Stereochemistry of Model Compounds for Pyridoxal-catalysed Reactions. Crystal Structures of the Hydrated Complexes Bis(pyridoxylidene-DL-valinato)nickel(II) and Bis(pyridoxylidene-L-valinato)zinc(II)

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Crystals of bis(pyridoxylidene-DL-valinato)nickel(II), (I), are orthorhombic, space group *Pccn*, with unit-cell parameters a = 17·69, b = 19·43, c = 20·83 (all ±0·01) Å, Z = 8. The structure has been solved by the heavy-atom method and refined to R 0·17 for 4784 independent reflections. Crystals of bis(pyridoxylidene-L-valinato)-zinc(II), (II), are tetragonal, space group $P4_22_12$, with Z = 8, in a unit cell of dimensions $a = b$ = 18·59 ± 0·02, c = 21·29 ± 0·04 Å. (II) Is strictly isomorphous with the related Co^{II} complex. A trial model for (II) was deduced from the structure of the nickel complex and refined to R 0·16 for 1568 independent reflections. Both (I) and (II) consist of discrete molecules with octahedral metal ions bonded to two terdentate Schiff bases, and are characterized by the presence of polar cavities in which partially disordered water molecules are located. The ligand is not planar, and the distortion is mostly due to a rotation of the carboxy-group. The stereospecificity of formation of crystalline complexes is discussed.

THE role played by metal ions in the nonenzymatic pyridoxal-dependent reactions of α-amino-acids has been examined by an increasing number of studies in solution.[1-5] Several years ago Christensen [6] prepared numerous metal chelates of the pyridoxylidene-amino-acids in crystalline form. Willstadter *et al.*[7] published the preliminary results of the crystal structure determination of bis(pyridoxylidene-DL-valinato)manganese(II). These authors claimed that the use of L-valine gave disordered crystals, which were not suitable for *X*-ray analysis. More recently the preliminary results of the *X*-ray structural determinations of (pyridoxylidene-DL-valin-

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[1] B. M. Guirard and E. E. Snell, in 'Comprehensive Biochemistry,' vol. 15, eds. M. Florkin and E. H. Stotz, Elsevier, New York, 1964, ch. V.

[2] O. A. Gansow and R. H. Holm, *J. Amer. Chem. Soc.*, 1969, **91**, 573.

[3] E. H. Abbott and A. E. Martell, *J. Amer. Chem. Soc.*, 1970, **92**, 1754.

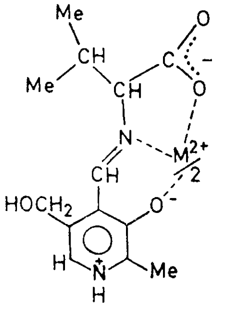
[4] W. L. Felty, C. G. Ekstrom, and D. L. Leussing, *J. Amer. Chem. Soc.*, 1970, **92**, 3006.

[5] E. H. Abbott and A. E. Martell, *J. Amer. Chem. Soc.*, 1970, **92**, 5845.

[6] H. N. Christensen, *J. Amer. Chem. Soc.*, 1957, **79**, 4073.

[7] E. Willstadter, T. A. Hamor, and J. L. Hoard, *J. Amer. Chem. Soc.*, 1963, **85**, 1205.

ato)copper(II)[8] and (pyridoxylidene-5-phosphate-DL-phenylalaninato)aquocopper(II)[9] have been published. Since the knowledge of the structure of the metal chelates of pyridoxylidene-amino-acids is of particular interest in understanding the role of intermediate species in pyridoxal-catalysed reactions, we have undertaken an *X*-ray study of cobalt(II), zinc(II), and nickel(II) complexes of pyridoxylidenevaline. We now report the three-dimensional *X*-ray structural analysis of bis-(pyridoxylidene-DL-valinato)nickel(II), (I), and bis-(pyridoxylidene-L-valinato)zinc(II), (II).



(I) $M^{2+} = Ni^{2+}$
(II) $M^{2+} = Zn^{2+}$

EXPERIMENTAL

Preparation of Complexes.—The complexes were prepared according to ref. 6, the concentration of reactants being adjusted in order to achieve a slow crystallization.

