U0418 2009/095

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UNIVERSITI SAINS MALAYSIA

UNIVERSITY RESEARCH GRANT FINAL REPORT
Geran Penyelidikan Universiti Laporan Akhir

A.	**TITLE OF RESEARCH:** *Tajuk penyelidikan:* Porous Metal-Carboxylate Compunds: Synthesis, Characterization And Host-Guest Properties
B.	**PERSONAL PARTICULARS OF RESEARCHER** / *MAKLUMAT PENYELIDIK:*
(i)	**Name of Research Leader:** *Nama Ketua Penyelidik:* PROF MADYAROHANA BINTI ADNAN
	Name of Co-Researcher *Nama Penyelidik Bersama:* AHMAD FAIZ BIN LATIF DRCOSWALD STEPHEN @ MOHD NASRI PROF MADYASHUKRI BIN SULAIMAN DR. NASER ELTAHER
(ii)	**School/Institute/Centre/Unit : PP S KIMIA** *Pusat Pengajian /Institut/Pusat/Unit :*

USM
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SAINS
MALAYSIA

Pejabat Pengurusan Dan Kreativiti Penyelidikan
Research Creativity and Management Office

Canselori,

Universiti Sains Malaysia
Aras 6, Bangunan Canselori
11800, USM Pulau Pinang
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L : www.research.usm.my

Ruj. Kami : 2009/095 (U0418)
Tarikh : 30 Mac 2011

Profesor Abdul Latif Ahmad
Dekan Penyelidikan
Pelantar Sains Fundamental
Pejabat Pelantar Penyelidikan
Universiti Sains Malaysia

Tuan,

PENILAIAN LAPORAN AKHIR GERAN UNIVERSITI PENYELIDIKAN

Dengan hormatnya perkara di atas dirujuk.

2. Adalah dimaklumakan bahawa projek penyelidikan di bawah seliaan **Prof. Madya Rohana Adnan** yang bertajuk ***Porus Metal-Carboxylate Compounds: Synthesis, Characterization And Host-Guest Properties*** telah selesai. Sehubungan itu, kerjasama tuan dipohon untuk menilai laporan akhir seperti tajuk di atas.

3. Bersama-sama ini disertakan deraf borang penilaian berserta laporan akhir projek untuk tindakan tuan selanjutnya. Untuk makluman tuan borang penilaian yang disertakan belum dimuktamatkan oleh Jawatankuasa Pengurusan Penyelidikan (JKPP). Buat masa ini Pejabat ini akan menggunakan deraf borang penilaian tersebut.

Sekian, terima kasih.

"BERKHIDMAT UNTUK NEGARA"
'Memastikan Kelestarian Hari Esok'

Yang menjalankan tugas,

(HAZLAN ABDUL HAMID)
Ketua Penolong Pendaftar
Pejabat Pengurusan & Kreativiti Penyelidikan
Bahagian Penyelidikan & Inovasi

s.k. Prof. Madya Rohana Adnan
Pusat Pengajian Sains Kimia
Universiti Sains Malaysia

Pegawai Teknologi Maklumat
Pejabat Pengurusan & Kreativiti Penyelidikan
Universiti Sains Malaysia

HAH/ds
My/Doc/Surat Penilaian Laporan Akhir – 811120 Rohana Adnan

C. **Research Platform (Please tick (/) the appropriate box):**
Pelantar Penyelidikan (Sila tanda (/) kotak berkenaan):

☐ A. **Life Sciences**
Sains Hayat

☑ B. **Fundamental**
Fundamental

☐ C. **Engineering & Technology**
Kejuruteraan & Teknologi

☐ D. **Social Transformation**
Transformasi Sosial

☐ E. **Information & Communications Technology (ICT)**
Teknologi Maklumat & Komunikasi

☐ F. **Clinical Sciences**
Sains Klinikal

☐ G. **Biomedical & Health Sciences**
Bioperubatan Sains Kesihatan

D. **Duration of this research :**
Tempoh masa penyelidikan ini :

***Duration :** 2 tahun
Tempoh :

From : ~~28~~ 1. 3. 2009 **To** : 28. 2. 2011
Dari: *Ke :*

E. **ABSTRACT OF RESEARCH**

(An abstract of between 100 and 200 words must be prepared in **Bahasa Malaysia and in English**. This abstract will be included in the Annual Report of the Research and Innovation Section at a later date as a means of presenting the project findings of the researcher/s to the University and the community at large)

Abstrak Penyelidikan

(Perlu disediakan di antara 100 - 200 perkataan di dalam **Bahasa Malaysia dan juga Bahasa Ingge** Abstrak ini akan dimuatkan dalam Laporan Tahunan Bahagian Penyelidikan & Inovasi sebagai satu ca untuk menyampaikan dapatan projek tuan/puan kepada pihak Universiti & masyarakat luar).

F.

SUMMARY OF RESEARCH FINDINGS

Ringkasan dapatan Projek Penyelidikan

Abstract This work investigated the reaction of between lantanide salts, potassium salt of 2,2'-biquinoline-4,4'-dicarboxylic acid (K_2bqdc) and 1,10-phenanthroline (phen) and Schiff bases with Zn and Mn salts in aqueous medium. The reactions afforded several new lanthanide bqdc and Zn and manganese-Schiff bases complexes. These complexes were characterized by elemental analyses, infrared spectroscopy, photoluminescene, x-ray crystallography and thermal gravimetric analysis. Thermogravimetric analysis performed on the complexes shows complexes have higher thermally stable up to above 450 °C which suggested higher coordination number and greater π-π interactions between the metals and the ligands and within ligands. The photoluminescence analysis run on these complexes indicated that Schiff base, bqdc and phen contribute to the emission of the complexes. The complexes were found to exhibit linker-based luminescence properties with Er, Terbium complexes exhibiting the highest luminescence intensity. Theoretical studies using the PM6 semi empirical method was also used to complement and explain the results.

Abstrak Penyelidikan ini mengkaji tindak balas antara garam lantanida dengan garam kalium 2,2'-bikuinolina-4,4'-dikarboksilik (K_2bqdc) dan 1,10-fenanthrolina (phen) dan tindak balas Schiff bes dengan garam Zn and Mn dalam meium akueous. Tindak balas tersebut menghasilkan beberapa kompleks lanthanida bqdc dan Zn and mangan-Schiff bes. Kompleks yang terhasil dicirikan dengan analisis unsur (CHN), spekstrokopi infra merah, fotoluminasi, kristalografi sinar x dan analisis termagravimetrik. Analisis termalgravimetrik yang dijalankan menunjukkan bahawa kompleks yang dihasilkan mempunyai kestabilan terma yang tinggi sehingga 450 °C yang mencadangkan bahawa nombor koordinatan yang tinggi dan interaksi π-π antara logam dan ligan dan juga antara ligan. Analisis fotoluminasi yang dijalankan ke atas kompleks menunjukkan bahawa ligan Schiff bes, bqdc dan phen menyumbang terhadap emisi kompleks dan menunjukkan sifat fotoluminasi *linker-based* dengan kompleks Er dan Terbium mempamerkan intesiti paling tinggi. Kajian teoritikal menggunakan kaedah semi empirik PM6 turut digunakan untuk menerangkan dapatan kajian.

