The Template Synthesis and Crystal and Molecular Structure of a Seven-co-ordinate Manganese(II) Complex with 2,6-Diacetylpyridine Mono(2-aminobenzoylhydrazone) †

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A new seven-co-ordinate manganese(II) complex $[Mn(HL)(OH_2)_2Cl]Cl{\cdot}H_2O$ has been synthesised with 2,6-diacetylpyridine mono(2-aminobenzoylhydrazone) (HL) by using a template reaction, and characterised by *X*-ray crystallography. The structure has been solved using direct methods and Fourier-difference techniques and refined by least squares to *R* 0.0470 for 1 862 observed diffractometer data. The co-ordination around the manganese atom is a pentagonal bipyramid, with a water molecule and a chlorine atom in the axial positions and four donor atoms (two nitrogens and two oxygens) of HL and a second water molecule in the equatorial plane. The molecular packing involves an extensive network of hydrogen bonds.

As part of a general program of investigation into the metal complexes of 2,6-diacetylpyridine bis(aroylhydrazones), a series of structure determinations has been undertaken with the aim of obtaining information about the stereochemistry of such complexes and the co-ordinating properties of the hydrazones. Our previous studies have revealed in the hydrazones a remarkable versatility for binding metal ions as well as a considerable tendency to act as quinquedentate planar ligands, so favouring seven-membered stereochemistries.[1–5]

In order to investigate further the molecular geometries of the metal complexes of 2,6-diacetylpyridine aroylhydrazones and to understand better the ligand behaviour of these molecules, we have extended our work to the 2,6-diacetylpyridine monohydrazones, by exploring the 2,6-diacetylpyridine mono(2-aminobenzoylhydrazone) (HL) obtained by a template reaction in the presence of manganese(II) chloride. The present note deals with the synthesis and the structural characterisation of $[Mn(HL)(OH_2)_2Cl]Cl{\cdot}H_2O$, which, as far as we are aware, is the first structurally characterised dicarbaldehyde or diketone monoaroylhydrazone metal complex.

Experimental

Preparation.—The template reaction was carried out by mixing 2,6-diacetylpyridine, 2-aminobenzohydrazide, and $MnCl_2{\cdot}4H_2O$ (1 : 1 : 1) in chloroform–ethanol (1 : 1 v/v) and refluxing the resulting solution for about 0.5 h. After cooling and slow evaporation of the solvent, the compound $[Mn(HL)(OH_2)_2Cl]Cl{\cdot}H_2O$ was isolated as yellow crystals.

Crystallography.—*Crystal data.* $C_{16}H_{22}Cl_2MnN_4O_5$, $M = 476.22$, triclinic, $a = 9.134(4)$, $b = 14.009(6)$, $c = 9.004(4)$ Å, $\alpha = 100.82(5)$, $\beta = 102.85(4)$, $\gamma = 108.50(5)°$ (by least-squares refinement of θ values for 25 automatically centred reflections), $U = 1\,022.8(9)$ Å^3, space group $P\bar{1}$, $Z = 2$, $D_c = 1.546$ g cm^{-3}, $F(000) = 490$, Mo-K_α radiation, $\lambda = 0.710\,69$ Å, μ(Mo-K_α) = 9.16 cm^{-1}.

Data collection and processing. A unique data set was measured in the range $6 < 2\theta < 50°$ with the θ—2θ scan method, using a Philips PW 1100 four-circle diffractometer fitted with a monochromatic Mo-K_α radiation source. Of the 3 436 unique reflections collected, 1 862 had $I > 3\sigma(I)$ and were used in the subsequent structure analysis. During data collection one standard reflection monitored every 90 min showed only random deviations about its mean value. Corrections for Lorentz and polarisation effects were applied. On the basis of a ψ-scan study there was no need to correct for absorption effects.

Structure determination and refinement. The structure was solved by multisolution direct methods (Mn and Cl atoms) followed by normal heavy-atom procedures. Refinement was by full-matrix least squares. All atoms were refined anisotropically, with the exception of the hydrogen atoms which were located in a ΔF map and included in the refinement with individual isotropic thermal parameters. Residuals R, R' at convergence were 0.0470, 0.0502, reflection weights being $[\sigma^2(F_o) + 0.005|F_o|^2]^{-1}$. The final difference synthesis showed no significant features. Neutral-atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion.[6] All calculations were performed on a CDC 76 Cyber computer with the SHELX 76 system of programs.[7] Final fractional atomic co-ordinates are given in Table 1, selected interatomic distances and angles in Table 2.

