

# The Coordination of Divalent Transition Metal Ions to a Sterically Constrained Chelating Pyrazole Derivative. The Crystal and Molecular Structure of Bis(azido)-(2,5-bis(3',5'-dimethylpyrazol-1'-ylmethyl)-2,5-diazahehexane)nickel(II), [Ni(C<sub>16</sub>H<sub>28</sub>N<sub>12</sub>)]

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## Abstract

The ligand 2,5-bis(3',5'-dimethylpyrazol-1'-ylmethyl)-2,5-diazahehexane (debd) reacts with divalent transition metal ions in combination with small, coordinating anions to form M(debd)X<sub>2</sub> (M = Mn, Fe, Co, Ni, Cu, Zn, Cd, X = NCS; M = Mn, Co, Ni, Co, Zn, Cd, X = N<sub>3</sub>; M = Mn, Cd, X = Cl, Br). The compound Ni(debd)(N<sub>3</sub>)<sub>2</sub> crystallizes in space group *P bcn*, *Z* = 4, *a* = 15.712(1) Å, *b* = 9.2398(3) Å, *c* = 14.4246(5) Å. The structure was solved to a final *R* value of 0.028. The nickel ion is octahedrally surrounded by four nitrogens of the ligand and the two azide anions, which are in a *cis* position. The molecule has a twofold symmetry axis. The other compounds have very similar structures, as is concluded from X-ray powder isomorphism and spectroscopic properties, including IR, NMR (<sup>1</sup>H and <sup>13</sup>C), ESR and NIR-Vis spectroscopy.

## Introduction

The coordination chemistry of simple heterocyclic compounds such as pyrazoles has been extensively studied [1–6]. Recently, attention has been focussed on the coordinating behaviour of pyrazole-containing ligands [7–9]. These ligands have been used to model the active site of metallo-enzymes [10, 11], as has been done with pyridine- [12, 13], imidazole- [14], and bezimidazole-containing [15–17] chelating ligands. To be able to design more effective chelating systems to mimic metallo-enzymes, deeper insight is needed in the coordination chemistry of this type of ligands.

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This paper describes the coordination behaviour of the ligand 2,5-bis(3',5'-dimethylpyrazol-1'-ylmethyl)-2,5-diazahehexane, abbreviated debd, towards divalent transition metal ions. This ligand contains, besides two amine nitrogens, two potentially coordinating heterocyclic (pyrazole) nitrogens, thus combining four nitrogen donor atoms in an orientation which could allow chelation to one metal ion. An additional property featured by this ligand is the substantial steric hindrance, introduced by the two methyl groups on each pyrazole and the methyl groups on the amine nitrogens. The coordinating flexibility of this ligand is rather restricted, as will be illustrated by the small structural variability of the compounds reported here. To prove the octahedral geometry of the compounds a crystal structure determination of a representative compound was undertaken.

## Experimental

### Starting Materials

Commercially available solvents and hydrated metal salts were used. The ligand debd was synthesized as described [18] by the condensation reaction of N-hydroxymethyl(3,5-dimethyl)pyrazole and the amine N,N'-dimethyl-ethylenediamine (Janssen Chimica) using acetonitril as a solvent. The ligand was obtained as a yellow oil and was used without further purification. The purity was checked by NMR.

### Synthesis of the Complexes

All complexes have the general formula M(L)X<sub>2</sub>. The halide complexes (M = Cd, Mn; X = Cl, Br) were synthesized by dissolving the appropriate metal halide in hot methanol (2.50 mmol in 50 ml or in the case of CdCl<sub>2</sub> 2.50 mmol in 75 ml) and a hot solution

of an equivalent amount of ligand in 15 ml methanol. Crystals of the desired metal complexes separated from the solution upon standing. Isothiocyanato complexes of the metals Mn, Co, Ni, Zn and Cd were synthesized using the nitrates as starting compounds. After mixing hot ethanolic solutions of the metal nitrate (2.50 mmol in 20 ml) and the ligand (2.50 mmol in 10 ml), a hot solution of an equivalent amount of  $\text{NH}_4\text{NCS}$  (5.00 mmol in 20 ml of a 1:1 mixture of ethanol and water) was added. The metal complexes separated from the solutions as microcrystalline compounds. The complex  $\text{Cu}(\text{debd})(\text{NCS})_2$  was synthesized by adding a hot ethanolic solution of the ligand (2.70 mmol in 15 ml) to a hot solution of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (2.70 mmol in 15 ml). To this deep blue solution was added 27 mmol of  $\text{NH}_4\text{NCS}$  (a five-fold excess), dissolved in 40 ml of a hot mixture of ethanol/water (1:1). Green crystals of the copper complex separated from the dark green solution upon standing overnight.

