Synthesis and Crystal Structure of Tris(morpholinecarbodithioato-*S,S'*)manganese(IV) Pentaiodide–Dichloromethane (2/1)†

Paola Deplano and Emanuele F. Trogu*
Istituto di Chimica Generale, Inorganica ed Analitica dell'Università di Cagliari, Via Ospedale 72, 09124 Cagliari, Italy
Francesco Bigoli and Maria Angela Pellinghelli
Istituto di Chimica Generale dell'Università di Parma, Centro Studio per la Strutturistica Diffrattometrica del C.N.R., Viale delle Scienze, 43100 Parma, Italy

The compound $[Mn(S_2CNC_4H_8O)_3]I_5 \cdot 0.5CH_2Cl_2$ has been prepared by reaction of tris(morpholinecarbodithioato-*S,S'*)manganese(III), $[Mn(S_2CNC_4H_8O)_3]$, with iodine in CH_2Cl_2 solution. The crystal structure has been determined by *X*-ray diffraction at 295 K. Crystals are monoclinic, space group $P2_1/c$, a = 20.451(9), b = 18.910(5), c = 18.714(5) Å, β = 109.68(2)°, U = 6 814(4) Å^3, and Z = 8. The structure comprises anionic layers composed of chains of V-shaped I_5^- units interposed by differently inclined $[Mn(S_2CNC_4H_8O)_3]^+$ cations.

We have recently investigated the reaction between iodine (I_2) and tris-dithiocarbamates of some metals(III) of the first transition row, showing that formation of 1:1 molecular complexes of the charge-transfer (c.t.) type generally occurs.[1–3] Moreover, c.t. complexes between the reagents may be key intermediates in the mechanism of oxidation of dithiocarbamato derivatives by means of I_2.[3,4]

In the case of manganese(III) conventional u.v.–visible spectrophotometric measurements show immediate formation of an intermediate which rapidly evolves to give a manganese(IV) species. Since stopped-flow measurements, to give a better investigation of the reaction mechanism, are in progress, in this paper we only report the synthesis and *X*-ray crystal structure of $[Mn(S_2CNC_4H_8O)_3]I_5 \cdot 0.5CH_2Cl_2$, obtained as the final product of the reaction between $[Mn(S_2CNC_4H_8O)_3]$ and I_2 in CH_2Cl_2.

Experimental

Materials.—Twice sublimed iodine was purchased from Carlo Erba. Tris(morpholinecarbodithioato)manganese(III) was prepared according to the literature.[5] Dichloromethane was Merck Reagent Grade and dried over 4 Å molecular sieves before use.

Synthesis.—The compound $[Mn(S_2CNC_4H_8O)_3]I_5 \cdot 0.5CH_2Cl_2$ was obtained as shining dark brown crystals by slow evaporation of a CH_2Cl_2 solution (100 cm^3) containing $[Mn(S_2CNC_4H_8O)_3]$ (100 mg) and iodine (150 mg). The crystals gave analytical results in accord with the formulation $[Mn(S_2CNC_4H_8O)_3]I_5 \cdot 0.5CH_2Cl_2$ and were suitable for an *X*-ray structure determination.

Elemental analyses were performed at the Istituto di Farmacia dell'Università di Cagliari. Infrared spectra were recorded using a Perkin-Elmer model 983 spectrophotometer. I.r. (KBr pellets): 2 970m, 2 914m, 2 853m, 1 509vs, 1 431s, 1 383m, 1 353m, 1 299s, 1 265s, 1 238vs, 1 108vs, 1 059m, 1 022vs, 994ms, 879m, 827w, 733w, 648w, 544s, 401s, 369ms, and 286w.

