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Synthesis and crystal structure of an infinite one-dimensional chain containing a poly-metallocage of Mn^{II} with 4,4′-bis(imidazol-1-ylmethyl)biphenyl

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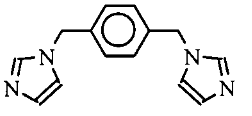
A new manganese(II) co-ordination polymer, $[Mn(bimb)_3][ClO_4]_2\cdot 2H_2O$ [bimb = 4,4′-bis(imidazol-1-ylmethyl)-biphenyl], was synthesized and characterized by X-ray crystallography, magnetic susceptibility and luminescent measurements. The cation structure of the complex is an infinite one-dimensional chain containing a poly-metallocage. Each Mn^{II} co-ordinates with six nitrogen atoms of six different bimb ligands with a distorted octahedral environment and each bimb ligand in turn binds to two Mn^{II}. The perchlorate counter ions and water molecules are incorporated between two adjacent chains through four C–H · · · O hydrogen bonds.

Introduction

Taking inspiration from the examples of biological systems, where simple units are organized into various intricate and beautiful structures with complex and efficient functions, many chemists are trying to design aggregates from molecular building blocks with some specific structures. The recent upsurge in the research devoted to co-ordination polymers was evoked by a fundamental interest in the development of approaches to the prediction of crystal structures and has subsequently been accelerated by the practical opportunities that are offered by new classes of functional materials. The control of molecular structure and topology is one of the major goals in supramolecular chemistry.[1,2] The generation of molecular architecture depends on the combination of several factors like the co-ordination geometry of metal ions, the nature of the ligands and the reaction conditions. The use of transition metal ions to control the assembly of supramolecular architectures has become a popular and rapidly growing discipline. Metal-containing polymers constitute a conspicuously large family of inorganic architectures. An enormous body of work has been published since the 1960s, such as helicates, racks, grids, rings, cages,[3] interlocking rings and molecular knots.[4] The employment of transition metal ions and appropriate bridging ligands has become a dominant theme in the construction of some interesting arrays.[5,6] Infinite complexes involving macrocyclic frameworks are often assembled through metal co-ordination of pyridone- or pyridine-based bridging ligands.[7]

In previous studies it has been reported that the flexible bridging ligand *N*,*N*′-tetramethylenebisimidazole formed an interpenetrating three dimensional network by reaction with manganese(II) tetrafluoroborate,[8] 1,4-bis(imidazol-1-ylmethyl)-benzene (bix) gave an infinite polyrotaxane network by reactions with silver nitrate[9] and zinc nitrate hexahydrate,[10] and an infinite 1-D network with manganese(II) nitrite.[11] In order further to investigate the influence of the bridging ligand on the formation of supramolecular complexes, we synthesized a novel ligand, 4,4′-bis(imidazol-1-ylmethyl)biphenyl (bimb) and its manganese(II) complex. The choice of biphenyl as a spacer is to detect the effect of π–π interaction on the conformation of the supramolecular structure and also to study the influence of the bridging spacer in the structure. The employment of rigid linkers represents an excellent alternative for further research.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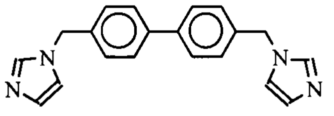
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The X-ray single crystal diffraction analysis of $[Mn(bimb)_3]$-$[ClO_4]_2\cdot 2H_2O$ and of the ligand was carried out.