The corresponding iron compound was prepared by adding a hot solution of 13 mmol of  $\text{NH}_4\text{NCS}$  in 20 ml of an ethanol/water mixture (1:1) to the hot reaction mixture of 2.90 mmol of  $\text{Fe}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  in 20 ml ethanol and 2.90 mmol of *debd* in 10 ml ethanol. A dark brown precipitate was filtered from the cooled reaction mixture. The clear, dark-red solution was allowed to stand, and after several days the desired iron complex could be obtained as a deep purple powder. Azido complexes of the metals Mn, Co, Ni, Zn and Cd were synthesized using nitrates as starting compounds. After mixing hot ethanolic solutions of the metal nitrate (3.40 mmol in 25 ml) and the ligand (3.40 mmol in 15 ml) a hot solution of a *ca.* 3-fold excess of  $\text{NaN}_3$  was added (21 mmol in 40 ml of a 1:1 ethanol/water mixture). The instantaneously-formed flocculent precipitate was filtered off and the clear solution was allowed to cool. The complexes separated from the solutions within a few hours in a microcrystalline form (Mn, Co, Zn, Cd) or overnight as crystals. Dopes of metals in isomorphous host lattices were prepared by starting from a mixture of the appropriate starting metal salts.

The compounds synthesized are listed in Table I, together with their colour, melting points, and X-ray and infrared type.

#### Spectroscopic Methods

IR spectra ( $2000\text{--}180\text{ cm}^{-1}$ ) were recorded on a Perkin-Elmer PE 380 instrument, using KBr pellets and nujol mulls between NaCl or polyethylene discs. Far-IR spectra ( $400\text{--}100\text{ cm}^{-1}$ ) of nujol mulls between polyethylene discs were measured at the University of Amsterdam on a Nicolet 7199B FT-IR spectrometer, using a globar source and a 6.25  $\mu$  Mylar beam splitter. Electronic spectra ( $2000\text{--}300\text{ nm}$ ) were measured on a Perkin-Elmer UV330

TABLE I. Melting Points, Colours, Infrared and X-ray Types of the *Debd* Compounds.

Compound	Melting point <sup>d</sup>	Colour	IR type	X-ray type
$\text{Mn}(\text{debd})(\text{NCS})_2$	234 °C	white	I	A
$\text{Fe}(\text{debd})(\text{NCS})_2$	234 °C	deep purple	I	A
$\text{Co}(\text{debd})(\text{NCS})_2^{\text{a}}$	224 °C	purple	I	A
$\text{Ni}(\text{debd})(\text{NCS})_2$	258 °C	blue	I	A
$\text{Cu}(\text{debd})(\text{NCS})_2$	171 °C	green	I	A
$\text{Zn}(\text{debd})(\text{NCS})_2$	180 °C	white	I	A
$\text{Cd}(\text{debd})(\text{NCS})_2$	212 °C	white	I	A
$\text{Mn}(\text{debd})(\text{N}_3)_2$	207 °C	white	II	B
$\text{Co}(\text{debd})(\text{N}_3)_2$	199 °C	red	II	B
$\text{Ni}(\text{debd})(\text{N}_3)_2^{\text{b}}$	258 °C	blue	II	B
$\text{Zn}(\text{debd})(\text{N}_3)_2$	165 °C	white	II	B
$\text{Cd}(\text{debd})(\text{N}_3)_2$	197 °C	white	II	B
$\text{Mn}(\text{debd})\text{Cl}_2^{\text{c}}$	198 °C	pink	III	C
$\text{Cd}(\text{debd})\text{Cl}_2$	203 °C	white	III	C
$\text{Mn}(\text{debd})\text{Br}_2$	210 °C	pink	III	D
$\text{Cd}(\text{debd})\text{Br}_2$	198 °C	white	III	D

<sup>a</sup>*Anal.* calcd. for  $\text{Co}(\text{C}_{16}\text{H}_{28}\text{N}_6)_2\text{N}_2\text{C}_2\text{S}_2$ : C, 44.26; H, 5.98; N, 22.9. Found: C, 43.83; H, 5.90; N 22.4%. <sup>b</sup>*Anal.* calcd. for  $\text{Ni}(\text{C}_{16}\text{H}_{28}\text{N}_6)_2\text{N}_6$ : C, 42.98; H, 6.31; N, 37.59. Found: C, 42.86; H, 6.29; N, 38.05%. <sup>c</sup>*Anal.* calcd. for  $\text{Mn}(\text{C}_{16}\text{H}_{28}\text{N}_6)\text{Cl}_2$ : C, 44.66; H, 6.56; N, 19.53. Found: C, 44.30; H, 6.51; N, 19.48. <sup>d</sup>All compounds decomposed upon melting.

instrument, operating in the diffuse reflectance mode with MgO as a reference.