X-Ray Crystal-structure Analysis.—*Crystal data.* $C_{15.5}H_{25}ClI_5MnN_3O_3S_6$, M = 1 218.66, monoclinic, a = 20.451(9), b = 18.910(5), c = 18.714(5) Å, β = 109.68(2)°, U = 6 814(4) Å^3, Z = 8, D_c = 2.376 g cm^{-3}, $F(000)$ = 4 528, Mo-K_α radiation (λ = 0.710 73 Å), μ(Mo-K_α) = 53.14 cm^{-1}, space group $P2_1/c$. The setting angles of 27 reflections in the range 11—17°, well centred on a Siemens AED single-crystal diffractometer, were used for the least-squares adjustment of the unit-cell parameters of a brownish prismatic crystal of dimensions 0.33 × 0.43 × 0.56 mm.

Intensity data. Diffraction measurements were made at 295 K on the same diffractometer, niobium-filtered Mo-K_α radiation and the θ—2θ scan mode being used. All the reflections were measured with θ in the range 3—23°. The crystal became damaged during intensity data collection, so corrections for decay were applied taking the intensity of one standard reflection checked every 50 reflections as the internal scaling reference.

Of a total of 9 731 measured reflections ($+h$, $+k$, $\pm l$), 3 110 having $I \geqslant 2\sigma(I)$ were considered observed and employed in the analysis. Data were converted to unscaled F_o values by application of the standard Lorentz and polarization factors. Corrections for absorption (maximum and minimum values 1.131 69, 0.856 59) and extinction (maximum and minimum values 1.070 23, 0.917 74) were applied using the method of Walker and Stuart.[6]

Structure determination and refinement. Initial co-ordinates of the iodine atoms were determined by a Patterson map. Repeated structure-factor calculations and difference-Fourier maps, phased on an increasing number of atoms, located the remaining non-hydrogen atoms, including those of the solvent molecule. The structure was refined first by full-matrix least squares on F using the SHELX 76 system of computer programs,[7] and then by anisotropic blocked full-matrix least squares. Only the iodine, manganese, and sulphur atoms were allowed to vibrate anisotropically. All the H atoms were placed in their geometrically calculated positions. The function minimized was $\Sigma w(F_o - F_c)^2$; unit weights were chosen in the first stages of the refinement and in the final cycles of the refinement a weight $w = k[\sigma^2(F_o) + gF_o^2]^{-1}$ was calculated, where k = 0.7689 and g = 0.001 616. Final convergence was reached at an R value of 0.0570 (R' = 0.0612), with a goodness-of-fit value of 0.7486. The final electron-density difference synthesis showed no peaks >0.96 and <−0.79 e Å^{-3}. Scattering factors and corrections for anomalous dispersion effects were taken from ref. 8.

The calculations were carried out on the CYBER 76 computer of Consorzio Interuniversitario Nord Est Calcolo

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx.

Table 1. Fractional atomic co-ordinates (× 10^4) with estimated standard deviations in parentheses for the non-hydrogen atoms

