

catena- μ -(3,5-Diamino-1,2,4-triazole- N_2, N_4)-bis(thiocyanato-N)-manganese(II). Synthesis, crystal structure, infrared and magnetic characterization

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Abstract

The title compound $((C_6H_{10}MnN_{12}S_2)_n = [Mn(dat)_2(SCN)_2]_n)$ was prepared and characterized by means of X-ray and IR spectroscopy. The crystals are orthorhombic, space group *Pbcn* (D_{2h}^{14} No. 60) with $a = 9.386(2)$, $b = 9.329(2)$, $c = 15.940(2)$ Å and $Z = 4$. The compound exhibits a two-dimensional Mn(II) network with the 1,2,4-triazole molecule acting as a bidentate bridging ligand. The structure consists of centrosymmetric units in which the manganese atoms are coordinated in distorted octahedral geometries by six nitrogen atoms. Each manganese atom is linked by four 1,2,4-triazole molecules, and two molecules of thiocyanate complete the octahedral coordination around the metal ion. Each 1,2,4-triazole molecule bridges between two manganese atoms. The NH and NH_2 group of the guanazole unit are involved in intermolecular hydrogen bonds. IR bands are diagnostic of the coordination environments around the metal atoms. Antiferromagnetic couplings, $J = -0.21(1)$ cm $^{-1}$, among manganese ions in the same layer occurs.

Introduction

Although 1,2,4-triazole and its 4- or 3,5- derivatives have been largely investigated as ligand in coordination complexes, 3,5-diamino-1,2,4-triazole (guanazole = dat) suggests not only 1,2- or 1,4-bidentate coordination behaviour due to the existence of the triazole in two tautomeric forms, but also the possibility of amino group coordination; even if the NH_2 group always has less basicity than the cyclic nitrogen atoms. Up to now 1,2,4-triazole and its 4- or 3,5-derivatives seem to form complexes with 1,2-N coordinated units [1–5], 2,4-bridging triazole units [6, 7], and bridging and monodentate units in the same complex [8, 9].

When the triazole units bridge paramagnetic metal ions they constitute an efficient pathway for the exchange interaction leading to interesting magnetic behaviours [10–12]. We have used the 3,5-diamino substituted 1,2,4-triazole as a ligand either to increase the efficiency in transmitting the magnetic interaction between metal ions or to increase the possibility of additional connections among the paramagnetic centres through the NH_2 groups.

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Experimental

Complex preparation

All chemicals were of reagent grade and used as received.

The manganese(II) derivative $[Mn(dat)_2(SCN)_2]_n$ was prepared by adding dropwise an aqueous solution of $Mn(SCN)_2 \cdot 5H_2O$ to an aqueous solution of guanazole in a 1:2 molar ratio with continued stirring. The resulting solution was allowed to stand for several weeks at room temperature; white crystals were formed. *Anal.* Calc. for $C_6H_{10}MnN_{12}S_2$: N, 45.5; C, 19.5; H, 2.7; S, 17.4. Found: N, 45.7; C, 19.3; H, 2.8; S, 17.5%. Carbon, hydrogen, nitrogen, and sulphur were determined with a Carlo Erba 1106 elemental analyzer.

Spectral measurements

The IR spectra were recorded in the solid state with a Bruker IFS 113v Fourier transform spectrophotometer using KBr pellets in the 4000–400 cm $^{-1}$ region and polyethylene pellets in the 400–40 cm $^{-1}$ region.

Magnetic measurements and EPR spectra

The magnetic susceptibility in the temperature range 2–30 K was measured by using a SQUID magnetometer

Metronique Ing. MS02 operating at 20 mT, while the high temperature data (12–300 K) were obtained operating at 0.5 T.

Polycrystalline EPR spectra were recorded on a Varian E-9 spectrometer at X-band frequency using a liquid helium continuous flow cryostat Oxford Instruments ESR9 to cool the sample down to 4.2 K.