ESR spectra of powder samples were measured on a Varian E-3 EPR spectrometer, using a 9.5 GHz microwave bridge, at room temperature and at 77 K. Spectra could be measured with fields varying between 375 Gauss and 6700 Gauss.

All NMR spectra were measured in *dms**-d*<sub>6</sub> solutions. Proton NMR spectra were recorded on a JEOL LNM PS 100 instrument, operating at 99.5 MHz with an external lock and using TMS as an internal reference. <sup>13</sup>C-NMR spectra were recorded on a JEOL JEC 980B instrument, operating at 50.1 MHz using <sup>2</sup>H as an internal lock and TMS as internal reference.

Röntgen powder diffraction patterns were obtained using a Guinier-type camera. Elemental analyses were performed at the Microanalytical Laboratory of the University College, Dublin, Rep. of Ireland.

#### Crystal Structure Determination

Crystals of  $\text{Ni}(\text{debd})(\text{N}_3)_2$  suitable for X-ray analysis were obtained from the reaction mixture. Crystal data and details of the structure determination are listed in Table II. The space group was determined to be *Pbcn* from Weissenberg photographs. A blue, transparent crystal mounted on a glass fiber was used to collect data on an Enraf-Nonius

TABLE II. Crystal Data and Details of the Structure Analysis of Ni(debd)(N<sub>3</sub>)<sub>2</sub>.

(a) Crystal data	
$M_r$	447.19 (C <sub>16</sub> H <sub>28</sub> N <sub>12</sub> Ni)
Crystal system	orthorhombic
Space group	<i>Pbcn</i>
<i>a</i> (Å)	15.712(1)
<i>b</i> (Å)	9.2398(3)
<i>c</i> (Å)	14.4246(5)
<i>U</i> (Å <sup>3</sup> )	2094.1(2)
<i>Z</i>	4
$D_x$	1.419 g cm <sup>-3</sup>
$D_m$	1.42 g cm <sup>-3</sup>
$F(000)$	944
$\mu(\text{MoK}\alpha)$	8.99 cm <sup>-1</sup>
Crystal size	(0 0 1)–(0 0 $\bar{1}$ ) 0.350 mm (1 1 0)–( $\bar{1}$ $\bar{1}$ 0) 0.575 mm (1 1 0)–(1 $\bar{1}$ 0) 0.525 mm
Crystal volume	0.122 mm <sup>3</sup>
No. of grid points	384
Max., min. transmission	0.75, 0.68
(b) Data collection	
Radiation	Zr-filtered MoK $\alpha$ , $\bar{\lambda} = 0.71073$ Å
Temperature	295 K
$\theta_{\text{min.}}$ , $\theta_{\text{max}}$ (°)	0.10, 27.50
$\omega/2\theta$ scan (°)	0.44 + 0.35 tan $\theta$
Horizontal and vertical apertures (mm)	3.4
Standard reflections	4 $\bar{4}$ 5, 5 $\bar{5}$ 3, 7 3 5
Total data	2961
Total unique data	2400
Observed data $I > 2.5\sigma(I)$	1815
$hkl$ range	0 < $h$ < 20, 0 < $k$ < 11, 0 < $l$ < 18
Final scan $\sigma(I)/I$	0.01
Max scantime (seconds)	90
(c) Refinement	
No. of refined parameters	189
Weighting scheme	$w^{-1} = \sigma^2(F)$
Final $R_F = \Sigma(F_o -  F_c ) / \Sigma F_c $	0.0275 for 1815 reflections 0.0451 for 2400 reflections
Final $R_{wF} = [(\Sigma w( F_o  -  F_c )^2) / \Sigma w F_o ^2]^{1/2}$	0.0374 for 1815 reflections 0.0390 for 2400 reflections
(Shift/error) <sub>max</sub>	for $z$ of N(1): 0.12
Residual electron density, min., max.	–0.13, 0.29 eÅ <sup>-3</sup>
$S =$	0.70
$F^{\text{corr}} = F_c(1 - gF_c^2/\sin \theta)$	$g = 1.1(2) \cdot 10^{-7}$

CAD-4F diffractometer. Unit cell parameters were derived by least-squares from the diffractometer settings of 25 reflections [19] in the range  $11^\circ < \theta < 15^\circ$ . During the data collection three standard reflections measured every hour showed no variation in intensity over 56 h of X-ray exposure time. Standard deviations in the intensities were increased according to an analysis of the variance of the standard reflections [20]:  $\sigma^2(I) = \sigma_{CS}^2(I) + (0.02 \times I)^2$ .

