pH Dependence of Binding Site in Complexation of Cu^II with Picolinamide Groups: Crystallographic Studies of Mono- and Binuclear Complexes with N,N'-Dipicolinoyl-1,3-propanediamine*

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Abstract

Three related copper complexes (a) $[Cu(C_{15}H_{14}N_4O_2)(H_2O)] . 2H_2O$, $M_r = 399 \cdot 90$, monoclinic, $P2_1/c$, $a = 11 \cdot 730$ (5), $b = 13 \cdot 097$ (7), $c = 12 \cdot 668$ (5) Å, $\beta = 119 \cdot 59$ (3)°, $U = 1692$ (1) Å^3, $Z = 4$, $D_m = 1 \cdot 59$, $D_x = 1 \cdot 570$ Mg m^{-3}, $T = 296$ K, final $R = 4 \cdot 6\%$ ($wR = 5 \cdot 4\%$) for 2279 independent reflections; (b) $[CuCl(C_{15}H_{16}N_4O_2)]_2SO_4 . 8H_2O$, $M_r = 1006 \cdot 82$, monoclinic, $P2_1/c$, $a = 14 \cdot 679$ (2), $b = 13 \cdot 070$ (2), $c = 23 \cdot 958$ (6) Å, $\beta = 111 \cdot 56$ (2)°, $U = 4275$ (2) Å^3, $Z = 4$, $D_m = 1 \cdot 53$, $D_x = 1 \cdot 564$ Mg m^{-3}, $T = 296$ K, final $R = 6 \cdot 1\%$ ($wR = 6 \cdot 6\%$) for 5415 independent reflections; and (c) $[Cu(SO_4)(C_{15}H_{16}N_4O_2)]_2 . 13H_2O$, $M_r = 1122 \cdot 06$, orthorhombic, $C222_1$, $a = 15 \cdot 42$ (1), $b = 24 \cdot 92$ (2), $c = 25 \cdot 73$ (2) Å, $U = 9885$ (13) Å^3, $Z = 8$, $D_m = 1 \cdot 52$, $D_x = 1 \cdot 51$ Mg m^{-3}, $T = 296$ K, were studied. In the monomeric complex (a) prepared in an alkaline solution, the Cu^II ion is surrounded by four N atoms of the two deprotonated amide and two pyridine moieties, and a water molecule at the apex, yielding a distorted square-pyramidal structure. Both complex cations in the dimeric complexes (b) and (c) obtained in acidic solution have approximate D_2 symmetry, the Cu^II ions being surrounded by the two N in pyridine rings and two amide O atoms in each half of two picolinoyl groups in an approximate plane, and two Cl$^-$ ions for (b) and SO$_4^{2-}$ ions for (c) occupying axial positions respectively. These structures are essentially consistent with those proposed from absorption and ESR studies.

Introduction

In a previous communication, the unique properties of N,N'-di(picolinoyl)-1,3-propanediamine [(1), H₂ppda] as a ligand were discussed (Kajikawa,

Mukai, Ishizu & Ojima, 1981). This potentially tetradentate amide reacts with copper(II) sulfate in alkaline solution to give a dark blue–violet CuN₄-type complex (Ojima, 1967). The color changes reversibly to blue upon acidification of the solution. The blue complex has been characterized by spectral studies as the dimeric CuN_2O_2 form having a spin triplet state. Particularly for the latter, the ESR study showed that the two equivalent Cu atoms stack together so that the *g* and *D* tensor axes coincide with each other and the distance between two metal ions was evaluated to be *ca* 4 Å. Such a color change and the pH dependence of the binding site are characteristic of biuret, polypeptides or proteins (Sigel & Martin, 1982).

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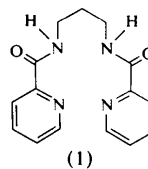
This investigation arose partly out of a general interest in copper–protein interaction and partly out of structural interest in a spin triplet Cu^II complex. Stephens and his coworkers have studied a series of Cu^II complexes with symmetrical picolinamide derivatives, including H₂ppda, prepared at high pH conditions (Chapman, Stephens & Vagg, 1980, 1981; Mulqi, Stephens & Vagg, 1981; Stephens & Vagg, 1981, 1982). The crystal structure determination of these complexes showed that the metal atoms were coordinated by two N atoms of the deprotonated amide and two N atoms of the pyridine moiety in all cases. For [Cu(ppda)] two different crystalline forms designated α and β were separated and the structure of the latter has been determined by Stephens & Vagg

Table 1. *Summary of intensity data collection and structure refinement*

Complex	(a)	(b)	(c)
Color	Dark blue-violet	Blue	Blue
Crystal dimensions (mm)	$0.30 \times 0.30 \times 0.20$	$0.30 \times 0.40 \times 0.40$	$0.30 \times 0.30 \times 0.07$
Crystal shape	Rhomboid	Short prismatic	Rhombic plate
$F(000)$	828	2080	4672
Absorption coefficient (μ) (cm^{-1})	13.2	12.4	10.3
Scan range	$\pm h, k, l$	$\pm h, k, l$	h, k, l
Standards	202, 006, 354	400, 080, 004	600, 0,12,0, 12,0,6
Max. 2θ (°)	55	55	40
No. of reflections observed $[\lvert F_o \rvert > 3\sigma(\lvert F_o \rvert)]$	3106	5857	940
No. of unique reflections	2831	5415	910
No. of unobserved reflections	951	4195	1620
No. of variables	307	661	294
R	0.046	0.061	0.20
R_w	0.054	0.066	0.18
H atoms	Included	Included	—
$(\Delta/\sigma)_{max}$ in final cycle	0.26	0.32*	

* Except for O(W8) which has a very large temperature factor.

(1982). However, the structure of the α form has not yet been obtained and there is no structural report on the dimeric ppda complex prepared in acidic medium.

