Structure and Magnetic Properties of Bis(diethyldithiocarbamato)-manganese(II)

By **Mario Ciampolini*** and **Carlo Mengozzi,** Istituto di Chimica Analitica dell'Università di Pisa, Laboratorio del C.N.R., 41 via Jacopo Nardi, Firenze
Pierluigi Orioli, Istituto di Chimica Generale dell'Università di Siena, Siena, Italy

A number of N-substituted bis(dithiocarbamato)manganese(II) complexes have been synthesized and their magnetic properties investigated. The X-ray crystal and molecular structure of bis(diethyldithiocarbamato)-manganese(II) has been determined by the heavy-atom method from diffractometer data. Crystals are triclinic, space group $P1$, with $a = 11.039(5)$, $b = 10.055(5)$, $c = 7.529(2)$ Å, $\alpha = 70.9(1)°$, $\beta = 83.7(1)°$, $\gamma = 82.2(1)°$, $Z = 2$. The structure was refined by least-squares techniques to R 0.062 for 1 023 observed reflections. The manganese is co-ordinated by six sulphur atoms in an elongated octahedral environment. Six-co-ordination is achieved through polymerization *via* sulphur atoms of adjacent planar molecules. The magnetic moment is temperature dependent which suggests a spin-sextet ground state with appreciable antiferromagnetic interactions. The other complexes exhibit similar magnetic properties, and a similar environment for manganese is also suggested for them.

IT has been recently reported that bis(diethyldithiocarbamato)manganese(II), [Mn(Et₂dtc)₂], has a square-planar structure and a spin-quartet ground state.[1] This is rather surprising since only one other example of a square-planar manganese(II) complex is known, this being phthalocyaninatomanganese(II),[2] whose stereochemistry is imposed by the steric requirements of the quadridentate macrocyclic ligand.

However, the square-planar structure for [Mn(Et₂dtc)₂] is only supported by its alleged isomorphism with the analogous nickel(II) complex,[1] [Ni(Et₂dtc)₂], whose square-planar stereochemistry (very common for this metal) has been demonstrated by a complete X-ray analysis.[3]

and to study thoroughly its magnetic properties, we have prepared a series of manganese(II) complexes with N-substituted dithiocarbamates of general formula R^1R^2-NCS_2^- ($R^1R^2dtc^-$), where R^1 and R^2 = H, Me, Et, Pr^i, Ph, or $R^1,R^2 = [CH_2]_4$. The chemical behaviour and magnetic properties of these compounds have been investigated. The crystal and molecular structure of the diethyl derivative has been determined by X-ray diffraction.

EXPERIMENTAL

Preparation of the Compounds.—All operations were performed under pure nitrogen with deoxygenated solvents.

The appropriate sodium dithiocarbamate (20 mmol) in

TABLE 1

Analytical data and magnetic moments for the compounds

Compound	Analyses (%)			$\mu_{eff}/$B.M.[a]
	C	H	N	
[Mn(H,Medtc)₂]	17.97 (17.1) [b]	3.01 (3.1) [b]	10.48 (9.1) [c]	5.70 (292)
[Mn(H,Etdtc)₂]	24.39 (24.4)	4.09 (4.0)	9.48 (9.3)	5.70 (292)
[Mn(H,Pr^{i}dtc)₂]	29.70 (29.7)	4.80 (5.0)	8.51 (8.7)	5.75 (293)
[Mn(H,Phdtc)₂]	42.95 (42.5)	3.09 (3.1)	7.15 (6.9)	5.65 (292)
[Mn(Me₂dtc)₂]	24.39 (25.2)	4.09 (4.3)	9.48 (8.8)	
[Mn(Me,Phdtc)₂]	45.80 (44.2)	3.84 (3.7)	6.67 (6.4)	
[Mn(Et₂dtc)₂] [c]	34.17 (34.2)	5.73 (5.6)	7.97 (7.9)	5.65 (293), 5.15 (84)
[Mn(Pr^{i}₂dtc)₂]	41.20 (41.3)	6.92 (7.0)	6.87 (6.4)	5.30 (294)
[Mn{(CH₂)₄dtc)₂}]	34.56 (34.3)	4.64 (4.6)	8.06 (8.2)	5.60 (292)
[Mn(Et₂dtc)₂],2py	47.13 (47.0)	5.93 (6.1)	10.99 (10.6)	5.95 (294)
[Mn(H,Phdtc)₂],py	48.50 (48.9)	3.64 (3.9)	8.93 (9.3)	6.15 (293)

[a] Temperature (K) in parentheses. [b] Found values in parentheses. [c] Mn content: Calc., 15.63; Found, 15.8.

