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Crystal structure and physico-chemical properties of cobalt(II) and manganese(II) complexes with imidazole-4-acetate anion

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Abstract

Crystal complexes of the general formula $[M(4\text{-iaa})_2(H_2O)_2]H_2O$ have been obtained from aqueous solutions containing a double excess of the sodium salt of imidazole-4-acetic acid ($Na\ 4\text{-iaa} \cdot H_2O$) with respect to the nitrates of cobalt(II) and manganese(II). The complexes have been characterized by X-ray studies, electronic UV–VIS–NIR spectra, IR spectra and the complex of manganese(II) by EPR spectra. In the present complexes the imidazole-4-acetate anion is a chelating ligand where an azomethine nitrogen atom of the imidazole ring and an oxygen atom of the carboxyl group are donor atoms. The immediate environment of the central ion in both complexes is described by distorted *cis*-octahedron.

Keywords: Imidazole-4-acetic acid; Cobalt(II) complexes; Manganese(II) complexes; X-ray structure; Absorption spectra; EPR spectra

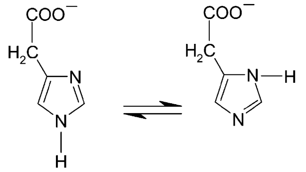
1. Introduction

Imidazole-4-acetic acid occurs in the brain of mammals [1–4]. It acts as a receptor activated by an inhibitor of neurotransmission – gamma-aminobutyric (GABA). It belongs to a newly separated class of receptors – $GABA_c$ receptors [5,6]. Since 1990 there has been a very keen interest in receptors of this kind. They have been satisfactorily characterized via a formidable combination of molecular biological, physiological, pharmacological and neurochemistry studies. The statement [6–10] that Ni^{2+}, Cu^{2+}, Cd^{2+}, Zn^{2+} cations modulate the action of $GABA_c$ receptors is noteworthy.

It is then advisable to consider the chemical interaction between imidazole-4-acetic acid and ions of transition metals.

The presence of the donor atom and azomethine nitrogen atom and oxygen atoms of the carboxyl group in a molecule of the present imidazole derivative makes it possible to form chelate complexes with metal ions. Considering the complex formation constants and spectroscopy data, the chelating character of 4-imidazole acetic acid with metal ions in aqueous solution has been demonstrated [11–15].

As a result of the transformation of the hydrogen atom between the nitrogen atoms of the heterocyclic ring, the present acetate derivatives of imidazole occurs as two tautomeric forms, imidazole-4(5)-acetate anion:



imidazole-4-acetate   imidazole-5-acetate

In the first tautomer the position of the donor atoms N(imidazole) and O(carboxyl) favours chelation because stable six-membered chelate rings can appear as a result of the presence of the substituent in position 4 in the coordinate bond. The explicit participation of the

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4-tautomer in the coordinate bond is shown by X-ray studies of the complexes of this ligand with metals ions in the solid state [16–19].

Coordination compounds of Co^{2+} and Mn^{2+} in the solid state have been of interest here. The structure and selected spectroscopic properties of the complexes are presented.

2. Experimental

2.1. Synthesis

The sodium salt of imidazole-4-acetic acid (Na(4-iaa)$\cdot H_2O$), $Co(NO_3)_2 \cdot 3H_2O$ and $Mn(NO_3)_2 \cdot xH_2O$ came from Aldrich Chemical Co.

Crystals suitable for X-ray analysis were obtained from an aqueous solution containing metal nitrates(V) and the sodium salt of 4-imidazole acetic acid (Na(4-iaa)$\cdot H_2O$) in the molar ratio 1:2. 25 cm^3 of the solution containing 1 mmol of metal nitrate was gradually added with constant stirring to the solution of 2 mmol Na(4-iaa)$\cdot H_2O$ dissolved in 25 cm^3 of water. The solutions were left to stand at room temperature for a few days.

