An unusual β-diketone coordination mode. Crystal structure of bis(1,3-bis(2-hydroxyphenyl)-1,3-propanedione)tetrakispyridine dimanganese(III)

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(Received May 7, 1990; revised July 25, 1990)

Abstract

An unusual β-diketone coordination mode is reported here for the first time. A dinuclear Mn(III) compound is obtained by reaction, in open atmosphere and basic medium, of a mononuclear, β-diketone like complex of the trinucleating ligand 1,3-bis(2-hydroxyphenyl)-1,3-propanedione with a Mn(II) salt. The aforementioned molecule is a potentially trinucleating ligand with three coordination sites: the most reactive is the central β-diketone moiety, while the outer are the less reactive. In the Mn(III) complex both metal ions are occupying the two outer sites. The compound bis(1,3-bis(2-hydroxyphenyl)-1,3-propanedione)tetrakispyridine dimanganese(III), $C_{50}H_{38}N_4O_8Mn_2$, is monoclinic, space group $P2_1/n$, $a=16.093(5)$, $b=17.062(4)$, $c=31.449(6)$ Å, $\beta=93.09(2)°$, $V=8622.7$ Å^3, $Z=8$, $D_x=1.44$ Mg m^{-3}, μ(Mo Kα)$=6.20$ cm^{-1}. 4516 final data for 259 refined parameters. $R=0.076$, $R_w=0.081$. Mn–Mn distance in the dinuclear compound is 5.295(2) Å.

Introduction

As part of our research program about polynuclear complexes and synthesis directing ligands, we have focused our interest on trinucleating ligands in order to synthesize linear homo (M–M–M) or heterotrinuclear complexes of the type M–M'–M or M'–M–M'. The compound 1,3-bis(2-hydroxyphenyl)-1,3-propanedione (bhppH$_3$) (Fig. 1) is an excellent ligand affording mononuclear complexes with divalent transition metal ions of formula M(bhppH$_2$)$_2$ [1]. In these complexes the metal ion is coordinated, in a square-planar fashion, by two ligands, through the central β-diketone fragments, [2], achieving the hexacoordination by solvent molecules. In the case of the lithium complex the coordination is tetrahedral [3]. The mononuclear divalent metal complexes are potential trinucleating ligands. Trinuclear complexes of the type UO$_2$–M–UO$_2$ have already been reported by us, M being first row divalent transition metal ions [4]. In all these cases, the most reactive coordination site appears to be the inner β-diketone moiety, so the first metallic ion to be coordinated is located at this position. Only by forcing the experimental conditions, a second and third ion, enter the less reactive outer coordination sites. Surprisingly, when any mononuclear complex [M(bhppH$_2$)$_2$] is treated with a Mn(II) salt in basic medium and in open atmosphere, a dinuclear Mn(III) is formed, where both metal ions are located at the outer coordination sites, the inner position becoming vacant. To the best of our knowledge this type of reactivity is completely unusual in the β-diketone chemistry and is reported for the first time in this paper.

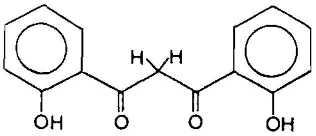

Fig. 1. 1,3-Bis(2-hydroxyphenyl)-1,3-propanedione.

Experimental

Starting materials

The ligand 1,3-bis(2-hydroxyphenyl)-1,3-propanedione (bhppH$_3$) was prepared following literature methods [1, 5]. The mononuclear complexes

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0020-1693/90/$3.50

[$M(bhppH_2)_2$, M = Co(II), Ni(II), Zn(II), Cd(II)] were prepared as already described by us [1, 2]. All operations were performed in open atmosphere. Reagents and solvents were commercial grade materials and were used without further purification. Microanalyses (C, H, N) were performed in our analytical laboratory on a Perkin-Elmer 240-B instrument. IR spectra were obtained on a Perkin-Elmer FT spectrophotometer as KBr pellets. Electronic spectra were run on a Shimadzu UV 240B spectrophotometer.

