Ferromagnetic and Antiferromagnetic Spin Coupling in Ni_4O_4 Cubane-type Clusters with 4-Amino-3,5-bis(hydroxymethyl)-1,2,4-triazole as a Ligand. The X-ray Structure of a New Dumbbell-like Double Cubane Cluster

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Abstract

The synthesis, spectroscopic and magnetic properties of two nickel clusters are described, $Ni_8(NCS)_8$-$(Hahmt)_6(H_2ahmt)_4(ahmt)(H_2O)_{12}$ (A) and Ni_4-$(Hahmt)_4(H_2ahmt)_2(NCS)_4(H_2O)_4$ (B) (H_2ahmt = 4-amino-3,5-bis(hydroxymethyl)-1,2,4-triazole). The X-ray structure of A has been determined. The compound crystallizes in the space group $C2/c$, a = 25.458(2), b = 15.466(2), c = 26.959(3) Å, β = 90.684(5)°. The structure was refined to R = 0.108 for 4169 observed reflections. The structure consists of two Ni_4O_4 cubane-type clusters, each consisting of four nickel atoms, three singly deprotonated and one doubly deprotonated ligands. Hahmt coordinates as a bidentate chelating ligand through its triazole-N_1 and its 3-oxymethyl-part. The doubly deprotonated ligand chelates in a bis-bidentate manner to two Ni_4 clusters. In this way dumbbell-like pairs of ligand bridged cubanes are formed. Along two opposite diagonals of the Ni_4O_4 cubanes a neutral ligand, coordinating through its triazole-N_1, N_2 atoms, forms a bridge between two nickel ions. The NiN_3O_3 chromophore is completed by a monodentate N-coordinating thiocyanate anion. Compound B, for which only partial structure determination was possible, has the same Ni_4O_4 cubane-type cluster, however, without the bridging ligand between the cubanes. The two types of Ni–Ni bridges result in two unequivalent superexchange pathways. In the compounds both ferromagnetic and antiferromagnetic interaction pathways are present, resulting in an overall antiferromagnetic behaviour. The nature of the interaction for the different pathways is related to the observed Ni–O–Ni angles. The intercluster exchange is much larger through the triazole bridge in A than it is in B, where only hydrogen bridges keep the clusters together.

Introduction

Recently a variety of coordination compounds containing 1,2,4-triazole derivatives have been investigated. Most communications deal with mono- or dialkyl-substituted 1,2,4-triazoles. Using these types of ligands many di- and trinuclear linear compounds have been obtained, in which the triazole nucleus behaves as a bidentate ligand, bridging between the metal centers. Triple ligand bridges are known in the case of unsubstituted or 4-alkylsubstituted 1,2,4-triazoles [1–7]. Using 3,5-dialkylsubstituted triazoles the metal ions are bridged by only two ligands and either a fluoride, or a thiocyanate anion, due to steric hindrance [8, 9]. Most of these compounds exhibit rather small antiferromagnetic exchange.

Only a few examples are known of chelating triazole compounds. With 3,5-bis(pyridin-2-yl)-1,2,4-triazole and derivatives dinuclear planar compounds are formed with two bridging ligands [10–12]. Oligonuclear compounds with triazole ligands containing more than three metal ions have not been reported sofar, except for a tetranuclear copper compound reported by Prins *et al.* [13]. 4-Amino-3,5-bis-(hydroxymethyl)-1,2,4-triazole (H_2ahmt) (Fig. 1) is the first example of a chelating triazole ligand with aliphatic side chains.

H_2ahmt can occur in three ways, *i.e.* neutral, singly deprotonated and doubly deprotonated, resulting in three modes of coordination. When deprotonated, the ligand contains the same chelating
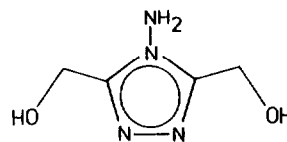

Fig. 1. Schematic drawing of 4-amino-3,5-bis(hydroxymethyl)-1,2,4-triazole (H_2ahmt).

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unit as the 1-oxymethylpyrazole anion, which has been reported by Paap *et al.* to form M_4O_4 cubane-type clusters (M = Co, Ni) [14].

This paper deals with two nickel thiocyanate compounds. In one of these compounds all three modes of coordination of H_2ahmt are present. The structure and magnetic properties of the compounds are reported.

Experimental

Synthesis of H_2ahmt

The ligand was synthesized using the method of Adàmek [15], with a few modifications. Glycolic acid and hydrazine hydrate in a 1:2 molar ratio were heated in a large beaker to 180 °C until evolution of water has ceased. The reaction mixture was solved in ethanol. The product crystallizes upon standing. A second crop can be obtained by evaporating the mother liquor and repeated heating and crystallisation. Melting point (m.p.): 197–200 °C (lit. 207 °C). Overall yield: 65%. NMR (dmso-d_6): 4.19 ppm ($-CH_2-$, doublet); 5.09 ppm (–OH, triplet); 5.61 ($-NH_2$, singlet).

Synthesis of $Ni_8(NCS)_8(ahmt)(Hahmt)_6(H_2ahmt)_4$-$(H_2O)_{12}$ (A) and of $Ni_4(NCS)_4(Hahmt)_4(H_2ahmt)_2$-$(H_2O)_4$ (B)

1 mmol of $NiCl_2 \cdot 6H_2O$ was dissolved in 5 cm^3 of water and added to a solution of 2 mmol of H_2ahmt and 2 mmol of ammonia in 5 cm^3 of water. After heating this solution another hot solution of 1 mmol NH_4NCS in 10 cm^3 of water was added. B crystallizes upon cooling down to room temperature within a day; A crystallizes, when the solution was cooled down very slowly, in about two weeks. Crystals, obtained in both ways, decompose in air. All determinations, except for the single crystal studies, were carried out on powders, formed upon drying the crystals. The decomposition of the crystals most likely does not affect the composition of the compound. It will be shown hereafter, that spectroscopic, analytical, magnetic and crystallographic data are all consistent with each other. Even the amount of lattice water molecules found in the crystal structure determination is in agreement with the composition of the compound calculated from the elemental analysis. *Anal.* A Found: Ni, 17.05; C, 23.03; H, 3.66; N, 26.05. Calc.: Ni, 17.22; C, 22.89; H, 3.99; N, 26.71%. B Found: Ni, 16.62; C, 24.09; H, 3.78; N, 27.37. Calc.: Ni, 16.78; C, 24.02; H, 3.75; N, 28.02%.

Analytical and Physical Measurements

C, H and N analyses were carried out by the Microanalytical Laboratory of University College, Dublin, Ireland. Nickel was determined using standard EDTA

titrations. Infrared spectra were recorded on a model 580B Perkin-Elmer spectrophotometer using KBr pellets in the range 4000–250 cm^{-1}. UV–Vis spectra were obtained on a Perkin-Elmer UV330 spectrophotometer using the diffuse reflectance technique with MgO as a reference.

