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Boron and Transition Metal Compounds Derived from 2-Uroylbenzimidazole

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ABSTRACT: *The coordination sites of 2-uroylbenzimidazole* **1** *toward diphenylborinic acid, as well as zinc, cadmium, copper, nickel and cobalt chlorides, bromides, and nitrates were investigated. The ligand is bonded in monodentate mode to $ZnCl_2$, $ZnBr_2$, $CdCl_2$, $CdBr_2$, and $Cd(NO_3)_2$, and in bidentate mode to all others. With diphenylborinic acid, two heterocycles are formed; in one, the boron is bonded to imidazole and the terminal NH_2 group, and in the other the boron is bonded to imidazole and to the oxygen atom. Boron, zinc, and cadmium derivatives were studied by NMR spectroscopy. The X-ray diffraction structure of 2-uroylbenzimidazole is reported.* © 1999 John Wiley & Sons, Inc. Heteroatom Chem 10: 577–584, 1999

INTRODUCTION

Herein we report the study of the coordinating behavior of 2-uroylbenzimidazole **1**, as shown in Figure 1. 2-Aminobenzimidazole derivatives are important compounds; they show interesting biological activities, especially as antiparasitic drugs, antihelmintics, fungicides, and biocides [1]. Their use in the treatment of neurocysticercosis was recently reported [2]. They are good coordinating ligands; an example of this coordinating ability was found in 2-guanidinobenzimidazole **2** (Figure 1), which forms stable derivatives with Lewis acids or metallic ions by coordinating to the lone pair of the imidazolic nitrogen atom and by substituting one acidic N-H of the guanidinic group [3–6]. Because of the closely related structures of 2-uroylbenzimidazole and **2**, we decided to investigate their coordinating properties. Compound **1** is a planar molecule bearing sp^2 nitrogen and oxygen atoms with lone pairs available for coordination. It is also a good model to establish a competition between oxygen and nitrogen coordination to boron or metal atoms. Thus, we have prepared the compounds derived from diphenylborinic acid because the diphenylborinium species

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$B(C_6H_5)_2^+$ functions as a covalent diamagnetic model for metal coordination, which can be studied in detail by NMR spectroscopy. We have also prepared the zinc(II), cadmium(II), copper(II), cobalt(II) and nickel(II) chloride, bromide, and nitrate complexes of **1**. We were unable to obtain good crystals of the new compounds to confirm the assigned structures by spectroscopy, but we could confirm our propositions with an X-ray diffraction structure of a cobalt compound derived from a similar ligand: methyl-2-benzimidazole carbamate.

