Transition-metal(II) Thiocyanate Coordination Compounds Containing 4-allyl-1,2,4-triazole. Structure and Magnetic Properties.

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Abstract

The synthesis and characterisation of a series of dinuclear and polynuclear coordination compounds with 4-allyl-1,2,4-triazole are described. Dinuclear compounds were obtained for Mn(II) and Fe(II) with composition $[M_2(Altrz)_5(NCS)_4]$, and for Co(II) and Ni(II) with composition $[M_2(Altrz)_4(H_2O)(NCS)_4](H_2O)_2$. The crystal structure of $[Co_2(Altrz)_4(H_2O)(NCS)_4](H_2O)_2$ was solved at room temperature. It crystallizes in the monoclinic space group $P2_1/n$. The lattice constants are $a = 18.033(3)$ Å, $b = 13.611(2)$ Å, $c = 15.619(3)$ Å, $\beta = 92.04(2)°$ and $Z = 4$. One cobalt ion has an octahedrally arranged donor set of ligands consisting of three vicinal nitrogens of 1,2-bridging triazoles (Co–N = 2.14–2.15 Å), one terminal triazole nitrogen (Co–N = 2.12 Å) and two N-bounded NCS anions (Co–N = 2.08 Å). The other Co(II) ion has the same geometry, but the terminal triazole ligand is replaced by H_2O (Co–O = 2.15 Å). The crystal structure is stabilised by hydrogen bonding through H_2O molecules, S-atoms of the NCS anions and the lone-pair electron of the monodentate triazole. The magnetic exchange in the Mn, Co and Ni compounds is antiferromagnetic with J-values of −0.4 cm^{-1}, −10.9 cm^{-1} and −8.7 cm^{-1} respectively. The Co compound was interpreted in terms of an Ising model. For $[Zn_2(Altrz)_5(NCS)_2]_\infty[Zn(NCS)_4]$, $[Cu_2(Altrz)_3(NCS)_4]_\infty$ and $[Cd_2(Altrz)_3(NCS)_4]_\infty$ chain structures are proposed. In the Cu compound thiocyanates appear to be present, bridging via the nitrogen atom, as deduced from the IR spectrum.

Introduction

A variety of coordination compounds with 1,2,4-triazoles are known [1–16]. Due to the ambidentate nature of these ligands, coordination compounds with several geometries are known. In the chain compound $[CuCl_2(Htrz)]_\infty$ [1] and in the linear trinuclear compound $[Ni_3(Htrz)_6(H_2O)_6](NO_3)_6(H_2O)_2$

[2] the triazoles are coordinating in a 1,2-bidentate fashion. The magnetic exchange in both compounds is antiferromagnetic [3–5]. Engelfriet [7] first described a series of layered structures in which the triazole ligands are bridging through the 2,4-nitrogen atoms. The compounds have a general composition $[M(Htrz)_2(NCS)_2]$ for the divalent metals Mn, Fe, Co, Ni, Cu and Zn. For the Mn, Fe, Co and Ni compounds an antiferromagnetic intralayer exchange is found, while the Cu compound appears to be slightly ferromagnetic. When a substituent is placed at the 4-position of the triazole ring, this ligand is forced to coordinate monodentately or in a 1,2-bidentate fashion, initially resulting in two well characterised compounds *i.e.* $[Mn_2(Metrz)_5(NCS)_4]$ [8] (Metrz: 4-methyl-1-2,4-triazole) and $[Co_2(Phtrz)_5(NCS)_4](H_2O)_{2.7}$ [9] (Phtrz: 4-phenyl-1,2,4-triazole). In both dinuclear compounds the metal centers are coupled antiferromagnetically.

Recently we reported a series of dinuclear compounds, which showed a remarkably asymmetrical occupation of the terminal coordination sites. The compounds have a general composition of $[M_2(Ettrz)_4(H_2O)(NCS)_4](H_2O)_2$ (Ettrz: 4-ethyl-1,2,4-triazole) for M = Mn, Fe, Co and Ni [10, 11]. In these compounds the metal centers are also coupled antiferromagnetically. Transition metal(II) thiocyanates with 4-t-butyl-1,2,4-triazole give rise to the formation of mono-, di- and tri-nuclear and chain compounds [12–14]. In the present paper transition metal(II) thiocyanate coordination compounds with 4-allyl-1,2,4-triazole (Altrz) are reported. These coordination compounds were prepared in order to study the influence of an unsaturated substituent at the ring on the coordination of the ligand, and on the magnetic properties of the resulting coordination compounds.

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TABLE I. Crystal and Diffraction Data for [Co$_2$(Altrz)$_4$-(H$_2$O)(NCS)$_4$](H$_2$O)$_2$.

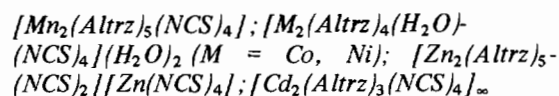|	
Space group	$P2_1/n$
Lattice constants	
a (A)	18.033(3)
b (A)	13.611(2)
c (A)	15.619(3)
β (°)	92.04(2)
Z	4
Crystal dimensions (mm)	0.20 × 0.25 × 0.35
θ-range (°)	2–23
Measured reflections	5502
Independent reflections	5306
Significant reflections	2457
Experimental density (Mg m^{-3})	1.46
Calculated density (Mg m^{-3})	1.4
μ (MoKα) (cm^{-1})	11.21
Final $R(R_w)$	0.046(0.047)

Experimental

Syntheses

4-allyl-1,2,4-triazole (Altrz)

The new ligand Altrz was synthesized using a method similar to that reported by Bayer et al. for the preparation of other 4-substituted 1,2,4-triazoles [16]. In this case allylamine (1 mol) was added slowly to the boiling solution of monoformyl-hydrazine (1 mol) and triethylorthoformate (1.5 mol) in 400 ml of anhydrous methanol. The solution was refluxed for 4 h and the solvent was then removed under reduced pressure. The remaining

liquid was distilled at 3 mm Hg. No polymerisation reactions were observed under these conditions. Altrz: yield: 57%; b.p.: 166–169 °C (3 mm Hg); NMR (CDCl$_3$): 4.50 ppm (d, 2H), 5.10 ppm (m, 2H), 5.70 ppm (m, 1H), 8.16 ppm (s, 2H). IR (cm^{-1}): 3110(vs), 3030(m), 2960(m), 2930(m), 2860(m), 1698(sh), 1679(s), 1647(s), 1532(vs), 1460(s), 1445(s,sh), 1430(s), 1381(s), 1368(m,sh), 1360(w,sh), 1350(w), 1332(m), 1295(m), 1275(m), 1251(vw), 1225(m,sh), 1185(vs), 1157(m,sh), 1125(w), 1078(s), 995(s), 978(s), 952(s), 941(s,sh), 871(s), 763(s), 749(s), 685(m), 638(vs), 585(m), 560(m), 515(w), 380(w).

