Synthesis and X-ray crystallography of diverse metal complexes derived from xanthone-crown ether

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A series of sandwich, monomeric, dimeric and polymeric complexes supported with 1,8-xanthone-18-crown-5 (L) were synthesised. Mass spectrum experiments suggested the existence of sandwich and monomeric complexes in solution. And the structure characterisations of six new complexes by single-crystal X-ray diffraction show the strong coordination of xanthone-18-crown-5 carbonyl oxygen with alkaline earth metal cation, which results high fluorescent increase in alkaline earth metal complexes.

Keywords: xanthone-crown; sandwich; crystal

Introduction

Fluorescent chemosensors capable of selectively recognising guest species are of particular interest due to their high sensitivity and ease of monitoring (*1*). As a result, many efforts have been devoted to the preparation of a variety of fluorescent sensors for special species (*2*). Among them, the crown ether sensors attract considerable attentions as receptors for the alkali metal and alkaline earth metal cations to form the host–guest complexes (*3*). Recently, 1,8-anthraquinone crown ether (*4*) and xanthone-crown ethers (*4, 5*) were found to be good sensors for alkaline earth metals or heavy metals. And in the two systems, photoinduced electron transfer (PET) is the current, dominant photophysical mechanism for the detection of metals. With this mechanism, molecules with a low-lying $n-\pi*$ transition generally do not luminesce; however, coordination of lumophor's-associated non-bonding electrons with electropositive centre raises the energy of the $n-\pi*$ transition above that of the corresponding $\pi-\pi*$ transition, and luminescence is switch 'on'. Based on this mechanism, Prodi et al. (*4*) reported that a series of xanthone-crown ethers are suitable for the construction of multisensory devices for the alkaline earth metal ions. They proposed the strong fluorescence results from the planar isomer (Chart 1), which is stabilised by coordination of metal cation. But this proposed mechanism was not verified by any complexes structures, or calculation experiments.

Because xanthone-crown ethers are good fluorescent chemosensors to alkaline earth metal cations, this promotes us to understand the real mechanism and do some research on the synthesis of xanthone-crown ether metal complexes. In the research progress, some interesting coordination chemistry of xanthone-crown ether was found. The structures of six new complexes gave some evidence for the fluorescent mechanism in this system (Table 1).

Results and discussion

Synthesis of complexes

The preparations of all complexes were done at room temperature with acetonitrile as solvent. In order to understand the difference between alkaline earth metal and other metal complexes, Na^+, Al^{3+} and Co^{2+} together with alkaline earth metal ions were chosen to synthesise serials of complexes. Four kinds of complexes can be formed with this xanthone-crown ether ligand, sandwich, monomer, dimer and polymer. It is easy to get pure monomeric complexes of Na^+, Mg^{2+}, Ca^{2+}, Sr^{2+}, dimeric complexes of Ba^{2+} and sandwich complexes of $Al(H_2O)_6^{3+}$ and $Co(H_2O)_6^{2+}$ in a highly pure crystalline form. Although sandwich complexes of sodium, magnesium, calcium, strontium and barium were always co-precipitated with some monomers or dimers, their existence was evidenced by the mass spectra in acetonitrile solution with the 1:2 ratio of metal to ligand. Fortunately, one crystal of calcium sandwich complex was obtained and analysed. Pure sodium polymeric complex can be obtained in crystalline form with the 2:1 ratio of metal to ligand, which has been reported in our previous work (*5*) (Scheme 1).

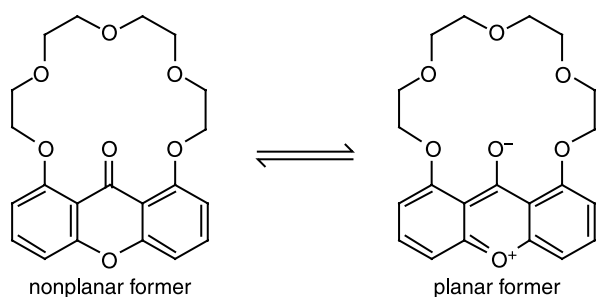*Corresponding author. Email: wujc@lzu.edu.cn

Chart 1.　Two isomers of 1,8-xanthone-18-crown-5.

X-ray crystal structures

Single crystals suitable for X-ray structure determination were obtained by slow vapour diffusion of acetonitrile/ether. Those different metal/ligand stoichiometries in the series of complexes were confirmed by the crystallographic results. An ORTEP drawing of molecular structure of [Na·L·ClO$_4$] **1** is given in Figure 1. The geometry around sodium is a distorted square pyramid with four ligand oxygen atoms including one perchlorate anion oxygen at axial position, and the intra-annular carbonyl oxygen on the equatorial positions. Least-squares planes defined by the two aromatic rings in the xanthone are offset by a dihedral angle of 9.80(15)° to one another, while in free ligand the dihedral angle is 14.49(12)° (*6*, *7*). The carbonyl double-bond distance of C12—O2, 1.227(5) Å is just slightly longer than the free ligand 1.212(2) Å. Other important bond distances are listed in Table 2. It is interesting that one chain disodium complex can also form with the ratio of 2:1 of Na$^+$ to ligand (*5*).

Calcium perchlorate that reacts with this ligand can form monomeric complex **9** with the 1:1 ratio of metal/ligand and sandwich complex **5** can be obtained with excess ligand. Monomeric calcium molecular structure is shown in Figure 2, the geometry around Ca was a distorted pentagonal bipyramid with nitrogen atom of acetonitrile and oxygen atom of carbonyl oxygen of ligand at axial position and other three oxygen atoms of ligand, one water and one perchlorate anion on the equatorial positions. Least-squares planes defined by the two aromatic rings in the xanthone are offset by a dihedral angle of 5.32(14)° to one another. This xanthone parent structure is more different from the free ligand with its planarity. On the other hand, the carbonyl double-bond distance of C12—O2, 1.241(3) Å is more lengthening than the free ligand 1.212(2) Å. Other important bond distances are listed in Table 2.

