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Syntheses, crystal structures and properties of Zn(II) and Cd(II) complexes derived from *N*-(*o*-nitrophenyl)-*N*′-(methoxycarbonyl) thiourea(H_2omt) and 2,2′-bipyridine(bpy) or *o*-phenanthroline(phen)

Xu Shen,*[a] Xianfa Shi,[a] Beisheng Kang,[b], Yu Liu,[b] Yexiang Tong,[b], Hualiang Jiang[c] and Kaixian Chen[c]

[a]Department of Chemistry, Tongji University, Shanghai 200092, People's Republic of China

[b]Department of Chemistry, Zhongshan University, Guangzhou 510275, People's Republic of China

[c]Shanghai Institute of Materia Medica, Chinese Academy of Sciences, Shangahi 200031, People's Republic of China

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Abstract—The chelating properties of *N*-(*o*-nitrophenyl)-*N*′-(methoxycarbonyl)thiourea (H_2omt) were investigated through the study of the crystal structures of Cd(Homt)$_2$(bpy), **1**, Zn(Homt)$_2$(phen), **2** and H_2omt (bpy = 2,2′-bipyridine, phen = *o*-phenanthroline). The cadmium(II) ion in **1** is in a distorted octahedral geometry contributed by the two N atoms from bipyridine and the two S and the two deprotonated amine N atoms from two Homt groups [Cd–N(bpy) = 2.329(3), Cd–N(amine) = 2.360(3) and Cd–S = 2.690(1) Å]. The Zn(II) ion in complex **2** is four-coordinated by the two N atoms from the *o*-phenanthroline and the two deprotonated amine N atoms from two Homt groups in a distorted tetrahedral fashion, in which the binding of S atom to the metal is not involved [Zn–N(phen) = 2.088(4), Zn–N(amine) = 1.998(3) Å]. © 1998 Elsevier Science Ltd. All rights reserved

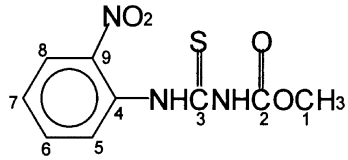
Keywords: syntheses; crystal structures; cadmium(II) complex; zinc(II) complex; *N*′-(*o*-nitrophenyl)-*N*′-(methoxycarbonyl)thiourea; bipyridine; *o*-phenanthroline.

INTRODUCTION

Recently, the derivative *N*-(*o*-nitrophenyl)-*N*′-(ethoxycarbonyl)thiourea (H_2oet) was isolated from the leaves of resistant *Pyricuiria oryzae cav*. rice variety [1] and the preliminary pharmacological tests showed its high antibacterial activity. In our previous work [2], several ligands similar to the basic structure of H_2oet were prepared and their Cu(I) complexes were prepared and crystallographically characterized. It is interesting to find that copper(I) complexes can be obtained from the copper(II) salts by *in situ* reduction in the presence of these thiourea derivatives. In fact, the biological activities of complexes with thiourea derivatives have been well documented and thiourea derivatives have been successfully screened for various biological actions [3–6] and some *N*-substituted-*N*′-alkoxycarbonyl thioureas have been used in commercial fungicides. To date, plenty of transition metal complexes with such thiourea derivatives have been reported and the structures with O,S-binding to the metal ions were well proposed in alkaline media based on a series of physicochemical properties [7–9]. Now, it has been a common knowledge that complexation with metal ions may enhance the biological activity of a wide variety of organic compounds. For example, the copper(II) complex of 2-ace-

* Author to whom correspondence should be addressed.

tyloxybenzoic acid (aspirin), a ligand used as an analgesic since the last century, was reported to be significantly more active as an anti-inflammatory agent than the free ligand (Refs [10,11]. and references cited therein). Complexes of metal ions containing a bidentate organic compound such as 2,2′-bipyridine (bpy) and phenanthrolinine (phen) have been well reported [12,13] and they serve as interesting models for the understanding enzyme–metal ion–substrate relationship, thus playing an important role in metalloenzyme-catalyzed biochemical reactions [14,15]. In our previous work, the chloroform solvated Cd(II) complex with the ligand *N*-(*o*-nitrophenyl)-*N*′-(methoxycarbonyl)thiourea (H_2omt) and *o*-phenanthroline was reported [16] and Zn(II) and other transition metal complexes [e.g. Cu(II), Co(II)] with H_2omt and bipyridine (bpy) were synthesized [17]. To make such work more complete, in this paper we report the crystal structures of Zn(II) and Cd(II) complexes with H_2omt and bpy for Cd(II) and phen for Zn(II).



N-(*o*-nitrophenyl)-N'-(methoxycarbonyl)thiourea (H_2omt) (**m. f.** $C_9H_9O_4N_3S$)
(carbon atoms labelling is for ^{13}C NMR assignments)

EXPERIMENTAL

Chemicals

All reactants were reagent grade and used without further purification.

