Investigation into Aroylhydrazones as Chelating Agents. Part 3.[1] Synthesis and Spectroscopic Characterization of Complexes of Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} with 2,6-Diacetylpyridine Bis(benzoylhydrazone) and *X*-Ray Structure of Aquachloro[2,6-diacetylpyridine bis(benzoylhydrazone)]manganese(II) Chloride †

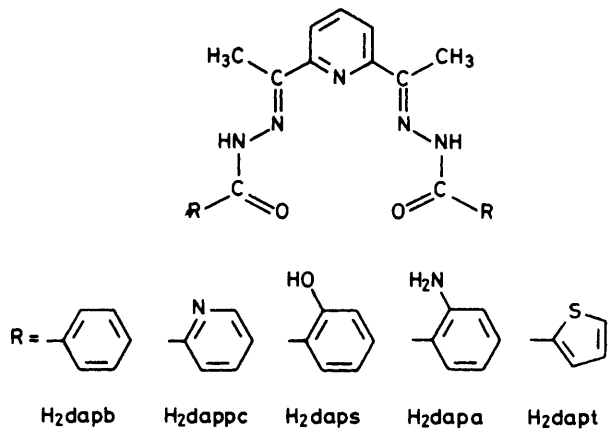
Carlo Lorenzini, Corrado Pelizzi, Giancarlo Pelizzi,* and Giovanni Predieri
Istituto di Chimica Generale ed Inorganica, Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Via M. D'Azeglio 85, 43100 Parma, Italy

The chelating behaviour of neutral and deprotonated 2,6-diacetylpyridine bis(benzoylhydrazone) (H_2dapb) has been investigated in some new complexes of Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}. An *X*-ray diffraction analysis was carried out on [Mn(H_2dapb)(OH_2)Cl]Cl. The crystals are monoclinic, space group $P2_1/c$, with unit-cell dimensions a = 7.065(6), b = 17.096(9), c = 19.446(13) Å, β = 96.89(8)°, and Z = 4. The structure was solved by the heavy-atom technique from 1 545 observed independent reflections recorded at room temperature on an automated diffractometer and refined to a final R value of 0.0329. The structure consists of [Mn(H_2dapb)(OH_2)Cl]$^+$ cations and Cl^- anions. The cation has a pentagonal-bipyramidal geometry, with H_2dapb forming the equatorial plane and the H_2O and Cl groups occupying the axial positions. The i.r. spectra suggest differences in the interaction of these metals with the hydrazone molecule.

We are currently investigating a series of metal complexes of 2,6-diacetylpyridine aroylhydrazones with the aim of obtaining general information about the structure and the stereochemistry of such complexes.

Earlier studies carried out on H_2dappc and H_2daps complexes [1-3] have revealed some interesting aspects such as the strong donor properties of the hydrazones in co-ordination to metals, their tendency to act as approximately planar quinquedentate ligands yielding seven-co-ordinate pentagonal-bipyramidal structures, and the ability to behave as neutral or deprotonated ligands.

The present paper describes the synthesis and the i.r. spectra of complexes of H_2dapb with Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}, and the *X*-ray diffraction analysis of [Mn(H_2dapb)(OH_2)Cl]Cl.



Experimental

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. Infrared spectra (4 000—200 cm^{-1}) for KBr discs were recorded on a Perkin-Elmer model 283 B spectrophotometer, mass spectra with a Varian CH-5 spectrometer (70 eV ≈ 1.12 × 10^{-17} J).

Materials.—2,6-Diacetylpyridine was used as received (Aldrich). Organic solvents were purified using published procedures.[4]

Benzohydrazide was prepared by treating hydrazine with methyl benzoate using the published procedure.[5] 2,6-Diacetylpyridine bis(benzoylhydrazone) (H_2dapb) was prepared by heating benzohydrazide and 2,6-diacetylpyridine (2 : 1 molar ratio) under reflux in absolute ethanol for 3 h. The white-yellow microcrystalline product obtained on cooling was recrystallized from methanol and identified by its C, H, and N elemental analysis, melting point (212 °C), and mass spectrum [*m/e*: 399 (2.4), 294 (26.2), 266 (8.3), 105 (100.0), 77 (39.3), and 51 (5.5%)].

The complexes of Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} were prepared by mixing ethanol solutions of H_2dapb and ethanol solutions of the metal salt (chloride or acetate) in 1 : 1 molar ratio. The mixture was refluxed for 1 h and then allowed to stand. When the acetates of Ni, Cu, and Zn were used, precipitation immediately occurred, while from metal chlorides a microcrystalline product was isolated only after slow evaporation of the solvents. The compounds were purified by washing with small portions of cold chloroform. Analytical and physical data are listed in Table 1.

Template Reaction.—A mixture (1 : 2 : 1 molar ratio) of 2,6-diacetylpyridine, benzohydrazide, and Zn(CH_3COO)$_2$·2H_2O was dissolved in ethanol and refluxed for 1 h. After cooling and slow evaporation of the solvent a yellow crystalline product was obtained for which the analytical data and i.r. spectrum agree with the formula Zn(dapb).

