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Structural Researches on Copper(II) Complexes with Vitamin B_6 Derivatives: X-Ray Structures of Bis(N-t-butyl-pyridoxylideneiminato)copper(II) and Bis(N-t-butyl-pyridoxylideneiminato)copper(II)–Methanol (1:1/3)

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The structures of bis(N-t-butyl-pyridoxylideneiminato)copper(II) (compound I) and bis(N-t-butyl-pyridoxylideneiminato)copper(II)–methanol (1:1/3) (compound II) were determined from three-dimensional X-ray data collected by counter methods. Crystals (I) are monoclinic, space group C2/c *with* $Z = 8$ *in a unit cell of dimensions* $a = 11.19(1)$, $b = 20.06(2)$, $c = 23.99(2)$ Å, $\beta = 99.7(1)°$. *Crystals (II) are trigonal, space group* $R\bar{3}c$ *with* $Z = 18$ *and cell dimensions* $a = 16.82(3)$, $c = 48.59(5)$ Å. *Compound (I) was refined to a final conventional* R *factor of 0.0403 for 2150 reflections with* $I \geqslant 2\sigma(I)$ *and compound (II) to a final* $R(F)$ *of 0.0475 for 543 reflections with* $F \geqslant 6\sigma(F)$. *Both compounds show a C2 symmetry but in (II) only, the copper atom lies on a crystallographic two-fold axis; the metal atom is chelated to two pyridoxylidene ligands through the imino N and the phenolato O in a flattened tetrahedral coordination with a* θ *value of* $52.9(3)°$ *for (I) and* $47.1(7)°$ *for (II). In (I) the* O–H···N *hydrogen bonds form layers while in (II) they determine a trimeric unit which hosts a methanol molecule as guest. The layers or the trimers are held together by weak Van der Waals interactions.*

Introduction

Pyridoxal is one of the most biologically active B_6 vitamins and plays an important part in some enzymatic reactions in the presence of metal ions. As part of a research program concerning the study of the ligand and in order to contribute to the definition of the chemical properties of vitamin B_6 derivatives, we have undertaken the determination of the structures of the Schiff's base of pyridoxal with t-butylamine. The results so far obtained with these compounds disclose various stereochemical arrangements of the ligands around the metal atom and different types of connections between the complexes.

Experimental

Syntheses of the Two Complexes

In attempting to prepare the copper(II) complex with the Schiff's base obtained from pyridoxal and t-butylamine following reference [1], two kinds of deep green crystals (prismatic and bipyramidal) were isolated after recrystallization from methanol. Elemental C, H, N. analyses of the two compounds, performed on a Perkin-Elmer Mod. 240 automatic analyser, were not sufficient to differentiate their stoichiometry and only the structural analyses showed their different empirical formulae.

Crystal Data

The most significant crystal data are given in Table I. Preliminary cell parameters determined by rotation and Weissenberg photographs were successively refined by a least squares procedure applied to the θ values of 16 reflections ($19 < \theta < 26°$) for crystal(I) and of 23 reflections ($8 < \theta < 14°$) for crystal(II) accurately measured on a Siemens AED single crystal diffractometer.

Intensity Data

Intensity data were collected at room temperature using Ni-filtered CuKα radiation for (I) and Zr-filtered MoKα radiation for (II) and the ω–2θ scan technique. In both types of data collection the intensity of a standard reflection was measured every 20 reflections to check the stability of the crystal

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TABLE I. Crystallographic Data.

	Compound (I)	Compound (II)
Stoichiometry	$Cu(C_{12}H_{17}O_2N_2)_2$	$Cu(C_{12}H_{17}O_2N_2)_2 \cdot 1/3CH_3OH$
Mr	506·103	516·784
Space group*	$C2/c$	$R\bar{3}c$
Cell constants	$a = 11.19(1)$ Å	$a = 16.82(3)$ Å
	$b = 20.06(2)$	$c = 48.59(5)$
	$c = 23.99(2)$	
	$\beta = 99.7(1)^\circ$	
U (Å^3)	5309(9)	11905(32)
Z	8	18
D_c (Mg m^{-3})	1.267	1.298
$F(000)$	2136	4914
μ(cm^{-1})	14.039	8.608
Radiation	CuKα ($\bar{\lambda} = 1.54178$ Å)	MoKα ($\bar{\lambda} = 0.71069$ Å)
θ up to	55°	24°
Independent reflections	3346	2303
Observed reflections**	2150	543

*From systematic absences and structural analysis. **2150 reflections with $I \geq 2\sigma(I)$ and 543 with $F \geq 6\sigma(F)$ were classified as observed for the crystal (I) and (II) respectively.

and the electronics. The structure amplitudes were obtained after the usual correction for Lorentz and polarization factors and the absolute scales were established by Wilson's method. No correction for absorption was applied.