In sandwich calcium complex **5**, the calcium atom is surrounded by two ligands (Figure 3). One ligand is strongly coordinated to calcium with the long carbonyl double-bond distance of C12—O2, 1.242(6) Å. And the two aromatic rings of the xanthone are almost on one plane with a dihedral angle of 0.66(33)°. It is worth noting that the other ligand was half-coordinated to Ca, which means that only one set of symmetric oxygen atoms in ligand, O9, O10, O11, O12, coordinate to Ca. Therefore, the dihedral angle of 11.99(30)° between the two aromatic rings of this xanthone is just slightly small to free ligand, and the long carbonyl double-bond distance of C33—O9, 1.232(6) Å is due to the carbonyl oxygen binding to Ca. π−π Interaction is also observed with 3.36 Å between the two xanthone ligands.

An ORTEP drawing of strontium complex **10** is given in Figure 4; the geometry around Sr is a distorted pentagonal bipyramid with the nitrogen atom of aceto-nitrile and oxygen atom of carbonyl oxygen of ligand at axial position and three oxygen atoms of ligand, one water and one perchlorate anion on the equatorial positions. Two aromatic rings in the xanthone give a dihedral angle of 7.49(13)°. The carbonyl double-bond distance of C12—O2, 1.240(3) Å is longer than the free ligand. Other important bond distances are listed in Table 2.

Figure 5 demonstrates the dimeric barium complex **11** molecular structure with two perchlorate anions as weak bridges. The barium atom was nine coordinated by one nitrogen atom of acetonitrile, four oxygen atoms of ligand including carbonyl oxygen and four oxygen atoms of perchlorate anion. Two aromatic rings in the xanthone give a dihedral angle of 2.02(30)°. The long carbonyl double-bond distance of C12—O2, 1.239(5) Å can also be found. Other important bond distances are listed in Table 2.

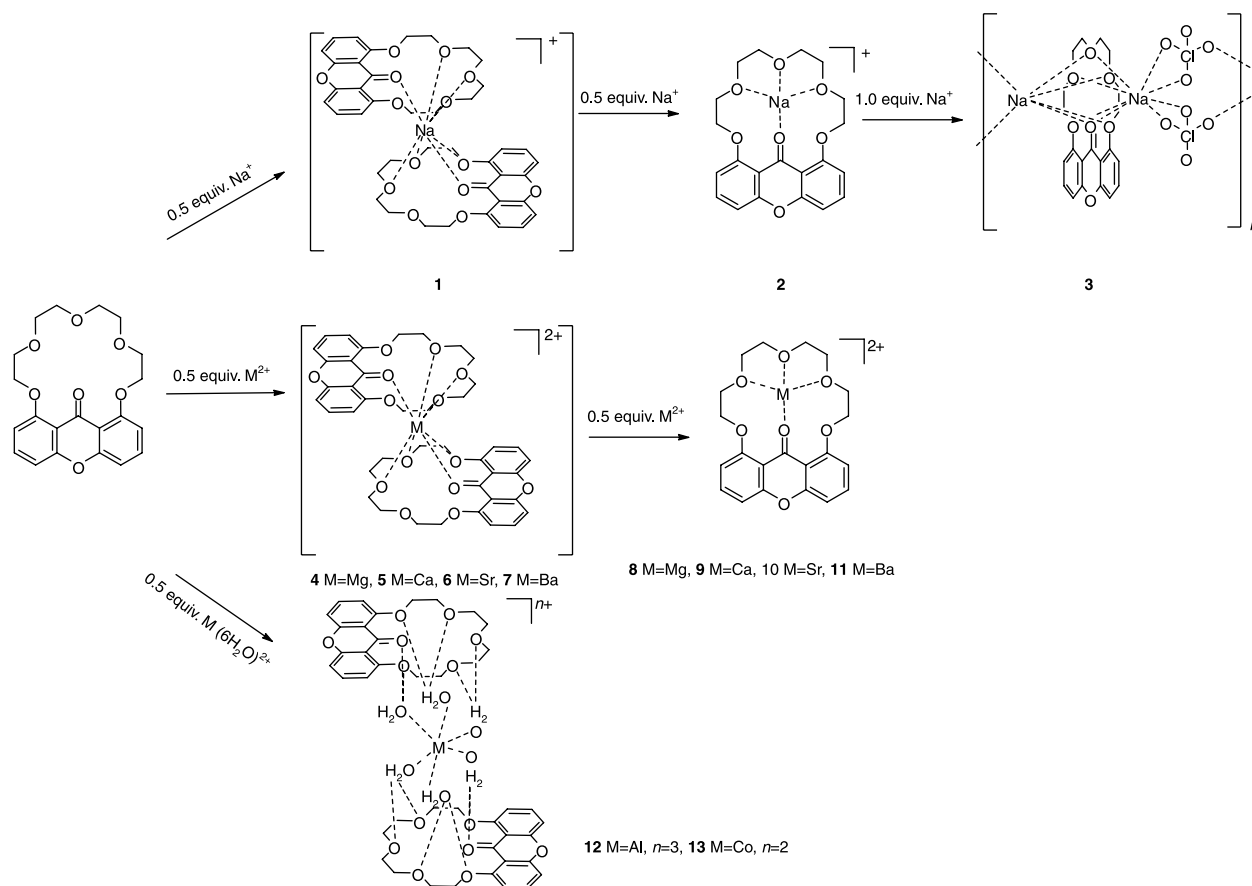The structure of the Co^{2+} complex **13** is more interesting (Figure 6). The Co^{2+} cation is hydrated by six water molecules and fine located in the centre of two xanthone-crown ether molecules through O—H···O hydrogen bonding interactions. This unexpected complex is perfectly sandwiched by two xanthone-crown ether molecules through well-defined hydrogen bonds that involve metal-coordinated water molecules and oxygen atoms of the xanthone-crown ether molecules. In this complex, the bond distance of C12—O2, 1.221(3) Å, and the dihedral angle, 18.44(13)° between the two aromatic ring planes of the xanthone are similar to free ligand, indicating the cobalt-hydrated cation does not affect the ligand geometry dramatically.

Mass spectrum

Because some sandwich, monomeric, dimeric and polymeric complexes were obtained in solid state, it promotes us to understand all kinds of complex species in solution, which is also worth for the studies of luminescence behaviour. Therefore, the electron spray ion mass spectrum experiments were performed in acetonitrile solution and shown in Figure 7.

Table 1. Crystal data and structure refinements for compounds.

