Synthesis, photophysics, electrochemistry and binding studies of zinc(II) dithiolate crown complexes

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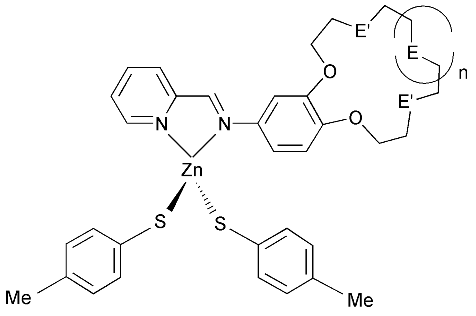
A series of zinc(II) dithiolate complexes containing ligands with benzo-15-crown-5 (dic), benzo-18-crown-6 (dic-18-6), 10-thiabenzo-15-crown-5 (dic-S), 10-selenabenzo-15-crown-5 (dic-Se) and 7,10,13-trithiabenzo-15-crown-5 (dic-3S) moieties have been synthesized and characterized, and their photophysics and electrochemistry studied. The metal ion-binding properties have been investigated by electronic absorption, emission and ^{1}H NMR spectroscopy. The X-ray crystal structure of [Zn(SC$_6$H$_4$-CH$_3$-*p*)$_2$(dic-3S)] (**5**) has also been determined.

Host-guest chemistry has been attracting much attention in the past two decades, which has led to a revival of interest in crown ether chemistry. Numerous studies have been performed that are reported in many papers and summarized in reviews and books.[1,2] Crown ethers with only hard oxygen atoms on the polyether cavities are used as 'probes' for alkali and alkaline earth metals, some other metal ions, oxonium ions, protonated amines including amino acids, and some neutral rod-like molecules such as acetonitrile.[3] Recently, increasing attention has been paid to variation of the donor atoms such as sulfur or selenium in place of the well-known all-oxygen combination in order to tune the crown ether cation binding ability.[4] Although there have been numerous reports on the complexation of alkali and alkaline earth metal ions,[2a,3] corresponding studies on the complexation of transition or late transition metal cations with acyclic or cyclic polythioethers are relatively less extensive. However, excellent examples of efficient ligands designed for these soft metal ions have been reported.[4,5]

In recent years there has been a growing interest in the study of fluorescent probes for soft metal ions, in particular the group IIB metal ions such as Zn^{2+} and Cd^{2+}.[6a–c] The biological activities of these ions are important. For example, zinc is a vital component in many cellular processes.[6d] The Zn^{2+} ion has the ability to modulate a variety of ion channels and may play an important role in gene expression and neurotransmission.[6e] Therefore, the availability of better and more specific probes for Zn^{2+} and Cd^{2+} would provide additional insights into the role played by these metal ions in neurobiology.

As a continuation of our studies on the copper(I) crown ether containing system,[7] herein we report the design and synthesis of a series of zinc(II) dithiolate crown ether containing complexes (Scheme 1) and the cation-binding properties of these complexes. Attempts have been made to tune their binding properties by varying the size as well as the donor properties of the crown ether cavity. Their electronic absorption, luminescence, electrochemistry and binding studies are also described.



n = 1, E = O, E' = O (**1**)
n = 2, E = O, E' = O (**2**)
n = 1, E = S, E' = O (**3**)
n = 1, E = Se, E' = O (**4**)
n = 1, E = S, E' = S (**5**)

Scheme 1 Schematic drawing of the zinc(II) dithiolate complexes with crown ether ligands.

Experimental

Reagents and materials

The ligands *N*-(2-pyridylmethylene)-4-aminobenzo-15-crown-5 (dic)[8a] and *N*-(2-pyridylmethylene)-4-aminobenzo-18-crown-6 (dic-18-6) were synthesized by modification of literature procedures.[8] 4′-(2″-Pyridinecarboxaldimino)benzo-10-thia-15-crown-5 (dic-S), 4′-(2″-pyridinecarboxaldimino)benzo-10-selena-15-crown-5 (dic-Se) and 4′-(2″-pyridinecarboxaldimino)benzo-7,10,13-trithia-15-crown-5 (dic-3S) were prepared according to previously reported procedures.[7]

p-Thiocresol was obtained from Lancaster Synthesis Ltd. Zinc tetrafluoroborate was purchased from Strem Chemicals Inc. Cadmium nitrate tetrahydrate was purchased from Acros. Zinc acetate dihydrate was obtained from Peking Reagent. Tetra-*n*-butylammonium hexafluorophosphate (^{n}Bu$_4$NPF$_6$;

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Lancaster, 98%) was purified by recrystallization with hot ethanol three times and vacuum dried for over 24 h before use. Sodium perchlorate (Aldrich, 98%), barium perchlorate (Aldrich, 97%), 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, after treatment with concentrated H_2SO_4 and aqueous $NaHCO_3$, was distilled over calcium hydride before use. All other reagents were of analytical grade and were used as received.

Synthesis

[Zn(SC$_6$H$_4$-CH$_3$-*p*)$_2$(dic)] (1). This complex was prepared according to a modified method.[9] A solution of dic (100 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 room temperature for 4 h during which the solution colour changed from colourless to yellow. After evaporation of the solvent under reduced pressure, the residue was dissolved in CH_2Cl_2 and diffusion of diethyl ether vapour into its concentrated solution gave **1** as yellow crystals. Yield: 110 mg (60%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.15 (s, 6H, CH_3), 3.80 (m, 10H, CH_2OCH_2), 3.98 (m, 4H, $C_6H_3OCH_2$, CH_2OCH_2), 4.18 (t, 2H, $J = 8.5$ Hz, $C_6H_3OCH_2$), 6.78 (d, 4H, $J = 7.6$ Hz, aryl H *ortho* to S), 6.82 (d, 1H, $J = 8.7$ Hz, C_6H_3), 7.08 (d, 4H, $J = 7.7$ Hz, aryl H *meta* to S), 7.15 (d, 1H, $J = 7.7$ Hz, C_6H_3), 7.35 (d, 1H, $J = 3.9$ Hz, C_6H_3), 7.58 (m, 2H, C_5H_4N), 8.00 (t, 1H, $J = 13.6$ Hz, C_5H_4N), 8.25 (s, 1H, C*H*=N), 8.65 (d, 1H, $J = 4.2$ Hz, C_5H_4N). Positive FAB-MS (*m*/*z*): 559 $\{M - SC_6H_4\text{-}CH_3\text{-}p\}^+$. Anal. calcd for $C_{34}H_{38}N_2O_5S_2Zn{\cdot}\frac{1}{2}H_2O$: C, 58.91; H, 5.67; N, 4.04; found: C, 58.89; H, 5.27; N, 3.61.

