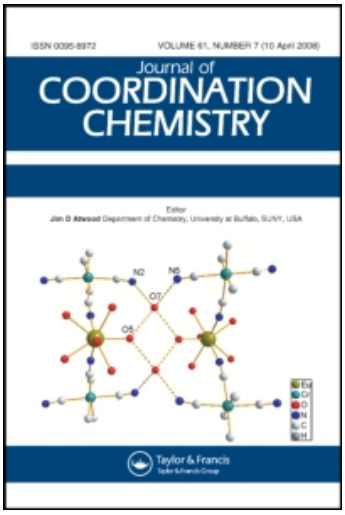

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SYNTHESES, CRYSTAL STRUCTURES AND PROPERTIES OF CADMIUM(II) AND MANGANESE(II) COMPLEXES DERIVED FROM *N*(*o*-NITROPHENYL)-N'-(METHOXYCARBONYL)THIOUREA AND *o*-PHENANTHROLINE (OR 2,2'-BIPYRIDINE)

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SYNTHESES, CRYSTAL STRUCTURES AND PROPERTIES OF CADMIUM(II) AND MANGANESE(II) COMPLEXES DERIVED FROM *N*-(*o*-NITROPHENYL)-*N'*-(METHOXYCARBONYL)THIOUREA AND *o*-PHENANTHROLINE (OR 2,2'-BIPYRIDINE)

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One cadmium(II) and one manganese(II) complexes derived from *N*-(*o*-nitrophenyl)-*N'*-(methoxycarbonyl)thiourea (H_2omt) and *o*-phenanthroline (phen) or 2,2'-bipyridine (bpy) have been synthesized: **1**, $[Cd(Homt)_2(phen)](CHCl_3)_2$; **2**, $[Mn(ocn)_2(bpy)_2]$ (ocn = *o*-nitrophenylcyanamido-*N*). The cadmium(II) ion in complex **1** has distorted octahedral geometry generated by the two N atoms from one phen and the two S atoms and the two deprotonated amide N atoms from two Homt groups. Complex **2** is formed by desulfurization and hydrolysis of the ligand H_2omt in alkaline media. The manganese(II) atom is six-coordinated with distorted octahedral geometry made up by four N atoms from two bpy ligands and two N atoms from two ocn ligands. Spectroscopic and electrochemical properties, as well as antibacterial and antifungal activities have been studied.

Keywords: Synthesis; X-ray structure; Cd(II) complex; carbodiimide Mn(II) complex; *N*-(*o*-nitrophenyl)-*N'*-(methoxycarbonyl)thiourea; *o*-phenanthroline; bipyridine

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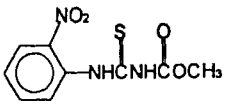
INTRODUCTION

The biological activities of complexes with thiourea derivatives have been well documented; thiourea derivatives have been successfully screened for various biological actions,[1] and some *N*-substituted-*N'*-alkoxycarbonyl thioureas have been used in commercial fungicides. To date, many transition metal complexes of thiourea derivatives have been reported and structures with O,S-binding to the metal ions have been proposed for alkaline media based on a series of physicochemical properties.[2] However, to our knowledge, no such crystal structure has been published. Recently, the derivative *N*-(*o*-nitrophenyl)-*N'*-(ethoxycarbonyl)thiourea (H_2oet) was isolated from the leaves of a resistant (*Pyricuiria oryzae cav.*) rice variety[3] and preliminary pharmacological tests showed its high antibacterial activity. In previous work,[4] several ligands similar to the basic structure of H_2oet were prepared, and it was found that copper(I) complexes can be obtained from the copper(II) salts by *in situ* reduction in the presence of these thiourea derivatives. It is 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-acetyloxybenzoic 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.[5] Ternary complexes of metal ions containing a bidentate organic base such as 2,2'-bipyridine (bpy) and phenanthrolinine (phen) have been well reported,[6] and they serve as interesting models for understanding enzyme–metal ion–substrate relationships which should play an important role in metalloenzyme-catalysed biochemical reactions.[7] With these facts in mind, a study of transition metal complexes with the new derivative *N*-(*o*-nitrophenyl)-*N'*-(methoxycarbonyl)thiourea would be interesting.



N-(*o*-nitrophenyl)-*N'*-(methoxycarbonyl)thiourea (H_2omt)

EXPERIMENTAL

Materials

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 instrument. IR data were collected by a Magna 750 spectrometer; electronic spectra were recorded on a Shimadzu UV-300 spectrometer. ^{1}H NMR spectra were determined with a Bruker AM 500 instrument in $CDCl_3$ solution with TMS as internal standard. The EPR spectrum of complex **2** was obtained on a Bruker 2000-SRC spectrometer operating at X-band frequencies at room temperature. Cyclic voltammetry was performed with a HDV-7B potentiostat and LZ3Q-204 recorder with an electrochemical cell containing a Pt wire working electrode, a Pt plate auxiliary electrode, and an SCE reference electrode.

