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Syntheses, structural characterizations and properties of 12-MC-4 organotin(IV) metallacrowns: [12-MC$_{RSn(IV)N(shi)}$-4] and [12-MC$_{RSn(IV)N(Clshi)}$-4] (R = Et, Bu, Ph; H_3shi = salicylhydroxamic acid; H_3Clshi = 5-chlorosalicylhydroxamic acid)

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ABSTRACT

Five 12-MC-4 organotin(IV) metallacrowns(MCs) with the types of [12-MC$_{RSn(IV)N(shi)}$-4] (R = Et (**1**), Bu (**2**), Ph (**3**); H_3Shi = salicylhydroxamic acid) and [12-MC$_{RSn(IV)N(Clshi)}$-4] (R = Et (**4**), Bu (**5**), H_3Clshi = 5-chlorosalicylhydroxamic acid) have been synthesized and characterized by elemental analyses, IR and TGA. X-ray single-crystal diffraction analyses were also carried out and showed that all complexes **1**–**5** contain a neutral 12-membered metallacrown ring which is formed by the succession of four repeating units of –[Sn–N–O]–, indicating the substituents on the tin(IV) atom are uninfluential in coordination of organotin(IV) centers with hydroxamic acid. Fluorescence properties of complexes **1**–**5** have been investigated, where complex **3** displays strong fluorescence emissions in the blue region. In addition, antitumor activities of complexes **4** and **5** have also been tested, and both the complexes exhibit weak activity towards human hepatocellular carcinoma cell line (Bel-7402) and Hela cell line.

1. Introduction

Since the first metallacrowns were reported in 1989 [1,2], metallacrown compounds have attracted considerable attentions owing to their diverse architectures [3], and their potential applications in host–guest, supramolecular chemistry [4], recognition reagents [5], bioactivities [6], single-molecular magnets (SMMs) and single-chain magnets (SCMs).[7] A series of traditional metallacrowns with $[-M-N-O-]_n$ repeat linkage including 9-MC-3, 12-MC-4, 15-MC-5, 18-MC-6 and 24-MC-8, which contain the planar, inverse, dimmer, fused and off-set stacked structures, have been reported until now. The metal centers of these reported metallacrowns are always transition ions, such as V(V), Cr(III), Mn(II, III), Fe(III), Co(II, III), Ni(II), Cu(II), Zn(II), etc. [8]. However, few metallacrowns have been prepared by the reaction of organometal centers and organic ligands so far.

On the other hand, organotin(IV) compounds have received much interest for their various coordination modes depending on the number and the nature (Me, Et, Bu, Ph) of the organic substituents on the central tin(IV) atom [9–12] as well as their potential biological activities [13–17]. It is reported that the biological activity of organotin(IV) compounds is greatly influenced by the structure of the molecule and the nuclearity of the complexes [18,19] and polynuclear organotin(IV) compounds may exhibit higher antitumor activity [20].

In order to expand the "periodic table" of the metallacrowns [3b] and obtain a deeper insight into the coordination of hydroxamic acid with organotin(IV) centres, we designed and successfully prepared five 12-MC-4 organotin(IV) metallacrowns with salicylhydroxamic acid and 5-chlorosalicylhydroxamic acid ligands, which are characterized by elemental analyses, IR, TGA and X-ray single-crystal diffraction analyses. Herein we report the synthesis and structural characterization of these [12-MC$_{[RSn(IV)]N(shi)}$-4] (R = Et(**1**), Bu(**2**), Ph (**3**); H_3Shi = salicylhydroxamic acid) and [12-MC$_{RSn(IV)N(Clshi)}$-4] (R = Et(**4**), Bu(**5**); H_3Clshi = 5-chlorosalicylhydroxamic acid) metallacrown complexes. Fluorescence properties of complexes **1**–**5** have been also investigated, where complex **3** displays strong fluorescence emissions in the blue region. In addition, antitumor activities of complexes **4** and **5** have been tested, and both the complexes exhibit weak activity towards human hepatocellular carcinoma cell line (Bel-7402) and Hela cell line.

2. Results and discussion

2.1. Syntheses

As shown in Scheme 1, the organotin(IV) metallacrowns [12-MC$_{[RSn(IV)]N(shi)}$-4] (R = Et(**1**), Bu(**2**), Ph(**3**); H_3Shi = salicylhydro

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xamic acid) and [12-$MC_{RSn(IV)N(Clshi)}$-4] (R = Et(**4**), Bu(**5**); H_3Clshi = 5-chlorosalicylhydroxamic acid) were obtained from the reactions between equimolar amounts of R_3SnCl and ligands in methanol and pyridine mixed solution. Complexes **1**–**5** were all colorless solid and stable in air. Complexes **1**–**3** are insoluble in water, chloroform, acetone, methanol, pyridine, DMSO and DMF, whereas complexes **4** and **5** are slightly soluble in DMSO and DMF.

2.2. IR spectroscopic data

The assignments of the IR bands of complexes **1**–**5** have been made by comparison with the IR spectra of the free ligand. For the five complexes, no ν(OH) and ν(N–H) bands were found, which appeared in the range of 3340–3079 cm^{-1} in free ligands, in accord with deprotonated and coordination to the tin ions of the three oxygens and one nitrogen of the ligand. The characteristic absorptions at about 1600, 1560 cm^{-1} are assigned to CO/CN stretching vibration [21–24]. While the medium-intensity absorption appearing at 430–433 cm^{-1} in the IR spectra, which is absent in the spectrum of the free ligand, is assigned to the Sn–O stretching vibration [25,26]; and the medium-intensity band appearing at 623–669 cm^{-1} is assigned to the Sn–N stretching vibration.

