Investigation into Aroylhydrazones as Chelating Agents. Part 7.[1] Synthesis and Spectroscopic Characterization of Complexes of Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} with 2,6-Diacetylpyridine Bis(2-aminobenzoylhydrazone) and *X*-Ray Structure of Chloro[2,6-diacetylpyridine bis(2-aminobenzoylhydrazone)](methanol)-manganese(II) Chloride Monohydrate

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A series of Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} complexes with 2,6-diacetylpyridine bis(2-aminobenzoylhydrazone) (H_2dapab) has been prepared from the reaction of the hydrazone with metal chlorides and acetates. The i.r. spectra are reported and evaluated to obtain information on the co-ordinating behaviour of the hydrazone. An *X*-ray diffraction analysis carried out on $[Mn(H_2dapab)(CH_3OH)Cl]Cl{\cdot}H_2O$ has shown it to possess pentagonal-bipyramidal geometry with the H_2dapab ligand occupying the equatorial plane and the Cl and CH_3OH groups at the axial sites. The structure has been refined to $R = 0.0676$ for 2 173 observed diffractometer data.

The chemical properties of hydrazones have been intensively investigated in several research fields owing to their chelating capability and their pharmacological activity.[2]

We are currently studying the ligand behaviour of acylhydrazones of aromatic aldehydes or ketones with the aim of obtaining information about the chemical and structural properties of the metal complexes, especially with regard to the stereochemistry of the metal and the effects of the co-ordination on the conformation of the hydrazone.

In preceding papers in this series we have considered the 2,6-diacetylpyridine bis(aroylhydrazones) (aroyl = benzoyl, picolinoyl, salicyloyl, 2-thenoyl), which were found to be of great interest because of their versatility in co-ordinating to metal atoms and the flexibility in assuming different conformations. Other interesting features of these molecules arise from their possibility of co-ordinating either in the neutral or in the anionic form and the tendency to yield seven-co-ordinate stereochemistries.

In a continuation of this work, which is carried out in order to obtain a fuller understanding of the influence exerted by the organic substituents on the chemical and structural properties of the compounds, we have turned our attention to the 2-aminobenzoyl moiety as aroyl group, by preparing 2,6-diacetylpyridine bis(2-aminobenzoylhydrazone) (H_2dapab). In a previous paper we reported the synthesis and *X*-ray crystal structure of two organotin(IV) complexes of H_2dapab[3] and here we present the preparation and the structural characterization of metal complexes obtained by reaction of H_2dapab with Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} chlorides and acetates, as well as the *X*-ray analysis of the manganese chloride derivative.

Experimental

Materials.—2,6-Diacetylpyridine and 2-aminobenzohydrazide were commercially available (Aldrich) and used without further purification. Organic solvents were purified using published procedures.[4]

Preparations.—2,6-Diacetylpyridine bis(2-aminobenzoylhydrazone) (H_2dapab) was prepared by refluxing 2-aminobenzohydrazide and 2,6-diacetylpyridine (2:1 molar ratio) in ethanol solution for *ca.* 2 h. A white-yellow microcrystalline product was isolated on cooling and standing overnight. The product was recrystallized from methanol and identified by C, H, and N elemental analyses, m.p. (187 °C), and mass spectrum[m/z 429 (6.3), 309 (12.5), 162 (12.5), 120 (100.0), 92 (20.3), and 66 (15.6%)]. Manganese(II), cobalt(II), nickel(II), copper(II), and zinc(II) complexes were prepared by mixing a hot chloroform solution of H_2dapab and a methanol solution of the metal chloride (or acetate) in 1:1 molar ratio. The solution was refluxed for *ca.* 1 h and then allowed to stand and slowly evaporate until a microcrystalline product was isolated. Analytical data are in Table 1.

Measurements.—Elemental (C, H, and N) analyses were carried out on Perkin-Elmer model 240 automatic equipment. Determination of metal was by atomic absorption spectroscopy on a Perkin-Elmer model 303-HGA 70 instrument. I.r. spectra (4 000—200 cm^{-1}) for KBr discs were recorded on a Perkin-Elmer model 283 B spectrophotometer. Mass spectra were determined with a Varian CH-5 spectrometer at 70 eV (*ca.* 1.12×10^{-17} J).

X*-Ray Data Collection, Structure Solution and Refinement.*—Orange crystals suitable for *X*-ray diffraction were obtained by recrystallisation from a MeOH–$CHCl_3$ mixture and are air stable.