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
I(1)	−38(1)	2 547(1)	5 136(1)	I(6)	5 051(1)	2 647(1)	5 239(1)
I(2)	−33(1)	2 405(1)	3 643(1)	I(7)	5 006(1)	2 676(1)	3 713(1)
I(3)	45(1)	2 177(1)	2 024(1)	I(8)	4 909(1)	2 614(2)	2 062(1)
I(4)	1 644(1)	2 515(1)	2 340(1)	I(9)	6 569(1)	2 465(1)	2 559(1)
I(5)	3 028(1)	2 794(1)	2 618(1)	I(10)	7 998(1)	2 392(1)	3 008(1)
Mn(1)	1 667(2)	−22(2)	2 265(2)	Mn(2)	7 239(2)	−73(2)	4 187(2)
S(11)	845(4)	−758(3)	2 493(4)	S(12)	6 628(4)	869(4)	4 428(4)
S(21)	1 292(4)	592(3)	3 131(4)	S(22)	8 087(4)	640(4)	5 027(4)
S(31)	2 579(4)	−674(4)	3 083(4)	S(32)	6 923(4)	−852(4)	4 983(4)
S(41)	2 627(4)	700(4)	2 522(4)	S(42)	7 963(4)	−1 036(4)	4 310(4)
S(51)	1 678(4)	−664(4)	1 200(4)	S(52)	6 293(4)	−412(4)	3 154(4)
S(61)	1 015(4)	655(3)	1 213(4)	S(62)	7 462(4)	368(4)	3 142(4)
O(11)	−809(9)	−104(9)	4 031(9)	O(12)	7 618(11)	3 237(10)	5 521(10)
O(21)	5 187(9)	65(10)	4 132(10)	O(22)	7 364(10)	−3 560(10)	4 967(11)
O(31)	984(9)	206(9)	−1 572(9)	O(32)	6 005(12)	−43(11)	332(12)
N(11)	327(10)	−143(10)	3 485(10)	N(12)	7 491(12)	1 809(11)	5 336(11)
N(21)	3 745(11)	57(11)	3 495(11)	N(22)	7 556(10)	−2 058(11)	4 995(10)
N(31)	953(10)	12(10)	−102(11)	N(32)	6 360(16)	170(14)	1 904(17)
C(11)	753(12)	−110(11)	3 095(12)	C(12)	7 425(14)	1 203(13)	4 959(14)
C(21)	−68(13)	−789(13)	3 504(13)	C(22)	6 912(16)	2 256(16)	5 342(16)
C(31)	−796(14)	−594(14)	3 449(15)	C(32)	6 996(18)	2 933(18)	5 041(18)
C(41)	−479(14)	522(14)	3 939(14)	C(42)	8 194(17)	2 823(17)	5 472(17)
C(51)	305(12)	390(12)	4 030(12)	C(52)	8 160(15)	2 097(15)	5 821(15)
C(61)	3 077(13)	38(12)	3 103(13)	C(62)	7 463(13)	−1 396(13)	4 787(14)
C(71)	4 119(15)	−505(15)	4 002(15)	C(72)	7 176(15)	−2 431(15)	5 457(15)
C(81)	4 842(15)	−593(14)	3 977(15)	C(82)	6 843(16)	−3 105(16)	5 046(16)
C(91)	4 868(16)	554(16)	3 597(16)	C(92)	7 678(15)	−3 260(15)	4 504(16)
C(101)	4 146(15)	735(14)	3 606(14)	C(102)	8 040(14)	−2 589(15)	4 810(15)
C(111)	1 198(12)	9(11)	654(12)	C(112)	6 682(15)	33(14)	2 634(17)
C(121)	1 089(14)	−592(13)	−539(14)	C(122)	5 678(21)	−127(20)	1 409(22)
C(131)	1 402(13)	−313(13)	−1 090(14)	C(132)	5 727(17)	−483(17)	786(19)
C(141)	938(14)	804(13)	−1 115(14)	C(142)	6 678(20)	184(19)	797(21)
C(151)	626(13)	622(13)	−555(13)	C(152)	6 681(17)	597(18)	1 397(19)
C(16)	3 535(20)	148(20)	1 155(20)				
Cl(1)	4 098(5)	896(5)	1 588(5)				
Cl(2)	3 834(6)	−586(6)	1 572(6)				

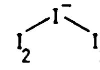
Automatico (Casalecchio, Bologna) with financial support from the University of Parma, and on the GOULD-SEL 32/77 computer of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R. (Parma). The programs ASSORB,[9] PARST,[10] PLUTO,[11] and ORTEP[12] were also used.

The final atomic fractional co-ordinates are given in Table 1; selected bond distances and angles are in Table 2.

Results and Discussion

Crystal and Molecular Structure.—The crystal-structure determination effectively confirms the stoicheiometry of the complex as being $[Mn(S_2CNC_4H_8O)_3]I_5{\cdot}0.5CH_2Cl_2$. The structure of this polyiodide salt is made up of anionic layers, lying approximately parallel to (010), interposed by tris(morpholinecarbodithioato-*S*,*S*′)manganese(IV) cations differently inclined. The anionic layer (Figure 1) is composed of chains of V-shaped I_5^- units, running parallel to [001] and with appreciable but not exceptional interactions between the units: I(1) ··· I(3′) 3.519(3) and I(6) ··· I(8′) 3.554(3) Å (prime indicates position: $x, \frac{1}{2} - y, \frac{1}{2} + z$). The roughly parallel chains are bonded by tertiary interactions [I(5) ··· I(7) 3.877(3) and I(10) ··· I(2″) 3.795(3) Å (double prime indicates position: $1 + x, y, z$)] approximately parallel to [100].

