

can be the ultimate product from the reaction between *fac*-(CH₃CN)₃Mo(CO)₃ and CH₃N(PF₂)₂. However, in the presence of limited quantities of hydrogen chloride the course of this reaction can be diverted to [CH₃N(PF₂)₂]₂Mo₂(CO)₃(PF₂NHCH₃)(PF₂)(Cl) (5). In addition, [CH₃N(PF₂)₂]₄Mo₂(CO)₃ has been shown to react readily with excess CH₃N(PF₂)₂ around 100 °C with replacement of two of its three carbonyl groups by a CH₃N(PF₂)₂ ligand to give [C-H₃N(PF₂)₂]₅Mo₂CO (6). In the absence of X-ray crystallographic structural data, we are reluctant to speculate on the structure of [CH₃N(PF₂)₂]₅Mo₂CO. However, the presence of an extremely low-field resonance at $\delta +43.6$ (doublet, $J = 1111$ Hz) in the otherwise very complicated fluorine-19 NMR spectrum of this complex supports our earlier suggestion³ that [CH₃N(PF₂)₂]₅Mo₂CO has a bridging PF₂ group like [C-H₃N(PF₂)₂]₂Mo₂(CO)₃(PF₂NHCH₃)(PF₂)(Cl) (5) and (CO)Fe₂(PF₂NCH₃)₂[μ -CH₃N(PF₂)₂]₃(μ -PF₂)²⁰ which also have relatively low-field fluorine-19 resonances.

Acknowledgment. The portion of this work performed at the University of Georgia was partially supported by the Petroleum Research Fund, administered by the American Chemical Society. The research performed at the Oak Ridge National Laboratory was sponsored by the Division of Materials Sciences, Office of Basic Energy Sciences, U.S. Department of Energy, under Contract W-7405-eng-26 with the Union Carbide Corp.

Registry No. 1, 17731-95-2; 3, 89460-03-7; 4, 79721-57-6; 5, 89346-98-5; 6, 79746-02-4; C₇H₈Mo(CO)₃, 12125-77-8; C₈H₈Mo(CO)₃, 12108-93-9; η^4 -C₈H₈Mo(CO)₃(PF₂)₂NCH₃, 89346-99-6; [CH₃N(PF₂)₂]₃Mo₂(CO)₅, 79721-55-4; [(C₂H₅)₃NH]Cl, 554-68-7; CH₃N(PF₂)₂, 17648-18-9; CH₃CN, 75-05-8; Mo, 7439-98-7.

Supplementary Material Available: For compound 5, listings of anisotropic thermal parameters, hydrogen atom coordinates, least-squares best planes, and observed and calculated values of F^2 with standard errors of the former (27 pages). Ordering information is given on any current masthead page.

Contribution from the Department of Chemistry, Gorlaeus Laboratories, State University Leiden; 2300 RA Leiden, The Netherlands

Synthesis, Spectroscopic Characterization, and Magnetic Properties of Unusual 3,5-Dialkyl-1,2,4-triazole Compounds Containing N-Bridging Isothiocyanato Ligands. X-ray Structure of Trinuclear

Bis(μ -thiocyanato-*N*)bis(μ -3,5-diethyl-1,2,4-triazole-*N*¹,*N*²)bis(thiocyanato-*N*)(3,5-diethyl-1,2,4-triazole-*N*¹)nickel(II)-*N*,*N*¹,*N*^{1'}]nickel(II) Dihydrate

GERARD A. VAN ALBADA, RUDOLF A. G. DE GRAAFF, JAAP G. HAASNOOT, and JAN REEDIJK*

Received July 15, 1983

The synthesis and characterization of a series of unusual trimeric and polymeric coordination compounds containing 3,5-dialkyl-1,2,4-triazoles are described. The compounds have the general formulas M₃(LH)₆(NCS)₆(H₂O)₂ (M = Mn²⁺, Co²⁺, Ni²⁺; LH = 3,5-dimethyl-1,2,4-triazole and 3,5-diethyl-1,2,4-triazole), Zn(NCS)(L⁻) (L⁻ is the deprotonated ligand LH), and Cd(NCS)₂(LH). The Zn and Cd compounds are polymeric, containing bridging triazole ligands and (bridging) thiocyanato ligands. The Mn, Co, and Ni compounds are mutually isomorphous and contain the linear trinuclear unit (NCS)₂(LH)M(LH)₂(NCS)M(LH)₂(NCS)M(LH)(NCS)₂, as deduced from a single-crystal X-ray analysis of the compound with M = Ni(II) and the 3,5-diethyl derivative. The title compound crystallizes in the orthorhombic space group *Pbca* with $a = 14.447$ (8) Å, $b = 23.047$ (8) Å, and $c = 18.613$ (9) Å and $Z = 4$. The structure was solved with use of Mo $K\alpha$ diffractometer data and standard heavy-atom and least-squares refinement techniques. Final residuals are 0.058 (R) and 0.063 (R_w). The trinuclear cations all have Ni(II) atoms with a NiN₆ chromophore (Ni-N distances are 2.02 (1)-2.18 (1) Å). The usual structural features are the N-bonding bridging NCS groups between the Ni(II) atoms and the 1,2-bridging triazole ligands (two between each pair of nickel ions). The magnetic-exchange interactions between the metal ions are small but significant. The Mn and Co compounds are antiferromagnetically coupled, but—surprisingly—the nickel trimers are ferromagnetic. The results are discussed on the basis of the structure determined.