2.3. Description of the structures of *1*–*3* [27]

The crystal structure of complexes **1**–**3** is illustrated in Fig. 1a–c, respectively. Selected bond lengths and angles are listed in Table 2. In the structure of **1**–**3**, four Sn atoms and four shi^{3-} ligands construct the formally neutral [12-$MC_{RSn(IV)N(shi)}$-4] metallacrown, each salicylhydroxamic acid ligand chelated to one Sn atom with the carbonyl O atom and hydroximate O atom, and is coordinated to an adjacent Sn atom through the phenolate O atom and imine N atom, thus μ-NO bridges are established. Complexes **1**–**3** all possess a vacant cavity in the center of the metallacrown. The bite distances of complexes **1**–**3** (3.474 Å for **1**, 3.387 Å for **2** and 3.437 Å for **3**) are longer than those observed in transition metal 12-MC-4 complexes, but the cavity sizes (0.66 Å for **1**, 0.62 Å for **2** and 0.55 Å for **3**) are consistent with the values of the 12-MC-4 metallacrowns constructed by the hydroxamic acid ligands (0.50–0.66 Å) [2,28–30].

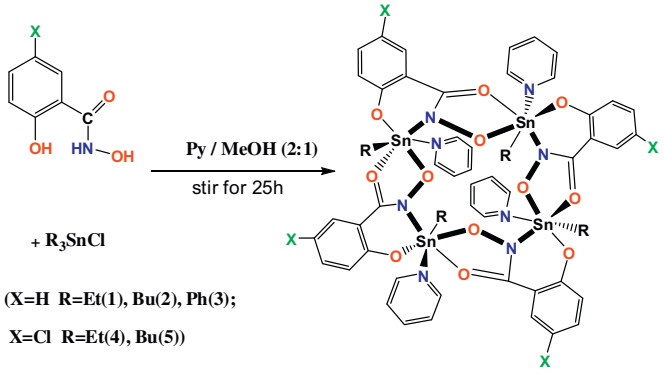
As shown in Fig. 2a, in complex **1**, adjacent metallacrown rings are connected into 2D supramolecular network parallel *ac* plane *via* C21–H21···O5(carbonyl)#1 [#1: $x + 1/2, -y + 1/2, z - 1/2$] and C22–H22···O3 (phenolate)#1, the distances between C21···O5, C22···O3 are 3.297(9) and 3.463(9) Å respectively, which both lie within the values in previous literature [31,32]; the angles of C(21)–H(21)···O(5), C(22)–H(22)···O(3) are 122.3° and 152.2° respectively. In complex **2**, carbonyl O atom and carbon atom C of pyridine molecule are provided as acceptors and donors respectively to form C–H···O weak interactions (C16···O5#1 [#1: $x + 1/2, -y + 1/2, z + 1/2$], 3.187 Å), which link the adjacent molecules into 2D network parallel *bc* plane (Fig. 2b). While more than one kind of weak interactions are present in complex **3**, adjacent metallacrown rings are assembled 2D supramolecular frameworks parallel *bc* plane *via* the C–H···O(C22···O3#1 [#1: $x - 1/2, -y + 1/2, z + 1/2$], 3.462(10) Å, 158.6°) and C28–H28···π interactions, which are future linked into a 3D network configuration by C–H···π interactions between ligand benzene carbon atom C6 and the phenyl ring (C25–C30) (Fig. 3a). The C–H···π distances between H6···Cg1 (Cg1, ring center of C25–C30 at $x - 1/2, -y + 1/2, -z + 1/2$) and H28···Cg2 (Cg2, ring center of C31–C36 at $-x + 1/2, y + 1/2, -z + 1/2$) are 3.068 and 3.142 Å, respectively, and they both lie within the common reported values for aromatic C–H···π interactions (2.59–3.39 Å) [33–47].

For analysing metal–organic networks sustained by coordination and/or hydrogen bonds, a widely used approach is the net-based approach, which reduces complicated structures to simple topological networks of multiply connected nodes. Each metallacrown is connected to four other ones through C22–H22···O3 and C28–H28···π interactions parallel *bc* plane and also interacted with other four ones through C6–H6···π interactions above and below the *bc* layer, respectively. Herein these supramolecular interactions and the metallacrown units are treated as an actual bond and the single node, respectively, as shown in Fig. 3b, the resulting 3-D structure can be topologically reduced to an 8-connecting net with a Schlafli symbol ($4^{24}6^4$), which is very similar to the **bcu** net (CsCl).

2.4. Description of the structures of *4* and *5*

The crystal structure of complexes **4** and **5** is illustrated in Fig. 1d and e. Selected bond lengths and angles are listed in Table 2. In complexes **4** and **5**, the triply deprotonated form of $Clshi^{3-}$ is similar to the shi^{3-} which act as tetradentate ligands to chelated two adjacent tin atoms with Sn–N–O linkages which are emphasized by bold bonds. The phenolate oxygen and imine nitrogen atoms are bound to one tin atom, and the carbonyl and hydroximate oxygen atoms are bound to an adjacent tin atom. Meanwhile, one Sn(IV) atom binds in a five-membered chelate ring formed through the hydroximate group, while a second Sn(IV) atom binds to the six-membered substituted iminophenolate ring and the basis of metallacrown ring is formed by these juxtapose five- and six-membered chelate rings through the $(Sn–N–O–)_4$ linkage. All the Sn atoms are hexa-coordinated in a distorted octahedron geometry, that is all the tin atoms possess the same coordination environments, with only minor differences in bond lengths and bond angles. In complexes **4** and **5**, the average distances of Sn–N(py), Sn–N(Clshi) and Sn–O(Clshi) in the complexes (2.328, 2.177 and 2.078 Å for **4** and 2.341, 2.179 and 2.081 Å for **5**) are in the normal range of organotin complexes [41]. The sum of the angles of Sn···Sn···Sn (79.08, 100.92, 79.08, 100.92° for **4**; 79.25, 100.75, 79.25, 100.25° for **5**) is 360°, so four Sn atoms site in a parallelogram geometry, the Sn···Sn diagonal distances within the Sn4 parallelogram are 7.673 and 6.335 Å for **4**; 7.667 and 6.348 Å for **5**, respectively, and the Sn···Sn adjacent distances are 4.968 and 4.982 Å for 4; 4.937 and 4.981 Å for **5**, respectively. There is an empty cavity in the center of the metallacrown and the bite distances of complexes **4** and **5** are 3.426 and 3.433 Å, respectively, which are longer than those observed in transition metal 12-MC-4 complexes; the cavity sizes (0.63 Å for **4** and 0.64 Å for **5**) are consistent with the values of the 12-MC-4 metallacrowns constructed by the hydroxamic acid ligands (0.50–0.66 Å) [2,28–30].

