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Hydrated manganese(II) cyanato complexes of 3- and 4-acetyl, carbomethoxy-, carboethoxy- and benzoylpyridine derivative ligands and crystal structure of *trans*-dicyanato-bis(4-acetylpyridine)diaquamanganese(II); [Mn(4-acetylpyridine)$_2$(NCO)$_2$(H$_2$O)$_2$]

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Abstract—A series of 1 : 2 manganese(II) cyanato complexes of 3-, 4-acetyl-, 3- and 4-benzoylpyridines, methyl and ethyl nicotinate and isonicotinates has been prepared and characterized. Except for L = ethyl isonicotinate, all other complexes crystallize with two water molecules. In the case of ethyl isonicotinate the complex crystallizes with two ethanol molecules. the IR and Raman spectral lines of diagnostic value are given and discussed, suggesting terminal *N*-bonded cyanato ligands and aqua molecules or bonded ethanol molecules in these manganese(II) complexes. The structure of [Mn(4-acetylpyridine)$_2$(OCN)$_2$(H$_2$O)$_2$] as determined by crystallographic methods features six-coordinate manganese(II) centres, pairs of *trans* aqua molecules [Mn—O = 2.202(3) Å], N-bonded cyanato ligands [Mn—N = 2.116(3) Å] and monodentate N-bonded carbonyl pyridine ligands [Mn—N = 2.322(3) Å]. The structure is further consolidated by hydrogen bonds between aqua oxygen atoms of acetyl groups or terminal oxygen atoms of cyanato ligands. These hydrogen bonds connect the polyhedra along the *cb* plane to form a layer-type structure. The EPR spectra of powder samples and solvent solutions at room temperature were recorded and discussed. © 1997 Elsevier Science Ltd

Keywords: manganese(II) complexes; cyanato complexes; crystal structure; preparation of; vibrational spectroscopy; physical properties.

Recently we established, as part of our continuing study of metal pseudohalide complexes of substituted pyridines [1,2], that manganese(II) azide forms with such ligands complexes which display a variety of structures [3–6]. Thus, when the ligand (L) is pyridine or 4-acetylpyridine, two-dimensional complexes of the type [MnL$_2$(N$_3$)$_2$]$_n$ containing only μ-1,3 bridging azido ligands are isolated [5,6], whereas L = ethyl isonicotinate gives a manganese(II) azide complex of the same type but possesses simultaneous μ-1,1 and μ-1,3 bridging azides [7]. These complexes show interesting magnetic properties. The cyanato ion which is isoelectronic with the azide can function in a similar manner, i.e. it can act as a terminal or as a bridging ligand between two metal atoms in the μ-*N*,*O* (or end-to-end) mode as well as μ-*O*,*O* and μ-*N*,*N* (or end-on) fashions [8–13]. It is therefore expected that the cyanate ion bridges two manganese(II) atoms in a similar way to the azide ion. In fact, the reactions between the manganese(II) ion and pyrazinic acid in the presence of azide ion or cyanate ion afforded complexes of the type [NaMn(pyrazinato)X$_2$(H$_2$O)$_2$]$_n$ (X = N$_3$ or OCN) having the same crystal structure [14,15]. Additionally, there is continuing interest in the synthesis and characterization of manganese(II) complexes, due to the identification of several manganese biomolecules that appear to contain di- and tetranuclear manganese units, including the water oxidation/oxygen evolution centres within the photo-

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synthesis apparatus of green plants and cyanobacteria [16], the manganese catalases [17] and even recently identified manganese ribonucleotide reductases [18]. As a consequence, we examined the complex formation between the manganese(II) ion and some carbonyl derivatives of pyridine in the presence of the cyanate anion. In this paper we report the synthesis and characterization of the title complexes as elucidated by different spectroscopic methods, together with the X-ray structure analysis of *trans*-[Mn(4-acetylpyridine)$_2$(NCO)$_2$(H$_2$O)$_2$], a typical member of this series.

EXPERIMENTAL

The organic pyridine derivative ligands were obtained from Aldrich and the other chemicals were of analytical-grade quality.

