Transition-metal(II) Thiocyanate Coordination Compounds with 4-t-Butyl-1,2,4-triazole. Structure and Magnetic Properties

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Abstract

The synthesis, spectroscopy and structure of a series of t-Butrz coordination compounds with varying geometries is described. [Zn(t-Butrz)$_2$(NCS)$_2$] is a mononuclear compound, in which the Zn(II) ion is coordinated tetrahedrally.

[Mn$_2$(t-Butrz)$_4$(H$_2$O)(NCS)$_4$] and its Fe(II) analogue are both asymmetrical dinuclear compounds. In the manganese compound a small antiferromagnetic exchange (J – 0.5 cm^{-1}) is present.

The crystal structure of [Co$_3$(t-Butrz)$_8$(NCS)$_4$](NCS)$_2$(H$_2$O)$_9$ was determined at room temperature. It crystallizes in the space group $P2_1/n$, with lattice constants a = 15.616(3) Å, b = 14.168(4) Å, c = 19.517(7) Å, and β = 90.48(2)°. The unit cell contains two trinuclear units. In the linear trimer the Co centers are linked by three 1,2-bicoordinating t-Butrz groups (Co–Co: 3.88 Å). The central Co(II) ion is therefore coordinated by 6 t-Butrz ligands.

For the terminal Co ions the octahedral coordination is completed by two N-donating thiocyanate anions (Co–N: 2.10 Å) and a monodentate coordinating t-Butrz (Co–N: 2.13 Å). The non-coordinating nitrogen atom of this triazole ligand is involved in hydrogen bonding (O–N: 2.98 Å). The magnetic properties of this compound can be described in terms of a S = 1/2 formalism. Application of the Ising model yields J = –13.2 cm^{-1} and $g_{/\!/}$ = 7.8. The magnetic interaction in the corresponding isostructural Ni compound is antiferromagnetic also (J = –10.0 cm^{-1}, g = 2.02). [Co$_3$(t-Butrz)$_4$(NCS)$_6$](H$_2$O)$_2$ is a linear trinuclear compound in which the central Co(II) ion is coordinated octahedrally, while the terminal Co ions reside in tetrahedral coordination sites. Attempts to replace the terminal Co ions by Zn(II) ions appeared to be successful. The magnetic exchange in [Cu(t-Butrz)$_2$(NCS)$_2$](H$_2$O)$_{0.5}$ is antiferromagnetic and unusually strong. Based on spectral data a layer structure is proposed for this compound. Cd(t-Butrz)$_{1.5}$(NCS)$_2$ is a linear-chain type compound, containing alternating units of bridging ligands and unusual bridging NCS anions.

Introduction

The first coordination compounds with 1,2,4-triazole were described as early as 1900 [1]. Until 1970 most papers on this subject dealt with copper compounds, especially [CuCl$_2$(Htrz)], [CuCl(trz)(H$_2$O)$_2$] and [Cu(trz)$_2$] [2–8], in which trz stands for the deprotonated form of 1,2,4-triazole. After 1970 a variety of triazole coordination compounds was reported, some of which showed interesting features, especially from a magnetochemistry point of view. Reimann and Zocchi [9] reported the crystal structure of the linear trinuclear compound [Ni$_3$(Htrz)$_6$(H$_2$O)$_6$](NO$_3$)$_6$(H$_2$O)$_2$. The magnetic properties of this compound were studied in detail by Mackey and Martin [10] and by Engelfriet *et al.* [11]. Both found an antiferromagnetic exchange between the nearest neighbours, but disagreed about the role of an interaction between the terminal Ni–ions, J_{31}, in the fitting procedure.

Engelfriet *et al.* [12–19] discovered a series of interesting layered structures with 1,2,4-triazole, in which the ligands are bridging through the 2,4-nitrogen atoms. The coordination compounds have a general composition of [M(Htrz)$_2$(NCS)$_2$] for M = Mn, Fe, Co, Ni, Cu and Zn. The M–Htrz–M links form a 2-dimensional network. The layers are separated by NCS$^-$ groups, which also provide an interlayer exchange path via hydrogen bonding with Htrz groups in neighbouring layers. The magnetic behaviour shows pronounced 2-dimensional characteristics with ratios of inter-to-intralayer exchange, $|J/J'|$, of the order of $\simeq 10^{-2}$–10^{-3}. For Mn, Fe, Co and Ni the intralayer exchange is antiferromagnetic, while for the Cu-compound a ferromagnetic exchange was found.

4-Substituted 1,2,4-triazoles are forced to coordinate monodentately or in a 1,2-bidentate fashion. Engelfriet *et al.* reported the first well-characterised coordination compounds with 4-R-

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1,2,4-triazoles, *i.e.*, $[Co_2(Phtrz)_5(NCS)_4](H_2O)_{2.7}$ [20] and $[Mn_2(Metrz)_5(NCS)_4]$ [21]. Both compounds are dinuclear and behave antiferromagnetically. Recently we reported a series of coordination compound with 4-ethyl-1,2,4-triazole [22–24] and 4-allyl-1,2,4-triazole [24, 25]. Predominantly dinuclear compounds were obtained, also showing an antiferromagnetic exchange between the metal centers. In this paper coordination compounds with 4-t-butyl-1,2,4-triazole are described. It is shown that the different electronic properties and the compact nature of the t-butyl group result in a series of coordination compounds with different geometries compared to the earlier-described coordination compounds [20–25].

Experimental

Syntheses

4-t-butyl-1,2,4-triazole

The ligand t-Butrz was prepared according to a method described by Bayer *et al.* [26]. A solution of 1.5 mol triethylorthoformate and 1 mol monoformylhydrazine in 400 ml of anhydrous methanol was refluxed for 3.5 h. Then 1 mol of t-butylamine was added slowly to the boiling solution. After the addition of the amine the solution was refluxed for another 4 h. The solvent was then removed under reduced pressure.

Finally the crude product was recrystallized from a CCl_4/diethylether mixture. Yield: 64%; melting point: ≈30 °C; NMR: 1.62 ppm (s, 9 H), 8.30 ppm (s, 2 H). The melting point could not be determined accurately, since the compound is very hygroscopic. Bayer *et al.* [26] reported a boiling point of 128–132 °C at 1 mm Hg.

Coordination Compounds

$[Mn_2(t\text{-}Butrz)_4(H_2O)(NCS)_4]$

10 mmol t-Butrz in 20 ml of water was added slowly to a hot solution of manganese(II) nitrate (5 mmol) and ammonium thiocyanate (10 mmol) in 20 ml of water. By boiling the solution its volume was reduced to 30 ml. On slowly cooling to ambient temperature the compound crystallized.

$[Fe_2(t\text{-}Butrz)_4(H_2O)(NCS)_4]$

7.5 mmol t-Butrz in 10 ml of hot water was added to a boiling solution of 3.75 mmol iron(II) chloride and 7.5 mmol ammonium thiocyanate in 40 ml of hot water. Sulfur dioxide was passed through the solution for 1 min. The compound crystallized upon standing at room temperature for a few days.

$[Co_3(t\text{-}Butrz)_8(NCS)_4](NCS)_2(H_2O)_9$

Cobalt(II) nitrate hydrate (1.37 mmol) and a small molecular excess of ammonium thiocyanate were dissolved in about 25 ml of warm water. A solution of 8.22 mmol t-Butrz in 25 ml of water was added slowly to the boiling solution of the metal salt. A few drops of concentrated ammonia were added and the volume of the solution was reduced to 40 ml. The solution was slowly cooled and, after standing for several days at ambient temperature, the compound crystallized.

$[Co_3(t\text{-}Butrz)_4(NCS)_6](H_2O)_2$

A hot solution of 2.63 mmol t-Butrz in 25 ml of water was added to a boiling aqueous solution (25 ml) of 1.75 mmol hydrated cobalt(II) nitrate and ammonium thiocyanate (3.5 mmol). The solution was acidified with a few drops of nitric acid. The volume of the solution was reduced to 40 ml by boiling. The compound crystallized upon standing at room temperature.

$[Ni_3(t\text{-}Butrz)_8(NCS)_4](NCS)_2(H_2O)_9$

A solution of 10 mmol t-Butrz in 25 ml of hot water was added slowly to a boiling solution of hydrated nickel(II) nitrate (2 mmol) and ammonium thiocyanate (4 mmol) in water (25 ml). The volume of the solution was reduced to 40 ml and, after cooling to ambient temperature, blue-purple crystals were formed after several days.

