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Supplementary Information

A Luminescent Linear Trinuclear Magnesium Complex Assembled from a Phosphorus-based *tris* Hydrazone Ligand

Vadapalli Chandrasekhar,*[a] Ramachandran Azhakar,[a] Jamie F. Bickley[b] and Alexander Steiner[b]

[a] *Department of Chemistry, Indian Institute of Technology, Kanpur, Kanpur-208016, India. Fax: 91 512 2590007/2597436; Tel: 91 512 2597259; E-mail: vc@iitk.ac.in*
[b] *Department of Chemistry, University of Liverpool, Liverpool-L69 7ZD, U.K.*

Synthesis of LH_3:

The ligand LH_3 was synthesized as reported in the literature. (*Inorg. Chem.*, 2003, **42**, 5989)

Synthesis of L_2Mg_3 complex:

To a solution of the ligand LH_3 (0.6 mmol) and triethylamine (6 mmol) in chloroform (30 mL) was added drop-wise a solution of the $MgCl_2.6H_2O$ (0.9 mmol) in methanol (30 mL) at room temperature and stirred for 6h. The metal complex precipitated out of the reaction mixture and was filtered. This was dissolved in a minimum amount of dichloromethane (5 mL) and *n*-hexane was added to it until a slight turbidity appeared. This was kept at 5 ° C to obtain a crystalline product.

Yield: 0.25g, 78.0%. Mp: >280 ^{o}C. UV-vis.(CH_2Cl_2) λ_{max}/nm (ε/ $Lmol^{-1}cm^{-1}$): 354 (18588), 286 (52215), 278 (51540). FT-IR (KBr) $\nu_{C=N}/cm^{-1}$: 1601cm^{-1}. ^{1}H NMR: 3.28(d, 9H, -N(C*H*$_3$); $^{3}J(^{1}H\text{-}^{31}P)$ =11.0Hz), 6.19-6.23(m, 3H, aromatic), 6.37-6.42(m, 3H, aromatic), 6.60-6.62(m, 3H, aromatic), 6.87-6.89(m, 3H, aromatic), 8.18(s, 3H, imino). ^{13}C NMR: 37.2 (N-*C*H$_3$), 114.9, 117.3, 122.6, 133.6, 163.9 (aromatic carbons), 165.7

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(N=*C*H). ^{31}P NMR: 69.1(s). FAB-MS: 1088(M^+). Anal. Calcd for $C_{48}H_{48}N_{12}O_6P_2S_2Mg_3$: C,53.00; H,4.45; N,15.45. Found: C,52.50; H,4.55; N,15.10.

Table 1.

Crystal and structure Refinement Data for L_2Mg_3 complex:

Parameters	L_2Mg_3
Empirical formula	$C_{51}\ H_{51}\ Cl_9\ Mg_3\ N_{12}\ O_6\ P_2\ S_2$
Formula Weight	1446.08
Temperature	213 (2) K
Wavelength	0.71073 Δ
Crystal system	Triclinic
Space group	P-1
Unit cell dimensions	a = 11.065 (3) Δ α= 72.67 (3)^0 b = 11.168 (3) Δ β = 83.03 (3)^0 c = 15.436 (3) Δ γ = 61.40 (2)^0
Volume, Z	1598.3 (6) Δ^3, 1
Density (Calculated)	1.502 Mg/m^3
Absorption coefficient	0.596 mm^{-1}
F (000)	740
Crystal size	0.5x 0.5 x 0.5 mm^3
θ range for data collection	2.10 to 24.25^0
Limiting indices	-12≤h≤12, -12≤k≤12, -17≤l≤17
Reflections collected	10130
Independent reflections	4733 (R_{int} = 0.0374)
Completeness to θ	91.8%
Refinement method	Full - matrix least - squares on F^2
Data/ restraints/ parameters	4733 / 27 / 406
Goodness - of - fit on F^2	1.083
Final R indices [I>2σ(I)]	R1 = 0.0532, wR2 = 0.1457
R indices (all data)	R1 = 0.0628, wR2 = 0.1532
Largest diff. peak and hole	1.019 and -0.619eΔ^{-3}

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Ortep Diagram of L_2Mg_3:

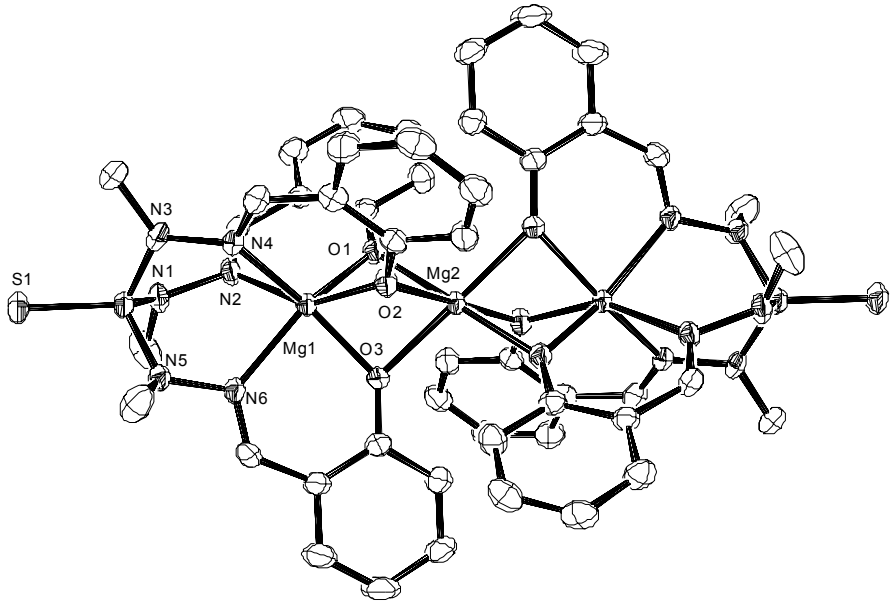


Table 2.

Important bond length (Å) and bond angles (^{o}) for L_2Mg_3 complex:

(a) bond length in Å

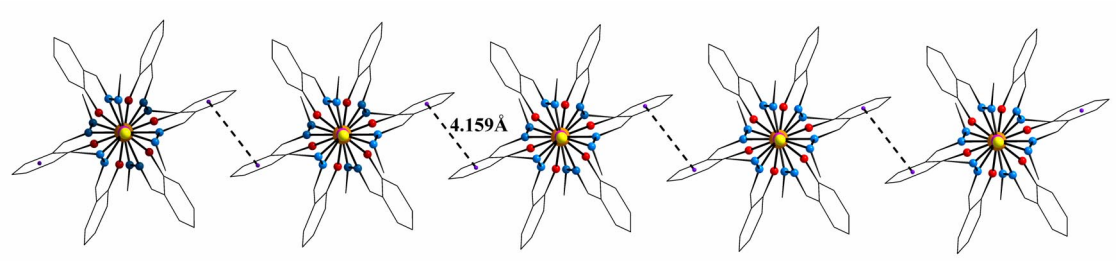
Mg(1)-O(2)	2.009(3)
Mg(1)-O(3)	2.039(3)
Mg(1)-O(1)	2.051(3)
Mg(1)-N(2)	2.145(3)
Mg(1)-N(6)	2.167(3)
Mg(1)-N(4)	2.249(3)
Mg(2)-O(1)	2.070(2)
Mg(2)-O(3)	2.091(2)
Mg(2)-O(2)	2.097(2)
Mg(1)-Mg(2)	2.7828(13)

(b) bond angles in ^{o}

O(2)-Mg(1)-O(3)	81.00(10)
O(2)-Mg(1)-O(1)	81.11(10)
O(3)-Mg(1)-O(1)	79.67(10)
O(2)-Mg(1)-N(2)	150.37(12)
O(3)-Mg(1)-N(2)	119.50(12)
O(1)-Mg(1)-N(2)	82.04(11)
O(2)-Mg(1)-N(6)	118.11(11)
O(3)-Mg(1)-N(6)	83.80(11)
O(1)-Mg(1)-N(6)	152.29(12)
N(2)-Mg(1)-N(6)	87.03(12)