[Zn(SC$_6$H$_4$-CH$_3$-*p*)$_2$(dic-18-6)] (2). Complex **2** was prepared similarly to **1** except that dic-18-6 was used in place of dic to give yellow crystals. Yield: 125 mg (63%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.15 (s, 6H, CH_3), 3.75 (m, 14H, CH_2OCH_2), 4.00 (m, 4H, $C_6H_3OCH_2$, CH_2OCH_2), 4.20 (t, 2H, $J = 8.2$ Hz, $C_6H_3OCH_2$), 6.68 (d, 4H, $J = 7.6$ Hz, aryl H *ortho* to S), 6.83 (d, 1H, $J = 8.4$ Hz, C_6H_3), 7.10 (d, 4H, $J = 7.5$ Hz, aryl H *meta* to S), 7.18 (d, 1H, $J = 7.4$ Hz, C_6H_3), 7.35 (d, 1H, $J = 4.0$ Hz, C_6H_3), 7.50 (d, 1H, $J = 4.2$ Hz, C_5H_4N), 7.62 (t, 1H, $J = 12.6$ Hz, C_5H_4N), 8.00 (t, 1H, $J = 12.9$ Hz, C_5H_4N), 8.27 (s, 1H, C*H*=N), 8.62 (d, 1H, $J = 4.5$ Hz, C_5H_4N). Positive FAB-MS (*m*/*z*): 603 $\{M - SC_6H_4\text{-}CH_3\text{-}p\}^+$. Anal. calcd for $C_{36}H_{42}N_2O_6S_2Zn{\cdot}H_2O$: C, 57.94; H, 5.94; N, 3.75; found: C, 58.06; H, 5.96; N, 3.51.

[Zn(SC$_6$H$_4$-CH$_3$-*p*)$_2$(dic-S)] (3). This complex was prepared similarly to **1** except that dic-S was used in place of dic to give **3** as yellow crystals. Yield: 118 mg (62%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.15 (s, 6H, CH_3), 2.85 (m, 4H, CH_2SCH_2), 3.80 (m, 8H, CH_2OCH_2), 3.90 (t, 2H, $J = 12.6$ Hz, $C_6H_3OCH_2$), 4.15 (t, 2H, $J = 6.4$ Hz, $C_6H_3OCH_2$), 6.65 (d, 4H, $J = 7.5$ Hz, aryl H *ortho* to S), 6.85 (d, 1H, $J = 7.8$ Hz, C_6H_3), 7.08 (m, 5H, aryl H *meta* to S, C_6H_3), 7.38 (d, 1H, $J = 4.0$ Hz, C_6H_3), 7.60 (m, 2H, C_5H_4N), 8.00 (t, 1H, $J = 12.3$ Hz, C_5H_4N), 8.25 (s, 1H, C*H*=N), 8.62 (d, 1H, $J = 4.1$ Hz, C_5H_4N). Positive FAB-MS (*m*/*z*): 575 $\{M - SC_6H_4\text{-}CH_3\text{-}p\}^+$. Anal. calcd for $C_{34}H_{38}N_2O_4S_3Zn{\cdot}CH_2Cl_2$: C, 55.79; H, 5.29; N, 3.77; found: C, 55.96; H, 5.40; N, 3.61.

[Zn(SC$_6$H$_4$-CH$_3$-*p*)$_2$(dic-Se)] (4). This complex was prepared similarly to **1** except that dic-Se was used in place of dic to give **4** as orange crystals. Yield: 81 mg (40%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.15 (s, 6H, CH_3), 2.87 (m, 4H, CH_2SeCH_2), 3.85 (m, 8H, CH_2OCH_2), 3.90 (t, 2H, $J = 4.3$ Hz, $C_6H_3OCH_2$), 4.20 (t, 2H, $J = 6.4$ Hz, $C_6H_3OCH_2$), 6.70 (d, 4H, $J = 7.6$ Hz, aryl H *ortho* to S), 6.85 (d, 1H, $J = 7.8$ Hz, C_6H_3), 7.10 (m, 5H, aryl H *meta* to S, C_6H_3), 7.38 (d, 1H, $J = 4.0$ Hz, C_6H_3), 7.60 (m, 2H, C_5H_4N), 8.00 (t, 1H, $J = 12.0$ Hz, C_5H_4N), 8.25 (s, 1H, C*H*=N), 8.70 (d, 1H, $J = 4.0$ Hz, C_5H_4N). Positive FAB-MS (*m*/*z*): 623 $\{M - SC_6H_4\text{-}CH_3\text{-}p\}^+$. Anal. calcd for $C_{34}H_{38}N_2O_4S_2SeZn{\cdot}H_2O$: C, 53.37; H, 5.27; N, 3.66; found: C, 53.14; H, 5.28; N, 3.46.