Data were corrected for Lorentz, polarization and absorption [21] effects.

The structure was solved by Patterson and Fourier methods and refined with full-matrix least-squares techniques on  $F$ . Atomic coordinates of all atoms, anisotropic thermal parameters of the non-hydrogen atoms and individual isotropic temperature parameters of the hydrogen atoms are available as supplementary material\*. Final positional parameters are listed in Table III. Scattering factors from Cromer and Mann [22] corrected for anomalous dispersion [23] were used. The values for H were taken from reference [24]. The data collection was performed

TABLE III. Final Refined Fractional Positional Parameters for Ni(debd)(N<sub>3</sub>)<sub>2</sub>.  $\times 10^5$  for Ni,  $\times 10^4$  for all other non-hydrogens,  $\times 10^3$  for hydrogen atoms.

Atom	$x/a$	$y/b$	$z/c$
Ni	0	–5035(3)	75000
N(1)	–1351(1)	–681(2)	7367(1)
N(2)	–1571(1)	–1492(2)	6614(1)
N(7)	–147(1)	–2288(2)	6523(1)
N(9)	6(1)	924(2)	6409(1)
N(10)	266(1)	2110(2)	6353(1)
N(11)	537(1)	3271(2)	6242(2)
C(3)	–2412(1)	–1797(2)	6595(1)
C(4)	–2755(1)	–1131(2)	7350(2)
C(5)	–2086(1)	–457(2)	7823(2)
C(6)	–902(1)	–1916(2)	5978(1)
C(8)	–297(1)	–3605(2)	7088(2)
C(31)	–2809(2)	–2720(3)	5868(2)
C(51)	–2129(2)	393(2)	8688(2)
C(71)	566(1)	–2498(3)	5869(2)
H(41)	–330(1)	–119(1)	754(1)
H(81)	–90(1)	–355(1)	733(1)
H(82)	–22(1)	–438(1)	670(1)
H(311)	–335(1)	–288(1)	600(1)
H(312)	–246(1)	–370(1)	576(1)
H(313)	–268(1)	–241(1)	529(1)
H(511)	–262(1)	15(1)	904(1)
H(512)	–177(1)	23(1)	910(1)
H(513)	–222(1)	142(2)	858(1)
H(611)	–76(1)	–105(1)	559(1)
H(612)	–113(1)	–278(1)	562(1)
H(711)	106(1)	–270(1)	619(1)
H(712)	52(1)	–338(1)	548(1)
H(713)	64(1)	–158(1)	550(1)

with a modified CAD-4F software package [19]. The calculations were carried out on an in-house DG-ECLIPSE S/230 mini-computer, using the programs of the ILIAS package (an adaptation and extension by A.L.S. of the SHELX76 package [25]), or the CDC-CYBER/175 of the University of Utrecht, with programs of the EUCLID package [26].

\*Supplementary material available from the Editor-in-Chief.

## Results and Discussion

### General

Despite several attempts with chlorides and bromides as anions, only the Mn and Cd compounds could be isolated. No efforts were made to isolate the  $\text{Fe}(\text{N}_3)_2$  compound.

The IR and X-ray types of the compounds are given in Table I. The infrared spectra of the azido compounds are all almost identical, only showing significant differences in the far-IR region and for the anion vibrations. In combination with the almost identical X-ray powder diffraction patterns it can be concluded that all azido compounds are isostructural. The halide compounds also show almost identical IR spectra, only different in the far IR region. Although the X-ray powder diffraction patterns are different for these compounds, indicating a different crystal packing, it can be concluded that the conformation of the ligand is the same in both series of compounds.

The isothiocyanate compounds form another isostructural series, as can be concluded from the similarity in the infrared spectra and the X-ray powder diffraction patterns. The main differences between the infra red spectra of the isothiocyanate compounds and the other compounds concern the far-IR region and the anion vibrations. Other, minor differences can also be noted in the spectra, e.g. in the region  $820\text{--}780\text{ cm}^{-1}$  (pyrazole (C–H) out of plane bending mode [47]). The similarity however, is large enough to justify the conclusion that in all compounds reported here the ligand has a similar conformation.