Physical measurements

C, H and N analyses were carried out on a Carlo Erba 1106 elemental analyzer. IR spectra were recorded on a Magna 750 spectrometer, UV spectral data were collected by a Shimadzu UV-300 spectrometer. NMR (^1H and ^{13}C) spectra were determined with a Bruker AM 500 instrument in DMSO-d_6 solution. Cyclic voltammetry was performed with a HDV-7B Potentiostat and LZ3Q-204 *X*–*Y* recorder with an electrochemical cell containing a Pt wire working electrode, a Pt plate auxiliary electrode and an SCE reference electrode.

X-ray crystallography

Pertinent crystal data, basic information about the data collection and structure refinement of the crystals of **1**, **2** and H_2omt are given in Table 1.

The structures were all solved by direct methods. Refinements were carried out by full-matrix least squares using anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were included as fixed contributions in structure factor calculations but not refined. All calculations were performed on a Compaq computer using the TEXSAN program package.

Biological activity

The antibacterial and antifungal activities of the ligand H_2omt and the metal complexes against the standard strains of *B. subtilis* 6633, *S. lutea*, *S. aureus* 209p, *P. diploccus*, *E. coli* and *P. aeruginosa* x313 and *S. Yake Sake* were determined using the plate method [18]. Each of the compounds was prepared at a concentration of 0.55 mM during the tests and the results are listed in Table 6.

Preparations

N-(o-Nitrophenyl)-N′-(methoxycarbonyl)-thiourea (*H_2omt*). The preparation of the ligand H_2omt was according to our previous method [7–9].

General preparation method for Cd(Homt)$_2$(bpy), **1**, *and Zn(Homt)$_2$(phen)*, **2**. A solution of $M(ClO_4)_2 \cdot 6H_2O$ (M = Cd and Zn) (3 mmol) in 20 cm^3 of methanol was added slowly to a methanolic solution of 2,2′-bipyridine or *o*-phenanthroline (3 mmol in 15 cm^3). This was warmed by stirring at 40–45°C for 30 min to give a clear solution which was cooled to room temperature and to it was added the clear methanolic solution (20 cm^3) containing H_2omt (6 mmol) and NaOH (6 mmol). A large amount of yellowish solids were precipitated, this resulting mixture was stirred at room temperature for a further 3 h and the solids were collected by filtration, washed thoroughly with water

Table 1. Summary of crystallographic data and structural parameters of the compounds H_2omt, **1** and **2**

Compound	H_2omt	**1**	**2**
Formula	$C_9H_9N_3O_4S$	$C_{28}H_{24}N_8O_8CdS_2$	$C_{30}H_{22}N_8O_8S_2Zn$
M	255.25	777.08	752.05
Crystal size (mm^3)	$0.25\times0.20\times0.15$	$0.45\times0.45\times0.25$	$0.25\times0.15\times0.15$
Crystal color and shape	yellow, prism	yellow, prism	yellow, prism
Crystal system	monoclinic	monoclinic	monoclinic
Space group	C2/c (# 15)	C2/c (# 15)	C2/c (# 15)
a (Å)	31.420 (5)	22.463 (5)	20.911 (5)
b (Å)	4.672(2)	9.681(4)	10.848(4)
c (Å)	15.226(2)	15.312(5)	15.508(4)
β (°)	97.47(1)	112.64(3)	113.50(2)
V ($Å^3$)	2216(1)	3073 (2)	3226(3)
Z	8	4	4
D_c ($g\cdot cm^{-3}$)	1.530	1.68	1.548
$F(000)$	1056	1568	1536
μ (cm^{-1})	2.86	8.99	9.63
Diffractometer	Rigaku AFC5R	Enraf-Nonius CAD4	Enraf-Nonius CAD4
2θ max. (°)	50.0	49.9	49.9
Scan width (°)	$0.85+0.35\tan\theta$	$0.95+0.35\tan\theta$	$0.85+0.45\tan\theta$
Scan speed (min^{-1})	<12.0	<5.85	<7.84
No. of unique reflections	2217	2888	3014
No. of observations	1460 [$I>2\sigma(I)$]	2326 [$I>3\sigma(I)$]	1927 [$I>2\sigma(I)$]
No. of variables	154	250	222
Temperature (°)	23	23	23
R	0.041	0.033	0.051
Rw	0.059	0.041	0.053
GOF	1.62	1.26	1.25
Max. shift in final cycle	0.002	0.00	0.0004
$\Delta\rho$ max., min. ($e\,Å^{-3}$)	0.21, −0.24	0.93, −0.60	0.29, −0.37

and methanol and dried *in vacuo*. Complex **1**, m.p. 243°C (decomp.). Yield, 89%. Found: C, 43.6; H, 4.1; N, 14.6. Calc. for $C_{28}H_{24}N_8O_8CdS_2$: C, 43.2; H, 3.1; N, 14.4%. Complex **2**, m.p. 227°C (decomp). Yield, 91%. Found: C, 47.8; H, 10; N, 14.6. Calc. for $C_{30}H_{22}N_8O_8S_2Zn$: C, 47.9; H, 2.9; N, 14.9%.