X-ray structure determination

The crystals were shaped as regular prisms. X-ray data were collected at room temperature on Enraf-Nonius CAD 4 diffractometers with Mo K α radiation. During the measurements the crystal decay was tested by detecting the intensity of standard reference reflections at intervals. MnC₆H₁₀N₁₂S₂, $M = 369.30$, orthorhombic, space group *Pbcn* (No. 60), $a = 9.386(2)$, $b = 9.329(2)$, $c = 15.940(3)$ Å, $U = 1395.7(8)$ Å³, $Z = 4$, $D_c = 1.76(1)$ ($D_m = 1.75(1)$ by flotation) g cm⁻³, $F(000) = 748$, graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å), $\mu(\text{Mo K}\alpha) = 11.8$ cm⁻¹, crystal dimensions $c. 0.10 \times 0.10 \times 0.07$ mm. Unit cell parameters were derived from a least-squares fit to the setting angles of 25 intense reflections in the 8–16° θ range. The intensity data were collected at room temperature on a CAD 4 Enraf-Nonius automatic diffractometer with the ($\omega - 2\theta$) scan technique in the range 2–26°, at a scan speed range of 1.0–4.1° min⁻¹, with a scan width of 0.7° + 0.35 tg θ . Two standard reflections were measured every 4 h, and the intensities showed no significant changes. No. of collected reflections: 3053, no. of observed reflections: 854 with $I > 3.0 \sigma(I)$ (after merge $R = 0.032$), no. of parameters: 111; $\Delta\rho = 0.4$ to -0.5 (max. to min.) e Å⁻³ near the heavy atoms. All data were recorded for Lorentz and polarization effects, and an empirical absorption correction, based on the ψ scan, was applied [13] (max., min. transmission factor = 0.99, 0.92).

The structure was solved by Patterson and Fourier methods, and refined by full-matrix least-squares calculations, with $\sum w(|F_o - F_c|)^2$ being minimized. Non-hydrogen atoms were treated anisotropically, whereas the hydrogen atoms were treated as fixed contributors at found positions assuming a temperature factor 1 Å² greater than that of the attached nitrogen atom.

This model converged at $R = 0.029$ and $R_w = 0.030$, $w = 1.2/[\sigma^2(F) + 0.0001F_o^2]$. Complex neutral-atom scattering factors [14] were employed throughout; major calculations were carried out on a Vax 6210 computer, using the SHELX 76 program package [15] and the ORTEP plotting program [16].

Final fractional coordinates for the non-hydrogen atoms are given in Table 1, bond distances and bond angles are given in Table 2. See also 'Supplementary material'.

TABLE 1. Final positional parameters of [Mn(dat)₂(SCN)₂]_n

Atom	<i>x/a</i>	<i>y/b</i>	<i>z/c</i>
Mn	0	0.22877(6)	1/4
S(1)	0.1829(2)	0.4014(1)	-0.01613(7)
N(1)	0.1656(3)	0.3910(3)	0.2840(2)
N(2)	0.2695(3)	0.3500(3)	0.3415(2)
N(3)	0.3487(3)	0.5484(3)	0.2854(2)
C(1)	0.2194(3)	0.5103(3)	0.2527(2)
C(2)	0.3754(3)	0.4420(3)	0.3408(2)
N(4)	0.4941(4)	0.4284(3)	0.3872(2)
N(5)	0.1522(3)	0.5908(3)	0.1947(2)
N(6)	0.0781(3)	0.2435(3)	0.1180(2)
C(3)	0.1202(4)	0.3078(4)	0.0613(2)

Results and discussion

The molecular structure of [Mn(dat)₂(SCN)₂]_n, Fig. 1, consists of four guanazole molecules and two thiocyanate groups linked to the metal ion. The manganese is surrounded by six nitrogen atoms in a distorted octahedral coordination. The guanazole molecules act as a bidentate ligand, with a N(2),N(4) coordination mode, giving a two-dimensional layer structure. The manganese atom is in a special dimensional position on a binary axis bisecting the N(1)–Mn–N(1)" angle. The two unique Mn–N (guanazole) bond distances 2.237(2) and 2.273(2) Å, respectively, are significantly different from each other; the bond difference may be influenced to some extent by the crystal packing. The terminal SCN groups are N bonded and the Mn–N–C angle is 151.9(2)°. The Mn–N distance is close to those already found: 2.233(3) Å.

The nearest-neighbour Mn–Mn distance within the polymeric molecule is 6.617(3) Å. The triazole rings are found to be planar within experimental error. Bond distances and angles of the ring compare well with those found by other authors [2, 17]. The dihedral angles between ring planes are 91.2, 116.1 and 125.5°. The vectors MnN(6) and MnN(6)' form with the coordination plane N(1)N(3)"N(3)'N(1)" an angle of 86.3(4). The atoms with apexes forming the plane and the vector have been submitted to the symmetry operations: ' = $x - 0.5, y - 0.5, 0.5 - z$; " = $0.5 - x, y - 0.5, z$; "' = $-x, y, 0.5 - z$.

