ON THE INTERACTION BETWEEN IMIDAZOLES AND ZINC SALTS. THE ROLE OF COUNTERIONS AND OF SUBSTITUENTS

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Abstract—The reactions between benzimidazole (L^1), 4-phenylimidazole (L^2), 4-methylimidazole (L^3), 2-phenylimidazole (L^4) and ZnX_2 ($X = Cl, Br, I, NO_3, ClO_4, CH_3COO, CF_3COO, CF_3SO_3$ or BF_4) have been investigated. 31 novel adducts were obtained and characterized by analytical (elemental analysis and conductivity measurements) and spectral (IR, far IR and 1H NMR) data. The ligands L^1 , L^2 , L^3 and L^4 behave always in the monodentate N-donor fashion yielding 2:1 (L_2ZnX_2 , $L = L^1$ and L^4), 3:1 (L_3ZnX_2 , $L = L^3$, L^1 and L^4), 4:1 (L_4ZnX_2 , $L = L^1, L^2, L^3$ and L^4), 5:1 ($[L_5Zn]X_2$, $L = L^1$) and 6:1 derivatives ($[L_6Zn]X_2$, $L = L^2$). The behavior of the adducts in acetone and chlorinated solvents is also discussed. Comparison has been made with related complexes of imidazoles.

1. Introduction

Zinc is recognized to be essential to all forms of life,¹⁻⁴ and a large number of diseases and congenital disorders have been traced to zinc deficiency. In 1940 carbonic anhydrase was shown to be a zinc enzyme, and in 1955 carboxypeptidase became the second recognized zinc enzyme. Since then more than 300 other zinc enzymes have been reported, and about 20 have known structures based on X-ray study in the crystalline state and/or NMR data for solutions,⁵ most of them being imidazole derivatives. In addition there are a number of cases in which Zn^{+2} ions are present to provide structural rigidity to a certain region of the protein.⁶ The most notable of these are the "zinc fingers" and some related "twists" and "clusters". These occur in DNA binding proteins where they stabilize the correct binding sites. Finally there are the metallothionines, which store zinc.⁷⁻⁸

On the other hand imidazole is a molecule of considerable interest as versatile donor and potential fungicide⁹ and also of great biochemical importance¹⁰⁻¹¹: this five-membered nitrogen heterocycle in fact occurs in proteins as part of the side chain of the amino acid histidine,¹² in nucleic acid structures as part of the purine moiety¹¹ of adenine and guanine, and in the vitamin B_{12} coenzyme as benzimidazole.¹⁴

Many studies have appeared in literature which describe the synthesis and characterization of imidazole-metal ion derivatives¹⁵ as model compounds in order to obtain indirect knowledge of the nature of the interactions involved in a proposed enzyme-metal-ion-substrate complex, but generally the simple imidazole heterocycle has been employed.

We have recently investigated the reactivity of variously substituted imidazoles with $Hg(II)$,¹⁶⁻¹⁸ $Au(I)$,¹⁹ $Cu(I)$,²⁰⁻²² $Ag(I)$,²³ $Sn(IV)$ ²⁴⁻²⁶ and of N-substituted imidazoles with $Zn(II)$ and $Cd(II)$.²⁹

The purpose of this paper is to extend the knowledge of the modes of action of substituted imidazoles towards zinc acceptors. Here we report the synthesis and spectroscopic characterization of new $Zn(II)$ derivatives of benzimidazole (L^1), 4-phenylimidazole (L^2), 4-methylimidazole (L^3) and 2-phenylimidazole (L^4) (Fig. 1). Factors affecting the stoichiometry and the coordination number are discussed and rationalized on the basis of steric and electronic arguments.

Fig. 1. Ligands employed in this work.

2. Experimental Section

The zinc(II) salts were purchased from Alfa (Karlsruhe) and Aldrich (Milwaukee) and used as received. The ligands benzimidazole (L^1), 4-phenylimidazole (L^2), 4-methylimidazole (L^3) and 2-phenylimidazole (L^4) were obtained from Aldrich and were crystallized from diethyl ether/petroleum ether (1:2). The samples were dried in vacuo to constant weight (20°C, ~ 0.1 Torr). Elemental analyses were carried out in-house with a Fisons Instruments 1108 CHNSO-elemental analyser. IR spectra from 4000 to 150 cm^{-1} were recorded with a Perkin Elmer System 2000 FT-IR instrument. ^1H NMR spectra (300 MHz) were recorded on a VXR-300 Varian Spectrometer operating at room temperature. The chemical shifts are reported in ppm from SiMe_4 (H calibration by internal deuterium solvent lock).

Melting points were taken on an IA 8100 Electrothermal Instrument. The electrical resistance of solutions were measured with a Crison CDTM 522 conductimeter at room temperature.

CAUTION. The perchlorato derivatives reported in this paper may explode by shock or heating when dry. Small quantities (< 0.5 g) of the dry products should be handled with all possible precaution.

Synthesis

All experiments were carried out under a dinitrogen atmosphere. Hydrocarbon solvents were dried by distillation from sodium-potassium, dichloromethane from calcium hydride and tetrahydrofuran from LiAlH_4 . All solvents were outgassed with dry dinitrogen prior to use.

[(Benzimidazole) $_2\text{ZnCl}_2$](H_2O) $_{0.5}$ (1). A suspension of benzimidazole (0.473 g, 4.0 mmol) in diethyl ether (30 ml) was treated with ZnCl_2 (0.136 g, 1.0 mmol) in ethanol (20 ml). The reaction was stirred at room temperature for 3 h. A colorless precipitate was formed which was filtered off and washed with diethyl ether (2 $\times$ 5 ml) (76% yield). M.p. 228–229°C. Found: C, 44.4; H, 3.4; N, 14.8. Calc. for $\text{C}_{14}\text{H}_{13}\text{Cl}_2\text{N}_4\text{O}_{0.5}\text{Zn}$, C, 44.1; H, 3.4; N, 14.7. IR (nujol, cm^{-1}): 3317s $\nu(\text{H}_2\text{O})$, 3142w $\nu(\text{C-H})$, 307s, 297s $\nu(\text{Zn-Cl})$, 230m $\nu(\text{Zn-N})$. ^1H NMR (Acetone): δ , 2.9 (br, 0.5H, H_2O), 7.29–7.38 (m, 4H, *Ph*), 7.91 (br, 4H, *Ph*), 8.76 (s, 2H, *H-2*), 12.4 (br, 2H, *NH*). $^{13}\text{C}\{^1\text{H}\}$ NMR (Acetone): δ , 117.0 (br, C-6 and C-9), 125.16 (C-7 and C-8), 137.0 (br, C-4 and C-5), 144.75 (C-2).

