FULL PAPER

Versatility of 2,6-diacetylpyridine (dap) hydrazones in stabilizing uncommon coordination geometries of Mn(II): synthesis, spectroscopic, magnetic and structural characterization[†]

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Five seven- or eight-coordinate manganese complexes of hydrazone ligands have been prepared. Three seven-coordinate neutral Mn^{II} complexes: [Mn(dapA₂)]_n (1), [Mn(dapB₂)(H₂O)₂] (2), [Mn(dapS₂)(H₂O)₂] (3) have been synthesized from the bis-Schiff bases of 2,6-diacetylpyridine: dap(AH)₂, dap(BH)₂ and dap(SH)₂ (AH = anthraniloyl hydrazide, BH = benzoyl hydrazide, SH = salicyloyl hydrazide), respectively. Two eight-coordinate Mn^{II} complexes: [Mn(dapS)₂] (4) and [Mn(dapB)₂]·3H₂O (5) have been synthesized from the mono-Schiff bases dapBH and dapSH, respectively. The complexes have been characterized by elemental analyses and by IR, UV-Vis., FAB mass, EI mass and EPR spectroscopy. The molecular structures of 1, 3·DMF and 4·DMF have been determined by single-crystal X-ray diffraction. The mono-Schiff bases are monoanionic and the bis-Schiff bases are dianionic. The octa-coordinated mono-Schiff base complex 4 adopts a dodecahedral geometry, while the hepta-coordinated bis-Schiff base complex 1 forms a one-dimensional linear polymeric chain. A weak antiferromagnetic exchange interaction (J = -0.15 cm⁻¹) between the Mn(II) ions in 1 is attributed to weak Mn ··· Mn interaction through the PhNH₂ moiety of the ligand, as indicated by extended-Hückel molecular orbital calculations. A good simulation of the EPR spectrum of a frozen solution (DMSO at 4 K) of compound 1 was obtained with g = 2.0, D = 0.1 cm⁻¹, E =0.01 cm⁻¹. The EPR spectrum of a powdered sample of compound 1 shows a large broadening of the signal, due in part, to the important zero-field splitting of the hepta-coordinated Mn(II) ion.

Introduction

Although interest in the coordination properties of hydrazone ligands towards transition metal ions and in the biological properties of their metal complexes has been growing in recent years,¹⁻⁶ the magnetic properties⁷ of polynuclear metal complexes of hydrazones have been only rarely studied.

2,6-Diacetylpyridine is an excellent precursor for synthesizing hydrazone Schiff bases, its versatile ligating behavior producing unusual geometries-specifically, high coordination numbersin its metal complexes including those of manganese.^{2,5,8} Generally bis-Schiff bases are known for 2,6-diacetylpyridine, and they behave as pentadentate ligands with a N_3O_2 donor set.^{2,5,9,10} However, there remains the possibility of generating new molecular architecture of these complexes by suitable substitution of the phenyl ring of the aroyl hydrazide, in order to provide additional donor atoms. With this in mind we used the bis-Schiff base of anthraniloyl hydrazide and salicyloyl hydrazide. In this paper we demonstrate that in the bis(anthraniloyl hydrazone) ligand the two -NH₂ groups in the ortho positions of the aroyl rings impart a heptadentate nature to the ligand spanning three Mn^{II} centers resulting in a linear polymeric chain. The bis(salicyloyl hydrazone) ligand behaves as a pentadentate N₃O₂ donor spanning only one Mn^{II} center. To our knowledge this is the first report of formation of a linear chain of Mn^{II} ions involving a heptadentate hydrazone ligand. The single-crystal

†Electronic supplementary information (ESI) available: Table ST1: Intermolecular contacts in **3**. Fig. SF1: Fourier difference map for **3**. Fig. SF2: View of the hydrogen bonding and other short contacts in **3**. Fig. SF3: MOs for the dimer model. See http://dx.doi.org/10.1039/b503891j X-ray structure of this complex $[Mn(dapA_2)]_n$ (1) and that of another bis-Schiff base complex $[Mn(dapS_2)(H_2O)_2]$ ·DMF (3·DMF) are reported here.

As a diketone, 2,6-diacetylpyridine retains the ability to form a mono-Schiff base.¹¹ In an attempt to explore this aspect of its chemistry, mono-Schiff bases with salicyloyl hydrazide and benzoyl hydrazide were prepared. Here the ligands are typically tetradentate and the resultant complexes have a strikingly different geometry compared to the bis-Schiff bases, with both ligands forming octa-coordinate complexes with Mn^{II} . A singlecrystal X-ray structure determination on $[Mn^{II}(dapS)_2]$ ·DMF (4·DMF) shows that Mn^{II} has dodecahedral geometry.

Experimental

Physical measurements

C, H, N analyses were performed on a Perkin-Elmer 2400 instrument. FTIR spectra (4000–600 cm⁻¹) were recorded as KBr discs on a JASCO 460 PLUS spectrophotometer. Electronic spectra were obtained using a JASCO 7850 spectrophotometer. Variable-temperature (2–300 K) magnetic measurements for polycrystalline samples of **1** were carried out with a Quantum Design SQUID MPMS-XL susceptometer, working in the range 2–300 K under a magnetic field of 500 G, at the "Servei de Magnetoquímica" (Universitat de Barcelona). Pascal's constants were used to estimate the diamagnetic corrections. The fit was performed by minimizing the function $R = \sum [(\chi_M T)_{exptl} - (\chi_M T)_{exptl}^2) \sum [\chi_M T)_{exptl}^2$. EPR spectra were recorded at X-band (9.4 G Hz) frequency with a Bruker ESP-300E spectrometer at the "Servei de Magnetoquímica" (Universitat de Barcelona).

