DALTON
FULL PAPER

Complexes of some transition metal ions with 2-methyl-1-vinylimidazole in aqueous solution and the solid state

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Received 2nd November 1999, Accepted 8th February 2000
Published on the Web 9th March 2000

The stability constants and structures of the complexes of Co^{2+}, Cu^{2+}, Zn^{2+}, Ni^{2+} and Cd^{2+} with 2-methyl-1-vinylimidazole in aqueous solution have been determined by potentiometric and spectrophotometric methods. The stability of the compounds depended much on the presence of the electron-attracting vinyl substituent contributing to the $\pi_{M \rightarrow L}$ back bonding. Further, nitrato complexes of cobalt(II) and copper(II) with 2-methyl-1-vinylimidazole (L) of general formulae $[CoL_3(H_2O)(NO_3)]NO_3$ **1**, $[CoL_2(NO_3)_2]$ **2**, $[CuL_4(NO_3)_2]\cdot 2H_2O$ **3** and $[CuL_2(NO_3)_2]$ **4** have been prepared in the solid state. Full single-crystal X-ray analyses have been accomplished for compounds **1** and **4** which enabled the determination of angles and bond lengths.The compounds were identified on the basis of elemental analyses, EPR spectroscopy, IR, FIR and VIS-NIR absorption spectra and magnetochemical data. The immediate environment of the central ions is described by a distorted tetragonal bipyramid.

Introduction

Imidazole compounds have aroused general interest owing to the presence of the imidazole entity in the structure of a variety of biologically important substances. The presence of a substituent in the imidazole ring affects the co-ordination processes with metal ions, in particular in those cases when it occurs at α position to the electron-donating endocyclic nitrogen atom of the 1,3-diazole. This influence is closely related to the inductive effect of the alkyl substituent and the steric effect. Owing to the steric hindrance, solid co-ordination compounds usually contain no more than four molecules of 2-substituted imidazole ligands. An exception to this rule is provided by an octahedral $[Cd(mim)_6]X_2$ complex (mim = 2-methylimidazole).[1,2] In this family of ligands a change in the structure of the co-ordination sphere from octahedral to tetrahedral has been reported for the cobalt(II) ion in aqueous solution. These structural transformations in aqueous solutions[3–7] have been attributed to contribution of the $\pi_{M \rightarrow L}$ back bonding. A compound with an electron-attracting vinyl group thus shows a stronger tendency towards formation of these bonds than a plain alkyl substituent. For this reason 2-methyl-1-vinylimidazole has been selected as the object of the present study.

Solid co-ordination compounds of vinylimidazoles with metal chlorides, sulfates and acetates, owing to their biological activity and interesting physico-chemical properties, have previously been obtained.[8–11] The co-ordination capacity of 1-vinylimidazole in relation to Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} in aqueous solution as well as the extractibility of the complexes of these metals with organic solvents have been reported.[12]

Experimental

Solution studies

Reagents. 2-Methyl-1-vinylimidazole (Aldrich-Europe) was purified by vacuum distillation. The concentrations of the solutions of nitric acid, metal nitrates and sodium hydroxide were determined by classical analytical methods.

Potentiometric measurements. Potentiometeric measurements of the metal ion systems were carried out using a PHM-84 pH meter (Radiometer) and a GK 2401 C combination electrode placed in a glass vessel thermostatted at 298 K in solution of constant ionic strength $I = 0.5$ mol dm^{-3} (with KNO_3). The electrode was calibrated by titration of a HCl solution of known titre with a NaOH solution according to ref. 13. The protonated ligand (HL^+) concentration in stock solutions used in potentiometric titations was 0.15 mol dm^{-3}. The metal ion : HL^+ molar ratios were 1 : 4 and 1 : 6. The pH-metric titration with a base solution was conducted over the pH range 3–7.5. The dissociation constants of the conjugate acid and stability constants, β_n, of the complexes were refined by the SUPERQUAD program.[14]

Visible range spectra. The visible-range absorption spectra of the Co^{2+}, Ni^{2+} and Cu^{2+} complexes in aqueous solutions were recorded on a Specord M.-40 (Carl Zeiss, Jena) spectrophotometer. The solutions used in these measurements were prepared in an analogous manner to those for the potentiometric titrations. The initial metal ion concentrations were 0.02 and 0.05 mol dm^{-3}. The highest concentration of the protonated ligand was 0.15 mol dm^{-3}. The metal : protonated ligand concentration ratios were different.

