DOI: 10.1002/zaac.200600064

The Novel Polymeric Complex of Manganese(II) with Picolinic Acid, $[Mn(pic)_2]_n$, a New Coordination Mode for Picolinic Acid

Zerrin Heren[a,*], Hümeyra Paşaoğlu[b], Gökhan Kaştaş[b], Cem Keser[a], Orkan Zafer Yeşilel[c] and Orhan Büyükgüngör[b]

Kurupelit, Samsun / Turkey, Ondokuz Mayıs University, Faculty of Arts and Sciences, [a] Department of Chemistry and [b] Department of Physics
[c] Eskişehir / Turkey, Eskişehir Osmangazi University, Faculty of Arts and Sciences, Department of Chemistry

Received February 17th, 2006.

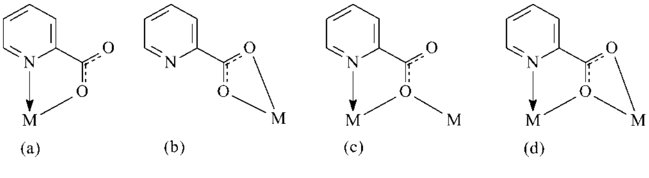
Abstract. A manganese(II) complex with novel coordination mode of picolinic acid (pic) has been synthesized and characterized by elemental analysis, magnetic susceptibility, FT-IR, thermal analysis (DTA and TG) and X-ray diffraction techniques. The complex crystallizes in the monoclinic space group $P2_1/c$ with unit cell parameters: a =10.4086 (6), b = 0.9524 (6), c =10.3570 (6) Å, β = 107.904 (4)° and Z = 4. In the complex all donor sites of picolinato ligands participated to the coordination. The ring nitrogen and one of the carboxylate oxygen atom of picolinato ligand form chelate ring with one Mn^{2+} ion, whereas the other carboxylate oxygen atom is coordinated to the other Mn^{2+} ion and forming a polymeric structure thermally stable up to 338 °C.

Keywords: Manganese; Picolinic acid; Thermal analyses; Crystal structures

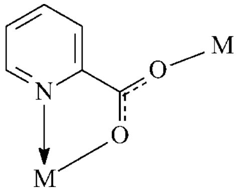
1 Introduction

Picolinic acid (2-pyridinecarboxylic acid) has been a widely investigated multidendate ligand and the general formula of the metal picolinic acid complexes may be given as $[M(C_5H_4NCOO)_2(H_2O)n]$ (n= 0, 2, 4) [1−9]. The picolinate ligand within the crystal structures of these complexes show several bonding modes (Scheme 1), from which the N,O- chelating formed with the central metal ions and hydrogen bonding between the carboxylate group and water molecules are dominant. Although picolinic acid has been studied extensively, both structurally and spectroscopically for many years [10−12], the polymeric complexes of this ligand have not been synthesized up to now.

In the present paper we report a novel crystalline coordination polymer of Mn^{2+} with picolinic acid, where a new bonding mode (Scheme 2) as well as the mode in Scheme 1c for picolinic acid was observed. In this structure, while the picolinato ligand forms a chelate ring through N,O donors by coordinating to one of the metal ions as bidentate, the carboxylate group bridges to the other metal ion.



Scheme 1 Possible coordination modes for picolinate ligand.



Scheme 2 New coordination mode for picolinate ligand.

2 Results and Discussion

2.1 IR Spectrum

The most characteristic bands in the IR spectrum correspond to the stretching vibrations of carbonyl group in the expected regions [13]. It is often used here to correlate the IR spectrum with the metal carboxylate structures by using the difference between the asymmetric and symmetric carboxylate stretches ($\Delta = \nu_{asym}(COO^-) - \nu_{sym}(COO^-)$) [14]. For the complex, $[Mn(pic)_2]_n$, two $\nu_{asym}(COO^-)$ values have been observed at 1675 and 1598 cm^{-1}, and two $\nu_{sym}(COO^-)$ values at 1411 and 1345 cm^{-1}. The corresponding $\Delta\nu$ values are 330 and 187 cm^{-1}, confirming the monodentate and bidentate coordination modes, respectively, of the (COO^-) groups [14]. This conclusion is consistent with the X-ray diffraction measurements. The

---

* Dr. Zerrin Heren
Department of Chemistry,
Faculty of Arts and Sciences,
Ondokuz Mayis University
TR−55139, Kurupelit, Samsun / Turkey
Telephone:+90 362 312 19 19
Fax: +90 362 457 60 81
E−mail : zheren@omu.edu.tr