### Description of the Structure of $\text{Ni}(\text{debd})(\text{N}_3)_2$

The Ni ion, residing on a two-fold axis (position 4(c) of space group  $Pbcn$ ), is in octahedral coordination with the *cis*-positioned mono-coordinated azido groups ( $\text{N}(9)\text{--Ni--N}(9\text{A})$ ,  $100.07(7)^\circ$ ;  $\text{Ni--N}(9)=\text{Ni--N}(9\text{A})$ ,  $2.053(2)\text{ \AA}$ ) (Fig. 1). The 2,5-bis(3',5'-dimethylpyrazol-1'-ylmethyl)-2,6-diazahexane serves as a N-tetradentate ligand coordinated to the Ni(II) ion *via* two tertiary amino atoms ( $\text{Ni--N}(7)=\text{Ni--N}(7\text{A})$ ,  $2.181(2)\text{ \AA}$ ) and the pyridine type of N atoms from two pyrazole rings ( $\text{Ni--N}(1)=\text{Ni--N}(1\text{A})$ ,  $2.138(2)\text{ \AA}$ ). Irregularity of the octahedron can be seen from the Ni–N bonding angles in the equatorial plane ( $\text{N}(7)$ ,  $\text{N}(7\text{A})$ ,  $81.79(6)^\circ$ ;  $\text{N}(7)$ ,  $\text{N}(9)$ ,  $89.48(6)^\circ$ ;  $\text{N}(9)$ ,  $\text{N}(9\text{A})$ ,  $100.07(7)^\circ$ ) although the mean value of these angles is  $90.28(6)^\circ$  (Table III). The two Ni–N(1) bonds are *trans*, deviating from linearity ( $171.20(7)^\circ$ ).

The Ni–azido bond can be compared with one of the values observed in the structure of di- $\mu$ -azido-bis(2,2',2''-triaminotriethylamine)dinickel(II) tetraphenylborate [27]. However, this dimer has *cis*-positioned, di-coordinate azido groups (forming

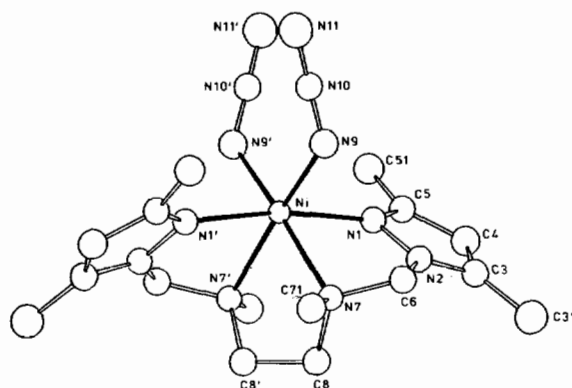


Fig. 1. ORTEP-projection of  $\text{Ni}(\text{debd})(\text{N}_3)_2$ . Hydrogen atoms have been omitted for clarity. The two equivalent parts of the complex are related by a twofold crystallographic symmetry axis.

with the metals an eight membered ring) with two different Ni–N(azido) bond lengths ( $2.069(8)$ ,  $2.195(7)\text{ \AA}$ ). In the dimer structure of  $[\text{Ni}_2(\text{N-tetramethylcyclam})_2(\text{N}_3)_3]^+$  [28] with a single end-to-end azide bridge, these bonds are  $2.11(1)$  and  $2.15(1)\text{ \AA}$ . The Ni–N(amino) bond of  $2.181(2)\text{ \AA}$ , as part of a large tetradentate ligand, can be compared with the analogous bonds in the macrocyclic tertiary amine complex [28] ( $2.15(1)$ ,  $2.16(1)\text{ \AA}$ ). The Ni–N(1) distance of  $2.138(2)\text{ \AA}$  is somewhat longer than in those structures where the pyrazole coordinates as an isolated ligand, e.g. hexakis(pyrazole)nickel(II)bis(tetrafluoroborate),  $2.098(3)\text{ \AA}$  [29], and can also be compared with distances found in compounds with other chelating pyrazole containing ligands [7, 30, 31].

The two mono-coordinated azido groups are identical, due to the operation of the two-fold axis. These groups are linear ( $\angle\text{N}(9)\text{--N}(10)\text{--N}(11)$ ,  $175.9(2)^\circ$ ) whereas the angle  $\text{Ni--N}(9)\text{--N}(10)$  is  $130.9(1)^\circ$ . In azido-coordinated complexes of various transition metals, as well as those of Ni(II) [27, 38, 32], the M–N=N angles varied between  $117$  and  $142^\circ$ . Such a wide range implies influence of steric factors and/or crystal packing on the geometry of a trigonally hybridized nitrogen. The azido group ( $1.172(3)$ ,  $1.165(3)\text{ \AA}$ ) is symmetrical with N–N bonds differing within  $3\sigma$ . In the structures of  $[\text{Ni}_2(\text{tren})(\text{N}_3)_2](\text{BPh}_4)_2$  [27] and  $[\text{Ni}_2(\text{N-tetramethylcyclam})_2(\text{N}_3)_3]\text{I}$  [28] the azido groups are symmetrical.