Investigation in the solid state

Synthesis of the complexes. The cobalt(II) and copper(II) complexes were prepared in 2-propanol solutions using the metal nitrates and 2-methyl-1-vinylimidazole. The metal-to-ligand molar ratio was either 1 : 2 or 1 : 4. The compounds were crystallised from 2-propanol. From a solution of Co^{2+} ions with a fourfold excess of the imidazole base, a complex with three molecules of the imidazole ligand was obtained. The results of its elemental analysis are as follows (%): **1** C, 41.0; H, 5.2; N, 21.4; calculated for $CoL_3(H_2O)(NO_3)_2$ C, 41.2; H, 5.0; N, 21.3; **2** C, 35.9; H, 3.9; N, 21.3; calculated for $CoL_2(NO_3)_2$ C, 36.1; H, 4.0; N, 21.0; **3** C, 44.0; H, 5.7; N, 21.6; calculated for $CuL_4(NO_3)_2\cdot 2H_2O$ C, 43.9; H, 5.5; N, 21.4; **4** C, 35.5; H, 4.1; N, 21.0; calculated for $CuL_2(NO_3)_2$ C, 35.7; H, 4.0; N, 20.8.

DOI: 10.1039/a908718d

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Table 1 Stability constants of some imidazole derivatives in aqueous solution at 298 K and ionic strength $I = 0.5$ mol dm^{-3} (KNO_3) (for imidazole, $I = 0.16$ mol dm^{-3} (KNO_3))

Ligand	Central ion	log β_1	log β_2	log β_3	log β_4	log β_5	Ref.
Imidazole	Co^{2+}	2.47	4.40	5.85	6.85		19, 20
pK_a = 7.12	Ni^{2+}	3.09	5.56	7.56	9.10		
	Cu^{2+}	4.31	7.84	10.76	12.90		
	Zn^{2+}	2.56	4.89	7.16	9.19		
	Cd^{2+}	3.11	5.80	8.10	10.00	11.60	
1-Ethylimidazole	Co^{2+}	2.32	4.17	5.42	7.02	7.42	21
pK_a = 7.25	Ni^{2+}	3.04	5.54	7.52	8.97	9.85	
	Cu^{2+}	4.40	7.99	10.98	13.22	14.20	
	Zn^{2+}	2.50	4.79	7.40	9.30	10.10	
1-Vinylimidazole	Co^{2+}	2.25	4.00	5.25	6.17	6.37	12
pK_a = 5.92	Ni^{2+}	2.94	5.34	7.24	8.43	9.10	
	Cu^{2+}	3.60	6.70	9.30	11.35	11.90	
	Zn^{2+}	2.08	3.68	4.78	7.08		
	Cd^{2+}	2.30	4.12	5.46	6.34	6.74	
2-Methyl-1-vinylimidazole	Co^{2+}	1.30(3)	2.40(3)				This work
pK_a = 6.98	Ni^{2+}	1.68(2)	2.91(4)				
	Cu^{2+}	3.20(2)	5.80(2)	7.80(3)	9.20(4)		
	Zn^{2+}	1.55(4)	3.60(4)	5.50(5)	6.50(6)		
	Cd^{2+}	2.06(2)	3.46(3)	4.26(3)			
2-Methylimidazole	Co^{2+}	1.73	3.05	3.84	6.16		22
pK_a = 8.10	Cu^{2+}	3.35	6.38	9.23	11.92	14.45	
	Zn^{2+}	1.88	3.99	7.49	9.32		
2-Methyl-1-propylimidazole	Co^{2+}	1.61(3)	2.00(3)	3.00(3)	5.40(4)		23
pK_a = 8.20	Ni^{2+}	2.05(2)	3.41(2)	4.19(3)			
	Cu^{2+}	3.67(2)	7.23(2)	9.65(3)	11.0(4)		
	Zn^{2+}	1.35(4)	4.40(5)	7.45(5)	9.41(6)	10.5(6)	

Physical measurements. Elemental analyses were run on a Model 240 Perkin-Elmer CHN Analyzer. The IR spectra were recorded on a Perkin-Elmer 180 (50–4000 cm^{-1}) spectrophotometer in Nujol and in KBr pellets, FIR spectra in Nujol mulls sandwiched between polyethylene plates, and electronic spectra (5000–25000 cm^{-1}) on a Cary UV-VIS-NIR spectrophotometer in Nujol mulls. Magnetic susceptibility data were obtained at room temperature and corrected for diamagnetism by Pascal's constants. The EPR spectra were recorded on a Bruker ESP 300E (Bruker, Germany) spectrometer operating at X-band and equipped with a Bruker NMR gaussmeter ER 035M and Hewlett-Packard microwave frequency counter HP 5350B at 77 K. Parameters were calculated by computer simulation of the experimental spectra using Bruker's WIN-EPR SimFonia Software Version 1.2.