Crystal Data.—Unit cell parameters were determined from precession and Weissenberg photographs. The data for (I) and (II) (Table 1) were refined by least-squares from sixteen 2θ values measured on an automatic Siemens diffractometer. The measured (flotation) densities of the crystals indicate the presence of 7·4 (I) and 8·1 (II) molecules of water per independent unit, but analytical data for (I) indicate a slightly larger water content [Found: C, 42·6; H, 6·1; N, 7·6; Ni, 7·6. Calc. for $Ni(C_{13}H_{17}N_2O_4)_2,7{\cdot}4H_2O$: C, 43·2; H, 6·7; N, 7·7; Ni, 8·1%]. (II) Is strictly isomorphous with the related Co^{II} complex. Crystal data for the DL salt of zinc show that it is also isomorphous with its Co^{II} and Mn^{II} analogues.[7]

TABLE 1

Crystal data for (I) and (II)

	(I)	(II)
System	Orthorhombic	Tetragonal
a/Å	17·69 ± 0·01	18·59 ± 0·02
b/Å	19·43 ± 0·01	18·59 ± 0·02
c/Å	20·83 ± 0·01	21·29 ± 0·04
U/Å^3	7160	7357
D_m/g cm^{-3}	1·34	1·34
Z	8	8
Space group	*Pccn* (No. 56)	$P4_22_12$ (No. 94)
μ/cm^{-1}	13·7 (Cu-K_α)	7·6 (Mo-K_α)

Data Collection and Structure Determination for (I) *and* (II).—Intensities for both complexes were recorded on an automatic Siemens diffractometer by the θ—2θ scan procedure. A total of 4784 independent reflections with intensities above background were measured for (I) by use of Cu-K_α radiation (λ = 1·5418 Å) and 1568 for (II) by use of Mo-K_α radiation (λ = 0·7107 Å). The dimensions of both crystals were *ca.* 0·6 × 0·4 × 0·2 mm. No correction for absorption was applied. The structure of (I) was solved by the heavy-atom technique.

After several cycles of structure-factor and Fourier synthesis calculations, all the non hydrogen atoms of the complex and five water molecules were located. For these atoms several cycles of block-diagonal least-squares refinement were carried out with individual isotropic temperature factors. The function minimized was $\Sigma w(F_o - |F_c|)^2$, with the weighting scheme $w = [4{\cdot}5 + F_o + 0{\cdot}006\, F_o^2]^{-1}$. The atoms O(2′) and the water molecules refined with high thermal parameters. A three-dimensional Fourier synthesis calculated at this stage in an attempt to locate the remaining water molecules showed two alternative positions for the atom O(2′) and a number of peaks of low electron density. These peaks were found in a cavity of the structure, which accommodates four of the five water molecules already located. An attempt to refine O(2′) in the two alternative positions with different occupancies and the positions of some of the peaks, which could reasonably be due to water molecules on the basis of steric considerations, did not give reliable results. In any case the molecular structure of the complex was not significantly influenced and *R* improved only slightly.

In view of the difficulty of handling the partially disordered structure of the water, it was decided to refine only the atoms of the complex, with O(2′) at the position of higher occupancy, and the five water molecules initially located. After several more cycles of least-squares refinement convergence was obtained with *R* 0·17. Final atomic parameters and their standard deviations are listed in Table 2. The numbering scheme of the atoms is shown in Figure 1.

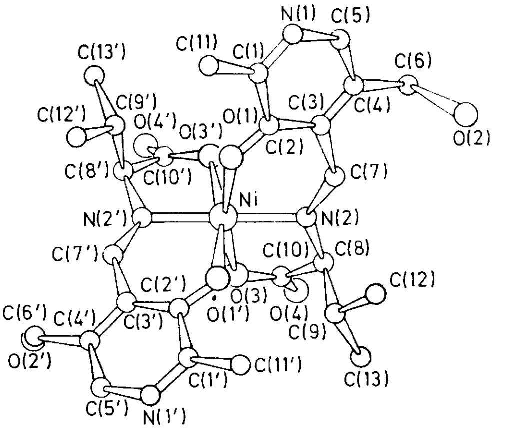


FIGURE 1 A perspective drawing of the nickel complex (I)

A trial structure for (II) was easily deduced from the structure of (I). After some cycles of least-squares refinement, the Fourier map showed that the part of the unit cell which contains most of the water molecules is even more disordered than in the nickel complex, and O(2′) could not be located at all. Therefore only the atomic parameters of the complex, excluding those of O(2′), and of one water molecule

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[8] J. F. Cutfield, D. Hall, and T. N. Waters, *Chem. Comm.*, 1967, 785.

