Investigation into Aroylhydrazones as Chelating Agents. Part 2.[1] Neutral and Deprotonated Ligand Behaviour of 2,6-Diacetylpyridine Bis-(picolinoylhydrazone) in Complexes of Mn^{II}, Co^{II}, Ni^{II}, and Zn^{II} and *X*-Ray Structure of Diaqua[2,6-diacetylpyridine bis(picolinoylhydrazonato)-(2−)]manganese(II)

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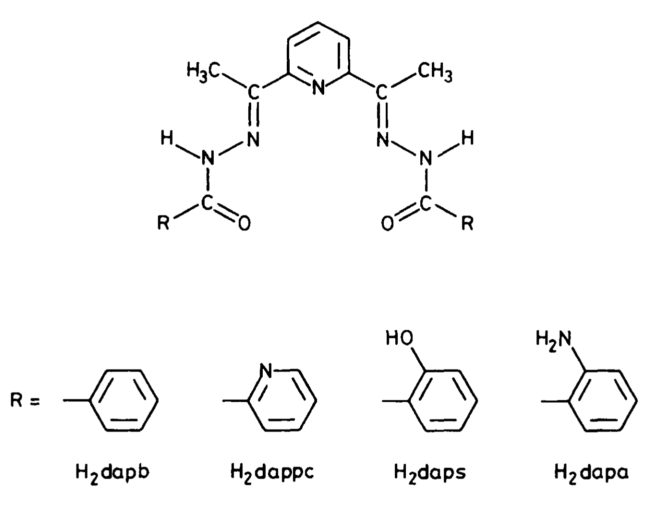
The co-ordinating properties of 2,6-diacetylpyridine bis(picolinoylhydrazone) (H_2dappc) have been investigated in some new complexes of Mn^{II}, Co^{II}, Ni^{II}, and Zn^{II} characterized by spectroscopic and magnetic techniques. An *X*-ray diffraction analysis was carried out on Mn(dappc)·$9H_2O$. The crystals are monoclinic, space group *C*2/*c*, with unit-cell dimensions a = 13.96(1), b = 15.25(2), c= 13.59(1) Å, β = 109.59(8)°, and Z = 4. A total of 1 161 observed reflections have been measured by single-crystal diffractometry and refined by full-matrix least squares to R = 0.050. The manganese ion is in a pentagonal-bipyramidal environment with the dappc ligand occupying the pentagonal girdle and two water molecules in the axial sites.

We have previously reported the synthesis and the characterization of several metal complexes of aroylhydrazones of general formula $[R^1C(O)NHN{=}CR^2]_nR^3$ ($n = 1$ or 2; R^1, R^3 = aryl or heteroaryl; R^2 = H or CH_3), with the aim of investigating the influence co-ordination exerts on their conformation and/or configuration in connection with the nature of the metal and of the counter ion.[2-6] A remarkable versatility in the chelation was observed when $n = 2$, as in 2,6-diacetylpyridine bis(picolinoylhydrazone) (H_2dappc), whose copper, $Cu_2(dappc)Cl_2{\cdot}H_2O$, and manganese, $Mn(H_2dappc)Cl_2{\cdot}5H_2O$, complexes were previously examined.[2,7]



H_2dapb H_2dappc H_2daps H_2dapa

We have now examined the chelating behaviour of H_2dappc in some new complexes of Mn^{II}, Co^{II}, Ni^{II}, and Zn^{II}, as well as its reactivity under different experimental conditions. The present paper deals with the synthesis and the physico-chemical characterization of these complexes and with the *X*-ray crystal structure of the Mn(dappc)·$9H_2O$ complex.

EXPERIMENTAL

Measurements.—Elemental C, H, and N analyses were made on Perkin-Elmer model 240 automatic equipment. Determination of metal was by atomic absorption spectroscopy on a Perkin-Elmer model 303 instrument. Infrared spectra (4 000—200 cm^{-1}) for KBr discs and electronic spectra (11 800—50 000 cm^{-1}) for ethanolic solutions were recorded on Perkin-Elmer model 283 B and 402 spectrophotometers respectively. The magnetic measurements were carried out on a Newport Instruments balance (Gouy method).

