

Linear Trinuclear Coordination Compounds with 4-Ethyl-1,2,4-triazole. Structure and Magnetic Properties

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Abstract

The synthesis and characterisation of a series of linear trinuclear coordination compounds containing 4-ethyl-1,2,4-triazole (Etrtz) are presented. The crystal structure of the first linear trinuclear Mn(II) compound $[\text{Mn}_3(\text{Etrtz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$ was determined at room temperature. The compound crystallizes in the space group $P31c$, with lattice constants $a = b = 14.545(2)$ Å and $c = 20.072(3)$ Å. In the linear trimer the metal ions are linked by three 1,2-bidentate coordinating triazole ligands. The manganese ions are coordinated octahedrally. For the terminal metal ions the octahedral coordination is completed by H_2O molecules. The coordination distances are: Mn–N 2.24 Å and Mn–O 2.19 Å. The Co(II), Ni(II) and Zn(II) compounds are X-ray isomorphous with the Mn(II) compound.

The magnetic exchange in the Mn, Co and Ni compounds is antiferromagnetic with J values of -0.6 cm^{-1} , -14.7 cm^{-1} (Ising approximation) and -9.4 cm^{-1} , respectively. An expression for the magnetisation and magnetic susceptibility of a linear Mn(II) trimer is presented.

The Cu(II) and Cd(II) compounds, with composition $[\text{M}_3(\text{Etrtz})_9(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_6(\text{H}_2\text{O})_x$, are also likely to be trinuclear. The terminal coordination sites in these compounds appear to be occupied by three monodentate coordinating triazole ligands and three water molecules. Surprisingly, the magnetic exchange in the Cu compound appears to be ferromagnetic.

Introduction

Several papers on the coordination chemistry of both substituted and unsubstituted 1,2,4-triazoles

have been reported [1–15]. The main interest in this field was focused on the interesting magnetic properties of these compounds.

Recently we reported a series of transition metal(II) thiocyanate coordination compounds with 4-substituted 1,2,4-triazoles [9–15]. Besides a number of unusual chain compounds [13, 14], mainly dinuclear compounds were obtained, showing an antiferromagnetic exchange between the metal centers.

In order to investigate the possible formation of linear chain compounds containing bridging triazole ligands, coordination compounds were synthesized, applying the non-coordinating anion trifluoromethanesulfonate. Trifluoromethanesulfonate was chosen because of its favourable properties [16], *i.e.*, the ion is inert to substitution, it forms non-explosive compounds and it is a poor oxidizing agent. Trifluoromethanesulfonates also have a disadvantage, *i.e.* their impact on the infrared spectrum. A number of intense anion absorptions dominate the infrared spectrum. A strong absorption at about 650 cm^{-1} makes it rather complicated and ambiguous to draw conclusions concerning the coordination modes of the triazole ligand, based on the out-of-plane ring vibrations. Nevertheless, based on an X-ray structure ligand field spectra and magnetic susceptibility data, the geometries of the synthesized coordination compounds could be determined.

The present paper shows that linear trinuclear coordination compounds are easily obtained from aqueous solutions with 4-ethyl-1,2,4-triazole.

Experimental

Synthesis

Commercially available chemicals were used without further purification. 4-Ethyl-1,2,4-triazole (Etrtz) was prepared according to the literature [9, 17]. The transition-metal(II) trifluoromethanesul-

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fonates were prepared by adding trifluoromethanesulfonic acid to a suspension of an equimolar amount of metal carbonate in acetonitrile [16].

The trifluoromethanesulfonate coordination compounds were all prepared by the same method, *i.e.* 1.25 mmol of hydrated metal(II) trifluoromethanesulfonate was dissolved in about 20 ml of hot water; 2.5 mmol Etrtz, dissolved in 10 ml of water was added slowly to the hot metal salt solution with continuous stirring. The compounds crystallized upon standing at ambient temperature. For the manganese compound the volume of the solution had to be reduced by evaporation to *ca.* 15 ml. Microcrystalline precipitates were filtered off, washed with water and ethanol, and dried under reduced pressure at room temperature. Crystals were carefully removed from the solution, washed with water, and dried on filter paper.

Analyses and Physical Measurements

Metal analyses were carried out by complexometric titrations [18], after prior decomposition of the compounds in boiling nitric acid. C, H and N analyses were carried out at Eindhoven University of Technology, The Netherlands.

The ligand-field spectra were recorded on a Beckman DK-2A UV-Vis spectrophotometer (350–2000 nm), using the diffuse reflectance method with MgO as a reference.

Infrared spectra were recorded on a Perkin-Elmer 580 B spectrophotometer (4000–180 cm^{-1}) both as KBr discs and Nujol mulls.

The EPR spectra of powdered samples were recorded at room temperature on a Varian E 3 at X-band frequencies, employing 100 kHz field modulation.