Both crystallographically independent pentaiodides are non-planar [maximum displacement 0.051(2) for I(2) and 0.062(2) Å for I(7)] and are of the 'interacting V-shaped ion' type, and can be approximately described as shown.



Excluding the corresponding distances I(4)–I(5) and I(9)–I(10) and the corresponding angles I(1)–I(2)–I(3) and I(6)–I(7)–I(8), all the other bond distances and angles in these I_5^- units show significant differences, the most considerable being observed for the value of the angle at the central atom [I(2)–I(3)–I(4) 100.2(1) and I(7)–I(8)–I(9) 90.5(1)°]. The distances to the terminal atoms, ranging from 2.751(3) to 2.827(3) Å, are significantly longer than in the crystalline I_2 [2.715(6) Å].[13] Each I–I distance is correlated with the adjacent distances: in fact the shorter the bond length, the longer the contacts involving the adjacent atoms. The I_5^- units have dimensions similar to those found in the discrete V-shaped pentaiodide ions,[14,15] in the interacting V-shaped pentaiodide ions,[16,17] and in the nearly linear units.[18–20]

The chains are connected in an arrangement to form slightly puckered layers containing a substructure based on 12-membered, square, and non-planar rings [maximum and minimum displacements 0.719(2), 0.022(2) Å], where each side includes four iodine atoms. A similar substructure was observed in 2,1,3-benzoselenadiazole–2,1,3-benzoselenadiazolium pentaiodide[21] and in diferrocenylselenium tri-iodide–iodine–dichloromethane (1/1/0.5);[22] in these compounds, however, no I_5^- units occur, and only I_3^- anions and I_2 molecules are present. One of the best measures of the degree of layer puckering is the value of the dihedral angle between the mean planes passing through the atoms of two adjacent square rings: 176.67(1)—