Preparation of the complexes

The complexes were prepared by dissolving $MnCl_2 \cdot 3H_2O$ (6 mmol) in distilled water (30 cm^3), followed by addition of the pyridine ligand (14 mmol) dissolved in ethanol (10 cm^3). NaNCO (12 mmol) dissolved in water (*ca* 6 cm^3) was then added and the final mixture filtered. Upon stirring the filtrate, a precipitate of the complex was obtained in cases of methyl and ethyl isonicotinates as well as ethyl nicotinate. The precipitate was filtered off and the filtrate allowed to stand in a refrigerator for several days until crystals of the complex separated. Some physical properties as well as the results of elemental analysis of the isolated complexes are given in Table 1.

Physical measurements

Raman spectra were obtained using a Perkin–Elmer System 2000 NIR FT–Raman spectrometer. The power of the laser beam used was approximately 30 mW. IR spectra were obtained using a Bruker IFS-25 model FT-IR spectrophotometer. Solid samples were measured as KBr pellets and liquid ligands as capillary films between KBr windows. The EPR spectra of solid samples and their solutions in water, ethanol and DMF were recorded using a Bruker ECS 106 ESR spectrometer. The experimental procedures and instruments used for other measurements are as described previously [19].

X-ray crystallography

A modified STOE four-circle diffractometer was used for single-crystal X-ray measurements. Orientation matrix and lattice parameters were obtained by least-squares refinement of the diffraction data from 28 reflections in the 2θ range 11–22°. Data were collected at 295(2) K using graphite crystal-monochromatized Mo-$K\alpha$ radiation ($\lambda = 0.71069$ Å) and the ω-scan technique. The intensities were corrected for Lorentz and polarization effects in the usual way. Crystallographic data are given in Table 2.

The structure was solved by Patterson superposition methods and subsequent Fourier analyses. Anisotropic displacement parameters were applied to the non-hydrogen atoms in full-matrix least-squares refinements based on F^2. Hydrogen-atom positions were obtained from ΔF maps and included in the final refinement cycles by use of geometrical restraints. The

Table 1. Some physical properties and analytical data for the complexes

Complex	Colour	M.p.t (°C)	Analytical: Found (Calc.) (%)				$\mu_{eff}{}^a$ (B.M.)
			C	H	N	Mn	
1, Mn(4-Acpy)$_2$(OCN)$_2$(H$_2$O)$_2$	Yellow	110	46.4	4.2	13.3	13.2	5.75
	crystals		(46.1)	(4.3)	(13.4)	(13.2)	
2, Mn(3-Acpy)$_2$(OCN)$_2$(H$_2$O)$_2$	Pale yellow	210	45.9	4.2	13.6	13.4	5.80
	needles	dec	(46.1)	(4.3)	(13.4)	(13.2)	
3, Mn(Et-ison)$_2$(OCN)$_2$(C$_2$H$_5$OH)$_2$	Bright yellow	150	50.7	5.4	10.5	10.1	5.83
	crystals		(49.5)	(5.6)	(10.5)	(10.3)	
4, Mn(Me-ison)$_2$(OCN)$_2$(H$_2$O)$_2$	Yellow microcrystals	225	42.6	4.2	12.1	12.4	5.78
		dec	(42.8)	(4.0)	(12.5)	(12.2)	
5, Mn(Et-nic)$_2$(OCN)$_2$(H$_2$O)$_2$	White fine	170	45.1	4.8	11.5	11.5	5.92
	needles	dec	(45.3)	(4.7)	(11.7)	(11.5)	
6, Mn(Me-nic)$_2$(OCN)$_2$(H$_2$O)$_2$	White fine	215	43.0	3.9	12.6	12.4	5.77
	needles		(42.8)	(4.0)	(12.5)	(12.2)	
7, Mn(4-Bzpy)$_2$(OCN)$_2$(H$_2$O)$_2$	Pale yellow	165	57.2	4.0	10.1	10.0	5.72
	microcrystals	dec	(57.7)	(4.1)	(10.3)	(10.2)	
8, Mn(3-Bzpy)$_2$(OCN)$_2$(H$_2$O)$_2$	Pale yellow–	160	57.5	4.3	10.4	10.0	5.84
	green powder	dec	(57.7)	(4.1)	(10.3)	(10.2)	

Abbreviations: Acpy = acetylpyridine, Et-ison = ethyl isonicotinate, Me-ison = methyl isonicotinate, Et-nic = ethyl nicotinate, Me-nic = methyl nicotinate, Bzpy = benzoylpyridine. [a] Room-temperature magnetic moments.