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A program written by Weihe¹² was used to simulate the EPR spectra. The simulation was performed by generating the energy matrix for each orientation of the molecule relative to the magnetic field. The resonance condition for each transition was then found by successive diagonalizations and iterations of the energy matrix, and the relative intensities were calculated from the eigenvectors multiplied by the appropriate Boltzmann factor at 4 K. Summation of all the transitions over the whole space, where each transition is represented by a differentiated Gaussian curve, gives the simulated spectrum. The spin-Hamiltonian used for the simulation include the ZFS parameters D and E. FAB and EI mass spectra of the samples were recorded on JEOL JMS600 instrument in *m*-nitrobenzyl alcohol as matrix.

Materials

2,6-Diacetylpyridine was obtained from Aldrich and used without further purification. Organic solvents were purified following published procedures.¹³

Ligand preparations

Aroyl hydrazides were prepared by reaction of hydrazine with corresponding methyl or ethyl esters using a published method.¹⁴

The bis-Schiff bases were prepared according to known methods.^{3,15} The mono-Schiff bases were prepared as described below.

DapSH. 2,6-Diacetylpyridine (0.815 g, 5 mmol) was dissolved in excess methanol (150 cm³). Salicyloyl hydrazide (0.76 g, 5 mmol) dissolved in methanol (75 cm³) was added dropwise with stirring to the former over a period of 2 h. After an additional hour of stirring a white solid separated, which was discarded. The filtrate was allowed to evaporate at room temperature. The light yellow product was thoroughly washed with hot methanol (4 × 25 cm³); yield: 0.63 g, 42%. Found (calc. for C₁₆H₁₅N₃O₃): C 64.23 (64.65), H 4.96 (5.05), N 14.68 (14.14)%. Selected IR bands (cm⁻¹): 3271w [ν_{NH} (amide)], 3200 br [ν_{OH}], 1697s [ν_{CO} (ketone)], 1647s [ν_{CO} (amide I)]. ¹H NMR (DMSO-d₆): δ 2.52 (s, 3H), 2.72 (s, 3H), 7.02–7.45 (m, 4H), 8.01–8.39 (m, 3H), 11.52 (s, 1H), 11.84 (s, 1H). FAB MS: *m/z* 298 [DapSH + H]⁺.

DapBH. To a methanolic solution (150 cm³) of 2,6diacetylpyridine (0.815 g, 5 mmol) a methanolic solution (75 cm³) of benzoyl hydrazide (0.680 g, 5 mmol) was added dropwise with stirring over 3 h. After an additional 1 h of stirring a white solid separated and was filtered off and discarded. The filtrate was concentrated by evaporation at room temperature, whereupon a white solid (0.600 g, 40%) appeared which was purified by column chromatography. The fraction which was eluted with (MeCN–CHCl₃ = 5 : 95) gives the expected compound DapBH. Found (calc. for C₁₆H₁₅N₃O₂): C 68.04 (68.33), H 5.15 (5.34), N 15.16 (14.95)%. Selected IR bands (cm⁻¹): 3188w [ν_{NH} (amide]], 1699s [ν_{CO} (ketone)], 1670s [ν_{CO} (amide I)], 1533 [δ_{NH} + ν_{CN} (amide II)]. ¹H NMR (CDCl₃): δ 2.55 (s, 3H), 2.76 (s, 3H), 7.49–7.59 (m, 4H), 7.83–8.03 (m, 3H), 9.15 (s, 1H). EI MS, m/z 281 (DapBH)⁺.

Preparation of the complexes

All the complexes were prepared using a general procedure described below for complex 1. The mono- and bis-Schiff base complexes were prepared by using metal and ligand ratios of 1:2 and 1:1, respectively.

[Mn(dapA₂)]_n (1). Addition of Et₃N (0.202 g, 2 mmol) to a suspension of dap(AH)₂ (0.429 g, 1 mmol) in methanol (30 cm³) produced a clear solution. To this solution a methanolic (10 cm³) solution of Mn(ClO₄)₂·6H₂O (0.362 g, 1 mmol) was added and the mixture was refluxed for 2 h. The orange solid that separated out was filtered off; yield: 0.366 g (76%). Diffraction-quality single crystals were obtained by concentration of a DMF solution of the orange material. Found (calc. for $C_{23}H_{21}N_7O_2Mn$): C 57.56 (57.26), H 4.30 (4.36), N 20.22 (20.33)%. Selected IR bands (cm⁻¹): 3376 ms [$\nu_{NH}(NH_2)$], 1612s [amide I], 1524vs [amide II]. Electronic spectrum in DMF solution, λ/nm (ε/dm^3 mol⁻¹ cm⁻¹): 425 (13040), 375 (24590). FAB MS, m/z 483 [Mn(dapA₂) + H]⁺.

[Mn(dapB₂)(H₂O)₂] (2). Yield: 80%. Found (calc. for $C_{23}H_{23}N_5O_4Mn$): C 55.92 (56.56), H 4.62 (4.71), N 14.41 (14.34)%. Selected IR bands (cm⁻¹): 3434 [ν_{OH} of H₂O], 1625m [amide I], 1525w [amide II]. Electronic spectrum in DMF solution, λ/nm (ε/dm^3 mol⁻¹ cm⁻¹): 390 (6244), 335 (13182), 310 (16882). FAB MS, m/z 453 [Mn(dapB₂) + H]⁺.