Intermolecular hydrogen-bond contacts, on which the crystal packing mainly depends, occur between the NH₂ and NH of a 3,5-diamino-triazole molecule and the S and N atoms of the NCS group.

A drawing of the unit cell packing diagram of [Mn(dat)₂(SCN)₂]_n complex is given in Fig. 2.

Vibration spectra

The position of the NH₂ bands indicate that there is no strong hydrogen bonding in these NH₂ groups

TABLE 2. Bond distance (Å) and bond angles (°) with e.s.d.s in parentheses

Mn–N(1)	2.237(2)	Mn–N(3)′	2.273(2)	Mn–N(6)	2.233(3)
C(3)–S(1)	1.622(4)	N(2)–N(1)	1.391(3)	C(1)–N(1)	1.320(3)
C(2)–N(2)	1.313(4)	C(1)–N(3)	1.369(3)	C(2)–N(3)	1.352(4)
C(2)–N(4)	1.344(4)	C(1)–N(5)	1.347(4)	C(3)–N(6)	1.154(4)
Mn–N(1)–N(2)	117.4(2)	Mn–N(1)–C(1)	138.1(2)		
Mn–N(6)–C(3)	151.9(2)	N(1)–Mn–N(1)	94.8(1)		
N(1)–Mn–N(6)	87.6(1)				
C(1)–N(1)–N(2)	102.3(2)	C(2)–N(2)–N(1)	110.2(2)		
C(2)–N(3)–C(1)	102.8(2)	N(3)–C(1)–N(1)	114.4(3)		
N(5)–C(1)–N(1)	123.4(3)	N(5)–C(1)–N(3)	122.2(3)		
N(3)–C(2)–N(2)	110.2(3)	N(4)–C(2)–N(2)	124.2(3)		
N(4)–C(2)–N(3)	125.6(3)	N(6)–C(3)–S(1)	178.0(3)		

Primed atoms (′) are related to unprimed by symmetry transformation $1.5+x, 1.5+y, 1.5-z$ of reference coordinates.

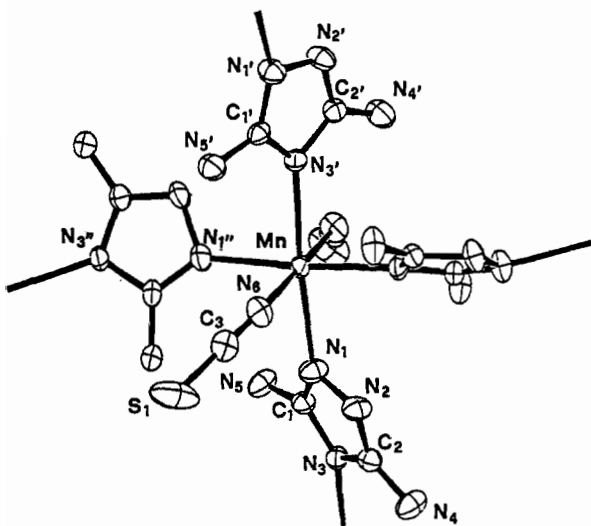


Fig. 1. ORTEP view of $[\text{Mn}(\text{dat})_2(\text{SCN})_2]_n$ showing the atom numbering and thermal motion ellipsoids (50%) for the atoms. The hydrogen atoms are not labelled for clarity.

(3463, 3453 asym, 3372 sym). The positions of the very strong νCN (2056 cm^{-1}), of the weak νCS (810 cm^{-1}), and of the $\delta(\text{NCS})$ bands of the thiocyanate group indicate either coordination through the nitrogen atoms, or the *trans* position of the NCS groups [18].

The metal–nitrogen stretching modes are clearly situated in the 262 and 214 cm^{-1} regions for the short (M–N) and longer (M–N) stretching modes, respectively. The deformation modes involving the thiocyanate group must be situated in the 200 cm^{-1} region.

Magnetic properties

The room temperature value of the product of the susceptibility with temperature is $4.12\text{ emu mol}^{-1}\text{ K}$ ($\mu_{\text{eff}} = 5.74$) a little lower than the value expected for an isolated $S = 5/2$ spin with $g = 2(4.375\text{ emu mol}^{-1}\text{ K})$. The χT product decreases smoothly on lowering the temperature but below 30 K the decrease becomes

