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Spectroscopic and Magnetic Properties of Transition Metal(II) Trifluoromethanesulfonate Compounds with Bridging Asymmetric 3,4-Dialkyl Substituted 1,2,4-Triazole Ligands

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Abstract

The spectroscopic and magnetic properties are described of coordination compounds with asymmetric 3,4-dialkyl substituted 1,2,4-triazoles. The ligands 3-methyl-4-ethyl-1,2,4-triazole and 3-methyl-4-t-butyl-1,2,4-triazole have been investigated. Using $M(CF_3SO_3)_2$ (M = Mn, Co, Ni, Cu, Zn) compounds have been obtained with a linear trinuclear structure, in which the metal ions are linked to each other by two pairs of three bridging triazoles. The coordination sphere around the terminal ligands is completed by monodentate ligands and/or water molecules. The structure has been confirmed by an X-ray structure determination of $[Co_3(metz)_6(H_2O)_6][Co_3(metz)_8(H_2O)_4](CF_3SO_3)_{12}(H_2O)_8$. This compound crystallizes in the space group $P\bar{1}$ with lattice constants $a = 13.793(4)$, $b = 14.401(3)$, $c = 23.258(4)$ Å, $\alpha = 80.58(2)$, $\beta = 83.23(2)$ and $\gamma = 64.33(2)°$. The unit cell contains two independent trinuclear clusters of different composition. These two clusters have the same overall structure. Differences are related to the presence of monodentately coordinating ligands as well as to the position of the C3-methyl substituent. The complete refinement of this structure was obstructed by disorder problems in the anions and the non-coordinating water molecules. The magnetic susceptibilities of the compounds have been recorded and could be fitted to theoretical expressions for linear trimers. The compound $[Ni_2(mtbtz)_5(H_2O)_4](CF_3SO_3)_4(H_2O)_4$ appears to be a dimeric species as concluded from its magnetic behaviour.

Introduction

Even though quite a number of coordination compounds containing 1,2,4-triazole derivatives as bridging ligands between the transition metal ions have been reported [1–9], very little is understood about the nature of the magnetic behaviour of this type of compounds. Crystallographic studies on 4-alkyl substituted 1,2,4-triazoles revealed that the N1–N2 bond has only slightly a double bond character. Therefore, it is very likely that the σ-framework represents the dominant pathway for the superexchange mechanism. This would be contradictory to the ideas of Ball and Blake [10], who suggested that an important part of the superexchange takes place via the π-electrons of the ligand. This makes it worthwhile extending the studies on this very wide class of ligands. From such studies a better insight may be obtained about the mechanism of magnetic interactions generally and through 1,2,4-triazole bridges in particular.

The relatively easy method of synthesis makes these ligands very suitable for detailed magnetochemical studies. Using 4-alkyl substituted 1,2,4-triazoles mainly di- and trinuclear compounds have been obtained, nearly all exhibiting weak antiferromagnetic exchange [1–9]. As a propagation of the investigations on this type of symmetric ligands the results with 3,4-dialkyl substituted triazoles are presented now. The major difference between those two groups of ligands is the asymmetry of the latter ones. For a first investigation 3-methyl-4-ethyl-1,2,4-triazole (abbreviated as metz) and 3-methyl-4-tert-butyl-1,2,4-triazole (abbreviated as mtbtz) were used. The ligand metz has been reported by Vercek *et al.* [11], who investigated the hydrazinolysis of some azolopyrazines.

The synthesis of the ligands used here was essentially the same as the one used for the 4-alkyl substituted 1,2,4-triazoles [8, 12], using acetylhydrazine instead of formylhydrazine in order to introduce the 3-methyl substituent. Based on the results with 4-alkyl-1,2,4-triazoles we started the investigations using metal(II) trifluoromethanesulfonates, the results of which are presented below, including a partial structure determination of $[Co_3(metz)_6(H_2O)_6][Co_3(metz)_8(H_2O)_4](CF_3SO_3)_{12}(H_2O)_8$.