Preparations

N-(o-nitrophenyl)-N'-(methoxycarbonyl)-thiourea (H_2omt)

To 20 cm^3 of acetone containing thiocyanate (2.0 g, 26.3 mmol) was added a solution of methyl chloroformate (2.5 g, 26.3 mmol) in 20 cm^3 of acetone dropwise. After the resulting mixture was stirred at 40°C for 30 min, the solution was cooled to 0–5°C in an ice bath. Then, *o*-nitrophenylamine (3.6 g, 26.3 mmol) was added dropwise, followed by stirring for two more hours at room temperature. The resulting mixture was filtered to yield a yellowish solution which was evaporated to dryness. The crude product was recrystallized from ethanol and dried *in vacuo*. Yield, 5.4 g (66%); m.p., 206–208°C; *Anal*: Calcd. for $C_9H_9N_3O_4S$(%): C, 42.3; H, 3.5; N, 16.5. Found: C, 42.1; H, 3.3; N, 16.3.

Complex 1, [Cd(Homt)$_2$(phen)](CHCl$_3$)$_2$

A solution of $Cd(ClO_4)_2 \cdot 6H_2O$ (0.1 g, 0.3 mmol) in 20 cm^3 of methanol was added slowly to a methanolic solution of *o*-phenanthroline (0.06 g, 0.3 mmol in 15 cm^3). This was warmed at 40–45°C with stirring for 15 min to obtain a colourless solution. When cooled to room temperature, to it was added a methanolic solution (20 cm^3) containing H_2omt (0.2 g, 0.6 mmol) and NaOH (0.02 g, 0.6 mmol). Large amounts of solids were precipitated. The resultant mixture was stirred at room temperature for a further 2 h, the solids were collected by filtration, washed thoroughly with water and methanol, and dried *in vacuo*. Yield, 0.3 g (89%); m.p., 243°C (decomp.); *Anal*: Calcd. for $C_{32}H_{26}CdCl_6N_8O_8S_2$(%): C, 37.0; H, 2.5; N, 10.8. Found: C, 36.7; H, 2.7; N, 10.3.

Single crystals suitable for X-ray analyses were obtained by slow diffusion of diethyl ether into a solution of complex **1** in chloroform over two weeks.

Complex 2, $Mn(ocn)_2(bpy)_2$

A solution of $Mn(ClO_4)_2 \cdot 6H_2O$ (0.6 g, 1.5 mmol) in 15 cm^3 of methanol was slowly added to a methanolic solution (10 cm^3) of 2,2′-bipyridine (0.2 g, 1.5 mmol). The resulting mixture was warmed with stirring at 40–45°C for 15 min. Upon cooling to room temperature, to it was added 20 cm^3 of a methanolic solution containing NaOH (0.1 g, 3.1 mmol) and H_2omt (0.8 g, 3.1 mmol). After the mixture was stirred at room temperature for 2 h, a small amount of insoluble brown solid was removed by filtration. The clear filtrate was left to evaporate slowly in air for about three weeks to deposit orange crystals. Yield, 0.5 g (32%); m.p., 271°C (decomp.); *Anal*: Calcd, for $C_{34}H_{24}N_{10}O_4Mn$(%): C, 59.0; H, 3.5; N, 20.2. Found: C, 59.4; H, 3.5; N, 20.1.

Biological Activity

The antibacterial and antifungal activities of the ligand H_2omt and the metal complexes **1** and **2** against the standard strains of *B. subtilis 6633*, *S. lutea*, *S. aureus 209p*, *P. diploccus*, *E. coli and P. aerruginosa x313* and *S. yake sake* were determined using the plate method.[8] Each of the compounds was prepared at a concentration of 0.55 mM during the tests, and the results are listed in Table V.

X-ray Crystallography

Pertinent crystal data, information on data collection and structure refinement of **1** and **2** are listed in Table I and non-hydrogen atomic coordinates and equivalent isotropic thermal parameters are listed in Table II.

Both structures were solved by direct methods. Refinement was carried out using full-matrix least-squares techniques 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. For complex **1**, one of the Cl atoms in the solvent chloroform molecules was disordered (Cl(4) and Cl(5)). All calculations were performed on a Compaq computer using the TEXSAN or SHELXTL-5 program package. Other crystallographic programs used in the structure determination have been cited elsewhere.[9]

TABLE I Summary of crystallographic data and structural parameters for **1** and **2**

	1, $[Cd(Homt)_2(phen)](CHCl_3)_2$	**2**, $Mn(ocn)_2(bpy)_2$
Formula	$C_{32}H_{26}CdCl_6N_8O_8S_2$	$C_{34}H_{24}N_{10}O_4Mn$
M	1039.83	691.57
Crystal size/mm	$0.20 \times 0.15 \times 0.10$	$0.20 \times 0.15 \times 0.15$
Crystal color and shape	Yellow, prism	Orange, prism
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$	$P2_1/n$ (# 14)
a/Å	10.965(3)	13.754(3)
b/Å	14.297(3)	30.02(1)
c/Å	14.811(3)	7.760(6)
α/°	82.641(2)	
β/°	70.94(2)	90.16(4)
γ/°	73.39(2)	
V/Å^3	2101.6(8)	3204(4)
Z	2	4
Dc/g cm^{-3}	1.640	1.434
$F(000)$	1036	1420
μ/cm^{-1}	10.57	4.48
Diffractometer	Siemens SMART CCD	Enraf-Nonius CAD4
2θ max./°	23.26×2	50.0
No. of unique reflections	5793	5879
No. of observations	4723 ($I > 2\sigma(I)$)	3885 (($I > 2\sigma(I)$)
No. of variables	523	442
Temperature/°	23	23
R	0.050	0.056
wR^2(R_w for **2**)	0.134	0.062
GOF	1.086	1.31
Max. shift in final cycle	−0.065	0.0002
$\Delta\rho$ max., min./eÅ^{-3}	1.109, −0.818	0.38, −0.33