[(Benzimidazole) $_2\text{ZnBr}_2$] (2). A suspension of benzimidazole (0.473 g, 4.0 mmol) in diethyl ether (30 ml) was treated with ZnBr_2 (0.225 g, 1.0 mmol) and CH_2Cl_2 (20 ml). The reaction was stirred at room temperature for 3 h. A colorless precipitate was formed which was filtered off and washed with diethyl ether (2 $\times$ 5 ml) (70% yield). M.p. 243–245°C. Found: C, 36.4; H, 2.6; N, 12.1. Calc. for $\text{C}_{14}\text{H}_{12}\text{Br}_2\text{N}_4\text{Zn}$, C, 36.8; H, 2.7; N, 12.1. IR (nujol, cm^{-1}): 3107wbr $\nu(\text{C-H})$, 229vs. ^1H NMR (Acetone): δ , 7.31–7.36 (m, 4H, *Ph*) 7.90 (br, 4H, *Ph*), 8.83 (s, 2H, *H-2*), 12.5 (br, 2H, *NH*).

2.2.3. [(Benzimidazole) $_2\text{ZnI}_2$](H_2O) $_{0.5}$ (3). A suspension of benzimidazole (0.473 g, 4.0 mmol) in diethyl ether (30 ml) was treated with ZnI_2 (0.319 g, 1.0 mmol) and CH_2Cl_2 (20 ml). The reaction was stirred at room temperature for 24 h. The solution was then concentrated under reduced pressure; the oily residue obtained was crystallized twice from CH_2Cl_2 /diethyl ether (60% yield). M.p. 100–103°C. Found: C, 42.0; H, 3.2; N, 14.0. Calc. for $\text{C}_{14}\text{H}_{12}\text{I}_2\text{N}_4\text{O}_{0.5}\text{Zn}$, C, 42.1; H, 3.4; N, 13.5. IR (nujol, cm^{-1}): 3367br $\nu(\text{H}_2\text{O})$, 3156w $\nu(\text{C-H})$, 201vs $\nu(\text{Zn-I})$, 227m $\nu(\text{Zn-N})$. ^1H NMR (Acetone): δ , 4.0 (br, 1H, H_2O), 7.24–7.32 (m, 8H, *Ph*), 7.75–7.77 (m, 8H, *Ph*), 8.57 (s, 4H, *H-2*).

[(Benzimidazole) $_2\text{Zn}(\text{NO}_3)_2$](H_2O) $_2$ (4). Compound 4 was prepared similarly to compound 3, by using $\text{Zn}(\text{NO}_3)_2$. Recrystallized from petroleum ether (78% yield). M.p. 85–88°C. Found: C, 36.4; H, 3.5; N, 18.2. Calc. for $\text{C}_{14}\text{H}_{16}\text{N}_6\text{O}_8\text{Zn}$, C, 37.2; H, 3.5; N, 18.1. IR (nujol, cm^{-1}): 3322wbr $\nu(\text{H}_2\text{O})$, 3168w $\nu(\text{C-H})$, 1750vw, 1734vw $\nu_1 + \nu_4(\text{NO}_3)$, 1377vs $\nu(\text{NO}_3)$, 287m, 273w $\nu(\text{Zn-O})$, 232m, 205m $\nu(\text{Zn-N})$. ^1H NMR (Acetone): δ , 3.70 (br, 4H, H_2O), 7.43–7.51 (m, 4H, *Ph*), 7.76–7.81 (m, 4H, *Ph*), 8.78 (s, 2H, *H-2*), 12.8 (br, 2H, *NH*). Cond. (Acetone, conc. $1.02 \times 10^{-3}\text{M}$): Λ_m 7.5 $\Omega^{-1}\text{cm}^2\text{mol}^{-1}$.

[(Benzimidazole) $_2\text{Zn}(\text{ClO}_4)_2$](H_2O) (5). Compound 5 was prepared similarly to compound 2, by using $\text{Zn}(\text{ClO}_4)_2$ (92% yield). M.p. 162–165°C. Found: C, 44.6; H, 3.5; N, 14.8. Calc. for $\text{C}_{14}\text{H}_{12}\text{Cl}_4\text{N}_4\text{O}_{10}\text{Zn}$, C, 44.7; H, 3.6; N, 14.8. IR (nujol, cm^{-1}): 3301mbr $\nu(\text{H}_2\text{O})$, 3114w $\nu(\text{C-H})$, 1155w, 1094vsbr, 1008w, 979w $\nu(\text{ClO}_4)$, 294m, 229m $\nu(\text{Zn-O})$. ^1H NMR (Acetone): δ , 2.22 (s, 2H, H_2O), 7.35–7.39 (m, 8H, *Ph*), 7.72–7.76 (m, 8H, *Ph*), 9.03 (s, 4H, *H-2*), 12.8 (br, 4H, *NH*). $^{13}\text{C}\{^1\text{H}\}$ NMR (Acetone): δ , 115.97 (C-6 and C-9), 125.65 (C-7 and C-8), 134.5, 136.0 (br, C-4 and C-5), 145.10 (C-2).

[(Benzimidazole) $_2\text{Zn}(\text{CH}_3\text{COO})_2$] (6). Compound 6 was prepared similarly to compound 1, by using $\text{Zn}(\text{CH}_3\text{COO})_2$ and washed with ethanol/diethyl ether (67% yield). Insoluble in all common organic solvents. M.p. 320–323°C. Found: C, 51.5; H, 4.3; N, 13.4. Calc. for $\text{C}_{18}\text{H}_{18}\text{Cl}_2\text{N}_4\text{O}_4\text{Zn}$, C, 49.6; H, 3.6; N, 15.2. IR (nujol, cm^{-1}): 3159wbr, 3081w $\nu(\text{C-H})$, 1610s, 1377vsbr $\nu(\text{COO})$, 285s $\nu(\text{Zn-O})$.

2.2.7. [(Benzimidazole) $_2\text{Zn}(\text{CF}_3\text{SO}_3)_2$] (7). Compound 7 was prepared similarly to compound 2, by using $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ (21% yield). M.p. 128–131°C. Found: C, 43.1; H, 2.9; N, 13.4. Calc. for $\text{C}_{30}\text{H}_{24}\text{F}_6\text{N}_8\text{O}_6\text{S}_2\text{Zn}$, C, 43.0; H, 2.8; N, 13.4. IR (nujol, cm^{-1}): 3143wbr $\nu(\text{C-H})$, 1303mbr, 640s, 516m $\nu(\text{SO}_3)$, 1168m $\nu(\text{C-F})$. ^1H NMR (Acetone): δ , 7.39–7.44 (m, 8H, *Ph*), 7.75–7.80 (m, 8H, *Ph*), 9.10 (s, 4H, *H-2*).