Hasil :

1. Syarifah Zati Hanani Syed Zubir, MSc thesis, to be submitted March 2011.
2. Naser El Taher, PhD thesis, completed
3. Raime, N.-N., Adnan, R., Rosli, M.M., Fun, H.-K. Poly[[diaqua-(3-carboxy-5-nitrobenzoato)(-5-nitrobenzene-1,3-dicarboxylato) neodymium(III)] 2.5-hydrate] Acta Crystallographica Section E: 65(9), 2009, m1108-m1109. (IF 0.310)
4. Naser E. Eltayeb, S.G. Teoh, R. Adnan, E. Kusrini, H. K. Fun, The manganese (III) complex with chelating Schiff base ligand: X-ray structure, spectroscopic and computational studies, Spectrochimica Acta, Part A: Molecular and Biomolecular Spectroscopy (2010), 75A, 453-457. (IF 1.510)
5. Eltayeb, N.E., Teoh, S.G., Adnan, R., Fun, H.-K., Chantrapromma, S. 2-Methyl-6-(6-methyl-1Hbenzimidazol-2-yl)phenol-2-methyl-6-(5-methyl- 1Hbenzimidazol-2-yl)phenol (3/1) *Acta Crystallographica Section E: Structure Reports Online* 2009, 65 (12), pp. o3227-o3228
6. Eltayeb, N.E., Teoh, S.G., Yeap, C.S., Fun, H.-K., Adnan, R. ,6'-Di-tert-butyl-2,2'-[1,2-phenylene-bis(nitrilo-methylidyne)]diphenol *Acta Crystallographica Section E: Structure Reports Online* 65 (12), pp. o3142-o3143
7. Syed-Zuber-Sharifah Zati Hanani, Rohana Adnan*, Ahmad-Faiz Abdul Latip, Hydrothermal synthesis, characterization and photoluminescence studies of three novel erbium 2,2'-biquinoline-4,4'-dicarboxylate complexes Submitted to Journal of Luminescence, under review, LUMIN-D-10-00864
8. S.Z.S. Zati-Hanani, R. Adnan*, A.F.A. Latip, C.S. Sipaut, Synthesis, Characterization and Thermal Properties of Two Novel Lanthanide 2,2'-biquinoline-4,4'-dicarboxylate Complexes Sains Malaysiana, telah diterima untuk diterbitkan versi June 2011.

G.

COMPREHENSIVE TECHNICAL REPORT

Laporan Teknikal Lengkap

Applicants are required to prepare a comprehensive technical report explaining the project.
(This report must be attached separately)
Sila sediakan laporan teknikal lengkap yang menerangkan keseluruhan projek ini.
[Laporan ini mesti dikepilkan]

List the key words that reflect your research:
Senaraikan kata kunci yang mencerminkan penyelidikan anda:

English	Bahasa Malaysia
Lanthanide dicarboxylate complexes	Kompleks lantanida dikarboksilat
Manganese Schiff base complex	Kompleks mangan Shiff bes
Photoluminescence	Fotoluminasi
Thermal property	Sifat termal

H.

a) Results/Benefits of this research
Hasil Penyelidikan

No. *Bil:*	Category/Number: *Kategori/ Bilangan:*	Promised	Achieved
1.	**Research Publications (Specify target journals)** *Penerbitan Penyelidikan (Nyatakan sasaran jurnal)*	2	4
2.	**Human Capital Development**		
	a. Ph. D Students		1*
	b. Masters Students	1*	
	c. Undergraduates (Final Year Project)		2
	d. Research Officers		1
	e. Research Assisstants		1
	f. Other: Please specify		
3.	**Patents** *Paten*		
4.	**Specific / Potential Applications** *Spesifik/Potensi aplikasin*		
5.	**Networking & Linkages** *Jaringan & Jalinan*		
6.	**Possible External Research Grants to be Acquired** *Jangkaan Geran Penyelidikan Luar Diperoleh*		

- Kindly provide copies/evidence for Category 1 to 6.

[2a] – partially supported through Graduate Research Assistant Scheme
[2b] - To submit thesis by March 2011

b) Equipment used for this research.
Peralatan yang telah digunakan dalam penyelidikan ini.

Items *Perkara*	Approved Equipment	Approved Requested Equipment	Location
Specialized Equipment Peralatan khusus	Digital Balance pH meter		PPS Kimia, USM
Facility Kemudahan	BET, XRD X-ray Crystallography FTIR TGA, CHN,		USM
Infrastructure Infrastruktur			

- Please attach appendix if necessary.

I. BUDGET / *BAJET*

Perbelanjaan :Expenditure

Project Account No. : 1001 / PKIMIA / 811120

Total Approved Budget : RM 99400

Total Additional Budget : RM

Grand Total of Approved Budget : RM 99400

Yearly Budget Distributed

Year 1 : RM 55200

Year 2 : RM 44200

Year 3 : RM

Additional Budget Approved

Year 1 : RM

Year 2 : RM

Year 3 : RM

Total Expenditure : RM 99388

Balance : RM 12

- **Please attach final account statement from Treasury**

11-3-2011

Signature of Researcher
Tandatangan Penyelidik

Date
Tarikh

Prof. Madya Dr. Rohana Adnan
Pusat Pengajian Sains Kimia
Universiti Sains Malaysia

H. COMMENTS OF PTJ'S RESEARCH COMMITTEE
KOMEN JAWATANKUASA PENYELIDIKAN PERINGKAT PTJ

General Comments:
Ulasan Umum:

Completed the work satisfactorily with numerous publications

Professor Norita Mohamed
Deputy Dean
(Research & Postgraduate Studies)
School of Chemical Sciences
Universiti Sains Malaysia

Signature and Stamp of Chairperson of PTJ's Evaluation Committee
Tandatangan dan Cop Pengerusi Jawatankuasa Penilaian PTJ

Date : 14/3/11
Tarikh :

Signature and Stamp of Dean/ Director of PTJ
Tandatangan dan Cop Dekan/ Pengarah PTJ

Date : 14/3/11
Tarikh :

Prof. Dr. Wan Ahmad Kamil Mahmood
Dekan
Pusat Pengajian Sains Kimia
Universiti Sains Malaysia

Acta Crystallographica Section E
Structure Reports
Online
ISSN 1600-5368

6,6′-Di-*tert*-butyl-2,2′-[1,2-phenylenebis(nitrilomethylidyne)]diphenol

Naser Eltaher Eltayeb,[a]‡ Siang Guan Teoh,[a] Chin Sing Yeap,[b]§ Hoong-Kun Fun[b]*¶ and Rohana Adnan[a]

[a]School of Chemical Science, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
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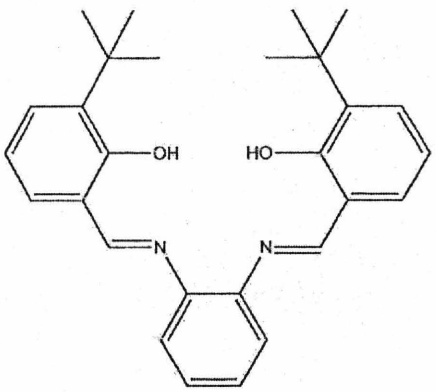
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.004 Å; R factor = 0.059; wR factor = 0.206; data-to-parameter ratio = 13.2.