$[Zn(t\text{-}Butrz)_2(NCS)_2]$

2.5 mmol hydrated zinc(II) nitrate and 5 mmol ammonium thiocyanate were dissolved in 25 ml of hot water. 5 mmol t-Butrz in 25 ml of hot water was added slowly to the boiling metal salt solution. The volume of the solution was reduced to 40 ml. The compound crystallized upon standing.

$[Cd_2(t\text{-}Butrz)_3(NCS)_4]_\infty$

5 mmol t-Butrz in 20 ml of water was added slowly to a hot solution of hydrated cadmium(II) nitrate (2.5 mmol) and ammonium thiocyanate (5 mmol) in 20 ml of water. After reduction of the volume to 30 ml, the solution was slowly cooled to room temperature. Crystallization occurred upon standing for several days.

Analyses and Physical Measurements

Metal analyses were carried out by complexometric titrations [27] after prior decomposition of the compounds in boiling nitric acid. C, H and N analyses were carried out by the Pascher Analytic Laboratory in Bonn, F.R.G.

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. Laser-Raman spectra in the solid state were recorded on a Cary-81 instrument, equipped with an Argon gas laser, using 100 mW power. The EPR spectra of powdered Cu samples were recorded at room temperature and at liquid nitrogen temperature on a Varian E3 at X-band frequencies, employing a 100 kHz field modulation. The NMR spectra were recorded on a JEOL PS-100 spectrophotometer in the Fourier transform mode, operating at 100 MHz. Magnetic susceptibility measurements from 80–300 K were performed by means of an automated Faraday balance, described by Arbouw [28]. Susceptibility measurements between 2 K and 80 K were carried out using a PAR vibrating sample magnetometer model 150A with a Janis cryostat described by Engelfriet [19]. X-ray powder diffraction patterns were recorded with a Philips PW 1050 powder diffractometer, using Cu-Kα radiation and a Nickel-filter.

X-Ray Data Collection for [Co_3(t-Butrz)$_8$(NCS)$_4$]-(NCS)$_2$(H_2O)$_9$

A single crystal, which appeared to be of good quality, was mounted on an Enraf Nonius CAD-4 diffractometer. Mo-Kα radiation, monochromatised by graphite, was used for the determination of the unit cell parameters as well as for measuring the reflection intensities. The data were corrected for Lorentz and polarisation effects and for absorption [29]. The experimental density was determined by the flotation method in a mixture of 1,2-dibromoethane and cyclohexane. Relevant crystal and diffraction data are given in Table I.

Solution of the Molecular Structure of hexakis-μ-(4-t-butyl-1,2,4-triazole-N^1,N^2)bis(4-t-butyl-1,2,4-triazole-N^1)tetrakis(thiocyanato-N)tricobalt-(II)bis(thiocyanate) nonahydrate

All calculations were carried out on the Leiden University Amdahl V7B computer, using a local set of programs written or modified by Mrs. E. Rutten-Keulemans, Dr. R. A. G. de Graaff and Mrs. S. Gorter. Scattering factors and anomalous dispersion corrections were taken from the International Tables for X-ray Crystallography [30]. The function minimized during the least-squares refinement was $\Sigma w(\Delta F)^2$, with $\Delta F = |F_o| - |F_c|$ and the weighting scheme $w = (\sigma_F)^{-2}$. Discrepancy indices referred to are defined as $R = \Sigma|\Delta F|/\Sigma|F_o|$ and $R_w = [\Sigma w(\Delta F)^2/\Sigma w F_o{}^2]^{1/2}$.

A three-dimensional Patterson synthesis yielded the position of two Co atoms. The program DIRDIF (direct methods on difference structure factors) [31] revealed almost the complete structure. Five cycles of isotropic refinement yielded $R = 0.186$ ($R_w = 0.227$). The t-butyl groups had large temperature factors because of their free rotational mobility. Therefore, they were difficult to refine and slack constraints had to be used [32]. Two extra oxygen atoms were found in a difference Fourier synthesis. After three cycles of anisotropic refinement for all atoms located, R decreased to 0.096 ($R_w = 0.144$). A new difference Fourier synthesis revealed a non-coordinating NCS^- group. The group showed disorder. The C atom of this group was located on or near an inversion centre (1/2, 0, 0). The matrix of the coefficients of the normal equations was divided into four separate blocks. The first block contained the Co atoms and the bridging t-Butrz groups, the second the N(1) coordinated t-Butrz. The third block contained the two coordinating NCS^- groups and the last block was holding all non-coordinating groups.

TABLE I. Relevant Crystal and Diffraction Data for [Co_3(t-Butrz)$_8$(NCS)$_4$](NCS)$_2$(H_2O)$_9$.

Space group	$P2_1/c$
Lattice constants	
a (A)	15.616(3)
b (A)	14.168(4)
c (A)	19.517(7)
β (°)	90.48(2)
Z	2
Crystal dimensions (mm)	0.2 × 0.3 × 0.5
θ range (°)	2–22
Measured reflections	5492
Independent reflections	5297
Significant reflections	2089 (2904^a)
Experimental density (Mg m^{-3})	1.28
Calculated density (Mg m^{-3})	1.30
Final R (R_w)	0.046 (0.045)
μ (Mo-Kα) (cm^{-1})	7.69

[a] Including low order reflections.

Several isotropic refinements of the free NCS^- group decreased R to 0.080 ($R_w = 0.117$). One NCS^- and $5H_2O$ molecules were still missing and the R value remained high. A difference Fourier synthesis of all significant reflections showed no peaks, which could be attributed to the missing thiocyanate group or the water molecules. A quarter of the unit cell was searched for empty spaces and one hole was found at about the fractional coordinates $x \approx 0.550$, $y \approx 0.310$–0.440 and $z \approx 0.050$. This hole was large enough to contain one NCS^- group. Examining difference Fourier synthesis again however showed nothing interpretable. The conclusion was that the remaining thiocyanate group and the H_2O molecules had to be in complete disorder. In order to support this conclusion, low order reflections ($\sin(\theta/\lambda) < 0.3$) were removed. Least-squares refinement now converged to $R = 0.048$ ($R_w = 0.048$), showing that the missing NCS^- and H_2O only contributes significantly to the low order reflections, in accordance with the conclusion given earlier.

The H atoms attached to the t-butyl groups could not be calculated due to the rotational motion of the methyl groups. The hydrogens belonging to the triazole rings were placed in the plane of the ring at a distance of 0.95 Å from the parent atoms. Three cycles of anisotropic refinement of the final model (for $\sin(\theta/\lambda) > 0.3$), yielded R = 0.046 ($R_w = 0.045$). The same model, but now using all significant reflections, gave an R of 0.080 ($R_w = 0.156$).

A final difference Fourier synthesis (for $\sin(\theta/\lambda) > 0.3$) showed only three small peaks, with a maximum height of 0.39 eÅ^{-3} (statistical noise level = 0.086 eÅ^{-3}). Two of these peaks lie near the third (free) NCS$^-$ group and one is located in the hole.

The positional parameters are listed in Table II[†].

TABLE II. Fractional Coordinates ($\times 10^4$) and Isotropic Temperature Factors (Å^2) of the Atoms of [Co_3(t-Butrz)$_8$(NCS)$_4$](NCS)$_2$(H_2O)$_9$.