Preparations.—The ligand H_2dappc was prepared by treating 2,6-diacetylpyridine with picolinohydrazide as described elsewhere.[7]

Cobalt(II), nickel(II), and zinc(II) complexes were prepared by mixing chloroform solutions of H_2dappc and ethanolic solutions of the metal chlorides in 1 : 1 molar ratio. The solution was refluxed for 3 h and then allowed to stand and slowly evaporate until a microcrystalline product was isolated. The compound was purified by washing the solid with small portions of cold chloroform.

The compound Mn(dappc)·$9H_2O$ was prepared by adding dropwise a 0.01 mol dm^{-3} NaOH solution to a warm ethanol–water solution (1 : 1 v/v) containing H_2dappc and $MnCl_2{\cdot}4H_2O$ (1 : 1 molar ratio) until pH *ca.* 8. During the addition, the colour gradually changed from yellow to orange. By slow evaporation of the solvents, a microcrystalline orange-red product was isolated. The same complex can be obtained from $Mn(H_2dappc)Cl_2{\cdot}5H_2O$ and NH_4OH in ethanol, under reflux for *ca.* 1 h, or from the reaction of H_2dappc, in anhydrous ethanol, with sodium ethanolate (1 : 2 molar ratio) under reflux for 3 h and successive addition of $MnCl_2{\cdot}4H_2O$ (1 : 1 molar ratio).

Template reaction. A mixture (1 : 2 : 1 molar ratio) of 2,6-diacetylpyridine, suspended in water, of picolinohydrazide, dissolved in ethanol, and of $MnCl_2{\cdot}4H_2O$, dissolved in water–ethanol (1 : 1 v/v), was refluxed for 3 h. After cooling and slow evaporation of the solvent, a yellow crystalline product was obtained. Analytical data agree with the formula $Mn(H_2dappc)Cl_2{\cdot}5H_2O$.

Reactions involving the copper ion were carried out under conditions similar to those previously described,[2] changing only the metal : ligand ratios.

X-Ray Data Collection and Determination and Refinement of the Crystal Structure of Mn(dappc)·$9H_2O$.—Preliminary photographs indicated monoclinic symmetry and systematic absences consistent with the space groups $C2/c$ or Cc (hkl, $h + k = 2n + 1$; $h0l$, $l = 2n + 1$). On the basis of the intensity statistics, $C2/c$ was adopted and the choice was confirmed by the successful refinement of the structure. Data were collected on an on-line Siemens AED single-crystal diffractometer using Mo-K_α ($\lambda = 0.710\ 69$ Å) radiation. The unit-cell parameters were obtained by a least-squares treatment of the 2θ values of 14 reflections, accurately centred on the diffractometer.

Crystal data. $a = 13.96(1)$, $b = 15.25(2)$, $c = 13.59(1)$ Å, $\beta = 109.59(8)°$, $U = 2\ 726(5)$ Å^3, $D_m = 1.49$ g cm^{-3}, $Z = 4$, $D_c = 1.502$ g cm^{-3}, $F(000) = 1\ 292$, μ(Mo-K_α) = 5.31 cm^{-1}.

Intensities were recorded at room temperature by the θ—2θ scan method, with θ between 3.0 and 23.0°. The automatic data-collection routine was modified so that the systematically absent reflections hkl, $h + k = 2n + 1$, were not collected. In this way only 2 071 reflections were measured; after symmetry-equivalent reflections had been merged, the number of unique data was 1 903, of which 1 161 with $I > 2\sigma(I)$ were considered observed and formed the basis of the structural refinement. No crystal decay was observed in the standard reflection monitored over the course of the experiment. Data were corrected for Lorentz and polarization factors, but not for absorption.