The raspberry-red crystals of the cobalt(II) complex and the colourless ones of the manganese(II) complex were filtered off and dried in the air. Results of the elemental analyses are as follows (%): cobalt(II) complex: C, 33.2; H, 4.6; N, 15.3. Calc. for [Co(4-iaa)$_2$(H_2O)$_2$]H_2O: C, 33.07; H, 4.44; N, 15.43. manganese(II) complex: C, 33.3; H, 4.6; N, 15.8. Calc. for [Mn(4-iaa)$_2$(H_2O)$_2$]H_2O: C, 33.44; H, 4.49; N, 15.60%.

2.2. Physical measurements

Elemental analyses were run on a Model 240 Perkin–Elmer CHN Analyzer. The IR spectra were recorded on a Perkin–Elmer 180 (spectral range 50–4000 cm^{-1}) spectrophotometer in Nujol and in KBr pellets. The far-IR spectra were obtained in Nujol mulls sandwiched between polyethylene plates. The electronic spectra (5000–30 000 cm^{-1}) were recorded on a Cary 5 UV–VIS–NIR spectrophotometer in Nujol mulls. Magnetic susceptibility data were obtained at room temperature with a Bruker BM-4 system and corrected for diamagnetism by Pascal's constants. The EPR spectra were recorded on a Bruker ESP 300E (Bruker, Germany) spectrometer.

2.3. Crystal data

X-ray measurements were performed on a Kuma KM4CCD diffractometer. The structures were solved by direct methods using the SHELX-97 [20] program and refined by full-matrix least-squares methods using the SHELXL-97 [21] program. Details of the crystal data and refinement for the present compounds are collected in Table 1.

Table 1
Crystal data and structure refinement for [Co(4-iaa)$_2$(H_2O)$_2$]H_2O and [Mn(4-iaa)$_2$(H_2O)$_2$]H_2O complexes

	[Co(4-iaa)$_2$(H_2O)$_2$]H_2O	[Mn(4-iaa)$_2$(H_2O)$_2$]H_2O
Empirical formula	$C_{10}H_{16}CoN_4O_7$	$C_{10}H_{16}MnN_4O_7$
Temperature (K)	85(1)	100(1)
Wavelength (Å)	0.71073	0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2(1)/c$	$P2(1)/c$
Unit cell dimensions		
a (Å)	9.638(2)	9.768(2)
b (Å)	7.461(2)	7.525(2)
c (Å)	19.367(4)	19.597(3)
β (°)	97.40(3)	97.82(3)
Volume (Å^3)	1381.1(5)	1427.2(3)
Z	4	4
Density (calculated) (Mg/m^3)	1.747	1.672
Absorption coefficient (mm^{-1})	1.286	0.967
F (000)	748	740
Crystal size (mm)	$0.15 \times 0.15 \times 0.20$	$0.20 \times 0.25 \times 0.25$
Theta range for data (°)	3.54–28.34	3.50–28.37
Index ranges	$-11 \leqslant h \leqslant 12$, $-9 \leqslant k \leqslant 9$, $-25 \leqslant l \leqslant 23$	$-11 \leqslant h \leqslant 13$, $-9 \leqslant k \leqslant 7$, $-26 \leqslant l \leqslant 26$
Reflections collected/unique	8705/3247 [$R_{int} = 0.0272$]	8824/3283 [$R_{int} = 0.0271$]
Data [$I > 2\sigma(I)$]/parameters	3031/263	3040/263
Goodness-of-fit on F^2	1.056	1.074
Final R indices [$I > \sigma(I)$]	$R_1 = 0.0232$, $wR_2 = 0.0590$	$R_1 = 0.0259$, $wR_2 = 0.0637$
R indices (all data)	$R_1 = 0.0258$, $wR_2 = 0.0603$	$R_1 = 0.0294$, $wR_2 = 0.0655$
Largest differential peak and hole e (Å^{-3})	0.328 and −0.519	0.383 and −0.565

3. Results and discussion

3.1. Description of structure

The present compounds of cobalt(II) and manganese(II) with imidazole-4-acetate are neutral, mononuclear, *cis*-octahedral complexes.

