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Metal Complexes of Virus Inhibitors. Part III*. Coordination Properties of 1-n-propyl-2-α-hydroxybenzylbenzimidazole and the X-ray Crystal Structure of $Ni(C_{17}H_{18}N_2O)_2(C_{17}H_{17}N_2O)_1(ClO_4)_1$

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Abstract

Complexes are described of Cobalt(II) and Nickel(II) salts with the title ligand L. The X-ray crystal structure is described of $NiL_2L'_1(ClO_4)_1$. One ligand molecule (L′) in this complex is deprotonated and the structure involves strongly hydrogen bonded dimers with O–H–O bonds = 2.56 Å and 2.62 Å and a Ni–Ni bond = 4.77 Å. The corresponding Cobalt complex is thought to be similar but no other compounds containing L′ were obtained.

Introduction

Benzimidazoles with hydroxy-substituents in the 2-position show a range of anti-viral activity which has been attributed to their ability to chelate with trace metal ions [2]. Such chelating ability has been shown for 2-α-hydroxybenzylbenzimidazole [3] and for its equally active O-methyl ether [1]. Substitution of a n-propyl group in the 1-position causes a marked improvement in anti-viral activity although it might be expected to have little influence on the donor ability of the chelation sites. It was therefore of interest to compare the coordination chemistry of 1-n-propyl-2-α-hydroxybenzylbenzimidazole with that of 2-α-hydroxybenzylbenzimidazole.

Experimental

Preparation of the Compounds

Analyses are given in Table I.

TABLE I. Analytical Results for the Complexes.

Complexes	Found			Calculated		
	C	H	N	C	H	N
NiL_2Cl_2	60.39	5.37	8.27	61.60	5.48	8.46
$NiL_2(NO_3)_2$	57.28	5.19	11.81	57.07	5.07	11.75
$NiL_2(SCN)_2$	60.84	5.16	11.69	60.10	5.13	11.88
$NiL_2L'_1(ClO_4)_1$	62.63	5.79	–	63.98	5.68	–
$CoL_{1.5}Cl_2$	57.38	5.00	7.97	57.84	5.14	7.98
$CoL_{1.5}Br_2$	49.39	4.31	7.01	49.53	4.40	6.80
CoL_2I_2	48.65	4.40	6.78	48.31	4.49	6.64
$CoL_2(NO_3)_2$	57.04	5.06	11.36	57.07	5.07	11.74
$CoL_2(SCN)_2$	60.77	5.20	11.92	61.09	5.13	11.88
$CoL_2L'_1(ClO_4)_1$	63.06	5.66	–	63.98	5.68	–

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1-n-propyl-2-α-hydroxybenzylbenzimidazole on a 'large scale' was synthesised as described in [4].

NiL_2Cl_2

L (5.1 g) and $NiCl_2 \cdot 6H_2O$ (2.4 g) were dissolved in nitromethane (25 cm^3) with vigorous shaking and warming and the solution filtered. The filtrate was evaporated to about 10 cm^3 and left standing. The pale green crystals that formed after several days were filtered off, crushed and dried *in vacuo.*

$NiL_2(NO_3)_2$

L (5.4 g) and $Ni(NO_3)_2 \cdot 6H_2O$ (2.9 g) were dissolved in acetone (50 cm^3) with warming and shaking to give a green solution which after filtration was evaporated to dryness and the residue dissolved in nitromethane (20 cm^3). This solution on standing for several days produced green crystals which were filtered off, crushed and dried *in vacuo.*

$NiL_2(SCN)_2$

L (2.7 g) was dissolved in hot absolute ethanol (25 cm^3) and to this was added $Ni(SCN)_2$ in absolute ethanol (17 cm^3). The green solid which crystallised out on standing overnight was filtered off and dried *in vacuo.*

