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The crystal structure and spectroscopic properties of *catena*-(2-methylimidazolium bis(μ_2-chloro)aquachloromanganese(II))

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Abstract: A novel manganese(II) coordination polymer, *catena*-(2-methylimidazolium bis(μ_2-chloro)aquachloromanganese(II)), $\{(C_4H_7N_2)[MnCl_3(H_2O)]\}_n$, was synthesized, structurally characterized by FTIR spectroscopy and confirmed by single crystal X-ray diffraction analysis. Thermogravimetric analysis and EPR spectroscopy of the compound were also performed. The colourless crystals of the complex were monoclinic, space group *P*21/*c*, with the cell parameters a = 11.298(2) Å, b = 7.2485(14) Å, c = 14.709(5) Å, β = 128.861(18)°, V = 938.0(5) Å^3, Z = 4 and R_1 = 0.03. The title compound consisted of one-dimensional infinite anionic chains $[MnCl_3(H_2O)]_n$ and isolated 2-methylimidazolium cations. The Mn(II) atom was octahedrally coordinated to four bridging chloride anions (Mn–Cl = 2.5109(6) – 2.5688(7) Å), one terminal chloride anion (Mn–Cl = 2.5068(11) Å) and a H_2O molecule (Mn–O = 2.2351(17) Å). A three-dimensional layer structure was constructed *via* hydrogen bonds and by weak π–π stacking interactions. A four-step thermal decomposition occurred in the temperature range 25–900 °C under nitrogen.

Keywords: manganese(II) complex; 2-methylimidazole; X-ray crystal structure; IR spectra; EPR spectra.

INTRODUCTION

Complexes of imidazole derivatives with transition metal ions have attracted much attention because of their biological and pharmacological activities, such as antiviral and antimicrobial,[1,2] antifungal and antimycotic,[3] antihistaminic and antiallergic,[4] anthelminthic,[5] antitumoural and antimetastatic properties.[6–13] The biological role of complexes containing an imidazole ring system can be connected with the two N atoms, which have different properties; the deprotonated N

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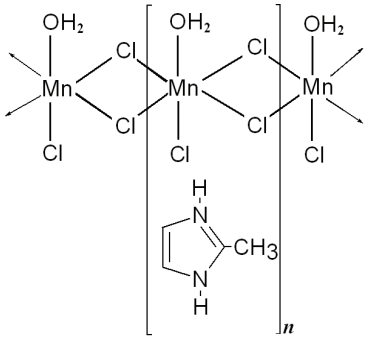
atom can coordinate with a transition-metal ion, whereas the protonated N atom participates in hydrogen bonding.[14–22]

2-Methylimidazole, a compound widely used as a chemical intermediate (the manufacture of pharmaceuticals, photographic and photothermographic chemicals, dyes and pigments, agricultural chemicals and rubber), has been detected in cigarette smoke, as a result of pyrolysis. It is also an undesirable by-product in food and forage coloured with caramel, such as beer, colas, caramel-coloured syrups and soy sauce.[23–27]

In previous papers, the crystal structures of 2-methylimidazole and diaquadichlorobis(1*H*-imidazole)manganese(II) were reported.[28,29] In this paper, the structural characterization of the polymeric complex, *catena*-(2-methylimidazolium bis(μ_2-chloro)aquachloromanganese(II)) (**I**), which was obtained in the reaction of manganese(II) chloride with 2-methylimidazole (Scheme 1), is reported. In this compound, a protonated 2-methylimidazole can cross-link manganese(II) complexes, $[MnCl_3(H_2O)]_n$, through two M–Cl···H–N interactions. Despite the simplicity of the ligands, no structural report of the title compound was found in a search of the Cambridge Structural Database (CSD, Version 5.31 of November 2009).[30] Moreover, only two manganese(II) complexes with 2-methylimidazolium cation have been investigated, *i.e.*, bis(2-methylimidazolium)-bis(2,6-pyridinedicarboxylato)manganese(II)[31] and *catena*-(bis(2-methylimidazolium)(μ_2-benzene-1,2,4,5-tetracarboxylato-*O*,*O*')tetraaquamanganese(II) pentahydrate).[32] The same $[MnCl_3(H_2O)]$ group was reported in the structure of $[H(2\text{-ampy})][MnCl_3(H_2O)]$.[33]



(I)

Scheme. 1. Structure of $\{(2\text{-met}H_2\text{Im})[MnCl_3(H_2O)]\}_n$.