	x/a	y/b	z/c	B_{iso}
Co(1)	0	0	0	2.51(3)
Co(2)	−1339.6(6)	899.2(7)	1534.6(5)	2.92(3)
N(11)	459(4)	138(4)	1025(3)	3.0(2)
N(12)	40(4)	434(4)	1556(3)	3.1(2)
C(13)	440(6)	407(6)	2095(4)	3.6(2)
N(14)	1223(4)	101(5)	1955(3)	3.6(2)
C(15)	1209(5)	−56(6)	1278(3)	3.3(2)
C(16)	1974(4)	2(6)	1439(3)	4.4(2)
C(17)	2516(10)	865(11)	1343(10)	12.0(6)
C(18)	2434(7)	−907(10)	2269(6)	9.4(5)
C(19)	1615(7)	−100(13)	3155(4)	9.2(5)
N(21)	−605(4)	1367(4)	75(3)	2.8(2)
N(22)	−1073(4)	1672(4)	618(3)	3.2(2)
C(23)	−1359(5)	2497(6)	460(4)	3.5(2)
N(24)	−1084(4)	2765(4)	−162(3)	3.5(2)
C(25)	−624(5)	2026(6)	−375(4)	3.4(2)
C(26)	−1316(4)	3637(4)	−563(3)	4.7(2)
C(27)	−1670(12)	4357(7)	−74(6)	9.6(5)
C(28)	−1967(7)	3348(8)	−1099(5)	7.2(3)
C(29)	−514(7)	3999(8)	−902(7)	7.9(4)
N(31)	−1147(4)	−631(4)	372(3)	2.9(2)
N(32)	−1625(4)	−297(4)	901(3)	3.4(2)
C(33)	−2257(5)	−868(6)	979(4)	3.8(2)
N(34)	−2233(4)	−1576(4)	515(3)	3.4(2)
C(35)	−1523(4)	−1381(6)	152(4)	3.5(2)
C(36)	−2833(4)	−2396(5)	415(3)	4.6(2)
C(37)	−2295(8)	−3280(6)	398(9)	9.2(5)
C(38)	−3445(8)	−2412(11)	1010(6)	8.9(4)
C(39)	−3285(9)	−2220(11)	−264(6)	9.4(5)
N(41)	−2637(4)	1362(5)	1513(3)	3.7(2)
N(42)	−3117(6)	1401(11)	945(4)	8.4(4)
C(43)	−3879(8)	1616(17)	1129(6)	10.1(6)
N(44)	−3917(4)	1737(7)	1823(4)	6.3(3)
C(45)	−3118(6)	1556(8)	2002(5)	5.2(3)
C(46)	−4681(5)	1877(11)	2273(5)	9.6(6)
C(47)	−4440(13)	2630(23)	2782(14)	23(2)
C(48)	−4865(14)	955(17)	2640(15)	20(2)
C(49)	−5447(9)	2121(21)	1835(10)	15(1)
N(1)	−965(6)	2058(6)	2135(4)	4.6(2)
C(1)	−445(8)	2479(7)	2440(5)	4.2(2)
S(1)	269(2)	3060(2)	2862(2)	6.4(1)
N(2)	−1642(4)	86(6)	2393(3)	4.4(2)
C(2)	−2029(6)	−439(7)	2734(4)	4.1(2)
S(2)	−2525(3)	−1146(2)	3224(2)	9.3(1)
O(1)	830(10)	2720(11)	1061(6)	12.8(5)
O(2)	7239(6)	4257(13)	4573(4)	11.9(5)
N(3)[a]	5188	318	−517	14.2(5)
C(3)[a]	5000	0	0	14.2(5)
S(3)[a]	4718	−407	732	14.2(5)
H(13)	259	592	2539	5.00[b]
H(15)	1683	−275	1022	5.00
H(23)	−1749	2830	742	5.00
H(25)	−345	1996	−805	5.00
H(33)	−2689	−800	1315	5.00
H(35)	−1325	−1754	−218	5.00
H(43)	−4351	1684	822	5.00
H(45)	−2922	1578	2464	5.00

[a] Parameters were found in a difference Fourier synthesis. Further refinement was not possible. [b] The isotropic thermal parameters of the hydrogen atoms were taken 5.00 and were not refined.

Results and Discussion

General

The synthesized coordination compounds are listed in Table III, together with colours, analyses, structure types and melting points. The infrared and ligand field data are listed in Tables IV and V, respectively. The compounds will be discussed separately.

[Zn(t-Butrz)$_2$(NCS)$_2$]

The compound [Zn(t-Butrz)$_2$(NCS)$_2$] is one of the few examples of coordination compounds with monodentately-coordinating 1,2,4-triazoles. The structure, of which the detailed results were published previously [33], consists of mononuclear units in which the Zn center is coordinated tetrahedrally by two N donating NCS$^-$ groups and two t-Butrz ligands coordinating by only one N atom. Other known mononuclear 1,2,4-triazole compounds are [Mn(Htrz)(H_2O)$_4$·SO_4] [34] and a series of Cr and W pentacarbonyl compounds with Phtrz and Metrz [35, 36].

[Zn(t-Butrz)$_2$(NCS)$_2$] clearly shows the strong symmetry-determining function of the t-butyl group with respect to the triazole ring. It is known

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[†] List of structure factors and anisotropic thermal parameters are available from the author on request.

TABLE III. Analytical Data, Colours, Structure Types and Melting Points of Coordination Compounds Containing t-Butrz.

Compound	Structure		Elemental analyses[a]				
	Type	Colour	% M	% C	% N	% H	m.p. (°C)
[Mn_2(t-Butrz)$_4$(H_2O)(NCS)$_4$]	A	white	12.5	38.8	26.4	5.3	205–207
			(12.8)	(39.1)	(26.0)	(5.4)	
[Fe_2(t-Butrz)$_4$(H_2O)(NCS)$_4$]	A	white	13.0				240–242
			(12.9)				
[Co_3(t-Butrz)$_8$(NCS)$_4$](NCS)$_2$(H_2O)$_9$	B	orange	10.6	38.1	24.6	5.9	144–148[b]
			(10.5)	(38.4)	(24.9)	(6.3)	
[Co_3(t-Butrz)$_4$(NCS)$_6$](H_2O)$_2$	C	dark-blue	16.7	33.3	24.0	4.6	>250
			(16.7)	(33.9)	(23.7)	(4.6)	
[Co_2Zn(t-Butrz)$_4$(NCS)$_6$](H_2O)$_2$	C	grey	Co: 9.6	33.2	23.6	4.7	241–243
			(11.0)	(33.7)	(23.6)	(4.5)	
			Zn: 6.9				
			(6.1)				
[CoZn$_2$(t-Butrz)$_4$(NCS)$_6$](H_2O)$_2$	C	orange	Co: 6.2	32.7	23.0	4.6	233–235
			(5.5)	(33.5)	(23.5)	(4.5)	
			Zn: 10.7				
			(12.2)				
[Ni_3(t-Butrz)$_8$(NCS)$_4$](NCS)$_2$(H_2O)$_9$	B	purple	10.3	38.0	25.3	6.3	>250
			(10.4)	(38.4)	(24.9)	(6.3)	
[Cu(t-Butrz)$_2$(NCS)$_2$](H_2O)$_{0.5}$	D	green	14.4	38.0	25.1	5.1	
			(14.5)	(38.3)	(25.5)	(5.3)	
[Zn(t-Butrz)$_2$(NCS)$_2$][c]	E	white	15.2	38.8	26.2	5.2	226–228
			(15.1)	(38.9)	(26.0)	(5.1)	
[Cd_2(t-Butrz)$_3$(NCS)$_4$]$_\infty$[c]	F	light-yellow	27.0	31.6	21.5	4.0	>250
			(27.0)	(31.7)	(21.9)	(4.0)	

[a] Calculated values in parentheses. [b] On heating the compound turns blue. [c] Single crystal X-ray structures are reported elsewhere [33, 57].

TABLE IV. Relevant Infrared Vibration Absorptions and Tentative Assignments of Coordination Compounds Containing t-Butrz.

Compound	ν(CN)	ν(CS)	δ(NCS)	γ(C–H)	τ	F.I.R.[a]
[Mn_2(t-Butrz)$_4$(H_2O)(NCS)$_4$]	2082 (sh)	792 (w)	500 (sh)	900 (vw)	685 (vw)	265 (m)
	2068 (vs)	785 (sh)	480 (m)	882(m)	660 (vs)	240 (s)
	2048 (sh)			870 (m)		220 (s)
						205 (s)
[Fe_2(t-Butrz)$_4$(H_2O)(NCS)$_4$]	2090 (sh)	794 (w)	499 (sh)	905 (vw)	688 (vw)	268 (m)
	2075 (vs)	785 (sh)	480 (m)	888 (m)	660 (vs)	244 (s)
	2059 (sh)			872 (m)		222 (s)
						203 (m)
[Co_3(t-Butrz)$_8$(NCS)$_4$](NCS)$_2$(H_2O)$_9$	2089 (vs)	789 (w)	480 (m)	905 (sh)	686 (vw)	235 (s)
	2057 (vs)		465 (w)	898 (m)	660 (vs)	195 (w)
[Co_3(t-Butrz)$_4$(NCS)$_6$](H_2O)$_2$	2120 (sh)	835 (w)	480 (m)	899 (m)	661 (vs)	305 (vs)
	2090 (s)		460 (sh)	860 (vw)		240 (m)
						205 (w)
[Co_2Zn(t-Butrz)$_4$(NCS)$_6$](H_2O)$_2$	2120 (sh)	818 (m)	478 (m)	898 (m)	659 (vs)	305 (sh)
	2093 (s)	470 (sh)				285 (s)
						235 (s)
[CoZn$_2$(t-Butrz)$_4$(NCS)$_6$](H_2O)$_2$	2120 (sh)	818 (m)	475 (m)	895 (m)	659 (vs)	285 (s)
	2093 (s)		465 (sh)			235 (s)
[Ni_3(t-Butrz)$_8$(NCS)$_4$](NCS)$_2$(H_2O)$_9$	2095 (vs)	790 (m)	487 (m)	902 (m)	690 (w)	267 (s)
	2075 (s)	740 (w)	472 (w)	865 (m)	661 (vs)	
[Cu(t-Butrz)$_2$(NCS)$_2$](H_2O)$_{0.5}$	2068 (s)	800 (w)	505 (w)	890 (m)	685 (vw)	325 (m)
	2045 (sh)	762 (m)	483 (m)	865 (sh)	659 (vs)	274 (s)
	2020 (vs)		460 (m)			246 (w)
						206 (w)

