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TWO Mn(II) CHLORIDE COMPLEXES CONTAINING GUEST MOLECULES

Solvothermal syntheses, crystal structures and thermal decomposition

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Two phenanthroline–manganese inclusion complexes with $[MnCl(H_2O)(phen)_2]^+$ core have been synthesized and characterized by single crystal X-ray diffraction, elemental analyses, IR spectra, thermogravimetric analyses. Uncoordinated 2-mercaptothiazole (tzdtH) and 2-mercaptobenzothiazole (bztzH) as guest molecules are included in the complexes with formulas $[MnCl(H_2O)(phen)_2]Cl\cdot tzdtH$ (**1**) and $\{[MnCl(H_2O)(phen)_2]Cl\}_2\cdot bztzH$ (**2**). X-ray structural analyses for complexes revealed that the complex **1** is triclinic, space group P1 with a=9.724(1) Å, b=11.858(1) Å, c=12.644(2) Å; β=89.056(2)°; Z=2, D_c=1.513 Mg m^{-3}, F(000)=638 and the complex **2** is triclinic, space group P1 with a=9.861(1) Å, b=11.476(1) Å, c=12.908(3) Å; β=84.991(2)°; Z=1, D_c=1.511 Mg m^{-3}, F(000)=600. Two complexes exhibit high stability up to 650°C. The molar specific heat capacities for the two complexes **1** and **2** can be estimated as being 96.175±0.332 and 72.505±0.364 J mol^{-1} K^{-1} at 298.15 K by RD496-III microcalorimeter, respectively.

Keywords: *crystal structure, manganese, 2-mercaptobenzothiazole, 2-mercaptothiazole, phenanthroline, thermal analysis*

Introduction

Manganese complexes have attracted considerable interest in recent years because of the presence of manganese element in variety biosystems [1–3]. Interest in the coordination chemistry of heterocyclic thiones arises from the presence of the heterocyclic skeleton in many biomolecules [4]. For heterocyclic thiones both the endocyclic nitrogen atom and exocyclic sulphur may act as donor, the ligands have great ability to adopt different bonding modes, unidentate, bidentate or bridging sometimes in more than one way in the same compound [5]. Metallo-complexes of 2-mercaptothiazole and the related 2-mercaptobenzothiazole have proved a fertile area for study over years, stimulated both by the diversity of their commercial application and the richness of their structural chemistry. As far as we know, few examples of Mn(II) complexes containing this kind of ligands have been reported [6, 7]. In order to investigate the bonding mode and the thermal behaviour of these complexes, we chose 2-mercaptothiazole (tzdtH) and 2-mercaptobenzothiazole (bztzH) reacting with 1,10-phenanthroline (phen), leading to two phen–manganese inclusion complexes in which neutral uncoordinated heterocyclic thiones are enclosed into the host molecules containing $[Mn(II)Cl(H_2O)(phen)_2]^+$ and Cl^- counter ions. We report here the synthesis, crystal structure, thermal stability and molar specific heat capacities of the title complexes.

Experimental

Materials

All chemicals used in the experiments were analytical grade and commercial available without further purification. C, H, N contents were determined on a Perkin-Elmer 2400 type elemental analyzer.

Synthesis of complex $[MnCl(H_2O)(phen)_2]Cl\cdot tzdtH$ (**1**)

A mixture of manganese chloride tetrahydrate (0.040 g, 0.2 mmol), 2-mercaptothiazole (0.048 g, 0.4 mmol), 1,10-phenanthroline (0.079 g, 4 mmol), water (4 mL) and methanol (4 mL) was combined in a 23 mL Teflon-lined stainless-steel Parr bomb, which was heated at 140°C for 48 h and then cooled to room temperature. Pale-yellow crystals were obtained in 72% yield based on manganese. For $C_{27}H_{23}N_5OS_2Cl_2Mn$, analysis calculated: C 52.01, H 3.72, N 11.23%; found: C 51.89, H 3.57, N 11.09%.

Synthesis of complex $\{[MnCl(H_2O)(phen)_2]Cl\}_2\cdot bztzH$ (**2**)

A mixture of manganese chloride tetrahydrate (0.040 g, 0.2 mmol), 2-mercaptobenzothiazole (0.067 g, 0.4 mmol), 1,10-phenanthroline (0.079 g, 4 mmol), water (4 mL) and methanol (4 mL) was combined in a 23 mL Teflon-lined stainless-steel Parr bomb, which was heated at 150°C for 60 h and then cooled to room temperature. Yellow crystals were obtained in 66% yield based on manganese. For $C_{55}H_{41}N_9O_2S_2Cl_4Mn_2$,

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analysis calculated: C 56.18, H 3.51, N 10.72%; found: C 56.44, H 3.42, N 10.58%.

