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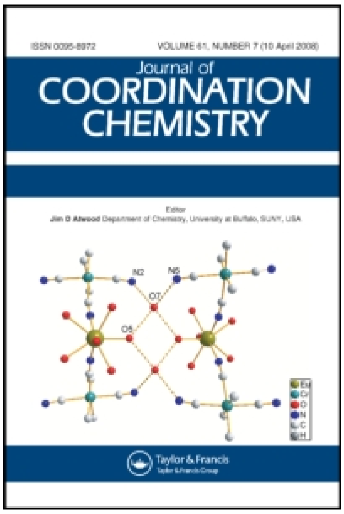

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PREPARATION, CRYSTAL STRUCTURE AND PROPERTIES OF [{MnL(PHEN)$_2$}(ClO$_4$)·1.25H$_2$O]$_{<i>n</i>}$ [HL = *N*-(1-CARBOXYPROPIONYL)AMINOPYRIDINE; PHEN = *O*-PHENANTHROLINE]

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PREPARATION, CRYSTAL STRUCTURE AND PROPERTIES OF $[\{MnL(PHEN)_2\}(ClO_4)\cdot 1.25H_2O]_n$ [HL = *N*-(1-CARBOXYPROPIONYL)AMINOPYRIDINE; PHEN = *O*-PHENANTHROLINE]

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(Received 29 July 1997)

The Mn(II) complex with *o*-phenanthroline $[MnL(phen)_2](ClO_4)\cdot 1.25H_2O$(HL = N-(1-carboxypropionyl)aminopyridine; phen = *o*-phenanthroline), was prepared and crystallographically characterized. The complex consists of a six-coordinate manganese(II) ion chelated by two bidentate carboxylato oxygen and four *o*-phenanthroline nitrogen atoms. The average Mn–O and Mn–N bond lengths are 2.229(3) and 2.254(3) Å and 2.210(4)–2.250(3) Å, respectively. The intermolecular hydrogen bonding interaction O(1)···N(5a) gives rise to crystal packing determined by an infinite chain along the *a* axis. Preliminary pharmacological tests demonstrated that this Mn(II) complex showed definite inhibition activity against *B. subtilis 6633, S. lutea, S. aureus 209p, P. diplococcus, C. Albicans (Robin) Berkh 50, S. Sake Yake* and P388 *in vitro*.

Keywords: Manganese(II); crystal structure; *o*-phenanthroline; N-(1-carboxypropionyl)aminopyridine; biological activity

The coordination behaviour of amide oxygen or deprotonated nitrogen atoms has been an area of interest and the metal to amide bond provides a simple model for more complex enzymes.[1–3] In previous work, a series of lanthanide(III) complexes derived from 1-(1-carboxypropionyl)thiosemicarbazide was synthesized and inhibition effects on human decidual cells

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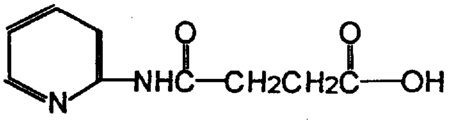
[*] Corresponding authors.

were reported.[4] Recently, the coordination chemistry of manganese in different oxidation states has received a great deal of attention because of the discovery of tightly bound manganese atoms in various biomolecules.[5] It has been found that *o*-phenanthroline (phen) and related bidentate ligands can form water-soluble neutral chelate complexes such as $M(phen)_2X_2$, which have found practical applications in medicine as, for example, antitumor agents. Thus, with these facts in mind, we have prepared a series of carboxypropionyl derivatives and their Mn(II) complexes. In this study the ligand *N*-(1-carboxypropionyl)aminopyridine (HL) and its manganese complex are reported with their biological activities and other properties.