The observed density of 1.49 g cm^{-3} is consistent with four molecules per unit cell. Thus, in the centric space group $C2/c$, the asymmetric unit contains only half a molecule with the molecule constrained to lie on an inversion centre or on a two-fold axis. The Patterson function indicated that the molecule shows crystallographic two-fold symmetry, with Mn as well as N(1) and C(3) lying on a two-fold axis. Anisotropic full-matrix least-squares refinement converged at $R = 0.050$ with unit weights. The hydrogen-atom positions could not be located convincingly from a Fourier difference map, and they were therefore omitted. Scattering factors for neutral Mn, O, N, and C were taken from ref. 8. A final difference synthesis was featureless.

The final atomic co-ordinates are given in Table 1, bond distances and angles in Table 2. Structure factors and thermal parameters are available as Supplementary Publication No. SUP 23288 (9 pp.).* All the calculations were performed on the Cyber 76 computer of the Consorzio per la Gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale (Casalecchio, Bologna).

DISCUSSION

The versatile co-ordinating behaviour of H_2dappc in the copper(II) and manganese(II) complexes, whose i.r. and X-ray data were reported previously,[2,7] suggested an expansion of our work both to different transition metals such as Co^{II}, Ni^{II}, and Zn^{II} and to a more thorough examination with the same metal atoms, by changing some experimental conditions.

Cobalt, Nickel, and Zinc Complexes.—From the analytical and spectroscopic data (Tables 3 and 4) it can be deduced that all the complexes show the general formula M^{II}(H_2dappc)Cl_2·nH_2O ($n = 5$ or 6), as already found in Mn(H_2dappc)Cl_2·$5H_2O$.[2] The magnetic moments (Table 3) of the complexes of Co^{II} and Ni^{II} are normal for three and two unpaired electrons respectively.[9]

TABLE 1

Fractional atomic co-ordinates (× 10^4) of Mn(dappc)·$9H_2O$

Atom	x	y	z
Mn	0	−80(1)	2 500
O(1)	−501(4)	−1 134(3)	1 346(3)
O(2)	1 457(4)	−93(3)	2 204(3)
N(1)	0	1 416(4)	2 500
N(2)	−841(4)	468(3)	878(4)
N(3)	−1 274(4)	−114(3)	67(3)
N(4)	−2 050(6)	−1 462(4)	−1 286(5)
C(1)	−469(5)	1 849(4)	1 614(5)
C(2)	−481(5)	2 752(4)	1 596(5)
C(3)	0	3 198(6)	2 500
C(4)	−947(5)	1 288(4)	693(5)
C(5)	−1 489(6)	1 680(4)	−360(6)
C(6)	−1 046(5)	−924(4)	424(5)
C(7)	−1 436(5)	−1 664(4)	−327(5)
C(8)	−1 197(6)	−2 481(4)	−36(5)
C(9)	−1 574(8)	−3 149(5)	−701(7)
C(10)	−2 212(8)	−2 968(6)	−1 675(7)
C(11)	−2 413(8)	−2 140(7)	−1 954(6)
O(3)	3 525(5)	133(5)	5 865(5)
O(4)	0	2 678(7)	7 500
O(5)	3 353(8)	543(6)	3 826(7)
O(6)	314(11)	5 660(7)	2 115(10)

All the complexes exhibit similar i.r. absorption bands (Table 4), the only differences concerning some small shifts (5—10 cm^{-1}). The i.r. spectroscopic analysis of H_2dappc in its free state and in the co-ordinated form reveals some differences which indicate the co-ordination mode of the hydrazone. Both amide I and amide II bands are lowered by *ca.* 60—30 and 12—2 cm^{-1} respectively, as compared with the values for the corresponding parent ligand, these variations being related to the co-ordination of the carbonylic oxygen atom to the metal.[10-15] The vibrational bands of these complexes are very similar to those observed in the spectrum of Mn(H_2dappc)Cl_2·$5H_2O$, so suggesting a similar co-