Introduction

Triazoles, and in particular 1,2,4-triazole, are versatile ligands that show a very interesting coordination chemistry.¹⁻⁵ After deprotonation all three nitrogens have lone pairs available and coordination to metal ions through several modes has been observed. Unsubstituted 1,2,4-triazole is known to yield a chain-type structure through 1,2-bridging in CuCl₂(trH) (trH = 1,2,4-triazole).² Changing the anion to NCS⁻ has led to the discovery of a new class of two-dimensional structures, M(NCS)₂(trH)₂, with very interesting magnetic

properties.³ When the experimental conditions were changed, a second isomer was observed, which turned out to be trimeric.⁴ Prevention of the deprotonation at N(4) by alkylation led Vos⁵ to the discovery of a large group of dimeric and trimeric species, all having the M(Rtr)₃M or the M(Rtr)₃M(Rtr)₃M unit (Rtr = 4-alkyl-1,2,4-triazole).

The use of thiocyanate anions proved to be useful in the above-mentioned studies, and in all cases N-bonded NCS⁻ groups were found. Thiocyanate is known to be versatile and ambidentate in its coordination behavior,⁶ and many other modes of coordination have been reported. In our previous studies we found that bridging occurs between two Cd(II) ions, using only the nitrogens of the NCS ions.⁷ Because of the unusual bridging mode of NCS and our interest in the magnetic exchange between transition-metal ions through small

- (1) Inoue, M.; Kubo, M. *Coord. Chem. Rev.* **1976**, *21*, 1.
- (2) Jarvis, J. A. *Acta Crystallogr.* **1962**, *15*, 964.
- (3) Engelfriet, D. W. Ph.D. Thesis, State University Leiden, 1979. Engelfriet, D. W.; Groeneveld, W. L.; Groenendijk, H. A.; Smit, J. J.; Nap, G. M. *Z. Naturforsch., A* **1980**, *35A*, 115.
- (4) Reimann, C. W.; Zocchi, M. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1971**, *B27*, 682.
- (5) Vos, G.; le Fèvre, R. A.; de Graaff, R. A. G.; Haasnoot, J. G.; Reedijk, J. J. *Am. Chem. Soc.* **1983**, *105*, 1682.

(6) Kabesova, M.; Gazo, J. *Chem. Zvesti* **1980**, *34*, 800.

(7) Groeneveld, L. R.; Vos, G.; Verschoor, G. C.; Reedijk, J. J. *Chem. Soc., Chem. Commun.* **1982**, 620.

Table I. Coordination Compounds of dmtrH and detrH with Metal Thiocyanates with Analytical Data, X-ray Powder Isomorphism, Melting Points, and Colors

formula	color	% metal		mp, °C	X-ray powder type
		calcd	found		
Mn ₃ (dmtrH) ₆ (NCS) ₆ (H ₂ O) ₂	white	14.6	14.8	160	A
Co ₃ (dmtrH) ₆ (NCS) ₆ (H ₂ O) ₂	red	15.2	15.6 ^a	230 dec	A
Ni ₃ (dmtrH) ₆ (NCS) ₆ (H ₂ O) ₂	blue	15.4	15.5 ^b	>250	A
Zn(NCS) ₂ (dmtr)	white	29.8	28.7 ^c	>250	
Cd(NCS) ₂ (dmtrH)	white	34.5	34.5	200 dec	
Mn ₃ (detrH) ₆ (NCS) ₆ (H ₂ O) ₂	white	12.7	12.1	155	A'
Co ₃ (detrH) ₆ (NCS) ₆ (H ₂ O) ₂	red	13.5	12.6	110 dec	A'
Ni ₃ (detrH) ₆ (NCS) ₆ (H ₂ O) ₂	blue	13.4	13.0 ^d	205 dec	A'
Zn(NCS) ₂ (detr)	white	21.4	21.3	>250	
Cd(NCS) ₂ (detrH)	white	31.8	30.0	180 dec	

^a Anal. Found (Calcd): C, 30.69 (31.49); H 4.06 (4.05); N, 28.7 (29.38); S, 17.1 (16.81). ^b Anal. Found (Calcd): C, 30.95 (31.51); H, 4.07 (4.06); N, 27.83 (29.40). ^c Anal. Found (Calcd): C, 27.52 (27.34); H, 2.94 (2.75); N, 25.21 (25.52). ^d Anal. Found (Calcd): C, 37.34 (38.45); H, 5.32 (5.38); N, 26.05 (25.62).

ligands,⁸ we have started an investigation into the synthesis and the properties of triazole compounds with small bridging anions, such as F, OH, and NCS. Consideration of space-filling molecular models already indicated that 3,5-disubstituted 1,2,4-triazoles might provide good cavities for small anions, when species such as M(LH)₂M are formed (LH = 3,5-disubstituted 1,2,4-triazoles).

Subsequent preparation and structural characterization of the compounds obtained has indeed shown that novel types of bridged systems can be obtained with use of this approach. The present paper describes the first results of these investigations, using transition-metal thiocyanates and 3,5-diethyl- and 3,5-dimethyl-1,2,4-triazole, including a crystal structure of a representative compound.