N-(1-carboxypropionyl)aminopyridine (HL)

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EXPERIMENTAL

Preparation of the Ligand HL

Succinic anhydride (0.61 g, 6.10 mmol) dissolved in glacial acetic acid ($35\,cm^3$) was added to 2-aminopyridine (0.57 g, 6.10 mmol). The reaction mixture was stirred at 50–60°C for 3 h, then concentrated *in vacuo* to about $6\,cm^3$. On cooling in ice, the precipitate formed was isolated by filtration, washed thoroughly with anhydrous ethanol and dried in air. It was purified by dissolving in Na_2CO_3 solution (5%) and reprecipitated by the addition of dilute HCl in the cold, then recrystallized from anhydrous ethanol and dried *in vacuo*. Yield, 0.68 g (57%); m.p. 143–145°C. Found: C, 55.73; H, 5.32; N, 14.48%. Calc. for $C_9H_{10}N_2O_3$: C, 55.6; H, 5.15; N, 14.42%.

Synthesis of the Manganese(II) Complex

To $15\,cm^3$ of a methanolic solution containing $Mn(ClO_4)_2{\cdot}6H_2O$ (0.24 g, 0.66 mmol) was added *o*-phenanthroline (0.13 g, 0.66 mmol). The resulting mixture was stirred at 40–45°C for 1 h to obtain a clear yellowish solution. When cooled to room temperature, the solution was added to a methanolic solution ($15\,cm^3$) containing NaOH (0.03 g, 0.75 mmol) and HL (0.13 g, 0.67 mmol). The reaction mixture was stirred at room temperature for 2–3 h. The yellowish solution obtained after filtration was left to evaporate slowly in air for several weeks to give yellowish crystals, which were collected and dried in air. Yield, 0.27 g (62%). m. p. 279–281°C (decomp.). Found: C, 54.6; H, 4.1; N, 11.7%. Calc. for $C_{33}H_{27.5}N_6O_{8.25}ClMn$: C, 54.2; H, 3.8; N, 11.5%.

Physical Measurements

Elemental analyses (C, H and N) were performed on a Carlo-Erba 1106 instrument. IR data were recorded on Magna 750 spectrophotometer in KBr discs in the range 4000–200 cm^{-1}. Electronic spectra were recorded using a Shimadzu UV-300 spectrophotometer in DMF solution and for solid samples. Magnetic moments were measured at room temperature with a CTP-F_{82} Faraday balance by the Guoy method with $CuSO_4 \cdot 5H_2O$ as calibrant. ESR spectra were recorded with a Bruker 2000-SRC spectrometer at room temperature by employing X-band radiation and in a cylindrical cavity with 100 KHz magnetic field modulation. Cyclic voltammograms were recorded on a HDV-7B potentiotat and an LZ3Q-204 X-Y recorder. Solutions of the compounds (1.0×10^{-4} mol dm^{-3}) in DMF with tetraethylammonium perchlorate (0.1 mol dm^{-3}) as supporting electrolyte were deoxygenated by a stream of nitrogen for at least 15 min. Platinum working and counter electrodes were used, together with an S.C.E. reference electrode.

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RESULTS AND DISCUSSION

X-ray Diffraction Analysis

A summary of data collection, crystallographic data and details of the structure refinement is listed in Table I. The atomic coordinates and thermal parameters of the non-hydrogen atoms are listed in Table II. The data were corrected for Lorentz and polarization effects, and the structure was solved by direct methods and Fourier techniques. The non-hydrogen atoms were refined anisotropically, while hydrogen atoms were refined isotropically. The O(5), O(6) and O(7) atoms were disordered with the occupancy of O(5A), O(5B), O(6A), O(6B), O(7A) and O(7B) being 50% each. All calculations were performed using the TEXSAN crystallographic software package of the Molecular Structure Corporation. An ORTEP plot of the cation with hydrogen atoms omitted is shown in Figure 1, and its packing in a unit cell is depicted in Figure 2. Selected atomic distances and bond angles are listed in Table III.

