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The synthesis, spectroscopic properties and X-ray structure of Zn(II) complexes with amino derivatives of chromone

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ABSTRACT

Three new Zn(II) complexes containing the ligands 5-amino-8-methyl-4*H*-chromen-4-one (**1**), 6- or 7-amino-2-phenyl-4*H*-chromen-4-one (**2**, **3**) were prepared. The new synthesised compounds were characterised by IR, ^{1}H NMR and MS spectroscopy. The crystal structure of complex **4** was determined with the use X-ray diffraction. The Zn(II) centre of **4** is linked by two chlorido and two *N*-bound aminochromone ligands, **1**, in a strongly distorted tetrahedral configuration with the dissymetric point group C_2. The protonation constants of the ligands **1**, **2** and **3** corresponded to 3.68, 3.88 and 6.83, respectively. The stability constants of the Zn(II) complexes were calculated from the potentiometric titration data. The complexes were found to have the formulae ML and ML_2 for ligands **1** and **2**, and ML for ligand **3**. Fluorescence spectroscopic properties were also studied; the strongest fluorescence in solution was exhibited by complex **6**.

1. Introduction

For a long time, we have been synthesising and investigating the X-ray structures, cytotoxic effect and lipophilicity of metal ion complexes [1–4]. Special effort has been focused on chromone (benzo-γ-pyrone) derivatives as ligands. Chromone and its derivative flavone (2-phenyl-4*H*-chromen-2-one) are of great interest due to their chemical properties in particular, with their reactivity towards nucleophilic reagents containing nitrogen, oxygen, sulphur and carbon [5]. Their pharmacological activity [6], such as anticancer [7–9] antioxidant [10], antimitotic [11], antiinflamatory [12] and many others [13,14] makes both molecules attractive for further backbone derivatisation and screening as novel therapeutic agents. Most of flavonoids are good metal chelators which can chelate many metal ions to form different complexes due to their conjugated system. It has been extensively reported that the interaction of some metals with flavonoids contributes to their antioxidant activity [15]. In recent years, metal ion complexes have played a very important role in medicine, pharmacy and diagnostics [16]. Zn(II) is a one of the most important metal ions in the human body. This ion is found at the active sites of over 200 types of enzymes, most of which catalyse the hydrolysis of esters (carboxylic or phosphate) and amides [17]. Moreover, Zn(II) is essential for the growth and development in all forms of life and has beneficial therapeutic and preventative effects on infectious diseases. Zn(II) ions play an important role as radioprotective agents, tumour photosensitizers and antidiabetic insulin-mimetic agents [18]. The coordination number and geometry of the compounds are therefore dependant on the size and charge of the ligand. In many complexes the Zn(II) cation prefers a tetrahedral coordination sphere [19]. Fluorescent imaging has been proven to be the most suitable technique for Zn(II) *in vivo* monitoring [20].

In the present work we have conducted the synthesis of three Zn(II) complexes with chromone or flavone derivatives, and characterised them using IR, ^{1}H NMR and MS spectroscopy. The X-ray crystal structure of one complex was determined. The coordination tendencies of the ligands towards the Zn(II) ions in solution were studied with potentiometric and spectrophotometric methods. We have been exploring the influence of the position of the electron donating group NH_2 in the molecule on the coordination behaviour of the ligands towards the Zn(II) centre. Moreover the ability of the ligands to enhance fluorescence through complexation may give the opportunity for the photochemical applications of these complexes.

2. Experimental

2.1. Materials and methods

All substances were used without further purification. Chloroform-d and DMSO-d_6 solvents for NMR spectroscopy were

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obtained from Dr. Glaser AG Basel. Solvents for the synthesis (acetonitrile, diethyl ether) were reagent grade or better and were dried according to standard protocols [21]. The melting points were determined using an Electrothermal Buechi540 apparatus and they are uncorrected. The IR spectra were recorded on a Pye-Unicam 200G spectrophotometer in KBr discs. The ^{1}H NMR spectra were registered at 300 MHz on a Varian Mercury spectrometer. The MS-FAB data were determined on Finnigan Matt 95 mass spectrometer (NBA, Cs^+ gun operating at 13 keV). For the new compounds satisfactory elemental analyses (0.4% of the calculated values) were obtained using a Perkin–Elmer PE 2400 CHNS analyser. 5-Amino-8-methyl-4*H*-chromen-4-one [22] was prepared as described in [23].

2.2. Synthesis of bis(5-amino-8-methyl-4H-chromen-4-one)-N5,N′5-dichlorido-zinc(II) ($Zn(L\mathbf{1})_2Cl_2$) (**4**)

A solution of $ZnCl_2$ (0.021 g, 0.15 mmol) in acetonitrile (10 ml) was added dropwise to a solution of the ligand **1** (0.052 g, 0.03 mmol) in acetonitrile (15 ml). The reaction mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure at room temperature to one-half of the initial volume. After 24 h, the precipitated yellow solid was filtered off, washed with diethyl ether and dried in the air. Yellow crystals of **4** suitable for X-ray diffraction were obtained after a few days by recrystallising the precipitated product from an acetonitrile solution. Yield: 41 mg (56.24%), mp: 191.5–192.8 °C. FT IR (KBr cm^{-1}): ν(C–NH_2) 3175, 3078; ν(C=O) 1641; ν(C=C) 1621, 1553, 1487; ν(M–N) 482. ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C) δ (ppm): 2.17 (s, 3H, CH_3), 6.11 (d, 1H_B, $^3J_{HH}$ = 5.77 Hz), 6.44 (d, 1H_D, $^3J_{HH}$ = 8.33 Hz), 7.2 (d, 1H_E, $^3J_{HH}$ = 8.33 Hz), 7.21 (s, 2H, NH_2), 8.09 (d, 1H_A, $^3J_{HH}$ = 5.75 Hz). MS-FAB (*m*/*z*): 452 (ZnL_2Cl^+), 276 ($ZnLCl^+$), 176 (100%, L).