Structure Determination and Refinement

For both compounds, three dimensional Patterson maps were computed and the positions of the Cu atoms determined. Successive Fourier syntheses revealed the positions of all other non-hydrogen atoms and the disordered distribution of methanol in (II). The refinements were carried out by full-matrix least-squares cycles using the SHELX-76 system of computer programs [2] with initially isotropic and then anisotropic thermal parameters. For compound (I) all the hydrogen atoms were located from a difference Fourier synthesis; at this stage a final blocked full-matrix least-squares cycle was computed, including the H atoms with isotropic thermal parameters. The best results were obtained using unit weights giving a final conventional $R(F) = 0.0403$ (observed reflections only).

For compound (II) all the hydrogen atoms were evident in a difference electron density distribution but, as many coordinates got worse in the least-squares refinement and in order to reduce the number of refined parameters, positional parameters were refined only for those hydrogens whose positions were not geometrically fixed (H_1, H_2, H_3). The methyl and methylene hydrogens were included in their geometrically constructed positions and all the groups were refined as rigid body with free thermal parameters in the last blocked full-matrix least-squares cycle. The number of observations is rather limited with respect to the number of refined parameters and this affects the accuracy of the geometrical parameters. The best results were here again obtained using unit weights giving a final conventional $R(F) = 0.0475$ (observed reflections only). Scattering factors for Cu^{2+}, C, H, N and O were taken from the International Tables for X-ray Crystallography and both the real and imaginary components of anomalous dispersions were included [3]. Final atomic coordinates and thermal parameters for non-hydrogen and for hydrogen atoms are given in Tables II, III and Tables IV, V for compounds (I) and (II) respectively. Lists of observed and calculated structure factors are available from the authors on request.

All the calculations were carried out on the CYBER 76 computer of the 'Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale', Casalecchio (Bologna), with the financial support of the University of Parma.

Results and Discussion

Both structures consist of Δ and Λ enantiomers as a consequence of the space groups to which they

TABLE II. Fractional Atomic Coordinates (×10^5 for Cu and ×10^4 for the Other Non-Hydrogen Atoms) and Anisotropic Thermal Parameters (×10^4) with e.s.ds. in Parentheses for Compound (I). Anisotropic Thermal Parameters are in the Form $\exp[-2\pi^2(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12})]$.

	x/a	y/b	z/c	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	16582(8)	−10032(4)	62204(3)	643(5)	489(5)	334(4)	−28(5)	4(3)	−19(4)
O(1)	2187(4)	−724(2)	5546(2)	820(36)	588(29)	421(26)	−196(26)	119(24)	−30(23)
O(2)	−400(5)	−2561(3)	4154(2)	703(36)	995(42)	805(39)	101(31)	−175(29)	−448(34)
O(3)	2293(4)	−1514(2)	6864(2)	885(32)	489(26)	462(24)	25(24)	−96(22)	12(20)
O(4)	3044(7)	651(3)	8170(2)	1753(63)	1302(49)	670(36)	584(46)	−267(38)	−501(34)
N(1)	523(5)	−1680(3)	5843(2)	546(36)	580(38)	431(32)	−57(30)	77(26)	−61(29)
N(2)	2799(6)	−1221(4)	4193(2)	725(47)	1274(69)	347(34)	−64(45)	143(31)	28(38)
N(3)	1873(4)	−138(2)	6616(2)	624(34)	454(30)	360(28)	51(25)	−14(25)	3(22)
N(4)	4139(5)	−1594(3)	8219(2)	824(42)	864(48)	439(32)	202(37)	−15(28)	121(33)
C(1)	617(6)	−1910(3)	5348(3)	496(45)	498(45)	516(42)	−67(37)	−55(35)	−41(35)
C(2)	1451(5)	−1683(3)	4984(2)	399(39)	550(45)	351(34)	59(34)	−3(29)	4(32)
C(3)	1516(6)	−2053(4)	4481(3)	483(43)	699(50)	377(37)	116(38)	−65(32)	−76(36)
C(4)	2207(7)	−1800(5)	4119(3)	716(55)	1066(68)	395(48)	−12(51)	11(41)	−94(47)
C(5)	2756(7)	−855(4)	4658(3)	631(49)	1003(71)	474(45)	−159(48)	14(37)	142(45)
C(6)	2117(6)	−1094(4)	5092(2)	483(41)	725(51)	308(36)	−61(39)	−2(29)	24(37)
C(7)	836(7)	−2690(4)	4341(3)	655(52)	736(55)	519(49)	172(43)	−123(41)	−213(45)
C(8)	3397(12)	−194(6)	4747(5)	1315(102)	1539(99)	720(71)	−833(89)	222(70)	82(67)
C(9)	−480(7)	−1961(4)	6124(4)	686(57)	865(67)	802(58)	−223(51)	325(48)	−115(53)
C(10)	−731(13)	−1448(7)	6562(6)	1190(106)	1514(115)	1192(92)	−488(87)	719(87)	−492(88)
C(11)	11(16)	−2611(7)	6432(8)	1537(132)	1190(102)	1674(143)	−255(95)	913(118)	501(104)
C(12)	−1626(12)	−2044(14)	5712(6)	754(79)	2606(300)	1301(107)	−591(130)	290(71)	−406(153)
C(13)	2524(6)	−85(3)	7108(2)	695(43)	470(43)	377(34)	−12(35)	65(30)	−69(32)
C(14)	3107(5)	−608(3)	7463(2)	502(39)	611(46)	306(31)	97(34)	35(27)	−14(30)
C(15)	3828(5)	−438(3)	7987(2)	557(40)	733(48)	352(34)	16(36)	101(29)	−58(34)
C(16)	4316(6)	−948(4)	8338(3)	607(46)	1066(62)	362(38)	143(48)	1(33)	56(43)
C(17)	3487(6)	−1762(4)	7733(3)	801(49)	690(57)	470(38)	171(42)	13(35)	128(38)
C(18)	2941(6)	−1282(3)	7328(2)	614(42)	641(43)	377(33)	79(35)	70(30)	41(32)
C(19)	4099(9)	277(4)	8166(3)	1021(67)	1037(61)	462(50)	−54(53)	−1(47)	−138(45)
C(20)	3300(14)	−2494(4)	7607(4)	1654(127)	713(51)	805(72)	244(63)	−220(76)	158(46)
C(21)	1281(7)	494(3)	6354(3)	905(55)	461(39)	558(41)	124(38)	−53(37)	75(33)
C(22)	338(10)	310(5)	5854(4)	1226(85)	901(72)	892(65)	384(71)	−453(60)	−80(58)
C(23)	2240(11)	925(6)	6176(6)	1435(93)	992(81)	1715(122)	−68(76)	70(89)	902(92)
C(24)	590(11)	844(5)	6784(4)	1643(103)	933(77)	929(68)	592(75)	57(68)	−141(58)