TABLE I Summary of crystal data, intensity collection and structure refinement parameters for the Mn(II) complex

Compound	$[MnL(phen)_2](ClO_4)\cdot 1.25H_2O$
Formula	$C_{33}H_{27.5}ClMnN_6O_{8.25}$
F.W	730.51
Crystal size/mm	0.65 × 0.25 × 0.25
Crystal shape/colour	Prism/yellow
Crystal system	Monoclinic
Space group	$C2/c$ (No. 15)
Cell constants	
a/Å	23.524(8)
b/Å	15.921(4)
c/Å	17.916(5)
β/°	90.27(2)
V/Å^3	6710(4)
Z	8
Dc/g cm^{-3}	1.446
Diffractometer	Enraf-nonius CAD4
μ(MoKα)/cm^{-1}	5.15
F(000)	3004
2θ max./°	50.0
Scan width/°	$0.40 + 0.35\tan\theta$
Scan speed/min^{-1}	< 4.5° (in ω)
No. of reflections with $I > 3\sigma(I)$	3911
No. of variables	487
R	0.057
R_w (unit weights)	0.066
GOF	1.64
Max. shift in final cycle	0.005
$\Delta\rho$ max., min./eÅ^{-3}	0.36, −0.55

As shown in Figure 1, the crystal structure comprises discrete $[MnL(phen)_2]^+$ cations and ClO_4^- anions. The manganese(II) ion is six coordinated by four N atoms from two chelate phen molecules and two O atoms from a bidentate carboxylato group, forming a distorted octahedron [N(1)–Mn–N(4) = 170.7(1)°, N(1)–Mn–N(3) = 103.8(1)°, N(2)–Mn–O(1) = 92.4(1)°, N(2)–Mn–O(2) = 143.5(1)°]. Mn and the phen group with N(1), N(2); Mn, phen with N(3) and N(4), respectively, are nearly coplanar, and the associated dihedral angle is 71.71°. Atoms O(1), O(2), C(25), C(26) are almost coplanar, and form dihedral angles of 80.91 and 69.39° with the above two planes. The Mn–N bond lengths from 2.210(4) to 2.250(3) Å are shorter than those found in *cis*-$[Mn(phen)_2(NCS)_2]$ [2.301(3)–2.294(2) Å],[6] *cis*-$[Mn(phen)_2Cl_2]$ [2.270(3)–2.355(4) Å],[7,8] and $[Mn(phen)(bet)(NO_3)(H_2O)_2]^+$ [2.302(4)–2.275(3) Å],[9] which may be caused by steric effects of the ligands. The Mn–O bond lengths of 2.229(3) and 2.254(3) Å are within the range for manganese(II) complexes with bidentate carboxylato groups.[10]

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TABLE II Positional parameters and *B*(*eq*) for the Mn(II) complex