Anal. Calc. for $C_{20}H_{18}N_2O_4ZnCl_2{\cdot}0.5H_20$ (495.66 g/mol) for **4**: C, 48.46; H, 3.86; N, 5.65. Found: C, 48.40; H, 3.39; N, 5.62%.

2.3. Synthesis of acetonitrile-bis(6-amino-2-phenyl-4H-chromen-4-one)-N6,N′6-dichlorido-zinc(II) ($Zn(L\mathbf{2})_2Cl_2$) (**5**)

Zn(II) chloride $ZnCl_2$ (56.2 mg, 0.41 mmol) was dissolved in 10 ml acetonitrile and then added dropwise to a stirred solution of the ligand 6-amino-2-phenyl-4*H*-chromen-4-one (**2**) (195.69 mg, 0.82 mmol) in acetonitrile (20 ml) at room temperature. The mixture was stirred for 10 min and a yellow precipitate was obtained. The solid was filtered off, washed with diethyl ether and dried *in vacuo* and over P_2O_5. Yield: 176.4 mg (70.44%), mp: 263.9–265.1 °C. FT IR (KBr cm^{-1}) (selected bands): ν(C–NH_2) 3281, 3117; ν(C=O) 1627; ν(C=C) 1612, 1573, 1487; ν(M–N) 481. ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C) δ (ppm): 5.52 (s, 2H, NH_2), 6.87 (s, 1H_B), 7.07 (d, 1H_E, $^3J_{HH}$ = 8.73 Hz), 7.086 (d, 1$H_{6'}$, $^3J_{HH}$ = 14.88 Hz), 7.493, 7.53 (dd, 1$H_{5'}$, $^3J_{HH}$ = 8.73 Hz, $^3J_{HH}$ = 13.09 Hz), 7.534 (d, 1H_F, $^3J_{HH}$ = 8.93 Hz), 7.55, 7.57 (dd, 1$H_{3'}$, $^3J_{HH}$ = 1.78 Hz, $^3J_{HH}$ = 1.98 Hz), 8.039 (s, 1H_C), 8.052, 8.041 (dd, 1$H_{4'}$, $^3J_{HH}$ = 5.36 Hz, $^3J_{HH}$ = 7.74 Hz). MS-FAB (*m*/*z*): 612 (5%, M^++2H), 577.6 (ZnL_2Cl^+), 304 (ZnL^{2+}), 238.2 (100%, L). *Anal.* Calc. for $C_{30}H_{22}N_2O_4ZnCl_2$ (610.72 g/mol) for **5**: C, 58.99; H, 3.63; N, 4.58. Found: C, 58.57; H, 3.49; N, 4.71%.

2.4. Synthesis of acetonitrile-bis(7-amino-2-phenyl-4H-chromen-4-one)-N7,N′7-dichlorido-zinc(II) ($Zn(L\mathbf{3})_2Cl_2CH_3CN$) (**6**)

To a solution of the ligand **3** (0.176 g, 0.74 mmol) in acetonitrile (20 ml) was added dropwise a solution of $ZnCl_2$ (0.51 g, 0.37 mmol) in acetonitrile (10 ml). The reaction mixture was stirred at room temperature for 24 h. The solvent was removed under reduced pressure at room temperature to one-half of the initial volume. After 3 h, a yellow solid precipitated and was filtered off, washed with diethyl ether and dried in air. Yield: 93 mg (37%), mp: 248.7–250.0 °C. FT IR (KBr cm^{-1}): ν(C–NH_2) 3345, 3228; ν(C≡N) 2200; ν(C=O) 1629; ν(C=C) 1607, 1580, 1517; ν(M–N) 485. ^{1}H NMR (300 MHz, DMSO-d_6, 25 °C) δ (ppm): 2.07 (s, 3H, CH_3CN), 6.33 (s, 2H, NH_2), 6.62 (s, 1H_B), 6.68 (d, 1H_D, $^3J_{HH}$ = 8.73 Hz), 6.675, 6.682 (dd, 1$H_{5'}$, $^3J_{HH}$ = 8.73 Hz, $^3J_{HH}$ = 8.53 Hz), 7.52, 7.545 (dd, 1$H_{3'}$, $^3J_{HH}$ = 5.55 Hz, $^3J_{HH}$ = 3.76 Hz), 7.556 (d, 1$H_{2'}$, $^3J_{HH}$ = 5.33 Hz), 7.58 (d, 1$H_{6'}$, $^3J_{HH}$ = 3.76 Hz), 7.69 (d, 1H_C, $^3J_{HH}$ = 8.73 Hz), 7.998 (s, 1H_F), 8.00, 8.011 (dd, 1$H_{4'}$, $^3J_{HH}$ = 7.73 Hz, $^3J_{HH}$ = 5.36 Hz). MS-FAB (*m*/*z*): 612 (1%, M^++2H), 577.8 [ZnL_2Cl^+], 371.3 ($ZnLCl_2$), 366.2 ($ZnLCl^+$), 238.2 (100%, L). *Anal.* Calc. for $C_{30}H_{22}N_2O_4$-$ZnCl_2{\cdot}CH_3CN$ (651.77 g/mol) for **6**: C, 58.96; H, 3.87; N, 6.44. Found: C, 58.75; H, 3.61; N, 6.12%.

2.5. Potentiometric studies

Potentiometric measurements were carried out in 1,4-dioxane/water (10:90) at 25 °C in a constant-temperature circulating water jacketed titration cell. Titrations were performed with an Alpha Titro-plus (Schott) equipped with a microcombination glass electrode and an Ag/AgCl reference electrode (BluLine 16pH, Schott). The electrode was calibrated in terms of [H^+] by titrating HNO_3 solutions with standard NaOH solutions and the pK_w value (13.77) was calculated by means of Gran's method. Carbonate-free standard NaOH solution (0.01 mol dm^3) was used as the titrant. The total concentration of each ligand ranged from 2.20×10^{-3} to 2.60×10^{-3} mol dm^{-3}. All the experiments were performed at constant ionic strength (0.1 mol dm^{-3} $NaClO_4$). Each titration was repeated (80–100 data points per titration) four times and the data were processed with the use of the HYPERQUAD2008 [24] program to compute the protonation constants. The distribution diagrams were plotted by the program HYSS 2006.