Synthesis of the dinuclear complexes

$Zn(bhppH_2)_2 \cdot 2Me(OH)$ (250 mg, 4 mmol) was dissolved in a mixture of methanol (150 ml) and triethylamine (TEA) (10 ml) at refluxing conditions. $Mn(CH_3COO)_2$ (200 mg) in methanol (10 ml) was added to the aforementioned clear solution and the colour of the mixture changed to dark red. The solution was concentrated to a third of its initial volume and water (200 ml) was added. A dark-yellow precipitate appeared which was filtered. This solid could never be satisfactorily characterized, chemical analyses indicating the presence of Zn and Mn in it. This uncharacterized solid was digested for 40 min with warm pyridine (60 °C) and finally the mixture was filtered. The resulting dark-red solution was concentrated and let to stand in open atmosphere until a dark-red crystalline precipitate appeared. The compound obtained was a Mn(III) complex. The same compound was obtained regardless of the nature of the mononuclear [$M(bhppH_2)_2$] complex used in the synthesis (M = Mn, Co, Ni, Zn, Cd). *Anal.* Calc. for $Mn_2(bhpp)_2 \cdot 4py$: C, 64.37; N, 6.00; H, 4.07. Found: C, 63.8; N, 5.9; H, 4.1%. Electronic spectra: 575 nm ($\epsilon = 500$).

Crystallography and structure determination

Red single crystals (green by reflected light) of $C_{50}H_{38}N_4O_8Mn_2$ were directly obtained from the synthesis process indicated above. They are monoclinic, space group $P2_1/n$, $a = 16.093(5)$, $b = 17.062(4)$, $c = 31.449(6)$ Å, $\beta = 93.09(2)°$, $V = 8622.7$ Å^3, $Z = 8$, $D_x = 1.44$ Mg m^{-3}, μ(Mo Kα) = 6.20 cm^{-1}. X-ray diffraction data at 293 K were collected with an Enraf-Nonius CAD4 diffractometer using graphite crystal monochromated Mo Kα radiation ($\lambda = 0.71069$ Å) on a 0.12×0.18×0.22 mm crystal. The number of independent reflections collected by using the ω–2θ technique and $2\theta < 47$ was 12 777, these are included between $-18 \leqslant h \leqslant 18$, $0 \leqslant k \leqslant 19$, $0 \leqslant l \leqslant 35$.

The non-unique data were averaged and the resulting intensities were corrected for Lorentz and polarization effects. The structure was solved by direct methods [6] and refined by full-matrix least-squares [7]. Due to the large number of atoms in the asymmetric unit (128 non-H atoms), only metallic and oxygen atoms have been refined using anisotropic thermal parameters, the remaining C and N atoms were refined isotropically. The final residuals for 259 refined parameters against 4516 data for which $F > 5\sigma(F)$ were $R = 0.076$ and $R_w = 0.081$ ($w = 1/(\sigma^2(F) + 0.001409F^2)$). In a final difference Fourier synthesis the maximum and minimum heights were 0.61 and -0.42 e Å^{-3}.

The scattering factors were taken from the International Tables for X-ray Crystallography [8]. Atomic coordinates with equivalent temperature factors are listed in Table 1. Bond distances and angles are listed in Table 2.

Magnetic measurements

Magnetic measurements were run in a Faraday type equipment in the 300–77 K temperature range. The balance was calibrated with standard $Hg[Co(SCN)_4]$. Pascal Tables were used for diamagnetic corrections, but no attempts were made to introduce TIP corrections.

Results and discussion

General chemistry

Mn(III) has a far more extensive chemistry than any of the other high oxidation states of this element. Mn(III) is fairly stable in fluoro, chloro, cyano, oxo, carboxylato, β-diketonate [9]. The Mn(III) dinuclear complexes described in this paper were synthesized by reaction of a mononuclear [$M(bhppH_2)_2$] complex with a Mn(II) salt (M = Zn(II), Cd(II), Ni(II), Co(II), Mn(II)). Regardless of the starting mononuclear complex used in the synthesis, the final complex obtained had the formula $Mn_2(bhpp)_2 \cdot 4py$. The reactions used are schematically represented in eqn. (1).

$$M(bhppH_2)_2 \cdot xROH + Mn(CH_3COO)_2 \xrightarrow[\text{TEA}]{\text{methanol}}$$

$$\text{'MnMMn(bhpp)}_2\text{'} \xrightarrow[\text{open vessel}]{\text{pyridine}} MnMn(bhpp)_2 \cdot 4py \qquad (1)$$

This scheme implies a complex set of reactions, involving replacement of the original central metal ion of the mononuclear complex and oxidation of the Mn(II) ion. This oxidation is favoured by the stabilization of the Mn(III) by ligands containing hard coordinating elements [9], such as O or N. On the other hand, several Mn(III) complexes with Schiff base ligands, prepared by bubbling O_2 through a solution of the appropriate Mn(II) complex [10–12], have been described in the literature. It is worth