[Mn(dapS₂)(H₂O)₂] (3)-DMF. Yield: 67%. Found (calc. for C₂₆H₃₀N₆O₇Mn): C 52.32 (52.61), H 5.11 (5.06), N 14.20 (14.17)%. Selected IR bands (cm⁻¹): 3400 br [ν_{0H} of H₂O], 1612vs [amide I], 1500w [amide II]. Electronic spectrum in DMF solution, λ /nm (ε /dm³ mol⁻¹ cm⁻¹): 395 (10738), 345 (31021). FAB MS, *m*/*z* 485 [Mn(dapS₂) + H]⁺.

[Mn(dapS)₂] (4)·DMF. Yield: 65%. Found (calc. for C₃₅H₃₅N₇O₇Mn): C 58.72 (58.33), H 4.71 (4.86), N 13.42 (13.61). Selected IR bands (cm⁻¹): 1697s [ν_{co} (ketone)], 1647s [amide I], 1546s [amide II]. Electronic spectrum in DMF solution, λ /nm (ε /dm³ mol⁻¹ cm⁻¹): 395 (15345), 348 (44035). FAB MS, *m*/*z* 648 [Mn(daps)₂ + H]⁺.

[Mn(dapB)₂] (5)·3H₂O. Yield: 50%. Found (calc. for $C_{32}H_{34}N_6O_7Mn$): C 56.97 (57.39), H 5.15 (5.08), N 12.72 (12.56)%. Selected IR bands (cm⁻¹): 3388br [ν_{OH} of H_2O], 1685s [ν_{CO} (ketone)], 1660m [amide I], 1556m [amide II]. Electronic spectrum in DMF solution, λ/nm (ϵ/dm^3 mol⁻¹ cm⁻¹): 375 (12365), 340 (15634). FAB MS, m/z 616 [Mn(dapB)₂ + H]⁺.

Crystallography

Single crystals suitable for X-ray diffraction were obtained by evaporation of solvent from concentrated DMF solution (for 1) or by slow diffusion of a DMF solution into diethyl ether (for 3 and 4). For 3 and 4 the crystals were obtained as DMF solvates with formulae 3·DMF and 4·DMF, respectively. Diffraction data for single crystals of 1, 3·DMF and 4·DMF were collected using a Bruker SMART CCD area diffractometer with graphitemonochromated Mo-K α radiation. The structures were solved using direct methods and refined by full-matrix least squares on F^2 using SHELXL97.¹⁶ The hydrogen atoms were refined using riding model. Crystallographic data are summarized in Table 1.

CCDC reference numbers 241988 (1), 258624 (3·DMF) and 241987 (4·DMF).

See http://dx.doi.org/10.1039/b503891j for crystallographic data in CIF or other electronic format.

Results and discussion

Syntheses

The bis-Schiff base ligands dap(BH)₂, dap(SH)₂ and dap(AH)₂ used in this study were prepared according to experimental procedures developed from earlier methods (Scheme 1).^{3,15} Owing to the availability of the two carbonyl groups, 2,6-diacetylpyridine may leave one carbonyl group free by condensing with only one hydrazide, resulting in a mono-Schiff base. This can be achieved by a modification of the method used to prepare the bis-Schiff base: a dilute methanolic solution of the hydrazide (1 equivalent) is added dropwise over 2–3 h to a very dilute solution of 2,6-diacetylpyridine (1 equivalent) with stirring at room temperature. Prolonged stirring of the solution gives the mono-Schiff base along with small amounts of the bis-Schiff base is obtained, as confirmed by spectroscopic measurements (IR, NMR and FAB and EI mass spectra).

Table 1 Details of data collection and structural refinement for 1, 3 DMF and 4 DMF

	1	3.DMF	4·DMF
Empirical formula	$C_{23}H_{21}N_7O_2Mn$	$C_{26}H_{30}N_6O_7Mn$	$C_{35}H_{35}N_7O_7Mn$
M	482.40	593.50	720.64
T/K	150(2)	150(2)	150(2)
$\lambda/\text{\AA}$	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	I2/a	<i>P</i> -1	$P2_{1}/c$
a/Å	12.663(4)	7.4635(8)	13.4258(13)
b/Å	10.626(3)	13.908(2)	15.749(2)
c/Å	16.510(5)	15.216(2)	16.267(2)
$a/^{\circ}$	90	114.421(2)	90
β/°	96.499(5)	96.351(2)	105.174(2)
y/°	90	102.314(2)	90
$U/Å^3, Z$	2207(2), 4	1369.5(3), 2	3319.6(7), 4
$D_{\rm c}/{\rm g~cm^{-3}}$	1.452	1.439	1.442
μ/mm^{-1}	0.634	0.500	0.459
Reflections collected:			
total, unique	12157, 9036	12210, 5886	30065, 7622
$R_{ m int}$	0.063	0.031	0.037
obs. $(I > 2.0\sigma(I))$	6771	4794	6379
Final R_1 , wR_2	0.0604, 0.182	0.0391, 0.106	0.0407, 0.115



IR Spectra

In all the ligands a broad band around 3300 cm⁻¹ indicates the presence of an amide proton. Lower values for some of the ligands may be due to the hydrogen bonding. In 1 and 4 the absence of this band indicate deprotonation of the amide proton. However, in other complexes (2, 3 and 5), the presence of a strong broad band (due to water) in this region precludes any conclusion about the presence or absence of the $v_{\rm NH}$ band. The $v_{\rm co}$ (amide I) band of the coordinated ligand is also shifted to lower wavelength compared to the free ligand due to coordination (in all the complexes) and deprotonation (in all the complexes except 3, see below). A sharp band around ~1700 cm⁻¹ indicates the presence of free carbonyl group in the mono-Schiff base ligands: this band is also shifted to lower energy upon coordination.