Single crystals suitable for X-ray analyses were obtained by slow diffusion of diethyl ether into the solution of **1** or **2** in chloroform over several weeks.

RESULTS AND DISCUSSION

Crystal structures

The structure of complex $Cd(Homt)_2(bpy)$, **1**, is depicted in Fig. 1, which shows that the Cd(II) ion is six-coordinated by two N atoms from bipyridine and two S and two N atoms from two Homt groups. Selected atomic distances and bond angles are listed in Table 2.

The bond lengths Cd–S(1) of 2.690(1) Å and Cd–N(1) of 2.360(3) Å are well within the range of the published results dealing with Cd–S (thiocarbonyl) [19] and Cd–N(amine) [20] and are also comparable to Cd–S (thiocarbonyl) [2.687(2) Å] and Cd–N(amine) [2.326(4), 2.330(4) Å] in our previous work [16]. The structural data within the 2,2′-bypyridine molecule are normal and Cd–N(4) of 2.329(3) Å is comparable to the reported values of Cd–N(bipy) elsewhere [21, 22]. The geometry of the six-coordinated cadmium(II) atom is distorted with the bond angles N(1)–Cd–S(1) = 61.59(7)°, N(1)–Cd–N(4) = 99.2(1)° and N(1)–Cd–N(4a) = 100.2(1)°. The molecule contains two four-membered (from Homt) and one five-membered chelate rings (from phen) and the metal ion deviates by 0.0313(2) Å from the plane N(1)C(2)S(1)Cd. The dihedral angle between the least squares planes N(1)C(2)S(1)Cd and N(4)C(14)C(14a)N(4a)Cd is 100.38(7)°.

The structure of complex $Zn(Homt)_2(phen)$, **2**, is shown in Fig. 2, and selected bond distances and angles are also listed in Table 2. The Zn(II) atom is four-coordinated by the two N atoms from the *o*-phenanthroline molecule and the two deprotonated amine N atoms from two Homt groups in a distorted tetrahedral geometry with N(4)–Zn–N(1) = 115.8°, N(4)–Zn–N(4a) = 79.8(3)° and N(1)–Zn–N(1a) = 128.9(2)°. The Homt ligand is monodentately coordinated to Zn(II) atom with the deprotonated amine nitrogen atom where the S atom does not bind to the metal ion, which is different from that in complex **1**. As Zn(II) ion is a harder acid relative to Cd(II) and

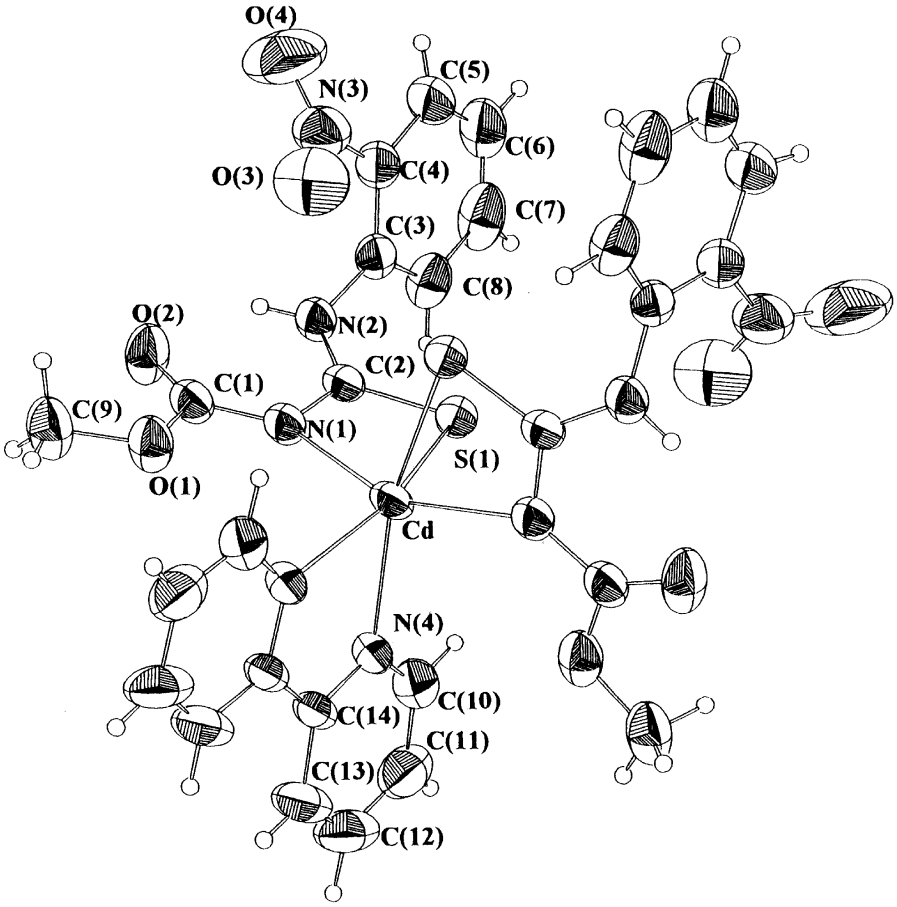


Fig. 1. ORTEP drawing of complex **1** with ellipsoids at 35% probability.