[Zn(SC$_6$H$_4$-CH$_3$-*p*)$_2$(dic-3S)] (5). This complex was prepared similarly to **1** except that dic-3S was used in place of dic to give **5** as red crystals. Yield: 130 mg (65%). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.15 (s, 6H, CH_3), 2.90 (m, 6H, CH_2SCH_2), 3.05 (m, 6H, CH_2SCH_2), 4.00 (t, 2H, $J = 4.8$ Hz, $C_6H_3OCH_2$), 4.30 (t, 2H, $J = 5.2$ Hz, $C_6H_3OCH_2$), 6.70 (d, 4H, $J = 7.8$ Hz, aryl H *ortho* to S), 6.85 (d, 1H, $J = 7.9$ Hz, C_6H_3), 7.10 (m, 5H, aryl H *meta* to S, C_6H_3), 7.42 (d, 1H, $J = 4.2$ Hz, C_6H_3), 7.59 (m, 2H, C_5H_4N), 8.00 (t, 1H, $J = 12.9$ Hz, C_5H_4N), 8.28 (s, 1H, C*H*=N), 8.62 (d, 1H, $J = 4.2$ Hz, C_5H_4N). Positive FAB-MS (*m*/*z*): 613 $\{M - SC_6H_4\text{-}CH_3\text{-}p\}^+$. Anal. calcd for $C_{34}H_{38}N_2O_2S_5Zn{\cdot}H_2O$: C, 54.42; H, 5.37; N, 3.73; found: C, 54.64; H, 5.21; N, 3.34.

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 are reported relative to Me_4Si. Positive-ion FAB mass spectra were recorded on a Finnigan MAT95 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 spectra 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 determinations 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} ^{n}Bu$_4$NPF$_6$) was added to maintain the ionic strength of the sample solution constant during the titration in order to avoid any effects arising from a change in the ionic strength of the medium. This is especially important for complexes showing a LLCT 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.[10a] 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.[10b]

Binding studies using both UV-vis and emission spectrophotometric measurements were performed by adding aliquots of the metal salt to a solution of the zinc(II) dithiolate crown ether containing complexes in the presence of supporting electrolyte (0.1 mol dm^{-3} ^{n}Bu$_4$NPF$_6$) while maintaining the concentration of the zinc complexes constant. Binding constants for 1 : 1 complexation were obtained by a nonlinear least-squares fit[10c] of the absorbance (X) *versus* the concentration of the metal ion added (c_M) according to eqn. (1):

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

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.

For emission titration studies, eqn. (1) can be modified to give eqn. (2), written as:

$$I = I_0 + \frac{I_{lim} - I_0}{2c_0}[c_0 + c_M + 1/K_S - [(c_0 + c_M + 1/K_S)^2 - 4c_0c_M]^{1/2}] \qquad (2)$$

where I_0 and I are the emission intensities of the complex at a selected wavelength λ in the absence and presence of the metal cation, respectively, and I_{lim} is the limiting value of emission intensity in the presence of excess metal ion.

For proton NMR titration experiments, a solution of Zn(II) crown ether containing complex was prepared. The initial ^{1}H NMR spectrum was recorded and aliquots of metal cations were added using a micro-syringe. 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 complex formation. The computer program EQNMR[10d] was used, which requires a knowledge of the concentration of each component and the observed chemical shift for each data point.

Crystal structure determination

Single crystals of **5** were obtained by vapour diffusion of diethyl ether into a concentrated dichloromethane solution of the complex. A red crystal of dimensions 0.40 × 0.20 × 0.10 mm mounted on a glass fibre was used for data collection at 28 °C on a Rigaku AFC7R diffractometer with graphite monochromatized Mo-Kα radiation ($\lambda = 0.71069$ Å) using $\omega - 2\theta$ scans with ω-scan angle $(0.73 + 0.35 \tan\theta)°$ at a scan speed of 16.0 deg min^{-1} [up to 6 scans for reflections with $I < 15\sigma(I)$]. The total number of reflections was 5769, of which 5460 were unique and $R_{int} = 0.034$. There were 3871 observed reflections with $I > 3\sigma(I)$, used in the structural analysis. The space group was determined based on a statistical analysis of intensity distribution and the successful refinement of the structure, which was solved by Patterson methods, expanded by Fourier methods (PATTY)[11a] and refined by full-matrix least-squares using the software package TeXsan[11b] on a Silicon Graphics Indy computer. Convergence for 416 variable parameters by least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.050F_o^2)^2]$ was reached at $R = 0.048$ and $wR = 0.071$.

Crystal data for 5. [$C_{34}H_{38}N_2O_2S_5Zn \cdot \frac{1}{2}CH_3OH \cdot \frac{1}{2}C_2H_5OH$], $M = 771.42$, triclinic, space group $P\bar{1}$ (No. 2), $a = 11.270(3)$, $b = 11.754(3)$, $c = 15.670(4)$ Å, $\alpha = 100.07(3)$, $\beta = 98.45(3)$, $\gamma = 111.88(3)°$, $U = 1844(1)$ Å^3, $Z = 2$, $D_c = 1.39$ g cm^{-3}, μ(Mo-Kα) = 9.9 cm^{-1}, $T = 301$ K.

CCDC reference number 181895. See http://www.rsc.org/suppdata/nj/b1/b109497c/ for crystallographic data in CIF or other electronic format.

Results and discussion

The ligands dic, dic-18-6, dic-S, dic-Se and dic-3S were synthesized by the condensation reaction of the corresponding 4′-aminobenzocrown and 2-pyridinecarboxaldehyde in ethanol, modified from the procedure reported for *N*-(2-pyridylmethylene)-4-aminobenzo-15-crown-5;[8] the procedures of which have been reported previously.[7] Reaction of $Zn(OAc)_2 \cdot 2H_2O$ with *p*-thiocresol and crown ether ligands in a molar ratio of 1 : 2 : 1 afforded a series of zinc(II) dithiolate crown complexes. All of them gave satisfactory elemental analyses and were characterized by ^{1}H NMR spectroscopy and positive-ion FAB mass spectrometry.