Magnetic susceptibility data were obtained on a PAR model 150A vibrating sample magnetometer in the temperature region 4–80 K. Magnetic data were fitted to theoretical expressions given below by means of a Simplex routine [16], using a computer program written by Prins. These calculations were carried out on a Commodore PC10 personal computer. All parameters $(g, J_1, J_2, \theta, zJ'$; *vide infra*) were independently varied in the fitting procedure.

Data Collection and Structure Determination of A

X-ray data were collected on an ENRAF-NONIUS CAD4-F diffractometer for a blue transparent block-shaped crystal of A*, that was mounted with some mother liquor in a Lindemann glass capillary to prevent severe decay of the crystal due to loss of water of crystallization. Crystal data and numerical details of the structure determination are given in Table I. Lattice parameters with standard deviations were determined from the setting angles of 19 reflections $(8 < \theta < 12°)$. The observed extinctions $(h0l:l = 2n + 1)$ indicated space group Cc or $C2/c$. The latter was chosen. Standard deviations in the intensities were increased according to an analysis of the variance of the reference reflections [17]: $\sigma^2(I) = \sigma_{cs}^2(I) + (0.07 \times I)^2$. The reflections were corrected for Lp and a linear decay of 10% over the 136 h of X-ray exposure time. The structure of the complex was solved by Patterson methods with the program SHELX84 [18] and refined on F with blocked full-matrix least-squares techniques using a large version of SHELX76 [19]. The lattice contains several isolated cavities that showed up in a difference Fourier map as areas with large residual density. A total of six independent water molecules of crystallization at hydrogen bond distances from O and N functions could be identified in those areas, of which three had high temperature factors. The latter probably indicates severe positional disorder. However, no satisfactory disorder model could be found to describe it. In addition two of the NCS groups and one of the alcohol chains showed positional disorder; this was included with a disorder model in the final refinements. A difference map calculated at this stage showed additional residual density in the solvent

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TABLE I. Crystal Data and Details of the Structure Determination of A

(a) Crystal data

Formula	$C_{52}H_{104}N_{52}Ni_8O_{34}S_8$
Molecular weight	2727.9
Crystal system	monoclinic
Space group	$C2/c$
a (Å)	25.458(2)
b (Å)	15.466(2)
c (Å)	26.959(3)
β (°)	90.684(5)
V (Å^3)	10614(2)
Z	4
D(obs.), D(calc.) (g cm^{-3})	1.70, 1.707
$F(000)$ electrons	5616
μ(Mo Kα) (cm^{-1})	16.35
Crystal size (mm)	0.25 × 0.30 × 0.33

(b) Data collection

θ_{min}, θ_{max} (°)	0.76, 25
Radiation (Å)	Mo Kα (Zr-filtered), 0.71073
$\omega/2\theta$ scan (°)	0.50 + 0.35 tan θ
Horizontal, vertical aperture, distance to crystal (mm)	3, 3, 173
Refined reflections	020; 00 −4; 400
Data set	h 0:30; k 0:18; l −31:31
Total data, unique data	9948, 9325
Observed data ($I > 2\sigma(I)$)	4169

(c) Refinement

N_O, N_V	4169, 670
R, R_w	0.108, 0.153
Weighting scheme	$w = 1/\sigma^2(F)$
$(\Delta/\sigma)_{av}$	0.1
Min. max. resolved density (e Å^{-3})	1.53, −0.91

areas, an indication for additional disorder, but did not show any reliable hydrogen atom positions. Convergence was reached at $R = 0.108$. Most atoms were refined with anisotropic thermal parameters. Final positional parameters and equivalent isotropic temperature factors for the non-hydrogen atoms are listed in Table II. Scattering factors were taken from Cromer and Mann [20] and anomalous dispersion terms from Cromer and Liberman [21]. Geometrical calculations were done with PLATO [22]. The calculations were done on an in-house μ-VAX-II. X-ray data of **B** have been collected in a similar way; **B** crystallizes in the spacegroup $I4_1/a$; cell parameters are $a = b = 15.60(1)$ and $c = 26.89(1)$ Å, $Z = 4$. Reflections could be measured only for $\theta < 16°$ (Mo Kα), probably due to severe disorder. See 'Supplementary Material'.

Results and Discussion

Description of the Structure of A

The monoclinic unit cell of **A** contains four discrete molecules of the complex (Fig. 2) on sites with twofold axial symmetry and 48 water molecules of crystallization in intermolecular cavities. The water molecules are on hydrogen bond distances from O and N atoms. Selected data on the geometry are given in Table III. A drawing of the asymmetric part of the molecule is presented in Fig. 3, together with the labelling of the atoms as used in Tables II and III.

Basically the structure consists of Ni₄O₄ cubane-type clusters, built up from two interpenetrating tetrahedrons of four nickel atoms and four oxygen atoms. The four oxygen atoms originate from the deprotonated hydroxymethyl-substituents on the triazole ring. These deprotonated ligands chelate through their N1 and oxymethyl-O atoms to a nickel ion, whereas those oxygen atoms also coordinate to two other nickel atoms. Two neutral ligands coordinating through their triazole N1 and N2 atoms only, form a bridge between two nickel atoms along two opposite diagonals of the distorted Ni₄O₄ cube. The coordination octahedron around nickel is completed by a thiocyanate anion coordinating through its nitrogen atom. In this way NiN₃O₃ chromophores have been formed.

The Ni₄O₄ cubanes are coupled in pairs by a doubly deprotonated ligand, which chelates to two different cubanes through its two substituents. In this way the dumbbell-like structure is formed. The cubane bridging ligand lies on the twofold axis.

Bond distances and bond angles within the triazole rings are of the same magnitude as those observed for 4-alkyl-1,2,4-triazoles [2–8]. On the contrary the angles between the Ni—N bonds and ligand N—N and N—C bonds show significant deviations. In the deprotonated chelating ligands, the Ni—N—C angle is much smaller than the Ni—N—N angle (*ca.* 112° resp. *ca.* 137°), whereas in 4-alkyl-1,2,4-triazoles, either monodentately or bidentately coordinating, these angles are almost the same (*ca.* 125°). In the ligand bridging between the cubanes the strongest deviation appears (107.9° resp. 145.8°). The decrease of the M—N—C angle and the increase of the M—N—N angle belonging to it, will be due to the chelating effect of the N—C—C—O-moiety. The small values of the triazole-N-nickel-oxymethyl-O angles of the same chelating ring (*ca.* 80°) originate from the same effect. Both features have also been observed for the chelating 3,5-bis(pyridin-2-yl)-1,2,4-triazole and derivatives [11–13].