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Experimental

Synthesis of the Ligands

A mixture of 156 g (1.53 mol) of acetylhydrazine and 385 g (2.3 mol) of triethylorthoformate in 600 ml of methanol p.a. was refluxed during 2½ h. After that, 100 ml (1.53 mol) ethylamine (boiling point (b.p.) 16.6 °C) using a N_2 gas stream (to obtain metz) or 160 ml (1.53 mol) t-butylamine (to obtain mtbtz) was added slowly to the boiling solution. After another 3 h of refluxing the solvent was removed by distillation and the residue heated to 170 °C for 2 h. Finally, the reaction mixture was distilled. Yields: metz: 102 g (0.9 mol, 60%); b.p. 135–150 °C (2 mm Hg); mtbtz: 85 g (0.6 mol, 40%); b.p. 150–160 °C (3.5 mm Hg). NMR (DMSO-d_6) metz: 1.10 ppm (t, 3H); 2.22 ppm (s, 3H); 3.91 ppm (q, 2H); 8.77 ppm (s, 1H). mtbtz: 1.57 ppm (s, 9H); 2.52 ppm (s, 3H); 8.37 ppm (s, 1H).

Synthesis of the Coordination Compounds

All coordination compounds crystallized within a few days upon standing at room temperatures. After crystallisation the compounds were filtered off, washed with a small amount of ethanol and dried in air.

$[Mn_3(metz)_6(H_2O)_6](CF_3SO_3)_6(H_2O)_3$

2 mmol of $Mn(CF_3SO_3)_2$ was dissolved in 4 ml of water. A solution of 4 mmol of metz in 6 ml of water was added.

$[M_3(metz)_6(H_2O)_6][M_3(metz)_8(H_2O)_4](CF_3SO_3)_{12}(H_2O)_8$ ($M = Co, Zn$)

2 mmol of $M(CF_3SO_3)_2$ was dissolved in 10 ml of water. A solution of 4 mmol of metz in 10 ml of water was added.

$[M_3(metz)_{12}](CF_3SO_3)_6$ ($M = Co, Ni$)

2 mmol of $M(CF_3SO_3)_2$ ($M = Co$, Ni) was dissolved in 6 ml of water. A solution of 12 mmol of metz in 6 ml of water was added.

$[Mn_3(mtbtz)_7(H_2O)_5](CF_3SO_3)_6(H_2O)$

2 mmol of $Mn(CF_3SO_3)_2$ was dissolved in 4 ml of water. A solution of 4 mmol of mtbtz in 6 ml of water was added.

$[Co_3(mtbtz)_7(H_2O)_5](CF_3SO_3)_6(H_2O)$

2 mmol of $Co(CF_3SO_3)_2$ was dissolved in 10 ml of water. A solution of 6 mmol of mtbtz in 10 ml of water was added.

$[Ni_2(mtbtz)_5(H_2O)_4](CF_3SO_3)_4(H_2O)_4$

2 mmol of $Ni(CF_3SO_3)_2$ was dissoved in 10 ml of ethanol: water (2:1). A solution of 6 mmol of mtbtz in 6 ml of the same mixture of solvents was added.

Analyses and Spectroscopic Measurements

Metal determinations were done using standard complexometric titrations. C, H, and N analyses were carried out by the Microanalytical Laboratory of University College, Dublin, Ireland. Infrared spectra (4000–180 cm^{-1}) were recorded as KBr pellets on a Perkin-Elmer 580 spectrophotometer. UV–Vis spectra were obtained on a Perkin-Elmer 330 spectrophotometer using the diffuse reflectance technique with MgO as a reference. Magnetic susceptibilities were measured on a PAR vibrating sample magnetometer model 150 in the temperature range 4–80 K.

Magnetic data were fitted to theoretical expressions as given in the literature (*vide infra*) by means of a Simplex routine [13]. The calculations were carried out on a Commodore PC10 personal computer, using a computer program written by R. Prins. All parameters (J, J', g, D; *vide infra*) were independently variable in the fitting procedure. All expressions for the magnetic susceptibility, which have been used to fit data, were based on spin Hamiltonian $\mathcal{H} = -2\Sigma J_{ij}\hat{S}_i\hat{S}_j$.