(continued overleaf)

TABLE IV *(continued)*

Compound	ν(CN)	ν(CS)	δ(NCS)	γ(C–H)	τ	F.I.R.[a]
[Zn(t-Butrz)$_2$(NCS)$_2$]	2099 (vs)	838 (w)	485 (m)	885 (s)	680 (vw)	288 (s)
	2084 (sh)			852 (m)	660 (vs)	223 (m)
						196 (m)
[Cd$_2$(t-Butrz)$_3$(NCS)$_4$]$_\infty$	2038 (vs)	802 (w)	525 (m)	895 (m)	660 (vs)	262 (m)
	1982 (vs)		498 (w)	880 (m)	653 (vs)	240 (m)
	1940 (sh)		480 (m)	855 (m)		185 (s)

[a] Unassigned absorptions in the far-infrared region.

TABLE V. Ligand Field Spectra (Diffuse Reflectance) of Coordination Compounds Containing t-Butrz.

Compound	Ligand field bands (cm^{-1})			Dq (cm^{-1})	B (cm^{-1})
Fe$_2$(t-Butrz)$_4$(H$_2$O)(NCS)$_4$]	10.950				
[Co$_3$(t-Butrz)$_8$(NCS)$_4$](NCS)$_2$(H$_2$O)$_9$	10.300	16.670	21.275	1125	815
[Co$_3$(t-Butrz)$_4$(NCS)$_6$](H$_2$O)$_2$	9.500	20.450		1040	810
	8.260	16.670		480	700
[Co$_2$Zn(t-Butrz)$_4$(NCS)$_6$](H$_2$O)$_2$	9.350	20.600		a	
	16.450				
[CoZn$_2$(t-Butrz)$_4$(NCS)$_6$](H$_2$O)$_2$	10.000	20.500			
	16.700				
[Ni$_3$(t-Butrz)$_8$(NCS)$_4$](NCS)$_2$(H$_2$O)$_9$	11.500	18.430		1155	b
[Cu(NCS)$_2$(t-Butrz)$_2$](H$_2$O)$_{0.5}$	15.950				

[a] σ_1(Oh) and σ_2(Td) coincide, which makes an accurate calculation of Dq and B impossible. [b] σ_3 is not observed, probably due to the different geometries for the Ni ions. Calculation of B based on σ_1 and σ_2 only yields an unreliable value for this parameter.

that 1,2,4-triazole with local C_{2v}-symmetry (1,2-bicoordination) has only one infrared active ring torsion vibration. When the symmetry is reduced to C_s the second out-of-plane ring vibration is supposed to become infrared active [37, 38]. For [Zn(t-Butrz)$_2$(NCS)$_2$], therefore, two ring torsion vibrations are to be expected in the infrared spectrum. Two absorptions are indeed observed (680 cm^{-1} and 660 cm^{-1}), but the high-frequency out-of-plane ring absorption is very weak. This implies that the C_{2v}-symmetry of the triazole ring is only slightly distorted by the monodentate coordination and that the symmetry of the ligand is mainly determined by the t-butyl group. The C–H out-of-plane absorption is split (885 and 852 cm^{-1}) and clearly shows the presence of monodentate t-Butrz. The ring–t-butyl stretching vibration was located with Raman spectroscopy and assigned to the 585 cm^{-1} frequency absorption.

The relatively high position of the M–N band at 288 cm^{-1} agrees with the tetrahedral coordination of the Zn center [39, 40]. The position of ν(CS) (838 cm^{-1}) also indicates the presence of thiocyanates in a tetrahedral environment. The ν(CN) absorption around 2090 cm^{-1} is in agreement with N donation of the thiocyanate group [41–43].

[M$_2$(t-Butrz)$_4$(H$_2$O)(NCS)$_4$] (M = Mn(II), Fe(II))

The infrared spectra of the mutually isostructural Mn(II) and Fe(II) compounds are similar. The absorption of the C–H out-of-plane vibration is split (900 (w), 882 (m), 870 (s) cm^{-1}) and two out-of-plane ring torsions are observed (685 (w), 660 (vs) cm^{-1}), suggesting the presence of both mono- and bidentate coordinating t-Butrz [37, 38]. The position of the ν(CN), ν(CS) and δ(NCS) absorptions (see Table IV) indicate that only N coordination of the thiocyanate groups [41–43] occurs. The asymmetry of the bands originating from the H$_2$O molecules suggests coordination of the solvent, or at least strong hydrogen bonding [44, 45]. The ligand field spectrum of the Fe(II) compound agrees with octahedral coordination of the Fe(II) ions (Table V). The position of the ligand field maximum of the asymmetric band (10.900 cm^{-1}) reveals that Fe(II) is in the high-spin state.

Based on the analyses, infrared and ligand field data, a dinuclear structure is proposed in which the metal ions are linked by three bridging t-Butrz ligands. The octahedron around one metal ion is completed by two N donating NCS$^-$ groups and a t-Butrz coordinating by only one N atom. At the second metal center, the terminal t-Butrz group is replaced by a coordinating H_2O molecule. Similar, asymmetrical structures have been found with Ettrz [22–24] and Altrz [24, 25]. Elemental analyses indicate the absence of non-coordinating H_2O molecules. In the Ettrz and Altrz compounds, non-coordinating water molecules stabilize the structures, by forming intermolecular hydrogen bridges [22–25].

The magnetic behaviour of $[Mn_2(t\text{-}Butrz)_4(H_2O)(NCS)_4]$ is in accordance with a dinuclear structure. The magnetic susceptibility data were fitted by means of the method of least-squares to the equation for χ, resulting from the spin Hamiltonian for an isotropic magnetic exchange, $H = -2J\vec{S}_1\cdot\vec{S}_2$, with $S_1 = S_2 = 5/2$ [46]. A reasonable fit was obtained, assuming $D = 0$, yielding $J = -0.5$ cm^{-1} and $g = 1.99$, indicating a weak antiferromagnetic exchange between the manganese centers. Since the Fe(II) in $[Fe_2(t\text{-}Butrz)_4(H_2O)(NCS)_4]$ is readily oxidized to Fe(III) after removal of the solvent, the magnetic data of this compound were not collected.

$[M_3(t\text{-}Butrz)_8(NCS)_4](NCS)_2(H_2O)_9$ (M = Co(II), Ni(II))

The structure of the trinuclear Co compound was determined by single-crystal X-ray diffraction techniques.

The structure consists of linear trinuclear units. The metal atoms are linked by three N^1,N^2-donating t-Butrz groups. The central Co(II) atom is surrounded by six t-Butrz groups. The coordination around the terminal metal ions is completed by two N-donating NCS^- groups and a t-Butrz coordinating with only one N atom.

The complete unit of $[Co_3(t\text{-}Butrz)_8(NCS)_4]^{2+}$ is depicted in Fig. 1, together with the atomic numbers. Relevant distances and angles are given in Tables VI and VII. As can be seen from Table VI, the CoN_6 octahedra of the terminal Co atoms are slightly distorted. The geometries of the t-Butrz rings are comparable with the trz rings in $[Ni_3(Htrz)_6(H_2O)_6](NO_3)_6(H_2O)_2$ [9] and in other coordination compounds with 4-substituted 1,2,4-triazoles [20–25].