O(2)-Mg(1)-N(4)	84.07(11)
O(3)-Mg(1)-N(4)	155.40(11)
O(1)-Mg(1)-N(4)	117.20(11)
N(2)-Mg(1)-N(4)	82.21(11)
N(6)-Mg(1)-N(4)	86.16(11)
O(2)-Mg(1)-Mg(2)	48.68(7)
O(3)-Mg(1)-Mg(2)	48.45(7)
O(1)-Mg(1)-Mg(2)	47.82(7)
N(2)-Mg(1)-Mg(2)	127.75(9)
N(6)-Mg(1)-Mg(2)	129.17(8)
N(4)-Mg(1)-Mg(2)	128.87(9)
O(1)#1-Mg(2)-O(1)	180.0
O(1)#1-Mg(2)-O(3)	101.98(9)
O(1)-Mg(2)-O(3)	78.02(9)
O(1)#1-Mg(2)-O(3)#1	78.02(9)
O(1)-Mg(2)-O(3)#1	101.98(9)
O(3)-Mg(2)-O(3)#1	180.000(1)
O(1)#1-Mg(2)-O(2)	101.39(9)
O(1)-Mg(2)-O(2)	78.61(9)
O(3)-Mg(2)-O(2)	77.77(9)
O(3)#1-Mg(2)-O(2)	102.23(9)
O(1)#1-Mg(2)-O(2)#1	78.61(9)
O(1)-Mg(2)-O(2)#1	101.39(9)
O(3)-Mg(2)-O(2)#1	102.23(9)
O(3)#1-Mg(2)-O(2)#1	77.77(9)
O(2)-Mg(2)-O(2)#1	180.000(1)
Mg(1)-Mg(2)-Mg(1)#1	180.0

Weak intermolecular π- π interactions of L_2Mg_3 complex in the solid state structure:



View of the supramolecular array along the inter-metal axis where the centroid-centroid distance of 4.159Å, shortest C-C distance of 3.313 Å and shortest C-centroid distance of 3.497 Å

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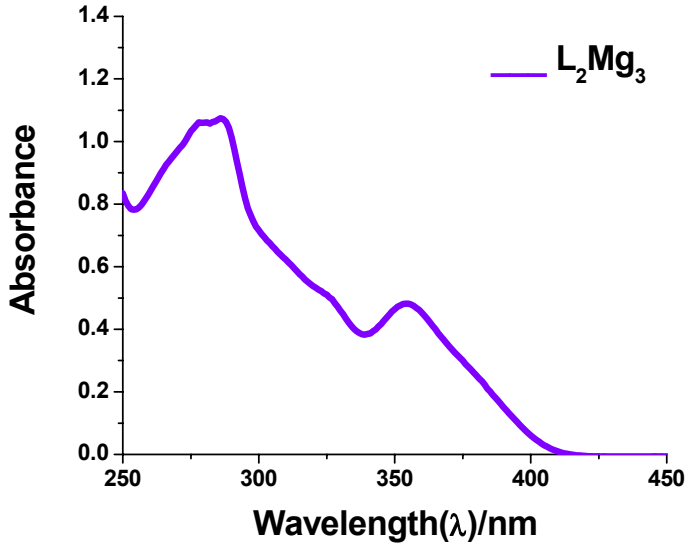
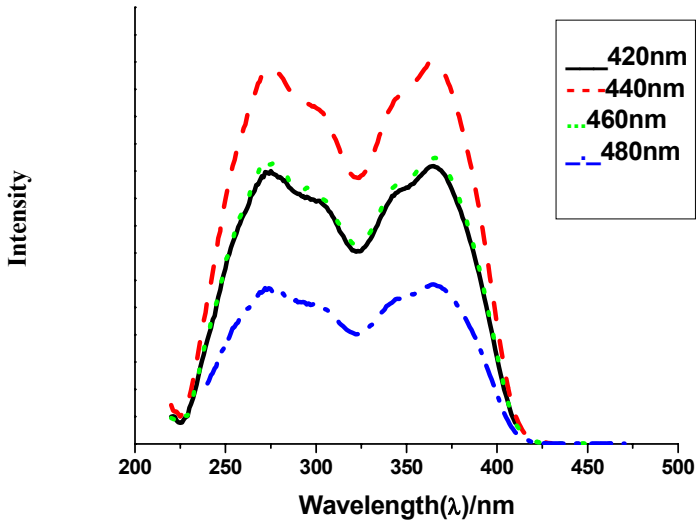
UV-vis spectrum of L_2Mg_3 complex (CH_2Cl_2):



Excitation spectrum of L_2Mg_3 complex recorded at different wavelength:

Excitation spectrum of L_2Mg_3 complex in CH_2Cl_2 solution recorded at four different wavelengths. The spectrum obtained at four different wavelength are represented in four different colors.



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TGA curve of L_2Mg_3 complex: