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Crystal Structure, Spectroscopy and Thermal Study of Manganese(II) Complex with Sarcosine

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A polymeric manganese(II) complex of sarcosine $[Mn(sar)_2(H_2O)_2]Cl_2$ (where sar = sarcosine) has been prepared and characterized by elemental, spectroscopic, thermal, magnetic and X-ray investigations. X-ray crystallographic study shows that the octahedral-coordinated manganese(II) ion is situated in the crystallographic center of symmetry and is bound to four carboxylate oxygen atoms of different sarcosine molecules and two water molecules. Two non-coordinated chloride ions are located between the chains. IR spectra of the free ligand and the complex have been discussed. This complex is stable up to 378 K, later loosing water and transforming into oxides. The gas-phase products of decomposition have been analyzed by FTIR spectra.

Key words: sarcosine complexes, manganese(II) ion, X-ray analysis

Investigations of manganese interaction with simple amino acids have been carried out with regard to an essential role of manganese in some biological systems [1–3]. As a continuation of our study on the Mn(II) complexes with natural amino acids [4–7], we discusses the properties and crystal structure of sarcosine (N-methylglycine) complex with manganese(II) ion. The sarcosine molecule acts as a bidentate-bridging or threedentate bridging-chelating ligand. In the complex of sarcosine with cadmium chloride, the zwitterionic sarcosine coordinates Cd(II) ion through both carboxylate oxygen atoms. Additionally, chloride ions take part in binding of the central atom [8]. The polymeric complex of Eu(III) with sarcosine is built of dimeric units $[Eu(sar)_3(H_2O)_2]_2^{6+}$. Two metal ions are linked by two bridging and two bridging-chelataing carboxylate groups from four sarcosine molecules. The units are further linked by two simple carboxylate bridges [9]. In the complex of Mn(III) ion with *N*-(5-nitro-2-hydroxybenzyl)sarcosine, nitrogen atom and one carboxylate oxygen from sarcosine coordinate the metal ion creating a five-member ring [10].

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EXPERIMENTAL

Crystals of $[Mn(sar)_2(H_2O)_2]Cl_2$ were grown by slow evaporation of an aqueous solution of sarcosine and manganese(II) chloride of the 1:2 molar ratio. Colourless crystals were formed after a few days. Crystals were isolated by washing with ethanol and dried in air at room temperature. Chemical analysis confirms the composition.

IR spectra of the free sarcosine and complex were recorded in the range 4000–400 cm^{-1} on a SPECORD M80 spectrophotometer at room temperature using the KBr pellet technique. Magnetic susceptibility measurement was conducted at 292±1 K by a magnetic susceptibility balance, using $[HgCo(SCN)_4]$ as calibrant. Susceptibility was corrected by Pascal`s constant. X-ray powder diffractogram of the complex was recorded with a HGZ4 X-ray diffractometer with CuKα radiation. Thermal measurements were performed with a derivatograph in a static air atmosphere, up to 1272 K. The products of decomposition were identified using a NETZCH TG 209 apparatus coupled with a Bruker FTIR IFSS spectrophotometer.

X-ray crystallography: Data were collected at 293 K temperature on a KappaCCD diffractometer, using graphite monochromated MoKα radiation. Crystallographic data and other pertinent information are given in Table 1. The crystal structure was solved by direct-atom methods using SHELXS-97 [11] and refined by full-matrix least squares method using SHELXL-97 program [12]. The carbon bonded H-atoms were included in the calculated positions and refined using a riding model. Isotropic temperature factors were taken as $1.2U_{eq}$ for H-atoms of CH_2 group and 1.5_{eq} for H-atoms of CH_3 group. H-atoms of the water molecules were located from difference Fourier map.

Table 1. Summary of data collection and crystal parameters.

Formula	$C_6H_{18}Cl_2MnN_2O_6$
M_r	340.06
Crystal system	triclinic
Space group	P-1
T(K)	293
Wavelength (Å)	0.71073
a (Å)	4.8220(4)
b (Å)	5.3790(6)
c (Å)	13.783(1)
α (°)	83.763(5)
β (°)	80.549(7)
γ (°)	87.581(6)
V (Å^3)	350.5(4)
Z	1
F(000)	175
D_{calc} (Mg m^{-3})	1.611
Absorption coefficient (mm^{-1})	1.338
Crystal dimensions (mm)	0.30×0.20×0.10
Reflections collected/unique	2997/1566
θ range for data collection	3.81 to 27.50
Index ranges	$-6 \le h \le 6, -6 \le k \le 6, -17 \le l \le 17$
R [$I > 2\sigma(I)$]	0.0763
wR	0.2446
GOF	1.123
Largest diff. peak and hole [e Å^{-3}]	1.977, –0.703

RESULTS AND DISCUSSION

The crystal structure of manganese(II) with the sarcosine complex was determined by single-crystal X-ray diffraction. The *catena*-poly[manganese(II)-diaqua-bis(μ-sarcosine-$\kappa^{2}0,0'$)] dichloride is built up from centrosymmetric linear chains as shown in Fig. 1. Manganese(II) ion displays octahedral geometry with water molecules occupying axial sites. The equatorial plane is defined by four oxygen atoms from four sarcosine molecules. The Mn–O$_{\text{carboxyl}}$ bond lengths are 2.147(4) and 2.208(4) Å. The axial Mn–O$_{\text{water}}$ distances are 2.182(4) Å. The valence angles in the octahedron differ from 90° by a maximum 4.79°. The selected bond lengths and angles are given in Table 2. Two chloride ions of outer coordination sphere fill the voids between the polymeric chains. Each manganese ion is connected with the neighboring manganese atom *via* two carboxylate bridges forming a polymeric chain. The carboxylate group of sarcosine has a bidentate-bridging character and forms syn-syn bonds with manganese(II) ions. The C(1)–O(1)–Mn(1) and C(1)$^{\text{ii}}$–O(2)–Mn(1) angles are 128.6(4) and 127.6(3)°, respectively. C–O bond lengths in the carboxylate group are 1.253(7) Å and 1.267(7) Å. O–C–O angle equals 126.6(5)°, typical for the bidentate-bridging carboxylate group [13].

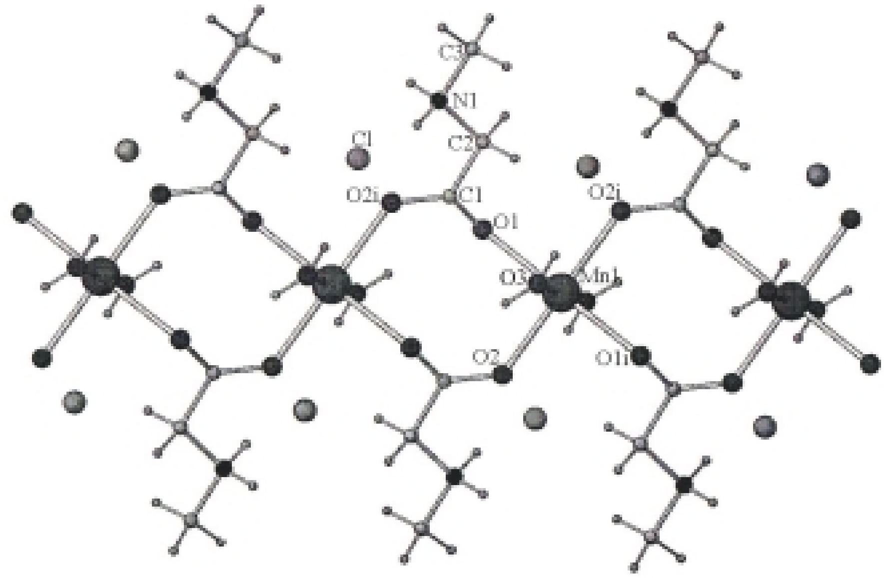

Figure 1. The crystal structure of $[Mn(sar)_2(H_2O)_2]Cl_2$.

Table 2. Selected bond lengths (Å) and angles (°) with e.s.d.'s in parentheses.

Mn(1)–O(1)	2.147(4)	N(1)–C(2)	1.474(8)
Mn(1)–O(3)	2.182(4)	N(1)–C(3)	1.486(8)
Mn(1)–O(2)	2.208(4)	C(1)–C(2)	1.512(8)
O(1)–C(1)	1.253(7)	C(1)–O(2)[a]	1.267(7)
O(1)–C(1)–O(2)[a]	126.6(5)		

[a] Symmetry code: –x, –y + 1, –z.

The sarcosine molecules exist in the zwitterionic form. The main chain of amino acid has a zigzag conformation. The valence angles in the sarcosine are in the range 112.5(5)–117.2(5)°. There is a small deviation from planarity in the main chain C(3)–N(1)–C(2)–N(1). The torsion angle equals 177.5(5)°.

The crystal structure of the complex is stabilized by a network of hydrogen bonds (Table 3). The water molecules and protonated NH_2^+ group occur as the proton donors in the hydrogen bonds. Carboxylate oxygen atoms and chloride ions take part in hydrogen bonds formation as proton acceptor. Each Cl^- ion is connected with two different sarcosine molecules *via* N–H···Cl hydrogen bonds. Additionally, chloride ion is hydrogen bonded with the coordinated water molecule through almost linear (173(7)°) O_{water}–H···Cl hydrogen bond. The shortest O–H···O hydrogen bond (2.869(6) Å) appears between the water molecule and carboxylate oxygen of sarcosine.

Table 3. Hydrogen bond lengths (Å) and angles (°) with e.s.d.'s in parentheses.

D–H···A	D–H	H···A	D···A	<D–H···A
O(3)–H(3BO)···O(2)[a]	0.95(11)	2.02(11)	2.869(6)	148(8)
O(3)–H(3AO)···Cl(1)[b]	0.88(8)	2.35(8)	3.231(5)	173(7)
N(1)–H(1B)···Cl(1)[c]	0.90	2.24	3.104(5)	161.6
N(1)–H(1A)···Cl(1)[d]	0.90	2.28	3.156(5)	163.6

[a] Symmetry code: x, y – 1, z.
[b] Symmetry code: –x + 1, –y, –z.
[c] Symmetry code: x, y, z.
[d] Symmetry code: x, y + 1, z.

The effective magnetic moment of the title complex is 5.70 B.M. (the spin-only μ_{eff} for Mn(II) is 5.92 B.M.). Thus, there is practically no magnetic interaction between the Mn(II) ions through the sarcosine bridges.

Spectroscopic data for sarcosine and the complex are summarized in Table 4. IR spectrum of free sarcosine exhibits a strong absorption band with two maxima at 3470 and 3408 cm^{-1}, which can be ascribed to the asymmetric and symmetric stretching vibrations of NH_2^+ group. In the complex spectrum these bands occur at lower frequencies 3000 and 2950 cm^{-1}, due to hydrogen bonds formation. The complex IR spectrum shows a broad absorption band at 3416 cm^{-1}, resulting from stretching vibrations of the hydrogen bonded water molecules. As expected from the zwitterionic structure of amino acid, the carboxylate stretching vibrations of carboxylate group appear both in the free ligand and the complex. For sarcosine the asymmetric ν_{as} and symmetric ν_{sym}

stretching vibrations of COO group appear at 1628 and 1408 cm^{-1}, respectively. For the complex the asymmetric stretching band of COO group is broadened and split by the deformation vibrations of water molecules and asymmetric deformation vibrations of NH_2^+ group [15]. We assume that the ν_{as} vibrations appear at 1600 cm^{-1}. The symmetric stretching vibrations band of coordinated carboxylate group appear at 1408 cm^{-1}. As can be seen, frequencies of stretching vibrations of COO group are different in comparison to the corresponding bands of the sarcosine due to the complex formation. The separation, $\Delta\nu = \nu_{as} - \nu_{sym}$ equals to 184 cm^{-1} and may be assumed as indicative for ionized or bidentate-bridging carboxylate group [13].

Table 4. The wavenumbers and assignment of the bands observed in the IR spectra of sarcosine and its manganese complex[a].

Sarcosine	$[Mn(sar)_2(H_2O)_2]Cl_2$	Vibration modes
	3416	O–H str hydrogen bonded
3470, 3408	3000, 2950	doublet NH_2^+ (asym str – sym str)
1628	1600	COO asym str
1584	1570, 1560	NH_2^+ asym def
1488	1472	CH_3 scissor
1408	1416	COO sym str
1390	1400	
1308	1328	CH_2 wag
1230		NH_2^+ rock
1210		C–H bend
1170, 1150		NH_2^+ rock
1064, 1010	1048	C–N str
968, 940, 868	970, 936, 864	C–C str, CH_3 rock
844	–	H_3C–C–N sym str
700, 620, 560	712, 690, 640	CH_2 rock, skeletel
500	500	COO wag

[a]Abbreviations: asym, asymmetric; sym, symmetric; str, strech; def, deformation; wag, wagging; rock, rocking.

The $[Mn(sar)_2(H_2O)_2]Cl_2$ complex is stable at room temperature. Upon heating, dehydration process begins at 378 K. A calculated weight loss, due to removal of the water molecules is 10.58%, while the weight losses measured are 10.00% (air atmosphere) and 10.49% (argon atmosphere). On the DTG curves two peaks at 395 K and 420 K are observed. This may indicate that the loss of water molecules is a double-step process. The evolved water molecules give characteristic bands on the FTIR spectra of gas-phase products of complex decomposition collected at 408 K. As follows from Fig. 2, the H_2O molecules absorb in the ranges: 3750–3500 cm^{-1} and 1900–1300 cm^{-1}, due to stretching and deformation vibrations respectively. When the complex is heated above 493 K, the subsequent decomposition of the complex with degradation of sarcosine takes place. On the TG curve two significant weight losses are observed between 493–623 and 623–918 K. The first step of decomposition of organic ligand is connected with a simultaneous release of H_2O, CO_2 and NH_3, which is reflected in the FTIR spectra recorded at 513 K (Fig. 2). Carbon dioxide molecules absorb in the wavenumber ranges: 2300–2250 and 750–600 cm^{-1}, due to deformation and valence vibration. The CO_2 band of deformation vibrations has an unusual shape, which points to an overlapping with another group. Deformation vibrations of gaseous NH_3 give very characteristic double peaks with the maxima at 966 and 923 cm^{-1} [16]. In the FTIR spectra collected at 558 K intensities of water, carbon dioxide and ammonia bands increase. On the other hand, the new broad band in the range 3100–2750 cm^{-1} with submaxima at 2962 and 2799 cm^{-1} is observed. This band is probably due to vibrations of degradation products of sarcosine molecules, *i.e.* acetonitrile [17]. At 573 K the bands with maxima at 3738, 3567, 1743, 1625, 1508, 1457, 1168 cm^{-1} are observed. Heating of the complex above 723 K causes a gaseous HCl release. Vibrations of hydrochloride give rise to the characteristic multi-peak band in the region 3100–2700 cm^{-1} [15].

