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Synthesis, luminescence and host–guest chemistry of copper(I) and zinc(II) complexes of dppzc (dppzc = dipyrido[3,2-a:2′,3′-c]phenazo-15-crown-5)☆

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Abstract

Copper(I) and zinc(II) complexes containing dipyrido[3,2-a:2′,3′-c]phenazo-15-crown-5 (dppzc) ligand have been synthesized and characterized, and their photophysics and electrochemistry studied. The crystal structure of $[Zn(SC_6H_4{-}CH_3\text{-}p)_2(dppzc)]$ (**2**) has been determined. The ion-binding properties of these complexes towards alkali metal ions have also been described. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Crystal structure; Luminescence; Electrochemistry; Ion-binding

1. Introduction

The fruitful discovery of crown ether ligands [1] led to numerous studies on cyclic and cage compounds that are capable of binding cations, anions or neutral molecules in their cavities and have led to the development of new fields in current chemistry such as host–guest and supramolecular chemistry [2] since Pedersen's initial observations [3] on the affinity of macrocyclic polyethers to alkali and alkaline earth cations. Apart from the successful applications of metal ion probes, pH sensors and molecular recognitions [4–7] in this field, crown ethers have also been used for the photocontrol of ion extraction and transport and construction of chemical switches [8]. However, most of the work has been confined to the organic host systems [3,9]. With the aim of advancing chemical sensor technology, considerable recent attention has been focused on the design of inorganic hosts with the awareness of interesting photophysical and metal ion-binding properties [10]. In this work, efforts have been made to study the binding of copper(I) and zinc(II) crown ether-containing complexes for lithium and sodium metal ions. The binding properties of these complexes were evaluated as a function of crown ether size and solvent polarity.

Dipyrido[3,2-a:2′,3′-c]phenazine (dppz) is an interesting ligand that has attracted growing attention in recent years [11a–c]. Its extended π-conjugation and planarity of the molecule have made it a promising candidate as a DNA intercalator. Recent works have focused on the syntheses of metal complexes containing dppz ligand to function as metallointercalators and DNA photoswitch [11]. Recently, we prepared a crown ether-containing dppz ligand, dipyrido[3,2-a:2′,3′-c]phenazo-15-crown-5 (dppzc), and studied the ion-binding properties of its ruthenium (II) complexes [12]. As an extension of our previous works on the binding studies of ruthenium polypyridine complexes with crown ether pendants, herein are reported the syntheses and characterization of copper(I) and zinc(II) dppzc complexes (Scheme 1). The electronic absorption, luminescence, electrochemistry and binding properties of these complexes towards metal cations have also been studied.

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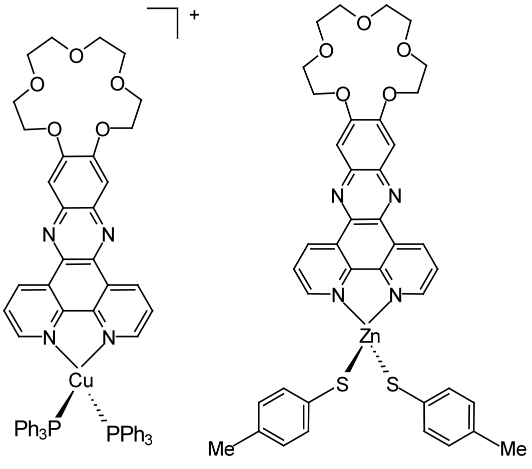

(1) **(2)**

Scheme 1. Schematic drawing of copper(I) and zinc(II) complexes of dppzc.

2. Experimental

2.1. Reagents and materials

p-Thiocresol was obtained from Lancaster Synthesis Ltd. Zinc acetate dihydrate was obtained from Peking Reagent. Dipyrido[3,2-a:2′,3′-c]phenazine (dppz) [13], dppzc [12], $[Cu(PPh_3)_2(MeCN)_2]PF_6$ [14a] and $[Cu(PPh_3)_2(dppz)]PF_6$ [14b] were prepared by a published procedure. Tetra-n-butylammonium hexafluorophosphate ($^nBu_4NPF_6$) (Lancaster, 98%) was purified by recrystallization from hot ethanol three times and vacuum dried for over 24 h before use. Sodium perchlorate (Aldrich, 98%), lithium perchlorate (Aldrich, 99.9%) and potassium hexafluorophosphate (Strem, 99.5%) were recrystallized from hot methanol and vacuum dried before use. Acetonitrile was distilled over calcium hydride before use. Dichloromethane was washed with conc. H_2SO_4 and distilled over calcium hydride. All other reagents were of analytical grade and were used as received.