TABLE 2

Bond distances (Å) and selected bond angles (°) in Mn(dappc)·$9H_2O$

Mn–N(1)	2.281(7)	N(2)–N(3)	1.386(6)
Mn–N(2)	2.280(5)	N(3)–C(6)	1.326(8)
Mn–O(1)	2.190(5)	O(1)–C(6)	1.270(7)
Mn–O(2)	2.202(6)	C(6)–C(7)	1.496(9)
N(1)–C(1)	1.336(7)	N(4)–C(7)	1.334(8)
C(1)–C(2)	1.377(9)	N(4)–C(11)	1.357(11)
C(2)–C(3)	1.367(8)	C(11)–C(10)	1.321(14)
C(1)–C(4)	1.478(8)	C(10)–C(9)	1.353(12)
C(4)–C(5)	1.501(9)	C(9)–C(8)	1.346(10)
N(2)–C(4)	1.274(8)	C(8)–C(7)	1.316(9)
N(1)–Mn–N(2)	68.5(2)	N(1)–C(1)–C(4)	115.0(6)
N(2)–Mn–O(1)	68.9(2)	C(1)–C(4)–N(2)	114.3(6)
O(1)–Mn–O(1^i)	85.6(2)	Mn–N(2)–C(4)	122.6(5)
O(2)–Mn–O(2^i)	179.0(3)	Mn–N(2)–N(3)	118.7(4)
Mn–N(1)–C(1)	119.6(4)	C(4)–N(2)–N(3)	118.7(6)
C(1)–N(1)–C(1^i)	120.8(5)	N(2)–N(3)–C(6)	108.6(5)
Mn–O(1)–C(6)	117.6(5)	O(1)–C(6)–C(7)	116.3(6)
O(1)–C(6)–N(3)	125.9(6)	N(3)–C(6)–C(7)	117.7(6)
C(6)–C(7)–N(4)	117.4(6)	C(6)–C(7)–C(8)	120.8(6)
C(7)–N(4)–C(11)	116.8(7)		

i = $\bar{x}, y, \frac{1}{2} - z$.

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

ordinating behaviour of H_2dappc. Probably, in the complexes of Co^{II}, Ni^{II}, and Zn^{II}, it acts as a ONNNO quinquedentate ligand giving rise to a pentagonal-bipyramidal co-ordination, as found in the manganese(II) complex, with the chloride ions or the water molecules occupying the apical positions.

Only one band at 18 180 and at 16 260 cm^{-1} for Co^{II} and Ni^{II} respectively is observed in the visible region (25 000—11 765 cm^{-1}), whose attribution is difficult and scarcely significant. In addition, although pentagonal-bipyramidal complexes of Co^{II} and Ni^{II} have been described,[16,17] nevertheless little information is available on their electronic spectra.[18,19] The spectra in the u.v. region (Table 3) are rather similar for the three complexes, showing a higher number of absorptions and a stronger intensity than those observed in the free-ligand spectrum. These bands are due to π–π^* electronic transitions and their high number can be justified by the presence of both keto- and iminol tautomeric forms.[3,20,21]

TABLE 3

Analytical [a] and physical data for cobalt, nickel, and zinc complexes

Complex	Analysis (%) M	C	H	N	$\tilde{\nu}$/cm^{-1} u.v.	visible	μ/B.M.[b]
Co(H_2dappc)Cl_2·5H_2O	10.0	40.8	4.7	15.7	43 500,	18 180,	4.0
	(9.5)	(40.6)	(4.7)	(15.8)	28 570,	15 870	
					22 220		
Co(H_2dappc)Cl_2·3H_2O	10.2	43.8	4.3	17.1	45 450,	18 200	—
	(10.1)	(43.1)	(4.3)	(16.7)	28 980,		
					27 030		
Ni(H_2dappc)Cl_2·5H_2O	9.8	40.1	4.5	15.6	45 450,	16 260	3.2
	(9.5)	(40.6)	(4.7)	(15.8)	33 330		
Zn(H_2dappc)Cl_2·6H_2O	10.4	39.8	4.4	15.1	43 480,	—	—
	(10.1)	(39.1)	(4.8)	(15.2)	30 770	—	—

[a] Calculated values are given in parentheses. [b] 1 B.M. ≈ 9.27×10^{-24} A m^2.