Experimental

General methods

4,4′-Bis(bromomethyl)biphenyl was prepared according to the reported procedures.[12] n-Butyllithium[13] was freshly prepared and titrated using the literature methods prior to use. Tetrahydrofuran (THF) and diethyl ether were dried by sodium–benzophenone and distilled before use. All other chemicals were of reagent grade quality from commercial sources and used without further purification. C, H and N analyses were carried out on a Perkin-Elmer 240C element analyzer at the analysis center of Nanjing University. 500 MHz ^1H NMR spectroscopic measurements were performed on a Bruker AM-500 NMR spectrometer, using TMS ($SiMe_4$) as an internal reference at 25 °C. Thermogravimetric and differential analyses were made on a simultaneous SDT 2960 thermal analyzer under flowing N_2 with a heating rate of 10 °C min^{-1}. Luminescence spectra were recorded on a Hitachi 850 fluorescence spectrophotometer at room temperature (25 °C). Magnetic measurements on powder samples were carried out using a CHAN-2000 Faraday magnetometer in the 75–300 K temperature range. The apparatus was calibrated with $[Ni(en)_3]S_2O_3$ (en = ethylenediamine). Diamagnetic corrections were made using Pascal's constants.

CAUTION: perchlorate salts of metal complexes with organic ligands are potentially explosive and should be handled with care.

Syntheses

4,4′-Bis(imidazol-1-ylmethyl)biphenyl (bimb). The ligand bimb was prepared under an argon atmosphere using standard Schlenk techniques. n-Butyllithium (7.2 mmol, 1.6 M solution in diethyl ether) was added slowly to a solution of imidazole

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(490 mg, 7.2 mmol) in dry THF (20 ml) at −78 °C, over about 0.5 hour. Then the solution of 4,4′-bis(bromomethyl)biphenyl (1.22 g, 3.6 mmol) in dry THF (20 ml) was added slowly to the above mixture at −78 °C with stirring in about 1 hour. Three hours later water (10 ml) was added dropwise to quench the reaction. The solvents were removed in vacuum, then 30 ml water were added to the residue to precipitate the ligand. The white powder was recrystallized from acetone. Yield 79%, mp 167–168 °C. ^{1}H NMR ($CDCl_3$, 25 °C): δ 5.18 (s, 4 H); 6.95 (s, 2 H); 7.14 (s, 2 H); 7.25 (d, 4 H); 7.70 (s, 2 H) and 7.55 (d, 4 H). These data agree with those of the literature.[14]

$[Mn(bimb)_3][ClO_4]_2\cdot 2H_2O$. A solution of $Mn(ClO_4)_2\cdot 6H_2O$ (12.06 mg, 0.033 mmol) in acetonitrile (10 ml) was added dropwise to a stirred solution of bimb (31.4 mg, 0.1 mmol) in methanol (10 ml) at 60 °C. Pale yellow single crystals suitable for X-ray diffraction were obtained by slow diffusion of diethyl ether into the clear filtrate for several days in 78% yield. Calc. for $C_{60}H_{58}Cl_2MnN_{12}O_{10}$: C, 58.44; H, 4.74; N, 13.63. Found: C, 58.50; H, 4.71; N, 13.46%.

$bimb\cdot 2HClO_4$. This compound was an unexpected product of the reaction of $MnCl_2\cdot 4H_2O$, $NaClO_4$ and the bimb ligand. A solution of $MnCl_2\cdot 4H_2O$ (6.6 mg, 0.033 mmol) in distilled water (1 ml) was added dropwise to a stirred solution of bimb (31.4 mg, 0.1 mmol) in methanol (10 ml) at 60 °C. 30 minutes later two drops of a saturated solution of $NaClO_4$ were added. Single crystals suitable for X-ray diffraction were obtained by slow evaporation from the filtrate at room temperature.

X-Ray crystallography

The X-ray diffraction measurements were performed on a Siemens P4 automatic four-circle diffractometer using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at room temperature. Intensity data were collected in the variable ω-scan mode. The structures were solved by direct methods using SHELXS 86[15] and refined by full-matrix least-squares calculation on F^2 with SHELXL 93.[16] All non-hydrogen atoms were refined anisotropically, whereas the hydrogen atoms were generated geometrically. Calculations were performed on a PC-586 computer using the Siemens SHELXTL program package.[17,18] Details of the crystal parameters, data collections and refinements are listed in Table 1, and selected bond distances and angles are given in Table 2.

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See http://www.rsc.org/suppdata/dt/b0/b002692l/ for crystallographic files in .cif format.