[9] G. A. Bentley, J. M. Waters, and T. N. Waters, *Chem. Comm.*, 1968, 988.

TABLE 2

Final positional ($\times 10^4$) and thermal parameters ($\times 10^2$) for (I) and (II), with standard deviations in parentheses *

	(I)				(II)			
	x/a	y/b	z/c	$B/\text{Å}^2$	x/a	y/b	$/zc$	$B/\text{Å}^2$
Ni/Zn	1003(1)	1220(1)	2526(1)	332(7)	1328(3)	6346(3)	2441(2)	284(5)
O(1)	2065(4)	1115(4)	2170(4)	271(13)	311(12)	6462(13)	2129(9)	379(56)
O(1′)	1158(4)	2209(4)	2790(4)	280(13)	1298(14)	5310(12)	2711(9)	386(54)
O(2)	3306(6)	−477(5)	4038(5)	463(19)	−1019(13)	7828(14)	4072(11)	537(69)
O(2′)	−1269(9)	2962(8)	1419(8)	812(35)				
O(3)	−15(4)	1135(4)	3073(4)	303(14)	2340(12)	6537(12)	3006(9)	318(52)
O(3′)	628(4)	262(4)	2084(4)	282(13)	1727(12)	7375(12)	1965(10)	334(53)
O(4)	−443(5)	503(5)	3886(5)	435(18)	2648(14)	7181(14)	3790(10)	466(63)
O(4′)	−306(5)	−9(4)	1416(4)	333(15)	2549(13)	7638(13)	1325(9)	354(47)
N(1)	3493(6)	−136(5)	1943(5)	355(19)	−1235(15)	7599(15)	1985(12)	341(64)
N(1′)	420(6)	3896(5)	2802(5)	305(17)	2220(15)	3646(17)	2840(12)	333(60)
N(2)	1384(5)	761(4)	3335(4)	230(14)	957(15)	6829(15)	3273(11)	294(62)
N(2′)	488(5)	1571(4)	1715(4)	211(3)	1845(15)	5980(15)	1618(11)	318(65)
C(1)	3063(7)	424(6)	1840(6)	304(20)	−748(19)	7088(19)	1804(15)	327(81)
C(1′)	823(7)	3338(6)	2967(6)	322(21)	1779(21)	4157(21)	2980(17)	411(87)
C(2)	2499(6)	597(5)	2314(5)	237(17)	−157(20)	6943(19)	2263(14)	350(85)
C(2′)	770(6)	2726(6)	2591(5)	245(17)	1706(18)	4758(18)	2539(17)	317(73)
C(3)	2473(6)	183(5)	2868(5)	259(18)	−145(20)	7348(20)	2853(15)	379(88)
C(3′)	290(6)	2749(5)	2053(5)	245(17)	2129(20)	4827(21)	1985(16)	342(84)
C(4)	2958(6)	−377(6)	2950(6)	299(19)	−673(22)	7865(23)	2913(18)	536(109)
C(4′)	−115(7)	3363(6)	1906(6)	310(20)	2592(20)	4177(20)	1886(16)	419(92)
C(5)	3449(8)	−535(7)	2456(6)	364(23)	−1234(19)	8003(19)	2484(16)	369(73)
C(5′)	−43(7)	3908(6)	2298(6)	323(20)	2628(18)	3626(20)	2392(15)	361(78)
C(6)	2977(8)	−839(7)	3524(7)	408(25)	−745(22)	8325(22)	3545(18)	583(113)
C(6′)	−650(8)	3416(8)	1339(7)	459(28)	3008(24)	4132(23)	1346(19)	646(123)
C(7)	1915(6)	331(6)	3380(5)	252(17)	394(17)	7264(18)	3326(13)	255(72)
C(7′)	196(7)	2178(6)	1619(5)	290(19)	2169(17)	5358(17)	1574(13)	283(77)
C(8)	873(7)	816(6)	3874(6)	302(20)	1449(18)	6818(18)	3797(14)	280(75)
C(8′)	354(6)	1041(5)	1232(5)	228(17)	1975(17)	6529(17)	1117(13)	205(68)
C(9)	1006(7)	1510(7)	4247(6)	349(22)	1355(22)	6082(19)	4099(14)	420(89)
C(9′)	1082(7)	961(7)	806(6)	344(22)	1314(20)	6618(17)	752(13)	302(76)
C(10)	97(7)	817(6)	3600(6)	295(19)	2222(19)	6831(18)	3478(15)	240(73)
C(10′)	203(6)	375(6)	1607(5)	256(18)	2090(20)	7235(20)	1488(13)	276(71)
C(11)	3188(8)	834(7)	1242(7)	398(25)	−792(20)	6614(20)	1238(15)	280(78)
C(11′)	1354(9)	3364(8)	3521(8)	464(28)	1288(22)	4078(20)	3567(16)	498(99)
C(12)	1823(10)	1540(9)	4485(8)	535(32)	572(24)	6011(25)	4337(19)	918(170)
C(12′)	1250(9)	1645(8)	452(8)	481(29)	1125(21)	5854(21)	428(16)	528(108)
C(13)	457(10)	1557(9)	4819(8)	543(33)	2024(22)	5946(22)	4593(17)	518(107)
C(13′)	951(10)	404(10)	306(9)	585(36)	1370(23)	7215(21)	251(15)	417(85)
W(1)	2500(—)	2500(—)	1698(10)	761(45)	0(—)	5000(—)	1522(14)	553(83)
W(2)	1600(10)	−901(9)	1661(8)	896(39)				
W(3)	1854(13)	−2067(12)	2379(10)	1114(54)				
W(4)	1052(11)	−2830(10)	1570(10)	1091(52)				
W(5)	1304(11)	−576(10)	4963(9)	1005(47)				