EXPERIMENTAL

Synthesis of $\{(C_4H_7N_2)[MnCl_3(H_2O)]\}_n$

All the employed chemicals were commercial products (Sigma-Aldrich and POCH S.A., Poland), which were used without further purification.

Hydrochloric acid (2 mg, 0.05 mmol), manganese(II) chloride (520 mg, 4 mmol) and 2-methylimidazole (640 mg, 8 mmol) were stirred in 2 ml of water until they had dissolved. The solution was filtered and the filtrate was left to stand undisturbed. After two days, colourless single crystals of **I**, suitable for X-ray crystallographic analysis, were collected and dried in air at room temperature (268.94 mg, yield: 24.92 %). Anal. Calcd. for $C_4H_9Cl_3MnN_2O$: C, 18.29; H, 3.43; N, 10.67 %. Found: C, 18.34; H, 3.39; N, 10.69%.

X-Ray crystal structure determination

The data were collected using an Oxford Diffraction kappa diffractometer with a Sapphire3 CCD detector and MoKα radiation (λ = 0.71073 Å) at 100 K. Accurate cell parameters were determined and refined using the CrysAlis CCD program.[34] For the integration of the collected data, the program CrysAlis RED was used.[34] Absorption corrections were realised using the multi-scan method.[34] The structure was solved by the direct method using SHELXS-97[35] and then the solution was refined by the full matrix least-squares method using SHELXL-97.[35] Non-hydrogen atoms were refined with anisotropic displacement factors. All hydrogen atoms attached to N and C were placed in the geometrically idealized positions (d(N–H) = 0.88 Å and U_{iso}(H) = 1.2U_{eq}(N) for N–H hydrogens; d(C–H) = 0.95 Å and U_{iso}(H) = 1.2U_{eq}(C) for C–H hydrogens; d(C–H) = 0.98 Å and U_{iso}(H) = 1.5U_{eq}(C) for CH_3 hydrogens). Hydrogen atoms attached to O atoms were located from the difference Fourier map and then refined as riding on their parent atoms.

Physical measurements

The IR spectrum of a polycrystalline sample of *catena*-(2-methylimidazolium bis(μ_2-chloro)aquachloromanganese(II)) dispersed in KBr was measured at room temperature using an FT-IR Nicolet Magna 560 spectrometer operating at a resolution of 4 cm^{-1}. The IR spectrum was recorded in the range of 4000–400 cm^{-1} using an Ever-Glo source, a KBr beam splitter and a DTGS detector. The thermal stability of the compound was studied by thermogravimetric analysis (TGA) from 298 to 1173 K at a heating rate of 10 K min^{-1} under a nitrogen atmosphere using a Perkin–Elmer Pyris thermogravimetric analyzer. The X-band electron paramagnetic resonance (EPR) spectrum (9.7 GHz) was recorded using a Bruker EMX spectrometer at room temperature. 2,2-Diphenyl-1-picrylhydrazyl (DPPH) was used as an internal field marker. For the EPR measurement, 0.1 mL of the sample solution was kept in closed quartz capillaries.

RESULTS AND DISCUSSION

The crystal data and final refinement details of the title compound are given in Table I.

The asymmetric unit of the title crystal structure comprises an anionic $[MnCl_3(H_2O)]$ fragment and a 2-methylimidazolium (2-metH_2Im) cation (Fig. 1). The crystal structure shows the formation of $[MnCl_3(H_2O)]_n$ polymeric chains developed parallel to axis *b*. The local geometry around Mn(II) ion can be seen as octahedral, involving four bridging chloride anions, one terminal chloride anion and one water molecule. The angles in the octahedron are distorted by less than 7.4° from the ideal values (Table II).

