Note

Coordination behaviour of Ar-SO_2-*N*-amino acids toward the Mn(II) ion. Crystal and molecular structure of [Mn(tsgln)$_2$] and [Mn(ts-DL-α-ala)$_2$(H_2O)]·2.78H_2O·0.92CH_3OH

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Abstract

A series of complexes of Ar-SO_2-*N*-amino acids (Ar-SO_2- = 4-toluensulfonyl- (hereafter abbreviated as tosyl) (ts), benzenesulfonyl (bs); amino acid = glycine (gly), DL-α- and β-alanine (α- and β-ala), asparagine (asn) and glutamine (gln)) with Mn(II) was synthesized and characterized by means of spectroscopic and thermal analyses. For two of them [Mn(ts-α-ala)$_2$(H_2O)]·2.78H_2O 0.92CH_3OH (**I**) and [Mn(tsgln)$_2$] (**II**) the crystal and molecular structure was also determined. **I** crystallizes in the orthorhombic *Pbcn* space group, with cell dimensions: $a = 31.212(3)$, $b = 11.248(2)$, $c = 9.051(2)$ Å, $Z = 4$. **II** crystallizes in the monoclinic *C*2 space group, with cell dimensions: $a = 17.490(3)$, $b = 5.259(2)$, $c = 17.432(2)$ Å, $\beta = 120.70(4)°$, $Z = 2$. In both compounds the Mn(II) atom is octahedrally coordinated by six oxygen atoms. In **I** the amino acid monoanion bridges two Mn atoms through the carboxyl group giving rise to a 1D polymer, the coordination to Mn is completed by two water molecules in a special position. In **II** each amino acid monoanion bridges two Mn atoms through the carboxyl group and binds a third Mn atom through the carbonyl oxygen of the terminal amide group, giving rise to a 2D polymer.

Introduction

Among first-row transition metals considered essential for life, manganese plays an important role because it is the metal centre in naturally occurring biomolecules such as concanavalin A [1], pyruvate kinase [1] and in the pseudo-catalase from *Lactobacillus plantarum* [2]. Consequently it is rather surprising that the literature data on Mn(II) interactions with amino acids, peptides and related molecules are confined to very few cases, both in the solid and solution state. The results on proline [3], glycine [4] and aspartic acid [5] suggest that the preferential active binding site on the amino acid is the carboxyl group, while the amino nitrogen remains uncoordinated, so it seems clear that Mn(II) displays a low tendency to form an N,O-chelate ring.

For example the overall formation constant of the bis(L-histidinato)Mn(II) complex is 6–12 orders of magnitude smaller with respect to other 3d-metal ions [6] and the same holds for peptide complexes of the type $MnLH^+$ where the only active binding site is the N-terminal amino group with log *K* in the range 1.79–2.47 [7].

Also in natural systems such as concanavalin A the Mn(II) ion is coordinated to aspartic and glutamic carboxylate oxygens and to imidazole nitrogen of the histidine residue and these amino acids act only as monodentate ligands [1]. Until now no reports are available on N-substituted amino acids although in 1979 an attempted structural characterization of Mn(II) hippurate [8] was announced. In the framework of a systematic investigation performed in our laboratory on metal(II) complexes with N-substituted amino acids, we separated a series of Mn(II) compounds with Ar-SO_2-*N*-amino acids of general formula Mn(Ar-SO_2-*N*-aminoacidate)$_2$·*x* solvent, where Ar-SO_2- = tosyl or benzenesulfonyl group. The crystal and molecular structure of the α-alanine and glutamine complexes is reported here.

Experimental

Preparation of the complexes

All the complexes were obtained by mixing 10 ml of a boiling aqueous solution of Mn(II) acetate trihydrate 10^{-1} mol/dm^3 and 10 ml of a methanolic solution 2×10^{-3} mol/dm^3 of the appropriate Ar-SO_2-*N*-amino acid, with Ar-SO_2 = 4-toluenesulfonyl (hereafter tosyl) (ts) and benzenesulfonyl (bs) group and amino acid: DL-α- and β-alanine (α- and β-ala), glycine (gly), asparagine (asn), glutamine (gln). In all cases crystalline compounds separated after slow cooling, but only tosyl-DL-α-alanine and tosyl-glutamine adducts were suitable for X-ray analysis.

