

Synthesis, X-ray Crystal Structure and Magnetism of $[\text{NiCl}_2\{\text{bis}(2\text{-benzimidazolyl})\text{propane}\}]_2 \cdot (\text{C}_2\text{H}_5\text{OH})_2$ – A Second Example of a Ferromagnetically Coupled Five-Coordinated High-Spin Dichloro-Bridged Nickel(II) Dimer

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The ligand bis(2-benzimidazolyl)propane coordinates to Ni^{II} with chloride as an anion, thereby forming a dinuclear compound with the formula: $[\text{NiCl}_2(\text{tbz})_2]_2(\text{C}_2\text{H}_5\text{O})_2$. This compound crystallizes in the space group $P2_1/c$. Each five-coordinated Ni^{II} ion has a distorted trigonal bipyramidal environment which consist of two asymmetrically bridging Cl anions with distances of 2.3556(17) and 2.4275(16) Å, a terminal Cl anion with a distance of 2.3496(17) Å and two nitrogen atoms of the ligand with distances of 2.022(4) and 2.000(4) Å. The Ni–Ni distance is 3.5891(12) Å, while the Ni–Cl–Ni angle is 97.23(6)°. The magnetic properties of the compound, as studied in the range 5–280 K, have been fitted

with a zero-field splitting parameter D (–14.3 cm^{-1}) and a ferromagnetic exchange between the Ni ions in the dinuclear unit ($J = +2.5 \text{ cm}^{-1}$). The title compound appears to be the second example for a five-coordinated ferromagnetic dinuclear Ni^{II} compound of this type, and its magnetic properties appear to correlate with the ligand structure. With the availability of an increasing number of examples of such species it appears that antiferromagnetic exchange is found for all cases with the chromophore $\text{N}_2\text{ClNiCl}_2\text{NiClN}_2$ where the MN_2 ring is 5-membered. In the case, where this ring is six-membered, the exchange is ferromagnetic.

During the last 2 decades only a few dichloro-bridged Ni^{II} dimers have been studied in detail both structurally and magnetically^{[1][6][7][8][9]}. Such compounds all contain a sterically crowded didentate amine or imine ligand (NN) resulting in the centrosymmetric chromophore (NN)ClNiCl₂NiCl(NN). The geometry of Ni^{II} in all cases is trigonal bipyramidal with varying degrees of distortion to tetragonal pyramidal^{[1][6][7][8][9]}. The NiCl_2Ni rectangle has Ni–Cl–Ni angles of $97.5 \pm 0.9^\circ$ and the Ni–Cl distances vary from 2.296 to 2.456 Å, Ni–Ni varies from 3.56 to 3.65 Å.

Magnetically these compounds are very interesting as both Ni ions interact, albeit weakly, through the Cl bridges. In fact, this only leaves the chelating ligand (NN) as a possible synthetic variable. Most of the earlier antiferromagnetically coupled systems have a rigid N–C–C–N structure with a five-membered chelate ring. Only one system^[1] has a flexible non-conjugated ligand with a six-membered chelate ring.

By using parameters for both the zero-field splitting (D) and the exchange J and zJ' (the latter being a parameter which describes lattice effects on the exchange), the low- T magnetic data can be fitted accurately. So far most compounds of this category $[\{\text{Ni}(\text{NN})\text{Cl}_2\}_2]$ have shown the commonly observed antiferromagnetic exchange and only

in one case^[1] has ferromagnetic exchange been reported. No correlations with any structural parameter (Ni–Cl–Ni angle, Ni–Cl distances) could be found at the time, although the more recently developed parameter^[2] to describe the degree of deviation from trigonal-bipyramidal (τ) gave a clue that an increased distortion towards square pyramidal could be the origin.