2.2. Synthesis of copper(I) and zinc (II) complexes of dppzc ligand

2.2.1. Synthesis of $[Cu(PPh_3)_2(dppzc)]PF_6$ (**1**)

This was prepared by modification of a literature procedure for related copper(I) complexes [15]. To a solution of dppzc (47 mg, 0.1 mmol) in dichloromethane (5 ml) was added a solution of $[Cu(PPh_3)_2(MeCN)_2]PF_6$ (120 mg, 0.1 mmol) in dichloromethane (5 ml) and the mixture was stirred at room temperature (r.t.) for 1 h during which the solution changed from colorless to yellow. After evaporation of the solvent, the residue was dissolved in dichloromethane and diffusion of diethyl ether vapor into its concentrated solution gave **1** as yellow crystals. Yield: 70 mg (62%). ^1H NMR (300 MHz, $CDCl_3$): δ 3.82 (m, 8H, CH_2OCH_2), 4.05 (t, 4H, $J = 7.8$ Hz, $C_6H_2OCH_2CH_2$), 4.45 (t, 4H, $J = 3.9$ Hz, $C_6H_2OCH_2$), 7.25 (m, 24H, PPh_3), 7.35 (m, 6H, PPh_3), 7.68 (s, 2H, C_6H_2), 8.02 (q, 2H, $J = 13.1$ Hz, pyridyl H's), 9.10 (dd, 2H, $J = 1.9$ Hz, $J = 4.8$ Hz, pyridyl H's), 9.70 (dd, 2H, $J = 1.4$ Hz, $J = 6.9$ Hz, pyridyl H's *ortho* to N). Positive ESI MS (*m*/*z*): 1058 $\{M\}^+$, 797 $\{M-PPh_3\}^+$. *Anal*. Calc. for $C_{62}H_{54}F_6N_4O_5P_3Cu$: C, 61.77; H, 4.52; N, 4.65. Found: C, 61.69; H, 4.43; N, 4.41%.

2.2.2. Synthesis of $[Zn(SC_6H_4-CH_3\text{-}p)_2(dppzc)]$ (**2**)

This was prepared by modification of a literature procedure for related zinc(II) complexes [16]. A solution of dppzc (129 mg, 0.27 mmol) in MeOH (5 ml) was added dropwise to a mixture of $Zn(OAc)_2 \cdot 2H_2O$ (60 mg, 0.27 mmol) and *p*-thiocresol (67 mg, 0.54 mmol) in MeOH (10 ml) and the mixture was stirred at r.t. for 4 h during which the solution changed from colorless to yellow. The isolation of the complex was similar to that for **1** to give **2** as yellow crystals. Yield: 105 mg (49%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.83 (s, 6H, CH_3), 3.75 (m, 8H, CH_2OCH_2), 4.00 (t, 4H, $J = 7.9$ Hz, $C_6H_2OCH_2CH_2$), 4.45 (t, 4H, $J = 7.9$ Hz, $C_6H_2OCH_2$), 6.45 (d, 4H, $J = 7.9$ Hz, aryl H *ortho* to S), 7.00 (d, 4H, $J = 8.0$ Hz, aryl H *meta* to S), 7.50 (s, 2H, C_6H_2), 7.95 (q, 2H, $J = 13.1$ Hz, pyridyl H's), 8.98 (dd, 2H, $J = 1.4$ Hz, $J = 4.5$ Hz, pyridyl H's), 9.65 (dd, 2H, $J = 1.5$ Hz, $J = 6.8$ Hz, pyridyl H's *ortho* to N). Positive FAB MS (*m*/*z*): 659 $\{M-SC_6H_4-CH_3\text{-}p\}^+$. *Anal*. Calc. for $C_{40}H_{38}N_4O_5S_2Zn$: C, 60.02; H, 4.88; N, 7.14. Found: C, 60.17; H, 4.76; N, 6.82%.