Relevant intermolecular distances are given in Table VIII. The only clear hydrogen bridge exists between O(2) and N(42) (O···N distance 2.89(1) Å). The existence of a hydrogen bond is the more probable as the fourth t-Butrz, which is otherwise free to rotate around the Co–N(41) axis, apparently does not do so. Three other examples of linear trimers with 1,2,4-triazoles have been described, *e.g.*: $[Ni_3(Htrz)_6(H_2O)_6](NO_3)_6(H_2O)_2$ [9], $[Ni_3(Htrz)_6(H_2O)_6](SO_4)_3(H_2O)_9$ [19] and $[Ni_3(Htrz)_6(NCS_6]$ [19]. No linear Co-trimers with 1,2,4-triazoles have been reported before.

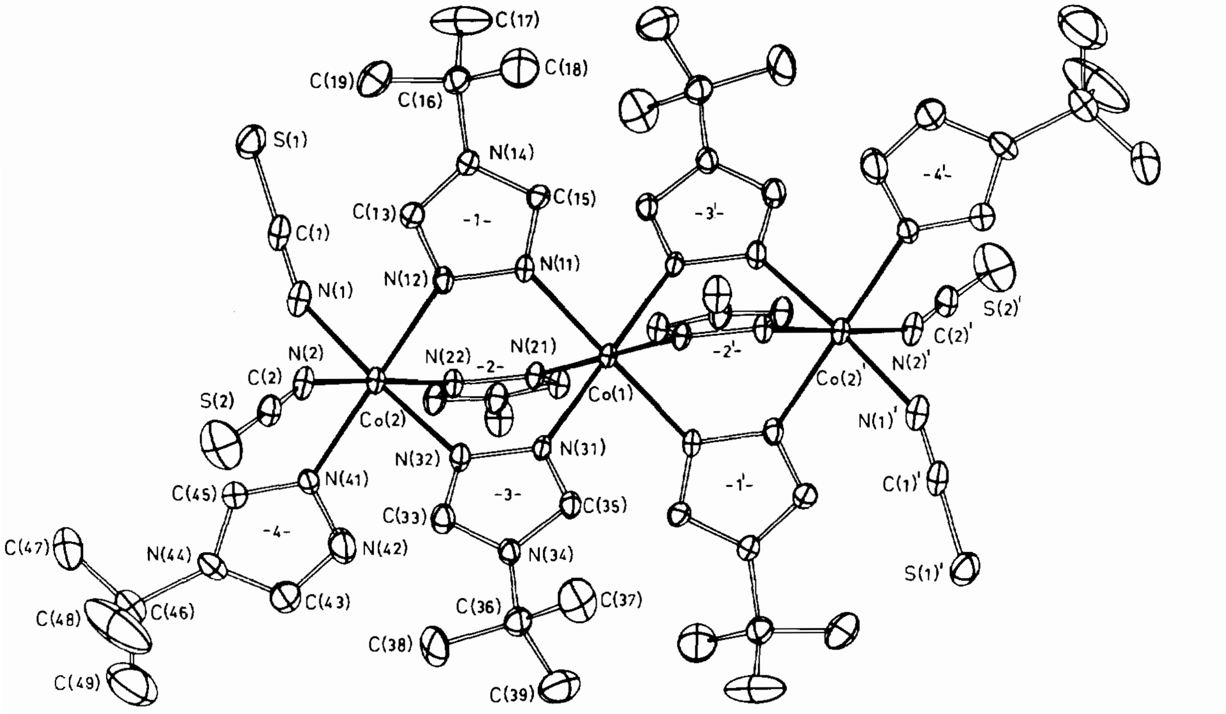

Fig. 1. Perspective view of the trinuclear unit of $[Co_3(t\text{-}Butrz)_8(NCS)_4]^{2+}$. The atom numbering cooresponds to that in Tables II, VI, VII and VIII. The t-Butrz rings have been numbered. Rings 1′, 2′, 3′ and 4′ are related to rings 1, 2, 3 and 4 by a reflection through the inversion center (0, 0, 0). The same applies too to the primed numbers of the NCS^- groups. The H atoms and the methyl groups of ring 2 have been left out for clarity.

TABLE VI. Intramolecular Distances (Å) and Angles (°) in $[Co_3(t\text{-}Butrz)_8(NCS)_4]^{2+}$ except t-Butrz Groups. Experimental Standard Deviations include Errors in the Cell Parameters.

Co(1)–Co(2)	3.8828(9)	Co(2)–N(41)	2.129(6)
Co(1)–N(11)	2.128(6)	Co(2)–N(1)	2.10(1)
Co(1)–N(21)	2.161(6)	Co(2)–N(2)	2.091(8)
Co(1)–N(31)	2.135(6)	N(1)–C(1)	1.17(1)
Co(2)–N(12)	2.134(6)	N(2)–C(2)	1.17(1)
Co(2)–N(22)	2.141(6)	C(1)–S(1)	1.61(1)
Co(2)–N(32)	2.143(6)	C(2)–S(2)	1.59(1)
N(11)–Co(1)–N(21)	89.9(2)	Co(1)–N(11)–N(12)	123.5(4)
N(11)–Co(1)–N(31)	90.3(2)	Co(1)–N(11)–C(15)	129.5(4)
N(21)–Co(2)–N(31)	89.1(2)	Co(1)–N(21)–N(22)	125.1(4)
N(12)–Co(2)–N(22)	89.0(2)	Co(1)–N(21)–C(25)	127.9(4)
N(12)–Co(2)–N(32)	87.7(3)	Co(1)–N(31)–N(32)	125.4(5)
N(12)–Co(2)–N(41)	179.9(1)	Co(1)–N(31)–C(35)	127.9(5)
N(12)–Co(2)–N(1)	88.2(3)	Co(2)–N(12)–N(11)	128.8(5)
N(12)–Co(2)–N(2)	92.0(2)	Co(2)–N(12)–C(13)	124.9(5)
N(22)–Co(2)–N(32)	87.9(3)	Co(2)–N(22)–N(21)	126.7(5)
N(22)–Co(2)–N(41)	91.0(2)	Co(2)–N(22)–C(23)	126.5(5)
N(22)–Co(2)–N(1)	90.7(3)	Co(2)–N(32)–N(31)	126.8(5)
N(22)–Co(2)–N(2)	176.5(3)	Co(2)–N(32)–C(33)	125.8(5)
N(32)–Co(2)–N(41)	92.2(3)	Co(2)–N(41)–N(42)	123.9(5)
N(32)–Co(2)–N(1)	175.8(3)	Co(2)–N(41)–C(45)	129.1(6)
N(32)–Co(2)–N(2)	88.8(3)	Co(2)–N(1)–C(1)	151.1(7)
N(41)–Co(2)–N(1)	91.8(3)	Co(2)–N(2)–C(2)	158.1(6)
N(41)–Co(2)–N(2)	88.0(3)	N(1)–C(1)–S(1)	178(1)
N(1)–Co(2)–N(2)	92.7(3)	N(2)–C(2)–S(2)	177.5(8)

TABLE VII. Bond Lengths (Å) and Angles (°) in the t-Butrz Groups in $[Co_3(t\text{-}Butrz)_8(NCS)_4]^{2+}$.

	ring 1	ring 2	ring 3	ring 4
N(1)–N(2)	1.369(8)	1.363(8)	1.363(8)	1.33(1)
N(2)–C(3)	1.29(1)	1.29(1)	1.29(1)	1.28(1)
C(3)–N(4)	1.33(1)	1.35(1)	1.35(1)	1.37(1)
N(4)–C(5)	1.338(9)	1.34(1)	1.35(1)	1.32(1)
C(5)–N(1)	1.30(1)	1.282(9)	1.29(1)	1.25(1)
N(4)–C(6)[a]	1.507(7)	1.505(7)	1.505(7)	1.500(8)
C(6)–C(7)[a]	1.500(9)	1.505(8)	1.509(8)	1.504(9)
C(6)–C(8)[a]	1.512(9)	1.509(8)	1.511(8)	1.518(9)
C(6)–C(9)[a]	1.517(8)	1.511(8)	1.516(8)	1.505(9)
N(1)–N(2)–C(3)	106.2(6)	106.8(6)	107.3(6)	107.0(8)
N(2)–C(3)–N(4)	111.8(6)	111.1(6)	111.2(6)	110(1)
C(3)–N(4)–C(5)	104.5(6)	103.6(6)	103.2(6)	100.9(8)
N(4)–C(5)–N(1)	110.5(6)	111.6(6)	111.6(6)	114.4(8)
C(5)–N(1)–N(2)	107.0(5)	107.0(6)	106.7(6)	106.7(7)
C(3)–N(4)–C(6)[a]	127.9(5)	128.5(6)	129.7(5)	129.7(9)
C(5)–N(4)–C(6)[a]	127.6(6)	127.6(5)	127.2(6)	128.7(9)
C(7)–C(6)–C(8)[a]	113(1)	112.0(9)	111.1(9)	110(1)
C(7)–C(6)–C(9)[a]	114(1)	111.0(9)	111.9(9)	114(1)
C(8)–C(6)–C(9)[a]	107.5(9)	110.2(7)	112.4(9)	108(1)

[a] Refined with constraints.