[(Benzimidazole) $_2\text{Zn}(\text{CF}_3\text{SO}_3)_2$] (8). Benzimidazole (0.709 g, 6.0 mmol) was added to an ethanol solution (30 ml) of $\text{Zn}(\text{CF}_3\text{SO}_3)_2$ (0.363 g, 1.0 mmol). The reaction was stirred at room temperature for 3 h. A colorless precipitate was formed, which was filtered off and washed with ethanol (3 $\times$ 5 ml) and recrystallized from CH_2Cl_2 /petroleum ether (60% yield). M.p. 97–100°C. Found: C, 46.6; H, 3.2; N, 14.7. Calc. for $\text{C}_{37}\text{H}_{30}\text{F}_6\text{N}_8\text{O}_6\text{S}_2\text{Zn}$, C, 47.6; H, 3.3; N, 14.8. IR (nujol, cm^{-1}): 3146wbr $\nu(\text{C-H})$, 1272vsbr, 638s, 515m $\nu(\text{SO}_3)$, 1168s $\nu(\text{C-F})$. ^1H NMR (Acetone): δ , 7.29–7.33 (m, 10H, *Ph*), 7.60–7.80 (m, 10H, *Ph*), 8.79 (s, 5H, *H-2*), 9.2 (br, 5H, *NH*).

Structural type	N. compound	L	X
2:1	1	L ¹	Cl
	2	L ¹	Br
	6	L ¹	CH ₃ COO
	23	L ⁴	Cl
	24	L ⁴	Br
3:1	10	L ²	Cl
	11	L ²	Br
	14	L ²	ClO ₄
	15	L ²	CH ₃ COO
	20	L ³	Cl
	27	L ⁴	ClO ₄
	31	L ⁴	BF ₄
4:1	5	L ¹	ClO ₄
	7	L ¹	CF ₃ SO ₃
	18	L ²	CF ₃ SO ₃
	30	L ⁴	CF ₃ SO ₃
4:1	3	L ¹	I
	9	L ¹	BF ₄
	12	L ²	I
	16	L ²	CH ₃ COO
	17	L ²	CF ₃ COO
	21	L ³	Br
	25	L ⁴	I
	29	L ⁴	CF ₃ COO

Scheme 1

[(Benzimidazole)₂Zn(BF₄)₂] (9). Benzimidazole (0.473 g, 4.0 mmol) was added to an ethanol solution (30 ml) of Zn(BF₄)₂ (0.239 g, 1.0 mmol). The reaction was stirred at room temperature for 3 h. A colorless precipitate was formed, which was filtered off and washed with ethanol (2 × 5 ml) and recrystallized from *n*-pentane (28% yield). M.p. 131-134°C. Found: C, 47.3; H, 3.4; N, 15.8. Calc. for C₂₇H₂₄B₂F₈N₈Zn, C, 51.0; H, 3.9; N, 17.0. IR (nujol, cm⁻¹): 3150wbr ν(C-H), 1154vs, 1078mbr, 1021mbr, 768w, 520w ν(BF₄), 200s ν(Zn-N), 280m, 268vw, 247w, 225w ν(Zn-F). ¹H NMR (Acetone): δ, 7.28-7.34 (m, 8H, *Ph*), 7.60-7.80 (m, 8H, *Ph*), 8.4 (br, 4H, *NH*), 8.75 (s, 4H, *H*-2).

[(4-phenylimidazole)₂ZnCl₂](H₂O) (10). An ethanol solution (20 ml) of ZnCl₂ (0.136 g, 1.0 mmol) was added to a diethyl ether suspension (30 ml) of 4-phenylimidazole (0.579 g, 4.0 mmol). The reaction was stirred at room temperature for 24 h. The solution was then concentrated under reduced pressure; the colorless precipitate obtained was recrystallized twice from CH₂Cl₂/diethyl ether (92% yield). M.p. 106-108°C. Found: C, 55.3; H, 4.5; N, 14.3. Calc. for C₂₇H₂₆Cl₂N₆OZn, C, 55.7; H, 4.7; N, 13.9. IR (nujol, cm⁻¹): 3123br ν(C-H), 303s, 280m ν(Zn-Cl), 224w ν(Zn-N). ¹H NMR (Acetone): δ, 2.9 (br, 2H, H₂O), 7.20-7.50 (m, 9H, C₆H₅), 7.56 (s, 3H, *H*-5), 7.78 (d, 6H, C₆H₅), 8.07 (s, 3H, *H*-2), 12.2 (br, 3H, *NH*). ¹³C{¹H} NMR (Acetone): δ, 120.53 (br, C-5), 125.83 (C-7 and C-11), 128.33 (C-9), 129.65 (C-8 and C-10), 132.0, 136.0 (br, C-5 and C-6), 138.11 (C-2). Cond. (CH₂Cl₂, conc. 1.04 × 10⁻³M): Λ_m 0.07 Ω⁻¹cm²mol⁻¹; (Acetone, conc. 1.09 × 10⁻³M): Λ_m 2.6 Ω⁻¹cm²mol⁻¹.

[(4-phenylimidazole)₂ZnBr₂](H₂O)₂ (11). A diethyl ether solution (20 ml) of ZnBr₂ (0.225 g, 1.0 mmol) was added to a dichloromethane solution (30 ml) of 4-phenylimidazole (0.579 g, 4.0 mmol). The reaction was stirred at room temperature for 24 h. The solution was then concentrated under reduced pressure; the colorless precipitate obtained was recrystallized from diethyl ether (76% yield). M.p. 103-107°C. Found: C, 49.3; H, 3.7; N, 12.8. Calc. for C₂₇H₂₄Br₂N₆Zn, C, 50.9; H, 4.2; N, 12.9. IR (nujol, cm⁻¹): 3129br ν(C-H), 304w, 226m ν(Zn-Br), 231m ν(Zn-N). ¹H NMR (Acetone): δ, 7.20-7.45 (m, 9H, C₆H₅), 7.59 (s, 3H, *H*-5), 7.79 (d, 6H, C₆H₅), 8.10 (br, 3H, *H*-2). ¹³C{¹H} NMR (Acetone): δ, 119.93 (br, C-5), 125.74 (C-7 and C-11), 128.13 (C-9), 129.59 (C-8 and C-10), 131.8, 136.0 (br, C-5 and C-6), 137.87 (C-2). Cond. (CH₂Cl₂, conc. 1.03 × 10⁻³M): Λ_m 0.1 Ω⁻¹cm²mol⁻¹; (Acetone, conc. 1.02 × 10⁻³M): Λ_m 1.9 Ω⁻¹cm²mol⁻¹.

[(4-phenylimidazole)₂ZnI₂](H₂O)₃ (12). A diethyl ether solution (20 ml) of ZnI₂ (0.319 g, 1.0 mmol) was added to a dichloromethane solution (30 ml) of 4-phenylimidazole (0.579 g, 4.0 mmol). The reaction was

stirred at room temperature for 24 h. The solution was then concentrated under reduced pressure; the oily residue obtained was recrystallized from diethyl ether (47% yield). M.p. 96-102°C. Found: C, 47.8; H, 3.7; N, 12.4. Calc. for $C_{36}H_{33}N_8O_{0.5}Zn$, C, 48.3; H, 3.9; N, 12.4. IR (nujol, cm^{-1}): 3398wbr $\nu(H_2O)$, 3124w $\nu(C-H)$, 201vs $\nu(Zn-I)$, 223m $\nu(Zn-N)$. 1H NMR (Acetone): δ , 3.0 (br, 1H, H_2O), 7.20-7.50 (m, 12H, C_6H_5), 7.62 (s, 4H, $H-5$), 7.79 (d, 8H, C_6H_5), 8.04 (br, 4H, $H-2$). Cond. (CH_2Cl_2 , conc. $1.01 \times 10^{-3}M$): Λ_m 0.9 $\Omega^{-1}cm^2mol^{-1}$; (Acetone, conc. $0.99 \times 10^{-3}M$): Λ_m 8.1 $\Omega^{-1}cm^2mol^{-1}$.