$NiL_2L'_1(ClO_4)_1$

L (4.0 g) and $Ni(ClO_4)_2 \cdot 6H_2O$ (1.9 g) were dissolved in hot acetone (25 cm^3), the solution filtered and the filtrate evaporated to about 15 cm^3. After standing for several weeks the green crystals which had formed were filtered off and some of it was crushed and dried *in vacuo.*

$CoL_{1.5}Cl_2$

L (5.4 g) and $CoCl_2 \cdot 6H_2O$ (2.4 g) were dissolved in acetone (50 cm^3) with vigorous shaking and the resulting deep blue solution was filtered. On standing for a short time a blue solid crystallised which was filtered off and dried *in vacuo.* This product was recrystallised several times from nitromethane and the small feather-like crystals dried *in vacuo.*

$CoL_{1.5}Br_2$

L (4.0 g) and $CoBr_2 \cdot 6H_2O$ (2.4 g) were dissolved in acetone (20 cm^3) and the resulting deep blue solution was filtered. The filtrate was evaporated to dryness and the residue dissolved in nitromethane (10 cm^3). The nitromethane solution on standing produced purple crystals which were filtered off, crushed and dried *in vacuo.*

CoL_2I_2

$Co(NO_3)_2 \cdot 6H_2O$ (1.5 g) and NaI (1.5 g) were dissolved in acetone (25 cm^3) and the precipitated $NaNO_3$ filtered off. The filtrate was evaporated to about 10 cm^3 and chilled overnight. L (2.7 g) was added to the clear CoI_2 solution and the resulting purple solution filtered. The filtrate was evaporated to dryness and the residue recrystallised from nitromethane.

$CoL_2(NO_3)_2$

L (5.4 g) and $Co(NO_3)_2 \cdot 6H_2O$ (2.9 g) were dissolved in acetone (50 cm^3) and after filtration the solution was evaporated to about 10 cm^3. On chilling overnight the dark red crystals that had formed were filtered off, dried *in vacuo* and recrystallised from acetone.

$CoL_2(SCN)_2$

The deep blue solution prepared by shaking together L (4.0 g) and $Co(SCN)_2$ (1.3 g) in acetone (50 cm^3), filtering and evaporating to about 20 cm^3, on standing produced pink crystals. The crystals were filtered off, gently crushed and dried *in vacuo.*

$CoL_2L'_1(ClO_4)_1$

L (4.0 g) and $Co(ClO_4)_2 \cdot 6H_2O$ (1.9 g) were dissolved in acetone (25 cm^3). The solution was filtered and evaporated to 10 cm^3. On standing for several weeks pink crystals formed which were filtered off and dried *in vacuo.*

X-Ray Crystal Structure Data

$NiC_{51}H_{53}N_6O_3ClO_4$, M = 956.1, monoclinic, a = 14.549(2), b = 19.812(3), c = 16.988(3), β = 96.05(1), U = 4869, space group $P2_1/n$, Z = 4, D_c = 1.31 g cm^{-3}, $\mu(Cu\text{-}K_\alpha)$ = 15 cm^{-1}. Refined unit cell parameters were obtained by centring 18 reflections on a Nicolet R3m diffractometer, 4615 independent reflections ($\theta \leqslant 50$) were measured for a single crystal (0.3 × 0.4 × 0.5 mm) with Cu-K_α radiation (λ = 1.54178 Å, graphite monochromated) and using the omega scan measuring routine. Of these 3915 had $|F_o| \geqslant 3\sigma(|F_o|)$ and were considered to be observed. The net count of the check reflections (the 321 and $3\bar{1}\bar{3}$) did not change significantly during the data collection indicating that no deterioration of the crystal had occured. The data were brought to a uniform arbitrary scale by use of these reflections and Lorentz, polarisation and numerical absorption correction applied.

The structure was solved by the heavy atom method and the non-hydrogen atoms refined anisotropically. The refinement showed there to be severe disorder in the perchlorate ion. This was partially compensated for by allowing the groups to refine as two discrete partial occupancy molecules (occupancy 0.8 and 0.2) with idealised tetrahedral geometries. There was also fairly high thermal motion in the terminal methyl carbons of the three n-propyl groups. The positions of the non-hydroxy hydrogen atoms were idealised (C–H = 0.96 Å), assigned isotropic

TABLE II. Atom Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($Å^2 \times 10^3$).