In complex **4**, adjacent molecules are assembled 2D network parallel *ab* plane (Fig. 4a) *via* C–H···O weak interactions



Scheme 1.

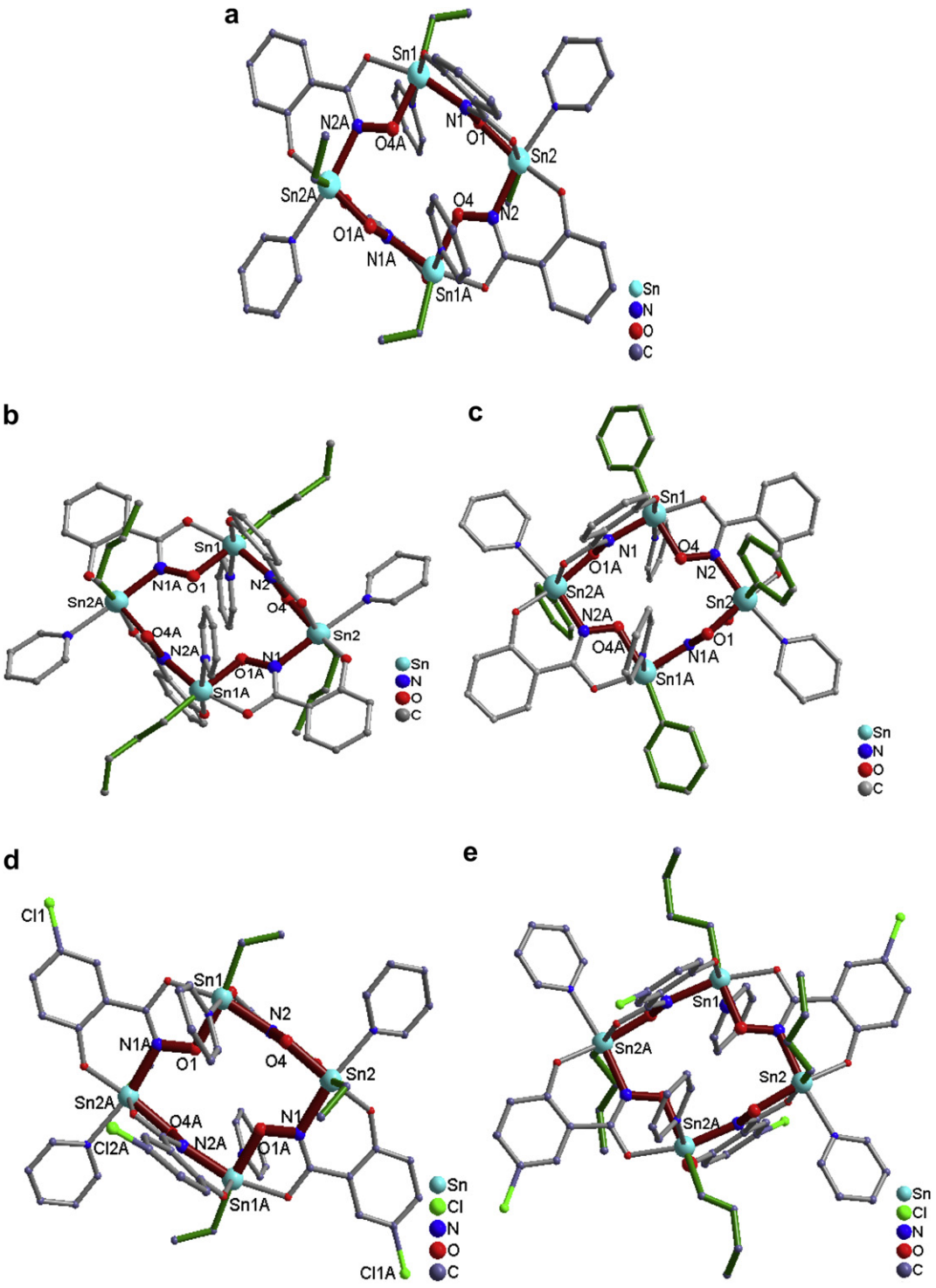


Fig. 1. The crystal structure of complexes **1**(a), **2**(b),**3**(c), **4**(d), **5**(e) in ORTEP view (the hydrogen atoms have been omitted for clarity).

(C22···O6#1[#1 1.5 − *x*, *y* − 0.5, −*z* + 0.5]; 3.557(11) Å) between phenolate oxygen atoms and carbon atoms of pyridine molecule. In complex **5**, adjacent molecules are assembled 2D supramolecular frameworks parallel *bc* plane by C—H···Cl weak interactions (Fig. 4b). The distances of H29B···Cl2#1 (#1 *x* − 1/2, −*y* − 1/2, *z* − 1/2) and H28C···Cl1#1 are 2.76 and 2.74 Å, respectively, which both lie within the values in previous literature [38,39].

On the whole, the structural analyses of complexes **1**–**5** show that the mild conditions of the reactions lead to dealkylation to obtain novel metallacrowns, which are few reported [40]. The donors (nitrogen and oxygen atoms) provided by the ligands to the ring organotin(IV) atoms play a key factor in the coordination of hydroxamic acid with organotin(IV), and the substituents on the central tin(IV) atom are uninfluential, although they are contributing in the spatial arranging of the metallacrown molecules. The cavity sizes of these five 12-MC-4 metallacrowns could encapsulate alkali metal and alkaline earth metal ions, transition metal ions and main group metal ions into the metallacrown rings, but complexes

Table 1
Crystal data and structure refinement parameters for complexes **1**–**5**.