TABLE 1. Fractional atomic coordinates ($\times 10^4$) with the equivalent temperature factors

	x/a	y/b	z/c	B_{eq}
Mn1	-3626(2)	-451(2)	2896(1)	4.54
Mn2	-6565(2)	-347(2)	2056(1)	4.40
O1	-2521(7)	-324(9)	2712(5)	5.46
O7	-4021(8)	-528(8)	2315(4)	4.29
O9	-5440(8)	-270(8)	1914(5)	4.46
O15	-6906(9)	-383(9)	1472(5)	5.12
O16	-7660(8)	-440(9)	2229(5)	5.92
O22	-6162(9)	-312(9)	2635(5)	5.16
O24	-4754(7)	-575(8)	3041(4)	4.56
O30	-3293(8)	-389(10)	3467(4)	5.97
Mn3	271(2)	-1491(2)	5145(1)	4.22
O31	82(8)	-2414(9)	4830(4)	4.84
O37	-33(9)	-879(8)	4675(5)	5.18
O39	-489(8)	539(8)	4557(4)	4.44
O45	565(8)	-2068(7)	5643(5)	5.00
Mn4	-10285(2)	-1501(2)	-119(1)	4.06
O46	573(9)	2096(8)	600(5)	4.59
O52	484(8)	571(8)	438(5)	4.62
O54	-34(9)	867(9)	-360(5)	4.93
O60	106(8)	2399(8)	-224(5)	4.40
C1	-2249(8)	-382(9)	2326(4)	4.80
C2	-1388(8)	-321(9)	2305(4)	4.98
C3	-1027(8)	-371(9)	1212(4)	7.04
C4	-1528(8)	-482(9)	1541(4)	7.17
C5	-2389(8)	-543(9)	1563(4)	5.25
C6	-2750(8)	-493(9)	1955(4)	3.41
C7	-3659(12)	-461(12)	1937(7)	4.29
C8	-4203(11)	-469(11)	1592(6)	3.55
C9	-5071(11)	-413(13)	1568(6)	4.14
C10	-5577(9)	-527(9)	1172(4)	4.15
C11	-5165(9)	-670(9)	801(4)	6.57
C12	-5621(9)	-801(9)	417(4)	8.25
C13	-6489(9)	-789(9)	405(4)	7.70
C14	-6901(9)	-646(9)	777(4)	6.39
C15	-6445(9)	-515(9)	1160(4)	5.92
C16	-7928(8)	-394(9)	2618(4)	4.86
C17	-8792(8)	-414(9)	2635(4)	5.79
C18	-9157(8)	-375(9)	3027(4)	6.23
C19	-8657(8)	-316(9)	3402(4)	5.88
C20	-7793(8)	-297(9)	3385(4)	5.11
C21	-7428(8)	-336(9)	2993(4)	4.48
C22	-6517(11)	-376(14)	2989(7)	5.51
C23	-6014(11)	-407(12)	3367(6)	4.29
C24	-5131(10)	-474(11)	3385(5)	3.76
C25	-4637(9)	-493(9)	3785(4)	4.38
C26	-5048(9)	-549(9)	4164(4)	6.63
C27	-4591(9)	-597(9)	4552(4)	6.69
C28	-3723(9)	-590(9)	4563(4)	8.45
C29	-3313(9)	-534(9)	4185(4)	7.90
C30	-3770(9)	-486(9)	3796(4)	5.57
N101	-3887(12)	864(11)	2878(6)	5.89
C102	-3467(15)	1355(17)	3175(9)	7.81
C103	-3612(18)	2180(19)	3154(10)	9.72
C104	-4163(19)	2466(19)	2854(10)	9.86
C105	-4642(17)	1995(19)	2573(10)	9.39
C106	-4485(15)	1158(16)	2597(8)	7.06
N107	8449(11)	3199(11)	2053(6)	5.46
C108	7756(16)	2819(17)	2192(8)	8.25