The molecule of the title Schiff base compound, $C_{28}H_{32}N_2O_2$, has a twisted geometry; the dihedral angles between the central benzene ring and the other two benzene rings being 29.12 (14) and 26.01 (14)°. Four intramolecular C—H⋯O hydrogen bonds and two intramolecular O—H⋯N hydrogen bonds stabilize the molecular structure. In the crystal packing, molecules are stacked along the a axis and stabilized by π–π interactions [centroid–centroid distance = 3.6724 (17) Å]. The crystal studied was found to be a non-merohedral twin, the refined ratio of twin components being 0.374 (5):0.626 (5).

Related literature

For biological applications of Schiff base derivatives, see: Dao *et al.* (2000); Eltayeb & Ahmed (2005*a*,*b*); Karthikeyan *et al.* (2006); Sriram *et al.* (2006). For related structures, see: Eltayeb *et al.* (2007*a*,*b*). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$C_{28}H_{32}N_2O_2$
M_r = 428.56
Triclinic, $P\bar{1}$
a = 6.8312 (9) Å
b = 13.9632 (16) Å
c = 14.0689 (15) Å
α = 116.615 (5)°
β = 99.068 (4)°
γ = 98.209 (4)°
V = 1149.6 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 0.08 mm^{-1}
T = 100 K
0.87 × 0.20 × 0.05 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.936, T_{max} = 0.996
4021 measured reflections
4021 independent reflections
3241 reflections with $I > 2\sigma(I)$

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.059
$wR(F^2)$ = 0.206
S = 1.19
4021 reflections
304 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.32 e Å^{-3}
$\Delta\rho_{min}$ = −0.39 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H⋯*A*	*D*—H	H⋯*A*	*D*⋯*A*	*D*—H⋯*A*
O2—H1*O*2⋯N2	0.91 (5)	1.73 (4)	2.584 (3)	156 (4)
O1—H1*O*1⋯N1	0.91 (5)	1.77 (6)	2.609 (3)	151 (5)
C22—H22*A*⋯O1	0.96	2.34	2.993 (3)	125
C23—H23*A*⋯O1	0.96	2.34	2.987 (4)	124
C26—H26*B*⋯O2	0.96	2.31	2.963 (4)	125
C27—H27*C*⋯O2	0.96	2.37	3.011 (4)	124

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

The authors thank the Malaysian Government, the Ministry of Higher Education, (MOHE) and Universiti Sains Malaysia (USM) for the FRGS and RU research grants (PKIMIA/815002 and PKIMIA/811120). The International University of

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§ Thomson Reuters ResearcherID: A-5523-2009.
¶ Thomson Reuters ResearcherID: A-3561-2009.

o3142 Eltayeb *et al.* doi:10.1107/S1600536809048922 *Acta Cryst.* (2009). E65, o3142–o3143

Africa (Sudan) is acknowledged for providing study leave to NEE. HKF and CSY thank USM for the Research University Golden Goose grant (1001/PFIZIK/811012). CSY thanks USM for the award of a USM Fellowship.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: LH2954).

References

Bruker (2005). *APEX2*, *SAINT* and *SADABS*. Bruker AXS Inc., Madison, Wisconsin, USA.

Cosier, J. & Glazer, A. M. (1986). *J. Appl. Cryst.* **19**, 105–107.

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Eltayeb, N. E., Teoh, S. G., Teh, J. B.-J., Fun, H.-K. & Ibrahim, K. (2007*b*). *Acta Cryst.* E**63**, o766–o767.

Karthikeyan, M. S., Prasad, D. J., Poojary, B., Bhat, K. S., Holla, B. S. & Kumari, N. S. (2006). *Bioorg. Med. Chem.* **14**, 7482–7489.

Sheldrick, G. M. (2008). *Acta Cryst.* A**64**, 112–122.

Spek, A. L. (2009). *Acta Cryst.* D**65**, 148–155.

Sriram, D., Yogeeswari, P., Myneedu, N. S. & Saraswat, V. (2006). *Bioorg. Med. Chem. Lett.* **16**, 2127–2129.

Acta Cryst. (2009). E**65**, o3142–o3143 Eltayeb *et al.* • $C_{28}H_{32}N_2O_2$ **o3143**

Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Poly[[diaqua(3-carboxy-5-nitrobenzoato)(μ-5-nitrobenzene-1,3-dicarboxylato)neodymium(III)] 2.5-hydrate]

Nurul-Nadia Raime,[a] Rohana Adnan,[a]‡ Mohd Mustaqim Rosli[b] and Hoong-Kun Fun[b]*§

[a]School of Chemical Sciences, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia, and [b]X-ray Crystallography Unit, School of Physics, Universiti Sains Malaysia, 11800 USM, Penang, Malaysia
Correspondence e-mail: hkfun@usm.my

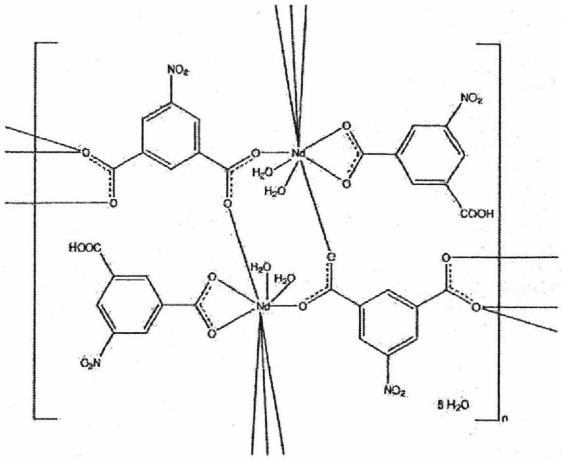
Received 27 July 2009; accepted 15 August 2009

Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.003 Å; disorder in main residue; R factor = 0.018; wR factor = 0.057; data-to-parameter ratio = 14.8.

In the title compound, $\{[Nd(C_8H_3NO_6)(C_8H_4NO_6)(H_2O)_2]\cdot 2.5H_2O\}_n$, the Nd^{III} ion is nine-coordinated by seven O atoms from five carboxylate groups and two water molecules. The $[Nd(C_8H_3NO_6)(H_2O)_2]^{2+}$ units are bridged by 5-nitroisophthalate dianions, forming polymeric sheets parallel to the ab plane. The polymeric sheets are linked into a three-dimensional network by O—H···O and C—H···O hydrogen bonds, and π–π interactions [centroid–centroid distance = 3.5533 (11) Å]. The 5-nitroisophthalate(1−) anion is disordered over three positions with an occupancy ratio of 0.68:0.23:0.09. Two of the uncoordinated water molecules are disordered over two positions, with occupancy ratios of 0.722 (15):0.278 (15) and 0.279 (6):0.221 (6), respectively.

Related literature

For related structures, see: Ye *et al.* (2008); Eddaoudi *et al.* (2001); Bünzli & Choppin (1989); Huang *et al.* (2008); Cui *et al.* (2002); Yan *et al.* (2005); Ren *et al.* (2006); Li *et al.* (2005). For the stability of the temperature controller used for the data collection, see: Cosier & Glazer (1986).