Methods

All TG-DTG tests were performed with a Perkin-Elmer thermogravimetric instrument.

All single crystal X-ray experiments were performed on a Bruker Smart-1000CCD diffractometer with graphite monochromated MoK_{α} radiation (χ=0.71073 Å) using ω and φ scan mode for structure measurement at 273 K. The single crystal structures of complexes were solved by direct methods and refined on F^2 by the full-matrix least-squares methods using the SHELXL-97 (Sheldrick, 1997) program package [8]. All non-hydrogen atoms were refined anisotropically and all the H atoms attached to the carbon were placed geometrically. The crystal data and refinement details of the complexes are summarized in Table 1.

Results and discussion

IR spectra

In complexes **1** and **2** the absence of ν_{SH} close to 2500 cm^{-1} [9] and the presence of ν_{NH} at approximate 3100 cm^{-1} [10], as well as the characteristic thioamide bands in the 1500, 1200–1300, 1000 and 600–700 cm^{-1} regions [11], confirm thione donation in the two complexes. There are no obvious shifts in the characteristic thioamide bands indicate that the ligands tzdtH and bztzH are uncoordinated in both the complexes **1** and **2**.

In contrast with those of (1617, 1587, 1561, 1504 cm^{-1}) and (854, 739 cm^{-1}) in the ligand phen, the skeleton vibration of benzene ring and the band vibration of C–H displays certain shifts in the complexes, indicating that two nitrogen atoms in the ligand phen coordinate to Mn^{2+}.

Shifts in these bands between the free ligand and the complexes results from a combination of factors such as electronic shifts within the ligand as well as hydrogen bonding effects. IR spectra of the complexes were consistent with the structure analyses from the X-ray diffraction.

Thermogravimetric analyses

Thermal gravimetric analyses (TG-DTG) for the crystal samples 1 and 2 were performed from 40 to 800°C

Table 1 Crystal data and structure refinement details of complexes **1** and **2**

Parameter	$C_{27}H_{23}N_5OS_2Cl_2Mn$ (**1**)	$C_{55}H_{41}N_9O_2S_2Cl_4Mn_2$ (**2**)
Formula mass	623.46	1175.77
Temperature/K	273(2)	273(2)
Crystal system	triclinic	triclinic
Space group	P1	P1
a, *b*, *c*/Å	9.724, 11.858(1), 12.644(2)	9.861(1), 11.476(1), 12.908(3)
β/°	89.056(2)	84.991(2)
V/Å^3	1368.8(3)	1292.1(3)
Z	2	1
F(000)	638	600
D_{calc}/Mg m^{-3}	1.513	1.511
Absorption coefficient/mm^{-1}	0.861	0.829
Crystal size/mm	0.31·0.28·0.094	0.28·0.22·0.17
Range *hkl* collected	$-11\leq h\leq 11$ $-14\leq k\leq 10$ $-15\leq l\leq 5$	$-11\leq h\leq 11$ $-13\leq k\leq 8$ $-15\leq l\leq 14$
Reflections collected	6991	6622
Completeness to theta=25.04	98.2	98.6
Independent reflections	4748 [R(int)=0.0218]	5546 [R(int)=0.0154]
Data/restraints/parameters	4748/0/355	5546/3/667
Goodness-of-fit on F^2	1.031	1.055
R_{int}	0.0218	0.0154
Final R indices [1>2σ(I)]	0.0382, 0.0298	0.0349, 0.0900
R indices (all data)	0.0573, 0.0974	0.0431, 0.0932
Largest different peak and hole/e Å^{-3}	0.331, –0.268	0.350, –0.300

at a heating rate of 10°C min^{-1} under a static air atmosphere (Figs 1 and 2) and the thermal decomposed procedure are deduced as Schemes 1 and 2.