[Mn$_2$(Altrz)$_5$(NCS)$_4$]; [M$_2$(Altrz)$_4$(H$_2$O)-(NCS)$_4$](H$_2$O)$_2$ (M = Co, Ni); [Zn$_2$(Altrz)$_5$-(NCS)$_2$][Zn(NCS)$_4$]; [Cd$_2$(Altrz)$_3$(NCS)$_4$]$_\infty$

Metal(II) thiocyanate (2.5 mmol) was dissolved in hot water (ca. 15 ml). The hot metal salt solution was filtered in the case of Ni(II) and Co(II) in order to remove insoluble impurities. Altrz (5 mmol), dissolved in water (10 ml), was added to the hot metal salt solution. The coordination compounds crystallized upon standing at room temperature.

[Fe$_2$(Altrz)$_5$(NCS)$_4$]
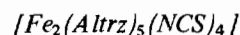
Ammonium thiocyanate (5 mmol) was dissolved in 15 ml of water. The solution was heated to boiling. After passing sulfur dioxide through the solution for 1 min, hydrated iron(II) ammonium sulfate (2.5 mmol) was added rapidly. Then Altrz (5 mmol) in water (10 ml) was added slowly to the boiling metal salt solution. Crystallization occurred while standing for several days at 4 °C.

TABLE II. Analytical Data, Colours, Structure Types and Melting Points of Transition Metal(II) Thiocyanate Coordination Compounds with Altrz.

Compound	Structure type	Colour	Elemental analyses[a]				m.p. (°C)
			%M	%C	%N	%H	
[Mn$_2$(Altrz)$_5$(NCS)$_4$]	A	white	12.3 (12.4)	39.0 (39.2)	30.4 (30.0)	4.0 (4.0)	181–183
[Fe$_2$(Altrz)$_5$(NCS)$_4$]	B	white	12.6 (12.6)				202–104
{Co$_2$(Altrz)$_4$(H$_2$O)(NCS)$_4$](H$_2$O)$_2$	C	red	14.0 (13.7)	34.2 (34.3)	26.3 (26.7)	4.1 (4.1)	184–186[b]
[Ni$_2$(Altrz)$_4$(H$_2$O)(NCS)$_4$](H$_2$O)$_2$	C	blue	13.6 (13.6)	34.9 (34.3)	26.7 (26.7)	3.9 (4.1)	235–238
[Cu$_2$(Altrz)$_3$(NCS)$_4$]$_\infty$	D	green	18.6 (18.5)	33.2 (33.2)	26.3 (26.5)	3.1 (3.1)	228–230
[Zn$_2$(Altrz)$_5$(NCS)$_2$]$_\infty$[Zn(NCS)$_4$]	E	white	17.6 (17.6)	33.0 (33.3)	26.4 (26.3)	3.4 (3.4)	112–114
[Cd$_2$(Altrz)$_3$(NCS)$_4$]$_\infty$	F	white	28.8 (28.7)	28.9 (29.1)	23.1 (23.2)	2.7 (2.7)	202–204

[a]Calculated values in parentheses.   [b]At 100–105 °C the compound looses H$_2$O and turns blue.

Microcrystalline precipitates were filtered, 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 at room temperature. Analytical data, colours, structure types and melting points of the coordination compounds obtained are listed in Table II.

Analyses and Physical Measurements

Metal analyses were carried out by complexometric titration [17, 18] 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, West-Germany.

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}) as KBr discs.

The EPR spectrum of a powdered sample of $[Cu_2(Altrz)_3(NCS)_4]_\infty$ was 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 automatized Faraday balance, described by Arbouw [19]. 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 [7].

X-ray powder diffraction patterns were recorded with a Philips PW 1050 powder diffractometer, using Cu—Kα radiation. The single crystal X-ray diffraction measurement was performed on an Enraf-Nonius CAD-4 diffractometer. All calculations were carried out on the Leiden University Amdahl V7B computer, using a local set of programs.

Mo-Kα radiation, monochromatised by graphite, was used to determine the reflection intensities. The data were corrected for Lorentz and polarisation effects. Reflections with intensities less than twice the standard deviation (calculated from counting statistics and inaccuracies of attenuation filters) were considered insignificant. After reduction of the intensities to structure factors, a Wilson plot was calculated in order to obtain starting values for the scale factor and the initial thermal parameter *B*. The experimental density was determined in a mixture of cyclohexane and 1,2-dibromoethane.

Relevant crystal and diffraction data are summarized in Table I.

Solution and Refinement of the Structure of Co₂-(Altrz)₄(H₂O)(NCS)₄(H₂O)₂

The function minimized during the least-squares refinement was $\Sigma w(|F_o| - |F_c|)^2$ with the weighting scheme $w = \sigma_F^{-2}$. Discrepancy indices are defined as $R = \Sigma|\Delta F|/\Sigma|F_o|$ and $R_w = [\Sigma w[(\Delta F)^2/\Sigma w F_o^2]^{1/2}$. Scattering factors and anomalous dispersion corrections were taken from International Tables for X-ray Crystallography [20]. A three-dimensional Patterson synthesis revealed the positions of the Co(II)-ions. A structure in which two Co-ions are bridged by three Altrz groups was generated by using the program DIRDIF [21]. Except for the coordinated nitrogen, the monodentate coordinating Altrz appeared to be in a disordered position. The positions of these atoms were treated with Waser constraints [22] and were not refined anisotropically. (see Fig. 2). The disorder was refined in an occupation ratio of 0.467(A) 0.467(A):0.533(8)(B). The allyl groups also show high thermal motions or disorder, and the positions did not refine to physically real values. Therefore all allyl groups were refined using Waser constraints [22].

The hydrogen atoms were placed at calculated positions (0.95 Å from the corresponding C atom) and with B_{iso} of this atom as temperature parameter. The calculation was repeated at the end of the refinement. In this way 4 out of 6 H atoms of the water molecules refined in the normal way. Isotropic refinement yielded $R = 0.135$ ($R_w = 0.151$). Six cycles of anisotropic refinement led to a final R value of 0.046 ($R_w = 0.047$) (significant reflections only) and $R = 0.138$ ($R_w = 0.051$) for all reflections. The positional parameters of the located atoms are listed in Table III.*

Results and Discussion

General

The obtained coordination compounds are listed in Table II, together with colours, analyses and some other relevant properties. Relevant infrared and ligand field data are listed in Tables VII and VIII. The compounds will be discussed in groups, according to their spectral properties or proposed structures.

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*A list of structure factors, Tables of isotropic thermal and hydrogen parameters have been deposited with the Editor-in-Chief.

TABLE III. Fractional Coordinates ($\times 10^4$) and Isotropic Temperature Factors ($A^2 \times 10^2$ for Co, $\times 10$ for the other Atoms of $[Co_2(Altrz)_4(H_2O)(NCS)_4](H_2O)_2$.