Experimental

Crystal data

$[Nd(C_8H_3NO_6)(C_8H_4NO_6)-(H_2O)_2]\cdot 2.5H_2O$
M_r = 644.55
Triclinic, $P\overline{1}$
a = 9.5748 (1) Å
b = 10.4634 (1) Å
c = 13.3285 (2) Å
α = 69.279 (1)°
β = 71.753 (1)°
γ = 66.046 (1)°
V = 1118.71 (2) Å^3
Z = 2
Mo $K\alpha$ radiation
μ = 2.41 mm^{-1}
T = 100 K
0.35 × 0.24 × 0.13 mm

Data collection

Bruker SMART APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.484, T_{max} = 0.742
22527 measured reflections
5879 independent reflections
5725 reflections with $I > 2\sigma(I)$
R_{int} = 0.019

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.018
$wR(F^2)$ = 0.057
S = 1.21
5879 reflections
398 parameters
115 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 1.18 e Å^{-3}
$\Delta\rho_{min}$ = −0.77 e Å^{-3}

Table 1
Selected bond lengths (Å).

Nd1—O7	2.3302 (13)	Nd1—O2W	2.4775 (15)
Nd1—O8^{i}	2.4214 (14)	Nd1—O2	2.5223 (13)
Nd1—O10^{ii}	2.4481 (14)	Nd1—O1	2.5743 (14)
Nd1—O1W	2.4612 (14)	Nd1—O10^{iii}	2.9332 (14)
Nd1—O9^{iii}	2.4708 (13)		

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x, -y+2, -z+1$; (iii) $x+1, y-1, z$.

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‡ Additional corresponding author, e_mail: r_adnan@usm.my.
§ Thomson Reuters ResearcherID: A-3561-2009.

doi:10.1107/S1600536809032486

Table 2
Hydrogen-bond geometry (Å, °).

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O5*A*—H5*A*···O3*W*$^{\rm iv}$	0.84	1.76	2.596 (5)	178
O1*W*—H1*W*1···O2$^{\rm v}$	0.74	1.99	2.731 (3)	175
O1*W*—H2*W*1···O4*WA*	0.94	2.00	2.849 (4)	149
O2*W*—H1*W*2···O4*WA*	0.84	1.86	2.667 (3)	159
O2*W*—H2*W*2···O1$^{\rm i}$	0.82	2.06	2.874 (3)	172
O3*W*—H1*W*3···O11$^{\rm vi}$	0.91	2.56	3.246 (3)	132
O3*W*—H1*W*3···O12$^{\rm vi}$	0.91	2.05	2.902 (3)	156
O3*W*—H2*W*3···O9$^{\rm iii}$	0.96	1.76	2.688 (2)	162
O4*WA*—H2*W*4···O3*W*	0.85	2.51	3.118 (6)	130
C12—H12*A*···O1$^{\rm ii}$	0.95	2.41	3.351 (2)	169

Symmetry codes: (i) $-x, -y+1, -z+1$; (ii) $-x, -y+2, -z+1$; (iii) $x+1, y-1, z$; (iv) $x-1, y, z+1$; (v) $-x+1, -y+1, -z+1$; (vi) $x, y-1, z$.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: CI2868).

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2-Methyl-6-(6-methyl-1*H*-benzimidazol-2-yl)phenol–2-methyl-6-(5-methyl-1*H*-benzimidazol-2-yl)phenol (3/1)

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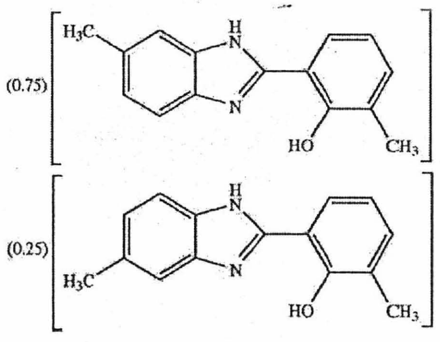
Key indicators: single-crystal X-ray study; T = 100 K; mean σ(C–C) = 0.002 Å; disorder in main residue; R factor = 0.046; wR factor = 0.131; data-to-parameter ratio = 20.1.

The title compound, $0.75C_{15}H_{14}N_2O\cdot0.25C_{15}H_{14}N_2O$, is a co-crystal of 2-methyl-6-(6-methyl-1*H*-benzimidazol-2-yl)phenol as the major component and 2-methyl-6-(5-methyl-1*H*-benzimidazol-2-yl)phenol as the minor component. The refined site-occupancy ratio is 0.746 (4)/0.254 (4). The conformations of both components are identical except for that of the methyl substituent on the benzene ring of the benzimidazole unit which is positionally disordered over two positions. The molecule is essentially planar, the dihedral angle between the benzimidazole plane and the benzene ring being 3.49 (4)°. An intramolecular O—H···N hydrogen bond generates an $S(6)$ ring motif. In the crystal packing, molecules are linked through N—H···O hydrogen bonds into chains along [201]. These chains are stacked approximately along the a-axis direction. The crystal packing is further stabilized by weak N—H···O and O···H···N hydrogen bonds, together with weak intermolecular C—H···π interactions. A π–π interaction with a centroid–centroid distance of 3.6241 (6) Å is also observed between the substituted phenyl ring and that of the benzimidazole system.

Related literature

For bond-length data, see: Allen *et al.* (1987). For hydrogen-bond motifs, see: Bernstein *et al.* (1995). For background to benzimidazoles and their bioactivity, see: Demirayak *et al.* (2002); Guven *et al.* (2007); Minoura *et al.* (2004); Pawar *et al.* (2005); Thakurdesai *et al.* (2007); Tomei *et al.* (2003). For related structures, see: Eltayeb *et al.* (2007, 2009*a*,*b*); Xiao *et al.* (2009). For the stability of the temperature controller used in the data collection, see Cosier & Glazer, (1986).



Experimental

Crystal data

$0.75C_{15}H_{14}N_2O\cdot0.25C_{15}H_{14}N_2O$
M_r = 238.28
Monoclinic, $P2_1/c$
a = 4.9231 (1) Å
b = 19.8900 (6) Å
c = 12.3199 (3) Å
β = 105.085 (1)°
V = 1164.80 (5) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 0.09 mm^{-1}
T = 100 K
0.59 × 0.17 × 0.10 mm

Data collection

Bruker APEXII CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2005)
T_{min} = 0.951, T_{max} = 0.992
34431 measured reflections
3703 independent reflections
3165 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.046
$wR(F^2)$ = 0.131
S = 1.07
3703 reflections
184 parameters
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.61 e Å^{-3}
$\Delta\rho_{min}$ = −0.20 e Å^{-3}

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H1N2···O1^{i}	0.936 (19)	2.095 (19)	2.9916 (12)	160.1 (18)
O1—H1O1···N1	0.93 (2)	1.74 (2)	2.6040 (12)	153 (2)
C15—H15C···$Cg3^{ii}$	0.96	2.66	3.5731 (16)	160
C15A—H15F···$Cg2^{iii}$	0.96	2.96	3.780 (4)	144

Symmetry codes: (i) $x-1, -y+\frac{3}{2}, z-\frac{1}{2}$; (ii) $x-1, y, z$; (iii) $-x+1, y+\frac{1}{2}, -z+\frac{1}{2}$. $Cg2$ and $Cg3$ are the centroids of the C1–C6 and C8–C13 rings, respectively.

Data collection: *APEX2* (Bruker, 2005); cell refinement: *SAINT* (Bruker, 2005); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Sheldrick, 2008); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL* and *PLATON* (Spek, 2009).