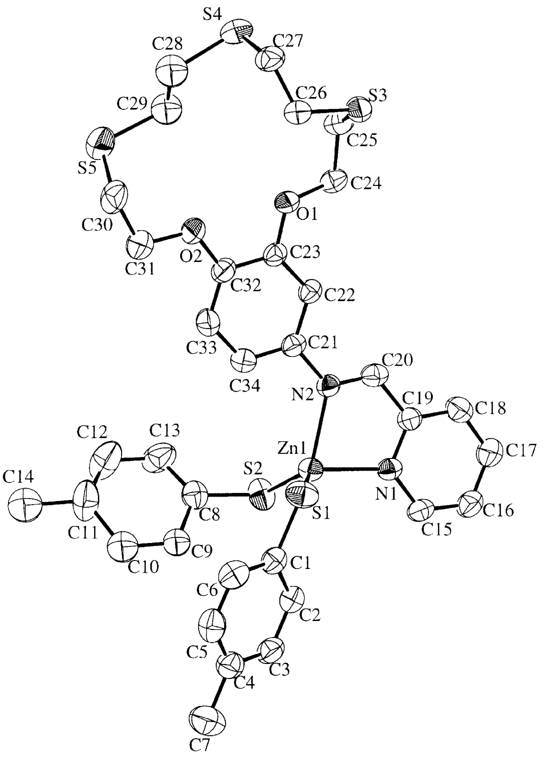


Fig. 1 Perspective drawing of **5** with the atomic numbering scheme. Hydrogen atoms have been omitted for clarity. Thermal ellipsoids are drawn at the 40% probability level.

X-Ray crystal structure determination

The crystal structure of complex **5** with atomic numbering is depicted in Fig. 1. Selected bond distances (Å) and bond angles (°) are displayed in Table 1. The Zn(II) centre adopts a distorted tetrahedral geometry with an S(1)–Zn(1)–S(2) angle of 129.08(6)° and a N(1)–Zn(1)–N(2) angle of 78.9(1)°. The average bond distances of Zn–S and Zn–N are 2.263(2) and 2.124(4) Å, respectively, which are found to be typical of related systems.[9b,12]

Electronic absorption and photophysical properties

The photophysical data for **1**–**5** are summarized in Table 2. All the complexes show low-energy absorption bands at

Table 1 Selected bond distances (Å) and angles (°) for **5**

Zn(1)–S(1)	2.268(2)	Zn(1)–S(2)	2.258(2)
Zn(1)–N(1)	2.112(4)	Zn(1)–N(2)	2.136(4)
S(1)–C(1)	1.788(6)	S(2)–C(8)	1.773(6)
S(3)–C(25)	1.813(6)	S(3)–C(26)	1.805(5)
S(4)–C(27)	1.783(6)	S(4)–C(28)	1.95(2)
S(5)–C(29)	1.86(2)	S(5)–C(30)	1.793(8)
S(1)–Zn(1)–S(2)	129.08(6)	S(1)–Zn(1)–N(1)	115.7(1)
S(1)–Zn(1)–N(2)	105.8(1)	S(2)–Zn(1)–N(1)	103.1(1)
S(2)–Zn(1)–N(2)	113.3(1)	N(1)–Zn(1)–N(2)	78.9(1)
Zn(1)–S(1)–C(1)	105.2(2)	Zn(1)–S(2)–C(8)	104.4(2)
Zn(1)–N(1)–C(15)	129.7(3)	Zn(1)–N(1)–C(19)	112.9(3)
Zn(1)–N(2)–C(20)	112.3(3)	Zn(1)–N(2)–C(21)	124.9(3)
C(25)–S(3)–C(26)	105.1(3)	C(27)–S(4)–C(28)	94.0(5)
C(29)–S(5)–C(30)	104.3(5)		

Table 2 Photophysical data for complexes **1**–**5**

	Medium (T/K)	λ_{abs}/nm (ε/dm^3 mol^{-1} cm^{-1})	λ_{em}/nm (τ_0/μs)
1	Solid (77)		570sh (<0.01)
	Glass (77)[a]		505
	MeCN (298)	250 (27,070), 376 (7,980)	524
	CH_2Cl_2 (298)	252 (26,140), 388 (8,760)	520
2	Solid (77)		525sh (<0.01)
	Glass (77)[a]		500
	MeCN (298)	262 (21,860), 394 (9,600)	516
	CH_2Cl_2 (298)	260 (29,600), 402 (10,630)	510
3	Solid (77)		554sh (<0.01)
	Glass (77)[a]		502
	MeCN (298)	262 (24,360), 388 (8,010)	496
	CH_2Cl_2 (298)	262 (29,500), 403 (10,730)	516
4	Solid (77)		595sh (<0.01)
	Glass (77)[a]		500
	MeCN (298)	262 (19,140), 386 (6,400)	492
	CH_2Cl_2 (298)	260 (25,080), 403 (11,680)	508
5	Solid (77)		568sh (<0.01)
	Glass (77)[a]		482
	MeCN (298)	270 (33,820), 390 (9,890)	490
	CH_2Cl_2 (298)	268 (35,480), 406 (11,780)	504

[a] EtOH : MeOH = 4 : 1 (v/v).

ca. 376–406 nm and a higher energy band at *ca.* 250–270 nm in both acetonitrile and dichloromethane solutions. The latter is tentatively assigned as intraligand (IL) transitions of thiolate ligands since free RS^- is found to absorb at similar energy. With reference to previous spectroscopic work on the related monomeric [Zn(phen)(SR)$_2$],[9,12c,e,13,14] the broad low-energy band at *ca.* 376–406 nm is suggested to be a mixture of ligand-to-ligand charge transfer [LLCT, $p_\pi(SR^-) \rightarrow \pi^*(L)$] and IL [$\pi(L) \rightarrow \pi^*(L)$ or $n \rightarrow \pi^*(L)$] transitions, where L = dic, dic-18-6, dic-S, dic-Se or dic-3S.

Similar to the related mononuclear [Zn(N–N)(SR)$_2$] system,[13] complexes **1–5** are found to be luminescent with emission maxima at *ca.* 490–525 nm both in 77 K glasses and at room temperature in degassed acetonitrile and dichloromethane solutions upon excitation at $\lambda > 350$ nm, but are only slightly emissive in the low temperature solid states. With reference to previous work on the related mononuclear [Zn(N–N)(SR)$_2$] system,[9,12c,14] the emissions are most probably derived from the lowest energy LLCT triplet excited state. The emission spectrum of **3** in a 77 K glass is depicted in Fig. 2.