The stability constant (β_{pqr}) of a complex $M_pL_qH_r$ refers to the formation of that complex from the participating species, i.e. the reaction: $pM + qL + rH = M_pH_qL_r$ (charges are omitted for simplicity). The indexes *p*, *q* and *r* are stoichiometric numbers; *p* and *q* are positive or zero value. *R* is a positive integer for protonated species, zero for neutral species and negative for hydroxo or deprotonated species.

2.6. Spectroscopic measurements

Fluorescence measurements were performed on a Shimadzu RF5301 spectrofluorimeter equipped with a 150 W Xenon lamp and 10 mm quartz cells. The absorption spectra were recorded on Shimadzu UV 2450 double-beam spectrophotometer equipped with 10 mm quartz cells at 25 °C and an ionic strength of 0.1 mol dm^{-3} ($NaClO_4$).

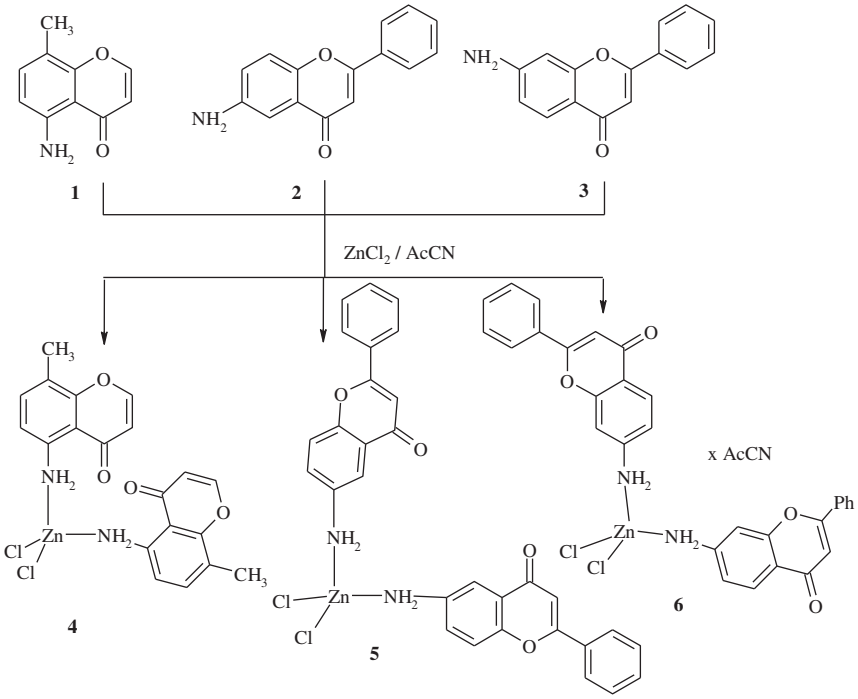
2.7. X-ray structure determination of **4**

The data were collected at 200 K by means of an Oxford Diffraction XCalibur diffractometer with graphite-monochromated Mo Kα radiation. The data have been corrected by a numerical absorption correction with XRED [25]. The structure has been solved with the direct method using SIR97 [26]. All non-hydrogen atoms were refined anisotropically, and the hydrogen atoms were generated in idealised positions, riding on their parent atoms [27].

3. Results and discussion

3.1. Chemistry

The complexes **4**–**6** were prepared by mixing $ZnCl_2$ with 5-amino-8-methyl-4*H*-chromen-4-one (**1**), 6-amino-2-phenyl-4*H*-chro-



Scheme 1. Synthesis of the Zn(II) complexes with aminochromone derivatives.

men-4-one (**2**) or 7-amino-2-phenyl-4*H*-chromen-4-one (**3**) in a 1:2 (M:L) molar ratio. The reactions were carried out in acetonitrile solution. Three new Zn(II) complexes **4**–**6** (see Scheme 1) of the aminochromones derivatives **1**–**3** have been obtained in good yield.

3.2. MS-FAB

All the compounds have been investigated by positive/negative mass spectrometric measurements, giving valuable structural information. The major structurally informative molecular ions and fragment ions in the positive-ion mode of compounds **4**–**6** are presented in Table 1. The molecular peaks relating to complexes **5** and **6** were observed at 612 $[M+2H]^+$ in the FAB-MS spectra. For complex **4**, we have not observed a molecular peak, but a strong peak at *m*/*z* 452 was attributed to $[M-Cl]^+$. The FAB mass spectrum of **6**, recorded in the positive ion mode, contains a peak at *m*/*z* 654 due to the $[M+2H]^+$ ion and at *m*/*z* 577.8 due to MCl^+. In addition, a predominant peak corresponding to the ligands **2** and **3** at *m*/*z* 238.2 [100%, L] was observed.

The data presented above are in good agreement with the results obtained from the elemental analysis and therefore confirm the proposed structure of investigated complexes by X-ray spectroscopy.

3.3. Infrared spectra

Some characteristic IR vibrations for the complexes are given in Table 2. Significant differences in the IR spectra of complexes **4–6** were observed in comparison with those of ligands **1**–**3**. The IR spectra of the ligands **1**, **2** and **3** (see Table 2) show prominent stretching vibrations at 3432, 3342 and 3345 cm^{-1} respectively, which were assigned to the asymmetric $\nu(NH_2)$ and at 3324, 3238 and 3228 cm^{-1} which were assigned to the symmetric $\nu(NH_2)$. These bands shift to lower energies (by 257 and 246 cm^{-1} for compound **4**; 61 and 121 cm^{-1} for compound **5**; 52 and 41 cm^{-1} for compound **6**, respectively), showing that coordination of the amino group has occurred. The strong $\nu(C{=}O)$ bands, occurring at 1641, 1627 and 1629 cm^{-1} for **4**, **5** and **6** respectively, are shifted only slightly compared to the free ligands (1648, 1642 and 1630 cm^{-1}). Several absorptions in the 1588–1411 cm^{-1} region can be assigned to aromatic vibrations. Ligands coordination to the metal centre is substantiated by bands appearing for ν(M–N) at 482, 481 and 485 cm^{-1} for **4–6**, respectively [28].