Results and Discussion

Three bis(aroylhydrazone)manganese(II) complexes, $Mn(H_2dappc)Cl_2{\cdot}5H_2O$ [H_2dappc = 2,6-diacetylpyridine bis(picolinoylhydrazone)],[8] $Mn(dappc){\cdot}9H_2O$,[4] and $Mn(H_2dapb)Cl_2{\cdot}H_2O$ [H_2dapb = 2,6-diacetylpyridine bis(benzoylhydrazone)],[5] have been synthesised so far and structurally characterised in our laboratory. In all of them the metal atom shows a seven-co-ordinate pentagonal-bipyramidal geometry, with the organic molecule always acting as a planar and quinquedentate ligand, in spite of its neutral or

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† *Supplementary data available* (No. SUP 56051, 6 pp.): thermal parameters, full bond lengths and angles. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Fractional atomic co-ordinates (× 10^4) for $[Mn(HL)(OH_2)_2Cl]Cl\cdot H_2O$

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Mn	9 398(1)	7 869(1)	5 798(1)	C(14)	5 606(8)	7 367(5)	5 159(7)
Cl(1)	8 630(2)	6 388(1)	3 430(2)	C(15)	6 174(9)	8 280(5)	4 513(8)
Cl(2)	11 415(2)	9 093(1)	11 429(2)	C(16)	5 017(11)	8 703(7)	3 719(12)
O(1)	11 826(5)	7 862(4)	6 990(5)	H(2)	10 786(72)	6 497(46)	9 188(76)
O(2)	7 620(6)	8 692(4)	4 661(6)	H(3)	17 450(73)	8 921(46)	10 046(65)
O(3)	10 047(8)	9 192(5)	7 875(8)	H(4)	17 661(71)	7 663(41)	11 234(66)
O(4)	10 994(6)	9 038(4)	4 880(7)	H(5)	15 391(68)	6 202(47)	11 034(69)
O(5)	11 148(7)	6 803(5)	1 557(6)	H(6)	12 888(91)	6 144(58)	9 553(86)
N(1)	14 957(11)	9 045(6)	8 214(10)	H(91)	6 634(83)	4 836(53)	8 018(75)
N(2)	10 655(6)	6 724(4)	8 257(6)	H(92)	8 480(110)	5 154(65)	8 582(104)
N(3)	9 225(6)	6 761(4)	7 447(6)	H(93)	7 977(138)	5 753(89)	9 733(152)
N(4)	6 805(6)	7 152(4)	5 984(6)	H(11)	4 667(77)	5 163(52)	7 103(78)
C(1)	13 594(7)	7 459(5)	8 910(7)	H(12)	2 439(84)	5 486(52)	5 392(78)
C(2)	15 026(8)	8 304(5)	8 997(8)	H(13)	3 308(84)	7 043(51)	4 466(80)
C(3)	16 525(9)	8 352(6)	9 890(9)	H(161)	5 619(98)	9 343(66)	3 482(95)
C(4)	16 646(9)	7 621(7)	10 640(9)	H(162)	4 151(108)	8 247(68)	2 892(104)
C(5)	15 279(9)	6 770(6)	10 548(9)	H(163)	4 490(99)	8 863(61)	4 443(101)
C(6)	13 785(9)	6 717(6)	9 703(8)	H(1N1)	13 971(112)	8 926(64)	7 599(103)
C(7)	11 999(8)	7 376(5)	7 999(7)	H(2N2)	15 661(103)	9 416(64)	8 384(100)
C(8)	7 865(7)	6 205(5)	7 584(7)	H(103)	10 453(92)	9 184(57)	8 651(87)
C(9)	7 666(10)	5 436(7)	8 554(10)	H(203)	9 610(108)	9 539(72)	7 962(107)
C(10)	6 455(7)	6 374(5)	6 687(7)	H(104)	11 195(79)	9 728(58)	5 147(78)
C(11)	4 853(8)	5 783(5)	6 547(8)	H(204)	11 061(76)	8 987(49)	4 138(75)
C(12)	3 621(9)	6 008(6)	5 675(8)	H(105)	10 571(88)	6 593(57)	1 813(88)
C(13)	3 984(9)	6 813(6)	4 997(9)	H(205)	11 203(96)	7 456(65)	1 611(94)

Table 2. Selected distances (Å) and angles (°)