Experimental Section

Starting Materials. Metal(II) nitrates, NH₄NCS, Zn(NCS)₂, and Cd(NCS)₂ were used as the commercially available salts. Hydrazine hydrate, acetic acid, and propionic acid were also obtained commercially.

Synthesis of the Ligands. Several procedures have been reported for the synthesis of 3,5-dimethyl-1,2,4-triazole (abbreviated dmtrH).⁹ The procedure described first by Byalkovskii-Krupin and Lopyrev¹⁰ and slightly modified by us was most suitable for the synthesis of both dmtrH and the 3,5-diethyl analogue (abbreviated detrH). In a typical preparation a 80% aqueous solution of 2.6 mol of hydrazine hydrate was added slowly to 2.0 mol of acetic acid (or propionic acid). The mixture was heated slowly and kept at 220 °C for about 3 h. When the mixture was cooled, the intermediate 4-amino-3,5-dialkyl-1,2,4-triazole (adat) was isolated (characterization by NMR). A solution of 0.7 mol of adat in 150 mL of HCl (6 M) was treated with a solution of 0.8 mol of sodium nitrite in 850 mL of water for about 2 h, during which time the temperature was kept at 25–30 °C. The resulting mixture was evaporated in vacuo. The final syrup was dissolved in ethanol and refluxed for 30 min. After vacuum evaporation of the ethanol, the yellow crystals of dmtrH were recrystallized from toluene. The final product consisted of white needles, mp 138–139 °C (lit.¹¹ mp 139–140 °C). Characterization was done by elemental analysis (C, H, N) and NMR (singlet at 2.19 ppm downfield from Me₄Si, solvent Me₂SO-*d*₆). In case of detrH a yellow liquid was purified by distillation in vacuo (110 °C at 1 mmHg). The resulting solid melted at 45–49 °C (lit.¹² mp 61–62 °C). Characterization by NMR in Me₂SO-*d*₆ yielded a triplet at 1.32 ppm and a quadruplet at 2.74 ppm downfield from Me₄Si.

Table II. Crystal and Diffraction Data of Ni₃(detrH)₆(NCS)₆(H₂O)₂

<i>M_r</i>	1311.7
space group	<i>Pbca</i>
cryst syst	orthorhombic
<i>a</i> , Å	14.447 (8)
<i>b</i> , Å	23.047 (8)
<i>c</i> , Å	18.613 (9)
<i>V</i> , Å ³	6197 (9)
<i>Z</i>	4 (trimers)
<i>D</i> _{measd} , Mg·m ⁻³	1.40 (1)
<i>D</i> _{calcd} , Mg·m ⁻³	1.41
<i>F</i> (000)	2469.9
θ range, deg	2–20
measd reflens	5646
indep reflens	2884
significant reflens (<i>I</i> > 2 σ)	1804
μ , cm ⁻¹	11.55
final <i>R</i> value ($\sum F_o - F_c / \sum F_o $)	0.058
final <i>R_w</i> value ($[\sum w(F_o - F_c)^2] / \sum w F_o ^2$) ^{1/2}	0.063
transmission range (azimuth scan)	0.75–0.94
diffractometer	CAD-4
radiation	Mo K α
monochromator	graphite

Synthesis of the Coordination Compounds. In the case of Mn, Co, and Ni(II) a solution of 5 mmol of M(NO₃)₂ in 15 mL of water was added rapidly to a solution of 10 mmol of NH₄NCS in 15 mL of water. The ligand (10 mmol) dissolved in 10 mL of water was slowly added to this solution. Upon standing, the metal thiocyanate compounds slowly crystallized. In the cases of Zn and Cd, the metal thiocyanates were used directly. The resulting compounds are listed in Table I. Despite the use of different metal–ligand ratios, the same products crystallize in all cases.

Characterization. The solid crystalline products obtained have been characterized by physical and analytical methods. Metal analyses were obtained by complexometric titrations or atomic absorption spectroscopy. Elemental analyses were carried out by commercial institutes. Infrared spectra were obtained as Nujol mulls and as KBr disks (4000–200 cm⁻¹) on a Perkin-Elmer 580 spectrophotometer. Ligand field spectra were obtained by the diffuse-reflectance method on the solid powders. Magnetic susceptibility measurements were performed between 2 and 80 K on a PAR vibrating-sample magnetometer using a Janis-type cryostat.

X-ray Data Collection and Refinement. A crystal of Ni₃(detrH)₆(NCS)₆(H₂O)₂ was grown from an aqueous ethanol solution of Ni(NO₃)₂, NH₄NCS, and detrH in stoichiometric amounts. Small light blue plates were isolated upon slow evaporation. A crystal of dimensions 0.5 × 0.35 × 0.06 mm³ was mounted and used for the data collection. Crystal data and relevant information about the data collection and refinement have been summarized in Table II. The data were corrected for Lorentz, polarization, and absorption effects.¹³ Scattering factors, including anomalous dispersion, were taken from

- (8) Reedyk, J.; Ten Hoedt, R. W. M. *Recl. Trav. Chim. Pays-Bas* **1982**, *101*, 49.
- (9) Weissberger, A.; Taylor, E. C., Eds. "Heterocyclic Compounds"; Wiley: New York; Vol. 37, p 380.
- (10) Byalkovskii-Krupin, K. L.; Lopyrev, V. A. *Metody Poluch. Khim. Reakt. Prep.* **1970**, No. 22, 92.
- (11) Postovskii, I. Y.; Vereshchagina, N. N. *Zh. Obshch. Chim.* **1959**, *29*, 2139.
- (12) Grüner, R.; Benes, Z.; Schubert, E.; Arman, M. *Monatsh. Chem.* **1927**, *48*, 37.