X-ray Structure Determination

A suitable crystal of $[Co_3(metz)_6(H_2O)_6][Co_3(metz)_8(H_2O)_4](CF_3SO_3)_{12}(H_2O)_8$ was mounted on an Enraf Nonius CAD4 diffractometer and data were collected at 293 K. Crystal data are: $C_{41}H_{81}Co_3F_{18}N_{21}O_{27}S_6$, $a = 13.793(4)$, $b = 14.401(3)$, $c = 23.258(4)$ Å, $\alpha = 80.58(2)$, $\beta = 83.23(2)$, $\gamma = 64.33(2)^\circ$, space group $P\bar{1}$, $D_m = 1.63$, $D_c = 1.628$, Mo Kα radiation (graphite monochromator), $T = 293$ K. Intensity data were collected in the range $2 \leqslant \theta \leqslant 20^\circ$. A total of 6621 unique reflections were collected of which 4427 were used in the refinement. The Co atoms were obtained by means of a Patterson synthesis. The heavy atoms of the ligands were located using the program AUTOFOUR [14].

Unfortunately, disordering problems obstructed the least squares refinement of the metal and ligand positions and also prohibited the location of the anion atoms from plotted weighted $2F_o - F_c$ Fourier maps, although these maps showed residual electron density in the anions areas. The lowest R value obtained was $R = 0.23$, based on a model including all atoms, except the hydrogen atoms, belonging to the cations and the sulfur atoms, one third of the carbon atoms and one sixth of the oxygen atoms belonging to the anions. ($R = \{\Sigma(||F_c| - |F_o||)/\Sigma|F_o|\}$. We were unable to collect enough diffraction data to take into account all disorder possibilities. However, the overall structure of the cations became quite clear and agrees with spectroscopic and magnetic techniques.

TABLE I. Analytical and Spectroscopic Data of Metal(II)trifluoromethanesulfonates with the Ligands metz and mtbtz

Compound	Colour	Elemental analysis[a]				X-ray type	Ligand field bonds ×10^3 (cm^{-1})			Dq[b] (cm^{-1})	B[b] (cm^{-1})	Melting point (°C)
		M	C	H	N							
$[Mn_3(metz)_6(H_2O)_6](CF_3SO_3)_3(H_2O)_3$	white	7.61 8.71	22.60 22.82	3.38 3.80	13.50 13.31	A						>250
$[Co_3(metz)_6(H_2O)_6][Co_3(metz)_8(H_2O)_4](CF_3SO_3)_{12}(H_2O)_8$	orange	8.67 8.77	24.41 24.41	3.85 4.02	14.68 14.58	B	9.79	20.5		1070	790	>250
$[Co_3(metz)_{12}](CF_3SO_3)_6$	orange	7.24 7.35				C	10.2	21.3		1125		210
$[Ni_3(metz)_{12}](CF_3SO_3)_6$	purple	7.02 7.32	32.43 32.89	4.69 4.48	21.41 20.93	C	11.1	18.0	28.8	1110	900	>250
$[Zn_3(metz)_6(H_2O)_6][Zn_3(metz)_8(H_2O)_4](CF_3SO_3)_{12}(H_2O)_8$	white	9.70 9.64				B						>250
$[Mn_3(mtbtz)_7(H_2O)_5](CF_3SO_3)_6(H_2O)$	white	7.70 7.68				D						166
$[Co_3(mtbtz)_7(H_2O)_5](CF_3SO_3)_6(H_2O)_4$	orange	7.48 7.99	29.88 29.84	5.01 4.93	13.69 13.29	E	9.39	20.9		1025	845	>200
$[Ni_2(mtbtz)_5(H_2O)_4](CF_3SO_3)_4(H_2O)_4$	purple	7.81 7.54	29.77 30.07	4.94 5.20	13.52 13.49	F	10.6	17.2	27.8	1060	840	>200

[a] The second line gives calculated values. [b] *Dq* and *B* values are calculated as in refs. 16 and 18.