Table 2. Crystallographic data and processing parameters

Empirical formula	$C_{16}H_{18}MnN_4O_6$
Molecular weight	417.28
Colour, habit	Yellow, irregular shaped
Crystal system	Monoclinic
a (Å)	7.508(3)
b (Å)	17.405(6)
c (Å)	7.534(4)
β (°)	107.35(3)
V (Å^3)	939.7(7)
Space group	$P2_1/c$ (No. 14)
Z	2
$F(000)$	430
D_{calc} (Mg m^{-3})	1.475
Approximate crystal size (mm)	$0.45 \times 0.28 \times 0.22$
μ(Mo-K_α) (mm^{-1})	0.742
Data collection limits	$\pm h,k,l$; $2\theta < 60°$;
Scan mode	ω-scan, $\Delta\omega = 1.5°$
Reflections collected	2640
Independant reflections	2090 ($R_{int} = 0.0500$)
Parameters/restraints	138/3
Goodness-of-fit on F^2	0.992
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0483$, $wR_2 = 0.0997$
R indices (all data)	$R_1 = 0.1071$, $wR_2 = 0.1179$
Weights a, b^a	0.0407, 0.0000
Residual electron density (e Å^{-3})	$+0.328/-0.434$

[a] $w = 1/[\sigma^2(F_o^2)+(aP)^2+bP]$, where $P = (F_o^2+2F_c^2)/3$.

programs SHELXTL [20] and PLATON [21] were used for computations. Analytical expressions of neutral-atom scattering factors were employed and anomalous dispersion corrections were incorporated [22]. Selected bond distances and bond angles are given in Table 3. Positional parameters, anisotropic displacement parameters, hydrogen-atom coordinates, a full list of bond lengths and angles have been deposited with the Editor as supplementary material.

RESULTS AND DISCUSSION

The reactions between manganese(II) ion and 3-, 4-acetyl-, benzoylpyridines, methyl and ethyl nicotinate and isonicotinates in the presence of the cyanate ion in aqueous/ethanolic medium afforded the manganese(II) complexes given in Table 1. Except the manganese(II) complex of ethyl isonicotinate, all other cyanato complexes contain two water molecules as inferred from their analytical data and IR spectra (see later). The 1 : 2 manganese(II) cyanato complex of ethyl isonicotinate crystallizes with two ethanol molecules rather than water. These cyanato complexes thus differ from the corresponding manganese(II) azido complexes of the same ligands which crystallize without any solvent [3,6,7]. These complexes are soluble in water, methanol, ethanol, DMSO and DMF, in some cases with turbidity, giving rise to non-conducting solutions.

The room-temperature magnetic moment values of 5.70 to 5.90 B.M. found for these complexes fall very well within the range reported for octahedrally coordinated manganese(II) complexes [23,24]. This result is consistent with the infrared and Raman spectral data given in Table 4. The IR spectra of these complexes show a broad band of medium-to-strong intensity over the range 3500–3200 cm^{-1} due to hydrogen-bonded coordinated water molecules [25,26]. The complex $Mn(Et\text{-}ison)_2(OCN)_2S_2$ (S = solvent) exhibit several medium bands at 3450, 3300, 3210, 3000 and 2800 cm^{-1}, which are absent from spectra of all other complexes, due to solvent molecules. The $\nu Mn—O(H_2O)$ or $\nu Mn—O(C_2H_5OH)$ absorption bands appear in the range 560–480 cm^{-1} [27]. Complex **3**, which contains two ethanol molecules, was heated up to 70°C for several hours. The weight loss was found to be *ca* 5%, which is lower than 8.5% required if the complex loses one solvent molecule only, or 7.75% for losing one cyanate anion. The IR spectrum of this sample shows the presence of the cyanates along with a splitting of the asymmetric stretching band with two peaks at 2260 and 2190 cm^{-1}. The 3200 cm^{-1} band disappears and the intensity of the bands 3000, 2800, 1560, 1250, 850, 690 and 550 cm^{-1} are reduced upon heating to 70°C. These bands disappear completely after gradual heating to 130°C. The total weight loss is *ca* 18.1%. This value is a little higher than that required when the complex loses two solvent molecules. We may assume that partial loss of one solvent molecule occurs around 70°C and two molecules at 130°C, as inferred from the IR spectra and percentage of the weight loss at both temperatures. The splitting of the ν_{as} (OCN) band which persists after heating of the sample to 130°C is an indication of the bridging nature of the cyanato groups in the dehydrated complex. The carbonyl stretching bands in the spectra of the present complexes appear at more or less the same positions when compared with the corresponding free ligands, suggesting monodentate 3- and 4-carbonyl derivatives of pyridine ligands. Thus, four coordination sites of the manganese(II) atom are occupied by two aqua (or two solvent) molecules and two *N*-monodentate pyridine ligands. The last two centres should be occupied by two terminal cyanato ligands. Table 4 shows that the complexes exhibit strong IR absorption bands in the range 2220–2180 cm^{-1} and medium bands in the range 1360–1300 cm^{-1}, due to ν_{as} and ν_s modes, respectively, of the cyanato groups. In fact, because of the similar masses of the atoms and similar force constants of the bonds in NCO, with consequent strong coupling between the NC and CO vibrations, one cannot identify ν_{as} simply with the NC vibration nor ν_s with the CO vibration and then make deductions about changes in bond order from the directions of changes of these frequencies [28,29]. The positions of these vibration frequencies, however, are very close to those reported for $[M(NCO)_4]^{2-}$, M = Mn, Fe, Co, Ni and Zn, possessing M—NCO bonds [27]. As seen from Table 4,