Cation binding studies

Upon addition of aliquots of alkali and alkaline earth metal salts such as $LiClO_4$, $NaClO_4$, KPF_6 or $Ba(ClO_4)_2$ to a solution of **1** or **2**, the absorption at 376–394 nm in acetonitrile shifts to higher energy. The observed blue shift upon cation binding may be suggestive of the dominant character of the IL $n \rightarrow \pi^*(L)$ transition, since the binding of a metal ion to the polyether cavity is expected to reduce the availability of the lone pair electrons on the oxygens, leading to a blue shift in the $n \rightarrow \pi^*$ transition. On addition of a large excess of free dic or dic-18-6 ligands to an acetonitrile solution of **1** or **2**, the spectral changes were reversible because of the competition of the large excess of free crown ethers with the complexes for the metal cations. The addition of metal cations to degassed MeCN solutions of this class of complexes led to almost no changes in the emission spectra. Therefore, the binding of the metal cations could not be studied by the emission spectrophotometric method. The change in absorbance of complex **1** upon addition of lithium ions is shown in Fig. 3. The insert shows the change of absorbance at 410 nm as a function of lithium ion concentration. For complex **1**, the stability constants for the binding of Li^+ and Na^+ ions are $\log K_s = 4.13$ and 3.73, respectively. The close agreement of the experimental data with the theoretical fit is supportive of a 1 : 1 stoichiometry, which is in accordance with the size match of Li^+ and Na^+ to the crown cavity, resulting in preferential binding (Table 3). With K^+ and Ba^{2+} ions, no well-defined isosbestic points were observed in the UV-visible absorption titration spectral traces, indicative of the formation of both 1 : 1 and 1 : 2 adducts in the solution mixture. No satisfactory fits to eqn. (1) were obtained.

For complex **2**, the Ba^{2+}, K^+ and Na^+ ions all gave a perfect fit to eqn. (1) in acetonitrile, based on 1 : 1 stoichiometry, with different $\log K_s$ values (Table 3), depending on the size match between the dic-18-6 crown cavity and the various metal ions.[4d,e,15] Barium ions gave the largest stability constant with $\log K_s = 4.69$, while the stability constants are $\log K_s = 4.26$ and 3.26 for potassium and sodium ions, respectively. Since the ionic diameters of Ba^{2+} and K^+ match the cavity size of

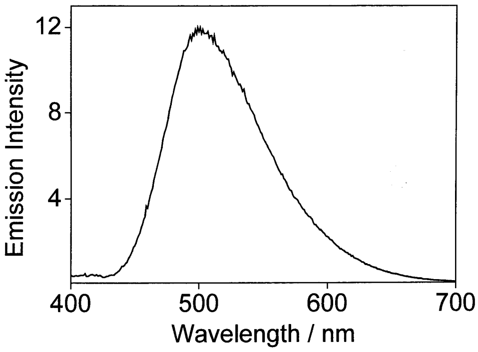


Fig. 2 Emission spectrum of **3** in ethanol–methanol (4 : 1 v/v) glass at 77 K.

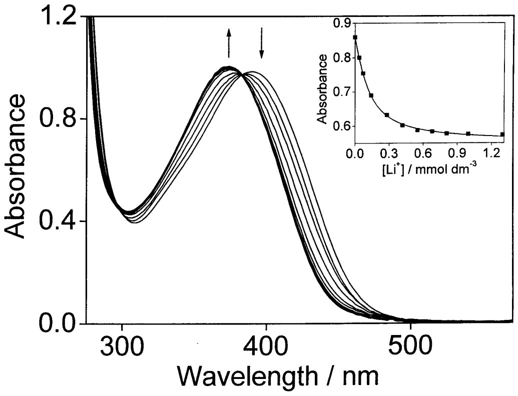


Fig. 3 The electronic absorption spectral traces of **1** (9×10^{-5} mol dm^{-3}) in acetonitrile (0.1 mol dm^{-3} $^nBu_4NPF_6$) upon addition of lithium perchlorate at 298 K. The insert shows a plot of absorbance *versus* [Li^+] monitored at $\lambda = 410$ nm (■) and the theoretical fit (——).

Table 3 Binding constants of complexes **1** and **2** for alkaline and alkaline earth metal cations in MeCN (0.1 mol dm^{-3} $^nBu_4NPF_6$) at 298 K

	$\log K_s$			
	Li^+	Na^+	Ba^{2+}	K^+
1	4.13[a]	3.73[a]	—[c]	—[c]
	4.06[b]	3.53[b]	—[c]	—[c]
2	1.86[a]	3.26[a]	4.69[a]	4.26[a]
	—[c]	3.19[b]	4.30[b]	—[c]

[a] From UV-visible spectrophotometric method. [b] From ^1H NMR spectroscopic method. [c] Not determined.

Table 4 Binding constants of complexes **3**–**5** for transition metal cations in MeCN (0.1 mol dm^{-3} ^{n}Bu$_4$NPF$_6$) at 298 K

	log K_s	
	Zn^{2+}	Cd^{2+}
3	3.43[a]	3.06[a]
	3.50[b]	2.99[b]
	3.62[c]	3.14[c]
4	4.41[a]	3.80[a]
	4.57[b]	3.58[b]
	4.22[c]	3.62[c]
5	3.41[a]	3.56[a]
	3.64[b]	3.49[b]

[a] From UV-visible spectrophotometric method. [b] From emission spectrophotometric method. [c] From ^{1}H NMR spectroscopic method.

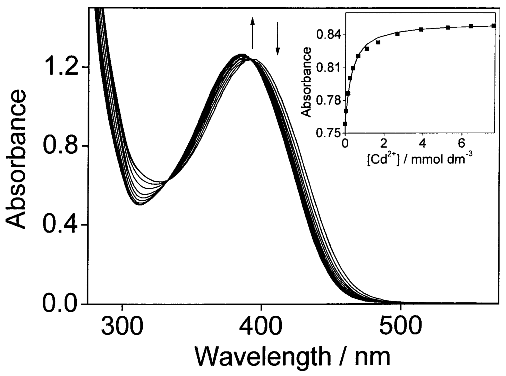


Fig. 4 The electronic absorption spectral traces of **5** (1 × 10^{-4} mol dm^{-3}) in acetonitrile (0.1 mol dm^{-3} ^{n}Bu$_4$NPF$_6$) upon addition of Cd^{2+} at 298 K. The insert shows a plot of absorbance *versus* [Cd^{2+}] monitored at $\lambda = 350$ nm (■) and the theoretical fit (——).