	Complex **1**	Complex **2**	Complex **3**	Complex **4**	Complex **5**
Empirical formula	$C_{56}H_{56}N_8O_{12}Sn_4$	$C_{64}H_{72}N_8O_{12}Sn_4$	$C_{72}H_{56}N_8O_{12}Sn_4$	$C_{56}H_{52}Cl_4N_8O_{12}Sn_4$	$C_{63.50}H_{67}Cl_4N_8O_{12}Sn_4$
Formula weight	1507.85	1620.06	1700.01	1645.62	1750.81
Temperature	298(2) K	298(2) K	298(2) K	298(2) K	298(2) K
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
space group	P2(1)/n	P2(1)/n	P2(1)/n	P2(1)1/n	P2(1)/n
a (Å)	12.2580(12)	12.8702(15)	13.1385(11)	12.2029(13)	12.7445(14)
b (Å)	19.159(2)	13.1065(16)	18.143(2)	19.8896(19)	13.0682(12)
c (Å)	12.748(2)	20.343(2)	13.8972(14)	12.7668(15)	21.419(2)
β	101.531(2)	108.083(2)	100.5320(10)	98.9020(10)	103.172
V (A^3)	2933.4(7)	3262.1(6)	3305.4(6)	3061.3(6)	3473.3(6)
Z	2	2	2	2	2
D (Mg/m^3)	1.707	1.649	1.708	1.785	1.674
F(000)	1488	1616	1680	1616	1736
Data/restraints/parameters	5165/0/363	5746/0/399	5835/0/433	5412/0/381	6122/0/484
Goodness-of-fit on F^2	0.976	1.000	0.999	1.000	0.999
Final *R* indices	$R_1 = 0.0528$	$R_1 = 0.0474$	$R_1 = 0.0447$	$R_1 = 0.0515$	$R_1 = 0.0503$
[$I > 2$sigma(I)]	$wR_2 = 0.0579$	$wR_2 = 0.1277$	$wR_2 = 0.0881$	$wR_2 = 0.0742$	$wR_2 = 0.1041$
Largest diff. peak and hole (e $Å^{-3}$)	0.984–0.792	1.167–1.276	0.838–0.570	0.640–0.440	0.979–0.589

1–**5** actually have a vacant cavity in the center of metallacrown rings, which may be influenced by the steric hindrance of the larger substitutes on the tin atoms.

2.5. Thermal stability

To evaluate the thermal stability of complexes **1**–**5**, thermogravimetric analyses (TGA) of complexes were performed in the temperature range of 30–500 °C under N_2 atmosphere. The TGA curves of complexes **1**–**5** showed the framework of these cyclic metallacrown host molecules can be intact up to 170 °C. On further heating, complexes **1**–**5** dramatically lose their weight from 170 °C to 490 °C.

2.6. Fluorescence properties

The fluorescence properties of complexes **1**–**5** and both ligands were measured at room temperature, and the fluorescent spectra are displayed in Fig. 5. As shown in Fig. 5a, when excited at 300 nm, the fluorescence emission bands of free salicylhydroxamic acid (H_3shi) are mainly located at 336 and 427 nm with shoulders at 460, 500 and 535 nm, which can be attributed to the $\pi^* \rightarrow$ n and $\pi^* \rightarrow \pi$ transitions. Compounds **1**–**3** exhibit emissions at 438, 412 and 400 nm which are red-shifted by 102, 76 and 64 nm respectively compared to the free ligand, which can be assigned tentatively to ligand-to-metal charge transfers (LMCT) [41]. The biggish red-shift of the energy of complexes in comparison to that of free ligand can be attributed to the coordination of the metal and the ligand; in addition, because of the extended π-conjugation of the phenyl groups, the emission intensity of complex **3** increases.

When excited at 300 nm (Fig. 5b), the free H_3Clshi ligand displays one strong fluorescence emission at 430 nm and complex **4** (excited at 320 nm) exhibits the emission at 439 nm, which should be attributed to the $\pi^* \rightarrow \pi$ transition of the free ligand, while complex **5** exhibits the emission at 390 and 560 nm respectively, when excited at 300 nm, which should be assigned to ligand-to-metal charge transfer. It is interesting that the emission wavelength of **5** undergoes a blue shift probably because the C–H···Cl interactions of the adjacent molecules decrease π-conjugation of complex.

All of complexes **1**–**5** display fluorescence properties in the blue region at room temperature, the emission intensity of these complexes are different and this suggests that the different interactions and dimensional architectures can result in the different HOMO–LUMO gap [42–44] and thus exhibit different luminescent properties. The emission bands of complexes **1**–**3** and **5** may be tentatively assigned to be charge transfer between metal and ligand. And complex **3** may be applied in light-emitting devices, since they are thermally stable and insoluble in common polar and non-polar solvents.

2.7. Antitumor activities

Owing to the insolubility in water and DMSO, the antitumor activities of complexes **1**–**3** are difficult to be formulated. Complexes **4** and **5** were screened for the in vitro tumor-inhibiting activity against human hepatocellular carcinoma cell line (Bel-7402) and Hela cell line. The inhibitory concentration IC_{50} has been assayed, for complexes **4** and **5**, the IC_{50} values for Bel-7402 and Hela cell lines are listed in Table 3, and the results show that complexes **4** and **5** exhibit weak activity towards both the tested tumor cell lines, which are greatly weaker than that of the reported polynuclear organotin(IV) compounds [19,20]. So we are currently turning to exploring the organotin(IV) metallacrown with the higher solubility in water or in DMSO to study the factors that influence the antitumor activities of organotin(IV) compounds.

3. Conclusions

In conclusion, we have successfully prepared five 12-MC-4 organotin(IV) metallacrowns with salicylhydroxamic acid (H_3shi) and 5-chlorosalicylhydroxamic acid (H_3Clshi) ligands, which were characterized by elemental analyses, IR, TGA and X-ray single-crystal diffraction. The structural analyses of complexes **1**–**5** exhibit that the donors provided by the ligands to the ring organotin(IV) atoms play a major role in the coordination of hydroxamic acid ligands with organotin(IV), and the organic substituents on the tin(IV) atom which are contributing in the spatial arrangement of the metallacrown molecules are little effective. All complexes **1**–**5** display fluorescence properties in the blue region at room temperature. Complexes **4** and **5** exhibit weak antitumor activity towards the human hepatocellular carcinoma (Bel-7402) and Hela cell lines.

4. Experimental section

4.1. Materials and measurements

All chemicals and solvents for the synthesis of the complexes are commercially available, and they were used without further purification. The melting point was obtained with a Kofler micro-melting point apparatus and was uncorrected. IR spectra were

Table 2
Selected bond lengths [Å] and angles [°] for complexes **1**–**5**.