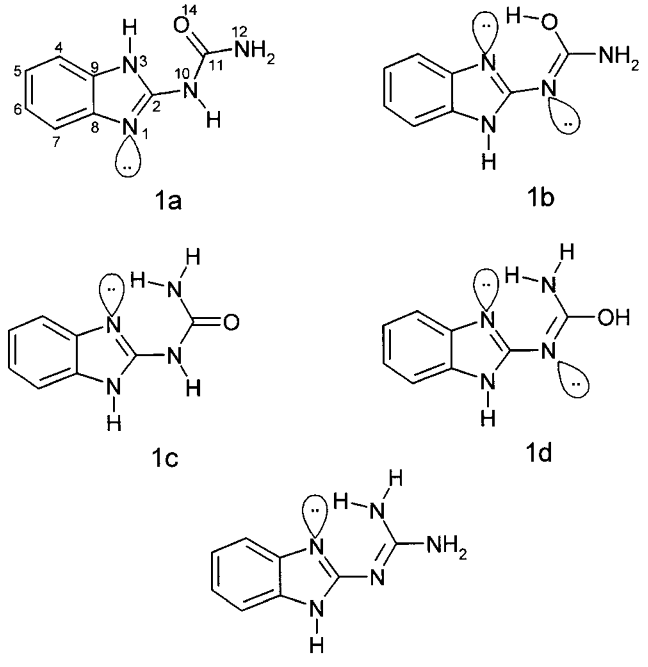
RESULTS AND DISCUSSION

Molecular Structure of 2-Uroylbenzimidazole

In order to understand the structures of the new coordination compounds, it was necessary to determine the structure of **1** because it can be depicted by several tautomers or conformers, which have an important influence in the coordination behavior of this polyfunctional ligand (Figure 1). In addition, the molecule can form intramolecular or intermolecular hydrogen bonds that can stabilize some of its isomers. Therefore, it was of interest to establish the presence of hydrogen bonds, which are competing for the coordination sites and are models for metal complexation. With this purpose in mind, we obtained the X-ray diffraction structure of compound **1** (Figure 2). Compound **1** crystallized from tetrahydrofuran (THF) in the monoclinic system C2/c. Its structure corresponds to conformer **1a** (Figure 1). It has a hydrogen bond between the imidazolic N-H and the carbonyl group (H–O intramolecular atoms distance, 2.205 Å), as well as an intermolecular hydrogen bond between the same groups (H–O intermolecular atoms distance, 2.151 Å) (Tables 1 and 2). In the IR spectra, several bands appear between 2838 and 3200 cm^{-1}, which can be attributed to inter- and intramolecular hydrogen bonds. It was deduced that, in solution, the same structure is preferred. In the ^{15}N NMR spectrum, ligand **1** presents two signals: a triplet (N12-H$_2$, $\delta = -298$, J(N-H) = 88.5 Hz), a doublet (N10-H, $\delta = -274.5$, (J(N-H) = 82 Hz); nitrogen atoms N-1 and N-3 were not easily observed because of their tautomeric equilibrium.

Boron Compounds

Compound **1** reacted with diphenylborinic acid under reflux in THF or with chlorodiphenylborane in THF in the presence of triethylamine. Two boron tautomeric heterocycles could be formed, **3a** and **3b**, and effectively the reaction with diphenylborinic acid in THF afforded both tautomers (Figure 3). From a mixture of water/THF, one tautomer crystallized to give white crystalline needles **3a**. In contrast, the reaction performed with chlorodiphenylborane afforded only one tautomer that was identified as isomer **3a**. Its structure was determined from ^1H, ^{13}C,



1a 1b 1c 1d 2

FIGURE 1 Tautomers and conformers of 2-uroylbenzimidazole **1** and 2-guanidinobenzimidazole **2**.

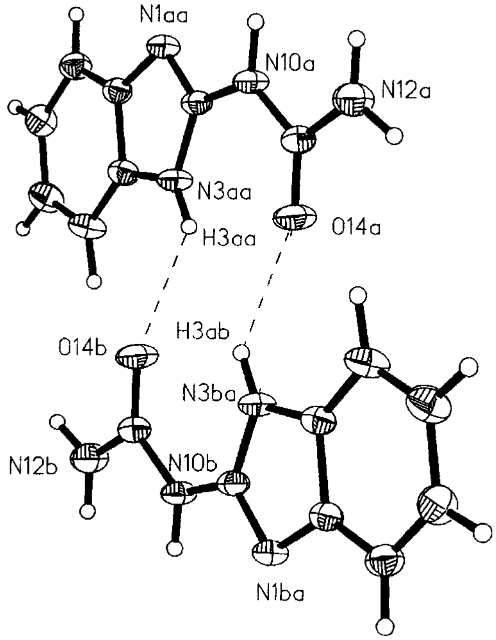


FIGURE 2 View of the association of the molecules of **1** via intermolecular hydrogen bonds.

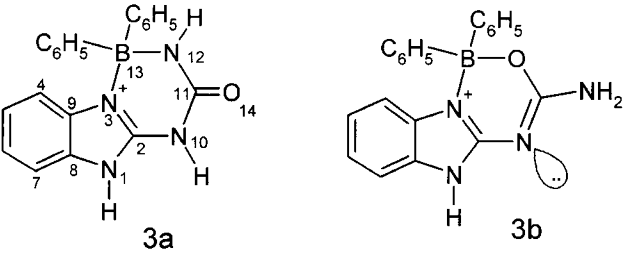
TABLE 1 Crystal Data of Compound **1** and **22**

Formula	$C_5H_8N_4O$	$C_{19}H_{18}Cl_2CoN_6O_5$
Formula weight	176.18 g·mol^{-1}	540.22
Cryst. Size	0.15 × 0.18 × 0.21	0.5 × 0.4 × 0.3
Space group	C 2/c	Triclinic P-1
a(Å)	23.8681(5)	8.594(2)
b(Å)	5.458(1)	9.294(2)
c(Å)	14.681(3)	14.714(3)
α(°)	90	89.75(3)
β(°)	127.42(3)	86.45(3)
γ(°)	90	74.14(3)
V(Å^3)	1507.0(5)	1128.2(4)
Z	8	2
d_c (g cm^3)	1.553	1.590
θ range (°)	1 to 25	1.39 to 24.97
Scan range (°)	0.8 + 0.345 tg θ	0-7 + 0-310 tg θ
Reflections collected	1420	4131
Unique reflections	1367	3967
Reflections observed 4σ	845	3992
Merging *R* factor	0.037	0-0174
Reflections with I > 3σI	828	2886
R	0.036	0.0386
R_w	0.034, w = 1.0	0.1042
Goodness of fit	1.048	1.042
Number of variables	119	298
$\Delta\rho$min (e/Å^3)	−0.49	−0.523
$\Delta\rho$max (e/Å^3)	0.61	0-447

Diffractometer CAD4-Enraf-Nonius, Radiation Mo/Kα (λ = 0.71069 Å), Scan type $\omega/2\theta$, measurements at room temperature. All hydrogen atoms were found by Fourier difference.