Magnetic susceptibility measurements between 80 K and 2 K were carried out using a PAR vibrating sample magnetometer model 150 A with a Janis cryostat described by Engelfriet [8]. Magnetic Saturation studies were performed at 1.13 K using equipment with magnetic fields up to 25 Tesla, as described elsewhere [19].

All calculations for the X-ray determination were carried out on a Leiden Amdahl V7B computer, using a local set of programs written.

X-ray Data Collection $[\text{Mn}_3(\text{Etrtz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$

A single crystal was selected and mounted on an Enraf-Nonius CAD-4 diffractometer. Mo-K α radiation monochromatised by graphite was used to determine the unit cell parameters, as well as the reflection intensities at room temperature, using the θ - 2θ scan method for all reflections with $2^\circ < \theta < 28^\circ$. The data were corrected for Lorentz and polarisation effects and for extinction. After reduction of the intensities to structure factors a Wilson plot was

calculated to obtain starting values for the scaling factor and the initial thermal parameter B . Only the 2280 reflections which had $I > 2\sigma(I)$ were used in the subsequent structure determination and refinement. The experimental density was determined in a mixture of 1,2-dibromoethane and cyclohexane.

The relevant diffraction data are listed in Table I.

TABLE I. Diffraction Data of $[\text{Mn}_3(\text{Etrtz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$.

Space group	$P\bar{3}1c$
Lattice constants	
<i>a</i> (Å)	14.545(2)
<i>b</i> (Å)	14.545(2)
<i>c</i> (Å)	20.072(3)
<i>V</i> (Å ³)	3678
Crystal dimensions (mm)	0.3 × 0.55 × 0.55
θ (°)	2–28
Measured reflections	9570
Independent reflections	3170
Significant reflections	2280
Experimental density (Mg m^{-3})	1.58
Calculated density (Mg m^{-3})	1.58
Final R (R_w)	0.085(0.095)
Z ($M = 1750$)	2

Solution and Refinement of the Structure of $[\text{Mn}_3(\text{Etrtz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$

A three dimensional Patterson synthesis revealed the positions of the Mn ions. The non-hydrogen atoms were located using the program DIRDIF [20]. Seven cycles of least-squares refinement with isotropic temperature factors resulted in $R = \Sigma|\Delta F|/\Sigma|F_o| = 0.162$. The scattering factors including the anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography [2]. The F atoms of the trifluoromethanesulfonate anion were in disorder. Alternative positions were introduced for these atoms, which refined with an occupation ratio of 52.5(5): 47.5(5). The bond distances and angles of the disordered CF_3SO_3^- group were treated with constraints [22]. The hydrogen atoms of the triazole ligand were placed at calculated positions, 0.95 Å from the corresponding carbon atom. The hydrogens of the water molecules could not be located. Twelve additional cycles of least-squares refinement with anisotropic temperature factors, except for the CF_3 atoms, resulted in $R = 0.085$ and $R_w = [\Sigma w(\Delta F)^2/\Sigma w F_o^2]^{1/2} = 0.095$ for 2280 significant reflections; $w = (\sigma_F)^{-2}$.

The positional parameters of the refined atoms are listed in Table II. Tables with observed and calculated structure factors are available from the authors.

TABLE II. Fractional Coordinates ($\times 10^4$) and Isotropic Thermal Parameters (\AA^2) of $[\text{Mn}_3(\text{Etrrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$ (Standard deviations are given in parentheses).

Atom	x/a	y/b	z/c	B_{iso}
Mn(1)	3333	6667	7500	1.93(4)
Mn(2)	3333	6667	5532(1)	1.44(4)
N(1)	4550(5)	7976(5)	6171(2)	2.2(2)
N(2)	4580(5)	7943(4)	6858(2)	2.1(1)
C(1)	5411(5)	8821(6)	7053(3)	2.8(2)
N(3)	5917(5)	9430(5)	6524(3)	2.9(2)
C(2)	5361(6)	8874(6)	5984(3)	2.8(2)
C(3)	6884(8)	10506(8)	6537(5)	5.2(3)
C(4)	6686(12)	11278(9)	6891(6)	9.9(6)
O(4)	4630(4)	6881(5)	4878(2)	3.3(2)
S(1)	9817(2)	13363(2)	5922(1)	3.9(7)
O(1)	10293(9)	14004(8)	6500(3)	8.8(5)
O(2)	8680(5)	12817(7)	5882(4)	7.0(3)
O(3)	10312(6)	13863(7)	5295(3)	6.9(3)
C(20)	10103(8)	12286(5)	6033(6)	10.9(5)
F(1)	11132(8)	12634(14)	5931(12)	13.4(2)
F(2)	9627(14)	11665(14)	6548(11)	13.4(2)
F(3)	9740(14)	11729(13)	5455(10)	13.4(2)
F(11) ^a	11132(8)	12665(14)	6134(13)	13.4(2)
F(22) ^a	9745(16)	11972(15)	6673(9)	13.4(2)
F(33) ^a	9555(14)	11426(11)	5673(14)	13.4(2)
H(1)	5626	9002	7503	5
H(2)	5539	9103	5536	5
H(3)	7460	10482	6753	5
H(4)	7109	10753	6089	5
H(5)	6666	11756	6577	5
H(6)	7230	11664	7208	5
H(7)	6021	10904	7112	5

^aThe disordered atoms with an occupation of 47.5%.