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

Mn(1)—N(1)	2.116(3)	Mn(1)—O(3)	2.202(3)
Mn—N(2)	2.322(3)	O(1)—C(1)	1.194(4)
O(2)—C(7)	1.203(5)	N(1)—C(1)	1.145(5)
N(2)—C(2)	1.329(4)	N(2)—C(6)	1.332(5)
C(2)—C(3)	1.369(5)	C(3)—C(4)	1.374(5)
C(4)—C(5)	1.373(4)	C(4)—C(7)	1.494(5)
C(5)—C(6)	1.366(5)	C(7)—C(8)	1.469(5)
N(1)—Mn(1)—O(3)	88.5(1)	N(1)—Mn(1)—N(2)	90.6(1)
O(3)—Mn(1)—N(2a)	89.1(1)	N(1)—Mn(1)—N(2a)	89.4(1)
O(3)—Mn(1)—N(2)	90.9(1)	O(3)—Mn(1)—N(1a)	91.5(1)
Mn(1)—N(1)—C(1)	164.4(3)	Mn(1)—N(2)—C(2)	122.8(2)
Mn(1)—N(2)—C(6)	120.3(2)	C(2)—N(2)—C(6)	116.8(3)
O(1)—C(1)—N(1)	179.4(4)	N(2)—C(2)—C(3)	123.7(3)
C(2)—C(3)—C(4)	118.8(3)	C(3)—C(4)—C(5)	118.1(3)
C(3)—C(4)—C(7)	123.1(3)	C(5)—C(4)—C(7)	118.8(3)
C(4)—C(5)—C(6)	119.3(3)	N(2)—C(6)—C(5)	123.3(3)
O(2)—C(7)—C(4)	118.4(3)	O(2)—C(7)—C(8)	121.3(3)
C(4)—C(7)—C(8)	120.3(3)		
Hydrogen bonds			
O(3)—H(8)	0.94(2)	O(3)—H(9)	0.95(2)
O(3)···O(2)	2.805(4)	O(3)···O(1)	2.763(4)
H(8)···O(2)	1.87(3)	H(9)···O(1)	1.82(2)
O(3)—H(8)···O(2)	172(3)	O(3)—H(9)···O(1)	176(3)

Symmetry code: (a) $-x$, $-y$, $-z$.

ν_{as} appears at higher frequencies in Raman spectra. Low energy (*ca* 1100–1250 cm^{-1}) ν_s bands have been reported in the literature [30,31] for systems potentially involving M—OCN bonding. Other evidence for Mn—NCO bonds in these cyanato complexes comes from their low-frequency Raman spectra. In the region 500–340 cm^{-1} two medium-to-weak bands are assignable [32,33] to the νMn—NCO stretch, similar to other metal cyanato complexes with M—NCO bonds [33]. The νMn—N(L) bands appear in a narrow range, 210–197 cm^{-1}, as expected compared with similar azido complexes of manganese(II). The conclusions given above are confirmed by the crystal structure analysis of the 1 : 2 manganese(II) cyanato complex of 4-acetylpyridine.