We report here the structures of monomeric Cu–ppda complex obtained at high pH $\{(a)\,[\text{Cu(ppda)}\,.\,(\text{H}_2\text{O})]\,.\,2\text{H}_2\text{O}\}$, which is the α form mentioned above, and two binuclear complexes $\{(b)\,[\text{CuCl(H}_2\text{ppda)}]_2\text{SO}_4\,.\,8\text{H}_2\text{O}$ and $(c)\,[\text{Cu(SO}_4)\,.\,(\text{H}_2\text{ppda)}]_2\,.\,13\text{H}_2\text{O}\}$ formed at pH 3·8.

Experimental

The monomeric complex (a) and the dimeric (c) were obtained from H$_2$ppda and CuSO$_4$ in alkaline and in acidic (pH = 3·8) aqueous solution, respectively, according to the reported procedure (Ojima, 1967; Kajikawa, Mukai, Ishizu & Ojima, 1981). The other dimeric complex (b) was prepared from a 1:1 mixture of (c) and the corresponding tetrachloride complex, [CuCl(H$_2$ppda)]$_2$Cl$_2$.2H$_2$O; the analytical data [found (%): C 35·57, H 4·65, N 11·04, S 3·00, Cl 7·00, Cu 12·62; calculated for C$_{30}$H$_{48}$Cl$_2$Cu$_2$N$_8$O$_{16}$S: C 35·79, H 4·81, N 11·13, S 3·18, Cl 7·04, Cu 12·62] indicate that two Cl atoms, one SO$_4$ group and eight water molecules are included per molecule of the complex. The crystal of (b) was sealed in a glass capillary, and the crystal of (c) coated with nail enamel and used for the diffraction study.

Intensity data collection: Rigaku AFC automated four-circle diffractometer, graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71073$ Å), ω and ω–2θ ($2\theta > 30°$) scans, scan rate 4·0° min^{-1}. Details of experimental conditions are listed in Table 1. Intensities corrected for Lorentz and polarization factors, but not for absorption. Three standard reflections measured every 100 reflections. Structures solved by the heavy-atom method for complex (a) and by the direct method for complexes (b) and (c) using MUL-TAN78 (Main, Hull, Lessinger, Germain, Declercq

& Woolfson, 1978). Refinements by block-diagonal least-squares procedure based on $\lvert F_o \rvert$ (Table 1). In complex (a), all H atoms were deduced from successive difference Fourier syntheses and the amide N atoms were found to have no H atoms. All non-hydrogen atoms anisotropic and H atoms isotropic.

The quality of the crystal of (c) is poor, despite its good appearance. Very few intensity data were obtained beyond $2\theta = 30°$ and the result of the structure analysis for (c) was not good enough to permit exact evaluation. Since the molecular shapes of the complex cations in crystals (b) and (c) were found to be very similar, only the geometry of the former is given. The atomic coordinates are listed in Table 2.* Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Max. heights in final difference Fourier maps 1·0 e Å^{-3} for (a) and 1·8 e Å^{-3} for (b). Crystallographic calculations performed on a FACOM M-380 computer of this Institute using the *UNICS*III program system (Sakurai & Kobayashi, 1979).

Discussion

Complex (a)

The shape of complex (a) is shown in Fig. 1. Although the molecular geometry is essentially the same as that of the β form, considerable differences are found in the angle between the two pyridyl planes and in the mode of molecular packing. The geometry about the Cu$^{\text{II}}$ is a distorted square pyramid whose base is surrounded by the tetradentate ligand, and a water molecule is at the apex. The complex has no

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Table 2. *Atomic parameters of complexes* (a) *and* (b)

Positional parameters are multiplied by 10^4. The equivalent isotropic temperature factor is defined by $B_{eq} = \frac{4}{3}\sum_i \sum_j \beta_{ij}\mathbf{a}_i \cdot \mathbf{a}_j$.