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$Mn(tsgly)_2 \cdot 4H_2O$. *Anal.* Found: C, 37.09; H, 4.90; N, 4.72. Calc. for $C_{18}H_{28}MnN_2O_{12}S_2$: C, 37.03; H, 4.84; N, 4.80%.

$Mn(ts\text{-}\alpha\text{-}ala)_2(H_2O) \cdot 2.78H_2O \cdot 0.92CH_3OH$. *Anal.* Found: C, 39.55; H, 4.45; N, 5.29. Calc. for $C_{20}H_{26}MnN_2O_9S_2 \cdot 2.78H_2O \cdot 0.92CH_3OH$: C, 40.56; H, 5.74; N, 4.53%.

$Mn(bs\text{-}\beta\text{-}ala)_2 \cdot 4H_2O$. *Anal.* Found: C, 37.35; H, 4.41; N, 4.29. Calc. for $C_{20}H_{32}MnN_2O_{12}S_2$: C, 37.03; H, 4.84, N, 4.80%.

$Mn(tsasn)_2 \cdot 3H_2O$. *Anal.* Found: C, 37.97; H, 4.49; N, 8.01. Calc. for $C_{22}H_{32}MnN_4O_{13}S_2$: C, 38.86; H, 4.75; N, 8.24%.

$Mn(tsgln)_2$. *Anal.* Found: C, 43.92; H, 4.72; N, 8.52. Calc. for $C_{24}H_{30}MnN_4O_{10}S_2$: C, 44.08; H, 4.65; N, 8.58%.

Physical measurements

IR spectra in the 4000–400 cm^{-1} spectral range were recorded as KBr pellets with a Bruker 113v FT-IR spectrometer. The thermogravimetric measurements were performed at a rate of 10 °C/min with a Mettler TA 3000 instrument.

X-ray analysis

Crystal data for compounds **I** and **II** are reported in Table 1. Intensity data were empirically corrected with the aid of ψ scan measurements and Lorentz and polarization corrections were applied as well. No significant change was observed in two reference intensities measured throughout the data collections.

The structures were solved by the heavy-atom method using SHELX86 [9] and refined with SHELX76 [10]. In the case of complex **I** the difference Fourier map indicated the presence of some additional atoms in the crystal lattice which could be interpreted as two water molecules and one methanol molecule. The Fourier maxima corresponded however to a rather low electron density thus suggesting a statistical occupancy of the crystal sites. The positions of these atoms were then refined together with their respective occupation factors. At the end of the refinement procedure the hydrogen atoms of the organic molecules were located at calculated positions and the last least-squares cycles were carried out by allowing these light atoms to ride around the bonded heavier atoms. Unit weights were adopted throughout the refinement procedure.

Results and discussion

Atomic fractional coordinates are reported in Tables 2 and 3 and the molecular geometries are described in Tables 4 and 5. In both complexes Mn is octahedrically coordinated with six oxygen atoms. In compound **I** this is achieved by surrounding each Mn atom with four different amino acid and two water molecules (see Fig. 1); each amino acid molecule, in its turn, bridges, through its carboxyl oxygens, two Mn atoms in a *syn–anti* type of configuration as commonly observed in polymeric Mn^{2+} complexes with α-amino acids [3, 4]. This gives