Table 1
MS data (*m*/*z*) of the complexes **4**–**6**.

Compound	Molecular ions	Fragment ions
4	–	452 (ZnL_2Cl^+), 276 ($ZnLCl^+$), 176 (100%, L)
5	612	577.6 (ZnL_2Cl^+), 304 (ZnL^{2+}), 238.2 (100%, L)
6	612	577.8 (ZnL_2Cl^+], 371.3 [$ZnLCl_2$], 366.2 [$ZnLCl^+$], 238.2 [100%, L]

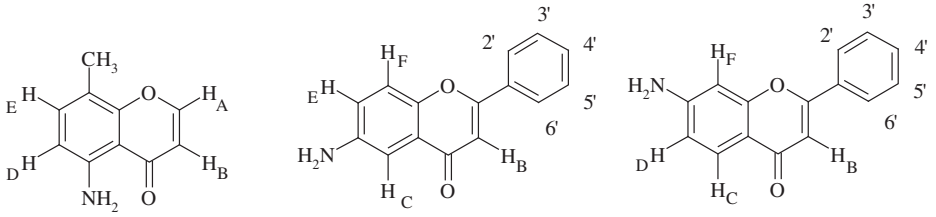
Table 2
IR data of the ligands and their complexes.

Compound	$\nu(NH_2)$	$\nu(C{=}O)$	ν_{aromat}	ν(M–N)
L1	3432, 3324	1648	1625, 1588, 1569	–
4	3175, 3078	1641	1621, 1553, 1487	482
L2	3342, 3238	1642	1581, 1565, 1487	–
5	3281, 3117	1627	1612, 1573, 1487	481
L3	3460, 3293	1630	1600, 1586, 1498	–
6	3345, 3228	1629	1607, 1580, 1517	485

3.4. ^1H NMR spectra

The ^1H NMR spectra of the complexes and their ligands were recorded after dissolution in d_6-DMSO, with TMS as an internal standard. Careful analysis of the ^1H NMR spectral data is summarised in Table 3. This data has been used to get information regarding the coordination mode of the ligands with the metal ion for complexes 4–6. For complexes **4–6**, the resonances of the amino group protons at positions 5, 6 and 7 were found at 7.23, 5.52 and 6.33 ppm respectively and they were shifted by 0.02, 001 and 0.03 ppm from their positions in the free ligands due to the coordi-

Table 3
^{1}H NMR data of the ligands and their Zn(II) complexes



1 2 3

	H_A	H_B	H_C	H_D	H_E	H_F	NH_2
L1	8.08, $^3J_{HH}$ = 5.75	6.12, $^3J_{HH}$ = 5.77	–	6.44, $^3J_{HH}$ = 8.33	7.20, $^3J_{HH}$ = 8.33	–	7.21
4	8.09, $^3J_{HH}$ = 5.75	6.11, $^3J_{HH}$ = 5.77	–	6.44, $^3J_{HH}$ = 8.33	7.21, $^3J_{HH}$ = 8.33	–	7.23
L2	–	6.87	8.04	–	7.20, $^3J_{HH}$ = 8.73	7.53, $^3J_{HH}$ = 8.93	5.53
5	–	6.87	8.039	–	7.20, $^3J_{HH}$ = 8.73	7.54, $^3J_{HH}$ = 8.93	5.52
L3	–	6.62	7.70, $^3J_{HH}$ = 8.53	6.68, $^3J_{HH}$ = 8.73	–	8.01	6.36
6	–	6.62	7.69, $^3J_{HH}$ = 8.73	6.68, $^3J_{HH}$ = 8.73	–	7.998	6.33

nation of the amino nitrogen atom with the metal centre. As is seen in Fig. 1, the ^{1}H NMR spectra of ligands **1**, **2** and **3** are almost indistinguishable from those of complexes **4**–**6**. The aromatic protons in all the spectra are observed around 6.11–8.08 ppm as singlets or doublets.

3.5. pH-metric and spectrophotometric measurements

The protonation constants of the ligands, which may be considered as monoprotic bases, were determined by potentiometric and spectrophotometric methods. The proton dissociation constants of the ligands **1**, **2** and **3** (Table 4) corresponded to 3.68, 3.88 and 6.83, respectively and were attributed to the deprotonation of the protonated amino group. The basicities of the ligands **1** and **2** are three orders of magnitude smaller than the basicity of ligand **3** due to the electron withdrawing effect of the C=O group. The basicity of amino derivatives of chromone depends on the electron density of the nitrogen atom. In the ligands strong intramolecular electron donor–acceptor interactions are possible. The most important interaction is hyperconjugation related to electron donation from the N atom of the NH_2 group to the anti-bonding acceptor σ^*(C–C) of the phenyl ring. Intramolecular hyperconjugative interactions are formed by the orbital overlap between π(C–C) and π^*(C–C) bond orbitals. Intramolecular charge transfer (ICT) resulting from hyperconjugation causes stabilization of the molecule. For 6-aminoflavone (**2**), a strong interaction between the ring oxygen atom and the neighbouring σ^*(C–C) orbitals has been observed [29]. A stronger hyperconjugative interaction could be expected to occur in the 7-aminoflavone molecule.

The pK_a values from the potentiometric study for ligands **1** and **2** were in good agreement with those obtained from the spectrophotometric titration. Because the ionizable –NH_2 group was remoted from the chromophore, the change in absorbance of 7-amino-2-phenyl-4*H*-chromen-4-one (ligand **3**) was very low, thus the protonation constant computation with the use spectrophotometric titration data was not possible.

The equilibrium constant values for the complexes formed between Zn(II) and the ligands were studied in the 1:1 and 1:2 metal–ligand systems (Fig. 2 for ligand **1** and its complexes). Analyses of the potentiometric curves with the use of the program HYPERQUAD allowed the determination of Zn(II) complex species in equilibrium and their formation constants. The best fit models included two complexes (ML_1 and ML_2) for ligands **1** and **2**. For the Zn(II)-ligand **3** systems, precipitation occurred above pH 5.5, so only the stability constant for M:L = 1:1 could be calculated.

