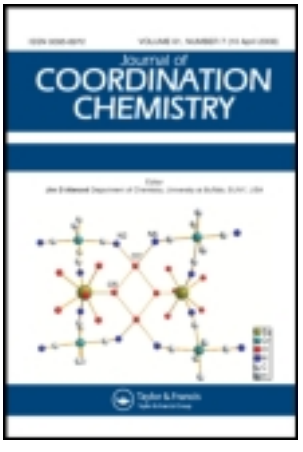

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Synthesis, characterization, and antibacterial activity of a manganese(II) complex of triaryltriazole

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Synthesis, characterization, and antibacterial activity of a manganese(II) complex of triaryltriazole

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A manganese(II) complex of 4-(4-methylphenyl)-3,5-bis(2-pyridyl)-4H-1,2,4-triazole (MBPT) was synthesized and characterized by X-ray crystallography. $[Mn(MBPT)_2(H_2O)_2](ClO_4)_2 \cdot 4H_2O$ is a divalent mononuclear manganese(II) complex with manganese coordinated to four nitrogens from two triazole ligands and two oxygens from two water molecules in a slightly distorted octahedral geometry. The complex and ligand were tested *in vitro* for their antibacterial activities. The title complex showed a wide range of bactericidal activities.

Keywords: Triazole; Manganese(II) complex; Crystal structure; Antibacterial

1. Introduction

Many compounds containing 1,2,4-triazole show antitumor, antibacterial, antiviral, and anti-inflammatory activities [1–6]. Some metal complexes of ligands containing 1,2,4-triazole were also reported to possess antimicrobial and anticancer activities [7–12]. Structures of transition metal (Cu, Zn, Co, Mn) complexes containing substituted 1,2,4-triazole ligands have been reported [13–16]. Some complexes with 4-(4-methylphenyl)-3,5-bis(2-pyridyl)-4H-1,2,4-triazole (MBPT) have also been studied [17–25]. In this article, a manganese(II) complex of MBPT was synthesized and characterized. The antibacterial activities against two Gram positive bacterial strains (*Bacillus subtilis* and *Staphylococcus aureus*) and two Gram negative bacterial strains (*Escherichia coli* and *Pseudomonas fluorescence*) were evaluated.

2. Experimental

2.1. *Materials and physical measurements*

All chemicals were of analytical grade. Solvents were purified by conventional methods. ^{1}H-NMR spectra were recorded on a Bruker DRX 500 model Spectrometer in

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DMSO-d_6. Chemical shifts (δ) for ^{1}H-NMR spectra were reported in parts per million to residual solvent protons. Electrospray ionization–mass spectrometry (ESI–MS) spectra were recorded on a Mariner System 5304 Mass spectrometer. Elemental analyses were performed on a CHN–O-Rapid instrument.

2.2. *Synthesis of MBPT*

The ligand (MBPT) was synthesized according to a similar method [25], m.p. 197–198°C. Yield: 65%. ^{1}H-NMR (500 MHz, DMSO-d_6, δ ppm): 2.38 (s, 3H); 7.20–7.38 (m, 6H); 7.82–7.84 (m, 2H); 8.20–8.23 (m, 2H); 8.45–8.47 (m, 2H). ESI–MS: 315.2 ($C_{19}H_{16}N_5^+$, $[M+H]^+$). Anal. Calcd for $C_{19}H_{15}N_5$ (%): C, 72.82; H, 4.82; N, 22.35. Found (%): C, 72.58; H, 4.88; N, 22.31.

2.3. *Synthesis of $[Mn(MBPT)_2(H_2O)_2](ClO_4)_2 \cdot 4H_2O$*

Manganese(II) perchlorate hexahydrate (36.1 mg, 0.1 mmol) and MBPT (62.6 mg, 0.2 mmol) were dissolved in acetonitrile (10 mL) by stirring. After allowing the resulting clear pale pink solution to stand at room temperature in air for 3 days, large blue crystals were formed at the bottom of the vessel on slow evaporation of the solvent. The crystals were isolated, washed thrce with acetonitrile, and dried in a vacuum desiccator using anhydrous $CaCl_2$ (yield 53%). Anal. Calcd for $C_{38}H_{42}Cl_2MnN_{10}O_{14}$ (%): C, 46.16; H, 4.28; N, 14.17. Found (%): C, 46.24; H, 4.25; N, 14.23.