Manganese Complex.—We have previously noted[2,7] the versatile co-ordinating properties of H_2dappc, which can act as chelating agent in its neutral or dianionic form. From the reaction of H_2dappc with the chlorides of Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, and Zn^{II} carried out under the same experimental conditions, only copper forms a complex containing the hydrazone in its dianionic form, Cu_2(dappc)Cl_2·H_2O.

With the aim of preparing other metal complexes containing the dappc^{2-} dianion we have changed some reaction conditions, using the manganese ion. First a ' template ' reaction was attempted with 2,6-diacetylpyridine, picolinohydrazide, and manganese(II) chloride (1 : 2 : 1 molar ratio) in ethanol solution; also, in this case, the main product of the reaction was Mn(H_2dappc)Cl_2·5H_2O, together with small amounts of a manganese(II) hydrazide complex.

Only by using an alkaline medium was it possible to obtain a manganese(II) complex with the hydrazone in its doubly deprotonated form, following three different reaction paths: (*a*) H_2dappc and $MnCl_2$·4H_2O in alkaline ethanol solution; (*b*) Mn(H_2dappc)Cl_2·5H_2O and an ethanol solution of NH_3; (*c*) $MnCl_2$·4H_2O and the sodium salt of H_2dappc. In all these cases a similar compound of formula Mn(dappc)·$n$$H_2O$ was isolated, containing a different number of water molecules ranging from five to nine. The different value of n causes only small differences in the i.r. spectra of the compounds; when $n = 9$ the product was isolated as orange crystals, which were suitable for *X*-ray analysis. The main differences between the vibrational bands of Mn(dappc)·9H_2O and of Mn(H_2dappc)Cl_2·5H_2O (Table 5) concern a strong decrease of the intensity and the frequency value of amide I band in the dappc complex. In spite of the deprotonated form of the ligand, no increase in the intensity of the band

TABLE 4

Comparison of the main i.r. bands in cobalt, nickel, and zinc complexes

H_2dappc	Co(H_2dappc)Cl_2·5H_2O	Ni(H_2dappc)Cl_2·5H_2O	Zn(H_2dappc)Cl_2·6H_2O	Assignment
	3 450 (sh)		3 600 (sh)	ν(NH), ν(OH)
	3 400m	3 400m, br	3 500 (sh)	
	3 340m	3 250br	3 330m	
3 325m	3 320 (sh)	3 180 (sh)	3 220 (sh)	
3 060w	3 060mw	3 060 (sh)	3 100 (sh)	ν(CH)
2 930w	3 040mw		3 070m	
2 850w	2 920w	2 920w	2 930w	
1 700vs	1 655vs	1 670vs	1 640vs	Amide I
	1 630 (sh)	1 620s		
1 587m	1 590m	1 590m	1 590m	Ring
1 570m	1 570w	1 570mw	1 570mw	
	1 510 (sh)		1 560 (sh)	
1 512vs	1 500vs	1 500vs, br	1 510vs, br	Amide II
1 470m	1 450 (sh)	1 450 (sh)	1 460m	Ring
1 450s	1 430vs	1 430s	1 430s	
1 435s	1 370m	1 380m	1 380m	
1 280m	1 280ms	1 285ms	1 285m	Amide III
1 230m	1 240m	1 275 (sh)	1 270m	

centred at about 1 600 cm^{-1} (due to the C=N–N=C moiety) was observed, as was previously reported in similar systems.[21-23] A medium-strong band at 1 040 cm^{-1} is present, which can be attributed to the ν(C–O) stretching vibration.[23,24]

The nine water molecules give rise to strong and broad absorptions, which prevent observation of the disappearance of the ν(NH) band, as compared to the spectra of H_2dappc in its free state and in Mn(H_2dappc)Cl_2·5H_2O. Noteworthy is the difference between the i.r. absorptions of Cu_2(dappc)Cl_2·H_2O and Mn(dappc)·9H_2O (Table 5); the manganese complex shows a more negative shift and a stronger decrease in frequency for amide I with respect to the copper compound. These differences are consistent with the results of the *X*-ray analysis, which has revealed the different behaviour of dappc^{2-}, *i.e.* nearly planar and ONNNO quinquedentate in the manganese compound, far from planar and octadentate in the copper compound.