	x	y	z	$B_{eq}(\text{Å}^2)$
Complex (a)				
Cu	1832·2 (0·5)	692·9 (0·4)	4284·4 (0·5)	2·27 (0·02)
O(W1)	2668 (3)	1928 (3)	3478 (3)	3·3 (0·1)
N(1)	550 (4)	1451 (3)	4688 (4)	2·8 (0·1)
C(2)	772 (5)	1962 (5)	5685 (5)	4·0 (0·2)
C(3)	-226 (5)	2420 (5)	5809 (5)	3·7 (0·2)
C(4)	-1491 (5)	2316 (4)	4896 (5)	3·0 (0·2)
C(5)	-1738 (4)	1763 (4)	3870 (4)	2·8 (0·2)
C(6)	-701 (4)	1345 (3)	3790 (4)	2·3 (0·1)
C(7)	-895 (4)	714 (4)	2719 (4)	2·6 (0·1)
O(8)	-2038 (3)	575 (3)	1850 (3)	4·1 (0·1)
N(9)	200 (3)	377 (3)	2807 (3)	2·5 (0·1)
C(10)	82 (5)	-253 (4)	1799 (4)	3·3 (0·2)
C(11)	1422 (5)	-468 (4)	1930 (4)	3·0 (0·2)
C(12)	2308 (5)	-1103 (4)	3050 (4)	2·5 (0·1)
N(13)	2767 (3)	-489 (3)	4155 (3)	2·2 (0·1)
O(14)	4513 (3)	-1560 (2)	5297 (3)	2·8 (0·1)
C(15)	3821 (4)	-780 (3)	5139 (4)	2·1 (0·1)
C(16)	4219 (4)	-40 (3)	6181 (4)	2·0 (0·1)
C(17)	5271 (5)	-213 (4)	7329 (4)	2·8 (0·2)
C(18)	5624 (5)	554 (4)	8194 (4)	3·2 (0·2)
C(19)	4979 (5)	1485 (4)	7865 (5)	3·1 (0·2)
C(20)	3935 (5)	1601 (4)	6707 (5)	2·9 (0·2)
N(21)	3519 (3)	835 (3)	5889 (3)	2·3 (0·1)
O(W2)	-4413 (3)	1626 (3)	887 (4)	4·1 (0·1)
O(W3)	-2959 (4)	-1217 (3)	421 (4)	4·7 (0·2)
Complex (b)				
Cu(1)	32·6 (0·7)	1233·4 (0·7)	1275·1 (0·4)	2·81 (0·03)
Cl(1)	-373 (1)	-587 (2)	1405 (1)	3·5 (0·1)
N(1)A	1026 (4)	1440 (4)	2082 (3)	2·6 (0·2)
C(2)A	2006 (5)	1352 (6)	2253 (3)	3·2 (0·2)
C(3)A	2619 (5)	1429 (6)	2846 (4)	3·5 (0·2)
C(4)A	2224 (6)	1591 (7)	3276 (3)	3·7 (0·2)
C(5)A	1216 (6)	1708 (6)	3106 (3)	3·3 (0·2)
C(6)A	641 (5)	1613 (5)	2505 (3)	2·6 (0·2)
C(7)A	-451 (5)	1711 (5)	2234 (3)	2·5 (0·2)
O(8)A	-856 (4)	1759 (4)	1668 (2)	3·3 (0·2)
N(9)A	-953 (4)	1736 (5)	2591 (3)	2·9 (0·2)
C(10)A	-2024 (5)	1843 (6)	2370 (3)	2·9 (0·2)
C(11)A	-2327 (5)	2850 (6)	2561 (3)	3·0 (0·2)
C(12)A	-1931 (5)	3791 (6)	2355 (3)	3·0 (0·2)
N(13)A	-2228 (4)	3813 (5)	1696 (2)	2·5 (0·2)
O(14)A	-705 (3)	4181 (4)	1722 (2)	3·0 (0·1)
C(15)A	-1594 (5)	3984 (5)	1434 (3)	2·3 (0·2)
C(16)A	-1941 (5)	3947 (5)	760 (3)	2·3 (0·2)
C(17)A	-2890 (5)	3854 (6)	367 (3)	2·7 (0·2)
C(18)A	-3059 (5)	3827 (6)	-244 (3)	3·2 (0·2)
C(19)A	-2284 (5)	3883 (6)	-438 (3)	3·2 (0·2)
C(20)A	-1361 (5)	3990 (6)	-20 (3)	3·2 (0·2)
N(21)A	-1182 (4)	4020 (4)	573 (2)	2·4 (0·2)
Cu(2)	96·3 (0·6)	4250·3 (0·7)	1216·8 (0·4)	2·60 (0·02)
Cl(2)	270 (1)	6120 (2)	1069 (1)	3·3 (0·1)
N(1)B	-921 (4)	1327 (5)	447 (2)	2·8 (0·2)
C(2)B	-1894 (5)	1292 (6)	274 (3)	3·2 (0·2)
C(3)B	-2495 (6)	1264 (7)	-321 (4)	3·6 (0·2)
C(4)B	-2076 (6)	1271 (7)	-750 (3)	3·9 (0·3)
C(5)B	-1073 (6)	1316 (6)	-575 (3)	3·4 (0·2)
C(6)B	-507 (5)	1345 (5)	22 (3)	2·6 (0·2)
C(7)B	580 (5)	1369 (5)	302 (3)	2·7 (0·2)
O(8)B	976 (4)	1345 (4)	867 (2)	3·3 (0·2)
N(9)B	1110 (4)	1403 (5)	-39 (3)	3·0 (0·2)
C(10)B	2176 (6)	1462 (6)	189 (3)	3·3 (0·2)
C(11)B	2531 (5)	2430 (6)	-20 (3)	3·0 (0·2)
C(12)B	2167 (5)	3426 (6)	151 (3)	3·0 (0·2)
N(13)B	2435 (4)	3536 (4)	804 (3)	2·4 (0·2)
O(14)B	883 (3)	3811 (4)	742 (2)	3·2 (0·2)
C(15)B	1781 (5)	3731 (5)	1041 (3)	2·4 (0·2)
C(16)B	2119 (5)	3887 (5)	1710 (3)	2·5 (0·2)
C(17)B	3064 (5)	3858 (6)	2115 (3)	3·3 (0·2)
C(18)B	3233 (6)	4011 (7)	2724 (4)	4·2 (0·3)
C(19)B	2459 (6)	4163 (7)	2903 (3)	3·7 (0·3)
C(20)B	1524 (5)	4178 (6)	2472 (3)	2·9 (0·2)
N(21)B	1357 (4)	4062 (4)	1892 (2)	2·4 (0·2)
S(1)	5095·1 (1.3)	3832·0 (1.5)	1240·8 (0·9)	2·91 (0·05)
O(S1)	5869 (4)	3192 (5)	1178 (3)	4·3 (0·2)
O(S2)	5533 (6)	4592 (6)	1710 (3)	6·9 (0·3)
O(S3)	4412 (4)	3171 (5)	1394 (3)	5·0 (0·2)
O(S4)	4580 (5)	4361 (5)	682 (3)	5·7 (0·2)
O(W1)	4925 (9)	1195 (8)	1808 (5)	11·3 (0·5)
O(W2)	4724 (8)	2981 (7)	4253 (5)	11·2 (0·5)
O(W3)	5930 (12)	1498 (12)	557 (10)	22·5 (1·1)
O(W4)	4255 (5)	1077 (5)	4499 (3)	5·6 (0·2)
O(W5)	6181 (6)	4644 (7)	2945 (3)	7·4 (0·3)
O(W6)	5580 (7)	2956 (8)	3434 (5)	10·1 (0·4)
O(W7)	5782 (8)	1055 (8)	3074 (5)	10·9 (0·5)
O(W8)	5005 (23)	2 (19)	800 (11)	31·3 (2·0)