	2	5	9	10	11	13
Formula	$C_{21}H_{22}ClNaO_{11}$	$C_{46}H_{50}CaCl_2N_2O_{22}$	$C_{23}H_{27}CaCl_2NO_{16}$	$C_{23}H_{27}Cl_2NO_{16}Sr$	$C_{46}H_{50}Ba_2Cl_4N_2O_{30}$	$C_{46}H_{62}ClCl_9N_2O_7$
Fw	508.83	1093.86	684.44	731.98	1527.34	1220.81
Temp	298(2)	298(2)	298(2)	298(2)	293(2)	273(2)
Crystal system	Monoclinic	Monoclinic	Triclinic	Triclinic	Triclinic	Monoclinic
Space group	$P2(1)/n$	$P2(1)/c$	$P\text{-}1$	$P\text{-}1$	$P\text{-}1$	$C2/c$
a (Å)	7.1486(10)	16.717(2)	8.0195(8)	8.070(3)	8.4880(2)	24.4425(17)
b (Å)	11.9293(16)	12.6429(11)	11.5806(12)	11.706(4)	10.9445(3)	16.2529(17)
c (Å)	26.451(4)	23.580(3)	16.9030(16)	17.104(5)	17.3063(4)	14.5626(12)
α	90.00	90.00	74.622(2)	75.494(5)	94.9500(10)	90.00
β (°)	96.102(2)	97.681(2)	87.488(3)	88.155(4)	104.1670(10)	107.311(2)
γ	90.00	90.00	70.489(2)	70.720(4)	112.778(2)	90.00
V (Å³)	2242.9(5)	4939.1(10)	1424.9(2)	1474.28	1407.46(6)	5523.1(8)
Z	4	4	2	2	1	4
Density (calcd, g/cm³)	1.507	1.471	1.595	1.649	1.802	1.468
Absorb. coeff. (mm⁻¹)	0.251	0.321	0.487	2.086	1.676	0.498
$F(000)$	1056	2280	708	744	760	2548
θ range	6.11–26	1.23–25	1.94–25	1.91–26	2.18–27.54	1.53–25
Index ranges	$-8 \leq h \leq 8,$ $-14 \leq k \leq 11,$ $-32 \leq l \leq 32$	$-18 \leq h \leq 19,$ $-15 \leq k \leq 15,$ $-28 \leq l \leq 23$	$-9 \leq h \leq 9,$ $-6 \leq k \leq 13,$ $-19 \leq l \leq 20$	$-9 \leq h \leq 9,$ $-6 \leq k \leq 14,$ $-19 \leq l \leq 21$	$-11 \leq h \leq 10,$ $-13 \leq k \leq 14,$ $-16 \leq l \leq 22$	$-29 \leq h \leq 25,$ $-19 \leq k \leq 19,$ $-17 \leq l \leq 17$
Observed reflns	1742	3253	3489	4660	3604	3298
Data/restr./param	3952/0/307	8646/0/698	4908/0/445	5697/0/445	5959/0/378	4879/0/387
GOF	0.906	0.956	1.019	1.007	0.768	1.149
Final R indices $[I > 2\sigma(I)]$	$R1 = 0.0778,$ $wR2 = 0.1959$	$R1 = 0.0676,$ $wR2 = 0.1369$	$R1 = 0.0406,$ $wR2 = 0.0941$	$R1 = 0.0342,$ $wR2 = 0.0802$	$R1 = 0.0386,$ $wR2 = 0.0797$	$R1 = 0.0460,$ $wR2 = 0.1256$
Peak and hole (e/Å³)	0.514 and −0.318	0.420 and −0.392	0.310 and −0.283	0.359 and −0.371	0.896 and −0.663	0.375 and −0.278
CCDC	692416	692418	692419	692415	694650	692417

Scheme 1.   Synthesis of 1,8-xanthone-18-crown-5 metal complexes.

When the ratio of alkaline earth metal to ligand is 1:1, there are two kinds of complex peaks attributed to $[M \cdot L]^{2+}$ and $[M \cdot L \cdot ClO_4]^+$ species. All intensities of $[M \cdot L]^{2+}$ are bigger than $[M \cdot L \cdot ClO_4]^+$, which means that the perchlorates weakly coordinate to the correspondence metal. The absence of $[Mg \cdot L \cdot ClO_4]^+$ peak demonstrates that perchlorates cannot coordinate to Mg^{2+} due to two coordinated waters (6). In the solution, there should have the complex dissociation equilibrium; consequently, two peaks due to the free ligand and a complex of $[2L + H_2O]$ from one water and two ligands can be found in the series mass spectra. When the ratio of metal to ligand changes to 1:2, peaks of sandwich complexes can be viewed in form of $[M \cdot 2L]^{2+}$ in strong intensities. The presence of small peak of $[M \cdot L]^{2+}$ owes to the equilibrium between monomer and sandwich complex. For calcium sandwich complex, the structure agrees well with the related mass spectrum. Sodium complex mass spectra were also measured, only $[Na \cdot L]^+$ specie was found with 1:1 ratio of Na to ligand. Changing ratio of Na to ligand to 1:2, three species of $[Na \cdot 2L]^+$, $[Na \cdot L]^+$ and free ligand were found, which demonstrates that

there is a reaction equilibrium between sandwich sodium complex and monomer sodium complex. In another words, sandwich sodium complex can be formed with the 1:2 ratio of metal to ligand. When the ratio of metal to ligand changes to 2:1, polymer complex $[2Na \cdot L \cdot 2ClO_4]_n$ can be obtained in solid state (5). But in solution, this polymer dissociates to $[Na \cdot L]^+$ evidenced by the same mass and ^1H NMR spectra of polymer and monomer. The mass spectra of the sandwich complex of $[Al(H_2O)_6 \cdot 2L]3ClO_4$ and $[Co(H_2O)_6 \cdot 2L]2ClO_4$ only give the peak of ligand, which shows that the two hydrated cations just weakly interact with two xanthone-crown ether ligands.

Therefore, a conclusion can be made that only sandwich and monomeric xanthone-crown ether complexes can really exist in the acetonitrile solution, which may be fluorescent-active species.