RESULTS AND DISCUSSION

Crystal Structures

The structure of [Cd(Homt)$_2$(phen)] with hydrogen atoms omitted is shown in Figure 1, and its packing in the unit cell is depicted in Figure 2. Selected atomic distances and bond angles are listed in Table III.

As can be seen from Figure 1, the Cd(II) atom is six-coordinated by two N atoms from one *o*-phenanthroline, and two S and two N atoms from two Homt groups. The bond lengths Cd–S(1) and Cd–S(2) of 2.687(2) Å are within the range of published results dealing with Cd–S (thiocarbonyl)[10] and the bond lengths Cd–N(3) of 2.326(4) Å and Cd–N(6) of 2.330(4) Å are comparable to reported values of Cu–N(amine).[11] The structural data within the *o*-phenanthroline molecule are normal, and the bond lengths Cd–N(phen) of 2.358(5) and 2.374(4) Å are consistent with Cd–N(phen or bpy) values reported elsewhere.[12]

TABLE II Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\times 10^3$) for **1**

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
Cd	12841(1)	11441(1)	2571(1)	39(1)
S	14537(1)	12529(1)	1630(1)	44(1)
S	13780(2)	10198(1)	3858(1)	50(1)
O(1)	13752(13)	6945(6)	2961(6)	197(5)
O(2)	13756(7)	5795(4)	3903(5)	110(2)
O(3)	13509(5)	9843(3)	790(3)	60(1)
O(4)	14600(5)	8408(3)	1293(3)	71(1)
O(5)	12305(6)	16860(4)	940(4)	89(2)
O(6)	11746(5)	16058(3)	2269(4)	71(1)
O(7)	10827(5)	13001(3)	4455(3)	66(1)
O(8)	11147(5)	14452(3)	3826(3)	72(1)
N(1)	10594(5)	11389(3)	3254(3)	44(1)
N(2)	11718(4)	11903(3)	1394(3)	43(1)
N(3)	13848(5)	9819(3)	2171(3)	41(1)
N(4)	14651(5)	8434(3)	3064(3)	47(1)
N(5)	14002(7)	6552(4)	3631(4)	71(2)
N(6)	12460(4)	12990(3)	3113(3)	39(1)
N(7)	13390(5)	14294(3)	2408(3)	42(1)
N(8)	12578(6)	16226(4)	1522(4)	54(1)
C(1)	12267(7)	12150(5)	498(5)	56(2)
C(2)	11571(8)	12400(5)	−169(5)	68(2)
C(4)	9651(7)	12108(4)	1046(5)	56(2)
C(5)	8286(7)	12058(5)	1389(6)	69(2)
C(6)	7745(7)	11804(5)	2303(7)	71(2)
C(7)	8477(6)	11575(5)	2976(5)	56(2)
C(8)	7939(7)	11334(5)	3938(6)	71(2)
C(9)	8715(7)	11137(5)	4535(6)	71(2)
C(10)	10020(7)	11166(5)	4170(5)	57(2)
C(11)	9829(5)	11606(4)	2656(4)	44(1)
C(12)	10419(5)	11876(4)	1676(4)	42(1)
C(13)	10266(8)	12390(6)	115(6)	74(2)
C(21)	14938(6)	7888(4)	3867(4)	43(1)
C(22)	14637(6)	6995(4)	4147(4)	49(2)
C(23)	14927(8)	6452(5)	4925(5)	69(2)
C(24)	15546(9)	6787(5)	5434(6)	78(2)
C(25)	15870(8)	7648(5)	5158(5)	70(2)
C(26)	15584(6)	8191(5)	4384(5)	56(2)
C(27)	14147(5)	9416(4)	2977(4)	40(1)
C(28)	14041(6)	9268(4)	1419(4)	47(1)
C(29)	13586(8)	9377(5)	−49(5)	74(2)
C(31)	14346(5)	14747(4)	1781(4)	39(1)
C(32)	13972(6)	15665(4)	1335(4)	43(1)
C(33)	14917(7)	16090(5)	699(5)	61(2)
C(34)	16254(8)	15628(5)	519(5)	69(2)
C(35)	16634(6)	14750(5)	962(5)	62(2)
C(36)	15682(6)	14325(4)	1601(5)	53(2)
C(37)	13386(5)	13349(4)	2435(4)	37(1)
C(38)	11473(6)	13563(4)	3790(4)	48(2)
C(39)	9716(10)	13504(6)	5235(6)	108(4)
C(01)	19180(9)	5098(6)	2530(7)	89(3)
C(02)	10174(15)	11402(8)	7692(11)	164(6)
Cl(1)	18316(4)	4207(3)	3028(3)	168(2)
Cl(2)	20032(3)	4849(3)	1342(3)	165(2)