The structure of the complex $[Mn(4\text{-}Acpy)_2(NCO)_2(H_2O)_2]$ as determined by X-ray crystallography is given in Fig. 1; selected bond lengths and bond angles are collected in Table 3. Each manganese(II) atom is octahedrally coordinated by the oxygen atoms of two aqua molecules [Mn—O(3) = 2.202(3) Å] and four nitrogen atoms; two nitrogen atoms of two 4-acetylpyridine molecules [Mn—N(2) = 2.322(3) Å] and the other two nitrogen atoms are the end atoms of two terminal N-bonded cyanato ligands [Mn—N(1) = 2.116(3) Å]. The ligands are centrosymmetrically arranged around the metal centre, which occupies the special position at the origin of the unit cell (Fig. 2) The structure is further consolidated by the existence of hydrogen bonds; a hydrogen bond between oxygen atoms O(3) of aqua molecules and oxygen atoms O(2) of the acetyl group, and another hydrogen bond between the aqua oxygen atom O(3) and an oxygen atom of a cyanato group (Table 3). These hydrogen bonds connect the polyhedra along the *cb* plane to form a layer type structure (Fig. 2).

The Mn—N(L) bond length found in the present structure is similar to a corresponding distance of 2.291(3) Å, reported in the structure of $[Mn(4\text{-}acetylpyridine)_2(N_3)_2]_n$ [6], but longer than that of 2.251(27) Å found in the structure of $[Mn(3\text{-}picoline)_2(N_3)_2(H_2O)_2]$ having a very closely similar structure [4]. This difference arises from the difference in the substituent groups. The electron-attracting acetyl group in the 4-position causes a decrease in the charge density on the nitrogen atom, which in turn weakens the Mn—N bond and therefore a long Mn—N distance is observed. In the case of 3-picoline complex the electron-releasing power of the methyl group increases the charge density of the nitrogen atom, and enhances and shortens the Mn—N bond when compared with the present structure.

The O(1)—C(1) bond length of 1.194(4) Å is a comparable with corresponding values found for M—OCN complexes [1.20(2)] [5] and falls into the range found for complexes containing M—OCN—M [1.19(2) to 1.22(2) Å] [10]. Also the N(1)—C(1) distance of 1.145(5) Å is in agreement with corresponding values reported for complexes containing μ(N,O) bridging cyanato groups [1.15(2)–1.18(2) Å] [13] and also with those found for M—OCN complexes [1.18(2)] [10].

Table 4. IR and Raman spectral data for the complexes

	νC=O		νMn—O(S)	ν_{as}(NCO)		ν_s(NCO)		δ(NCO)		νMn—NCO	MN—L
Complex	IR	Raman	IR	IR	Raman	IR	Raman	IR	Raman	Raman	Raman
$Mn(4\text{-}Acpy)_2(OCN)_2(H_2O)_2$	1680 vs	1693 vs	550 m	2210 vs	2248 m	1360 m	1358 m	640 m	642 wm	426 w 366m	205 ms
$Mn(3\text{-}Acpy)_2(OCN)_2(H_2O)_2$	1669 vs	1679 vs	484 wm	2200 vs	2235 wm	1356 m	1330 w 1315 m	637 m	639 m	426 w 392 w	200 m
$Mn(Et\text{-}ison)_2(OCN)_2(S)_2$	1720 vs	1731 vs	550w, br	2200 vs[a]	2240 wm	1360 m	1358 ms	620 m	642 w	430 w 366 wm	220 m
$Mn(Me\text{-}ison)_2(OCN)_2(H_2O)_2$	1725 vs	1720 vs	500 w	2220 m 2180 vs	2232 wm	1320 m	1329 wm	655 wm	669 m	371 m 350 w	227 m
$Mn(Et\text{-}nic)_2(OCN)_2(H_2O)_2$	1714 vs	1718 vs	515 wm, br	2225 s 2190 vs	2245 wm	1356 m	1330 w	656 wm 631 m	644 m	400 w 340 m	215 m 200 m
$Mn(Me\text{-}nic)_2(OCN)_2(H_2O)_2$	1730 vs	1718 vs	500 wm	2220 s 2190 vs	2240 wm	1330 m	1330 w	635 m	665 ms	400 w 337 m	215 m
$Mn(4\text{-}Bzpy)_2(OCN)_2(H_2O)_2$	1650 s	1655 vs	530 w	2200 s 2180 vs	2235 wm	1370 m	1335 wm	644 ms	652 ms	412 m 380 m	210 m
$Mn(3\text{-}Bzpy)_2(OCN)_2(H_2O)_2$	1646 vs	1650 vs	510 w[a]	2210 s 2175 vs	2240 wm		1340 m	653 m 630 wm	630 m	390 w 338 m	205 m

Abbreviations: w = weak, m = medium, s = strong, br = broad, (S) = solvent, H_2O or C_2H_5OH.