In contrast with these results, Fackler and Holah[4] had previously reported that [Mn(Et₂dtc)₂] is isomorphous with the analogous copper(II) and zinc(II) complexes, whose dimeric five-co-ordinated structure has been ascertained by X-ray investigations.[5]

Studies on toluene solutions of [Mn(Et₂dtc)₂] showed no e.s.r. signal.[6] This was taken to imply a spin-doublet ground state.[6]

In order to elucidate the structure of [Mn(Et₂dtc)₂]

water (*ca.* 100 ml) was added to MnCl₂,4H₂O (10 mmol) in water (20 ml). The yellow solid which immediately separated was washed first with water and then with ethanol–diethyl ether (2 : 1), and allowed to dry *in vacuo*. These compounds soluble in hot ethanol were recrystallized from it.

All the compounds are yellow crystalline solids. Analytical data are reported in Table 1. Compounds with $R^1 = R^2 = $ Et; $R^1 = $ H, $R^2 = $ Et, Pr^i, or Ph; $R^1 = $ Me, $R^2 = $ Ph, are slightly soluble in methanol, ethanol, acetone,

[1] S. Lahiry and V. K. Anand, *Chem. Comm.*, 1971, 1111.
[2] J. M. Robertson, *J. Chem. Soc.*, 1935, 615; 1937, 219.
[3] M. Bonamico, G. Dessy, C. Mariani, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, 1965, **19**, 619.
[4] J. P. Fackler and D. G. Holah, *Inorg. Nuclear Chem. Letters*, 1966, **2**, 251.

[5] M. Bonamico, G. Dessy, A. Mugnoli, A. Vaciago, and L. Zambonelli, *Acta Cryst.*, 1965, **19**, 886; M. Bonamico, G. Massone, A. Vaciago, and L. Zambonelli, *ibid.*, p. 898.
[6] N. S. Garifianov, S. E. Kamenev, B. M. Kazirev, and I. V. Ovcinnikov, *Doklady Akad. Nauk. U.S.S.R.*, 1967, **177**, 880.

dichloromethane. Those with $R^1 = H$, $R^2 = Me$; $R^1 = R^2 = Me$; $R^1 = R^2 = Pr^i$; $R^1,R^2 = [CH_2]_4$, are insoluble in those solvents. All the compounds are very soluble in pyridine from which they are precipitated by addition of n-hexane as mono- or bi-adducts.

All the compounds are immediately oxidized by oxygen when moist or in solution. When dry they are stable in air from some hours to some weeks. The most readily oxidizable compound is bis(diethyldithiocarbamato)manganese(II), which darkens instantaneously in the presence of traces of oxygen. With the dry material, oxidation takes place in a few minutes on the surface of the crystals, but, in the bulk, crystals are not oxidized for a few days.

Magnetic Measurements.—Magnetic susceptibility measurements in the temperature range 84—298 K were carried out with a Gouy balance as previously described.[7] All operations were performed under pure nitrogen.

Crystal Data.—[Mn(Et$_2$dtc)$_2$], $C_{10}H_{20}MnN_2S_2$, $M = 287.40$, Triclinic, $a = 11.039(5)$, $b = 10.055(5)$, $c = 7.529(2)$ Å, $\alpha = 70.9(1)°$, $\beta = 83.7(1)°$, $\gamma = 82.2(1)°$, $U = 780.76$ Å^3, $D_c = 1.23$, $Z = 2$. $\lambda(Mo-K_\alpha) = 0.7107$ Å, $\mu(Mo-K_\alpha) = 10.9$ cm^{-1}. Space group $P\bar{1}$.