TABLE II (*Continued*)

Atom	*x/a*	*y/b*	*z/c*	*U(eq)*
Cl(3)	18104(3)	6244(2)	2625(2)	146(1)
Cl(4)	9911(6)	10583(3)	8693(5)	230(2)
Cl(5)	9079(6)	11084(4)	7207(5)	231(2)
Cl(6)	11269(9)	11336(7)	6492(8)	207(4)
Cl(7)	11880(9)	11034(7)	7599(9)	211(5)

Atomic coordinates and thermal parameters of the non-hydrogen atoms for **2**

Atom	*x/a*	*y/b*	*z/c*	*B(eq)*
Mn	0.02400(4)	0.14708(2)	0.10236(8)	2.91(3)
O(1)	−0.3480(3)	0.02329(14)	0.5685(5)	6.8(2)
O(2)	−0.4714(3)	0.04972(13)	0.4373(5)	6.8(2)
O(3)	0.0268(5)	0.3237(2)	0.8552(7)	11.9(4)
O(4)	0.1614(5)	0.2954(2)	0.8200(6)	14.6(5)
N(1)	0.0011(2)	0.09900(11)	−0.1317(4)	3.2(2)
N(2)	−0.0762(2)	0.18040(11)	−0.0901(4)	3.3(2)
N(3)	0.1629(2)	0.16651(11)	−0.0407(4)	3.4(2)
N(4)	0.1533(3)	0.11517(11)	0.2408(4)	3.6(2)
N(5)	−0.0744(3)	0.10280(12)	0.2267(5)	4.4(2)
N(6)	−0.2239(3)	0.06416(12)	0.3089(4)	3.9(2)
N(7)	−0.3941(3)	0.02999(12)	0.4377(5)	4.0(2)
N(8)	0.0257(3)	0.20161(13)	0.2732(5)	5.0(2)
N(9)	0.0704(3)	0.25580(12)	0.4954(5)	4.5(2)
N(10)	0.0964(5)	0.31464(15)	0.7654(6)	6.2(3)
C(1)	0.0339(3)	0.05732(15)	−0.1368(6)	4.3(2)
C(2)	−0.0056(4)	0.02470(15)	−0.2401(6)	4.7(2)
C(3)	−0.0845(4)	0.03541(16)	−0.3381(6)	4.7(2)
C(4)	−0.1205(3)	0.07819(15)	−0.3335(5)	3.7(2)
C(5)	−0.0740(3)	0.10951(13)	−0.2324(5)	3.0(2)
C(6)	−0.1051(3)	0.15690(13)	−0.2277(5)	3.2(2)
C(7)	−0.1574(4)	0.17598(16)	−0.3603(6)	4.6(2)
C(8)	−0.1821(4)	0.22054(18)	−0.3485(7)	5.5(3)
C(9)	−0.1544(4)	0.24410(16)	−0.2080(7)	5.4(3)
C(10)	−0.1015(4)	0.22330(15)	−0.0812(6)	4.5(2)
C(11)	0.1638(3)	0.18903(15)	−0.1887(6)	4.3(2)
C(12)	0.2469(4)	0.19792(18)	−0.2814(7)	5.3(3)
C(13)	0.3333(4)	0.1829(2)	−0.2199(8)	6.2(3)
C(14)	0.3339(3)	0.15947(18)	−0.0662(7)	5.3(3)
C(15)	0.2482(3)	0.15213(14)	0.0224(6)	3.6(2)
C(16)	0.2431(3)	0.12780(13)	0.1898(5)	3.3(2)
C(17)	0.3236(3)	0.11873(15)	0.2905(6)	4.2(2)
C(18)	0.3119(4)	0.09632(17)	0.4433(7)	5.2(3)
C(19)	0.2214(4)	0.08341(17)	0.4955(6)	5.2(3)
C(20)	0.1431(4)	0.09336(16)	0.3914(6)	4.6(2)
C(21)	−0.1468(3)	0.08350(14)	0.2560(5)	3.5(2)
C(22)	−0.2689(3)	0.03175(13)	0.2122(5)	3.0(2)
C(23)	−0.2365(3)	0.01630(14)	0.0504(5)	3.5(2)
C(24)	−0.2902(4)	−0.01452(15)	−0.0406(6)	4.4(2)
C(25)	−0.3763(4)	−0.03143(16)	0.0261(6)	4.9(3)
C(26)	−0.4099(3)	−0.01669(15)	0.1812(6)	4.3(2)
C(27)	−0.3555(3)	0.01359(13)	0.2729(5)	3.1(2)
C(28)	0.0481(3)	0.22891(14)	0.3735(6)	3.9(2)
C(29)	0.0862(3)	0.30006(14)	0.4535(6)	3.5(2)
C(30)	0.0884(3)	0.31791(15)	0.2889(6)	4.3(2)
C(31)	0.1007(4)	0.36279(17)	0.2575(7)	5.6(3)
C(32)	0.1115(4)	0.39167(17)	0.3948(9)	6.4(3)
C(33)	0.1109(4)	0.37581(17)	0.5600(8)	6.3(3)
C(34)	0.0986(3)	0.33048(15)	0.5866(6)	4.3(2)