Two complete data sets were taken at different times with a computer-controlled Siemens AED three-circle diffractometer using Mo-K_α radiation ($\lambda = 0.710\,69$ Å). The first set (small crystal, θ range 3—21°, reflections measured 3 291, reflections observed 1 445), though yielding a solution of the structure, was not able to give a fully satisfactory refinement, probably because of the relatively few observed data. A further data set was then collected from a larger crystal which successfully refined the structure.

An automatic peak-search routine located and centred 29 reflections that could be indexed as monoclinic.

Crystal Data.—$C_{24}H_{29}Cl_2MnN_7O_4$, $M = 605.38$, monoclinic, $a = 8.855(4)$, $b = 15.462(6)$, $c = 20.332(8)$ Å, $\beta = 97.24(4)°$, $U = 2\,762(2)$ Å^3, $Z = 4$, $D_c = 1.456$ g cm^{-3}, $F(000) = 1\,252$, μ(Mo-K_α) = 6.95 cm^{-1}.

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† *Supplementary data available* (No. SUP 56294, 2 pp.): thermal parameters. 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. Analytical data for metal complexes of H_2dapab

	Analysis * (%)			
Compound	M	C	H	N
[Mn(H_2dapab)(CH_3OH)Cl]Cl·H_2O	9.9 (9.1)	47.3 (47.6)	5.0 (4.8)	16.7 (16.2)
[Co(H_2dapab)Cl_2]·4H_2O	8.8 (9.3)	43.7 (43.8)	4.7 (5.0)	15.4 (15.5)
[Cu(H_2dapab)Cl_2]·H_2O	11.2 (10.9)	47.7 (47.5)	4.1 (4.2)	16.0 (16.9)
[Zn(H_2dapab)Cl_2]·4H_2O	11.0 (10.3)	43.5 (43.3)	5.2 (4.9)	15.7 (15.4)
[Co(dapab)]	11.3 (12.1)	56.4 (56.8)	4.3 (4.4)	19.8 (20.2)
[Cu(dapab)]	13.2 (12.9)	56.0 (56.3)	4.0 (4.3)	19.7 (20.0)
[Zn(dapab)]	12.9 (13.3)	56.7 (56.1)	4.5 (4.3)	19.7 (19.9)

* Calculated values are given in parentheses.

Table 2. Fractional atomic co-ordinates (× 10^4) for [Mn(H_2dapab)(CH_3OH)Cl]Cl·H_2O

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Mn	4 507(2)	69(1)	1 710(1)	C(10)	7 809(9)	633(5)	1 464(4)
Cl(1)	3 079(3)	1 239(2)	1 089(1)	C(11)	9 208(11)	1 050(7)	1 541(5)
Cl(2)	2 389(3)	2 343(2)	−1 491(1)	C(12)	9 515(10)	1 582(7)	2 090(6)
O(1)	3 390(8)	−930(5)	1 036(3)	C(13)	8 487(10)	1 697(6)	2 555(5)
O(2)	2 653(7)	−244(4)	2 302(3)	C(14)	7 125(9)	1 242(5)	2 435(4)
O(3)	5 656(8)	−1 129(4)	2 223(3)	C(15)	5 954(10)	1 257(6)	2 878(4)
N(1)	5 373(10)	−878(5)	455(4)	C(16)	6 211(11)	1 762(7)	3 528(5)
N(2)	5 996(9)	−276(4)	912(4)	C(17)	2 490(9)	175(6)	2 802(4)
N(3)	6 806(7)	729(4)	1 901(3)	C(18)	1 201(10)	64(6)	3 173(4)
N(4)	4 775(7)	816(5)	2 678(3)	C(19)	8(11)	−522(7)	2 925(6)
N(5)	3 565(8)	764(5)	3 039(4)	C(20)	−1 227(12)	−618(9)	3 303(6)
N(6)	954(12)	−1 897(7)	724(7)	C(21)	−1 227(15)	−182(10)	3 885(7)
N(7)	37(17)	−969(10)	2 379(7)	C(22)	−82(15)	379(8)	4 115(6)
C(1)	1 709(10)	−2 139(6)	202(4)	C(23)	1 120(11)	502(7)	3 778(5)
C(2)	984(10)	−2 755(6)	−228(4)	C(24)	5 171(15)	−1 617(8)	2 756(5)
C(3)	1 727(10)	−3 096(6)	−735(4)	O(4)	2 390(25)	2 139(15)	5 006(11)
C(4)	3 195(10)	−2 821(6)	−812(4)	O(5)	5 000(0)	0(0)	5 000(0)
C(5)	3 920(10)	−2 204(6)	−382(4)	H(1N)	5 982(96)	−981(55)	115(44)
C(6)	3 177(10)	−1 863(6)	125(4)	H(5N)	3 440(96)	1 313(56)	3 199(42)
C(7)	3 996(13)	−1 208(6)	572(5)	H(71N)	1 077(107)	−893(57)	2 123(42)
C(8)	7 324(11)	20(6)	918(4)	H(72N)	−436(128)	−1 157(87)	2 059(66)
C(9)	8 404(12)	−218(7)	432(5)				

