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Structure and Magnetic Exchange in Di-μ-chloro-Bridged Nickel(II) Dimers. Crystal and Molecular Structure of Di-μ-chloro-dichlorobis(bis(3,5-dimethylpyrazolyl)methane)dinickel(II)

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The crystal and molecular structure of di-μ-chloro-dichlorobis(bis(3,5-dimethylpyrazolyl)methane)dinickel(II), $[NiCl_2N_4C_{11}H_{16}]_2$, has been determined by a single-crystal X-ray analysis using three-dimensional diffractometer data. The compound crystallizes in the triclinic space group $P\bar{1}$, with one dimeric unit in a cell of dimensions $a = 8.944$ (4) Å, $b = 11.015$ (5) Å, $c = 7.864$ (4) Å, $\alpha = 75.96$ (4)°, $\beta = 83.17$ (5)°, and $\gamma = 110.48$ (6)°. The structure was solved by using Patterson and Fourier techniques and refined by full-matrix least-squares procedures. The resulting conventional R factor based on 3249 unique reflections is 0.035. Each Ni(II) ion is in a geometry intermediate between a trigonal bipyramid and a square pyramid. In a trigonal-bipyramid description the Ni(II) ion lies 0.04 Å from the equatorial plane through the two chlorine atoms and one nitrogen atom belonging to the organic ligand. The axial sites are occupied by the second nitrogen atom of the ligand and a chlorine atom belonging to the closest symmetry related molecule, thereby forming a dimeric unit, $[NiCl_2(CH_2(dmpz)_2)]_2$. The terminal Ni–Cl distance (2.319 (1) Å) and the shortest bridging Ni–Cl distance (2.318 (1) Å) are normal, whereas the longest, axial bridging Ni–Cl distance (2.456 (1) Å) is relatively large compared to similar compounds. The Ni–N distances are 2.034 (3) and 2.099 (3) Å. The magnetic interaction between the Ni(II) ions can be described by a dimeric model assuming isotropic intradimer interactions, including both single-ion zero-field splittings and an interdimer exchange in the molecular field approximation. The intradimer coupling ($J = +2.6$ (5) cm^{-1}) is compared with the coupling observed in similar five-coordinated Ni(II) dimers. The present compound shows ferromagnetic exchange interaction, whereas the earlier compounds are all antiferromagnetic. A possible origin for this different behavior is given.

Introduction

Superexchange coupling in coordination compounds has become of considerable interest to inorganic chemists, as evidenced by the increasing number of papers on the subject in the chemical literature. Unfortunately, the mechanism of the superexchange interaction still is not understood completely and thus far it has not been possible to predict the magnitude and kind of interaction (antiferromagnetic or ferromagnetic) even in a simple system, like the dimeric Ni(II) compounds. However, Barraclough and Brookes[1] conclude that the bridge angle (Ni–Cl–Ni) determines to a great extent the exchange interaction. In copper(II) hydroxo-bridged compounds Hatfield et al.[2] even found a linear relationship between the value of the exchange integral, J, and the bridge angle, θ. For chlorine-bridged Ni(II) dimers such a relationship does not seem to exist, as already noticed by Hendrickson and coworkers.[3] Recently, Sinn et al.[4] on the other hand conclude that a decrease in bridge angle coincides with a decrease in the coupling constant from positive (ferromagnetic) to negative (antiferromagnetic).

Preliminary results on the present compound showed[5] that the magnetic coupling is ferromagnetic in nature, whereas so-far reported compounds having five-coordinate Ni(II) with a Cl_3N_2 core, i.e., $Ni_2(biq)_2Cl_4$,[4] $Ni_2(dmp)_2Cl_4$,[4] $Ni_2(dmp)_2Cl_4{\cdot}2CHCl_3$,[6] and $Ni_2(qnqn)_2Cl_4$,[3] show antiferromagnetic exchange interactions. To find out the origin of the observed ferromagnetism, we have undertaken a detailed magnetic and structural study of $[Ni(CH_2(dmpz)_2)Cl_2]_2$, in which $CH_2(dmpz)_2$ stands for bis(3,5-(dimethylpyrazolyl)-methane).

Experimental Section

Compound Preparation. Samples of $Ni(CH_2(dmpz)_2)Cl_2$ were prepared as previously reported.[5] The crystals used in the magnetic and X-ray studies were grown by slow evaporation from chloroform solution.

Collection and Reduction of the Intensity Data. The crystals used for X-ray analysis measured approximately 0.3 × 0.3 × 0.1 mm. Weissenberg photographs taken with Cu Kα radiation showed no systematic absences, which implied that the space group is either $P1$ or $P\bar{1}$. The unit cell dimensions are deduced from measurements on a Nonius automatic single-crystal diffractometer (CAD-3).