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The manganese(III) complex with chelating Schiff base ligand: X-ray structure, spectroscopic and computational studies

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ABSTRACT

A new Mn(III) complex, $[MnCl(H_2O)(L)]\cdot H_2O\cdot C_2H_5OH$, where L = 2,2′-{1,2-phenylenebis[nitrilomethylylidene]}bis(6-methoxyphenolate), has been synthesized and characterized by single-crystal X-ray diffraction. There is a good agreement between calculated and experimental structural data. The complex is crystallized in orthorhombic with space group *Pbca*. The Mn1 atom is coordinated with one Schiff base ligand, one water molecule and one chloride anion, forming a six-coordination number. The electronic and fluorescence spectra of the complex were also studied.

1. Introduction

Organic-metal-chelate complexes generally offer many attractive properties, such as displaying a double role of electron transport and light emission, high thermal stability, and ease of sublimation. Since the first example reported by Tang and Van Slyke [1,2], OLEDs have received vast attention and become an active field of research because of their potential applications in flat panel displays [3–6]. Thus, organic-metal-chelate complexes in particular have attracted a lot of attention. However, the low electron transport ability and the lack of suitable blue emitting complexes is one of the major disadvantages of metal-chelate complexes [7].

The structure of salicylaldehyde Schiff base is similar to the 8-hydroxyquinoline molecule [8]. Both molecules have one hydroxyl group, a coordinating nitrogen atom and a delocalized π-system. Interestingly, the structure of the Schiff base molecule is more flexible than that of 8-hydroxyquinoline. Therefore, organic-metal complexes of salicylaldehyde Schiff base molecules are expected to show good luminescent properties [8,9].

With the improvement of computational methods and computer power, methods such as semi-empirical PM6 and ZINDO/S can be used for the calculation of molecular geometry as well as electronic properties of the complex. Utilizing the single-crystal X-ray diffraction, the computational study of the complex was also investigated. In this paper, we study of the structure, electronic and luminescence properties of Mn(III) complex with the 2,2′-{1,2-phenylenebis[nitrilomethylylidene]}bis(6-methoxyphenolate) ligand.

2. Experimental

2.1. Materials

$MnCl_2\cdot 4H_2O$ was purchased from Acros (New Jersey, USA). *O*-phenylenediamine and triethylamine were purchased from Merck (Darmstadt, Germany). 3-Methoxysalicylaldehyde was purchased from Fluka (Buchs, Switzerland). Other chemicals were of at least analar grade and were used without further purification.

2.2. Physical measurements

Elemental analyses were performed on a Perkin-Elmer 2400II elemental analyzer. UV–vis spectra were obtained using a JASCO V-500 spectrophotometer in acetonitrile solution. FT-IR spectra were recorded on Perkin-Elmer 2000 FT-IR with samples prepared as KBr pellets. Conductivity was measured by using a Cyberscan500 con in acetonitrile solution. Fluorescence spectra were measured by using a JASCO spectrofluorometer FP-750 in DMF solution.

2.3. Preparation of the $[MnCl(H_2O)(L)]\cdot H_2O\cdot C_2H_5OH$ complex

The complex was prepared by refluxing a mixture of the 3-methoxysalicylaldehyde (4 mmol, 0.604 g) and *o*-phenyl-

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enediamine (2 mmol, 0.216 g) in ethanol (20 mL) for 30 min. Then $MnCl_2 \cdot 4H_2O$ (2 mmol, 0.397 g) in 10 ml ethanol was added, followed by 0.5 ml triethylamine. The mixture was stirred for 3 h at room temperature. The brown precipitate was obtained by filtration, washed with ethanol about (5 mL), then washed by copious amount of diethyl ether and dried. The single crystals were obtained by a slow evaporation in ethanol:chloroform (1:2, v/v) solvent. Yield: 46.2% with weight 0.459 g. m.p. >300 °C. IR (ν, cm^{-1}): ν(O–H) 3422; ν(Ar) 3058; $\nu(CH_3)$ 2938, 2837; ν(C=N) 1640; ν(C=C) 1579, 1547. Anal. calc.: C, 52.71; H, 5.16; N, 5.12, Mn, 10.05%. Found: C, 53.17; H, 4.26; N, 5.86; Mn, 9.52%. Conductivity: 55.93 Ω^{-1}. UV–vis (acetonitrile, λ_{max} nm, ε $dm^3\ mol^{-1}\ cm^{-1}$): 239 (22.88×10^3), 305 (13.43×10^3), 360 (12.93×10^3).

2.4. Crystallographic data collection and refinement

X-ray diffraction data was collected from single crystal by using a Bruker APEX2 area-detector diffractometer with a graphite monochromatic Mo Kα radiation source and a detector distance of 5 cm. Data was analyzed with APEX2 software [10]. The collected data was reduced by using the SAINT program and the empirical absorption corrections were applied using the SADABS program [10]. The structure was solved by direct methods and refined with the full-matrix least-squares method SHELXTL program [11]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms in the carbon atoms were added from theory calculation and the hydrogen atoms in the oxygen atoms were added from Fourier maps and were isotropically refined. The final refinement converged well. Data for publications were prepared with SHELXTL [11] and PLATON [12]. The summary of crystallographic data and details of the structure refinement is listed in Table 1. The selected bond lengths and bond angles are given in Table 2.

2.5. Computational methods

Calculations were carried out by using Mopac 2007 [13], Gaussian 03 [14] and HyperChem 8.0 [15]. GaussView 3.09 was used for visualization, while AOMix [16] and Swizard [17] were used for molecular orbital analysis and calculation of electronic spectra, respectively. Calculations were performed using a Gaussian03 program [14] at the unrestricted Hartree-Fock level of computation with 6-31 + G(3d, 3pd) basis set. The orbital diagrams were generated by use of the GaussView 3.09 software. Unrestricted calculation was performed for the Mn(III) complex, because it is a d4 complex, in which the Mn(III) metal ion in high spin state with quintet multiplicity [18,19].

Table 1

.Crystal data, data collection and structure refinement parameters for the complex.

Empirical formula	$C_{24}H_{28}ClMnN_2O_7$
Formula weight	546.87
Temperature (K)	100
Crystal system	Orthorhombic
Space group	*Pbca*
Unit cell dimensions	
a (Å)	17.102(3)
b (Å)	16.765(3)
c (Å)	16.026(3)
$\alpha = \beta = \gamma$ (°)	90
Volume (Å^3)	4594.9(14)
Z	8
Dcalc. ($g\ cm^{-3}$)	1.581
μ (mm^{-1})	0.741
F(000)	2272
Crystal size (mm)	0.29 × 0.26 × 0.18
θ (°)	2.12–25.00
h, k, l	−20/20, −19/19, −19/19
Reflections collected/unique	51,741/4040 [R(int) = 0.1030]
Completeness to theta = 29.61	99.9%
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	4040/2/313
Goodness-of-fit on F^2	1.270
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.1275$, $wR2 = 0.3156$
R indices (all data)	$R1 = 0.1435$, $wR2 = 0.3340$
Largest difference peak and hole (eÅ^{-3})	1.535 and −0.879

3. Results and discussion

3.1. Spectral and conductivity studies

Upon complexation, the typically absorption stretching bands of ν(O–H), ν(C–C), ν(C=C) and ν(C=N) were shifted towards the frequencies of free Schiff base ligand. The strong peak of ν(O–H) stretching frequency in the free Schiff base ligand was shifted higher value of 6 cm^{-1}, indicating the chelation of the phenolic oxygen atoms to the Mn(III) ion. The absorption stretching band ν(C=N) in the complex (1640 cm^{-1}) was shifted higher frequency relative to the frequency of free Schiff base ligand (1611 cm^{-1}), which may be due to the coordination effects. The molar conductivity for the complex in acetonitrile solvent was 55.93 Ω^{-1} indicating that the complex to be non-electrolyte nature [20].