Atom	*x/a*	*y/b*	*z/c*	*B*(*eq*)
Mn	0.32035(3)	0.01716(4)	0.51784(3)	3.29(3)
O(1)	0.41497(12)	0.01376(18)	0.53814(15)	3.9(1)
O(2)	0.35800(12)	0.05583(18)	0.62696(15)	3.9(1)
O(3)	0.4793(2)	0.2051(3)	0.5922(3)	9.5(3)
N(1)	0.30463(15)	−0.1056(2)	0.57240(18)	3.4(2)
N(2)	0.32562(14)	−0.0794(2)	0.42654(18)	3.4(2)
N(3)	0.23449(15)	0.0716(2)	0.50497(18)	3.4(2)
N(4)	0.33207(15)	0.1301(2)	0.44584(18)	3.4(2)
N(5)	0.53074(17)	0.1425(3)	0.5029(2)	5.0(2)
N(6)	0.5459(2)	0.1771(4)	0.3822(3)	7.5(3)
C(1)	0.2924(2)	−0.1169(3)	0.6437(2)	4.2(2)
C(2)	0.2902(2)	−0.1967(3)	0.6755(2)	4.8(2)
C(3)	0.3024(2)	−0.2645(3)	0.6339(3)	4.6(2)
C(4)	0.31604(18)	−0.2551(3)	0.5583(2)	3.7(2)
C(5)	0.3288(2)	−0.3236(3)	0.5097(3)	5.1(3)
C(6)	0.3398(2)	−0.3109(3)	0.4377(3)	5.1(3)
C(7)	0.33924(19)	−0.2280(3)	0.4056(2)	3.9(2)
C(8)	0.3485(2)	−0.2121(3)	0.3305(3)	5.0(3)
C(9)	0.3450(2)	−0.1324(4)	0.3050(2)	4.9(3)
C(10)	0.3340(2)	−0.0685(3)	0.3551(2)	4.4(2)
C(11)	0.32734(16)	−0.1602(3)	0.4519(2)	3.1(2)
C(12)	0.31546(16)	−0.1733(2)	0.5297(2)	3.0(2)
C(13)	0.1869(2)	0.0427(3)	0.5338(3)	4.2(2)
C(14)	0.1336(2)	0.0757(3)	0.5147(3)	5.5(3)
C(15)	0.1304(2)	0.1430(3)	0.4676(3)	5.2(3)
C(16)	0.1801(2)	0.1760(3)	0.4382(2)	3.7(2)
C(17)	0.1808(2)	0.2488(3)	0.3906(3)	4.7(2)
C(18)	0.2289(2)	0.2800(3)	0.3646(2)	4.4(2)
C(19)	0.2824(2)	0.2420(2)	0.3823(2)	3.4(2)
C(20)	0.3346(2)	0.2712(3)	0.3561(2)	4.4(2)
C(21)	0.3833(2)	0.2311(3)	0.3750(3)	4.5(2)
C(22)	0.3804(2)	0.1600(3)	0.4194(3)	4.3(2)
C(23)	0.28353(18)	0.1699(2)	0.4279(2)	3.1(2)
C(24)	0.23091(18)	0.1389(2)	0.4577(2)	3.1(2)
C(25)	0.4070(2)	0.0384(3)	0.6040(2)	3.6(2)
C(26)	0.4567(2)	0.0461(4)	0.6565(2)	5.1(2)
C(27)	0.5116(2)	0.0660(4)	0.6154(3)	5.3(3)
C(28)	0.5060(2)	0.1448(4)	0.5698(3)	5.3(3)
C(29)	0.5333(2)	0.2062(4)	0.4497(4)	6.0(3)
C(30)	0.5510(3)	0.2363(8)	0.3278(5)	11.0(6)
C(31)	0.5445(5)	0.3216(9)	0.3408(8)	13.2(9)
C(32)	0.5316(4)	0.3466(7)	0.4092(9)	12.2(7)
C(33)	0.5258(3)	0.2902(5)	0.4663(5)	8.3(4)
Cl	0.18360(8)	−0.00849(10)	0.77226(9)	6.82(9)
O(4)	0.2145(3)	0.0504(3)	0.7322(3)	13.1(4)
O(5A)	0.2319(4)	−0.0637(5)	0.7978(4)	9.9(5)
O(5B)	0.1793(14)	−0.0854(10)	0.7590(13)	10(2)
O(6A)	0.1565(6)	−0.0613(11)	0.7250(9)	16(1)
O(6B)	0.1346(8)	0.0427(13)	0.7396(15)	12(1)
O(7A)	0.1545(7)	0.0193(11)	0.8306(8)	13(1)
O(7B)	0.1870(18)	0.0129(17)	0.8454(15)	13(2)
O(8)	0.0322(6)	−0.2285(11)	0.7621(12)	22(2)
O(9)	0.0476(8)	−0.0323(11)	0.6349(9)	20(1)
O(10)	0.0368(9)	−0.0660(13)	0.835(2)	16(2)