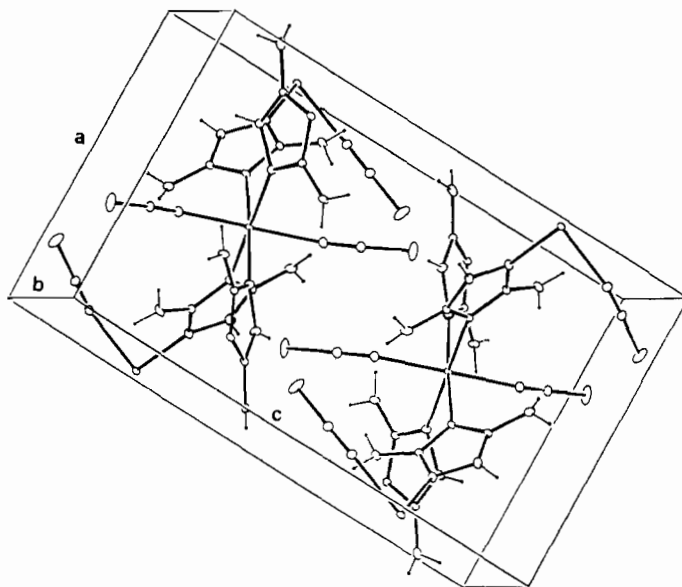


Fig. 2. Drawing of the unit cell packing diagram of the $[\text{Mn}(\text{dat})_2(\text{SCN})_2]_n$ complex.

faster and faster tending to zero at 0 K , as can be seen in Fig. 3. More information can be obtained by the behaviour of the magnetic susceptibility in low field and at low temperature shown in the inset of Fig. 3. The susceptibility in fact goes through a round maximum at *c.* 5.7 K but apparently does not tend to zero as the temperature goes to zero.

In the polycrystalline EPR spectra at room temperature a line centred at $g = 2$ with linewidth $\Delta H_{\text{pp}} = 140\text{ Gauss}$ is observed as well as a much weaker absorption at $g = 4$. On lowering the temperature the linewidth increases reaching $\Delta H_{\text{pp}} = 340\text{ Gauss}$ at 4.2 K . At this temperature the line is slightly asymmetric and the weak transition at $g = 4$ has completely disappeared.

The triazole ligands are known to be able to transmit magnetic interaction when bridging paramagnetic metal ions. In the present case the extended structure generated by the symmetry of the crystal lattice suggests

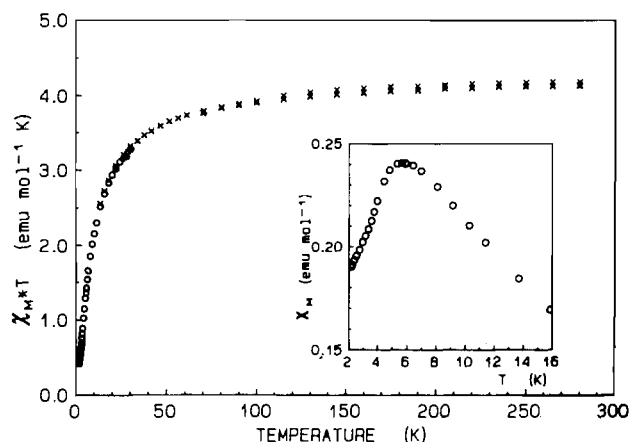


Fig. 3. Temperature dependence of magnetic susceptibility measured with a field of 0.5 T (x) and 20 mT (o) reported in the χT form. The low field susceptibility is shown in the inset.

that magnetic interaction between the spin $S=5/2$ of the manganese(II) ions is not restricted to a finite number of spins. The magnetic data above 30 K follow the Curie–Weiss law rather well and can be satisfactorily reproduced by using $\Theta = -9.1$ K and $g_{Mn} = 1.98$. The mean field model of antiferromagnetism is however inadequate to reproduce the behaviour at lower temperatures.

The main pathway for the exchange interaction is in fact supposed to be through the bridging guanazole molecules, which connect each metal ion to four nearest neighbours, thus forming a quadratic bidimensional magnetic lattice. The manganese atoms belonging to different layers are farther from each other than those within a layer, as shown by the shortest Mn–Mn contact (9.041 versus 6.617 Å). The planes are connected through hydrogen bonds between the terminal sulfur atom of a thiocyanate and a hydrogen of a guanazole molecule of the adjacent plane, but the inter-layer interaction through this exchange pathway is expected to be negligible compared to the intra-layer one.

Bidimensional magnetic behaviour is also observed in the EPR spectra where a half-field line, corresponding to the forbidden $\Delta m = 2$ transition, can be observed, because the exchange narrowing regime is not fully attained when the exchange interaction is active only in one or two dimensions. More information could be obtained by single crystal EPR spectra, however they are not available due to the small size of the crystals.