TABLE 2 Bond Lengths (Å) and Bond Angles (°) for **1**

Atoms	*Distances*	*Atoms*	*Angles*
N10-C11	1.340(3)	C11-N10-C2	127.5(2)
N10-H10	0.90(3)	C2-N3-C9	108.3(2)
N3-C9	1.376(3)	C2-N1-C8	106.8(2)
N1-C2	1.279(3)	O14-C11-N10	121.8(2)
O14-C11	1.156(3)	O14-C11-N12	123.2(2)
N12-H12	0.89(3)	N10-C11-N12	115.0(2)
N10-C2	1.363(3)	C8-C9-N3	105.2(2)
N3-C2	1.294(3)	C4-C9-N3	134.7(2)
N3-H3	0.87(3)	N1-C2-N3	111.2(2)
N1-C8	1.375(3)	N1-C2-N10	123.7(2)
C11-N12	1.342(4)	N3-C2-N10	125.1(2)
C9-C8	1.327(3)	C9-C8-N1	108.5(2)
		C7-C8-N1	132.3(2)



3a 3b

FIGURE 3 Tautomers of diphenylboron amides from 2-uroylbenzimidazole.

TABLE 3 ^{1}H NMR Data, δ(ppm), DMSO-d6

Compound	*H-1*	*H-10*	*H-12*	*H-4*	*H-5*	*H-6*	*H-7*
1a	11.47	9.79	6.75	7.00	7.34	7.34	7.00
3a	12.53	10.87	6.35	6.63	6.93	7.1	7.42
3b	12.30	–	–	6.63	6.92	–	–
4	–	–	6.63	6.63	7.0	7.0	6.63
5	–	10.9	6.87	7.0	7.43	7.43	7.0
7	11.7	9.8	6.92	7.1	7.55	7.55	7.1
8	–	10.2	6.98	7.1	7.55	7.55	7.1

^{15}N, ^{11}B, and HMQC (heteronucler multiple-quantum correlation) NMR experiments. The isolated isomer **3a** has a borate structure, as denoted by the signal at δ = −2.5 in the ^{11}B NMR spectrum. If tautomer **3a** is present, three different N-H signals of the same intensity should be found in the ^{1}H NMR spectrum; on the other hand, compound **3b** should show two signals (N-H and NH_2 in a 1 to 2 ratio). Examination of the spectrum showed three N-H signals with the same intensity: imidazolic N-H at δ = 12.53, N12-H at δ = 6.38, and N10-H at δ = 10.91. ^{1}H/^{15}N Hetcor NMR experiments allowed the correlation of the N10-H signal at δ = −277 and N12-H at δ = −271. No NH_2 group could be detected in the ^{1}H or ^{15}N NMR spectra. By a long-distance-correlation experiment, HMQC, ^{1}H/^{13}C interaction of N10-H with C-2 confirmed the assignment. All other ^{13}C and ^{1}H signals were unequivocally assigned by NMR experiments and by comparison with analogous compounds (Tables 3–5).

In the ^{1}H and ^{13}C NMR spectra of the mixture of tautomers, the second tautomer **3b** was identified, (δ ^{11}B = +4, broad). Compound **3b** presents a shift for C-11 to higher frequencies (δ = 164.6), which shows that the oxygen atom is bonded to the boron atom. We could not identify the N-H proton resonances, but we obtained ^{15}N NMR data with resonances at δ = −252, doublet *J*(N-H) = 81, and at δ = −290, triplet *J*(N-H) = 90 Hz, (Figure 3, Tables 3–5).

Mass spectra obtained by FAB (fast atom bombardment) or CID (collision-induced dissociation) methods, applied to pure **3a** and to the mixture of **3a** and **3b**, present the molecular peaks (341 or 340, respectively) in agreement with the proposed structures. The IR spectra of **3a** showed the characteristic

TABLE 4 ^{13}C NMR Data, δ(ppm), DMSO-d6

Compound	*C-2*	*C-4*	*C-5*	*C-6*	*C-7*	*C-8*	*C-9*	*C-11*
1a	155.7	113.4	120.4	120.4	113.4	136.5	136.5	148.3
3a	153.0	112.4	123.0	123.0	114.8	133.4	131.2	147.7
3b	154.9	111.0	122.1	122.3	113.3	133.6	130.8	164.6
4	155.2	113.8^{a}	121.7	121.7	113.8^{a}	135.1^{a}	135.1^{a}	148.2
5	155.4	114.1^{a}	121.7	121.7	114.1^{a}	135.9^{a}	135.9^{a}	148.4^{a}
7	155.0	113.5^{a}	120.6	120.6	113.9^{a}	135.6^{a}	135.6^{a}	148.1^{a}
8	155.2	113.8^{a}	121.3	121.3	113.8^{a}	135.2^{a}	135.2^{a}	147.5^{a}
C_6H_5B	*ipso*	*ortho*	*meta*	*para*				
3a	151.0	133.4	127.3	126.0				
3b	149.0	133.0	127.2	125.9				

^{a}Broad and short signals.