- (13) de Graaff, R. A. G. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 298.

Table III. Atomic Fractional Coordinates ($\times 10^4$ for Ni and S; $\times 10^3$ for C, N, and O) and Isotropic Thermal Parameters ($B_{\text{iso}} = \frac{8}{3} \pi^2 \text{ trace } (U)$) of $\text{Ni}_3(\text{detrH})_6(\text{NCS})_6(\text{H}_2\text{O})_2^c$

atom	x/a	y/b	z/c	$B_{\text{iso}}, \text{\AA}^2$
Ni(1) ^a	0	0	0	171 (7)
Ni(2)	1982 (1)	683 (1)	493 (3)	219 (5)
N(1)	93 (1)	7 (1)	85 (2)	21 (4)
C(1)	97 (1)	-18 (1)	140 (3)	29 (5)
S(1)	1018 (4)	-502 (5)	2142 (9)	92 (2) ^b
N(2)	193 (1)	110 (1)	145 (2)	34 (4)
C(2)	185 (1)	126 (1)	203 (3)	28 (5)
S(2)	1726 (3)	1493 (4)	2852 (8)	525 (15)
N(3)	303 (1)	16 (1)	86 (2)	30 (4)
C(3)	336 (1)	-25 (1)	109 (3)	38 (6)
S(3)	3913 (3)	-819 (4)	1416 (10)	70 (2)
N(11)	1 (1)	91 (1)	-5 (2)	21 (3)
N(12)	80 (1)	120 (1)	16 (2)	19 (4)
C(13)	62 (1)	175 (1)	27 (2)	26 (5)
N(14)	-30 (1)	185 (1)	10 (2)	24 (4)
C(15)	-67 (1)	133 (1)	-9 (3)	26 (5)
C(16)	-163 (1)	121 (1)	-35 (3)	41 (5) ^b
C(17)	-231 (1)	155 (2)	7 (4)	87 (8)
C(18)	127 (1)	223 (1)	49 (3)	38 (5) ^b
C(19)	89 (1)	252 (1)	118 (3)	61 (6)
N(21)	115 (1)	-6 (1)	-68 (2)	18 (3)
N(22)	197 (1)	22 (1)	-48 (2)	17 (3)
C(23)	266 (1)	3 (1)	-88 (3)	23 (5)
N(24)	229 (1)	-35 (1)	-136 (2)	25 (4)
C(25)	136 (1)	-39 (1)	-123 (3)	28 (5)
C(26)	75 (1)	-82 (1)	-163 (3)	30 (5) ^b
C(27)	78 (1)	-68 (1)	-245 (3)	50 (5) ^b
C(28)	366 (1)	18 (1)	-83 (3)	33 (5) ^b
C(29)	427 (1)	-37 (1)	-79 (3)	48 (6) ^b
N(31)	285 (1)	130 (1)	1 (2)	23 (4) ^b
N(32)	261 (1)	149 (1)	-68 (2)	31 (4)
C(33)	316 (1)	194 (1)	-85 (3)	38 (5)
N(34)	374 (1)	206 (1)	-28 (2)	31 (4) ^b
C(35)	354 (1)	165 (1)	22 (3)	28 (5)
O(W)	135 (1)	109 (1)	-174 (2)	91 (5)
C(36)	403 (1)	156 (1)	93 (3)	40 (5)
C(37A)	483 (1)	197 (1)	102 (4)	55 (5)
C(37B)	394 (1)	210 (1)	139 (4)	55 (5)
C(38)	313 (1)	230 (1)	-153 (3)	57 (6) ^b
C(39A)	371 (4)	195 (4)	-207 (7)	100 (14)
C(39B)	328 (4)	191 (4)	-217 (7)	128 (14)

^a Special position. ^b These atoms show high thermal anisotropy. ^c Estimated standard deviations in the least significant digits are given in parentheses.

ref 14. The structure was solved with use of standard heavy-atom techniques; several of the non-hydrogen atoms, however, were only found after application of direct methods (program DIRDIF¹⁵). The quality of the data did not allow the determination of the hydrogen atom positions. The ethyl groups of the terminal triazole ligands appeared to have large thermal parameters, which are ascribed to disorder. Therefore, Waser constraints¹⁶ were used to refine these ligand parts.