2.2.3. Synthesis of $[Zn(SC_6H_4-CH_3\text{-}p)_2(dppz)]$ (**3**)

Complex **3** was prepared similarly to **2** except dppz was used in place of dppzc to give yellow crystals. Yield: 113 mg (70%). ^1H NMR (300 MHz, $CDCl_3$): δ 1.81 (s, 6H, CH_3), 6.45 (d, 4H, $J = 7.8$ Hz, aryl H *ortho* to S), 6.98 (d, 4H, $J = 6.4$ Hz, aryl H *meta* to S), 8.02 (m, 4H, C_6H_4), 8.40 (q, 2H, $J = 17.3$ Hz, pyridyl H's), 9.02 (dd, 2H, $J = 3.4$ Hz, $J = 6.2$ Hz, pyridyl H's), 9.73 (dd, 2H, $J = 6.7$ Hz, $J = 9.7$ Hz, pyridyl H's *ortho* to N). Positive FAB MS (*m*/*z*): 469 $\{M-SC_6H_4-CH_3\text{-}p\}^+$. *Anal*. Calc. for $C_{32}H_{24}N_4S_2Zn$: C, 64.70; H, 4.07; N, 9.43. Found: C, 64.48; H, 3.91; N, 9.20%.

2.3. Crystal structure determination

Single crystals of **2** were obtained by vapor diffusion of diethyl ether into a concentrated dichloromethane solution of the complex.

Crystal data for **2**: $[C_{40}H_{38}N_4O_5S_2Zn]$, $M = 784.26$, monoclinic, space group $P2_1/c$ (No. 14), $a = 12.796(2)$, $b = 12.411(2)$, $c = 23.304(3)$ Å, $\beta = 100.90(2)°$, $U = 3534(1)$ Å^3, $Z = 2$, $D_{calc} = 1.433$ g cm^{-3}, μ(Mo Kα) $= 8.42$ cm^{-1}, $F(000) = 1632$, $T = 301$ K. A pale yellow crystal of dimensions 0.35 × 0.15 × 0.07 mm mounted on a glass fibre was used for data collection at 28 °C on a MAR diffractometer with a 300 mm image plate detector using graphite monochromatized Mo Kα radiation ($\lambda = 0.71073$ Å). 6562 unique reflections were obtained from a total of 28360 measured reflections ($R_{\text{int}} = 0.062$). 4076 reflections with $I > 3\sigma(I)$ were considered observed and used in the structural analysis. The space group was uniquely determined based on systematic absences and the structure was solved by direct methods (SIR92) [17a] and expanded by Fourier method and refinement by full-matrix least-squares using the software package TEXSAN [17b] on a Silicon Graphics Indy Computer. Convergence for 467 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.020F_o^2)^2]$ for 4076 reflections with $I > 3\sigma(I)$ was reached at $R = 0.052$ and $wR = 0.072$ with a goodness-of-fit of 2.22 $(\Delta/\sigma)_{\max} = 0.05$ except for the disordered C atoms. The final difference Fourier map was featureless, with maximum positive and negative peaks of 0.93 and 0.32 e Å^{-3}, respectively.

2.4. Physical measurements and instrumentation

^{1}H NMR spectra were recorded on a Bruker DPX-300 FT-NMR spectrometer in $CDCl_3$ at 298 K and chemical shifts were reported relative to Me_4Si. Positive ion FAB MS were recorded on a Finnigan MAT95 mass spectrometer and positive ESI MS on a Finnigan LCQ mass spectrometer. Elemental analyses of the new complexes were performed on a Carlo Erba 1106 elemental analyzer at the Institute of Chemistry, Chinese Academy of Sciences.

UV–Vis absorption spectra in acetonitrile, acetone or methanol were obtained on a Hewlett–Packard 8452A diode array spectrophotometer, and steady-state excitation and emission spectra on a Spex Fluorolog 111 spectrofluorimeter. The electronic absorption spectral titration for binding constant determination was performed with a Hewlett–Packard 8452A diode array spectrophotometer at 25 °C which was controlled by a Lauda RM6 compact low-temperature thermostat. Supporting electrolyte (0.1 mol dm^{-3} $^nBu_4NPF_6$) was added to maintain the ionic strength of the sample solution constant during the titration in order to avoid any changes arising from a change in the ionic strength of the medium. This is especially important for complexes showing a charge transfer transition since their absorption characteristics are usually rather sensitive to the nature of the solution medium.

Cyclic voltammetric measurements were performed by using a CH Instruments, Inc. CHI 620 electrochemical analyzer interfaced to an IBM-compatible PC. The electrolytic cell used was a conventional two-compartment cell. The salt bridge of the reference electrode was separated from the working electrode compartment by a Vycor glass bridge. A Ag–$AgNO_3$ (0.1 mol dm^{-3} in CH_3CN) reference electrode was used. The ferrocenium–ferrocene couple ($FeCp_2^{+/0}$) was used as the internal reference in the electrochemical measurements [18a]. The working electrode was a glassy carbon (Atomergic Chemetals V25) electrode with a platinum foil acting as the counter electrode. Treatment of the electrode surfaces was as reported previously [18b].