2.4. *Structure determination*

Diffraction intensities for the Mn triazole complex were collected on a Bruker SMART APEX CCD diffractometer equipped with graphite-monochromated Mo-Kα ($\lambda = 0.71073$ Å) radiation. Corrections for Lorentz-polarization and absorption were made. The program SAINT was used for integration of the diffraction profiles. The crystal structure was solved by direct methods using the SHELXS program of the SHELXTL package and refined by full-matrix least-squares with SHELXL [26]. All non-hydrogen atoms were refined anisotropically. Hydrogens were generated geometrically and allowed to ride on their parent carbons. Hydrogens on carbons were included in the riding model approximation with C–H = 0.93–0.97 Å, and with $U_{iso}(H) = 1.2\,U_{eq}(C)$. All hydrogens attached to oxygens were placed in geometrically idealized positions and constrained to ride on their parent atoms, with O–H distances of 0.90, and $U_{iso}(H) = 1.5\,U_{eq}(O)$. The manganese triazole is monoclinic crystal with space group $P2_1/c$. The crystallographic data are listed in table 1. The selected bond distances and bond angles are given in table 2.

2.5. *Antibacterial activity*

The antibacterial activity of the synthesized compounds was tested against *B. subtilis*, *E. coli*, *P. fluorescence*, and *S. aureus* using MH medium (Mueller–Hinton medium: casein hydrolysate 17.5 g, soluble starch 1.5 g, beef extract 1000 mL). The minimum

Table 1. Crystallographic and experimental data for the complex.

Empirical formula	$C_{38}H_{42}Cl_2MnN_{10}O_{14}$
Formula weight	988.66
Temperature (K)	298(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell dimensions (Å)	
a	9.139(3)
b	15.480(6)
c	16.240(6)
α	90
β	95.168(7)
γ	90
Volume (Å^3), Z	2288.1(15), 2
Calculated density (g cm^{-3})	1.435
Absorption coefficient (mm^{-1})	0.480
$F(000)$	1022
θ range for data collection (°)	1.82/25.02
Limiting indices	$-10 \le h \le 7$; $-18 \le k \le 18$; $-19 \le l \le 18$
Reflections collected/unique	11,835/4036
R(int)	0.0732
Max. and min. transmission	0.9581 and 0.9101
Data/restraints/parameters	4036/16/296
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0718$, $wR_2 = 0.1778$
Largest difference peak and hole (e Å^{-3})	0.653 and −0.317

$R_1 = \sum||F_o|-|F_c|/\sum|F_o|$, $wR_2 = [\sum[w(F_o^2-F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$.

Table 2. Selected bond lengths (Å) and angles (°) for the complex.

Mn(1)–N(2)	2.061(5)	Mn(1)–O(1W)	2.071(4)
Mn(1)–N(4)	2.105(5)		
N(2)–Mn(1)–O(1W)	90.57(19)	N(2)#1–Mn(1)–O(1W)	89.43(19)
N(2)–Mn(1)–N(4)#1	102.2(2)	N(2)–Mn(1)–N(4)	77.8(2)
O(1W)#1–Mn(1)–N(4)#1	90.96(19)	O(1W)–Mn(1)–N(4)#1	89.04(19)

Symmetry code: $\#1 - x+1, -y+1, -z+1$.

inhibitory concentrations (MICs) of the test compounds were determined by a colorimetric method using the dye MTT [3-(4,5-dimethylthiazol-2-yl)-2,5-diphenyl tetrazolium bromide] [27]. A stock solution of the synthesized compound (50 μg mL^{-1}) in dimethyl sulfoxide (DMSO) was prepared and graded quantities (50, 25, 12.5, 6.25, 3.13, 1.56, 0.78, and 0.39 μg mL^{-1}) of the test compounds were incorporated in a specified quantity of sterilized liquid MH medium. A specified quantity of the medium containing the compound was poured into microtitration plates. Suspension of the microorganism was prepared to contain approximately 10^5 cfu mL^{-1} and applied to microtitration plates with serially diluted compounds in DMSO to be tested and incubated at 37°C for 24 h. After the MICs were visually determined on each of the microtitration plates, 50 μL of phosphate buffered saline (PBS) (0.01 mol L^{-1}, pH 7.4: $Na_2HPO_4 \cdot 12H_2O$ 2.9 g, KH_2PO_4 0.2 g, NaCl 8.0 g, KCl 0.2 g, distilled water 1000 mL) containing 2 mg of MTT mL^{-1} was added to each well. Incubation was continued at room temperature for 4–5 h. The content of each well was removed and 100 μL of

Table 3. MICs of the synthetic compounds.

	MICs ($\mu g\,mL^{-1}$)			
	Gram positive		Gram negative	
Compounds	*B. subtilis*	*S. aureus*	*E. coli*	*P. fluorescence*
MBPT	12.5	6.25	6.25	12.5
Mn(II) complex	1.56	1.56	3.13	3.13
Penicillin	0.78	3.13	>100	>100
Kanamycin	0.39	1.56	6.25	6.25

isopropanol containing 5% 1 mol L^{-1} HCl was added to extract the dye. After 12 h of incubation at room temperature, the optical density (OD) was measured with a microplate reader at 550 nm. The observed MIC values are presented in table 3. Data are reported as means of three experiments.