The changes in the bond angles concerning the neutral ligands are opposite to those concerning the deprotonated ligands. The Ni—N—N angles are decreased (*ca.* 111°) and the Ni—N—C angles are increased (*ca.* 140°). This leads to a reduction of the

TABLE II. Final Positional and Equivalent Isotropic Thermal Parameters for the Non-hydrogen Atoms of $Ni_8(NCS)_8(Hahmt)_6$-$(H_2ahmt)_4(ahmt)(H_2O)_{12}$

Atom	x	y	z	U_{eq} or U (Å^2)
Ni(1)	0.40888(8)	0.3396(2)	0.11839(9)	0.047(1)
Ni(2)	0.35087(8)	0.1764(2)	0.1173(1)	0.051(1)
Ni(3)	0.30768(8)	0.3252(2)	0.18849(9)	0.0421(8)
Ni(4)	0.40635(8)	0.2377(1)	0.22071(9)	0.0387(8)
S(1)	0.5781(2)	0.4699(5)	0.1311(3)	0.112(4)
S(2)	0.1785(2)	0.0858(7)	0.0712(3)	0.133(4)
S(3)	0.2657(9)	0.6225(8)	0.1594(6)	0.104(4)*
S(4)	0.407(1)	−0.054(1)	0.2541(9)	0.159(6)*
O(1)	0.1431(8)	0.446(2)	0.145(1)	0.17(1)
O(2)	0.0305(7)	0.123(1)	0.3667(8)	0.124(8)
O(3)	0.1987(9)	0.376(2)	0.4412(9)	0.17(1)
O(4)	0.021(1)	0.585(2)	0.009(1)	0.24(2)
O(5)	0.164(2)	0.653(3)	0.037(2)	0.30(2)
O(6)	0.126(2)	0.187(3)	0.323(2)	0.33(2)
O(11)	0.3861(4)	0.3560(6)	0.1906(4)	0.040(4)
O(21)	0.3337(4)	0.1949(7)	0.1896(4)	0.039(4)
O(22)	0.084(1)	0.174(3)	0.232(2)	0.31(3)
O(31)	0.3290(4)	0.3048(7)	0.1169(4)	0.041(4)
O(32)	0.371(2)	0.652(3)	−0.005(2)	0.22(2)*
O(41)	0.4243(4)	0.2183(7)	0.1484(4)	0.042(4)
O(42)	0.455(2)	−0.200(3)	0.154(2)	0.34(2)*
O(51)	0.2325(8)	0.431(2)	0.329(1)	0.25(2)
O(52)	0.3938(8)	0.143(1)	0.373(1)	0.15(1)
O(61)	0.326(1)	0.092(2)	−0.0480(9)	0.20(2)
O(62)	0.509(1)	0.345(2)	−0.028(1)	0.22(2)
N(1)	0.4826(6)	0.382(1)	0.1238(6)	0.062(5)
N(2)	0.2818(6)	0.134(1)	0.0914(6)	0.072(6)
N(3)	0.2822(6)	0.443(1)	0.1830(7)	0.064(8)
N(4)	0.4288(7)	0.123(1)	0.2482(8)	0.068(8)
N(11)	0.4736(4)	0.3167(8)	0.2422(5)	0.034(4)
N(13)	0.5(−)	0.450(1)	0.25(−)	0.040(6)
N(14)	0.5(−)	0.545(1)	0.25(−)	0.067(8)
N(21)	0.2385(5)	0.262(1)	0.1898(6)	0.046(5)
N(22)	0.1837(5)	0.282(1)	0.1840(7)	0.061(5)
N(23)	0.1947(6)	0.142(1)	0.2016(7)	0.070(6)
N(24)	0.1820(7)	0.055(1)	0.2104(7)	0.094(8)
N(31)	0.3735(6)	0.446(1)	0.0903(6)	0.064(6)
N(32)	0.3894(8)	0.533(1)	0.0807(8)	0.083(8)
N(33)	0.3117(7)	0.507(1)	0.0535(6)	0.070(6)
N(34)	0.2598(8)	0.519(1)	0.0257(8)	0.11(1)
N(41)	0.3912(6)	0.057(1)	0.1248(7)	0.064(8)
N(42)	0.3814(7)	−0.024(1)	0.1176(7)	0.074(6)
N(43)	0.4662(7)	−0.007(1)	0.1248(9)	0.087(8)
N(44)	0.5229(7)	−0.019(1)	0.127(1)	0.12(1)
N(51)	0.3142(5)	0.3172(9)	0.2672(5)	0.045(5)
N(52)	0.3609(5)	0.2766(9)	0.2813(5)	0.042(5)
N(53)	0.3158(7)	0.306(1)	0.3455(7)	0.067(6)
N(54)	0.2999(8)	0.315(2)	0.3973(7)	0.12(1)
N(61)	0.3860(6)	0.200(1)	0.0465(6)	0.073(6)
N(62)	0.4124(6)	0.279(1)	0.0472(7)	0.71(8)
N(63)	0.4112(8)	0.225(2)	−0.0260(7)	0.097(8)
N(64)	0.423(1)	0.255(2)	−0.0788(8)	0.15(2)
C(1)	0.5225(7)	0.420(1)	0.1264(8)	0.06(1)
C(2)	0.2370(7)	0.117(2)	0.0826(8)	0.08(1)
C(3)	0.269(1)	0.509(1)	0.1734(8)	0.09(1)
C(4)	0.429(1)	0.056(2)	0.250(2)	0.17(2)

TABLE II. *(continued)*

Atom	x	y	z	U_{eq} or U (Å^2)	
C(11)	0.4596(6)	0.399(1)	0.2358(7)	0.043(5)	
C(14)	0.4080(6)	0.423(1)	0.2174(7)	0.050(6)	
C(21)	0.2434(7)	0.183(1)	0.2017(6)	0.047(6)	
C(22)	0.1587(7)	0.206(2)	0.1926(8)	0.07(1)	
C(23)	0.096(1)	0.208(3)	0.188(1)	0.16(2)	
C(24)	0.2957(6)	0.141(1)	0.2105(7)	0.047(6)	
C(31)	0.3280(7)	0.432(1)	0.0723(7)	0.053(6)	
C(32)	0.349(1)	0.560(2)	0.055(1)	0.09(1)	
C(33)	0.346(2)	0.657(2)	0.036(1)	0.15(2)	
C(34)	0.3004(7)	0.351(1)	0.0781(8)	0.063(8)	
C(41)	0.4430(7)	0.071(1)	0.1305(8)	0.060(6)	
C(42)	0.428(1)	−0.065(2)	0.117(1)	0.10(1)	
C(43)	0.435(2)	−0.168(2)	0.115(2)	0.17(2)*	
C(44)	0.4643(7)	0.162(1)	0.1341(8)	0.060(8)	
C(51)	0.2854(7)	0.335(1)	0.3063(8)	0.07(1)	
C(52)	0.3624(6)	0.272(1)	0.3297(8)	0.055(8)	
C(53)	0.403(1)	0.236(2)	0.362(1)	0.10(1)	
C(54)	0.223(2)	0.364(2)	0.308(1)	0.18(2)	
C(61)	0.3865(9)	0.169(2)	0.004(1)	0.08(1)	
C(62)	0.4272(9)	0.291(2)	0.002(1)	0.08(1)	
C(63)	0.458(1)	0.383(2)	0.012(1)	0.14(2)	
C(64)	0.364(1)	0.077(2)	−0.012(1)	0.12(1)	
Minor disorder positions					Pop. par.
S(3')	0.2347(8)	0.604(1)	0.1523(6)	0.104(4)*	0.499(17)
S(4')	0.453(1)	−0.053(1)	0.2573(9)	0.159(6)*	0.480(20)
O(32')	0.318(5)	0.689(8)	0.001(4)	0.22(2)*	0.270(40)