TABLE 5 ^{15}N and ^{11}B NMR

Data, δ(ppm), DMSO-d6

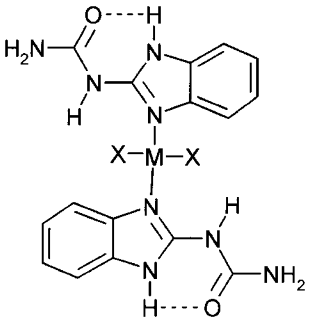
Compd.	N-12	N-10	N-1	B
1a	−298	−274.5	–	–
J(N-H)	88.5	82	–	–
3a	−271	−277	−233	−2.0
3b	−290	−252	–	+4.0
J(N-H)	90	–	–	–

signals for ν C=O at 1680 and ν B-N at 1183 and 1151 cm^{-1}. From the mixture of **3a** and **3b**, some of the bands of **3b** could be assigned; ν C-O appears at 1588 and ν B-O at 1366 and 1346 cm^{-1}, in accord with our proposition.

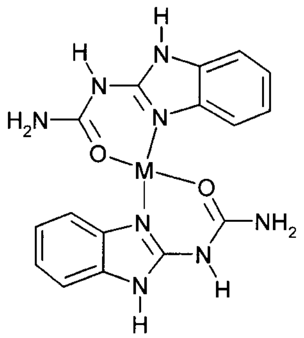
Zinc and Cadmium Compounds

We have reacted compound **1** with $ZnCl_2$, $ZnBr_2$, $Zn(NO_3)_2$, $CdCl_2$, $CdBr_2$, and $Cd(NO_3)_2$ in methanol. The reactions afforded compounds **4–9,** which were characterized by IR, thermogravimetric (TGA), and elemental analysis (Figure 4). For all zinc complexes, a tetrahedral geometry at the metal center is proposed. From the IR spectra, it is deduced that compounds **4** and **5** are coordinated through the pyridinic-type nitrogen atom to the metal ion. In the IR spectra, ν (C=C) shifted on complexation of **1** from 1646 to 1630 cm^{-1}; both compounds exhibited a shifting of the ν(C=O) vibration from 1706 in the ligand to ca. 1720 cm^{-1} in the complexes, indicating that the oxygen is not coordinated to the Zn(II) atom (Table 7). For the zinc compound **4** in its far IR spectrum, bands for ν(Zn-Cl) at 331 and 274 cm^{-1} were observed. It is proposed for both zinc(II) halide compounds that the ligands are monodentate with two halides bonded to the zinc(II) atom in a tetrahedral geometry. The stabilization of this geometry is due to a hydrogen bond between the carbonyl oxygen atom and the imidazolic N-H of the ligand, which were observed in their IR spectra as several broad bands centered at 3280 cm^{-1}. Similar behavior of the ligand was found in the cadmium(II) complexes **7–9;** the counteranions are coordinated to the metal, and as a consequence, the ligand is monodentate. In order to confirm the monodentate behavior of the ligand and the proposed hydrogen bonds, we analyzed the X-ray diffraction structure of a similar ligand in a dichloride cobalt compound: the methyl 2-benzimidazolecarbamate cobalt(II) chloride (Figure 5, Tables 1 and 6). This structure was previously reported by Sokol et al.[7], but we crystallized the complex with a methanol molecule and obtained a better resolution in the X-ray-diffraction analysis. In the structure, the cobalt(II) atom was in a tetrahedral geometry, and several intra- and intermolecular hydrogen bonds were found. The carbonyl oxygen atoms are interacting with two hydrogen atoms of the methyl groups (2.657, 2.814, 2,669, and 2.882 Å), with the imidazolic hydrogen (2.174 and 2.141 Å) and with the methanol OH group (O · · · O 3.068 Å); one of the aromatic protons (H104) is bonded to the methanol oxygen atom (3.018 Å); the amidic NH groups are bonded to the chlorine atoms (2.266 and 2.402 Å) and form a spiranic array around the cobalt(II): the interplanar angle is 65°. Intermolecular hydrogen bonds, between the aromatic proton (H10c) and the carbonyl oxygen from another molecule (2.44 Å) were also found.