TABLE III. Fractional Atomic Coordinates (×10^3) and Isotropic Thermal Parameters (×10^3) for the Hydrogen Atoms with e.s.d.s in Parentheses for Compound (I).

	x/a	y/b	z/c	U
H(1)	−47(6)	−276(3)	385(3)	103(23)
H(2)	−4(5)	−223(3)	520(2)	69(17)
H(3)	225(5)	−205(3)	372(3)	107(20)
H(4)	120(5)	−298(3)	404(3)	86(19)
H(5)	103(6)	−301(3)	466(3)	69(21)
H(6)	380(7)	−4(4)	447(4)	150(30)
H(7)	409(7)	−16(4)	512(4)	197(29)
H(8)	270(8)	12(4)	463(4)	185(36)
H(9)	−140(8)	−158(5)	672(4)	163(39)
H(10)	−85(9)	−100(5)	625(4)	165(36)
H(11)	−13(8)	−141(5)	677(4)	73(42)
H(12)	−68(9)	−276(5)	661(4)	155(40)
H(13)	83(9)	−257(6)	668(4)	279(51)
H(14)	−23(9)	−293(5)	605(4)	256(48)
H(15)	−232(9)	−219(5)	592(4)	175(40)
H(16)	−136(11)	−249(6)	558(5)	108(61)
H(17)	−173(11)	−145(6)	555(5)	192(64)
H(18)	332(7)	84(4)	857(3)	107(28)
H(19)	264(5)	34(3)	727(2)	47(16)
H(20)	499(5)	−85(3)	868(2)	107(18)
H(21)	479(5)	30(3)	858(3)	71(19)
H(22)	457(6)	46(3)	794(3)	97(23)
H(23)	360(6)	−263(4)	729(3)	111(29)
H(24)	245(7)	−255(4)	752(3)	112(35)
H(25)	394(6)	−274(4)	790(3)	147(24)
H(26)	−19(6)	72(4)	571(3)	127(25)
H(27)	−35(6)	−5(4)	597(3)	161(27)
H(28)	59(7)	10(4)	559(3)	107(29)

(continued overleaf)

TABLE III. *(continued)*

	x/a	*y/b*	*z/c*	*U*
H(28)	59(7)	10(4)	559(3)	107(29)
H(29)	210(7)	124(4)	602(4)	172(32)
H(30)	288(8)	70(4)	593(4)	129(41)
H(31)	267(8)	107(4)	660(4)	228(35)
H(32)	25(7)	134(4)	655(3)	202(26)
H(33)	122(7)	97(4)	718(3)	170(27)
H(34)	−27(7)	48(4)	678(3)	210(31)

belong. The molecular structures and atom numbering schemes of the two Δ enantiomers are shown in Figs. 1 and 2 for compounds (I) and (II) respectively. Bond distances and angles for the non-hydrogen atoms are given in Tables VI and VII. In both compounds the Cu atoms are chelated to two pyridoxylidene ligands through the imino nitrogen and the phenolate oxygen atoms in a flattened tetrahedral coordination. They show a C_2 symmetry but only in (II) does the Cu atom lie on a crystallographic two-fold axis. The dihedral angles (θ) between the CuON planes of the chelate rings are 52.9(3) and 47.1(7)° for (I) and (II) respectively. The configuration distorted towards tetrahedron is due to the imino N-substituent which is sufficiently bulky to prevent the normal square planar complex. Moreover the pyridine substituents and the intermolecular forces could also be responsible for this distortion. There are small