Results and discussion

Description of the structures

Fig. 1(a) shows the ORTEP[19] representation of the cation structure of $[Mn(bimb)_3]^{2+}$ with the atom numbering scheme. It is clear that the repeat unit of the complex contains one $[Mn(bimb)_3]^{2+}$ cation, two perchlorate anions and two crystal water molecules. Each manganese atom is co-ordinated by six imidazole nitrogen atoms from six different bimb ligands with the N–Mn–N bond angles varying from 87.9 (4) to 177.1 (5)° as listed in Table 2. Therefore the co-ordination environment of the manganese atom can be regarded as distorted octahedral with the Mn–N bond distances ranging from 2.206(11) to 2.301(11) Å and with the average 2.250(10) Å (Table 2).[20] Each bimb ligand has an extended geometry with "Z" shape since the two terminal imidazole groups are at in opposite direction with reference to the average biphenyl plane and serve to link two adjacent Mn. As a result, three bimb ligands and two Mn form a cage and two adjacent cages share a manganese atom and such units form an infinite 1-D chain (Fig. 1b and 1c). In the structure of $[Mn(bix)_3(H_2O)_2][NO_2]_2\cdot 2H_2O$,[11] the Mn^{II} is co-ordinated with four nitrogen atoms from two bridging and two terminal bix groups, and two waters, forming a 1-D chain. It has also been reported that 4,4′-bis(4-pyridylmethyl)biphenyl forms a [2]catenane by assembly with $Pd(en)(NO_3)_2$.[21] In the present case the infinite 1-D polymeric chain can be regarded as a poly-cage as illustrated in Fig. 1(c). Most recently, a highly porous metal co-ordination polymer $[Cu_3(TMA)_2(H_2O)_3]_n$ (TMA = benzene-1,3,5-tricarboxylate) was reported by Williams and co-workers.[22] The distance between Mn and MnA is 16.96 Å and the thickness of the cage can roughly be estimated from the triangles formed by methylene carbons of

Table 1 Summary of crystal data and refinement results for $[Mn(bimb)_3][ClO_4]_2\cdot 2H_2O$ and $bimb\cdot 2HClO_4$

Empirical formula	$C_{60}H_{58}Cl_2MnN_{12}O_{10}$	$C_{10}H_{10}ClN_2O_4$
Formula weight	1233.02	257.65
Crystal system	Orthorhombic	Monoclinic
Space group	$Pca2_1$	$P2_1/c$
a/Å	33.921(11)	4.8950(10)
b/Å	10.103(2)	15.164(2)
c/Å	17.915(4)	14.904(2)
β/°		97.210(10)
V/Å^3	6140(3)	1097.5(3)
Z	4	4
T/°C	23(2)	15(2)
μ/mm^{-1}	0.369	0.353
Measured/independent reflections	6423/5577	2341/1928
R_{int}	0.0407	0.0137
$R1$ ($I > 2\sigma(I)$)	0.0496	0.0777
wR_2 ($I > 2\sigma(I)$)	0.0754	0.2276