The Mn–Cl distances are in the range from 2.5068(11) to 2.5688(7) Å. The bridging Mn–Cl bond distances, *viz.* Mn–Cl2 and Mn–Cl3, are slightly longer than the terminal one (Mn–Cl1, Table II). The latter bond length Mn–Cl1 bond is

comparable with the corresponding value in other hexacoordinated Mn(II) complexes.[33,36,37] The Mn–O bond length of 2.2351(17) Å is slightly longer than the value found in other manganese(II) structures, *i.e.* [H(2-ampy)][$MnCl_3(H_2O)$] (2.171(2) Å),[33] $Mn_2L_2Cl_4(H_2O)_2$ (where L is 2-(2'-pyridyl)quinoxaline) (2.190(2) Å)[38] and than the average value specified by Orpen *et al.*[36] for a Mn–O distance (terminal OH_2 group = 2.190 Å). The Mn(II) atoms are separated by a distance of 3.6386(7) Å, which is quite large and seems to rule out any strong direct metal–metal interaction.

TABLE I. Crystal data and structure refinement details of $\{(C_4H_7N_2)[MnCl_3(H_2O)]\}_n$ (**I**)

Property	Value
Chemical formula	$[MnCl_3(H_2O)\cdot C_4H_7N_2]$
Compound weight	262.42
Crystal system	Monoclinic
Space group	$P2_1/c$
Crystal dimension, mm^3	0.56 × 0.22 × 0.21
Crystal form, colour	Polyhedron, colourless
Unit cell parameters	
a / Å	11.298(2)
b / Å	7.2485(14)
c / Å	14.709(5)
β / °	128.861(18)
V / $Å^3$	938.0(5)
Z	4
D_c / g cm^{-3}	1.858
$F(000)$	524
θ range for data collection, °	3.33–34.45
Data collection method	ω scan
Absorption coefficient, mm^{-1}	2.208
Final R indices ($I > 2\delta(I)$)	R_1 = 0.0304, wR_2 = 0.1101
R indices (all data)	R_1 = 0.0334, wR_2 = 0.1117
Reflections collected/unique	13649/3653 [R_{int} = 0.0201]
Limiting indices	$-17 \le h \le 17$, $-11 \le k \le 6$, $-23 \le l \le 22$
Refinement method	Full-matrix least-squares on F^2
S	1.0
Parameters refined	104
Extinction method	0.146(5)
$\Delta\rho_{max}$, $\Delta\rho_{min}$ / e $Å^{-3}$	1.42–0.99

The 2-methylimidazolium cations are planar (mean deviation = 0.0013 Å) and canted 88.64(6)° from the chains formed by the anions (*vs.* the plane formed by the two Mn atoms and the bridging Cl atoms). The internal geometry of the 2-metH_2Im cation is different from that in the free 2-methylimidazole (2-metHIm) molecule.[28] The N–C bond distances in **I** show some significant variations. The N1–C2 distance (N1–C2 1.325(3) Å) is shorter than the corresponding bond in

2-metHIm and, conversely, the C2–N3 bond is longer (1.384(3) Å *vs*. 1.3283(11) Å in 2-metHIm). This indicates that the π electrons of C2=N3 and C4=C5 exhibit significant delocalization compared with those of pure 2-metHIm.