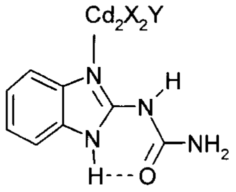
On the other hand, in compound **6,** the ionic character [$\nu_{as}(NO_3)$ 1392 cm^{-1}] of the nitrates and the ν(C=O) band shift from 1706 to 1684 cm^{-1} indicate a bidentate coordination of the ligand (Figure 4). Therefore, it is proposed that the structure of this complex is similar to that of the zinc(II) coordination compound derived from 2-guanidinobenzimidazole and determined by X-ray diffraction [4]. We



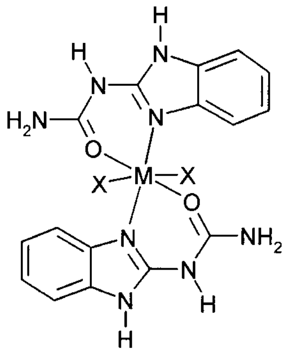
4 M = Zn, X = Cl
5 M = Zn, X = Br
9 M = Cd, X = NO_3



6 M = Zn
14, **15** = M = Cu



7 X = Cl, Y = H_2O
8 X = Br, Y = CH_3OH



10 M = Ni, X = Cl
11 M = Ni, X = Br
12 M = Ni, X = H_2O
13 M = Ni, X = OAc
16 M = Cu, X = NO_3
17 M = Cu, X = OAc
18 M = Co, X = Cl
19 M = Co, X = Br
20 M = Co, X = H_2O
21 M = Co, X = OAc

FIGURE 4 Compounds derived from 2-uroylbanzimidazole and metal ions.

TABLE 7 Selected Infrared Data

Compound	$\nu(C{=}O)$	$\nu(C{=}C)$	$\nu(C{=}N)$	$\nu(N\text{-}H)$	$\nu(N\text{-}H_2)$	$\nu_{\alpha\sigma}(COO^-)$ $\nu_{sym}(COO^-)$
1	1706	1646	1574	3360	3488	
4	1720	1630	1576	3166, 3256	3350	
5	1722	1628	1576	3282, 3366	3502, 3570	
6	1684	1634	1586	3202, 3346	3386	
7	1718	1674	1634	3304	3458	
8	1718	1678	1632	3316	3438	
9	1718	1602	1578		3410	
10	1688	1636	1652	3326, 3423	3500	
11	1678	1636	1578	3348	3450	
12	1682	1636	1588	3344	3406	
13	1670	1630	1564	3174	3325	1579, 1415
14	1672	1630	1562	3166, 3256	3400	
15	1670	1630	1560	3166, 3256	3380	
16	1676	1630	1574	3180, 3314		
17	1670	1630	1564	3174	3325	1564, 1458
18	1684	1636	1578	3322	3480	
19	1682	1634	1578	3328	3462	
20	1684	1634	1586	3346, 3394		
21	1693	1654	1577	3353, 3202	3426	1579, 1415

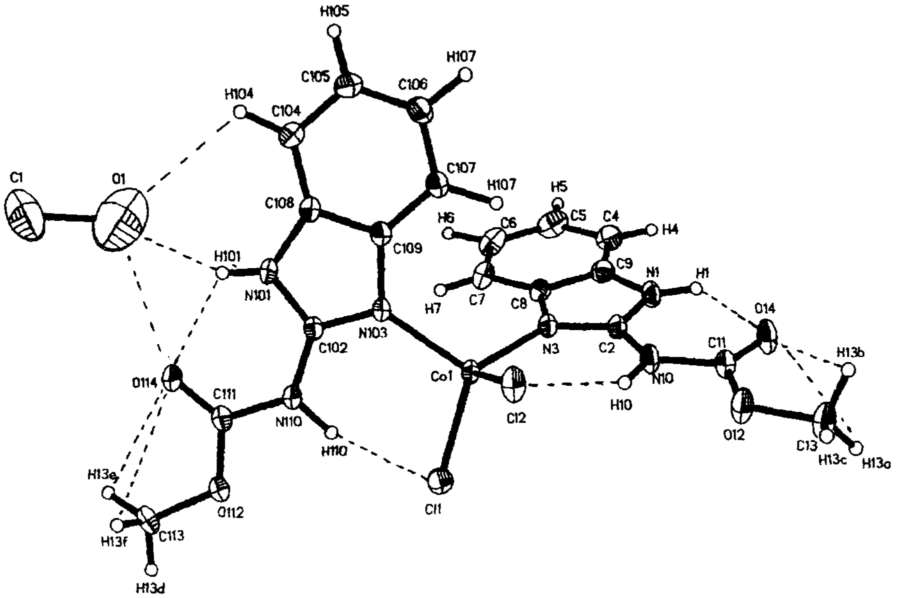


FIGURE 5 X-ray diffraction structure for methyl 2-benzimidazole carbamate cobalt(II) chloride, the dashed lines show the hydrogen bonds.