Crystal data. X-Ray measurements were performed on Kuma KM4 (complex **1**) and KM4CCD (**4**) diffractometers. The structures were solved by direct methods using SHELXS 86[15] and SHELX 97[16] and refined by full-matrix least-squares methods using SHELXL 93[17] and SHELXL 97[18] programs (respectively for cobalt(II) and copper(II) complexes). Details of the crystal data and refinement for compounds **1** and **4** are given in Table 3.

CCDC reference number 186/1850.

See http://www.rsc.org/suppdata/dt/a9/a908718d/ for crystallographic files in .cif format.

Results and discussion

Investigation in aqueous solution

On the basis of the pH-metric measurements, the dissociation constants of protonated 2-methyl-1-vinylimidazole were determined ($c = 1.05 \times 10^{-7}$ mol dm^{-3} at $I = 0.5$ mol dm^{-3}, at 298 K). Dissociation constants for imidazole and other previously studied 1- and 2-substituted imidazole derivatives are summarised in Table 1. The weaker basicity of 1-vinylimidazole (pK_a = 5.92)[12] relative to the unsubstituted imidazole (pK_a = 7.12)[19,20] and 1-ethylimidazole (pK_a = 7.25)[21] is due to the electron-attracting nature of the vinyl group. With 2-methyl-1-vinylimidazole, both substituents have an influence on the basicity, the 1-vinyl suppressing the basicity, whereas the methyl group adjacent to the electron-donating nitrogen atom at position 3 enhances electron density on the atom by virtue of the inductive effect. The interplay of these opposite effects in the imidazole molecule causes the basicity of 2-methyl-1-vinylimidazole (pK_a 6.98) to be comparable with that of the unsubstituted imidazole molecule (pK_a 7.12).

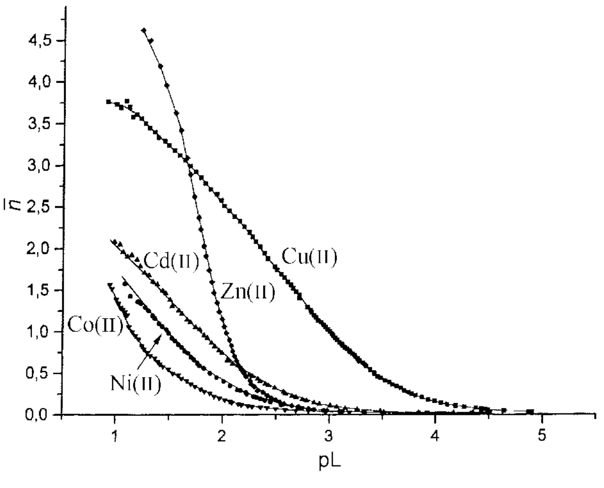

Fig. 1 Formation curves of 2-methyl-1-vinylimidazole complexes with Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+}.

The complexation reactions of Co^{2+}, Cu^{2+}, Ni^{2+}, Cd^{2+} and Zn^{2+} were conducted in solutions of pH ranging from 3 to 7.5. On the basis of the pH measurements and the dissociation constant of 2-methyl-1-vinylimidazole, plots of $\bar{n} = f(-\log[L])$ were drawn for each investigated system (Fig. 1). The shapes of the curves are independent of concentrations of particular metals thus revealing that only mononuclear species have been formed. On the basis of the mean ligand number, $\bar{n}$ and the equilibrium ligand concentration [L], stability constants of the complexes could be determined (Table 1). The literature evidence[22–26] shows that the stability of the metal–imidazole complexes is affected by the position of the substituent relative to the electron-donating 3-nitrogen atom. The α substituent weakens the complexes due to the steric effect, while that located on the

Table 2 The values of the log $^*\beta_1$ parameter for the complexes of Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} and Cd^{2+} with some imidazole derivatives

Ligand	Co^{2+}	Ni^{2+}	Cu^{2+}	Zn^{2+}	Cd^{2+}	pK_a
1-Ethylimidazole	−4.93	−4.21	−2.85	−4.75		7.25
1-Vinylimidazole	−3.67	−2.98	−2.32	−3.84	−3.60	5.92
2-Methyl-1-propylimidazole	−6.59	−6.15	−4.53	−6.85		8.20
2-Methyl-1-vinylimidazole	−5.68	−5.30	−3.78	−5.15	−4.92	6.98

Table 3 Crystal data and structure refinement for cobalt(II) **1** and copper(II) **4** complexes with 2-methyl-1-vinylimidazole