X-*Ray Analysis of* [Mn(H_2dapb)(OH_2)Cl]Cl.—Preliminary Weissenberg and rotation photographs established monoclinic symmetry. The space group $P2_1/c$ was deduced from systematic absences. The *X*-ray analysis was done at room

† *Supplementary data available* (No. SUP 23509, 16 pp.): thermal parameters, structure factors. See Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

Table 1. Analytical * and physical data

Compound	Colour	Melting point (°C)	Analysis (%) M	C	H	N
H_2dapb	Pale yellow	212		68.8 (69.2)	5.5 (5.3)	17.3 (17.5)
[Mn(H_2dapb)(OH_2)Cl]Cl	Yellow-orange	>290	10.3 (10.1)	51.1 (50.8)	4.6 (4.3)	12.7 (12.9)
Co(H_2dapb)Cl_2·3H_2O	Yellow-green	290 (decomp.)	9.8 (10.1)	47.4 (47.4)	4.3 (4.7)	11.9 (12.0)
Ni(H_2dapb)Cl_2·3H_2O	Yellow	230 (decomp.)	9.9 (10.1)	47.5 (47.4)	4.4 (4.7)	11.9 (12.0)
Zn(H_2dapb)Cl_2·3H_2O	Yellow	245 (decomp.)	10.7 (11.1)	47.1 (46.8)	4.8 (4.6)	12.0 (11.9)
Mn(dapb)·4H_2O	Orange	>290	10.7 (10.5)	52.4 (52.7)	5.5 (5.2)	13.2 (13.4)
Co(dapb)·2H_2O	Orange	>290	11.7 (12.0)	55.4 (56.1)	4.7 (4.7)	13.7 (14.2)
Ni(dapb)	Dark brown	>290	12.8 (12.9)	60.8 (60.6)	4.2 (4.2)	15.1 (15.4)
Cu(dapb)	Brown	>290	14.2 (13.8)	60.1 (59.9)	4.5 (4.2)	15.0 (15.2)
Zn(dapb)	Yellow	>290	14.4 (14.1)	59.5 (59.7)	4.3 (4.1)	14.8 (15.1)

* Calculated values are given in parentheses.

Table 2. Comparison of the main i.r. bands (cm^{-1}) in the complexes M(H_2dapb)Cl_2·nH_2O

Assignment	H_2dapb	[Mn(H_2dapb)(OH_2)Cl]Cl	Co(H_2dapb)Cl_2·3H_2O	Ni(H_2dapb)Cl_2·3H_2O	Zn(H_2dapb)Cl_2·3H_2O
			3 500m	3 500 (sh)	
ν(OH)		3 400m	3 380 (sh)	3 430m	3 450m,br
ν(NH)	3 280m,br	3 300m	3 300m	3 330m,br	3 300m,br
		3 220 (sh)	3 200 (sh)	3 200 (sh)	3 200 (sh)
		3 170m			
ν(CH)(aryl)	3 080w				
	3 050w	3 060mw	3 060mw	3 060w	3 060mw
	3 020w	3 005w	3 005w	3 010w	3 005w
ν(CH)(alkyl)	2 960w	2 970 (sh)			
	2 910w	2 905mw	2 910w	2 920w	2 915w
		2 800w	2 750m,br	2 750w	2 750w
Amide I	1 670 (sh)			1 680s	1 645 (sh)
	1 660vs,br	1 635vs	1 630vs	1 635vs	1 630vs,br
ν(C=N)	1 615m (sh)	1 625vs	1 615 (sh)		
Ring	1 600m (sh)	1 600m	1 600ms	1 600ms	1 600m
	1 580ms	1 575m	1 575s	1 580ms	1 580s
	1 565ms			1 550w	
	1 530vs				
Amide II	1 520vs	1 515vs,br	1 520vs,br	1 510vs	1 520vs,br
Ring	1 485ms	1 485s	1 485s	1 480ms	1 485s
	1 450s	1 460m	1 450m	1 450m	1 450ms
		1 445m			
	1 425 (sh)	1 430m	1 425m	1 425m	1 430ms
δ(NCO)	1 370ms	1 370w	1 375mw	1 375m	1 380m
	1 340ms				
ν(C–O)	1 310w	1 305 (sh)	1 325 (sh)	1 310 (sh)	1 310 (sh)
Amide III	1 275vs,br	1 285vs	1 300vs	1 285vs	1 295vs
			1 280vs	1 270vs	1 280vs
ν(N–N)	1 025m	1 028m	1 025m	1 025m	1 025 (sh)

temperature on a Siemens AED three-circle diffractometer under the control of a General Automation Jumbo 220 computer, using Mo-K_α ($\bar{\lambda}$ = 0.710 69 Å) radiation. Unit-cell parameters were determined by a least-squares treatment of the diffractometer setting angles of 18 strong reflections.

Crystal data. a = 7.065(6), b = 17.096(9), c = 19.446(13) Å, β = 96.89(8)°, U = 2 332(3) Å^3, Z = 4, D_c = 1.548 g cm^{-3}, F(000) = 1 116, μ(Mo-K_α) = 8.10 cm^{-1}.

Two octants of reciprocal space were surveyed with 2.5 < θ < 24.0°, using profile analysis. A total of 3 984 reflections were collected. After systematic absences had been deleted, merging of equivalent reflections gave 3 525 unique intensities of which 1 545 with $I > 2\sigma(I)$ were considered observed and retained for refinement. A standard reflection measured after every 50 reflections showed no significant change in intensity. Data were corrected for Lorentz and polarization effects, but not for absorption.

The structure was solved by the heavy-atom method and refined by full-matrix least-squares calculations, with all non-hydrogen atoms assigned anisotropic thermal parameters, to a conventional R index of 0.0501. A difference-Fourier map computed at this stage revealed all the hydrogen atoms which were refined isotropically. In the final cycles the weighting scheme $w = [\sigma^2(F_o) + 0.005(F_o)^2]^{-1}$ was introduced and refinement converged smoothly to give final residuals R = 0.0329 and R' = 0.0285. A final difference map was devoid of any chemically significant features.