TABLE 5

Comparison of the main i.r. bands of Mn(H_2dappc)Cl_2·5H_2O, Mn(dappc)·9H_2O, and Cu_2(dappc)Cl_2·H_2O

Mn(H_2dappc)Cl_2·5H_2O	Mn(dappc)·9H_2O	Cu_2(dappc)Cl_2·H_2O	Assignment
3 620 (sh)			
3 400s, br	3 500—	3 400m	ν(NH), ν(OH)
	3 200s, br		
3 050m	3 050mw	3 060w	ν(CH)
3 010 (sh)	3 010w	2 920w	
2 930w	2 920w	2 840w	
1 650vs	1 595m	1 640s	Amide I
		1 630s	
1 590s	1 585m (sh)	1 603s	Ring
1 572m	1 555m	1 580vs	
1 530 (sh)			
	1 530vs	1 560vs	ν(CN)
	1 500s		
1 500vs	—	—	Amide II
1 460s	1 470m	1 473m	Ring
1 430vs	1 420mw	1 455m	
1 380m	1 370s	1 380s	

The electronic spectrum in ethanol solution shows two absorptions at 45 455 and 31 750 with shoulders at 37 040 and at 28 990 cm^{-1}. No absorptions are observed in the visible region, owing to the spin-forbidden nature of the *d–d* transitions for manganese(II) and to the low solubility of the complex.[25]

The Structure of Mn(dappc)·9H_2O.—Our earlier *X*-ray studies on aroylhydrazones as chelating agents in metal complexes have shown [1,2] the tendency of these molecules to favour a seven-co-ordinate pentagonal-bipyramidal geometry, defining the equatorial plane of the bipyramid, the apices of which are occupied by univalent inorganic anions, solvent molecules, or σ-bonded organic groups. Such co-ordination has been now found in the title complex, whose structure is illustrated in Figure 1 together with the atomic labelling used. The doubly deprotonated dappc molecule acts as a quinquedentate ligand, encircling the manganese atom, and two water molecules span the axial positions of the pentagonal bipyramid. The metal atom and the five atoms of the pentagonal donor set are almost coplanar, the maximum deviation from the MnO_2N_3 least-squares plane being 0.09 Å.

It is of interest to compare the present compound (1) with the analogous Mn(H_2dappc)Cl_2·5H_2O (2),[2] in which the hydrazone is neutral. The two compounds are seen to be very similar with respect to: (*a*) the geometry of the co-ordination polyhedron; (*b*) the ligand behaviour of dappc which gives rise to four five-membered rings; (*c*) the apical L–Mn–L′ angle which is linear in both compounds [179.0(3)° in (1), 179.4(3)° in (2)] with the difference that in (2) one of the two water molecules is disordered and shares 50% occupancy with a chloride ion; (*d*) the values of the Mn–N bond distances [2.280(5), 2.281(7) Å in (1), 2.265(9), 2.266(11), and 2.271(8) Å in (2)]. These values compare fairly well with those found for Mn–$N_{eq.}$ bonds in seven-co-ordinate pentagonal-bipyramidal manganese(II) compounds {*e.g.* 2.22, 2.26, and 2.30 Å in a 15-membered N_5 macrocycle;[26] 2.244(9), 2.214(8), and 2.254(10) Å in a 15-membered N_3O_2 macrocycle;[27] 2.310(7), 2.303(9), and 2.273(8) Å in the [Mn(dapsc)Cl(H_2O)]$^+$ cation [dapsc = 2,6-diacetylpyridine bis(semicarbazone)][28]}. As far as the Mn–O bond distances are concerned, there is no significant difference between the equatorial [2.190(5) Å] and the axial [2.202(6) Å] bonds. Both these values are comparable to those found in the above dapsc derivative [Mn–$O_{eq.}$