Atom	*x*	*y*	*z*	U^a
Ni	1329(1)	559(1)	634(1)	34(1)
N(1)	2532(2)	351(2)	128(2)	37(1)
C(2)	3223(3)	722(2)	−181(2)	43(2)
C(3)	3562(3)	1373(2)	−15(3)	56(2)
C(4)	4227(4)	1616(3)	−470(3)	78(2)
C(5)	4538(4)	1227(3)	−1071(3)	86(3)
C(6)	4249(4)	596(3)	−1227(3)	75(2)
C(7)	3579(3)	340(3)	−772(3)	53(2)
N(8)	3102(3)	−259(2)	−807(2)	49(1)
C(9)	2488(3)	−226(2)	−259(2)	38(2)
C(10)	1818(3)	−765(2)	−99(2)	43(2)
O(11)	1213(2)	−465(1)	411(2)	41(1)
C(12)	3242(4)	−820(3)	−1361(3)	67(2)
C(13)	4108(4)	−1211(3)	−1109(3)	88(3)
C(14)	4262(6)	−1749(4)	−1696(5)	142(4)
C(15)	2280(3)	−1377(2)	307(3)	56(2)
C(16)	2753(4)	−1307(3)	1051(3)	71(2)
C(17)	3163(4)	−1849(3)	1446(4)	93(3)
C(18)	3097(5)	−2467(3)	1093(4)	125(3)
C(19)	2666(5)	−2552(3)	354(5)	134(4)
C(20)	2233(4)	−2002(3)	−42(4)	96(3)
N(21)	1413(2)	1581(2)	545(2)	40(1)
C(22)	1875(3)	2118(2)	934(2)	44(2)
C(23)	2416(3)	2132(2)	1655(3)	62(2)
C(24)	2812(4)	2741(3)	1886(3)	80(2)
C(25)	2688(4)	3316(3)	1417(3)	85(2)
C(26)	2164(4)	3299(2)	699(3)	72(2)
C(27)	1760(3)	2687(2)	465(3)	51(2)
N(28)	1212(3)	2490(2)	−216(2)	50(1)
C(29)	1034(3)	1827(2)	−133(2)	37(2)
C(30)	452(3)	1388(2)	−715(2)	39(1)
O(31)	470(2)	725(1)	−400(1)	36(1)
C(32)	852(4)	2943(2)	−863(3)	71(2)
C(33)	−138(5)	3154(3)	−803(4)	107(3)
C(34)	−304(6)	3471(4)	−44(4)	134(4)
C(35)	730(3)	1388(2)	−1551(2)	37(1)
C(36)	1625(3)	1289(2)	−1697(3)	57(2)
C(37)	1859(4)	1231(3)	−2460(3)	65(2)
C(38)	1195(4)	1277(2)	−3084(3)	66(2)
C(39)	299(4)	1376(2)	−2951(3)	64(2)
C(40)	54(3)	1432(2)	−2184(2)	53(2)
N(41)	1723(2)	427(2)	1822(2)	36(1)
C(42)	2559(3)	354(2)	2306(2)	37(2)
C(43)	3456(3)	359(2)	2140(3)	50(2)
C(44)	4137(3)	258(3)	2753(3)	64(2)
C(45)	3922(4)	156(2)	3530(3)	62(2)
C(47)	2343(3)	254(2)	3084(2)	44(2)
C(46)	3034(4)	158(2)	3706(3)	55(2)
N(48)	1389(3)	269(2)	3058(2)	44(1)
C(49)	1060(3)	375(2)	2290(2)	34(1)
C(50)	54(3)	411(2)	1992(2)	41(2)
O(51)	1(2)	403(1)	1146(1)	39(1)
C(52)	863(3)	232(2)	3745(2)	52(2)
C(53)	838(4)	914(2)	4153(3)	65(2)
C(54)	201(4)	918(3)	4811(3)	91(3)
C(55)	−426(3)	1034(2)	2258(2)	43(2)
C(56)	−146(4)	1662(2)	2052(3)	67(2)
C(57)	−582(4)	2242(3)	2287(3)	90(3)
C(58)	−1298(4)	2174(3)	2738(4)	103(3)
C(59)	−1587(4)	1549(3)	2956(3)	91(3)
C(60)	−1152(3)	977(3)	2707(3)	66(2)
Cl	1914(1)	5008(1)	−1046(1)	79(1)
O(61)	1240(3)	4741(3)	−625(2)	175(4)
O(62)	1802(3)	4779(2)	−1809(1)	173(4)
O(63)	1846(5)	5702(1)	−1038(3)	248(6)
O(64)	2771(3)	4817(3)	−693(2)	182(4)
O(61′)	1503(4)	5169(2)	−1788(2)	96(7)
O(62′)	1242(3)	4818(2)	−575(3)	32(3)
O(63′)	2522(4)	4485(3)	−1097(3)	217(18)
O(64′)	2375(4)	5562(3)	−718(2)	57(5)