The ligand field and infrared data are in agreement with the crystal structure. The ligand field spectra show an octahedral coordination of the metal ions with a Dq value of 1125 cm^{-1} for the Co compound and of 1155 cm^{-1} for the Ni compound (see Table V). The splitting of ν(CN) and ν(CS) (for the Ni compound) indicates the presence of both N donating and non-coordinating ionic thiocyanate groups

TABLE VIII. Relevant Intermolecular Distances (Å) (<3.00 Å) between Neighbouring Trimeric Units in $[Co_3(t\text{-}Butrz)_8(NCS)_4(H_2O)_4]^{2+}$.

O(2)–H(15)	2.16(1)
O(2)–N(42)	2.89(1)
S(1)–H(25)	2.782(7)

(Table IV) [41–43]. The splitting of the C–H out-of-plane absorptions is not very clear, but the observation of two ring torsion absorptions (Table IV) confirms the presence of both mono and bidentate t-Butrz groups [37, 38]. For both compounds, one strong M–N absorption is observed (Table IV).

Magnetic susceptibility data were collected for both the Co and Ni compounds between 2 K and 80 K. For a linear trinuclear Ni compound, the magnetic susceptibility can be calculated using the Hamiltonian $H = -2J[(\vec{S}_1\cdot\vec{S}_2) + (\vec{S}_2\cdot\vec{S}_3)] - 2J_{31}(\vec{S}_3\cdot\vec{S}_1)$ where the subscripts refer to the individual Ni-ions which are numbered in sequence. The magnetic data of $[Ni_3(t\text{-}Butrz)_8(NCS)_4](NCS)_2(H_2O)_9$ were compared with Ginsberg's formula [47], taking $J_{31} = 0$. Zero-field splittings and intercluster interactions were supposed to be negligible and g was assumed to be equal for all the individual Ni-ions. The least-squares fit of the inverse powder susceptibility is depicted in Fig. 2. The change in slope is characteristic for linear trimers having antiferromagnetic exchange between nearest neighbours. A good fit is obtained, yielding $J = -10.0$ cm^{-1} with $g = 2.02$. For the trinuclear compounds $[Ni_3(Htrz)_6(H_2O)_6](NCS)_6(H_2O)_2$ [10, 11], $[Ni_3(Htrz)_6(H_2O)_6](SO_4)_3(H_2O)_9$ [19] and $[Ni_3(Htrz)_6(NCS)_6]$ [19] the magnetic exchange interaction has about the same magnitude.

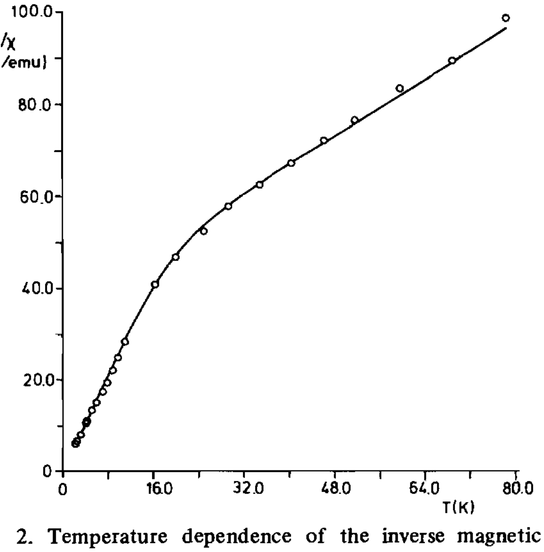

Fig. 2. Temperature dependence of the inverse magnetic susceptibility of a polycrystalline sample of $[Ni_3(t\text{-}Butrz)_8(NCS)_4](NCS)_2(H_2O)_9$ measured at H = 11.94 kOe. The curve is the prediction for a linear trinuclear compound with an isotropic exchange ($J = -10.0$ cm^{-1}, $g = 2.02$).

Linear trinuclear Co(II) compounds have been described before [48, 49], but surprisingly, for none of the reported compounds has a detailed study of their magnetic properties been undertaken. Therefore, no equations for the susceptibility of such a system are available. Assuming that at low temperatures (<40 K) only the lowest Kramers' doublet is populated, an $S = 1/2$ formalism with anisotropic g-values can be applied. In the case of an orthorhombic anisotropy the Heisenberg model will be appropriate to describe the magnetic properties of a linear trinuclear Co(II) compound. The magnetic susceptibility formula for a linear Cu(II) trimer may be applied, keeping in mind that an isotropic g-value is obtained. Least-squares fitting of the susceptibility data of $[Co_3(t\text{-}Butrz)_8(NCS)_4](NCS)_2(H_2O)_9$ to the equation of a linear Heisenberg $S = 1/2$ trimer [50], taking $J_{31} = 0$, provided a fit of rather poor quality, with $J = -9.0$ cm^{-1} and $g = 4.5$ (Fig. 3). We derived the equation for the Ising model according to a method by which Bonner *et al.* [51] calculated the Ising equation for the trinuclear Co(II) acetylacetonate compound. The magnetic susceptibility per Co-atom according to the Ising approximation, assuming $J_{31} = 0$, is given by [52]:

$$\chi_A = \frac{Ng^2\beta^2}{6kT}\,\frac{2 + 9e^x + e^{-x}}{12 + 6e^x + 6e^{-x}}$$

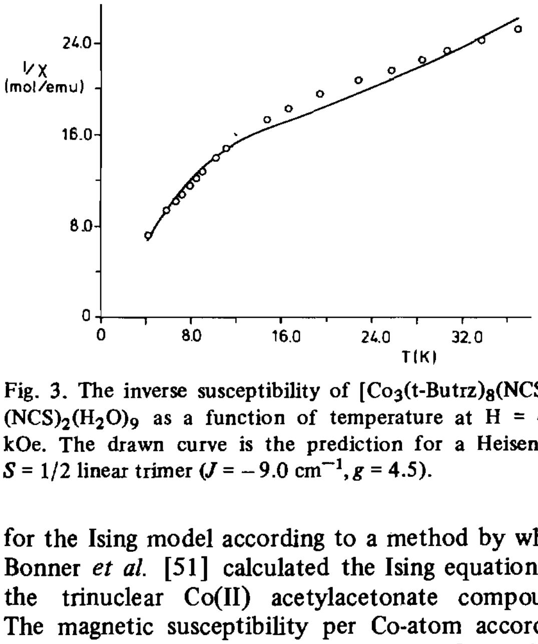

Fig. 3. The inverse susceptibility of $[Co_3(t\text{-}Butrz)_8(NCS)_4](NCS)_2(H_2O)_9$ as a function of temperature at H = 4.80 kOe. The drawn curve is the prediction for a Heisenberg $S = 1/2$ linear trimer ($J = -9.0$ cm^{-1}, $g = 4.5$).

Application of the Ising fit resulted in a slightly better fit, yielding $J = -13.2$ cm^{-1} and $g_{/\!/} = 7.8$ (see Fig. 4).