To investigate whether this hypothesis is useful, a new system had to be investigated. Bis(2-benzimidazoles) have been shown to be useful tools in the coordination chemistry of azoles which act as ligands in the context of mimicking biological systems^[3]. The ligands bis(2-benzimidazolyl)propane and bis(2-benzimidazolyl)butane form dinuclear alkoxo-bridged compounds^[4] with Cu^{II} and less strong anions, such as tetrafluoroborate, triflate, perchlorate, and nitrate. With strong anions, such as the halides, mononuclear Cu^{II} compounds are formed^[5]. With Ni^{II} chloride, bis(2-benzimidazolyl)propane (abbreviated as tbz) yields a dinuclear chloride-bridged compound. As this compound has the flexible ligand chelate ring, it was expected to yield a ferromagnetically coupled system, if our hypothesis were true. Therefore the title compound was studied both structurally and magnetically in detail. The results which are described below, show that they indeed agree with our hypothesis.

Results and Discussion

Description of the Crystal Structure of $[\text{NiCl}_2(\text{tbz})_2]_2(\text{C}_2\text{H}_6\text{O})_2$

The dinuclear unit consists of two $\text{NiCl}_2(\text{tbz})_2$ units, which are related by the crystallographic center of symmetry. Each unit consists of a five-coordinate Ni^{II} ion, surrounded by two N atoms of the ligand [$\text{Ni1}-\text{N13}$ 2.022(4), $\text{Ni1}-\text{N23}$ 2.000(4) Å], a terminal Cl ion [$\text{Ni1}-\text{Cl2}$ 2.3496(17) Å], a bridging Cl ion [$\text{Ni1}-\text{Cl1}$ 2.3556(17) Å], and a second bridging Cl ion [$\text{Ni1}-\text{Cl1a}$ 2.4275(16) Å], belonging to the other half of the dimer, resulting in a slightly asymmetric bridge.

The structure is depicted in Figure 1. The Ni–Ni distance is 3.5891(12) Å, while the Ni–Cl–Ni angle is 97.23(6). The Ni–Cl distances and angles are comparable with those distances known for such Ni^{II} species^{[1b][6a][7a]}, while the distances and angles of the ligand are comparable with other structures known for this ligand^[4].

Figure 1. ORTEP plot showing the structure $[\text{NiCl}_2(\text{tbz})_2]_2$ with atom-labeling scheme; ethanol molecules are omitted for clarity; atoms marked with an "a" are generated by an inversion centre

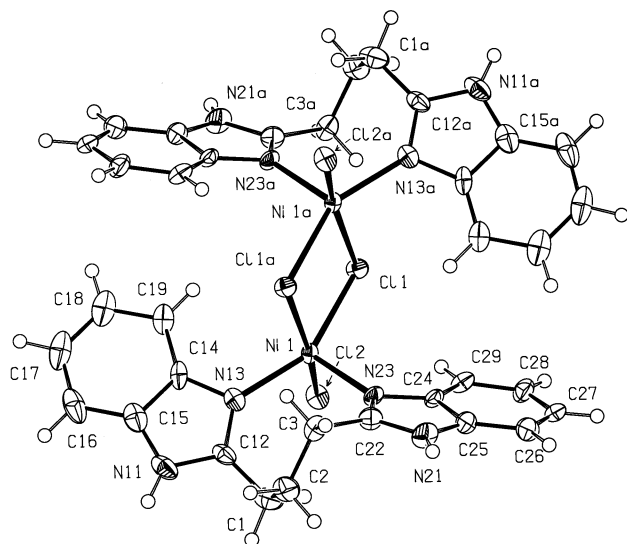


Table 1. Ligand field and far-infrared data of five-coordinated dimeric chloro-bridged Ni^{II} units

Compound	Ligand field ^[a] (10 ³ cm ⁻¹)						FIR [cm ⁻¹]		
							Ni–N	Ni–Cl	Ni–Cl _(br)
1. [Ni(qnqn)Cl ₂] ₂	6.5		13.0	19.6(sh)	22.8	^[d]	285	228	^[d]
2. [Ni(dmp)Cl ₂] ₂	6.4	10.6(w)	13.8	19.8(sh)	23.3	^[b]	294	260	198 ^[b]
3. [Ni(biq)Cl ₂] ₂	6.3	10.5(w)	13.8	19.8(sh)	23.4	^[c]	298	275	203 ^[c]
4. [Ni(CH ₂ (dmpz) ₂)Cl ₂] ₂	7.0		12.5	19.2(sh)	21.7	^[e]	290	267	210 ^[e]
5. [Ni(tbz)Cl ₂] ₂ (C ₂ H ₆ O) ₂	6.1		12.5(vbr)	19.6(sh)	22.0		289	245	218