(*a*) Co-ordination sphere

Mn–Cl(1)	2.468(3)	Mn–O(4)	2.240(6)	Cl(1)–Mn–O(3)	179.0(2)	N(4)–Mn–O(2)	67.5(2)
Mn–O(1)	2.243(5)	Mn–N(3)	2.335(6)	O(1)–Mn–N(3)	67.9(2)	O(2)–Mn–O(4)	77.2(2)
Mn–O(2)	2.430(6)	Mn–N(4)	2.319(6)	N(3)–Mn–N(4)	67.4(2)	O(4)–Mn–O(1)	79.6(2)
Mn–O(3)	2.189(7)						

(*b*) Ligand

N(1)–C(2)	1.369(12)	Mn–O(1)–C(7)	121.6(5)	C(9)–C(8)–C(10)	120.9(7)
C(1)–C(7)	1.461(9)	N(2)–C(7)–C(1)	118.3(6)	N(4)–C(10)–C(8)	115.3(6)
C(7)–O(1)	1.245(9)	O(1)–C(7)–C(1)	122.1(6)	Mn–N(4)–C(14)	120.0(5)
C(7)–N(2)	1.375(9)	O(1)–C(7)–N(2)	119.6(6)	Mn–N(4)–C(10)	119.4(5)
N(2)–N(3)	1.369(8)	N(3)–N(2)–C(7)	114.1(5)	C(10)–N(4)–C(14)	119.4(6)
N(3)–C(8)	1.287(8)	Mn–N(3)–N(2)	116.3(4)	N(4)–C(14)–C(15)	113.7(7)
C(8)–C(9)	1.502(12)	N(2)–N(3)–C(8)	121.3(6)	C(14)–C(15)–C(16)	120.9(7)
C(8)–C(10)	1.473(10)	Mn–N(3)–C(8)	122.3(5)	O(2)–C(15)–C(14)	119.4(7)
C(10)–N(4)	1.349(9)	N(3)–C(8)–C(10)	114.3(6)	O(2)–C(15)–C(16)	119.6(7)
N(4)–C(14)	1.332(9)	N(3)–C(8)–C(9)	124.8(7)	Mn–O(2)–C(15)	117.4(5)
C(14)–C(15)	1.495(10)				
C(15)–C(16)	1.483(14)				
C(15)–O(2)	1.226(9)				

(*c*) Hydrogen bonding

N(1) · · · O(1)	2.654(9)	O(4) · · · O(2$^{\rm III}$)	2.933(8)	N(1)–H(1N1)–O(1)	137(8)	O(4)–H(104)–O(2$^{\rm III}$)	157(7)
N(2) · · · O(5$^{\rm I}$)	2.880(8)	O(4) · · · Cl(2$^{\rm IV}$)	3.227(7)	N(2)–H(2)–O(5$^{\rm I}$)	149(6)	O(4)–H(204)–Cl(2$^{\rm IV}$)	171(7)
O(3) · · · Cl(2)	3.212(8)	O(5) · · · Cl(1)	3.117(7)	O(3)–H(103)–Cl(2)	170(9)	O(5)–H(105)–Cl(1)	160(9)
O(3) · · · Cl(2$^{\rm II}$)	3.129(8)	O(5) · · · Cl(2$^{\rm IV}$)	3.165(8)	O(3)–H(203)–Cl(2$^{\rm II}$)	170(9)	O(5)–H(205)–Cl(2$^{\rm IV}$)	172(7)

$^{\rm I}$ $x, y, z + 1$; $^{\rm II}$ $2 - x, 2 - y, 2 - z$; $^{\rm III}$ $2 - x, 2 - y, 1 - z$; $^{\rm IV}$ $x, y, z - 1$.

deprotonated form, the axial positions being occupied by chloride ions and/or water molecules depending on the nature of the complex.

In the present compound, whose structure is illustrated in Figure 1, the manganese atom is in a distorted pentagonal-bipyramidal environment with two nitrogen and two oxygen atoms of the organic ligand and a water molecule occupying the pentagonal girdle and a second water molecule and a chloride ion in the axial positions. It is interesting that we again have a seven-co-ordinate complex, in spite of the fact that HL is now acting in a quadridentate manner, unlike bis(aroylhydrazones) which always behave as quinquedentate ligands.