Luminescence spectra

Although the xanthone-crown ether shows only a very weak fluorescence in acetonitrile solution at room
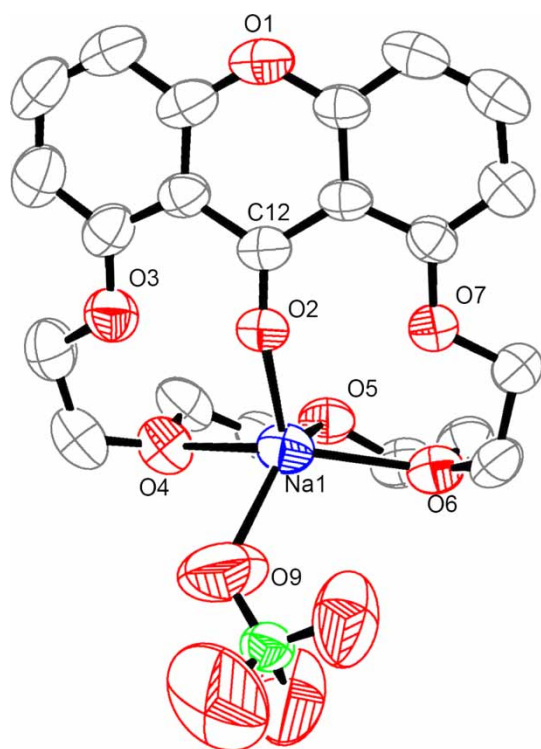
Figure 1. Thermal ellipsoid (50%) diagram of **2**. Perchlorate anions and hydrogen atoms have been excluded for clarity.
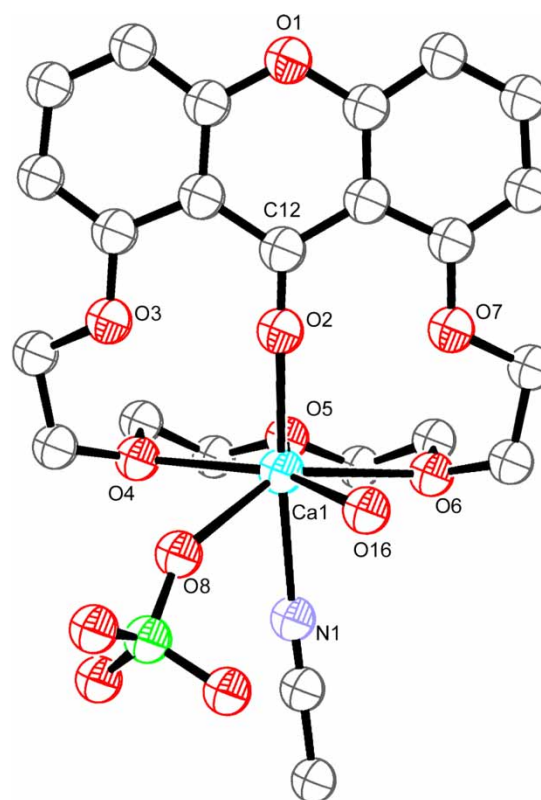

Figure 2. Thermal ellipsoid (50%) diagram of **9**. Perchlorate anions and hydrogen atoms have been excluded for clarity.

temperature, the addition of alkaline earth metal perchlorates to the solution produced a strong increase in fluorescence band at 445 nm excited at 310 nm, especially for Ca^{2+} (see Figure 8 for Ca^{2+}). The emission intensity crested with the addition of 1 equiv. of alkaline earth metal ions, indicating the stoichiometry of 1:1 luminescent complex form as monomer.

Figure 9 compares the selectivity of xanthone-crown ether with different perchlorate salts. Two equivalents of a perchlorate salt were added to xanthone-crown ether and the emission spectra were recorded. Emission change is most sensitive for the addition of calcium ion. Zn^{2+}, containing a full complement of d electrons, also shows strong luminescence enhancement due to its similarity to Mg^{2+} (*8*).

The results of bond valence sum analyses show the distribution of the more positive charge density on carbonyl oxygen in alkaline earth metal and zinc complexes than sodium, aluminium and cobalt complexes, which agrees well with the severely lengthened double bond of carbonyl group and more planar parent xanthone in alkaline earth metal complexes that Prodi et al. have proposed. Although there is strong interaction between Cu^{2+} and xanthone-crown ether, Cu^{2+} shows minimal luminescence enhancement (*9*). In fact, the transition metal ions of Ni^{2+}, Mn^{2+} and Fe^{3+} show minimal

luminescence enhancements too, which was due to the presence of low-lying d–d transitions that effectively quench emission internally. Therefore, the critical feature responsible for initiating luminescence in this xanthone-crown ether ligand is the degree of electropositive charge experienced by the intra-annular carbonyl oxygen, which in turn controls the inversion of $n\pi*$ and $\pi\pi*$ excited states in the lumophore and as a consequence, the xanthone-crown ether changes to be more planar.

Conclusions

The syntheses of several new sandwich, monomer, dimer and even polymer metal complexes have been described, and the coordination model between xanthone-crown ether and metal cation has been demonstrated with different ratios of metal to ligand. Evidenced by the structure analyses of the series of metal complexes, the PET sensor mechanism for xanthone-crown ether to alkaline earth metal ions results from the strong coordination between alkaline earth metal and carbonyl oxygen, which changes parent xanthone to be planar and inverts $n\pi*$ and $\pi\pi*$ excited states in the lumophore.

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Table 2. Selected bond distances (Å).

2(Na)	Na1—O2	2.241(4)	Na1—O5	2.406(4)	Na1—O9	2.342(7)
	Na1—O4	2.374(5)	Na1—O6	2.408(5)	C12=O2	1.227(5)
	Ca1—O2	2.2672(19)	Ca1—O6	2.553(2)	Ca1—N1	2.477(3)
9(Ca)	Ca1—O4	2.503(2)	Ca1—O8	2.455(2)	C12=O2	1.241(3)
	Ca1—O5	2.468(2)	Ca1—O16	2.343(2)		
	Ca1—O2	2.277(4)	Ca1—O9	2.362(4)	C12=O2	1.242(6)
5(Ca)	Ca1—O4	2.555(4)	Ca1—O10	2.578(4)	C33=O9	1.232(6)
	Ca1—O5	2.522(4)	Ca1—O11	2.552(4)		
	Ca1—O6	2.588(4)	Ca1—O12	2.457(4)		
	Sr1—O2	2.4183(19)	Sr1—O6	2.6458(19)	Sr1—N1	2.648(3)
10(Sr)	Sr1—O4	2.635(2)	Sr1—O8	2.500(2)	C12=O2	1.240(3)
	Sr1—O5	2.6306(19)	Sr1—O9	2.568(2)		
	Ba1—O2	2.555(4)	Ba1—O8	2.752(3)	Ba1—N1	2.906(5)
	Ba1—O4	2.738(3)	Ba1—O13	2.678(9)	C12=O2	1.239(5)
11(Ba)	Ba1—O5	2.835(3)	Ba1—O14	3.266(12)		
	Ba1—O6	2.849(3)	Ba1—O15	3.158(11)		
	Co1—O8	2.101(2)	C12=O2	1.221(3)	O6···H—O8	2.805(4)
13(Co)	Co1—O9	2.087(2)	O2···H—O9	2.754(3)	O4···H—O8	2.778(3)
	Co1—O10	2.085(2)	O2···H—O10	2.805(3)		