Results and Discussion

General

In contrast to the 4-alkyl substituted 1,2,4-triazoles [6, 7, 9] very little information about the coordination mode of the 3,4-dialkyl substituted triazoles can be obtained from the infrared spectra. In the case of the symmetric N4-substituted triazoles the C_{2v} symmetry is lowered to C_s symmetry upon monodentate coordination, whereas the symmetry is retained upon bidentate coordination. This affects the out-of-plane C–H and the ring torsion vibrations. In the case of the now used asymmetric metz and mtbtz ligands the coordination mode does not influence the symmetry of the ligand. Therefore no straightforward structural information is to be expected from IR spectra as such. An additional problem in the interpretation of the IR spectra originates from the domination of the trifluoromethanesulfonate anion vibrations on the IR spectra. This anion does not generally coordinate to transition-metal ions. From the IR spectra it is impossible to see whether the anion is coordinated or hydrogen bridges are formed between the anion and solvent molecules. All anion absorptions observed in the compounds in the present study lie in the same range (1280, 1252, 1210, 1168, 1031, 760, 640, 573 and 518 cm^{-1}). Based on the non-coordinating behaviour of $CF_3SO_3^-$ in $[Co_3(metz)_6(H_2O)_6][Co_3(metz)_8(H_2O)_4](CF_3SO_3)_{12}(H_2O)_8$, we assume that the triflate anions are not coordinated to the metal ions in all other compounds described in this paper.

The analytical, spectroscopic and magnetic results of the compounds obtained with metz as well as with mtbtz and the $CF_3SO_3^-$ anion have been summarized in Table I.

As can be seen from Table I three types of compounds have been formed with the ligand metz, which will be discussed hereafter.

$[Mn_3(metz)_6(H_2O)_6](CF_3SO_3)_6(H_2O)_3$

According to its composition, and because of the analogy with the results obtained with 4-ethyl-1,2,4-triazole (ettrz) [9], a trinuclear structure is proposed for this compound, with the same three-dimensional arrangement of metal, ligands and water molecules as known to occur in $Mn_3(ettrz)_6(H_2O)_3(CF_3SO_3)_6$ [9]. The trinuclear nature of the compound is confirmed by the magnetic susceptibility measurements, which can be fitted to an expression for the magnetic susceptibility of a linear trinuclear manganese compound as derived by Vos [9]. The least-squares fit of the χ^{-1} *versus* T curve results in $J = -0.5(1)$ cm^{-1} and $g = 2.1(1)$, where J stands for next-neighbour interaction; the nearest next-neighbour interaction is assumed to be zero as has been done and confirmed for linear trinuclear compounds with ettrz [6, 9].

$[M_3(metz)_6(H_2O)_6][M_3(metz)_8(H_2O)_4](CF_3SO_3)_{12}(H_2O)_8$ ($M = Co, Zn$)

The above discussed Mn compound and these Co and Zn compounds have very similar IR spectra. This leads us to the assumption that these compounds also exist as trinuclear units in which some of the water molecules are replaced by monodentately coordinating ligands. The differences in the IR spectra originate from the occurrence of both bidentate and monodentate metz. This assumption has in fact been confirmed by an X-ray structure determination of the Co compound. Surprisingly, the unit cell contains two independent and different trinuclear clusters, which even have different compositions. In both units the three cobalt atoms are in a linear arrangement with a triple triazole bridge between the central and each of the two terminal Co atoms. In one of the two clusters (cluster 2) six water molecules are coordinated at both ends of the trimer, whereas in the other one (cluster 1) two of those water molecules have been replaced by monodentate ligands. The two clusters also differ in the position of the methyl substituents on C3. In cluster 1 all these methyl groups are pointing to the terminal parts of the cluster, whereas in the other cluster two of the six substituents are positioned near the central cobalt ion. An ORTEP [15] drawing of cluster 2 is given in Fig. 1, together with the numbering of the atoms as used in Tables II and III. The atoms in cluster 1 are labelled in an equivalent way; triazole ring 4 coordinates monodentately, rings 1, 2 and 3 bidentately. The atomic parameters of metal and ligand atoms are given in Table II (see also 'Supplementary Material'). Selected bond distances and bond angles are tabulated in Table III. All distances and angles observed are in a reasonable range. Unfortunately, it appeared to be impossible to complete the refinement of the atom positions due to disordering problems as described in 'Experimental'. During the refinement