counter anion. These results agree with the proposed CuN_4 square-planar chargeless model except for the apical coordination (Ojima, 1967; Kajikawa, Mukai, Ishizu & Ojima, 1981). The bond parameters around Cu are summarized in Table 3, in which those of the dimeric complexes are also given. In the present structure the complex has a pair of chemically equivalent bonds, and the bond lengths in the pair are generally in fair agreement, but some torsion angles differ as shown in Fig. 2. This is due to strain caused by steric repulsion between *ortho* H atoms in the two adjacent pyridyl rings. The conformation is described with reference to a least-squares plane through four donor N atoms, indicating the relative positions of the other atoms above or below this plane [Fig. 2(ii)]. This shows that the diagonal atom pair N(1),N(13) is below the plane, while the pair N(9),N(21) is above and the Cu atom lies 0·263 Å (0·24 Å in the β form) out of the plane toward the apical O atom. The dihedral angle between the two planes N(1)–N(9)– N(21) and N(13)–N(9)–N(21) is 17·8°. The coordination form is displaced 27% from a square-pyramidal (s.p.) conformation toward trigonal bipyramidal (t.b.) along the Berry coordinate (Holmes & Deiters, 1977).

The $Cu-N_{amide}$ (av. 1·950 Å) and $Cu-N_{pyridine}$ (av. 2·048 Å) bond lengths, and the displacement of Cu from the basal N_4 plane are similar to those found in the β form and in the related complexes studied by Stephens and coworkers (Chapman, Stephens & Vagg, 1980, 1981; Mulqi, Stephens & Vagg, 1981; Stephens & Vagg, 1981, 1982). The apical Cu–O length [2·369 (1) Å] is longer than the 2·268 (4) Å in the β form. In the Cu^{II} complexes with glycylgly-cylglycine (Cu–ggg; Freeman, Schoone & Sime, 1965), and with biuret (Freeman, Smith & Taylor, 1961), formed at higher pH, the corresponding $Cu-N_{amide}$ bond lengths show similar values (1·94 and 1·93 Å respectively). The amide groups are planar within 0·006 Å. The six-membered chelate ring has a boat-like form with C(11) at the bow toward the apex as in the β form.

The steric strain due to the *ortho* H atoms of the two pyridyl rings is partially relieved by : (i) a reduction of the angles N(1)–Cu–N(13) or N(9)–Cu–N(21), (ii) expansion of the angle between the two pyridyl rings and (iii) twisting of the pyridyl planes with respect to each other. Molecular models suggest
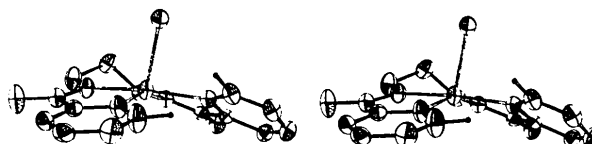

Fig. 1. A stereoscopic drawing of complex (a). H atoms other than those in the *ortho* positions of the pyridyl rings have been omitted for clarity.

that these movements are restricted by the rigid 5-6-5-membered chelate ring system formed by coordination. As a result, the intramolecular contact between two *ortho* H atoms in the pyridyl rings [H(C2)···H(C20)] is short [1·95 (9) Å]. In the β form the separation is only 1·86 Å. A marked difference is observed between the α and β forms in the dihedral angles between the two pyridyl planes; 42·3 (2) and 26·4° respectively.

The present complex {(a)[Cu(ppda)(H₂O)]. 2H₂O} may be compared with a more flexible complex of N,N'-di(2-pyridyl)-2,6-diazaheptane, which has no carbonyl group and the same 5-6-5-membered chelate ring system (Bailey, McKenzie & Mullins, 1970). The geometry about Cu is t.b., the six-membered chelate ring takes the usual chair form,
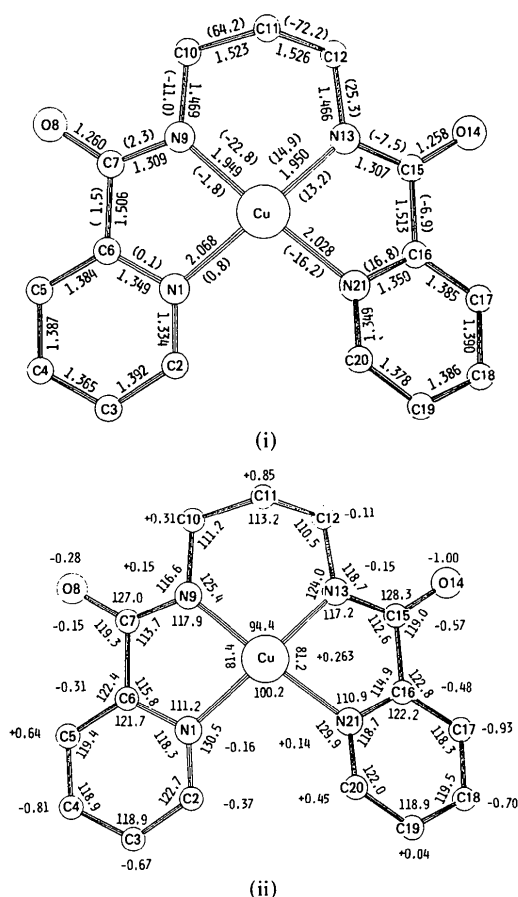

(i)

(ii)

Fig. 2. The bond parameters in complex (a). (i) Bond lengths (Å) and torsion angles (°). Torsion angles around the chelate rings are given in parentheses. Other values are bond lengths. (ii) Bond angles (°) and atomic displacements (Å) from the N₄ mean plane; the atomic displacements are the values with positive or negative signs, indicating respectively the relative positions of the other atoms above or below this plane. The standard deviations are: bond lengths: Cu–N 0·005, N–C 0·008, C–C (pyridine ring) 0·01, C–C 0·007, C=O 0·006, C–N 0·007, C–C (aliphatic) 0·009 Å; torsion angles: 0·6°; bond angles: in the chelate rings 0·6, others 0·3 ~ 0·5°. Atomic displacements: 0·002 Å for Cu and ~0·01 Å for other atoms.