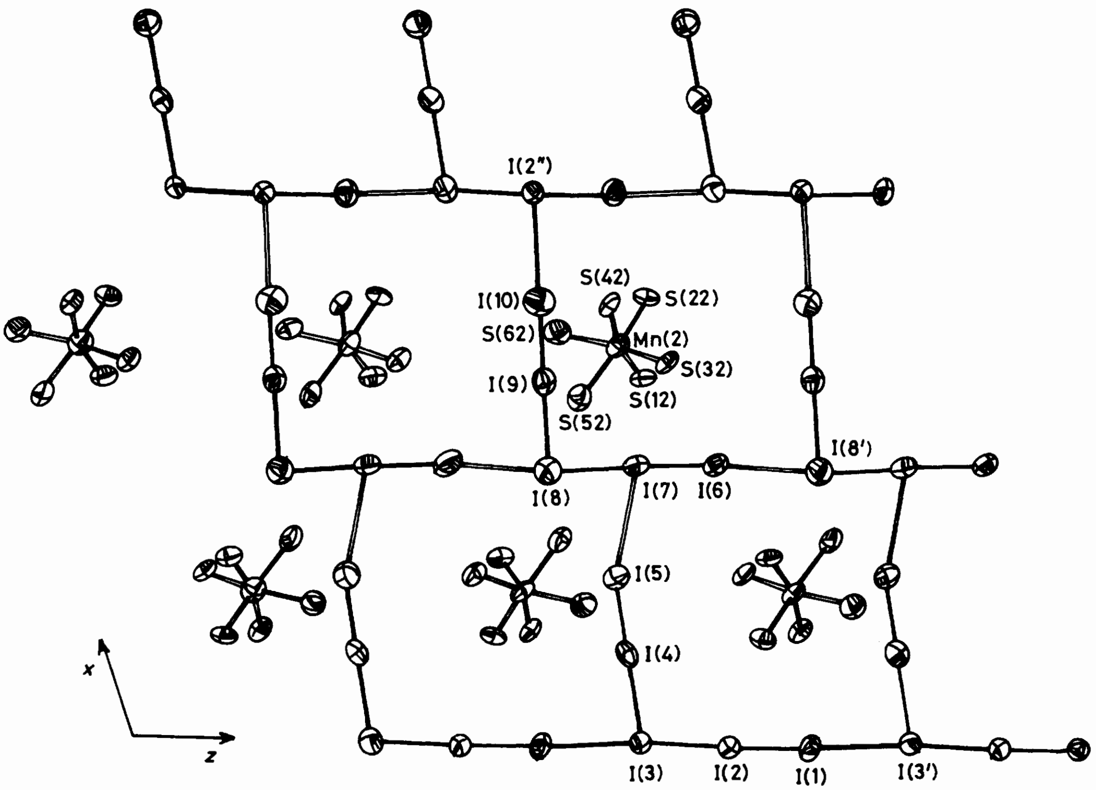


Figure 1. Projection of the anionic layer viewed along *b* showing the cation 2 in the channel

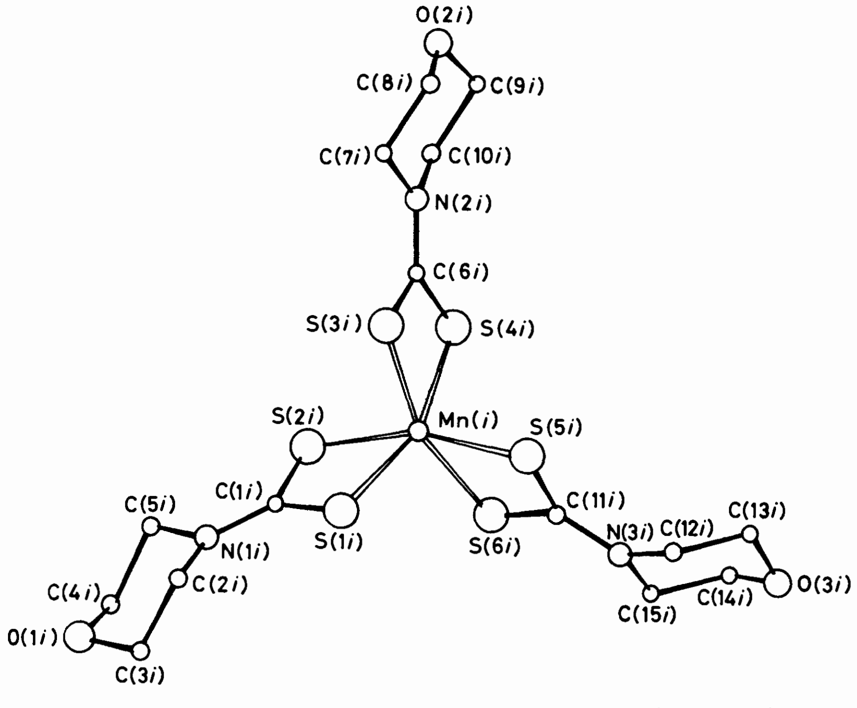


Figure 2. Perspective view of the cations (*i* = 1 or 2 for cation 1 and 2 respectively). Thermal ellipsoids are drawn at the 50% probability level

177.9(1)° in both [100] and [001] directions. In the two independent square rings, besides the above-mentioned angles at the central atom of the I_5^- units, the directions of the tertiary interactions between the chains are very different: I(4)–I(5)–I(7) 155.9(1) and I(9)–I(10)–I(2″) (1 + *x*, *y*, *z*) 176.7(1)°. This must be the result of steric interaction with cation 2, which does not lie parallel to anionic layers, as cation 1, but occupies the channels formed by anionic layers, as shown in Figure 1.