Binding studies using UV–Vis measurement were performed by adding aliquots of the metal salt to a solution of the copper (I) and zinc(II) crown ether-containing complexes in the presence of supporting electrolyte (0.1 mol dm^{-3} $^nBu_4NPF_6$) while maintaining the concentration of the metal complexes constant. Binding constants for 1:1 complexation were obtained by a nonlinear least-squares fit [19a] of the absorbance (X) versus the concentration of the metal ion added (c_M) according to Eq. (1):

$$X = X_0 + \frac{X_{\lim} - X_0}{2c_0}[c_0 + c_M + 1/K_S - [(c_0 + c_M + 1/K_S)^2 - 4c_0c_M]^{1/2}] \tag{1}$$

where X_0 and X are the absorbance of the complex at a selected wavelength in the absence and presence of the metal cation, respectively, c_0 is the concentration of the complex, c_M is the concentration of the metal cation, $X_{\lim}$ is the limiting value of absorbance in the presence of excess metal ion and K_S is the stability constant. The experiments for binding studies were performed in duplicate and the average binding constants obtained.

For proton NMR titration experiments, a solution of Cu(I) crown ether-containing complex was prepared. The initial ^{1}H NMR spectrum was recorded and aliquots of metal cations were added using a microsyringe. After each addition and mixing, the spectrum was recorded and changes in the chemical shift of certain protons were noted. The results of the experiment were expressed as a plot of chemical shift as a function of the amount of cation added, which was subjected to analysis by curve fitting since the shape of the titration curve is indicative of the stability constant for the complex formation. The computer program EQNMR [19b] was used which requires a knowledge of the concentration of each component and the observed chemical shift for each data point.

3. Results and discussion

All the synthesized copper(I) and zinc(II) crown complexes have been well characterized by ^{1}H NMR spectroscopy and positive ion FAB MS or ESI MS and gave satisfactory elemental analyses. The coordination of ligands to the metals has been confirmed by the down-field shift of ^{1}H NMR signals for those protons adjacent to nitrogen atoms (dppzc, 9.57 ppm; **1**, 9.70 ppm; **2**, 9.65 ppm; dppz, 9.63 ppm; **3**, 9.73 ppm). The X-ray crystal structure of **2** has also been determined.

3.1. Crystal structure

The perspective drawing of **2** with atomic numbering is depicted in Fig. 1. The crystallographic data of **2** are summarized in Table 1. Selected bond distances (Å) and bond angles (°) are displayed in Table 2. The Zn(II) center adopts a distorted tetrahedral geometry with a S(1)–Zn(1)–S(2) angle of 130.15(5)° and a N(1)–Zn(1)–N(4) angle of 79.0(2)°. The average bond distances of Zn–S and Zn–N are 2.268(7) and 2.108(4) Å, respectively, which are found to be typical of related systems [16b,20]. For complex **2**, π–π stacking interactions between the aromatic rings of thiolate ligand and dppzc are observed with the interplanar separations in the range of 3.09–3.60 Å.

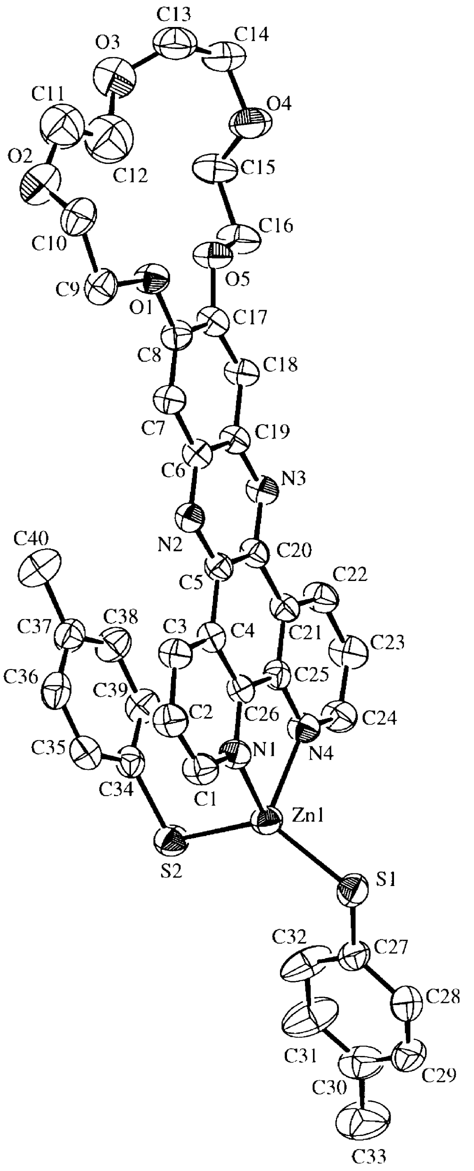

Fig. 1. Perspective drawing of **2** with the atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 40% probability level.