3.2. X-ray structure of the Mn(III) complex

The $[MnCl(H_2O)(L)] \cdot H_2O \cdot C_2H_5OH$ complex, where L = 2,2′-{1,2-phenylenebis[nitrilomethylylidene]}bis(6-methoxyphenolate) is crystallized in orthorhombic with space group *Pbca* (Table 1). The Mn1 atom is coordinated with one Schiff base ligand, one water molecule and one chloride anion, forming a six-coordination

Table 2

Selected bond lengths (Å), bond angles (°) and torsion angles (°) in the complex.

Bond	Length (Å)	Bond	Angles (°)	Atom	Torsion angles (°)
Mn1–O1	1.869(7)	O1–Mn1–O2	91.5(3)	Mn1–O1–C14–C19	−174.0(7)
Ln1–O2	1.891(7)	O1–Mn1–N1	92.6(4)	Mn1–O1–C14–C15	1.6(17)
Mn1–O1W	2.289(7)	O2–Mn1–N2	92.4(4)	Mn1–O2–C13–C8	−0.4(15)
Mn1–Cl1	2.576(3)	N1–Mn1–N2	83.3(4)	Mn1–O2–C13–C12	178.2(7)
Mn1–N1	1.993(9)	O1–Mn1–O1W	90.8(3)	N1–C1–C6–N2	2.5(14)
Mn1–N2	1.992(9)	O2–Mn1–O1W	93.5(3)	C20–N1–C1–C6	175.3(10)
		N1–Mn1–O1W	84.1(3)	C7–N2–C6–C5	0.5(17)
		N2–Mn1–O1W	82.9(3)	C6–N2–C7–C8	−177.6(11)
		O2–Mn1–Cl1	93.6(2)		
		O1–Mn1–Cl1	93.7(2)		
		N1–Mn1–Cl1	90.9(3)		
		N2–Mn1–Cl1	89.7(3)		
		OW1–Mn1–Cl1	171.5(2)		
		O2–Mn1–N1	173.6(4)		
		O1–Mn1–N2	174.8(4)		

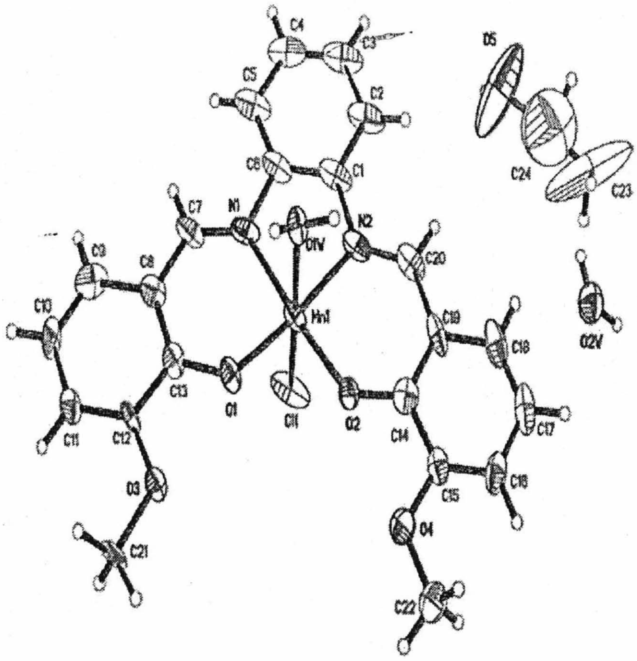

Fig. 1. Molecular structure of the Mn(III)-Schiff base complex with thermal ellipsoid of 50%.

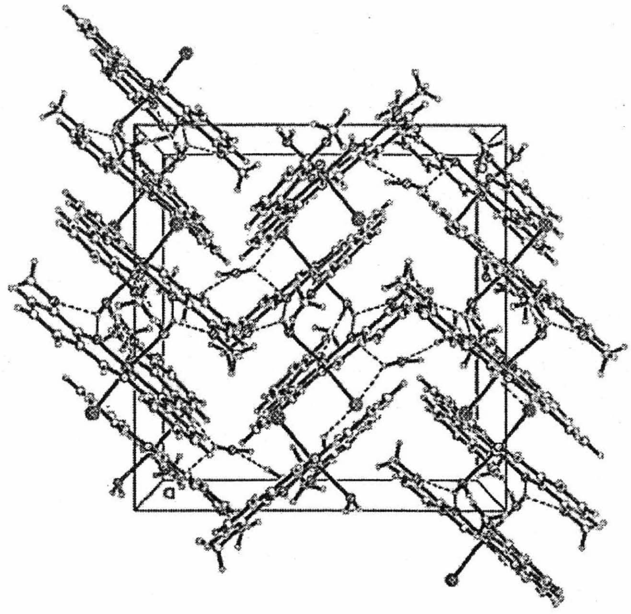

Fig. 2. Crystal packing of complex viewed down the c-axis exhibiting 3D hydrogen bonding network as shown by the dashed lines (- - -).

number (Fig. 1). The phenolic groups (O1 and O2) of the Schiff base ligand are coordinated to the Mn1 atom indicating that the deprotonation has taken place. The molecular structure of complex with mirror plane symmetry was observed. Fig. 1 shows the chloride anion (Cl1) and water molecule (O1W) are coordinated to the Mn1 atom in the axial positions and four donor atoms of the Schiff base ligand form the equatorial plane of N1–N1–O1–O2. In addition, the O1W–Mn1–Cl1 bond angle is almost linear [171.5(2)°]. The Mn1 atom is coplanar with O1, O2, N1 and N2 atoms with maximum deviation of 0.054(9) Å for the N1 atom. The remaining two alkoxy terminal chains are akin to a hanging tail and the conformation of structure is opened (Fig. 1). The coordination geometry around the Mn1 atom can be as described as an octahedral, with four donor atoms of the Schiff base forming the equatorial plane and the axial positions are occupied by a water molecule and a chloride anion (Figure S1).

The average of Mn–O bond lengths [1.880(7) Å] is shorter than to the average of Mn–N [1.993(9) Å], Mn–OW [2.289(7) Å] and Mn–Cl [2.576(3) Å] bond lengths (Table 2). The averages Mn–O and Mn–N bond lengths are quite similar with the values found in the dimethoxy(5,10,15,20-tetraphenylporphinato)manganese(IV) complex (1.838 and 2.012(3) Å) [21]. The Mn–Cl bond length is similar with the MnCl{2,2′-[(1s,2s)-1,2-diphenyl-1,2-ethanediylbis(nitrilomethylidyne)]-diphenolato-*O,N,N′,O′*}·C_2H_6O [22] and [MnCl(5,5′-Cl-salen)(H_2O)] complexes [23]. Further confirmation of the Mn(III) complex is a six-coordination number exhibiting nearly identical bond lengths. The bond angles of the adjacent coordinated atoms to Mn1 atom are all close to 90° except N1–Mn1–N2 [83.3(4)°], which is smaller than expected. On the other hand, the bond angle of O1W–Mn1–Cl1 [171.5(2)°] is also a little less than the ideal value [24]. These values however, are close to that of the $MnC_{16}H_{14}N_2O_3ClBr_2$ complex [25]. The N1–C1–C6–N2 torsion angle indicates that the *o*-phenylenediamine is slightly not coplanar with Mn1 atom. This is due to the maximum deviation of 0.018(12) Å for the C1 atom. The corresponding N–C–C–N torsion angle of 2.5(14)° is significantly smaller than those found in the MnCl{2,2′-[(1s,2s)-1,2-diphenyl-1,2-ethanediylbis(nitrilomethylidyne)]-diphenolato-*O,N,N′,O′*}·C_2H_6O complex of 43.86(17)° [22]. This suggests that the central phenyl ring substituents govern the coplanarity of the equatorial plane in the inner-coordination sphere.