C109	7612(17)	2014(18)	2118(9)	8.84
C110	8140(16)	1598(16)	1868(8)	7.50
C111	8850(16)	1969(16)	1733(8)	7.67
C112	8958(15)	2770(16)	1842(8)	7.56
N201	-6378(11)	-1670(12)	2028(6)	6.39
C202	-5691(15)	-1949(15)	2257(8)	7.51
C203	-5474(20)	-2755(21)	2202(10)	11.00
C204	-6008(19)	-3173(18)	1941(10)	9.09
C205	-6661(20)	-2922(20)	1739(10)	10.36
C206	-6922(17)	-2077(18)	1773(9)	8.76
N207	-6642(11)	1005(11)	2026(6)	5.46
C208	-6804(15)	1444(16)	2376(8)	7.65
C209	-6882(16)	2274(18)	2328(9)	9.32
C210	-6691(16)	2600(18)	1938(10)	7.64
C211	-6515(17)	2174(19)	1581(10)	10.06
C212	-6501(14)	1307(16)	1646(9)	6.97
C31	-184(8)	-2490(9)	4426(3)	3.77
C32	-192(8)	-3255(9)	4270(3)	5.13
C33	-458(8)	-3403(9)	3848(3)	6.48
C34	-717(8)	-2786(9)	3582(3)	6.55
C35	-708(8)	-2020(9)	3738(3)	6.02
C36	-442(8)	-1872(9)	4160(3)	4.00
C37	-394(13)	-1045(10)	4315(7)	3.67
C38	-702(11)	-415(13)	4045(6)	4.30
C39	-693(11)	390(13)	4168(7)	3.55
C40	-915(8)	1013(8)	3865(5)	4.60
C41	-1211(8)	814(8)	3454(5)	6.02
C42	-1384(8)	1400(8)	3153(5)	6.61
C43	-1262(8)	2186(8)	3263(5)	6.54
C44	-966(8)	2385(8)	3674(5)	4.75
C45	-793(8)	1799(8)	3975(5)	4.79
N301	1075(11)	1401(14)	4660(6)	6.41
C302	1514(17)	2059(16)	4551(8)	8.01
C303	2370(17)	1917(17)	4398(9)	8.68
C304	2661(18)	1169(19)	4384(9)	9.12
C305	2243(16)	528(16)	4501(9)	7.86
C306	1395(15)	686(16)	4663(8)	6.60
N307	8360(11)	1449(11)	5049(7)	5.04
C308	8172(14)	1658(15)	5439(8)	5.52
C309	7325(16)	1734(15)	5568(8)	6.88
C310	6704(15)	1591(17)	5278(9)	7.06
C311	6908(15)	1351(15)	4871(9)	6.19
C312	7743(14)	1260(14)	4763(7)	5.85
C46	0771(8)	1849(9)	999(3)	3.96
C47	903(8)	2457(9)	1291(3)	4.74
C48	1124(8)	2288(9)	1716(3)	5.12
C49	1214(8)	1511(9)	1849(3)	5.50
C50	1083(8)	903(9)	1556(3)	4.64
C51	861(8)	1072(9)	1131(3)	4.47
C52	667(11)	398(13)	825(7)	3.71
C53	695(11)	-369(13)	972(6)	4.30
C54	429(13)	-988(12)	718(7)	3.28
C55	491(8)	-1827(7)	879(5)	4.50
C56	812(8)	-1967(7)	1293(5)	5.76
C57	817(8)	-2726(7)	1458(5)	7.99
C58	502(8)	-3346(7)	1209(5)	5.52
C59	181(8)	-3206(7)	795(5)	4.57
C60	175(8)	-2447(7)	630(5)	5.11
N401	1646(10)	1401(11)	9914(6)	4.67