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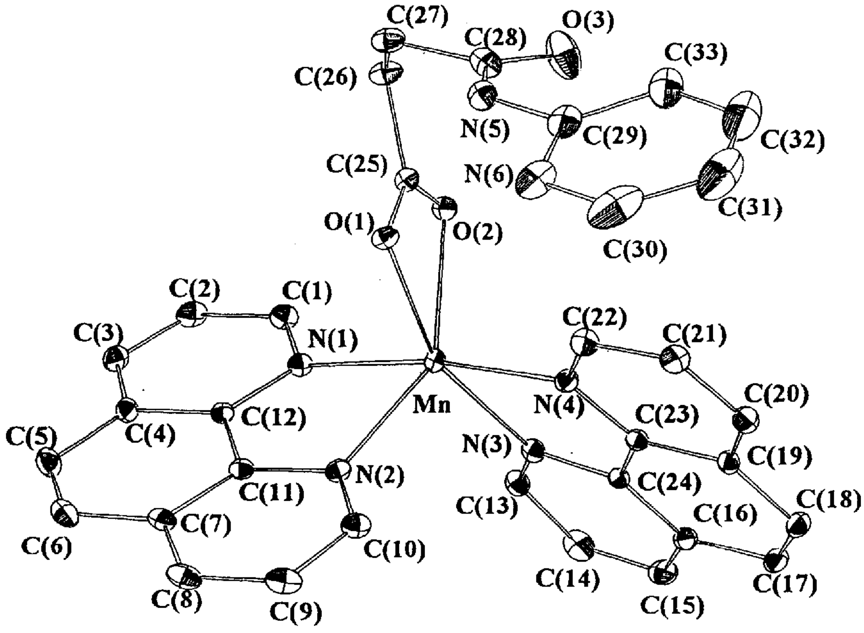

FIGURE 1 Perspective view showing the structure of action $[\mathrm{MnL(phen)_2}]^+$.

The intermolecular contact O(1)$\cdots$N(5a) (2.895(5) Å) (O(1)$\cdots$H(21a)-N(5a) = 167.7°, O(1)$\cdots$H(21a) = 2.149 Å; symmetry code: $1-x$, $-y$, $1-z$) is a normal hydrogen bond for O$\cdots$H–N,[11] thus leading to a crystal packing determined by an infinite chain of hydrogen bonds along the *a* axis as shown in Figure 2.

IR and Electronic Spectra

In the IR spectra of the ligand HL and its manganese complex, the frequencies at about 3109–3234 and 1670 cm^{-1} are attributed to ν(NH) and the amide-I band, respectively. The absorption ν(OH)(COOH) at 2769–2484 cm^{-1} of the ligand HL is found to have disappeared in the complex, confirming the complexation of the carboxylate group to the metal ion. In the spectrum of the ligand HL, the band for ν(C=O)(COOH) appears at 1695 cm^{-1}, and is absent in the complex. The newly formed bands ν_{as}(COO) at 1576 cm^{-1} and ν_s(COO) at 1344 cm^{-1} indicate that the coordination moeity for the carboxylate group to the metal ion is bidentate,[12] consistent with the X-ray crystallographic results.

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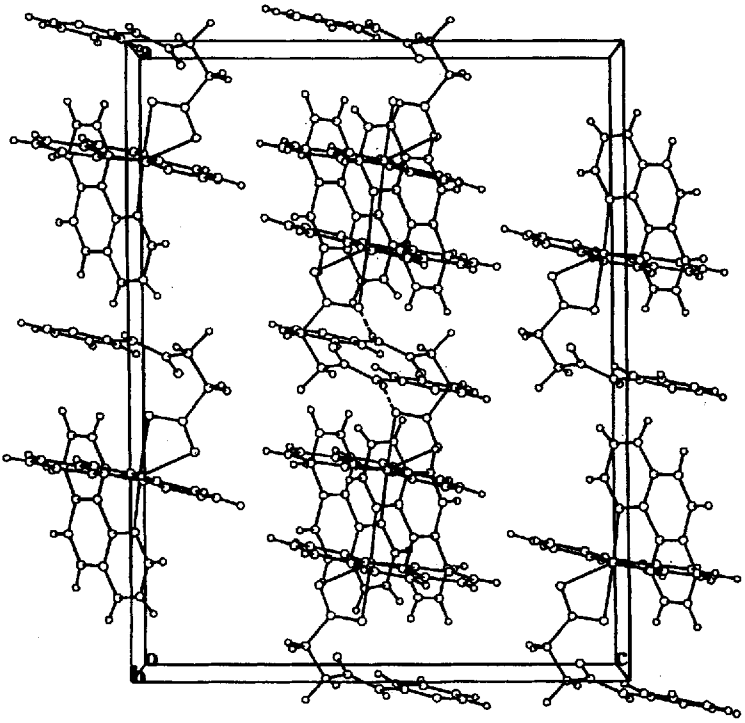