	1 $[CoL_3(H_2O)(NO_3)]NO_3$	**4** $[CuL_2(NO_3)_2]$
Empirical formula	$C_{18}H_{26}CoN_8O_7$	$C_{12}H_{16}CuN_6O_6$
Molecular weight	525.40	403.85
T/K	293(2)	100(2)
Radiation	Mo-Kα (λ = 0.71069 Å)	Mo-Kα (λ = 0.71069 Å)
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/n$ (no. 14)	$P\bar{1}$ (no. 2)
a/Å	11.363(2)	7.261(2)
b/Å	12.633(3)	7.931(2)
c/Å	17.013(3)	14.743(3)
α/°		103.78(3)
β/°	93.80(3)	95.39(3)
γ/°		94.78(3)
V/Å^3	2436.8(8)	816.0(3)
Z	4	2
μ/mm^{-1}	0.758	1.382
Reflections collected	4391	5089
Independent reflections	4391	3437, R(int) = 0.0195
Final $R1$, $wR2$ [$I > 2\sigma(I)$]	0.0353, 0.0840	0.0313, 0.0783

pyrrolic nitrogen atom makes the stability comparable with that of the imidazole compounds. Within the family of similarly substituted imidazoles, information on factors influencing the stability of the complexes, with the exception of basicity, is provided by a parameter of proton substitution in HL^+ for a metal ion (log $^*\beta_1$ = log β_1 − pK_a)[27] (Table 2). Numerical values of this parameter for all metal ions are higher for 2-methyl-1-vinylimidazole than for 2-methyl-1-propylimidazole (the increase is opposite to that of basicity). It can thus be concluded that the stability of complexes with the ligand carrying the unsaturated electron-accepting vinyl group is affected by some additional interactions. They are likely to involve an additional contribution of the $\pi_{M\rightarrow L}$ back bonding to the linkage between a metal ion and the 2-methyl-1-vinylimidazole molecule.[3–7] Again, alkyl substituents suppress the π-acceptor capacity of the imidazole ring owing to the mesomeric effect. Therefore the stability of their complexes is lower than would be expected based on their basicities. In the visible absorption spectra of the nickel(II) complexes a characteristic band emerges assignable to octahedral compounds of the metal ion, corresponding to the $^3A_{2g}(F) \longrightarrow {}^3T_{1g}(P)$ electronic transition. It is displaced towards shorter wavelengths in relation to that of the aqua complex (15 400 cm^{-1}). Under these conditions the utmost displaced band appears at 16500 cm^{-1} with molar absorptivity ε = 7.2 dm^3 mol^{-1} cm^{-1}.

The spectra of the copper(II) complexes of the ligand are typical for a tetragonal structure of the ion. The band due to the $^2E_g \longrightarrow {}^2T_{2g}$ electronic transition is displaced towards higher energies in relation to that of $Cu(H_2O)_6^{2+}$ (12 600 cm^{-1}). During the measurements the band was displaced up to 17 300 cm^{-1} (ε = 64 dm^3 mol^{-1} cm^{-1}). Such a spectral pattern of the nickel(II) and copper(II) complexes with 2-methyl-1-vinylimidazole leads to a conclusion that the immediate surrounding of the copper(II) ion is described by a tetrahedrally distorted octahedron, while the nickel(II) complexes are pseudo-octahedral. The results of our earlier studies have shown that, in aqueous solutions of the cobalt(II) complexes with 2-alkylimidazoles, configurational tetrahedron–octahedron equilibria are set up. In the absorption spectra of the cobalt(II) complexes with 2-methyl-1-vinylimidazole a bathochromic shift of the octahedral absorption band ($^4T_{1g}(F) \longrightarrow {}^4T_{1g}(P)$) is observed accompanied by a change in shape of the spectrum. Upon raising the ligand : metal ratio (5 : 1) a new band emerges at 17 900 cm^{-1}, corresponding to the $^4A_1(F) \longrightarrow {}^4T_{1g}(P)$ electronic transition. This finding may be indicative of a change in the co-ordination sphere of cobalt(II) in solution. However, in this case the tetrahedron–octahedron equilibrium is clearly displaced towards the six-co-ordinate species, as shown by the failure to obtain spectra with a distinctly separated band assignable to the tetrahedral species. It can thus be speculated that stabilisation of the six-co-ordinate cobalt(II) complexes is achieved by a massive contribution from π back bonding. A similar picture was observed by Nelson and co-workers[5–7] with the cobalt(II)–pyridine complexes. In the case of the zinc(II) co-ordination compounds there is no distinct influence of the π bonding on the structure. The steep shape of the formation curve and the irregularity of variations of the successive stability constants (log K_1 to log K_n) are due to the change in structure of the co-ordination sphere of the central ion from octahedral to tetrahedral. A similar irregularity of the K_n changes in the system Zn^{II}–ammonia has been attributed by Orgel[28] to identical structural transformations. Also, a similar picture was observed with imidazole and its derivatives (Table 1).