[a] A slightly splitted band.

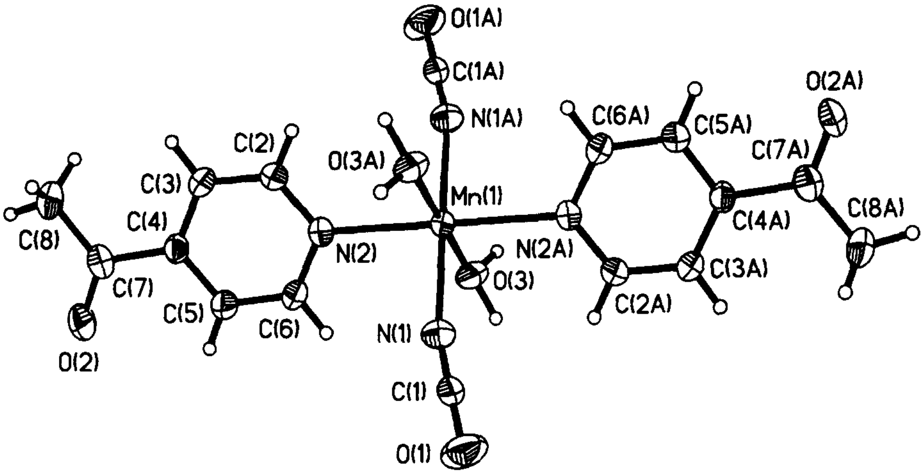

Fig. 1. Molecular geometry and atom labelling scheme of $Mn(4\text{-acetylpyridine})_2(OCN)_2(H_2O)_2$.

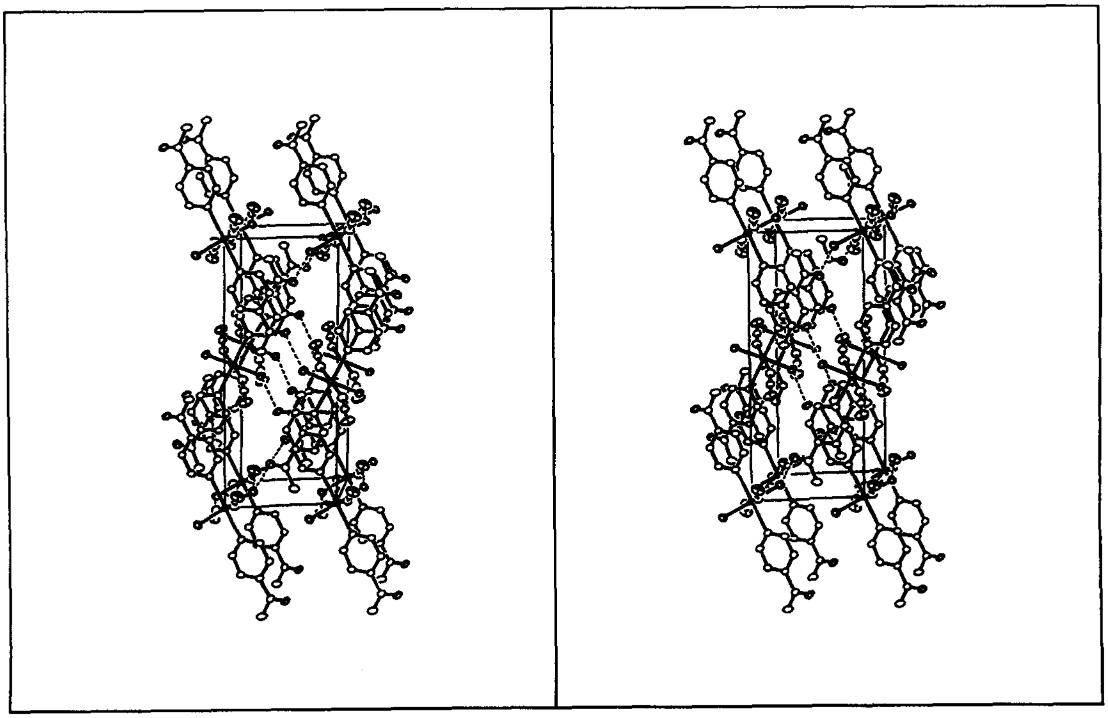

Fig. 2. Unit-cell plot (stereo) of $Mn(4\text{-acetylpyridine})_2(OCN)_2(H_2O)_2$, viewed along the *c*-axis of the unit cell. Hydrogen bonds are indicated by broken lines.