[a] U is defined as one third of the trace of the orthogonalised U_{ij} tensor.

thermal parameters, $U(H) = 12\ U_{eq}(C)$ and allowed to ride on their parent carbon atoms. The methyl groups were refined as idealised rigid bodies. The positions of the O–H hydrogen atoms were derived from a F map and these atoms refined isotropically. Refinement was by block cascade full matrix least-squares to $R = 0.052$, $R_w = 0.054$, $[w^{-1} = \sigma^2(F) + 0.0004F^2]$. Computations were carried out on an Eclipse S140 computer using the SHELXTL program system [5]. Fractional atomic coordinates and isotropic thermal parameters are listed in Table II. Table III lists selected values of bond lengths and bond angles.

Spectroscopic and Magnetic Measurements

These were carried out as described previously [6].

Results and Discussion

The ligand L coordinates to a variety of nickel(II) and cobalt(II) salts, forming complexes containing 2 or 3 mol of L. In all cases it appears to chelate through the imino nitrogen and the hydroxylic oxygen. The anions are uncoordinated in the ML_3 compounds and monodentate in ML_2X_2. In this respect there is a strong similarity to 2-α-hydroxybenzylbenzimidazole. In detail however the differences are significant.

With the perchlorates of both nickel(II) and cobalt(II), isomorphous complexes were obtained which analysed as $ML_2L'_1(ClO_4)_1$, and which behaved as 1:1 electrolytes in nitrobenzene, although the metal ions were still in the 2+ oxidation state. It appeared that one mol of the ligand had been deprotonated, giving a cation $[ML_2L'_1]^+$. In view

TABLE III. Selected Bond Lengths and Bond Angles.