Investigation in the solid state

The structure of $[CoL_3(H_2O)(NO_3)]NO_3$ 1. In the six-co-ordinate cobalt(II) complex **1** three molecules of 2-methyl-1-vinylimidazole, a bidentate nitrato ligand and a water molecule are co-ordinated to the central ion (Fig. 2). The 2-methyl-1-vinylimidazole ligands are bound through the 'pyridine' nitrogen atom of the ring. In the chelating nitrato group the Co–O(2) and Co–O(1) bonds are symmetric, the difference in their lengths being as small as *ca.* 0.044 Å (Table 4). Owing to the chelation, the O(1)–N(1)–O(2) angle is 3.8° smaller than the trigonal value of 120°. Another nitrato ligand is linked through hydrogen bonding to the water molecule. Hydrogen bond lengths and bond angles are shown in Table 5. The immediate array of the cobalt(II) ion is thus made up of the N(11), N(21)

Table 4 Selected bond lengths (Å) and bond angles (°) for complex **1**, $[CoL_3(H_2O)(NO_3)]NO_3$

Co–O(7)	2.056(2)	O(1)–N(1)	1.261(3)
Co–N(31)	2.085(2)	O(2)–N(1)	1.253(3)
Co–N(11)	2.125(2)	O(3)–N(1)	1.213(3)
Co–N(21)	2.147(2)	O(4)–N(2)	1.237(4)
Co–O(1)	2.190(2)	O(5)–N(2)	1.240(5)
Co–O(2)	2.234(2)	O(6)–N(2)	1.200(4)
O(7)–Co–N(31)	103.0(1)	N(11)–Co–O(1)	90.3(1)
O(7)–Co–N(11)	91.1(1)	N(21)–Co–O(1)	88.1(1)
N(31)–Co–N(11)	93.1(1)	O(7)–Co–O(2)	95.1(1)
O(7)–Co–N(21)	88.4(1)	N(31)–Co–O(2)	161.7(1)
N(31)–Co–N(21)	91.3(1)	N(11)–Co–O(2)	89.1(1)
N(11)–Co–N(21)	175.5(1)	N(21)–Co–O(2)	86.5(1)
O(7)–Co–O(1)	152.8(1)	O(1)–Co–O(2)	57.7(1)
N(31)–Co–O(1)	104.1(1)		

Table 5 Hydrogen bond lengths (Å) and bond angles (°) for complex **1**

D–H···A	D–H	H···A	D···A	DHA
O(7)–H(1)···O(4)	0.89	1.87	2.736(4)	166.5
O(7)–H(2)···O(5^i)	0.94	1.80	2.714(4)	162.2

Symmetry code: ^{i} $-x + 1, -y, -z$.

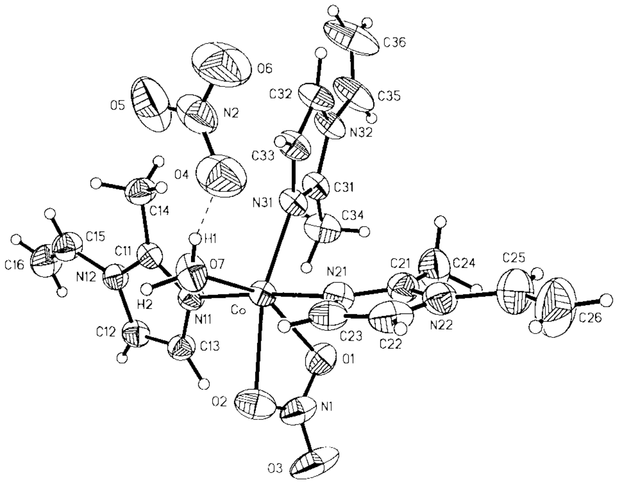

Fig. 2 The molecular structure of the cobalt(II) complex with 2-methyl-1-vinylimidazole, $[CoL_3(H_2O)(NO_3)]NO_3$ **1**.

and N(31) nitrogen atoms belonging to three imidazole rings with respective bond lengths of 2.125(2), 2.147(2) and 2.085(2) Å, two oxygen atoms O(1) and O(2) of the bidentate nitrato ligand and an oxygen atom O(7) of the water molecule. The bonds lengths Co–O(1), Co–O(2), Co–O(7) are 2.190(2), 2.234(2), 2.056(2) Å , respectively.