3. Results and discussion

3.1. *Synthesis and characterization of the Mn complex*

The triazole ligand MBPT reacts with $Mn(ClO_4)_2$ in a 2 : 1 molar ratio to afford a mononuclear Mn(II) complex, which is air stable at room temperature. The molecular structure of this Mn(II) triazole complex is constrained by a crystallographic center of inversion. As shown in figure 1, each formula unit consists of a $[Mn(MBPT)_2(H_2O)_2]^{2+}$, two ClO_4^-, and four lattice water molecules. This is consistent with the elemental analysis. MBPT coordinates to Mn *via* N2 of the triazole and N4 of a pyridyl ring leaving N3 of the triazole and N5 of another pyridyl ring uncoordinated, similar to the coordination in another MBPT complex [25]. Mn(II) is coordinated to four nitrogens from two MBPT in the equatorial plane and two oxygens from two water molecules in axial positions, forming a slightly distorted octahedral geometry. The Mn–N bond lengths are comparable to other Mn–N contacts (2.03–2.10 Å) in similar manganese complexes [28]. However, the Mn–N bond to triazole nitrogen is 2.061(5) Å, 0.044 Å shorter than that to the pyridyl nitrogen 2.105(5) Å, comparable with those observed for other MBPT complexes [25]. The bond angles around Mn illustrate that this complex displays a slightly distorted octahedral geometry, similar to the Ni and Co complexes of this ligand reported by others [25].

3.2. *Antibacterial activity*

MBPT and its Mn(II) complex were screened for antibacterial activity against two Gram-positive bacterial strains (*B. subtilis* and *S. aureus*) and two Gram-negative bacterial strains (*E. coli* and *P. fluorescence*) by MTT method. The MICs of the compounds are presented in table 3. The antibiotics kanamycin and penicillin were included as references. The results revealed that MBPT and its Mn(II) complex showed

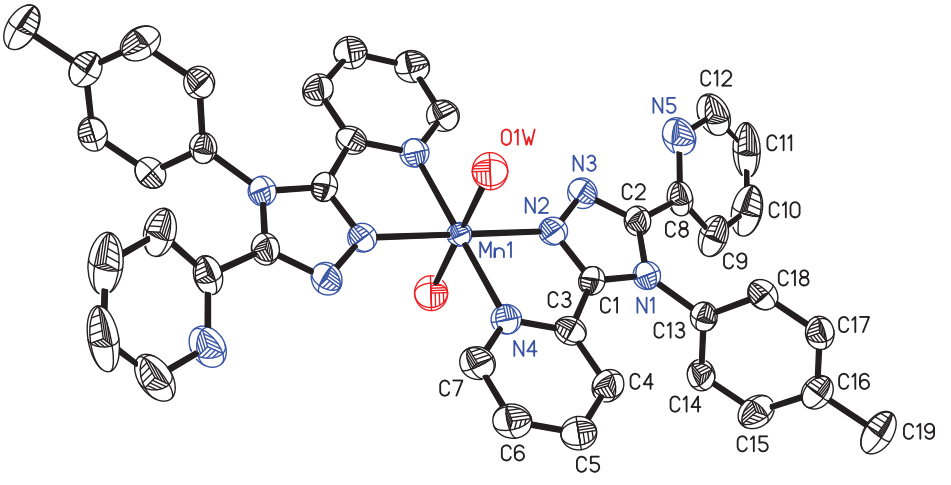

Figure 1. The molecular structure of the complex. Lattice waters, anions, and hydrogens are omitted for clarity.

broad-spectrum antibacterial activities against the tested two Gram-positive and two Gram-negative bacteria. The Mn(II) complex exhibited better antibacterial activities than its ligand MBPT, which was more potent than or similar with commercial antibiotics (kanamycin and penicillin). There has been no report about the antibacterial study of Mn complex with MBPT ligand. When compared with macrocyclic complexes of Mn (the central Mn atom is five coordinate by four nitrogens from a 14-membered macrocyclic Schiff-base ligand and an oxygen atom from an acetate) reported by Singh *et al*. [29, 30], we found that the antibacterial activities of this Mn(II) triazole complex are more potent.

Supplementary material

Crystallographic data for the title complex have been deposited with the Cambridge Crystallographic Data Centre (CCDC 804703).

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References

[1] Q. Zhang, Y. Peng, X.-I. Wang, S.M. Keenan, S. Arora, W.J. Welsh. *J. Med. Chem*., **50**, 749 (2007).
[2] J.H. Cho, D.L. Bernard, R.W. Sidwell, E.R. Kern, C.K. Chu. *J. Med. Chem*., **49**, 1140 (2006).