Numbers in parentheses are e.s.d.s in the least significant digit. $U_{eq} = 1/3 \Sigma\Sigma U_{ij} a_i^* a_j^* a_i a_j$. Atoms with an asterisk have been refined isotropically.
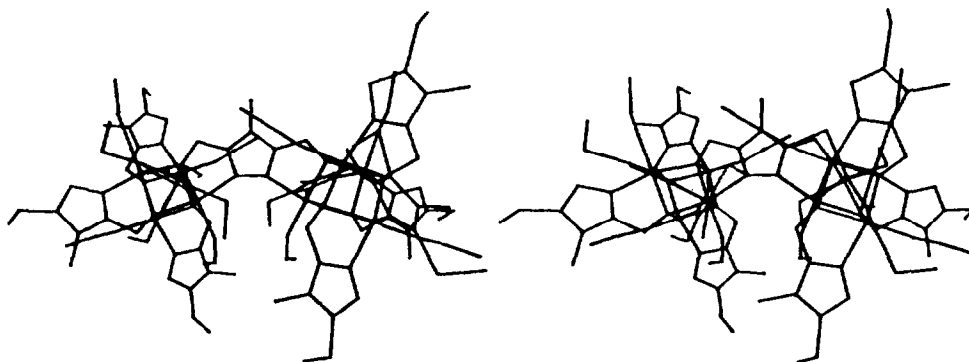

Fig. 2. Stereo drawing of the dumbbell-like double cluster A.

Ni(1)—Ni(2) and the Ni(3)—Ni(4) distances. These distances are about 0.22 Å smaller than the other Ni—Ni distances in the Ni₄O₄ cubane and 0.8 Å smaller than in coordination compounds with N(1), N(2)-coordinating 4-alkyl-1,2,4-triazoles [2–8]. The origin of the shortening of these Ni—Ni distances is not well understood yet.

Ni₄O₄ cubanes have been reported earlier in the literature [14, 23–26]. The first crystallographic study of a Ni₄O₄ cubane was published by Andrew

and Blake [24]. Only in the compound reported by Paap *et al.* [14] the bridging oxygen atoms are part of a chelating ligand, namely 1-(hydroxymethyl)-3,5-dimethylpyrazole. In all other reported Ni₄O₄ cubanes the Ni atoms are bridged by methoxy groups. Another uncommon feature of the described structure is the occurrence of the bridging triazole ligands along the diagonals of the distorted cube. All nickel ions are coupled to each other by means of oxygen bridges. Additionally, two pairs of Ni atoms also

TABLE III. Selected Data on the Geometry of A

Bond distances (Å)

Ni(1)–Ni(2)	2.924(4)	S(4)–C(4)	1.79(3)	N(33)–N(34)	1.52(3)
Ni(1)–Ni(3)	3.221(3)	S(3')–C(3)	1.80(3)	N(33)–C(32)	1.25(3)
Ni(1)–Ni(4)	3.178(3)	S(4')–C(4)	1.80(4)	N(41)–N(42)	1.29(2)
Ni(1)–O(11)	2.05(1)	O(11)–C(14)	1.38(2)	N(41)–C(41)	1.34(2)
Ni(1)–O(31)	2.10(1)	O(21)–C(24)	1.40(2)	N(42)–C(42)	1.35(2)
Ni(1)–O(41)	2.08(1)	O(22)–C(23)	1.34(6)	N(43)–C(41)	1.35(2)
Ni(1)–N(1)	1.99(2)	O(31)–C(34)	1.45(2)	N(43)–C(42)	1.34(3)
Ni(1)–N(31)	2.02(2)	O(32)–C(33)	1.28(6)	N(43)–N(44)	1.46(3)
Ni(1)–N(62)	2.14(2)	O(41)–C(44)	1.40(2)	N(51)–N(52)	1.39(2)
Ni(2)–Ni(3)	3.200(4)	O(42)–C(43)	1.26(7)	N(51)–C(51)	1.32(2)
Ni(2)–Ni(4)	3.251(4)	O(51)–C(54)	1.20(4)	N(52)–C(52)	1.31(3)
Ni(2)–O(31)	2.06(1)	O(52)–C(53)	1.49(3)	N(53)–C(52)	1.37(2)
Ni(2)–O(41)	2.14(1)	O(61)–C(64)	1.38(4)	N(53)–C(51)	1.38(3)
Ni(2)–O(21)	2.02(1)	O(62)–C(63)	1.49(4)	N(53)–N(54)	1.47(3)
Ni(2)–N(2)	2.00(2)	O(32')–C(33)	1.3(1)	N(61)–N(62)	1.39(2)
Ni(2)–N(41)	2.12(2)	N(1)–C(1)	1.17(2)	N(61)–C(61)	1.24(3)
Ni(2)–N(61)	2.15(2)	N(2)–C(2)	1.19(2)	N(62)–C(62)	1.29(3)
Ni(3)–Ni(4)	2.974(3)	N(3)–C(3)	1.10(2)	N(63)–N(64)	1.46(3)
Ni(3)–O(11)	2.05(1)	N(4)–C(4)	1.04(3)	N(63)–C(62)	1.33(4)
Ni(3)–O(21)	2.12(1)	N(11)–N(11A)	1.40(1)	N(63)–C(61)	1.35(4)
Ni(3)–O(31)	2.04(1)	N(11)–C(11)	1.33(2)	C(11)–C(14)	1.45(2)
Ni(3)–N(3)	1.94(2)	N(13)–N(14)	1.47(2)	C(21)–C(24)	1.50(2)
Ni(3)–N(21)	2.01(1)	N(13)–C(11)	1.35(2)	C(22)–C(23)	1.60(3)
Ni(3)–N(51)	2.13(1)	N(21)–N(22)	1.44(2)	C(31)–C(34)	1.45(2)
Ni(4)–O(11)	2.06(1)	N(21)–C(21)	1.27(2)	C(32)–C(33)	1.59(4)
Ni(4)–O(21)	2.13(1)	N(22)–C(22)	1.36(3)	C(41)–C(44)	1.51(2)
Ni(4)–O(41)	2.03(1)	N(23)–N(24)	1.40(2)	C(42)–C(43)	1.60(4)
Ni(4)–N(4)	2.00(2)	N(23)–C(21)	1.39(2)	C(51)–C(54)	1.65(5)
Ni(4)–N(11)	2.18(1)	N(23)–C(22)	1.37(3)	C(52)–C(53)	1.45(3)
Ni(4)–N(52)	2.10(1)	N(31)–N(32)	1.43(2)	C(61)–C(64)	1.59(4)
S(1)–C(1)	1.62(2)	N(31)–C(31)	1.27(2)	C(62)–C(63)	1.67(4)
S(2)–C(2)	1.59(2)	N(32)–C(32)	1.30(3)		
S(3)–C(3)	1.80(2)	N(33)–C(31)	1.33(2)		

Bond angles (°)