Atom	x/a^a	y/b	z/c	$B_{(iso)}$
Co(1)	7971(1)	8637(1)	−1256(1)	345(3)
Co(2)	7824(1)	9415(1)	1141(1)	348(3)
N(1)	8331(4)	7267(6)	−1637(4)	45(2)
C(1)	8507(5)	6483(8)	−1696(5)	46(3)
S(1)	8769(2)	5339(2)	−1795(2)	93(1)
N(2)	8535(4)	9412(6)	−2174(4)	48(2)
C(2)	8942(5)	9887(7)	−2545(5)	43(3)
S(2)	9535(2)	10539(2)	−3046(2)	79(1)
N(3)	8323(4)	10672(6)	1660(4)	49(3)
C(3)	8662(5)	11346(8)	1860(5)	43(3)
S(3)	9154(2)	12308(2)	2135(2)	80(1)
N(4)	8186(4)	8561(6)	2173(4)	49(3)
C(4)	8472(5)	8161(7)	2728(5)	41(3)
S(4)	8883(2)	7579(2)	3534(2)	65(1)
N(11)	8876(4)	8766(5)	−345(4)	34(2)
N(12)	8822(4)	9073(5)	506(4)	33(2)
C(13)	9484(5)	9046(6)	851(5)	37(3)
N(14)	9983(3)	8757(5)	269(4)	37(2)
C(15)	9581(5)	8575(6)	−456(5)	38(3)
C(16)	10788(3)	8605(5)	428(5)	48(3)
C(17)	10968(4)	7591(7)	726(6)	79(5)
C(18)	11301(7)	6953(7)	356(8)	121(7)
N(21)	7313(4)	7919(5)	−327(4)	35(2)
N(22)	7302(4)	8170(5)	534(4)	36(2)
C(23)	6862(5)	7539(7)	891(5)	44(3)
N(24)	6585(4)	6898(5)	318(5)	44(2)
C(25)	6891(5)	7150(9)	−438(5)	44(3)
C(26)	6064(4)	6081(6)	475(6)	66(4)
C(27)	6440(6)	5118(6)	589(9)	87(5)
C(28)	7087(7)	4906(8)	482(10)	116(6)
N(31)	7556(4)	10032(5)	−811(4)	34(2)
N(32)	7474(3)	10271(5)	46(4)	34(2)
C(33)	7202(5)	11163(7)	55(6)	39(3)
N(34)	7106(3)	11507(5)	−756(5)	41(2)
C(35)	7335(4)	10782(7)	−1269(5)	41(3)
C(36)	6810(5)	12478(5)	1021(6)	55(3)
C(37)	5993(5)	12507(7)	1148(7)	78(5)
C(38)	5528(5)	11921(10)	−952(9)	134(7)
N(41)	6822(3)	9744(5)	1749(3)	40(2)
N(42A)	6134(4)	9519(13)	1367(7)	47(2)
N(42B)	6106(4)	9782(13)	1391(5)	47(2)
C(43A)	5638(3)	9848(20)	1880(12)	61(2)
C(43B)	5663(3)	9865(20)	2028(6)	61(2)
N(44A)	5960(4)	10366(10)	2528(7)	43(2)
N(44B)	6046(4)	9863(9)	2784(5)	43(2)
C(45A)	6698(4)	10267(12)	2430(7)	44(2)
C(45B)	6766(4)	9761(13)	2581(4)	44(2)
C(46A)	5581(7)	10782(15)	3273(8)	74(4)
C(46B)	5734(7)	9775(10)	3645(6)	74(4)
C(47A)	6088(12)	11260(15)	3911(9)	89(5)
C(47B)	5834(12)	10658(13)	4185(7)	89(5)
C(48A)	6130(20)	11170(20)	4680(10)	161(9)
C(48B)	6050(20)	11470(10)	4068(10)	161(9)
O(1)	7054(4)	8518(6)	−2173(5)	53(2)
O(2)	5658(5)	9447(9)	−346(6)	126(4)
O(3)	5656(5)	8164(9)	−1727(7)	125(5)

aEstimated standard deviations in the least significant digits are given in parentheses.

$[M_2(Altrz)_4(H_2O)(NCS)_4](H_2O)_2$ $(M = Co(II), Ni(II))$

The two compounds appear to have the same infrared spectrum and X-ray powder diagram, and are therefore considered as isomorphous and iso-structural. The X-ray structure of the Co compound shows the presence of dimeric units, in which the metal ions are linked by three 1,2-bicoordinating Altrz groups. Two N donating NCS^- groups and a monodentate Altrz complete the CoN_6 octahedron around one metal ion. For the other metal ion the sixth ligand is a water molecule, instead of the monodentate Altrz. The stereochemistry of one unit of $[Co_2(Altrz)_4(H_2O)(NCS)_4]$ is shown in Fig. 1 with the labeling of the atoms, used in the Tables III, IV, V and VI. The disorder in the monodentate coordinating Altrz is depicted separately in Fig. 2. Intermolecular distances and bond angles are listed with their e.s.d.s in Tables IV and V. This structure is similar to the structure of $[Ni_2(Ettrz)_4(H_2O)-(NCS)_4](H_2O)_{2.25}$ [11], which also has this remarkable asymmetrical coordination.

Engelfriet et al. described somewhat related di-nuclear compounds with Phtrz [9] and Metrz [8], but in these cases no H_2O molecule is coordinat-ing and the geometry is much more symmetrical. Hydrogen bonding is expected to play an important role in the stabilisation of the structure. Not all hydrogen atoms belonging to H_2O molecules could be located however; consequently, it is difficult to localize the hydrogen bridges. Never-theless, based on calculated distances, a number of hydrogen bridges can be indicated (Table VI).

The coordination sphere of Co(1) is linked through H-bridges between O(1) and O(3), O(3) and O(2), O(2) and N(42), with the coordination sphere of Co(2). The bond between O(1) and O(3) is quite strong $(O(1)\cdots O(3) = 2.68$ Å). Hydrogen bonding to the non-coordinating nitrogen of a mono-dentate triazole group has also been observed [14] in the structure of $[Co_3(t\text{-}Butrz)_8(Ncs)_4](NCS)_2$-$(H_2O)_4$. The hydrogen bridge between O(1) and S(1) links two different molecules.