TABLE IV. Fractional Atomic Coordinates (×10^4) and Anisotropic or Isotropic Thermal Parameters (×10^4) with e.s.d.s. in Parentheses for Compound (II). Anisotropic Thermal Parameters are in the Form $\exp[-2\pi(h^2a^{*2}U_{11} + \ldots + 2hka^*b^*U_{12}]$.

	x/a	*y/b*	*z/c*	U_{11} or U	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cu	2782(2)	2782(2)	2500	407(28)	468(51)	285(16)	234(25)	70(22)	141(43)
O(1)	1988(10)	2930(11)	2735(3)	599(111)	813(129)	394(92)	406(105)	86(83)	236(82)
O(2)	2831(10)	1113(10)	3495(3)	486(109)	498(119)	423(86)	236(100)	−167(78)	−54(82)
O(3)	322(67)	0	2500	2386(501)					
N(1)	3534(11)	2722(11)	2811(3)	451(127)	330(104)	351(97)	210(95)	−107(91)	7(81)
N(2)	593(13)	1963(12)	3338(4)	476(147)	657(151)	424(114)	276(122)	84(111)	19(97)
C(1)	3195(17)	2516(14)	3056(4)	681(194)	461(156)	133(119)	290(141)	2(134)	89(111)
C(2)	2312(14)	2326(14)	3145(4)	347(146)	423(145)	285(105)	221(104)	−10(101)	−74(101)
C(3)	1984(15)	1943(14)	3409(4)	454(166)	514(178)	342(131)	296(142)	−26(118)	−75(122)
C(4)	1156(16)	1780(15)	3493(4)	491(168)	400(168)	411(153)	234(123)	105(131)	209(125)
C(5)	884(16)	2348(15)	3091(5)	464(186)	614(171)	499(150)	376(148)	37(141)	−99(126)
C(6)	1738(14)	2546(14)	2978(4)	360(154)	401(139)	443(126)	123(124)	6(117)	−38(109)
C(7)	2543(15)	1719(16)	3598(4)	492(159)	560(182)	264(107)	298(138)	0(107)	37(112)
C(8)	237(16)	2547(19)	2921(4)	600(165)	805(230)	666(162)	462(149)	49(144)	67(165)
C(9)	4485(13)	2879(16)	2759(4)	201(124)	630(182)	471(136)	202(107)	14(112)	105(129)
C(10)	4884(16)	3538(15)	2525(4)	478(143)	594(149)	527(130)	238(122)	153(107)	230(107)
C(11)	4414(18)	1961(15)	2689(5)	559(213)	746(170)	858(185)	452(149)	−51(148)	−187(140)
C(12)	5113(15)	3304(17)	3011(4)	304(169)	967(204)	547(134)	334(155)	−204(120)	9(133)
C(13)	61(270)	340(489)	2732(27)	2482(921)					

TABLE V. Fractional Atomic Coordinates (×10^3) and Isotropic Thermal Parameters (×10^3) for the Hydrogen Atoms with e.s.d.s. in Parentheses for Compound (II).

	x/a	*y/b*	*z/c*	*U*
H(1)	233(13)	59(13)	345(3)	98(54)
H(2)	350(12)	249(11)	323(3)	25(57)
H(3)	90(12)	139(11)	369(3)	55(57)
H(4)	318	235	363	
H(5)	223	142	379	
H(6)	62	295	275	
H(7)	16	299	307	
H(8)	−43	202	286	
H(9)	555	366	246	
H(10)	495	416	262	
H(11)	443	334	235	
H(12)	501	193	263	
H(13)	394	177	252	

TABLE V. *(continued)*

	x/a	*y/b*	*z/c*	*U*
H(14)	409	150	286	
H(15)	584	362	297	
H(16)	490	274	315	
H(17)	497	381	310	

TABLE VI. Bond Distances (Å) and Angles (°) with e.s.d.s for Compound (I).