Table 3. *Bond parameters around copper* (Å *and* deg)

Complex	(a)		(b)
		Cl(1)	Cl(2)
X	O(W1)	N(1)A, N(1)B	N(21)B, N(21)A
N, N'	N(1), N(13)	O(8)B, O(8)A	O(14)A, O(14)B
Y, Y'	N(9), N(21)		
Cu···X	2·369 (1)	2·500 (2)	2·496 (2)
X···Cu···N	106·5 (2)	97·6 (2)	97·1 (2)
X···Cu···Y	98·7 (2)	92·4 (2)	104·3 (2)
X···Cu···N'	97·8 (2)	94·1 (2)	99·0 (2)
X···Cu···Y'	87·9 (1)	112·0 (2)	95·2 (2)
N···Cu···N'	155·7 (2)	168·2 (3)	163·9 (2)
Y···Cu···Y'	172·6 (2)	155·6 (2)	160·5 (2)
Cu from basal plane	0·263 (2)	0·324 (3)	0·308 (3)

and the short non-bonded contact between *ortho* H atoms is 2·76 Å.

The related analogous Cu complex of N,N'-dipicolinoyl-1,2-ethylenediamine {[Cu(peda)-(H₂O)]. H₂O} obtained at higher pH has a 5-5-5 chelate ring system (Ojima, 1967; Chapman, Stephens & Vagg, 1981). When the structures of the Cu–ppda and Cu–peda complexes are compared, the following points should be noted (as summarized in Table 4). Red shift in the d–d transition band, a larger N_{amide}–Cu–N_{amide} angle and a smaller $N_{pyridine}$–Cu–$N_{pyridine}$ angle, and less separation of the two *ortho* H atoms and/or more twisting of the two pyridyl planes are observed in the Cu–ppda complex. These mean that a complex of picolinamide having a 5-6-5 chelate ring system has more strain than that with a 5-5-5 system.

A projection of the crystal structure along the a axis is shown in Fig. 3, where hydrogen bonds are indicated by broken lines. All the amide O atoms, and the coordinated and crystalline water molecules participate in the hydrogen bonds. Details are listed in Table 5. Whereas the hydrogen bonds in a crystal
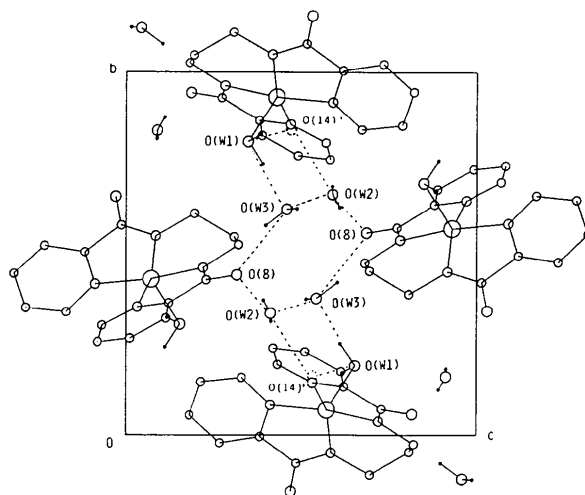

Fig. 3. Crystal structure of complex (a) projected along a. Dashed lines indicate hydrogen bonds.

Table 4. *Separation of ortho* H *atoms and twisting in two pyridine rings for* Cu–ppda *and* Cu–peda *complexes*

	d–d transition ν_{max} (cm^{-1}) (ε)*	N_{amide}–Cu–N_{amide} (°)	$N_{pyridine}$–Cu–$N_{pyridine}$ (°)	H$\cdots$H distance (Å)	Twisting of pyridine rings (°)
Cu–ppda, α form†	17700 (97)	94·4	100·2	1·95	42·3
Cu–ppda, β form‡		93·7	101·1	1·86	26·4
Cu–peda, A§	18700 (212)	82·3	112·7	2·27	10·8
Cu–peda, B		82·8	110·8	2·24	26·8

* Measured in aqueous solution (Ojima, 1967).
† Complex (a) (present work).
‡ Stephens & Vagg (1982).
§ The crystal contains two independent molecules, A and B (Chapman, Stephens & Vagg, 1981).

Table 5. *Hydrogen-bond distances* (Å) *in complex* (a)

For symmetry code see Table 6.

O$\cdots$O		O$\cdots$O	
O($W1$)$\cdots$O(14^{ii})	2·917 (5)	O(8)$\cdots$O($W3^{i}$)	2·831 (6)
O($W1$)$\cdots$O($W3^{iii}$)	2·737 (6)	O(14)$\cdots$O($W2^{iii}$)	2·780 (5)
O(8)$\cdots$O($W2^{i}$)	2·791 (5)	O($W2$)$\cdots$O($W3^{iv}$)	2·737 (5)

of the β form connect the molecules perpendicular to the b axis, the molecules in this complex are linked by hydrogen bonds along the b axis.

Other intermolecular contacts are normal. The closest approach, O(14)$\cdots$C(19), is 3·311 (8) Å.