Short O···O and O··· Cl contacts, intermolecular O–H···O, O–H···Cl and C–H···O hydrogen bonds, π–π interactions, C–H···π, and O–H···π interactions are observed. The packing diagram of complex in the *ab*-plane exhibits O–H···O, C–H···O and O–H···Cl hydrogen bonds by three-dimensional (3D) network (Fig. 2). In addition, the coordinated and solvated water molecules also take part in three bifurcated hydrogen bonds (Table 3). The disorder of the O5 and C24 atoms has been stabilized by intermolecular hydrogen bonding. The solvated ethanol molecule is also involved in hydrogen bonding interactions with C23–H23B···O5 [2.5996 Å] and C23–H23A···O2W [2.000 Å].

The aromatic rings of the Schiff base ligand are coplanar with the Mn1 atom with maximum deviation of −0.059(2) Å for the Mn1 atom. These aromatic sequences also formed dihedral angles of 4.1(4)°, 3.5(4)° and 2.6(4)° for Cg1–Cg2, Cg1–Cg3 and Cg2–Cg3, respectively, where Cg1, Cg2 and Cg3 denote Mn1–N1–N2–C1–C6, Mn1–O1–N1–C7–C8–C13, and Mn1–O2–N2–C14–C19–C20. The three aromatic rings of the ligand (Cg4, Cg5 and Cg6) are essentially planar with maximum deviation about 0.020(14) Å for the C2

Table 3
Selected intermolecular hydrogen bonding in the complex.

D–H···A	D–H (Å)	H···A (Å)	D···A (Å)	D–H···A (°)
O5–H5B···Cl1[i]	0.821	2.739	3.268	123.9
O1W–H11W···O2[ii]	0.851	2.128	2.896(9)	150.0
O1W–H11W···O4[ii]	0.851	2.345	2.934(11)	126.8
O1W–H21W···O1[ii]	0.851	2.556	2.894(10)	104.9
O1W–H21W···O3[ii]	0.851	2.021	2.862(9)	169.7
O2W–H22W···Cl1[iii]	0.993	2.398	3.219(10)	139.6
O2W–H22W···O2[iii]	0.993	2.384	3.146(12)	133.0
C23–H23B···O5[iv]	0.961	2.600	3.144	116.2
C23–H23A···O2W[v]	0.960	2.000	2.93(3)	164.1
C2–H2A···O5[v]	0.9296	2.4231	3.3163	161.1

Symmetry codes: (i) 1/2 − *x*, 1 − *y*, −1/2 + *z*; (ii) 1 − *x*, 1 − *y*, 1 − *z*; (iii) *x*, 1/2 − *y*, −1/2 + *z*; (iv) 1 − *x*, 1 − *y*, −*z*; (v) *x*, *y*, *z*.

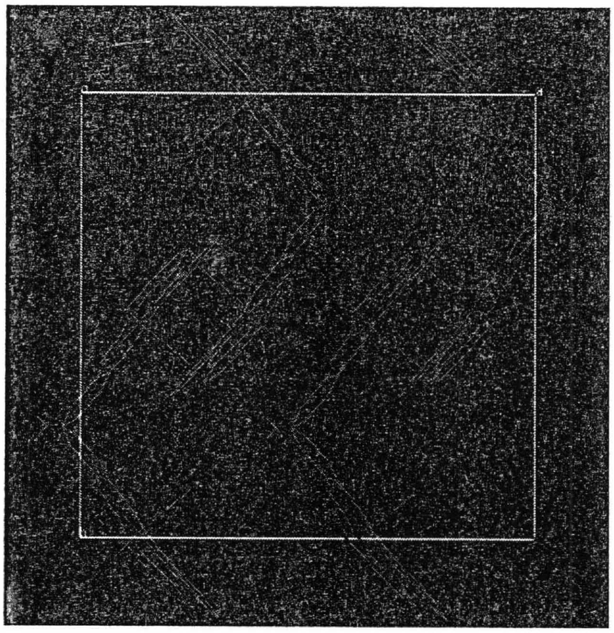

Fig. 3. Arrangement the π–π stacking interaction between the rings of Schiff base ligand in face to face mode viewed down *c*-axis.

atom, 0.020(11) Å for the C12 atom, and −0.008(12) Å for the C16 atom, respectively.

Some π–π interactions were established between the adjacent aromatic rings of the Schiff base ligand located in neighboring complexes. The rings of Schiff base ligand involved in the intermolecular π–π stacking interactions are arranged in face to face mode with the shortest distance and dihedral angle between two planes being 3.643(7) Å and 6.30° (Fig. 3). The π–π interactions between Cg5 and Cg6 with the centroids distance of 3.643(7) Å (symmetry code $1-x$, $1-y$, $1-z$), where Cg5 and Cg6 are defined by the aromatic rings of (C8–C13) and (C14–C19), respectively. Meanwhile, the π–π stacking interactions between the Cg5 and Cg4 rings with centroids distance of 4.056(7) Å (symmetry code of $1/2-x$, $1-y$, $1/2+z$), where the two planes makes a dihedral angle of 11.97° and Cg4 is defined by the aromatic ring of (C1–C6), is longer than that found in the Cg5–Cg6 interaction.

There exist some weak C–H···Cg interactions, i.e. C2–H2A···Cg5 [3.186 Å, 92.74°, $1/2-x$, $1-y$, $-1/2+z$], C4–H4A···Cg6 [3.082 Å, 150.20°, $1/2-x$, $1/2+y$, z], and C21–H21B···Cg4 [3.044 Å, 137.93°, $1/2-x$, $1-y$, $1/2+z$], where Cg4, Cg5 and Cg6 are defined by the aromatic rings of Schiff base ligand. In addition, some weak O–H···Cg interactions, namely O5–H5B···Cg2 [3.1725 Å, 160.66°, $1/2-x$, $1-y$, $-1/2+z$], O1W–H11W···Cg2 [3.0926 Å, 68.74°, x, y, z], and O1W–H21W···Cg3 [2.8268 Å, 92.11°, x, y, z], where Cg2 and Cg3 are defined by the aromatic rings of [Mn1–O1–N1–C7–C8–C13] and [Mn1–O2–N2–C14–C19–C20], were observed.

3.3. Computational study

The optimized geometric parameters obtained from semi-empirical method PM6 in MOPAC2007 [13] represent a good approximation with those of the crystal structure, and they are the bases for calculating other parameters, such as molecular orbitals and electronic absorption spectra.