The spectral and magnetic data obtained are in agreement with the dinuclear structure. The splitting of the C–H out-of-plane absorption in the infrared spectrum (see Table VII) indicates the presence of both mono- and bi-dentate Altrz ligands [6, 24]. The observation of the second weak out-of-plane ring torsion absorption at about 640 cm^{-1} exhibits a shoulder, again in agreement with the presence of different types of Altrz groups. The position of $\nu(CN)$ and $\nu(CS)$ (Table VII) are in accordance with the presence of N-donating thio-cyanate groups [25–28]. Shoulders observed at the $\nu(H–O)$ absorptions of the H_2O mole-cules suggest coordination and/or strong hydro-gen bonding of at least part of the H_2O mole-
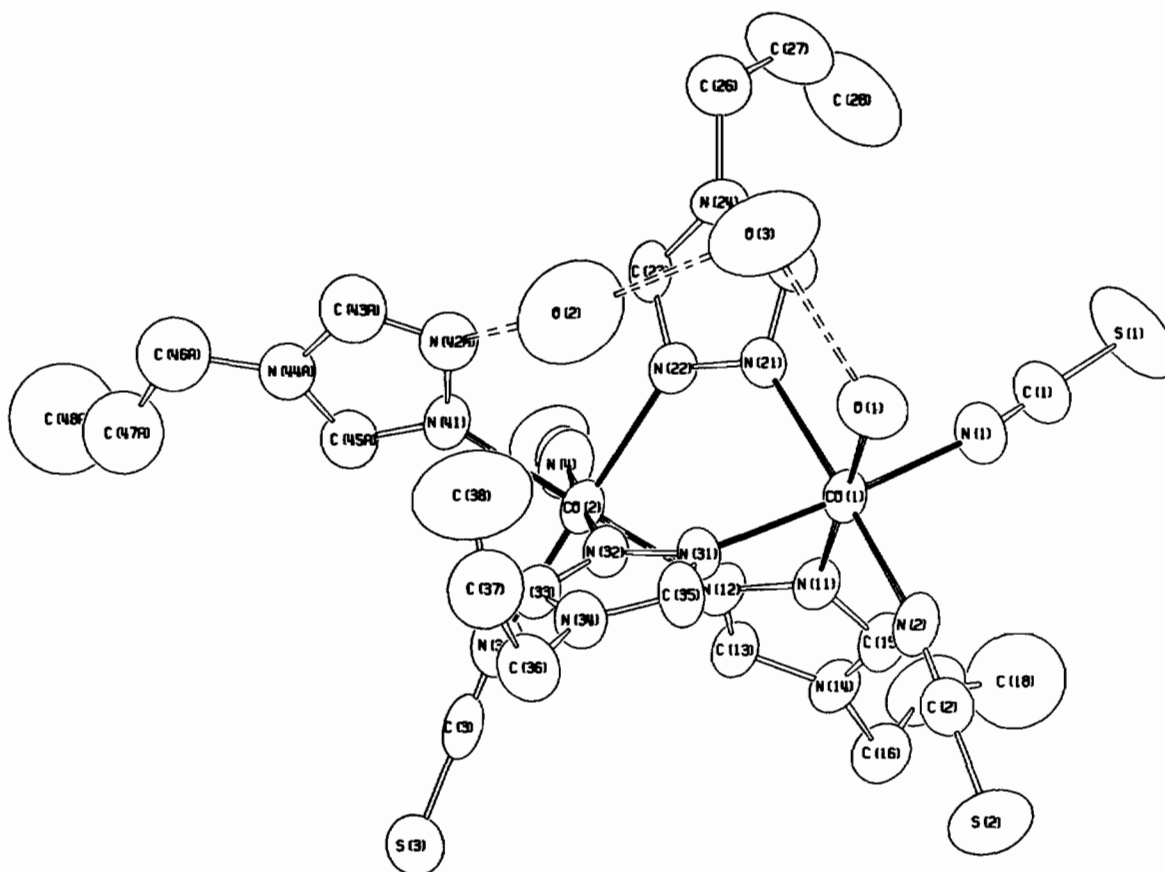
Fig. 1. ORTEP drawing [23] and numbering system of the dinuclear unit of $[Co_2(Altrz)_4(H_2O)(NCS)_4]$. The hydrogen atoms and the disorder in Altrz group 4 have been omitted for reasons of clarity.

TABLE IV. Relevant Intramolecular Distances (Å) and Angles (°) in $[Co_2(Altrz)_4(H_2O)(NCS)_4](H_2O)_2$ Except Altrz Groups.

Co(1)–Co(2)	3.909(2)	N(1)–C(1)	1.118(9)
Co(1)–N(1)	2.069(8)	C(1)–S(1)	1.636(11)
Co(1)–N(2)	2.075(7)	N(2)–C(2)	1.150(9)
Co(1)–O(1)	2.154(7)	C(2)–S(2)	1.613(10)
Co(1)–N(11)	2.135(6)	N(3)–C(3)	1.140(10)
Co(1)–N(21)	2.143(7)	C(3)–S(3)	1.630(11)
Co(1)–N(31)	2.164(7)	N(4)–C(4)	1.132(9)
Co(2)–N(3)	2.084(8)	C(4)–S(4)	1.643(10)
Co(2)–N(4)	2.075(8)		
Co(2)–N(41)	2.118(4)		
Co(2)–N(12)	2.137(6)		
Co(2)–N(22)	2.143(7)		
Co(2)–N(32)	2.145(7)		
N(1)–Co(1)–N(2)	95.3(3)	N(3)–Co(2)–N(4)	92.2(3)
N(1)–Co(1)–O(1)	89.0(3)	N(3)–Co(2)–N(41)	90.9(3)
N(1)–Co(1)–N(11)	91.4(3)	N(3)–Co(2)–N(12)	90.0(3)
N(1)–Co(1)–N(21)	88.3(3)	N(3)–Co(2)–N(22)	176.5(3)
N(1)–Co(1)–N(31)	177.0(3)	N(3)–Co(2)–N(32)	88.6(3)
N(2)–Co(1)–O(1)	87.9(3)	N(4)–Co(2)–N(41)	91.2(3)
N(2)–Co(1)–N(11)	92.1(3)	N(4)–Co(2)–N(12)	89.5(3)
N(2)–Co(1)–N(21)	175.2(3)	N(4)–Co(2)–N(22)	91.3(3)

TABLE IV. *(continued)*

N(2)–Co(1)–N(31)	87.7(3)	N(4)–Co(2)–N(32)	178.1(3)
O(1)–Co(1)–N(11)	179.5(3)	N(41)–Co(2)–N(12)	178.9(2)
O(1)–Co(1)–N(21)	89.2(3)	N(41)–Co(2)–N(22)	89.9(3)
O(1)–Co(1)–N(31)	90.8(3)	N(41)–Co(2)–N(32)	90.6(3)
N(11)–Co(1)–N(21)	90.8(3)	N(12)–Co(2)–N(22)	89.2(3)
N(11)–Co(1)–N(31)	88.8(3)	N(12)–Co(2)–N(32)	88.7(2)
N(21)–Co(1)–N(31)	88.7(3)	N(22)–Co(2)–N(32)	88.0(3)
Co(1)–N(1)–C(1)	167.7(8)	Co(2)–N(41)–C(45A)	130.8(4)
Co(1)–N(2)–C(2)	166.2(7)	Co(2)–N(41)–C(45B)	123.2(4)
Co(1)–N(11)–N(12)	125.4(5)	Co(2)–N(12)–N(11)	126.5(5)
Co(1)–N(11)–C(15)	128.0(6)	Co(2)–N(12)–C(13)	126.4(6)
Co(1)–N(21)–N(22)	124.8(6)	Co(2)–N(22)–N(21)	127.0(5)
Co(1)–N(21)–C(25)	127.8(6)	Co(2)–N(22)–C(23)	126.5(6)
Co(1)–N(31)–N(32)	124.4(6)	Co(2)–N(32)–N(31)	127.0(6)
Co(1)–N(31)–C(35)	127.8(6)	Co(2)–N(32)–C(33)	126.5(6)
Co(2)–N(3)–C(3)	171.0(8)	N(1)–C(1)–S(1)	179.2(9)
Co(2)–N(4)–C(4)	170.7(8)	N(2)–C(2)–S(2)	178.1(9)
Co(2)–N(41)–N(42A)	121.5(4)	N(3)–C(3)–S(3)	179.1(8)
Co(2)–N(41)–N(42B)	128.5(4)	N(4)–C(4)–S(4)	179.7(10)

TABLE V. Bond Distances (Å) and Angles (°) of the Altrz Groups in $[Co_2(Altrz)_4(H_2O)(NCS)_4](H_2O)_2$.