Complex (b)

A perspective view of the molecular conformation and the bond parameters are shown in Figs. 4 and 5 respectively. The structure consists of a parallel array of the binuclear complex perpendicular to the b axis with no unusually close intermolecular approaches except for hydrogen bonds. Each Cu^{II} ion has a distorted s.p. coordination containing two half-ligand molecules in *trans* positions and a Cl$^-$ ion at the apex. The ligands coordinate to the Cu through the amide O atoms and the N atoms in the pyridine moieties. The geometries about the two Cu^{II} ions are not exactly the same (see Table 3), and the displacements from the s.p. toward t.b. conformation are 28 and 11% respectively. The shifts of the Cu^{II} ions from the basal planes are 0·32 and 0·31 Å respectively. Except for the shorter Cu–N$_{pyridine}$ average values of 1·969 Å, the other bonds show similar lengths to the monomeric series. The mean Cu–O bond length, 1·981 Å, is comparable to the value for the peptide linkage in the Cu–ggg complex formed at lower pH (1·987 Å; Freeman, Robinson & Schoone, 1964), and is longer than that in the CuO$_4$ biuret complex (1·935 Å; Freeman & Smith, 1966). The presence of protons on the aliphatic amide N atoms at N(13) was confirmed by a difference Fourier synthesis, and the protons were found to be involved in hydrogen bonds with O of SO$_4$. Although the presence of H atoms at N(9) was equivocal in the analysis, they seem to be involved in hydrogen bonding to the Cl$^-$ ions as given in Table 6.

Table 6. *Hydrogen-bond distances* (Å) *in complex* (b)

O,N$\cdots$O,Cl		O$\cdots$O	
N(9)$A\cdots$Cl(2^{iii})	3·097 (6)	O($W1$)$\cdots$O($W7^{i}$)	2·83 (2)
N(9)$B\cdots$Cl(1^{iv})	3·227 (6)	O($W1$)$\cdots$O($W8^{i}$)	2·91 (3)
N(13)$A\cdots$O($S1^{vi}$)	2·730 (7)	O($W1$)$\cdots$O($W5^{x}$)	2·79 (2)
N(13)$B\cdots$O($S3^{i}$)	2·760 (7)	O($W2$)$\cdots$O($W4^{i}$)	2·70 (1)
O($S1$)$\cdots$O($W3^{i}$)	2·69 (2)	O($W2$)$\cdots$O($W6^{i}$)	2·69 (1)
O($S2$)$\cdots$O($W5^{i}$)	2·76 (1)	O($W2$)$\cdots$O($W3^{ix}$)	3·05 (2)
O($S2$)$\cdots$O($W7^{vii}$)	2·90 (1)	O($W2$)$\cdots$O($W8^{vii}$)	2·68 (2)
O($S3$)$\cdots$O($W1^{i}$)	2·77 (1)	O($W3$)$\cdots$O($W8^{i}$)	2·57 (3)
O($S4$)$\cdots$O($W4^{viii}$)	2·76 (1)	O($W5$)$\cdots$O($W6^{i}$)	2·79 (1)
O($S4$)$\cdots$O($W4^{vii}$)	2·95 (1)	O($W6$)$\cdots$O($W7^{i}$)	2·68 (1)

Symmetry code

(i)	x, y, z	(vi)	$-1+x, y, z$
(ii)	$1-x, -y, 1-z$	(vii)	$1-x, \frac{1}{2}+y, \frac{1}{2}-z$
(iii)	$-x, \frac{1}{2}+y, -z+\frac{1}{2}$	(viii)	$x, \frac{1}{2}-y, -\frac{1}{2}+z$
(iv)	$-1-x, -y, -z$	(ix)	$x, \frac{1}{2}-y, \frac{1}{2}+z$
(v)	$-x, -y, -z$	(x)	$1-x, -\frac{1}{2}+y, \frac{1}{2}-z$

The two amide groups, C(6)–O(8)–C(7)–N(9) and C(16)–O(14)–C(15)–N(13), are planar within 0·005 Å. Such planar structural units containing Cu–O$_{amide}$ bonds may tend to stack together owing to geometrical requirements and electrostatic interactions. There are two possible different stacking modes: each half-ligand coordinates with two different Cu^{II} ions in *anti* and *syn* fashions as shown in Fig. 6; the *anti* type has D_2 symmetry and stacks with its mirror-image form. The former is the case. Two Cu^{II} ions are aligned coaxially with a base-to-base arrangement of the s.p. conformations and the complex resembles a spinning-wheel having pseudo D_2 symmetry. The connecting lines Cl(1)–Cu(1)–Cu(2) and Cl(2)–Cu(2)–Cu(1) are not exactly straight:
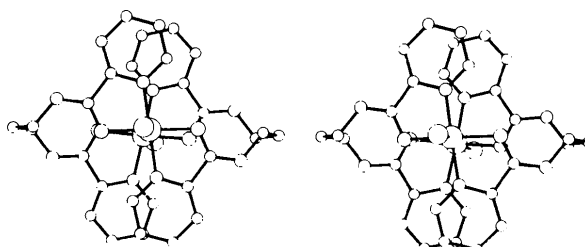

Fig. 4. A stereodrawing of complex (b).

164·75 (7) and 171·11 (7)° respectively. In agreement with the estimation from ESR, the Cu–Cu distance in the dimeric group is 3·948 (1) Å. The closest distances between these stacking pyridine rings are 3·46 (1) and 3·59 (1) Å at C(3)B···C(19)A and C(3)A···C(19)B respectively.

Projections of the crystal structure along the a and b axes are shown in Fig. 7(i), (ii). The structure consists of complex cations, Cl⁻ and SO$_4^{2-}$ anions, and water molecules, which are held together via a three-dimensional network of hydrogen bonds. The hydrogen-bond parameters are listed in Table 6. The molecules are stacked in a layer parallel to the ac plane. The Cu–Cu vector in the dimer is approxi-