Mn picolinato complex has a polymeric structure, where the two picolinate ligands coordinate to the Mn^{2+} metal ion in different manners. One of the (COO^-) groups is in monodentate form, while the second is in bidentate form and bridges two neighboring Mn^{2+} ions. Apart from that the bands observed at 1653, 1631, 1576, 1477 and 1433 cm^{-1} might be attributed to the vibration modes of ν_{asym} and ν_{sym} of C=C/C=N. The bands observed at 641 cm^{-1} and 443 cm^{-1} can be assigned to the in- plane ring deformation and out-of-plane deformation of the coordinated pyridine ring, respectively [13]. These bands are observed to shift to higher frequencies respect to its free ligand. The band around 1000 cm^{-1} assigned to the ring breathing in the IR spectrum of the free picolinic acid is appeared at 1015 cm^{-1} in the complex.

2.2 *Magnetic susceptibility*

The solubility of this complex in a number of solvents such as water, methanol, ethanol, acetone, DMF, DMSO was found to be too low. Due to the very low solubility, it was not possible to record UV-vis spectrum for the complex.

Magnetic susceptibility value of the complex is μ_{eff} = 2.27 BM. This low value may be explained by a strong interac tion between Mn^{2+} ions in the polymeric structure.

2.3 *Thermal analysis*

Thermal analysis curves of the complex (DTA and TG) are given in Figure 1. Thermal behavior of the complex was followed up to 900 °C in a static atmosphere. The thermal stability of the complex is very high. The polymeric complex is thermally stable in air up to 338 °C and begins to decompose without melting at 345 °C. In this consecutive stage (DTA peaks at 400, 430, 450 °C), picolinato ligands decompose and the organic residue burns. The final decom position product black MnO_2 was identified by IR spectroscopy (found 83.76; calc. 84.42 %).

2.4 *Crystallography*

The crystal structure analysis indicates that the complex has a polymeric two-dimensional network. The asymmetric unit consists of $Mn(pic)_2$-monomer together with two picolinato ligands (Fig. 2).

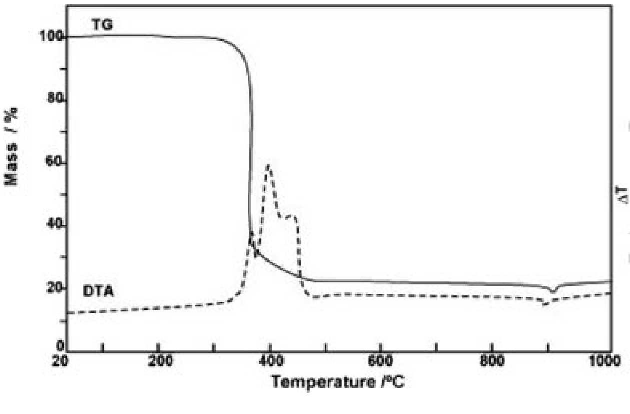


Fig. 1 The TG and DTA curves of $[Mn(pic)_2]_n$.

It should be underlined that the pic ligands adopt two unusual coordination modes in the crystal structure. In the first case, the carboxylate group (O1/C1/O2) is in a monodentate mode, and bridges ion Mn1 to a neighboring ion $Mn1^{ii}$ through carboxyl atom O2, with the $Mn1\cdots Mn1^{ii}$ distance of 3.4908(5) Å. In the second case, the carboxylate group (O3 C7 O4) is in a bidentate mode, and links $Mn1^{i}$ ion to the ion Mn1 through atom O3, and chelates ion $Mn1^{i}$ through atom O4 and pyridine atom N2 (Fig. 3). Atom O2 lies out of the plane of the pyridine ring by 0.198 Å in the opposite direction of Mn1 ion, as might be expected from its bridging coordination to the $Mn1^{ii}$ ion.

The Mn^{2+} ion is six-coordinated by two N and four O atoms from four pic ligands, yielding a distorted octahedral environment (Fig. 3). The bond distances and angles are given in Table 1. The Mn−O distances range from 2.1083 (12)−2.2212 (11) Å, and are shorter than Mn−N distances. This is similar to the situation reported for the related structures [15−18]. The average C−C (1.380 Å) and C−N (1.336 Å) distances in the pyridine ring are typical. The angles around the Mn^{2+} ion are significantly distorted from