Results and Discussion

General

The obtained coordination compounds, together with their melting points, analyses and other relevant properties are listed in Table III. Mn(II), Fe(II), Co(II), Ni(II) and Zn(II) form an isostructural series of coordination compounds. Due to the special features of the Fe(II) compound (HS–LS transition) the detailed data have been discussed in previous papers [12, 23].

The structures of the Cu(II) and Cd(II) compounds differ from the other compounds and are therefore discussed separately in this paper.

$[\text{M}_3(\text{Etrrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$ ($M = \text{Mn(II)}, \text{Co(II)}, \text{Ni(II)}, \text{Zn(II)}$)

$[\text{M}_3(\text{Etrrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$ represents a series of isomorphous linear trinuclear compounds. The crystal structures of $[\text{Mn}_3(\text{Etrrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$ and its Zn(II) analogue were determined by X-ray diffraction techniques. The structural data of the Mn compound are presented in this paper, while those for the Zn compound have been published previously [24].

The compounds consist of linear trinuclear units in which the metal ions are linked by three 1,2-N donating Etrrz groups. The central metal ion is surrounded by six triazole ligands. The octahedral coordination around the terminal metal ions is completed by H_2O molecules.

A complete trinuclear unit is depicted in Fig. 1, with the atomic numbers used in the several tables. Relevant bond distances and angles are given in Table

TABLE III. Colours, Structure Types, Analyses and Melting Points of Transition Metal(II) Trifluoromethanesulfonate Coordination Compounds Containing Etrrz.

Compound	Structure type	Colour	Elemental analyses ^a				M.p. (°C)
			%M	%C	%N	%H	
$[\text{Mn}_3(\text{Etrrz})_6(\text{H}_2\text{O})_2](\text{CF}_3\text{SO}_3)_6$	A	colourless	9.4 (9.4)	20.6 (20.6)	14.4 (14.4)	3.1 (3.1)	>250
$[\text{Fe}_3(\text{Etrrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$	A	white	9.4 (9.6)	20.2 (20.6)	14.4 (14.4)	3.1 (3.1)	>250
$[\text{Co}_3(\text{Etrrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$	A	light-orange	9.9 (10.0)	20.7 (20.5)	14.3 (14.3)	3.2 (3.1)	>250
$[\text{Ni}_3(\text{Etrrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$	A	purple-blue	10.1 (10.0)	20.7 (20.5)	14.1 (14.3)	3.1 (3.1)	>250
$[\text{Cu}_3(\text{Etrrz})_9(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_6$	B	light-blue	9.6 (9.5)	24.9 (25.1)	18.9 (18.8)	3.4 (3.5)	216–219
$[\text{Zn}_3(\text{Etrrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$	A	white	10.9 (11.0)				>250
$[\text{Cd}_3(\text{Etrrz})_9(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_6(\text{H}_2\text{O})_3$	C	white	15.6 (15.2)	22.8 (22.8)	17.2 (17.1)	3.3 (3.4)	>250

^aCalculated values in parentheses.

TABLE IV. Bond Distances (Å) and Angles (Degrees) in $[\text{Mn}_3(\text{Ettrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$.^a

Mn(1)–Mn(2)	3.950(2)	N(3)–C(3)	1.492(9)
Mn(1)–N(2)	2.241(5)	C(3)–C(4)	1.47(2)
Mn(2)–N(1)	2.244(5)	S(1)–O(1)	1.432(8)
Mn(2)–O(4)	2.194(5)	S(1)–O(2)	1.436(7)
N(1)–N(2)	1.381(6)	S(1)–O(3)	1.452(7)
N(2)–C(1)	1.303(8)	S(1)–C(20)	1.824(9)
C(1)–N(3)	1.343(9)	F(1)–C(20)	1.33(1)
N(3)–C(2)	1.351(9)	F(2)–C(20)	1.314(9)
C(2)–N(1)	1.303(9)	F(3)–C(20)	1.364(9)
N(2)–Mn(1)–N(2A)	90.4(2)	C(1)–N(3)–C(3)	127.7(7)
N(2)–Mn(1)–N(2C)	90.3(2)	C(2)–N(3)–C(3)	127.7(7)
N(2)–Mn(1)–N(2E)	178.4(3)	N(3)–C(3)–C(4)	111.6(9)
N(1)–Mn(2)–O(4)	175.2(2)	F(1)–C(20)–F(2)	119(1)
N(1)–Mn(2)–O(4A)	94.0(2)	F(1)–C(20)–F(3)	98(1)
O(4)–Mn(2)–O(4A)	87.7(2)	F(2)–C(20)–F(3)	110.9(9)
Mn(1)–N(2)–N(1)	125.1(4)	F(1)–C(20)–S(1)	110.3(9)
Mn(1)–N(2)–C(1)	127.5(4)	F(2)–C(20)–S(1)	114(1)
Mn(2)–N(1)–N(2)	124.6(4)	F(3)–C(20)–S(1)	103(1)
Mn(2)–N(1)–C(2)	128.3(4)	C(20)–S(1)–O(1)	103.0(6)
N(1)–N(2)–C(1)	107.1(5)	C(20)–S(1)–O(2)	103.0(5)
N(2)–C(1)–N(3)	110.1(6)	C(20)–S(1)–O(3)	105.2(6)
C(1)–N(3)–C(2)	105.7(6)	O(1)–S(1)–O(2)	117.0(6)
N(3)–C(2)–N(1)	109.9(6)	O(1)–S(1)–O(3)	114.8(5)
C(2)–N(1)–N(2)	107.1(5)	O(2)–S(1)–O(3)	111.9(5)