Two molecules of the azole ligand and two molecules of water are connected with the central ion. The third molecule of water is not involved in the coordinate bond. It is connected via a hydrogen bond with the oxygen atom of a coordinating molecule of water and with the oxygen atom of the carboxyl group.

The molecular structure determined shows that, like in the complexes studied before [11–19], the coordination reactions favour the isomer containing the acetate substituent in the immediate proximity of the azomethine nitrogen atom, i.e. the 4-iaa tautomer. It is a bidentate ligand. One electron pair for the coordinate bond is provided by the oxygen atom of the carboxyl group, the other one by the azomethine nitrogen atom of the heterocyclic ring.

The six coordinate environment of the central ion in both the present complexes (chromophores MeN_2O_4) is different from the regular *cis*-octahedral geometry. The structural arrangement and the atom numbering scheme for the present complexes are shown in Fig. 1. Selected bond lengths and bond angles are compiled in Table 2.

Lengths of metal–nitrogen bonds in the cobalt(II) complex are 2.071(1) and 2.092(1) Å. In the manganese(II) complex bonds are slightly longer – 2.214(1) and 2.194(1) Å.

The oxygen atom of the carboxyl group forms bonds of the lengths 2.128(1) and 2.135(1) Å with the cobalt(II) ion and of the lengths 2.197(1) and 2.220(1) Å with the manganese(II) ion.

Owing to the participation of the oxygen O(2) atom in the intramolecular hydrogen bond with a molecule of water not involved in the coordination, the lengthening of the bonds of Co–O(2) (2.194 Å) compared with those of Co–O(1) (2.072(1) Å) is observed. The same refers to the complex of manganese(II) where the lengths are Mn–O(2) 2.258(1) Å and Mn–O(1) 2.148(1) Å.

Owing to the chelation, the angles of bonds of donor atoms of the azole ligand with the central ion get distorted. The angles of the nitrogen–metal–oxygen bond in six-membered chelatic rings are 85.34(4)° and 84.48(4)° in the cobalt(II) complex and 81.50(4)° and 82.81(4)° in the manganese(II) complex.

The angles of the O(11)–M–O(21) bond are 93.88(4)° for the cobalt(II) complex and 96.08(4)° for the manganese(II) one.

In the carboxyl group the lengths of carbon–oxygen bonds are observed to be slightly different. Owing to the contribution of the oxygen atom of the carboxyl group to the bond with the central ion, the bond C(17)–O(11) and C(27)–O(21) grows longer compared with the carbon – non-coordinating oxygen bond C(17)–O(12) and C(27)–O(22).

The crystal structure of the present cobalt(II) and manganese(II) complexes $[M(4\text{-iaa})_2(H_2O)_2]H_2O$ is stabilized by intramolecular and intermolecular hydrogen bonds. Lengths and angles of the bonds are given in