mately parallel to the b axis. In spite of the large number of crystalline water molecules, all are involved in a hydrogen–bonding network which incorporates the O atoms of SO$_4$, forming a layer, and stabilizes the crystal arrangement. The complex cations are held together by hydrogen bonds of N(9)–H···Cl⁻ type, forming a layer structure. The hydrophobic cation layer cross-links with two different water layers via hydrogen bonds between N(13)A···O(S1) and N(13)B···O(S3). Some of the hydrogen-bond lengths are considerably shorter than those in the monomeric complex (a). These are good examples of the cooperative shortening of a water cluster (Newton, 1983).
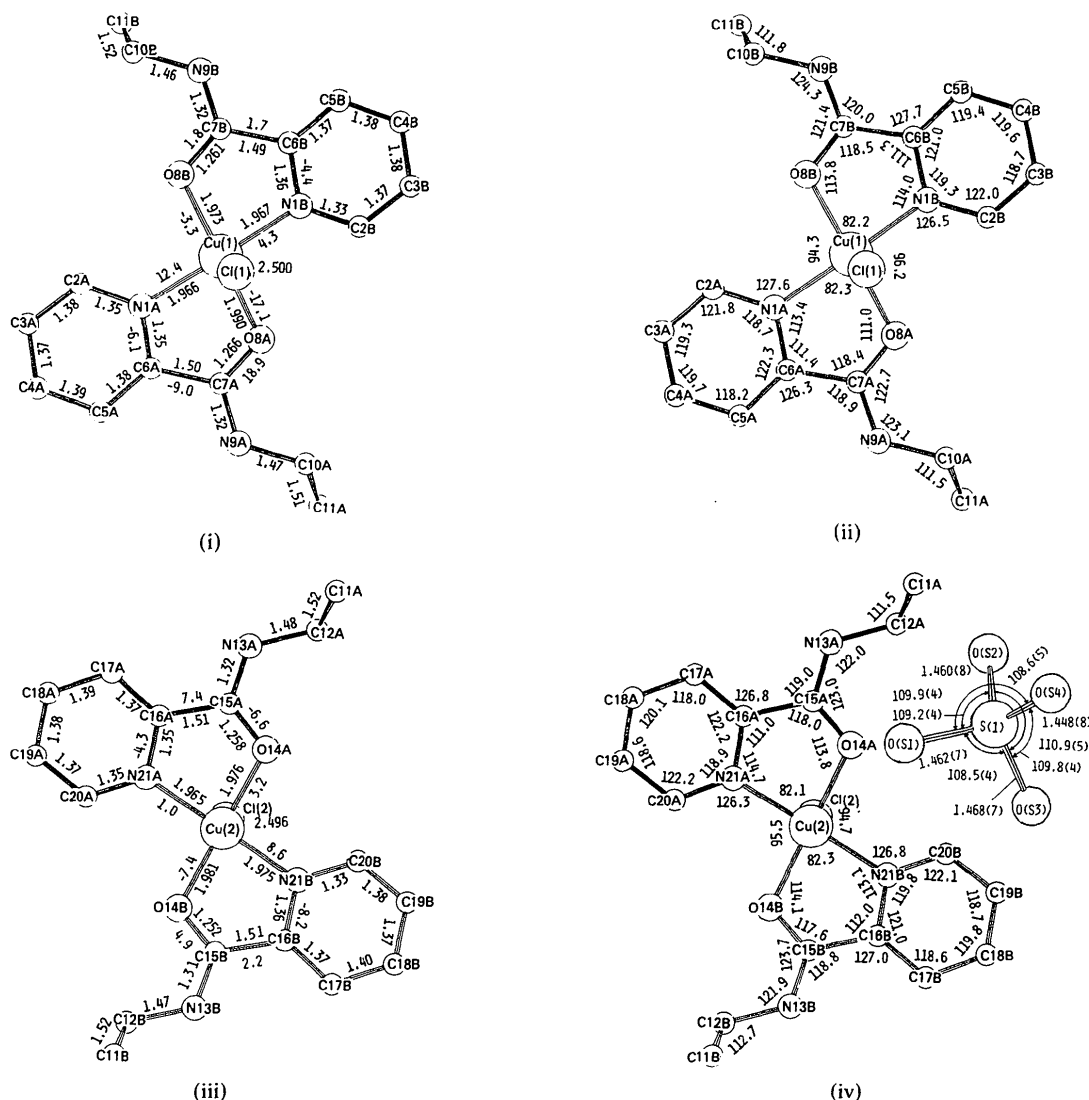

(i)

(ii)

(iii)

(iv)

Fig. 5. The bond parameters in complex (b). (i) Bond lengths (Å) and torsion angles (°), and (ii) bond angles (°) about Cu(1). (iii) Bond lengths (Å) and torsion angles (°), and (iv) bond angles (°) about Cu(2), and the bond parameters of the sulfate ion with their estimated standard deviations. Torsion angles around the chelate rings are expressed by the figures outside the rings. Other values are bond lengths. The standard deviations are: bond lengths: Cu–N and Cu–O 0·006, N–C and C–C (pyridine ring) 0·01, C=O 0·009, others 0·01 Å; torsion angles: 0·1°; bond angles: in pyridine ring 0·1, others 0·8°.

Complex (c)

Since the final R index is 20%, only the general features of the structure are described. There are two crystallographically independent molecules in the asymmetric unit. Their molecular shapes are similar to that observed in complex (b). Two half-picolinoyl groups form the basal plane and an O of the SO$_4$ group is at the apex. The packing of the molecules in the crystal is shown in Fig. 8.