Complex neutral-atom scattering factors were used, those for the non-hydrogen atoms being corrected for anomalous dispersion.[6] For all the computations, the SHELX package [7] of crystallographic programs was used. The final atomic fractional co-ordinates are given in Table 4, selected bond distances and angles in Table 5.

Results and Discussion

With the aim of testing the co-ordination behaviour of 2,6-diacetylpyridine bis(benzoylhydrazone) (H_2dapb) in neutral or

Table 3. Comparison of the main i.r. bands (cm^{-1}) in the complexes M(dapb)

Assignment	Mn(dapb)·4H_2O	Co(dapb)·2H_2O	Ni(dapb)	Cu(dapb)	Zn(dapb)
ν(OH)	3 560m				
	3 450m,br	3 300m,br			
	3 200m				
ν(CH)(aryl)	3 060w	3 080w	3 080w	3 080w	3 080w
		3 040w	3 050w	3 050w	3 060w
ν(CH)(alkyl)	2 910w	2 900w	2 910w	2 905w	2 910w
	1 640 (sh)				
δ(OH), amide I	1 630ms				1 610w
	1 600 (sh)		1 595 (sh)	1 595 (sh)	
	1 580ms	1 580s	1 585m	1 585ms	1 585m
Ring	1 560 (sh)	1 560 (sh)			
ν(C=O), ν(C=N)	1 545vs	1 550m	1 550s	1 550s	1 550m
	1 535vs	1 510 (sh)	1 495 (sh)	1 500 (sh)	1 500 (sh)
Ring	1 490s	1 500vs,br	1 485vs	1 485vs	1 490vs,br
	1 450 (sh)		1 455m	1 460s	1 450m
	1 420s,br	1 410s	1 425s	1 430s	1 430m
δ(NCO)	1 360vs,br	1 375vs,br	1 365vs,br	1 370vs	1 365vs,br
				1 355vs	
ν(C–O)	1 320w	1 330s	1 325s	1 330s	1 325m
	1 310w	1 300 (sh)	1 300m	1 300ms	1 300m
Amide III	1 290s	1 295m	1 285s	1 290ms	1 285m
		1 270w	1 260mw	1 260m	1 260mw
ν(N–N)	1 050m	1 050m	1 050s	1 050s	1 045m

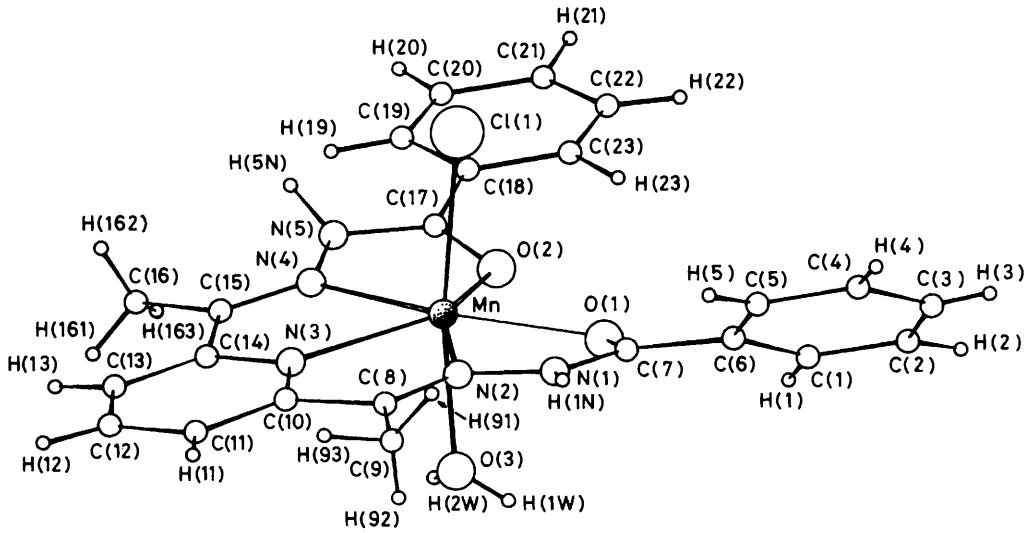


Figure 1. Structure of $[Mn(H_2dapb)(OH_2)Cl]^+$ showing the atom-numbering scheme

deprotonated form and of comparing its spectroscopic properties in different metal complexes we have treated the hydrazone with the chlorides of Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II}. Moreover, we have also prepared the corresponding complexes with the metal acetates, the synthesis and physicochemical properties of which have recently been reported.[8] From the analytical data (Table 1) it is to be noted that, whereas the reaction of the acetates invariably leads to the formation of chelates containing bideprotonated ligand, $dapb^{2-}$, the chlorides form complexes of formula $M(H_2dapb)Cl_2 \cdot nH_2O$ (n = 1 or 3) when M = Mn, Co, Ni, and Zn. When M = Cu a green-brown product was isolated which could not be freed from impurities, and in this case the main product seems to be the same as that isolated from the reaction with copper acetate, *i.e.* Cu(dapb). Elemental analysis established that all the complexes have 1 : 1 metal to ligand stoicheiometry.