The final R value was 0.058 for 1804 significant reflections. Atomic positions of the non-hydrogen atoms are listed in Table III. Listings of F_o and F_c values and the thermal parameters of the non-hydrogen atoms are available as supplementary material.¹⁷

Results and Discussion

General Considerations. The compounds listed in Table I appeared to be the only compounds that could be isolated in the present solvent system, irrespective of the used molar ratio of ligands and metals. No pure compounds could be obtained so far with use of Fe(II) and Cu(II) salts. The infrared spectra of the Mn(II), Co(II), and Ni(II) compounds are essentially

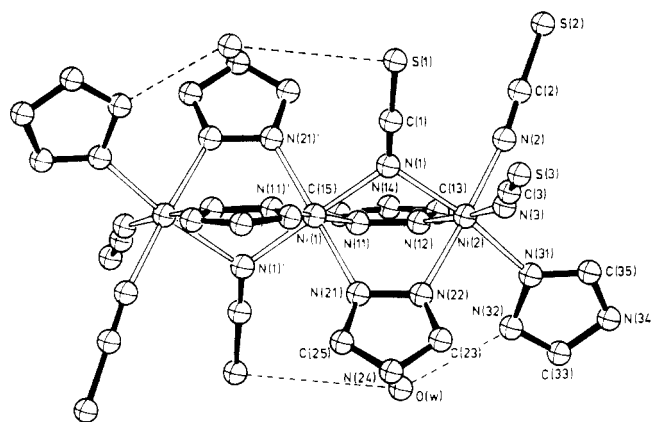


Figure 1. ORTEP drawing of $\text{Ni}_3(\text{NCS})_6(\text{detrH})_6 \cdot 2\text{H}_2\text{O}$, showing the numbering system, the position of the water molecules relative to the ligands, and the intramolecular hydrogen bridges (dotted lines). Primed atoms are generated by $-x, -y, -z$. Ethyl groups of triazole ligands have been omitted for clarity. The numbering of the ethyl groups as mentioned in Table III is as follows: attached to C(n3) are C(n8)–C(n9) and to C(n5) are C(n6)–C(n7), where n denotes the number of the ring. Disordered positions have been given the labels A and B (e.g. C(39A) and C(39B) are both attached to C(38).

Table IV. Bond Lengths (Å) and Bond Angles (deg) of the Coordination Part in $\text{Ni}_3(\text{detrH})_6(\text{NCS})_6(\text{H}_2\text{O})_2$

Ni(1)–Ni(2)	3.39 (1)	Ni(2)–N(12)	2.16 (1)
Ni(1)–N(11)	2.11 (1)	Ni(2)–N(22)	2.10 (1)
Ni(1)–N(21)	2.10 (1)	Ni(2)–N(31)	2.10 (1)
Ni(1)–N(1)	2.09 (1)	Ni(2)–N(2)	2.02 (1)
Ni(2)–N(1)	2.18 (1)	Ni(2)–N(3)	2.05 (1)
N(1)–C(1)	1.18 (1)	C(2)–S(2)	1.63 (1)
C(1)–S(1)	1.57 (1)	N(3)–C(3)	1.14 (1)
N(2)–C(2)	1.15 (1)	C(3)–S(3)	1.65 (1)
Ni(1)–N(11)–N(12)	117.7 (9)	Ni(2)–N(22)–N(21)	118.4 (9)
Ni(1)–N(21)–N(22)	118.4 (9)	Ni(2)–N(31)–N(32)	117.0 (9)
Ni(2)–N(12)–N(11)	118.5 (9)		
Ni(1)–N(1)–Ni(2)	105.5 (5)	Ni(2)–N(3)–C(3)	157.6 (9)
Ni(2)–N(2)–C(2)	169.0 (9)		
N(1)–Ni(1)–N(21)	87.1 (4)	N(21)–Ni(1)–N(1)	92.9 (4)
N(1)–Ni(1)–N(21)	92.9 (4) ^a	N(1)–Ni(2)–N(22)	85.6 (4)
N(1)–Ni(1)–N(11)	87.3 (4)	N(1)–Ni(2)–N(12)	83.9 (4)
N(21)–Ni(1)–N(11)	87.7 (4)		
N(1)–C(1)–S(1)	178.8 (9)	N(3)–C(3)–S(3)	176.5 (9)
N(2)–C(2)–S(2)	178.4 (9)		

^a Primed atoms are generated by $-x, -y, -z$.

similar for each of the ligands (apart from a few far-IR bands, vide infra), suggesting a similar structure for each of the compounds. Also the X-ray powder patterns of the three compounds are the same with respect to line positions and intensities. Even the patterns for the detrH and dmtrH compounds closely resemble each other. Because the ligand field spectra also indicate the same ligand environment for each of the Co(II) and Ni(II) compounds, we assume that all compounds with the stoichiometry $\text{M}_3(\text{ligand})_6(\text{NCS})_6(\text{H}_2\text{O})_2$ have the same basic structure. The compounds $\text{Zn}(\text{dmtr})(\text{NCS})$ and $\text{Zn}(\text{detr})(\text{NCS})$, although not isomorphous, are also believed to have similar structures. The high melting points indicate a polymeric structure. The pair of compounds $\text{Cd}(\text{ligand})(\text{NCS})_2$ may also have similar structures, as will be discussed below in the section about the spectral properties.

Molecular Structure of $\text{Ni}_3(\text{detrH})_6(\text{H}_2\text{O})_2$. The centrosymmetric trimeric species is shown in Figure 1, together with the atomic labeling system used. Relevant bond lengths and angles are listed in Table IV. Bond distances and angles of the triazole rings are normal and are given as supplementary material.¹⁷ The central nickel ion is surrounded by four

(14) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.