Cu–O(1)	1.898(5)	Cu–O(3)	1.889(5)
Cu–N(1)	1.972(6)	Cu–N(3)	1.973(5)
O(1)–C(6)	1.309(8)	O(3)–C(18)	1.308(7)
N(1)–C(1)	1.295(9)	N(3)–C(13)	1.283(7)
C(1)–C(2)	1.455(9)	C(13)–C(14)	1.437(8)
C(2)–C(3)	1.429(9)	C(14)–C(15)	1.416(7)
C(3)–C(4)	1.355(11)	C(15)–C(16)	1.378(9)
C(4)–N(2)	1.334(12)	C(16)–N(4)	1.335(10)
N(2)–C(5)	1.343(10)	N(4)–C(17)	1.311(8)
C(5)–C(6)	1.441(10)	C(17)–C(18)	1.430(9)
C(6)–C(2)	1.398(10)	C(18)–C(14)	1.395(9)
C(3)–C(7)	1.496(11)	C(15)–C(19)	1.513(10)
C(7)–O(2)	1.404(9)	C(19)–O(4)	1.400(12)
C(5)–C(8)	1.506(15)	C(17)–C(20)	1.507(12)
N(1)–C(9)	1.512(11)	N(3)–C(21)	1.517(8)
C(9)–C(10)	1.530(17)	C(21)–C(22)	1.504(12)
C(9)–C(11)	1.553(17)	C(21)–C(23)	1.495(15)
C(9)–C(12)	1.491(15)	C(21)–C(24)	1.557(14)
O(1)–Cu–N(1)	94.7(3)	O(3)–Cu–N(3)	94.9(3)
O(1)–Cu–N(3)	96.9(2)	O(3)–Cu–N(1)	97.3(3)
O(1)–Cu–O(3)	136.7(4)	N(1)–Cu–N(3)	147.5(4)
Cu–O(1)–C(6)	123.9(5)	Cu–O(3)–C(18)	125.5(4)
Cu–N(1)–C(1)	121.4(6)	Cu–N(3)–C(13)	121.3(4)
Cu–N(1)–C(9)	121.4(5)	Cu–N(3)–C(21)	121.8(4)
C(1)–N(1)–C(9)	117.2(6)	C(13)–N(3)–C(21)	116.9(5)
O(1)–C(6)–C(2)	126.1(6)	O(3)–C(18)–C(14)	125.1(6)
O(1)–C(6)–C(5)	116.4(7)	O(3)–C(18)–C(17)	116.8(6)
C(2)–C(6)–C(5)	117.5(6)	C(14)–C(18)–C(17)	118.0(6)
N(1)–C(1)–C(2)	126.8(7)	N(3)–C(13)–C(14)	128.0(6)
C(1)–C(2)–C(3)	118.3(7)	C(13)–C(14)–C(15)	119.0(6)
C(1)–C(2)–C(6)	122.0(6)	C(13)–C(14)–C(18)	122.7(5)
C(3)–C(2)–C(6)	119.6(6)	C(15)–C(14)–C(18)	118.2(5)
C(2)–C(3)–C(4)	117.5(8)	C(14)–C(15)–C(16)	118.1(6)
C(3)–C(4)–N(2)	124.4(8)	C(15)–C(16)–N(4)	124.1(7)
C(4)–N(2)–C(5)	120.0(8)	C(16)–N(4)–C(17)	118.7(7)
N(2)–C(5)–C(6)	120.7(8)	N(4)–C(17)–C(18)	122.8(7)
C(2)–C(3)–C(7)	122.5(7)	C(14)–C(15)–C(19)	122.5(6)
C(4)–C(3)–C(7)	120.0(7)	C(16)–C(15)–C(19)	119.4(6)
N(2)–C(5)–C(8)	121.1(8)	N(4)–C(17)–C(20)	117.8(7)
C(6)–C(5)–C(8)	118.2(8)	C(18)–C(17)–C(20)	119.4(7)
C(3)–C(7)–O(2)	110.5(7)	C(15)–C(19)–O(4)	112.4(8)
N(1)–C(9)–C(10)	106.9(8)	N(3)–C(21)–C(22)	108.9(6)
N(1)–C(9)–C(11)	107.2(9)	N(3)–C(21)–C(23)	108.5(7)
N(1)–C(9)–C(12)	111.5(9)	N(3)–C(21)–C(24)	109.5(6)
C(10)–C(9)–C(11)	109.2(1.1)	C(22)–C(21)–C(23)	110.8(8)
C(10)–C(9)–C(12)	107.1(1.0)	C(22)–C(21)–C(24)	106.2(8)
C(11)–C(9)–C(12)	114.7(1.2)	C(23)–C(21)–C(24)	112.9(8)

TABLE VII. Bond Distances (Å) and Angles (°) with e.s.d.s. for Compound (II).

Cu–O(1)	1.87(2)	C(6)–C(2)	1.44(4)
Cu–N(1)	2.01(2)	C(3)–C(7)	1.49(4)
O(1)–C(6)	1.31(2)	C(7)–O(2)	1.42(4)
N(1)–C(1)	1.29(2)	C(5)–C(8)	1.53(4)
C(1)–C(2)	1.42(4)	N(1)–C(9)	1.51(3)

(continued overleaf)