TABLE 1. Crystal data for **I** and **II**

Compound	**I**	**II**
Formula	$MnS_2O_8N_2C_{20}H_{24} \cdot 3.78H_2O \cdot 0.92CH_3OH$	$MnS_2O_{10}N_4C_{24}H_{30}$
Formula weight	637.0	653.6
Crystal system	orthorhombic	monoclinic
a (Å)	31.212(3)	17.490(3)
b (Å)	11.248(2)	5.259(2)
c (Å)	9.051(2)	17.432(2)
β (°)		120.70(4)
V (Å^3)	3177.6(8)	1378.7(6)
Z, D_{calc} (g cm^{-3})	4, 1.33	2, 1.57
Space group	*Pbcn*	*C*2
F(000)	1299.4	678
Radiation (graphite monochromated)	Mo Kα	Mo Kα
μ(Mo Kα) (cm^{-1})	5.75	6.65
2θ Range (°)	5–50	5–48
Scan method	ω	ω
Scan interval	$0.7+0.35\ tg\theta$	$0.7+0.35\ tg\theta$
Collected octants	h,k,l	$\pm h,k,l$
No. data collected	1226	1206
No. data used ($I>3\sigma(I)$)	1193	678
Crystal size (mm)	$0.25 \times 0.25 \times 0.20$	$0.15 \times 0.15 \times 0.20$
R^a	0.064	0.054
No. variable parameters	192	101
GOF^b	3.64	3.17

Unit weights were adopted in the refinement procedure. [a] $R=[\Sigma(F_o-k|F_c|)^2/\Sigma F_o]$. [b] $GOF=\sqrt{[\Sigma(F_o-k|F_c|)^2/(N_{obs}-N_{var})]}$.

TABLE 2. Fractional atomic coordinates ($\times 10^4$), equivalent isotropic thermal parameters and occupation factors (o.f.) for all non-hydrogen atoms of compound **I**

Atom	x	y	z	B_{eq} (Å^2)	o.f.
Mn	0(0)	590(2)	2500(0)	3.9(2)	0.5
S	−1480(1)	1954(3)	3776(3)	4.8(2)	1
O(1)	−1432(2)	2730(5)	2509(8)	6.0(6)	1
O(2)	−1358(2)	2418(6)	5189(8)	6.6(7)	1
O(3)	−418(2)	703(6)	4425(6)	4.5(5)	1
O(4)	582(2)	566(6)	3786(6)	4.7(5)	1
O(5w)	0	−1348(9)	2500	8.9(14)	0.5
O(6w)	0	2543(8)	2500	7.1(10)	0.5
O(7w)	5674(4)	−1042(12)	1803(22)	11.2(24)	0.54(1)
O(8m)	5470(8)	1772(24)	748(30)	14.0(11)	0.46(2)
O(9w)	4782(13)	1649(34)	791(43)	17.8(22)	0.35(3)
N	−1231(2)	753(7)	3363(7)	4.2(6)	1
C(1)	−2024(3)	1521(8)	3920(10)	4.3(2)	1
C(2)	−2282(3)	2108(9)	4925(11)	5.3(2)	1
C(3)	−2712(3)	1811(9)	4950(12)	6.2(2)	1
C(4)	−2890(3)	945(9)	4090(11)	5.5(2)	1
C(5)	−2626(3)	363(9)	3078(11)	6.4(2)	1
C(6)	−2178(3)	647(9)	2997(11)	6.1(2)	1
C(7)	−3356(3)	591(10)	4177(15)	8 7(13)	1
C(8)	−1131(3)	−121(8)	4516(9)	4.3(2)	1
C(9)	−1190(4)	−1343(10)	3921(13)	7 1(3)	1
C(10)	−668(2)	30(9)	5075(11)	3 7(1)	1
C(11m)	5741(13)	1018(34)	1485(45)	14.0(11)	0.46(2)

TABLE 3. Fractional atomic coordinates ($\times 10^4$) and equivalent isotropic thermal parameters for non-hydrogen atoms of compound **II**