Table 1
Crystal and structure determination data for **2**

Formula	[$C_{40}H_{38}N_4O_5S_2Zn$]
Formula weight	784.26
T (K)	301
a (Å)	12.796(2)
b (Å)	12.411(2)
c (Å)	23.304(3)
β (°)	100.90(2)
V (Å^3)	3534(1)
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
Z	2
F(000)	1632
D_{calc} (g cm^{-3})	1.433
λ, Å (graphite monochromated, Mo Kα)	8.42
Number of data collected	28360
Number of unique data	6562
Number of data used in refinement, m	4076
Number of parameters refined, p	467
R [a]	0.052
R_w [a]	0.072
Goodness-of-fit, S	2.22
Maximum shift, $(\Delta/\sigma)_{max}$	0.05
Residual extrema in final different map (e Å^{-3})	+0.93, −0.32

[a] $w = 4\ F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.020F_o^2)^2]$ with $I \geq 3\sigma(I)$.

Table 2
Selected bond distances (Å) and bond angles (°) for **2**

Bond distances			
Zn(1)–S(1)	2.257(1)	Zn(1)–S(2)	2.280(2)
Zn(1)–N(1)	2.115(4)	Zn(1)–N(4)	2.101(4)
S(1)–C(27)	1.764(6)	S(2)–C(34)	1.781(5)
O(1)–C(8)	1.369(5)	O(1)–C(9)	1.436(6)
O(5)–C(16)	1.442(6)	O(5)–C(17)	1.354(5)
Bond angles			
S(1)–Zn(1)–S(2)	130.15(5)	S(1)–Zn(1)–N(1)	115.4(1)
S(1)–Zn(1)–N(4)	110.7(1)	S(2)–Zn(1)–N(1)	104.5(1)
S(2)–Zn(1)–N(4)	105.0(1)	N(1)–Zn(1)–N(4)	79.0(2)
Zn(1)–S(1)–C(27)	107.3(2)	Zn(1)–S(2)–C(34)	98.3(2)
Zn(1)–N(1)–C(1)	128.2(3)	Zn(1)–N(1)–C(26)	111.6(3)
Zn(1)–N(1)–C(24)	128.1(3)	Zn(1)–N(4)–C(25)	112.4(3)

3.2. Electronic absorption and luminescence properties

The electronic absorption spectrum of complex **1** shows a higher energy band at ≈260–300 nm and a vibronic-structured low-energy absorption band at ≈384–408 nm in both acetonitrile and dichloromethane solutions. The low-energy band with vibrational progressional spacings of ≈1260–1290 cm^{-1}, typical of the skeletal vibrational mode of the aromatic ring in the excited state, is tentatively assigned as metal-to-ligand charge transfer [MLCT, $d_\pi(Cu) \rightarrow \pi^*(dppzc)$] transition with some mixing of an intraligand [IL, $\pi \rightarrow \pi^*$ (dppzc) or $n \rightarrow \pi^*$ (dppzc)] transition, as similar assignments have been suggested in other related systems [15]. Complex **2** also displays similar vibronic-structured low-energy absorption bands at approximately 384–404 nm in the electronic absorption spectra in both acetonitrile and dichloromethane solutions. The close resemblance of the low-energy vibronic bands in complexes **1** and **2** is suggestive of an electronic transition that is dominated by the IL transition of dppzc. Similar to other related Zn(II) complexes with thiolate and diimine ligands [16,20c,21], the low-energy bands observed in the visible region of the spectrum of **2** are likely to involve some mixing of a ligand-to-ligand charge transfer [LLCT, $p_\pi(SR^-) \rightarrow \pi^*(dppzc)$] character. The electronic absorption spectral data are collected in Table 3.

Upon excitation of complexes **1** and **2** in the solid state, glass, acetonitrile and dichloromethane solutions at $\lambda > 350$ nm, emission bands at ≈ 520–615 nm are observed (Table 3). The emissions are tentatively assigned as originating from the $^3IL/^3MLCT$ and $^3IL/^3LLCT$ mixed states for **1** and **2**, respectively. Fig. 2 shows the emission spectrum of **1** in the solid state at 77 K. The inset shows the electronic absorption spectrum in acetonitrile at 298 K. The close resemblance of the emission band between **1** and **2** is again suggestive of the domination of an IL character for their origin. A vibrational progressional spacing of ≈ 1300–1354 cm^{-1}, typical of the skeletal vibrational mode of the aromatic ring in the ground state, together with the emission pattern in the solid state and glass at 77 K appearing as a mirror image of the absorption band, is in accord with an IL assignment, probably with some mixing of a ^3MLCT character in **1** and a ^3LLCT character in **2**.