TABLE 6 Selected Bond Lengths (Å) and Bond Angles (°) for Methyl 2-Benzimidazolecarbamate Cobalt(II) Chloride

Atoms	*Distances*	*Atoms*	*Distances*
Co1-N103	2.008(3)	014-H1	2.141
Co1-N3	2.012(3)	014-H13b	2.657
Co1-C11	2.257(1)	014-H13a	2.814
Co1-C12	2.257(1)	01-H104	3.018
C2-N3	1.331(4)	01-H101	2.137
N3-C8	1.398(4)	0114-H101	2.174
N103-C109	1.405(4)	0114-H13e	2.669
N103-C102	1.329(4)	0114-H13f	2.882
Cl-2-H10	2.402	0114-01	3.068
Cl-1-H110	2.266		
	Angles		Angles
N103-Co1-N3	111.6(1)	N103-Co1-C11	107.9(1)
N3-Co1-C11	112.61(9)	N103-Co1-C12	108.5(1)
N3-Co1-C12	106.3(1)	C11-Co1-C12	109.8(1)

have recorded ^{1}H and ^{13}C NMR spectra of zinc and cadmium complexes **4**, **5**, **7**, and **8**. The compounds were only soluble in DMSO-d_6. The ligand is in tautomeric equilibrium, and the benzimidazolic hydrogen and carbon atoms presented δ averaged values. Resonances of carbon atoms were not as significatively shifted by the presence of the metal ion as those of the hydrogen atoms (Tables 3–4).

Ni, Cu, and Co Compounds

Reactions of $NiCl_2$, $NiBr_2$, $Ni(NO_3)_2$, $Ni(OAc)_2$, and 2-uroylbenzimidazole **1** afforded green compounds (**10–13**, respectively), which exhibited the characteristic bands for octahedral nickel(II) complexes in their electronic spectra (Figure 4, Table 7). Their IR data indicates a bidentate coordination of the ligand (Table 8). There are two ligands bonded to the nickel(II) atom and two counterions completing the hexacoordination, with exception of the nitrate compound, where the water molecules occupy these positions [$\nu_{as}(NO_3^-)$ 1388 cm^{-1}].

The 2-uroylbenzimidazole metal complexes (**14–16**) derived from $CuCl_2$, $CuBr_2$, and $Cu(NO_3)_2$ are green. In the reflectance spectra, the two halide compounds showed a band in the expected region for a tetrahedral geometry of Cu(II) (Table 7) with two bidentate ligands. The nitrate compound **16** exhibited a band assigned to an octahedral geometry for the copper(II) ion, the two nitrate groups being bonded to the copper atom (two sharp bands are observed at 1384 and 1328 cm^{-1}). A structure similar to **16** was found for the acetate compound **17** (Figure 4).

The cobalt(II) complexes **18–21** exhibited a reflectance spectra corresponding to cobalt(II) in an octahedral geometry with two bidentate ligand molecules (confirmed by the IR data) and two anions in the coordinating sphere with exception of 20 where two H_2O molecules are coordinated.

EXPERIMENTAL

All reagents are of commercial quality and were used without further purification. Melting points were measured on a Gallenkamp apparatus and are un-

TABLE 8 Electronic Spectra[a] and Effective Magnetic Moments

Compound	*Band position cm^{-1}*	*Geometry*	*μeff MB*
10$[Ni(2\text{-}UB)_2Cl_2]\cdot 5H_2O$	24880, 13850, 8355	Octahedral	3.00
11$[Ni(2\text{-}UB)_2Br_2]\ 6H_2O$	27473[b], 15360, 9515	Octahedral	3.12
12$[Ni(2\text{-}UB)_2(H_2O)_2]\cdot(NO_3)_2$	24750, 15850, 9500	Octahedral	2.90
13$[Ni(2\text{-}UB)_2(OAc)_2]\cdot 3H_2O$	26221, 15488, 10156	Octahedral	
14$[Cu(2\text{-}UB)_2]\cdot Cl_2$	11490	Dist. tetrahedral	1.83
15$[Cu(2\text{-}UB)_2]\cdot Br_2$	11530	Dist. tetrahedral	2.02
16$[Cu(2\text{-}UB)_2(No_3)_2]$	15200	Octahedral	1.94
17$[Cu(2\text{-}UB)_2(OAc)_2]\cdot 3H_2O$	15751,	Octahedral	1.94
18$[Co(2\text{-}UB)_2Cl_2]\cdot 2H_2O$	19700, 8000	Octahedral	4.60
19$[Co(2\text{-}UB)_2Br_2]\cdot 3H_2O$	19520, 9380	Octahedral	4.67
20$[Co(2\text{-}UB)_2(H_2O)_2]\ (NO_3)_2$	19800, 9060	Octahedral	4.51
21$[Co(2\text{-}UB)_2(OAc)_2]\cdot 4H_2O$	20 554, 9000	Octahedral	5.04

[a] Solid state.