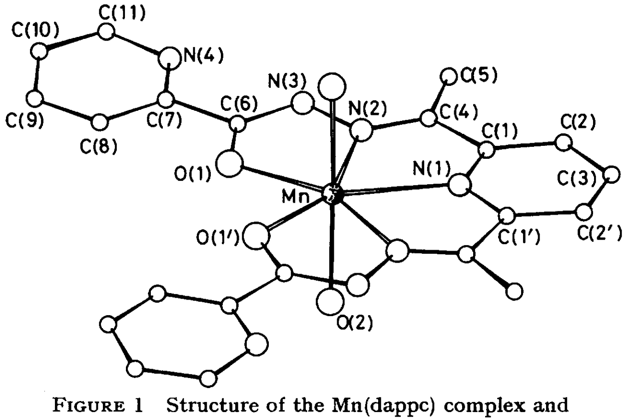

FIGURE 1 Structure of the Mn(dappc) complex and the atom-numbering scheme

2.212(7), 2.220(7); Mn–O$_{ax.}$ 2.222(8) Å], but shorter than those found in (2) [Mn–O$_{eq.}$ 2.255(8), 2.252(9); Mn–O$_{ax.}$ 2.227(8) Å]. If one compares the dappc molecule in the two manganese complexes, worthy of note are the bond angle at N(3) which is narrower [108.6(5)°] in (1) than in (2) [112.7(7), 114.7(7)°], as a consequence of deprotonation, and the OCNNCCN system which is more π-delocalized in (1) than in (2). Incidentally, it can be added that the ligand behaviour of dappc in these two compounds is quite different from that observed in Cu$_2$(dappc)Cl$_2$·H$_2$O (metal–ligand ratio 2 : 1), in which the ligand, present in its deprotonated form, acts in an octadentate manner towards the two non-equivalent copper atoms, both five-co-ordinate.

As illustrated in Figure 2, the structure consists of parallel layers of symmetry-related complex molecules interspaced with the unco-ordinated water molecules. The latter, one of which, O(4), lies on a two-fold axis and another, O(6), is disordered over two positions, link the complex molecules through an intricate hydrogen-bonding network (Table 6).