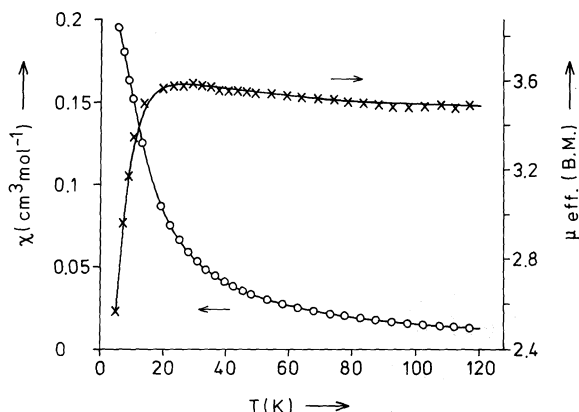
^[a] Abbreviations: sh = shoulder, w = weak, vbr = very broad. – ^[b] Synthesized according to ref.^[9] and re-measured. – ^[c] Synthesized according to ref.^[7a] and re-measured, the bridging Ni–Cl vibration can be at 198 cm⁻¹ or at 203 cm⁻¹, as a ligand vibration occurs in this area. – ^[d] Data from ref.^[6b], assignment of the FIR vibrations is uncertain as the compound was measured in CsI to ca. 200 cm⁻¹. This compound could not be synthesized to be re-measured. – ^[e] Data from ref.^[1a] and ^[1c].

Table 2. Comparison between structural and magnetic data of five-coordinated dimeric chloro-bridged Ni^{II} units

Compound ^[a]	Ni–Cl [Å]	Ni–Ni [Å]	Ni–Cl–Ni [°]	Largest angles [°] α, β (τ) ^[b]	J [cm ⁻¹]	D [cm ⁻¹]	g	ref. (s = structure, m = magnetism)
[Ni(qnqn)Cl ₂] ₂ (1)	2.408(2) 2.422(2) 2.296(2)	3.652(1)	98.23(5)	160.55(6), 158.00(7) ($\tau = 0.04$)	–4.4	–7.0	2.25	^{[8](m)} , ^{[6a](s)}
[Ni(dmp)Cl ₂] ₂ (2)	2.378(1) 2.414(1) 2.307(1)	3.600(1)	97.4(1)	168.5(1), 155.41(5) ($\tau = 0.21$)	–5.1	–8.8	2.20	^{[7a](s)} , ^[c] , ^{[8](m)}
[Ni(biq)Cl ₂] ₂ (3)	2.372(1) 2.400(1) 2.306(1)	3.563(1)	96.68(2)	164.03(2), 157.55(5) ($\tau = 0.10$)	–10.45 –7.74	–33.7 –18.43	2.21 2.31	^{[7b](m)} ^{[7a](s)} , ^{[7b](m)}
[Ni(CH ₂ (dmpz) ₂)Cl ₂] ₂ (4)	2.319(1) 2.318(1) 2.456(1)	3.587(2)	97.36(4)	144.2(1), 173.8(3) ($\tau = 0.49$)	+2.58	2.17	2.31	^{[1b](s, m)}
[Ni(tbz)Cl ₂] ₂ (C ₂ H ₆ O) ₂ (5)	2.3556(17) 2.3496(17) 2.4275(16)	3.5891(12)	97.23(6)	162.85(7), 150.00(14) ($\tau = 0.21$)	+2.49	–14.3	2.14	this work

^[a] Ligand abbreviations: qnqn = *trans*-2(2'-quinoly)methylene-3-quinuclidinone, dmp = 2,9-dimethyl-1,10-phenantroline (neocuproine), biq = 2,2'-biquinolyl, CH₂(dmpz)₂ = bis(3,5-dimethylpyrazolyl)methane. – ^[b] See ref.^[2], τ = defined as $\alpha - \beta/60$. – ^[c] Another crystal structure with this ligand was solved, i.e. [Ni(dmp)Cl₂]₂ · 2 CHCl₃; ^[9] some distances slightly differ from those from the [Ni(dmp)Cl₂]₂ compound.