	ring 1	ring 2	ring 3	ring 4A	ring 4B
N(1)–N(2)	1.400(7)	1.388(8)	1.390(8)	1.392	1.390
N(2)–C(3)	1.293(9)	1.309(9)	1.310(9)	1.302	1.303
C(3)–N(4)	1.359(9)	1.334(9)	1.356(9)	1.349	1.347
N(4)–C(5)	1.346(9)	1.364(9)	1.346(9)	1.353	1.353
C(5)–N(1)	1.314(9)	1.302(9)	1.302(9)	1.307	1.309
N(4)–C(6)	1.479(4)	1.482	1.479	1.482	1.482
C(6)–C(7)	1.488	1.484	1.480	1.478	1.475
C(7)–C(8)	1.213	1.217	1.205	1.211	1.209
N(1)–N(2)–C(3)	107.9(6)	106.3(7)	106.3(7)	106.4	106.4
N(2)–C(3)–N(4)	110.7(7)	111.2(7)	110.2(8)	110.8	111.0
C(3)–N(4)–C(5)	105.5(6)	105.3(7)	105.8(7)	105.2	105.2
N(4)–C(5)–N(1)	110.3(7)	109.9(7)	110.0(7)	110.1	110.0
C(5)–N(1)–N(2)	106.6(6)	107.3(7)	107.8(7)	107.1	107.2
C(3)–N(4)–C(6)	126.7(7)	127.1(8)	127.1(8)	126.2	126.6
C(5)–N(4)–C(6)	127.7(7)	127.6(8)	127.1(8)	127.6	127.0
N(4)–C(6)–C(7)	112.6	113.1	114.1	114.0	114.3
C(6)–C(7)–C(8)	128.5	128.9	130.4	130.0	130.4

TABLE VI. Hydrogen bridges in $[Co_2(Altrz)_4(H_2O)(NCS)_4](H_2O)_2$.

	Distance (Å)
O(1)···S(1)[a]	3.282(8)
O(1)···O(3)	2.68(1)
O(3)···O(2)	2.78(2)
O(2)···N(42A)	2.78(1)
O(2)···N(42B)	2.84(1)

[a]Position $1\frac{1}{2} - x$, $\frac{1}{2} + y$, $-\frac{1}{2} - z$.

cules [29, 30], which is in accordance with the determined crystal structure of the Co compound. The ligand field data of the octahedrally coordinated Co and Ni ions are given in Table VIII.

The X-ray data show that the octahedra are slightly distorted, although this is not reflected in the ligand field spectra. To see whether or not magnetic exchange is present in the compounds, the magnetic susceptibility of both compounds was studied in the range of 2–80 K. The susceptibility data of

TABLE VII. Relevant Infrared Absorptions with Tentative Assignments of Coordination Compounds Containing Altrz.

Compound	ν(CN)	ν(CS)	δ(NCS)	γ(CH)	τ	F.I.R.[a]
$[Mn_2(Altrz)_5(NCS)_4]$	2070(vs)	799(m)	481(m)	902(w,sh)	685(w)	290(w,sh)
				876(s)	638(vs)	230(vs)
$[Fe_2(Altrz)_5(NCS)_4]$	2065(vs)	798(m)	478(m)	895(m)	682(w)	245(vs)
				885(w,sh)	631(vs)	
				870(w)		
$[Co_2(Altrz)_4(H_2O)(NCS)_4](H_2O)_2$	2105(sh)	792(m)	480(m)	900(s)	689(w)	250(vs)
	2095(vs)			873(m)	641(vs)	
					632(s,sh)	
$[Ni_2(Altrz)_4(H_2O)(NCS)_4](H_2O)_2$	2105(sh)	788(m)	478(m)	890(s)	687(w)	265(vs)
	2095(vs)		470(sh)	870(m)	640(vs)	
					630(s,sh)	
$[Cu_2(Altrz)_3(NCS)_4]_\infty$	2090(vs)	830(sh)	510(w)	830(sh)	647(s)	300(s)
	2030(vs)	825(m)	485(m)		639(vs)	250(m)
	1995(sh)		475(m,sh)			230(m)
$[Zn_2(Altrz)_5(NCS)_2]_\infty[Zn(NCS)_4]$	2090(vs)	883(w)	476(m)	900(w)	675(vw)	288(vs)
	2038(w,sh)			880(m)	635(vs)	225(vs)
$[Cd_2(Altrz)_3(NCS)_4]_\infty$	2098(s)	790(w)	485(w,sh)	882(s)	637(vs)	230(s)
	2042(s)		472(w)			
			455(w)			

[a]Unassigned absorptions in the far-infrared region, most likely due to M–L stretch vibrations.

TABLE VIII. Ligand Field Spectra (Diffuse Reflectance) of Coordination Compounds Containing Altrz.

Compound	Ligand field bands (cm^{-1})			Dq (cm^{-1})	B (cm^{-1})
$[Fe_2(Altrz)_5(NCS)_4]$	11.630				
$[Co_2(Altrz)_4(H_2O)(NCS)_4](H_2O)_2$	9.760	20.830		1065	815
$[Ni_2(Altrz)_4(H_2O)(NCS)_4](H_2O)_2$	10.990	17.860		1100	a
$[Cu_2(Altrz)_3(NCS)_4]_\infty$	15.500				
Co^{2+} in $[Zn_2(Altrz)_5(NCS)_2]_\infty[Zn(NCS)_4]$	10.810	21.500		1175	790
Co^{2+} in $[Cd_2(Altrz)_3(NCS)_4]_\infty$	10.200	16.670	21.500	1115	835

[a]σ_3 is not observed. The origin for this might be distortion from octahedral geometry and/or the asymmetry of the dimer. Calculation of B, based on σ_1 and σ_2 yields an unreliable value for this parameter.
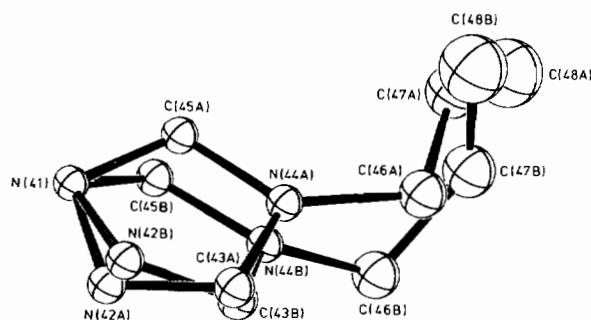

Fig. 2. ORTEP drawing [23] of the disordered monodentate coordinating Altrz group in $[Co_2(Altrz)_4(H_2O)(NCS)_4]$-$(H_2O)_2$. The refined occupation ratio is 0.46(A):0.54(B).

$[Ni_2(Altrz)_4(H_2O)(NCS)_4](H_2O)_2$, which show a maximum in the χ vs. T curve at 26.1 K, were fitted to the theoretical expression for Ni(II) dimers [31], assuming an isotropic magnetic exchange. The fit, which is of good quality, is presented in Fig. 3. Least-squares fitting results in $J = -8.7$ cm^{-1}, $g = 1.98$ and $zJ = +2.3$ cm^{-1}. Inclusion of zero-field splitting effects in the fitting procedure did not improve the quality of the fit. The small g-value cannot be explained. The presence of zero-field splittings (assumed to be zero in the fit) may be responsible for this.