Table I. Crystal Data and Experimental Parameters of Di-μ-chloro-dichlorobis(bis(3,5-dimethylpyrazolyl)-methane)dinickel(II)

A. Crystal Data	
formula $(NiCl_2N_4C_{11}H_{16})_2$	$V = 686.12$ Å^3
fw 666	$Z = 1$
$a = 8.944$ (4) Å	density (obsd) = 1.6 g/cm^{-3}
$b = 11.015$ (5) Å	density (calcd) = 1.61 g/cm^{-3}
$c = 7.864$ (4) Å	space group: $P\bar{1}$
$\alpha = 75.96$ (4)°	μ(Mo Kα) = 17.9 cm^{-1}
$\beta = 83.17$ (5)°	
$\gamma = 110.48$ (6)°	
B. Experimental Parameters	
radiation: Mo Kα (Kα_1)	max (sin θ)/λ: 0.7210
λ 0.709 26 Å	data collected: 4550
monochromator: graphite	data with $I > 2.85\sigma(I)$: 3249
takeoff angle: 4.4°	

The intensities were measured up to $\theta = 30°$ with the θ–2θ scan mode using Mo Kα radiation. The applied scan angle was $\Delta w = 0.8 + 0.4(\tan\theta)°$. The background was recorded in an additional scan area of $\Delta w/4°$ on each side of the main scan. Scanning times were 10° min^{-1}, whereas the background was scanned at both ends of the scan at half of the scan time. From the 4550 measured reflections, 3249 were significantly ($>2.85\sigma(I)$) different from the background intensity. In the reduction of the intensities to the structure factors, no correction for absorption has been applied ($\mu_{MoK\alpha} = 17.9$ cm^{-1}). Estimated minimum and maximum correction factors are less than 10%. All crystal data and experimental data are summarized in Table I.

Solution and Refinement of the Structure. The structure was solved by the heavy-atom method and refined by (blocked) full-matrix least-squares calculations using unit weights. The form factors used

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Table II. Final Fractional Atomic Coordinates and Thermal Parameters[a]

atom	x/a	y/b	z/c	10^2U_{11}	10^2U_{22}	10^2U_{33}	10^2U_{12}	10^2U_{13}	10^2U_{23}
N1	0.02293 (5)	0.84123 (4)	0.07096 (5)	2.89 (2)	1.90 (2)	2.79 (2)	1.30 (1)	−0.66 (1)	−0.88 (1)
Cl(1)	0.0888 (1)	1.03919 (7)	0.1522 (1)	4.80 (4)	2.57 (3)	3.99 (4)	2.04 (3)	−2.03 (3)	−1.62 (3)
Cl(2)	−0.1887 (1)	0.63912 (7)	0.0910 (1)	3.96 (4)	2.36 (3)	5.39 (5)	1.11 (3)	−1.71 (4)	−1.06 (3)
C1	0.1893 (4)	0.6395 (3)	0.0689 (5)	3.9 (2)	2.7 (1)	4.0 (2)	1.9 (1)	−0.9 (1)	−1.4 (1)
C11	0.3576 (4)	0.9769 (3)	−0.2113 (5)	3.7 (2)	3.2 (1)	4.0 (2)	1.5 (1)	−0.1 (1)	−0.8 (1)
C12	0.4878 (4)	0.9411 (4)	−0.2616 (6)	3.5 (2)	4.3 (2)	5.1 (2)	1.5 (1)	0.3 (2)	−1.0 (2)
C13	0.4401 (4)	0.8062 (3)	−0.1682 (5)	3.3 (2)	4.4 (2)	4.4 (2)	2.1 (1)	−1.1 (1)	−2.1 (2)
C111	0.3504 (6)	1.1143 (4)	−0.2760 (7)	5.3 (2)	3.3 (2)	6.8 (3)	1.8 (2)	1.1 (2)	0.2 (2)
C131	0.5263 (5)	0.7125 (5)	−0.1728 (7)	3.9 (2)	5.5 (2)	7.4 (3)	3.0 (2)	−1.3 (2)	−2.8 (2)
N11	0.2341 (3)	0.8704 (2)	−0.0935 (4)	3.6 (1)	2.7 (1)	3.6 (1)	1.9 (1)	−0.6 (1)	−1.0 (1)
N12	0.2884 (3)	0.7656 (2)	−0.0693 (4)	3.3 (1)	3.0 (1)	3.6 (1)	1.9 (1)	−0.7 (1)	−1.2 (1)
C21	0.1004 (4)	0.7322 (3)	0.4535 (4)	3.8 (2)	3.2 (1)	3.1 (2)	1.2 (1)	−1.0 (1)	−0.9 (1)
C22	0.1807 (5)	0.6491 (4)	0.5225 (5)	4.7 (2)	4.2 (2)	3.5 (2)	1.8 (2)	−1.8 (2)	−0.8 (1)
C23	0.2289 (4)	0.6042 (3)	0.3880 (5)	3.5 (2)	3.0 (1)	4.2 (2)	1.5 (1)	−1.4 (1)	−0.3 (1)
C211	0.0251 (6)	0.8055 (4)	0.5483 (6)	6.8 (3)	4.8 (2)	3.4 (2)	2.7 (2)	−1.0 (2)	−1.7 (2)
C231	0.3231 (6)	0.5154 (5)	0.3816 (7)	5.4 (2)	4.9 (2)	6.1 (3)	3.3 (2)	−1.5 (2)	−0.2 (2)
N21	0.0983 (3)	0.7383 (2)	0.2830 (4)	3.9 (1)	2.7 (1)	3.3 (1)	1.9 (1)	−1.1 (1)	−1.2 (1)
N22	0.1794 (3)	0.6596 (2)	0.2437 (4)	3.9 (1)	2.6 (1)	3.5 (1)	2.0 (1)	−0.9 (1)	−0.8 (1)