[(4-phenylimidazole) $_2$ Zn(NO $_3$) $_2$](H $_2$ O) $_{0.5}$ (13). A diethyl ether suspension (20 ml) of $Zn(NO_3)_2$ (0.189 g, 1.0 mmol) was added to a dichloromethane solution (30 ml) of 4-phenylimidazole (0.579 g, 4.0 mmol). The reaction was stirred at room temperature for 24 h. A colorless precipitate was formed, which was filtered off and washed with diethyl ether (2×5 ml) (72% yield). M.p. 157-161°C. Found: C, 51.2; H, 4.0; N, 17.7. Calc. for $C_{27}H_{25}N_8O_6.5Zn$, C, 51.4; H, 4.0; N, 17.8. IR (nujol, cm^{-1}): 3542w, 3486w $\nu(H_2O)$, 3145wbr, 3121w $\nu(C-H)$, 1753vw $\nu_1+\nu_4(NO_3)$, 1377vs $\nu(NO_3)$, 304vw, 273vw $\nu(Zn-O)$, 215w $\nu(Zn-N)$. 1H NMR (Acetone): δ , 2.7 (br, 1H, H_2O), 7.37-7.51 (m, 9H, C_6H_5), 7.71 (s, 3H, $H-5$), 7.79 (d, 6H, C_6H_5), 8.37 (s, 3H, $H-2$). Cond. (Acetone, conc. $1.01 \times 10^{-3}M$): Λ_m 16.2 $\Omega^{-1}cm^2mol^{-1}$.

[(4-phenylimidazole) $_2$ Zn(ClO $_4$) $_2$](H $_2$ O) (14). Compound 14 was prepared similarly to compound 12, by using $Zn(ClO_4)_2$. Recrystallized from CH_2Cl_2 /diethyl ether (60% yield). M.p. 107-110°C. Found: C, 45.4; H, 3.7; N, 11.8. Calc. for $C_{27}H_{25}Cl_2N_8O_9Zn$, C, 45.8; H, 4.1; N, 11.8. IR (nujol, cm^{-1}): 3317wbr $\nu(H_2O)$, 3145w $\nu(C-H)$, 1150wbr, 1075mbr, 969w, 644m, 617vs $\nu(NO_3)$, 226w $\nu(Zn-O)$. 1H NMR (Acetone): δ , 2.9 (br, 2H, H_2O), 7.30-7.52 (m, 9H, C_6H_5), 7.76 (s, 3H, $H-5$), 7.80 (d, 6H, C_6H_5), 8.53 (s, 3H, $H-2$), 11.5 (br, 3H, NH).

[(4-phenylimidazole) $_2$ Zn(CH $_3$ COO) $_2$](15). A diethyl ether suspension (20 ml) of $Zn(CH_3COO)_2$ (0.183 g, 1.0 mmol) was added to a dichloromethane solution (30 ml) of 4-phenylimidazole (0.579 g, 4.0 mmol). The reaction was stirred at room temperature for 24 h. The solution was then concentrated under reduced pressure; the oily residue obtained was recrystallized from $CHCl_3$ (60% yield). M.p. 231-234°C. Found: C, 59.9; H, 4.9; N, 13.8. Calc. for $C_{31}H_{30}N_8O_4Zn$, C, 60.4; H, 4.9; N, 13.6. IR (nujol, cm^{-1}): 3126wbr $\nu(C-H)$, 1582sbr, 1376vs $\nu(COO)$, 271mbr $\nu(Zn-O)$, 201w $\nu(N-N)$. 1H NMR (Acetone): δ , 1.95 (s, 6H, CH_3COO), 7.10-7.40 (m, 9H, C_6H_5), 7.50-7.90 (m, 6H, C_6H_5), 7.55 (br, 3H, $H-5$), 7.70 (br, 3H, $H-2$).

[(4-phenylimidazole) $_2$ Zn(CH $_3$ COO) $_2$](H $_2$ O) (16). A dichloromethane suspension (20 ml) of $Zn(CH_3COO)_2$ (0.183 g, 1.0 mmol) was added to an ethanol solution (30 ml) of 4-phenylimidazole (0.579 g, 4.0 mmol). The reaction was stirred at room temperature for 24 h. The solution was then concentrated under reduced pressure; the yellow precipitate obtained was recrystallized from diethyl ether (59% yield). M.p. 106-109°C. Found: C, 61.7; H, 5.2; N, 14.4. Calc. for $C_{40}H_{40}N_8O_5Zn$, C, 61.2; H, 5.2; N, 14.2. IR (nujol, cm^{-1}): 3362br $\nu(H_2O)$, 3170wbr $\nu(C-H)$, 1560sbr, 1376vs $\nu(COO)$, 298vs $\nu(Zn-O)$. 1H NMR ($CDCl_3$): δ , 1.9 (br, 2H, H_2O), 2.01 (s, 6H, CH_3COO), 6.97 (br, 4H, $H-5$), 7.10-7.34 (m, 12H, C_6H_5), 7.35 (br, 4H, $H-2$), 7.50-7.70 (m, 8H, C_6H_5), 13.5 (br, 4H, NH).

[(4-phenylimidazole) $_2$ Zn(CF $_3$ COO) $_2$](H $_2$ O) (17). 4-phenylimidazole (0.579 g, 4.0 mmol) was added to an ethanol solution (30 ml) of $Zn(CF_3COO)_2$ (0.291 g, 1.0 mmol). The reaction was stirred at room temperature for 24 h. The solution was then concentrated under reduced pressure; the oily residue obtained was recrystallized from diethyl ether/ CH_2Cl_2 (58% yield). M.p. 154-157°C. Found: C, 55.3; H, 3.7; N, 12.9. Calc. for $C_{40}H_{34}F_6N_8O_5Zn$, C, 56.1; H, 3.9; N, 12.7. IR (nujol, cm^{-1}): 3134w, 3113m, 3058m $\nu(C-H)$, 1654vsbr, 1377vs $\nu(COO)$, 1125vsbr $\nu(C-F)$, 266m, 276m $\nu(Zn-O) + \nu(Zn-N)$. 1H NMR (Acetone): δ , 5.0 (br, 2H, H_2O), 8.50-8.70 (m, 12H, C_6H_5), 8.88 (s, 4H, $H-5$), 9.04 (d, 8H, C_6H_5), 9.36 (s, 4H, $H-2$). Cond. (Acetone, conc. $1.02 \times 10^{-3}M$): Λ_m 6.8 $\Omega^{-1}cm^2mol^{-1}$.