The unit-cell parameters were obtained from a least-squares fit of the diffractometer settings of 28 intense reflections. From the systematic extinctions (*h*0*l* absent with *l* odd, and 0*k*0 absent with *k* odd) the space group was unambiguously determined as $P2_1/c$.

A total of 4 780 reflections ($+h$, $+k$, $+l$) were measured in the range $3 < \theta < 24°$. Following removal of systematically absent and redundant reflections, 4 411 unique data remained, 2 177 of which having $I > 2\sigma(I)$ were judged to be 'observed' and, after corrections for Lorentz and polarization factors, were used in subsequent calculations. The θ–2θ scan method was used, and the intensities were measured with the profile technique. A standard reflection was periodically remeasured to account for crystal stability and long-term drift. No crystal decomposition was noted during the data collection.

The structure was solved by a combination of direct methods and Fourier techniques. The *E*-map computed with the phases of the set having the highest reliability index (parachor) revealed the positions of Mn and Cl atoms. All the other non-hydrogen atoms, including two half-occupancy water molecules of solvation, were found after a few cycles of structure factor calculations and difference Fourier syntheses. Isotropic unit-weighted full-matrix least-squares refinement of the positional parameters for all atoms gave $R = 0.1133$. Further refinement was then carried out, with all the atoms, except the two water molecules, assigned anisotropic thermal parameters. Rigid-group refinement was used for the C(1)–C(6) phenyl ring which was found to exhibit modest disorder problems. At this point a ΔF synthesis was computed, which only revealed the positions of four hydrogen atoms [those bonded to N(1), N(5), and N(7)]. These H atoms were included in the refined model, with their isotropic thermal parmeters allowed to refine freely. Attempts to locate the remaining hydrogens were unsuccessful. The final agreement factors were $R = 0.0676$ and $R' = 0.0734$, with a goodness-of-fit value of 0.4985. The ratio observations: variables was 2 173:343 = 6.3:1. Four bad reflections were rejected from the last calculations. An extinction correction was also applied. The function minimized in the least-squares refinement was $\Sigma w(F_o - F_c)^2$, where the weighting scheme used throughout was of the form $w = k/\sigma^2(F_o) + g|F_o|^2$. Maximum and minimum peak heights on the final difference Fourier map were 0.26 and −0.19 e $Å^{-3}$, respectively.

Scattering factors and anomalous dispersion corrections were taken from ref. 5. Computations were carried out on a GOULD-SEL 32/77 computer using the SHELX system of programs[6] and some locally developed programs. The molecular plots were drawn with PLUTO.[7]

Atomic positional parameters are listed in Table 2; selected interatomic distances and angles are in Table 3.

Results and Discussion

Some physical data for H_2dapab and its metal complexes are given in Table 4. Elemental analysis established that all the complexes have 1:1 metal:ligand stoicheiometry. As previously observed for 2,6-diacetylpyridine 2-picolinoyl-, 2-

Table 3. Selected distances (Å) and angles (°)