Bond lengths (Å)			
Ni–N(1)	2.072(3)	Ni–O(11)	2.066(3)
Ni–N(21)	2.035(3)	Ni–O(31)	2.072(2)
Ni–N(41)	2.055(3)	Ni–O(51)	2.222(3)
N(1)–C(2)	1.392(5)	N(1)–C(9)	1.316(5)
C(2)–C(3)	1.400(6)	C(2)–C(7)	1.400(6)
C(3)–C(4)	1.387(7)	C(4)–C(5)	1.393(8)
C(5)–C(6)	1.337(8)	C(6)–C(7)	1.401(7)
C(7)–N(8)	1.373(6)	N(8)–C(9)	1.358(5)
N(8)–C(12)	1.484(6)	C(9)–C(10)	1.490(6)
C(10)–O(11)	1.428(5)	C(10)–C(15)	1.516(6)
C(12)–C(13)	1.502(7)	C(13)–C(14)	1.492(10)
C(15)–C(16)	1.381(7)	C(15)–C(20)	1.371(7)
C(16)–C(17)	1.370(8)	C(17)–C(18)	1.362(9)
C(18)–C(19)	1.354(10)	C(19)–C(20)	1.396(9)
Bond angles (deg.)			
N(1)–Ni–O(11)	77.5(1)	N(1)–Ni–N(21)	96.1(1)
O(11)–Ni–N(21)	165.2(1)	N(1)–Ni–O(31)	98.0(1)
O(11)–Ni–O(31)	88.3(1)	N(21)–Ni–O(31)	79.3(1)
N(1)–Ni–N(41)	102.8(1)	O(11)–Ni–N(41)	93.7(1)
N(21)–Ni–N(41)	100.8(1)	O(31)–Ni–N(41)	159.0(1)
N(1)–Ni–O(51)	160.5(1)	O(11)–Ni–O(51)	83.0(1)
N(21)–Ni–O(51)	103.2(1)	O(31)–Ni–O(51)	83.2(1)
N(41)–Ni–O(51)	76.3(1)	Ni–N(1)–C(2)	136.6(3)
Ni–N(1)–C(9)	112.4(3)	C(2)–N(1)–C(9)	105.6(3)
N(1)–C(2)–C(3)	131.7(4)	N(1)–C(2)–C(7)	108.7(4)
C(3)–C(2)–C(7)	119.6(4)	C(2)–C(3)–C(4)	117.3(4)
C(3)–C(4)–C(5)	121.1(5)	C(4)–C(5)–C(6)	122.9(5)
C(5)–C(6)–C(7)	116.9(5)	C(2)–C(7)–C(6)	122.2(5)
C(2)–C(7)–N(8)	106.0(4)	C(6)–C(7)–N(8)	131.8(4)
C(7)–N(8)–C(9)	107.1(4)	C(7)–N(8)–C(12)	125.0(4)
C(9)–N(8)–C(12)	127.9(4)	N(1)–C(9)–N(8)	112.5(4)
N(1)–C(9)–C(10)	122.0(4)	N(8)–C(9)–C(10)	125.5(4)
C(9)–C(10)–O(11)	105.5(3)	C(9)–C(10)–C(15)	112.9(3)
O(11)–C(10)–C(15)	109.3(3)	Ni–O(11)–C(10)	118.5(2)
N(8)–C(12)–C(13)	111.9(4)	C(12)–C(13)–C(14)	111.0(5)
C(10)–C(15)–C(16)	119.3(4)	C(10)–C(15)–C(20)	121.7(4)
C(16)–C(15)–C(20)	119.0(5)	C(15)–C(16)–C(17)	121.2(5)
C(16)–C(17)–C(18)	118.9(5)	C(17)–C(18)–C(19)	121.6(6)
C(18)–C(19)–C(20)	119.5(6)	C(15)–C(20)–C(19)	119.8(6)

of this unusual stoichiometry a full X-ray crystal structure determination was carried out on the nickel complex. The geometry about the Ni is that of a distorted octahedron with the oxygen and nitrogen atoms facial (Fig. 1). The angles at the Ni range between 76.3° and 103.2°, and between 159.0° and 165.2° *cf.* 90° and 180° for a regular octahedron. However despite these large departures from ideal geometry the spread of values within the two faces containing only oxygen or nitrogen atoms is much smaller. The ONiO angles are all acute (83.2° to 88.3°) and the NNiN angles are all obtuse (96.1° to 102.8°). Similar contractions of the ONiO angles with respect to the NNiN angles have been observed before, *e.g.* in the structure of bis(2-aminoethanol)(2-aminoethanolato)nickel(II)perchlorate the ONiO angles are 89.4° and the NNiN angles 96.7° [7]; also in the structure of tris(glycinato)nickel(II) the ONiO angles are 88.6°, 88.2° and 90.5° and the NNiN angles are 98.2°, 97.3° and 99.6° respectively [8]. The principal distortion in $NiL_2L'(ClO_4)$ is a rotation of 17° from a normal staggered relationship between the oxygen and nitrogen atoms about the vector joining the centroids of the two faces.