The two independent cations, which are depicted in Figure 2, are similar. In fact in both cations the manganese has a trigonally distorted octahedral environment, as indicated by the S–Mn–S angle values, the bond distances and angles are in good

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

(*a*) I_5^- anions

I(1)–I(2)	2.810(3)	I(6)–I(7)	2.827(3)
I(2)–I(3)	3.117(3)	I(7)–I(8)	3.031(3)
I(3)–I(4)	3.186(3)	I(8)–I(9)	3.216(3)
I(4)–I(5)	2.751(3)	I(9)–I(10)	2.759(3)
I(1)–I(2)–I(13)	176.4(1)	I(6)–I(7)–I(8)	176.2(1)
I(2)–I(3)–I(4)	100.2(1)	I(7)–I(8)–I(9)	90.5(1)
I(3)–I(4)–I(5)	179.5(1)	I(8)–I(9)–I(10)	177.7(1)

(*b*) Cations:

	cation 1 *i* = 1	cation 2 *i* = 2
Mn(*i*)–S(1*i*)	2.330(9)	2.306(9)
Mn(*i*)–S(2*i*)	2.324(9)	2.337(8)
Mn(*i*)–S(3*i*)	2.328(8)	2.336(9)
Mn(*i*)–S(4*i*)	2.305(9)	2.309(9)
Mn(*i*)–S(5*i*)	2.340(9)	2.318(7)
Mn(*i*)–S(6*i*)	2.351(7)	2.308(9)
S(1*i*)–C(1*i*)	1.72(2)	1.72(3)
S(2*i*)–C(1*i*)	1.71(2)	1.69(3)
S(3*i*)–C(6*i*)	1.68(3)	1.64(3)
S(4*i*)–C(6*i*)	1.71(2)	1.71(3)
S(5*i*)–C(11*i*)	1.72(2)	1.68(4)
S(6*i*)–C(11*i*)	1.73(2)	1.68(3)
C(1*i*)–N(1*i*)	1.31(4)	1.33(3)
C(6*i*)–N(2*i*)	1.32(3)	1.31(3)
C(11*i*)–N(3*i*)	1.33(3)	1.33(4)
S(1*i*)–Mn(*i*)–S(2*i*)	75.1(3)	75.6(3)
S(1*i*)–Mn(*i*)–S(3*i*)	91.8(3)	94.5(3)
S(1*i*)–Mn(*i*)–S(4*i*)	158.7(3)	164.0(3)
S(1*i*)–Mn(*i*)–S(5*i*)	93.5(3)	91.2(3)
S(1*i*)–Mn(*i*)–S(6*i*)	103.8(3)	99.3(3)
S(2*i*)–Mn(*i*)–S(3*i*)	100.7(3)	103.7(3)
S(2*i*)–Mn(*i*)–S(4*i*)	90.9(3)	94.7(3)
S(2*i*)–Mn(*i*)–S(5*i*)	162.4(4)	160.5(3)
S(2*i*)–Mn(*i*)–S(6*i*)	94.9(3)	92.7(3)
S(3*i*)–Mn(*i*)–S(4*i*)	74.9(3)	75.2(3)
S(3*i*)–Mn(*i*)–S(5*i*)	92.9(3)	91.4(3)
S(3*i*)–Mn(*i*)–S(6*i*)	160.4(4)	160.8(3)
S(4*i*)–Mn(*i*)–S(5*i*)	103.5(3)	101.1(3)
S(4*i*)–Mn(*i*)–S(6*i*)	93.2(3)	93.8(3)
S(5*i*)–Mn(*i*)–S(6*i*)	74.6(3)	75.0(3)
Mn(*i*)–S(1*i*)–C(1*i*)	86.5(8)	85.8(1.0)
Mn(*i*)–S(2*i*)–C(1*i*)	86.8(8)	85.3(1.0)
Mn(*i*)–S(3*i*)–C(6*i*)	86.3(9)	84.3(1.0)
Mn(*i*)–S(4*i*)–C(6*i*)	86.4(9)	83.7(1.0)
Mn(*i*)–S(5*i*)–C(11*i*)	87.4(8)	85.4(1.1)
Mn(*i*)–S(6*i*)–C(11*i*)	86.8(8)	85.6(1.1)
S(1*i*)–C(1*i*)–S(2*i*)	111.6(1.3)	113.0(1.5)
S(3*i*)–C(6*i*)–S(4*i*)	112.3(1.5)	115.7(1.5)
S(5*i*)–C(11*i*)–S(6*i*)	111.1(1.2)	114.0(1.7)
S(1*i*)–C(1*i*)–N(1*i*)	124.8(1.7)	122.1(2.2)
S(2*i*)–C(1*i*)–N(1*i*)	123.6(1.7)	124.5(2.2)
S(3*i*)–C(6*i*)–N(2*i*)	122.8(1.8)	125.2(2.1)
S(4*i*)–C(6*i*)–N(2*i*)	124.8(1.9)	119.0(2.1)
S(5*i*)–C(11*i*)–N(3*i*)	124.7(1.7)	121.9(2.5)
S(6*i*)–C(11*i*)–N(3*i*)	124.0(1.7)	123.8(2.4)