atom	x/a	y/b	z/c	U, Å^2	atom	x/a	y/b	z/c	U, Å^2
H11	0.082 (5)	0.604 (4)	0.041 (5)	4.31[b]	H1313	0.554 (6)	0.692 (5)	−0.066 (7)	7.09
H12	0.245 (4)	0.582 (4)	0.064 (5)	4.31	H221	0.198 (5)	0.634 (4)	0.636 (6)	5.07
H121	0.595 (5)	1.005 (4)	−0.345 (6)	5.57	H2111	−0.060 (6)	0.806 (5)	0.506 (7)	6.46
H1111	0.253 (6)	1.108 (4)	−0.318 (6)	6.46	H2112	−0.018 (5)	0.755 (5)	0.662 (7)	6.46
H1112	0.437 (5)	1.173 (4)	−0.371 (6)	6.46	H2113	0.103 (6)	0.875 (5)	0.550 (6)	6.46
H1113	0.347 (6)	1.146 (5)	−0.175 (7)	6.46	H2311	0.426 (6)	0.567 (5)	0.314 (7)	6.84
H1311	0.626 (6)	0.757 (5)	−0.253 (7)	7.09	H2312	0.324 (6)	0.479 (5)	0.484 (7)	6.84
H1312	0.465 (6)	0.634 (5)	−0.214 (7)	7.09	H2313	0.284 (6)	0.449 (5)	0.312 (7)	6.84

[a] Estimated standard deviations are in parentheses. The anisotropic thermal parameters are in the form $t = \exp\{-2\pi^2\Sigma_i\Sigma_j u_{ij}h_ih_ja_i^*a_j^*\}$.
[b] Parameter is held fixed.

for Ni, Cl, N, and C were obtained from Cromer and Mann[7] as were $\Delta f'$ and $\Delta f''$ for anomalous dispersion due to Ni and Cl and those for H from Stewart et al.[8] Assigned isotropic temperature factors of the hydrogen atoms were not refined. The final conventional R index $(\Sigma||F_o| - |F_c||/\Sigma|F_o| \times 100)$ based on 3249 reflections is 0.035. All calculations were performed on an IBM 370/158 computer, using the computer programs from X-RAY 72.[9] The final set of atomic and thermal parameters is given in Table II. A table of observed and calculated structure factors is available.[10]

Magnetic Susceptibility Measurement. Variable-temperature (4.2–90 K) magnetic susceptibility measurements were performed with a Princeton Applied Research Model 155 vibrating sample magnetometer operating at 3.8 kG and calibrated as described in a previous paper.[11] All data were corrected for diamagnetism[12] and temperature-independent paramagnetism, TIP (taken as 200×10^{-6} emu/Ni dimer). Least-squares fitting of the magnetic susceptibilities to the equations, given in detail by Ginsberg et al.,[13] was performed with a computer program written in FORTRAN IV by D. Knetsch (University of Leyden).

Results and Discussion

Description of the Structure. Figure 1 provides an illustration of the dimeric molecule. The dimer is made up by two $NiCl_2(CH_2(dmpz)_2)$ units, which are related by the crystallographically imposed center of symmetry. Each unit consists of a five-coordinate Ni(II) ion, surrounded by the organic bidentate ligand, a terminal Cl ion, a bridging Cl ion, and a second bridging Cl ion, belonging to the other half of the dimer. The bridging Cl ions and the Ni ions are all in the same plane.