Many authors have found positive linear correlations between the ligand basicity and the stability constants of complexes [30,31], but high pK_a values do not always ensure more stable complexes [32]. In Fig. 3, the first stepwise stability constants for the Zn(II) complexes **4**–**6** are represented as a negative linear function of the basicity of ligands. This linear relationship is exclusively obeyed by similar ligands with the same electron-donor atom relative to both the metal ion and the proton [30].

The influence other than ligand basicity factors on the stability of the complexes could be illustrated by the values of log $^*\beta_1$ (Eqs. (1)–(3)).

$$[Zn(H_2O)_6]^{2+} + HL^+ \leftrightarrow [Zn(H_2O)_5L]^{2+} + H_3O^+ \quad (1)$$

$$\beta^* = \frac{[Zn(H_2O)_5L]^{2+}[H_3O^+]}{[Zn(H_2O)_6]^{2+}[HL^+]} \quad (2)$$

$$\log {}^*\beta_1 = \log \beta_1 - pK_a \quad (3)$$

Similar to log β_1, the log $^*\beta_1$ values significant decrease with increasing basicity of the ligands. The negative slope of the dashed line (Fig. 3) is close unity (−1.15), which means that the stability of the complexes is weakly affected by a contribution of $\pi_{M \rightarrow L}$ bonding to the M–L bonds. The log $^*\beta_1$ values for chromone derivatives decrease in the order: **1** > **2** >> **3**. This can be caused by a reduction of the π-acceptor properties of the ligands resulting from an increase in electron density on the donor N-atom of the NH_2 group [30].

The spectrophotometric titration was carried out under the same conditions as the potentiometric titration, except for the concentration of the ligands (10 times lower in the spectrophotometric measurements). Representative species-distribution diagrams for the Zn(II)-**1**, Zn(II)-**2** and Zn(II)-**3** systems are shown in Fig. 4. From Fig. 4 it can be seen that the protonated form (LH) of the ligands **1** and **2** exist in the acidic medium at pH <2 and under pH 4 for ligand **3**. The complexation process for both 5-amino-8-methyl-4*H*-chromen-4-one and 6-amino-2-phenyl-4*H*-chromen-4-one began at low pH due to the formation of ZnL and ZnL_2 species. The complex ML_2 was a predominant species over pH 4.5–5.0.

The spectrophotometric titration of the ligands **1** and **2** is shown in Figs. 5 and 6, respectively. The spectra were recorded in the region 220–500 nm and between pH 2 and 10. The absorption spectra of the ligand **1** with the pH <5.0 have two characteristic peaks, with the maxima at 300 and 370 nm. The absorption band at

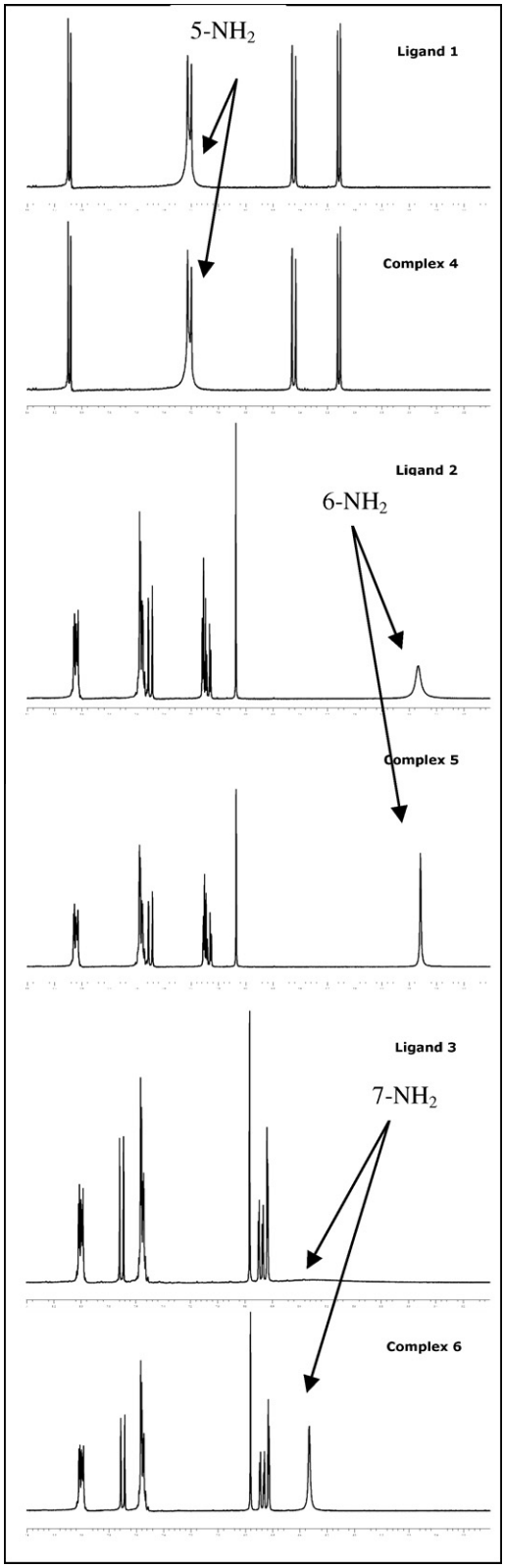


Fig. 1. ^{1}H NMR spectra of the ligands and their Zn(II) complexes.

300 nm was associated with the protonated form of the ligand and this peak gradually decreased during the titration and disappeared at pH >5.0. In the range pH 5.0–8.1 no changes were observed in the absorption spectra.

Table 4
The values of the overall protonation constants (pK_a) of the ligands and the stability constants (log β) of the Zn(II) complexes from potentiometric titrations.