Data Collection.—A thin yellow needle, 0.3 mm long, was mounted on an automatic Philips diffractometer, the elongation axis c being approximately coincident with the diffractometer axis. Philips automatic routines [8] readily gave the Dirichlet reduced cell which was refined together with the orientation matrix by the use of 19 accurately centred reflections. With a ω—2θ scan technique, the intensities of 1 438 reflections were measured within $2\theta = 40°$ and 1 023 of these, having $I > 2\sigma(I)$, were used for the structure determination and refinement. The standard deviation $\sigma(I)$ of the corrected intensity I was estimated according to the following expression: $\sigma(I) = [P + 0.25(B_1 + B_2)(T_p/T_b)^2 + (kI)^2]^{\frac{1}{2}}$ where P is the peak count, B_1 and B_2 are the background counts and T_p and T_b are the count times on the peak and background respectively. The factor k was determined by a least-squares fit of three standard reflections monitored regularly. The intensities of these reflections did not show any systematic drift during the experiment, although the crystal had turned brown at the end of data collection. This meant that the oxidation process involved only a thin layer at the surface of the crystal.

Intensities were corrected for Lorentz-polarization effects. Absorption effects were neglected.

Structure Determination and Refinement.—The structure was solved by heavy-atom methods with the use of Patterson and Fourier syntheses. Refinement was performed by least squares with anisotropic temperature factors for Mn and S atoms and isotropic ones for the other atoms. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$ with weights according to Hughes' scheme: ($F_o \leqslant 32$, $\sqrt{w} = 1$; $F_o > 32$, $\sqrt{w} = 32/F_o$). Final R and R' factors were 0.062 and 0.078 {R' is defined as $(\Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2)^{\frac{1}{2}}$. Atomic scattering factors were taken from ref. 9, those for manganese and sulphur being corrected for the real and imaginary part of anomalous dispersion effects.[10] Final atomic parameters with their estimated standard deviations are listed in Tables 2 and 3. Observed and calculated structure

* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1974, Index issue (items less than 10 pp. are supplied as full-size copies).

[7] L. Sacconi, R. Cini, M. Ciampolini, and F. Maggio, *J. Amer. Chem. Soc.*, 1960, **82**, 3487.

[8] Philips, 'Serving Science and Industry,' 1972, **18**, No. 2, 22.

Positional parameters and isotropic thermal parameters ($\times 10^4$), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	$U/Å^2$
Mn(1)	0	0	0	*
Mn(2)	0	0	5 000	*
S(1)	−320(3)	1 939(3)	1 573(5)	*
S(2)	1 829(3)	1 412(4)	−929(5)	*
S(3)	2 290(3)	−28(4)	4 727(5)	*
S(4)	971(3)	−1 805(3)	3 297(5)	*
N(1)	1 614(8)	3 427(10)	707(14)	327(26)
N(2)	3 388(9)	−1 755(11)	2 888(15)	397(28)
C(1)	1 111(10)	2 361(12)	467(17)	318(31)
C(2)	984(12)	4 331(14)	1 852(19)	420(34)
C(3)	1 503(13)	3 916(16)	3 764(22)	550(42)
C(4)	2 849(12)	3 763(15)	−205(21)	498(39)
C(5)	2 770(13)	4 845(16)	−2 188(22)	570(42)
C(6)	2 329(11)	−1 220(14)	3 550(19)	365(35)
C(7)	3 500(13)	−2 884(16)	1 988(22)	557(43)
C(8)	3 639(15)	−2 272(18)	−143(25)	712(51)
C(9)	4 587(13)	−1 275(15)	3 045(21)	510(39)
C(10)	5 171(16)	−2 174(19)	4 825(26)	789(54)

* Anisotropic parameters, see Table 3.