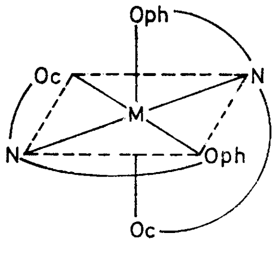
* Unprimed and primed units here and in subsequent Tables refer to the two chemically but not structurally equivalent moieties of the complexes. Oxygen atoms of water molecules are indicated by the symbol W.

were refined by least-squares, using isotropic thermal parameters for all atoms. The final R factor was 0·16. The molecular parameters of the zinc complex are less accurate because the number of reflections per parameter is less than half that of the nickel complex. However there is no evidence of disorder in the part of the unit cell containing the molecule of the complex, whose important structural aspects can be considered well established. Table 2 lists the final atomic parameters and their estimated standard deviations. Atomic scattering factors were taken from ref. 10. All calculations were carried out on an IBM 360 44 computer with programmes written by A. Immirzi.[11] Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 21010 (28 pp., 1 microfiche).†

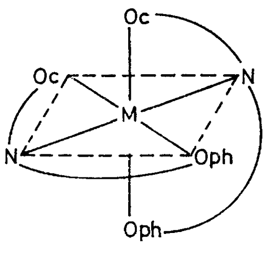
DISCUSSION

The structures of (I) and (II) consist of discrete molecules with octahedral co-ordinated metal ions bonded to two terdentate Schiff bases.

The bis(terdentate) complexes have the *abf* structure for which two enantiomorphous forms A and B are possible. The donor atoms are the imine nitrogen (N), the phenolic (O_{ph}) and the carboxy (O_c) oxygens of the pyridoxylidene groups.



A



B

The co-ordination polyhedron of (I) can be described as a distorted octahedron with approximate C_2 symmetry.

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† See Notice to Authors No. 7 in *J.C.S. Dalton*, 1973, Index ssue.

[10] D. T. Cromer and J. M. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[11] A. Immirzi, personal communication.