(15) Beurskens, P. T.; Bosman, W. P.; Doesburg, H. M.; Gould, R. O.; Van der Hark, T. E. M.; Prick, P. A. J. Technical Report, Laboratory for Crystallography, Nijmegen, The Netherlands, 1980.

(16) Waser, J. *Acta Crystallogr.* 1963, 16, 1091.

(17) Supplementary material.

Table V. Magnetic Susceptibility Data for Some of the Compounds $M_3(LH)_6(NCS)_6(H_2O)_2$ with $M = Mn, Co, Ni$ and $LH = detrH$ and $detrH$

compd	$\mu(80\text{ K}), \mu_B$	Θ, K	g	J, cm^{-1}
$Mn_3(detrH)_6(NCS)_6(H_2O)_2$	5.25 (5)	-21 (2)	2.01 (1) ^a	-1.33 (3)
$Co_3(detrH)_6(NCS)_6(H_2O)_2$	4.85 (5)	-25 (2)	5.69 (2) ^b	-7.0 (3)
$Co_3(detrH)_6(NCS)_6(H_2O)_2$	4.60 (5)	-20 (2)	5.16 (3) ^b	-4.7 (3)
$Ni_3(detrH)_6(NCS)_6(H_2O)_2$	3.50 (5)	8 (1)	2.24 (1) ^c	5.3 (4)
$Ni_3(detrH)_6(NCS)_6(H_2O)_2$	3.50 (5)	14 (4)	2.20 (1) ^c	9.6 (1)

^a Determined for a Heisenberg trimer $S = 5/2$. ^b Determined for a Heisenberg trimer $S' = 1/2$. ^c Determined for a Heisenberg trimer $S = 1$, assuming $D = 0$.

(bridging) triazole ligands and two NCS anions. The NCS ions bridge to the terminal nickel ions through nitrogen only. The terminal nickel atoms are also octahedrally coordinated. Apart from the three bridging nitrogens (two from triazole and one from NCS⁻) three terminal ligands are present (two terminal NCS ligands and one monodentate triazole ligand). The two water molecules are held intramolecularly between the S atom of the bridging NCS and the noncoordinating nitrogen of the terminal, monodentate triazole ligand but are not coordinated to the nickel ions. The Ni-Ni distance within the trimers amounts to 3.39 (1) Å. The Ni-N distances and N-Ni-N angles are all within the range known for octahedral NiN_6 chromophores. Bridging of triazoles through N(1) and N(2) has been observed before^{4,5,7,18} and seems to be a general phenomenon. However, bridging when substituents are present on carbon atoms C(3) and C(5) is unprecedented. Bridging of thiocyanato ligands is a general phenomenon and has been reviewed.⁶ The most common bridging mode is through both nitrogen and sulfur, resulting in M-NCS-M linkages. Bridging by sulfur only has also been observed.^{6,19} Bridging through nitrogen only, on the other hand, is highly unusual and has only been reported in a few compounds,^{7,20} such as in $(Re_2(NCS)_{10})^{3-}$ and in $Cd(NCS)_2(butr)_{1.5}$, and very recently²¹ also in a dinuclear Co(II) macrocyclic compound. The present compound is the first case in which nickel(II) is bridged in this way. The bridging angle Ni-N-Ni amounts to 105.5 (5)°. The terminal NCS groups are N bonded, as expected. The Ni-N≡C angles are close to linear (160–170°). The molecular is further stabilized by intramolecular and intermolecular hydrogen bonding between O (with S(1), S(2), and N(32)), N(14) (with N(34)), and N(24) (with S(2)). Although no proton positions could be located in the refinement, all "acid" hydrogens must be involved in hydrogen bonding with lone pairs of other atoms. The O-N, O-S, N-S, and N-N contacts are in the range observed for intermediate hydrogen contacts (i.e. N(14)⋯N(34) = 2.88 (1) Å; O⋯N(32) = 2.83 (1) Å; N(24)⋯S(2) = 3.33 (1) Å; O⋯S(1) = 3.76 (1) Å; O⋯S(3) = 3.51 (1) Å).²² Some of the intramolecular hydrogen bonds are indicated in Figure 1 as dotted lines. This was not investigated further, due to the limited quality of the data set.

Magnetic Properties. Because of the trinuclear nature of the nickel compound and the isomorphism (vide supra) of the Mn, Co, and Ni compounds, a study of the magnetic susceptibility was undertaken, to see to what extent magnetic-exchange interaction within the trimers occurs. The results are summarized in Table V. As can be seen from this table, considerable magnetic exchange occurs in all compounds. The exchange is antiferromagnetic in the Mn and Co compounds but, surprisingly, ferromagnetic in the nickel compounds. A