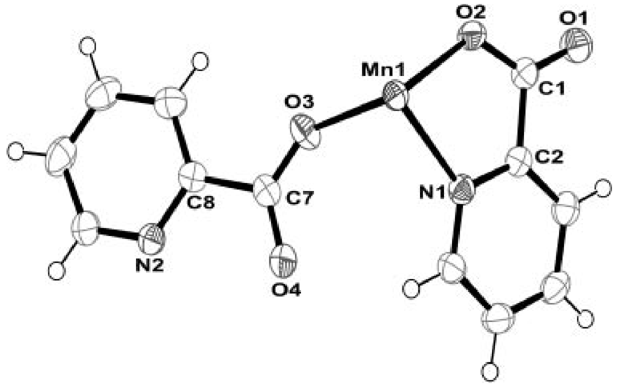


Fig. 2 The perspective view and atom labelling scheme of $[\text{-}C_{12}H_8MnN_2O_4\text{-}]_n$. Atomic displacement ellipsoids are drawn at the 50 % probability level.

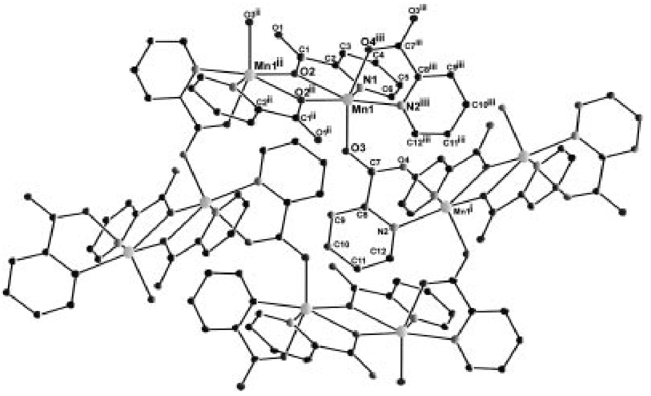


Fig. 3 Part of the crystal structure of $[\text{-}C_{12}H_8MnN_2O_4\text{-}]_n$, showing the formation of two-dimensional polymer chain. Symmetry codes: (i) x, 3/2−y, z−1/2; (ii) 1−x, 1−y, 2−z; (iii) x, 3/2−y, 1/2+z.

Table 1 Selected bond lengths /Å and bond angles /° for [-$C_{12}H_8MnN_2O_4$-]$_n$

Mn1−N1	2.2699(14)	Mn1^{i}−N2	2.2884(14)
Mn1−O2	2.2212(11)	Mn1^{ii}−O2	2.1469(11)
Mn1−O3	2.1083(12)	Mn1^{i}−O4	2.2100(12)
Mn1−O2^{ii}	2.1469(11)	Mn1−O4^{iii}	2.2100(12)
Mn1−N2^{iii}	2.2884(14)	C1−C2	1.516(2)
C1−O1	1.219(2)	C2−N1	1.345(2)
C1−O2	1.280(2)	C7−O3	1.250(2)
N1−Mn1−N2^{iii}	115.36(5)	O2^{ii}−Mn1−N2^{iii}	97.58(5)
O3−Mn1−O2	113.05(5)	O4^{iii}−Mn1−N2^{iii}	72.51(5)
O3−Mn1−O4^{iii}	160.15(5)	O3−Mn1−O2^{ii}	96.89(5)
O2−Mn1−N2^{iii}	154.98(5)	O2^{ii}−Mn1−O4^{iii}	96.29(5)
O2^{ii}−Mn1−N1	145.56(5)	O3−Mn1−N1	92.47(5)
Mn1^{ii}−O2−Mn1	106.09(5)	O3−Mn1−N2^{iii}	91.07(5)
O2^{ii}−Mn1−O2	73.91(5)	O4^{iii}−Mn1−N1	84.93(5)
O4^{iii}−Mn1−O2	84.88(5)	O2−Mn1−N1	71.92(4)
C7−O3−Mn1	134.97(12)	O4−C7−O3	126.4(2)
O1−C1−O2	126.3(2)		

octahedral configuration. This is mainly caused by the coordination of the bridging O atom to another metal ion. The bond angles of carboxylate groups are nearly equal [O1−C1−O2 = 126.3(2)° and O4−C7−O3 = 126.4(2)°]. These values are greater than those observed in the related structures [15, 16]. The angle between the planes through the pic ligands is 36.13(5)°. The torsion angles of the O1−C1−C2−N1 [174.8(2)°], O2−C1−C2−C3 [170.9(2)°], O3−C7−C8−N2 [177.3(2)°] and O4−C7−C8−C9 [178.3(2)°] suggest that the pic groups are nearly planar. The chelate ring (Mn1−O2−C1−C2−N1) is close to planar, with an r.m.s deviation of 0.1057 Å. In this chelate ring, the bridging O2 atom has a maximum deviation [0.146(9) Å].