For Co(II) the situation is more complicated since the orbital moment is only partly quenched [32–35]. To study the magnetic interaction in
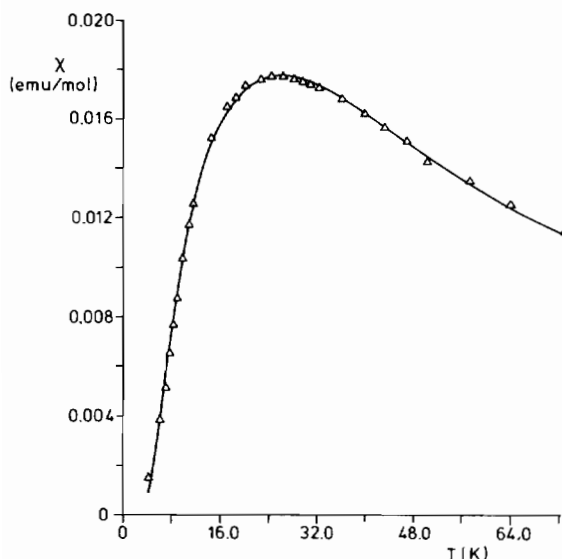
Fig. 3. Magnetic susceptibility of $Ni_2(Altrz)_4(H_2O)(NCS)_4$-$(H_2O)_2$ as a function of temperature, measured at H = 11.17 kOe. The drawn curve is the prediction for a dinuclear compound with isotropic interaction. ($J = -8.7$ cm^{-1}, g = 1.98, zJ = +2.3 cm^{-1}).

Fig. 4. Temperature dependence of the magnetic susceptibility of a polycrystalline sample of $[Co_2(Altrz)_4(H_2O)$-$(NCS)_4](H_2O)_2$, measured at H = 11.72 kOe. The curve is the prediction for the parallel susceptibility of an Ising dimer. ($J = -10.9$ cm^{-1}, $g_\parallel = 7.16$, zJ = +0.02 cm^{-1}).

dinuclear Co(II) compounds, one should consider the Hamiltonian for the dimer:

$$H = -2J_{12}(a\vec{S}_{1x}\cdot\vec{S}_{2x} + b\vec{S}_{1y}\cdot\vec{S}_{2y} + c\vec{S}_{1z}\cdot\vec{S}_{2z})$$

For the cases $a = b = 0$, $c = 1$ and $a = b = c$ this equation refers to the Ising [36] and Heisenberg [37] Hamiltonian respectively, whereas the case $a = b = 1$, $c = 0$ corresponds to the (less well known) XY model [38]. The combined action of spin-orbit coupling and the low-symmetry ligand field results in a splitting of the $^4T_{1g}$-level into six Kramers' doublets. The magnetic properties at low temperatures ($T < 40$ K) will be determined by the ground doublet, since at these temperatures this doublet will be the only populated level in the single-ion approximation. An effective S = ½ formalism will then apply and the anisotropy in the effective g-tensor for this doublet would indicate which of the model Hamiltonians will be appropriate. In case of a strong uniaxial anisotropy, the cases $g_\parallel \gg g_\perp$ and $g_\perp \gg g_\parallel$ would then apply to the Ising and XY model respectively. For the more general case of an ortho-rhombic anisotropy, the full expression should be applied.

Unfortunately, no single crystals of sufficient size for magnetic susceptibility measurements could be prepared. Therefore, in the absence of information on the anisotropy of the g-tensor, the magnetic data were fitted to the predictions for the susceptibility of a Heisenberg dimer and the parallel susceptibility of an Ising dimer, both with S = ½. Application

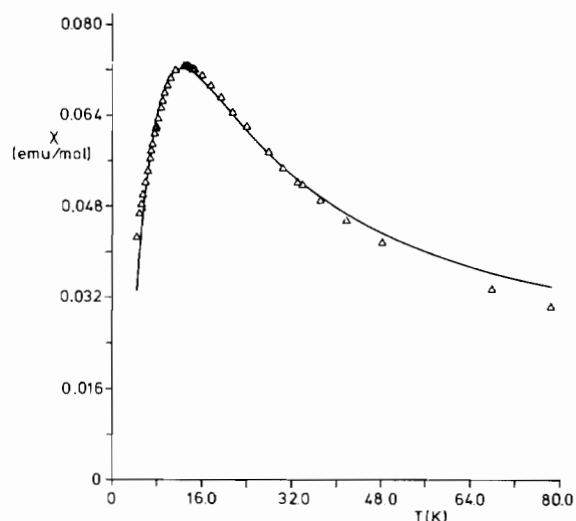of the Ising model provided the best fit, resulting in $J = -10.9$ cm^{-1}, $g_\parallel = 7.16$ and zJ = +0.02 cm^{-1} (solid curve Fig. 4). The deviation below 6 K may be due to paramagnetic impurities [7]. On powdering or heating the Co-compound turns blue, which is most probably caused by a loss of H_2O molecules, also observed for the similar Ettrz compound [11]. Although the sample was only slightly compressed in the sample holder, a small amount of the blue paramagnetic phase may have formed. The rather poor fit above 50 K is attributed to a neglect of $\chi_\perp$, and to the fact that at higher temperatures the lowest Kramers' doublet will not be the only populated level. The magnetic data suggest the existence of a weak ferromagnetic inter-dimer exchange, which probably occurs via the intermolecular hydrogen bridge $O(1)\cdots S(1)$.

[M₂(Altrz)₅(NCS)₄] (M = Mn(II), Fe(II))

The infrared spectrum of $[Mn_2(Altrz)_5(NCS)_4]$ shows two out-of-plane ring torsion absorptions (638(vs), 681(w) cm^{-1}), indicating the presence of both mono- and bi-dentate Altrz ligands [6, 24]. The splitting of the C–H out-of-plane absorption (876(s), 902(w,sh) cm^{-1}), although not very clear, agrees with this conclusion [6, 24]. The position of ν(CN) (2070(vs) cm^{-1}) and ν(CS) (799(m) cm^{-1}) are indicative for N-donation by the thiocyanate groups [25–28].

The magnetic susceptibility data, collected down to 2 K at a field of 1.72 kOe, are consistent with a dinuclear structure. The data were fitted by means of least-squares to the formula for the paramagnetic

susceptibility, which results from the spin Hamiltonian for an isotropic magnetic exchange with $S_1 = S_2 = 5/2$ (see ref. 39) without zero-field splitting. A fit of reasonable quality was obtained, resulting in $J = -0.4$ cm^{-1} and $g = 1.99$. No maximum in the χ vs. T curve was observed, since the small J value would result in a maximum below 2 K, a temperature which cannot be reached with our equipment.

Based on the infrared and magnetic susceptibility data a dinuclear structure is proposed for $[Mn_2-(Altrz)_5(NCS)_4]$. The metal ions are linked by three 1,2-bidentate coordinating Altrz ligands. The terminal coordination sites of the octahedrally surrounded Mn(II)-ions are occupied by two N-donating thiocyanates and an Altrz ligand coordinating by only one N atom. This compound has a higher symmetry than does the dinuclear Co- and Ni-compounds, as the coordinating H_2O molecule is replaced by a monodentate Altrz, resulting in the presence of a center of symmetry. A similar geometry has been reported [8, 9] for $[Co_2(Phtrz)_5(NCS)_4](H_2O)_{2.7}$ and $[Mn_2(Metrz)_5(NCS)_4]$. For this Mn-compound a J-value of -0.4 cm^{-1} was obtained with $g = 2.0$ [7].

