helical complex, some factors must be considered: (1) an adequate distribution of the ligand donor set is indispensable; (2) the co-ordination geometry of the metal ion, (3) the metal ion radius and (4) substituent effects (the presence of substituents at crucial positions can also control the assembly process [9].

Complex (**2**)

The IR spectrum of (**2**) is quite different from that of (**1**) and ligand L_I. The ligand L_I does not contain electron-withdrawing phenyl groups, so the move of electronic charge from the pyridine rings to the metal ion in (**2**) is very large, and the absorption bands of pyridine ring undergoes serious bathochromic shifts ($\Delta\gamma_{=CH}$ 48, $\Delta\gamma_{C=C,C=N}$ 38, $\Delta\sigma_{=CH}$ 17 cm^{-1}). The two bands at 619 and 652 cm^{-1} are assigned to the stretching of the oxygen of the perchlorate ion.

The FAB mass spectrum of (**2**) shows peaks at 627 and 528 corresponding to the species $[CdL_I][ClO_4]$ and $[CdL_I]$, respectively. No fragments containing two Cd atoms were observed. These data combined with the elemental analysis suggest that the molecular formula of (**2**) should be $[CdL_I][ClO_4]_2$, a mononuclear complex.

The complex (**2**) is diamagnetic, its ^1H NMR spectrum consists of nine well-resolved resonance signals, indicative of a highly symmetric configuration on the NMR time scale.

The X-ray crystal structure of (**2**) has been determined. The structure of the cation $[CdL_I]^{2+}$ in (**2**) and labeling scheme of atoms and planes are shown in Fig. 3. Bond lengths between Cd atom and donor nitrogen atoms and N—Cd—N bond angles in (2) are shown in Table 2.

In (**2**) all the pyridine rings are in *cis* conformations, Cd^{II} coordinates not only with all the nitrogen atoms of the pyridine rings, but also with two oxygen atoms of two perchlorate ions. The molecule has a C_2 symmetrical axis passing through atoms Cd, C^{16} and N^{17} and bisects the molecule into two equivalent portions. The bond lengths of Cd(1)—O(3) and O(3a) are rather longer than Cd(1) to the other donor atoms. Hence Cd is a pentagonal bipyramid configuration having O(3) or O(3a) situated at the apex. The twist angles of pyridine rings in (**2**) is influenced by steric

Table 2. Selected bond lengths (Å) and bond angles (°) for complexes (**1**) and (**2**)

Complex (**1**)			
Cu(1)—Cu(2)	3.953		
Cu(1)—N(1)	2.031(5)		
Cu(1)—N(2)	2.055(5)		
Cu(1)—N(6)	2.012(5)		
Cu(1)—N(7)	2.062(5)		
Cu(2)—N(3)	2.272(5)		
Cu(2)—N(4)	1.950(5)		
Cu(2)—N(5)	2.239(5)		
Cu(2)—N(8)	2.309(3)		
Cu(2)—N(9)	1.966(5)		
Cu(2)—N(10)	2.329(6)		
N(1)—Cu(1)—N(2)	81.7(2)	N(1)—Cu(1)—N(6)	136.1(2)
N(2)—Cu(1)—N(6)	121.9(2)	N(1)—Cu(1)—N(7)	112.2(2)
N(2)—Cu(1)—N(7)	131.0(2)	N(6)—Cu(1)—N(7)	81.3(2)
N(3)—Cu(2)—N(4)	77.0(2)	N(3)—Cu(2)—N(5)	154.7(2)
N(4)—Cu(2)—N(5)	77.8(2)	N(3)—Cu(2)—N(8)	103.9(2)
N(4)—Cu(2)—N(8)	105.0(2)	N(5)—Cu(2)—N(8)	84.0(2)
N(3)—Cu(2)—N(9)	101.6(2)	N(4)—Cu(2)—N(9)	178.0(2)
N(5)—Cu(2)—N(9)	103.5(2)	N(8)—Cu(2)—N(9)	76.7(2)
N(3)—Cu(2)—N(10)	82.2(2)	N(4)—Cu(2)—N(10)	101.0(2)
N(5)—Cu(2)—N(10)	101.3(2)	N(8)—Cu(2)—N(10)	154.0(2)
N(9)—Cu(2)—N(10)	77.3(2)		
Complex (**2**)			
Cd(1)—O(3)	2.460(8)		
Cd(1)—O(3a)	2.460(8)		
Cd(1)—N(7)	2.445(5)		
Cd(1)—N(7a)	2.445(5)		
Cd(1)—N(13)	2.345(5)		
Cd(1)—N(13a)	2.345(5)		
Cd(1)—N(17)	2.388(7)		
O(3)—Cd(1)—N(7)	79.4(2)	O(3)—Cd(1)—N(13)	104.1(2)
N(7)—Cd(1)—N(13)	68.7(2)	O(3)—Cd(1)—N(17)	94.7(1)
N(7)—Cd(1)—N(17)	132.9(1)	N(13)—Cd(1)—N(17)	67.7(1)
O(3)—Cd(1)—O(3a)	170.7(2)	N(7)—Cd(1)—O(3a)	94.1(2)
N(13)—Cd(1)—O(3a)	79.5(2)	N(17)—Cd(1)—O(3a)	94.7(1)
O(3)—Cd(1)—N(7a)	94.1(2)	N(7)—Cd(1)—N(7a)	94.2(2)
N(13)—Cd(1)—N(7a)	151.7(2)	N(17)—Cd(1)—N(7a)	132.9(1)
O(3a)—Cd(1)—N(7a)	79.4(2)	O(3)—Cd(1)—N(13a)	79.5(2)
N(7)—Cd(1)—N(13a)	151.7(2)	N(13)—Cd(1)—N(13a)	135.3(2)
N(17)—Cd(1)—N(13a)	67.7(1)	O(3a)—Cd(1)—N(13a)	104.1(2)
N(7a)—Cd(1)—N(13a)	68.7(2)		