TABLE VII. *(continued)*

C(2)–C(3)	1.42(3)	C(9)–C(10)	1.49(3)
C(3)–C(4)	1.34(4)	C(9)–C(11)	1.53(4)
C(4)–N(2)	1.36(4)	C(9)–C(12)	1.54(3)
N(2)–C(5)	1.34(3)	O(3)–C(13)	1.43(52)
C(5)–C(6)	1.41(4)		
O(1)–Cu–N(1)	93.3(7)	C(2)–C(3)–C(4)	119.8(2.1)
O(1)–Cu–O(1^i)	146.2(7)	C(3)–C(4)–N(2)	123.7(2.0)
O(1)–Cu–N(1^i)	96.4(8)	C(4)–N(2)–C(5)	118.7(2.4)
N(1)–Cu–N(1^i)	146.3(7)	N(2)–C(5)–C(6)	123.1(2.3)
Cu–O(1)–C(6)	124.1(1.6)	C(2)–C(3)–C(7)	121.4(2.2)
Cu–N(1)–C(1)	120.2(1.9)	C(4)–C(3)–C(7)	118.8(2.0)
Cu–N(1)–C(9)	120.4(1.2)	N(2)–C(5)–C(8)	117.6(2.3)
C(1)–N(1)–C(9)	119.3(1.9)	C(6)–C(5)–C(8)	119.3(2.1)
O(1)–C(6)–C(2)	122.8(2.1)	C(3)–C(7)–O(2)	116.7(1.8)
O(1)–C(6)–C(5)	120.3(2.1)	N(1)–C(9)–C(10)	107.6(2.0)
C(2)–C(6)–C(5)	116.9(1.9)	N(1)–C(9)–C(11)	108.7(1.9)
N(1)–C(1)–C(2)	127.8(2.0)	N(1)–C(9)–C(12)	111.7(1.8)
C(1)–C(2)–C(3)	120.2(2.2)	C(10)–C(9)–C(11)	111.1(1.8)
C(1)–C(2)–C(6)	121.9(1.9)	C(10)–C(9)–C(12)	108.2(1.9)
C(3)–C(2)–C(6)	117.8(2.1)	C(11)–C(9)–C(12)	109.6(2.0)

Key to symmetry operation: (*i*) *y*, *x*, ½ – *z*

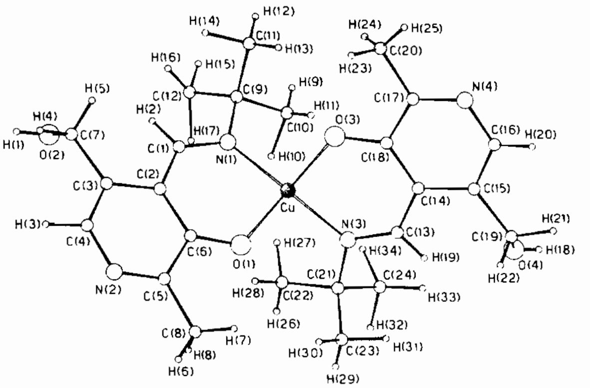

Fig. 1. Projection of the Δ enantiomer of complex (I) along the pseudo two-fold axis.

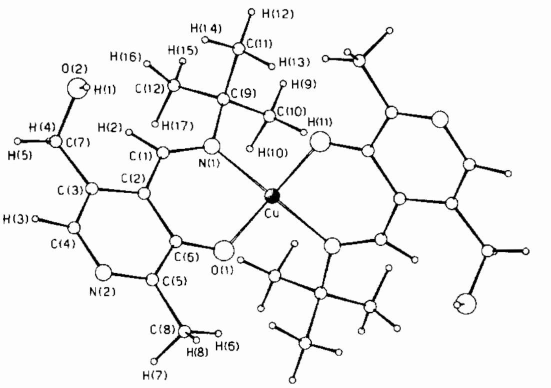

Fig. 2. Projection of the Δ enantiomer of complex (II) along the two-fold axis.

differences between the 'bite' and 'non-bite' distances in the coordination polyhedrons ('bites' (I): O(1)···N(1) = 2.846(8), O(3)···N(3) = 2.846(6) Å; 'non-bites' (I): O(1)···N(3) = 2.898(7), O(3)···N(1) = 2.898(7) Å; 'bite' (II) O(1)···N(1) = 2.82(3), 'non-bite' O(1)···N(1^i) = 2.89(2) Å, *i* = *y*, *x*, ½ – *z*). The Cu–O and Cu–N bond distances (Tables VI, VII) agree with the values observed in similar bis-(N-R-salicylideneiminato)copper(II) complexes [4, 5] and in our previously studied *trans*-bis(N-n-butyl-pyridoxylideneiminato)copper(II) [6]. From now on this latter complex will be mentioned as (III). In (III) the complex has a crystallographic C_2 symmetry and the distortion from the tetrahedral stereochemistry is greater (θ = 15.9(2)°) than in (I) and (II) and the 'bite' and 'non-bite' distances are obviously shorter.

The bendings along the 'bites' of the ligand are considerable. In (I) the dihedral angles between the mean planes passing through Cu, O(1), N(1) and N(1), C(1), C(2), C(6), O(1) and between Cu, O(3), N(3) and N(3), C(13), C(14), C(18), O(3) are 160.2(3)° and 166.7(3)° with the Cu atom out of the first and second chelate rings by 0.455(4) and 0.305(5) Å respectively. The corresponding dihedral angle and the deviation of the

TABLE VIII. Intra- and Intermolecular Contacts with e.s.d.s.