If we neglect the inter-layer interactions the value of the antiferromagnetic coupling constant within the plane can be estimated from the temperature at which the maximum in magnetic susceptibility occurs and from the value of χ at the maximum using the relations established by de Jongh and Miedema [19]:

$$T(\chi_{\max})/|J|(S(S+177)) = 2.05(1)$$

$$\chi_{\max}|J|/Ng^2\mu_B^2 = 0.0551(1)$$

For the present compound we observe $T_{\max} = 5.7$ K, which corresponds to $J = -0.22$ cm $^{-1}$, while from $\chi_{\max} = 0.241$ emu/mol we can estimate $J = -0.21$ cm $^{-1}$. These values are lower than those observed when triazole molecules bridge in a μ -1,2 fashion [10, 12] due to the less efficiency of the super-exchange mechanism that involves three rather than two atoms. This value is however a little higher than that observed in another manganese(II) compound containing a μ -2,4 bridging triazole, $J = -0.17$ cm $^{-1}$ [7], and whose structure is not too dissimilar from the present one.

From the present results we can conclude that the introduction of two NH $_2$ groups, which add electron density on the triazole molecule, has induced a sensible increase in the intra-layer exchange interaction but has not provided additional connections between the planes that could lead to magnetic ordering.

Supplementary material

Table 1S listing thermal parameters; Table 2S and 3S containing positional and thermal parameters, and bond distances, angles, and bonding interactions for hydrogen atoms; and Table 4S of some selected least-square planes and atomic deviations therefrom, are available from the authors on request.

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References

- 1 L. Antolini, A. Benedetti, A. C. Fabretti, A. Giusti and M. C. Menziani, *J. Chem. Soc., Dalton Trans.*, (1988) 1075.
- 2 C. W. Reinmann and M. Zocchi, *Acta Crystallogr., Sect. B*, 27 (1971) 682.
- 3 W. L. Groeneveld, G. Vos, G. C. Verschoor and J. Reedijk, *J. Chem. Soc. Chem. Commun.*, (1982) 620.
- 4 L. Antolini, A. C. Fabretti, D. Gatteschi, A. Giusti and R. Sessoli, *Inorg. Chem.*, 29 (1990) 143.
- 5 L. Antolini, A. C. Fabretti, D. Gatteschi, A. Giusti and R. Sessoli, *Inorg. Chem.*, 30 (1991) 4858.
- 6 D. W. Engelfriet, J. G. Haasnoot and W. L. Groeneveld, *Z. Naturforsch., Teil A*, 32 (1977) 783.
- 7 D. W. Engelfriet and W. L. Groeneveld, *Z. Naturforsch., Teil A*, 33 (1978) 848.

- 8 D. W. Engelfriet, W. Den Brinker, G. C. Verschoor and S. Gorter, *Acta Crystallogr., Sect. B*, 35 (1979) 2922.
- 9 G. A. van Albada, R. A. G. de Graaff, J. G. Haasnoot and J. Reedijk, *Inorg. Chem.*, 23 (1984) 1404.
- 10 G. Vos, J. G. Haasnoot, G. C. Verschoor, J. Reedijk and P. E. L. Schaminee, *Inorg. Chim. Acta*, 105 (1985) 31.
- 11 L. R. Groeneveld, R. A. le Febre, R. A. G. de Graaff, J. G. Haasnoot, G. Vos and J. Reedijk, *Inorg. Chim. Acta*, 102 (1985) 69.
- 12 W. Vreugdenhil, J. G. Haasnoot, M. F. J. Schoondergang and J. Reedijk, *Inorg. Chim. Acta*, 130 (1987) 235.
- 13 A. C. T. North, D. C. Phillips and F. S. Mathews, *Acta Crystallogr., Sect. A*, 24 (1968) 351.
- 14 *International Tables for X-Ray Crystallography*, Vol. 4, Kynoch, Birmingham, UK, 1974, p. 174.
- 15 G. M. Sheldrick, *SHELX 76*, Program for crystal structure determination, University Chemical Laboratory, Cambridge, UK, 1976.
- 16 C. K. Johnson, *ORTEP, Rep. ORNL-3794*, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.
- 17 R. Prins, R. A. G. de Graaff, J. G. Haasnoot, C. Vader and J. Reedijk, *J. Chem. Soc., Chem. Commun.*, (1986) 1430.
- 18 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compound*, Wiley, New York, 4th edn., 1986.
- 19 L. J. de Jongh and A. R. Miedema, *Adv. Phys. C*, 5 (1972) 1675.