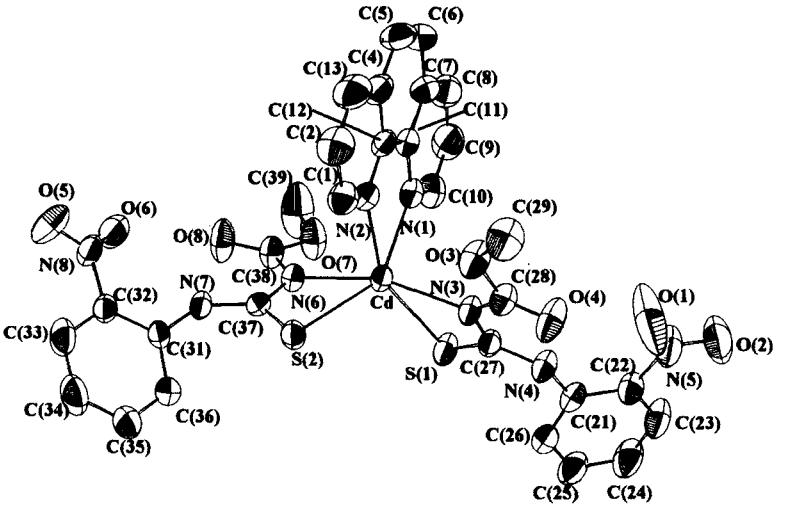


FIGURE 1 ORTEP drawing of $[Cd(Homt)_2(phen)]$ with ellipsoids at 45% probability level (hydrogen atoms are omitted for clarity).

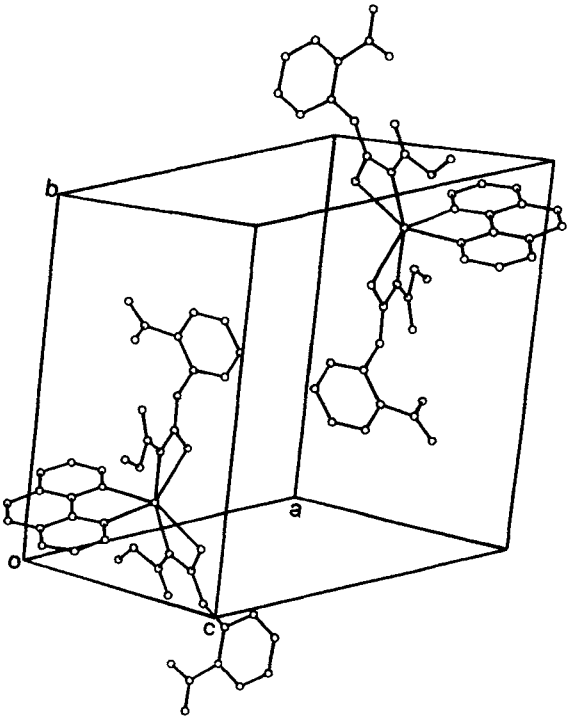


FIGURE 2 Packing of $[Cd(Homt)_2(phen)]$ in the unit cell.