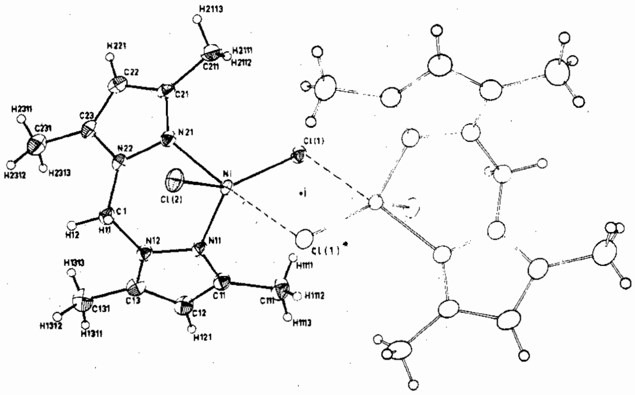

Figure 1. Molecular structure of NIDI, together with atomic numbering scheme for the asymmetric half of the dimer.

The separation between the Ni ions is 3.587 (2) Å, and the Ni–Cl–Ni angle is 97.36 (4)°. All the relevant interatomic distances and angles are listed in Table III. The values for the ligand molecules are all in the range observed in similar compounds;[14] this is also the case for the Ni–N and Ni–Cl distances, although the bridging Ni–Cl distances of 2.318 (1) and 2.456 (1) Å in fact reveal the most asymmetric bridge observed so far in five-coordinated dimeric Ni(II) compounds. The main structural features of the other known chloro-bridged Ni(II) dimers[2–6,15–20] are compared in Table IV, together with

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Table III. Interatomic Distances (Å) and Angles (deg)

N11–C11	1.333 (3)	N21–C21	1.327 (5)
N11–N12	1.383 (4)	N21–N22	1.375 (5)
C11–C12	1.398 (6)	C21–C22	1.400 (6)
C11–C111	1.501 (6)	C21–C211	1.487 (7)
C111–H1111	0.96 (5)	C211–H2111	0.86 (5)
C111–H1112	0.92 (4)	C211–H2112	0.88 (5)
C111–H1113	0.94 (6)	C211–H2113	0.84 (5)
C12–H121	1.00 (3)	C22–H221	0.91 (5)
C12–C13	1.372 (5)	C22–C23	1.357 (6)
C131–H1311	0.92 (5)	C231–H2311	0.91 (4)
C131–H1312	1.00 (5)	C231–H2312	0.81 (5)
C131–H1313	0.90 (6)	C231–H2313	1.00 (6)
C13–N12	1.342 (4)	C23–N22	1.352 (5)
C13–C131	1.493 (7)	C23–C231	1.502 (7)
Ni–Cl(1)	2.319 (1)	C1–N12	1.439 (3)
Ni–Cl(2)	2.318 (1)	C1–N22	1.441 (5)
Ni–Cl(1)^a	2.456 (1)	C1–H11	0.98 (4)
Ni–N11	2.033 (3)	C1–H12	0.94 (5)
Ni–N21	2.099 (3)		
Cl(1)–Ni–Cl(2)	144.23 (5)	C13–C131–H1313	108 (4)
Cl(1)–Ni–N11	103.50 (9)	H1311–C131–H1312	105 (4)
Cl(1)–Ni–N21	94.88 (9)	H1311–C131–H1313	103 (5)
Cl(1)–Ni–Cl(1)^a	82.64 (4)	H1312–C131–H1313	117 (4)
Cl(2)–Ni–N11	112.08 (9)	C12–C13–C131	130.2 (3)
Cl(2)–Ni–N21	90.26 (7)	C12–C13–N12	106.6 (4)
Cl(2)–Ni–Cl(1)^a	88.48 (5)	N12–C13–C131	123.1 (3)
N11–Ni–N21	87.6 (1)	C13–N12–N11	111.9 (2)
N11–Ni–Cl(1)^a	98.56 (9)	N11–N12–C1	117.9 (3)
N21–Ni–Cl(1)^a	173.8 (3)	C13–N12–C1	129.7 (3)
Ni–Cl(1)–Ni^a	97.36 (4)	Ni–N21–N22	116.8 (2)
N12–C1–N22	110.6 (3)	Ni–N21–C21	137.7 (3)
N12–C1–H11	108 (2)	C21–N21–N22	105.3 (3)
N12–C1–H12	105 (2)	N21–C21–C22	109.9 (4)
N22–C1–H11	113 (2)	N21–C21–C211	122.3 (4)
N22–C1–H12	108 (3)	C22–C21–C211	127.8 (4)
H11–C1–H12	111 (4)	C21–C211–H2111	107 (4)
Ni–N11–N12	118.8 (2)	C21–C211–H2112	109 (4)
Ni–N11–C11	135.8 (3)	C21–C211–H2113	106 (4)
C11–N11–N12	104.5 (3)	H2111–C211–H2112	103 (4)
N11–C11–C12	110.8 (3)	H2111–C211–H2113	125 (5)
N11–C11–C111	122.4 (4)	H2112–C211–H2113	106 (5)
C12–C11–C111	126.9 (3)	C21–C22–C23	107.1 (3)
C11–C111–H1111	111 (3)	C21–C22–H221	124 (3)
C11–C111–H1112	112 (4)	C23–C22–H221	129 (3)
C11–C111–H1113	106 (3)	C23–C231–H2311	109 (4)
H1111–C111–H1112	107 (4)	C23–C231–H2312	108 (4)
H1111–C111–H1113	108 (5)	C23–C231–H2313	115 (3)
H1112–C111–H1113	113 (4)	H2311–C231–H2312	111 (5)
C11–C12–C13	106.3 (3)	H2311–C231–H2313	100 (4)
C11–C12–H121	125 (3)	H2312–C231–H2313	113 (5)
C13–C12–H121	129 (3)	C22–C23–C231	131.1 (4)
C13–C131–H1311	111 (4)	C22–C23–N22	106.3 (4)
C13–C131–H1312	113 (3)	N22–C23–C231	122.5 (4)
		C23–N22–N21	111.3 (3)
		N21–N22–C1	118.6 (3)
		C23–N22–C1	129.9 (3)