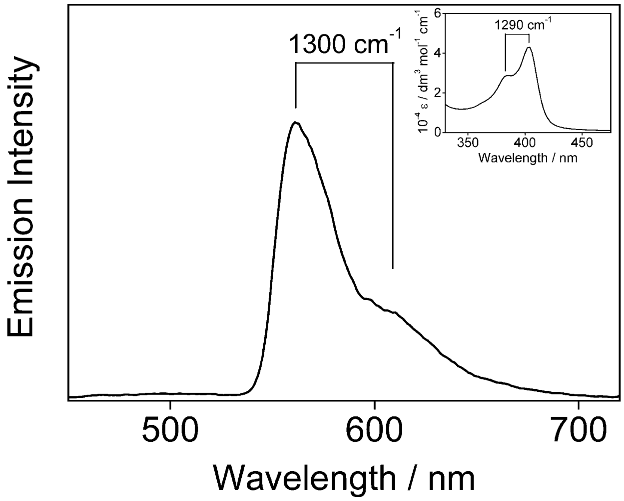

Fig. 2. Emission spectrum of **1** in the solid state at 77 K. The inset shows an electronic absorption spectrum in acetonitrile at 298 K.

3.3. Cation binding studies

Upon addition of lithium ions to **1** and **2** in acetonitrile solution, an obvious electronic absorption spectral change was observed. The bands at ≈ 408 nm in **1** and 404 nm in **2** undergo a blue shift in energy with increasing lithium ion concentration. Similar changes were also observed upon addition of sodium ions. These shifts were attributed to the binding of the cations to the crown ether cavity as similar effects were absent for the crown-free analogues, $[Cu(PPh_3)_2(dppz)]PF_6$ and $[Zn(SC_6H_4-CH_3\text{-}p)_2(dppz)]$. The spectral changes were reversible on addition of an excess of free dppzc ligands to an acetonitrile solution of **1** and **2**. With K^+ ions, no satisfactory fits to Eq. (1) were obtained and no well-defined isosbestic points could be found in the electronic absorption spectral traces upon addition of potassium ions to a solution of both complexes, indicative of the formation of both 1:1 and 1:2 adducts in the solution mixture. The electronic absorption spectral traces of **2**

Table 3
Photophysical data for complexes **1** and **2**

Complex	Medium (T(K))	λ_{abs} (nm) (ε ($dm^3\ mol^{-1}\ cm^{-1}$))	λ_{em} (nm) (τ_0 (μs))
1	Solid (298)		554 (< 0.01)
	Solid (77)		535, 575sh [b]
	Glass (77) [a]		534, 572sh [b]
	CH_3CN (298)	260 (54,030), 290 (83,890), 384sh (28,450), 404 (42,700)	534sh (< 0.01)
	CH_2Cl_2 (298)	264 (43,130), 300 (68,560), 388sh (24,150), 408 (36,220)	615 (< 0.01)
2	Solid (298)		535 (< 0.01)
	Solid (77)		562, 608sh [b]
	Glass (77) [a]		524, 564sh [b]
	CH_3CN (298)	265 (7,150), 292 (9,660), 385sh (4,530), 403 (6,480)	520sh (< 0.01)
	CH_2Cl_2 (298)	295 (17,650), 388sh (6,430), 404 (11,720)	– [c]

[a] EtOH, MeOH = 4:1 (v/v).
[b] Vibronic-structured.
[c] Non-emissive.

on sequential addition of Li^+ to an acetonitrile solution of the complex are shown in Fig. 3. The inset in Fig. 3 shows the changes of absorbance at 404 nm as a function of lithium ion concentration. The curve shows a gradual decrease in absorbance on increasing the cation concentration, reaching saturation at higher cation concentration. The binding constants of **1** and **2** are tabulated in Table 4.

The effect of solvents on the binding abilities was investigated using identical methods at 298 K in three different solvents with different polarity: acetonitrile, acetone and methanol. The choice of solvents was limited by the solubility of the complex, the alkali metal ions and the bound species. It is found that the binding constants for lithium and sodium ions in different solvents are in the order of acetonitrile > acetone > methanol. The binding constants of **1** for Li^+ and Na^+ ions in acetonitrile and acetone are in the order: $Li^+ > Na^+$ and $Na^+ > Li^+$, respectively.