TABLE III Selected bond lengths (A) and angles (°) for **1** and **2**

1					
N(1)–Cd	2.358(5)	N(3)–Cd	2.326(4)	S(1)–Cd	2.687(2)
N(2)–Cd	2.374(4)	N(6)–Cd	2.330(4)	S(2)–Cd	2.687(2)
N(1)–Cd–N(2)	70.3(2)	N(2)–Cd–N(3)	97.9(2)	N(3)–Cd–S(1)	61.90(12)
N(1)–Cd–N(3)	100.4(2)	N(2)–Cd–N(6)	98.2(2)	N(3)Cd–S(2)	109.03(12)
N(1)–Cd–N(6)	93.9(2)	N(2)–Cd–S(1)	154.14(12)	N(6)–Cd–S(1)	104.89(11)
N(1)–Cd–S(1)	96.24(12)	N(2)–Cd–S(2)	89.93(12)	N(6)–Cd–S(2)	61.57(11)
N(1)–Cd–S(2)	146.63(11)	N(3)–Cd–N(6)	161.3(2)	S(1)–Cd–S(2)	111.17(5)
C(1)–N(2)–Cd	125.1(4)	C(27)–N(3)–Cd	101.9(3)	C(37)–N(6)–Cd	102.2(3)
C(10)–N(1)–Cd	125.5(4)	C(27)–S(1)–Cd	80.2(2)	C(37)–S(2)–Cd	80.0(2)
C(11)–N(1)–Cd	116.5(4)	C(28)–N(3)–Cd	135.6(4)	C(38)–N(6)–Cd	135.0(4)
C(12)–N(2)–Cd	116.4(4)				
Intramolecular hydrogen bonds					
N(4)···O(1)	2.628	N(7)···O(6)	2.676		
N(4)···O(4)	2.646	N(7)···O(6)	2.633		
2					
N(1)–Mn	2.314(4)	N(3)–Mn	2.288(4)	N(5)–Mn	2.131(4)
N(2)–Mn	2.262(3)	N(4)–Mn	2.285(4)	N(8)–Mn	2.107(4)
N(1)–Mn–N(2)	71.3(1)	C(10)–N(2)–Mn	123.4(3)		
N(1)–Mn–N(3)	83.8(1)	N(2)–Mn–N(8)	94.5(1)	C(6)–N(2)–Mn	118.2(3)
N(1)–Mn–N(4)	102.1(1)	N(3)–Mn–N(4)	71.7(1)	C(11)–N(3)–Mn	123.9(3)
N(1)–Mn–N(5)	83.2(1)	N(3)–Mn–N(5)	155.7(1)	C(15)–N(3)–Mn	118.2(3)
N(1)–Mn–N(8)	165.7(1)	N(3)–Mn–N(8)	95.7(1)	C(20)–N(4)–Mn	122.0(3)
N(2)–Mn–N(3)	94.3(1)	N(4)–Mn–N(5)	91.2(1)	C(16)–N(4)–Mn	117.0(3)
N(2)–Mn–N(4)	165.3(1)	N(4)–Mn–N(8)	91.3(1)	C(21)–N(5)–Mn	159.3(4)
N(2)–Mn–N(5)	100.8(1)	N(5)–Mn–N(8)	101.9(2)	C(28)–N(8)–Mn	164.7(4)

In complex **1**, the bond angles vary from those of a regular octahedron with N(1)–Cd–S(1) = 96.24(12)°, N(1)–Cd–S(2) = 146.63(11)°, N(1)–Cd–N(3) = 100.4(2)°; thus the geometry of the six-coordinated cadmium(II) atom is highly distorted. The molecule contains two four-membered (from Homt) [CdN(6)C(37)S(2) and CdS(1)C(27)N(3)] and one five-membered (from phen) [CdN(1)C(11)C(12)N(2)] chelate rings. The dihedral angle between the two four-membered least-squares planes is 110.72°, while the dihedral angles between the four-membered and the five-membered ones are 99.57 and 96.35° respectively. There are strong hydrogen bonds between the amine N atom and the carbonyl and nitro oxygen atoms (Table III).

The structure of complex **2**, $Mn(ocn)_2(bpy)_2$, is shown in Figure 3 and its unit cell packing is presented in Figure 4. Selected bond lengths and angles are also listed in Table III. It is found that desulfurization and hydrolysis of the ligand H_2omt has taken palce during the formation reaction. The bond N(6)–C(21) of 1.278(6) Å, C(21)–N(5) of 1.175(5) Å, N(8)–C(28) of 1.171(6) Å, and C(28)–N(9) of 1.281(5) Å and the nearly linear arrangement

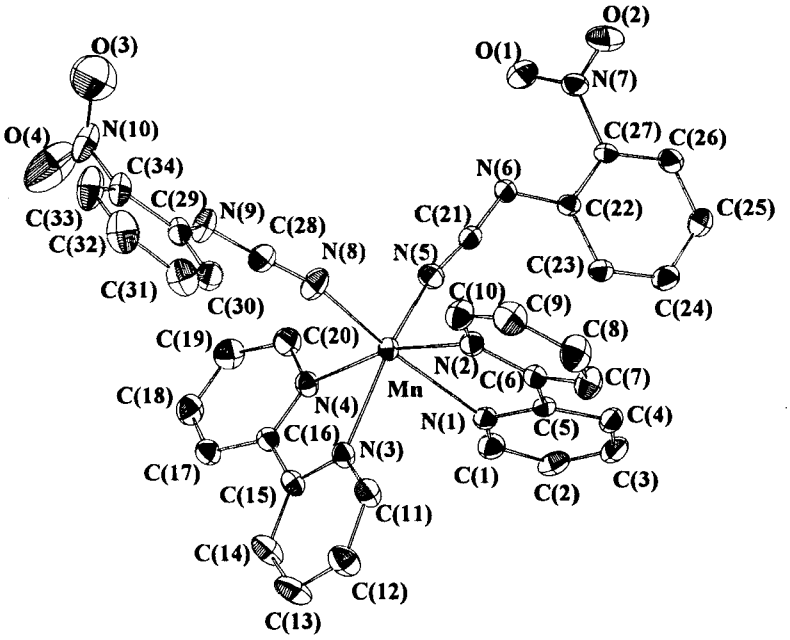


FIGURE 3 ORTEP drawing of $[Mn(ocn)_2(bpy)_2]$.