Atom	x	y	z	B_{eq} (Å^2)
Mn	0	0	0	1.4(2)
S	−41(3)	8155(10)	2992(2)	1.8(3)
O(1)	−340(7)	6426(23)	3414(7)	2.9(2)
O(2)	−93(7)	10826(20)	3111(7)	2.6(3)
O(3)	−48(8)	6789(23)	808(8)	2 4(3)
O(4)	−128(8)	2626(27)	858(8)	3 2(3)
O(5)	−3546(6)	4908(28)	839(6)	2.5(2)
N(1)	−626(7)	7650(25)	1921(7)	1.7(2)
N(2)	−3241(9)	687(27)	1123(9)	3.1(3)
C(1)	1093(9)	7495(32)	3358(10)	2.2(3)
C(2)	1517(10)	9133(34)	3090(11)	3.0(4)
C(3)	2437(10)	8681(36)	3437(10)	3.5(4)
C(4)	2849(11)	6654(38)	3964(11)	3 2(4)
C(5)	2402(10)	4951(54)	4208(10)	4 0(3)
C(6)	1499(10)	5375(40)	3881(10)	3.3(4)
C(7)	3861(13)	6189(43)	4381(13)	4 8(5)
C(8)	−689(7)	5074(35)	1609(7)	1.2(2)
C(9)	−1664(9)	4174(29)	1069(9)	1.9(3)
C(10)	−247(7)	4813(36)	1045(8)	1 5(2)
C(11)	−2043(9)	3830(32)	1663(11)	2.4(3)
C(12)	−2995(9)	3138(36)	1213(9)	1.9(2)

TABLE 4 Molecular dimensions for **I**

Bond lengths (Å)	
Mn–O(3)	2.181(5)
Mn–O(4b)	2 156(5)
Mn–O(5w)	2.180(10)
Mn–O(6w)	2.196(9)
S–O(1)	1.448(7)
S–O(2)	1.433(7)
S–N	1.603(8)
S–C(1)	1.774(9)
O(3)–C(10)	1.235(11)
O(4)–C(10)	1.258(11)
O(8)–C(11)	1.370(48)
N–C(8)	1.467(11)
C(1)–C(2)	1.381(13)
C(1)–C(6)	1 377(13)
C(2)–C(3)	1.384(14)
C(3)–C(4)	1.365(14)
C(4)–C(5)	1 395(14)
C(4)–C(7)	1.510(14)
C(5)–C(6)	1.435(14)
C(8)–C(9)	1.487(15)
C(8)–C(10)	1.543(12)
Bond angles (°)	
O(3)–Mn–O(3a)	173.3(3)
O(3)–Mn–O(4b)	94.3(2)
O(3)–Mn–O(4c)	85.8(2)
O(3a)–Mn–O(5w)	93.3(2)
O(3a)–Mn–O(6w)	86.7(2)
O(4b)–Mn–O(4c)	178 5(3)
O(4c)–Mn–O(5w)	89 3(2)
O(4c)–Mn–O(6w)	90.7(2)
O(5w)–Mn–O(6w)	180.0
N–S–C(1)	104.5(8)
O(2)–S–C(1)	106.8(7)
O(2)–S–N	112 7(7)
O(1)–S–C(1)	108.8(7)
O(1)–S–N	105 8(6)
O(1)–S–O(2)	117 4(8)
Mn–O(3)–C(10)	136.2(6)
S–N–C(8)	120 1(7)
N–C(8)–C(1)	111.0(1.0)
O(4)–C(10)–C(8)	114.1(1.1)
O(3)–C(10)–C(8)	120.1(1 0)
O(3)–C(10)–O(4)	125 7(1 3)
Selected torsion angles (°)	
N–S–C(1)–C(2)	147.6(1.1)
C(1)–S–N–C(8)	−79.0(1.1)
S–N–C(8)–C(9)	141.2(1.0)
N–C(8)–C(10)–O(3)	−9.4(1.6)

(a) $\bar{x}$, y, $\frac{1}{2}-z$. (b) $\bar{x}$, $\bar{y}$, $1-z$ (c) x, $\bar{y}$, $z-\frac{1}{2}$. (w) water.

rise to a linear 'polymeric' sequence propagating along *c* as illustrated in Fig. 1. Figure 2 shows, in more detail, the asymmetric unit together with the numbering scheme. The 'free' water and methanol molecules are located in an uncrowded zone of the crystal lattice and no particularly short contact is detected except for a possible hydrogen bond between O(7w) and O(1) ($-x$, $y-\frac{1}{2}$, z), with O...O distance of 2.81 Å. In compound **II** the octahedral coordination is achieved through a