TABLE 3

Bond lengths (Å), valency angles (°), with their estimated standard deviations in parentheses

(*a*) Bond lengths in (I)

	Unprimed unit	Primed unit
Ni–O(1)	2·03(1)	2·02(1)
Ni–O(3)	2·14(1)	2·18(1)
Ni–N(2)	2·02(1)	2·04(1)
O(1)–C(2)	1·30(1)	1·28(1)
C(2)–C(1)	1·44(2)	1·43(2)
C(1)–C(11)	1·49(2)	1·49(2)
C(1)–N(1)	1·35(2)	1·34(2)
N(1)–C(5)	1·32(2)	1·33(2)
C(5)–C(4)	1·38(2)	1·34(2)
C(4)–C(3)	1·40(2)	1·42(2)
C(4)–C(6)	1·49(2)	1·51(2)
C(6)–O(2)	1·41(2)	1·42(2)
C(3)–C(7)	1·48(1)	1·44(1)
C(7)–N(2)	1·26(1)	1·30(1)
N(2)–C(8)	1·45(2)	1·46(1)
C(8)–C(9)	1·57(2)	1·57(2)
C(9)–C(12)	1·53(2)	1·55(2)
C(9)–C(13)	1·54(2)	1·52(2)
C(8)–C(10)	1·49(2)	1·53(2)
C(10)–O(3)	1·27(1)	1·26(1)
C(10)–O(4)	1·28(2)	1·24(1)

(*b*) Valency angles in (I)

	Unprimed unit	Primed unit
O(1)–Ni–N(2)	87·2(3)	88·1(3)
N(2)–Ni–O(3)	78·6(3)	78·5(3)
O(1)–Ni–O(3)	165·2(6)	165·8(6)
O(1)–Ni–(O(3′)	92·5(3)	92·4(3)
O(1)–Ni–N(2′)	98·4(3)	98·5(3)
O(3)–Ni–N(2′)	95·2(3)	94·4(3)
Ni–O(1)–C(2)	122·7(6)	125·8(6)
O(1)–C(2)–C(1)	115·5(4)	116·1(5)
C(2)–C(1)–C(11)	123·2(6)	119·7(6)
N(1)–C(1)–C(11)	118·7(5)	120·4(6)
N(1)–C(1)–C(2)	118·1(5)	119·9(5)
C(1)–N(1)–C(5)	124·8(6)	122·8(6)
N(1)–C(5)–C(4)	120·6(6)	121·6(5)
C(5)–C(4)–C(3)	117·9(6)	118·8(6)
C(2)–C(3)–C(4)	121·8(5)	120·1(5)
C(1)–C(2)–C(3)	116·7(5)	116·8(5)
C(3)–C(4)–C(6)	125·5(6)	122·5(5)
C(5)–C(4)–C(6)	116·6(6)	118·6(6)
C(4)–C(6)–O(2)	108·5(5)	110·4(5)
C(4)–C(3)–C(7)	118·1(4)	116·9(5)
O(1)–C(2)–C(3)	127·8(5)	127·1(5)
C(2)–C(3)–C(7)	120·0(4)	123·0(5)
C(3)–C(7)–N(2)	124·8(4)	123·7(5)
C(7)–N(2)–Ni	127·1(7)	127·4(7)
C(7)–N(2)–C(8)	117·2(4)	118·0(4)
N(2)–C(8)–C(10)	106·2(4)	105·9(4)
C(8)–C(10)–O(3)	118·4(5)	116·2(5)
C(8)–C(10)–O(4)	120·6(6)	118·2(5)
O(3)–C(10)–O(4)	121·1(5)	125·6(5)
C(10)–O(3)–Ni	111·4(6)	111·4(5)
Ni–N(2)–C(8)	114·0(5)	114·0(4)
N(2)–C(8)–C(9)	110·8(4)	109·1(4)
C(10)–C(8)–C(9)	109·1(5)	110·2(4)
C(8)–C(9)–C(12)	109·5(6)	109·9(5)
C(8)–C(9)–C(13)	109·8(6)	110·3(5)
C(12)–C(9)–C(13)	110·2(6)	108·3(6)

(*c*) Bond lengths in (II)

	Unprimed unit	Primed unit
Zn–O(1)	2·02(3)	2·01(3)
Zn–O(3)	2·26(3)	2·29(3)
Zn–N(2)	2·10(3)	2·11(3)

(*d*) Valency angles in (II)

	Unprimed unit	Primed unit
O(1)–Zn–N(2)	85·7(7)	86·6(7)
N(2)–Zn–O(3)	76·0(8)	75·8(8)
O(1)–Zn–O(3)	159·9(13)	159·4(12)
O(1)–Zn–O(3′)	93·9(7)	91·2(7)
O(1)–Zn–N(2′)	100·8(8)	99·2(8)
O(3)–Zn–N(2′)	96·5(8)	97·0(8)

The two terdentate ligands have the same configuration and in the solid state the racemic co-ordination compounds A(LL),B(DD)[*] are present. In the case of (II) only the A(LL) diastereoisomer has been found in the solid state.