[3] H. Bayrak, A. Demirbas, S.A. Karaoglu, N. Demirbas. *Eur. J. Med. Chem.*, **44**, 1057 (2009).
[4] M. De Braccio, G. Grossi, G. Roma, D. Piras, F. Mattioli, M. Gosmar. *Eur. J. Med. Chem.*, **43**, 584 (2008).
[5] S.-J. Yan, Y.-J. Liu, Y.-L. Chen, L. Liu, J. Lin. *Bioorg. Med. Chem. Lett.*, **20**, 5225 (2010).
[6] Z.-Y. Cheng, W.-J. Li, F. He, J.-M. Zhou, X.-F. Zhu. *Bioorg. Med. Chem.*, **15**, 1533 (2007).
[7] S. Tardito, O. Bussolati, M. Maffini, M. Tegoni, M. Giannetto, V. Dall'Asta, R. Franchi-Gazzola, M. Lanfranchi, M.A. Pellinghelli, C. Mucchino, G. Mori, L. Marchiò. *J. Med. Chem.*, **50**, 1916 (2007).
[8] U. Ghani, N. Ullah. *Bioorg. Med. Chem.*, **18**, 4042 (2010).
[9] G.B. Bagihalli, P.G. Avaji, S.A. Patil, P.S. Badami. *Eur. J. Med. Chem.*, **43**, 2639 (2008).
[10] G.B. Bagihalli, S.A. Patil. *J. Coord. Chem.*, **62**, 1690 (2009).
[11] P.G. Avaji, S.A. Patil, P.S. Badami. *J. Coord. Chem.*, **61**, 1884 (2008).
[12] A.S. Ramasubramanian, B.R. Bhat, R. Dileep. *J. Coord. Chem.*, **63**, 3108 (2010).
[13] B. Ding, E.-C. Yang, X.-J. Zhao, X.G. Wang. *J. Coord. Chem.*, **61**, 3793 (2008).
[14] J.G. Małecki, R. Kruszynski, M. Jaworska, P. Lodowski. *J. Coord. Chem.*, **60**, 741 (2007).
[15] B. Ding, L. Yi, P. Cheng, H.-B. Song, H.-G. Wang. *J. Coord. Chem.*, **57**, 771 (2004).
[16] Y.-Y. Liu. *J. Coord. Chem.*, **60**, 2597 (2007).
[17] S.C. Shao, D.R. Zhu, T.W. Wang, Y. Zhang, S.S.S. Raj, H.K. Fun. *Chin. Chem. Lett.*, **11**, 93 (2000).
[18] D.-R. Zhu, T.-W. Wang, S.-L. Zhong, Y. Xu, X.-Z. You. *Chin. J. Inorg. Chem.*, **20**, 508 (2004).
[19] D.-R. Zhu, Z.-X. Wang, J. Song, Y.-Z. Li, D.-Y. Lan. *Chin. J. Inorg. Chem.*, **21**, 128 (2005).
[20] J. Klingele, H. Scherer, M.H. Klingele. *Z. Anorg. Allg. Chem.*, **635**, 2279 (2009).
[21] J.A. Kitchen, N.G. White, M. Boyd, B. Moubaraki, K.S. Murray, P.D.W. Boyd, S. Brooker. *Inorg. Chem.*, **48**, 6670 (2009).
[22] S.-C. Shao, Z.-D. Liu, H.-L. Zhu. *Acta Crystallogr.*, **E60**, m1815 (2004).
[23] M.H. Klingele, S. Brooker. *Eur. J. Org. Chem.*, **16**, 3422 (2004).
[24] D. Zhu, Y. Xu, Z. Yu, Z. Guo, H. Sang, T. Liu, X. You. *Chem. Mater.*, **14**, 838 (2002).
[25] D.-R. Zhu, Y. Song, Y. Xu, Y. Zhang, S.S.S. Raj, H.-K. Fun, X.-Z. You. *Polyhedron*, **19**, 2019 (2000).
[26] G.M. Sheldrick. *SHELXTL, Crystallographic Software Package, (version 5.1)*, Bruker-AXS, Madison, Wisconsin, USA (1998).
[27] J. Meletiadis, J.F. Meis, J.W. Mouton, J.P. Donnelly, P.E. Verweij. *J. Clin. Microbiol.*, **38**, 2949 (2000).
[28] H.-L. Zhu, Y.-X. Tong, X.-L. Yu, X.-M. Chen. *J. Coord. Chem.*, **55**, 843 (2002).
[29] D.P. Singh, K. Kumar, C. Sharma. *Eur. J. Med. Chem.*, **45**, 1230 (2010).
[30] D.P. Singh, K. Kumar, C. Sharma. *Eur. J. Med. Chem.*, **44**, 3299 (2009).