Ligand	pK_a (HL)	Log β_1 (ML)	Log β_2 (ML_2)	Log $^*\beta_1$
1	3.68(7)	6.83(3)	9.71(10)	3.15
2	3.88(6)	6.75(8)	9.47(12)	2.87
3	6.83(8)	3.26(6)	–	−3.57

Values in parentheses are the standard deviations in the last significant digit.

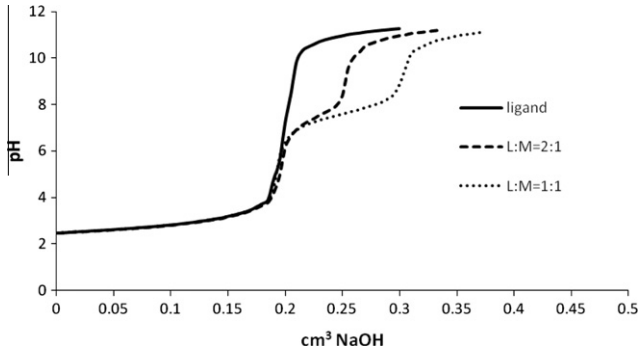


Fig. 2. Potentiometric titration curves of ligand **1** in the absence and presence of Zn(II) ions.

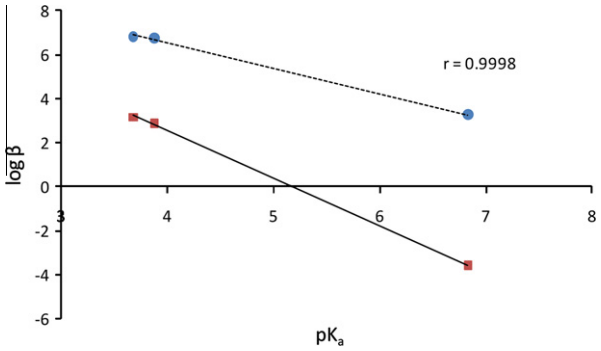


Fig. 3. Stability constants log β_1 (solid line) and log $^*\beta_1$ (dashed line) of the Zn(II) complexes as function of the pK_a values of the ligands.

The UV–Vis spectra of ligand **2** changed significantly in pH range 2.8–5.0, and over pH 5.0 no change was observed. The unprotonated form of ligand **2** has three bands, with the maxima at 280, 315 and 370 nm. During the protonation process (decreasing pH) the band at 280 nm showed a bathochromic shift to 300 nm coupled with decreasing absorbance.

3.6. Fluorescensce spectra

The fluorescence properties of ligands **1**–**3** and their complexes with Zn(II) (**4**–**6**) were measured in the polar solvents 10% 1,4-dioxane in water and methanol at room temperature. Ligand **1** and complex **4** did not show any fluorescence features, whereas 6-aminoflavone (**2**), 7-aminoflavone (**3**) and their complexes with Zn(II) ions exhibited fluorescence in both solvents. Both complexes **5** and **6** exhibited stronger fluorescence than their respective ligands. For the Zn(II) complexes, no emissions originating from metal-centred excited states were expected, because the Zn(II) ion is difficult to oxidise or reduce due to its stable d^{10} configuration [33,34]. Thus excited states after metal ion complexation are typically ligand centred in nature. In the absence of any Zn(II) ions

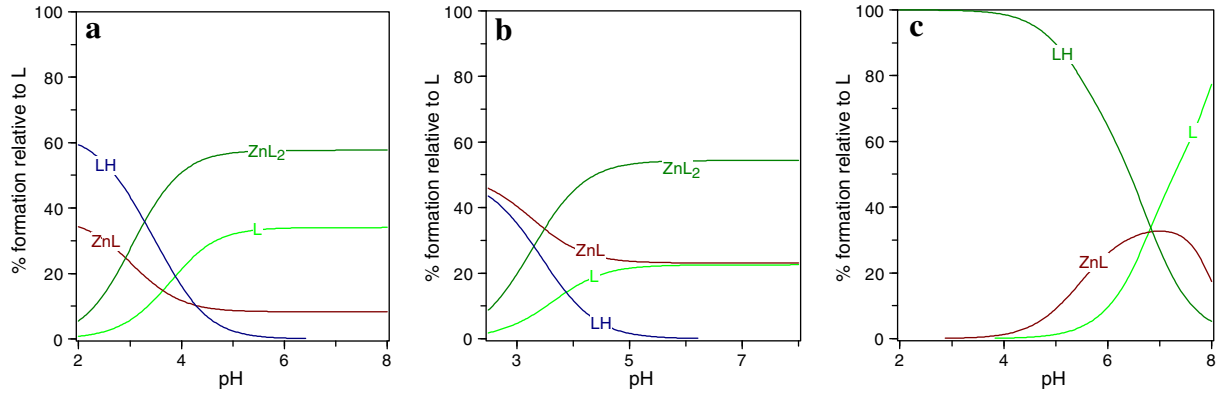


Fig. 4. Species distribution curves for a 1:2 metal to ligand molar ratio of (a) Zn-**1**, (b) Zn-**2** and (c) Zn-**3** systems at 25 °C and $I = 0.1$ mol dm^{-3} in 10% 1,4-dioxane in water.

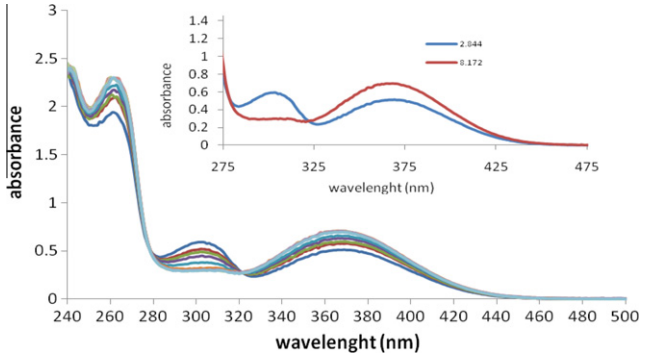


Fig. 5. Absorption spectra for 5-amino-8-methyl-4*H*-chromen-4-one at various pH (2.844–8.172) conditions, $c = 2.10 \times 10^{-4}$ mol dm^{-3} in 10% 1,4-dioxane in water, $I = 0.1$ mol dm^{-3}.