Ni(2)–Ni(1)–Ni(3)	62.54(9)	N(2)–Ni(2)–N(41)	99.8(6)
Ni(2)–Ni(1)–Ni(4)	64.23(8)	Ni(1)–Ni(3)–Ni(2)	54.19(8)
Ni(2)–Ni(1)–O(11)	88.2(3)	Ni(1)–Ni(3)–Ni(4)	61.58(7)
Ni(2)–Ni(1)–O(31)	44.8(3)	Ni(1)–Ni(3)–O(11)	38.3(3)
Ni(2)–Ni(1)–O(41)	47.0(3)	Ni(1)–Ni(3)–O(21)	79.8(3)
Ni(2)–Ni(1)–N(1)	139.5(5)	Ni(1)–Ni(3)–O(31)	39.7(3)
Ni(2)–Ni(1)–N(31)	118.5(4)	Ni(1)–Ni(3)–N(3)	99.2(5)
Ni(3)–Ni(1)–Ni(4)	55.38(7)	Ni(1)–Ni(3)–N(21)	138.5(5)
Ni(3)–Ni(1)–O(11)	38.3(3)	Ni(2)–Ni(3)–Ni(4)	63.44(8)
Ni(3)–Ni(1)–O(31)	38.2(3)	Ni(2)–Ni(3)–O(11)	80.9(3)
Ni(3)–Ni(1)–O(41)	81.8(3)	Ni(2)–Ni(3)–O(21)	38.4(3)
Ni(3)–Ni(1)–N(1)	137.7(5)	Ni(2)–Ni(3)–O(31)	39.0(3)
Ni(3)–Ni(1)–N(31)	85.4(5)	Ni(2)–Ni(3)–N(3)	138.3(6)
Ni(4)–Ni(1)–O(11)	39.6(3)	Ni(2)–Ni(3)–N(21)	88.2(4)
Ni(4)–Ni(1)–O(31)	82.0(3)	Ni(4)–Ni(3)–O(11)	43.9(3)
Ni(4)–Ni(1)–O(41)	38.8(3)	Ni(4)–Ni(3)–O(21)	45.7(3)
Ni(4)–Ni(1)–N(1)	97.4(5)	Ni(4)–Ni(3)–O(31)	88.4(3)
Ni(4)–Ni(1)–N(31)	135.7(5)	Ni(4)–Ni(3)–N(3)	136.9(5)
O(11)–Ni(1)–O(31)	76.5(4)	Ni(4)–Ni(3)–N(21)	120.6(4)
O(11)–Ni(1)–O(41)	78.3(4)	O(11)–Ni(3)–O(21)	85.2(4)
O(11)–Ni(1)–N(1)	99.6(6)	O(11)–Ni(3)–O(31)	78.0(4)
O(11)–Ni(1)–N(31)	97.2(5)	O(11)–Ni(3)–N(3)	96.2(5)
O(31)–Ni(1)–O(41)	87.4(4)	O(11)–Ni(3)–N(21)	164.2(5)

TABLE III. *(continued)*

O(31)–Ni(1)–N(1)	174.6(6)	O(21)–Ni(3)–O(31)	77.3(4)
O(31)–Ni(1)–N(31)	77.0(5)	O(21)–Ni(3)–N(3)	176.2(6)
O(41)–Ni(1)–N(1)	95.5(5)	O(21)–Ni(3)–N(21)	79.2(5)
O(41)–Ni(1)–N(31)	164.4(5)	O(31)–Ni(3)–N(3)	99.6(6)
N(1)–Ni(1)–N(31)	100.1(6)	O(31)–Ni(3)–N(21)	100.6(6)
Ni(1)–Ni(2)–Ni(3)	63.28(9)	N(3)–Ni(3)–N(21)	99.5(6)
Ni(1)–Ni(2)–Ni(4)	61.68(8)	Ni(1)–Ni(4)–Ni(2)	54.09(8)
Ni(1)–Ni(2)–O(31)	46.0(3)	Ni(1)–Ni(4)–Ni(3)	63.04(7)
Ni(1)–Ni(2)–O(41)	45.3(3)	Ni(1)–Ni(4)–O(11)	39.4(3)
Ni(1)–Ni(2)–O(21)	89.0(3)	Ni(1)–Ni(4)–O(21)	80.7(3)
Ni(1)–Ni(2)–N(2)	136.9(5)	Ni(1)–Ni(4)–O(41)	39.9(3)
Ni(1)–Ni(2)–N(41)	120.4(4)	Ni(1)–Ni(4)–N(4)	138.7(6)
Ni(3)–Ni(2)–Ni(4)	54.89(7)	Ni(1)–Ni(4)–N(11)	85.9(4)
Ni(3)–Ni(2)–O(31)	38.4(3)	Ni(2)–Ni(4)–Ni(3)	61.67(8)
Ni(3)–Ni(2)–O(41)	81.5(3)	Ni(2)–Ni(4)–O(11)	79.5(3)
Ni(3)–Ni(2)–O(21)	40.6(3)	Ni(2)–Ni(4)–O(21)	37.3(3)
Ni(3)–Ni(2)–N(2)	98.0(5)	Ni(2)–Ni(4)–O(41)	40.0(3)
Ni(3)–Ni(2)–N(41)	137.6(5)	Ni(2)–Ni(4)–N(4)	100.3(6)
Ni(4)–Ni(2)–O(31)	80.7(3)	Ni(2)–Ni(4)–N(11)	136.4(4)
Ni(4)–Ni(2)–O(41)	37.6(3)	Ni(3)–Ni(4)–O(11)	43.6(3)
Ni(4)–Ni(2)–O(21)	39.6(3)	Ni(3)–Ni(4)–O(21)	45.5(3)
Ni(4)–Ni(2)–N(2)	140.2(5)	Ni(3)–Ni(4)–O(41)	89.2(3)
Ni(4)–Ni(2)–N(41)	88.1(5)	Ni(3)–Ni(4)–N(4)	138.4(5)
O(31)–Ni(2)–O(41)	86.8(4)	Ni(3)–Ni(4)–N(11)	118.8(3)
O(21)–Ni(2)–O(31)	78.9(4)	O(11)–Ni(4)–O(21)	84.8(4)
O(31)–Ni(2)–N(2)	94.5(5)	O(11)–Ni(4)–O(41)	79.1(4)
O(31)–Ni(2)–N(41)	165.7(5)	O(11)–Ni(4)–N(4)	177.6(6)
O(21)–Ni(2)–O(41)	77.1(4)	O(11)–Ni(4)–N(11)	78.4(4)
O(41)–Ni(2)–N(2)	177.1(6)	O(21)–Ni(4)–O(41)	77.3(4)
O(41)–Ni(2)–N(41)	78.9(5)	O(21)–Ni(4)–N(4)	96.5(6)
O(21)–Ni(2)–N(2)	100.6(6)	O(21)–Ni(4)–N(11)	163.2(4)
O(21)–Ni(2)–N(41)	98.1(6)	O(41)–Ni(4)–N(4)	99.1(7)
O(41)–Ni(4)–N(11)	98.8(5)	N(44)–N(43)–C(42)	130.(2)
N(4)–Ni(4)–N(11)	100.3(6)	Ni(3)–N(51)–N(52)	110.7(9)
Ni(1)–O(11)–Ni(3)	103.3(5)	Ni(3)–N(51)–C(51)	138.(1)
Ni(1)–O(11)–Ni(4)	101.0(4)	N(52)–N(51)–C(51)	111.(1)
Ni(1)–O(11)–C(14)	118.(1)	Ni(4)–N(52)–N(51)	113.(1)
Ni(3)–O(11)–Ni(4)	92.5(4)	Ni(4)–N(52)–C(52)	139.(1)
Ni(3)–O(11)–C(14)	125.2(9)	N(51)–N(52)–C(52)	108.(1)
Ni(4)–O(11)–C(14)	111.3(9)	C(51)–N(53)–C(52)	112.(2)
Ni(2)–O(21)–Ni(3)	101.1(5)	N(54)–N(53)–C(51)	123.(2)
Ni(2)–O(21)–Ni(4)	103.1(5)	N(54)–N(53)–C(52)	126.(2)
Ni(2)–O(21)–C(24)	117.(1)	Ni(2)–N(61)–N(62)	110.(1)
Ni(3)–O(21)–Ni(4)	88.8(4)	Ni(2)–N(61)–C(61)	140.(2)
Ni(3)–O(21)–C(24)	110.7(9)	N(62)–N(61)–C(61)	110.(2)
Ni(4)–O(21)–C(24)	129.(1)	Ni(1)–N(62)–N(61)	112.(1)
Ni(1)–O(31)–Ni(2)	89.2(4)	Ni(1)–N(62)–C(62)	143.(2)
Ni(1)–O(31)–Ni(3)	102.2(5)	N(61)–N(62)–C(62)	105.(2)
Ni(1)–O(31)–C(34)	111.3(9)	C(61)–N(63)–C(62)	107.(2)
Ni(2)–O(31)–Ni(3)	102.7(5)	N(64)–N(63)–C(61)	134.(3)
Ni(2)–O(31)–C(34)	128.(1)	N(64)–N(63)–C(62)	119.(3)
Ni(3)–O(31)–C(34)	118.(1)	S(1)–C(1)–N(1)	178.(2)
Ni(1)–O(41)–Ni(2)	87.8(4)	S(2)–C(2)–N(2)	175.(3)
Ni(1)–O(41)–Ni(4)	101.3(5)	S(3)–C(3)–N(3)	165.(2)
Ni(1)–O(41)–C(44)	126.(1)	S(3′)–C(3)–N(3)	167.(2)
Ni(2)–O(41)–Ni(4)	102.4(5)	S(3)–C(3)–S(3′)	28.(1)
Ni(2)–O(41)–C(44)	110.(1)	S(4)–C(4)–N(4)	161.(3)
Ni(4)–O(41)–C(44)	122.(1)	S(4′)–C(4)–N(4)	160.(3)
Ni(1)–N(1)–C(1)	169.(1)	S(4)–C(4)–S(4′)	38.(1)