(*continued*)

TABLE 1. (*continued*)

	x/*a*	*y*/*b*	*z*/*c*	B_{eq}
C402	1866(15)	1677(15)	9535(8)	6.49
C403	2722(17)	1761(16)	9447(9)	7.16
C404	3307(15)	1553(16)	9750(9)	6.59
C405	3102(19)	1262(19)	10142(11)	9.61
C406	2233(16)	1201(16)	10215(8)	6.71
N407	−1049(11)	1455(15)	320(6)	6.40
C408	−1385(21)	2134(20)	460(10)	9.29
C409	−2208(21)	2100(22)	634(11)	10.87
C410	−2529(17)	1394(22)	713(9)	9.37
C411	−2172(20)	675(20)	567(10)	9.90
C412	−1421(18)	769(18)	373(9)	7.58

TABLE 2. Bond lengths (Å) and bond angles (°)

Bond lengths		Bond lengths	
O1–Mn1	1.911(13)	C21–C20	1.395(17)
O7–Mn1	1.909(13)	C22–C21	1.468(22)
O24–Mn1	1.908(13)	C23–C22	1.402(27)
O30–Mn1	1.847(14)	C24–C23	1.425(24)
N101–Mn1	2.282(19)	C25–C24	1.454(21)
N107–Mn1	2.390(24)	C26–C25	1.395(19)
O9–Mn2	1.892(13)	C30–C25	1.395(20)
O15–Mn2	1.890(15)	C27–C26	1.395(18)
O16–Mn2	1.878(14)	C28–C27	1.395(20)
O22–Mn2	1.899(15)	C29–C28	1.395(19)
N201–Mn2	2.280(21)	C30–C29	1.395(18)
N207–Mn2	2.311(19)	C102–N101	1.402(33)
C1–O1	1.317(19)	C106–N101	1.366(31)
C7–O7	1.354(25)	C103–C102	1.427(44)
C9–O9	1.291(23)	C104–C103	1.351(43)
C15–O15	1.282(20)	C105–C104	1.396(43)
C16–O16	1.323(19)	C106–C105	1.452(41)
C22–O22	1.285(26)	C108–N107	1.382(32)
C24–O24	1.278(22)	C112–N107	1.306(31)
C30–O30	1.331(19)	C109–C108	1.411(41)
C2–C1	1.395(19)	C110–C109	1.384(39)
C6–C1	1.395(16)	C111–C110	1.392(37)
C3–C2	1.395(17)	C112–C111	1.417(38)
C4–C3	1.395(16)	C202–N201	1.370(30)
C5–C4	1.395(19)	C206–N201	1.348(33)
C6–C5	1.395(17)	C203–C202	1.432(44)
C7–C6	1.463(23)	C204–C203	1.359(44)
C8–C7	1.358(27)	C205–C204	1.272(44)
C9–C8	1.397(25)	C206–C205	1.508(46)
C10–C9	1.464(22)	C208–N207	1.368(32)
C11–C10	1.395(19)	C212–N207	1.334(33)
C15–C10	1.395(20)	C209–C208	1.430(41)
C12–C11	1.395(18)	C210–C209	1.397(42)
C13–C12	1.395(20)	C211–C210	1.380(44)
C14–C13	1.395(19)	C212–C211	1.494(43)
C15–C14	1.395(18)	O31–Mn3	1.876(15)
C17–C16	1.395(19)	O37–Mn3	1.852(15)
C21–C16	1.395(17)	O45–Mn3	1.889(15)
C18–C17	1.395(17)	C31–O31	1.325(16)
C19–C18	1.395(17)	C37–O37	1.277(26)
C20–C19	1.395(19)	C39–O39	1.274(26)

(*continued*)

TABLE 2. (*continued*)

Bond lengths		Bond lengths	
C32–C31	1.395(21)	C52–O52	1.271(27)
C36–C31	1.395(19)	C47–C46	1.395(19)
C33–C32	1.395(15)	C51–C46	1.395(22)