Anisotropic thermal parameters * (Å^2 $\times 10^3$), with estimated standard deviations in parentheses

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Mn(1)	39(2)	36(2)	42(2)	−10(1)	0(1)	−17(2)
Mn(2)	25(2)	41(2)	37(2)	−2(1)	−2(1)	−13(1)
S(1)	28(2)	31(2)	35(2)	−4(1)	−1(1)	−9(2)
S(2)	37(2)	39(2)	39(2)	−8(2)	6(2)	−16(2)
S(3)	31(2)	41(2)	50(2)	−5(2)	−1(2)	−23(2)
S(4)	31(2)	30(2)	36(2)	−7(1)	−2(1)	−12(2)

* Anisotropic thermal factors are of the form: $\exp(-2\pi^2 \sum_{i=1}^{3} \sum_{j=1}^{3} h_i h_j a_i^* a_j^* U_{ij})$.

factors are listed in Supplementary Publication No. SUP 21404 (3 pp., 1 microfiche).*
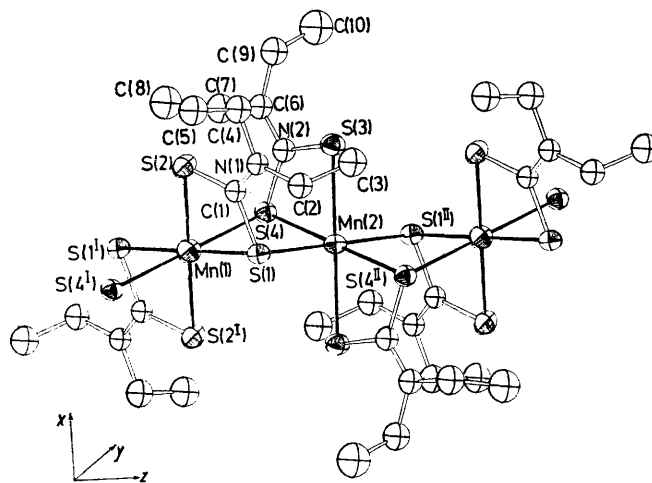

FIGURE 1 The packing of the molecules of [Mn(Et$_2$dtc)$_2$] and the labelling of the atoms

RESULTS AND DISCUSSION

Description of the Structure.—The structure of [Mn(Et$_2$dtc)$_2$] (Figure 1) consists of two independent centrosymmetric molecules, linked into infinite chains by the

[9] D. T. Cromer and J. T. Waber, *Acta Cryst.*, 1965, **18**, 104.

[10] 'International Tables for X-Ray Crystallography,' vol. III, 1962, Kynoch Press, Birmingham.

sharing of some of the S atoms between the two Mn atoms. The manganese atom is co-ordinated by four sulphur atoms of the chelate rings coplanar, mean Mn–S 2.55 ± 0.05 Å, and two further sulphur atoms from neighbouring molecules at a mean distance of 2.74 ± 0.04 Å completing a distorted octahedron. Octahedral chains are shown schematically in Figure 2. The man-
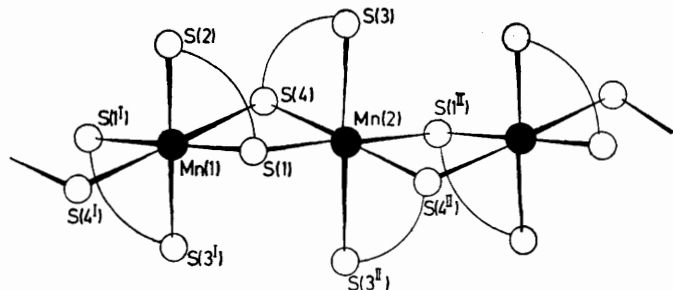

FIGURE 2   Schematic drawing showing the octahedral chain linkage in $[\mathrm{Mn(Et_2dtc)_2}]$

ganese atoms lie in centres of symmetry at 0,0,0 and 0,0,1/2 so that the $[\mathrm{Mn(Et_2dtc)_2}]$ moieties possess C_i crystallographic symmetry. There are two crystallographically non-equivalent molecules in the triclinic cell. The two independent co-ordination polyhedra around the manganese atoms show some significant differences in bond lengths and angles very likely attributable to packing forces (Table 4).