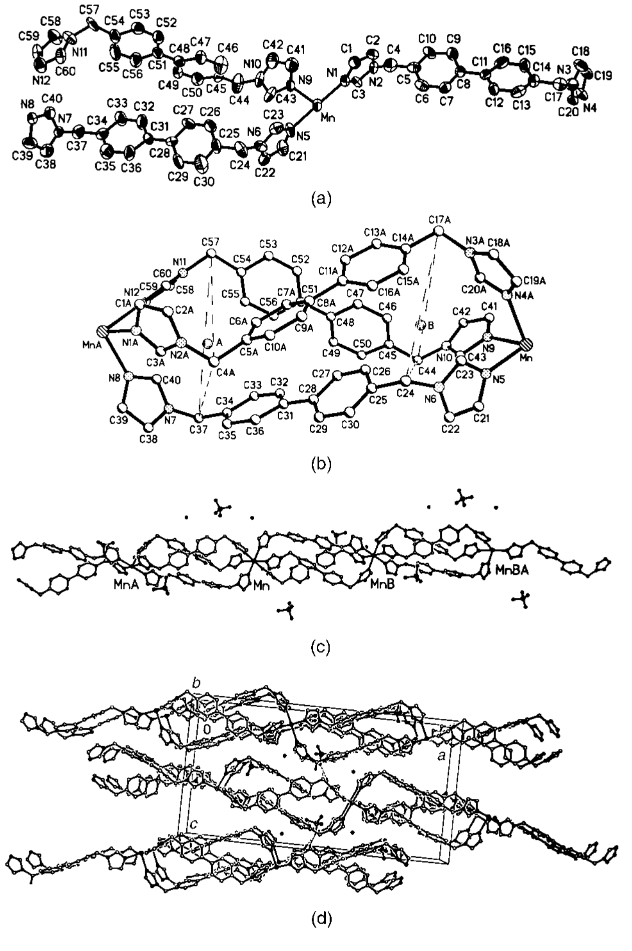

Fig. 1 (a) Crystal structure of the repeat unit of cationic moiety of $[Mn(bimb)_3][ClO_4]_2\cdot 2H_2O$ with the ellipsoids drawn at the 50% probability level. (b) An individual cage formed by two Mn^{II} and three bimb ligands. (c) Poly-cage structure. (d) Crystal packing diagram on the ac plane with hydrogen bonds indicated by dashed lines.

the bimb ligands as indicated by dashed lines in Fig. 1(b). The average edge lengths of the two triangles C4A, C37, C57 and C17A, C24, C44 are 6.62 and 6.72 Å, respectively. The centroid–centroid distances of A–B (Fig. 1b) and dihedral angle between these two triangles are 8.73 Å and 20.7°, respectively. The two benzene ring planes of each biphenyl group are near coplanar since the dihedral angles between the two benzene ring planes are 19.2 (for planes containing C5, C6, C7, C8, C9, C10 and C11, C12, C13, C14, C15, C16), 18.1 (for planes containing C25, C26, C27, C28, C29, C30 and C31, C32, C33, C34, C35, C36) and 13.2° (for planes containing C45, C46, C47, C48, C49, C50 and C51, C52, C53, C54, C55, C56), respectively. The dihedral angles between each two imidazole ring planes related to the corresponding biphenyl listed above are 27.0, 28.3 and 19.9°, respectively. The counter ions of perchlorate are disposed between the two adjacent cationic chains by the formation of four C–H ··· O hydrogen bonds (Fig. 1d). There are three C-H ··· O hydrogen bonds generated between the three different methylene CH_2 groups and oxygen atoms of ClO_4^-, r(C ··· O) = 3.377(14), 3.390(13), 3.260(16) Å, and one C–H ··· O hydrogen bond formed between CH of the imidazole group and the oxygen atom of ClO_4^- anion with r(C ··· O) = 3.453(16) Å. The solvate water molecules are disordered between the adjacent chains.

The polymeric structure of the synthesized complex is also stabilized by close face-to-face and T-type edge-to-face π–π interactions. For example, the centroid–centroid distance between the planes of C11A–C12A–C13A–C14A–C15A–C16A and C25–C26–C27–C28–C29–C30 with a dihedral angle of 14.3° is 5.18 Å, and the distance and dihedral angle between C5A–C6A–C7A–C8A–C9A–C10A and C31–C32–C33–C34–C35–C36 are 5.05 Å and 8.7°, respectively. The related centroid–centroid distances and dihedral angles are listed in Table 3.

The crystal structure of bimb·$2HClO_4$ is shown in Fig. 2(a) with the atom numbering scheme. The repeat unit of the compound is half a molecule with protonation of the imidazole group. The two phenyl rings and the two imidazole groups of bimb are parallel with each other. The dihedral angle of C5–C6–C7–C8–C9–C10 and N1–N2–C1–C2–C3 is 79.3°. The stacking diagram of bimb·$2HClO_4$ is shown in Fig. 2(b). The cations pack in parallel mode with the centroid–centroid distance between the two nearest benzene ring planes of 3.38 Å, which indicates the existence of π–π interactions. The perchlorate counter ions form three hydrogen bonds with adjacent protonated imidazole rings, two N–H ··· O bonds are 2.982(7) and 2.972(7) Å and one C–H ··· O is 3.145(9) Å.