Experimental

General procedures

Chemicals were purchased commercial sources and used without further purification. 1,8-(3,6,9-Trioxaundecane-1,11-diyldioxy)xanthone (L), abbreviated as 1,8-xanthone-18-crown-5, was prepared according to the literatures (*5*, *6*). The preparation of the complexes **3**, **8** and **12** has been reported in our recent paper (*6*). Elemental analyses were conducted using an Elementar Vario EL mass spectroscopic data were obtained from a

Bruker APEX FT-ICR-MS and ^{1}H NMR spectra were recorded using a Varian Mercury Plus 400 spectrometer. Crystals were mounted on a Bruker SMART APEX CCD diffractometer for data collection using Mo Kα radiation.
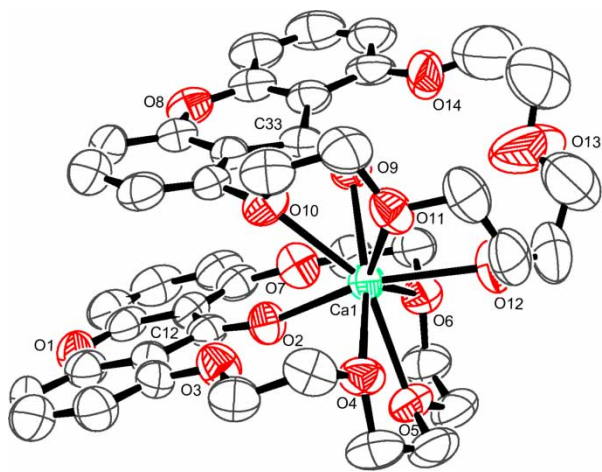

Figure 3. Thermal ellipsoid (50%) diagram of **5**. Perchlorate anions and hydrogen atoms have been excluded for clarity.
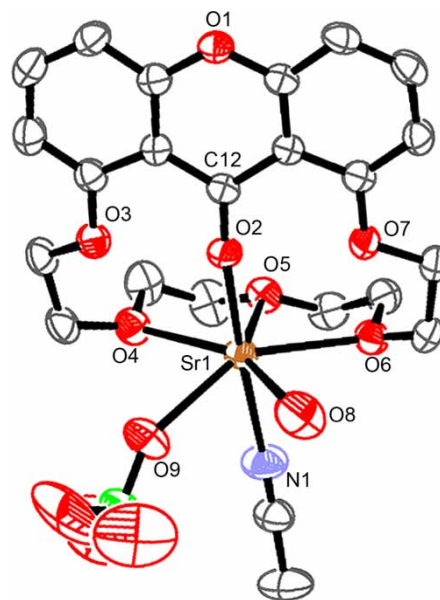

Figure 4. Thermal ellipsoid (50%) diagram of **10**. One perchlorate anion and hydrogen atoms have been excluded for clarity.
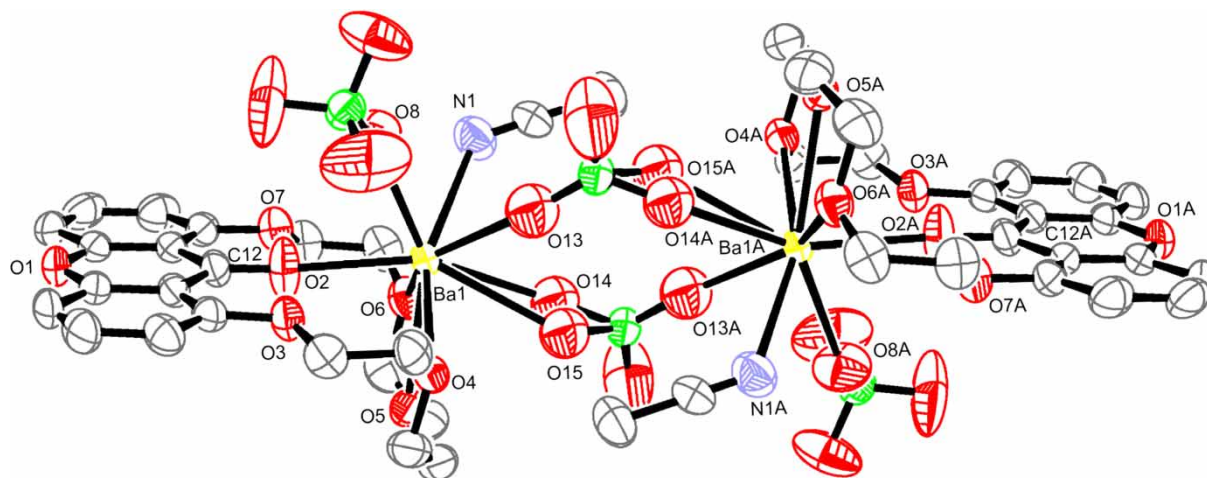
Figure 5. Thermal ellipsoid (50%) diagram of dimeric **11**. Perchlorate anions and hydrogen atoms have been excluded for clarity.

Preparation of compounds

[Na·L·ClO₄] (2)

L (77.2 mg, 0.2 mmol) was dissolved in acetonitrile (5 ml). Sodium (I) perchlorate monohydrate (28.1 mg, 0.2 mmol) was dissolved in acetonitrile (2 ml) and added dropwise. The mixture was stirred for 2 h. All the solvents were evaporated under reduced pressure. The residue was dissolved in acetonitrile (2 ml) and layered with diethyl ether. Fine yellow block crystals were obtained. Yield: 80% (81.4 mg). ESI-MS: $m/z = 409.7$ [Na·L]⁺. ¹H NMR (400 MHz, CD₃COCD₃, 25°C): δ 3.76 (m, 4H, CH₂−O), 3.88 (m, 4H, CH₂−O), 4.04 (m, 4H, CH₂−O), 4.34 (m, 4H, CH₂−O), 7.03 (d, 2H, Ar-H), 7.14 (d, 2H, Ar-H), 7.73 (t, 2H, Ar-H). IR (cm⁻¹, KBr): 3446 (w), 2933 (m), 1662 (m), 1599 (m), 1279 (m), 1231 (m), 1090 (s), 771 (m), 621 (m). Elemental anal. calcd for $C_{21}H_{22}ClNaO_{11}$: C, 49.57; H, 4.36%. Found: C, 49.31; H, 3.98%.