^aA indicates symmetry operation $1 - y, 1 + x - y, z$; E indicates symmetry operation $1 - y, 1 - x, \frac{1}{2} - z$; C indicates symmetry operation $y - x, y, \frac{1}{2} - z$.

TABLE V. Relevant Infrared Absorptions and Tentative Assignments.

Compound	Absorptions (cm^{-1})		
	$\gamma\text{C-H}$	τ	FIR
$[\text{Mn}_3(\text{Ettrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$	916(m) 870(w)	635(vs)	230(s) 205(m)
$[\text{Fe}_3(\text{Ettrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$	910(m)	685(vw) 638(vs)	260(sh), 241(s) 205(m)
$[\text{Co}_3(\text{Ettrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$	915(m) 895(vw)	690(vw) 641(vs)	272(s), 245(sh) 205(s)
$[\text{Ni}_3(\text{Ettrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$	910(s) 889(m)	690(vw) 639(vs)	282(s), 208(s) 195(sh)
$[\text{Cu}_3(\text{Ettrz})_9(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_6$	921(m) 885(sh)	685(vw) 639(vs)	285(sh), 273(s) 250(s), 215(m)
$[\text{Zn}_3(\text{Ettrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$	915(m) 891(vw)	688(vw) 640(vs)	210(s) 192(sh)
$[\text{Cd}_3(\text{Ettrz})_9(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_6(\text{H}_2\text{O})_3$	910(m) 890(sh)	641(s) 631(s)	208(s)

IV. The unit cell contains two trinuclear units. These units are located on a position with 32-site symmetry. The water molecules in the structure donate their hydrogen atoms to the O atoms of the CF_3SO_3^- -anions. The hydrogen bridge distances (Å) are: O(4)–O(1): 2.696(9) and O(4)–O(2): 2.773(9). No crystal structure of a linear trinuclear Mn(II) compound has been described before.

The infrared spectra of these compounds are mutually similar. The C–H out-of-plane absorption is located around 915 cm^{-1} and shows (in most cases) a weak shoulder around 890 cm^{-1} . The triazole out-of-plane ring absorption is observed at about 640 cm^{-1} , accompanied by a very weak absorption at $685\text{--}690 \text{ cm}^{-1}$. This last absorption is not observed for the manganese compound. The

TABLE VI. Ligand Field Data of Trifluoromethanesulfonate Coordination Compounds with Etrtz.

Compound	Ligand field bands (cm ⁻¹)	Dq (cm ⁻¹)	B (cm ⁻¹)
[Fe ₃ (Etrtz) ₆ (H ₂ O) ₆](CF ₃ SO ₃) ₆ ^a	11.400 18.000		
[Co ₃ (Etrtz) ₆ (H ₂ O) ₆](CF ₃ SO ₃) ₆	10.050 21.280	1100	
[Ni ₃ (Etrtz) ₆ (H ₂ O) ₆](CF ₃ SO ₃) ₆	11.100 17.590	1110	835 ^b
[Cu ₃ (Etrtz) ₉ (H ₂ O) ₃](CF ₃ SO ₃) ₆	16.050		

^aRecorded at liquid nitrogen temperature. ^b σ_3 is not observed, possibly due to the different chemical environments for the metal ions. Calculation of B based on σ_1 and σ_2 yields an unreliable value for this parameter.