The structure mode of a complex optimized by the semi-empirical PM6 method with the MOPAC2007 software is presented in Fig. 4. The coordination geometry around the Mn(III) ion is a distorted octahedral with two oxygen and two nitrogen from the Schiff base ligand. The base ligand occupies the equatorial position, and the axial position was occupied by chloride anion and water molecule. The averages calculated values of Mn–O, Mn–N, Mn–Cl, and Mn–OW bond lengths are 1.951, 1.875, 1.968, and 2.146 Å, respectively. The calculated bond lengths and bond angles are slightly smaller compared to the experimental values. Comparison of calculated and experimental bond lengths data are presented in Figure S2. The calculated angles of O2–Mn1–Cl1, O1–Mn1–Cl1, N1–Mn1–Cl1, N2–Mn1–Cl1, OW1–Mn1–Cl1, O1–Mn1–O2, and N1–Mn1–N2 are 94.8°, 96.8°, 98.5°, 100.2°, 162.1°, 79.5°, and 87.3°, respectively, which are slightly larger compared to their respective experimental values. The larger angles in the prediction is because the contribution of the crystal packing forces effect, which is absent in calculation. The expected results as the molecule complex in the crystal lattice are also subjected to some constrains, and they do not exist in the solution and gas phases.

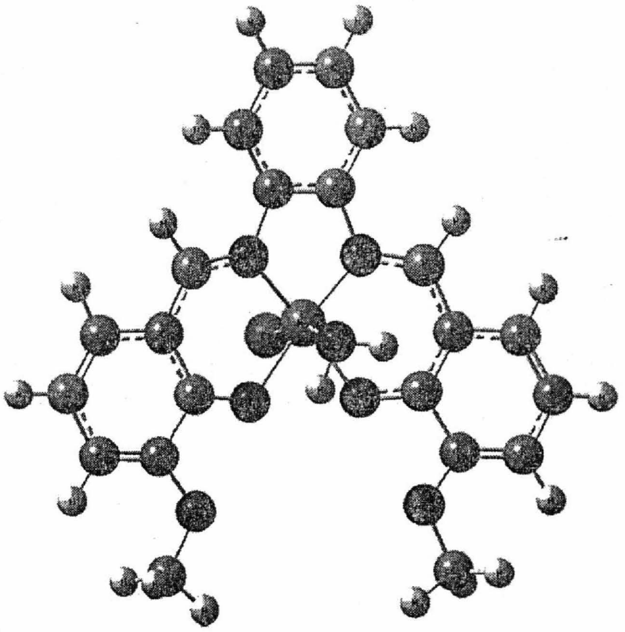

Fig. 4. Molecular structure of the Mn(III)-Schiff base complex from computational calculation.

The results of molecular orbital (MO) calculations showed that the electron density in the HOMO and LUMO are delocalized over the benzene rings (Fig. 5). The contour plots of HOMO and LUMO for the Mn(III) complex are presented in Figure S3. The methoxy

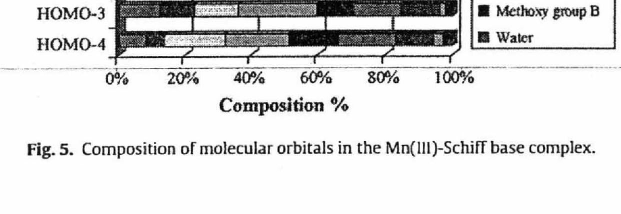

Fig. 5. Composition of molecular orbitals in the Mn(III)-Schiff base complex.

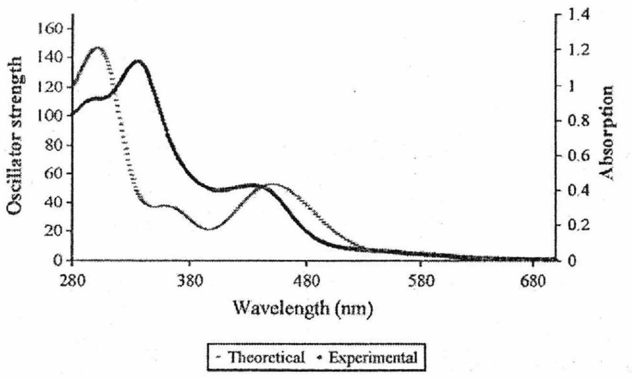

Fig. 6. Comparison of calculated and experimental electronic absorption for the complex.

group plays a main role in the solubility of this kind of compounds in common solvents. This group provides the facility to form an extended intermolecular H-bond network, due to the polarity of the methoxy group. However, their contribution to HOMO and LUMO densities is very little and almost negligible. On the other hand, the role of the Mn(III) ion shows a high contribution to the molecular orbital surfaces.

3.4. UV–vis and emission properties

The electronic spectrum of the complex in acetonitrile solution has four maxima peaks at 239, 305, 360 and 450 nm, which essentially show the absorption of the Schiff base ligand (Fig. 6). The absorptions at 240 and 305 nm can be related to the spin-allowed π–π^* azomethane intraligand transition [26]. The weak bands at 360 and 450 nm in the UV–vis region can be assigned to spin-allowed metal to the ligand charge transfer (MLCT) transition [26–28]. No d–d absorption bands were observed due to the presence of strong tail of the charge transfer band at lower energy.

The electronic absorption spectra were calculated by ZINDO/S method incorporated in HyperChem [15], based on the PM6 optimized structure. Fig. 6 shows the comparison between the calculated and the experimental results. Three bands of the electronic transitions at 300, 350 and 450 nm were observed. These results are in a good agreement with experimental data. By comparing the experimental spectrum with the calculated absorption spectrum of the complex, we notice that the calculated and experimental data are good in term of band positions.

The fluorescence spectra of the free Schiff base ligand and its complex were evaluated in DMF solution at room temperature with λ_{ex} at 330 nm. The free Schiff base ligand exhibits an intense broad emission band at 484 nm. Comparison with the free ligand, the complex had a red-shift emission peak from 430 to 600 nm with the center peak at 492 nm. The red-shift emission peak is probably due to the intraligand fluorescence emission [29,30].

4. Conclusion

In summary, we report the synthesis, spectroscopic and computational studies of $[MnCl(H_2O)(L)]\cdot H_2O\cdot C_2H_5OH$ complex, where L = 2,2′-{1,2-phenylenebis[nitrilomethylylidene]}bis(6-methoxyphenolate). The Schiff base ligand has an important role in the electronic and emission properties of complex. Computational study confirms the high degree of accuracy of the computational methods.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.saa.2009.11.006.

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PENYATA PERBELANJAAN PADA 31 MEI 2010

NAMA PROJEK :

POROUS METAL-CARBOXYLATE COMPOUNDS: SYNTHESIS, CHARACTERIZATION AND HOST-GUEST PROPERTIES
TEMPOH:
KETUA PENYELIDIK: DR ROHANA ADNAN
PENYELIDIK BERSAMA: DR COSWALD STEPHEN SIPAUT, ENCIK AHMAD FAIZ LATIF, PROFESOR MADYA SHUKRI SULAIMAN
PUSAT PENGAJIAN SAINS KIMIA

AKAUN	**PTJ**	**PROJEK**	**DONOR**	**PERUNTUKAN PROJEK**	**PERBELANJAAN TERKUMPUL SEHINGGA THN LALU**	**PERUNTUKAN SEMASA**	**TANGUNGAN SEMASA**	**BAYARAN SEMASA**	**BELANJA SEMASA**	**BAKI PROJEK**
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Maaf tak ada salinan
[illegible]

Baki akhir b/b
Rm 12

SENARAI JUMLAH-JUMLAH KECIL :

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330	ASET	16,000.00	0.00	16,000.00	5,587.90	0.00	5,587.90	10,412.10
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