Complex **1**			
Sn(1)–O(3)	2.048(4)	Sn(1)–O(4)	2.062(4)
Sn(1)–C(25)	2.107(8)	Sn(1)–O(5)	2.115(4)
Sn(1)–N(1)	2.151(5)	Sn(1)–N(3)	2.336(6)
Sn(2)–O(6)#1	2.044(5)	Sn(2)–O(1)	2.065(4)
Sn(2)–O(2)	2.107(4)	Sn(2)–C(27)	2.113(7)
Sn(2)–N(2)#1	2.176(5)	Sn(2)–N(4)	2.291(6)
N(2)–Sn(2)#1	2.176(5)	O(6)–Sn(2)#1	2.044(5)
O(3)–Sn(1)–O(4)	90.80(18)	O(3)–Sn(1)–O(5)	95.26(17)
O(4)–Sn(1)–O(5)	76.30(17)	O(3)–Sn(1)–N(1)	83.38(19)
O(4)–Sn(1)–N(1)	88.93(18)	O(5)–Sn(1)–N(1)	165.16(19)
O(3)–Sn(1)–N(3)	171.8(2)	O(4)–Sn(1)–N(3)	81.95(19)
O(5)–Sn(1)–N(3)	86.76(18)	N(1)–Sn(1)–N(3)	92.6(2)
O(6)#1–Sn(2)–O(1)	162.71(17)	O(6)#1–Sn(2)–O(2)	87.48(17)
O(1)–Sn(2)–O(2)	75.83(16)	O(6)#1–Sn(2)–N(2)#1	84.4(2)
O(1)–Sn(2)–N(2)#1	99.20(18)	O(2)–Sn(2)–N(2)#1	87.98(18)
O(6)#1–Sn(2)–N(4)	82.5(2)	O(1)–Sn(2)–N(4)	91.0(2)
O(2)–Sn(2)–N(4)	83.36(18)	N(2)#1–Sn(2)–N(4)	164.6(2)
Complex **2**			
Sn(1)–O(3)	2.056(7)	Sn(1)–O(4)#1	2.065(6)
Sn(1)–O(5)#1	2.108(6)	Sn(1)–C(25)	2.117(10)
Sn(1)–N(1)	2.135(7)	Sn(1)–N(3)	2.343(9)
Sn(2)–O(6)	2.021(6)	Sn(2)–O(1)	2.067(6)
Sn(2)–O(2)	2.099(7)	Sn(2)–C(29)	2.127(15)
Sn(2)–N(2)	2.169(7)	Sn(2)–N(4)	2.307(8)
O(4)–Sn(1)#1	2.065(6)	O(5)–Sn(1)#1	2.108(6)
O(3)–Sn(1)–O(4)#1	90.5(3)	O(3)–Sn(1)–O(5)#1	93.0(3)
O(4)#1–Sn(1)–O(5)#1	76.9(2)	O(3)–Sn(1)–N(1)	84.9(3)
O(4)#1–Sn(1)–N(1)	88.6(2)	O(5)#1–Sn(1)–N(1)	165.3(2)
O(3)–Sn(1)–N(3)	171.4(3)	O(4)#1–Sn(1)–N(3)	81.0(3)
O(5)#1–Sn(1)–N(3)	84.8(3)	N(1)–Sn(1)–N(3)	95.2(3)
O(6)–Sn(2)–O(1)	162.6(3)	O(6)–Sn(2)–O(2)	86.5(3)
O(1)–Sn(2)–O(2)	76.4(3)	O(6)–Sn(2)–N(2)	84.4(3)
O(1)–Sn(2)–N(2)	97.6(3)	O(2)–Sn(2)–N(2)	89.1(3)
O(6)–Sn(2)–N(4)	83.9(3)	O(1)–Sn(2)–N(4)	91.0(3)
O(2)–Sn(2)–N(4)	81.3(3)	N(2)–Sn(2)–N(4)	165.3(3)
Complex **3**			
Sn(1)–O(4)#1	2.060(4)	Sn(1)–O(3)	2.067(4)
Sn(1)–O(5)#1	2.107(4)	Sn(1)–C(25)	2.125(7)
Sn(1)–N(1)	2.141(5)	Sn(1)–N(3)	2.311(6)
Sn(2)–O(6)	2.046(5)	Sn(2)–O(1)	2.069(4)
Sn(2)–O(2)	2.109(4)	Sn(2)–C(31)	2.164(8)
Sn(2)–N(2)	2.165(5)	Sn(2)–N(4)	2.274(6)
O(4)–Sn(1)#1	2.060(4)	O(5)–Sn(1)#1	2.107(4)
O(4)#1–Sn(1)–O(3)	89.87(18)	O(4)#1–Sn(1)–O(5)#1	77.11(16)
O(3)–Sn(1)–O(5)#1	92.15(18)	O(4)#1–Sn(1)–N(1)	90.26(18)
O(3)–Sn(1)–N(1)	85.16(19)	O(5)#1–Sn(1)–N(1)	167.11(18)
O(4)#1–Sn(1)–N(3)	81.66(18)	O(3)–Sn(1)–N(3)	171.1(2)
O(5)#1–Sn(1)–N(3)	88.48(19)	N(1)–Sn(1)–N(3)	92.3(2)
O(6)–Sn(2)–O(1)	160.56(19)	O(6)–Sn(2)–N(2)	83.9(2)
O(6)–Sn(2)–O(2)	85.26(19)	O(1)–Sn(2)–O(2)	75.60(17)
O(1)–Sn(2)–N(2)	98.89(18)	O(2)–Sn(2)–N(2)	88.97(18)
C(31)–Sn(2)–N(2)	93.8(2)	O(6)–Sn(2)–N(4)	83.0(2)
O(1)–Sn(2)–N(4)	91.8(2)	O(2)–Sn(2)–N(4)	84.99(19)
Complex **4**			
Sn(1)–O(6)	2.052(6)	Sn(1)–O(1)	2.063(5)
Sn(1)–C(25)	2.102(9)	Sn(1)–O(2)	2.114(5)
Sn(1)–N(2)	2.170(7)	Sn(1)–N(3)	2.347(8)
Sn(2)–O(3)	2.049(6)	Sn(2)–O(4)#1	2.084(5)
Sn(2)–O(5)#1	2.105(6)	Sn(2)–C(27)	2.131(10)
Sn(2)–N(1)	2.184(7)	Sn(2)–N(4)	2.308(7)
O(4)–Sn(2)#1	2.084(5)	O(5)–Sn(2)#1	2.105(6)
O(6)–Sn(1)–O(1)	91.9(2)	O(6)–Sn(1)–C(25)	93.3(3)
O(1)–Sn(1)–C(25)	170.2(3)	O(6)–Sn(1)–O(2)	93.2(2)
O(1)–Sn(1)–O(2)	76.6(2)	C(25)–Sn(1)–O(2)	94.8(3)
O(6)–Sn(1)–N(2)	84.8(3)	O(1)–Sn(1)–N(2)	87.5(2)
C(25)–Sn(1)–N(2)	101.2(3)	O(2)–Sn(1)–N(2)	164.0(2)
O(6)–Sn(1)–N(3)	173.3(3)	O(1)–Sn(1)–N(3)	81.6(3)
C(25)–Sn(1)–N(3)	93.4(3)	O(2)–Sn(1)–N(3)	86.9(3)
N(2)–Sn(1)–N(3)	93.3(3)	O(3)–Sn(2)–O(4)#1	160.2(2)
O(3)–Sn(2)–O(5)#1	84.4(2)	O(4)#1–Sn(2)–O(5)#1	75.9(2)
O(3)–Sn(2)–C(27)	103.3(3)	O(4)#1–Sn(2)–C(27)	96.0(3)
O(5)#1–Sn(2)–C(27)	169.6(3)	O(3)–Sn(2)–N(1)	83.7(2)
O(4)#1–Sn(2)–N(1)	98.0(2)	O(5)#1–Sn(2)–N(1)	89.0(2)
C(27)–Sn(2)–N(1)	98.8(3)	O(3)–Sn(2)–N(4)	82.8(3)
O(4)#1–Sn(2)–N(4)	92.9(3)	O(5)#1–Sn(2)–N(4)	84.1(3)
C(27)–Sn(2)–N(4)	89.8(3)	N(1)–Sn(2)–N(4)	165.3(3)
Complex **5**			
Sn(1)–O(4)#1	2.067(4)	Sn(1)–O(3)	2.069(6)
Sn(1)–C(25)	2.10(13)	Sn(1)–O(5)#1	2.122(5)
Sn(1)–N(1)	2.166(6)	Sn(1)–N(3)	2.365(8)
Sn(2)–O(6)	2.051(5)	Sn(2)–O(1)	2.077(5)
Sn(2)–O(2)	2.104(5)	Sn(2)–C(29)	2.118(11)
Sn(2)–N(2)	2.193(5)	Sn(2)–N(4)	2.315(6)
O(4)–Sn(1)#1	2.067(4)	O(5)–Sn(1)#1	2.122(5)
O(4)#1–Sn(1)–O(3)	91.6(2)	O(4)#1–Sn(1)–C(25)	168(4)
O(3)–Sn(1)–C(25)	90(3)	O(4)#1–Sn(1)–O(5)#1	76.79(18)
O(3)–Sn(1)–O(5)#1	94.1(2)	C(25)–Sn(1)–O(5)#1	91(4)
O(4)#1–Sn(1)–N(1)	87.55(19)	O(3)–Sn(1)–N(1)	84.6(2)
C(25)–Sn(1)–N(1)	105(4)	O(5)#1–Sn(1)–N(1)	164.3(2)
O(4)#1–Sn(1)–N(3)	81.6(2)	O(3)–Sn(1)–N(3)	173.2(2)
C(25)–Sn(1)–N(3)	96(3)	O(5)#1–Sn(1)–N(3)	85.3(2)
N(1)–Sn(1)–N(3)	94.2(3)	O(6)–Sn(2)–O(1)	160.9(2)
O(6)–Sn(2)–O(2)	84.9(2)	O(1)–Sn(2)–O(2)	76.2(2)
O(6)–Sn(2)–C(29)	103.8(3)	O(1)–Sn(2)–C(29)	94.7(3)
O(2)–Sn(2)–C(29)	170.1(3)	O(6)–Sn(2)–N(2)	84.0(2)
O(1)–Sn(2)–N(2)	98.2(2)	O(2)–Sn(2)–N(2)	87.3(2)
C(29)–Sn(2)–N(2)	98.0(3)	O(6)–Sn(2)–N(4)	84.0(2)
O(1)–Sn(2)–N(4)	90.3(2)	O(2)–Sn(2)–N(4)	82.9(2)
C(29)–Sn(2)–N(4)	93.4(3)	N(2)–Sn(2)–N(4)	165.1(2)