FIGURE 2 Packing of the cation $[MnL(phen)_2]^+$ in the unit cell.

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In the electronic spectra of the ligand HL and its Mn(II) complex the absorption bands at 272 nm for the ligand HL and 262 nm for the complex are attributed to an n → π* transition of the pyridine ring, and the bands at 252 nm for the ligand HL and 234 nm for the complex are ascribed to n → π* transition of the amide group.[13] The band observed at 408 nm for powder samples of the manganese complex is due to an LMCT transition while the *d-d* transition of the Mn(II) (d^5) is weak.[14]

Magnetic and ESR Properties

At room temperature,.the magnetic moment of the manganese complex was found to be 5.84 B. M., indicating the existence of five unpaired electrons for Mn(II). The X-band ESR spectrum was measured for powder samples at room temperature. The spectrum displayed a very anisotropic g tensor with $g_x = 3.7171$, $g_y = 2.0456$ and $g_z = 1.2645$. Based on the above facts, a high-spin state with $S = 5/2$ is expected for Mn^{2+}

TABLE III Selected bondlengths (Å) and angles (°) for the Mn(II) complex

Mn–N(1)	2.217(3)	N(1)–C(1)	1.323(5)	N(4)–C(22)	1.321(5)
Mn–N(2)	2.250(3)	N(1)–C(12)	1.348(5)	N(4)–C(23)	1.344(5)
Mn–N(3)	2.210(4)	N(2)–C(10)	1.307(5)	N(5)–C(28)	1.335(6)
Mn–N(4)	2.230(3)	N(2)–C(11)	1.364(5)	N(5)–C(29)	1.394(7)
Mn–O(1)	2.254(3)	N(3)–C(13)	1.318(5)	N(6)–C(29)	1.330(8)
Mn–O(2)	2.229(3)	N(3)–C(24)	1.368(5)	N(6)–C(30)	1.36(1)
N(1)–Mn–N(2)	74.2(1)	C(11)–N(2)–Mn	113.8(2)	O(1)–C(25)	1.259(5)
N(1)–Mn–N(4)	170.7(1)	C(12)–N(1)–Mn	115.0(3)	O(2)–C(25)	1.256(5)
N(1)–Mn–N(3)	103.8(1)	C(13)–N(3)–Mn	126.9(3)	O(3)–C(28)	1.217(6)
N(1)–Mn–O(1)	94.2(1)	C(22)–N(4)–Mn	127.3(3)	N(4)–C(22)–C(21)	123.0(4)
N(1)–Mn–O(2)	85.6(1)	C(23)–N(4)–Mn	114.3(3)	N(4)–C(23)–C(19)	122.5(4)
N(2)–Mn–N(3)	104.3(1)	C(24)–N(3)–Mn	115.2(3)	N(4)–C(23)–C(24)	118.8(4)
N(2)–Mn–N(4)	97.1(1)	C(25)–O(1)–Mn	89.5(3)	N(5)–C(28)–C(27)	115.2(5)
N(2)–Mn–O(1)	92.4(1)	C(25)–O(2)–Mn	90.7(2)	N(6)–C(30)–C(31)	123(1)
N(2)–Mn–O(2)	143.5(1)	N(1)–C(1)–C(2)	121.7(4)	N(6)–C(29)–C(33)	124.3(7)
N(3)–Mn–N(4)	74.8(1)	N(1)–C(12)–C(4)	122.5(4)	N(6)–C(29)–N(5)	112.2(6)
N(3)–Mn–O(1)	158.1(1)	N(1)–C(12)–C(11)	118.2(3)	C(1)–N(1)–C(12)	118.9(4)
N(3)–Mn–O(2)	110.0(1)	N(2)–C(10)–C(9)	124.6(4)	C(10)–N(2)–C(11)	116.5(4)
N(4)–Mn–O(2)	103.6(1)	N(2)–C(11)–C(7)	122.6(4)	C(13)–N(3)–C(24)	117.7(4)
N(4)–Mn–O(1)	89.4(1)	N(2)–C(11)–C(12)	117.0(4)	C(22)–N(4)–C(23)	118.4(4)
O(1)–Mn–O(2)	58.5(1)	N(3)–C(13)–C(14)	122.3(4)	C(28)–N(5)–C(29)	127.9(5)
C(1)–N(1)–Mn	125.6(3)	N(3)–C(24)–C(16)	122.9(4)	C(29)–N(6)–C(30)	115.4(7)
C(10)–N(2)–Mn	129.1(3)	N(3)–C(24)–C(23)	116.6(4)	C(33)–C(29)–N(5)	123.4(7)