According to the TG-DTG curve, the decomposition process of the complex **1** can be divided into four steps. The first step in the range of 86 to 128°C is confirmed as the loss of coordinated water (calculated value: 2.89%), which is consistent with the absence of the 3413 cm^{-1} in IR spectrum of the middle product at 130°C. The second step from 165 to 253°C is considered as the break of the tzdtH with the loss of 19.69% which is in good agreement with the calculated value 19.69%. This process has been confirmed by IR spectrum of the residue at 260°C with the disappearance of the vibrations at 1503, 1295, 1049 and 703 cm^{-1} compared with those of the complex. The third step is the loss of one phen with 36.90% (calculated value: 37.06%). Finally, the compound is completely converted to Mn_2O_3 with the loss of 27.54% (calculated value: 27.70%) at 650°C, which is consistent with the standard IR spectrum of Mn_2O_3.

$$[\mathrm{MnCl_2(phen)_2(H_2O)}]\cdot\mathrm{tzdtH} \xrightarrow{86\sim104\sim128℃;\,2.88\%\ (2.89\%)}$$

$$[\mathrm{MnCl_2(phen)_2}]\cdot\mathrm{tzdtH} \xrightarrow{165\sim239\sim253℃;\,19.69\%\ (19.69\%)}$$

$$\mathrm{MnCl_2(phen)_2} \xrightarrow{323\sim378\sim430℃;\,36.90\%\ (37.06\%)}$$

$$\mathrm{MnCl_2(phen)} \xrightarrow{462\sim573\sim650℃;\,27.54\%\ (27.70\%)} \mathrm{Mn_2O_3}$$

Scheme 1 Thermal decomposed procedure for the complex **1**

$$\{[\mathrm{MnCl(H_2O)(phen)_2]Cl}\}_2\cdot\mathrm{bztzH} \xrightarrow{113-161-198℃;\,2.99\%\ (3.06\%)}$$

$$\{[\mathrm{MnCl(phen)_2]Cl}\}_2\cdot\mathrm{bztzH} \xrightarrow{197-221-248℃;\,14.59\%\ (14.67\%)}$$

$$\{[\mathrm{MnCl(phen)_2]Cl}\}_2 \xrightarrow{299-358-392℃;\,36.92\%\ (37.06\%)}$$

$$\{[\mathrm{MnCl(phen)]Cl}\}_2 \xrightarrow{443-520-650℃;\,31.60\%\ (31.78\%)} \mathrm{Mn_2O_3}$$

Scheme 2 Thermal decomposed procedure for the complex **2**

The TG-DTG curves of complex **2** is similar to the complex **1**. Figure 2 shows four obvious mass losses: The first step in the range of 113 to 198°C is the loss of two coordinated water (calculated value: 3.06%), which is consistent with the absence of the 3445 cm^{-1} in IR spectrum of the middle product at 200°C. The second step from 197 to 248°C is the loss of uncoordinated bztzH (calculated value: 14.67%), which has been confirmed by IR spectrum of the residue at 260°C with the disappearance of the vibration at 1494, 1316, 1028 and 662 cm^{-1}. The third step is the loss of two phen with 36.92% (calculated value: 37.06%) and the fourth step is considered as the complex completely converted to Mn_2O_3 of 31.60% (calculated value: 31.78%) at 650°C, which is consistent with the standard IR spectrum of Mn_2O_3. These results show the two complexes exhibit the similar high stability up to 650°C.

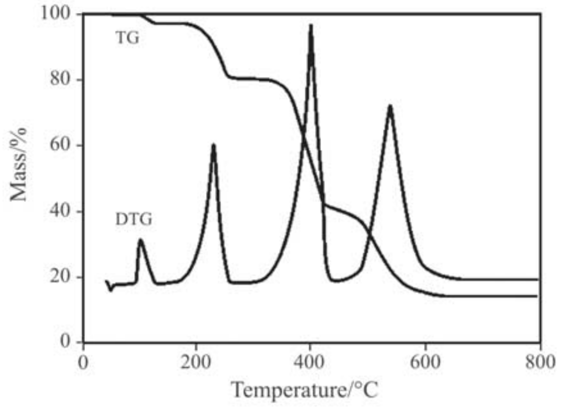

Fig. 1 TG and DTG curves for the complex **1**

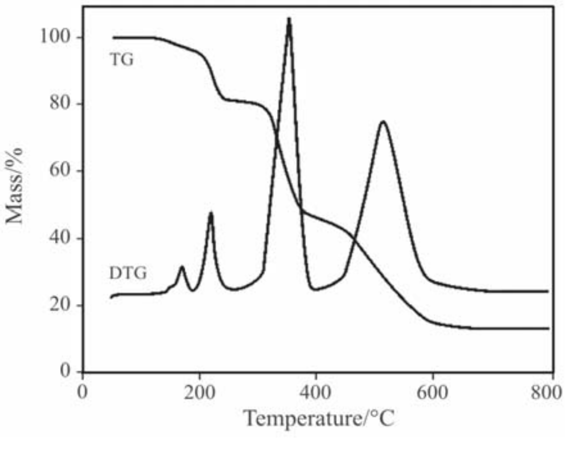

Fig. 2 TG and DTG curves for the complex **2**

Molar specific heat capacities of complexes

The molar specific heat capacities of the complexes were measured according to reference [12] (measuring 6 times for each sample), and their molar specific heat capacities were calculated from the data in Table 2 and presented in Table 3.