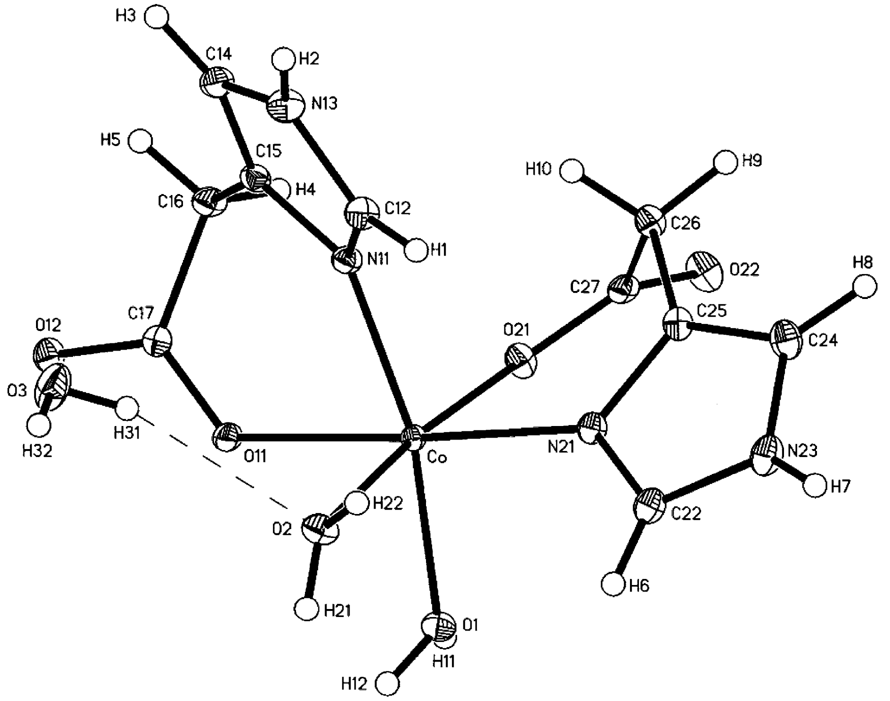

Fig. 1. The structure and numbering scheme of the studied cobalt(II) and manganese(II) complexes.

Table 2
Selected bond lengths [Å] and angles [°] for $[Co(4\text{-iaa})_2(H_2O)_2]H_2O$ and $[Mn(4\text{-iaa})_2(H_2O)_2]H_2O$ complexes

	$[Co(4\text{-iaa})_2(H_2O)_2]H_2O$	$[Mn(4\text{-iaa})_2(H_2O)_2]H_2O$
Bond lengths		
M–N(21)	2.071(1)	2.194(1)
M–O(1)	2.072(1)	2.148(1)
M–N(11)	2.092(1)	2.214(1)
M–O(21)	2.128(1)	2.197(1)
M–O(11)	2.135(1)	2.220(1)
M–O(2)	2.194(1)	2.258(1)
O(11)–C(17)	1.278(2)	1.274(2)
N(11)–C(15)	1.383(2)	1.385(2)
C(15)–C(16)	1.499(2)	1.504(2)
Bond angles		
C(16)–C(17)	1.530(2)	1.533(2)
N(21)–M–O(1)	96.8(1)	100.4(1)
N(21)–M–N(11)	92.8(2)	92.1(1)
O(1)–M–N(11)	168.3(1)	164.9(1)
N(21)–M–O(21)	85.3(1)	82.8(1)
O(1)–M–O(21)	89.5(2)	92.3(1)
N(11)–M–O(21)	98.0(1)	97.6(1)
N(21)–M–O(11)	177.0(1)	173.4(1)
O(1)–M–O(11)	86.1(1)	86.2(1)
N(11)–M–O(11)	84.5(1)	81.5(1)
O(21)–M–O(11)	93.9(1)	96.1(1)
N(21)–M–O(2)	90.0(1)	88.8(1)
O(1)–M–O(2)	87.6(2)	87.1(1)
N(11)–M–O(2)	85.6(2)	84.8(1)
O(21)–M–O(2)	174.2(1)	171.4(1)
O(11)–M–O(2)	90.9(1)	92.5(1)
C(17)–O(11)–M	130.2(1)	132.0(1)
C(15)–N(11)–M	124.1(1)	124.1(1)
N(11)–C(15)–C(16)	121.8(1)	122.1(1)
C(15)–C(16)–C(17)	113.5(1)	113.8(1)

Tables 3 and 4. Fig. 2 shows the packing of molecules of the complex in the unit cell.

3.2. The infrared spectra

The bond of the carboxyl group with the metal ion is marked in the IR spectra by two separate bands assigned to asymmetric and symmetric stretching vibrations (v_{as} and v_s, respectively). For the present cobalt(II) and manganese(II) complexes the bands are placed at $v_{as} = 1580$ cm^{-1} and $v_s = 1400$ cm^{-1}.