Table 3. The twist angles (°) between pyridine planes for complexes (**1**) and (**2**)

Angles between pyridine planes (°)	Complex (**1**)	Complex (**3**) [3] $[Cu_2L_2][PF_6]_3 \cdot 2CH_3CN$	Complex (**2**)
Ligand 1			
1–2	19.6	12.0	7.8
2–3	133.9	48.3	10.3
3–4	22.4	17.4	10.3
4–5	14.2	11.3	7.8
Ligand 2			
A–B	15.5	6.1	
B–C	129.6	47.7	
C–D	8.3	27.8	
D–E	28.5	9.0	

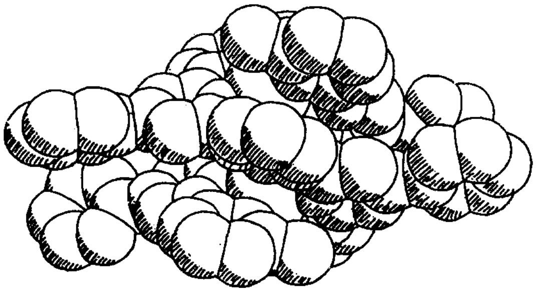

Fig. 2. Double helical configuration of the ligand molecules of (**1**).

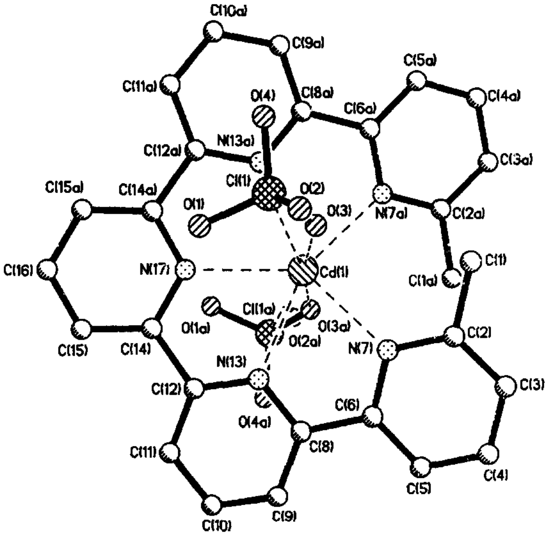

Fig. 3. The structure of $[CdL_1]^{2+}$.

interaction between the two terminal methyl groups as shown in Table 3. Hence the structure of (**2**) may be regarded as monohelical, being analogous to the Ag(1) complex of quinquepyridine [1]. The Cd^{II} ion is of the correct size (r = 1 Å) [14] for the cavity of quinquepyridine in the all *cis* conformation (r = 1 Å) [15] therefore a mononuclear complex is easily formed, while the size of copper ions is too small, only part of the pyridine nitrogen atoms in the ligand is coordinated to one copper ion and the remaining pyridine rings are twisted about the annular C—C bond in a fashion that may lead to coordination with another copper ion to form a binuclear double helical $[Cu_2L_2]^{3+}$ ion.

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