^{a} $-x, -y, -z$.

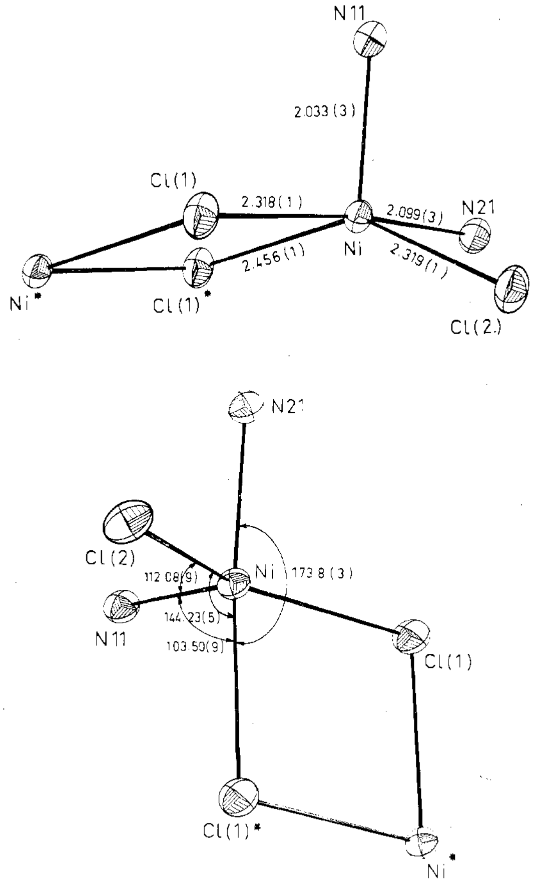

Figure 2. Basic geometry around Ni(II) depicted as a trigonal-bipyramid and as a square-pyramidal polyhedron, together with distances and angles.

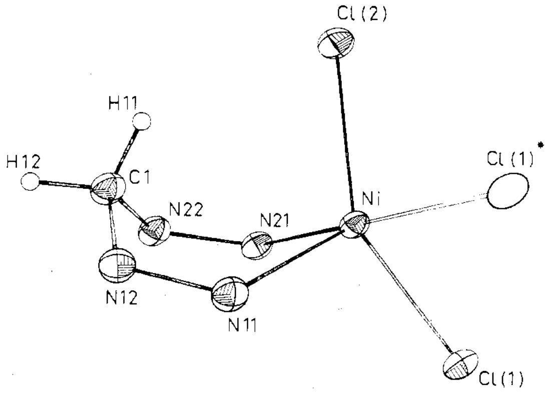

Figure 3. Schematic drawing showing the short H11–Cl(2) distance of 2.6 Å. For clarity the pyrazole carbons have been omitted.

the magnetic exchange parameters (to be discussed below).

In the present compound each Ni(II) ion is in a geometry intermediate between trigonal bipyramidal (tbp) and square pyramidal (sp). The most typical angles of sp (2 × 160–170° and 4 × 95–100°) and of tbp (1 × 180° and 3 × 120°) can both be used in a first approximation to describe the coordination geometry. This is depicted in detail in Figure 2, together with some bond distances and angles around Ni(II).