Structures

[Mn(dapA₂)]_{*n*} (1). In 1 Mn(II) occupies a distorted pentagonal bipyramidal environment (Fig. 1) with the axial bonds much longer than the equatorial bonds. The equatorial Mn–N and Mn–O bond distances (Table 2) are similar to those observed for other complexes having similar geometry.^{8,9,17,18} The equatorial plane is somewhat distorted, with Mn, N(8), N(8#2), N(1) along with N(9) and N(9#2) [symmetry code #2: -x + 3/2, y, -z + 2] constituting a good least squares mean plane, with $\chi^2 = 94.3$ and the maximum deviation of any atom being \pm 0.009(2) Å [for N(8#2) and N(8), respectively]. The other two coordinating atoms O(10) and O(10#2) deviate by 0.262(2) and -0.262(2) Å, respectively, from the above plane.

The bite angles of the chelate rings are within the range of $67-70^{\circ}$, whereas the O(10)–Mn–O(10#2) angle [86.65(8)°] deviates

Table 2 Selected bond lengths (Å) and angles (°) for 1

Mn-O(10)	2.2100(16)	Mn-N(1)	2.337(2)
Mn-N(8)	2.269(2)	Mn-N(16#1)	2.3611(19)
$\begin{array}{l} O(10)-Mn-O(10\#2)\\ O(10\#2)-Mn-N(8)\\ O(10)-Mn-N(1)\\ O(10)-Mn-N(16\#1)\\ N(8)-Mn-N(16\#1)\\ N(1)-Mn-N(16\#1)\\ \end{array}$	86.65(8) 154.51(6) 136.68(4) 82.42(6) 89.50(7) 90.21(4)	$\begin{array}{l} O(10)-Mn-N(8)\\ N(8)-Mn-N(8\#2)\\ N(8)-Mn-N(1)\\ O(10\#2)-Mn-N(16\#1)\\ N(8\#2)-Mn-N(16\#1)\\ N(16\#1)-Mn-N(16\#3) \end{array}$	69.86(6) 134.87(9) 67.44(5) 97.28(6) 90.65(7) 179.59(9)

Symmetry transformations used to generate equivalent atoms: #1 x - 1/2, -y, z; #2 -x + 3/2, y, -z + 2; #3 -x + 2, -y, -z + 2.



Fig. 1 Ellipsoid plot of the linear chain of **1**. Displacement ellipsoids are drawn at the 50% probability level.

appreciably from that of an ideal pentagon (72°). Similarly, the *trans* angles are 134.87(9)° [N(8)–Mn–N(8#2)] and 154.51(6)° [N(8)–Mn–O(10#2)], deviate by about 10° from the ideal angle of 144°. A strong N(16#1)–H(16B) \cdots N(9) hydrogen bond is characterised by an N(9) \cdots N(16#1) distance of 2.680(3) Å and an N(16#1)–H(16B) \cdots N(9) angle is 128° [symmetry code #1: x - 1/2, -y, z]. Each asymmetric unit is then connected to two other such units through axial coordination of the NH₂ groups, resulting in a linear chain of [Mn(dapA₂)]_n.

 $[Mn(dapS_2)(H_2O)_2]$ (3)-DMF. As in 1, the Mn(II) is in a pentagonal bipyramidal environment (Fig. 2). The basal plane is occupied by N₃O₂ donor atoms of the pentadentate bis(aroyl hydrazone) ligand, while two water molecules occupy the axial positions. All the metal-ligand bond distances in the basal

Table 3 Distances (Å) and angles	$(^{\circ})$ for 3 ·DMF
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Mn–O(1W)	2.1361(15)	Mn–O(2W)	2.1516(15)
Mn–O(10)	2.2462(15)	Mn–O(20)	2.2176(17)
Mn-N(1)	2.360(2)	Mn-N(8)	2.3174(19)
Mn-N(18)	2.3275(17)		
O(1W)–Mn–O(2W)	176.87(7)	O(1W)-Mn-O(10)	88.74(6)
O(1W)-Mn-O(20)	87.11(6)	O(1W) - Mn - N(1)	92.52(6)
O(1W)-Mn-N(8)	87.11(6)	O(1W)-Mn-N(18)	91.79(6)
O(2W)–Mn–O(10)	89.88(6)	O(2W)-Mn-O(20)	90.02(6)
O(2W)-Mn-N(1)	90.42(6)	O(2W)-Mn-N(8)	95.05(6)
O(2W)-Mn-N(18)	88.40(6)	O(10) - Mn - O(20)	87.47(6)
O(10) - Mn - N(1)	135.95(6)	O(10) - Mn - N(8)	69.68(6)
O(10) - Mn - N(18)	157.20(6)	O(20) - Mn - N(1)	136.57(6)
O(20) - Mn - N(8)	156.53(6)	O(20) - Mn - N(18)	69.80(6)
N(1)-Mn-N(8)	66.43(6)	N(1) - Mn - N(18)	66.80(6)
N(8)–Mn–N(18)	133.12(7)		