There are no $\mathrm{Mn^{II}}$–S distances available from the literature for comparison. However, if from the Mn–Cl distance (2.51 Å) in the $[\mathrm{MnCl_6}]^{4-}$ ion [11] we subtract the covalent radius of chlorine (0.99 Å) [12] and add that of sulphur (1.04 Å) [12] we obtain 2.56 Å, which is very close to the mean of our chelate Mn–S distances.

All atoms of both independent molecules, apart from the terminal methyl groups, lie approximately in a plane, the maximum and mean deviations from which are 0.085 and 0.029 Å. Planarity and bond length values in the ligand molecule (Table 4) indicate conjugation with sp^2 hybridization of the valence orbitals of C(1), N(1), C(6), and N(2). All the bond lengths and angles in the ligand are in agreement with analogous values from X-ray investigations on other metal dithiocarbamates.[3,5] There are no unusual intermolecular distances.

The structure of $[\mathrm{Mn(Et_2dtc)_2}]$ is different from those of the analogous nickel(II), copper(II), and zinc(II) complexes. In fact, the structure of the nickel(II) complex consists of discrete molecules in which the nickel shows square-planar co-ordination.[3] Both the copper(II) and zinc(II) analogues are dimers in which the copper and zinc atoms show distorted five-co-ordinate stereochemistry.[5]

Magnetic Properties.—Lahiry and Anand report 3.8 and 4.1 B.M. at 98 and 298 K, respectively, for the magnetic moment of $[\mathrm{Mn(Et_2dtc)_2}]$.[1] They consider these values to be consistent with a pure spin-quartet ground state ($S\ 3/2$).[1]

On the present compound magnetic susceptibility measurements give a different result (Table 2, Figure

TABLE 4

Bond lengths (Å) and angles (°), with estimated standard deviations in parentheses

(a) Distances

Mn(1)–S(1)	2.562(4)	Mn(2)–S(4)	2.605(4)
Mn(1)–S(2)	2.530(3)	Mn(2)–S(3)	2.511(3)
Mn(1)–S(4)	2.778(3)	Mn(2)–S(1)	2.704(3)
S(1)–C(1)	1.74(1)	S(3)–C(6)	1.70(2)
S(2)–C(1)	1.71(1)	S(4)–C(6)	1.73(1)
C(1)–N(1)	1.34(2)	C(6)–N(2)	1.34(2)
N(1)–C(2)	1.50(2)	N(2)–C(7)	1.49(2)
N(1)–C(4)	1.49(2)	N(2)–C(9)	1.50(2)
C(2)–C(3)	1.52(2)	C(7)–C(8)	1.52(2)
C(4)–C(5)	1.54(2)	C(9)–C(10)	1.51(2)

(b) Angles

S(1)–Mn(1)–S(2)	71.2(1)	S(3)–Mn(2)–S(4)	70.7(1)
S(4$^\mathrm{I}$)–Mn(1)–S(2)	93.3(1)	S(1)–Mn(2)–S(3$^\mathrm{II}$)	94.7(1)
S(4$^\mathrm{I}$)–Mn(1)–S(1)	87.5(1)	S(1)–Mn(2)–S(4$^\mathrm{II}$)	88.2(1)
S(1)–Mn(1)–S(2$^\mathrm{I}$)	108.7(1)	S(4$^\mathrm{II}$)–Mn(2)–S(3)	109.3(1)
S(4)–Mn(1)–S(1)	92.5(1)	S(1)–Mn(2)–S(4)	91.8(1)
S(4)–Mn(1)–S(2)	86.7(1)	S(1)–Mn(2)–S(3)	85.3(1)
Mn(1)–S(4)–Mn(2)	88.7(1)	Mn(1)–S(1)–Mn(2)	91.2(1)
Mn(1)–S(1)–C(1)	84.2(5)	Mn(2)–S(3)–C(6)	86.8(4)
Mn(1)–S(2)–C(1)	85.9(4)	Mn(2)–S(4)–C(6)	83.2(5)
S(1)–C(1)–S(2)	118.6(8)	S(3)–C(6)–S(4)	119.2(7)
S(1)–C(1)–N(1)	119.7(9)	S(3)–C(6)–N(2)	121.3(1.1)
S(2)–C(1)–N(1)	121.7(8)	S(4)–C(6)–N(2)	119.5(1.2)
C(1)–N(1)–C(2)	123.2(9)	C(6)–N(2)–C(7)	124.2(1.2)
C(1)–N(1)–C(4)	119.5(1.1)	C(6)–N(2)–C(9)	121.8(1.3)
C(2)–N(1)–C(4)	117.2(1.1)	C(7)–N(2)–C(9)	114.0(1.1)
N(1)–C(2)–C(3)	111.3(1.0)	N(2)–C(7)–C(8)	111.3(1.3)
N(1)–C(4)–C(5)	111.7(1.1)	N(2)–C(9)–C(10)	111.7(1.2)