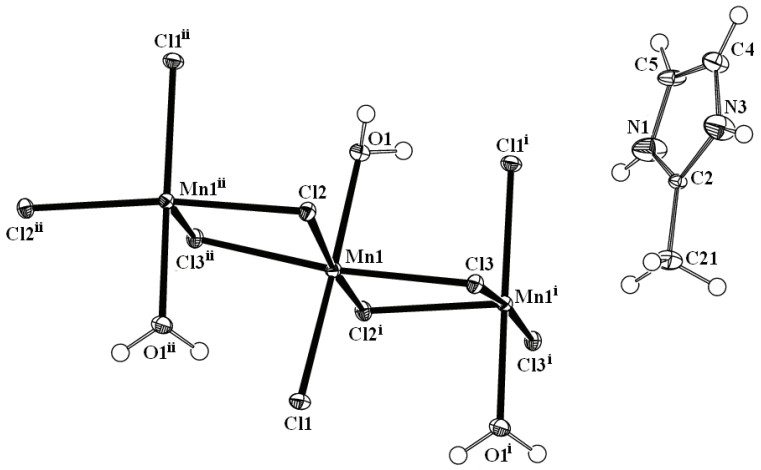


Fig. 1. A view of the molecular structure of **I**, showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 50 % probability level. H atoms are shown as small spheres of arbitrary radius (symmetry codes: *i*) $-x$, $-1/2 + y$, $1/2 - z$; *ii*) $-x$, $1/2 + y$, $1/2 - z$).

Table II. Selected bond lengths (Å), bond angles (°) and torsion angles (°) of $\{(C_4H_7N_2)[MnCl_3(H_2O)]\}_n$. Symmetry codes: *i*) $-x$, $-1/2 + y$, $1/2 - z$; *ii*) $-x$, $1/2 + y$, $1/2 - z$

Bond lengths, Å			
Mn1–O1	2.2351(17)	N1–C2	1.325(3)
Mn1–Cl1	2.5068(11)	N1–C5	1.325(3)
Mn1–Cl2	2.5109(6)	N3–C2	1.384(3)
Mn1–Cl2^i	2.5220(6)	N3–C4	1.358(3)
Mn1–Cl3	2.5567(6)	C4–C5	1.364(3)
Mn1–Cl3^i	2.5688(7)	C2–C21	1.455(3)
Bond angles, °			
O1–Mn1–Cl1	178.01(4)	Cl1–Mn1–Cl3^{ii}	92.93(2)
O1–Mn1–Cl2	86.92(4)	Cl2–Mn1–Cl3^{ii}	87.74(2)
Cl1–Mn1–Cl2	94.05(2)	Cl2^i–Mn1–Cl3^{ii}	91.75(2)
O1–Mn1–Cl2^i	85.66(4)	Cl3–Mn1–Cl3^{ii}	172.754(12)
Cl1–Mn1–Cl2^i	93.37(2)	C2–N1–C5	108.53(18)
Cl2–Mn1–Cl2^i	172.583(12)	C2–N3–C4	106.86(17)
O1–Mn1–Cl3	87.38(4)	N1–C2–N3	108.41(17)
Cl1–Mn1–Cl3	94.32(2)	N1–C2–C21	126.62(17)
Cl2–Mn1–Cl3	91.80(2)	N3–C2–C21	124.96(17)
Cl2^i–Mn1–Cl3	87.77(2)	N3–C4– C5	106.68(18)
O1–Mn1–Cl3^{ii}	85.37(4)	N1–C5–C4	109.53(18)

The packing shows four potentially active H atoms, *viz* the methylimidazolium N–H and the aqua H atoms involved in hydrogen bonds with Cl atoms, forming a three-dimensional hydrogen-bonded network (Fig. 2 and Table III). The $[MnCl_3(H_2O)]$ units are connected in the crystal lattice through O1–H1O···Cl1^{i} and O–H2O···Cl1^{iii} hydrogen bonds (symmetry codes: *i*) $-x$, $-1/2 + y$, $1/2 - z$; *iii*) x, $3/2 - y$, $-1/2 + z$), which are formed between two terminal chloride anions and the hydrogen atoms of the coordinated water molecule. The result of these interactions is the formation of eight-membered rings, with a graph-set motif of $R_4^2(8)$,[39,40] in the *bc* plane. Moreover, each of the $[MnCl_3(H_2O)]$ moieties is also linked to two 2-metH_2Im cations by weaker N1–H1···Cl2^{iv} and N3–H3···Cl1^{v} hydrogen bonds (symmetry codes: *iv*) x, $-1 + y$, z; *v*) $1 - x$, $1 - y$, $1 - z$), joining the molecules into a three-dimensional network. The N–H···Cl interactions are formed to one bridging halogen and one terminal halogen (Fig. 3). In addition, there are weak contacts between the C–H groups of the 2-metH_2Im ring and the Cl, as well as O atoms of the $[MnCl_3(H_2O)]$ unit of neighbouring molecules (Table III). The alternate stacking of the 2-metH_2Im rings results in ring separations of 3.841 Å, indicating weak π–π interactions (Fig. 3).[41]