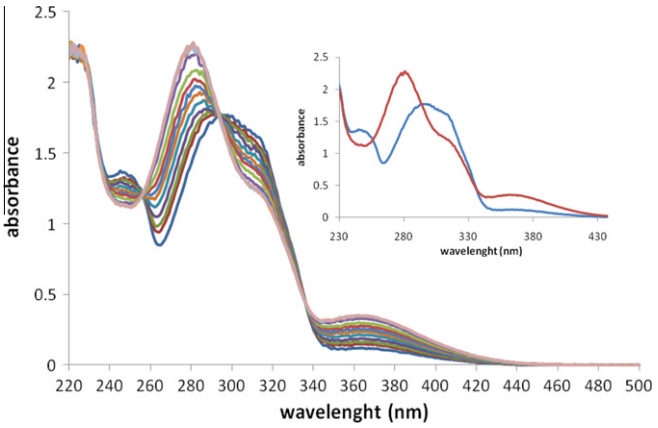


Fig. 6. Absorption spectra of 6-amino-2-phenyl-4*H*-chromen-4-one at various pH (2.756–10.079) conditions, $c = 2.62 \times 10^{-4}$ mol dm^{-3} in 10% 1,4-dioxane in water, $I = 0.1$ mol dm^{-3}.

photo-induced electron transfer (PET) due to the presence of a lone pair of electrons on the donor atom may cause quenching of the ligand fluorescence [20]. The chelation of the ligand to Zn(II) prevents the PET process and increases the rigidity of the ligand, and hence increases the fluorescence intensity.

The excitation and emission spectra of ligand **3** (7-aminoflavone) and complex **6** in dioxane-water solution are shown in Fig. 7. The absorption band of ligand **3** at 418 nm shifted to 410 nm for complex **6** (a blue-shift of 10 nm). Both compounds emitted fluorescence at the same wavelength, 505 nm. The coordination of the ligand with the zinc atom caused a significant enhancement of the fluorescence. As can be seen in Fig. 6, the complex with Zn(II) showed the same level of fluorescence with a 10 times lower concentration than that of the free ligand. The excitation and emission wavelengths were the same for compounds **3** and **6** in methanol solution, and the fluorescence enhancement was comparable to that in the dioxane-water solution.

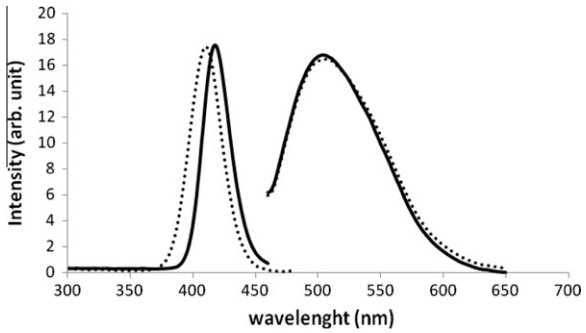


Fig. 7. The excitation and emission spectra of 7-amino-2-phenyl-4*H*-chromen-4-one (**3**) (solid line) and its complex (dashed line) with Zn(II) ions (**6**) in 10% 1,4-dioxane in water; [L] = 8.688×10^{-3} mol dm^{-3}, [ML_2Cl_2] = 6.55 × 10^{-4} mol dm^{-3}.

The fluorescence spectra of ligand **2** (6-aminoflavone) and the complex with Zn(II) (**5**) were recorded in 10% dioxane in water solution and in methanol, on excitation at 445 and 438 nm for the ligand and complex, respectively. A blue shift (7 nm) of the excitation band was observed, but the emission band maximum was at the same wavelength (555 nm) for both the ligand and the complex.

6-Aminoflavone (**2**) emitted fluorescence at a wavelength red-shifted by about 50 nm in relation to 7-aminoflavone (**3**). This suggests that the position of the amine group in the ligand molecules strongly affects their fluorescence properties. As in coumarins [35] and quinolinones [36], a donor substituent (e.g. methoxy, NH_2) in position 6 has a more pronounced bathochromic effect than that in position 7.

3.7. X-ray structure analysis of *4*

The molecular structure of complex **4** was determined by X-ray structure analysis. The corresponding details are summarised in Table 5 and selected geometrical parameters are gathered in Table 6. As shown in Fig. 8, the zinc centre of **4** is linked by two chlorido and two N-bound aminochromone ligands (**1**) in a strongly distorted tetrahedral configuration, with the dissymmetric point group C_2. Thus, the bond angle Cl–Zn–Cl_a of 117.17(3)° is much lar-

Table 5
Crystallographic data of Zn(II) complex **4**.

Net formula	$C_{20}H_{18}Cl_2N_2O_4Zn$
M_r (g mol^{-1})	486.66
Crystal size (mm)	0.35 × 0.12 × 0.12
T (K)	200(2)
Radiation	Mo Kα
Diffractometer	'Oxford XCalibur'
Crystal system	monoclinic
Space group	$C2/c$
a (Å)	12.8390(7)
b (Å)	17.6268(10)
c (Å)	8.8660(6)
α (°)	90
β (°)	102.184(6)
γ (°)	90
V (Å^3)	1961.3(2)
Z	4
D_{calc} (g cm^{-3})	1.64816(17)
μ (mm^{-1})	1.555
Absorption correction	Numerical
Transmission factor range	0.6306–0.8903
Reflections measured	5171
R_{int}	0.0359
Mean $\sigma(I)/I$	0.0747
θ Range	3.99–26.37
Observed reflections	1313
x, y (weighting scheme)	0.0284, 0
Hydrogen refinement	Constr
Reflections in refinement	1989
Parameters	133
Restraints	0
$R(F_{obs})$	0.0282
$R_w(F^2)$	0.0618
S	0.914
Shift/error$_{max}$	0.001
Maximum electron density (e Å^{-3})	0.381
Minimum electron density (e Å^{-3})	−0.364

Table 6
Selected structural parameters of complex **4**.