The X-band EPR spectra of powdered samples of complexes **1–8** at room temperature have been recorded. The spectra of complexes **4–8**, which are similar, show a broad intense isotropic signal centred at $g = 2.0$ [Fig. 3(a)]. The peak-to-peak line widths of **4** and **6** is 391 G, that of **5** equals 320 G, but for **7** and **8** the values are 248 and 266, respectively. The spectrum of **7**, however, shows weak features at $g = 1.64$ and 2.52. On the other hand, the room-temperature spectra of complexes **1** and **2** exhibit a hyperfine structure of six components [Figs 3(b) and (c)]. The corresponding hyperfine structure of complex **3** is not clear, which may be due to poor resolution.

All of these complexes were dissolved in water, ethanol and DMF and their room-temperature spectra were recorded; the spectra of **3** in ethanol and **1** in water are reported in Figs 3(d) and (e). These spectra are very similar to each other and to that of solid complex **1** and all of them show the hyperfine structure. Thus, the isotropic signal centred at $g = 2.0$ of the solid complexes **4–8** splits into six lines when dissolved in any of the three solvents, due to hyperfine

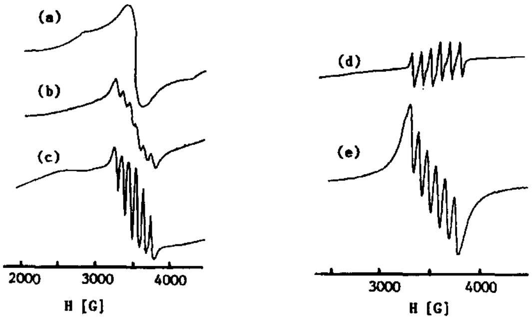

Fig. 3. First derivative EPR spectra (X-band, 9.83 GHz) at room temperature: (a), (b) and (c) **7**, **2** and **1**, respectively, in polycrystalline form; (d) **1** in water; (e) **3** in ethanol.

structure of Mn^{II} ($I = 5/2$). In some of these solvents each of the six components appears split into two small bands. Such splitting may be due to the coupling with the N(py) ($I_N = 1$). The splitting factor (A) for solid complexes **1** and **2** increases from 95.5 to 97.8 G. All of these complexes exhibit the same value of the splitting factor in the same solvent. The influence of the solvent on these spectra reflects itself in the decrease in the splitting factor from 96.7 to 93.4 to 87.3 G for water, ethanol and DMF solvents, respectively. These spectra of solid complexes as well as DMF solutions are very similar to those of hexa-coordinate manganese(II) complexes with ground state $^6S_{5/2}$ [34,35].