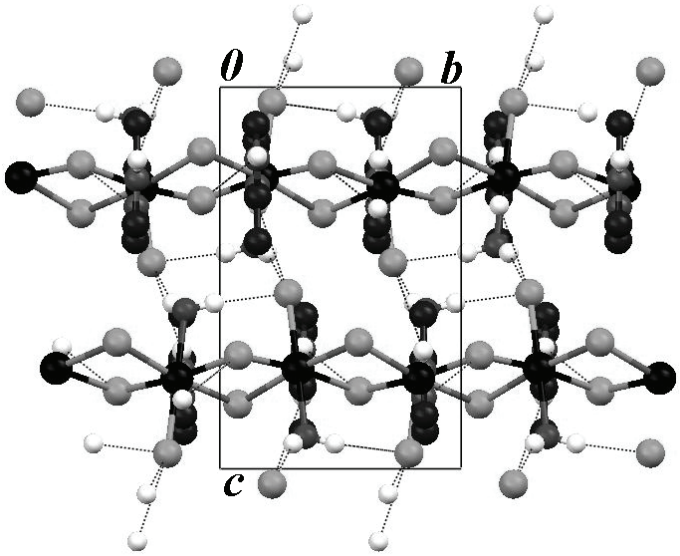


Fig. 2. Packing in the crystal structure of $\{(2\text{-met}H_2Im)[MnCl_3(H_2O)]\}_n$ viewed along the *a* axis. For the sake of clarity, all H atoms bonded to C atoms were omitted.

The structure of the presented complex differs considerably from that of $[MnCl_2(C_3H_4N_2)_2(H_2O)_2]$ (in which the Mn(II) atom was octahedrally coordinated by the monodentate ligands, *i.e.* two *N*-coordinated imidazole groups, two

chloride anions and two O atoms of water molecules) and other Mn(II) systems with imidazole ligands.[29,37,42–47] Thus, the introduction a methyl substituent at the C2 position of imidazole seems to prevent it from being incorporated into the lattice of **I**.

Table III. Hydrogen bonding geometry for $\{(C_4H_7N_2)[MnCl_3(H_2O)]\}_n$. Symmetry codes: *iii*) $x, 1.5 - y, -1/2 + z$; *i*) $-x, -1/2 + y, 1/2 - z$; *iv*) $x, -1 + y, z$; *v*) $1 - x, 1 - y, 1 - z$; *vi*) $x, 1/2 - y, -1/2 + z$;; *vii*) $-x, 1 - y, -z$

Bond	*d* (D–H) / Å	*d* (H···A) / Å	*d* (D···A) / Å	<DHA/ °
O1–H2O···Cl1^{iii}	0.90	2.33	3.1917(16)	161
O1–H2O···Cl1^{i}	0.91	2.26	3.1596(16)	172
N1–H1···Cl2^{iv}	0.88	2.87	3.492(2)	129
N3–H3···Cl1^{v}	0.88	2.87	3.601(2)	141
C5–H5···Cl3^{vi}	0.95	2.47	3.233(2)	138
C5–H5···O1^{vii}	0.95	2.30	2.993(3)	129