Since the compound very readily turns blue on powdering, the sample was only slightly compressed into the sample holder. When the crystals

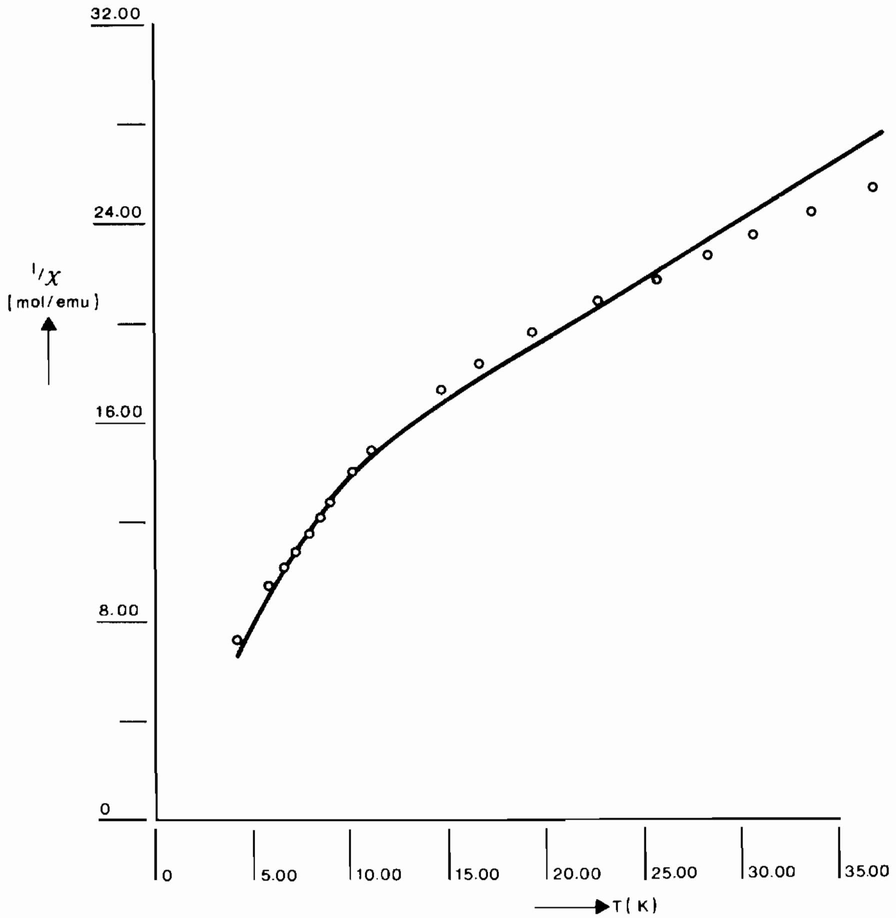

Fig. 4. The inverse susceptibility of $[Co_3(t\text{-}Butrz)_8(NCS)_4](NCS)_2(H_2O)_9$ as a function of temperature. The drawn curve is the prediction for an Ising linear trimer ($J = -13.2$ cm^{-1}, $g_{/\!/} = 7.8$).

are not powdered an accurate measurement of the magnetic susceptibility is more difficult, which in the g-values will differ for the central and the Furthermore it is quite possible that the anisotropy in the g-values will differ for the central and the terminal Co(II) ions. The applied procedures therefore have to be regarded as rough approximations only.

$[Co_3(t\text{-}Butrz)_4(NCS)_6](H_2O)_2$

For $[Co_3(t\text{-}Butrz)_4(NCS)_6](H_2O)_2$ a trinuclear structure is proposed, in which the metal centers are linked by two 1,2-bidentate t-Butrz ligands. Based on the infrared data (Table IV), the presence of monodentate triazole ligands can not be excluded completely. The positions of ν(CN), ν(CS) and δ(NCS) (Table IV), on the other hand provide no indication for bridging thiocyanate groups, which implies that the Co centers must be linked by t-Butrz groups. N-bonded NCS$^-$ groups complete the octahedral coordination around one Co center, most probably the central ion, and the tetrahedral coordination around the remaining two terminal Co ions. This mixed coordination is in agreement with the ligand field data of the compound (Table IV). The spectrum shows bands which may be attributed to an octahedral coordination (9500 cm^{-1} and 20.450 cm^{-1}) and a tetrahedral (8260 cm^{-1} and 16.670 cm^{-1}) coordination. The bands assigned to σ_1(Oh) and σ_2(Td) partly coincide, which makes it difficult to calculate the ligand field maxima accurately.

The infrared spectrum provides no indication for coordination of water molecules.

The magnetic susceptibility data are in agreement with the proposed trinuclear structure. A change of slope in the $1/\chi$ *vs.* T curve is observed, which is characteristic for a linear trinuclear compound, having antiferromagnetic exchange between nearest neighbours. On applying the Heisenberg model for linear $S = 1/2$ trimers, which cannot be entirely valid, a very poor fit is obtained resulting in $J = -5.6$ cm^{-1} and $g = 5.0$. Using the Ising model a slightly better fit is obtained ($J = -8.5$ cm^{-1},

$g_{\parallel}$ = 9.0). These values should be regarded as estimates only. The exchange in this compound, however, is significantly weaker than the exchange in $[Co_3(t\text{-}Butrz)_8(NCS)_4](NCS)_2(H_2O)_9$ for which a *J*-value of -13.2 cm^{-1} (Ising) is obtained. This conclusion is supported by the determination of the θ-values for both compounds. For $[Co_3(t\text{-}Butrz)_8(NCS)_4](NCS)_2(H_2O)_9$ $\theta \simeq -25$ *K*, while for $[Co_3(t\text{-}Butrz)_4(NCS)_6](H_2O)_2$ a θ-value of about -18 *K* is obtained, which indeed indicates a weaker antiferromagnetic exchange for the blue Co compound. In this compound, the metal ions are linked by two bridging t-Butrz units while in $[Co_3(t\text{-}Butrz)_8(NCS)_4](NCS)_2(H_2O)_9$ the Co(II) centers are bridged by three t-Butrz groups. This is most likely the origin of the difference in the magnitude of the exchange.

The combination of 4 and 6 coordination in $[Co_3(t\text{-}Butrz)_4(NCS)_6](H_2O)_2$ makes this structure very suitable for the synthesis of mixed metal coordination compounds. It seems possible to selectively replace a Co(II) ion in an octahedral or tetrahedral site. It was therefore tried to obtain trimers with Zn–Co–Co and Zn–Co–Zn units, by applying the related metal-salt mixtures in the preparation of the compounds, assuming, that the central Co(II) ion is indeed coordinated octahedrally. Grey and orange compounds were obtained respectively. Both appeared to be X-ray and IR-isomorphous with the title compound. The grey compound (Zn–Co–Co) shows and asymmetric band at about 9.350 cm^{-1}, due to σ_1(Oh) and σ_2(Td) and bands at 16.450 cm^{-1} (σ_3(Td)) and 20.600 cm^{-1} (σ_3(Oh)). The orange compound (Zn–Co–Zn) exhibits only bands at 10.000 cm^{-1} (σ_1(Oh)) and 20.500 cm^{-1} (σ_3(Oh)). A very weak band at 16.700 cm^{-1} indicates the presence of a very small amount of tetrahedrally coordinated Co(II)-ions, which is in agreement with the metal analyses.

Further evidence for the proposed substitution may be derived from the far-infrared data. For $[Co_3(t\text{-}Butrz)_4(NCS)_6](H_2O)_2$ the Co–N absorptions are located at 305 cm^{-1}, 240 cm^{-1} and 205 cm^{-1}. The absorption at 305 cm^{-1} can be attributed to the Co(II) ions in the tetrahedral coordination sites. On replacement of the Co(II) centers by Zn(II) ions, the related M–N absorption is expected to shift downfield [53], which is in full agreement with the observed data. In the Zn–Co–Co compound the Co–N absorption is located at 305 cm^{-1}, while the Zn–N absorption is observed at 285 cm^{-1}. For the Zn–Co–Zn compound no absorption is found around 305 cm^{-1}, indicating that the terminal metal sites are occupied by Zn(II) ions (band at 285 cm^{-1}).

The melting points of the three compounds are also in agreement with the expected behaviour. The smaller ion radius of Co(II) compared to Zn(II) should result in a higher lattice energy and therefore in a higher melting point. On replacement of Co(II) by Zn(II) a decrease in melting point is indeed observed (Table III).

The metal analyses for the grey and orange compounds are respectively: Co: 9.6 (11.0); Zn: 6.9 (6.1) and Co: 6.2 (5.5); Zn: 10.7 (12.2). The calculated values, based on Zn–Co–Co and Zn–Co–Zn, are given in parentheses. These values indicate that the substitution pattern varies slightly within both compounds but, in spite of this, it is obvious that it is possible to replace the terminal Co centers by Zn(II)-ions. No attempts were undertaken to improve the syntheses to obtain highly pure mixed-metal species.