The structure of $[CuL_2(NO_3)_2]$ 4. The numbering of atoms and the structure of complex **4** are shown in Fig. 3, whereas in Fig. 4 the molecular packing of $[CuL_2(NO_3)_2]$ in the unit cell is presented. Two molecules of the imidazole base are linked to the central ion *via* 'pyridine' nitrogen atoms with Cu–N bond lengths of 1.960(2) and 1.967(2) Å (Table 6). The remaining four sites in this six-co-ordinate complex are occupied by four oxygen atoms O(1), O(2), O(3), O(5) of the nitrato groups acting as chelating ligands. In both groups the Cu–O bonds are asymmetric, the differences in lengths of the first and second nitrato groups being 0.393 and 0.406 Å. Such asymmetric bonds of bidentate nitrate are typical for this central ion.[29,30] The immediate environment of the copper(II) ion is not described by a regular polyhedron, because the chelating ONO_2 group distorts both the angles and the bonds. For this reason, the co-ordinational polyhedron assumes a distorted tetragonal bipyramid.

Table 6 Selected bond lengths (Å) and bond angles (°) for complex **4**, $[CuL_2(NO_3)_2]$

Cu–N(11)	1.967(2)	O(1)–N(1)	1.296(2)
Cu–N(12)	1.960(2)	O(2)–N(1)	1.253(2)
Cu–O(4)	2.011(2)	O(3)–N(1)	1.223(2)
Cu–O(5)	2.417(2)	O(4)–N(2)	1.290(2)
Cu–O(1)	2.032(1)	O(5)–N(2)	1.245(2)
Cu–O(2)	2.425(2)	O(6)–N(2)	1.226(2)
N(11)–Cu–N(21)	92.96(7)	N(1)–O(1)–Cu	100.84(10)
N(11)–Cu–O(4)	96.36(7)	N(1)–O(2)–Cu	83.89(10)
N(21)–Cu–O(4)	162.82(7)	N(2)–O(4)–Cu	102.07(11)
N(11)–Cu–O(1)	155.05(6)	O(3)–N(1)–O(1)	118.80(16)
N(21)–Cu–O(1)	91.49(6)	O(3)–N(1)–O(2)	123.84(17)
O(4)–Cu–O(1)	86.13(6)	O(1)–N(1)–O(2)	117.36(15)
N(11)–Cu–O(2)	97.43(6)	O(5)–N(2)–O(6)	122.77(17)
N(21)–Cu–O(2)	103.44(7)	O(5)–N(2)–O(4)	116.06(15)
O(4)–Cu–O(2)	89.66(6)	O(6)–N(2)–O(4)	121.15(17)
O(1)–Cu–O(2)	57.69(5)		

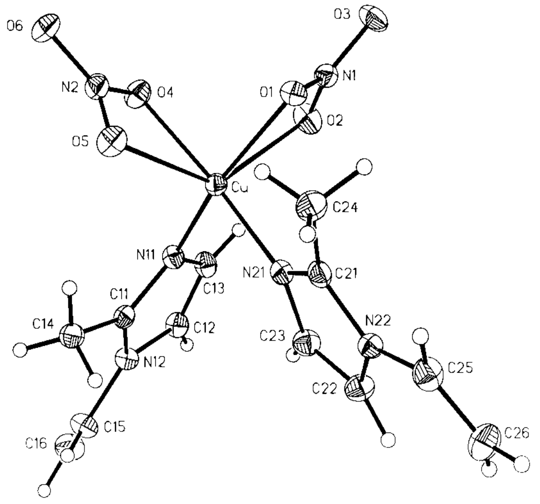

Fig. 3 The molecular structure of the copper(II) complex with 2-methyl-1-vinylimidazole, $[CuL_2(NO_3)_2]$ **4**.

EPR spectra of complexes 3 and 4. The EPR spectra of the polycrystalline compounds and their frozen ethanolic solutions are shown in Fig. 5. It is noteworthy that copper hyperfine splitting is observed also for polycrystalline complex **3** (Fig. 5 2b), however the hyperfine lines are broader than those observed for an ethanolic solution of this complex (Fig. 5 2a). The broadening effect caused by dipole–dipole interactions between copper(II) centres at relatively close positions usually leads to loss of the hyperfine structure as is observed for polycrystalline $[CuL_2(NO_3)_2]$ (Fig. 5 1b). All spectra have axial character with $g_{zz} = g_{\parallel} \gg g_{xx} \approx g_{yy} = g_{\perp} > 2.0023$ and $A_{zz} = A_{\parallel} \gg A_{xx} \approx A_{yy} = A_{\perp}$ typical for a tetragonal (or square planar symmetry) of the formed complexes and the $d_{x^2-y^2}$ orbital of copper containing an unpaired electron. As a consequence, $g_{\parallel}$ and $A_{\parallel}$ parameters are predominantly modified by the change in copper unpaired electron density affected by interactions with the ligands bound in the copper(II) plane.[31] The EPR parameters derived from polycrystalline and frozen solution anisotropic spectra exhibit similar trends depending on the compound. A characteristic increase of $A_{\parallel}$ and decrease of $g_{\parallel}$ parameters (Table 7) is consistent with the change in donor set around Cu^{II} from N_2O_2 in $[CuL_2(NO_3)_2]$ to N_4 in $[CuL_4(NO_3)_2]\cdot 2H_2O$. The co-ordination environment is not affected by the solvent molecules upon dissolution of crystalline complexes. The distinct dissimilarity in the EPR spectral parameters (Table 7) as well as in ^{14}N hyperfine splitting (at the high field line of perpendicular