The facial geometry results in a flattening of the molecule as a whole with respect to the oxygen face. This can be seen in the space-filling drawing of the

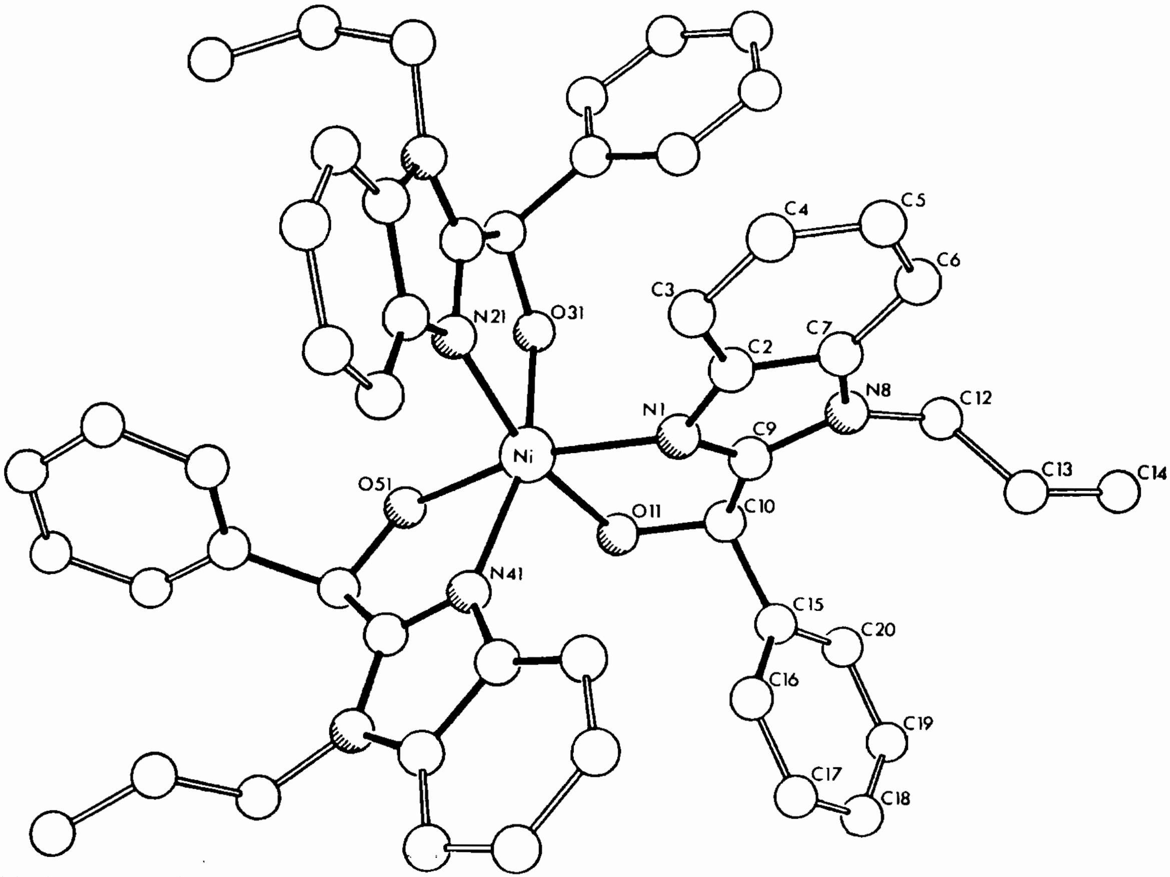


Fig. 1. Geometry about the Ni atom.