Infrared Spectra.—Table 2 lists selected vibrational bands and assignments of H_2dapb in its free state and in the neutral co-ordinated form. The hydrate nature of the complexes is always well evident by the presence of strong and broad absorptions in the 3 500 cm^{-1} region; these bands partially disappear when the complexes are heated at 120 °C for several hours. In all the complexes the amide I band, ν(C=O), shifts towards lower frequency values (Δν *ca.* 30 cm^{-1}), while the amide II, ν(C=O) + δ(NH), and the amide III, δ(NH) + ν(C=O), bands shift slightly to lower (Δν *ca.* 15 cm^{-1}) and higher (Δν *ca.* 20 cm^{-1}) frequencies, respectively.[9,10] The assignment of the amide III band is not always certain, owing to the complicated nature of the spectrum in the 1 300—1 100 cm^{-1} region. The vibrations at about 1 620 cm^{-1} are assigned to ν(C=N) of the azomethine group which undergoes a downward shift (Δν *ca.* 15 cm^{-1}), indicating that the azomethine

Table 4. Fractional atomic co-ordinates ($\times 10^4$) of $[Mn(H_2dapb)(OH_2)Cl]Cl$

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Mn(1)	1 645(1)	3 019(0)	7 102(0)	C(19)	5 019(8)	5 088(3)	9 094(3)
Cl(1)	4 666(2)	3 375(1)	6 624(1)	C(20)	5 450(8)	5 835(3)	9 339(3)
Cl(2)	1 603(2)	−1 520(1)	5 921(1)	C(21)	4 901(9)	6 486(3)	8 952(3)
O(1)	−106(5)	3 630(2)	6 235(2)	C(22)	3 880(8)	6 393(3)	8 308(3)
O(2)	1 997(6)	4 187(2)	7 667(2)	C(23)	3 383(8)	5 651(3)	8 062(3)
O(3)	−1 164(5)	2 964(2)	7 545(2)	H(1N)	−470(92)	2 221(35)	5 278(32)
N(1)	−266(7)	2 509(2)	5 626(2)	H(5N)	5 119(91)	3 597(34)	8 781(31)
N(2)	495(6)	2 147(2)	6 231(2)	H(1)	−2 354(97)	4 620(39)	5 602(37)
N(3)	2 085(6)	1 723(2)	7 423(2)	H(2)	−3 240(100)	5 425(41)	4 607(34)
N(4)	3 287(6)	2 883(2)	8 176(2)	H(3)	−2 529(101)	4 959(38)	3 580(36)
N(5)	3 917(6)	3 571(2)	8 509(2)	H(4)	−1 128(98)	3 799(38)	3 354(39)
C(1)	−2 106(8)	4 447(3)	5 123(3)	H(5)	−243(101)	2 994(39)	4 288(32)
C(2)	−2 669(9)	4 917(3)	4 558(3)	H(91)	363(98)	971(38)	5 281(35)
C(3)	−2 247(9)	4 689(3)	3 914(3)	H(92)	−1 159(112)	715(43)	5 759(39)
C(4)	−1 325(8)	3 989(3)	3 825(3)	H(93)	532(94)	300(40)	5 809(32)
C(5)	−783(8)	3 513(3)	4 395(3)	H(10)	3 594(89)	664(34)	8 756(31)
C(6)	−1 165(7)	3 744(3)	5 041(2)	H(11)	1 274(87)	−56(33)	6 838(31)
C(7)	−476(8)	3 296(3)	5 681(3)	H(12)	2 728(87)	−361(36)	7 977(29)
C(8)	586(8)	1 401(3)	6 281(3)	H(161)	3 849(102)	1 761(40)	9 452(33)
C(9)	−101(9)	832(3)	5 730(3)	H(162)	5 602(104)	2 014(39)	9 221(32)
C(10)	1 470(8)	1 140(3)	6 983(3)	H(163)	4 075(104)	2 573(40)	9 522(34)
C(11)	1 649(9)	360(3)	7 175(3)	H(19)	5 378(99)	4 617(40)	9 350(34)
C(12)	2 486(9)	183(3)	7 831(3)	H(20)	6 230(103)	5 923(37)	9 765(36)
C(13)	3 115(8)	781(3)	8 286(3)	H(21)	5 349(99)	7 024(39)	9 110(33)
C(14)	2 878(8)	1 545(3)	8 061(3)	H(22)	3 430(100)	6 820(39)	8 005(32)
C(15)	3 546(8)	2 234(3)	8 499(3)	H(23)	2 544(99)	5 610(38)	7 628(37)
C(16)	4 390(9)	2 153(3)	9 239(3)	H(1W)	−2 113(95)	3 095(35)	7 280(31)
C(17)	3 225(9)	4 232(3)	8 170(3)	H(2W)	−1 118(87)	3 174(32)	8 033(31)
C(18)	3 933(8)	4 989(3)	8 447(3)				