For the Fe-compound a similar structure is proposed. Magnetic measurements and C, H, N, analyses were not carried out for $[Fe_2(Altrz)_5(NCS)_4]$, since the Fe(II)-ion is readily oxidized to Fe(III). The infrared spectrum and the X-ray powder diffractogram show some small differences with the data of the manganese compound, but these may originate from the presence of a fairly large quantity of the Fe(III).

The splitting of the C–H out-of-plane absorption in the infrared spectrum, which is a strong indication for the presence of both mono- and bi-dentate coordinating Altrz [6, 24], is more pronounced for $[Fe_2(Altrz)_5(NCS)_4]$ than for the Mn-compound (see Table VII). The asymmetric ligand field band of the Fe-compound exhibits a maximum at 11.600 cm^{-1}, which shows that Fe(II) is in the high-spin state. No high-spin low-spin transition is observed upon cooling to liquid nitrogen temperature.

[Zn₂(Altrz)₅(NCS)₂]∞[Zn(NCS)₄]
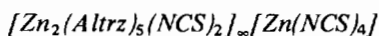
The formula of the Zn-compound per metal ion is $Zn(Altrz)_{5/3}(NCS)_2$. This suggests the presence of trinuclear units, in which the metal ions are linked by two bridging Altrz ligands. The central Zn ion would then be in an octahedral environment, which is completed by N donating thiocyanates. The terminal Zn ions would be coordinated tetrahedrally, with three isothiocyanates on the four terminal coordination sites, and an Altrz coordinating by only one N atom. This structure would imply that one thiocyanate group will

be not coordinating, *i.e.* ionic. A weak $\nu(CN)$ absorption at 2038 cm^{-1} is in agreement with this assumption, but this absorption can also originate from an isotopic satellite (^{13}C) [40]. Other collected data, however, are strongly in conflict with this trinuclear model.

The ligand field spectrum of the isostructural Co^{2+} dope (Table VIII) shows an octahedral environment of the metal centers. The high Dq value (1175 cm^{-1}) indicates that at least five of the ligands must be Altrz groups.

The infrared spectrum provides no absolute clarity about the coordination modes of the Altrz groups. Two out-of-plane ring torsions are present, but the absorption at 675 cm^{-1} is very weak. Two C–H out-of-plane absorptions are observed, but again one of them is weak (Table VII). These data suggest the presence of both mono- and bidentate Altrz ligands [6, 24].

The ^1H NMR spectrum, recorded in propylene carbonate, shows a singlet at 8.60 ppm. For Group VI metal coordination compounds with 4-substituted 1,2,4-triazoles containing monodentately coordinating triazoles, the ^1H NMR spectra show two singlets, indicating the unequivalence of the triazole ring protons [41].

In $[Zn(t-Butrz)_2(NCS)_2]$ [12], also containing triazole ligands coordinating through only one nitrogen atom, the ring protons give rise to only one singlet in the ^1H NMR spectrum. This suggests a rapid shuttling in solution of the coordination to the metal ion between N1 and N2 for divalent transition metal ions. Monodentate coordination of the Altrz ligand can therefore not be deduced from the ^1H NMR data.

The formula $[Zn_2(Altrz)_5(NCS)_2]_\infty[Zn(NCS)_4]$ seems very probable, especially from a detailed analysis of the infrared spectrum. In the far-infrared region, two strong absorptions are observed: 288 cm^{-1} and 225 cm^{-1}. Sabatini *et al.* [42] and Forster *et al.* [43] showed that an absorption around 280 cm^{-1} is indicative for $[Zn(NCS)_4]^{2-}$ species. A $\nu(CS)$ absorption at about 830 cm^{-1} was also observed by Sabatini for $(Et_4N)_2-Zn(NCS)_4$ [42]. Therefore, the presence of $[Zn(NCS)_4]^{2-}$ seems very likely in this case. The unit $[Zn_2(Altrz)_5(NCS)_2]^{2+}$ may present a polynuclear chain, in which the Zn ions are linked alternately by two and three 1,2-bicoordinating Altrz groups. The octahedra around the Zn centers are completed by an N-donating NCS^- group. The splitting of the C–H out-of-plane absorption is probably caused by the asymmetric coordination around the metal centers, as observed for the alternating zig-zag chain $[Cd_2(t-Butrz)_3(NCS)_4]_\infty$ [13]. Alternative structures cannot be excluded. Single crystals of the Zn compound have not been prepared so far.

[Cu₂(Altrz)₃(NCS)₄]∞

The infrared spectrum of [Cu₂(Altrz)₃-(NCS)₄]∞ shows only one γ(C—H) absorption (898 cm⁻¹), while the strong out-of-plane ring torsion is split (647 cm⁻¹, 639 cm⁻¹). The observation of only one C—H out-of-plane absorption, and the absence of the out-of-plane ring torsion which becomes infrared active with *C*-symmetry of the triazole ligand, indicates the presence of only bridging Altrz groups [6, 24]. The splitting of the strong out-of-plane ring torsion is most probably caused by a very asymmetric coordination around the Cu(II) centers, as is also observed for [Cd₂(t-Butrz)₃-(NCS)₄]∞ [13]. The ν(CN), ν(CS) and δ(NCS) absorptions are clearly split, showing the presence of different kind of thiocyanate groups. The observed shoulder at 1995 cm⁻¹ (ν(CN)) and the absorption at 510 cm⁻¹ (δ(NCS)) are in agreement with the presence of thiocyanates, bridging solely via the nitrogen atom. Evidence for the existence of such a bridging mode is presented elsewhere [13] for the crystal structure of [Cd₂(t-Butrz)₃(NCS)₄]∞. The remaining thiocyanate absorptions may be assigned to N-donating thiocyanate groups [25—28].

The ligand field spectrum shows an asymmetric band at 15.500 cm⁻¹, indicating a distorted six coordination around the Cu(II) centers.

The EPR spectrum shows one signal having a g-value of 2.13. Hyperfine splittings remain unresolved. On cooling to liquid nitrogen temperature only a slight sharpening of this signal is observed. The presence of a weak 'half-field' signal suggests the presence of dinuclear units.

The magnetic susceptibility data, collected between 10 K and 240 K, show a maximum in the susceptibility curve around 88 K. The data were fitted by means of least-squares to the Bleaney and Bowers equation for Cu(II) dimers [44]. Taking J = −48.6 cm⁻¹ and g = 2.00, a reasonable fit is obtained. Including zJ in the fitting procedure, a very good fit is obtained yielding J = −53.5 cm⁻¹, zJ = +0.03 cm⁻¹ and g = 2.04. The susceptibility data of |Cu₂(Altrz)₃(NCS)₄]∞ and the calculated values for both models are presented in Fig. 5.