Crystal structures of the complexes

The X-ray structure analysis reveals that the asymmetric unit of 1 consists of a aquachlorobis(1,10-phenanthroline) manganese(II) cation, one uncoordinated chloride anion and a tzdtH molecule – as shown in Fig. 3 and the Mn(II) atom is coordinated by one chloride anion, one O atom of water and four N atoms of two phen ligands, forming a distorted octahedral coordination geometry. Through the hydrogen bonding between N5 atom of the uncoordinated tzdtH ligand and Cl anion, O atom of coordinated water and Cl anion, along with S2 atom of the uncoordinated tzdtH

Table 2 Data of the heat and heat capability of the empty cell and the standard substances (298.15 K)[a]

Heats of disequilibrium and specific heat capacity	The empty cell	Standard α-Al_2O_3	Sublimed benzoic acid
$q(1)$/mJ	3689.151	3825.725	3909.248
$q(2)$/mJ	3686.060	3827.302	3912.490
$q(3)$/mJ	3687.238	2829.849	3911.858
$q(4)$/mJ	3690.008	3827.946	3908.362
$q(5)$/mJ	3691.445	3830.873	3912.998
$q(6)$/mJ	3691.994	3830.667	3914.650
q mean±SD/mJ	3689.316±0.495	3828.727±0.842	3911.601±0.968
The relative standard deviation	$2.578\cdot10^{-4}$	$2.200\cdot10^{-4}$	$2.476\cdot10^{-4}$
Specific heat capacity		78.724±1.377	145.891±1.003
c/J mol^{-1} K^{-1}		79.03 [13]	145.327 [14]

$${}^{a}SD=\sqrt{\frac{\sum(x_1-\bar{x})^2}{n-1}}$$

Table 3 Data of the specific heat capacities of the complexes (298.15 K)[b]

Complexes	m/g	q (mean±SD)/mJ	c (mean±SD)/J mol^{-1} K^{-1}
1	2.02369	3689.353±0.325	96.175±0.332
2	2.22575	3777.353±0.332	72.505±0.364

$${}^{b}SD=\sqrt{\frac{\sum(x_1-\bar{x})^2}{n-1}}$$

ligand and C21 of phen, building up a supramolecular network, presented in Fig. 4.

As shown in Fig. 5, the asymmetric unit of **2** consists of a neutral $\{[MnCl(H_2O)(phen)_2]Cl\}_2$ molecule and a discrete bztzH molecule. In the neutral molecule $\{[MnCl(H_2O)(phen)_2]Cl\}_2$, the Mn(II) is six coordinate, involving one chloride atom, one O atom of water and four N atoms of two phen ligands, forming a distorted octahedral coordination geometry. In complexe **2**, there exists π–π stacking supramolecular interactions with a distance of 3.32 Å between intramolecular two adjacent phen. The discrete molecule interacts with the neutral molecule via hydrogen bonds, presented in Fig. 6.

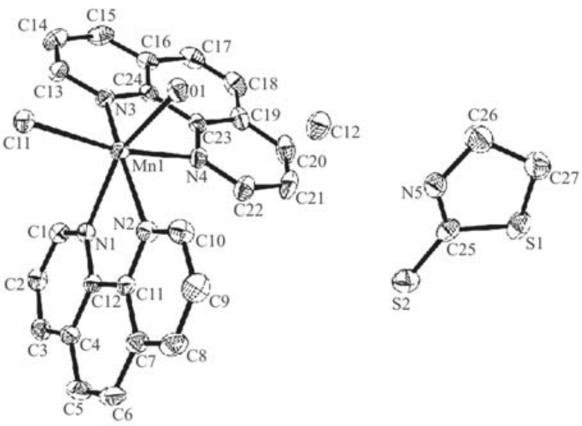

Fig. 3 A view of the asymmetric unit of complex **1**, showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level. H atoms have been omitted for clarity