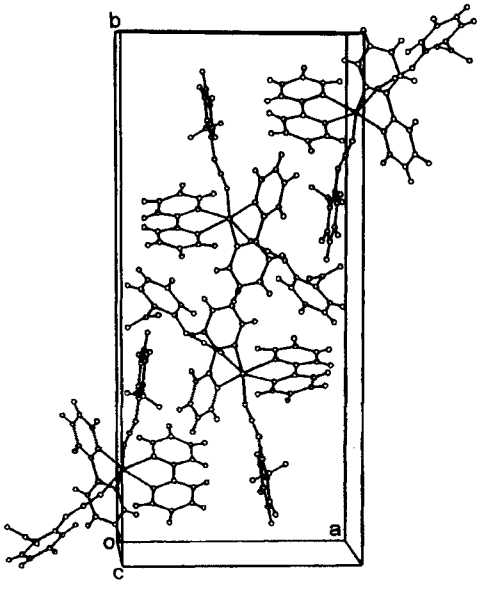


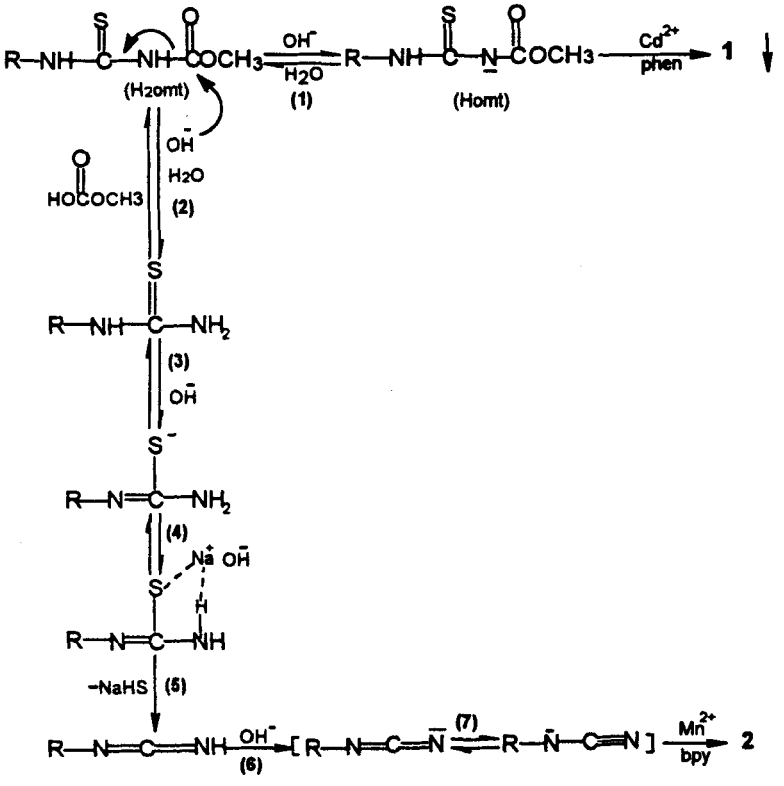
FIGURE 4 Packing of $[Mn(ocn)_2(bpy)_2]$ in the unit cell.

of the angles N(6)–C(21)–N(5) of 172.3(4)° and N(9)–C(28)–N(8) of 174.0(5)° are comparable to results for cyanamido-*N* Cu(II) complexes,[13] suggesting the existence of [–N–C≡N] in the structure; this could be confirmed by the bond angles C(22)–N(6)–C(21) of 121.3(4)° and C(29)–N(9)–C(28) of 118.0(4)°, characteristic of sp^2 hybridization of N(6) and N(9).

The Mn(II) atom is six-coordinated with distorted octahedral geometry and the bond lengths of N(5)–Mn (2.131(4) Å) and N(8)–Mn (2.107(4) Å) are much shorter than those of N(bpy)–Mn (2.314(4), 2.262(3), 2.288(4), 2.285(4) Å) which are found to lie in the range of the published results for Mn–N(bpy or phen).[14]

It is suggested that the formation of complexes **1** and **2** can be depicted in Scheme 1 as shown below.

As shown in Scheme 1, the formation of **1** with low solubility in methanol drove the equilibrium (**1**) to the right, favouring the formation of normal Homt structural products.



SCHEME 1 The formation of complexes **1** and **2** derived from the ligand H_2omt.

In fact, a reaction similar to equation (**2**) has been reported for the preparation of *N*-heteroaryl-thioureas and acyl-thioureas.[15] During the formation of complex **2**, it is proposed that the hydrolysis and desulfurization might have taken place in the presence of NaOH as depicted according to (**3**), (**4**), (**5**) and (**6**). Additionally, it has been shown that the alkaline decomposition of thiourea and *N*-ethylthiourea is first order in thiourea and NaOH,[16] and the exchange reactions with $Na^{35}SH$ and $^{35}S_8$ have been used for the preparation of ^{35}S-labelled thioureas.[17]