[(4-phenylimidazole) $_2$ Zn(CF $_3$ SO $_3$) $_2$](18). A diethyl ether solution (20 ml) of $Zn(CF_3SO_3)_2$ (0.363 g, 1.0 mmol) was added to a dichloromethane solution (30 ml) of 4-phenylimidazole (0.865 g, 6.0 mmol). The reaction was stirred at room temperature for 24 h. The solution was then concentrated under reduced pressure; the colorless precipitate obtained was recrystallized from CH_2Cl_2 /petroleum ether (33% yield). M.p. 92-96°C. Found: C, 48.5; H, 3.4; N, 11.9. Calc. for $C_{38}H_{33}F_6N_8O_6S_2Zn$, C, 49.0; H, 3.7; N, 13.3. IR (nujol, cm^{-1}): 3144mbr $\nu(C-H)$, 1302mbr, 635sbr, 514mbr $\nu(SO_3)$, 1155m $\nu(C-F)$. 1H NMR (Acetone): δ , 7.30-7.50 (m, 12H, C_6H_5), 7.76 (d, 8H, C_6H_5), 7.81 (s, 4H, $H-5$), 8.55 (s, 4H, $H-2$).

[(4-phenylimidazole) $_2$ Zn(BF $_4$) $_2$](H $_2$ O) (19). Compound 19 was prepared similarly to compound 17 by using $Zn(BF_4)_2$. Recrystallized from diethyl ether (60% yield). M.p. 166-170°C. Found: C, 57.8; H, 4.5; N, 15.0. Calc. for $C_{34}H_{30}B_2F_8N_8O_2Zn$, C, 57.3; H, 4.5; N, 15.1. IR (nujol, cm^{-1}): 3608mbr, 3318vsbr $\nu(H_2O)$, 3128mbr $\nu(C-H)$, 1126vs, 1028vsbr, 966s, 755s, 518s $\nu(BF_4)$, 205s $\nu(Zn-N)$, 279m, 247m, 227m $\nu(Zn-F)$. 1H NMR (Acetone): δ , 7.20-7.50 (m, 18H, C_6H_5), 7.71 (s, 6H, $H-5$), 7.77 (d, 12H, C_6H_5), 8.26 (s, 6H, $H-2$), 9.9 (br, 6H, NH).

[(4-methylimidazole) $_2$ ZnCl $_2$](H $_2$ O) $_{0.5}$ (20). A diethyl ether suspension (20 ml) of $ZnCl_2$ (0.136 g, 1.0 mmol) was added to an ethanol solution (30 ml) of 4-methylimidazole (0.328 g, 4.0 mmol). The reaction was stirred at room temperature for 24 h. The solution was then concentrated under reduced pressure; the oily residue obtained was washed from CH_2Cl_2 /diethyl ether (50% yield). Found: C, 36.8; H, 5.6; N, 21.5. Calc. for $C_{12}H_{19}Cl_2N_6O_{0.5}Zn$, C, 37.1; H, 5.8; N, 21.5. IR (nujol, cm^{-1}): 3380mbr $\nu(H_2O)$, 3133mbr $\nu(C-H)$, 303s $\nu(Zn-Cl)$, 227w $\nu(Zn-N)$, 200s $\nu(N-N)$. 1H NMR (Acetone): δ , 2.23 (s, 9H, CH_3), 6.90 (s, 3H, $H-5$), 7.86 (s, 3H, $H-2$).

[(4-methylimidazole) $_2$ ZnBr $_2$](H $_2$ O) $_{1.5}$ (21). A diethyl ether suspension (20 ml) of $ZnBr_2$ (0.225 g, 1.0 mmol) was added to a CH_2Cl_2 solution (30 ml) of 4-methylimidazole (0.328 g, 4.0 mmol). The reaction was stirred at room temperature for 24 h. The solution was then concentrated under reduced pressure; the oily residue obtained was washed from CH_2Cl_2 /diethyl ether (40% yield). Found: C, 33.0; H, 4.7; N, 19.1. Calc. for $C_{16}H_{27}Br_2N_8O_{1.5}Zn$, C, 33.3; H, 4.7; N, 19.4. IR (nujol, cm^{-1}): 3129mbr $\nu(C-H)$, 226m $\nu(Zn-Br)$, 201w $\nu(N-N)$. 1H NMR (Acetone): δ , 2.24 (s, 12H, CH_3), 5.0 (br, 3H, H_2O), 6.89 (s, 4H, $H-5$), 7.84 (s, 4H, $H-2$).

$[(4\text{-methylimidazole})_3\text{Zn}(\text{NO}_3)_2](\text{H}_2\text{O})_{1.5}$ (**22**). Compound **22** was prepared similarly to compound **20**, by using $\text{Zn}(\text{NO}_3)_2$. The oil obtained was washed from *n*-pentane (40% yield). Found: C, 31.1; H, 4.6; N, 24.2. Calc. for $\text{C}_{12}\text{H}_{21}\text{N}_8\text{O}_{7.5}\text{Zn}$, C, 31.0; H, 4.6; N, 24.1. IR (nujol, cm^{-1}): 3321wbr $\nu(\text{H}_2\text{O})$, 3144wbr $\nu(\text{C-H})$, 1750vw, 1734vw $\nu_1+\nu_4(\text{NO}_3)$, 1376vs $\nu(\text{NO}_3)$, 286w, 274w $\nu(\text{Zn-O})$, 236m, 206s $\nu(\text{Zn-N})$, 200w $\nu(\text{N-N})$. ^1H NMR (Acetone): δ , 2.27 (s, 9H, CH_3), 3.20 (br, 3H, H_2O), 7.01 (s, 3H, $H-5$), 8.10 (s, 3H, $H-2$).

Structural type	N. compound	L	O ^o O
2:1	4	L^1	NO_3
	26	L^4	NO_3
3:1	13	L^2	NO_3
	22	L^3	NO_3

Scheme 2

Structural type	N. compound	L	X
5:1	8	L^1	CF_3SO_3
6:1	19	L^2	BF_4

Scheme 3

$[(2\text{-phenylimidazole})_3\text{ZnCl}_2](\text{H}_2\text{O})_{0.5}$ (**23**). ZnCl_2 (0.136 g, 1.0 mmol) was added to a diethyl ether solution (30 ml) of 2-phenylimidazole (0.579 g, 4.0 mmol). The reaction was stirred at room temperature for 24 h. A colorless precipitate was formed, which was filtered off and washed with diethyl ether (2×5 ml) (40% yield). M.p. 229-232°C. Found: C, 49.9; H, 3.9; N, 12.9. Calc. for $\text{C}_{18}\text{H}_{17}\text{Cl}_2\text{N}_4\text{O}_{0.5}\text{Zn}$, C, 49.6; H, 3.9; N, 12.9. IR (nujol, cm^{-1}): 3243mbr $\nu(\text{H}_2\text{O})$, 3127w, 3051vw $\nu(\text{C-H})$, 321m, 289vs $\nu(\text{Zn-Cl})$, 235m $\nu(\text{Zn-N})$. ^1H NMR (Acetone): δ , 2.97 (br, 1H, H_2O), 7.15-7.50 (m, 10H, C_6H_5 , $H-4$ and $H-5$), 7.63 (d, 4H, C_6H_5), 12.0 (br, 2H, NH).