(*a*) Co-ordination sphere of Mn			
Mn–O(1)	2.215(7)	Mn–N(2)	2.279(8)
Mn–O(2)	2.208(7)	Mn–N(3)	2.266(6)
Mn–O(3)	2.300(6)	Mn–N(4)	2.268(7)
		Mn–Cl(1)	2.462(3)
O(1)–Mn–N(2)	69.5(3)	O(2)–Mn–N(4)	69.0(2)
N(2)–Mn–N(3)	68.8(3)	O(1)–Mn–O(2)	83.1(3)
N(3)–Mn–N(4)	68.3(3)	Cl(1)–Mn–O(3)	173.6(2)
(*b*) Ligands			
N(6)–C(1)	1.38(2)	N(7)–C(19)	1.31(2)
C(6)–C(7)	1.49(1)	C(17)–C(18)	1.46(1)
O(1)–C(7)	1.22(1)	O(2)–C(17)	1.23(1)
N(1)–C(7)	1.37(1)	N(5)–C(17)	1.36(1)
N(1)–N(2)	1.38(1)	N(4)–N(5)	1.38(1)
N(2)–C(8)	1.26(1)	N(4)–C(15)	1.27(1)
C(8)–C(9)	1.51(2)	C(15)–C(16)	1.53(1)
C(8)–C(10)	1.48(1)	C(14)–C(15)	1.46(1)
N(3)–C(10)	1.34(1)	C(13)–C(14)	1.39(1)
C(10)–C(11)	1.39(1)	N(3)–C(14)	1.35(1)
C(11)–C(12)	1.39(1)	O(3)–C(24)	1.43(1)
C(12)–C(13)	1.40(2)		
Mn–O(1)–C(7)	121.2(7)	Mn–O(2)–C(17)	120.6(6)
O(1)–C(7)–N(1)	119.4(9)	O(2)–C(17)–N(5)	119.7(8)
N(2)–N(1)–C(7)	115.0(8)	N(4)–N(5)–C(17)	114.0(7)
Mn–N(2)–N(1)	114.8(6)	Mn–N(4)–N(5)	115.5(5)
N(1)–N(2)–C(8)	123.0(8)	N(5)–N(4)–C(15)	121.6(7)
Mn–N(2)–C(8)	122.1(6)	Mn–N(4)–C(15)	122.9(6)
N(2)–C(8)–C(9)	125.0(9)	N(4)–C(15)–C(16)	125.4(8)
N(2)–C(8)–C(10)	114.9(8)	N(4)–C(15)–C(14)	114.5(8)
C(9)–C(8)–C(10)	120.1(8)	C(14)–C(15)–C(16)	120.2(8)
C(8)–C(10)–C(11)	123.5(8)	C(13)–C(14)–C(15)	123.5(8)
N(3)–C(10)–C(8)	114.5(8)	N(3)–C(14)–C(15)	114.5(7)
N(3)–C(10)–C(11)	122.0(8)	N(3)–C(14)–C(13)	121.9(8)
C(10)–C(11)–C(12)	116.6(9)	C(12)–C(13)–C(14)	116.1(9)
C(11)–C(12)–C(13)	122.7(9)	C(10)–N(3)–C(14)	120.7(7)
Mn–N(3)–C(10)	119.5(5)	Mn–N(3)–C(14)	119.7(5)
Mn–O(3)–C(24)	127.6(7)		
(*c*) Possible hydrogen bonding			
N(6) ··· O(1)	2.64(1)	N(5) ··· Cl(2^{ii})	3.29(1)
N(7) ··· O(2)	2.60(1)	N(7) ··· Cl(2^{iii})	3.38(1)
O(3) ··· Cl(2^{i})	3.063(7)	O(4) ··· Cl(1^{ii})	3.34(2)
		O(4) ··· Cl(2^{ii})	3.15(2)

i $1 - x, \bar{y}, \bar{z}$; ii $x, \frac{1}{2} - y, z + \frac{1}{2}$; iii $\bar{x}, \bar{y}, \bar{z}$.

benzoyl-, and 2-thenoyl-hydrazones, in this case also the complexes with the metal chlorides contain the hydrazone in its neutral form, the formula being $M(H_2dapab)Cl_2{\cdot}nH_2O$ (n = 1—4), while the metal acetates give rise to complexes [M(dapab)] containing the hydrazone in its doubly deprotonated form. All the complexes are obtained in high yields and appear to be stable both in the solid state and in solution. Both types of complexes are scarcely soluble, although the [M(dapab)] derivatives are slightly more so, in polar solvents such as alcohols and dimethyl sulphoxide: for this reason, no absorptions are observed in the visible region in alcohol solution.