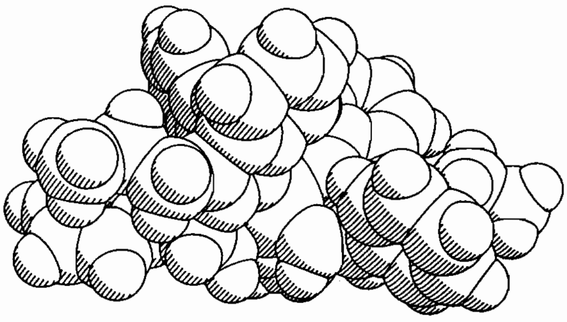
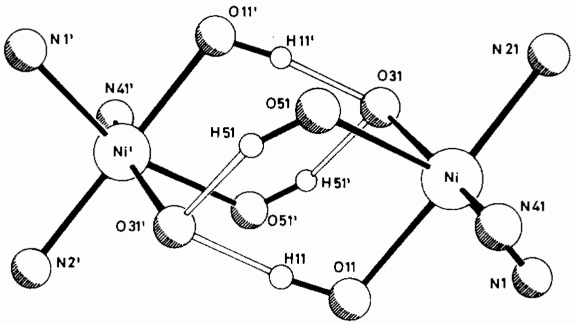


Fig. 2. Space-filling drawing of the molecule.



Ni'–O(31')–H(51)	114°	O(31')–O(51)	2.62 Å
O(31')–H(51)–O(51)	154°	O(31')–H(51)	1.76 Å
O(31')–H(11)–O(11)	165°		

Fig. 3. Pattern of hydrogen bonding.

molecule (Fig. 2). A consequence of this flattened geometry is that not only are both the protonated and deprotonated oxygen atoms in an exposed position on the surface of the molecule, but also another molecule is able to approach close enough to form a strongly hydrogen bonded face-to-face dimer.

The successful location and refinement of the hydroxy hydrogen atom positions has permitted the pattern of hydrogen bonding to be defined (Fig. 3).

The two molecules are linked across a crystallographic centre of symmetry by four hydrogen bonds. Two of these, between O(31) and O(11′) and also between O(31′) and O(11) are short (2.50 Å), and the other two between O(51) and O(31′) and between O(31) and O(51′) are slightly longer (2.62 Å).

TABLE IV. Diffuse Reflectance Spectra of the Complexes (cm^{-1}).

NiL_2Cl_2	24,100; 23,300sh; 20,000sh; 14,200; 12,500sh; 8350
$NiL_2(NO_3)_2$	25,650; 23,000sh; 15200; 12,800sh; 9,250
$NiL_2(SCN)_2$	25,000; 21,000sh; 15,400; 13,100sh; 8950.
$NiL_2L'_1(ClO_4)_1$	25,650; 15,050; 12,900sh; 9,100
$CoL_{1.5}Cl_2$	20,200sh; 18,850; 15,800sh; 14,700; 8,000sh; 6,200; 5,400; 5,200; 4,850; 4,700sh
$CoL_{1.5}Br_2$	20,000sh; 18,600; 14,900; 13,900; 7,800; 5,700; 5,000; 4,700; 4,500sh
CoL_2I_2	18,500sh; 17,400; 15,900; 9,500; 6000
$CoL_2(NO_3)_2$	21,000sh; 19,600; 15,400sh; 10,500; 6,700
$CoL_2(SCN)_2$	20,500sh; 18,600; 16,400sh; 8,700; 7,700sh
$CoL_2L'_1(ClO_4)_1$	20,800sh; 18,450; 9,100; 7,600

