

# A luminescent linear trinuclear magnesium complex assembled from a phosphorus-based tris-hydrazone ligand†

Vadapalli Chandrasekhar,<sup>\*a</sup> Ramachandran Azhakar,<sup>a</sup> Jamie F. Bickley<sup>b</sup> and Alexander Steiner<sup>b</sup>

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A novel linear trinuclear magnesium complex  $\{P(S)[N(CH_3)N=CHC_6H_4-o-O]_3\}_2Mg_3$  was prepared by the reaction of  $P(S)[N(CH_3)N=CHC_6H_4-o-OH]_3$  with  $MgCl_2 \cdot 6H_2O$  in the presence of triethylamine. The trinuclear magnesium complex is fluorescent in solution as well as in the solid-state.

Among the various biologically important metal ions,  $Mg^{2+}$  occupies a prominent position. The favorable charge-size ratio of  $Mg^{2+}$  coupled with the dramatic change in its ionic radius (0.65 Å) *vis-à-vis* its hydrated radius (4.76 Å) is believed to be responsible for the many crucial roles of  $Mg^{2+}$  ions in various biological processes.<sup>1</sup> These include not only catalytic processes such as phosphate ester hydrolysis but also a structural role in which the  $Mg^{2+}$  ion is important for stabilizing the conformations of biological molecules. Thus, it is believed that  $Mg^{2+}$  helps to fold RNA into specific structures and assists ribozyme activity.<sup>2</sup> In view of the above, a study of the coordination chemistry of  $Mg^{2+}$  in general and that of multi-nuclear magnesium complexes in particular, assumes considerable importance. We have recently designed a tris-hydrazone ligand,  $P(S)[N(CH_3)N=CHC_6H_4-o-OH]_3$  ( $LH_3$ ), built on a phosphorus support and have shown its efficacy towards divalent transition metal ions.<sup>3</sup> Herein we report the synthesis, structure and spectroscopy of a novel linear trinuclear magnesium complex  $\{P(S)[N(CH_3)N=CHC_6H_4-o-O]_3\}_2Mg_3$  ( $L_2Mg_3$ ). Apart from its structural novelty, this compound shows luminescent properties both in solution as well

as in the solid-state and is therefore of interest in view of the recent thrust in new organic light emitting diodes (OLEDs).<sup>4</sup>

The tris-hydrazone ligand  $LH_3$  reacts with  $MgCl_2 \cdot 6H_2O$  in a 2 : 3 stoichiometric ratio in the presence of  $Et_3N$  to afford the linear trinuclear magnesium complex,  $L_2Mg_3$ . The  $^{31}P$  NMR chemical shift of this diamagnetic complex appears at 69.1 ppm, which is deshielded with respect to the ligand ( $^{31}P$  NMR of  $LH_3$ : 71.7 ppm).  $L_2Mg_3$  shows a prominent molecular ion peak ( $M^+$ : 1088) in its FAB mass spectrum.

The molecular structure of  $L_2Mg_3$  was determined by single-crystal X-ray crystallography and is shown in Fig. 1.† Two molecules of the tris-hydrazone ligand are completely deprotonated and provide a ligand environment with a total of six negative charges ( $O^-$ ). The two trianionic ligands cumulatively bind a linear array of three magnesium ions each of which is present in an oxidation state of +2. This generates a neutral trinuclear magnesium complex. The terminal magnesium ions in this complex ( $Mg_t$ ) are encapsulated in a facial  $N_3O_3$  coordination environment. The geometry around the terminal metal centers can be described as distorted octahedral. The central magnesium ion is also present in a distorted octahedral environment. However, its ligand environment is composed of only phenolic oxygen atoms (6O). The disposition of the aromatic groups in the metal complex  $L_2Mg_3$  gives rise to a paddle wheel type of structural arrangement when the molecule is viewed through the inter-metal axis, Fig. 1(d). There is a noticeable change in the bond parameters of the complex when compared with the ligand. Thus, the  $N-N_{(avg)}$  bond distance increases from 1.388(5) Å ( $LH_3$ ) to 1.437(4) Å in  $L_2Mg_3$ . The other metric parameters (average values) are as follows:  $Mg_t-N_{(im)} = 2.187(3)$  Å,  $Mg_t-O = 2.033(3)$  Å and  $Mg_c-O = 2.085(2)$  Å. The bond parameters are comparable to those of other  $Mg^{2+}$  complexes.<sup>5</sup> The inter-metal distance ( $Mg_t-Mg_c$ ) is 2.7828(13) Å.