agreement and the usual distorted chair conformation adopted by the morpholinic rings[23] is observed.

There are significant differences in the value of the angle between the $\mathrm{Mn}\langle^{\mathrm{S}}_{\mathrm{S}}$ and $^{\mathrm{S}}_{\mathrm{S}}\rangle\mathrm{C{-}N}$ planes: 0.5(4), 1.8(4), and 0.2(6)° in cation 1 and 3.2(5), 10.6(5), and 7.2(7)° in cation 2 respectively. The co-ordination around the metals and the Mn–S bond lengths, ranging from 2.305(9) to 2.351(7) Å, agree with those found in tris(pentamethylenedithiocarbamato)manganese(IV) perchlorate.[24] On the contrary, in the analogous complexes of manganese(III), tris(4-morpholinedithiocarbamato)manganese(III)–trichloromethane[25] and tris(4-morpholinedithiocarbamato)manganese(III)–dichloromethane,[26] Jahn-Teller effects are responsible for the tetragonal distortion in the manganese environment and for a significant lengthening of the Mn–S bond distances, in the range 2.344(1)—2.584(1) and 2.385(3)—2.534(3) Å respectively. The absence of approximate D_3 symmetry in the cations can be seen clearly in Figure 2 and is due to intermolecular contacts involving the O atoms of the morpholinic rings, the adjacent cations, and solvent molecules: O(11) $\cdots$ C(51) $(-x, -y, 1-z)$ 3.46(3), O(21) $\cdots$ C(71) $(1-x, -y, 1-z)$ 3.40(3), O(31) $\cdots$ C(31) $(-x, -y, -z)$ 3.48(3), O(12) $\cdots$ C(131) $(1-x, \frac{1}{2}+y, \frac{1}{2}-z)$ 3.35(3), O(22) $\cdots$ C(16) $(1-x, y-\frac{1}{2}, \frac{1}{2}-z)$ 3.34(4), and O(32) $\cdots$ C(16) $(1-x, -y, -z)$ 3.23(5) Å.

The dichloromethane molecule shows only non-bonding contacts with the cations. The other shortest interactions which determine the packing are: C(22) $\cdots$ I(6) 3.82(3), C(72) $\cdots$ I(5) $(1-x, -y, 1-z)$ 3.83(3), C(82) $\cdots$ I(6) $(1-x, -y, 1-z)$ 3.83(3), C(141) $\cdots$ S(11) $(-x, -y, -z)$ 3.69(2), C(51) $\cdots$ S(22) $(1-x, -y, 1-z)$ 3.72(2), C(31) $\cdots$ S(42) $(x-1, y, z)$ 3.53(3), C(82) $\cdots$ Cl(1) $(1-x, y-\frac{1}{2}, \frac{1}{2}-z)$ 3.56(3), and C(91) $\cdots$ Cl(1) 3.61(3) Å.

Extensive use of the 'Cambridge Structural Database Files' was made for bibliography.

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