Table 2 Selected bond distances (Å) and angles (°) for the complex $[Mn(bimb)_3][ClO_4]_2{\cdot}2H_2O$

Mn–N(8)#1	2.206(11)	Mn–N(1)	2.262(10)
Mn–N9	2.238(10)	Mn–N(4)#2	2.301(11)
Mn–N(5)	2.243(10)	Mn–N (average)	2.250(10)
Mn–N(12)#1	2.252(10)		
N(8)#1–Mn–N(9)	89.1(3)	N(5)–Mn–N(1)	176.6(5)
N(8)#1–Mn–N(5)	93.8(4)	N(12)#1–Mn–N(1)	89.6(4)
N(9)–Mn–N(5)	89.5(4)	N(8)#1–Mn–N(4)#2	176.4(4)
N(8)#1–Mn–N(12)#1	90.0(4)	N(9)–Mn–N(4)#2	88.5(3)
N(9)–Mn–N(12)#1	177.1(5)	N(5)–Mn–N(4)#2	88.8(4)
N(5)–Mn–N(12)#1	87.9(4)	N(1)–Mn–N(4)#2	89.0(4)
N(8)#1–Mn–N(1)	88.5(4)	N(12)#1–Mn–N(4)#2	92.6(4)
N(9)–Mn–N(1)	93.1(4)		

Symmetry transformations used to generate equivalent atoms: #1 $x + \frac{1}{2}, -y, z$; #2 $x - \frac{1}{2}, -y, z$.

Magnetic and thermal properties

The magnetic susceptibility of $[Mn(bimb)_3][ClO_4]_2{\cdot}2H_2O$ as a function of temperature between 75 and 300 K was measured. At 300 K the effective moment is 5.79 μ_B ($\mu_B \approx 9.27 \times 10^{-24}$ J T^{-1}) which is close to the value of 5.92 μ_B expected for isolated