The main difference between structures (b) and (c) is the mode of packing. The crystal of (c) contains
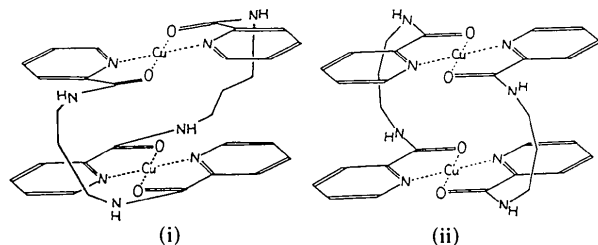
Fig. 6. Two possible coordinations for the dimeric complex. (i) *anti* form. (ii) *syn* form.
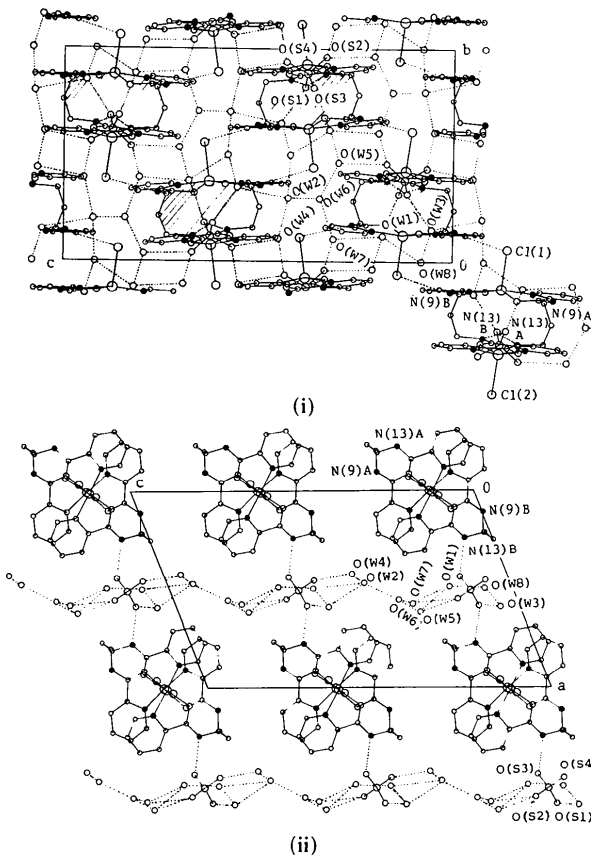
Fig. 7. Crystal structure of complex (b) projected (i) along **a**, and (ii) along **b**. Broken lines indicate hydrogen bonds. In (ii), only half of the atoms in the unit cell are drawn for the sake of clarity. The other half are obtained by the inversion operation.

13 water molecules in the asymmetric unit. In contrast to the rigid hydrogen network in (b), the water molecules in (c) easily escape from the crystal. Thus both the data collection and the structure analysis become very difficult. These water molecules, however, magnetically isolate the atoms of the Cu–Cu pair from each other and we observed a well resolved hyperfine structure in the ESR spectrum of a single crystal without ESR-silent host lattice even at room temperature, as if the molecular structure in solution is carried into the crystal phase. The similarity of the ESR parameters obtained in solution and in the single crystal is evidence for an analogous molecular structure in both states.

The ESR investigation of these complexes in a single-crystal state will be described elsewhere (Kajikawa, Sakurai, Azuma, Kohno, Tsuboyama, Kobayashi, Mukai & Ishizu, 1984).
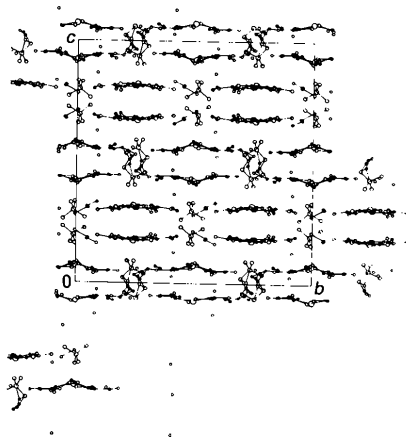
Fig. 8. Crystal structure of complex (c) projected along **a**.

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Crystalline-State Reaction of Cobaloxime Complexes by X-ray Exposure. VIII. Effect of the Cooperative Motion on the Reaction Rate

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Abstract

Crystals of [(R)-1-cyanoethyl]bis(dimethylglyoximato)(4-methylpyridine)cobalt(III) (dimethylglyoximato = 2,3-butanedione dioximato), $C_{17}H_{25}CoN_6O_4$, $[Co(C_3H_4N)(C_6H_7N)(C_4H_7N_2O_2)_2]$, reveal crystalline-state racemization on exposure to X-rays. At the initial stage, the crystal is monoclinic, space group $P2_1$, with $a = 8·875$ (7), $b = 28·525$ (10), $c = 8·695$ (5) Å, $\beta = 115·59$ (6)°, $V = 1985$ (2) Å^3, $M_r = 436·4$, $D_m = 1·47$, $D_x = 1·508$ g cm^{-3} for $Z = 4$ and μ(Mo $K\alpha$) = 9·69 cm^{-1}. $R = 0·063$ for 3255 observed reflections. The two crystallographically independent molecules are related by a pseudo inversion center. On irradiation with X-rays, the unit-cell dimensions gradually change, converging to $a = 8·691$ (10), $b = 28·05$ (2), $c = 8·864$ (7) Å, $\beta = 114·49$ (7)° and $V = 1966$ (3) Å^3 without degradation of crystallinity. The space group is transformed to $P2_1/a$. $R = 0·120$ for 2452 observed reflections. One of the two cyanoethyl groups in the crystallographically independent molecules changes its configuration from R to S. The volume of the cavity for the reactive cyanoethyl group

(12·61 Å^3) is greater than that for the non-reactive group (11·05 Å^3). The rate constant of the racemization, $0·57 \times 10^{-6}$ s^{-1}, is smaller than those for related crystals, although the cavity for the reactive group is larger than the corresponding ones of those crystals. This is due to the smaller contribution of the non-reactive group to the inversion of the reactive group through the cooperative motion in the racemization process.

Introduction

It has been found that the modes of racemization of the chiral 1-cyanoethyl group in crystals of bis(dimethylglyoximato)cobalt, cobaloxime, complexes are divided into two classes: order-to-disorder and order-to-order racemization. Crystals of [(R)-1-cyanoethyl][(S)-α-methylbenzylamine]cobaloxime, R-cn-S-mba (Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1981), and [(S)-1-cyanoethyl][(S)-α-methylbenzylamine]cobaloxime, S-cn-S-mba (Ohashi, Sasada & Ohgo, 1978), reveal the first mode of racemization. Crystals of [(R)-1-cyanoethyl](tributylphosphine)cobaloxime, R-cn-tbp, and [(R)-1-cyanoethyl](triphenylphosphine)cobaloxime, R-cn-tpp, also belong to the first, although the

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