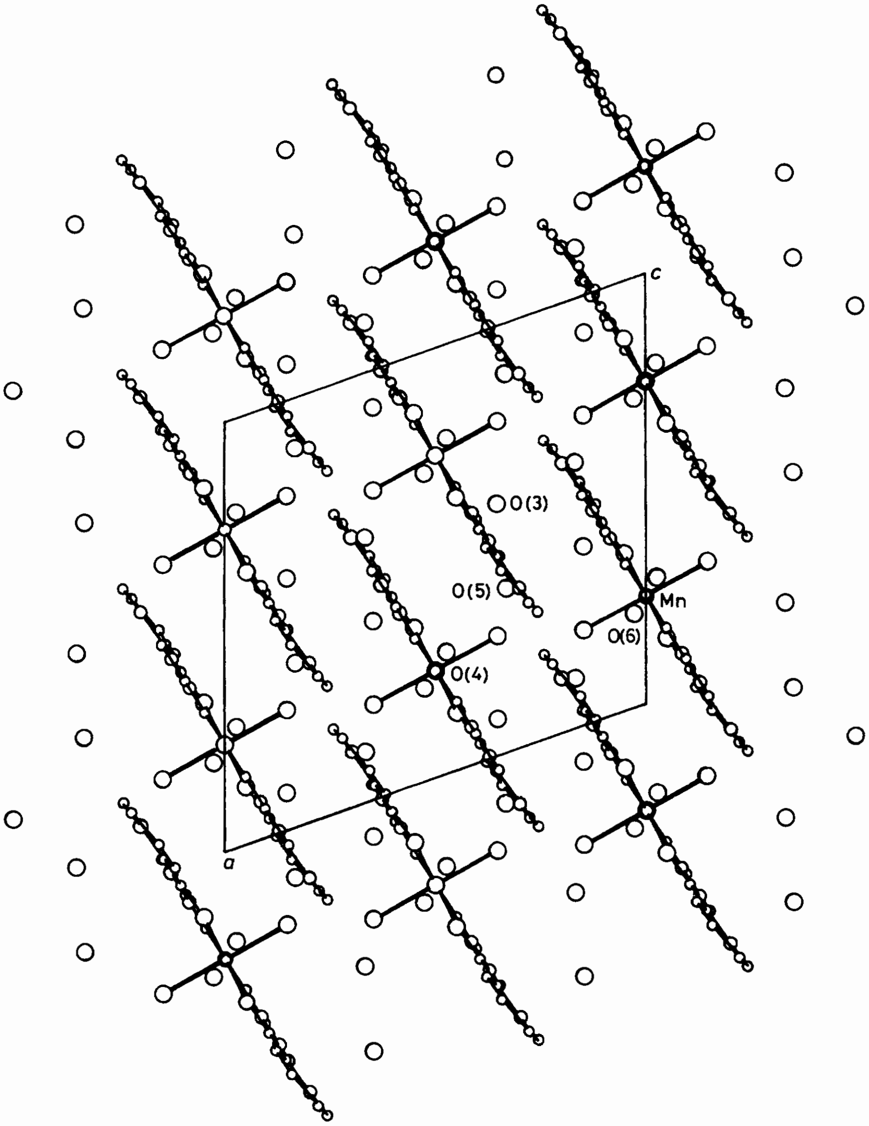

FIGURE 2 Diagrammatic projection of the structure along [010] showing the crystal packing

Copper Complex.—The stoicheiometry and the chelating behaviour of H$_2$dappc in Cu$_2$(dappc)Cl$_2$·H$_2$O [7] differ from those observed in the other complexes. In view of this, we have again investigated the Cu^{II}–H$_2$dappc reaction with the aim of determining whether Cu$_2$(dappc)Cl$_2$·H$_2$O is the only such complex that copper is able to form. Reactions with 2 : 1, 1 : 1, and 1 : 2 metal : ligand molar ratios were carried out, and in all cases Cu$_2$(dappc)Cl$_2$·H$_2$O was the only product, together with unreacted ligand.

From the electronic spectra (5 000—25 000 cm^{-1}) of ethanol solutions containing different molar ratios of the metal to the ligand, it can be noted that: (*a*) when the ligand : metal ratio is 1 : 2 the spectrum is similar to that of free H_2dappc (43 480 and 31 950 cm^{-1}), with the exception of a weak shoulder at 39 215 cm^{-1}; (*b*) for 1 : 1, 3 : 2, and 2 : 1 molar ratios a gradual increase in intensity of the band at 39 215 cm^{-1} and a decrease of that at 31 950 cm^{-1} are observed; (*c*) solutions containing 5 : 2 and 1 : 3 molar ratios show spectra similar to that of 2 : 1 molar ratio.

TABLE 6

Possible hydrogen bonds (Å)

O(2) ··· O(5)	2.98(1)	O(3) ··· O(6^{iii})	2.78(1)
O(2) ··· N(3^{ii})	3.03(1)	O(3) ··· O(6^{iv})	2.94(1)
O(2) ··· N(4^{ii})	2.93(1)	O(4) ··· O(1^{v})	2.79(1)
O(3) ··· N(3^{i})	2.99(1)	O(4) ··· O(6^{vi})	2.65(1)
O(3) ··· O(5)	2.77(1)	O(5) ··· O(6^{vii})	2.59(2)

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

If we consider the band at 39 215 cm^{-1} as an absorption produced by co-ordination of the hydrazone molecule, we can deduce that the 2 : 1 molar ratio is the preferred one, also in solution.

The tendency of H_2dappc to react with the copper ion at 2 : 1 molar ratio was also shown by means of an extraction process. Equimolar amounts of Cu^{II}, Ni^{II}, and Zn^{II} in aqueous solutions were extracted by a chloroform solution of H_2dappc. After evaporation of the organic phase and its decomposition by adding concentrated sulphuric acid, the amounts of metals in the solution were determined by atomic absorption spectroscopy. The data showed that the amount of copper extracted in the organic phase was nearly double that of the other two metals. This experiment has revealed that H_2dappc does not show a different affinity towards copper, nickel, or zinc, the results being consistent with the different ligand : metal molar ratios.

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