No unusual phenomena are observed in the coordinated *debd* ligand. Angles of the carbon atoms bonded to the tertiary amino nitrogen show a normal trigonal geometry; all three C–N bonds are equal within  $4\sigma$  (Table IV). Bond lengths and angles of the pyrazole ring can be influenced by coordination sphere requirements, since there are no hydrogen bonds or other significantly short intermolecular contacts in the crystal structure. The pyrazole ring

TABLE IV. Bond Distances (Å) and Angles (°) of Ni(debd)-(N<sub>3</sub>)<sub>2</sub><sup>a</sup>.

Within the Ni-coordination			
Ni-N(1)	2.138(2)	N(1)-Ni-N(7)	77.22(6)
Ni-N(7)	2.181(2)	N(1)-Ni-N(9)	89.14(6)
Ni-N(9)	2.053(2)	N(1)-Ni-N(1A)	171.20(7)
		N(1)-Ni-N(7A)	96.04(6)
		N(1)-Ni-N(9A)	96.52(6)
		N(7)-Ni-N(9)	89.48(6)
		N(7)-Ni-N(7A)	81.79(6)
		N(7)-Ni-N(9A)	168.58(6)
		N(9)-Ni-N(9A)	100.07(7)
Within the ligands			
N(1)-N(2)	1.364(2)	Ni-N(1)-N(2)	111.4(1)
N(1)-C(5)	1.345(3)	Ni-N(1)-C(5)	142.8(1)
N(2)-C(3)	1.352(2)	N(2)-N(1)-C(5)	104.9(2)
N(2)-C(6)	1.449(2)	N(1)-N(2)-C(3)	112.2(1)
N(7)-C(6)	1.464(3)	N(1)-N(2)-C(6)	118.0(1)
N(7)-C(71)	1.477(3)	C(3)-N(2)-C(6)	129.8(1)
N(7)-C(8)	1.483(3)	Ni-N(7)-C(6)	104.8(1)
N(9)-N(10)	1.172(3)	Ni-N(7)-C(8)	106.4(1)
N(10)-N(11)	1.165(3)	Ni-N(7)-C(71)	115.6(1)
C(3)-C(4)	1.362(3)	C(6)-N(7)-C(8)	111.0(1)
C(3)-C(31)	1.489(3)	C(6)-N(7)-C(71)	107.6(1)
C(4)-C(5)	1.399(3)	C(8)-N(7)-C(71)	111.3(2)
C(5)-C(51)	1.476(4)	Ni(1)-N(9)-N(10)	130.9(1)
C(8)-C(8A)	1.511(3)	N(9)-N(10)-N(11)	175.9(2)
		N(2)-C(3)-C(4)	106.1(1)
		N(2)-C(3)-C(31)	122.9(2)
		C(4)-C(3)-C(31)	131.0(2)
		C(3)-C(4)-C(5)	107.1(2)
		N(1)-C(5)-C(4)	109.8(2)
		N(1)-C(5)-C(51)	122.3(2)
		C(4)-C(5)-C(51)	127.9(2)
		N(2)-C(6)-N(7)	108.1(1)
		N(7)-C(8)-C(8A)	109.5(1)

<sup>a</sup>Symmetry code: A = -x, y, 3/2 - z.

is planar with the maximal displacement from the least squares plane of 0.01(1) Å (for C(4) and N(2)). The geometry of this coordinated, substituted pyrazole ring differs from the non-coordinated, unsubstituted pyrazole [33] only by the values of the C-C-C angle (107.1(2) vs. 104.4°, respectively) and the C(3)-C(4) bond (1.362(3), 1.398 Å, respectively).

The crystal structure is composed of discrete molecules separated at van der Waals distances. The shortest contacts observed in the structure involve the terminal azido nitrogen: N(11)···C(4), 3.411(3) Å [1/2 - x, 1/2 + y, 3/2 - z] and N(11)···C(8), 3.397(3) Å [-x, y, 3/2 - z].

### Infrared Spectra

Some relevant IR data are listed in Table V. The vibrations of the azide anion ( $\nu_a(\text{N-N})$ ,  $\nu_s(\text{N-N})$  and  $\delta(\text{NNN})$ ) are found in the expected regions [34]. The  $\nu(\text{C-N})$  and  $\delta(\text{NCS})$  vibrations of the

thiocyanates are as expected for N-bonded octahedral complexes, which is the usual coordination mode for first-row transition metals [35]. The weak  $\nu(\text{C-S})$  vibration (expected in the region 798–816  $\text{cm}^{-1}$ ) is not observed, but is probably obscured by the stronger [47] pyrazole (C-H) out of plane vibration which lies in the same region. Possibly this accounts for the differences in this IR region between the isothiocyanate complexes and the other compounds.