X-Ray Structure of $[Mn(H_2dapab)(CH_3OH)Cl]Cl{\cdot}H_2O$.—The structure consists of discrete cations $[Mn(H_2dapab)(CH_3OH)Cl]^+$, chloride anions, and water molecules. Figure 1 shows a view of the cation along with the numbering system adopted and Figure 2 a diagram of the molecular packing, projected down *a*.

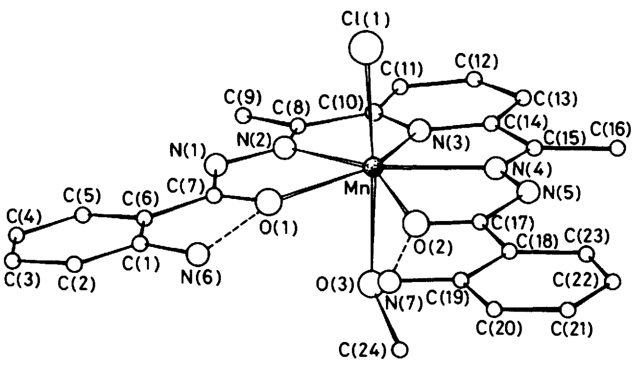

Figure 1. A perspective drawing of the $[Mn(H_2dapab)(CH_3OH)Cl]^+$ cation, showing the atom-numbering scheme

The manganese atom has a co-ordination geometry which approximates to pentagonal bipyramidal (ideally, of D_{5h} symmetry), this being the commonest seven-co-ordinate stoicheiometry for Mn^{II}.[8]

The H_2dapab, which is present in its neutral form, behaves as a quinquedentate ligand through three N and two O atoms encircling the metal atom and occupying the equatorial belt. The apices of the bipyramid are filled by a Cl ion and the O atom from the co-ordinated methanol solvent.

Valency angles at Mn show small, but significant, distortions from an ideal pentagonal-bipyramidal arrangement. Four of the five angles subtended at Mn by adjacent equatorial atoms are only slightly smaller than the ideal value of 72°, their range being 68.3(3)—69.5(3)°, while the fifth, namely that involving the two O atoms, is larger by *ca.* 11°. The range of the equatorial to axial angles is 81.7(2)—98.6(2)°; the interaxial angle is reduced from a theoretical 180 to 173.6(2)°.

The N_3O_2 basal set of atoms is nearly coplanar with a maximum displacement from the mean least-squares plane of 0.07 Å; the Mn atom lies 0.19 Å above this plane in the direction of the chlorine. An angle of 4.6(2)° is formed between the normal to this plane and the direction of the Mn–Cl bond; the corresponding angle for the Mn–O(3) bond is 4.2(2)°.

With regard to the Mn–O bonds, the two equatorial distances are essentially equal, 2.215(7) and 2.208(7) Å, while the axial distance, 2.300(6) Å, is significantly longer, as expected. The three Mn–N distances are practically equivalent at 2.266(6), 2.268(7), and 2.279(8) Å. All these values are well within the range previously reported for pentagonal-bipyramidal arrangements in manganese(II) compounds.[8] The observed Mn–Cl bond distance is 2.462(3) Å, which is in very good agreement with 2.468(3) Å found in the manganese(II) complex of 2,6-diacetylpyridine mono(2-aminobenzoylhydrazone);[1] both these values are slightly but significantly shorter than those observed for $Mn–Cl_{axial}$ bonds [range 2.503(3)—2.532(3) Å] in other pentagonal-bipyramidal manganese(II) compounds.[8]

There are four, five-membered chelate rings in the structure, all of which are slightly twisted [4.8(2)—6.1(1)°] out of the N_3O_2 donor plane. The atoms of the two MnNCCN rings slightly deviate from overall planarity with maximum deviations of 0.04 Å; the rings are at an angle of 3.9(2)° to each other and inclined 5.9(2) and 9.3(2)° to the plane of the respective adjacent MnOCNN chelate ring. One of these rings, MnO(1)C(7)N(1)N(2), is essentially planar (maximum deviation 0.02 Å), while some puckering of the other one, MnO(2)C(17)N(4)N(5), is observed, the largest deviation of any of the constituent atoms from the least-squares plane being 0.08 Å.