C34–C33	1.395(19)	C48–C47	1.395(15)
C35–C34	1.395(21)	C49–C48	1.395(22)
C36–C35	1.395(15)	C50–C49	1.395(19)
C37–C36	1.494(24)	C51–C50	1.395(15)
C38–C37	1.440(28)	C52–C51	1.522(26)
C39–C38	1.427(31)	C53–C52	1.387(32)
C40–C39	1.460(26)	C54–C53	1.378(29)
C41–C40	1.395(20)	C55–C54	1.521(23)
C45–C40	1.395(19)	C56–C55	1.395(21)
C42–C41	1.395(20)	C60–C55	1.395(18)
C43–C42	1.395(19)	C57–C56	1.395(17)
C44–C43	1.395(20)	C58–C57	1.395(18)
C45–C44	1.395(20)	C59–C58	1.395(21)
C302–N301	1.381(35)	C60–C59	1.395(17)
C306–N301	1.324(35)	C402–N401	1.347(32)
C303–C302	1.503(39)	C406–N401	1.345(30)
C304–C303	1.361(44)	C403–C402	1.428(36)
C305–C304	1.345(42)	C404–C403	1.351(36)
C306–C305	1.506(36)	C405–C404	1.385(43)
C308–N307	1.327(33)	C406–C405	1.433(40)
C312–N307	1.344(29)	C408–N407	1.362(41)
C309–C308	1.448(35)	C412–N407	1.328(38)
C310–C309	1.338(36)	C409–C408	1.462(49)
C311–C310	1.402(39)	C410–C409	1.339(51)
C312–C311	1.412(34)	C411–C410	1.442(48)
C46–O46	1.345(18)	C412–C411	1.391(44)
Bond angles		Bond angles	
O7–Mn1–O1	89.1(0.6)	C15–O15–Mn2	126.9(1.1)
O24–Mn1–O1	176.1(0.6)	C16–O16–Mn2	12.83(1.1)
O24–Mn1–O7	87.1(0.6)	C22–O22–Mn2	133.1(1.3)
O30–Mn1–O1	93.6(0.6)	C24–O24–Mn1	133.4(1.2)
O30–Mn1–O7	177.3(0.6)	C30–O30–Mn1	126.8(1.0)
O30–Mn1–O24	90.3(0.6)	C2–C1–O1	114.9(1.1)
N101–Mn1–O1	93.1(0.7)	C6–C1–O1	125.1(1.2)
N101–Mn1–O7	89.5(0.6)	C6–C1–C2	120.0(1.1)
N101–Mn1–O24	86.5(0.6)	C3–C2–C1	120.0(1.1)
N101–Mn1–O30	90.7(0.7)	C4–C3–C2	120.0(1.2)
O15–Mn2–O9	90.2(0.6)	C5–C4–C3	120.0(1.1)
O16–Mn2–O9	176.8(0.6)	C6–C5–C4	120.0(1.1)
O16–Mn2–O15	92.9(0.6)	C5–C6–C1	120.0(1.2)
O22–Mn2–O9	86.7(0.6)	C7–C6–C1	124.0(1.3)
O22–Mn2–O15	176.9(0.6)	C7–C6–C5	115.5(1.3)
O22–Mn2–O16	90.2(0.6)	C6–C7–O7	116.1(1.6)
N201–Mn2–O9	86.0(0.6)	C8–C7–O7	114.2(1.6)
N201–Mn2–O15	87.8(0.7)	C8–C7–C6	129.2(1.8)
N201–Mn2–O16	93.2(0.7)	C9–C8–C7	130.0(1.8)
N201–Mn2–O22	91.7(0.7)	C8–C9–O9	118.1(1.6)
N207–Mn2–O9	88.3(0.6)	C10–C9–O9	118.8(1.5)
N207–Mn2–O15	88.9(0.7)	C10–C9–C8	123.1(1.6)
N207–Mn2–O16	92.7(0.7)	C11–C10–C9	117.9(1.3)
N207–Mn2–O22	91.3(0.7)	C15–C10–C9	122.1(1.3)
N207–Mn2–N201	173.4(0.7)	C15–C10–C11	120.0(1.2)
C1–O1–Mn1	129.2(1.0)	C12–C11–C10	120.0(1.3)
C7–O7–Mn1	134.2(1.1)	C13–C12–C11	120.0(1.2)
C9–O9–Mn2	132.5(1.2)	C14–C13–C12	120.0(1.2)