Table 2. Selected bond lengths (Å) and angles (°) of complexes **1** and **2**

1					
N(1)–Cd	2.360(3)	N(4)–Cd	2.329(3)	S(1)–Cd	2.690(1)
N(1)–Cd–N(1a)	156.2(1)	N(4)–Cd–N(1a)	100.3(1)	C(1)–N(1)–Cd	135.8(2)
N(1)–Cd–N(4)	99.2(1)	N(4)–Cd–N(4a)	70.0(1)	C(2)–S(1)–Cd	80.0(1)
N(1)–Cd–S(1)	61.59(7)	N(4)–Cd–S(1)	101.21(8)	C(2)–N(1)–Cd	100.8(2)
N(1a)–Cd–S(1)	101.07(8)	N(4)–Cd–S(1a)	159.13(7)	C(10)–N(4)–Cd	122.8(3)
S(1a)–Cd–S(1)	92.89(5)			C(14)–N(4)–Cd	118.2(2)
2					
Zn–N(1)	1.998(3)	Zn–N(4)	2.088(4)		
N(1)–Zn–N(4)	115.8(1)	N(4)–Zn–N(1)i	103.0(2)	C(1)–N(1)–Zn	122.9(3)
N(1)–Zn–N(4)i	103.1(2)	N(4)–Zn–N(4)i	79.8(3)	C(2)–N(1)–Zn	113.1(3)
N(1)–Zn–N(1)i	128.9(2)			C(10)–N(4)–Zn	128.6(4)
				C(15)–N(4)–Zn	112.7(4)

Symmetry operator: a: $1-x$, y, $1/2-z$; i: $1-x$, $-y$, $-z$.

thus less thiophilic, the Homt ligand tends to ligate only through the N atoms with Zn–N(1) 1.998(3) Å like a normal Zn–N(amine) bond [23]. The structural data within the phenanthroline molecule are without much change and the bond Zn–N(4) of 2.088(4) Å is well within the values Zn–N(phen) [24].

The structure of the ligand H_2omt is shown in Fig. 3. The coordination behavior of the Homt group is

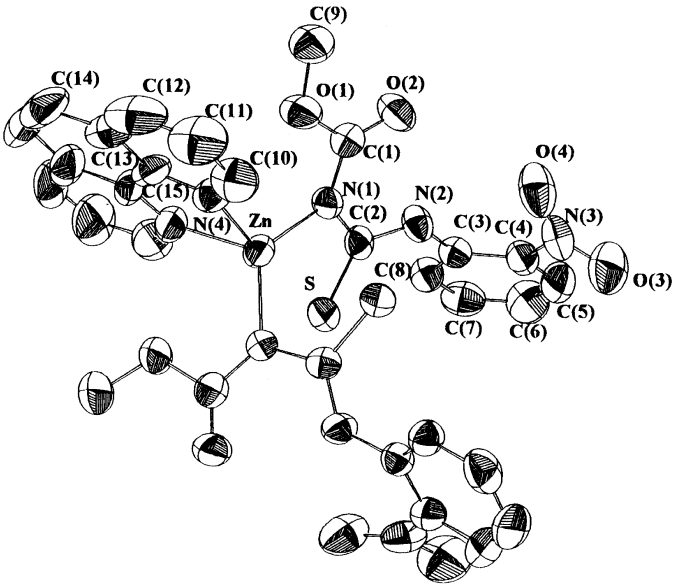


Fig. 2. ORTEP drawing of complex **2** with ellipsoids at 35% probability.

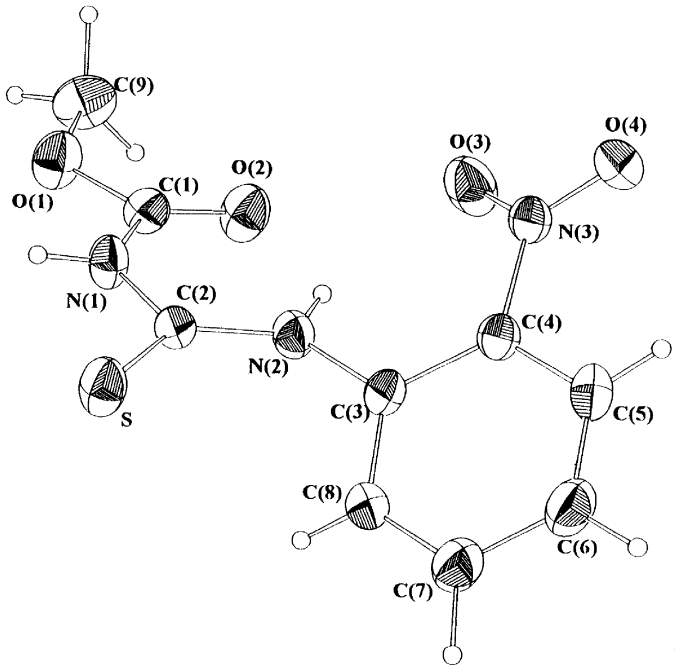


Fig. 3. ORTEP drawing of H_2omt with ellipsoids at 50% probability.