When looking in detail at the five compounds (Table IV) having five-coordinate chloro-bridged Ni(II) with a N–N bidentate ligand, it is observed that all compounds have N as the apical ligand in sp description. The present compound, however, deviates quite strongly on a few points. The structural differences of the present compound compared with the four previously reported five-coordinated chloride-bridged Ni(II) dimers can be summarized as follows: a distortion of the geometry from pseudo tetragonal pyramidal to trigonal bipyramidal (This is most clearly seen by the N–Ni–Cl angle of 174° (compared to 155–158° in the other compounds) and by the Cl–Ni–Cl angle of 144° (compared to 161–169° in the other compounds).), a quite strong asymmetry in the $NiCl_2Ni$ bridge (Although such an asymmetry of the bridge was reported before in other dimeric compounds (Table IV), this asymmetry can be related to the geometry around Ni(II), resulting in a lengthening of the "axial" Ni–Cl bond (in a trigonal-bipyramidal geometry) with respect to the equatorial Ni–Cl bonds. It should also be noted that the asymmetry in the $NiCl_2Ni$ unit differs from the symmetry in the other

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Table IV. Comparison between Structural and Magnetic Data of Chloro-Bridged Ni(II) Dimers (Esd Values in Parentheses)

compds	coordination geometry	Ni–Cl–Ni, deg	Ni–Ni, Å	Ni–Cl_t, Å	Ni–Cl_{b1}, Å	Ni–Cl_{b2}, Å	N–Ni–N, deg	Cl_t–Ni–Cl_{b2}, deg	Cl_{b1}–Ni–N, deg	J, cm^{-1}
$Ni(Qnqn)Cl_2$[a,3]	NiN_2Cl_3	98.23 (5)	3.652 (1)	2.296 (2)	2.408 (2)	2.422 (2)	97.6 (1)	160.6 (1)	158.0 (1)	−4.4
$Ni(dmp)Cl_2·CHCl_3$[a,6]	NiN_2Cl_3	98.0 (1)	3.602 (1)	2.316 (3)	2.378 (3)	2.384 (3)	81.7 (4)	162.2 (1)	157.2 (3)	?
$Ni(dmp)Cl_2$[a,3,4]	NiN_2Cl_3	97.4 (1)	3.600 (1)	2.307 (1)	2.378 (1)	2.414 (1)	82.0 (1)	168.5 (1)	155.4 (1)	−5.0
$Ni(biq)Cl_2$[a,4]	NiN_2Cl_3	96.68 (2)	3.563 (1)	2.306 (1)	2.372 (1)	2.400 (1)	80.4 (1)	164.0 (1)	157.6 (1)	−5.4[i]
$Ni(CH_2(dmpz)_2)Cl_2$[b]	NiN_2Cl_3	97.36 (4)	3.587 (2)	2.318 (1)	2.456 (1)	2.319 (1)	87.6 (1)	144.2 (1)	173.8 (3)	+2.6
$(NiCl_4)_2^{4-}$[19]	$NiCl_5$	99.29 (6)	3.669 (2)	2.283 (2)[h]	2.366 (2)	2.449 (2)				−2[3]
$Ni(en)_2Cl_2$[a,13,18]	NiN_4Cl_2	94.1[c]	3.67		2.485	2.522				+9[3]
		96.6 (1)[d]			2.461	2.551				+5.0[20]
$Ni(EG)_2Cl_2$[a,15–17]	NiO_4Cl_2	92.89[e]	3.452 (1)		2.382 (1)	2.382 (1)				+5.5[15a]
		93.03[f]	3.458 (1)		2.383	2.383				
$(Ni(H_2O)Cl_4)_2$[g]	$NiOCl_5$	95.0 (1)	3.602 (2)	2.405 (2)[h]	2.427 (2)	2.458 (2)				+7.2

[a] Ligand abbreviations are Qnqn = *trans*-2(2′-quinolyl)methylene-3-quinuclidinone, dmp = 2,9-dimethyl-1,10-phenantroline, biq = 2,2′-biquinolyl, en = ethylenediamine, and EG = ethylene glycol. [b] Present work. [c] From the compilation of Hendrickson and Long.[3] [d] Structure determined by Bottomley.[18] [e] Structure determined by van Ingen Schenau.[15b] [f] From the compliation of Hendrickson and Long[3] based on the structure of Antti.[16] [g] C. P. Landee and R. D. Willett, Washington State University, unpublished results. [h] The shortest Ni–Cl_t bond has been listed. [i] Recently reported by R. J. Butcher, C. J. O'Connor, and E. Sinn, *Inorg. Chem.*, 18, 492 (1979).

compounds. The "long" NiCl is *axial* in TBP description, compared to *equatorial* in the other compounds listed in Table IV.), an unusually short distance of 2.6 Å between the terminal Cl ligand and a hydrogen of the methylene bridge between the pyrazole fragments (This is depicted separately in Figure 3. This distance is even a little smaller than the sum of the van der Waals radii of hydrogen and chlorine.[21] In fact this CH_2 group prevents the Cl(terminal) anion to be located in a position "needed" for a square-pyramidal geometry. If this Cl ligand would be placed in a position as observed in the four other five-coordinated dimeric $[NiCl_2Ni]$ compounds, the H···Cl distance would be as short as 2.2 Å.). So, the presence of the CH_2 bridge in the ligand in fact hampers the formation of a geometry observed in the related compounds and decreases the Cl–Ni–Cl angle to the relatively small value of 144°. In addition an increase of Cl–Ni–N to 174° and a lengthening of Ni–Cl to 2.456 Å are observed. All other intraatomic distances and angles appear normal and will not be discussed in detail. From the details of the coordination geometry around Ni(II), it is evident that this particular compound is easily transformed to the tetrahedral monomeric species at high temperatures[5] and in solution, by breaking the long Ni–Cl bond.