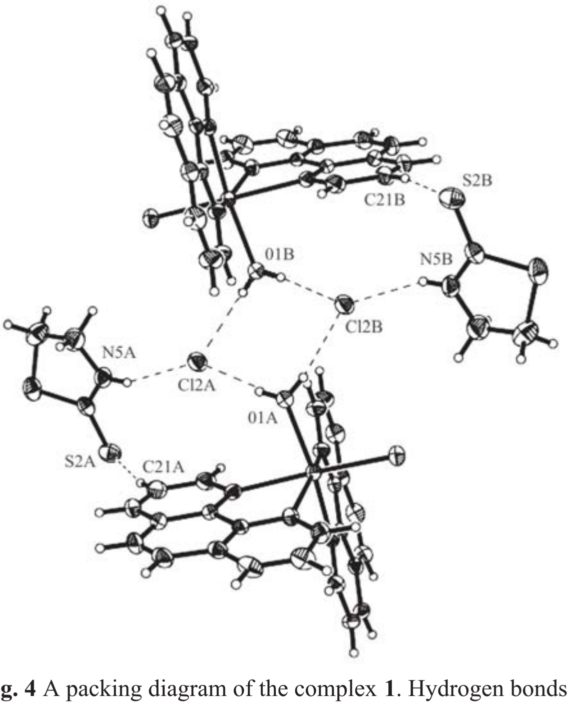

Fig. 4 A packing diagram of the complex **1**. Hydrogen bonds are indicated by dotted lines

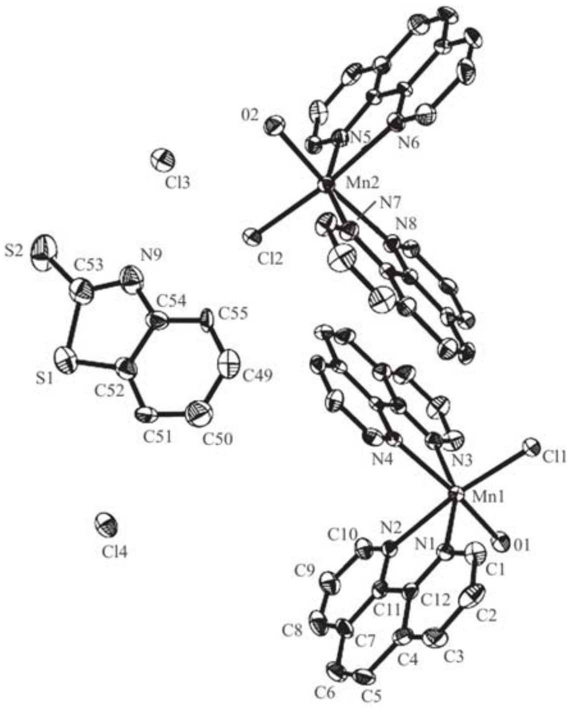

Fig. 5 A view of the asymmetric unit of **2**, showing the atom-numbering scheme and displacement ellipsoids at the 30% probability level. H atoms have been omitted for clarity

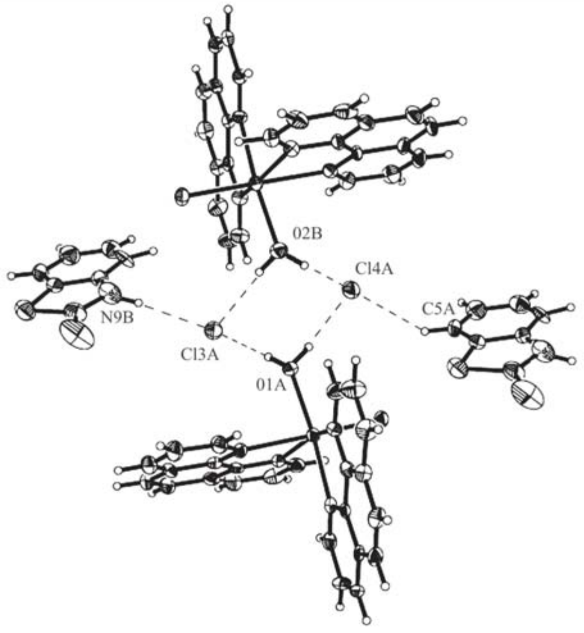

Fig. 6 A packing diagram of the complex **2**. Hydrogen bonds are indicated by dotted lines

Conclusions

In summary, we have prepared successfully the title complexes. X-ray diffraction analyses indicated that the existence of the heterocyclic thiones as guest molecules in the phen/Mn structure for the two complexes. Two complexes exhibit high stability up to 650°C. The molar specific heat capacities at 298.15 K for the two complexes are 96.175±0.332 and 72.505±0.364 J mol^{-1} K^{-1}, respectively.

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