The major aim of these investigations was to obtain additional evidence for the proposed structure. This compound, however, can provide the basis for future research on mixed metal coordination compounds with 1,2,4-triazoles, which might be very interesting from a magnetochemistry point of view.

$[Cu(t\text{-}Butrz)_2(NCS)_2](H_2O)_{0.5}$

The interpretation of the spectral data of $[Cu(t\text{-}Butrz)_2(NCS)_2](H_2O)_{0.5}$ is very complicated. In the infrared spectrum the C–H out-of-plane absorption at 865 cm^{-1} exhibits a shoulder at 890 cm^{-1}. The out-of-plane ring absorptions are observed at 659 cm^{-1} (vs) and 685 cm^{-1} (vw). The infrared data suggest the presence of both mono- and bidentate coordinating triazole ligands. The significant splitting of ν(CN) and δ(NCS) absorptions indicate the occurrence of different kind of NCS$^-$ groups (see Table III).

The ligand field spectrum exhibits one asymmetric band at 15.950 cm^{-1}, showing a distorted octahedral coordination of the Cu(II)-ions. The E.P.R. spectrum shows one signal having a *g* value of 2.15. Due to exchange narrowing, hyperfine splittings remain unresolved [54].

The magnetic behaviour of this Cu compound is quite surprising (Fig. 5). For the data between 120 K and 300 K a θ-value of about –320 K is obtained, indicating an unusually strong antiferromagnetic interaction between the Cu centers. The observed strong exchange makes it rather likely, that not only triazole groups act as bridging ligands. No maximum is observed in the χ *vs.* T curve, which implies that the compound is not an infinite chain or a finite chain containing an even number of metal ions. Based on the μ_{eff} *vs.* T curve a trinuclear structure can also be ruled out. Based on the collected data a layer structure seems likely. In such a structure Cu(II) chains, in which the Cu(II) ions are bridged by two 1,2-bicoordinating t-Butrz ligands, are mutually linked by thiocyanate groups, bridging via the nitrogen and sulfur atoms. This structure could account for the strong antiferromagnetic

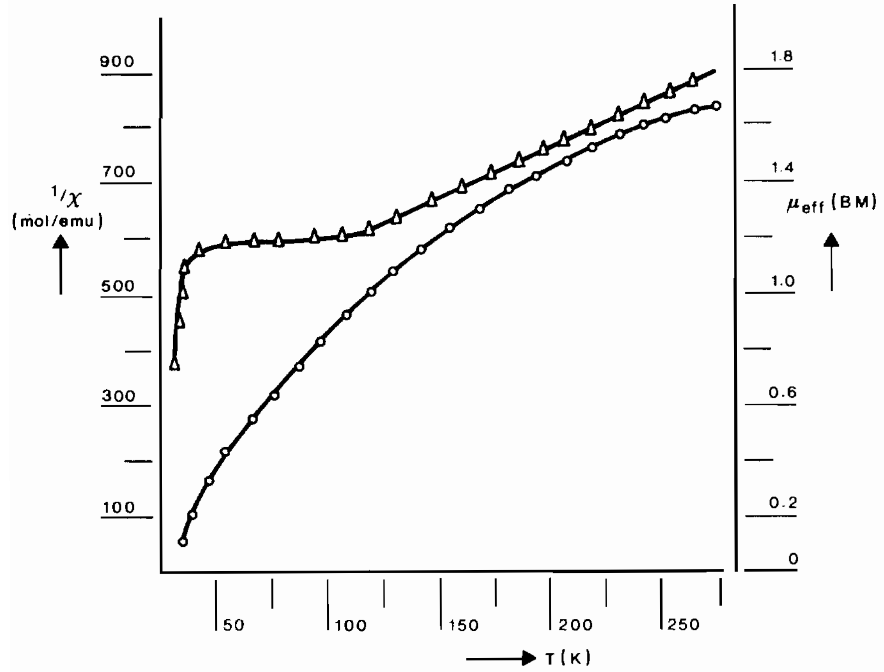

Fig. 5. Temperature dependence of the inverse susceptibility (△) and the effective magnetic moment (○) of $[Cu(t\text{-}Butrz)_2(NCS)_2](H_2O)_{0.5}$.

exchange. This structure implies that half of the thiocyanate groups is non-coordinating but ionic, which is in agreement with the infrared spectrum.

The ν(CN) absorption at 2068 cm^{-1} accounts for the bridging thiocyanate groups, while the absorption at 2020 cm^{-1} belongs to the non-coordinating thiocyanates. Usually thiocyanates bridging via the N and S atoms result in a ν(CN) absorption above 2100 cm^{-1} [6–9]. In $[Cu(py)_2(NCS)_2]$, which also contains NCS bridging units, however, the ν(CN) absorption is observed at 2072 cm^{-1} [39, 40]. The asymmetry of the γ(C–H) absorption and the presence of the second, weak, out-of-plane ring absorption at 685 cm^{-1} may be due to the asymmetrical coordination around the Cu(II)-ions as is also observed for the Cd compound. The non-coordinating thiocyanates and H_2O molecules are located in the holes of the crystal structure. The infrared spectrum indicates the involvement of the H_2O molecules in hydrogen bonding.

Other possible structures, however, cannot be excluded. It is obvious that the compound must have a very interesting structure, especially from a magnetochemistry point of view. Unfortunately, no single crystals of this compound could be prepared.

$[Cd_2(t\text{-}Butrz)_3(NCS)_4]_\infty$

The X-ray analysis of $[Cd_2(t\text{-}Butrz)_3(NCS)_4]_\infty$ showed the existence of a very unusual zig-zag chain. The detailed results of this crystal structure determination were published elsewhere [57]. The Cd-ions are connected, alternatingly, by three 1,2-bicoordinating t-Butrz groups and two thiocyanate groups, bridging via the nitrogen atom. The six coordination around each Cd-ion is completed by a single bonded N donating thiocyanate. The observed bridging mode of the thiocyanates is highly unusual and was only observed previously for the metal–metal bonded compound $[Re_2(NCS)_{10}]$.

A strong indication for this bridging coordination mode of the thiocyanates appears to be the position of the ν(CN) and δ(NCS) absorptions in the infrared spectrum. For $[Cd_2(t\text{-}Butrz)_3(NCS)_4]_\infty$, ν(CN) is observed as a doublet at 2038 cm^{-1} and 1982 cm^{-1}. The lower absorption may be assigned to the bridging isothiocyanate group, while the 2038 cm^{-1} absorption is attributed to the monodentately bonded isothiocyanate. For the Re compound, bands were observed at 1920 cm^{-1} and 1885 cm^{-1}, which at first were erroneously assigned to CO vibrations. The δ(NCS) absorptions of the Cd compound are located at 525 cm^{-1}, 498 cm^{-1} and 480 cm^{-1} (see Table IV). A δ(NCS) absorption clearly above 500 cm^{-1} has not been observed before and it seems justified therefore, to assign this absorption to the bridging isothiocyanate groups. No indicative ν(CS) absorption could be located, which is not surprising since this absorption is often rather weak. A few other compounds containing such a bridging NCS are known. From recent work from our and other laboratories a crystal structure determination has been reported for a trinuclear Ni(II) compound [58].

Conclusion

In this paper a variety of coordination compounds are described, which clearly show interesting features of the coordination chemistry of 1,2,4-triazoles. In combination with the ambidentate thiocyanate ligand a mononuclear and a layer compound and di- and trinuclear compounds are obtained. The magnetic exchange in the compounds containing paramagnetic metal ions is antiferromagnetic. For $[Cu(t\text{-}Butrz)_2(NCS)_2](H_2O)_{0.5}$ further research is recommended. Solving the crystal structure would not only reveal the, undoubtedly interesting, geometry of this compound, but would also make it possible to provide an adequate explanation for the observed strong antiferromagnetic exchange.

For the linear trinuclear compound $[Co_3(t\text{-}Butrz)_4(NCS)_6](H_2O)_2$ it is shown that it is possible to replace the terminal Co(II) ions by Zn(II) ions. Mixed metal compounds are especially interesting from a magnetic chemistry point of view, since it is possible to gain a better insight in the mechanisms through which the magnetic interactions take place in these triazole coordination compounds. Therefore, investigations on this field are in progress. The infrared spectrum of the mononuclear compound $[Zn(t\text{-}Butrz)_2(NCS)_2]$ shows that it is difficult to determine the coordination mode of the triazole ligand based on infrared data only.

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