Roman numeral superscripts denote the following equivalent positions relative to the reference molecule at x, y, z:

$\quad$ I $\ \bar{x}, \bar{y}, \bar{z}$ $\qquad$ II $\ \bar{x}, \bar{y}, 1 - z$

3). The value of μ_{eff} increases with the temperature from 5.15 B.M. at 84 K to 5.65 B.M. at 293 K. These values approach the spin-only value for five unpaired electrons ($S\ 5/2$), *i.e.* 5.92 B.M., and are much higher than those expected for $S\ 3/2$. Considering also the
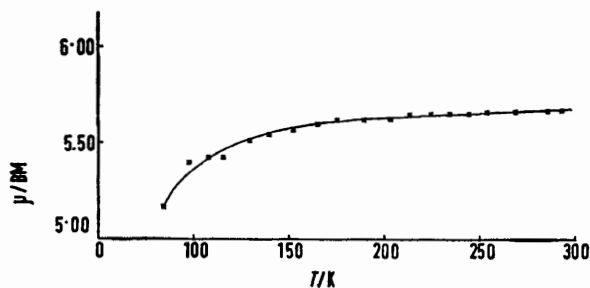

FIGURE 3   Magnetic moment for $[\mathrm{Mn(Et_2dtc)_2}]$ *vs.* temperature

polymeric octahedral structure of the $\mathrm{MnS_6}$ chromophore of the present compound, the magnetic values appear to be typical of a spin-sextet ground state with appreciable antiferromagnetic interactions. The distance between the manganese atoms (3.76 Å) is too large to allow a direct metal–metal exchange. It is suggested that superexchange interactions occur *via*

[11] *Chem. Soc. Special Publ.* No. 11, 1958.
[12] L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, New York, 1960.

bridging sulphur atoms. With bis(diethyldithiocarbamato)copper(II), which has a binuclear five-co-ordinated structure, magnetic coupling between the two copper atoms leads to ferromagnetic interactions.[13] By contrast, bis(diethyldithiocarbamato)chromium(II), which is reported to be isomorphous with the copper analogue, shows antiferromagnetic interactions.[14]

The other compounds of the series all show analogous magnetic behaviour at room temperature, the μ_{eff} value ranging from 5.30 to 5.75 B.M. This suggests aground state with S 5/2 for these compounds also, and the occurrence of superexchange interactions. It is thus likely that the structures of the other compounds also show some degree of polymerization. For the compounds less soluble in ethanol it is likely that a different kind of polymerization may occur, such as the formation of a three-dimensional polymeric network. The two pyridine adducts exhibit magnetic moments close to the spin-only value of S 5/2. This suggests that the pyridine molecules are co-ordinated to the manganese atoms, thus preventing polymerization.

Previous literature reports have not been confirmed by the present investigation. Although the occurrence of several isomeric forms of bis(diethyldithiocarbamato)-manganese(II) cannot be excluded, we found no evidence of this during our numerous preparations. It must be stressed that the extreme sensitivity of this compound towards oxidation in solution or in the powdered state makes its handling difficult.

[13] J. F. Villa and W. E. Hatfield, *Chem. Comm.*, 1971, 101.
[14] L. F. Larkworthy and R. R. Patel, *Inorg. Nuclear Chem. Letters*, 1972, **8**, 139.