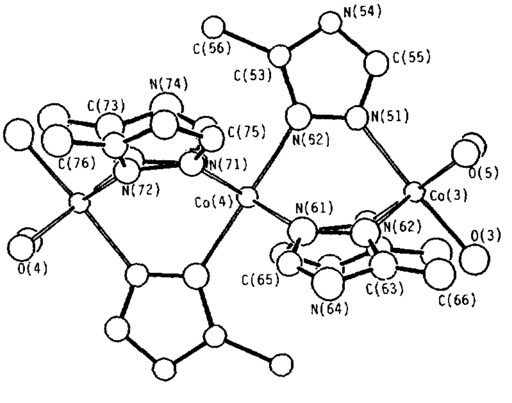

Fig. 1. ORTEP [15] drawing of the cation $[Co_3(metz)_6(H_2O)_6]^{6+}$, with the labelling of the atoms. The ethyl groups at N4 have been omitted for clarity.

TABLE II. Fractional Atomic Coordinates and Isotropic Thermal Parameters (Å^2) of Metal and Ligand Atoms (×10^4 for Co; ×10^3 for other atoms) for $[Co_3(metz)_6(H_2O)_6][Co_3(metz)_8(H_2O)_4](CF_3SO_3)_{12}(H_2O)_8$

Cluster 1					Cluster 2				
Atom[a]	x/a	y/b	z/c	B_{iso}	Atom[a]	x/a	y/b	z/c	B_{iso}
Co(1)	7355(4)	3576(4)	5990(2)	12(2)	Co(3)	2881(5)	728(4)	8894(2)	19(2)
Co(2)*	5000	5000	5000	15(1)	Co(4)*	5000	0	10000	220(1)
N(11)	659(3)	483(2)	476(1)	19(7)	N(41)	886(2)	237(2)	587(1)	16(7)
N(12)	747(3)	433(3)	511(2)	26(8)	N(42)	919(3)	188(3)	537(2)	36(9)
C(13)	830(4)	437(3)	474(2)	31(10)	C(43)	1013(4)	119(4)	543(2)	39(11)
N(14)	802(3)	496(3)	427(1)	22(7)	N(44)	1056(3)	128(3)	592(2)	40(9)
C(15)	692(4)	519(4)	422(2)	37(11)	C(45)	962(4)	216(3)	616(2)	26(9)
C(16)	959(4)	383(4)	496(2)	43(12)	C(46)	1098(4)	55(4)	488(2)	39(11)
C(17)	867(4)	528(4)	382(2)	36(11)	N(51)	301(3)	−24(3)	970(1)	22(7)
C(18)	855(4)	617(4)	384(2)	50(13)	N(52)	375(3)	−56(3)	1009(2)	28(8)
N(21)	500(3)	543(2)	584(1)	15(6)	C(53)	346(5)	−115(5)	57(3)	60(14)
N(22)	593(3)	492(3)	625(2)	24(7)	N(54)	261(3)	−130(3)	1040(2)	52(10)
C(23)	561(3)	544(3)	666(2)	13(8)	C(55)	232(5)	−64(5)	987(3)	6(1)
N(24)	460(2)	622(2)	659(1)	16(7)	C(56)	389(7)	−153(7)	125(4)	12(2)
C(25)	425(3)	619(3)	607(2)	27(10)	N(61)	528(3)	−28(3)	915(2)	36(9)
C(26)	632(4)	520(4)	718(2)	34(10)	N(62)	455(3)	−2(3)	870(2)	37(9)
N(31)	560(3)	342(3)	535(1)	22(7)	C(63)	510(4)	−28(4)	818(2)	34(11)
N(32)	648(3)	291(2)	571(1)	17(7)	N(64)	625(3)	−79(3)	833(2)	44(10)
C(33)	647(4)	197(4)	581(2)	38(11)	C(65)	622(5)	−69(5)	884(3)	6(1)
N(34)	580(3)	180(2)	553(1)	19(7)	C(66)	464(4)	−16(4)	768(2)	42(12)
C(35)	528(4)	272(4)	524(2)	40(11)	N(71)	389(3)	150(3)	972(2)	26(8)
C(36)	735(4)	96(4)	628(2)	40(11)	N(72)	298(3)	180(3)	935(2)	29(8)
O(1)	728(2)	295(2)	688(1)	24(6)	C(73)	246(3)	285(3)	936(2)	27(9)
O(2)	824(2)	443(2)	626(1)	35(7)	N(74)	292(3)	321(3)	971(2)	32(8)
					C(75)	376(4)	238(3)	995(2)	26(10)
					C(76)	145(4)	359(4)	908(2)	41(11)
					O(3)	270(2)	165(2)	810(1)	39(7)
					O(4)	114(2)	141(2)	903(1)	31(6)
					O(5)	266(2)	−35(2)	847(1)	33(7)