$[(2\text{-phenylimidazole})_3\text{ZnBr}_2]$ (**24**). A diethyl ether suspension (20 ml) of ZnBr_2 (0.225 g, 1.0 mmol) was added to a CH_2Cl_2 solution (30 ml) of 2-phenylimidazole (0.865 g, 6.0 mmol). The reaction was stirred at room temperature for 24 h. The solution was then concentrated under reduced pressure; the colorless precipitate obtained was recrystallized from CH_2Cl_2 (61% yield). M.p. 95-98°C. Found: C, 44.1; H, 3.1; N, 11.2. Calc. for $\text{C}_{18}\text{H}_{16}\text{Br}_2\text{N}_4\text{Zn}$, C, 44.6; H, 3.4; N, 11.6. IR (nujol, cm^{-1}): 3127m $\nu(\text{C-H})$, 215vs $\nu(\text{Zn-Br})$, 244s, 229w $\nu(\text{Zn-N})$. ^1H NMR (Acetone): δ , 7.10-7.60 (m, 10H, C_6H_5 , $H-4$ and $H-5$), 7.65 (d, 4H, C_6H_5), 12.0 (br, 2H, NH).

[(2-phenylimidazole)₂ZnI₂](H₂O)_{1.5} (25). A diethyl ether suspension (20 ml) of ZnI₂ (0.319 g, 1.0 mmol) was added to a CH₂Cl₂ solution (30 ml) of 2-phenylimidazole (0.579 g, 4.0 mmol). The reaction was stirred at room temperature for 24 h. The solution was then concentrated under reduced pressure; the yellow precipitate obtained was recrystallized from CH₂Cl₂/diethyl ether (61% yield). M.p. 112–115°C. Found: C, 46.9; H, 3.8; N, 12.1. Calc. for C₃₆H₃₅I₂N₈O_{1.5}Zn, C, 46.8; H, 4.0; N, 11.8. IR (nujol, cm⁻¹): 3159wbr ν(C-H), 233m ν(Zn-N). ¹H NMR (Acetone): δ, 5.6 (br, 3H, H₂O), 7.0–7.6 (m, 20H, C₆H₅, H-4 and H-5), 7.76 (br, 8H, C₆H₅), 12.0 (br, 4H, NH).

[(2-phenylimidazole)₂Zn(NO₃)₂](H₂O)_{1.5} (26). Compound 26 was prepared similarly to compound 23, by using Zn(NO₃)₂ (36% yield). M.p. 178–181°C. Found: C, 42.5; H, 3.8; N, 16.6. Calc. for C₁₈H₁₉N₆O_{7.5}Zn, C, 42.1; H, 3.8; N, 16.5. IR (nujol, cm⁻¹): 3539w, 3485w, 3369wbr ν(H₂O) + ν(NH), 3156wbr ν(C-H), 1751vw ν₁+ν₄(NO₃), 1377vs ν(NO₃), 274mbr ν(Zn-O). ¹H NMR (Acetone): δ, 3.4 (br, 3H, H₂O), 7.20–7.50 (m, 14H, C₆H₅, H-4 and H-5), 12.1 (br, 2H, NH). Cond. (Acetone, conc. 1.10 × 10⁻³M): Λ_m 13.7 Ω⁻¹cm²mol⁻¹.

[(2-phenylimidazole)₂Zn(ClO₄)₂](H₂O) (27). A diethyl ether suspension (20 ml) of Zn(ClO₄)₂ (0.264 g, 1.0 mmol) was added to a CH₂Cl₂ solution (30 ml) of 2-phenylimidazole (0.579 g, 4.0 mmol). The reaction was stirred at room temperature for 24 h. The colorless precipitate obtained was recrystallized from CH₂Cl₂/diethyl ether (76% yield). M.p. 204–208°C. Found: C, 45.4; H, 3.7; N, 11.9. Calc. for C₃₇H₃₆Cl₂N₈O₅Zn, C, 45.2; H, 3.8; N, 12.3. IR (nujol, cm⁻¹): 3252sbr ν(H₂O), 3130m, 3060w ν(C-H), 1120vsbr, 1064vsbr, 1000w, 621s, 617vs ν(ClO₄), 278vw, 237m ν(Zn-O), 208m ν(N-N). ¹H NMR (Acetone): δ, 7.2–8.0 (br, 15H, C₆H₅, H-4 and H-5), 9.0 (br, 6H, C₆H₅), 12.0 (br, 3H, NH).

[(2-phenylimidazole)₂Zn(CH₃COO)₂](H₂O) (28). Compound 28 was prepared similarly to compound 27, by using Zn(CH₃COO)₂ (55% yield). M.p. 192–195°C. Found: C, 54.0; H, 4.9; N, 11.4. Calc. for C₂₂H₂₄N₄O₅Zn, C, 54.0; H, 4.9; N, 11.4. IR (nujol, cm⁻¹): 3370vwbr ν(H₂O), 3134vwbr, 3062vwbr ν(C-H), 1560vsbr, 1377m ν(COO), 292vsbr ν(Zn-O). ¹H NMR (Acetone): δ, 1.95 (s, 6H, CH₃COO), 2.84 (br, 2H, H₂O), 7.15 (s, 4H, H-4 and H-5), 7.30–7.50 (m, 6H, C₆H₅), 7.99 (d, 4H, C₆H₅), 11.6 (br, 2H, NH).

[(2-phenylimidazole)₂Zn(CF₃COO)₂](29). A diethyl ether suspension (20 ml) of Zn(CF₃COO)₂ (0.291 g, 1.0 mmol) was added to a CH₂Cl₂ solution (30 ml) of 2-phenylimidazole (0.579 g, 4.0 mmol). The reaction was stirred at room temperature for 24 h. The solution was then concentrated under reduced pressure; the colorless precipitate obtained was recrystallized from CH₂Cl₂/diethyl ether (81% yield). M.p. 129–132°C. Found: C, 55.3; H, 3.7; N, 12.9. Calc. for C₄₀H₃₂F₆N₈O₄Zn, C, 55.4; H, 3.8; N, 13.2. IR (nujol, cm⁻¹): 3159mbr ν(C-H), 1652mbr, 1374vs ν(COO), 1154vs ν(C-F), 272s ν(Zn-O), 216w ν(Zn-N). ¹H NMR (Acetone): δ, 7.20–7.40 (m, 20H, C₆H₅, H-4 and H-5), 7.70 (br, 8H, C₆H₅).

[(2-phenylimidazole)₂Zn(CF₃SO₃)₂](30). Compound 30 was prepared similarly to compound 29, by using Zn(CF₃SO₃)₂. Recrystallized from diethyl ether (50% yield). M.p. 128–131°C. Found: C, 48.8; H, 3.4; N, 11.9. Calc. for C₃₈H₃₂F₆N₈O₆S₂Zn, C, 49.2; H, 3.6; N, 11.7. IR (nujol, cm⁻¹): 3147wbr, 3059vw ν(C-H), 1290mbr, 637vs, 514m ν(SO₃), 1157vs ν(C-F). ¹H NMR (Acetone): δ, 7.2–8.0 (br, 28H, C₆H₅, H-4 and H-5).