A drawing of the nickel complex (I), viewed along the pseudodiad axis (approximately parallel to [110]), is shown in Figure 1; primed and unprimed units refer to the two chemically but not structurally equivalent moieties of the molecule. It can be seen that only the two –CH_2–OH groups are in different conformations, caused by different interactions with water molecules. Bond lengths and valency angles are reported in Table 3. For (II) only the data for the co-ordination of the zinc atom are reported, since the lower accuracy of the structural parameters does not allow a meaningful comparison of bond lengths and angles. For (II) the agreement between chemically equivalent parameters appears good, considering the degree of disorder caused by the water molecules and the rather poor overall refinement of the structure.

The angles O(1)–Ni–O(3) and O(1′)–Ni–O(3′) are largely less than 180° because of the dimensions of the central ion with respect to the terdentate ligand. The ligand itself is not planar, and the distortion from planarity is mostly due to a rotation of the carboxy-group around the C(8)–C(10) bond. Some least-squares planes and dihedral angles between them are listed in Table 4. Very similar distortions are found in the zinc

TABLE 4

(*a*) Some least-squares planes

Plane	(I)	(I′)	(II)	(II′)	(III)	(III′)
a	11·86	13·39	10·47	14·64	−3·67	11·48
b	11·65	6·16	13·64	5·42	15·82	−9·37
c	9·52	−11·90	8·08	−10·13	10·37	−12·25
d	−5·87	0·36	−5·17	0·17	−4·99	2·08

(*b*) Deviations of atoms (Å)

	(I)	(I′)	(II)	(II′)	(III)	(III′)
Ni	−0·85	−0·55	−0·42	−0·26	−0·81	−1·01
C(1)	0·01 *	−0·01 *	0·10	0·18	−3·53	−3·74
C(2)	0·00 *	−0·01 *	0·13	0·15	−2·56	−2·76
C(3)	0·01 *	0·00 *	−0·01 *	0·00 *	−2·63	−2·68
C(4)	0·01 *	0·01 *	−0·20	−0·11	−3·61	−3·54
C(5)	−0·06 *	−0·02 *	−0·30	−0·10	−4·55	−4·44
N(1)	−0·03 *	−0·01 *	−0·13	0·06	−4·47	−4·52
C(6)	0·04 *	0·00 *	−0·35	−0·29	−3·75	−3·50
C(11)	0·07 *	0·06 *	0·31	0·41	−3·55	−3·83
O(1)	−0·05 *	−0·05 *	0·27	0·23	−1·73	−2·08
C(7)	0·01 *	0·04 *	0·02 *	0·00 *	−1·66	−1·72
N(2)	−0·16	−0·06	0·01 *	0·00 *	−0·83	−0·93
C(8)	−0·19	0·01	−0·01 *	0·00 *	0·00 *	0·00 *
C(10)	−1·37	−1·05	−1·05	−0·96	0·00 *	−0·01 *
O(3)	−1·64	−1·12	−1·16	−0·88	0·00 *	0·00 *
O(4)	−2·11	−1·74	−1·81	−1·72	0·00 *	0·00 *

Equations of the planes are referred to crystallographic axes and are expressed in the form: $ax + by + cz + d = 0$. Distances with asterisk refer to atoms defining the plane.