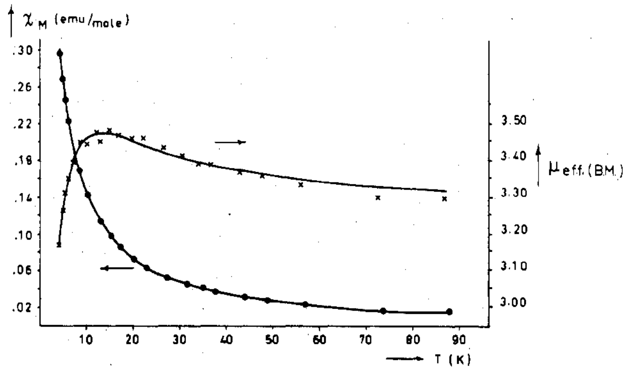

Figure 4. Molar susceptibility (●) and effective magnetic moment per Ni(II) ion (×) of NIDI as a function of temperature; the full curves represent the theoretical curves for $J = +2.58\ cm^{-1}$, $D = 2.17\ cm^{-1}$, $zJ' = -0.39\ cm^{-1}$, and $g = 2.310$, according to Ginsberg et al. (see text).

Magnetic Susceptibility Measurements. Magnetic susceptibility data in the range of 4.2–90 K were collected for finely ground single crystals of $(Ni(CH_2(dmpz)_2)Cl_2)_2$. The corrected molar susceptibility data set is plotted in Figure 4. In this figure also the μ_{eff} (effective moment defined as $(8\chi_M T)^{1/2}$) values and the results of the fitting procedure are included. The magnetic susceptibility apparently increases monotonically down to 4.2 K; however, in the plot of the effective moment vs. T a maximum is observed, occurring at about 13 K. A qualitatively similar behavior has been observed for the other structurally established di-μ-chlorine bridged dimers with octahedrally coordinated Ni(II), i.e., $(Ni(en)_2Cl_2)_2$[15,16] and $(Ni(EG)_2Cl_2)_2$.[13,18] For these latter compounds this behavior could be interpreted by assuming ferromagnetic superexchange coupling between the chlorine-bridged Ni(II) ions. The decreasing magnetic moment at the lowest temperatures can be explained by antiferromagnetic interdimer interactions, zero-field splitting effects, and/or saturation effects. The presence of saturation effects is easily excluded from the measurements by choosing the field strength below those values for which the susceptibility becomes field dependent. In the present compound the susceptibility was found to be field independent up to about 6 kG. At higher fields the susceptibility markedly decreased. For the description of the susceptibility data a model is needed which includes intra- and interdimer exchange, as well as zero-field splitting. Ginsberg et al.[13] published a susceptibility equation obtained from calculations based on the Hamiltonian

$$\mathcal{H} = -2J\hat{s}_1\cdot\hat{s}_2 - D(\hat{s}_{1z}^{\,2} + \hat{s}_{2z}^{\,2}) - 2ZJ'\hat{S}_i\langle\hat{S}_i\rangle - g_i\beta H\hat{S}_i \qquad (1)$$

in which the symbols have their usual meanings.[13] J denotes the isotropic intradimer exchange interaction, D the axial zero-field splitting, and ZJ' the interdimer exchange interaction parameter (molecular field approximation). Computer fitting of the theoretical susceptibility equation obtained from eq 1[13] to the data yielded $J = 2.58\ cm^{-1}$, $D = 2.17\ cm^{-1}$, $ZJ' = -0.39\ cm^{-1}$, and $g = 2.310$. In Figure 4 the plots of the theoretical susceptibility and the effective magnetic moment vs. T for this set of parameters are given as solid lines. Preliminary results[5] on this compound were slightly different, since at that time the measurements were performed at a field strength of about 18 kG; furthermore, at that time no single crystals were available and the possible presence of small amounts of monomeric impurities could have influenced the data.