2.2.31. [(2-phenylimidazole)₂Zn(BF₄)₂](31). Compound 31 was prepared similarly to compound 27, by using Zn(BF₄)₂ (27% yield). M.p. 269–272°C. Found: C, 48.5; H, 3.6; N, 12.9. Calc. for C₃₇H₃₄B₂F₈N₆Zn, C, 48.9; H, 3.6; N, 13.3. IR (nujol, cm⁻¹): 3299vsbr, 3138mbr, 3062w ν(C-H), 1121vs, 1052vsbr, 1014s, 778vs, 522m ν(BF₄), 202s ν(Zn-N), 280w, 250m, 222w ν(Zn-F). ¹H NMR (Acetone): δ, 7.0–7.8 (m br, 21H, C₆H₅, H-4 and H-5), 12.1 (br, 3H, NH). Cond. (Acetone, conc. 1.02 × 10⁻³M): Λ_m 176.7 Ω⁻¹cm²mol⁻¹.

3. Results and Discussion

Synthesis of the Zn(II) complexes

Benzimidazole (L¹), 4-phenylimidazole (L²), 4-methylimidazole (L³) or 2-phenylimidazole (L⁴) react in ethanol, diethyl ether or ethanol/diethyl ether solution/suspension with ZnX₂ acceptors (X = Cl, Br, I, NO₃, ClO₄, CH₃COO, CF₃COO, CF₃SO₃ or BF₄) affording derivatives 1–31 (schemes 1, 2 and 3):

$$(n = 2, 3, 4, 5 \text{ or } 6; m = 1; x = 0.5, 1, 1.5 \text{ or } 2)$$

Some of these zinc(II) complexes retain or absorb solvent molecules. Derivatives of 4-methylimidazole (20–22) are amorphous below 30°C and oils up to 30°C, whereas all the other compounds are air stable microcrystalline solids with sharp melting points (Experimental Section). They are generally soluble in DMSO, enough soluble in acetone and acetonitrile, poor soluble in chlorinated solvents such as chloroform and dichloromethane, insoluble in diethyl ether, alcohols and water. The solubility is function of the counterion (the dihalide and tetrafluoroborate derivatives are less soluble of the nitrate, perchlorate, and acetate complexes) and primarily of the ligand (the presence of a phenyl group generally increases the solubility of the complexes).

The derivative [(L¹)₄Zn(CF₃SO₃)₂] (7) was obtained from the reaction of benzimidazole (L¹) with Zn(CF₃SO₃)₂, in diethyl ether, using a 4/1 ligand/metal ratio, whereas the derivative [(L¹)₅Zn(CF₃SO₃)₂] (8) was obtained from the reaction of benzimidazole with Zn(CF₃SO₃)₂, in ethanol, using a 6/1 ligand/metal ratio; analogously, the derivative [(L²)₃Zn(CH₃COO)₂] (15) was obtained from the reaction of 4-phenylimidazole (L²) with Zn(CH₃COO)₂, in dichloromethane/diethyl ether, whereas the derivative

$[(L^2)_4Zn(CH_3COO)_2]$ (**16**), was obtained from the reaction of 4-phenylimidazole with $Zn(CH_3COO)_2$ in ethanol/diethyl ether, using the same ligand/metal ratio.

IR data

Selected IR and far-IR data of derivatives **1-31** are reported in the Experimental Section. The spectra are recorded in Nujol mull.

In the region $3200-3000\text{ cm}^{-1}$ we have found the $\nu(C-H)$ of azoles always shifted to higher frequencies (at least 50 cm^{-1}) with respect to the $\nu(C-H)$ of aromatic rings and generally shifted of $5-10\text{ cm}^{-1}$ with respect to the corresponding vibrations in the free ligands. In the region $1650-1500\text{ cm}^{-1}$ the $\nu(C=N)$ and $\nu(C=C)$ absorptions, while the bending vibrations typical of the ligands and the Whiffen absorptions^{30, 31} are observed in the region $600-500\text{ cm}^{-1}$; no changes have been observed with respect to the same absorptions in the free ligands.

The di-halo-metal adducts **1-3**, **10-12**, **20**, **21** and **23-25** show two M-X stretching vibrations as expected for a pseudo-tetrahedral (C_{2v} symmetry) structure in the case of four-coordinate **1**, **2**, **23** and **24** or for a *cis*- X_2 arrangement in the case of five- or six-coordinate **3**, **10-12**, **20**, **21** and **25**. In our case, the assignments of the M-halogen symmetric and asymmetric stretching vibrations are red-shifted on going from M-Cl ($310-280\text{ cm}^{-1}$) to M-Br ($250-225\text{ cm}^{-1}$) and to M-I ($230-185\text{ cm}^{-1}$).³² The medium absorptions in the range $250-200\text{ cm}^{-1}$ can be assigned to $\nu(M-N)$ stretching modes;³² in the di-chloro- and di-iodo-zinc derivatives the $\nu(M-N)$ modes can be assigned without much ambiguity, but for the di-bromo-zinc derivatives they lie close to the $\nu(Zn-Br)$ region and coupling must be appreciable.³³

The IR spectra of zinc-nitrate derivatives (**4**, **13**, **22** and **26**) are in accordance with the stoichiometries and the structures proposed. The derivatives containing 3 N-ligands and 2 nitrate groups (**13** and **22**) should have a seven-coordinate N_3ZnO_4 core, reached through the chelation of both the nitrate groups.³⁴⁻³⁶ Derivatives **4** and **26**, with a ligand-metal ratio 2:1, possess an octahedral geometry in the solid state with both the counterions bidentate; the IR data (the $\nu_1-\nu_4$ stretching modes, the combination band $\nu_1 + \nu_4$) are in accordance with this evidence.^{35, 36} In no case the spectra are in accordance with a ionic formulation of the nitrate group.³⁶

The perchlorato derivatives (**5**, **14** and **27**) exhibit two different trends: In **14** and **27** the ligands L^2 and L^4 are not able to completely substitute the perchlorato ion in the coordination sphere of the metal; on the other hand the derivative of L^1 (**5**) is ionic in the solid state (N_4Zn^{+2}) and shows a broad absorption at 1094 cm^{-1} and a sharp and strong band at 622 cm^{-1} , both typical of a XY_4 ionic group.²⁹

On the basis of IR data we can hypothesize a six-coordinate geometry for derivative **9** in the solid state, with both BF_4^- groups unidentate: in fact ν_3 mode splits into two broad bands (1170 and 1154 cm^{-1}). We observed also two bands at 768 and 722 cm^{-1} due to ν_1 and ν_4 respectively.^{37, 38} Moreover, the absorptions at $245-280\text{ cm}^{-1}$ could be tentatively assigned to $\nu(Zn-F)$ modes. In the spectrum of **31** we observe a strong broad absorption in the region $980-1150\text{ cm}^{-1}$, several broad bands in the range $680-780\text{ cm}^{-1}$ and absorptions at $250, 280\text{ cm}^{-1}$ that could be tentatively assigned to $\nu(Zn-F)$ modes, in accordance with a penta-coordinate geometry in the solid state, with both BF_4^- groups unidentate. However in acetone the derivative **31** shows a conductance value typical of 1:1 ionic species (see Experimental Section), suggesting that in solution this compound dissociates only one of the two BF_4^- groups. On the other hand **19** is ionic in the solid state with the BF_4^- groups likely linked through hydrogen bond to the H_2O molecule.