Fig. 2 Ellipsoid plot of **3**·DMF, showing the atom numbering scheme. Displacement ellipsoids are drawn at the 50% probability level.

plane e.g. Mn-N_{py} (2.360(2) Å), Mn-N_{amide} (av. 2.322 Å) and Mn-O (av. 2.232 Å) for this complex is larger than those in complex 1 (Table 3). This is probably due to the fact that, although in both these complexes the basal plane is occupied by a doubly deprotonated bis(aroyl hydrazone) ligand, the sites of deprotonations in these complexes are different. While in complex 1 the amide protons are deprotonated and the ligand is coordinated in its tautomeric enolate form, in complex 3 it is the phenolic protons attached to O(16) and O(26), which are deprotonated. This is clearly demonstrated by the Fourier difference map (ESI,† Fig. SF1). The higher C-N_{amide} bond distance (av. 1.361 Å) and the lower C-O (1.245 Å) bond distances in complex 3, compared to the corresponding C-N [1.339(3) Å] and C-O [1.270(3) Å] bond distances in complex 1 also support this conclusion. The bite angles are in the range $66-70^{\circ}$, while the *trans* angles are in the range of $136-157^{\circ}$. The pentagonal basal plane is distorted and one can not define a good least square mean plane containing Mn and the donor atoms of the basal plane. The best available least squares basal plane consists of Mn, O(10), O(20), N(18) and N(19) $[\chi^2 = 728.5,$ deviation of Mn = -0.033(1) Å], and N(1) deviates from this plane by -0.103(2) Å.

There is strong intra-molecular hydrogen bonding between the amide hydrogens H(9A) and H(19A) and the phenolate oxygens O(16) and O(26). In addition, there is strong intermolecular hydrogen bonding between the hydrogen atoms attached to two axial water molecules and the phenolate oxygens of the adjacent complex moieties (ESI,† Table ST1). These intermolecular hydrogen bonds along with several intermolecular $C \cdots H$, $C \cdots C$, $H \cdots H$ short contacts results in a three-dimensional supramolecular network (Fig. 3; ESI,†Fig. SF2).



Fig. 3 Intra and inter-molecular hydrogen bonds in complex 3.

[Mn(dapS)₂] (4)·DMF. Unlike complexes 1 and 3 where a bis(aroyl hydrazone) of 2,6-diacetylpyridine provides five donor atoms (N_3O_2) in a basal plane, the ligand used here is the mono(salicyloylhydrazone) of 2,6-diacetylpyridine, which can provide four donor atoms (N₂O₂). The crystal structure determination of the manganese(II) complex of this ligand shows Mn(II) in an octa-coordinated environment comprising an N_4O_4 donor set (Fig. 4). Six of these donor atoms (N_4O_2) are provided by the hydrazone part of the Schiff base along with the pyridine nitrogens. The Mn-O and Mn-N bond distances vary between 2.25 and 2.32 Å (Table 4), which is similar to the values in other octa-coordinated Mn complexes.20 The other two bonds are rather long Mn–O bonds (av. 2.54 Å) formed by the acetyl oxygens. This eight donor atoms form a dodecahedron (Fig. 5) around the Mn(II) centre. It is interesting to note that whereas in complex 3 the ligand was found to be deprotonated at the phenolic oxygens, here the deprotonation has occurred at the



Fig. 4 PLUTON¹⁹ diagram of 4 DMF showing the atom numbering scheme.

Table 4 Selected bond lengths (Å) and angles (°) for 4.DMF

Mn–O1 Mn–N3 Mn–N2′	2.2474(12) 2.3314(13) 2.2747(14)	Mn–N2 Mn–O1' Mn–N3'	2.2487(13) 2.2504(12) 2.3073(14)
Mn–O3′	2.5148(13)	WIII-143	2.5075(14)
O1-Mn-N2	70.06(5)	O1-Mn-O1'	94.40(5)
N2-Mn-O1'	84.33(5)	O1-Mn-N2'	87.51(5)
N2-Mn-N2'	143.90(5)	O1'-Mn-N2'	69.13(5)
O1-Mn-N3'	85.92(5)	N2-Mn-N3'	133.19(5)
O1'-Mn-N3'	138.68(5)	N2'-Mn-N3'	69.60(5)
O1-Mn-N3	139.10(5)	N2-Mn-N3	69.05(5)
O1'-Mn-N3	82.02(5)	N2'-Mn-N3	127.50(5)
N3'-Mn-N3	122.91(5)	O1–Mn–O3′	94.16(5)
N2-Mn-O3'	76.02(4)	O1'-Mn-O3'	154.39(4)
N2'-Mn-O3'	135.37(5)	N3'-Mn-O3'	66.06(5)
N3–Mn–O3′	75.75(4)		

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Fig. 5 High-symmetry dodecahedral geometry of complex 4.

amide nitrogen. This is reflected in the longer C–O [av. 1.259 Å for C(1)–O(1) and C(1')–O(1')] bond length and shorter C–N [av. 1.343 Å for C(1)–N(1) and C(1')–N(1')] bond length in complex 4 compared to those in complex 3 (average of C–O and C–N bond lengths are 1.245 and 1.361 Å, respectively).