Table 5. Selected intramolecular distances (Å) and angles (°) within the cation

Mn–Cl(1)	2.503(3)	N(3)–C(14)	1.334(7)	C(10)–C(11)	1.386(7)
Mn–O(1)	2.228(4)	N(4)–N(5)	1.390(5)	C(11)–C(12)	1.374(8)
Mn–O(2)	2.278(4)	N(4)–C(15)	1.277(6)	C(12)–C(13)	1.390(8)
Mn–O(3)	2.258(4)	N(5)–C(17)	1.369(6)	C(13)–C(14)	1.381(7)
Mn–N(2)	2.328(4)	C(1)–C(2)	1.381(8)	C(14)–C(15)	1.496(7)
Mn–N(3)	2.313(4)	C(1)–C(6)	1.392(7)	C(15)–C(16)	1.496(8)
Mn–N(4)	2.276(4)	C(2)–C(3)	1.378(8)	C(17)–C(18)	1.466(7)
O(1)–C(7)	1.220(7)	C(3)–C(4)	1.383(8)	C(18)–C(19)	1.403(8)
O(2)–C(17)	1.230(7)	C(4)–C(5)	1.391(8)	C(18)–C(23)	1.387(7)
N(1)–N(2)	1.380(5)	C(5)–C(6)	1.374(7)	C(19)–C(20)	1.384(7)
N(1)–C(7)	1.359(6)	C(6)–C(7)	1.492(7)	C(20)–C(21)	1.373(7)
N(2)–C(8)	1.280(6)	C(8)–C(9)	1.485(8)	C(21)–C(22)	1.377(8)
N(3)–C(10)	1.351(6)	C(8)–C(10)	1.499(8)	C(22)–C(23)	1.386(7)
N(3)–Mn–N(4)	67.5(2)	Mn–O(1)–C(7)	119.3(4)	O(1)–C(7)–C(6)	120.7(5)
N(2)–Mn–N(3)	66.8(1)	Mn–O(2)–C(17)	117.7(4)	O(1)–C(7)–N(1)	121.3(5)
O(3)–Mn–N(4)	91.2(2)	N(2)–N(1)–C(7)	114.3(4)	N(2)–C(8)–C(10)	112.2(5)
O(3)–Mn–N(3)	87.3(2)	Mn–N(2)–N(1)	113.5(3)	N(2)–C(8)–C(9)	126.1(5)
O(3)–Mn–N(2)	90.3(2)	N(1)–N(2)–C(8)	121.5(5)	C(9)–C(8)–C(10)	121.8(5)
O(2)–Mn–N(4)	68.5(2)	Mn–N(2)–C(8)	124.9(4)	N(3)–C(10)–C(8)	115.1(5)
O(2)–Mn–O(3)	84.4(2)	Mn–N(3)–C(14)	119.8(3)	C(8)–C(10)–C(11)	123.1(5)
O(1)–Mn–N(2)	68.7(2)	Mn–N(3)–C(10)	120.9(4)	C(13)–C(14)–C(15)	123.1(5)
O(1)–Mn–O(3)	82.8(2)	C(10)–N(3)–C(14)	119.2(4)	N(3)–C(14)–C(15)	114.7(5)
O(1)–Mn–O(2)	88.4(2)	Mn–N(4)–C(15)	124.5(4)	N(4)–C(15)–C(14)	112.8(5)
Cl(1)–Mn–N(4)	90.1(2)	Mn–N(4)–N(5)	116.1(3)	C(14)–C(15)–C(16)	122.4(5)
Cl(1)–Mn–N(3)	103.9(2)	N(5)–N(4)–C(15)	119.1(5)	C(16)–C(15)–N(4)	124.8(5)
Cl(1)–Mn–N(2)	97.1(2)	N(4)–N(5)–C(17)	113.5(4)	O(2)–C(17)–N(5)	120.6(5)
Cl(1)–Mn–O(3)	168.3(1)	C(5)–C(6)–C(7)	122.3(5)	N(5)–C(17)–C(18)	117.7(5)
Cl(1)–Mn–O(2)	85.3(2)	C(1)–C(6)–C(7)	117.4(5)	O(2)–C(17)–C(18)	121.6(5)
Cl(1)–Mn–O(1)	91.5(2)	N(1)–C(7)–C(6)	118.0(5)		

nitrogen atom is co-ordinated to the metal atom.[11,12] It is worthy that the amide I band is split for the complex $Ni(H_2dapb)Cl_2·3H_2O$; this apparently anomalous behaviour had already been observed for $[Ni(H_2dapb)(OH_2)_2][NO_3]_2·2H_2O$,[13] where a large difference in the Ni–O bond lengths explains the splitting of the C=O frequency values.

In the spectra of the M(dapb) complexes (Table 3) a remarkable shift ($\Delta\nu$ *ca.* 70 cm^{-1}) towards lower frequency

Table 6. Comparison between structural parameters (distances in Å, angles in degrees) in pentagonal-bipyramidal manganese(II) compounds

Complex	$Mn-L_{eq}$	$Mn-L_{ax}$	$L_{ax}-Mn-L_{ax}$	Sum of the angles in pentagonal girdle
(1)	2.30(1), 2.26(4), 2.22(1) [a]	2.30(4) [b]		
(2)	2.271(8), 2.266(11), 2.265(9) [a] 2.255(8), 2.252(9) [b]	2.227(8) [b] 2.506(7) [c]	179.4(3)	359.8
(3)	2.429(6) 2.385(6), 2.385(6), 2.354(5), 2.311(5) [a]	2.294(7), 2.174(7) [a]	170.8(2)	364.4
(4)	2.41(3)—2.34(3) [a]	2.24(2), 2.20(2) [b]		
(5)	2.254(10), 2.244(9), 2.214(8) [a] 2.296(8), 2.270(7) [b]	2.277(13), 2.254(13) [a]	172.3(4)	360.2
(6)	2.422(9) [a] 2.417(6), 2.303(7), 2.247(8) 2.178(8) [b]	2.182(8), 2.177(9) [b]	175.7(3)	361.7
(7)	2.310(7), 2.303(9), 2.273(8) [a] 2.220(7), 2.212(7) [b]	2.222(8) [b] 2.532(3) [c]	177.8(2)	360.0
(8)	2.281(7), 2.280(5) [a] 2.190(5) [b]	2.202(6) [b]	179.0(3)	360.4
(9)	2.328(4), 2.313(4), 2.276(4) [a] 2.278(4), 2.228(4) [b]	2.258(4) [b] 2.503(3) [c]	168.3(1)	359.9