The frequency difference of the vibrations ($\Delta = v_{as} - v_s = 180$ cm^{-1}) is not characteristic of either the monodentate group or the bidentate one COO^- [22]. The intermediate value Δ is accounted for by the contribution of oxygen atoms to hydrogen bonds. The contribution of the non-coordinating oxygen atom (O(12), O(22)) to the hydrogen bond with the molecule of water makes the carboxyl group a “pseudo-bridging” ligand.

In the far-IR spectra two new bands, not detected in the spectrum of the sodium salt of the azole ligand, are observed. They are placed at 378 and 318 cm^{-1} for the cobalt(II) complex and at 362 and 318 cm^{-1} for the manganese(II) complex. Bands of such higher frequencies as 378 cm^{-1} for the cobalt(II) complex and 362 cm^{-1} for the manganese(II) complex are bands of stretching vibrations v_a (metal–oxygen), whereas the band at 318 cm^{-1} for the present complexes is assignable to v_a (metal–nitrogen) [22]. The broad and complicated absorption between 3200 and 2800 cm^{-1} confirms the presence of water and hydrogen bonds in the complexes.

3.3. The d–d electronic spectra and magnetic properties

The UV absorption band observed for the present cobalt(II) complexes ($[Co(4\text{-iaa})_2(H_2O)_2]H_2O$) is broad and irregular. The exact position of the maximum of these spectra was determined by the Gaussian distribution. The bands appear at 46 000, 35 600 and 31 000 cm^{-1}. The first one can be observed in the spectrum of the sodium salt of the ligand, being a substrate for obtaining the present cobalt(II) complex. It corresponds to the $\pi \rightarrow \pi^*$ transmission in the ligand. The next two are ligand–metal charge-transfer (LMCT) bands (imidazole→Co(II)).

Within the visible range the maximum of absorption corresponding to the d–d bands for the present cobalt(II) complex appears at 19 700 cm^{-1}, whereas the band of low intensity is observed at 9000 cm^{-1} in the near-IR region. Considering the distortion of the

Table 3
Hydrogen-bonds for the cobalt(II) complex [Å and °]

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
N(13)–H(2)···O(3)a	0.87(2)	2.06(2)	2.8875(17)	158(2)
N(23)–H(7)···O(21)b	0.83(2)	2.00(2)	2.7382(16)	147(2)
O(1)–H(11)···O(22)c	0.81(2)	1.93(2)	2.7458(15)	175(2)
O(1)–H(12)···O(12)d	0.85(2)	1.95(2)	2.8015(16)	178(2)
O(2)–H(21)···O(11)d	0.83(2)	1.90(2)	2.7200(16)	173(2)
O(2)–H(22)···O(12)b	0.78(3)	2.10(3)	2.8719(15)	170(2)
O(3)–H(31)···O(2)	0.81(3)	2.34(3)	3.0566(16)	149(2)
O(3)–H(31)···O(11)	0.81(3)	2.61(2)	3.1905(17)	130(2)
O(3)–H(32)···O(22)e	0.78(3)	2.02(3)	2.7974(16)	178(2)

Symmetry transformations used to generate equivalent atoms: a = $-x, y+1/2, -z+1/2$; b = $x, y+1, z$; c = $-x+1, -y, -z$; d = $-x+1, y+1/2, -z+1/2$; e = $x, -y+1/2, z+1/2$.

Table 4
Hydrogen-bonds for the manganese(II) complex [Å and °]

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
N(13)–H(2)···O(3a)	0.86(2)	2.09(2)	2.905(2)	158(2)
N(23)–H(7)···O(21b)	0.85(2)	2.00(2)	2.758(2)	148(2)
O(1)–H(11)···O(22c)	0.84(2)	1.88(2)	2.718(2)	178(2)
O(1)–H(12)···O(12d)	0.85(2)	1.95(2)	2.798(2)	177(2)
O(2)–H(21)···O(11d)	0.84(3)	1.89(3)	2.727(2)	174(2)
O(2)–H(22)···O(12b)	0.79(2)	2.09(2)	2.876(2)	172(2)
O(3)–H(31)···O(2)	0.81(3)	2.47(3)	3.193(2)	148(3)
O(3)–H(31)···O(11)	0.81(3)	2.62(3)	3.204(2)	130(2)
O(3)–H(32)···O(22e)	0.82(2)	1.98(2)	2.795(2)	176(2)