[b] Broad, under a charge transition band.

TABLE 9 Elemental Analyses

			Found (*Calcd.*)		
Compound	*Color*	*Yield* (*%*)	*C*	*H*	*N*
3a$C_{20}H_{17}N_4OB\ 1/2H_2O$	White	80	68.55 (68.79)	5.30 (4.91)	15.98 (16.05)
4$[Zn(2\text{-}UB)_2Cl_2]\ H_2O$	White	82	38.03 (37.93)	3.64 (3.57)	22.61 (22.10)
5$[Zn(2\text{-}UB)_2Br_2]\cdot H_2O$	White	60	32.17 (32.27)	2.97 (3.03)	18.65 (18.81)
6$[Zn(2\text{-}UB)_2]\ (NO_3)_2\cdot 2H_2O$	White	44	33.21 (33.26)	3.49 (3.49)	24.23 (24.24)
7$[Cd(2\text{-}UB)Cl_2H_2O]$	White	80	26.66 (26.73)	2.10 (2.24)	15.30 (15.58)
8$[Cd(2\text{-}UB)Br_2CH_3OH]$	White	57	21.97 (22.40)	1.87 (2.07)	12.00 (11.66)
9$[Cd(2\text{-}UB)_2(NO_3)_2]$	White	53	32.79 (32.64)	2.73 (2.74)	23.94 (23.79)
10$[Ni(2\text{-}UB)_2Cl_2]\cdot 5H_2O$	Green	85	35.85 (36.35)	4.56 (4.23)	20.90 (21.14)
11$[Ni(2\text{-}UB)_2Br_2]\cdot 6H_2O$	Green	63	27.80 (28.30)	3.60 (4.1)	15.95 (16.50)
12$[Ni(2\text{-}UB)_2(H_2O)_2]\cdot(NO_3)_2$	Green	56	33.17 (33.62)	3.52 (3.52)	23.92 (24.52)
13$[Ni(2\text{-}UB)_2(OAc)_2]\cdot 3H_2O$	Blue	75	41.71 (41.19)	5.40 (4.84)	19.34 (19.21)
14$[Cu(2\text{-}UB)_2]\cdot Cl_2$	Green	40	39.49 (39.48)	3.48 (3.31)	22.24 (23.02)
15$[Cu(2\text{-}UB)_2]\cdot Br_2$	Green	66	33.44 (33.38)	2.73 (2.80)	19.07 (19.46)
16$[Cu(2\text{-}UB)_2(NO_3)_2]$	Green	56	36.12 (35.59)	3.12 (2.99)	25.48 (25.95)
17$[Cu(2\text{-}UB)_2(OAc)_2]\cdot 3H_2O$	Green	41	40.68 (40.85)	4.07 (4.80)	19.40 (19.06)
18$[Co(2\text{-}UB)_2Cl_2]\cdot 2H_2O$	Violet	40	37.56 (37.08)	3.87 (3.89)	21.79 (21.62)
19$[Co(2\text{-}UB)_2Br_2]\cdot 3H_3O$	Violet	63	30.99 (30.74)	3.42 (3.55)	17.91 (17.92)
20$[Co(2\text{-}UB)_2(H_2O)_2](NO_3)_2$	Pink	40	33.12 (33.64)	3.46 (3.53)	24.08 (24.52)
21$[Co(2\text{-}UB)_2(OAc)_2]\cdot 4H_2O$	Pink	46	40.41 (39.94)	4.07 (4.80)	18.86 (18.63)

corrected. Diffuse reflectance spectra were recorded on a Cary 5E UV/VIS/NIR spectrophotometer over the range 250–2500 nm. The IR spectra were collected on a Nicolet FT-IR spectrophotometer using KBr pellets in the range 4000 to 400 cm^{-1} and polyethylene pellets in the range 700 to 70 cm^{-1}. Magnetic susceptibility measurements of powdered samples were recorded on a Johnson Matthey balance using the Gouy method. Elemental analyses were performed by the Microanalytical Department, University College, London and Oneida Research Services. The TGA studies were performed on a thermoanalyser Shimadzu TGA-50 under a nitrogen atmosphere; finely ground samples between 5 and 10 mg were heated from 20 to 350°C at the heating rate of 5°C min^{-1}. ^1H and ^{13}C, ^{11}B and ^{15}N NMR spectra were recorded on Jeol GSX-270 and Eclipse 400 spectrometers. Chemical shifts (δ) are reported in ppm and coupling constants. (J) are given in hertz. Solvents were freshly distilled before use according to established procedures. Elemental analyses and yields are presented in Table 9.