Complexes: (1), diperchlorato{10,11,12,13-tetrahydrodibenzo[*b*,*k*]pyrido[*g*,*f*][1,4,7,10,13]penta-azacyclopentadecin-N^5,N^{10},N^{13},N^{18},N^{19b}}-manganese;[16] (2), aquachloro[2,6-diacetylpyridine bis(picolinoylhydrazone)]manganese chloride tetrahydrate;[2] (3), {2,15-dimethyl-3,7,10,-14,20-penta-azabicyclo[14.3.1]eicosa-1(20),2,14,16,18-pentaene}bis(isothiocyanato)manganese;[17] (4), diaqua{2,14-dimethyl-3,6,10,13,19-penta-azabicyclo[13.3.1]nonadeca-1(19),2,13,15,17-pentaene}manganese perchlorate-1,10-phenanthroline–ethanol (2/2/1);[18] (5), {2,13-dimethyl-6,9-dioxa-3,12,18-triazabicyclo[12.3.1]octadeca-1(18),2,12,14,16-pentaene}di-isothiocyanatomanganese;[19] (6) tetra-aquapurpuratomanganese purpurate hexahydrate;[20] (7) aquachloro[2,6-diacetylpyridine bis(semicarbazone)]manganese chloride dihydrate;[21] (8) diaqua[2,6-diacetylpyridine bis(picolinoylhydrazonate)(2−)]manganese heptahydrate;[3] (9), this work.

[a] N donor atom. [b] O donor atom. [c] Cl donor atom.