[Ca·L·ClO₄·CH₃CN·H₂O]ClO₄ (9)

L (77.2 mg, 0.2 mmol) was dissolved in acetonitrile (5 ml). Calcium (II) perchlorate tetrahydrate (62.0 mg, 0.2 mmol) was dissolved in acetonitrile (10 ml) and added dropwise. The mixture was stirred for 1 h. All the solvents were evaporated under reduced pressure. The residue was dissolved in acetonitrile (2 ml) and layered with diethyl ether. Yellow crystals were obtained. Yield: 65% (86.5 mg). ESI-MS: $m/z = 213.4$ [Ca·L]²⁺, 525.5 [Ca·L·ClO₄]⁺. ¹H NMR (400 MHz, CD₃COCD₃, 25°C): δ 3.98 (d, 8H, CH₂−O), 4.31 (s, 4H, CH₂−O), 4.53 (s, 4H, CH₂−O), 7.12 (d, 2H, Ar-H), 7.18 (d, 2H, Ar-H), 7.78 (t, 2H, Ar-H, $J = 8.8$ Hz). IR (cm⁻¹, KBr): 3407 (w), 2929 (m), 1635 (m), 1602 (m), 1478 (m), 1277 (m), 1082 (s), 770 (m), 625 (m). Elemental anal. calcd for $C_{23}H_{27}CaCl_2NO_{16}$: C, 40.36; H, 3.98; N, 2.05%. Found: C, 40.12; H, 3.64; N, 1.95%.
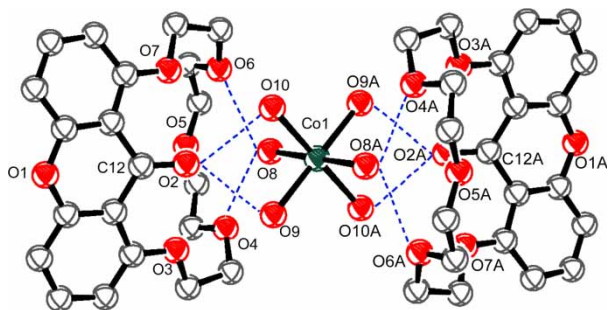
[Sr·L·ClO₄·CH₃CN·H₂O]ClO₄ (10)

L (77.2 mg, 0.2 mmol) was dissolved in acetonitrile (5 ml). Strontium (II) perchlorate dihydrate (64.4 mg, 0.2 mmol) was dissolved in acetonitrile (10 ml) and added dropwise. The mixture was stirred for 2 h. All the solvents were evaporated under reduced pressure. The residue was dissolved in acetonitrile (2 ml) and layered with diethyl ether. Yellowish coloured crystals were obtained. Yield: 70% (102.3 mg). ESI-MS: $m/z = 237.4$ [Sr·L]²⁺, 573.4 [Sr·L·ClO₄]⁺. ¹H NMR (400 MHz, CD₃COCD₃, 25°C): δ 4.02 (d, 8H, CH₂−O), 4.35 (s, 4H, CH₂−O), 4.51 (t, 4H, CH₂−O, $J = 4.8$ Hz), 7.12 (d, 2H, Ar-H), 7.20 (d, 2H, Ar-H), 7.81 (t, 2H, Ar-H, $J = 8.8$ Hz). IR (cm⁻¹, KBr): 3406 (w), 2933 (m), 1653

Figure 6. Thermal ellipsoid (50%) diagram of **13**. Perchlorate anions and hydrogen atoms have been excluded for clarity.

(m), 1601 (m), 1479 (m), 1279 (m), 1087 (s), 770 (m), 627 (m). Elemental anal. calcd for $C_{23}H_{27}Cl_2NO_{16}Sr$: C, 37.74; H, 3.72; N, 1.91%. Found: C, 37.48; H, 3.88; N, 1.97%.

[2Ba·2L·4ClO₄·2CH₃CN] (11)

L (77.2 mg, 0.2 mmol) was dissolved in acetonitrile (5 ml). Barium (II) perchlorate trihydrate (78.0 mg, 0.2 mmol) was dissolved in acetonitrile (10 ml) and added dropwise. The mixture was stirred for 2 h. All the solvents were evaporated under reduced pressure.