These findings are in line with that commonly observed for benzo-15-crown-5 type compounds in MeCN [9]. This is in close resemblance to the order of charge density of the cations: $Li^+ > Na^+$. The small size of the lithium ion bears the highest charge density while sodium cations of lower charge density also give rise to large binding constant as the hole size of the crown cavity would best fit that of sodium ions [3d].

Unlike the case of acetonitrile, the selectivity of metal ion binding to the crown cavity in methanol was higher in Na^+ than that of Li^+. Methanol is of the highest polarity among the three solvents studied. The extent of solvation by solvent molecules is larger for Li^+ ions than that for Na^+ ions. In view of this, Li^+ cations are well-solvated by methanol solvent molecules, and thus seeking a binding site in the crown cavity was no longer a necessity to stabilize the cations in methanol and, therefore, the binding constants of **1** for Li^+ ions in acetonitrile and acetone would be larger than that in the protic methanol solvent. The binding constants of the metal cations to complexes **1** and **2** could not be determined using emission spectrophotometric method due to insignificant changes in the emission intensities upon addition of metal ions. The stability constants obtained by ^1H NMR spectroscopic method are comparable to those determined using UV–Vis spectrophotometric method for complex **1** in acetonitrile, acetone and methanol (Table 4). Since complex **2** is not very soluble in acetone and methanol, the effect of solvents on the binding abilities in this complex has not been investigated.

Table 4
Binding constants of complexes **1** and **2** for alkali metal ions in different solvents (0.1 mol dm^{-3} $^nBu_4NPF_6$) at 298 K

		log K_s	
Complex	Medium	Li^+	Na^+
1	MeCN	3.37 ± 0.02 [a]	2.72 ± 0.04 [a]
		3.07 ± 0.01 [b]	3.00 ± 0.01 [b]
	Acetone	1.97 ± 0.01 [a]	2.51 ± 0.02 [a]
		1.75 ± 0.01 [b]	2.41 ± 0.01 [b]
	MeOH	– [c]	1.58 ± 0.03 [a]
			1.66 ± 0.01 [b]
2	MeCN	3.76 ± 0.02 [a]	3.36 ± 0.02 [a]

[a] From UV–Vis spectrophotometric method.
[b] From ^1H NMR spectroscopic method.
[c] Cannot be determined.

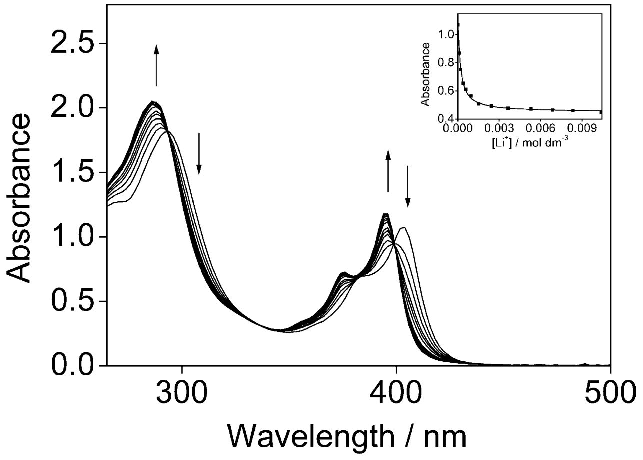

Fig. 3. The electronic absorption spectral traces of **2** (4.7×10^{-5} mol dm^{-3}) in acetonitrile (0.1 mol dm^{-3} $^nBu_4NPF_6$) upon addition of Li^+ at 298 K. The inset shows a plot of absorbance versus $[Li^+]$ monitored at $\lambda = 404$ nm (■) and its theoretical fit (—).

3.4. Electrochemical properties

Fig. 4 depicts the cyclic voltammograms of **1** in acetonitrile (0.1 mol dm^{-3} $^nBu_4NPF_6$). The electrochemical data are summarized in Table 5. The cyclic voltammograms of **1** and **2** display a quasi-reversible reduction couple at −1.31 and −0.91 V versus SCE, respectively, corresponding to the reduction of the dppzc ligand. An irreversible oxidation wave occurs at +1.25 V versus SCE in **1**, tentatively assigned as the metal-based oxidation, similar to related systems [15]. For **2**, the irreversible and quasi-reversible oxidation couples at +1.60 to +1.87 V versus SCE are likely to be derived from the thiolate ligand-centered oxidations [21c].