As mentioned in the Introduction, two other H_2dapab metal complexes have been characterized recently in our laboratory by *X*-ray diffraction, namely [SnBuCl(dapab)] and [SnPh₂-

Table 4. Physical data and selected vibrational bands (cm^{-1}) of the ligand and metal complexes

	Colour	M.p. (°C)	ν(NH),ν(OH)	ν(NH)	ν(CH)$_{aryl}$	ν(CH)$_{alkyl}$	amide I	ν(CC),δ(NH)	ν(CN),δ(NH)	δ(CH),ν(CN)	δ(NH),ν(CN)
H$_2$dapab	Pale yellow	187	3 500w 3 450m 3 340s	3 220m	3 060w 3 020w	2 920w	1 660vs	1 615 (sh) 1 600m 1 580m 1 550 (sh)	1 530vs	1 480m 1 450s 1 425m	1 250vs
[Mn(H$_2$dapab)(CH$_3$OH)Cl]Cl$\cdot$H$_2$O	Orange	> 250	3 440m 3 400 (sh) 3 300m	3 180m	3 060w	2 920w	1 620vs	1 582s 1 542ms	1 515s	1 475m 1 445m 1 425m	1 250vs
[Co(H$_2$dapab)Cl$_2$]$\cdot$4H$_2$O	Yellow-orange	> 250	3 420w 3 320w	3 180w	3 060w	2 920w	1 625vs	1 580s 1 560 (sh) 1 550s	1 510s	1 480 (sh) 1 450m 1 430m	1 250vs
[Ni(H$_2$dapab)Cl$_2$]$\cdot$H$_2$O	Pale green	> 250	3 450w 3 360w	3 180m	3 060w	2 920w	1 660 (sh) 1 625vs	1 580m 1 570 (sh) 1 550 (sh)	1 510m	1 485m 1 465m 1 425m	1 250m
[Cu(H$_2$dapab)Cl$_2$]$\cdot$H$_2$O	Dark brown	215	3 600m 3 400m	3 180 (sh) 3 120m	3 050w	2 920w	1 655s 1 610vs	1 580m 1 560m 1 500 (sh)	1 510m	1 485m 1 405m	1 300m 1 255m
[Zn(H$_2$dapab)Cl$_2$]$\cdot$4H$_2$O	Yellow	250	3 600w 3 420m 3 280w	3 180w	3 070w	2 920w	1 620vs	1 580s 1 550s	1 510vs	1 480m 1 450m 1 430m	1 250vs
[Mn(dapab)]	Orange	> 250	3 450 (sh) 3 360m	—	3 040m 3 000 (sh)	2 960 (sh)	1 608m	1 585m 1 570 (sh) 1 540 (sh)	1 525s	1 490s 1 450wm 1 430 (sh)	1 315s 1 250br
[Co(dapab)]	Yellow-orange	> 250	3 450 (sh) 3 360m	—	3 060m,br	2 920w	1 610m	1 590ms 1 545 (sh) 1 535vs	1 500s	1 450m	1 330s 1 270 (sh)
[Ni(dapab)]	Brown	> 250	3 450m 3 390m 3 250m	—	3 060w	2 920w	1 665m 1 610s	1 580s 1 550 (sh)	1 490vs	1 450m 1 430m	1 300m 1 260m
[Cu(dapab)]	Brown	> 250	3 450m 3 390m 3 260m	—	3 060w	2 920w	1 665m 1 610s	1 580s 1 550 (sh)	1 490vs	1 460 (sh) 1 425m	1 255s
[Zn(dapab)]	Orange	> 250	3 440br 3 260w	—	3 060w	2 920w	1 610s	1 580s 1 550w	1 490vs	1 460m 1 425m	1 250s