A large amount of papers have appeared about the theories concerning the mechanism of exchange coupling via intermediate diamagnetic ions (superexchange). However, to date it seems not possible to describe the superexchange interactions in a quantitative way. On the superexchange pathways for the exchange in the Ni_2Cl_2 unit, Ginsberg[13] and Barraclough and Brookes,[1] using a configuration interaction method, take into account three ferromagnetic and three antiferromagnetic pathways. The net exchange then should be largely dependent

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(21) J. H. Huheey, "Basic Principles of Inorganic Chemistry", Harper and Row, New York, 1972.

upon the bridging Ni–Cl–Ni angle. More recently, Sinn and co-workers[4] conclude also that the bridging angle determines the magnetic exchange coupling, saying that a decrease in the Ni–Cl–Ni angle is coinciding with a decrease in J from positive to negative values. Very recently, Motida[19] pointed out that an exchange integral between d_ϵ and p_σ orbitals plays the main role in ferromagnetic interactions obeying the Kanamori–Goodenough rules. The structural parameters of our dichloride-bridged Ni dimer will now be used to discuss the differences in magnetic behavior compared with the other, similar compounds. In Table IV some relevant data have been listed. The first six compounds are all five-coordinate with geometries between square pyramidal and trigonal bipyramidal (sp and tbp, respectively), whereas the last three are coordinate with octahedral Ni(II) ions. It is noticed that the J values should only be regarded as an estimate of the exchange interaction, since the J values can be affected slightly by other parameters (see above). It is seen that no clear correlation exists between the Ni–Cl–Ni angle and J; in two cases this angle is 97.4° ($(\mathrm{Ni(dmp)Cl_2})_2$ and $\mathrm{Ni(CH_2(dmpz)_2Cl_2)_2}$) whereas the interaction is antiferro- and ferromagnetic, respectively. Therefore, the bridging angle does not, a priori, determine the value of the exchange constant; also the Ni–Ni distance and the Ni–Cl distances do not seem to influence J greatly. Another difference between our compound and the other five-coordinate dimers is the asymmetry in the $\mathrm{NiCl_2Ni}$ unit. To study this effect we have added some six-coordinate dimers to Table IV. If such an asymmetry were to influence J to a great extent, larger differences in J would be expected for the compounds $[\mathrm{Ni_2(en)_4Cl_2}]\mathrm{Cl_2}$ and $[\mathrm{Ni_2(EG)_4Cl_2}]\mathrm{Cl_2}$. The nature of the chelating ligands (all N–N bidentate donors) also is quite similar in all four compounds, so only small differences in charge densities on nickel can be expected for these $(\mathrm{NiCl_2(LL)})_2$ compounds.

In fact the only significant structural difference between our compound and the previously reported Ni dimers is the deviation from square-pyramidal geometry; the present compound has a coordination geometry approaching trigonal-bipyramidal geometry.

From recent work of Kahn et al.[22] it has become clear that the sign and the magnitude of the magnetic exchange coupling are very sensitive to the orientation of the unpaired electrons on both metal ions in dimers. Because it is well-known that different geometries usually result in different energies (and orientation) of the orbitals containing the unpaired electrons, it seems likely that such a different orientation of the d orbitals in our compound is responsible for the different magnetic behavior.

Further evidence for different energies of the orbitals containing the unpaired electrons comes from the ligand field spectra of this group of compounds with a chromophore $[\mathrm{NiN_2Cl_3}]$. In case of the square-pyramidal $\mathrm{Ni(qnqn)Cl_2}$ ligand field maxima are observed at 13.0 and 22.8 $\mathrm{cm^{-1}} \times 10^3$,[23] whereas the structurally established tbp species $\mathrm{Ni(dabco)_2Cl_3^+}$ shows ligand field maxima at 10.7 and 20.4 $\mathrm{cm^{-1}} \times 10^3$.[24] The title compound, however, has maxima between those values (at 12.5 and 21.7 $\mathrm{cm^{-1}} \times 10^3$ [5]), suggesting also a different orbital energy with respect to the square-pyramidal species.

A similar orbital orientation effect has been described recently for imidazole-bridged copper(II) dimers[25] and for Cu(II) and Co(II) halogen-bridged linear-chain compounds with heterocyclic ligands.[26]

Concluding Remarks

The results of the present study have confirmed that five-coordinate Ni(II) halogen-bridged dimers are easily formed with N-donor chelates having bulky substituents near the donor sites. In the title compound, the usually formed square-pyramidal coordination geometry is distorted toward a trigonal-bipyramidal geometry, apparently caused by the steric effect of the methylene bridge between the pyrazolyl groups. As a result of this distortion the magnetic coupling between the Ni(II) ions is ferromagnetic, instead of antiferromagnetic, as observed in previously reported five-coordinate Ni(II) dimers. For a more complete understanding, however, more structural and magnetic data on related compounds are needed.

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Registry No. $[\mathrm{NiCl_2(CH_2(dmpz))_2}]_2$, 66350-75-2.

Supplementary Material Available: A listing of structure factor amplitudes (14 pages). Ordering information is given on any current masthead page.

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