Symmetry transformations used to generate equivalent atoms: (**1**) #1: $-x+2$, $-y+1$, $-z$ (**2**) #1: $-x+1$, $-y$, $-z$; (**3**) #1: $-x+1$, $-y$, $-z+1$; (**4**) #1: $-x+1$, $-y+2$, $-z+1$; (**5**) #1: $-x+1$, $-y$, $-z+1$.

recorded on a Nicole-5700 spectrophotometer using KBr discs and sodium chloride optics. Elemental analyses were performed with a PE-2400II apparatus. TGA was carried out with a Perkin–Elmer Pyris-1 instrument with a heating rate of 10 °C min^{-1} from 30 to 500 °C and with a 20.0 cm^3 min^{-1} nitrogen gas flow. Fluorescent data were collected on an Edinburgh FLS-920 instrument.

4.2. Syntheses

4.2.1. [12-$MC_{[EtSn(IV)]N(shi)}$-4] **1**

0.3 mmol portion of salicylhydroxamic acid (0.046 g) was dissolved in the solution of pyridine (20 mL) and methanol (10 mL), and 0.3 mmol of triethyltin(IV) chloride (0.072 g) was added, The mixture was stirred for 25 h at room temperature. After filtration the solvent volatilized in air and the colourless crystals were separated out about two weeks later. Yield, 43%. M.p. >300 °C. Analytical data: Found C, 44.39; H, 3.98; N, 7.19%. $C_{56}H_{56}N_8O_{12}Sn_4$ (1507.85) requires C, 44.60; H 3.74; N 7.43%. IR (KBr, cm^{-1}): (CO/NC),1598(s), 1568(s); (N–O), 927(s); (Sn–N), 668(m); (Sn–C), 591 (m); (Sn–O), 432(m).