Table 7 The EPR parameters of Cu^{2+} complexes with L = 2-methyl-1-vinylimidazole

Complex	Polycrystalline sample		Ethanol solution	
	$g_{\parallel}$	$A_{\parallel}$/ 10^{-4} cm^{-1}	$g_{\parallel}$	$A_{\parallel}$/ 10^{-4} cm^{-1}
$[CuL_2(NO_3)_2]$	2.325	—	2.314	154
$[CuL_4(NO_3)_2]\cdot 2H_2O$	2.285	175	2.272	182
$[Cu(1\text{-}Bz\text{-}2CH_2OHIm)_4]^{2+}$ [32]	2.275	180	2.273	178

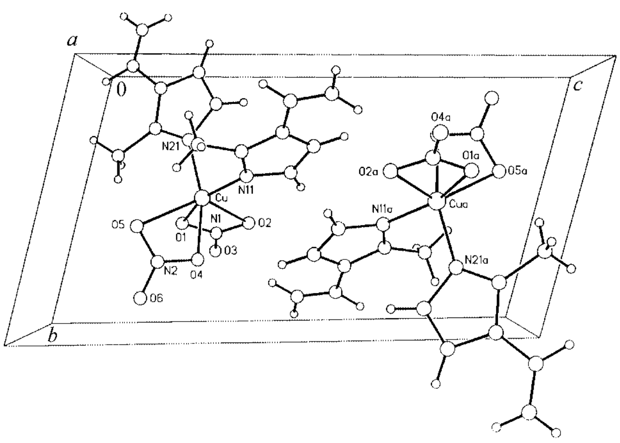

Fig. 4 Molecular packing of $[CuL_2(NO_3)_2]$ in the unit cell.

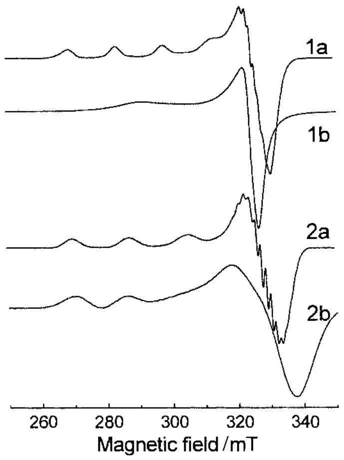

Fig. 5 The EPR spectra of complexes **3** (2) and **4** (1) measured for ethanolic solution (1a and 2a) and for polycrystalline samples (1b and 2b) at 77 K.

orientation for the frozen solution spectra in Fig. 5) are in a excellent agreement with the difference between copper(II) co-ordination spheres formed by two and four monodentate imidazole ligands, respectively. The EPR parameters for **3** presented in Table 7 resemble quite closely those found recently for $[Cu(1\text{-}Bz\text{-}2\text{-}CH_2OHIm)_4][NO_3]_2$ (1-Bz-2-CH_2OHim = 1-benzyl-2-hydroxymethylimidazole)[32] the molecular structure of which characterised by X-ray studies indicates a N_4 donor set of the ligands. The co-ordination properties of imidazole containing ligands are usually studied by EPR in solution.[24,33] A limited number of EPR data is known for the complexes simultaneously studied by X-ray crystallography,[32] especially when less than 4 imidazole ligands are co-ordinated. This is the case of $[CuL_2(NO_3)_2]$. The possibility to correlate the EPR data and molecular structure of the crystals allows for unambiguous assignment of the spectral properties to a particular copper(II) co-ordination sphere.