Synthesis of Boron Compounds **3a** *and* **3b**

A solution of 250 mg (1.4 mmol) of **1** in 3 mL of methanol and 100 mL of THF was reacted with 320 mg (1.7 mmol) of diphenylborinic acid dissolved in

30 mL of methanol under a dry nitrogen atmosphere for one hour. The solvent was evaporated in vacuum; a white solid was obtained, and the NMR spectra were recorded, the reaction product being a mixture of compounds **3a** and **3b.** Then, the white solid was dissolved in 50 mL of THF, and 20 mL of water was added, and the solution was kept over night, yielding white needles that were isolated, compound **3a** being obtained pure. Reaction of 250 mg (1.4 mmol) of **1** with 340 mg (1.7 mmol) of chlorodiphenylboron in 50 mL of THF and 10 mL of triethylamine for 4 hours afforded **3a** as a pure compound.

Data for compound **3a**: m.p. 220–222°C. MS (EI 20eV): [M^+] 339 (0.2), [M − C_6H_5] 263 (100), [M −2 C_6H_5] 185 (80.8). MS (FAB): 340 (5), 341 (18), 342 (5), M^+, 262, (16), 263 (58), 264 (10), [M − C_6H_5]$^+$, 154, (100).

Preparation of the Metal Complexes Derived from 2-Uroylbenzimidazole

All compounds were prepared using two equivalents of ligand **1** and one of each metal salt $ZnCl_2$, $ZnBr_2$, $Zn(NO_3)_2 \cdot 6H_2O$, $CdCl_2 \cdot H_2O$, $CdBr_2 \cdot 4H_2O$, $Cd(NO_3)_2 \cdot 4H_2O$, $NiCl_2 \cdot 6H_2O$, $Ni(NO_3)_2 \cdot 6H_2O$, $CuCl_2 \cdot 2H_2O$, $CuBr_2$, $Cu(Ac)_2 \cdot 2H_2O$, $Cu(NO_3)_2 \cdot 3H_2O$, $CoCl_2 \cdot 6H_2O$, $CoBr_2$, $Co(NO_3)_2 \cdot 6H_2O$, and $Co(Ac)_2 \cdot 6H_2O$. The metal salts (0.5 mmol) were dissolved in boiling methanol (10 mL) and added to a hot methanol solution (10 mL) of **1** (1.0 mmol, 176 mg). The mixture was stirred for ten minutes and then set aside at room temperature until a precipitate formed. The resulting precipitate was filtered off and dried under vacuum. It was not possible to obtain the melting points for all compounds because they decomposed under heating. Coordinated and crystallization water molecules were determined by TGA.

REFERENCES

[1] Katritzky, A. R. Comprehensive Heterocyclic Chemistry; Pergamon Press: Oxford, 1984, Vol 1, 181–202.

[2] (a) Jung, H.; Hurtado, M.; Sánchez, M.; Medina, M. T.; Sótelo, J. J Clin Pharmacol 1992, 32, 28; (b) Jung, H.; Sánchez, M.; González-Astiarazan, A.; Martínez, J. M.; Suástegui, R.; González-Esquivel, D. F. Am J Therap 1997, 4, 23; (c) Jung, H.; Medina, L.; García, L.; Fuentes, I.; Moreno-Esparza, R. J Pharm Pharmacol 1998, 50, 43.

[3] Barba-Behrens, N.; Vázquez-Olmos, A.; Castillo-Blum, S. E.; Hojer, G.; Meza-Hojer, S.; Hernández, R. M.; Rosalez-Hoz, M. J.; Vicente, R.; Escuer, A. Trans Met Chem 1996, 21, 397.

[4] Andrade-López, N.; Ariza-Castolo, A.; Contreras, R.; Vázquez-Olmos, A.; Barba-Behrens, N.; Tlahuext, H. Heteroat Chem 1997, 8, 397.

[5] Andrade-López, N.; Cartas-Rosado, R.; García-Baéz, E.; Contreras, R. Heteroat Chem 1998, 9, 399.

[6] Fialon, M. P.; Andrade-López, N.; Barba-Behrens, N.; Contreras, R. Heteroat Chem 1998, 9, 637.

[7] Sokol, V. J.; Davydov, V. V.; Porai-Koshits, M. A.; Zaitsev, B. E.; Palishkin, M. V.; Kukalenko, S. S. Russ J Inorg Chem 1989, 34, 496.