Figure 2. Molar susceptibility (\circ) and effective magnetic moment per Ni^{II} ion (\times) of [NiCl₂(tbz)₂](C₂H₆O)₄ as a function of the temperature; the full curves represent the theoretical curves for $J = +2.5$ cm⁻¹, $D = -14.3$ cm⁻¹, $zJ' = -0.36$ cm⁻¹ and $g = 2.14$ (see text), with an R value of $3.20 \cdot 10^{-3}$ (in which $R = \sum \chi_{\text{obs}} - \chi_{\text{calc}} / \sum \chi_{\text{obs}}$)



cm⁻¹. Compound 4, however, shows a ferromagnetic behaviour, as is also the case in the title compound 5. In fact, such a weak ferromagnetic interaction was also observed

in another compound [Ni(dae)Cl₂]₂^[11] {dae = *N,N'*-[2-(3,5-dimethyl-1-pyrazolyl)ethyl]ethylamine}, but in this case, the J value had not been reported.

For di- μ -hydroxo-bridged copper compounds a well-known correlation holds between the J vs. the bridging Cu–O–Cu angle and for a change of 1° a change of approx. 40 cm⁻¹ is expected in the J value^{[12][15]}. As seen from Table 2, for di- μ -chloride-bridged Ni^{II} compounds a quantitative correlation is not found. However, it appears that antiferromagnetic exchange is found for all cases with the chromophore N₂ClNiCl₂NiClN₂ where the MN₂ ring is 5-membered. In the case, where this ring is six-membered, the exchange is ferromagnetic. In general the variation in the extreme values of the exchange parameter J vary between -10 cm⁻¹ and $+19$ cm⁻¹, the geometries of the Ni^{II} compounds are often difficult to compare, from hexacoordinate octahedral to pentacoordinate trigonal bipyramide intermediates. Different geometries usually result in different energies (and orientation) of the orbitals of the unpaired electrons. This in contrary to the di- μ -hydroxo-bridged copper compounds where the variation in the J value vary from $+172$ cm⁻¹ to -509 cm⁻¹^[15] and the geometries are mostly all square planar. It must also

be pointed out that the energy differences are very weak (ca. 10 cm^{-1}) and the J value itself must be regarded as an estimate of the exchange interaction, since the J value can be affected slightly by other parameters^[12] (see compound **2** in Table 2 in ref.^[1b]).

Although we did find, for the first time, a qualitative structure-magnetism relation for 5-coordinated di- μ -chloronickel(II) species, a quantitative conclusion about the magnetic behaviour in relation to the structural component for such Ni^{II} compounds cannot be drawn at this moment.

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Experimental Section

General: C, H, N, and Ni determinations: Microanalytical Laboratory of University College, Dublin, Ireland. – UV/Vis spectra: Perkin-Elmer 330 spectrophotometer using the diffuse reflectance technique, with MgO as a reference. – FTIR spectra: Bruker 113v infrared spectrophotometer, polyethylene mulls ($600\text{--}100 \text{ cm}^{-1}$, mirror velocity 0.099 cm/s , resolution 2 cm^{-1} , Mylar 3.5μ beam splitter). – Magnetic susceptibility: The title compound was measured in the temperature range $4.2\text{--}300 \text{ K}$ with a fully automated Manics DSM-8 susceptometer equipped with a TBT continuous-flow cryostat and a Drusch EAF 16 NC electromagnet, operating at ca. 1.4 T . Data were corrected for magnetization of the sample holder and for diamagnetic contributions, which were estimated from the Pascal constants^[16]. Magnetic data were fitted to a theoretical expression minimizing the function $R = \sum |\chi_{\text{obs}} - \chi_{\text{calc}}|^2 / \sum |\chi_{\text{obs}}|^2$.