Magnetic properties

The magnetic susceptibility of **1** was measured in the range 2–300 K (Fig. 6). The $\chi_M T$ value of 4.51 cm³ mol⁻¹ K at room temperature is in agreement with the expected value for an isolated Mn(II) ion. On cooling below about 50 K, a more rapid decrease in the value of $\chi_M T$ could be observed, whereas the χ_M *vs. T* plot increases on cooling, without reaching a maximum in the temperature range studied.



Fig. 6 $\chi_M T vs. T$ plot for compound 1. The solid line is the best fit to the experimental data.

The shape of the $\chi_{\rm M}T$ vs. T plot is characteristic of a weak antiferromagnetic coupling, but it could be also due to the presence of zero-field splitting. In general, for Mn(II) ions, the zero-field splitting is very small. Nevertheless, in 1, the coordination polyhedron of each Mn(II) ion is a pentagonal bipyramid, and the ZFS could be significant. On the other hand, the magnetic interaction between the Mn(II) ions could be very small, due to the long $Mn \cdots Mn$ distance (6.40 Å), and the type of the bridging ligand (the dap A_2^{2-} ligand). The magnetic susceptibility data were analysed in two ways: as isolated Mn(II) ions with ZFS and as a one-dimensional system. In the first case, it was not possible to find a good fit of the experimental magnetic susceptibility data. The magnetic susceptibility data were analysed using the analytical expression derived by Fisher²¹ for an infinite chain of classical spins based on the Hamiltonian $H = -J\sum S_i S_{i+1}$, for local spin values S = 5/2: $\chi_M T = [Ng^2\beta^2 S(S+1)(1+U)]/[3kT(1-U)]$ where U = $\operatorname{coth}[JS(S+1)/kT] - [kT/(JS(S+1))]$. The best fit corresponds to J = -0.15 cm⁻¹, g = 2.02 and $R = 6.1 \times 10^{-4}$.

The weak magnetic interaction between the Mn(II) centres could be mediated either by the axially bridging NH₂–Ph groups or through π -stacking interactions between pyridine and phenyl rings separated by a centroid–centroid distance of 3.93 Å.

Extended-Hückel calculations for 1

With the aim of clarifying the origin of the magnetic interaction, extended Hückel calculations with the crystallographic coordinates for compound **1** were carried out with the CACAO program.²² Taking in consideration the one-dimensional structure of this compound, only a dinuclear fragment (two Mn(II) ions and two ligands) was considered. In each manganese ion one of the axial ligands (NH₂-coordinated) was replaced by a NH₃ group so that the model system used was [MnL(NH₃)]₂, where the L ligands "bridge" both Mn(II) ions (Scheme 2). For each d orbital of the manganese ions, two MOs could be obtained (symmetric and antisymmetric combination), with similar contribution of both metal ions. Fig. 7 shows one MO of each pair, and for clarity, the drawing shows only the







Fig. 7 Drawings of the MO fragments around one Mn(II) ion; the axial ligands are omitted for clarity.

fragment around one manganese ion (A complete MO diagram is deposited in ESI[†] as Fig. SF3).

With 10 metal d orbitals, a total of 10 MOs with major contribution from the metal ion would be expected. However, we found at least 14 MOs with more than a 10% contribution from each manganese ion (Fig. 8, Scheme 3), indicative of some delocalisation of the metal electronic density to the ligand. There are two pairs of MOs (155/156, 161/162) with more than 10% of contribution of each Mn(II) ion along with appreciable concentration of bridging PhNH₂ ligands but where the contributions of the axial NH₃ ligands are small. Two other pairs of MOs, 157/158 and 159/160, correspond to the terminal Ph–NH₂ groups in the studied binuclear system, with 157/158 having appreciable contribution from Mn(II), while 159/160 have only minor contribution from the metal ion. Fig. 8 shows the energy and composition of the MO pairs.



Fig. 8 Energy diagram and composition of the MOs with major contribution from Mn(II) ions. N–Ph symbolises the N atom of the ligand coordinated in axial position; N*–Ph symbolises the N atom of the ligand in a terminal position (not coordinated to the Mn(II) ion in this study). The percentage values correspond to one Mn(II) ion and one ligand.



Scheme 3

In the actual one-dimensional compound, this terminal group is coordinated to another Mn(II) ion. Then, in the real system these MO pairs must also participate in the Mn \cdots Mn interaction through the axial ligand. Substantial difference in the Mn–N_{axial} overlap population was observed between the NH₃ group (0.053) and the NH₂–Ph ligand (0.099), in spite of the same Mn–N distance. Greater values of overlap population with the ligands in the equatorial plane were observed (0.2–0.33) in agreement with the smaller Mn–L distances.

Using these results, we can attribute the variation of the $\chi_M T$ vs. T as being due to a weak Mn · · · Mn interaction, through the ligand. However, of the five Mn(II) electrons, only three of

them are placed in orbitals with an orientation favourable to the interaction.

EPR spectra of 1

EPR spectra recorded on powdered sample show, at room temperature, a broad signal centred at g = 2.06 ($\Delta H_{pp} = 560$ G). On cooling, a considerable broadening of the signal was observed, reaching a $\Delta H_{pp} = 1200$ G at 4 K (Fig. 9).



Fig. 9 EPR spectra of the polycrystalline 1 at three different temperatures.

EPR spectra of one-dimensional systems are difficult to interpret, even from a qualitative point of view. Several factors influence the line-width of the EPR spectra,²³ *e.g.* the dipolar interaction, the exchange interaction and the ZFS. The effect of the dipolar interaction is the broadening of the main line of the spectrum. When the exchange interaction is present a narrowing of the bands may be observed.²⁴ If the dipolar interaction is more important than the exchange interaction, a broadening of the spectra is observed. Additional broadening mechanisms are the hyperfine coupling and single-ion ZFS effects.