Based on the infrared, ligand field, EPR and magnetic susceptibility data the proposed structure is an infinite, alternating chain. The Cu(II) centers are alternately linked by three 1,2-bicoordinating Altrz units and two thiocyanate groups bridging via the nitrogen atom. This structure is similar to that of [Cd₂(t-Butrz)₃(NCS)₄]∞ [13]. Based on the splitting of the ν(CN) absorption (2090 cm⁻¹ and 2030 cm⁻¹), however, the orientation of the non-bridging thiocyanate groups will be *cis* rather than *trans*. If the proposed structure is valid, it is not clear why the γ(C—H) absorption is not split, as observed for the above-mentioned Cd compound with t-Butrz.
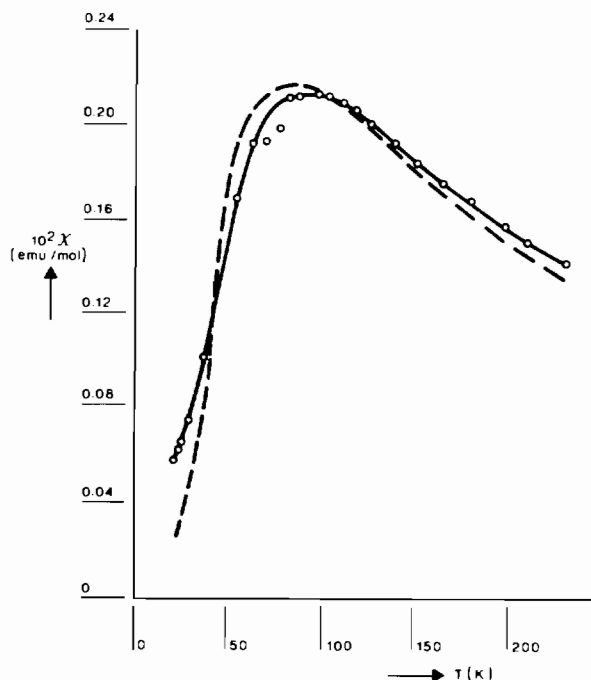

Fig. 5. Magnetic susceptibility per Cu(II)-ion of [Cu₂-(Altrz)₃(NCS)₄]∞ as a function of temperature. The curves represent the theoretical predictions for J = −48.6 cm⁻¹ and g = 2.00 (– – –) and for J = −53.5 cm⁻¹, zJ = +0.03 cm⁻¹ and g = 2.04 (———), according to Bleaney and Bowers [44].

It seems likely that the strong antiferromagnetic exchange represents the magnetic interaction between the triazole bridged Cu(II) centers. This would imply that the alternating chain may be interpreted, from a magnetochemistry point of view, in terms of a series of weakly coupled dinuclear units, which is in agreement with magnetic susceptibility and E.P.R. data. The proposed structure could not be verified by means of X-ray analysis. A series of crystals were investigated on their suitability for X-ray analysis, but unfortunately no single crystal of sufficient quality could be obtained.

[Cd₂(Altrz)₃(NCS)₄]∞

For [Cd₂(Altrz)₃(NCS)₄]∞ a chain structure is proposed. The Cd ions are linked alternately by three 1,2-bidentate coordinating Altrz groups and two bridging NCS groups. The six coordination around each Cd center is completed by a single bonded N donating thiocyanate. No single crystal of this compound has been prepared so far.

In the infrared spectrum the C—H out-of-plane vibration is observed as a rather strong asymmetric absorption at 882 cm⁻¹. Only one out-of-plane ring torsion absorption is present (637 cm⁻¹). These data strongly suggest the presence of bridging Altrz ligands only |6, 24].

The ¹H NMR spectrum of this compound, recorded in deuterated DMSO, shows only one signal (8.60

ppm) for the triazole ring hydrogens. As explained in the case of the Zn compound, however, mono-dentate coordination of the triazole ligand cannot be excluded, based on this observation only.

The ligand field spectrum of the isostructural Co^{2+} dope shows band at 10.200 cm^{-1}, 16.670 cm^{-1} and 21.500 cm^{-1} (Dq = 1115 cm^{-1}), indicating an octahedral coordination of the metal centers. This implies that bridging thiocyanates must be present. The major problem with this compound is the determination of the bridging mode of the thio-cyanate groups.

In $[Cd_2(t\text{-}Butrz)_3(NCS)_4]_\infty$ [13] thiocyanate groups are bridging via the nitrogen atom. This very unusual bridging mode results in characteristic infra-red absorptions at 1985 cm^{-1} ($\nu(CN)$) and 528 cm^{-1} ($\gamma(NCS)$). For $[Cd_2(Altrz)_3(NCS)_4]_\infty$ such a bridging mode is very unlikely, since the anion absorptions in this compound are located at: $\nu(CN)$: 2098 cm^{-1}(s) and 2042 cm^{-1}(s); $\nu(CS)$; 790 cm^{-1}(w); $\delta(NCS)$: 485 cm^{-1}(w,sh), 472 cm^{-1}(w), 455 cm^{-1}(w).

It is very likely that the thiocyanate bridges in this compound are formed by M–NCS–M units. In $[Cd(morpholine)_2(NCS)_2]$, which contains the same thiocyanate bridging mode, the observed anion absorptions are: $\nu(CN)$: 2090 cm^{-1}(s); $\nu(CS)$: 785 cm^{-1}, $\delta(NCS)$: 460 cm^{-1}(w) [45]. For $[Cd(Htrz)_2(NCS)_2]$ absorptions have been observed at 2095 cm^{-1}, 765 cm^{-1} and 476 cm^{-1} [46].

In all known examples of M–NCS–M bridging modes two bridges occur between the metal centers [45–49], which makes it very unlikely that three bridges are present in this Cd compound. Further-more, the significant splitting of the $\nu(CN)$ absorp-tion shows the presence of different types of thio-cyanates. It is to be expected, therefore, that the remaining thiocyanate is coordinating monodentately via the nitrogen atom, resulting in a $\nu(CN)$ absorp-tion at 2042 cm^{-1}. This frequency seems rather low for single-bonded N-donating thiocyanates. The same band position, however, has been observed for $[Cd_2(t\text{-}Butrz)_3(NCS)_4]_\infty$ for which structural evidence is obtained by X-ray diffraction techniques [13].

An alternative composition may be $[Cd(Altrz)_3]_\infty \cdot [Cd(NCS)_4]$. The occurrence of $[Cd(NCS)_4]^{2-}$ would account for the rather high Cd–N absorp-tion in the infrared spectrum (230 cm^{-1}) and for the presence of a small amount of tetrahedral spe-cies in the Cd compound, doped with Co(II) (see Table VIII). For tetrahedral Cd-species, a $\nu(CS)$ absorption above 800 cm^{-1} is to be expected. This absorption, however, is not observed.

Conclusions

In this paper a number of di- and poly-nuclear coordination compounds are described. The Co and Ni compounds are isostructural with a series of dinuclear compounds with Ettrz, reported prev-iously [10, 11]. The allyl group appears to have no significant effect on both the ring and the coordi-nation geometry, as they are essentially the same as in the Ettrz compounds [10]. The magnetic ex-change is also of the same magnitude as in the corresponding Ettrz compounds, *i.e.* −12.1 cm^{-1} and −9.5 cm^{-1} for the Co and Ni compound with Ettrz respectively and −10.9 cm^{-1} and −8.7 cm^{-1} respectively, for the corresponding compounds with Altrz.

For the Zn, Cd and especially the Cu compound further research is needed in order to provide evidence for the proposed structures. Numerous attempts to synthesize single crystals of these com-pounds have been unsuccessful so far. Furthermore, a detailed study of the Cu chain could give more information about the interesting magnetic proper-ties of this compound.

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