Spectroscopic Properties of the Compounds H_2omt, 1 and 2

IR and Electronic Spectra

For the compounds H_2omt and **1**, bands at about 3140 cm^{-1} are usually attributed to ν(NH), while for complex **2**, the band above 3100 cm^{-1} was not observed, indicating the absence of NH. The intense band arising from the amide-I stretching vibration at 1732 cm^{-1} for H_2omt is red-shifted when ligation occurs in complex **1** (1648 cm^{-1}). The C=S band at 867 cm^{-1} for the free ligand H_2omt has shifted to 845 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).[18] In addition, the coordination of the deprotonated nitrogen atom to Cd(II) in **1** is observed by the presence of bands at *ca* 320 cm^{-1}, assignable to ν(Cd–N).[19] Unlike the spectra of H_2omt and **1**, a very strong absorption at 2135 cm^{-1} appears in the spectrum of **2** showing the presence of the C≡N group.[20] N–Mn stretching is found at *ca* 335 cm^{-1}.[19]

The electronic spectra of the ligand H_2omt, complex **1** and **2** show bands at about 275 nm which are ascribed to the ^{1}L(b) absorption of the aromatic ring. Signals around 300 nm are ascribed to the absorption of the NO_2 group, and the $n \rightarrow \pi^*$ absorptions of C=O are observed near 345 nm. For the complexes, all the absorptions show a bathochromical shift relative to those of the free ligand caused by the coordination of metal ions to the ligand. The absorption at 403 nm in **2** is attributed to ligand-to-metal charge transfer. By virtue of the fact that the spin and Laporte-forbidden d–d transitions of the $t_{2g}^3 e_g^2$ manganese(II) compound are very weak,[21] such transitions are quite difficult to observe. Additionally, the band at 251 nm in **2** is assigned to the ^{1}L(a) absorption, which was absent in the other two compounds (H_2omt and **1**), this may be due to solvent effects. The $n \rightarrow \pi^*$ excitation of C=S is not observed in either H_2omt and **1**, in agreement with the report by Barret *et al.*[22]

TABLE IV ^{1}H NMR data for compounds H_2omt and **1** (in ppm)

Compound	*Assignment*[a]				
	Ar–NHC(s)	*HNC*(o)	OCH_3	*Aromatic ring*	2($CHCl_3$)
H_2omt	9.36(s, 1H)	8.3(s, 1H)	3.32(s, 3H)	7.40–8.34(m, 4H)	
1	9.46(s, 1H)		3.45(s, 3H)	7.21–8.51(m, 12H)	7.31(s, 2H)

[a] s = singlet, m = multiplet.

^{1}H NMR Spectra

Because of the strong paramagnetic nature of complex **2**, it is hard to interpret its ^{1}H NMR spectral data. ^{1}H NMR data for H_2omt and **1** are listed in Table IV. Most proton signals are observed to shift downfield in **1** relative to the free ligand. The absence of δ(NH) (s, 1H, HN–C(O)) in the complex shows the coordination of deprotonated amine to the Cd(II) ion.

ESR Spectra

The X-band ESR spectrum of complex **2** was determined in DMF solution at room temperature. The spectrum displays a six-line manganese(II) (I = 5/2) hyperfine pattern centered at $g = 2.003$, $A = 92.2$ G, indicating an odd unpaired electron system S = 5/2 with the g, A tensors isotropic arising from "allowed" transitions ($\Delta m_s = \pm 1$, $\Delta L = 0$).[23]

Electrochemical Studies

Cyclic voltammograms of H_2omt, **1** and **2** exhibit one irreversible anodic peak at about +0.74 V; it is tentatively suggested that such oxidation may correspond to the oxidation of the nitrophenyl groups. As for H_2omt and **1**, it is suggested that reversible redox couples at −1.09 and −1.06 V (H_2omt), −1.14 and −1.11 V (**1**) as well as irreversible cathodic peaks at −1.50 V (H_2omt) and −1.47 V (**1**) are ascribed to reduction and oxidation of the Homt ligand. As far as **2** is concerned, the irreversible cathodic peak at −0.68 V corresponds to the reduction of Mn(II).[24]

Biological Activities

The antibacterial and antifungal activities of the compounds are listed in Table V, showing that the free ligand H_2omt was inactive against *B. subtilis 6633*, *S. lutea*, *S. aureus 209p*, *P. diploccus* and *P. aerruginosa x313*, but slightly active against *E. coli* and *S. yake sake*. Both the metal complexes exhibited inhibition activities against the tested bacteria and fungus, and the

TABLE V Antibacterial and antifungal activity of the compounds H_2omt **1** and **2**[a]

Bacterium or fungus	*H_2omt*	**1**	**2**
B. subtilis 6633	0	5.8	5.9
S. lutea	0	7.6	7.6
S. aureus 209p	0	9.5	10.3
P. diploccus	0	10.2	6.9
E. coli	5.2	8.0	5.5
P. aerruginosa x313	0	11.6	10.3
S. yake sake	3.4	7.7	5.4

[a] The concentration of each tested compound was 0.55 mM. The inhibition zone is given in mm.

enhancement of the biological activities of the complexes is related to the coordination of the metal ion and the bpy or phen molecule.

Supplementary Material

Atomic coordinates, bond lengths and angles, and thermal parameters are available from the authors on request.

Acknowledgements

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