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Electrochemical Studies

Cyclic voltammograms of the ligand HL and its manganese complex were measured in DMF. The ligand HL showed one *quasi*-reversible redox couple and one irreversible oxidation wave. It is believed that the anodic peak at +1.28 V *vs* SCE is due to the oxidation of the carboxylate anion.[15] With respect to the cyclic voltammogram of the manganese(II) complex, it is found that the cathodic peak at −1.45 V *vs* SCE and anodic peaks at −0.78 and +1.00 V *vs* SCE correspond to the ligand as discussed above, suggesting that the complex is not stable in solution and HL can be easily dissociated from it. As for the cathodic peak at −0.70 V *vs* SCE, this may be ascribed to the reduction of manganese(II) to metallic manganese.[16]

Biological Activity

Preliminary antibacterial and antifungal activities, as well as the inhibition rate of P388 *in vitro* of the ligand HL and the manganese(II) complex were determined according to the plate and MTT (MTT = 3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyltetrazoiiumbromide) methods, respectively.[17,18] During the tests, a concentration of 5 mM was maintained for the compounds. Results are shown in Table IV.

TABLE IV Antibacterial and antifungal activities of the ligand HL and the Mn(II) complex[a]

Bacterium or fungus	*HL*	*Mn(II) complex*
B. subtilis 6633	0	13.0
S. lutea	0	12.1
S. aureus 209P	0	12.9
P. diplococcus	0	12.8
C. albicans (Robin) Berkh 50	0	7.4
S. Sake Yake	0	7.6

[a] The inhibition zone is expressed in mm.

As can be seen in Table IV, the ligand HL is inactive against the tested bacteria and fungi, while the complex showed definite antibacterial and antifungal activities. With regard to the antitumor activity of the compounds, the ligand HL is also inactive in the tests, whereas the Mn(II) complex exhibited an inhibition rate of 31.6% ($1 \times 10\,\mu M$), 19.4% ($1 \times 1\,\mu M$) and 15.4% ($1 \times 0.1\,\mu M$) against P388 *in vitro*. It is believed that the increase of antibacterial, antifungal and antitumor activities for the metal complex in comparison with the free ligand is mainly due to two factors, the coordination of the metal ion to the cells, and the ease of binding of proteins to the phen group. More detailed work on these aspects is in progress.

Supplementary Material

Atomic coordinates, bondlengths and angles, thermal parameters and observed and calculated structure factors are available from the authors on request.

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