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REFERENCES

1. Goher, M. A. S., Hasanein, A. A. and El-Subruiti, G. M., *Bull. Soc. Chim. Fr.*, 1982, I-221; Goher, M. A. S., Hasanein, A. A. and Soliman, S. M., *Bull. Soc. Chim. Fr.*, 1984, I-169.
2. Goher, M. A. S. and Mak, T. C. W., *Inorg. Chim. Acta*, 1984, **85**, 117; Goher, M. A. S. and Mak, T. C. W., *Inorg. Chim. Acta*, 1984, **89**, 119. Goher, M. A. S. and Mak, T. C. W., *Inorg. Chim. Acta*, 1985, **99**, 223.
3. Goher, M. A. S. and Abu-Youssef, M. A. M., *Acta Chim. Hung.*, 1987, **124**, 749.
4. Mautner, F. A. and Goher, M. A. S., *Cryst. Res. Technol.* 1990, **25**, 1271.
5. Goher, M. A. S. and Mautner, F. A., *Croat. Chim. Acta*, 1990, **63**, 559.
6. Escuer, A., Vicente, R., Goher, M. A. S and Mautner, F. A., *Inorg. Chem.*, 1995, **34**, 5707.
7. Escuer, A., Vicente, R., Goher, M. A. S. and Mautner, F. A., *Inorg. Chem.*, 1996, **35**, 6386.
8. Mallal, T., Kahn, O., Gouteron, J., Jeannin, S., Jeannin, Y. and O'Conner, J. C., *Inorg. Chem.*, 1987, **26**, 1375.
9. Mikuriya, M., Kida, S. and Murase, I., *Bull. Chem. Soc. Jpn*, 1987, **60**, 1355; Mallal, T., Boillot, M. -L., Kahn, O., Gouteron, J., Jeannin, S. and Jeannin, Y., *Inorg. Chem.*, 1986, **25**, 3058.
10. Walz, L. and Haase, W., *J. Chem. Soc., Dalton Trans.*, 1985, 1243; Julve, M., Verdaguer, M., de Munno, Ge, Real, J. A. and Bruno, G., *Inorg. Chem.*, 1993, **32**, 795.
11. Pohl, K., Wieghardt, K., Nuber, B. and Weiss, J., *J. Chem. Soc., Dalton Trans.*, 1987, 187.
12. Valach, F. and Dunaj-Jurco, M., *Acta Cryst.*, 1982, **B38**, 2145.
13. Vicente, R., Escuer, A., Penalba, E., Solans, X. and Front-Bardia, M., *J. Chem. Soc., Dalton Trans.*, 1994, 3005.
14. Goher, M. A. S., Mautner, F. A. and Popitsch, A., *Polyhedron*, 1993, **12**, 2557.
15. Goher, M. A. S., Al-Salem, N. A. and Mautner, F. A., *Polyhedron*, 1996, **15**, 3575.
16. Goindjee, T. K. and Coleman, W., *Photochem. Photobiol.*, 1985, **42**, 187; Amesz, J., *Biochem. Biophys. Acta*, 1983, **1**, 726.
17. Beyer Jr, W. F. and Fridovich, I., *Biochemistry*, 1985, **24**, 6460; Franko, R. M., Ponner-Hahn, J. E. and Bender, C. J., *J. Am. Chem. Soc.*, 1988, **110**, 7554.
18. Willing, A., Follman, H. and Auling, G., *Eur. J. Biochem.*, 1988, **170**, 603.
19. Goher, M. A. S., Wang, R. -J. and Mak, T. C. W., *Polyhedron*, 1992, **11**, 829.
20. Sheldrick, G. M., *SHELXTL/PC v.* 5.03 *Reference Manual.* Siemens Industrial Automation Inc., WI, U.S.A., 1994.
21. Spek, A. L., in *Computational Crystallography*, ed. D. Sayre. Clarendon Press, Oxford, 1982, p. 528.
22. *International Tables for Crystallography*, Vol. C, Tables 4.2.6.8. and 6.1.1.4., Kluwer Academic Publishers, Dordrecht, 1992.
23. Figgis, B. N. and Lewis, J., *Prog. Inorg. Chem.* 1964, **6**, 37.
24. Goher, M. A. S., Abu-Youssef, M. A. M. and Mautner, F. A., *Polyhedron*, 1993, **12**, 1751.
25. Gelfand, L. S., Pytlewski, L. L., Speca, A. N., Mikulski, C. M. and Karayannis, N. M., *J. Inorg. Nucl. Chem.*, 1980, **42**, 209.
26. Yoshida, S. and Asai, M., *Chem. Pharm. Bull. Jpn*, 1959, **5**, 162; Nakagawa, I. and Shimanouchi, T., *Spectrochim. Acta*, 1964, **20**, 429.
27. Nakamoto, K., *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd edn. John Wiley, New York, U.S.A., 1970.
28. Nelson, J. and Nelson, S. M., *J. Chem. Soc. (A)*, 1969, 1597.
29. Maki, A. and Decius, J. C., *J. Chem. Phys.*, 1959, **31**, 772.
30. Bailey, R. A. and Kozak, S. L., *J. Inorg. Nucl. Chem.*, 1969. **31**, 689.
31. Burmeister, L., Deardorff, E. A. and van Dyke, C. E., *Inorg. Chem.*, 1969, **8**, 170.
32. Chughtal, A. R. and Keller, R. N., *J. Inorg. Nucl. Chem.*, 1969, **31**, 633.
33. Sabatini, A. and Bertini, I., *Inorg. Chem.*, 1965, **4**, 959.
34. Srinivasan, B. R. and Sakar, S., *Inorg. Chem.*, 1990, **29**, 3898.
35. Lobana, T. S. and Bala, N., *Trans. Met. Chem.* 1994, **19**, 115; Batra, G. and Mathur, P., *Trans. Metal Chem.*. 1994, **19**, 160.