The  $\nu(\text{C-N})$  and  $\nu(\text{N-N})$  vibrations are split by ca. 10  $\text{cm}^{-1}$ , confirming a *cis* configuration for the azido as well as the isothiocyanato compounds [34, 35].

The  $\nu(\text{M-N})$  stretch vibrations for the isothiocyanate compounds show the expected Irving-Williams trend throughout the series Mn-Fe-Co-Ni-Cu-Zn-Cd, except for copper, which is probably due to a Jahn-Teller distortion [36]. The  $\nu(\text{M-N})$  stretch vibration was stronger and broader for the azido compounds. The metal-halide stretch vibrations lie in the region expected for this type of octahedral complexes [35, 37].

### NIR-Vis Spectra

The electronic transitions of some of the complexes are listed in Table VI. The nickel complexes show typical octahedral spectra, with a Dq value of 1030  $\text{cm}^{-1}$  for the isothiocyanate compound, somewhat larger than the Dq value of 950  $\text{cm}^{-1}$  for the azido compound due to the stronger ligand field of  $\text{SCN}^-$  vs.  $\text{N}_3^-$  [38]. The cobalt compounds show similar properties (Dq = 935  $\text{cm}^{-1}$  and 955  $\text{cm}^{-1}$  for the azido and isothiocyanate compound), which confirms the structural similarity between the cobalt and the nickel compounds, as well as between the azido and isothiocyanate compounds.

The low-energy transitions for the iron [39] and the copper [40] compounds have values usual for this type of compound. The high energy band in the spectrum of the copper compound can be assigned to a Cu-NCS charge transfer absorption. The high energy band in the spectrum of the iron compound is probably due to a small amount of strongly-absorbing Fe(NCS) species [41].

For  $\text{Mn}^{2+}$  compounds, d-d transitions are not only Laporte-forbidden but are spin-forbidden as well, resulting in very low intensities for transitions from the  ${}^6\text{A}_1$  ground state to the various quartet excited states [42]. The transitions and their assignments are in agreement with those found for similar octahedral complexes [43].

### NMR Spectroscopy

Some of the complexes appeared to be sufficiently dissolved in dmsO to allow NMR spectra to be recorded. Relevant data are listed in Table VII. The ligand is numbered as in Fig. 1.

TABLE V. Some of the Infrared Data of the debd Compounds (values in  $\text{cm}^{-1}$ ).

Compound	$\nu(\text{C}-\text{N}), \nu_{\text{a}}(\text{N}-\text{N})$	$\nu_{\text{s}}(\text{N}-\text{N})$	$\delta(\text{NNN}), \delta(\text{NCS})$	$\nu(\text{M}-\text{X})^{\text{b}}$
Mn(debd)(NCS) <sub>2</sub>	2070; 2060		479	245
Fe(debd)(NCS) <sub>2</sub>	2077; 2069		478	250
Co(debd)(NCS) <sub>2</sub>	2085; 2077		481	255
Ni(debd)(NCS) <sub>2</sub>	2103; 2090		478	260
Cu(debd)(NCS) <sub>2</sub>	2095; 2073		474	270
Zn(debd)(NCS) <sub>2</sub>	2090; 2077		482	230
Cd(debd)(NCS) <sub>2</sub>	2071; 2061		476	225
Mn(debd)(N <sub>3</sub> ) <sub>2</sub>	2065; 2040	1338	631	a
Co(debd)(N <sub>3</sub> ) <sub>2</sub>	2058; 2038	1339	639	a
Ni(debd)(N <sub>3</sub> ) <sub>2</sub>	2061; 2035	1341	645	a
Zn(debd)(N <sub>3</sub> ) <sub>2</sub>	2060; 2035	1343	642	a
Cd(debd)(N <sub>3</sub> ) <sub>2</sub>	2053; 2037	1334	640	a
Mn(debd)Cl <sub>2</sub>				254
Cd(debd)Cl <sub>2</sub>				247, 232
Mn(debd)Br <sub>2</sub>				210
Cd(debd)Br <sub>2</sub>				168

<sup>a</sup>The  $\nu(\text{M}-\text{N})$  in these compounds is a broad absorption in the region 275–295  $\text{cm}^{-1}$ . <sup>b</sup>M–debd ligand vibrations have been omitted.

TABLE VI. Electronic Transitions (values in 1000  $\text{cm}^{-1}$ ) of the debd Compounds.

Compound	$\sigma_1$	$\sigma_2$	$\sigma_3$	Other
Ni(debd)(N <sub>3</sub> ) <sub>2</sub>	9.52	15.5	25.6	
Ni(debd)(NCS) <sub>2</sub>	10.3	16.8	27.5	
Co(debd)(N <sub>3</sub> ) <sub>2</sub>	8.57		19.6	
Co(debd)(NCS) <sub>2</sub>	9.11		19.6	
Cu(debd)(NCS) <sub>2</sub>	13.1			25.4 <sup>a</sup>
Fe(debd)(NCS) <sub>2</sub>	9.96			19.2 <sup>a</sup>

<sup>a</sup>Assignments, see text.