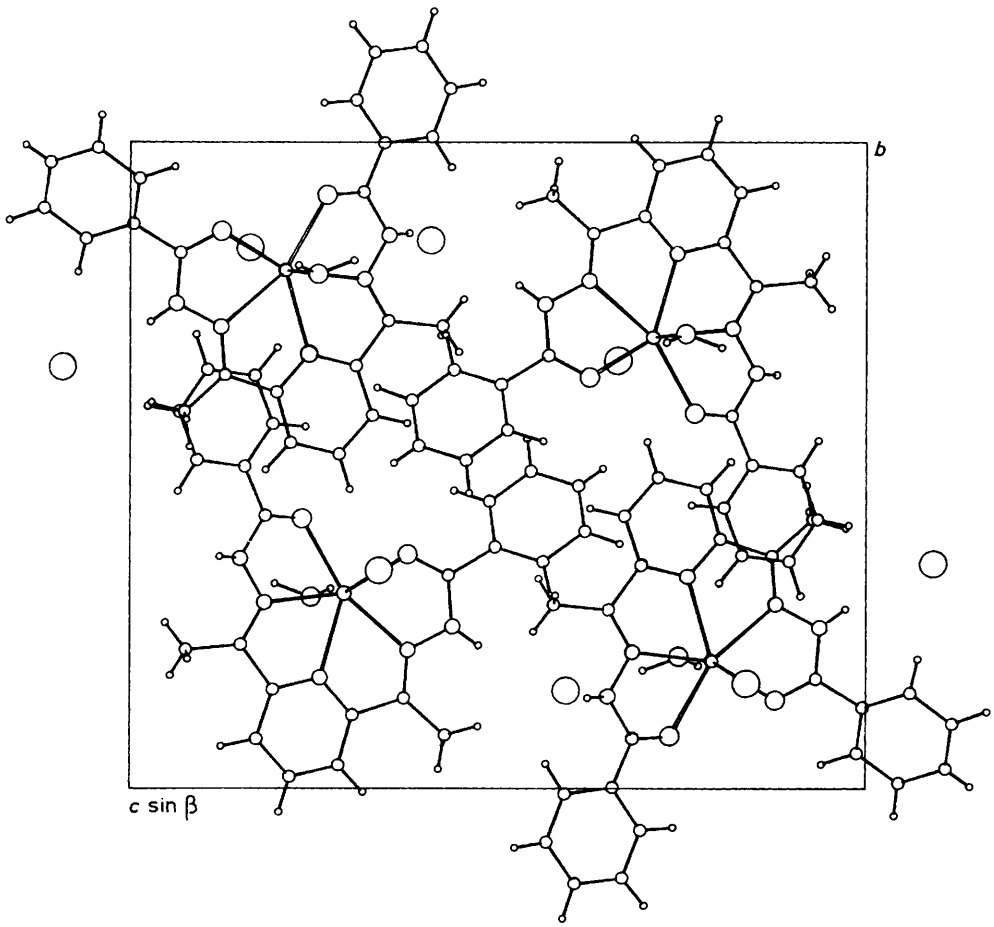


Figure 2. Projection of the structure along [100] showing the crystal packing

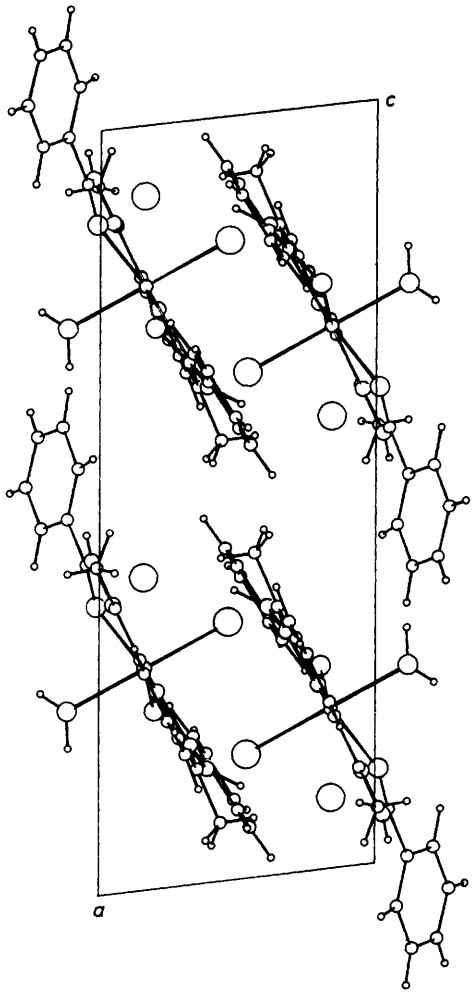


Figure 3. Projection of the structure along [010] showing the crystal packing

values, together with a decrease of the absorption intensity, was observed for the amide I band as compared with the values for the H_2dapb complexes. The loss of the hydrogen atom in both NH groups produces the appearance of a new band *ca.* 25 cm^{-1} to higher frequency with respect to the amide II band. The sharp band at 1 590—1 580 cm^{-1} can be also attributed to the presence of the >C=N–N=C< group, suggesting that the amide-oxygen atom co-ordinates in its enolic form upon deprotonation. This is supported by the presence of the bands in the 1 550 and 1 360 cm^{-1} regions, which are characteristic of the δ(NCO) vibration.

X-Ray Structure of [Mn(H_2dapb)(OH_2)Cl]Cl.—The molecular structure of the title compound consists of discrete [Mn(H_2dapb)(OH_2)Cl]$^+$ cations and Cl^- anions. The structure of the cation is presented in Figure 1, together with the atom-numbering scheme. The co-ordination sphere surrounding the central manganese atom is essentially pentagonal bipyramidal, the axial positions being occupied by one chloride ion and the water molecule, with the quinquedentate H_2dapb ligand forming the equatorial plane. The N_3O_2 donor set of atoms, which form the pentagon, are approximately coplanar, the maximum deviation from the least-squares plane being 0.13 Å. The Mn atom is 0.12 Å above this plane and 0.24 Å off the straight line running through the axial

Table 7. Hydrogen bonding and shorter van der Waals interactions; distances in Å, angles in degrees

O(3) · · · Cl(1^{I})	3.334(5)	O(3)–H · · · Cl(1^{I})	170
O(3) · · · Cl(2^{II})	3.161(6)	O(3)–H · · · Cl(2^{II})	167
N(1) · · · Cl(2^{III})	3.481(6)	N(1)–H · · · Cl(2^{III})	169
N(5) · · · Cl(2^{IV})	3.229(6)	N(5)–H · · · Cl(2^{IV})	159
O(1) · · · C(3^{V})	3.350(7)	O(2) · · · C(11^{II})	3.308(8)
C(8) · · · C(21^{VI})	3.277(10)	C(9) · · · C(20^{VI})	3.305(10)
C(8) · · · C(22^{VII})	3.347(9)		

Roman numeral superscripts refer to the following symmetry codes: I $x-1, y, z$; II $\bar{x}, \frac{1}{2}+y, \frac{3}{2}-z$; III $\bar{x}, \bar{y}, 1-z$; IV $1-x, \frac{1}{2}+y, \frac{3}{2}-z$; V $\bar{x}, 1-y, 1-z$; VI $1-x, y-\frac{1}{2}, \frac{3}{2}-z$; VII $\bar{x}, y-\frac{1}{2}, \frac{3}{2}-z$.

groups; this line is nearly perpendicular to the equatorial plane, making an angle of 86.5° with the plane. The structure possesses four five-membered chelate rings. Least-squares planes drawn through the two MnOCNN rings show deviations from planarity ranging from 0.04 to 0.12 Å. In both the rings the manganese atom lies on the opposite side with respect to the co-ordinated atoms. The two MnNCCN rings are planar within experimental error and practically coplanar, the dihedral angle being 3.0°.

A survey of *X*-ray structure determinations of seven-co-ordinate manganese compounds has revealed the persistence of a pentagonal-bipyramidal environment for the metal, the two exceptions being two ethylenediaminetetra-acetatomanganate(II) derivatives,[14,15] in which the metal atom has a distorted monocapped trigonal-prismatic geometry. Table 6 lists comparative structural data for the co-ordination sphere in all nine of the structurally characterized pentagonal-bipyramidal seven-co-ordinate complexes.[2,3,16–21] Summarizing: (*i*) eight complexes, including the present one, have a quinquedentate ligand in the pentagonal plane and a unidentate inorganic anion or water in the axial positions {compound (6) shows a [M(tridentate ligand) (unidentate ligand)$_4$] stoicheiometry}; (*ii*) atoms of small size, *i.e.* N or O, always span the equatorial positions, N_5, N_3O_2, and NO_4 donor sets being present in three, five, and one compound, respectively; (*iii*) the axial sites are occupied preferentially by nitrogen atoms, and, to a lesser extent, by oxygens or chlorines; (*iv*) the axis of the bipyramid is approximately linear, the angle L_{ax}–Mn–L_{ax} being less than 170° only in the title compound; (*v*) the sum of the five angles in each pentagonal girdle ranges from 359.8 to 364.4°. As regards the compounds containing a quinquedentate ligand it can be added that distortions from planarity are relatively small in each girdle (maximum deviation 0.15 Å), while they are considerably greater for compound (3), in which four N atoms are coplanar with Mn, the pyridine-nitrogen atom being 0.92 Å from this plane.

There are only two H_2dapb complexes of first-row transition elements which can be compared with the present one, namely [Co(H_2dapb)(OH_2)(NO_3)]NO_3 and [Ni(H_2dapb)(OH_2)$_2$][NO_3]$_2$·2H_2O.[13] The dimensions within the organic ligand as well as its geometry are almost the same in the three compounds. Some small structural differences involve mainly the N–N bond distances which are longer in the manganese compound [1.380(5), 1.390(5) Å] than in those of Co [1.365(4), 1.376(4) Å] and Ni [1.369(6), 1.366(6) Å], and the two M–O(ligand) bonds which differ by 0.050, 0.079, and 0.195 Å in the compounds of Mn, Co, and Ni, respectively.