TABLE 5. Molecular dimensions for **II**

Bond lengths (Å)	
Mn–O(4)	2.129(15)
Mn–O(3b)	2.228(14)
Mn–O(5a)	2.193(8)
S–O(1)	1.427(15)
S–O(2)	1.429(12)
S–N(1)	1.629(11)
S–C(1)	1.780(17)
O(3)–C(10)	1.233(23)
O(4)–C(10)	1.242(23)
O(5)–C(12)	1.256(20)
N(1)–C(8)	1.443(22)
N(2)–C(12)	1.343(23)
C(8)–C(10)	1.534(22)
C(8)–C(9)	1.543(17)
C(9)–C(11)	1.499(29)
C(11)–C(12)	1.478(20)
Bond angles (°)	
O(4)–Mn–O(3d)	170.7(5)
O(4)–Mn–O(3b)	89.8(5)
O(4)–Mn–O(4e)	99.1(5)
O(3b)–Mn–O(3d)	81.4(5)
O(5c)–Mn–O(4)	88.2(5)
O(5a)–Mn–O(3d)	90.8(5)
O(5a)–Mn–O(3b)	88.9(4)
O(5a)–Mn–O(5c)	179.7(6)
O(5a)–Mn–O(4)	92.0(5)
N(1)–S–C(1)	108.2(8)
O(2)–S–C(1)	106.3(8)
O(2)–S–N(1)	106.1(7)
O(1)–S–C(1)	109.0(8)
O(1)–S–N(1)	107.8(7)
O(1)–S–O(2)	119.0(8)
S–N(1)–C(8)	117.9(9)
O(4)–C(10)–O(3)	125.2(15)
O(3)–C(10)–C(8)	117.4(16)
N(1)–C(8)–C(10)	111.0(14)
C(10)–C(8)–C(9)	110.0(10)
N(1)–C(8)–C(9)	111.4(13)
S–C(1)–C(6)	119.8(14)
C(8)–C(9)–C(11)	110.9(12)
O(5)–C(12)–N(2)	122.4(15)
N(2)–C(12)–C(11)	120.4(16)
O(5)–C(12)–C(11)	116.8(16)
C(9)–C(11)–C(12)	116.0(13)
Selected torsion angles (°)	
N(1)–S–C(1)–C(2)	69.3(1.5)
C(1)–S–N(1)–C(8)	66.3(1.3)
S–N(1)–C(8)–C(10)	−115.4(1.2)
N(1)–C(8)–C(10)–O(4)	168.6(1.4)
N(1)–C(8)–C(9)–C(11)	−69.7(1.6)
C(9)–C(8)–C(10)–O(4)	−67.5(1.8)
C(8)–C(9)–C(11)–C(12)	176.0(1.4)
C(9)–C(11)–C(12)–N(2)	93.1(1.9)

(a) $x+\frac{1}{2}, y-\frac{1}{2}, z$ (b) $x, y-1, z$. (c) $\bar{x}-\frac{1}{2}, y-\frac{1}{2}, \bar{z}$ (d) $\bar{x}, y-1, \bar{z}$. (e) $\bar{x}, y, \bar{z}$

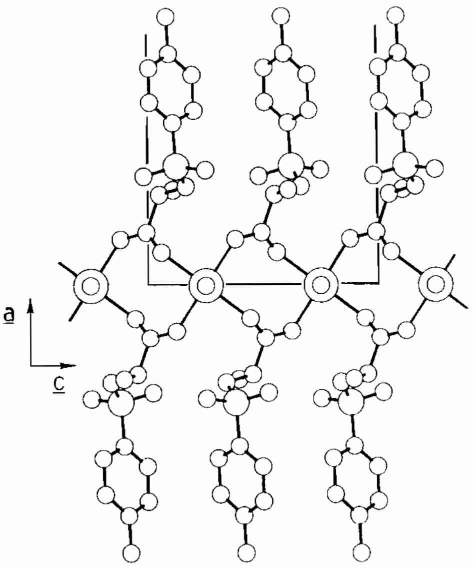
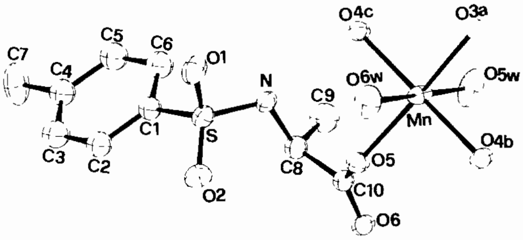