(continued)

TABLE III. *(continued)*

Ni(2)–N(2)–C(2)	168.(2)	N(11)–C(11)–C(14)	122.(1)
Ni(3)–N(3)–C(3)	171.(2)	N(11)–C(11)–N(13)	109.(1)
Ni(4)–N(4)–C(4)	155.(3)	N(13)–C(11)–C(14)	129.(1)
Ni(4)–N(11)–C(11)	107.1(9)	O(11)–C(14)–C(11)	110.(1)
Ni(4)–N(11)–N(11A)	145.8(9)	N(21)–C(21)–C(24)	123.(2)
N(11A)–N(11)–C(11)	107.(1)	N(21)–C(21)–N(23)	111.(2)
N(14)–N(13)–C(11)	125.8(8)	N(23)–C(21)–C(24)	126.(1)
C(11)–N(13)–C(11A)	108.(1)	N(22)–C(22)–N(23)	110.(2)
Ni(3)–N(21)–N(22)	138.(1)	N(22)–C(22)–C(23)	116.(3)
Ni(3)–N(21)–C(21)	113.(1)	N(23)–C(22)–C(23)	134.(3)
N(22)–N(21)–C(21)	109.(1)	O(22)–C(23)–C(22)	99.(2)
N(21)–N(22)–C(22)	105.(1)	O(21)–C(24)–C(21)	107.(1)
C(21)–N(23)–C(22)	105.(2)	N(31)–C(31)–C(34)	123.(2)
N(24)–N(23)–C(21)	130.(2)	N(31)–C(31)–N(33)	106.(2)
N(24)–N(23)–C(22)	125.(2)	N(33)–C(31)–C(34)	130.(2)
Ni(1)–N(31)–N(32)	135.(1)	N(32)–C(32)–N(33)	114.(2)
Ni(1)–N(31)–C(31)	114.(1)	N(32)–C(32)–C(33)	121.(3)
N(32)–N(31)–C(31)	111.(2)	N(33)–C(32)–C(33)	125.(3)
N(31)–N(32)–C(32)	100.(2)	O(32)–C(33)–C(32)	101.(3)
C(31)–N(33)–C(32)	109.(2)	O(32')–C(33)–C(32)	129.(6)
N(34)–N(33)–C(31)	124.(2)	O(32)–C(33)–O(32')	70.(6)
N(34)–N(33)–C(32)	126.(2)	O(31)–C(34)–C(31)	105.(1)
Ni(2)–N(41)–N(42)	138.(1)	N(41)–C(41)–C(44)	121.(1)
Ni(2)–N(41)–C(41)	110.(1)	N(41)–C(41)–N(43)	106.(1)
N(42)–N(41)–C(41)	111.(2)	N(43)–C(41)–C(44)	133.(2)
N(41)–N(42)–C(42)	107.(2)	N(42)–C(42)–N(43)	109.(2)
C(41)–N(43)–C(42)	107.(2)	N(42)–C(42)–C(43)	125.(3)
N(44)–N(43)–C(41)	123.(2)	N(43)–C(42)–C(43)	126.(3)
O(42)–C(43)–C(42)	114.(4)	O(51)–C(54)–C(51)	93.(3)
O(41)–C(44)–C(41)	110.(1)	N(61)–C(61)–N(63)	108.(2)
N(51)–C(51)–N(53)	103.(1)	N(61)–C(61)–C(64)	126.(2)
N(51)–C(51)–C(54)	128.(2)	N(63)–C(61)–C(64)	126.(2)
N(53)–C(51)–C(54)	127.(2)	N(62)–C(62)–N(63)	110.(2)
N(52)–C(52)–N(53)	106.(2)	N(62)–C(62)–C(63)	119.(2)
N(52)–C(52)–C(53)	129.(2)	N(63)–C(62)–C(63)	132.(2)
N(53)–C(52)–C(53)	125.(2)	O(62)–C(63)–C(62)	98.(2)
O(52)–C(53)–C(52)	112.(2)	O(61)–C(64)–C(61)	107.(2)

A prime indicates atoms of the minor disorder positions. A indicates the symmetry operation $1 - x, y, \frac{1}{2} - z$.

bridged by a triazole-nucleus are formed. As a matter of fact these two different types of Ni–Ni bridges result in different magnetic exchange parameters (*vide infra*).