4.2.2. [12-$MC_{[BuSn(IV)]N(shi)}$-4] **2**

This complex was prepared in a similar way to **1** except for substituting tributyltin(IV) chloride (0.098 g) for triethyltin(IV) chloride. Colorless crystals were separated out in 68% yield. M.p. >300 °C. Analytical data: Found C, 47.21; H, 4.76; N 6.69%. $C_{64}H_{72}N_8O_{12}Sn_4$ (1620.06) requires C, 47.45; H, 4.48; N, 6.92%; IR (KBr cm^{-1}): (CO/NC),1599(s), 1568(s); (N–O), 928(s); (Sn–N), 668 (m); (Sn–C), 589(m); (Sn–O), 434(m).

4.2.3. [12-$MC_{[PhSn(IV)]N(shi)}$-4] **3**

This complex was prepared in a similar way to **1** except for substituting triphenyltin(IV) chloride (0.116 g) for triethyltin(IV) chloride, colorless crystals were isolated in 53% yield. M.p. >300 °C. Analytical data: Found C, 50.62; H, 3.59; N 6.36%. $C_{72}H_{56}N_8O_{12}Sn_4$ (1700.01) requires C, 50.87; H, 3.32; N, 6.15%; IR (KBr cm^{-1}): (CO/

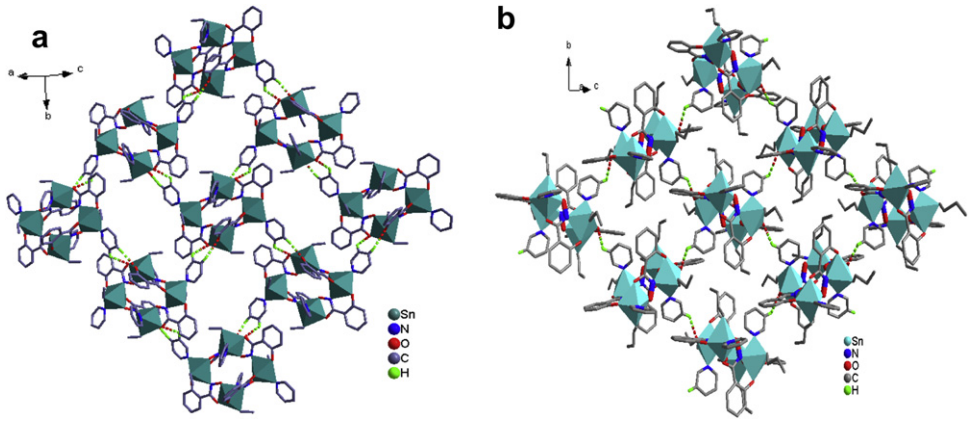


Fig. 2. 2D network of complex **1**(a) and **2**(b) formed by C–H···O interactions.

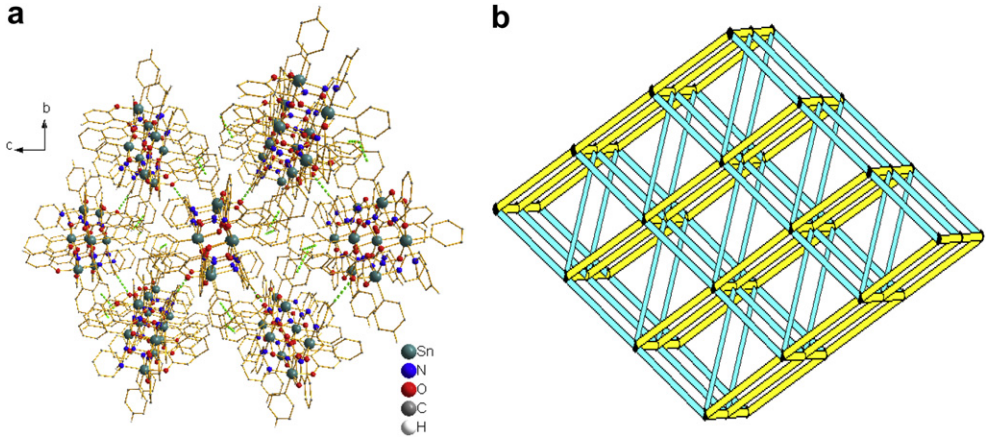


Fig. 3. (a) The 3D supramolecular structure of complex **3** and (b) 8-connecting 3D topological structure of complex **3**. yellow and blue lines indicate C22–H22···O/C28–H28···π and C6 H6···π interactions, respectively

NC),1599(s), 1568(s); (N–O), 929(s); (Sn–N), 669(m); (Sn–C), 594 (m); (Sn–O), 432(m).

4.2.4. *[12-MC$_{[EtSn(IV)]N(Clshi)}$-4]* **4**

0.3 mmol portion of 5-chlorosalicylhydroxamic acid (0.056 g) was dissolved in the solution of pyridine (20 mL) and methanol (10 mL), and 0.3 mmol of triethyltin(IV) chloride (0.072 g) was added, The mixture was stirred for 25 h at room temperature. After filtration the solvent volatilized in air and the colorless crystals were separated out about two weeks later. Yield, 39%. M.p. >300 °C. Analytical data: Found C, 40.53; H, 3.40; N, 6.56. $C_{56}H_{52}Cl_4N_8O_{12}Sn_4$ (1645.71) requires C, 40.87; H, 3.18; N, 6.81. IR (KBr cm^{-1}): (CO/