† Electronic supplementary information (ESI) available: synthesis, UV-vis spectrum, excitation spectrum, TGA of the  $L_2Mg_3$  complex. See <http://www.rsc.org/suppdata/cc/b414353a/>  
\*vc@iitk.ac.in

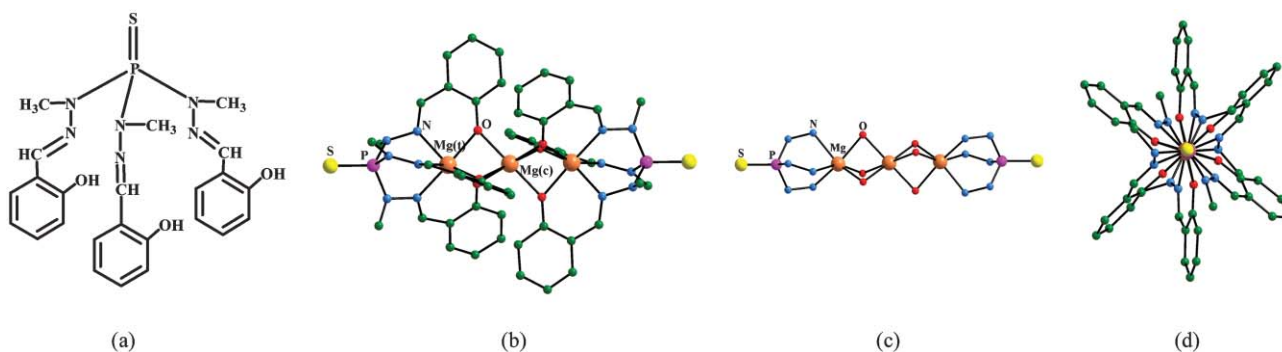
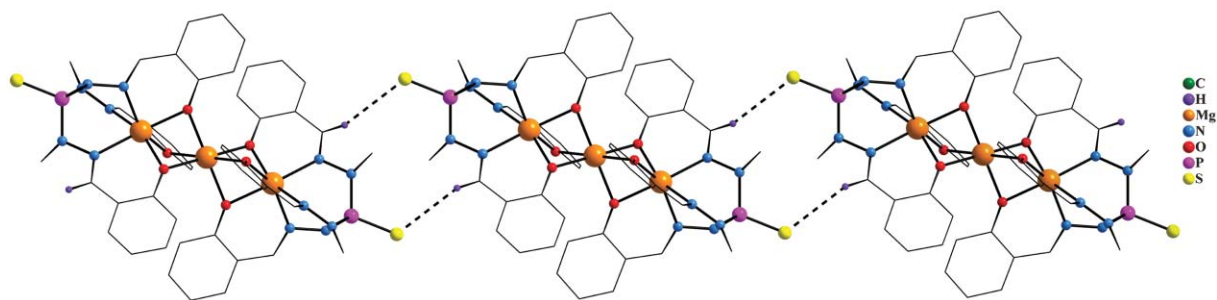


Fig. 1 (a) The ligand  $LH_3$ . (b) The molecular structure of the complex  $L_2Mg_3$ . (c) Side view of the core of  $L_2Mg_3$ . (d) Paddle wheel type of arrangement of  $L_2Mg_3$  viewed along the inter-metal axis.

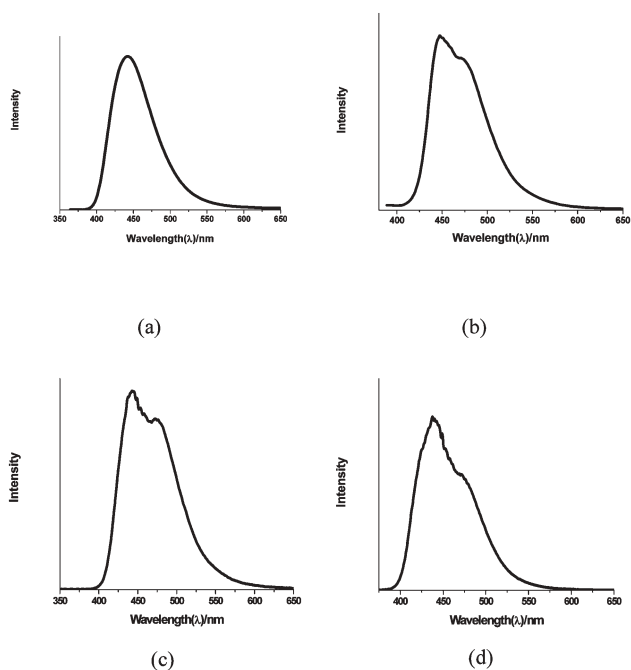


**Fig. 2** Intermolecular C–H···S=P interactions in the  $L_2Mg_3$  complex. All the hydrogen atoms which are not involved in the hydrogen bonding have been omitted for clarity. The bond parameters for the C–H···S contact are C–H 0.94(1) Å, H···S 3.013(54) Å and C···S 3.909(65) Å and C–H···S 159.92(20)°. The symmetry is  $-x, 2-y, -z$ .

The perfect linearity of the trinuclear magnesium array can be gauged by the  $Mg_t-Mg_c-Mg_t$  angle, which is 180°.