(*continued*)

TABLE 2. (*continued*)

Bond angles		Bond angles	
C15–C14–C13	120.0(1.3)	C211–C210–C209	124.7(2.9)
C10–C15–O15	127.0(1.3)	C212–C211–C210	114.4(2.7)
C14–C15–O15	113.0(1.3)	C211–C212–N207	120.2(2.4)
C14–C15–C10	120.0(1.2)	O37–Mn3–O31	91.4(0.6)
C17–C16–O16	114.2(1.1)	O45–Mn3–O31	91.50.6)
C21–C16–O16	125.8(1.3)	O45–Mn3–O37	176.8(0.7)
C21–C16–C17	120.0(1.1)	C31–O31–Mn3	128.6(1.2)
C18–C17–C16	120.0(1.1)	C37–O37–Mn3	132.1(1.3)
C19–C18–C17	120.0(1.2)	C32–C31–O31	115.1(1.2)
C20–C19–C18	120.0(1.1)	C36–C31–O31	124.9(1.4)
C21–C20–C19	120.0(1.1)	C36–C31–C32	120.0(1.0)
C20–C21–C16	120.0(1.2)	C33–C32–C31	120.0(1.2)
C22–C21–C16	121.3(1.3)	C34–C33–C32	120.0(1.3)
C22–C21–C20	118.5(1.3)	C35–C34–C33	120.0(1.0)
C21–C22–O22	119.7(1.7)	C36–C35–C34	120.0(1.2)
C23–C22–O22	118.4(1.6)	C35–C36–C31	120.0(1.3)
C23–C22–C21	121.7(1.7)	C37–C36–C31	120.6(1.2)
C24–C23–C22	124.4(1.7)	C37–C36–C35	119.3(1.4)
C23–C24–O24	119.7(1.5)	C36–C37–O37	120.7(1.6)
C25–C24–O24	117.9(1.4)	C38–C37–O37	118.9(1.7)
C25–C24–C23	122.2(1.5)	C38–C37–C36	120.2(1.7)
C26–C25–C24	118.6(1.3)	C39–C38–C37	124.1(1.8)
C30–C25–C24	121.3(1.3)	C38–C39–O39	116.7(1.9)
C30–C25–C26	120.0(1.2)	C40–C39–O39	121.6(1.8)
C27–C26–C25	120.0(1.3)	C40–C39–C38	121.6(1.8)
C28–C27–C26	120.0(1.2)	C41–C40–C39	119.2(1.4)
C29–C28–C27	120.0(1.2)	C45–C40–C39	120.7(1.4)
C30–C29–C28	120.0(1.3)	C45–C40–C41	120.0(1.3)
C25–C30–O30	126.9(1.2)	C42–C41–C40	120.0(1.3)
C29–C30–O30	113.0(1.3)	C43–C42–C41	120.0(1.3)
C29–C30–C25	120.0(1.2)	C44–C43–C42	120.0(1.3)
C102–N101–Mn1	119.3(1.5)	C45–C44–C43	120.0(1.3)
C106–N101–Mn1	120.0(1.6)	C44–C45–C40	120.0(1.3)
C106–N101–C102	120.6(2.1)	C306–N301–C302	123.2(2.1)
C103–C102–N101	119.2(2.3)	C303–C302–N301	116.0(2.3)
C104–C103–C102	119.2(2.8)	C304–C303–C302	119.0(2.6)
C105–C104–C103	123.7(3.1)	C305–C304–C303	125.1(2.7)
C106–C105–C104	116.4(2.6)	C306–C305–C304	115.0(2.5)
C105–C105–N101	120.6(2.3)	C305–C306–N301	121.4(2.3)
C112–N107–C108	115.9(2.1)	C312–N307–C308	119.2(1.9)
C109–C108–N107	122.2(2.3)	C309–C308–N307	123.2(2.1)
C110–C109–C108	119.5(2.5)	C310–C309–C308	118.2(2.4)
C111–C110–C109	118.7(2.5)	C311–C310–C309	118.2(2.4)
C112–C111–C110	117.2(2.4)	C312–C311–C310	121.7(2.2)
C111–C112–N107	126.3(2.3)	C311–C312–N307	119.4(2.1)
C202–N201–Mn2	115.3(1.5)	C47–C46–O46	113.6(1.3)
C206–N201–Mn2	116.7(1.7)	C51–C46–O46	126.4(1.2)
C206–N201–C202	127.9(2.2)	C51–C46–C47	120.0(1.0)
C203–C202–N201	117.7(2.3)	C48–C47–C46	120.0(1.4)
C204–C203–C202	115.2(2.7)	C49–C438–C47	120.0(1.2)
C205–C204–C203	127.2(3.2)	C50–C49–C48	120.0(1.0)
C206–C205–C204	120.8(2.9)	C51–C50–C49	120.0(1.4)
C205–C206–N201	111.1(2.3)	C50–C51–C46	120.0(1.2)
C208–N207–Mn2	121.7(1.6)	C52–C51–C46	121.0(1.2)
C212–N207–Mn2	114.3(1.6)	C52–C51–C50	118.9(1.5)
C212–N207–C208	124.0(2.1)	C51–C52–O52	117.3(1.8)
C209–C208–N207	118.5(2.3)	C53–C52–O52	122.6(2.0)
C210–C209–C208	117.7(2.6)	C53–C52–C51	120.0(1.8)

(*continued*)

TABLE 2. (*continued*)

Bond angles		Bond angles	
C54–C53–C52	121.7(1.9)	C403–C402–N401	120.7(2.1)
C55–C54–C53	121.0(1.8)	C404–C403–C402	118.6(2.5)
C56–C55–C54	119.2(1.3)	C405–C404–C403	122.2(2.5)
C60–C55–C54	120.7(1.4)	C406–C405–C404	116.7(2.6)
C60–C55–C56	120.0(1.1)	C405–C406–N401	121.5(2.4)
C57–C56–C55	120.0(1.2)	C412–N407–C408	121.2(2.4)
C58–C57–C56	120.0(1.4)	C409–C408–N407	118.1(2.9)
C59–C58–C57	120.0(1.1)	C410–C409–C408	118.2(3.2)
C60–C59–C58	120.0(1.2)	C411–C410–C409	122.8(2.9)
C59–C60–C55	120.0(1.4)	C412–C411–C410	114.3(2.9)
C406–N401–C402	120.3(1.9)	C411–C412–N407	124.4(2.8)

noticing here that the reaction of the free ligand (bhppH$_3$) with a Mn(II) salt or first row divalent metal ion, gives only the isomerically pure divalent metal mononuclear complex, the metal atom being placed in the central β-diketone moiety [1–3]. Further reaction in strong basic conditions with Mn(II) salts in open atmosphere give the dinuclear Mn(III) complexes.