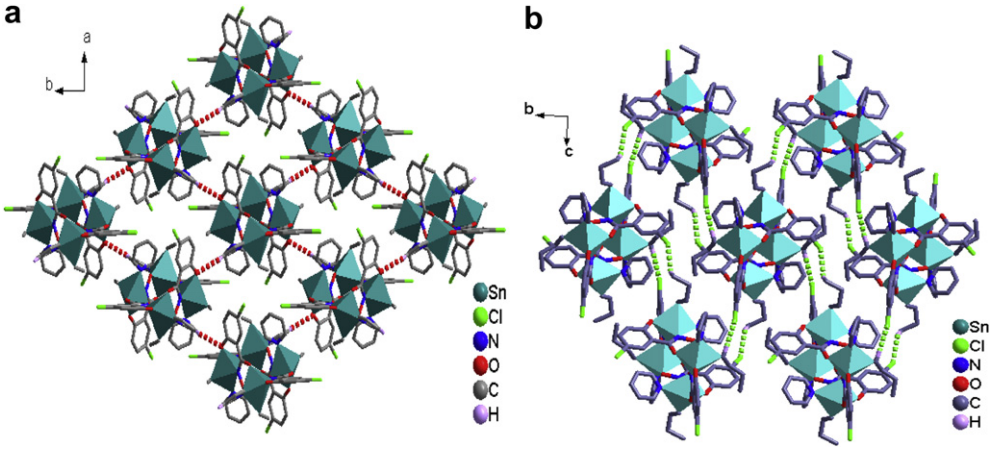


Fig. 4. 2D network of complex **4**(a) formed by C–H···O interactions (red dashed) parallel *ab* plane, and the complex **5**(b) formed by C–H···Cl interactions (green dashed) parallel *bc* plane. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.).

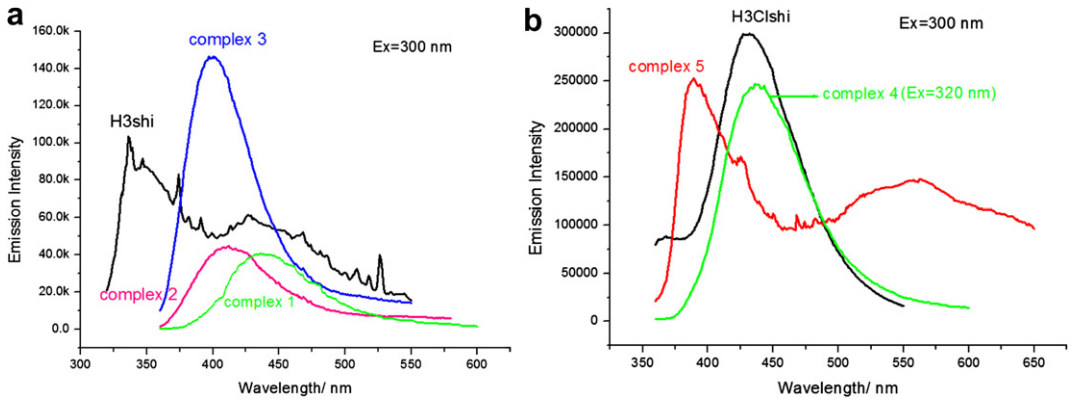


Fig. 5. Fluorescent spectra of ligands and complexes measured at room temperature. (a) H_3shi and complexes **1**–**3**; (b) H_3Clshi and complexes **4**–**5**

NC),1606(s), 1560(s); (N–O), 881(s); (Sn–C), 727(m); (Sn–N\), 623 (m); (Sn–O), 432(m).

4.2.5. *[12-MC$_{[BuSn(IV)]N(Clshi)}$-4]* ***5***

This complex was prepared following the procedure for **4** tributyltin(IV) chloride (0.098 g) was used instead of triethyltin(IV) chloride. Yield, 61%. M.p. >300 °C. Analytical data: Found C, 43.28; H, 4.06; N, 6.19. $C_{63.50}H_{67}Cl_4N_8O_{12}Sn_4$ (1750.91) requires C, 43.56; H, 3.86; N, 6.40. IR (KBr cm^{-1}): (CO/NC),1606(s), 1560(s); (N–O), 880(s); (Sn–C), 726(m); (Sn–N), 623(m); (Sn–O), 433(m).

4.3. *Crystal structures of complexes **1**–**5***

Suitable single crystals of the five complexes were mounted. Diffraction data were collected with a Bruker SMART CCD diffractometer with Mo-Kα (λ = 0.71073 Å) radiation at room temperature. During the intensity data collection, no significant decay was observed. The intensities were corrected for Lorentz-polarization effects and empirical absorption with the SADABS program [45]. The structures were solved by direct methods using the SHELXS-97 program and refined with SHELXL-97 [46]. All non-hydrogen atoms were found from difference Fourier syntheses. The H atoms were included in calculated positions with isotropic thermal parameters related to those of the supporting carbon atoms but were not included in the refinement. All calculations were performed using the WinGX System-Version 1.80.03 [47]. Crystal data and experimental details of the structure determinations are listed in Table 1.

4.4. *In vitro antitumor activity*

The human tumor cell lines which were used for screening were grown and maintained in RPMI-1640 medium supplemented with 10% fetal bovine serum at 37 °C in humidified incubators in an atmosphere of 5% CO_2. Cell proliferation in compound-treated cultures was evaluated by using a system based on the tetrazolium compound (MTT) [48] in the School of Medicine and Pharmacy, Ocean University of China. The Hela cell line was seeded into 96 well plates at a concentration of about 50 000 cells/mL and was incubated in an atmosphere of 5% CO_2 for 24 h. Then, 20 μL of the sample (organotin complexes) DMSO solution was added and further incubation was carried out at 37 °C for 48 h. The compounds were serially diluted (in four to six steps) with DMSO and added to cell incubation medium at the final concentration of 1.0% DMSO in the medium. 50 μL of 0.1% MTT was added to each well. After 4 h incubation, the culture medium was removed, and 150 μL of isopropanol was added to dissolve the insoluble blue formazan precipitates produced by MTT reduction. The plate was shaken for 20 min on a plate shaker to ensure complete dissolution. The optical density of each well was measured at 570 nm wavelength. The antitumor activity was determined three times in independent experiments.

Table 3
Half maximal inhibitory concentration (IC_{50} μM) of complexes **4** and **5** against tumor cell lines.

Tumor cell line	Complex **4**	Complex **5**
Bel-7402	15.38	15.20
Hela	12.04	11.18

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Appendix A. supplementary data

CCDC-748381, 738610, 738607, 748379, 738613 contain the supplementary crystallographic data for complexes **1**–**5** respectively. These data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html

Supplementary information associated with this article can be found in the online version, at doi:10.1016/j.jorganchem.2010.05.027.

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