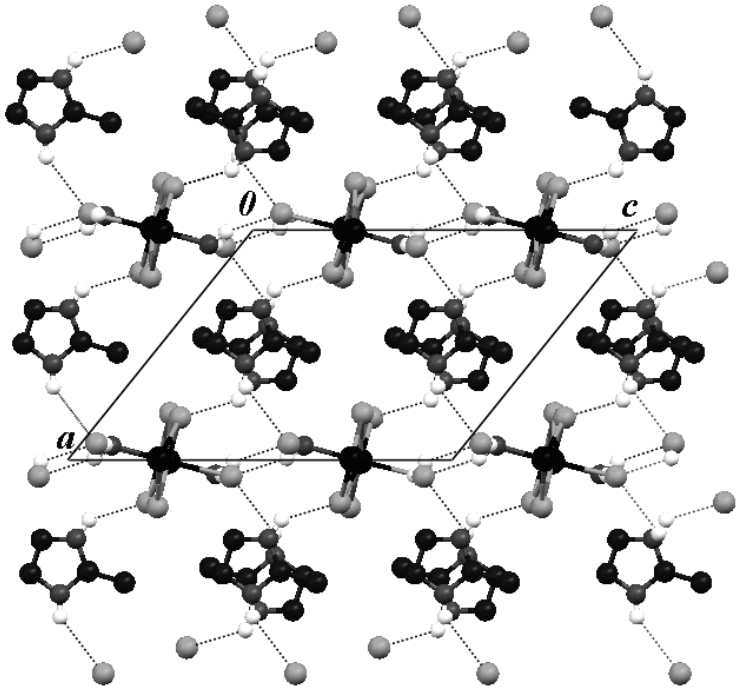


Fig. 3. Structure of a layer of $[MnCl_3(H_2O)]^-$ chains cross-linked by $[2\text{-met}H_2Im]^+$. For the sake of clarity, all H atoms bonded to C atoms were omitted.

IR spectrum of compound ***I***

The IR spectrum of the complex shows a strong and broad band extending over the frequency range 3600–2000 cm^{-1} (Fig. 4). The band in this region is attributed to the stretching vibrations, ν_{O-H}, of the hydroxyl groups in the water

molecules. The essential features of the band in this region indicate the presence of hydrogen bond involving the uncoordinated N–H groups of the 2-metH_2Im cation and aqua H atoms, with Cl atoms. From Raman spectra measurements of free 2-methylimidazole, it is known that the narrow bands at 3127 and 3102 cm^{-1}, disturbing the $\nu_{N–H}$ and $\nu_{O–H}$ band contour shapes of compound **I**, correspond to the $\nu_{C–H}$ stretching modes of the 2-metH_2Im ring.[28] The bands at 1613, 1579 and 1542 cm^{-1} can be due to the stretching of the short Cl···HO bonds.[48] The vibrational bands from 1438 to 1002 cm^{-1} can be assigned to the ring stretching frequency of the 2-metH_2Im cation.[49] The $\nu_{C=N}$ mode can be found at 1438 cm^{-1}. The bands remaining in the 859–686 cm^{-1} region can be associated with deformations of the imidazole ring. The peak at 477 cm^{-1} may be assigned to the bending vibration of the hydrogen bond.[48]

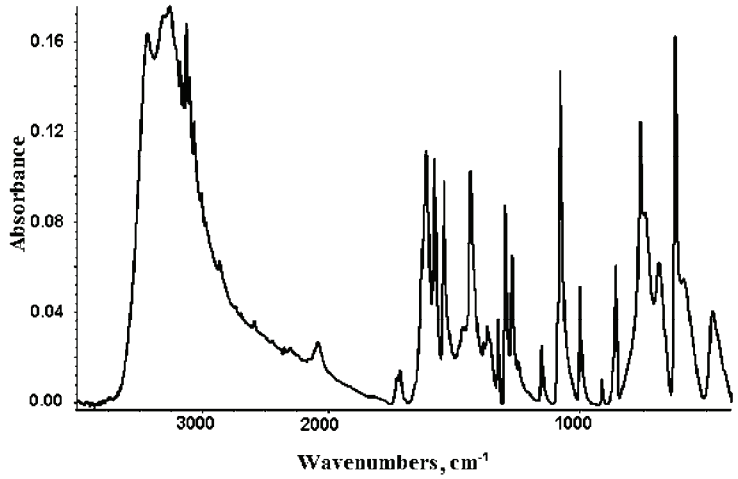


Fig. 4. The IR spectrum of *catena*-(2-methylimidazolium bis(μ_2-chloro)-aquachloromanganese(II)) sample dispersed in a KBr pellet.