For compound 1, several factors favour the broadening of the EPR band. As the exchange interaction is weak, no narrowing effect can operate. The presence of hyperfine coupling for the manganese ions ($I_{Mn} = 5/2$) contributes to a broad spectrum, whereas the contribution of the dipolar interaction must be moderate, due to the long Mn··· Mn distance (6.4 Å). On the other hand, a degree of ZFS could be present due to the seven-coordination of the Mn(II) ion. A manganese chain described in the literature, MnMn(EDTA)·9H₂O,²⁵ also shows a seven-coordinated Mn(II) ion, and with quite similar Mn··· Mn distances: for this compound the authors found that the most important effect to the broadening of the bands is the ZFS.²⁵ Therefore, for compound 1, with a small J value and similar Mn··· Mn distance, the broadening of the spectra could also be attributed to the presence of ZFS.

The EPR spectra of a DMSO solution of compound 1 were recorded at different temperatures (Fig. 10). Important differences, of intensity and position of the bands, are observed between the spectrum at room temperature and the spectra at low temperatures. In a general way, we can differentiate three regions of the spectra: ~ 1300 , ~ 2300 and ~ 3300 G. While at room temperature the most important signal appears at $g \sim 2$, at 135 K and lower temperatures, the most important band is found in the second region of the spectra, ~ 2300 G ($g \sim 2.9$). Some differences are also observed between the EPR spectra in the temperature range of 135 to 4 K. The ratio between the intensity of the first two peaks, (~ 1300 and ~ 2300 G) remains constant in the range 4 to 13 K, but increase at higher temperatures. The EPR spectrum in solution remains unchanged after a week, indicating the stability of the complex in DMSO.

Taking into consideration the weak $Mn \cdots Mn$ antiferromagnetic coupling, the spectra in solution could be due to an isolated Mn(II) ion in a pentagonal-bipyramidal geometry. For



Fig. 10 EPR spectra of a DMSO solution of compound 1 at different temperatures.

a Mn(II) ion, with a very small ZFS ($D \sim 0$) the five transitions $|5/2, -5/2\rangle \rightarrow |5/2, -3/2\rangle$; $|5/2, -3/2\rangle \rightarrow |5/2, -1/2\rangle$; $|5/2, -1/2\rangle \rightarrow |5/2, +1/2\rangle$; $|5/2, +1/2\rangle \rightarrow |5/2, +3/2\rangle$ and $|5/2, +3/2\rangle \rightarrow |5/2, +5/2\rangle$ occur in the same region, and only a broad band could be observed at $g \sim 2$. For small D values ($D \ll g\beta H$) the position of the five transitions differs and these transitions in x, y and z directions could also appear at different positions.

A quite good simulation¹² of the EPR spectrum at 4 K has been obtained, assuming an isolated spin state S = 5/2, with isotropic g = 2.0, D = 0.1 cm⁻¹ and E = 0.01 cm⁻¹, with a bandwidth of 300 G (Fig. 11). The broadness of the bands and absence of hyperfine splitting could be due to dipole–dipole interaction and ZFS, similar to that in the solid state.



Fig. 11 EPR spectra at 4 K of a DMSO solution of compound 1 (solid line) and simulated spectra (dashed line) with g = 2.00, D = 0.1 cm⁻¹, E = 0.01 cm⁻¹ and bandwidth of 300 G.

A spectra quite similar to that of compound 1 was reported for the mononuclear compound $[MnL(H_2O)_2]Cl_2$ (L = 2,13dimethyl-3,6,9,12,18-pentaazabicyclo[12.3.1]octadeca-(18),2,12, 14,16-pentaene),²⁶ where the Mn(II) ion is also in a distorted pentagonal-bipyramidal geometry, and the most intense features of the spectra appears at g > 2. The reported values of the ZFS parameters ($D = 0.07 \text{ cm}^{-1}$, $E = 0.008 \text{ cm}^{-1}$) are close to the *D* and *E* values used to simulate the spectrum of compound 1 at 4 K. To the best of our knowledge, EPR studies of systems with a hepta-coordinated Mn(II) ion are very limited. For the one-dimensional system MnMn(EDTA)·9H₂O,²⁵ the reported ZFS parameters are also comparable ($D \sim 0.11-0.13 \text{ cm}^{-1}$ and $E/D \sim 0.03$), while for the one-dimensional system [Mn(bpy)(H₂O)(TDB)]_n²⁷ the X-band EPR spectrum show the six-line manganese hyperfine pattern centered at g = 2.

Conclusions

Mn(II) is normally found in an octahedral coordination environment, and structurally characterized hepta- and especially octacoordinated Mn(II) complexes are relatively uncommon. Most of the structurally characterized octa-coordinated Mn(II) complexes involve macrocyclic ligands and there is no report of any such complex using aroyl hydrazones. Furthermore, the monohydrazones of 2,6-diacetylpyridine comprise a rarely studied system, and there is only one report¹¹ of an iron(III) complex of mono (theonyl hydrazone) of 2,6-diacetylpyridine, though the compound was not structurally characterized. Thus ours is the first report of a structurally characterized Mn(II) complex of mono-Schiff base of 2,6-diacetylpyridine, and moreover it is an octa-coordinated species.