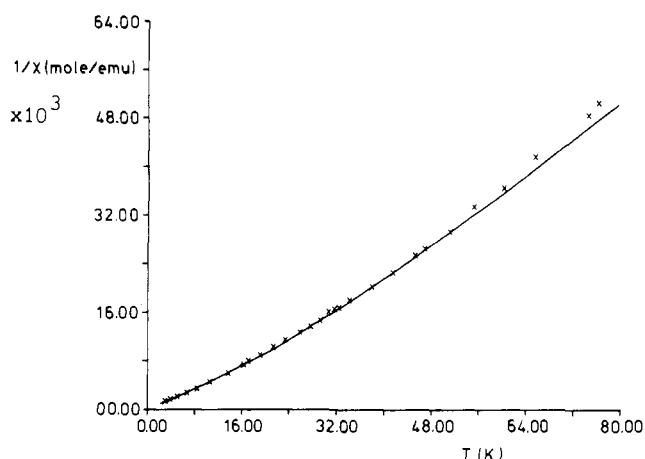


Figure 2. Plot of the inverse magnetic susceptibility ($1/\chi$) vs. temperature of $Ni_3(detrH)_6(NCS)_6(H_2O)_2$. The curve drawn is the theoretical one for our trimer of $S = 1$ ions with the parameters $g = 2.20$ (1) and $J = 9.6$ (1) (assuming J_{13} to be negligible).

fit of the inverse susceptibility for the Ni compound of detrH is redrawn in Figure 2, for the region below 80 K. Data obtained at higher temperature are insensitive to change in J . Since the structures of the six compounds are basically the same, the different magnetic behavior for the nickel compounds is likely to result from small structural changes in going from Mn(II), via Co(II), to Ni(II). Linear trinuclear compounds containing magnetic ions have been reported to a limited extent and have been studied by magnetic exchange in only a few cases,^{5,18,23–25} mainly for nickel(II) trimers. The magnetic exchange in such trimers is usually described by the Hamiltonian $H = -2J_{12}[(S_1 \cdot S_2) + (S_2 \cdot S_3)] - 2J_{13}(S_1 \cdot S_3)$, in which J_{12} represents the coupling between adjacent metal ions and J_{13} that between terminal ions. The value of the latter parameter has been the subject of some dispute^{5,24} and has been taken to be zero in our compounds, since the Ni-Ni distance between the terminal ions is very large. When, however, J_{13} is not neglected in the fit, finite values may result, but the uncertainties are on the order of 5 cm^{-1} . The effect of zero-field splittings of the individual ions has also been neglected, because it is expected to be different for the central and the terminal ions. The Heisenberg treatment is only an approximation for the cobalt trimers at low temperatures, and therefore the obtained J value cannot be accurate. It is well-known now that the sign and magnitude of the magnetic exchange in superexchange-coupled systems are determined by the overlap between the magnetic orbitals, their energy gap, and their two-electron exchange integral.²⁶ Small differences in the geometry of the dinuclear units are known to have large effects upon the magnetic exchange.^{26–28} It therefore is likely

(18) Vos, G.; De Kok, A. J.; Verschoor, G. C. Z. *Naturforsch. B: Anorg. Chem., Org. Chem.* **1981**, *36B*, 809.

(19) Nelson, S. M. *Inorg. Chem. Acta* **1982**, *62*, 39.

(20) Cotton, F. A.; Davison, A.; Ilsley, W. H.; Trop, H. S. *Inorg. Chem.* **1979**, *18*, 2719.

(21) Drew, M. G. B.; Esho, F. S.; Nelson, S. M. *Inorg. Chim. Acta* **1983**, *76*, L269.

(22) Schuster, P.; Zudel, G.; Sandorfy, G., Eds. "The Hydrogen Bond"; North-Holland: Amsterdam, 1978.

(23) Long, G. J.; Lindner, D.; Lintvedt, R. L.; Guthrie, J. W. *Inorg. Chem.* **1982**, *21*, 1431.

(24) Ginsberg, A. P.; Martin, R. L.; Sherwood, R. C. *Inorg. Chem.* **1968**, *7*, 932.

(25) Boyd, P. D. W.; Martin, R. L. *J. Chem. Soc., Dalton Trans.* **1979**, 92.

(26) Mackey, D. J.; Martin, R. L. *J. Chem. Soc., Dalton Trans.* **1978**, 702. Boyd, P. W. D.; Martin, R. L. *Ibid.* **1981**, 1069. Kahn, O. *Inorg. Chim. Acta* **1982**, *62*, 3.

Table VI. Infrared and Ligand Field Maxima of the Triazole Coordination Compounds (cm⁻¹)^a

compd	$\nu_{\text{NCS}}(\text{N bridging})$	$\nu_{\text{NCS}}(\text{other})$	ligand field max
Ni ₃ (dmtrH) ₆ (NCS) ₆ (H ₂ O) ₂	1997	2110, 2082	10 580, 13 400 (w), 17 240
Co ₃ (dmtrH) ₆ (NCS) ₆ (H ₂ O) ₂	2003	2101, 2069	9520, 18 800, 20 200, 21 980
Mn ₃ (dmtrH) ₆ (NCS) ₆ (H ₂ O) ₂	1995	2087, 2055	
Cd(NCS) ₂ (dmtrH)		2135, 2107, 2079	
Zn(NCS)(dmtr)		2088	
Ni ₃ (detrH) ₆ (NCS) ₆ (H ₂ O) ₂	1992	2120, 2090	9900, 13 160 (w), 17 240
Co ₃ (detrH) ₆ (NCS) ₆ (H ₂ O) ₂	1997	2107, 2083	9480, 18 150, 19 920, 21 280
Mn ₃ (detrH) ₆ (NCS) ₆ (H ₂ O) ₂	1996	2091, 2074	
Cd(NCS) ₂ (detrH)		2117 (br), 2067	
Zn(NCS)(detr)		2078	

^a Abbreviations: br = broad; w = weak.

that the alteration in the magnetic behavior as one goes from Co (and Mn) to Ni originates from a slight change in geometry (e.g. the M–N–M angle). Since we have only one crystal structure available, this hypothesis cannot be studied in further detail. It seems likely, however, that the magnetic-exchange pathways go at least via the NCS groups. Magnetic exchange via the triazoles, on the other hand, has also been reported in related compounds,^{3,4} with only triazole bridges.