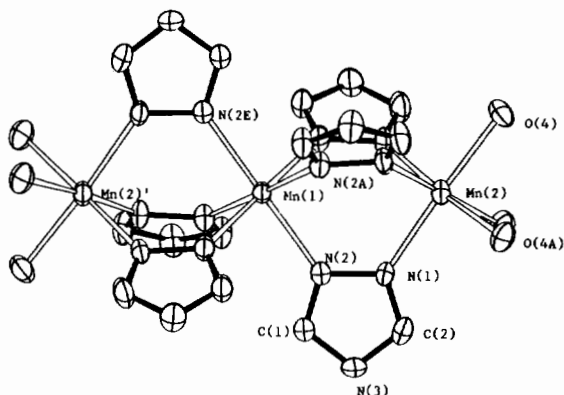


Fig. 1. Projection of the trimeric unit [(H₂O)₃Mn(Etrtz)₃-Mn(Etrtz)₃Mn(H₂O)₃]⁶⁺. Only the skeletal atoms are given for clarity.

absorptions mentioned, together with the metal–ligand absorptions, are listed in Table V. Based on these data the presence of monodentate coordinating Etrtz cannot be excluded. The single crystal X-ray analyses, however, show the occurrence of only 1,2-bidentate coordinating triazole ligands.

The presence of the second weak out-of-plane ring absorption and the splitting of the C–H out-of-plane absorption is not understood. The coordination of solvent molecules is clearly shown by the infrared spectra. Relatively sharp bands are observed at 3475 cm⁻¹ and 3365 cm⁻¹ (OH stretching) and at 1660 cm⁻¹ (H–OH bending). The ligand field data, which are listed in Table VI, show an octahedral coordination of the metal centers. The environment of the central metal ion is significantly different from that of the terminal ions. The rather symmetrical, but broad, bands in the ligand field spectra, however, do not show clearly these different ‘metal sites’. The obtained ligand field parameters are, therefore, an average for the three metal centers.

The trinuclear nature of these compounds is confirmed by the results of the magnetic susceptibility and magnetisation measurements. The inverse susceptibility vs. temperature curves for the Mn, Co

and Ni compounds exhibit the change in slope, which is characteristic for linear trimers having an antiferromagnetic exchange between nearest neighbours. The susceptibilities were fitted by means of least-squares methods to the theoretical expressions resulting from the Hamiltonians for linear trinuclear clusters, taking $J_{31} = 0$. The g-tensor was assumed to be equal for all the individual metal ions and intercluster interactions were assumed to be negligible.

Since no linear trinuclear Mn(II) compound has been described before, no expression for the susceptibility of such a compound has been reported. Earnshaw [25] supposed that the equation for χ of a linear trinuclear compound is similar to that of a trimer, in which the metal ions are arranged at the corners of an equilateral triangle. This is however rather unlikely, since the equation for the susceptibility of a linear Mn(II) trimer and a triangular system are not equal. We derived the equation for the susceptibility of a linear Mn(II) trimer based on the rules given by Kambe [26]. The Hamiltonian of such a system can be written in the form:

$$\mathcal{H} = -2J[(\hat{S}_1 \cdot \hat{S}_2) + (\hat{S}_2 \cdot \hat{S}_3)] - 2J_{31}(\hat{S}_3 \cdot \hat{S}_1)$$

In previous papers [12, 23] we described the magnetic behaviour of the isomorphous compound [Fe₃(Etrtz)₆(H₂O)₆](CF₃SO₃)₆. Upon cooling the central Fe(II) ion in this compound undergoes a high-spin–low-spin transition. When the Fe(II) ion is in the low-spin state (<190 K) there is no significant magnetic coupling present in the compound. This strongly suggests that the magnetic interaction between the terminal metal ions in these compounds can be ignored ($J_{31} = 0$). Based on this assumption the energy levels under the Hamiltonian, in the case of $S_1 = S_2 = S_3 = S$ are:

$$E(S'S^*) = -J[(S'(S' + 1) - S^*(S^* + 1) - S(S + 1))]$$

From this equation the formula for the susceptibility of a linear Mn(II) trimer can be calculated to be:

$$\begin{aligned} \chi_A = [Ng^2\beta^2/9kT] \times [& (105 + 2040e^{25x} + 1860e^{10x} \\ & + 1365e^{20x} + 858e^{7x} + 858e^{15x} + 495e^{4x} \\ & + 252e^x + 252e^{5x} + 858e^{-3x} + 495e^{-4x} \\ & + 498e^{-14x} + 252e^{-23x} + 252e^{-13x} + 252e^{-5x} \\ & + 105e^{-30x} + 108e^{-20x} + 105e^{-12x} + 105e^{-6x} \\ & + 105e^{-2x} + 30e^{-25x} + 30e^{-17x} + 30e^{-11x} \\ & + 30e^{-7x}) / (12 + 32e^{25x} + 48e^{10x} + 28e^{20x} \\ & + 24e^{7x} + 24e^{15x} + 20e^{4x} + 16e^x + 16e^{5x} \\ & + 24e^{-3x} + 20e^{-4x} + 24e^{-14x} + 16e^{-23x} \\ & + 16e^{-13x} + 16e^{-5x} + 12e^{-30x} + 16e^{-20x} \\ & + 12e^{-12x} + 12e^{-6x} + 12e^{-2x} + 8e^{-25x} \\ & + 8e^{-17x} + 8e^{-11x} + 8e^{-7x})] \end{aligned}$$

Using this equation a good fit is obtained, yielding $J = -0.6 \text{ cm}^{-1}$ and $g = 2.05$ (see Fig. 2). Application of the formula proposed by Earnshaw [25] resulted in a very poor fit.