X-ray data of **B** have also been collected. Although the crystals appeared to be of very poor quality, the existence of a Ni_4O_4 cubane was evident. Together with its composition and the similarity between the compounds with respect to the spectroscopic and magnetic data, it was assumed to have the same Ni_4O_4 cubane type structure. However, no bridging ligand can be present between the cubanes. The clusters in **B** must therefore be linked together through hydrogen bridges.

Spectroscopy

The IR spectra of **A** and **B** show only marginal differences, mainly in the intensities of some ligand vibrations. From the crystal structure determination it is quite clear, that the thiocyanate anion is N-coordinated to nickel. The $\nu(CN)$ vibration at 2100 cm^{-1} resembles this coordination mode. The $\nu(CS)$ and $\delta(NCS)$ vibrations could be assigned to the absorptions at 790 and 470 cm^{-1} respectively, all in agreement with N-coordinated thiocyanate. The absorptions observed at 442 and 340 cm^{-1} are tentatively assigned to Ni–O stretchings [25]. The compounds show typical octahedral ligand field spectra (σ_1, 9500; σ_2, 16 200; σ_3, 25 700 cm^{-1} for **A** and σ_1. 9700; σ_2, 16 200; σ_3, 25 700 cm^{-1} for **B**) with Dq values, that could be expected for a NiO_3N_3 chromophore [27].

Magnetic Measurements

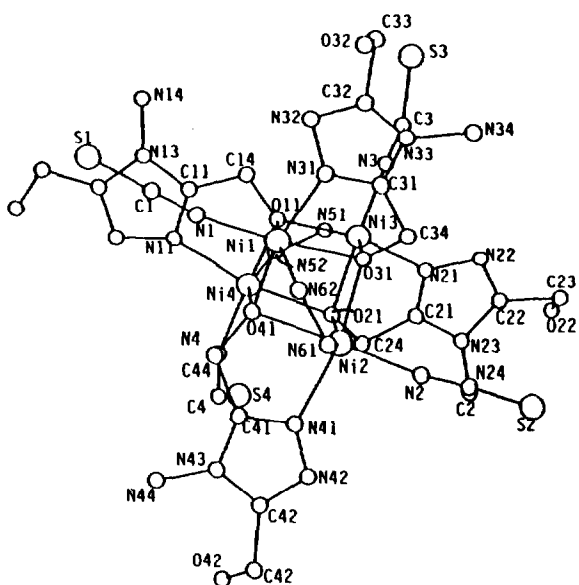Magnetic susceptibilities of the compounds were measured in the range 4–80 K. The χ *versus* T plots

Fig. 3. PLUTO drawing of the asymmetric part of A. The atom numbering corresponds to the numbering used in Tables II and III. The non-coordinating atoms of ligands 5 and 6 have been omitted for clarity; the atom numbering in this ligands is equivalent to that in all other ligands. N13 and N14 are on the twofold axis.

Fig. 4. Schematic representation of the Ni_4O_4 cubane cluster, showing the exchange integrals; the pseudo S_4 symmetry axis is also indicated.

clearly show antiferromagnetic exchange, whereas all Ni_4O_4 cubanes reported sofar exhibit ferromagnetic intracluster exchange. Andrew and Blake [24] and Bertrand *et al.* [26] have derived an expression for the magnetic susceptibility of tetranuclear nickel clusters with tetrahedral symmetry. That means, that all six super exchange pathways are equivalent. As has been pointed out above, two different exchange pathways are to be expected in the now described Ni_4O_4 cubanes. For this reason, the formulae given in refs. 24 and 26 are not suitable for the problem under consideration.

In order to describe the intracluster exchange, a formula for the magnetic susceptibility was derived using the Heisenberg–Dirac–Van Vleck method. The intercluster exchange through the doubly deprotonated ligand was assumed to be small and therefore neglected in first instance. To diminish the number of parameters local S_4 symmetry was assumed for the cluster. The eigenvalues of the Hamiltonian

$$\mathcal{H} = -2J_1\{S_1S_4 + S_1S_3 + S_2S_3 + S_2S_4\}$$
$$- 2J_2\{S_1S_2 + S_3S_4\}$$

were calculated, where J_1 stands for the exchange interaction between Ni ions bridged by two oxygen atoms only and J_2 for the exchange between Ni ions bridged by two oxygen atoms and the triazole nucleus (see Fig. 4). By taking $S' = S_1 + S_2$, $S^* = S_3 + S_4$ and $S^T = S' + S^*$, where S' and S^* can take the
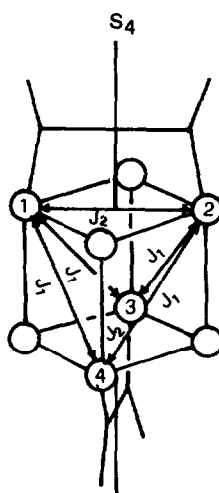
values 2, 1, 0 and S^T can take the values $S' + S^*, \dots, S' - S^*$, we have

$$\mathcal{H} = -J_1\{(S^T)^2 - (S')^2 - (S^*)^2\} - J_1\{(S')^2 + (S^*)^2$$
$$- S_1^2 - S_2^2 - S_3^2 - S_4^2\}$$

and the corresponding energy equation

$$E = -J_1\{S^T(S^T + 1) - S'(S' + 1) - S^*(S^* + 1)\}$$
$$- J_2\{S'(S' + 1) + S^*(S^* + 1) - 4S(S + 1)\}$$

Taking all possible values for S' and S^* and the corresponding values for S^T, one may calculate the eigenvalues for the Hamiltonian. Substituting the eigenvalues into Van Vlecks equation one obtains an expression for the magnetic susceptibility

$$\chi = Ng^2\beta^2[30 \exp(8x + 4y) + 14 \exp(4y)$$
$$+ 5 \exp(-6x + 4y) + \exp(-10x + 4y)$$
$$+ 28 \exp(4x) + 10 \exp(-2x) + 2 \exp(-6x)$$
$$+ 10 \exp(-2y) + 5 \exp(2x - 4y)$$
$$+ \exp(-2x - 4y) + 2 \exp(-6y)]/2kT[9 \exp(8x$$
$$+ 4y) + 7 \exp(4y) + 5 \exp(-6x + 4y)$$
$$+ 3 \exp(-10x + 4y) + \exp(-12x + 4y)$$
$$+ 14 \exp(4x) + 10 \exp(-2x) + 6 \exp(-6x)$$
$$+ 10 \exp(-2y) + 5 \exp(2x - 4y)$$
$$+ 3 \exp(-2x - 4y) + \exp(-4x - 4y)$$
$$+ 6 \exp(-6y) + \exp(-8y)]$$
$$(x = J_1/kT; \quad y = J_2/kT) \qquad (1)$$

TABLE IV. Comparison of Best-fit Parameters[a] for Susceptibility *vs.* Temperature Data