The ring of the five equatorially co-ordinating atoms shows the following displacements from the mean least-squares plane: O(1), −0.06; N(3), −0.01; N(4), 0.10; O(2), −0.13; and O(4), 0.15 Å; Mn is displaced 0.17 Å above this plane towards the axial chlorine ligand. If we consider only the four atoms of HL, the maximum deviation is 0.05 Å, the O(4) water oxygen being out of the plane by 0.34 Å. The sum of the

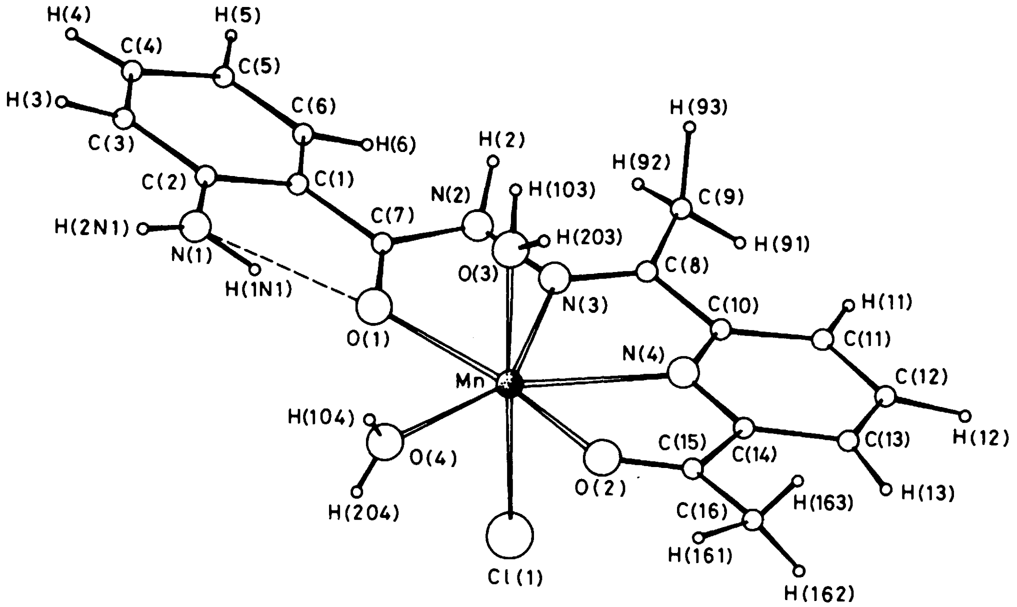

Figure 1. Perspective view of the $[Mn(HL)(OH_2)_2Cl]^+$ cation with the atom-numbering scheme

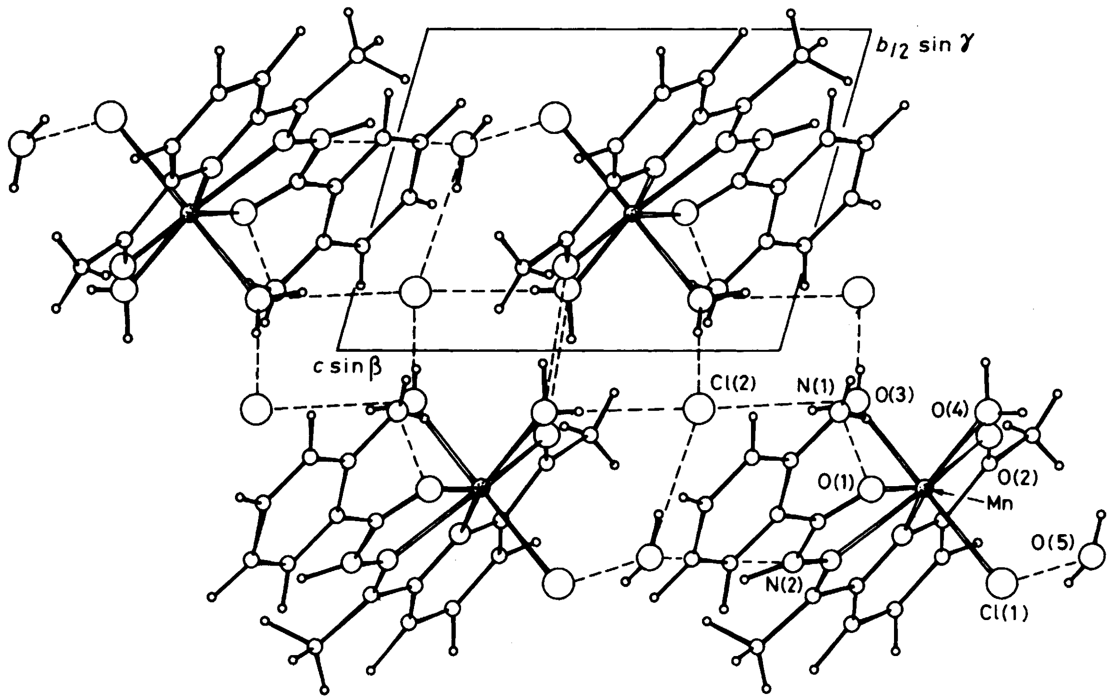

Figure 2. Crystal packing diagram of $[Mn(HL)(OH_2)_2Cl]Cl{\cdot}H_2O$ viewed from the *a* direction