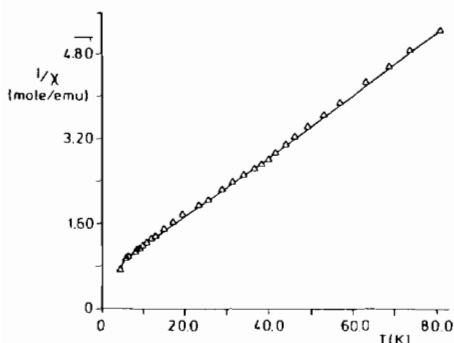


Fig. 2. The inverse susceptibility of $[\text{Mn}_3(\text{Ettrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$ measured at $H = 1.91 \text{ kOe}$. The drawn curve is the theoretical prediction for a linear $S = 5/2$ trimer ($J = -0.6 \text{ cm}^{-1}$, $g = 2.05$).

For a further check of the magnetism of this unusual compound, the magnetisation at very low T was studied.

The isothermal magnetisation (M) per trimer at $T = 1.13 \text{ K}$ up to very high fields ($H = 22 \text{ T}$) was measured using a pulsed field magnet [19]. In Fig. 3 the magnetisation isotherm is shown, obtained by collecting the results of three pulses. For fields higher than 15 T the compound is saturated, as may be concluded from the magnetisation which reaches the maximum value of the trimer, $M = 3gS = 15.5 \pm 0.5 \mu_B$, yielding $g = 2.07 \pm 0.06$ for $S = 5/2$, in agreement with the susceptibility result. Saturation

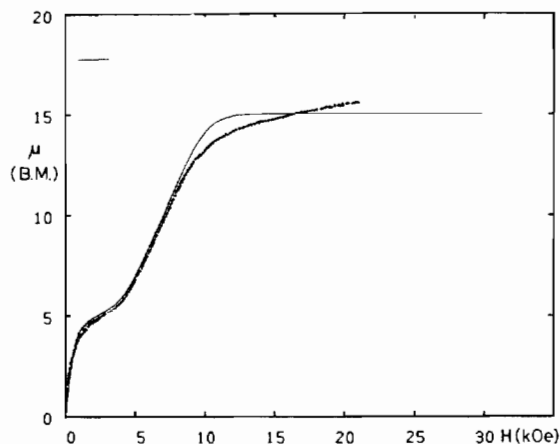


Fig. 3. Magnetization curve of $[\text{Mn}_3(\text{Ettrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$ at 1.13 K compared with calculations for the Heisenberg $S = 5/2$ trimer with $J = 0.6 \text{ cm}^{-1}$ and $g = 2.0$.

is achieved in two steps, which reflects the trimer character of the compound.

In the first step ($0 < H < 2T$), one third of the saturation moment is reached. Since a trimer in its antiferromagnetic groundstate carries a net spin of $5/2$, we interpret the first step as an alignment of the trimers along the applied field axis. The second step involves the field-induced transition from the antiferromagnetic to the ferromagnetic trimer state. We may estimate the exchange constant J by equating the exchange energy of the central spin $2zJS^2$ to its field energy at the inflection point $g\mu_B H_i S$. From this equation we get $J = -0.6 \text{ cm}^{-1}$ for $H_i = 6.5 \text{ T}$, which is in good agreement with the J -value obtained from the $1/\chi$ vs. T curve.

In order to explain in more detail the experimental data, we calculated the magnetization isotherms of a trimer, as governed by the Hamiltonian:

$$\mathcal{H} = -2J[\hat{S}_1\hat{S}_2 + \hat{S}_2\hat{S}_3] + g\mu_B H(\hat{S}_1 + \hat{S}_2 + \hat{S}_3)$$

In this description, only nearest neighbour interactions within the trimer have been taken into account (see above). Diagonalization of this Hamiltonian is easily performed and the result for the magnetisation calculated for parameter values $J = 0.6 \text{ cm}^{-1}$ and $g = 2.0$ is shown in Fig. 3.

The agreement is reasonable, although some small differences between theory and experiment are found at the highest field values. These may be ascribed to spin-lattice relaxation effects, which may appear with the pulsed-field technique as soon as the spin-lattice relaxation time approaches the rate at which the field changes [27].