Compound	Eqn. (1)[b]				Eqn. (2)					Eqn. (3)				
	J_1	J_2	g	ssr[c]	J_1	J_2	g	θ	ssr	J_1	J_2	g	zJ'	ssr
A	−8.5	4.2	2.12	4.5×10^{-5}	−5.5	7.6	2.02	−11.1	1.3×10^{-6}	−8.4	4.6	2.05	0.3	4.5×10^{-5}
B	−8.0	6.3	2.13	1.4×10^{-5}	−6.0	7.4	2.03	−5.2	5.6×10^{-6}	−8.5	3.1	2.47	−1.6	1.3×10^{-6}

[a]The meaning of J_1, J_2, θ and zJ' is explained in the text.   [b]Equations (1), (2) and (3) are as given in the text.   [c]ssr means sum of square residuals.
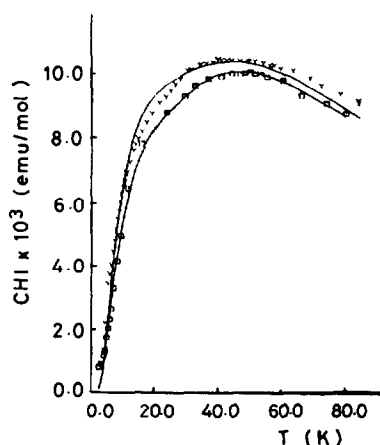
Fig. 5. Temperature dependence of the magnetic suscepti-bilities of A (□) and B (Y). Full curves are calculated using eqn. (2) with the parameters as given in Table III.

Taking $J_1 = J_2$, *i.e.* assuming T_d symmetry, the formula reduces to the one given by Andrew and Blake [24] and Bertrand *et al.* [26], which in fact could be expected.

The effect of intercluster exchange could be taken into account by replacing T with $T - \theta$ in the factor and Lines [28], who derived expressions for both temperature-dependent and temperature-independent intercluster exchange. This exchange could be taken into account by replacing T with $T - \theta$ in the factor $Ng^2\beta^2/kT$ in the expression for the susceptibility. For small intercluster exchange θ is assumed to be a constant yielding eqn. (2) (not given), whereas for larger values a temperature dependent expression has been derived:

$$\theta = \{2zJ'k^{-1}SS(S + 1)(2S + 1) \exp[-E(S)/kT]\}/$$

$$\{S(2S + 1) \exp[-E(S)/kT]\} \qquad (3)$$

The best fit parameters are summarized for both compounds in Table IV and visualized in Fig. 5 (for eqn. (2)).

It is quite clear from Fig. 5, that rather large deviations occur between calculated and observed X values, even when intercluster exchange is taken into account. This might originate from two assump-

tions that have been made, namely, that the Ni_4O_4 cubanes have S_4 symmetry instead of C_1 symmetry and that the zero-field splitting of the individual nickel ions is zero. The values of J_1 and J_2 obtained with either eqn. (1), (2) or (3) are of the same magnitude for both compounds. As could be expected from the structural differences between the two compounds, significant differences occur with respect to the intercluster exchange. Assuming temperature independent intercluster exchange (eqn. (2)) the magnitude of the intercluster exchange is smaller in compound B than in A. In B the intercluster exchange can take place via the hydrogen bridge contacts which will exist between the clusters. In A the main part of the intercluster exchange originates from the bridging ligand between two pairs of Ni_4O_4 cubanes. On the other hand weaker exchange pathways will exist through hydrogen bridges between the different pairs of Ni_4O_4 cubanes. Applying eqn. (3) ... . compounds smaller values are obtained for the intercluster exchange, which is in agreement with the results of Ginsberg and Lines [28]. In A zJ' is even positive. The reason for this is not understood as yet.

The magnetic exchange parameters resulting from the above discussed model are clearly opposite to the results obtained for Ni_4O_4 cubanes, as well as to those for triazole-bridged Ni compounds. Ni_4O_4 cubanes reported sofar all exhibit ferromagnetic exchange. Triazole-bridged transition metal compounds show antiferromagnetic interaction. Nevertheless, we calculate a ferromagnetic exchange between the nickel ions bridged both by the triazole nucleus and the bridging oxygen atoms and an antiferromagnetic exchange between the nickel ions bridged by oxygen atoms only.

The interaction through the triazole bridges is assumed to be very small compared to the interaction through the oxygen atoms. The basis for this assumption is the small value of the Ni−N−N angles observed around the coordinating nitrogen atoms of the triazole ring. This diminishes the overlap between the magnetic orbitals through the triazole nucleus.

For planar oxygen-bridged copper dimers it is clear, that the sign of the magnetic interaction depends on the value of the Cu−O−Cu angle.

Hatfield *et al.* [29] have found, that the singlet—triplet splitting in $Cu_2(OH)_2$ units will vanish for a bridging angle near 97.5°. For larger angles antiferromagnetic interaction is observed, where as for smaller angles ferromagnetic interaction will occur. Kahn *et al.* [30] have rationalized this effect in terms of the magnitude of the overlap integral between the magnetic orbitals. The same effect can be expected for oxygen bridged nickel atoms, as has already been argumented by Martin [31] and Cairns [32] and in fact has been observed in this and earlier work [33]. It can be seen from Table III, that the mean value of the Ni—O—Ni angles between the nickel atoms that are bridged by both oxygen and triazole, is significantly smaller than the mean value of the Ni—O—Ni angle between the purely oxygen bridged Ni atoms (89.69° and 102.11° respectively). A ferromagnetic interaction has been found to correspond to the smaller angles and an antiferromagnetic interaction to the larger ones.

This qualitative relation between the nature of the Ni—Ni interaction and the corresponding Ni—O—Ni angles also holds for the other reported Ni_4O_4 cubane clusters. In spite of this excellent result, these cubane-type compounds seem not to be suitable to derive a quantitative relation between the strength of the Ni—Ni interaction and the Ni—O—Ni angle, as has been done for planar $Cu-(O)_2-Cu$ systems. The reason for this is the nonplanarity of the Ni—$(O)_2$—Ni units and the low symmetry of the clusters, resulting into many parameters and the fact, that the number of structurally similar compounds is expected to be very small.

Conclusion

It has been pointed out again, that using 1,2,4-triazole derivatives interesting coordination compounds can be obtained. Quite often compounds have been synthesized, which show unprecedented characteristics [3,5,13,34]. It has been shown now, that chelating triazoles with aliphatic side chains also yield novel types of compounds. It is challenging to continue the investigations in this part of the triazole research, because the N—C/N—CH₂—O— moiety clearly appears to stabilize M_4O_4 clusters. The symmetry of the ahmt-ligand resulted in the ligand bridged Ni_4O_4 cubane structure. It may be interesting to investigate the asymmetric 3-hydroxymethyl-1,2,4-triazole, which has nearly the same structure as 1-hydroxymethylpyrazole [14]. With the latter ligand cubane-type clusters have been obtained with nickel and cobalt and with chloride and bromide as coordinating anions. Using H₂ahmt it was not possible to obtain similar structures with other metals and or anions than nickel and thiocyanate.

Supplementary Material

Listings of anisotropic temperature factors, all bond angles and torsion angles and observed and calculated structure factors are available from one of the authors (A.L.S.).

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