Compound (I)		Compound (II)	
a) Significant bond distances (Å) and angles (°) for the hydrogen bonds			
O(2)$\cdots$N(4^{iv})	2.789(8)	O(2)$\cdots$N(2^{ii})	2.79(2)
H(1)$\cdots$N(4^{iv})	1.98(7)	H(1)$\cdots$N(2^{ii})	1.91(16)
O(4)$\cdots$N(2^{v})	2.763(8)	O(2)–H(1)$\cdots$N(2^{ii})	172(4)
H(18)$\cdots$N(2^{v})	1.86(8)	H(1)–O(2)$\cdots$N(2^{ii})	6(3)
O(2)–H(1)$\cdots$N(4^{iv})	165(6)		
H(1)–O(2)$\cdots$N(4^{iv})	10(5)		
O(4)–H(18)$\cdots$N(2^{v})	145(6)		
H(18)–O(4)$\cdots$N(2^{v})	23(6)		
b) Selected interactions (Å)			
O(1)$\cdots$C(21)	3.379(9)	O(1)$\cdots$C(9^{i})	3.31(3)
O(1)$\cdots$C(22)	3.106(12)	O(1)$\cdots$C(10^{i})	3.26(2)
O(2)$\cdots$C(1)	3.179(9)	O(1)$\cdots$C(11^{i})	3.25(3)
O(2)$\cdots$C(2)	3.157(8)	O(2)$\cdots$C(1)	3.01(3)
O(2)$\cdots$C(4)	3.306(11)	O(2)$\cdots$C(2)	3.10(3)
O(2)$\cdots$C(12^{vi})	3.488(16)	C(8)$\cdots$O(2^{iii})	3.42(2)
O(3)$\cdots$C(9)	3.425(15)		
O(3)$\cdots$C(10)	3.342(9)		
O(3)$\cdots$C(11)	3.398(17)		
O(4)$\cdots$C(13)	2.917(8)		
O(4)$\cdots$C(14)	3.050(8)		
C(2)$\cdots$C(7^{vii})	3.430(10)		
C(6)$\cdots$C(7^{vii})	3.464(11)		

Key to symmetry operations:

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

metal atom in (II) are 155.6(7)° and 0.549(4) Å respectively.

The conformation of one of the chelate rings in compound (I) is of the 'sofa' type (ΔC_s(C(2) = 5°), in the other it is intermediate between the 'sofa' and the 'half-chair' one (ΔC_s(C(14)) = 5° and ΔC_2 (C(13)–C(14)) = 6°) while in compound (II) it is of the 'half-chair' type (ΔC_2(C(1)–C(2)) = 6°) [7]. In these (pyridoxylideneiminato)copper(II) complexes the six-membered chelate rings show some flexibility but the greatest deviation from the weighted least-squares planes is always observed for the metal atom.

As regards the seam between the pyridine and chelate ring, a different twist degree is observed as can be seen from a) the torsion angles implying the seam [τ[C(1)–C(2)–C(6)–O(1)] = 8(1), τ[C(13)–C(14)–C(18)–O(3)] = 3(1)° for compound (I) and τ[C(1)–C(2)–C(6)–O(1)] = 0(4)° for compound (II), τ[C(3)–C(2)–C(6)–C(5)] = 6(1), τ[C(15)–C(14)–C(18)–C(17)] = 1(1)° for (I) and τ[C(3)–C(2)–C(6)–C(5)] = −1(3)° for (II)] and b) the angles between the seam C(2)–C(6), or C(14)–C(18), and the intersection line of the two weighted least-squares planes through the chelate ring atoms and the pyridine moiety (78.8(4)°, 39.8(5)° for (I) and 20(1)° for (II)). These last values indicate that the twist decreases when the conformation changes from the 'sofa' to the intermediate 'sofa'–'half-chair', and to the 'half-chair' one. The twist around the bite

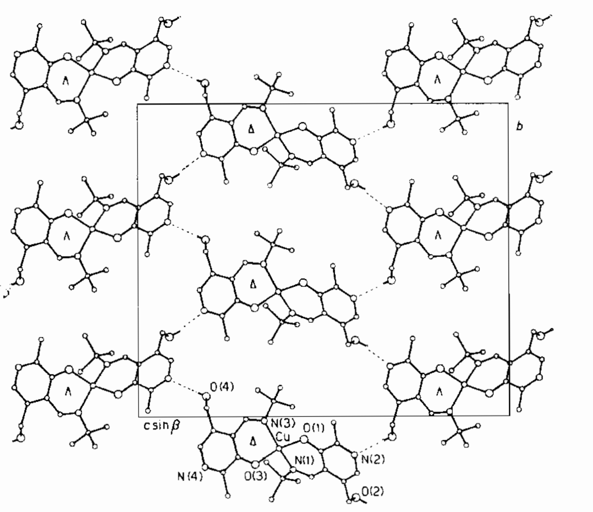

Fig. 3. Projection of the structure of compound (I) along *a* showing a layer parallel to (1 $\bar{1}$ 0).