(*c*) Interplanar angles (°) between planes

(I)–(II)	8·4	(II)–(III)	45·7	(I′)–(III′)	47·6
(I)–(III)	51·3	(I′)–(II′)	6·7	(II′)–(III′)	46·4

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[*] A and B stand for the two possible enantiomorphous forms of the complex, D and L refer to the configuration of the two Schiff bases.

complex. In both compounds the metal–carboxy-oxygen distances are systematically longer than the metal-phenolic-oxygen distances. A comparison of the planarity of the Schiff-base chelated to different metal ions is useful. Copper ion, having a mean co-ordination bond < 2Å, occupies the centre of a nearly planar terdentate ligand.[8,9,12,13] The increased co-ordination bond lengths in the manganese, nickel, and zinc complexes, result in increased ring-strain which determines the puckering of the chelated Schiff-bases. The Schiff-base bonded to copper ion, which shows the greatest activity in nonenzymatic reactions,[14] satisfies more properly the stereochemical requirements of the postulated reaction mechanism.[1]

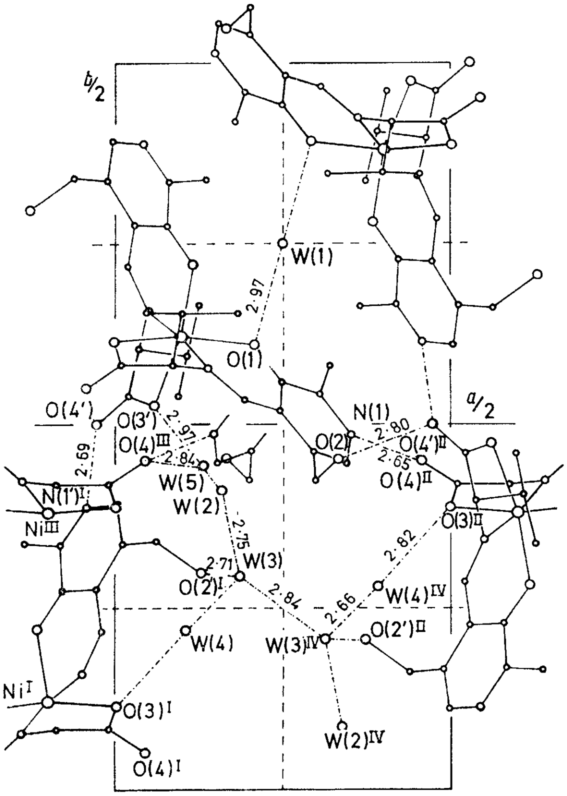

FIGURE 2 Part of the crystal structure of the nickel complex (I) viewed along the c axis

Figure 2 shows a projection on (001) of part of the crystal structure of (I). The molecules are held together through a network of hydrogen bonds, involving the protonated nitrogens of the pyridine rings and the phenolic and carboxy-oxygens. The molecules related by the screw axes and connected by hydrogen bonds [O(4') · · · N(1')^{I} 2·69, N(1) · · · O(4)^{II} 2·65, and O(2) · · · O(4')^{II} 2·80 Å] leave a canal parallel to the c axis, in which most of the polar groups of the ligand protrudes. W(1), located on the two-fold axis at $1/4,1/4,z$, is hydrogen-bonded to the phenolic oxygen of two different molecules. In the canal, only four out of the seven water molecules per asymmetric unit, as obtained from density and analytical data, have been located unambiguously. These molecules are hydrogen-bonded to each other and to the oxygens of the polar groups on the surface of the canal. Hydrogen-bond lengths are reported in Table 5.

TABLE 5

Hydrogen bonds (Å)

W(1) · · · O(1)	2·97	W(4) · · · O(3^{I})	2·82
W(2) · · · O(3')	2·97	W(5) · · · O(4^{III})	2·84
W(2) · · · W(3)	2·75	O(4') · · · N(1'^{I})	2·69
W(3) · · · W(3^{IV})	2·84	O(2) · · · O(4'^{II})	2·80
W(3) · · · O(2'^{I})	2·71	N(1) · · · O(4^{II})	2·65
W(3) · · · W(4)	2·66		

Roman numeral superscripts indicate the following equivalent positions:

I $-x, -\frac{1}{2} + y, \frac{1}{2} - z$	III $-x, -y, 1 - z$
II $\frac{1}{2} + x, -y, \frac{1}{2} - z$	IV $\frac{1}{2} - x, -\frac{1}{2} - y, z$

Figure 3 shows a schematic projection on (001) of the structure of (II). The packing is closely related to that of the nickel complex. In this case the only water molecule located is placed on the 4_2 axis.