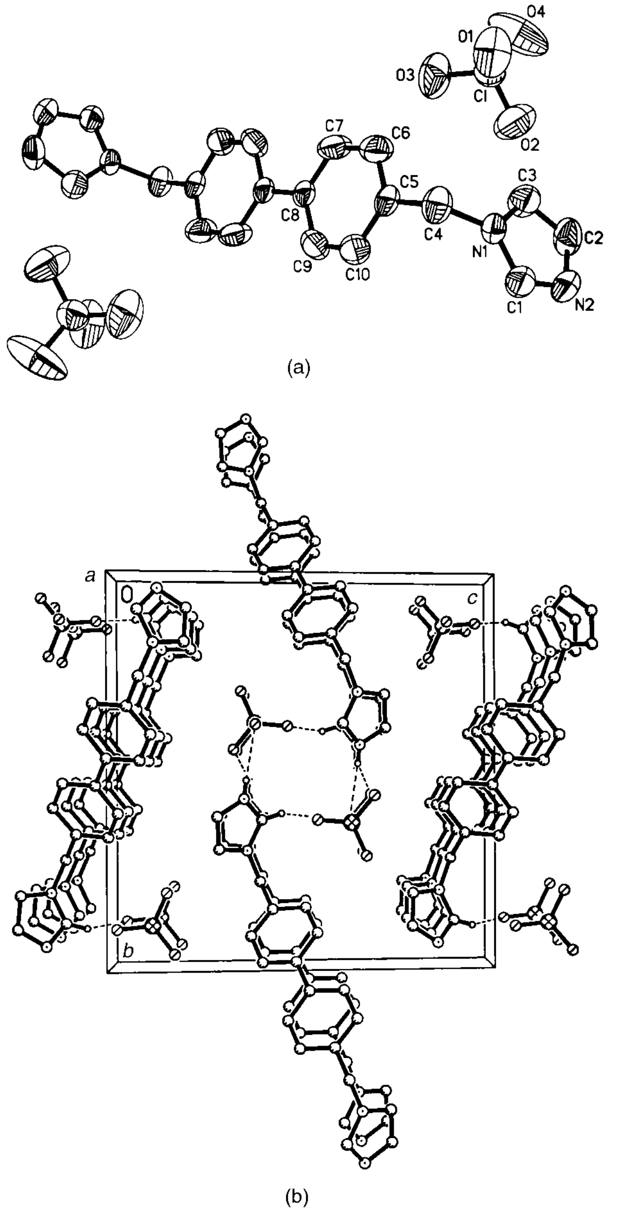

Fig. 2 (a) An ORTEP drawing of the structure of bimb·$2HClO_4$. (b) Crystal packing diagram with hydrogen bonds indicated by dashed lines.

Table 3 The centroid–centroid distances and dihedral angles between the benzene planes of the complex $[Mn(bimb)_3][ClO_4]_2{\cdot}2H_2O$

Plane 1	Plane 2	Distance/Å	dihedral angle/°
C5A–C6A–C7A–C8A–C9A–C10A	C31–C32–C33–C34–C35–C36	5.05	8.7
C5A–C6A–C7A–C8A–C9A–C10A	C51–C52–C53–C54–C55–C56	5.21	90.8
C31–C32–C33–C34–C35–C36	C51–C52–C53–C54–C55–C56	5.41	86.5
C11A–C12A–C13A–C14A–C15A–C16A	C25–C26–C27–C28–C29–C30	5.18	14.3
C11A–C12A–C13A–C14A–C15A–C16A	C45–C46–C47–C48–C49–C50	5.55	93.6
C25–C26–C27–C28–C29–C30	C45–C46–C47–C48–C49–C50	5.17	96.2

high-spin Mn^{II} ($S = 5/2$). The effective moment remains almost unchanged over the measured temperature range. The results indicate that there is practically no magnetic interaction between the neighboring manganese(II) ions through the bridging bimb ligand, because of the long intermetallic distance as revealed by the crystal structure.

The complex was further characterized by thermal analysis. It was stable up to 75 °C. The DTA curve shows that the complex lost weight in two steps; the TG curve shows initial endothermic loss of the water molecule between 75 and 130 °C, followed by exothermic loss of one bimb per formula unit (300 −390 °C).

Luminescence properties

The good response of the manganese(II) $^4T_1(^4G)$ state to the change of ligand field strength, symmetry and the high sensitivity of luminescence techniques, *e.g.* time resolved luminescence spectroscopy, make the Mn^{2+} $[^4T_1(^4G) \longrightarrow {}^6A_1]$ emission attractive as a diagnostic tool for co-ordination characteristics of this metal ion.[23] However, manganese(II) complexes may emit photoluminescence at low temperature and their luminescent properties at room temperature are rarely reported.[24] In our case the complex in the powdered solid state shows photoluminescence with an emission maximum at 418 nm upon excitation at 359 nm. Besides classical four- and six-co-ordinate oxide and halide species,[23] the result expands the range of manganese(II) co-ordination environments accessible by luminescence techniques.

Conclusion

A novel co-ordination polymer of the bimb ligand with manganese(II) was prepared and characterized by single crystal X-ray diffraction. An infinite 1-D cationic chain, which can also be regarded as a poly-cage, is formed by assembly of the bimb ligand with $Mn(ClO_4)_2$. The ClO_4^- ions and H_2O molecules are incorporated between the adjacent chains forming C–H···O hydrogen bonds. The polymeric structure is stabilized by close face-to-face and T-shape edge-to-face π–π interactions. The result of this study illustrates that the geometry and the rigidity of the ligand play an important role in the construction of the network structure. Systems formed by the bimb ligand with other metal ions are now being explored in our laboratory.

Acknowledgements

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