Figure 4 shows the least-squares fit of the magnetic susceptibilities of $[\text{Ni}_3(\text{Ettrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$ to Ginsberg's formula for linear trinuclear compounds with $S = 1$, taking $J_{31} = 0$. With

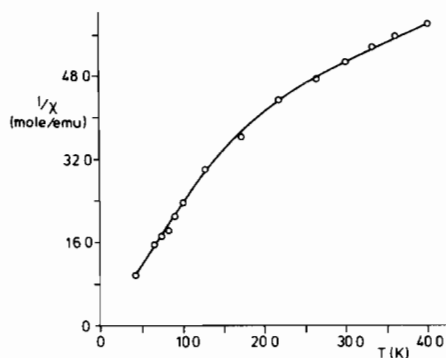


Fig 4 The inverse magnetic susceptibility of $[\text{Ni}_3(\text{Ettrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$ as a function of temperature, measured at $H = 9.67$ kOe. The full line represents the prediction for a linear Ni(II)-trimer with $J = -9.4$ cm^{-1} and $g = 2.15$.

$J = -9.41$ cm^{-1} and $g = 2.15$ a good fit is obtained. This Ni compound resembles $[\text{Ni}_3(\text{Htrz})_6(\text{H}_2\text{O})_6](\text{NO}_3)_6(\text{H}_2\text{O})_2$, described by Reimann and Zocchi [5]. The magnetic behaviour of the latter was first studied by Mackey and Martin [29], who obtained a reasonable fit taking $J = -8.7$ cm^{-1} , $g = 2.05$ and $J_{31} = +4.8$ cm^{-1} . Engelfriet [30] repeated the experiment assuming J_{31} to be zero. This model appeared to be in good agreement with the experimental data resulting in $J = -8.3$ cm^{-1} and $g = 2.13$.

For the magnetic susceptibility data (below 40 K) of the linear trinuclear Co compound a $S = \frac{1}{2}$ formalism was applied. Assuming a Heisenberg model the data were fitted to the equation of a linear Cu(II) trimer [31]. Taking both J and g as variable parameters in the least-squares procedure, J and g refined to -9.5 cm^{-1} and 4.9 respectively (dashed curve in Fig 5). J refined to -11.2 cm^{-1} when a fixed value of 5.1 was taken for the g -tensor (full line in Fig 5).

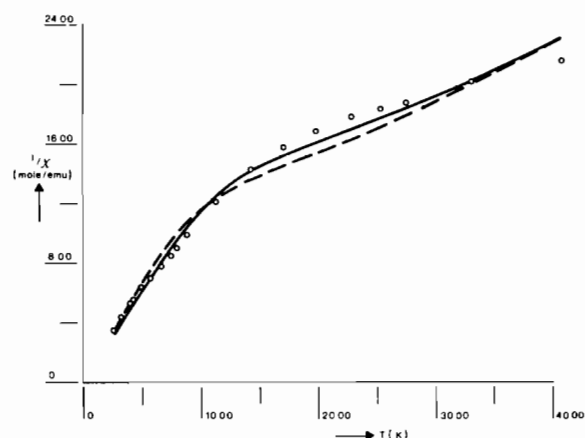


Fig 5 Inverse magnetic susceptibility as a function of temperature for $[\text{Co}_3(\text{Ettrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$ measured at $H = 3.40$ kOe. The dashed and full lines represent the theoretical prediction for a linear $S = \frac{1}{2}$ Heisenberg trimer (---- $J = 9.5$ cm^{-1} , $g = 4.9$ — $J = -11.2$ cm^{-1} , $g = 5.1$).

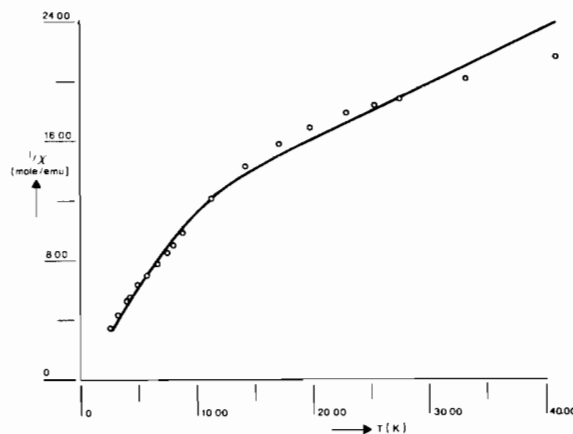


Fig 6 Inverse magnetic susceptibility as a function of temperature for $[\text{Co}_3(\text{Ettrz})_6(\text{H}_2\text{O})_6](\text{CF}_3\text{SO}_3)_6$ measured at $H = 3.40$ kOe. The full line represents the prediction for a linear $S = \frac{1}{2}$ Ising trimer with $J = 14.7$ cm^{-1} and $g_{\perp} = 6.2$.

The magnetic susceptibility data were fitted to the equation for the Ising model, the equation for the susceptibility for which has been presented in a previous paper [32].

$[\text{M}_3(\text{Ettrz})_9(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_6(\text{H}_2\text{O})_x$ ($M = \text{Cu(II)}$, Cd(II))

The Cu and Cd compounds are also believed to be linear trimers. The values of x are 0 and 3 for the Cu and Cd compound respectively. The dominant role of the CF_3SO_3^- absorptions in the infrared spectra, already mentioned in the introduction of this paper, is demonstrated clearly by these compounds. Although the geometries must be significantly different from the compounds mentioned earlier, the infrared spectra are similar and only very small differences are observed.