O···N is smaller but the bend, as previously seen, is greater than around C(2)–C(6), or C(14)–C(18). In fact the angles between the seam O···N and the intersection line of the weighted CuON plane with the weighted least-squares plane through the chelate ring atoms are 1.5(2) and 1.6(3)° for the first and the second chelate ring of (I) and 4.1(7)° for (II). Bond distances and angles in the pyridoxylidene moieties are in good agreement with those found in (III) and in other compounds containing the same moiety. The most significant differences are found in the torsion angles of the alcoholic groups. The C(3), C(7), O(2), H(1) fragment in (II) adopts an helicoidal geometry as in (III); in fact both the oxygen and the hydrogen of the alcoholic group, in the Δ enantiomers, are –synclinal with regard to C(2) and C(3) respectively (τ[C(2)–C(3)–C(7)–O(2)] = –56(3) and τ[C(3)–C(7)–O(2)–H(1)] = –59(14)°). In (I), O(2) and O(4) are +synclinal to C(2) and C(14) respectively while H(1) and H(18) are +anticlinal to C(3) and C(15) (τ[C(2)–C(3)–C(7)–O(2)] = +75(1), τ[C(14)–C(15)–C(19)–O(4)] = +57(1), τ[C(3)–C(7)–O(2)–H(1)] = +125(5) and τ[C(15)–C(19)–O(4)–H(18)] = +130(4)°). The alcoholic groups conformation in (I) is not energetically favourable, the hydroxylic hydrogen being eclipsed with regard to the methylene one but this conformation is realized in order to form intermolecular hydrogen bonds (Table VIII) with the pyridinic N joining the complexes in layers.

The packings are quite different. In (I) the abovementioned hydrogen bonds form layers roughly lying in planes parallel to (1 $\bar{1}$ 0). The sequence along [1 1 0] is of type Λ Λ Λ ... alternate with Δ Δ Δ ... enantiomers (Fig. 3). The layers are held together by weak Van der Waals interactions (Table VIII). In (II) the hydrogen bonds determine a trimeric unit of the same type of enantiomers with a Δ, Λ, Δ, ... sequence along [0 0 1]. Every trimeric unit (Fig. 4) forms a hollow which hosts a methyl alcohol molecule. These trimers are held together by weak Van der Waals contacts.

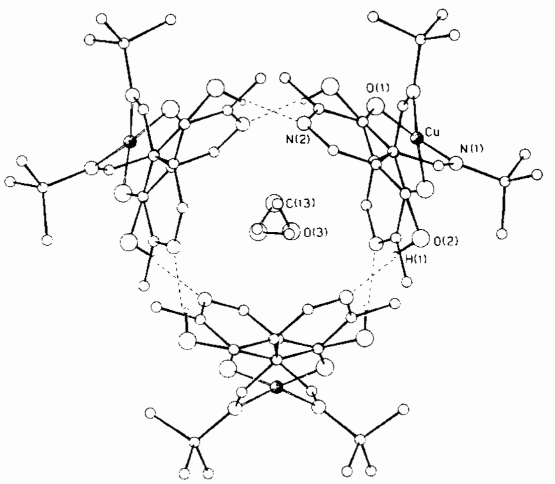

Fig. 4. Projection of the structure along *c* showing the trimeric arrangement of complex (II) determined by hydrogen bonds and the cavity occupied by the methanol guest.

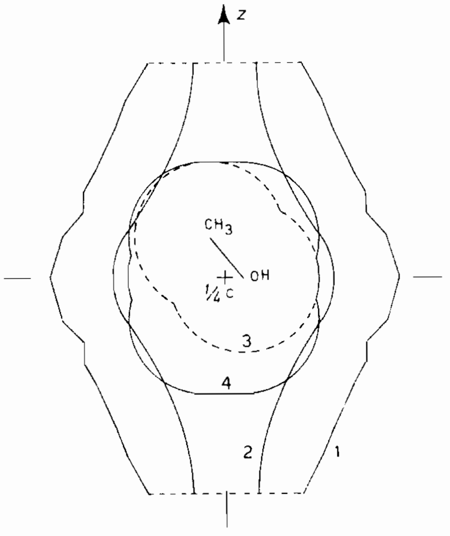

Fig. 5. Section of the internal rotation surface around *c* of the trimeric unit host (line 1). The inner line 2 refers to the cavity rotation surface calculated by considering the Van der Waals radii. The dashed line 3 depicts the Van der Waals overall size of one methanol molecule while the continuous line 4 represents the rotation surface section of the overall encumbrance of the six statistical positions of methanol.

The difference Fourier synthesis revealed some disorder of the guest molecule and the best refinement was obtained by distributing the alcohol molecule in six positions. The doubt about the kind of guest disorder (statistical or dynamic) persists. It could be the result of either a free rotation (dynamic disorder) or of the simultaneous existence of different positions (statistical disorder). The dimension of the cavity, formed by the trimeric unit, and the overall size of the solvent distributed in six positions have been calculated in accordance with the Van der Waals radii. As can be seen from Fig. 5, the hollow is greater than the encumbrance of a single methanol molecule and this fact could explain the disorder. Owing to the two narrowings at the two extremities the guest remains included and unable to get out.

Extensive use of Cambridge Crystallographic Data Files was made for the bibliography.

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