*Thermal analysis of compound **I***

The thermogravimetric data in Fig. 5 show a four-step decomposition. The first one, in the temperature range of 298–406 K, seems to correspond to the removal of one coordinated water molecule with a weight loss of 8.92 % (Calcd. 6.86 %). The next mass loss of 34.26 % (Calcd. 31.63 %), occurring in the range 406–558 K, can be attributed to 2-metH_2Im destruction. Further decomposition of the compound of 35.88 % (Calcd. 40.53 %), with the successive release of Cl_2, begins at 558 K and ends at 894 K. The final total mass loss of 78.80 % is much more than the calculated value of 72.97 %. Similarly to other Mn(II) complexes, the final product of the decomposition of $\{(C_4H_7N_2)[MnCl_3(H_2O)]\}_n$ seems to be MnO.[50–53]

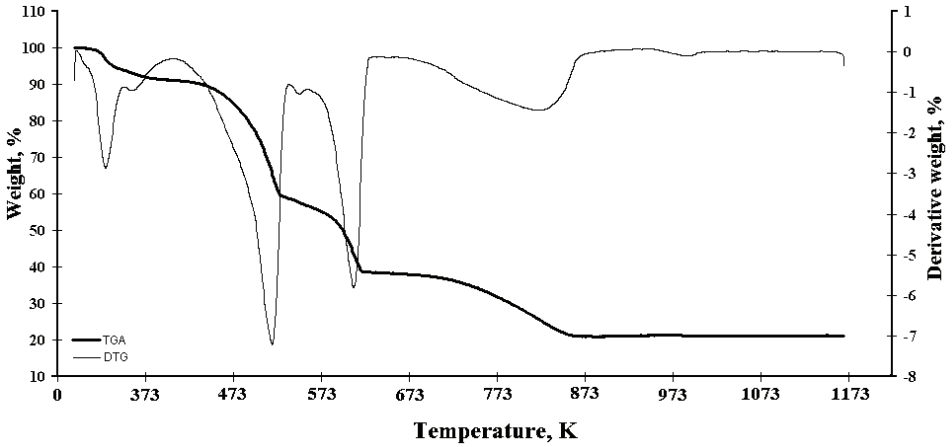


Fig. 5. TGA–DTG curves for compound **I** under a dynamic nitrogen atmosphere at a heating rate of 10 K min^{-1}.

*EPR spectrum of complex **I***

The solid-state EPR spectrum of compound **I** at room temperature shows only one isotropic signal at g = 2.03147, corresponding to manganese(II) in a weakly distorted octahedral environment (predicted by crystal structure analysis). Such an isotropic spectrum consisting of a broad signal without a hyperfine pattern is due to intermolecular dipole–dipole interactions and enhanced spin lattice relaxation.[54] When the manganese ion is magnetically diluted, the hyperfine interaction can be detected.

The EPR spectrum of $\{(C_4H_7N_2)[MnCl_3(H_2O)]\}_n$ in aqueous solution at 298 K brings more detailed information about the coordination sphere of the Mn(II) centre. The ground state of the Mn(II) ion ($3d^5$) is $^6S_{5/2}$. The EPR of Mn(II) ions can be adequately described by the spin-Hamiltonian:

$$H = g\mu_B BS + D(S_z^2 - (1/3)S(S + 1)) + E(S_{x^2} - S_{y^2}) + ASI$$

where: S = 5/2 and I = 5/2; D and E are fine structure (fs) parameters; the last term means that the hyperfine interaction; the g-factor and the hyperfine structure parameter A are isotropic.