A further investigation of the  $L_2Mg_3$  complex shows weak intermolecular C–H···S=P and  $\pi-\pi$  interactions in the solid-state leading to supramolecular architectures. In comparison to other weak intermolecular hydrogen bonds, C–H···S=P contacts are rare and only three examples are reported thus far to the best of our knowledge.<sup>3,6,7</sup> The imino protons ( $CH=N$ ) interact with the terminal P=S units leading to a double-bridged zig-zag one-dimensional polymeric chain (Fig. 2). In addition to these contacts, intermolecular  $\pi-\pi$  interactions between the aromatic six-membered rings are also observed which augment the one-dimensional polymeric chain<sup>8</sup> (see ESI†).

The optical behavior of  $L_2Mg_3$  is quite interesting. Although the ligand  $LH_3$  does not show any fluorescence, the complex shows emission behavior both in solution and in the solid-state. The emission spectra of  $L_2Mg_3$  in solution ( $CH_2Cl_2$ ;  $\lambda_{ex} = 354$  nm) and in the solid-state (powder in a quartz tube;  $\lambda_{ex} = 325$  nm) are shown in Figs. 3(a) and (b). In dichloromethane solution,



**Fig. 3** Emission spectra of the  $L_2Mg_3$  complex (a) in solution state (b) in solid-state (c) in thin film (d) in doped polymer.

an intense emission with a peak maximum at 442 nm is observed. In comparison, the solid-state emission peak occurs at 448 nm.

The excited state emission spectrum of  $L_2Mg_3$  obtained by different excitation wavelengths is similar to its UV–vis absorption spectrum with intense peaks around 275 and 365 nm, indicating that the emission is from the vertically excited state and that the molecular structure of the complex remains invariant in the excited state<sup>9</sup> (see ESI†). The luminescent properties of  $L_2Mg_3$  were investigated in its thin film as well as in a polymer matrix. Thus, a spin-coated thin-film sample of  $L_2Mg_3$  was prepared from its dichloromethane solution and its emission spectrum was studied [Fig. 3(c)]. We also prepared doped polymer thin films from a solution of 90% polystyrene and 10%  $L_2Mg_3$  complex in dichloromethane. The emission spectrum of such a polymer film is shown in Fig. 3(d). The luminescent properties of both the solid thin films and the polymer-doped thin films are nearly similar to that observed in solution and in the solid-state. It is observed from TGA that the  $L_2Mg_3$  complex starts to decompose at 425 °C (see ESI†). This clearly indicates that the  $L_2Mg_3$  complex is thermally quite stable.

The ability of  $L_2Mg_3$  to be uniformly dispersed in a polymer medium and the retention of its luminescent properties in such a matrix augurs well for exploring its OLED applications. To the best of our knowledge, this represents the first time that luminescent behavior has been observed for multi-nuclear magnesium complexes. Hitherto, fluorescent probes have been utilized for detecting magnesium ions. In the present instance the ligand itself is non-fluorescing and it is only on the formation of the trinuclear complex that the fluorescence behavior is manifested. The tunability of the ligand in terms of electronic and steric properties should allow the assembly of other trinuclear complexes with varying emission properties.

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Vadapalli Chandrasekhar,<sup>\*a</sup> Ramachandran Azhakar,<sup>a</sup> Jamie F. Bickley<sup>b</sup> and Alexander Steiner<sup>b</sup>

<sup>a</sup>Department of Chemistry, Indian Institute of Technology-Kanpur, Kanpur 208016, India. E-mail: vc@iitk.ac.in; Fax: +91-512-2590007/2597436

<sup>b</sup>Department of Chemistry, University of Liverpool, Liverpool, UK L69 7ZD

## Notes and references

‡ Crystal data for  $L_2Mg_3$ :  $C_{51}H_{51}Cl_9Mg_3N_{12}O_6P_2S_2$ .  $M = 1446.08$ , triclinic,  $P\bar{1}$  (no. 2),  $a = 11.065(3)$ ,  $b = 11.168(3)$ ,  $c = 15.436(3)$  Å,  $\alpha = 72.67(3)$ ,  $\beta = 83.03(3)$ ,  $\gamma = 61.40(2)^\circ$ ,  $V = 1598.3(6)$  Å<sup>3</sup>,  $Z = 1$ ,  $F(000) = 740$ ,  $\rho = 1.502$  g cm<sup>-3</sup>,  $\lambda = 0.71073$  Å,  $T = 213(2)$  K,  $\mu = 0.596$  mm<sup>-1</sup>, 10130 reflections collected, 4733 unique ( $R_{int} = 0.0374$ ),  $R = 0.0532$  [ $I > 2\sigma(I)$ ],  $R_w = 0.0628$  (all data). CCDC 251534. See <http://www.rsc.org/suppdata/cc/b4/b414353a/> for crystallographic data in .cif or other electronic format.

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