The packing of Mn(pic)$_2$ moieties in the crystal structure is shown in Figure 4. The polymer chains extend through the *bc* plane. It is interesting to see that the dinuclear $Mn_2(\mu\text{-}O)_2$ moiety has different directions in the crystal structure, that is, there are two bridges which are approximately perpendicular to each other.

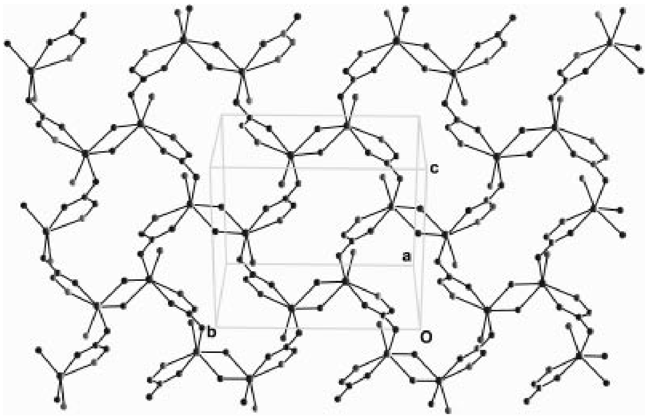


Fig. 4 The unit-cell packing of the complex, [-$C_{12}H_8MnN_2O_4$-]$_n$, parallel to *bc* plane.

3 Experimental Section

3.1 *Preparation of the complex [Mn(pic)$_2$]$_n$*

A solution of picolinic acid (8 mmol) in methanol was added drop wisely upon stirring to a solution of [Mn(ac)$_2$]·4H_2O (2 mmol) in absolute ethanol. The solution was heated to 60 °C in a temperature-controlled bath and stirring for 5 h. The resulting solution was left to slowly evaporate at r.t. Well-shaped light brown crystals, suitable for X-ray structure analysis, were collected after a week by filtration, washed with water and acetone and finally dried in vacuo. $C_{12}H_8MnN_2O_4$ (299.14); C 48.68 (calc. 48.13); H 2.46 (2.67); N 9.82 (9.36) %.

IR (KBr): υ_{asym} (COO$^-$) 1675 vs, 1598 vs, υ_{sym} (COO$^-$) 1411 vs, 1345 vs cm^{-1}, υ_{asym} and υ_{sym} (C=C/C=N) 1653 s, 1631 vs, 1576 s, 1477 m, 1433 m cm^{-1}, β(C=N) 641 m cm^{-1}, γ(C=N) 443 m cm^{-1}, ring breath 1015 s cm^{-1}.

3.2 *Materials and measurements*

All chemicals used were analytical reagent grade products. Manganese(II) acetate tetrahydrate salt was obtained from Merck. Picolinic acid was purchased from ACROS organics.

Magnetic susceptibility measurement at room temperature was performed using a Sherwood Scientific MXI model Gouy magnetic balance. The IR spectrum was recorded in the 4000−400 cm^{-1} region with a Mattson 1000 FT−IR spectrometer using KBr pellets. TG8110 thermal analyzer was used to record simultaneous TG and DTA curves in static air atmosphere at a heating rate of 10 Kmin^{-1} in the temperature range 20−1000 °C using platinum crucibles. Highly sintered α−Al_2O_3 was used as a reference and the DTG sensitivity was 0.05 mgs^{-1}. The elemental analysis was carried out at the TÜBİTAK Marmara Research Centre.

3.3 *Crystallographic analysis*

Diffraction experiments were carried out at 296 K on a Stoe IPDS diffractometer. The structure was solved by direct methods and refined using the programs SHELXS97 and SHELXL97 [19]. All non-hydrogen atoms were refined anisotropically by full-matrix least-squares methods [SHELXL-97]. The hydrogen atoms were placed in geometrically idealized positions and refined as riding atoms. The relevant crystal data and experimental conditions along with the final parameters are summarized in Table 2. Data collection: X-Area, cell refinement: X-Area, data reduction: X-RED [20]; program(s) used for molecular graphics: ORTEP-3 for Windows [21]; software used to prepare material for publication: WinGX [22].

Supplementary Material: Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 295003. Copies of 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).

Acknowledgements. We wish to acknowledge the Faculty of Arts and Sciences, Ondokuz Mayıs University, Turkey, for the use of the STOE IPDS-II diffractometer (purchased under grant F.279 of the University Research Fund).