Fig. 1. *ac* projection of the crystal structure of compound **I** showing the polymeric propagation along *c*



(a) $\bar{x}, y, \frac{1}{2}-z$ (b) $\bar{x}, \bar{y}, 1-z$. (c) $x, \bar{y}, z-\frac{1}{2}$. (w) water

Fig 2. Arbitrary view of structure **I** with the numbering scheme.

layer structure where each Mn atom is surrounded by six different amino acid molecules each one being linked, in its turn, to three different Mn atoms through the carboxyl oxygens and the amide oxygen, the carboxyl group bridges two Mn atoms in a *syn–syn* type of configuration. The layers are oriented parallel to the *ab* plane. In Fig. 3 we show the *ac* section of the layer showing the connections between the Mn atoms and the organic molecules together with the numbering scheme. Figure 4 shows a different projection of the structure in order to illustrate the connections of the two carboxyl oxygens with two different Mn atoms.

In both compounds the octahedral coordination is significantly distorted as may also be inferred by an inspection of the bond angles on the Mn atom reported in Tables 4 and 5 for compounds **I** and **II**, respectively. As an example we may consider the angle of 173.3(3)° (O(3)–Mn–O(3a), compound **I**) which deviates of 6.7° from the ideal value of 180° and the angle of 170.7(5)° (O(4)–Mn–O(3d), compound **II**) where the deviation rises to 9.3°. The r.m.s. deviations of observed valence angles from the theoretical ones in octahedra are 3.6 and 5.8° for compounds **I** and **II**, respectively. Mn–O bond distances are sharply distributed in **I** with a mean value of 2.178 Å, while in **II** they are broadly distributed around an average value of 2.183 Å, but in both cases