The residue was dissolved in acetonitrile (3 ml) and layered with diethyl ether. Fine colourless block crystals were obtained. Yield: 70% (106.8 mg). ESI-MS: $m/z = 262.4$ [Ba·L]$^{2+}$, 623.3 [Ba·L·ClO₄]$^+$. ^{1}H NMR (400 MHz, CD₃COCD₃, 25°C): δ 3.98 (s, 8H, CH₂−O), 4.16 (s, 4H, CH₂−O), 4.38 (s, 4H, CH₂−O), 6.98 (d, 2H, Ar-H), 7.10 (d, 2H, Ar-H), 7.73 (t, 2H, Ar-H, $J = 8.0$ Hz). IR (cm^{-1}, KBr): 3396 (w), 2928 (m), 1649 (m), 1602 (m), 1463 (m), 1274 (m), 1085 (s), 770 (m), 624 (m). Elemental anal. calcd for $C_{23}H_{25}BaCl_2NO_{15}$: C, 36.17; H, 3.30; N, 1.83%. Found: C, 36.31; H, 3.54; N, 1.92%.
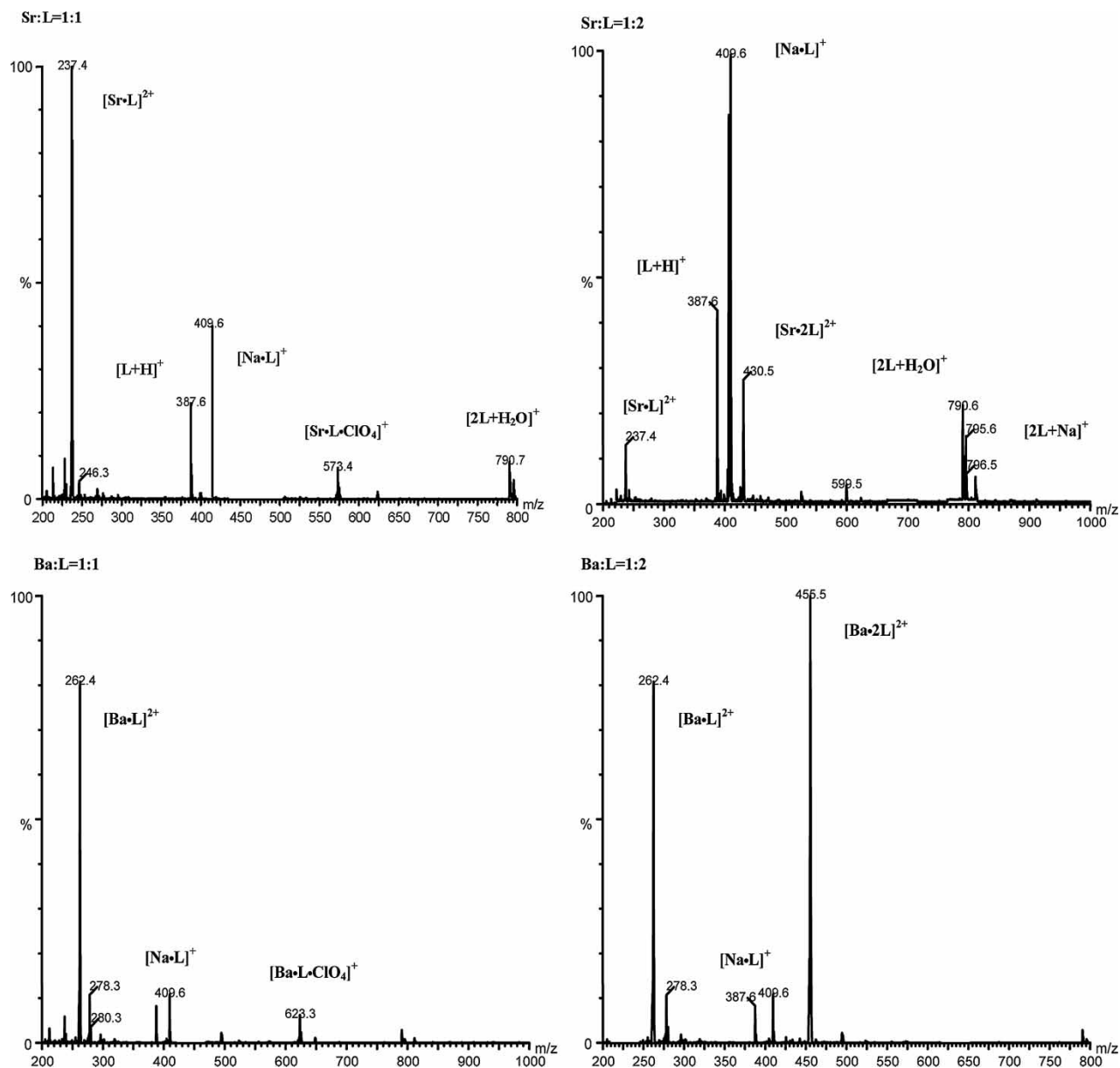

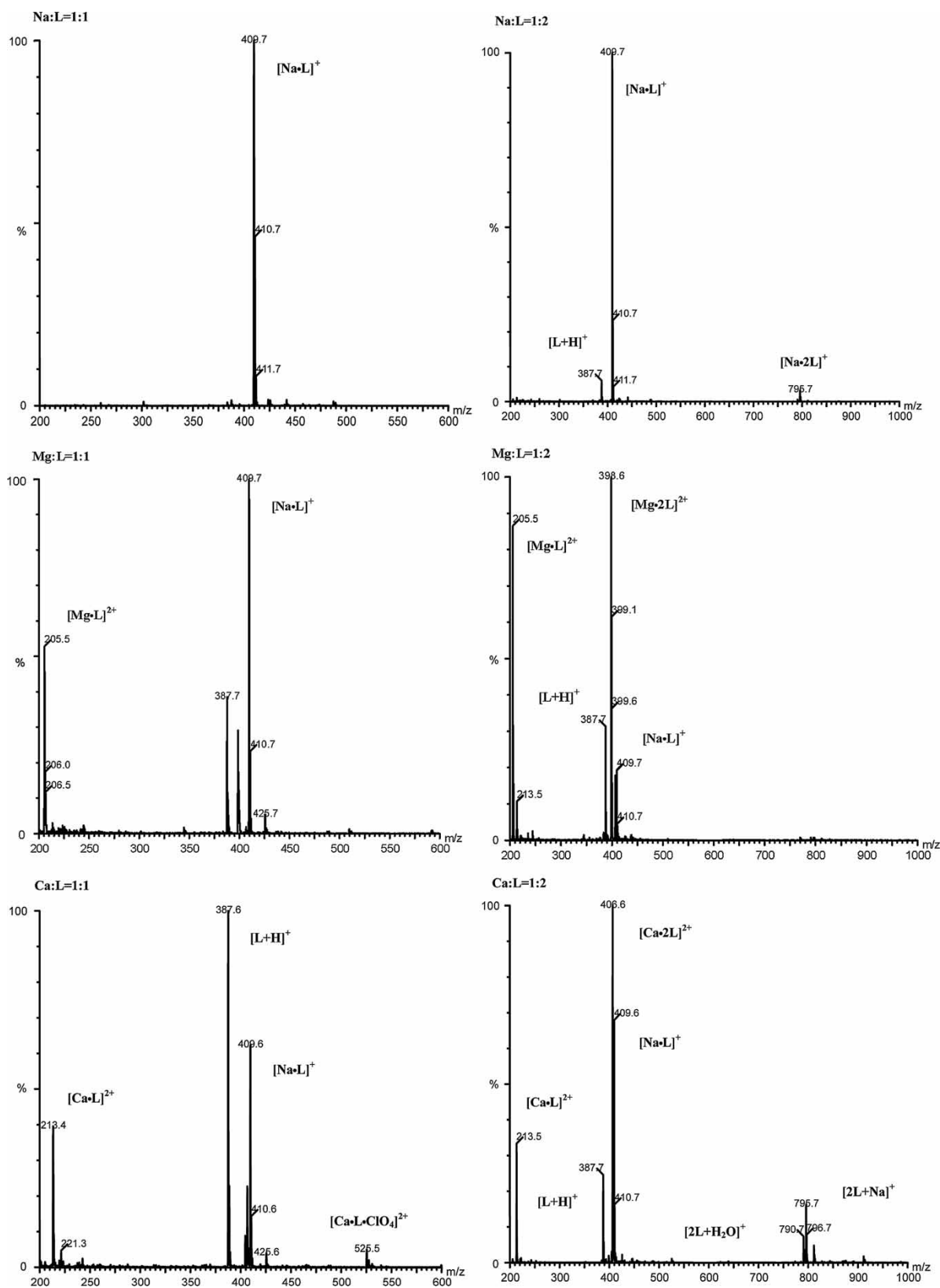Figure 7.   Electron spray ion mass spectra of complexes **1**−**11** (except polymer (**3**)) in acetonitrile solution.
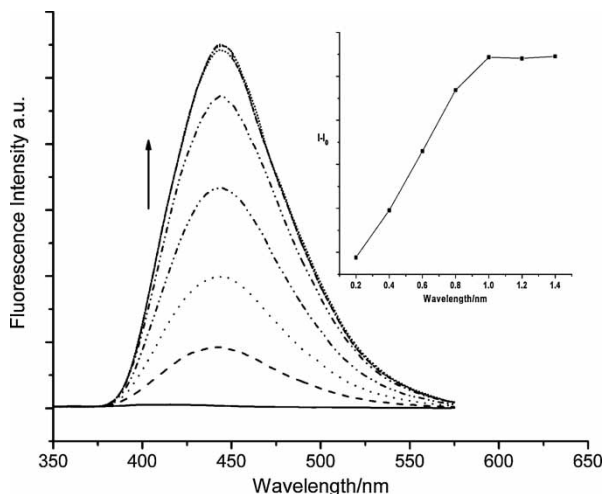
Figure 7. (continued).