different in each of the complexes, with either mono- or bidentate coordination. In the free ligand H_2omt, the thiourea moiety SO(1)O(2)N(1)N(2)C(1)C(2)C(9) is almost planar and N(3) is in the plane of the phenyl group, these two planes form a dihedral angle of 44.37°. In complex **1**, N(2) is also in the plane of the phenyl group, and the dihedral angle between this plane and the least squares plane SO(1)O(2)N(1)N(2)C(1)C(2) is 70.51°. With respect to complex **2**, the dihedral angle between the plane of N(2) and the phenyl group and the plane O(1)O(2)N(1)C(1)C(2)C(9) is 54.55°. Comparative bond distances and angles involving Homt group for the free ligand H_2omt and complexes **1** and **2** are listed

Table 3. Comparative bond distances (Å) and angles (°) involving Homt group for the compounds H_2omt, **1** and **2**

	H_2omt	**1**	**2**
C(9)–O(1)	1.444(4)	1.428(5)	1.433(6)
O(1)–C(1)	1.322(3)	1.341(4)	1.340(5)
C(1)–O(2)	1.200(3)	1.211(4)	1.210(5)
C(1)–N(1)	1.374(3)	1.366(4)	1.363(6)
N(1)–C(2)	1.374(3)	1.345(4)	1.361(5)
C(2)–S	1.666(3)	1.710(3)	1.674(4)
C(2)–N(2)	1.342(3)	1.347(4)	1.348(5)
N(2)–C(3)	1.421(3)	1.421(4)	1.396(5)
C(3)–C(4)	1.402(4)	1.385(5)	1.390(6)
C(4)–C(5)	1.385(4)	1.382(5)	1.374(7)
C(5)–C(6)	1.379(4)	1.360(7)	1.354(8)
C(6)–C(7)	1.383(5)	1.361(7)	1.361(8)
C(7)–C(8)	1.376(4)	1.392(6)	1.363(7)
C(8)–C(3)	1.379(4)	1.375(5)	1.393(6)
C(4)–N(3)	1.471(3)	1.455(5)	1.464(7)
N(3)–O(3)	1.225(3)	1.212(5)	1.214(6)
N(3)–O(4)	1.217(3)	1.210(5)	1.222(5)
C(9)–O(1)–C(1)	116.1(2)	116.0.(3)	117.3(4)
O(1)–C(1)–O(2)	124.9(3)	121.9(3)	122.5(4)
O(1)–C(1)–N(1)	109.9(2)	108.5(3)	108.0(4)
O(2)–C(1)–N(1)	125.2(3)	129.7(3)	129.4(4)
C(1)–N(1)–C(2)	128.5(2)	121.6(3)	123.0(4)
N(1)–C(2)–S	118.2(2)	116.2(2)	117.2(3)
N(1)–C(2)–N(2)	115.1(2)	122.1(3)	119.0(4)
N(2)–C(3)–C(4)	121.7(2)	121.1(3)	122.4(4)
N(2)–C(3)–C(8)	121.2(2)	121.3(3)	120.6(4)
C(3)–C(8)–C(7)	121.9(3)	119.8(4)	120.7(5)
C(8)–C(7)–C(6)	120.1(3)	121.0(4)	120.7(5)
C(7)–C(6)–C(5)	119.8(3)	120.4(4)	120.5(5)
C(6)–C(5)–C(4)	119.3(3)	118.6(5)	119.5(5)
C(5)–C(4)–C(3)	121.7(2)	122.5(4)	121.6(5)
C(3)–C(4)–N(3)	122.1(2)	120.9(3)	120.6(4)
C(5)–C(4)–N(3)	116.2(2)	116.5(4)	117.8(5)
C(4)–N(3)–O(3)	119.0(2)	118.8(4)	117.3(5)
C(4)–N(3)–O(4)	118.0(3)	117.3(4)	118.3(5)
O(3)–N(3)–O(4)	122.9(2)	123.8(4)	124.3(5)
S–C(2)–N(2)	126.6(2)	121.6(2)	123.7(3)
C(8)–C(3)–C(4)	117.1(3)	117.7(3)	117.0(4)
C(2)–N(2)–C(3)	126.3(2)	123.4(3)	129.5(4)

in Table 3. As shown in Table 3, there is general agreement of the values. The shorter bond N(1)–C(2) for complex **1** can be caused by the formation of S–Cd bond. For the same reason, complex **1** has the longest C(2)–S bond. The different conformation of the compounds arising from the binding of the metal ions to H_2omt gives rise to the following bond angles sequences: (i) O(1)–C(1)–O(2): (H_2omt) > (**1**) ≈ (**2**); (ii) O(2)–C(1)–N(1): (H_2omt) < (**1**) ≈ (**2**); (iii) C(1)–N(1)–C(2): (H_2omt) > (**1**) > (**2**); (iv) N(1)–C(2)–N(2): (H_2omt) < (**2**) < (**1**); (v) S–C(2)–N(2): (H_2omt) > (**2**) > (**1**); (vi) C(2)–N(2)–C(3): (**2**) > (H_2omt) > (**1**).