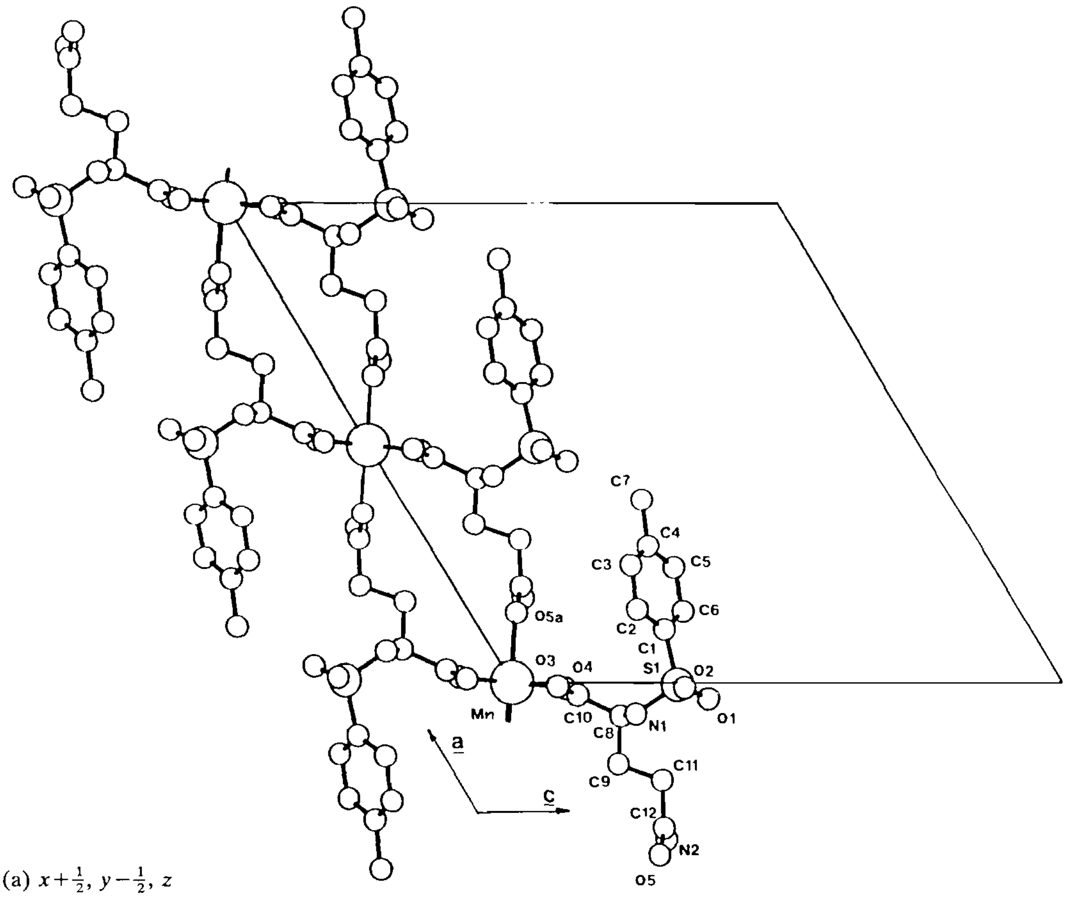


Fig. 3 *ac* projection of the crystal structure of compound **II** with the numbering scheme

the Mn–O distances fall in the range 2.091–2.287 Å, observed in other structurally known Mn(II) complexes with O-donor ligands [3, 4, 11–16]. We may conclude therefore that the octahedral coordination in **II** is less regular than in **I**, both of them showing however significant discrepancies from a regular octahedron. The shortest Mn...Mn distance is 4.525 Å in **I** (*c*/2) whereas in **II** it is 5.259 Å (*b*), consequently any direct magnetic interaction between metal ions can be ruled out; in addition in both cases, although this distance involves a double bridge (see Figs. 1 and 4), it is formed by the carboxyl oxygens and it is generally assumed [17] that the carboxylates are rather ineffective in transmitting the exchange interaction. The conformations of the molecules are summarized by the selected torsion angles reported in Tables 4 and 5. We point out the rather unusual torsion angle of 93.1° around the C(11)–C(12) bond observed in **II**, which may be interpreted with the need of bringing O(5) at the right coordination distance from the Mn atom.

Packing in **I** and **II** brings the aromatic rings in contact with each other. In compound **I** the interannular intra-chain distance is about 3.7 Å, and the chains are separated by the solvent molecules, while in the anhydrous compound **II** ring–ring intra- and inter-layer contacts of about 3.6 Å are present, which give rise to a much ordered structure.

Density data (see Table 1) indicate a much more effective space filling for **II** than for **I**. This is also confirmed by the tendency of **I** to include extraneous molecules within the crystal lattice.

The structure of the tsgln complex confirms the binding ability of amide oxygen, as observed in the [Cu(bipy)(tsasnN,O,O)]·H_2O (bipy = 2,2′-bipyridine, tsasnN,O,O = *N*-tosylasparaginate dianion) [18] and $[Cu(acvalO,O)_2]_n$ (acvalO,O = *N*-acetylvalinate monoanion) [19] complexes and indicates that its donor strength is comparable with that of carboxyl oxygens. The metal coordination of the amide oxygen enables the formation of a 2D polymeric arrangement whose layers are held together by short contacts between aromatic rings which are mainly responsible for the crystal stability so that the compound is stable up to 250 °C.