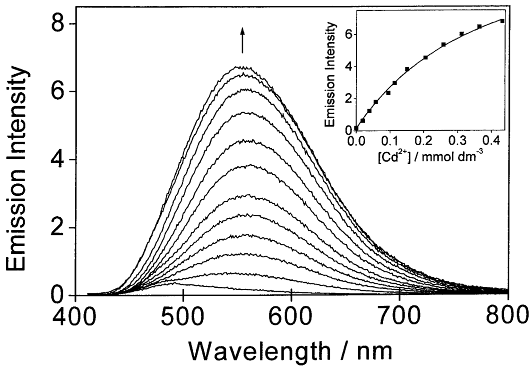


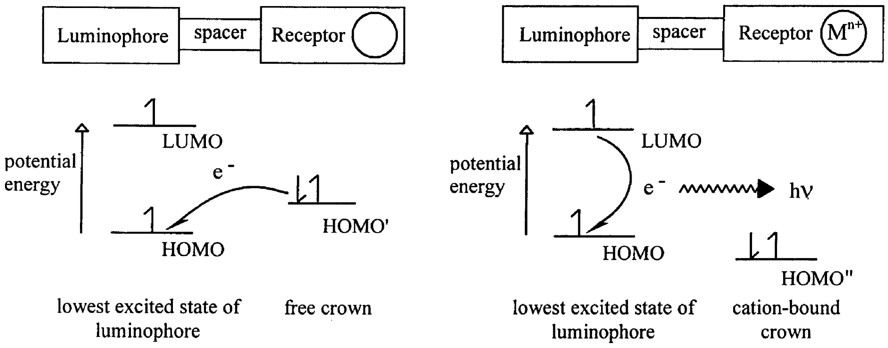
Fig. 5 Emission spectral changes of **5** in acetonitrile (0.1 mol dm^{-3} ^{n}Bu$_4$NPF$_6$) upon addition of Cd^{2+} at 298 K. Excitation was at the isosbestic wavelength of 392 nm. The insert shows a plot of emission intensity *versus* [Cd^{2+}] monitored at $\lambda = 558$ nm (■) and the theoretical fit (——).

dic-18-6 best,[4d,15] a higher affinity of **2** for these cations relative to Na$^+$ ion is expected. The larger binding constant for Ba^{2+} than K$^+$ is in line with the higher positive charge on Ba^{2+}. The binding constant of **2** for Li$^+$ ions is the smallest (log $K_S = 1.86$) compared to that of Na$^+$, K$^+$ and Ba^{2+} ions, in line with its smallest size.

The ion-binding experiments have also been carried out using ^{1}H NMR spectroscopy. A shift in the proton signals of the polyether cavity has been observed upon metal ion binding and the stability constants were determined using the EQNMR program.[10d] The stability constants for **1** and **2** thus determined are also given in Table 3.

Unlike complexes **1** and **2**, addition of aliquots of alkali and alkaline earth metal cations to an acetonitrile solution of complexes **3**–**5** gave no observable changes in the UV-visible spectra. However, a blue shift in energy was observed upon addition of the transition metal ions Zn^{2+} and Cd^{2+}. The shift in absorption energy for zinc(II) crown ether-containing complexes was found to be larger compared to that for a related copper(I) system.[7] The stability constants determined for complexes **3**–**5** are collected in Table 4. The electronic absorption spectra of complex **5** upon addition of Cd^{2+} ions are depicted in Fig. 4. The insert shows the change of absorbance at 350 nm as a function of Cd^{2+} ion concentration.

Complexes **3**–**5** in degassed acetonitrile solution show only one emission with maxima at *ca.* 490–496 nm upon excitation at $\lambda > 350$ nm. Addition of Zn^{2+} or Cd^{2+} ions to the degassed MeCN solution of this class of complexes gave rise to a dramatic enhancement of the emission intensities with a shift of emission maxima from 490 to 560 nm upon excitation at the isosbestic wavelength. Such an enhancement in the emission intensity could be explained by the blocking of the reductive intramolecular electron-transfer quenching mechanism (Scheme 2). The stability constants obtained using emission and ^{1}H NMR methods are comparable to those determined using the UV-visible spectrophotometric method, and are also summarized in Table 4. However, the ^{1}H NMR method could not be employed for the binding studies of **5** due to the low solubility of the complex. Fig. 5 displays the changes in the emission spectra of complex **5** in acetonitrile upon addition of Cd^{2+} at 298 K. The insert shows the changes in emission intensity as a function of Cd^{2+} ion concentration monitored at 558 nm. The close resemblance of the experimental data to the theoretical fits using both the UV-visible and emission methods is supportive of a 1 : 1 complexation model. Similar findings have also been reported in a related copper(I) system.[7]



Scheme 2

Table 5 Electrochemical data for complexes **1**–**5**[a]

	Oxidation	Reduction
	$E_{1/2}$[b] or E_{pa}[c]/V *vs.* SCE (in cation)	$E_{1/2}$[b]/V *vs.* SCE (in cation)
1	+1.50[b] (+1.51)[d] +1.17[c] (+1.17)[d]	−1.06 (−0.95)[d]
2	+1.49[b] (+1.49)[e] +1.19[c] (+1.18)[e]	−1.11 (−1.03)[e]
3	+1.46[b] (+1.46)[f] +1.22[c] (+1.21)[f]	−1.09 (−0.77)[f]
4	+1.50[b] (+1.49)[f] +1.24[c] (+1.22)[f]	−1.10 (−0.96)[f]
5	+1.48[b] (+1.47)[f] +1.24[c] (+1.24)[f]	−1.08 (−0.86)[f]

[a] In acetonitrile (0.1 mol dm^{-3} ^{n}Bu$_4$NPF$_6$). Working electrode: glassy carbon; ΔE_{p} of Fc$^+$/Fc ranges from 60–64 mV; scan rate, 100 mV s^{-1}. [b] $E_{1/2} = (E_{pa} + E_{pc})/2$ where E_{pa} and E_{pc} are the anodic and cathodic peak potentials of the quasi-reversible reduction and oxidation couples. [c] E_{pa} refers to the anodic peak potential of the irreversible oxidation wave. [d] $E_{1/2}$ *vs.* SCE in the presence of excess NaClO$_4$. [e] $E_{1/2}$ *vs.* SCE in the presence of excess KPF$_6$. [f] $E_{1/2}$ *vs.* SCE in the presence of excess Zn(BF$_4$)$_2$.