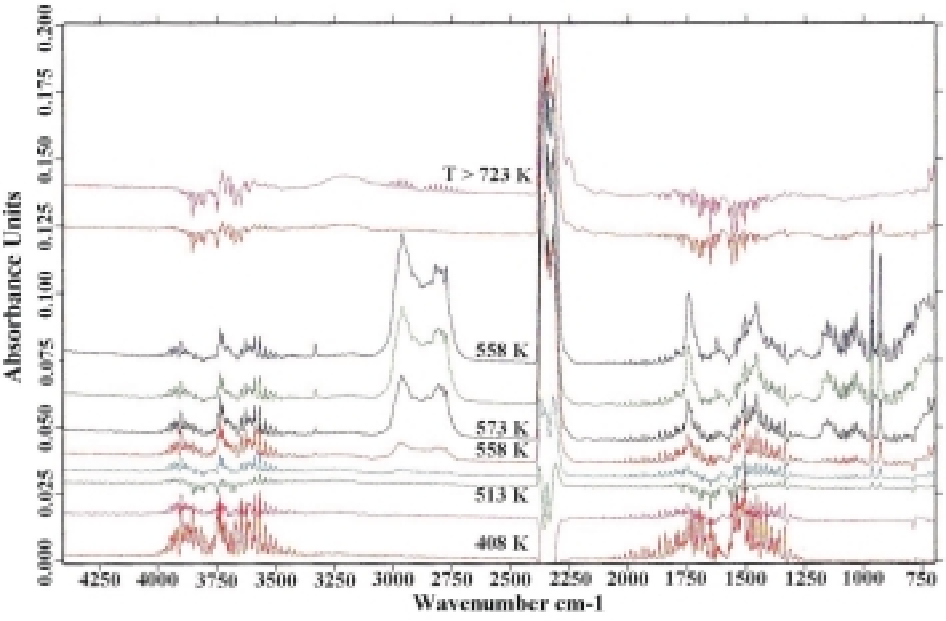

Figure 2. FTIR spectra of gaseous products of thermal decomposition of $[Mn(sar)_2(H_2O)_2]Cl_2$.

For comparison, the FTIR spectra of the gaseous products of sarcosine decomposition were also recorded. The temperature of NH_3 evolution is lower when the complex decomposes, *i.e.* 478 K. This suggests the formation of intermediate solid compounds, containing bonded nitrogen atoms.

Further heating of the complex leads to oxides. Between 918–998 K probably MnO_2 is formed, which transforms *via* Mn_2O_3 into Mn_3O_4 [18]. Mn_3O_4 formed at 1223 K is the final product of the complex decomposition (found weight loss 78.00%, calculated 77.6%).

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre (CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK) as deposition No. 145722.

REFERENCES

1. Holm R.H, Kenneohl P. and Solomon E.J., *Chem. Rev.,* **96**, 2239 (1996).
2. Siegel H., Fisher B.E. and Prijs B., *J. Am. Chem. Soc*., **99**, 4489 (1977).
3. Kanyo Z.F., Scolnick L.R., Ash D.E. and Christianson D.W., *Nature*, **383**, 554 (1996).
4. Rzączyńska Z., Mrozek R. and Głowiak T., *J. Chem. Crystallogr*., **27(7)**, 417 (1997).
5. Mrozek R., Rzączyńska Z. and Głowiak T., *Monatsh. Chem*., **129**, 129 (1998).
6. Mrozek R., Rzączyńska Z., Sikorska-Iwan M. and Głowiak T., *J. Chem. Crystallogr*., **29(7)**, 803 (1999).
7. Mrozek R., Rzączyńska Z., Sikorska-Iwan M., Jaroniec M. and Głowiak T., *Polyhedron*, **18**, 2321 (1999).
8. Krishnakumar R.V., Rameela M.P. and Natarajan S., *Cryst. Res. Technol.,* **31(2)**, 203 (1996).
9. Gawryszewska P.P., Jerzykiewicz L., Sobota P. and Legendziewicz J., *J. Alloys Comp.*, **300-301**, 275 (2000).
10. Shongwe M.S., Mikuriya M., Nukada R., Ainscough E.W., Brodie A.M. and Waters J.M., *Inorg. Chim. Acta*, **290**, 228 (1999).
11. Sheldrick G.M., SHELXS 97, *Acta Cryst.,* **A 46**, 467 (1990).
12. Sheldrick G.M., SHELXL 97, Program for Refinement of Crystal Structures, University of Gőttingen, Gőttingen, 1994.
13. Deacon G.B. and Philips R.J., *Coord. Rev.,* **33**, 227 (1980).
14. Silverstein R.M., Spectrometric Identification of Organic Compounds, Wiley&Sons, NY, 1998, p. 82.
15. Holly S. and Sohar P., Absorption Spectra in the Infrared Region, Akademiai Kiado, Budapest, 1975, pp. 117–169.
16. Guelachivili G. and Narahari Rao K., Handbook of Infrared Standards, Academic Press Inc., London 1986, p. 120.
17. Horak M. and Papoušek D., Infračervena spektra a struktura molekul, Akademia Praha 1976, p. 534.
18. Shaheen W.M. and Selim M.M., *J. Therm. Anal. Cal.*, **59**, 961 (2000).