The ts-α-ala complex shows a different thermal behaviour and the loss of solvent molecules begins at ≅30 °C, with the maximum in the DTG curve centred at 110 °C; the complete dehydration is immediately

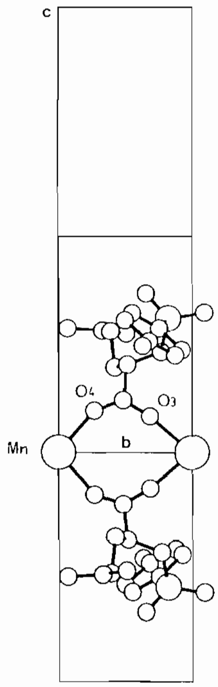


Fig. 4 *bc* projection of the crystal structure of compound **II** showing the complexation of one carboxyl group with two different metal ions.

followed by decomposition at 220 °C. In fact, in the temperature range 30–220 °C the weight loss is 14.55% with a calculated value of 15.77%. This behaviour can be justified by the presence of lattice solvent molecules which do not form strong bonding interactions. A strictly similar behaviour is displayed by the bs-β-ala complex. For $Mn(tsasn)_2 \cdot 3H_2O$ and $Mn(tsgly)_2 \cdot 4H_2O$ the weight loss takes place in the 130–210 °C temperature range and the experimental values of 7.77 and 12.57%, respectively, are in good agreement with the 8.17 and 12.35% calculated ones; the anhydrous tsgly complex is stable up to 240 °C, while the tsasn complex decomposes at 220 °C.

The IR spectra (Table 6) of the hydrate complexes show one or two broad bands in the region of ν(OH), and in all the spectra the stretching vibrations of the NH_2 and NH groups are almost unchanged with respect to the free ligands, excluding also for the tsgly, bs-β-ala and tsasn compounds any direct involvement of nitrogen atoms in metal coordination.

In the tsgln complex the two intense bands at 1632 and 1608 cm^{-1} are assigned to $\nu(COO)_{as}$ and $\nu(CO)_{amide}$, respectively, in the light of the *syn–syn* bridge of the carboxyl group which shifts the vibration to higher energy relative to the monodentate bonding mode and of the metal coordination of the amide oxygen which shifts the ν(CO) to lower energy relative to the uncoordinated amide group.

In the IR spectrum of the tsasn compound, the band at 1670 cm^{-1}, close to the position of $\nu(CO)_{amide}$ in the free ligand (1679 cm^{-1}), is similarly assigned. The possible assignment of this band to $\nu(COO)_{as}$ may be excluded because its value is too close to the absorption of a neutral COOH group.

For the remaining complexes the coordination of the amino acid through the carboxylate group seems reasonable as in the already structurally known ts-α-ala and tsgln species, but it is hazardous to infer their bonding mode on the basis of the IR data alone.

Supplementary material

List of observed and calculated structure factors, complete bond distances and angles, anisotropic thermal parameters for non-hydrogen atoms, and hydrogen atoms parameters (20 pages) are available from the authors on request.

TABLE 6. More relevant IR bands (cm^{-1})

	ν(OH)	ν(NH)	$\nu(COO)_{as}$	$\nu(COO)_s$	$\nu(SO_2)_{as}$	$\nu(SO_2)_s$	ν(SN)
$Mn(tsgly)_2 \cdot 4H_2O$	3571mb 3438mb	3282sh 3205s	1589vs	1403s	1319vs 1311vs	1160vs	869ms
$[Mn(ts\text{-}\alpha\text{-}ala)_2(H_2O)] \cdot 2.78H_2O \cdot 0.92CH_3OH$	3550mb 3495mb	3320sh	1641s	1368s	1312, 1256s 1285s	1155 1142s	980ms
$Mn(bs\text{-}\beta\text{-}ala\text{-})_2$ $4H_2O$	3534s	3306s	1566vs	1411s	1330s 1320s	1159vs	950s

	ν(OH)	$\nu(NH_2)$	ν(NH)	$\nu(CO)_{am}$	$\nu(COO)_{as}$	$\delta(NH_2)$	$\nu(COO)_s$	$\nu(SO_2)_{as}$	$\nu(SO_2)_s$	ν(SN)
$Mn(tsasn)_2 \cdot 3H_2O$	3538s	3384vs 3294s	3180vs	1670vs	1635vs 1619s		1382vs	1308s 1294s	1155vs	982 968ms
$[Mn(tsgln)_2]$		3497vs 3331s	3240vs	1608s	1632vs	1565s	1398s	1339s 1330s	1187s 1178vs	964ms

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