Synthesis of the Compound: The synthesis of the ligand bis(2-benzimidazoly)propane has been described earlier^[4c]. The nickel compound was prepared according to the following procedure: 1.2 mmol of Ni^{II} chloride and 1.2 mmol of the ligand were each dissolved in 10 ml of ethanol. The Ni^{II} salt solution was then added slowly to the ligand solution preventing any precipitation, filtered to remove any solids and after a few days the yellow-orange crystals separated. – $\text{C}_{19}\text{H}_{22}\text{Cl}_2\text{N}_4\text{NiO}$ (452.0): calcd. C 50.49, H 4.91, N 12.39, Ni 12.99; found C 50.25, H 4.60, N 12.80, Ni 13.80.

Crystal Structure Determination and Refinement of the Structure: The X-ray diffraction data were collected with an Enraf-Nonius CAD4T diffractometer at 150 K [rotating anode, 60 kV , 50 mA , graphite-monochromated Mo- K_α radiation, ω -scan mode]. Unit-cell parameters were checked for the presence of higher lattice symmetry^[17]. The structure was solved by Direct Methods DIRDIF^[18]. Neutral atom scattering factors and anomalous dispersion factors were taken from ref.^[19]. Calculations were performed with programs SHELXL93^[20] and PLATON^[21] on a DEC-5000 cluster. The structure was refined on F^2 to $R1 = 0.0612$ for 2093 reflections for with $F_o > 4 \sigma(F_o)$. ($wR2 = 0.105$ for 3562 unique reflections, $S = 0.968$, $-0.49 < \Delta\rho < 0.41$). A summary of the crystallographic data is given in Table 3. Anisotropic thermal parameters were used for all non-hydrogen atoms. Hydrogen atoms were included in the

Table 3. Crystal data and details of the structure determination

Compound	$\text{C}_{34}\text{H}_{32}\text{Cl}_4\text{N}_8\text{Ni}_2 \cdot (\text{C}_2\text{H}_6\text{O})_2$
Mol. wt.	904.02
Crystal system	monoclinic
Space group	$P2_1/c$ (No. 14)
a [Å]	13.0105(10)
b [Å]	8.3307(5)
c [Å]	19.6619(14)
β (°)	108.833(10)
V [Å ³]	2017.0(3)
Z	2
$D_{\text{calcd.}}$ [g cm ⁻³]	1.489
$F(000)$	936
μ [cm ⁻¹]	12.4
Crystal size [mm], colour	$0.12 \times 0.18 \times 0.17$, red-orange
T [K]	150
θ_{max}	25
$\Delta\omega$ [°]	$0.66 + 0.35 \tan$
index ranges, h, k, l	$-15/16, -10/0, -25/14$
Total data, total unique data	5347, 3562
Observed data	2093 [$I > 2 \sigma(I)$]
No. of refined refl. and params.	3562, 249
Final $R1, wR2$ ^[a]	0.0612, 0.105
G.o.F. ^[b]	0.968
$(\Delta/\sigma)_{\text{av}}$ and $(\Delta/\sigma)_{\text{max}}$ in final cycle	$< 0.001, < 0.001$

^[a] $R1 = \sum |F_o| - |F_c| / \sum |F_o|$; $wR2 = \sum [w(F_o^2 - F_c^2)^2] / [\sum w(F_o^2)^2]^{0.5}$. – ^[b] G.o.F. = $\{\sum [w(F_o^2 - F_c^2)^2] / (n - p)\}^{0.5}$.

refinement cycle at calculated positions, riding on their carrier atoms except for the one on the ethanol molecule that was located from a difference map and its parameters refined.

Atomic positional and thermal parameters, lists of bond lengths and angles, and F_o/F_c values are available as supplementary material from one of the authors (A. L. S.). Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-101365. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) + 44(1223)336-033, E-mail: deposit@ccdc.cam.ac.uk].