[a]Special positions are marked with an asterisk.

it became clear that disorder occurs in the position of the triflate anions, as well as in the position of the N4-substituents. Both features have been observed before [4, 7]. Besides that it cannot be excluded, that the positions of the two different units are also slightly disordered. Nevertheless, the overall structure of the compound as obtained from the crystal structure determination is quite clear and has in fact been confirmed by spectroscopic and magnetic measurements. The ligand field strength of the Co compound (1070 cm^{-1}), as well as the broad absorptions observed in the UV–Vis spectrum, agree with a mixture of CoN_6-, CoN_3O_3- and CoN_4O_2-chromophores [16].

The inverse magnetic susceptibilities could be fitted to a Heisenberg model, using $S = 1/2$ formalism [13]. A reasonable fit giving $J = -11(1)$ cm^{-1} and $g = 4.5(3)$ was obtained only for temperatures below 40 K. Reasonable fitting in the low temperature range only has been observed before for Co compounds and is a result of the population of low-lying excited states at higher temperatures. In this particular case poor fitting could also be ascribed to the existence of two different trinuclear units, each having its own magnetic parameters.

$[M_3(metz)_{12}](CF_3SO_3)_6$ (M = Co, Ni)

The infrared spectra of these two X-ray isomorphous compounds differ only slightly from the IR spectra of $[Co_3(metz)_6(H_2O)_6][Co_3(metz)_8(H_2O)_4](CF_3SO_3)_{12}(H_2O)_8$. The intensity of the ν(C–H) at 860 cm^{-1} is increased, whereas the intensity of the water vibrations has disappeared. The absorptions belonging to the anion are somewhat sharpened and no splitting of the absorption at 1270 cm^{-1} into two bands at 1280 and 1250 cm^{-1} has been observed in this compound, which is ascribed to the absence of hydrogen bridges to the CF_3SO_3 anion.

The strong ligand field indicates a MN_6 chromophore ($Dq = 1125$ (Co) and 1110 (Ni) cm^{-1}). Combining these results a linear trinuclear cluster is proposed in which again the metal ions are bridged

TABLE III. Selected Bond Distances and Bond Angles for $[Co_3(metz)_6(H_2O)_6][Co_3(metz)_8(H_2O)_4](CF_3SO_3)_{12}(H_2O)_8$, Estimated Standard Deviations are in Parentheses[a]