The six terminal coordination sites in the Cu and Cd trimers are occupied by three water molecules and three Ettrz groups coordinating by only one N atom, which implies a surprisingly asymmetrical coordination. Unfortunately the presence of monodentate coordinating Ettrz is not revealed clearly by the infrared data (see Table V).

Only the splitting of the intensive out-of-plane ring torsion, observed in the spectrum of the Cd compound, can be regarded as an indication for the presence of both monodentate and bidentate coordinating triazole ligands. The infrared spectra provide no indication for coordination of the anion. Coordination of water molecules is confirmed by the infrared data.

The X-ray powder diffractograms of the Cd and Cu compound are not identical, which may originate from the difference in the number of H_2O molecules. Another explanation might be a difference in the distribution of the terminal ligands, which, however, is rather unlikely.

The ligand field spectrum of $[\text{Cu}_3(\text{Ettrz})_9(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_6$ shows one asymmetrical band at 16.050 cm^{-1} , indicating a distorted octahedrally based coordination of the Cu(II) centers.

The EPR spectrum shows one signal having a g -value of 2.09. Due to exchange narrowing, the hyperfine splittings remain unresolved.

The magnetic susceptibility data of $[\text{Cu}_3(\text{Ettrz})_9(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_6$ were fitted by means of least-squares methods to the theoretical prediction [31] for a linear Heisenberg trimer with $S = \frac{1}{2}$, taking $J_{31} = 0$.

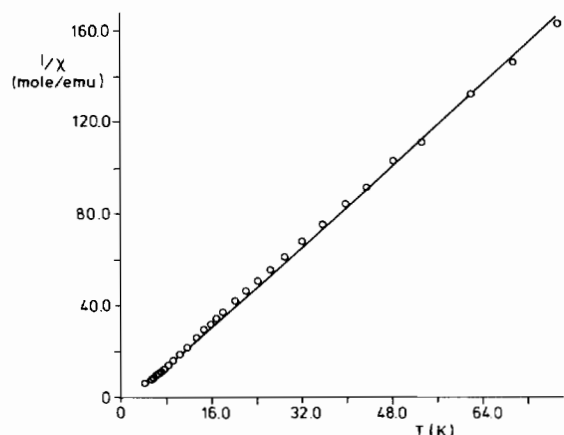


Fig. 7. Inverse magnetic susceptibility of $[\text{Cu}_3(\text{Ettrz})_9(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_6$ as a function of temperature measured at $H = 2.38 \text{ kOe}$. The drawn curve represents the theoretical prediction for a linear $S = \frac{1}{2}$ trimer with $J = +6.8 \text{ cm}^{-1}$ and $g = 2.11$.

Figure 7 shows the fit obtained, resulting in $J = +6.8 \text{ cm}^{-1}$ and $g = 2.1$. Hence a ferromagnetic exchange between nearest neighbours exists, which is rather surprising. The reason for the occurrence of a triplet ground state is not clear. Close examination of the geometry of this compound is necessary but unfortunately unsuccessful. A similar magnetic phenomenon is observed for the layer compounds $[\text{M}(\text{Htrz})_2(\text{NCS})_2]$ [8]. All paramagnetic first-row transition metals give rise to compounds with an antiferromagnetic intralayer exchange, except for the Cu compound which appeared to be slightly ferromagnetic.

Conclusion

In this paper a series of linear trinuclear transition metal(II) coordination compounds are described. Trifluoromethanesulfonate has been shown to be a very good choice for a non-coordinating anion. It is relatively simple to obtain single crystals of transition metal(II) coordination compounds using this anion, which makes a detailed study of the

geometries by X-ray analysis possible. The triflate anions do not coordinate, but are very suitable acceptors for hydrogen bonding. Consequently the obtained trinuclear structures are very stable. So far only linear trinuclear species have been obtained with this anion. It is not clear why no polynuclear ($n > 3$) compounds have been found with 3 bridging triazole ligands between the metal centers. Although no clear structural reasons are apparent, the strain in such structures could be large. Therefore, solvent molecules or monodentate coordinating triazole ligands limit the chain length by occupying the terminal coordination sites in the trinuclear compounds. Working under the appropriate experimental conditions it should be possible, however, to obtain long(er) polynuclear units.

The magnetic exchange coupling in the Mn(II), Co(II) and Ni(II) compounds is antiferromagnetic, which is in accordance with the magnetic coupling in previously described triazole-bridged coordination compounds [8, 9, 15, 23, 29, 32].

$[\text{Cu}_3(\text{Ettrz})_9(\text{H}_2\text{O})_3](\text{CF}_3\text{SO}_3)_6$ shows, surprisingly, a ferromagnetic exchange between the metal centers. Further attempts in preparing single crystals of this compound must be undertaken, in order to provide a more profound basis for the interpretation of the magnetic data.

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