Molecular structure and spectral properties of bis(2,6-dimethoxybenzoato)(2,2′ : 6′,2″-terpyridine)manganese(II): a five-coordinate Mn(II) complex

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The mixed complex formed by Mn(II), 2,6-dimethoxybenzoate (dmb) and 2,2′ : 6′,2″-terpyridine (terpy) was isolated in the solid state and characterised by single crystal X-ray diffraction, IR and EPR, and thermogravimetric analysis. The complex is fivefold co-ordinated with a geometry shifted toward the limiting form of the trigonal bipyramid. Two carboxylate groups and the central nitrogen atom of terpy occupy the equatorial plane, while the distal nitrogen atoms are in the axial positions. The normalised bite, the angle formed by distal nitrogen (N_d and $N_{d'}$) atoms at the metal ion, the manganese–nitrogen distances, and the tilt angles between the pyridine rings were compared with those of other terpyridine complexes. Owing to the large dimensions of the Mn(II) ion, the distortions observed in the N_d–Mn–$N_{d'}$ angles and in those between the pyridine rings are the largest so far observed with first-row transition metal ions. The metal-central nitrogen and metal-distal nitrogens distances are longer than with other metal ions.

The manganese complexes of carboxylic and nitrogenous ligands provide models for the active sites of manganese enzymes. In this light, much efforts has been directed towards the synthesis of Mn(II), (III) and (IV) complexes with ligands like 2,2′-bipyridine (bpy), 1,10-phenanthroline (phen) and 2,2′ : 6′,2″-terpyridine (terpy).[1–3] A dinuclear complex with 2,2′-bipyridine, $[Mn_2(dmb)_4(bpy)_2(H_2O)_2] \cdot bpy$(dmb = 2,6-dimethoxybenzoate) was prepared in our laboratory and characterised through single crystal X-ray analysis.[4]

We have isolated the compound $[Mn^{II}(dmb)_2(terpy)]$, which exhibits a characteristic fivefold co-ordination with a distorted trigonal bipyramidal geometry. Although various co-ordination geometries are accessible to high-spin d^5 metal ions, this stereochemistry is still rare for Mn(II), which prefers octahedral hexa-co-ordinated arrangements. Only a few examples of a trigonal bipyramidal environment involving a monodentate ligand are known: $[MnCl_2(2\text{-Meim})_3]$(2-Meim = 2-methylimidazole),[5] $[Mn(dmu)_3Br_2]$(dmu = *N*,*N*′-dimethylurea)[6] and $[Mn(OBz)(3,5\text{-}i\text{-}Pr_2pzH)\{HB(3,5\text{-}i\text{-}Pr_2pz)_3\}]$ [3,5-iPr$_2$pz = 3,5-diisopropylpyrazole and HB(3,5-i-Pr$_2$pz) = hydrotris(3,5-diisopropylpyrazolylborate)].[7] This co-ordination geometry arouses great interest because binuclear or mononuclear divalent manganese complexes with N_3 ligands are structural analogues for the active site of Mn containing proteins. For instance, a trigonal bipyramidal arrangement, with an N_3O_2 ligand donor set, is adopted by Mn(II) in Mn-SOD.[8] A five-co-ordinate geometry is stabilised in the mixed complexes formed by a tridentate ligand, like terpy, and a unidentate ligand. An analysis of complexes of the type Mn(II)LX_2 (L = tridentate, X = unidentate) showed that the geometry is irregular and corresponds neither to a trigonal bipyramid of C_{2v} symmetry nor to a regular square pyramid of C_s symmetry.[9] In this study the structure of $[Mn(dmb)_2(terpy)]$ has been determined by single crystal X-ray diffraction. The co-ordination mode of terpyridine is discussed comparatively with those of other structures. Further insights derive from the spectral properties (IR and EPR) and the thermogravimetric behaviour.

Experimental

Synthesis

$[Mn(dmb)_2(H_2O)_3]_n \cdot nH_2O$ was prepared as described previously.[10] 2,2′ : 6′,2″-Terpyridine was used as commercially available. Equimolar amounts (1 mmol) of $[Mn(dmb)_2(H_2O)_3]_n \cdot nH_2O$ and terpy were dissolved in 20×10^{-3} dm^3 of absolute EtOH under stirring. A yellow crystal-like precipitate formed by slow evaporation at room temperature. It was filtered off, washed with EtOH and air-dried at room temperature. $[Mn(dmb)_2(terpy)]$: Anal. calcd. for $MnC_{33}H_{29}O_8N_3$: C, 60.93; H, 4.49; N, 6.46; Mn_2O_3, 12.1%. Found C, 60.70; H, 4.61; N, 6.48; Mn_2O_3 11.8%.

Physical measurements

Elemental analyses (C, H and N) were obtained with a Perkin–Elmer 240 B elemental analyser. IR spectra were recorded with a FT Bruker IFS-66 interferometer using KBr (4000–600 cm^{-1}) or polyethylene (500–100 cm^{-1}) disks. Thermogravimetric data were obtained with a Perkin–Elmer TGS-2 apparatus in air and under nitrogen flow. X-band EPR spectra (9.15 GHz) were recorded on polycrystalline samples at 298 K with a Varian E-9 spectrometer and simulated by use of the Bruker WIN-EPR SimFonia program. Magnetic susceptibility data were obtained at room temperature with a Bruker BM-4 system and corrected for diamagnetism using Pascal's constants.

Crystal structure analysis

A summary of crystal parameters and details of the data collection are given in Table 1; selected bond lengths and angles are listed in Table 2.

Intensity data were taken on an Enraf–Nonius MACH3 computer-controlled diffractometer.[11] Data reduction was carried out with XCAD4.[12] The structure was solved by the SIR-97 software[13] and refined on F^2 by the program SHELXL93.[14] The $P2_1/a$ space group assigned to the compound is consistent with the setting originally determined. Of

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Table 1 Crystal data experimental details for [Mn(dmb)$_2$(terpy)]

Formula	$MnC_{33}H_{29}O_8N_3$
Formula weight	650.53
Crystal system	Monoclinic
Space group	$P2_1/a$
a/Å	13.559(2)
b/Å	14.745(3)
c/Å	16.186(1)
β(°)	111.93(2)
U/Å^3	3001.9
Z	4
μ/mm^{-1}	0.498
T/K	293(2)
Measured reflections	4612
Independent reflections	4235
Reflections with $I > 2\sigma(I)$	2070
R_{int}	0.01
R (F)	0.0588
wR (F^2) [$I > 2\sigma(I)$]^a	0.1085
wR (F^2) (all data)^a	0.1475

^{a} $w = 1/[\sigma^2 (F_0^2) + (0.0371\ P)^2 + 6.6740\ P]$ where $P = (F_0^2 + 2\ F_c^2)/3$.

course, it could be transformed to the standard $P2_1/c$ setting. The best data set involved more than half of the reflections with I less than $2\sigma(I)$. However, this factor is not critical as the R value, the residual electron density, the data-parameter ratio, *etc.* are very good. Atomic scattering factors were taken from ref. 15. No extinction corrections were applied. The software used to prepare material for publication was WINGX.[16] All non-hydrogen atoms were anisotropically refined. Hydrogen atoms were placed in their calculated positions and refined using a riding model.

CCDC reference number 440/196. See http://www.rsc.org/suppdata/nj/b0/b002119i/ for crystallographic files in .cif format.

Results and discussion

Structure of [Mn(dmb)$_2$(terpy)]

The Mn(II)LX$_2$ (L = tridentate ligand, X = unidentate ligand) stereochemistry has been studied in terms of a repulsion energy model.[9,17] A distinctive parameter is the normalized bite, defined as $b = 2\ \sin(\delta/2)$, where δ is the average angle formed by the axes joining the metal ion to the central and to the distal donors of the tridentate ligand. For $b < 1.40$ the stereochemistry is close to trigonal bipyramid with the tridentate ligand spanning axial-equatorial-axial sites. With $b = 1.55$ the stereochemistry is square pyramid with the tridentate ligand spanning basal-apical-basal sites. At $b = 1.73$ the stereochemistry reverts to trigonal bipyramid with the tridentate ligand bound in the three equatorial sites.

Table 2 Selected bond lengths (Å) and angles (°)

Mn–O(1″)	2.099(4)	C(7′)–O(1′)	1.259(7)
Mn–O(1′)	2.156(4)	C(7′)–O(2′)	1.249(7)
Mn–N(2)	2.226(5)	C(7″)–O(1″)	1.255(7)
Mn–N(3)	2.248(5)	C(7″)–O(2″)	1.223(7)
Mn–N(1)	2.310(5)		
O(1″)–Mn–O(1′)	99.9(2)	C(15)–N(3)–Mn	123.4(5)
O(1″)–Mn–N(1)	86.1(2)	C(1)–N(1)–C(5)	119.6(6)
O(1′)–Mn–N(1)	99.4(2)	C(6)–N(2)–C(10)	119.5(6)
O(1″)–Mn–N(2)	108.0(2)	C(11)–N(3)–C(15)	117.5(5)
O(1′)–Mn–N(2)	149.7(2)	N(1)–C(5)–C(6)	116.1(6)
O(1″)–Mn–N(3)	117.8(2)	N(2)–C(6)–C(5)	114.7(6)
O(1′)–Mn–N(3)	106.2(2)	N(2)–C(10)–C(11)	113.7(6)
N(1)–Mn–N(2)	71.6(2)	N(3)–C(11)–C(10)	115.2(5)
N(1)–Mn–N(3)	140.4(2)	C(4)–C(5)–C(6)	121.9(7)
N(2)–Mn–N(3)	71.1(2)	C(5)–C(6)–C(7)	124.3(7)
C(1)–N(1)–Mn	123.8(5)	C(9)–C(10)–C(11)	123.6(6)
C(5)–N(1)–Mn	116.0(4)	C(10)–C(11)–C(12)	123.8(6)
C(6)–N(2)–Mn	119.3(4)	O(1′)–C(7′)– O(2′)	122.1(7)
C(10)–N(2)–Mn	121.1(5)	O(1″)–C(7″)– O(2″)	125.5(6)
C(11)–N(3)–Mn	118.7(4)		

A perspective view of the molecular structure of [Mn(dmb)$_2$(terpy)] with atom numbering is presented in Fig. 1. The metal ion is in the center of a distorted trigonal bipyramid. The equatorial plane is occupied by the O(1′) and O(1″) atoms of the carboxylate groups of dmb and the central nitrogen (N$_c$) atom of terpy, N(2). The distal nitrogen atoms (N$_{d,\ d'}$) of terpy are in the axial positions, N(1) and N(3). The magnitude of the normalized bite of the terpy ligand is 1.17. The angle formed by the Mn–O bonds is 99.9°. The Mn–O(1′) bond (2.156 Å) is longer than Mn–O(1″) (2.099 Å). In addition, the angle O(1′)–Mn–N(2) (149.7°) is much greater than O(1″)–Mn–N(2) (108.0°). The stereochemistry is distorted toward a square pyramid with the N(1), N(2), N(3) and O(1″) atoms approaching planarity. The Mn(II) distance from the O(1′)–O(1″)–N(2) plane is 0.18 Å; the torsion angle of O(1′)–O(1″)–N(2)–Mn is 8°. The angle between N(1)–N(2)–N(3)–Mn and O(1′)–O(1″)–N(2)–Mn planes is 78.7°.

The magnitude of the N$_d$–Mn–N$_{d'}$ angle is reduced from 180°, as is found in other mono- and bis-terpy complexes.[18–25] Because of the larger size of the Mn(II) ion, the deviation is greater than for other first-row transition metal ions (Table 3). The N$_{d,\ d'}$–M–N$_c$ angle follows closely the size of the metal ion, the angle being smaller the larger is the cation. Indeed, large metal ions give rise to longer M–N distances and to a greater distortion of the terpyridine molecule.

The manganese(II)–nitrogen bonds are normal, though the Mn–N$_c$ distance (2.226 Å) is shorter than the average Mn–N$_{d,\ d'}$ (2.279 Å) bond length. This distortion is always observed in terpy complexes and is attributed to a more efficient overlap of the metal t_{2g} orbitals with the π^* orbitals of the central pyridyl moiety in comparison with the distal pyridyl rings.[26] In our complex the difference in bond lengths (0.05 Å) is smaller than seen for other first-row transition metal ions (Table 3) and comparable with that observed for high-spin [Mn^{II}(terpy)$_2$](I$_3$)$_2$ (0.06 Å).[19]

A linear correlation may be found between the magnitude of the N$_d$–N$_c$–N$_{d'}$ angle and the average M–N distance (see Fig. 2 in ref. 23). The angle of 109° is well correlated to the average Mn–N distance of our structure (2.261 Å). A linear correlation between the normalised bite and the average M–N distance was also established (see Fig. 2 in ref. 23). The distance of 2.261 Å is in fairly good agreement with the ligand bite of 1.17.

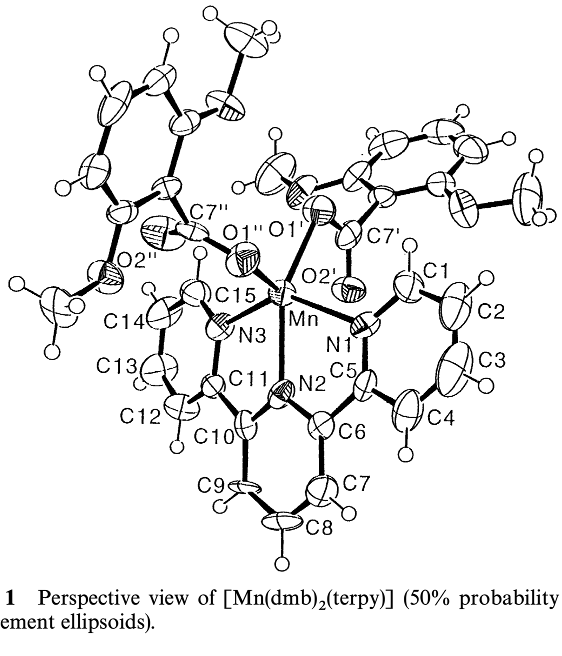

Fig. 1 Perspective view of [Mn(dmb)$_2$(terpy)] (50% probability displacement ellipsoids).

Table 3 Metrical details of terpy complexes (average values)

	Ionic radius/Å	$N_{d,d'}$–M–N_c/°	N_d–M–$N_{d'}$/°	M–N_c/Å	M–$N_{d,d'}$/Å	Δ^a/Å	$\Delta_{ring}{}^b$/°	Ref.
$[Cr^{III}(terpy)_2]ClO_4$	0.63	78.7	157.3	1.975	2.056	0.081		18
$[Mn^{II}(terpy)_2](I_3)_2$	0.80	72.3	144.5	2.19	2.25	0.06	9.7	19
$[Mn^{II}(dmb)_2(terpy)]$	0.80	71.3	140.4	2.226	2.279	0.053	10.4–13.5	This work
$[Fe^{II}(terpy)_2](ClO_4)_2$	0.74	80.6	161.1	1.891	1.988	0.097	<2	20
$[Co^{II}(terpy)_2]I_2 \cdot 2H_2O$	0.72	78.9	157.9	1.927	2.094	0.167	2.6	21
$[Co^{II}(terpy)_2](ClO_4)_2 \cdot 1.3H_2O$	0.72	76.7	153.6	2.028	2.137	0.109	1.4–2.7	22
$[Co^{III}(terpy)_2]Cl_3$	0.63	82.1	164.3	1.858	1.928	0.07	1.9–4.4	23
$[Ni^{II}(terpy)(NCO)_2(H_2O)]$	0.69	77.5	154.8	2.047	2.159	0.112		24
$[Cu^{I}(PPh_3)_2(terpy)]ClO_4$	0.96	73.0	146.1	2.102	2.460	0.358	27.5–31.3	29
$[Cu^{II}(terpy)_2](NO_3)_2$	0.72	77.4	154.7	1.988	2.085	0.097		25

[a] Difference between M–$N_{d,d'}$ and M–N_c. [b] Dihedral angle between the adjacent NC_5 rings in terpy.

The pyridyl rings are planar with a maximum deviation of 0.014 Å. The rings are tilted with respect to each other in order to permit the accommodation of the Mn–N bonds. The dihedral angles between the adjacent N(1), N(2) and N(2), N(3) rings are 13.5° and 10.4°, respectively, if the planes are defined as the rms planes with all the atoms: [N(1), C(1), C(2), C(3), C(4), C(5)], [N(2), C(6), C(7), C(8), C(9), C(10)], and [N(3), C(11), C(12), C(13), C(14), C(15)]. Smaller deviations from planarity are observed in terpyridine co-ordinated to metal ions of smaller size (Table 3). Dihedral angles in the range 0.65–3.29° are measured between the pyridyl rings of terpy complexes of Cu(II).[27,28] In contrast, angles of 27.5 and 31.3° are measured with the larger Cu(I) ion.[29]

A significant strain is evident at the junctions between the adjacent pyridine rings as a decrease of up to 6.3° from the ideal 120° value is measured in the inter-ring angles. In contrast, the deviations in the intra-ring angles are generally less than 2.0° and, at most, 4.1°. The distortion of the pyridine rings is indicated by the magnitude of the angles at the nitrogen atoms. The C(6)–N(2)–C(10) angle in the central ring is almost regular (119.5°), whereas the corresponding angles at N(1) and N(3) are 119.6 and 117.5°, respectively. It can be seen that the smallest C–N–C angle is C(11)–N(3)–C(15). Nevertheless, N(3) is close to Mn as N(2). Instead, N(1) and N(2) exhibit similar angles in spite of the very different bond lengths. The angles Mn–N(2)–C(*i*) (*i* = 6, 10) (average value = 120.2°) are more regular than Mn–N(1)–C(5) and Mn–N(3)–C(11) (average value = 117.3°) and than Mn–N(1)–C(1) and Mn–N(3)–C(15) (average value = 123.6°). Similar values are observed for $[Fe(terpy)_2](ClO_4)_2$.[20] The largest distortions involve the decrease of N–C–C angles within the chelated rings. To improve the overlap between the orbitals of terpy and those of Mn(II), the inter-pyridine angles decrease from 120° to an average value of 114.9° for N(1)–C(5)–C(6), C(5)–C(6)–N(2), N(2)–C(10)–C(11) and C(10)–C(11)–N(3). In comparison, values of 112.8° and 112.7° were measured in $[Fe(terpy)_2](ClO_4)_2$[20] and $[Co(terpy)_2]Cl_3$,[23] respectively, as an effect of a shorter metal–nitrogen distance and a more efficient orbital overlap. As a consequence, the inter-ring "external" angles C(4)–C(5)–C(6), C(5)–C(6)–C(7), C(9)–C(10)–C(11) and C(10)–C(11)–C(12) increase to 121.9–124.3°.

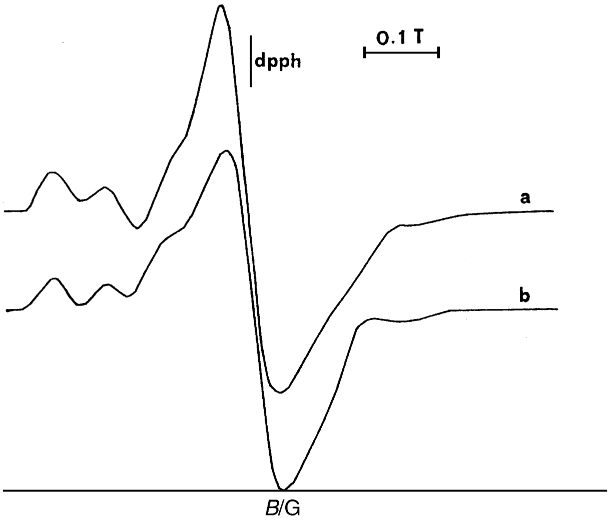

Fig. 2 (*a*) Experimental and (*b*) simulated EPR spectra recorded on a polycrystalline sample of $[Mn(dmb)_2(terpy)]$ at the X-band frequency.

The metrical details of the 2,6-dimethoxybenzoato ligand are normal.[4] The Mn–O(1″) and Mn–O(1′) distances are 2.099 and 2.156 Å, respectively, consistent with the distortion of the trigonal bipyramid toward the square pyramid with the longer Mn–O(1′) bond pointing along the axial direction.

Infrared and thermal properties

The terpyridine vibration modes do not shift appreciably upon complex formation. Indeed, the absorption bands of bpy, phen and terpy are not very metal-sensitive, since they originate from the heterocyclic or aromatic ring of the ligand. Thus, the main interest may be focused on the ν(M–N) vibrations. For a Mn(II) ion in high-spin configuration the stretch of the metal–nitrogen bond is expected in the 180–290 cm^{-1} region. Our compound displays an absorption at 234 cm^{-1}, comparable with that observed at 224 cm^{-1} for $[Mn(bpy)_3]^{2+}$.[30] Distinctive IR bands are the stretching vibrations of the carboxylate (ν_{as} and ν_s: 1593 and 1437 cm^{-1}, respectively). The value of $\Delta(\nu_{as} - \nu_s)$, 156 cm^{-1}, is in agreement with the monodentate co-ordination of dmb.[4,10]

Thermogravimetric measurements performed on the nitrogenous adducts of $Mn(dmb)_2$, like $[Mn(dmb)_2(2\text{-}Mepz)_2(H_2O)_2]$ and $[Mn_2(dmb)_4(bpy)_2(H_2O)_2] \cdot bpy$,[9] indicated that the release of the water molecules and nitrogenous bases, yielding a binary Mn(II)-dmb complex, occurs below 170 °C, whereas the final decomposition occurs above 230 °C.[31] The behaviour of $[Mn(dmb)_2(terpy)]$ is different and confirms the stable tridentate co-ordination of terpy. Indeed, the decomposition occurs at about 340 °C in a very narrow temperature range, giving directly a Mn_2O_3 residue. This indicates that the strong binding of terpyridine to manganese enhances the thermal stability of the complex.

Magnetic data

A magnetic moment of 6.02 μ_B was measured at room temperature, consistent with the expected spin-only value of an $S = 5/2$ Mn(II) complex. For a high-spin d^5 metal ion the following spin Hamiltonian may be considered:

$$H = \beta \mathbf{S} \cdot \mathbf{g} \cdot \mathbf{H} + D[S_z{}^2 - 1/3S(S+1)] + E(S_x{}^2 - S_y{}^2)$$

The higher terms are usually negligible and could be omitted. *D* and *E* correspond to the tetragonal and rhombic distortion, respectively. The $\lambda = E/D$ ratio ranges from 0, in the case of an axial symmetry, to 1/3, in the limit of the maximum rhombic distortion.

The main features of the polycrystalline EPR spectrum of our compound, collected at the X-band frequency and shown in Fig. 2, are a strong band around $g_{\mathrm{eff}} \sim 2$, three bands at $\sim$0.070, $\sim$0.150 and $\sim$0.230 T and two resonances above 0.400 T, a shoulder at $\sim$0.460 T and a band at 0.570 T. These features indicate $0 < \lambda < 0.33$, consistent with a structure intermediate between the trigonal bipyramid and the square pyramid. Based on the diagrams published by Dowsing and Gibson,[32] the position of the high-field absorption gives an indication of the D value: the higher the field value of the band, the higher is the value of D. In our case the position of the high-field absorption at 0.570 T is characteristic of a D value approximately in the range 0.05–0.08 cm^{-1}. A reasonably good fit of the EPR spectrum was obtained with the following parameters: $g_x = 2.01$, $g_y = 2.01$, $g_z = 2.05$, $D = 0.0567$ cm^{-1} and $E = 0.0104$ cm^{-1} ($\lambda = 0.183$), see Fig. 2.

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