Figure 8. Fluorescence titration of L with $Ca(ClO_4)_2$. Each addition is 0.2 equiv. of $Ca(ClO_4)_2$ in acetonitrile. Excitation at 310 nm. Inset is a plot of emission intensity versus equivalents of Ca^{2+} added. $[L] = 1.0 \times 10^{-5}$ M.
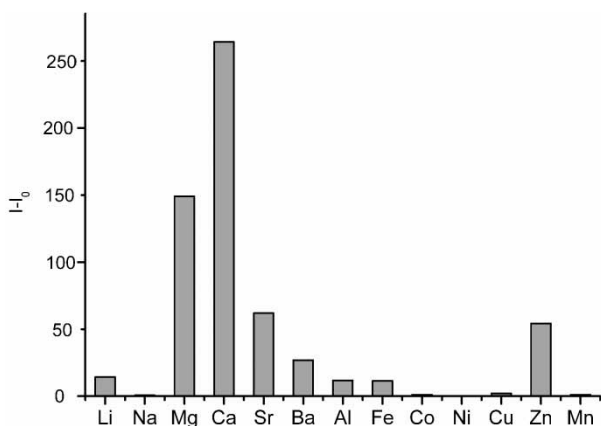

Figure 9. Fluorescence changes of L after addition of 2 equiv. of metal perchlorate salts. Excitation wavelength was 310 nm and the emission intensity changes were calculated at 445 nm. $[L] = 1.0 \times 10^{-5}$ M; $M^{2+} = 2.0 \times 10^{-5}$ M.

$[Co(H_2O)_6 \cdot 2L](ClO_4)_2$ (13)

L (77.2 mg, 0.2 mmol) was dissolved in acetonitrile (5 ml). Cobalt(II) perchlorate hexahydrate (36.5 mg, 0.1 mmol) was dissolved in acetonitrile (5 ml) and added dropwise. The mixture was stirred for 2 h. All the solvents were evaporated under reduced pressure. The residue was dissolved in acetonitrile (2 ml) and layered with diethyl ether. Fine orange-coloured crystals were obtained. Yield: 83% (77.9 mg). ESI-MS: $m/z = 387.1$ $[L+H]^+$. IR (cm^{-1}, KBr): 3409 (w), 2924 (m), 1649 (m), 1604 (m), 1476 (m), 1281 (m), 1087 (s), 767 (m), 624 (m). Elemental anal. calcd for $C_{23}H_{31}ClCo_{0.50}NO_{14}$: C, 45.26; H, 5.12; N, 2.29%. Found: C, 45.02; H, 5.03; N, 2.41%.

Acknowledgements

References

(1) de Silva, A.P.; Gunaratne, H.Q.N.; Gunnlaugsson, T.; Huxley, A.J.M.; McCoy, C.P.; Rademacher, J.T.; Rice, T.E. *Chem. Rev.* **1997**, *97*, 1515–1566.
(2) Kadarkaraisamy, M.; Sykes, A.G. *Inorg. Chem.* **2006**, *45*, 779–789.
(3) Liu, Y.; Han, M.; Zhang, H.-Y.; Yang, L.; Jiang, X.W. *Org. Lett.* **2008**, *10*, 2873–2876.
(4) Prodi, L.; Bolletta, F.; Zaccheroni, N.; Watt, I.F.; Mooney, J.N. *Chem. Eur. J.* **1998**, *4*, 1090–1094.
(5) Shen, R.; Pan, X.B.; Wang, H.F.; Yao, L.H.; Wu, J.C.; Tang, N. *Dalton Trans.* **2008**, *27*, 3574–3581.
(6) Mills, S.; Mooney, N.J.; Robinson, P.M.; Watt, C.F.; Box, B.G. *J. Chem. Soc., Perkin Trans.* **1995**, *2*, 697–708.
(7) Beddoes, R.S.; Cox, B.G.; Mills, O.S.; Mooney, N.J.; Watt, C.F.; Kirkland, D.; Martin, D. *J. Chem. Soc., Perkin Trans.* **1996**, *2*, 2091–2098.
(8) Shen, R.; Pan, X.B.; Wang, H.F.; Wu, J.C.; Tang, N. *Inorg. Chem. Commun.* **2008**, *11*, 318–322.
(9) Shen, R.; Wang, H.F.; Wu, J.C.; Tang, N. Unpublished results.