The axial Mn–O(3) of 2.258(4) Å to OH_2 is somewhat longer (0.04—0.08 Å) than axial Mn–O bonds in pentagonal-bipyramidal manganese(II) compounds.[1,3,21]

The molecular packing in the present complex is illustrated in Figures 2 and 3, down the [100] and [010] axes, respectively. All the four hydrogen atoms capable of hydrogen bonding, namely the two from the amide N(1) and N(5) atoms and the two from the water molecule, form hydrogen bonds involving the chloride ions. The distances and angles of these hydrogen bonds are summarized in Table 7, together with some significant van der Waals interactions.

Conclusions

Bearing in mind the *X*-ray data and the i.r. assignments, it can be deduced that, in all the complexes containing neutral H_2-dapb, both the oxygen atoms participate in co-ordination.[22-24] Moreover, there is a striking resemblance between the i.r. spectra of the complexes of Co and Zn and that of the manganese derivative, and this suggests that H_2dapb is quinquedentate in all the complexes, with a pentagonal-bipyramidal stereochemistry as revealed by the present *X*-ray analysis.

Also in M(dapb) complexes the shifts in the amide-group vibrations are consistent with co-ordination of the oxygen atoms to the metal, but in this case a pentagonal-bipyramidal metal environment should be excluded, owing to the absence of water molecules which could occupy the axial positions; consequently, a lower-symmetry stereochemistry should be present, which probably prevents $dapb^{2-}$ maintaining its planarity.

The immediate precipitation which occurs during the preparation of the $dapb^{2-}$ complexes, and the lower solubility in polar solvents and the higher melting points shown by the M(dapb) complexes with respect to those containing the neutral hydrazone, may be due to polymerization.

In conclusion, we can confirm that H_2dapb, as previously noted for H_2dappc and H_2daps, shows strong co-ordinating properties whether neutral or bideprotonated. The ' template ' reaction, carried out on the zinc complex, is further evidence of the ability of H_2dapb to form stable chelates in good yield.

The chemical and structural characterization of complexes of Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} with H_2daps, H_2dapt, and H_2dapa are in progress in our laboratory.[25]

References

1 Part 2, C. Pelizzi, G. Pelizzi, G. Predieri, and S. Resola, *J. Chem. Soc., Dalton Trans.*, 1982, 1349.
2 M. Nardelli, C. Pelizzi, and G. Pelizzi, *Transition Met. Chem.*, 1977, **2**, 35.
3 C. Pelizzi and G. Pelizzi, *J. Chem. Soc., Dalton Trans.*, 1980, 1970.
4 D. D. Perrin, W. L. F. Armarego, and D. R. Perrin, ' Purification of Laboratory Chemicals,' Pergamon Press, Oxford, 1966.
5 E. H. Rodd, 'Chemistry of Carbon Compounds ' Elsevier, London, 1954, vol. 3, part A, p. 556.
6 ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1975, vol. 4.
7 G. M. Sheldrick, SHELX-76, Program for Crystal Structure Determination, University of Cambridge, 1976.
8 S. E. Livingstone and J. E. Oluka, *Transition Met. Chem.*, 1980, **5**, 77.
9 K. K. Narang and A. Aggarwal, *Inorg. Chim. Acta*, 1974, **9**, 137.
10 M. P. Teotia, J. N. Gurtu, and V. B. Rana, *J. Inorg. Nucl. Chem.*, 1980, **42**, 821.
11 D. K. Rastogi, S. K. Sahni, V. B. Rana, and S. K. Dua, *J. Coord. Chem.*, 1978, **8**, 97.
12 R. L. Dutta and A. K. Sarkar, *J. Inorg. Nucl. Chem.*, 1981, **43**, 57.
13 T. J. Giordano, G. J. Palenik, R. C. Palenik, and D. A. Sullivan, *Inorg. Chem.*, 1979, **18**, 2445.
14 S. Richards, B. Pedersen, J. V. Silverton, and J. L. Hoard, *Inorg. Chem.*, 1964, **3**, 27.
15 N. N. Anan'eva, T. N. Polynova, and M. A. Porai-Koshits, *Zh. Strukt. Khim.*, 1974, **15**, 261.
16 N. W. Alcock, D. C. Liles, M. McPartlin, and P. A. Tasker, *J. Chem. Soc., Chem. Commun.*, 1974, 727.
17 M. B. G. Drew, A. H. Othman, S. G. McFall, P. D. A. McIlroy, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1977, 438.
18 M. G. B. Drew, A. H. Othman, S. G. McFall, and S. M. Nelson, *J. Chem. Soc., Chem. Commun.*, 1977, 558.
19 M. G. B. Drew, A. H. Othman, S. G. McFall, P. D. A. McIlroy, and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1977, 1173.
20 M. C. Favas, D. L. Kepert, A. H. White, and A. C. Willis, *J. Chem. Soc., Dalton Trans.*, 1977, 1350.
21 G. J. Palenik and D. W. Wester, *Inorg. Chem.*, 1978, **17**, 864.
22 N. S. Biradar and B. R. Havinale, *Inorg. Chim. Acta*, 1976, **17**, 157.
23 C. Pelizzi and G. Predieri, *Gazz. Chim. Ital.*, 1975, **105**, 413.
24 M. F. Iskander, L. El-Sayed, and S. Saddeck, *Transition Met. Chem.*, 1981, **6**, 27.
25 C. Lorenzini, Thesis, University of Parma, 1982.

Received 22nd *July* 1982; *Paper* 2/1254