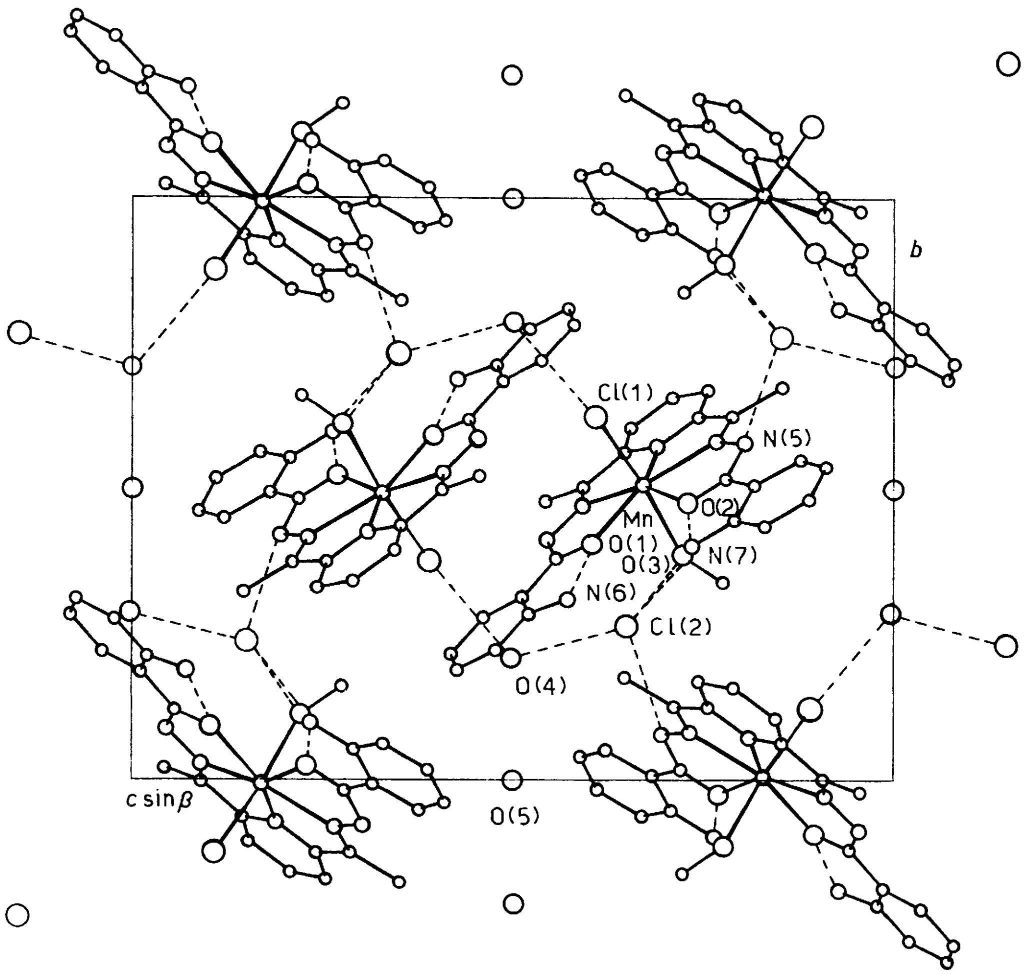

Figure 2. Molecular packing of the structure viewed along the *a* axis

(dapab)], in both of which the ligand was found to be present in its doubly deprotonated form.[3] Another remarkable feature that distinguishes the title structure from those mentioned above is the conformation of the two NH_2 groups. As also indicated by the torsion angles O(1)–C(7)–C(6)–C(1) [3(1)°] and O(2)–C(17)–C(18)–C(19) [−4(1)°] in the manganese compound, both the NH_2 groups are in a *syn* position with respect to the O atoms of the CO groups. As a consequence of this conformation, the molecule has two strong intramolecular $N\text{–}H \cdots O$ hydrogen bonds. In contrast to the present compound, in [SnBuCl(dapab)] the two NH_2 groups are both in a *syn* position with respect to the hydrazidic N atom, while an intermediate situation has been found in [$SnPh_2$(dapab)], where one NH_2 is positioned *syn* to the O atom and the other *syn* to the N atom of the hydrazide group. It is reasonable to relate these effects to the different form, neutral or deprotonated, of the hydrazone as well as to the nature of the metal.

Except for the two C(phenyl)–N(amino) distances, which are somewhat different, the chemically-equivalent bond distances and angles in the two hydrazone chains are in good agreement with each other.

Even if the absence of most hydrogen-atom positions prevents a full description, nevertheless we can observe that the molecular packing (see Figure 2 and Table 2) is mainly dictated by a three-dimensional hydrogen-bonding network involving cations, anions, and water molecules. The Cl(2) ion, which remains outside the co-ordination sphere of Mn, is linked through hydrogen bonding to three atoms of the cation, *i.e.* two N atoms of the hydrazone ligand and the O atom of the co-ordinated methanol solvent. In addition to accepting these three hydrogen bonds, Cl(2) is involved in a further hydrogen bond with O(4) of the water molecule. Concerning the two water molecules, they are both present in the crystal lattice as water of crystallization, as they are not directly bonded to the metal atom. One water molecule, O(4), is engaged in hydrogen bonding as it directs its hydrogens to Cl(2) and, more weakly, to Cl(1); the other, O(5), which lies disordered about a centre of symmetry, does not take part in any hydrogen-bonding interaction. The rather high thermal parameter of O(5) is fully consistent with the absence of hydrogen bonding. In addition, we particularly note the $O(4) \cdots C(2)$ ($\bar{x}$, $\frac{1}{2} + y$, $\frac{1}{2} - z$) intermolecular distance of 3.08(2) Å, which is less than the sum of the van der Waals radii and probably has to be ascribed to the disorder involving the C(1)—C(6) phenyl ring.