Electrochemical properties

The electrochemical data for complexes **1**–**5** in acetonitrile (0.1 mol dm^{-3} ^{n}Bu$_4$NPF$_6$) are tabulated in Table 5. The cyclic voltammogram of **5** is shown in Fig. 6. Cyclic voltammetric studies of complexes **1**–**5** in acetonitrile show similar cyclic voltammograms with a quasi-reversible and an irreversible oxidation wave, tentatively assigned as thiolate ligand-centred oxidations, and a quasi-reversible reduction couple, probably attributable to the diimine ligand-centred reduction.[12e] The similarity of the oxidation potentials is in accord with an assignment of a thiolate ligand-centred oxidation since all the complexes possess the same thiolate ligand. It is interesting to find that upon addition of metal ions, the crown-based reduction potential was shifted anodically by about 80–320 mV while the oxidation waves remain more or less undisturbed. This further supports the assignment of the reduction process as a diimine-crown ligand-centred reduction, in which binding of metal ions into the crown cavity would give rise to a perturbation of the reduction potential to less cathodic values, in line with the increased π-accepting ability of the dic-type ligands upon metal ion binding (Fig. 6).

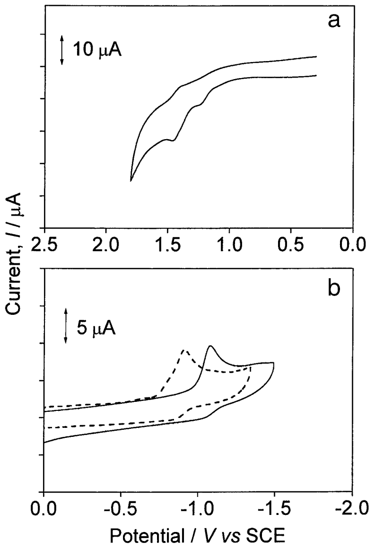


Fig. 6 Cyclic voltammograms showing (*a*) the oxidation (scan rate, 100 mV s^{-1}) and (*b*) reduction (scan rate, 100 mV s^{-1}) of **5** in acetonitrile (0.1 mol dm^{-3} ^{n}Bu$_4$NPF$_6$) in the absence of Zn^{2+} (solid line) and in the presence of excess Zn^{2+} (dashed line).

Conclusion

A series of zinc(II) dithiolate crown ether-containing complexes have been successfully synthesized. The electronic absorption, emission, electrochemical and binding properties of these systems have been studied. The crystal structure of [Zn(SC$_6$H$_4$-CH$_3$-*p*)$_2$(dic-3S)] (**5**) has also been determined. The low energy absorption bands of these complexes are suggested to be a mixture of ligand-to-ligand charge transfer [LLCT, $p_\pi(SR^-) \rightarrow \pi^*(L)$] and IL [$\pi(L) \rightarrow \pi^*(L)$ or $n \rightarrow \pi^*(L)$] transitions. The emissions are thought to be associated with the lowest energy LLCT triplet excited state. The ion-binding stability constants obtained from UV-visible, emission and ^{1}H NMR experiments were found to be in good agreement with each other.

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References

1 (*a*) M. Hiraoka, *Crown Compounds: Their Characteristics and Applications*, Kodansha, Japan, 1978; (*b*) Y. Inoue and G. W. Gokel, *Cation Binding by Macrocycles*, Marcel Dekker, New York, 1990.

2 (*a*) R. M. Izatt, J. S. Bradshaw, S. A. Nielsen, J. D. Lamb and J. J. Christensen, *Chem. Rev.*, 1985, **85**, 271; (*b*) R. M. Izatt, J. S. Bradshaw and R. L. Bruening, *Chem. Rev.*, 1991, **91**, 1721; (*c*) J. C. Ma and D. A. Dougherty, *Chem. Rev.*, 1997, **97**, 1303; (*d*) K. A. Connors, *Chem. Rev.*, 1997, **97**, 1325; (*e*) F. P. Schmidtchen and M. Berger, *Chem. Rev.*, 1997, **97**, 1609; (*f*) M. M. Conn and J. Rebek, *Chem. Rev.*, 1997, **97**, 1647; (*g*) F. Zeng and S. C. Zimmermann, *Chem. Rev.*, 1997, **97**, 1681; (*h*) A. Ikeda and S. Shinkai, *Chem. Rev.*, 1997, **97**, 1713; (*i*) V. W. W. Yam and K. K. W. Lo, *Coord. Chem. Rev.*, 1999, **184**, 157.

3 (*a*) C. J. Pedersen, *J. Am. Chem. Soc.*, 1967, **89**, 7017; (*b*) J. D. Lamb, R. M. Izatt, J. J. Christensen and D. J. Eatough, in *Coordination Chemistry of Macrocyclic Compounds*, ed. G. A. Melson, Plenum Press, New York, 1979, p. 145; (*c*) J. D. Lamb, R. M. Izatt, C. S. Swain and J. J. Christensen, *J. Am. Chem. Soc.*, 1980, **102**, 475; (*d*) J. Simon, M. K. Engel and C. Soulie, *New J. Chem.*, 1992, **16**, 287; (*e*) C. J. Pedersen, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1021; (*f*) P. D. Beer, O. Kocian, R. J. Mortimer and C. Ridgway, *J. Chem. Soc., Dalton Trans.*, 1993, 2629.