The spectrum of **I** exhibits a six line manganese hyperfine pattern centred at g = 1.98093 (Fig. 6). These six hyperfine lines arise from the interaction of the electron spin with the nuclear spin (^{55}Mn, I = 5/2) and correspond to m_I = ±5/2, ±3/2, ±1/2, resulting from allowed transitions (Δm_s = ±1, Δm_I = 0). The observed g values are close to the free electron spin value of 2.0023, which is suggestive of the absence of spin–orbit coupling in the ground state, $^6A_1$.[55–58]

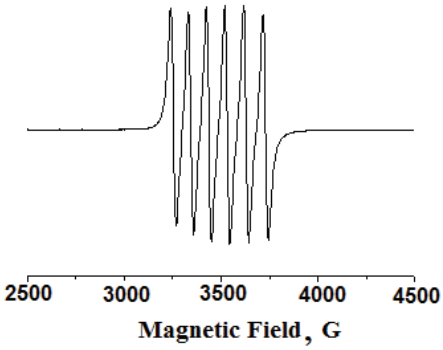


Fig. 6. X-band EPR spectrum of $\{(2\text{-metH}_2\text{Im})[MnCl_3(H_2O)]\}_n$ in aqueous solution.

CONCLUSIONS

In the present paper, the synthesis, crystal structure, thermal and spectroscopic properties of a novel manganese(II) coordination polymer, $\{(C_4H_7N_2)[MnCl_3(H_2O)]\}_n$, which can easily be prepared by the reaction of manganese(II) chloride and 2-methylimidazole, are reported. In the compound, each manganese ion is connected with the neighbouring metal *via* chloride atoms forming a polymeric chain of $[MnCl_3(H_2O)]_n$ anions hydrogen bonded to 2-metH$_2$Im cations, thus forming a three-dimensional hydrogen-bonded network. The substitution of imidazole by 2-methylimidazole during the synthesis is reflected in the structure and properties of the manganese complex in which the cation is not a metal complex but a protonated 2-methylimidazole ligand. Thus, the imidazole methyl group seems to be a steric feature impeding its insertion in the Mn coordination polymer. Moreover, the above-discussed compound shows the structural role of protonated 2-methylimidazole on the self-assembly of metal complexes through N–H···Cl–M hydrogen bonds.

SUPPLEMENTARY DATA

CCDC-755577 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre (CCDC), 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44(0)1223-336033; e-mail: deposit@ccdc.cam.ac.uk

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ИЗВОД

КРИСТАЛНА СТРУКТУРА И СПЕКТРОСКОПСКА КАРАКТЕРИЗАЦИЈА *catena*-(2-МЕТИЛИМИДАЗОЛИЈУМ-БИС(μ_2-ХЛОРО)АКВАХЛОРОМАНГАНА(II))

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Синтетизован је нови координациони полимер мангана(II), *catena*-(2-метилимидазолијум-бис(μ_2-хлоро)аквахлороманган(II)), $\{(C_4H_7N_2)[MnCl_3(H_2O)]\}_n$, и окарактерисан помоћу FT-IR спектроскопије и рендгенске структурне анализе. Такође, приказани су резултати термогравиметријске анализе и EPR спектроскопије испитиваног комплекса. Безбојни кристали комплекса су моноклинични, просторна група $P2_1/c$, са параметрима јединичне ћелије: a = 11,298(2) Å, b = 7,2485(14) Å, c = 14,709(5) Å, β = 128,861(18)°, V = 938,0(5) Å^3, Z = 4 и R_1 = 0,03. Наслovљено једињење се састоји од бесконачних једнодимензионалних $[MnCl_3(H_2O)]_n$ анјонских ланаца и изолованих 2-метилимидазолијум катјона. Mn(II) атом је октаедарски координован за четири мосна хлоридна анјона (Mn–Cl = 2,5109(6) – 2,5688(7) Å), један терминални хлоридни анјон (Mn–Cl = 2,5068(11) Å) и H_2O молекул (Mn–O = 2,2351(17) Å). Тродимензионална слојевита структура је изграђена помоћу водоничних веза и слабих π–π стекинг интеракција. Декомпозициона реакција испитиваног комплекса у струји азота се одвија у четири фазе при температурском интервалу 25–900 °C.

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