Infrared Spectra.—A comparison of the main vibrational bands of H_2dapab in its free state and in the co-ordinated form is reported in Table 3.

In the series of M(H_2dapab)$Cl_2 \cdot nH_2O$ complexes, the essentially similar spectroscopic pattern shown by the manganese, cobalt, and zinc derivatives indicates that an ONNNO-quinquedentate H_2dapab, as found from the *X*-ray study in the manganese complex, is also present in the other two compounds. Co-ordination mainly affects the amide I and amide II bands which undergo a negative shift of *ca.* 35 and 20 cm^{-1} respectively.[9] The i.r. spectra of the nickel and copper complexes show some significant differences when compared with those of manganese, cobalt, and zinc. In particular, the amide I band in both the complexes is split in two bands which differ by 35 and 50 cm^{-1} for nickel and copper derivatives, respectively. The higher absorption band shows in both cases a frequency value (*ca.* 1 660 cm^{-1}) similar to that observed in the spectrum of the free ligand. This fact could be explained as the effect of the participation in the co-ordination to metal of only one CO group. On the other hand, a similar splitting of the CO frequency value has been already observed in nickel complexes of 2,6-diacetylpyridine acylhydrazones and explained by a large difference in the Ni–O bond lengths.[8,10] The same explanation could also be acceptable for the copper complex, even if no examples on this subject are reported.

Examination of the vibrational bands of [M(dapab)] complexes and comparison with those of $M(H_2dapab)Cl_2{\cdot}nH_2O$ reveal a higher negative shift ($\Delta\nu \simeq 50$ cm^{-1}) and a decrease of the absorption intensity for the amide I band as a consequence of the deprotonated nature of the hydrazone and of the co-ordination to metal.[11] On the basis of the absorption values in the manganese and cobalt complexes both the CO groups are involved in the co-ordination. In nickel and copper complexes a split of the amide I band is observed, the difference being 55 cm^{-1} in both cases, which can be explained in a similar manner as that described above for the corresponding $M(H_2dapab)Cl_2{\cdot}nH_2O$ derivatives. In the zinc complex, which shows only one ν(CO) band in its spectrum, the structure could be similar to that recently observed in $[Zn_2(dapt)_2]$ [H_2dapt = 2,6-diacetylpyridine bis(2-thenoylhydrazone)][12] and in $[Zn_2(dapp)_2]$ [H_2dapp = 2,6-diacetylpyridine bis(2-pyridylhydrazone)].[13]

Conclusions

The *X*-ray data and the i.r. assignments confirm for H_2dapab the strong chelating properties that this kind of ligand shows towards different transition metal ions.

As regards the type of stereochemistry, the spectroscopic data for $[M(H_2dapab)Cl_2]{\cdot}nH_2O$ (M = Co, Ni, or Zn) are consistent with a structure resembling that of $[Mn(H_2dapab)(CH_3OH)Cl]Cl{\cdot}H_2O$, in which H_2dapab behaves as a quinquedentate ligand and the metal atom is at the centre of a distorted pentagonal bipyramid. A lower symmetry should be present in all the other complexes.

In addition, the structural situation of both NH_2 groups in $[Mn(H_2dapab)(CH_3OH)Cl]Cl{\cdot}H_2O$ suggests the possibility to carry out a template reaction with a dialdehyde or a diketone in order to form a NNNNN-quinquedentate macrocyclic ligand. Moreover, manganese is a transition metal ion capable of acting as template for ring closure to yield macrocyclic molecules.[14] Studies in this research field are now in progress in our laboratory.

Acknowledgements

Support from the Ministero della Pubblica Istruzione, Roma, is gratefully acknowledged.

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Received 4*th February* 1985; *Paper* 5/193