interior angles in the pentagonal girdle is 538.4°, only slightly smaller than the 540° corresponding to planarity. The angle between the axial bond and the equatorial plane is 86.6°.

In the context of seven-co-ordination and the Mn^{II} oxidation state (see Table 6, ref. 5), the Mn–Cl (axial) bond distance of 2.468(3) Å observed in this compound is slightly, but significantly, shorter than the corresponding tabulated values, which range from 2.503(3) to 2.532(3) Å. The two O (ligand) atoms are not bonded with the same strength to manganese. That Mn–O(2) is longer than Mn–O(1) by a significant 0.2 Å is consistent with the different nature of the two atoms, hydrazidic O(1) and ketonic O(2). The occurrence in the i.r. spectrum of two intense bands at 1 670 and 1 635 cm^{-1} is in accord with this. The two Mn–N bond distances are nearly equivalent at 2.335(6) and 2.319(6) Å; these values fall in the range quoted for Mn–N (equatorial) bonds in seven-co-ordinate manganese(II) compounds. The length of the Mn–O bond to the axial water [Mn–O(3) 2.189(7) Å] is at the low end of the range of distances observed for Mn^{II}–O$_w$ (axial) bonds (seven-co-ordination) and slightly shorter than the corresponding bond involving the equatorial water, Mn–O(4) 2.240(6) Å. The latter value is comparable to those, 2.178(8) and 2.247(8) Å, observed in tetra-aquapurpuratomanganese(II) purpurate hexahydrate.[9]

The HL ligand co-ordinates to the metal in a slightly unsymmetrical quadridentate manner through two N and two O atoms giving rise to three different five-membered chelate rings, one of which, MnO(1)C(7)N(2)N(3), shows only slight deviations from planarity (maximum 0.05 Å) while the other two, MnN(3)C(8)C(10)N(4) and MnN(4)C(14)C(15)O(2), show somewhat larger deviations (0.09—0.10 Å). The central chelate ring makes angles of 4.5 and 9.4° with the adjacent (chelate) rings. The pyridine ring is planar within experimental error, with both the attached carbon atoms displaced slightly below the plane [C(8), −0.02; C(15), −0.05 Å]. The phenyl ring is strictly planar with C(7) lying in the plane, while N(1) deviates only by up to 0.05 Å from it. For a better indication of the planarity of the HL molecule, one may distinguish two parts, having the aminic N(2) atom in common, *i.e.* N(1)C(2)C(3)C(4)C(5)C(6)C(1)C(7)O(1)N(2) and N(2)N(3)C(8)C(9)C(10)C(11)C(12)C(13)C(14)N(4)C(15)-C(16)O(2); the maximum displacement from the mean least-squares plane is of the same order of magnitude in the two parts, 0.22 and 0.18 Å respectively. The two moieties slightly but significantly deviate from coplanarity, the dihedral angle being 7.0(1)°.

The nitrogen atom N(1) of the amino-group is involved in a intramolecular hydrogen bond with the oxygen atom O(1) of the hydrazidic group, the two groups being located in a *syn* position, as indicated also by the torsion angle O(1)–C(7)–C(1)–C(2) which is 17(1)°.

It is of interest to compare this structural situation with that previously observed in two organotin(IV) complexes of 2,6-diacetylpyridine bis(2-aminobenzoylhydrazone) (H_2-dapa);[1] in $SnPh_2$(dapa) one of the two NH_2 groups shows a similar conformation, being *syn* with respect to the hydrazidic oxygen atom, while the other is in a *syn* position with respect to the hydrazidic nitrogen atom. In SnBuCl(dapa) both the NH_2 groups show the last conformation.

The molecular packing is dominated by an extensive network of hydrogen bonds involving the complex cation, the Cl^- anion, and the un-co-ordinated water. All the H atoms available for hydrogen bonding, except one of the two belonging to the NH_2 group, participate in hydrogen bonding as can be seen from Table 2 and Figure 2.

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