Cluster 1		Cluster 2	
Bond distance (Å)			
Co(1)–N(12)	2.17(4)	Co(3)–N(51)	2.12(3)
Co(1)–N(22)	2.19(4)	Co(3)–N(62)	2.10(4)
Co(1)–N(32)	2.05(3)	Co(3)–N(72)	2.07(4)
Co(1)–N(41)	2.07(3)	Co(3)–O(3)	2.07(3)
Co(1)–O(1)	2.13(3)	Co(3)–O(4)	2.17(3)
Co(1)–O(2)	2.27(3)	Co(3)–O(5)	2.12(3)
Co(2)–N(11)	2.11(3)	Co(4)–N(52)	2.17(4)
Co(2)–N(21)	2.14(3)	Co(4)–N(61)	2.03(4)
Co(2)–N(31)	2.11(3)	Co(4)–N(71)	2.09(3)
Bond angles (°)			
N(12)–Co(1)–N(22)	93(1)	N(51)–Co(3)–N(62)	92(1)
N(12)–Co(1)–N(32)	91(1)	N(51)–Co(3)–N(72)	88(1)
N(12)–Co(1)–N(41)	91(1)	N(51)–Co(3)–O(3)	177(1)
N(12)–Co(1)–O(1)	174(1)	N(51)–Co(3)–O(4)	90(1)
N(12)–Co(1)–O(2)	86(1)	N(51)–Co(3)–O(5)	90(1)
N(22)–Co(1)–N(32)	94(1)	N(62)–Co(3)–N(72)	95(1)
N(22)–Co(1)–N(41)	168(1)	N(62)–Co(3)–O(3)	90(1)
N(22)–Co(1)–O(1)	84(1)	N(62)–Co(3)–O(4)	174(1)
N(22)–Co(1)–O(2)	83(1)	N(62)–Co(3)–O(5)	90(1)
N(32)–Co(1)–N(41)	97(1)	N(72)–Co(3)–O(3)	94(1)
N(32)–Co(1)–O(1)	95(1)	N(72)–Co(3)–O(4)	91(1)
N(32)–Co(1)–O(2)	176(1)	N(72)–Co(3)–O(5)	176(1)
N(41)–Co(1)–O(1)	90(1)	O(3)–Co(3)–O(4)	89(1)
N(41)–Co(1)–O(2)	86(1)	O(3)–Co(3)–O(5)	88(1)
O(1)–Co(1)–O(2)	88(1)	O(4)–Co(3)–O(5)	85(1)
N(11)–Co(2)–N(21)	94(1)	N(52)–Co(4)–N(61)	89(1)
N(11)–Co(2)–N(31)	90(1)	N(52)–Co(4)–N(71)	91(1)
N(11)–Co(2)–N(21)$^{\#}$	86(1)	N(52)–Co(4)–N(52)*	180.0(0)
N(11)–Co(2)–N(31)$^{\#}$	90(1)	N(52)–Co(4)–N(61)*	91(1)
N(11)–Co(2)–N(11)$^{\#}$	180.0(0)	N(52)–Co(4)–N(71)*	89(1)
N(21)–Co(2)–N(31)	91(1)	N(61)–Co(4)–N(71)	89(1)
N(21)–Co(2)–N(21)$^{\#}$	180.0(0)	N(61)–Co(4)–N(61)*	180.0(0)
N(21)–Co(2)–N(31)$^{\#}$	89(1)	N(61)–Co(4)–N(71)*	91(1)
N(31)–Co(2)–N(31)$^{\#}$	180.0(0)	N(71)–Co(4)–N(71)*	180.0(0)

[a] # Indicates symmetry operation $1 - x, 1 - y, 1 - z$. *Indicates symmetry operation $1 - x, -y, 2 - z$.

by triple triazole bridges. At both sides of the trinuclear unit three ligands coordinate monodentately, completing the MN_6 chromophore.

The magnetic measurements are consistent with this structure. Fitting χ^{-1} *versus* T with the theoretical predictions [17, 6] results in $J = -7.0(1)$ cm^{-1} and $g = 2.3(1)$ for Ni and $J = -12.0(1)$ cm^{-1} and $g = 4.5(3)$ for Co (Heisenberg; $S = 1/2$).

The analytical, spectroscopic and magnetic data of the compounds formed with mtbtz have already been given in Table I. Some comments on these results will be given hereafter.

$[Mn_3(mtbtz)_7(H_2O)_5](CF_3SO_3)_6(H_2O)$

According to its composition and the analogy with the results obtained with metz, a trinuclear structure is proposed for this compound. The magnetic measurements from 4–80 K have been fitted on a model for a trinuclear manganese compound. The fitting of $1/\chi$ *versus* T resulted in $J = -1.1(1)$ cm^{-1} and $g = 2.0(1)$.

$[M_3(mtbtz)_7(H_2O)_5](CF_3SO_3)_6(H_2O)_4$ ($M = Co, Zn$)

As follows from the results of the magnetic measurements on the cobalt compound these are also trinuclear clusters. Fitting the data to the expression for a Heisenberg trinuclear compound with $S = 1/2$, resulted in $J = -14.4(1)$ cm^{-1} and $g = 4.7(1)$. The observed and calculated inverse susceptibility *versus* temperature curves for this compound are represented in Fig. 2 as typical examples of the shape of these curves for linear trinuclear clusters with antiferromagnetic exchange between next-neighbour metal ions.