Spectroscopic Properties. All compounds have also been characterized by infrared and ligand field spectra. Some relevant data are listed in Table VI. First of all it appears that—for each given ligand—the Mn, Co, and Ni compounds have almost identical infrared spectra, as would be expected when the same trinuclear species is present. The most striking aspect of the infrared spectra are the bands near or just below 2000 cm⁻¹; these bands can now be assigned to the ν_{CN} of the bridging isothiocyanato group. Similar vibrations have been found in only a few compounds.^{7,20,21} The amount of data that is now available, including our results, allows us to state that such a low CN stretching frequency is diagnostic for a NCS ligand bridging via the nitrogen atom only. The other vibrations between 2055 and 2120 cm⁻¹ are assigned to the terminal NCS ligands; the mutual cis geometry (Figure 1) explains the doublet character. The order also follows the Irving Williams sequence for each trio of compounds. Both zinc compounds have only one CN stretching vibration. The position agrees with nitrogen coordination only,⁶ so that the remaining donor atoms must come from the deprotonated triazole ligands, resulting in a—probably—tetrahedrally coordinated metal ion. The infrared spectra of both cadmium compounds are not very informative on the structure of the compounds. Both monodentate N-bonding and bridging N,S-bonding thiocyanate anions may be present in addition to bidentate (bridging) triazole ligands. No attempts were undertaken for further structural elucidation of these Zn and Cd compounds, as it appeared impossible to grow single crystals. Ligand field spectra of the (colored) Co and Ni compounds (Table VI) are in agreement with octahedral co-

ordination geometry for these metal ions.^{29,30} The deviations from ideal octahedral geometry are not reflected in clear and band splittings, although the three bands near 20 000 cm⁻¹ for the two Co(II) compounds at least suggest a lower symmetry.

Concluding Remarks. The results described in the present paper have shown that substituted 1,2,4-triazole ligands can form bridges between metal ions, even when substituents are present at positions 3 and 5 in the ring. When two such ligands form a bridge between two metal ions (as is the case in our trinuclear compounds), only a small space is left for a third bridging ligand. This seems to be the main driving force to the formation of our novel trinuclear compounds containing the N-bridging thiocyanate ligands. Related work in our laboratory has shown that fluoride ions may bridge in a similar way between transition-metal ions already containing bridging 3,5-disubstituted triazoles.³¹ Thiocyanate ligands that are bridging through nitrogen only appear to be formed when only a small space is available between two metal ions. If this is realized, it should be possible to prepare other compounds of this type. This study has also made clear that easy detection of N-bridging thiocyanate is possible through analysis of the infrared spectra.

Acknowledgment. The authors are indebted to Drs. G. C. Verschoor, S. Gorter, B. van der Griendt, and F. J. Rietmeijer for experimental assistance with the X-ray data collection and the magnetic susceptibility measurements.

Registry No. Mn₃(dmtrH)₆(NCS)₆, 89231-70-9; Co₃(dmtrH)₆(NCS)₆, 89210-77-5; Ni₃(dmtrH)₆(NCS)₆, 89210-78-6; Zn(NCS)(dmtr), 89210-83-3; Cd(NCS)₂(dmtrH), 89210-86-6; Mn₃(detrH)₆(NCS)₆, 89210-79-7; Co₃(detrH)₆(NCS)₆, 89210-80-0; Ni₃(detrH)₆(NCS)₆(H₂O)₂, 89210-81-1; Zn(NCS)(detr), 89210-85-5; Cd(NCS)₂(detrH), 89210-87-7.

Supplementary Material Available: Listings of observed and calculated structure factors, anisotropic thermal parameters, and bond lengths and angles of the triazole ligands in Ni₃(detrH)₆(NCS)₆(H₂O)₂ (8 pages). Ordering information is given on any current masthead page.

- (27) Crawford, V. H.; Richardson, H. W.; Wasson, J. R.; Hodgson, D. J.; Hatfield, W. E. *Inorg. Chem.* **1976**, *15*, 2107.
 (28) Felthouse, T. R.; Laskowski, E. J.; Hendrickson, D. N. *Inorg. Chem.* **1977**, *16*, 1077.

- (29) Reedijk, J.; Driessen, W. L.; Groeneveld, W. L. *Recl. Trav. Chim. Pays-Bas* **1969**, *88*, 1095.
 (30) Reedijk, J.; Van Leeuwen, P. W. N. M.; Groeneveld, W. L. *Recl. Trav. Chim. Pays-Bas* **1968**, *87*, 129.
 (31) Rietmeijer, F. J.; Den Hartog, A. J.; Reedijk, J., to be submitted for publication.