In the case of carboxylate derivatives it is generally accepted³⁹ that it is possible to distinguish between ionic, unidentate, chelating bidentate or bridging bidentate groups on the basis of Δ value [where $\Delta = \nu_s(COO^-) - \nu_s(COO)$], the following trend being found:

$$\Delta_{\text{unidentate}} > \Delta_{\text{ionic}} > \Delta_{\text{bridging bidentate}} > \Delta_{\text{chelating bidentate}}$$

where Δ_{ionic} is *ca.* $160-170\text{ cm}^{-1}$ for acetates and *ca.* $220-230\text{ cm}^{-1}$ for trifluoroacetates³⁷. In the derivatives **6**, **15**, **16** and **28** we predict a unidentate coordinating behaviour of CH_3COO^- , Δ being in the range $180-235\text{ cm}^{-1}$. In the spectra of tri-fluoroacetates **17** and **29** the Δ values are 277 and 278 cm^{-1} respectively, in accordance with a unidentate formulation of the CF_3COO^- groups. In all carboxylato derivatives we have also found a new band in the range $266-298\text{ cm}^{-1}$ likely due to $\nu(M-O)$.

The CF_3SO_3 group in derivatives **7**, **8**, **18** and **30** shows a spectroscopic behaviour typical of a ionic outer-sphere group. The vibrations of the SO_3 and CF_3 groups are similar to those observed in the spectra of analogous derivatives of bis(pyrazolyl)alkanes.⁴⁰

¹H and ¹³C NMR data

The proton NMR spectra of derivatives **1-31** have been recorded in deuterated chloroform or acetone (see Experimental Section). The choice of the solvent was dictated by the solubility of the compounds.

The signals of the azole ring protons of the ligands have always been found shifted to lower field upon coordination. The same trend has been observed for the proton signals of the R groups bonded in the 2-

and 4-positions of the imidazole ring ($R = \text{Me}$ or Ph) and for the condensed ring in L^1 derivatives. However, the deshielding observed is attenuated at positions remote from the metal. The Δ observed is likely due to a σ -charge donation from the N-donor to zinc(II) acceptor and is evidence of the existence of the complexes in solution. The Δ value is also function of the counterion: for example the greatest Δ values are observed in the zinc(II) derivatives containing good leaving groups (ClO_4 , BF_4 and CF_3SO_3).

Also if one would expect in many of these compounds the existence in solution of more than one isomer, or the presence of not equivalent ligands, in all the ^1H NMR spectra of **1-31** we found only one set of signals (in some cases the resonances are large, *ca.* 1 ppm) for each equivalent proton group. This is likely due to a rapid exchange between free and bound ligand or between different metal coordination sites. This rapid exchange is operative also at low temperature.

The spectra of derivatives containing imidazoles with aryl substituents often present signals shifted to higher field with respect to the analogous ligands with alkyl substituents. This is probably due to the nearness of these protons to the deshielding cone of the aromatics rings.^{26, 27}

The ^{13}C NMR spectra have been recorded in deuterated acetone only for selected compounds (**1**, **5**, **10** and **11**) due to the poor solubility of most of adducts obtained (see Experimental Section).

In the benzimidazole complexes **1** and **5** the signals of theazole ring carbons have always been found shifted to lower field upon coordination and the same trend has been observed for the carbon signals of the condensed ring. It is very interesting to note that some carbon signals of the condensed ring, broad in the spectrum of the ligand, are sharp in the corresponding zinc derivatives. This is likely due to the fact that the concomitant prototropy and metallotropy, generally observed inazole complexes,^{20, 41-43} is slow with respect to the prototropy operating in the ligand.

Finally in the 4-phenylimidazole complexes **10** and **11** the signals of theazole ring carbons have also been found shifted to lower field upon coordination, while no change has been found for the carbon signals of the aromatic ring. In all complexes the carbon signals generally are broad likely due to a fluxional behaviour operating in solution, which makes equivalent all the ligands coordinated.

Conductivity data

Conductivity measurements have been performed in dichloromethane or acetone solution for several derivatives (see Experimental Section).

Derivatives **10** and **11** are non electrolytes. Derivatives **4**, **12**, **13**, **17** and **26** for which a non-ionic structure has been observed in the solid state (see the IR data Section) show conductance values in acetone, in accordance with only partial ionic dissociation in this solvent. The dissociation seems to be dependent upon concentration of the solutions.

Finally, in the case of **31** ionic species can be postulated in solution, with the counterions BF_4^- out of the inner coordination sphere of the metal.

Conclusions

The combined evidence from measurements carried out in-solid state and in solution (medium and far IR, conductivity, NMR spectra) gives here a complete picture about the interaction of imidazole-type ligands and Zn(II) acceptors.

The ligand/metal ratio $m:n$ has been found to vary in a wide range, so that different compounds can be obtained depending on:

1. nature of the counter-ion: in some cases it is possible to obtain, with the same ligand and in the same reaction conditions, derivatives characterized by different stoichiometries, geometries and coordination numbers.
2. steric hindrance and basicity of the ligand: for example from the interaction of the sterically hindered benzimidazole and 2-phenylimidazole with ZnCl_2 we generally obtained derivatives with a 2:1 ligand/metal ratio; instead the ligands 4-methylimidazole and 4-phenylimidazole, without direct steric demand on the metal, gives also 3:1 adducts.
3. reaction conditions (solvent, temperature, ligand to metal ratio employed) which can help to modify structures and properties of complexes

Several interesting trends emerge: in our conditions the dichloride and dibromide complexes give generally the adducts with lower ligand/metal ratio (2:1 and 3:1); only from the reaction of diiodozinc acceptors with L^1 , L^2 and L^4 we have obtained compounds with 4:1 ligand/metal ratio. A pseudooctahedral 6:1 adduct (MN_6) is found only with the 4-phenylimidazole ligand and a good acceptor such as the tetrafluoroborate. In the case of nitrato and bis(acetato) derivatives the compounds are covalent with a 2:1, 3:1 or 4:1 ligand/metal ratio.

The compounds obtained are less soluble in common organic solvents and in water in conditions similar to the fisiologic ones and moreover they often presents hydrogen bond; these observations make

imidazoles potential models for the study of biological systems, overall with acceptors such as ZnCl_2 and $\text{Zn}(\text{CH}_3\text{COO})_2$.

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