Spectroscopic properties of the compounds

IR and UV spectra For the compounds of H_2omt, **1** and **2**, the bands at *ca.* 3140 cm^{-1} are usually attributed to the stretching frequency ν(NH), while for complex **3**, the band above 3100 cm^{-1} was not observed, indicating the absence of NH group. The intense band arising from the amide-I stretching vibration at 1732 cm^{-1} for H_2omt is red-shifted when ligation occurs in the Cd(II) (1648 cm^{-1}) and Zn(II) (1661 cm^{-1}) complexes. The C=S band at 867 cm^{-1} for the free ligand H_2omt has shifted to 855 cm^{-1} in complex **1**, indicative of the binding via the thiolato sulfur atom to Cd(II) ion, which is also indicated by the presence of a band of 310 cm^{-1}, assignable to ν(Cd–S) [25]. Therefore, the nearly unchanged ν(C=S) band at 868 cm^{-1} in complex **2** implicates the non-coordination of thiolate sulfur, in agreement with the X-ray crystallographic results. In addition, the coordination of nitrogen atom to Cd(II) or Zn(II) ion in complex **1** or **2** is observed by the presence of bands at *ca.* 320 ~ 335 cm^{-1}, assignable to ν(Cd–N) or ν(Zn–N) [26].

The UV spectra of the ligand H_2omt and complexes **1** and **2** are shown in Fig. 4. For all three compounds, the bands at about 278 nm are ascribed to ^{1}L(b) absorption of the aromatic ring. The signals around

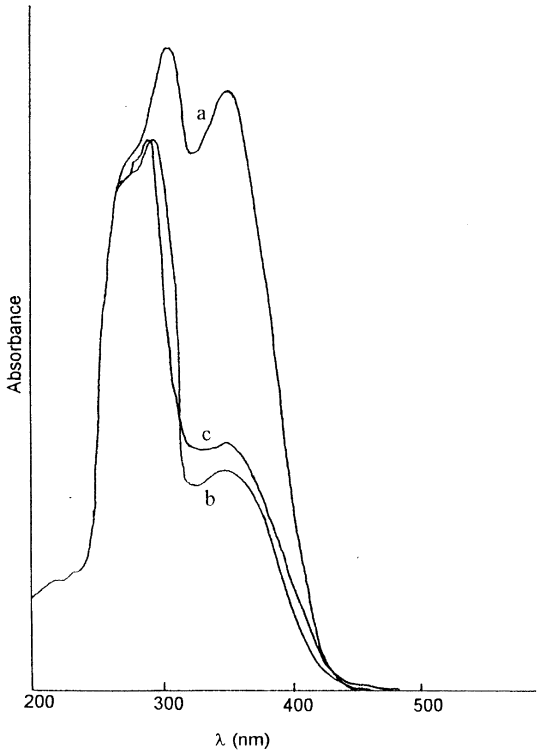


Fig. 4. UV spectra of the compounds in chloroform (a, H_2omt; b, **1**; c, **2**).

Table 4. ^{1}H NMR spectra of compounds H_2omt, **1** and **2** (in ppm)

Compound	Assignment[a]			
	Ar–NHC(S)	HNC(O)	OCH_3	aromatic ring
H_2omt	12.52 (s, 1H)	8.3 (s, 1H)	3.9 (s, 3H)	7.39 ~ 8.47 (m, 4H)
1	12.81 (s, 1H)	–	3.5 (s, 3H)	7.27 ~ 9.06 (m, 12H)
2	12.95 (s, 1H)	–	3.3 (s, 3H)	7.24 ~ 9.58 (m, 12H)

[a] s = single, m = multiple.

300 nm are attributed to the absorption of the NO_2 group. As for the $n\rightarrow\pi^*$ absorptions of C=O, they are near 345 nm. All the absorptions shown a bathochromical shift for the complexes relative to those of the free ligand are caused by the coordination of metal ions to the ligand. The $n\rightarrow\pi^*$ excitation of C=S is not observed in any of the compounds, in agreement with that reported by Barret *et al*. [27].

^{1}H and ^{13}C NMR spectra The ^{1}H and ^{13}C NMR spectra of the ligand H_2omt and complexes **1** and **2** are listed in Tables 4 and 5, respectively.