4 (*a*) H. K. Frensdorff, *J. Am. Chem. Soc.*, 1971, **93**, 600; (*b*) J. J. Christensen, D. J. Eatough and R. M. Izatt, *Chem. Rev.*, 1974, **74**, 351; (*c*) M. Oue, K. Akama, K. Kimura, M. Tanaka and T. Shono, *J. Chem. Soc., Perkin Trans. 1*, 1989, 1675; (*d*) S. Sato, Y. Habata, M. Sato and S. Akabori, *Bull. Chem. Soc. Jpn.*, 1989, **62**, 3963; (*e*) A. J. Blake, G. Reid and M. Schröder, *J. Chem. Soc., Chem. Commun.*, 1992, 1074; (*f*) G. Wu, W. Jiang, J. D. Lamb, J. S. Bradshaw and R. M. Izatt, *J. Am. Chem. Soc.*, 1991, **113**, 6538; (*g*) J. W. Sibert, S. J. Lange, C. L. Stern, A. G. M. Barrett and B. M. Hoffman, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 2020; (*h*) J. Ishikawa, H. Sakamoto, T. Mizuno and M. Otomo, *Bull. Chem. Soc. Jpn.*, 1995, **68**, 3071.

5 (*a*) R. M. Izatt, R. E. Terry, L. D. Hansen, A. G. Avondet, J. S. Bradshaw, N. K. Dalley, T. E. Jensen and J. J. Christensen, *Inorg. Chim. Acta*, 1978, **30**, 1; (*b*) R. D. Hancock, *Pure Appl. Chem.*, 1986, **58**, 1445; (*c*) K. R. Adam, C. W. G. Ansell, K. P. Dancey, L. A. Drummond, A. J. Leong, L. F. Lindoy and P. A. Tasker, *J. Chem. Soc., Chem. Commun.*, 1986, 1011; (*d*) J. Clarkson,

R. Yagbasan, P. J. Blower, S. C. Rawle and S. R. Cooper, *J. Chem. Soc., Chem. Commun.*, 1987, 950; (*e*) L. F. Lindoy, *Pure Appl. Chem.*, 1989, **61**, 1575; (*f*) R. M. Izatt, G. Wu, W. Jiang and N. K. Dalley, *Inorg. Chem.*, 1990, **29**, 3828.

6 (*a*) S. C. Burdette, G. K. Walkup, B. Spingler, R. Y. Tsien and S. J. Lippard, *J. Am. Chem. Soc.*, 2001, **123**, 7831; (*b*) G. K. Walkup, S. C. Burdette, S. J. Lippard and R. Y. Tsien, *J. Am. Chem. Soc.*, 2000, **122**, 5644; (*c*) Y. Sun, M. D. Wong and B. P. Rosen, *J. Biol. Chem.*, 2001, **276**, 14 955; (*d*) B. L. Vallee and K. H. Falchuk, *Physiol. Rev.*, 1993, **73**, 79; (*e*) K. H. Falchuk, *Mol. Cell. Biochem.*, 1998, **188**, 41.

7 V. W. W. Yam, Y. L. Pui, W. P. Li, K. K. W. Lo and K. K. Cheung, *J. Chem. Soc., Dalton Trans.*, 1998, 3615.

8 (*a*) V. W. W. Yam, K. K. W. Lo and K. K. Cheung, *Inorg. Chem.*, 1995, **34**, 4013; (*b*) D. W. Johnson, H. K. Mayer, J. P. Minard, J. Banaticla and C. Miller, *Inorg. Chim. Acta*, 1988, **144**, 167.

9 (*a*) K. A. Truesdell and G. A. Crosby, *J. Am. Chem. Soc.*, 1985, **107**, 1781; (*b*) K. J. Jordan, W. F. Wacholtz and G. A. Crosby, *Inorg. Chem.*, 1991, **30**, 4588.

10 (*a*) R. R. Gagne, C. A. Koval and G. C. Lisensky, *Inorg. Chem.*, 1980, **19**, 2854; (*b*) C. M. Che, K. Y. Wong and F. C. Anson, *J. Electroanal. Chem., Interfac. Electrochem.*, 1987, **226**, 221; (*c*) J. Bourson, J. Pouget and B. Valeur, *J. Phys. Chem.*, 1993, **97**, 4552; (*d*) M. J. Hynes, *J. Chem. Soc., Dalton Trans.*, 1993, 311.

11 (*a*) PATTY: P. T. Beurskens, G. Admiral, G. Beursken, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits and C. Smykalla, The DIRDIF Program System, Technical Report of the Crystallography Laboratory, University of Nijmegen, The Netherlands, 1992; (*b*) TeXsan: Crystal Structure Analysis Package, Molecular Structure Corp., The Woodlands, TX, USA, 1985 and 1992.

12 (*a*) A. D. Watson, C. P. Rao, J. R. Dorfman and R. H. Holm, *Inorg. Chem.*, 1985, **24**, 2820; (*b*) I. L. Abrahams and C. D. Garner, *J. Chem. Soc., Dalton Trans.*, 1987, 1577; (*c*) K. Halvorsen, G. A. Crosby and W. F. Wacholtz, *Inorg. Chim. Acta*, 1995, **228**, 81; (*d*) K. S. Anjali, J. T. Sampanthar and J. J. Vittal, *Inorg. Chim. Acta*, 1999, **295**, 9; (*e*) V. W. W. Yam, Y. L. Pui and K. K. Cheung, *Inorg. Chem.*, 2000, **39**, 5741.

13 G. A. Crosby, R. G. Highland and K. A. Truesdell, *Coord. Chem. Rev.*, 1985, **64**, 41.

14 R. G. Highland, J. G. Brummer and G. A. Crosby, *J. Phys. Chem.*, 1986, **90**, 1593.

15 H. G. Hansma and D. E. Laney, *Biophys. J.*, 1996, **70**, 1933.