The electronic spectra could assist in assigning the oxidation state of the metal ion in the complex. Unfortunately, the intense charge transfer bands of the bhppH$_3$ ligand make the analysis of the spectra difficult. The Mn(III) complex Mn(acac)$_3$ displays one band at 575 nm ($\epsilon = 200$), while no band is observed for the Mn(II) complex Mn(bhppH$_2$)$_2$ at the same frequency ($\epsilon = 4$); on the contrary, the dinuclear Mn(III) complex shows a shoulder in this region (575 nm, $\epsilon = 500$).

Molecular structure of Mn$_2$(bhppH)$_2$·4py

The asymmetric unit is made up of two molecules, one complete and two halves, $C_{50}H_{40}N_4O_8Mn_2$. Each of these two halves becomes a complete molecule through a symmetry centre. These two general symmetry centres are at (0,0,0) and (½,0,0). Figure 2 shows a perspective view of the molecule located at the general crystallographic site.

The coordination polyhedra around the Mn atoms are octahedral, where the basal plane is formed by the oxygen atoms of the ligand and the apical positions occupied by nitrogen atoms of the pyridine groups. The most intriguing fact of the structure is the non-occupancy of the ligand's central β-diketone position, which is the normal coordination site for mononuclear and trinuclear complexes, as we have already shown [1–4]. The C–O distances of the β-diketone moiety give interesting structural evidence for the keto-enol character of these types of molecules. In the Zn complex, Zn(bhppH$_2$)$_2$ [2], these distances are 1.305(7), 1.298(8), 1.286(8) and 1.310(8) Å. The same distances in the tetrahedral Li complex are 1.29(2),

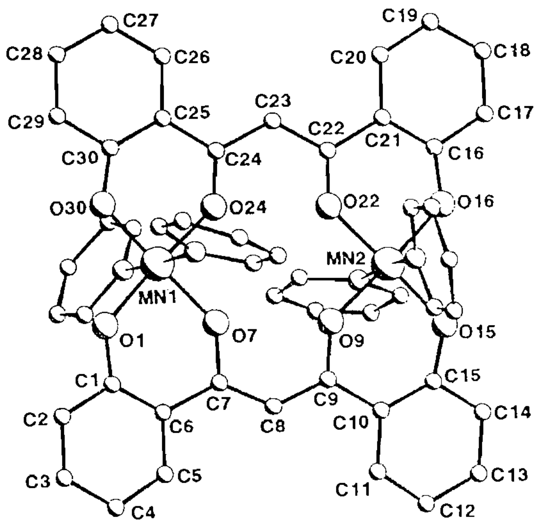

Fig. 2. Perspective view and atom numbering of the title molecule at general crystallographic position.

1.31(2), 1.27(2) and 1.29(2) Å [3]. In the centrosymmetric trinuclear complexes UO_2–Ni–UO_2 and UO_2–Co–UO_2, the corresponding distances are 1.295(12), 1.282(12) (Ni) and 1.289(40), 1.427(43) (Co) [4]. In the present centrosymmetric Mn(III) dinuclear complex the C–O distances are in the range 1.271(27)–1.354(25) Å. Similarly, the C–C distances of the β-diketone moiety are comparable, suggesting a similar chemical behaviour of the β-diketone fragment of the molecule, irrespective of the presence or absence of a metal ion in the central cavity.

Magnetic susceptibility measurements

We have run susceptibility measurements for this compound down to liquid nitrogen temperature. The complex exhibits a typical Curie–Weiss behaviour in this range of temperature as expected for a high spin d^4 ion. Assuming a spin value of 2, the Curie constant is 3.14 and the g value 2.0. These values are typical for high spin Mn(III) complexes with a ^5E_g ground term [13]. The effective magnetic moment is 4.7 at room temperature (300.2 K) and 3.9 at 79.3 K. These changes are probably due to the interaction between both Mn(III) ions in this exchange coupled system. The magnetic data processing was not satisfactory assuming a high spin d^5 configuration [Mn(II)]. A Curie constant of 3.1 and a g value of 1.7 were obtained in this case. The magnetic measurements confirm the presence of Mn(III) in this dinuclear complex. A further study down to liquid helium is in progress in order to calculate the magnetic coupling constant and the superexchange mechanism.

Supplementary material

Tables of anisotropic thermal parameters and observed and calculated structure factors (27 pages) are available from the authors on request.

Acknowledgement

This work was supported in part through CICYT (Ministerio de Educación y Ciencia, Spain) Grant MAT88-0179-C02-01.

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