As shown in Table 4, most of their proton signals are observed to shift to down fields in complexes **1** and **2** relative to those of the free ligand due to the binding of the metal ions. The absence of δ(NH) [s, 1H, HN–C(O)] in the complexes shows the coordination of deprotonated amine to Cd(II) or Zn(II) ion.

In comparison with the ^{13}C NMR spectrum of the ligand H_2omt (Table 5), C_2 has shifted to a lower field at δ 186.34 for **1** and 186.98 for **2**; C_3 to δ 159.31 (**1**) and 159.14 (**2**). However, C_1 is found to have shifted to a higher field at δ 51.85 for **1** and 51.68 for **2**.

Electrochemical studies

The cyclic voltammograms of the compounds H_2omt, **1** and **2** are shown in DMF and CH_3CN solutions at a scan rate of 0.1 V s^{-1} in the scan ranges 0 to +1.8 and −1.8 to 0 V are shown in Figs 5 and 6, respectively. As can be seen from Fig. 5, it is found that each of three compounds exhibit two irreversible cathodic peaks with −0.43 and −1.53 V for H_2omt, −0.30 and −1.40 V for **1** as well as −0.53 and −1.57 V for **2**, and one reversible redox couples at −1.13 and −1.08 V for H_2omt, −0.93 and −0.90 V for **1** and −1.13 and −1.05 V for **2**. Thus, it is tentatively suggested that all these peaks are ascribed to the reduction and oxidation process of the Homt group. In terms of the cyclic voltammograms of the compounds in CH_3CN solution as shown in Fig. 6, each of the compounds display an anodic peak (H_2omt, 1.28 V; **1**, +1.39 V; **2**, +1.39 V) one cathodic peak (H_2omt, −0.83 V; **1**, −0.55 V; **2**, −0.5 V) and one reversible redox couple (H_2omt, −1.15 and −1.13 V; **1**, −0.90 and −0.85 V; **2**, −0.92 and −0.87 V). In addition, it is interesting to find that there is a cathodic peak appearing at −1.50 V for H_2omt, while such a peak is absent for either of the two complexes, suggesting that the cyclic voltammogramms of the compounds are affected by the solvent.

Biological activities

The antibacterial and antifungal activities of the compounds are listed in Table 6, showing that the free

Table 5. ^{13}C NMR spectra of the compounds H_2omt, **1** and **2** (in ppm)

Compound	Assignment[a]								
	C_1[b]	C_2	C_3	C_4	C_5	C_6	C_7	C_8	C_9
H_2omt	53.78	178.68	152.48	142.21	125.15	133.49	126.73	128.16	132.48
1	51.85	186.34	159.31	141.96	124.69	135.04	125.39	128.40	133.05
2	51.68	186.98	159.14	141.76	124.69	134.91	126.61	128.52	132.97

[a] The signals of 2,2′-bipyridinyl ring for **1** appear at δ 150.71, 149.96, 139.37, 121.15 and 120.74, while the ones of *o*-phenanthrolinyl ring for **2** are observed at δ 149.76, 140.98, 138.27, 132.16, 125.07 and 124.60.

[b] The positions of the carbon atoms are denoted in the structure of the free ligand H_2omt.

Table 6. Antibacterial and antifungal activity of the compounds H_2omt, **1** and **2**[a]

Bacterium or fungus	H_2omt	**1**	**2**
B. subtilis 6633	0	5.3	3.8
S. lutea	0	7.5	7.4
S. aureus 209p	0	9.5	11.1
P. diploccus	0	9.2	6.5
E. coli	5.0	7.1	7.7
P. aeruginosa x313	0	9.3	9.3
S. Yake Sake	3.2	6.0	6.9

[a](1) The concentration of each tested compound was given in 0.55 mM. (2) The inhibition zone was given in mm.

ligand H_2omt was inactive against *B. subtilis* 6633, *S. lutea*, *S. aureus* 209p, *P. diploccus* and *P. aeruginosa* x313, but slightly active against *E. coli* and *S. Yake Sake*. Both the metal complexes exhibited inhibition activities against the tested bacteria and fungus, indicating that the enhancement of the biological activities of the complexes is related to the coordination of the metal ion and the bpy or phen molecule.