Symmetry transformations used to generate equivalent atoms: $a = -x, y + 1/2, -z + 1/2$; $b = x, y + 1, z$; $c = -x + 1, -y, -z$; $d = -x + 1, y + 1/2, -z + 1/2$; $e = x, -y + 1/2, z + 1/2$.

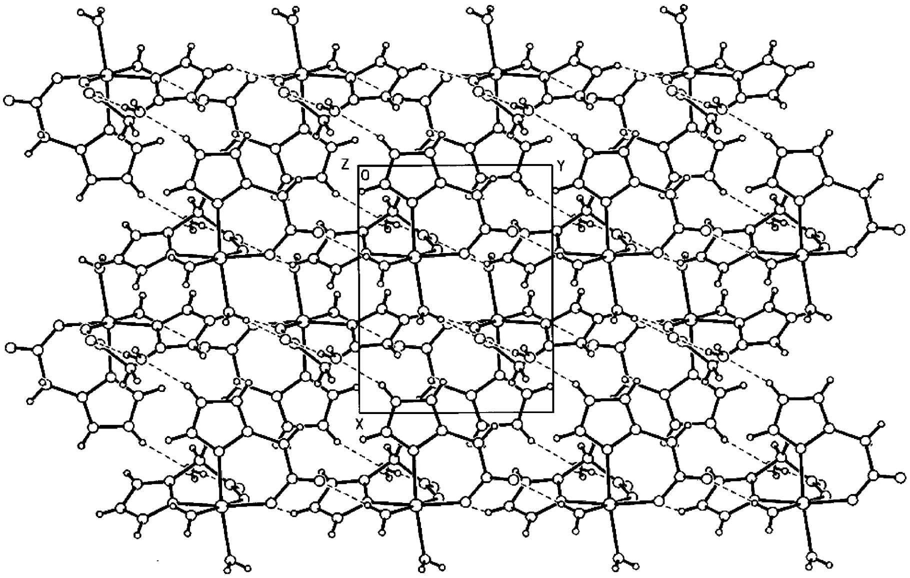

Fig. 2. The packing of molecules of the complexes in the unit cell.

coordinate polyhedron mostly resulting from the chelating character of the azole ligand, successive electronic transitions cannot be assigned to these bands at the present stage of investigations.

Magnetic moments of 4.77 and 5.82 B.M were measured at room temperature, for $[Co(4\text{-iaa})_2(H_2O)_2]H_2O$ and $[Mn(4\text{-iaa})_2(H_2O)_2]H_2O$, respectively, indicating the high-spin nature of these complexes.

3.4. The EPR spectra of the manganese complex

The EPR spectrum of the complex $[Mn(4\text{-iaa})_2(H_2O)_2]H_2O$ in a powdered sample exhibits one strong symmetrical line ($g_{\mathrm{eff}} = 1.996$) at 298 and 77 K, corresponding to manganese(II) in a weakly distorted octahedral environment, a geometry predicted by crystal structure analysis. For manganese(II) in a highly distorted octahedral geometry, a more complicated pattern of broad lines around $g \approx 2$ was observed. In that case a coordination sphere around Mn(II) ion (consisting of three imidazoles from one tridentate ligand, two carboxylate co-ligands and one water molecule) was distorted due to two bond angles significantly smaller than 90° (72° and 76°) and one apparently longer metal–ligand distance 2.41 Å [23].

4. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 203403 and 203404 for $[CoL_2(H_2O)_2]H_2O$ and $[MnL_2(H_2O)_2]H_2O$, respectively. Copies this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033: e-mail: deposit @ccdc.cam.ac.uk or www: http://www.ccdc.cam. ac.uk).

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