- [1] ^[1a] J. Reedijk, J. Verbiest, *Transition Met. Chem.* **1978**, *3*, 51–52. – ^[1b] J. C. Jansen, H. van Koningsveld, J. A. C. van Ooijen, J. Reedijk, *Inorg. Chem.* **1980**, *19*, 170–174. – ^[1c] J. Reedijk, J. Verbiest, *Transition Met. Chem.* **1979**, *4*, 239–243.
- [2] A. W. Addison, T. N. Rao, J. Reedijk, J. van Rijn, G. C. Verschoor, *J. Chem. Soc., Dalton Trans.* **1984**, 1349–1356.
- [3] ^[3a] J. Reedijk, *Comprehensive Coordination Chemistry* (Ed.: Sir Geoffrey Wilkinson), Pergamon Press, London, **1987**, p. 73–98. – ^[3b] E. Bouwman, W. L. Driessen, J. Reedijk, *Coord. Chem. Rev.* **1990**, *104*, 143–172.
- [4] ^[4a] G. Bernardinelli, A. Kübel-Pollak, S. Rüttimann, A. F. Williams, *Chimia* **1992**, *46*, 155–158. – ^[4b] G. Bernardinelli, A. Kübel-Pollak, S. Rüttimann, A. F. Williams, *Z. Kristallogr.* **1993**, *203*, 132–134. – ^[4c] G. A. van Albada, M. T. Lakin, N. Veldman, A. L. Spek, J. Reedijk, *Inorg. Chem.* **1995**, *34*, 4910–4917.
- [5] ^[5a] M. A. Pujar, T. D. Bharamgoudar, *Transition Met. Chem.* **1988**, *13*, 423–425. – ^[5b] N. Donappa, S. B. Naikar, *Asian J. Chem.* **1993**, *5*, 995–997. – ^[5c] G. A. van Albada, unpublished results.
- [6] ^[6a] G. J. Long, E. O. Schlemper, *Inorg. Chem.* **1974**, *13*, 279–285. – ^[6b] G. J. Long, D. L. Coffen, *Inorg. Chem.* **1974**, *13*, 270–278.
- [7] ^[7a] R. J. Butcher, E. Sinn, *Inorg. Chem.* **1977**, *16*, 2334–2343. – ^[7b] R. J. Butcher, C. J. O'Connor, E. Sinn, *Inorg. Chem.* **1979**, *18*, 492–497.
- [8] E. J. Laskowski, T. R. Felthouse, D. N. Hendrickson, G. J. Long, *Inorg. Chem.* **1976**, *15*, 2908–2911.

- [9] H. S. Preston, C. H. L. Kennard, *J. Chem. Soc. A* **1969**, 2682–2685.
- [10] A. P. Ginsberg, R. L. Martin, R. W. Brookes, R. C. Sherwood, *Inorg. Chem.* **1972**, *11*, 2884–2889.
- [11] W. L. Driessen, R. M. de Vos, A. Etz, J. Reedijk, *Inorg. Chim. Acta* **1995**, *235*, 127–133.
- [12] T. Bkouche-Waksman, Y. Journaux, O. Kahn, *Transition Met. Chem.* **1981**, *6*, 176–180 and references cited therein.
- [13] J. R. Ferraro, *Low-Frequency vibrations of Inorganic and Coordination compounds*, Plenum Press, New York, **1971**.
- [14] R. Carballo, A. Castiñeiras, W. Hiller, J. Strähle, *Polyhedron* **1993**, *12*, 1083–1092.
- [15] O. Kahn, *Molecular Magnetism*, Chapter 8.6., VCH Publishers, New York, **1993**, and references cited therein.
- [16] I. M. Kolthoff, P. J. Elving, *Treatise on Analytical Chemistry*, Interscience Publ., New York, **1963**, vol. 4, part 1.
- [17] A. L. Spek, *J. Appl. Cryst.* **1988**, *21*, 578–579.
- [18] P. T. Beurskens, G. Admiraal, G. Beurskens, W. P. Bosman, S. Garcia-Granda, R. O. Gould, J. M. M. Smits, C. Smykalla, C. The DIRDIF program system, Technical report of the Crystallography Laboratory. University of Nijmegen, The Netherlands, **1992**.
- [19] A. J. C. Wilson (Ed.), *International Tables for Crystallography*, vol. C, Kluwer Academic Publ., Dordrecht, The Netherlands, **1992**.
- [20] G. M. Sheldrick, *SHELXL93, Program for crystal structure refinement*, University of Göttingen, Germany, **1993**.
- [21] A. L. Spek, *Acta Crystallogr.* **1990**, *A46*, C34.

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