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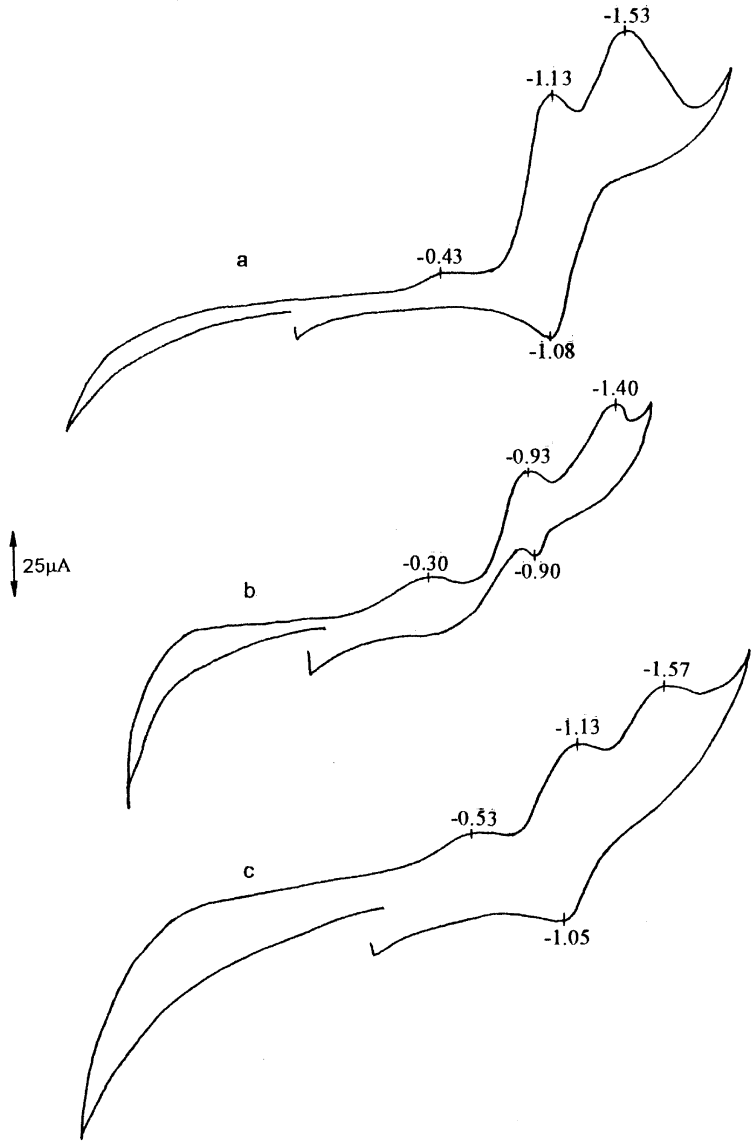

Fig. 5. Cyclic voltammograms of compounds H_2omt (a), **1** (b), **2** (c). (Measured in DMF, 1×10^{-4} mol · dm^{-3}, scan rate 100 mV · s^{-1}).

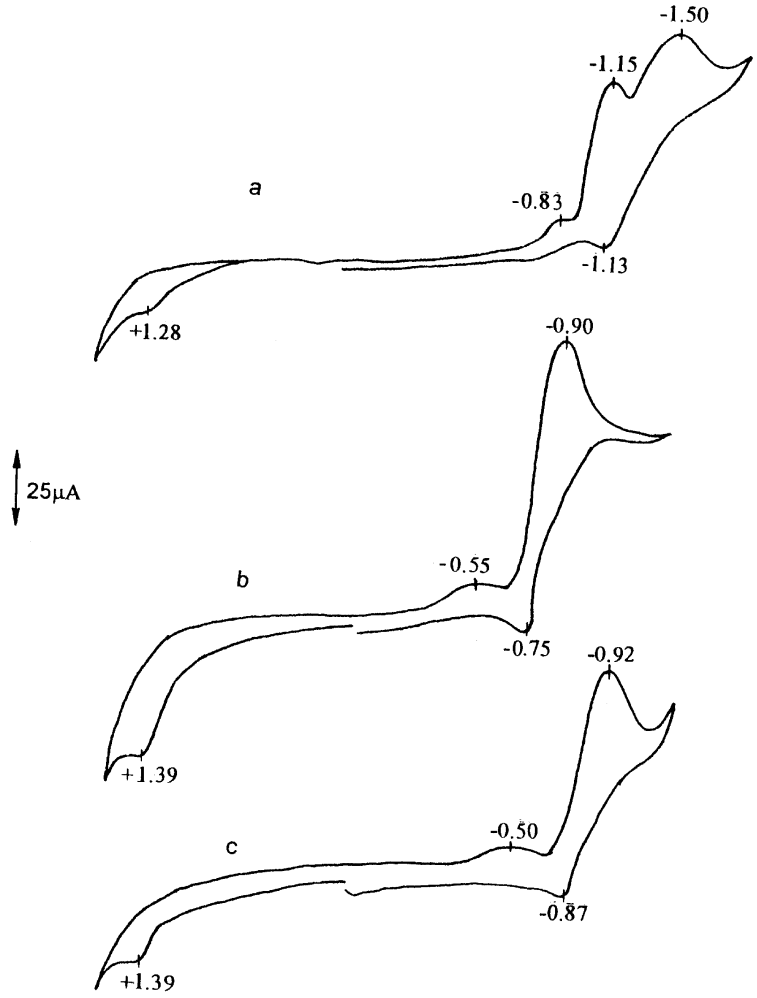

Fig. 6. Cyclic voltammograms of compounds H_2omt (a), **1** (b), **2** (c). (Measured in CH_3CN, 1×10^{-4} mol · dm^{-3}, scan rate 100 mV · s^{-1}).

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