From the  $C_2$  symmetry of the Ni(debd)(N<sub>3</sub>)<sub>2</sub> species and its similarity with the other compounds only one resonance is expected for each carbon atom in the <sup>13</sup>C spectrum. This is indeed observed for all carbon atoms of all three measured complexes, thereby confirming a symmetrical structure similar to the structure of Ni(debd)(N<sub>3</sub>)<sub>2</sub>. In the <sup>1</sup>H NMR spectra, only one resonance is expected for each set of methyl protons and for the pyrazole protons. This is not expected for protons 61 and 62, and 81 and 82, which do not *a priori* have to be equivalent. Protons 61 and 62 appear as a broad resonance, in con-

TABLE VII. <sup>13</sup>C and <sup>1</sup>H NMR Data of the Ligand and the Cd and Zn Compounds ( $\delta$  in ppm with TMS as reference). Ligand numbering as in Fig. 1.

Compound:	Ligand	Cd(debd)Br <sub>2</sub>	Cd(debd)(NCS) <sub>2</sub>	Zn(debd)(NCS) <sub>2</sub>	Zn(debd)(N <sub>3</sub> ) <sub>2</sub>	Cd(debd)(N <sub>3</sub> )
Carbon atom						
5	145.6	149.5	150.0	148.8		
3	139.3	141.7	142.7	141.3		
NCS			134.3	133.6		
4	105.0	106.3	106.6	107.1		
6	68.6	66.1	66.4	66.6	a	a
8	51.6	47.2	47.5	49.4		
71	39.5	39.7	39.7	b		
51	13.3	13.2	12.7	12.8		
31	10.7	10.1	10.1	10.0		
Proton						
4	5.81	6.09	6.17	6.16	6.11	6.24
61, 62	4.64	4.75	4.71	4.65	4.70	4.80
81, 82	2.59	b	b	b	b	b
71	2.21	2.31	2.36	2.31	2.29	2.37
51	2.25	2.40	2.36	2.33	2.31	2.34
31	2.15	2.15	2.16	2.15	2.15	2.16

<sup>a</sup>Insufficiently soluble. <sup>b</sup>Not observed.

trast to the other resonances which are sharp. The resonances of the protons 82 and 81 are probably obscured by the strong signal of monoprotonated dms<sub>o</sub>-d<sub>6</sub>, present in the solvent.

The resonances of the thiocyanate carbons are in agreement with the expected value for N-bonded, octahedral complexes [44]. In the <sup>13</sup>C as well as in the <sup>1</sup>H spectra the influence of the anion is most clearly seen from methyl group 51, which protrudes out towards the 'anion' side of the molecule. This probably indicates steric interaction between the methyl group and the anion and/or metal, as through-bond effects are very unlikely.

#### ESR Spectroscopy

The ESR spectrum of powdered Cu(debd)(NCS)<sub>2</sub> shows one, broad, isotropic resonance at room temperature ( $g = 2.15$ ). The spectrum of a Cu(II) dope in the isomorphous compound Zn(debd)(NCS)<sub>2</sub> provides more information. Two transitions are observed;  $g_{\parallel} = 2.26$ ,  $A_{\parallel} = 155$  Gauss,  $g_{\perp} = 2.11$ , showing a small rhombic splitting. This type of spectra is typical for (rhombically distorted) octahedral complexes [40].

The ESR powder spectra of the Mn(II) compounds are all indicative of a distorted octahedral geometry. With X = N<sub>3</sub> the distortion is hardly visible (MnN<sub>6</sub> chromophore), and for the isothiocyanate compound with a similar chromophore the distortion is also small. The halide compounds have a MnN<sub>4</sub>X<sub>2</sub> chromophore which leads to a large distortion, and a clearly rhombic signal ( $g = 4.3$ ) is observed [45, 46].

#### Conclusions

It is remarkable how the ligand debd shows an almost identical coordination behaviour towards all the described metal centers. Apparently, steric factors greatly favour the described configuration of the ligand around the metal. Steric interactions, as evidenced by NMR, allow the coordination of two additional small ligands such as SCN<sup>-</sup> and N<sub>3</sub><sup>-</sup>. Only in the case of the larger metal ions Mn<sup>2+</sup> and Cd<sup>2+</sup> is the coordination of relatively large anions such as Cl<sup>-</sup> and Br<sup>-</sup> observed.

The possibility of coordinating other small ligands is presently being investigated.

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