Bond lengths (Å)		*Bond angles (°)*		
Zn–Cl	2.2382(6)	Cl–Zn–N	115.20(5)	
Zn–N	2.048(2)	Cl–Zn–Cl$_a$	117.17(3)	
O1–C7	1.237(3)	Cl$_a$–Zn–N	100.00(5)	
O2–C5	1.379(3)	N–Zn–N$_a$	109.80(8)	
O2–C9	1.352(3)	Cl$_a$–Zn–N$_a$	115.20(5)	
N–C1	1.445(3)	Zn–N–C1	120.10(13)	
N–H	0.92	Zn–N–H	107	
C1–C2	1.378(3)	C1–N–N	107	
C1–C6	1.403(3)	O2–C5–C4	114.8(2)	
C2–C3	1.381(3)	O2–C9–C8	124.2(2)	
C3–C4	1.375(3)	C5–O2–C9	118.3(2)	
C4–C10	1.503(3)	C6–C7–C8	114.5(2)	
C4–C5	1.394(3)	O1–C7–C6	123.1(2)	
C5–C6	1.404(3)	O1–C7–C8	122.4(2)	
C6–C7	1.472(3)			
C7–C8	1.432(3)			
C8–C9	1.327(3)			
Torsion angles (°)				
Zn–N–C1–C2	−69.7(2)	C2–C1–C6–C7	−179.2(2)	
Zn–N–C1–C6	110.2(2)	C2–C1–C6–C5	0.6(3)	
N–C1–C6–C5	−179.2(2)	C9–O2–C5–C4	−179.0(2)	
N–C1–C6–C7	1.0(3)	C9–O2–C5–C6	0.2(3)	
Hydrogen bonds (Å, °)				
D–H···A	D–H	H···A	D···A	D–H···A
N–H11···O1	0.92	1.94	2.717(3)	141
N–H12···Cl$_b$	0.92	2.36	3.272(2)	172
C10–H10$_b$···01c	0.98	2.55	3.496(3)	162

Symmetry code: (a) 1 − x, y, 3/2 − z, (b) 1 − x, 1 − y, 1 − z, (c) ½ + x, ½ − y, −½ + z.

ger that that of N–Zn–N$_a$ (109.80(8)°). Both the mixed angles, however, N–Zn–Cl (115.20(5)°) and N$_a$–Zn–Cl (100.00(5)°) differ extremely from each other. The bond lengths Zn–Cl (2.2382(6) Å) and Zn–N (2.048(2) Å) are pairwise equal. The amino chromone ligand is bent off the Zn–N axis by the angle Zn–N–C1 of 120.10(13)°. Whereas the benzoic ring shows relatively equal C–C distances (1.389(3) Å), the quinoide ring exhibits two different sets of values (C6–C7 and C7–C8 1.472(3) and 1.432(3) Å), both contrary to the very short one of C8–C9 1.327(3) Å. The longest C–C bond is given by the single bond C4–C10 (1.503(3) Å). In comparison to the exocyclic C7–O1 carbonyl bond (1.237(3) Å), the two cyclic ones C5–O2 and C9–O2 (1.379(3) and 1.352(3) Å) are significantly longer. Both oxygen atoms O1 and O2 lie within the plane of the chromone ligand, as the torsion angles indicate. One strong *intra*molecular hydrogen bond (N–H11–O1) as well as two weaker *inter*molecular ones (N–H12–Cl$_b$ and C10–H10$_b$–O1$_c$) were found.

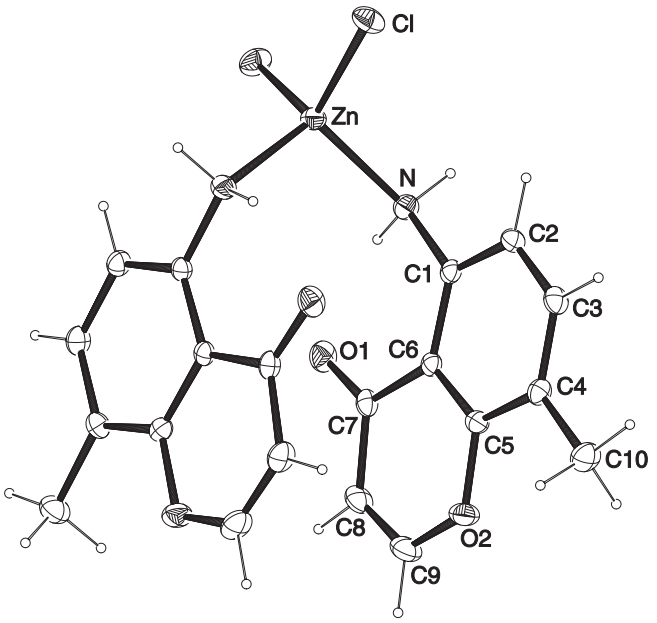


Fig. 8. An ORTEP drawing of the molecular structure of **4** with the atom numbering and 30% probability ellipsoids. The non-labelled atoms of the C_2-symmetric molecule are generated by the symmetry operation $x + 1$, y, $-z + 3/2$.

4. Conclusions

In this paper we have conducted the synthesis and investigated the spectroscopic properties and X-ray structure of Zn(II) complexes. The structure of the complexes was confirmed by spectral and elemental analyses. All the ligands created neutral complexes of the general type ML_2Cl_2.

The results of potentiometric studies indicate that both the ML and ML_2 Zn(II) complexes with ligands **1** and **2** exhibited similar stability in polar (10% 1,4-dioxane in water) solution. Ligand **3** only formed one complex (ML) which had a lower stability than the respective complexes of ligands **1** and **2**. The formation of a precipitate above pH 5.5 prevented the formation of the ML_2 complex.

The fluorescence properties of ligands **1**–**3** and their Zn(II) complexes **4**–**6** were measured in polar solvents at room temperature. The most significant fluorescence enhancement after Zn(II) complexation was exhibited by 7-aminoflavone (complex **6**).

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Appendix A. Supplementary data

CCDC 800462 contains the supplementary crystallographic data for complex **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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