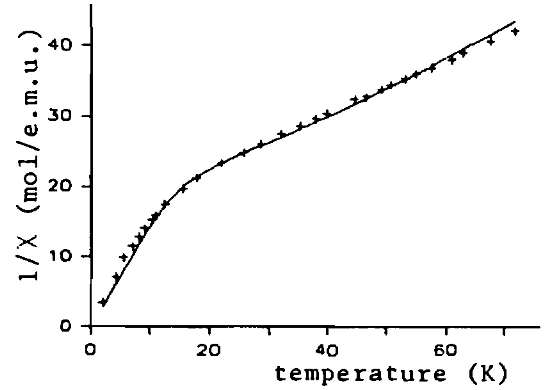

Fig. 2. The inverse susceptibility of $[Co_3(mtbtz)_7(H_2O)_5]$-$(CF_3SO_3)_6(H_2O)_4$ as a function of temperature. The full curve has been calculated with the parameters as given in the text.

Although the composition of these compounds closely resembles the composition of the Co compound with the metz ligand, it was not possible to decide whether the structure was identical or not. That means, from the results now available it is not possible to conclude that these compounds also consist of two independent clusters with different composition. Asymmetric compounds with a terminal monodentate ligand at one side of the cluster have been obtained earlier with 4-allyl-1,2,4-triazole [7].

$[Ni_2(mtbtz)_5(H_2O)_4](CF_3SO_3)_4(H_2O)_4$

The magnetic data recorded for this compound clearly shows that it differs largely from the other compounds in the present study. The χ *versus* T curve shows a maximum at about 28 K, indicating a dimeric compound. The data could in fact be fitted to the expression given by Ginsberg *et al.* [17] for a dinuclear Ni-compound, including zerofield splitting and intercluster exchange; the results were $J = -12.4(1)$ cm^{-1}, $g = 2.3(1)$, $J' = -2.9(1)$ cm^{-1}, $D = -11.6(1)$ cm^{-1}. The elemental analyses also agrees with such a dinuclear structure. Therefore a structure is proposed in which the nickel ions are bridged by three triazole ligands, two ligands coordinate monodentately and the coordination sphere around Ni is completed by two coordinating water molecules.

Compared to $Ni_3(metz)_{12}(CF_3SO_3)_6$ the ligand field strength of $[Ni_2(mtbtz)_5(H_2O)_4](CF_3SO_3)_4$-$(H_2O)_4$ is smaller ($Dq = 1110$ *versus* 1060 cm^{-1}), which is in agreement with the difference in coordination sphere, NiN_4O_2 *versus* NiN_6 [18].

Other Metals

The use of copper with metz resulted into two different compounds with composition $Cu(metz)_2$-$(CF_3SO_3)_2(H_2O)_3$ and $Cu_3(metz)_{10}(CF_3SO_3)_6(H_2O)_6$, respectively. The structure of these compounds as well as their magnetic behaviour are not well understood yet, but they are still under investigation. The syntheses of iron(II) compounds with these two ligands were unsuccessful.

Conclusion

The use of the non-coordinating $CF_3SO_3^-$ anion leads in most cases to the synthesis of trinuclear compounds. All these compounds have the same overall structure, three metal ions in a linear arrangement, linked to each other by two pairs of three bridging triazole ligands. The coordination sphere around the two terminal metal ions is completed by water and/or monodentately coordinated ligands. Because of the poor crystal structure resolution it is not possible to derive conclusions about the superexchange pathway in the now used ligands.

However, all exchange parameters lie in the same range as observed for 4-substituted triazoles, which might be expected from the similarity of the overall structures of the several compounds. The research on the now introduced type of asymmetric triazole ligands appears to be promising, and both the effect of other anions, like the coordinating thiocyanate anion, and the effect of changing the N4-substituent are inviting for further investigations. Such investigations should also spread more light on the effect of the C3 substituent on the difference of the coordination sites. It also seems likely for synthesizing heterotrinuclear compounds of the type M'-M-M', in which M'(II) has a larger ion radius than M(II), based on the trinuclear structure as described above. The positions of methyl substituents will favor the coordination of larger ions on the terminal coordination sites.

Supplementary Material

A table with fractional parameters of the other atoms has been deposited with the Editor-in-Chief.

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