The cation recognition properties of **1** were further demonstrated by addition of Na^+ into an acetonitrile (0.1 mol dm^{-3} $^nBu_4NPF_6$) solution of the complexes. Electrochemical changes were observed and included in Table 5. It is interesting to note that changes occurred in the potential of the crown-based reduction couples upon addition of metal cations, with no obvious changes in the oxidation waves. The crown-based reduction couple was shifted anodically. The anodic shift observed may

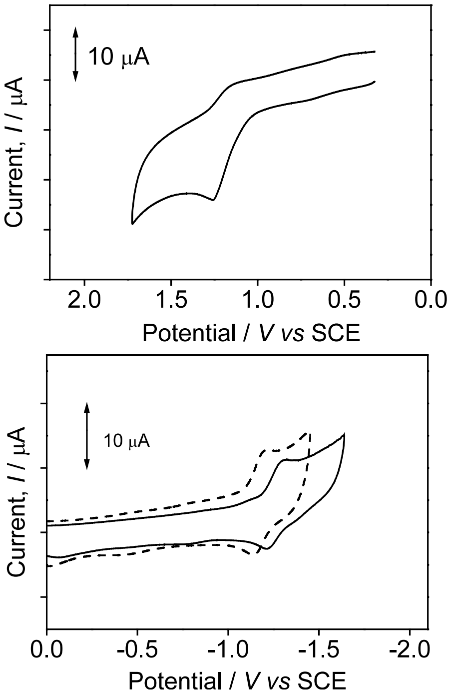

Fig. 4. Cyclic voltammograms showing (a) the oxidation (scan rate, 100 mV s^{-1}) and (b) reduction (scan rate, 100 mV s^{-1}) of **1** in acetonitrile (0.1 mol dm^{-3} $^{n}Bu_4NPF_6$) in the absence of Na^+ ions (solid line) and in the presence of Na^+ ions (dashed line).

Table 5
Electrochemical data for complexes **1** and **2**

Complex	Oxidation, $E_{1/2}$ [a] or E_{pa} [b](V vs. SCE), ($E_{1/2}$ in Na^+) [c]	Reduction, $E_{1/2}$ [a](V vs. SCE), ($E_{1/2}$ in Na^+) [c]
1	+1.25 [b] (+1.24) [c]	−1.31 (−1.21) [c]
2	+1.87 [a]	−0.91
	+1.60 [b]	

In acetonitrile (0.1 mol dm^{-3} $^{n}Bu_4NPF_6$). Working electrode, glassy carbon; ΔE_p of Fc^+–Fc ranges from 63 to 64 mV; scan rate, 100 mV s^{-1}.

[a] $E_{1/2} = (E_{pa} + E_{pc})/2$ where E_{pa} and E_{pc} are the anodic and cathodic peak potentials of the quasi-reversible reduction and oxidation couples.

[b] Anodic peak potential of the irreversible oxidation wave.

[c] $E_{1/2}$ value vs. SCE in the presence of $NaClO_4$ in acetonitrile (0.1 mol dm^{-3} $^{n}Bu_4NPF_6$).

probably be attributed to the binding of cations into the crown cavity as similar observations have been reported in other crown compounds [12,22]. Moreover, such shift was absent in similar studies with the crown-free analogue, $[Cu(PPh_3)_2(dppz)]PF_6$. This is expected since the metal cations bound to the crown pendant would act as an electron withdrawing group, giving rise to an increased ease of the diimine-crown reduction. The cyclic voltammograms of **1** in the presence of Na^+ ions are depicted in Fig. 4.

4. Conclusion

$[Cu(PPh_3)_2(dppzc)]PF_6$ **1** and $[Zn(SC_6H_4{-}CH_3\text{-}p)_2(dppzc)]$ **2** have been successfully synthesized. The electronic absorption, emission, electrochemical and binding properties of these systems have been studied. The crystal structure of $[Zn(SC_6H_4{-}CH_3\text{-}p)_2(dppzc)]$ has also been determined. The low energy absorptions of the copper(I) and zinc(II) dppzc complexes were assigned as predominantly intraligand [IL, $\pi(L) \rightarrow \pi^*(L)$ or $n \rightarrow \pi^*(L)$] transitions, probably with some mixing of a MLCT and LLCT character in the copper(I) and zinc(II) complexes, respectively. The binding of alkali metal cations by the cavity of the crown ether-containing complexes has been investigated by electronic absorption spectrophotometry, ^1H NMR spectroscopy and electrochemical measurements.

5. Supplementary material

Crystallographic data for the structural analysis for complex **2** have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 182397. Copies of this information may be obtained from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1233-336 033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk.

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