The infrared spectra. In the infrared absorption spectra of the complexes remarkable are new bands assigned to symmetric and antisymmetric stretching vibrations of the nitrato group which are obviously missing in the spectrum of 2-methyl-1-vinylimidazole. Positions of these bands for particular compounds are shown in Table 8. The bidentate nature of the nitrato ligand is highlighted by the strongest bands at 1472, 1480 and 1490 cm^{-1} for compounds **1**, 2 and **4** respectively.[30,34] Entirely different is the nature of the nitrato group in **3** (1350 cm^{-1}) and of one of these groups in compound **1** (1310 cm^{-1}). According to the previously suggested structure of complex **1**, the 1310 cm^{-1} band should be assigned to the nitrato group associated by hydrogen bonding with the water molecule. Again, in the spectrum of compound **3**, a very strong band a 1350 cm^{-1} is assignable to the stretching vibration of the monodentate ONO_2 group.[30,34] Water stretches yield broad absorption bands centred at 3320 and 3439 cm^{-1} for **1** and **3** respectively. Usually in such cases an accompanying weak band assignable to out-of-plane OH vibrations emerges at *ca.* 1640 cm^{-1}. However, in the spectrum of these complexes the band could hardly be identified owing to the overlapping band of the vinyl group. Sometimes in the far-IR spectra of aqua complexes a band due to a metal–oxygen stretch appears at *ca.* 400 cm^{-1}. Unfortunately, in the spectrum of complex **1** such a band could not be detected. However, in this spectral range new bands emerged at *ca.* 300 cm^{-1} (Table 8) in the spectra of all the complexes studied, thus confirming the participation of the "pyridinic" nirogen atom of the imidazole ring in its binding to the metal ion.

The IR spectral data show that the nature of the nitrato groups in the complexes is differentiated. In **1**, **2** and **4** they occur as bidentate ligands, whereas in **3** the monodentate group occurs. Again, in compound **1** one of the nitrato groups does not co-ordinate to the central ion at all. Bearing in mind this finding and the results of elemental analyses, the following formulae can be assigned to the complexes: $[CoL_3(H_2O)(NO_3)]NO_3$ **1**, $[CoL_2(NO_3)_2]$ **2**, $[CuL_4(NO_3)_2]\cdot 2H_2O$ **3**, $[CuL_2(NO_3)_2]$ **4**.

Electronic d–d spectra and magnetic properties of the complexes. Absorption bands due to d–d electronic transitions for the complexes are presented in Table 8. The position of this band for cobalt(II) at 17200 and 17600 cm^{-1} for **1** and **2** respectively is typical for six-co-ordinate complexes of the metal ion.[35] The spectra of the studied cobalt(II) and copper(II) complexes are diffuse and asymmetric, thus indicating overlap of several bands. For closer examination of these spectra a Gauss distribution could be applied. The positions of individual bands for the complexes, obtained from such an analysis, are shown in Table 8. In the spectrum of $[CuL_2(NO_3)_2]$ **4** the band is displaced towards near infrared. In that of compound **3** the band appears at a considerably higher energy (17 800 cm^{-1}), its components emerging at 16 000, 18 000 and 21 500 cm^{-1}. This observation, accompanied by the IR and EPR data, led us to assign a tetragonal stereochemistry for the $[CuL_4(NO_3)_2]\cdot 2H_2O$ complex. For the six-co-ordinate tetragonal chromophore CuN_4O_2 the ground state is provided by the $d_{x^2-y^2}$ (spectroscopic state $^2B_{1g}$). Energies of the remaining orbitals decrease in the order $d_{z^2} > d_{xy} > d_{xz},d_{yz}$ ($^2A_{1g} > {}^2B_{2g} > {}^2E_g$). Successive bands correspond to the $d_{x^2-y^2} \longrightarrow d_{xy}$, $d_{x^2-y^2} \longrightarrow d_{xy},d_{yz}$ and $d_{x^2-y^2} \longrightarrow d_{z^2}$ transitions.[36] In the remaining cobalt(II) and copper(II) complexes the bidentate nitrato ligand causes deformation of both the angles and bond lengths in the co-ordination polyhedra, thus precluding assignment of electronic transitions to constituent bands.

Effective magnetic moments of the cobalt(II) complexes at room temperature are 4.70 and 4.80 μ_B for **1** and **2** respectively. These values are consistent with high-spin six-co-ordinate complexes. Both copper(II) complexes are paramagnetic with magnetic moments of 2.01 and 1.81 μ_B corresponding to one unpaired electron.

Table 8 Principal infrared frequencies and electronic bands of complexes (in cm^{-1})

	Infrared spectra		Electronic spectra		
Complex	$\nu(NO_3)$	ν(M–N)	λ_{max}	Gauss analysis	Assignment
1 $[CoL_3(H_2O)(NO_3)]NO_3$	1472, 1310	290	17200	17100	
				21000	
2 $[CoL_2(NO_3)_2]$	1480	286	17600	17600	
				21100	
					$d_{x^2-y^2}$
3 $[CuL_4(NO_3)_2]\cdot 2H_2O$	1350	310	17800	16000	d_{xy}
				18000	d_{xz}, d_{yz}
				21500	d_{z^2}
					D_{4h}
4 $[CuL_2(NO_3)_2]$	1490	312	13800	10200	
				13400	
				16900	

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Paper a908718d