The results of this investigation allow elucidation of some interesting structural aspects of metal chelates of pyridoxylidene amino-acids. In the solid state of (I) the racemic co-ordination compounds A(LL),B(DD) are present. For (II) only the A(LL) diastereoisomer is found, and the same must be true for the isomorphous cobalt complex. Willstadter *et al.*[7] found that the octahedral bis(pyridoxylidene-DL-valinato)manganese(II) possesses crystallographic two-fold symmetry, which

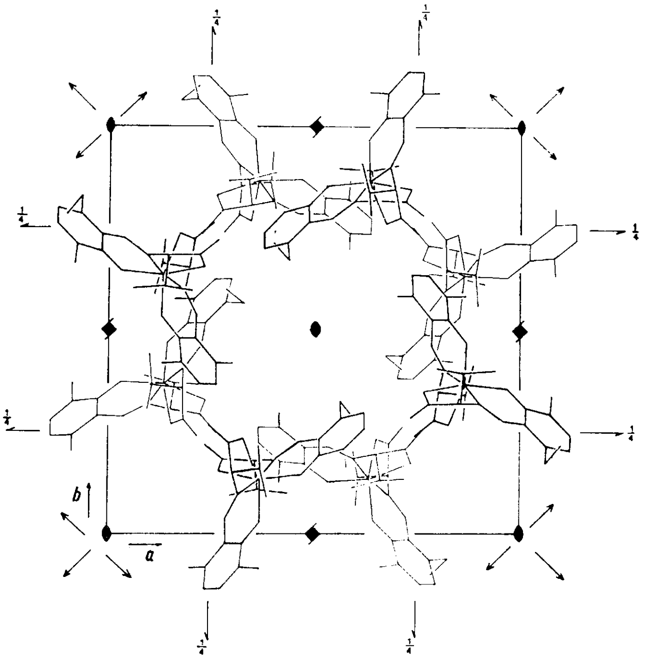

FIGURE 3 The crystal structure of the zinc complex (II) viewed along the c axis

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[12] T. Ueki, T. Ashida, Y. Sasada, and M. Kakudo, *Acta Cryst.*, 967, **22**, 870.

[13] T. Ueki, T. Ashida, Y. Sasada, and M. Kakudo, *Acta Cryst.*, 1969, **B25**, 328.

[14] J. B. Longenecker and E. E. Snell, *J. Amer. Chem. Soc.*, 1957, **79**, 142.

rules out structures such as A(DL) or B(DL). However they do not specify whether the enantiomorphous pairs A(LL),B(DD) or A(DD),B(LL) are present in the crystal. On the basis of the structure of the nickel complex, it seems likely that the enantiomorphous pair A(LL),B(DD) is also present in the isomorphous series of bis-complexes between manganese(II), cobalt(II), zinc(II), and pyridoxylidene-DL-valine. These results indicate that the formation of crystalline complexes is stereospecific and does not imply the racemization of the optically active amino-acid. The absence of racemization is in agreement with the fact that the valine racemization is much slower than that of other α-amino-acids. Thus it appears likely that the poor quality of the crystals of bis-complexes from pyridoxylidene-L-valine, ascribed by Willstadter *et al.* to an incomplete racemization before crystallization, is due to internal disorder of the water molecules, which are present in a quantity in the crystals.

This conclusion is evidenced from the behaviour of crystals of Fe^{III} pyridoxylidene-L-valine chelates. Indeed these crystals, which, according to the quoted authors, showed ' an astonishing internal disorder,' give a diffraction pattern as good as other chelates when mounted in a sealed capillary in the presence of the mother liquor.[15] However in the case of other L-amino-acids, the racemization can be an important factor influencing crystal disorder. The structures of octahedral complexes indicate that the stereospecificity cannot be explained by differences in the steric requirements for A(LL) and B(LL). This suggests that the mechanism of formation must involve an activated complex of lower energy for A(LL) than for the other diastereoisomer, in agreement with the mechanism suggested for aluminium pyridoxylidenevaline chelates.[5] Thus the A(LL) isomer, which is initially formed in greater quantity, separates in the solid state. With racemic Schiff bases, however, mixed-ligand complexes, such as A(DL) or B(DL), can form with the same velocity as A(LL) and B(DD). In this case an easier crystallization of the racemic complexes A(LL) and B(DD) must be invoked.

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[15] Unpublished results.