The non hydrogen-bonded O(11)····O(51) and O(51)····O(11′) contacts are 3.02 Å. All four hydrogen bonds are asymmetric; the deprotonated O(31) acts as an acceptor to two hydrogen bonds and the protonated O(11) and O(51) act as donors. Details of the hydrogen bonding geometries are given in the figure legend. A similar hydrogen bonded dimeric relationship between two facial Ni complexes was observed in the structure of bis(2-aminoethanol)(2-aminoethanolato)nickel(II)perchlorate [7]. There, however, the structure was slightly disordered and the nature of the hydrogen bonding between the molecules could not be deduced. The O···O approach distances were 2.74 Å indicating a weaker hydrogen bonding arrangement. The three Ni–N and two of the Ni–O bond distances are similar (Table III). The third Ni–O bond [to O(51)] is however very much longer, at 2.22 Å than the other two at 2.07 Å. Initially it was thought that this might indicate which of the oxygens had been deprotonated. However, location of the OH hydrogen positions showed this not to be the case and we can see no reason for the longer Ni–O(51) bond length. This asymmetry is confined to this one bond, *e.g.* the geometries of the three imidazole rings are not affected. Comparison of the bonds in these three rings and also of those linking them to the oxygen atoms shows them to be, within statistical significance, identical for the three ligands. The formation of a hydrogen bonded dimer also brings the three oxygens of the symmetry related molecule, O(11′), O(31′) and O(51′) to within 4 Å of the Ni. The Ni–O distances being 3.94 Å, 3.64 Å and 3.91 Å respectively. The Ni–Ni distance is 4.77 Å.

The highly distorted stereochemistry about the nickel ion is not reflected in its electronic spectrum (Table IV), which shows no splitting of the three bands predicted for regular octahedral geometry. The isomorphous cobalt compound however shows marked splitting of the $\nu_1(^4T_{1g} \rightarrow {}^4T_{2g})$ transition as does the corresponding complex with 2-α-hydroxybenzylbenzimidazole (HBB) as ligand [3]. Indeed the similarity of the two spectra tends to confirm the stoichiometry of $CoHBB_2HBB'_1(ClO_4)_1$. There is no evidence for any magnetic coupling between the two nickel ions within the dimer, the room temperature magnetic moment being 3.28. For the cobalt complex the moment of 4.73 is somewhat lower than the values commonly found for octahedral complexes, but this could be due to the quenching of orbital contribution by the low symmetry ligand field. No such reduction would be expected in the nickel complex with a $^3A_{2g}$ ground state and a virtually unsplit $^3T_{2g}$ level.

The cobalt(II) complexes with nitrate and thiocyanate as anions which are of stoichiometry CoL_2X_2 also show splitting of ν_1, whereas the isomorphous nickel complexes do not. These nickel complexes have slightly more intense bands than is usual in centrosymmetric complexes suggesting that they have *cis* geometry. It seems that in complexes of this type the $^4T_{2g}$ level of the cobalt ion is much more sensitive to distortion of the structure than is the $^3T_{2g}$ state of the nickel ion.

Reaction of L with cobalt chloride and bromide always gave compounds of stoichiometry $CoL_{1.5}X_2$. Their electronic spectra contain bands readily assigned to tetrahedral CoX_4^{2-} anions, plus weaker bands probably derived from an octahedral species (Table IV). The nature of this species could not be decided unambiguously because its bands were partially obscured by the CoX_4^{2-} bands but it appeared to be independent of the halide. It seems reasonable to formulate these compounds as $[CoL_3^{2+}][CoX_4^{2-}]$ with no deprotonation of the ligand. With the nickel halides, complexes NiL_2X_2 with essentially octahedral geometry were obtained.

In view of the unusual nature of the perchlorates attempts were made to prepare complexes with other non-coordinating anions. No other complexes were obtained in which the ligand was deprotonated. The fluorosilicates gave complexes with somewhat variable analyses but approximating to $ML_{2.5}SiF_6$. Crystals were obtained for the nickel compound but these deteriorated in the X-ray beam when structural investigation was attempted. Sufficient data were collected to show that the stoichiometry was in fact NiL_3SiF_6 although even on this sample the carbon analysis was low. No accurate Ni–Ni distances could be obtained but the minimum Ni–Ni distance is about 9.0 Å. The ligand is not deprotonated and there is no dimer formation. The cobalt complex was not isomorphous with the nickel one and its stoichiometry remains uncertain.

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