A survey of the structurally characterized metal complexes of bis-Schiff bases 2,6-diacetylpyridine reveals that in most of the cases discrete seven-coordinated complexes are obtained. Two binuclear Ni(II) complexes9 and a binuclear Fe(III) complex11 represent the only known examples of binuclear complexes using such ligands, but magnetic studies were reported only for the Ni(II) complexes. In fact the magnetochemistry of aroyl hydrazone complexes is not very well studied, and thus the effect of various factors on the magnetic properties of such metal complexes is yet to be fully understood. Again our paper for the first time reports that, using a bis-Schiff base of aroyl hydrazone as the only ligand, with suitable ortho substituents in the phenyl ring of the aroyl hydrazide moiety, it is possible to molecular engineer a one-dimensional chain of Mn(II) compounds, in which Mn(II) ions are coupled by weak antiferromagnetic interactions. In fact, we have demonstrated here that by changing the *ortho* substituents in the phenyl ring of the aroyl hydrazide moiety, e.g., replacing -NH₂ by -OH, one may control the supramolecular architecture, from a one-dimensional covalently linked chain to a three-dimensional hydrogen bonded network.

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References

- 1 C. Carini, G. Pelizzi, P. Tarasconi, C. Pelizzi, K. C. Molloy and P. C. Waterfield, J. Chem. Soc., Dalton Trans., 1989, 289.
- 2 A. Bonardi, C. Carini, C. Merlo, C. Pelizzi, G. Pelizzi, P. Tarasconi, F. Vitali and F. Cavatorta, J. Chem. Soc., Dalton Trans., 1990, 2771.
- 3 C. Pelizzi and G. Pelizzi, J. Chem. Soc., Dalton Trans., 1980, 1970.
- 4 D. Wester and G. J. Palenik, Inorg. Chem., 1976, 15, 755.
- 5 C. Pelizzi, G. Pelizzi and F. Vitali, J. Chem. Soc., Dalton Trans., 1987, 177.
- 6 E. C. Constable, in *Comprehensive Supramolecular Chemistry*, ed. J. L. Atwood, J. E. D. Davies, D. D. McNicol, J. P. Vogtle, J. P. Sauvage and M. W. Hosseini, Pergamon, Oxford, 1996, vol. 9, p. 213.
- 7 R. Sumita, D. D. Mishra, R. V. Maurya and N. Nageswara, *Polyhedron*, 1987, 16, 1825.
- 8 C. Pelizzi, G. Pelizzi, G. Predieri and S. Resola, J. Chem. Soc., Dalton Trans., 1982, 1349.
- 9 M. R. Bermejo, M. Fondo, A. M. Gonzàlez, O. L. Hoyos, A. Sousa, C. A. McAuliffe, W. Hussain, R. Pritchard and V. M. Novotorsev, *J. Chem. Soc., Dalton Trans.*, 1999, 2211.
- 10 G. F. Sousa and V. M. Deflon, Transition Met. Chem., 2003, 28, 74.

- 11 A. Bonardi, C. Merlo, C. Pelizzi, G. Pelizzi, P. Tarasconi and F. Cavatorta, J. Chem. Soc., Dalton Trans., 1991, 1063.
- 12 The simulation software package is freely distributed by Dr. H. Weihe; for more information see the www page: http://so-phus.kiku.dk/software/epr/epr.html.
- 13 D. D. Perrin, W. L. F. Armarego and P. R. Perrin, in *Purification of Laboratory Chemicals*, Pergamon Press, Oxford, 1966.
- 14 E. H. Rodd, in *Chemistry of Carbon Compounds*, Elsevier, London, 1954, vol. 3, part A, p. 556.
- 15 C. Lorenini, C. Pelizzi, G. Pelizzi and G. Predieri, J. Chem. Soc., Dalton Trans., 1983, 721.
- 16 G. M. Sheldrick, SHELXL97, University of Göttingen, Göttingen, Germany, 1998.
- 17 C. Pelizzi, G. Pelizzi, G. Predieri and F. Vitali, J. Chem. Soc., Dalton Trans., 1985, 2378.
- 18 M. Nardelli, C. Pelizzi and G. Pelizzi, *Transition Met. Chem.*, 1977, 2, 35.

- 19 PLATON, A. L. Spek, University of Utrecht, The Netherlands, 1999.
- 20 M. Mikuriya, Y. Hatano and E. Asato, Bull. Chem. Soc. Jpn., 1997, 70, 2495.
- 21 M. E. Fisher, Am. J. Phys., 1964, 32, 343.
- 22 CACAO (Computer Aided Composition of Atomic Orbitals) Program, Version 5.0, 1998; C. Mealli and D. M. Proserpio, J. Chem. Educ., 1990, 67, 399.
- 23 A. Bencini and D. Gatteschi, *EPR Exchange Coupled Systems*, Springer-Verlag, Berlin, 1990.
- 24 C. H. Weng, PhD Dissertation, Carnegie-Mellon University, Pittsburg, PA, 1968.
- 25 J. J. Borras-Almenar, R. Burriel, E. Coronado, D. Gatteschi, C. J. Gomez-Garcia and C. Zanchini, *Inorg. Chem.*, 1991, **30**, 947.
- 26 O. J. Sandoval, D. R. Rosales, M. J. R. Hoz, M. E. S. Torres and R. Z. Ulloa, *J. Chem.Soc., Dalton Trans.*, 1998, 1551.
- 27 X. S. Tan, D. F. Xiang, W. X. Tang and J. Sun, *Polyhedron*, 1996, 16, 689.