Table 2 Crystal data and structure refinement parameters for $[\text{-}C_{12}H_8MnN_2O_4\text{-}]_n$

Empirical formula	$C_{12}H_8MnN_2O_4$
Formula weight	299.14
Temperature /K	296
Wavelength /Å	0.71073 MoK_α
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions	
a, b, c /Å	10.4086 (6); 10.9524 (6); 10.3570 (6)
β /°	107.904 (4)
V /Å^3	1123.51 (11)
Z	4
Absorption coefficient /mm^{-1}	1.186
D_{calc} /Mg m^{-3}	1.769
Crystal size /mm	0.35 × 0.27 × 0.13
Theta range for data collection (deg)	2.1−26.0
Measured reflections	15886
Independent reflections	2213
Absorption correction	Integration
Refinement method	Full-matrix least-squares on F^2
Final R indices [$F^2 > 2\sigma(F^2)$]	$R_1 = 0.024$, $wR_2 = 0.066$
R indices (all data)	$R_1 = 0.028$, $wR_2 = 0.067$
Goodness-of-fit on F^2	1.060
Largest difference peak and hole (e Å^{-3})	0.206; −0.288

References

[1] B. N. Figgis, C. L. Raston, R. P. Sharma, A. H. White, *Aust. J. Chem*. **1978**, *31*, 2545.

[2] D. H. R. Barton, S. D. Bèvière, W. Chavasiri, D. Doller, W. G. Liu, J. H. Reibenspies, *New J. Chem*. **1992**, *16*, 1019.

[3] S. C. Chang, J. K. H. Ma, J. T. Wang, N. C. Li, *J. Coord. Chem*. **1972**, *2*, 31.

[4] H. Loiseseleur, *Acta Crystallogr.* **1972**, *B28*, 816.

[5] R. Faure, H. Loiseleur, G. Thomas-David, *Acta Crystallogr.* **1972**, *B28*, 1890.

[6] P. LLumme,G. Lundgrem, W. Mark, *Acta Chem. Scand*. **1969**, *23*, 3011.

[7] J. P. Deloume, H. Loiseleur, *Acta Crystallogr.* **1974**, *B30*, 607.

[8] J. P. Deloume, H. Loiseleur, G. Thomas, *Acta Crystallogr.* **1973**, *B29*, 668.

[9] A. Alvarez-Larena, J. F. Piniella, J. Pons, R. March, J. Casabò, *Z. Kristallogr*. **1994**, *209*, 695.

[10] R. March, W. Clegg, R. A. Coxall, L. Cucurull-Sánchez, L. Lezama, T. Rojo, P. González- Duarte, *Inorg.Chim. Acta* **2003**, *353*, 8, 129.

[11] S. L. Jain, P. Bhattacharyya, H. L. Milton, A. M. Z. Slawin, J. D. Woollins, *Inorg. Chem.Comm.* **2004**, *7*, 423.

[12] S. Basu, S.-M. Peng, G.-H. Lee, S. Bhattacharyya, *Polyhedron* **2005**, *24*,157.

[13] K. Nakamato, Infrared and Raman Spectra of Inorganic and Coordination Compounds, p. 232, Wiley & Sons, New York (1986).

[14] G. B. Deacon, R. J. Phillip, *Coord. Chem. Rev.* **1980**, *33*, 227.

[15] B. Żurowska, J. Ochocki, J. Mirozinski, Z. Ciunik, J. Reedijk, *Inorg. Chim. Acta* **2004**, *357*, 755.

[16] A. Şengül, O. Büyügüngör,*Acta Crystallogr.* **2005**, *C61*, m119.

[17] P. Segl'a, M. Jamnický, M. Koman, J. Šima T. Glowiak, *Polyhedron* **1998**, *17*, 4525.

[18] G.-Q. Bian, T. Kuroda-Sowa, H. Konaka, M. Maekawa, M. Munakata, *Acta Crystallogr.* **2004**, *C60*, m338.

[19] G. M. Sheldrick, SHLEXS-97 and SHELXL-97. Program for Refinement of Crystal Structures, University of Göttingen, Germany, 1997.

[20] Stoe & Cie (2002). X-Area (Version 1.18) and X-Red32 (Version 1.04). Stoe & Cie, Darmstadt, Germany, 2001.

[21] L. J. Farrugia, ORTEP-III. Program For Molecular Drawing. *J. Appl. Crystallogr*. **1997**, *30*, 565.

[22] L. J. Farrugia, WinGX Suite for Single Crystal Small Molecule Crystallography, *J. Appl. Crysallogr*. **1999**, *32*, 837.