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Dichlorotetrakis(pyridine)nickel(II)

By Robert E. Bachman and Kenton H. Whitmire*
Department of Chemistry, Rice University, PO Box 1892, *Houston, Texas* 77251, *USA*

and Subrata Mandal and Parimal K. Bharadwaj
Department of Chemistry, Indian Institute of Technology Kanpur, PO IIT, Kanpur – 208016, *India*

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Abstract. $[NiCl_2(C_5H_5N)_4]$, $M_r = 446.01$, tetragonal, $I4_1/acd$, $a = 15.783\,(3)$, $c = 16.965\,(8)$ Å, $V = 4226\,(2)$ Å^3, $Z = 8$, $D_x = 1.402$ Mg m^{-3}, Mo $K\alpha$ radiation (graphite-crystal monochromator), $\lambda = 0.71069$ Å, $\mu = 1.19$ mm^{-1}, $F(000) = 1840$, $T = 193$ K, final conventional $R = 0.039$ for 741 unique observed $[I > 3\sigma(I)]$ reflections and 83 variables. The Ni has an octahedral coordination with the Cl ligands in a *trans* relationship. The Ni—Cl distance is 2.433 (1) Å and the Ni—N distance is 2.121 (3) Å. The average N—Ni—Cl angle is 90.0 (9)°.

Experimental. A blue–green crystal (0.50 × 0.50 × 0.50 mm), obtained from the reaction of the Ni salt with pyridine, was mounted on glass fiber and used for data collection on a Rigaku AFC-5*S* single-crystal diffractometer with graphite-crystal-monochromated Mo $K\alpha$ radiation. Unit-cell dimensions were determined from angular settings of 25 reflections with 2θ between 37 and 42°. The space group was determined to be $I4_1/acd$ (No. 142) from the systematic absences. 3249 reflections were measured ($-10 < h < 21$, $0 < k < 21$, $0 < l < 22$; $4.0 < 2\theta < 55.0°$) with 741 unique reflections observed $[I > 3\sigma(I)]$; $R_{\rm int} = 0.024$. The ω–2θ-scan technique was employed with a 16.0° min^{-1} scan rate. Weak reflections $[I < 10\sigma(I)]$ were rescaned (maximum two rescans) and the counts accumulated to assure good counting statistics. Stationary background counts were recorded on each side of the reflection. Crystal and diffractometer stability was checked by monitoring three standard reflections every 150 reflections. Only random deviations were observed over the course of data collection. No decay correction was applied. An empirical absorption correction, based on ψ scans, was applied with correction factors ranging from 0.96 to 1.00. The data were also corrected for Lorentz and polarization effects. The structure was solved by direct methods employing the program *MITHRIL* (Gilmore, 1984) and Fourier synthesis, both of which are part of the *TEXSAN*2.0 program package (Molecular Structure Corporation, 1989). Least-squares refinement followed by an additional Fourier synthesis enabled the location of all the H atoms.

During the final stages of refinement the positional and anisotropic displacement parameters of all non-H atoms were refined. All H atoms were refined isotropically. The final conventional agreement factors were $R = 0.039$, $wR = 0.049$ and $S = 1.91$ for the 741 observed reflections and 83 variables. The function minimized was $\sum w(F_o - F_c)^2$ where $w = 1/\sigma^2(F_o)$ with $\sigma(F_o)$ from counting statistics. The maximum shift/e.s.d. in the last full-matrix least-squares cycle was less than 0.0002. The final difference Fourier map showed no peaks higher than 1.21 e Å^{-3} or deeper than -0.21 e Å^{-3}. All programs used in the structure solution and refinement are contained in the *TEXSAN*2.0 package (Molecular Structure Corporation, 1989). The plot was made using *ORTEP*II (Johnson, 1976). The atomic scattering factors included with the software package are from *International Tables for X-ray Crystallography* (1974, Vol. IV). The final positional and equivalent isotropic displacement parameters are given in Table 1.† Table 2 contains the molecular geometry data. Fig. 1 illustrates the metal coordination and the numbering scheme.

Related literature. The Ni—O bond length in tetrakis(3,5-dimethylpyridine)nickel(II) perchlorate is reported as 2.187 (4) Å and it shows paramagnetism (Madaule-Aubry & Brown, 1968). Conversely, the N—O distance in the 3,4-dimethyl derivative is

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* Author to whom correspondence should be addressed.

† Lists of structure factors, anisotropic thermal parameters, intra- and intermolecular bond distances, intramolecular bond angles and torsion angles, least-squares planes and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55161 (16 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH0615]

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Table 1. *Atomic coordinates and equivalent isotropic displacement parameters* (Å^2 × 10^2), *with e.s.d.'s in parentheses*

$$B_{eq} = (8\pi^2/3)\sum_{i=1}^{3}\sum_{j=1}^{3} U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Ni(1)	1.0000	$\frac{1}{4}$	$\frac{1}{8}$	1.99 (2)
Cl(1)	0.39099 (6)	0.6410	$\frac{1}{8}$	1.08 (3)
N(1)	1.0682 (2)	0.3161 (2)	0.0366 (2)	2.3 (1)
C(1)	1.1066 (3)	0.2758 (3)	−0.0223 (2)	3.1 (2)
C(2)	1.1502 (3)	0.3180 (4)	−0.0804 (3)	4.1 (3)
C(3)	1.1565 (3)	0.4036 (4)	−0.0780 (3)	4.2 (3)
C(4)	1.1179 (3)	0.4460 (3)	−0.0180 (3)	3.4 (2)
C(5)	1.0747 (3)	0.4009 (3)	0.0377 (2)	2.7 (2)

Table 2. *Bond lengths* (Å) *and angles* (°), *with e.s.d.'s in parentheses*

Ni(1)—Cl(1)	2.433 (1)	C(1)—C(2)	1.373 (6)
Ni(1)—N(1)	2.121 (3)	C(2)—C(3)	1.356 (7)
N(1)—C(1)	1.330 (5)	C(3)—C(4)	1.362 (6)
N(1)—C(5)	1.342 (5)	C(4)—C(5)	1.366 (5)
Cl(1)—Ni(1)—Cl(1*)	180.00	C(1)—N(1)—C(5)	116.9 (3)
Cl(1)—Ni(1)—N(1)	90.63 (9)	N(1)—C(1)—C(2)	122.3 (4)
Cl(1)—Ni(1)—N(1*)	89.37 (9)	C(1)—C(2)—C(3)	119.9 (5)
N(1)—Ni(1)—N(1*)	90.0 (2)	C(2)—C(3)—C(4)	118.6 (4)
Ni(1)—N(1)—C(1)	121.8 (3)	C(3)—C(4)—C(5)	119.0 (4)
Ni(1)—N(1)—C(5)	121.3 (3)	N(1)—C(5)—C(4)	123.2 (4)

* Indicates symmetry related atom.

3.343 (7) Å, well beyond the proximity needed for chemical bonding, and it shows diamagnetic behavior. The Ni—Cl distance, 2.433 (1) Å, in the title compound indicates that a chemical bond does exist and therefore the compound should be paramagnetic. The structural characterization of this compound, as well as the related Co compound, has been previously reported (Porai-Koshits, 1954). The present study determines all the relevant parameters to a higher degree of accuracy. A partial study has also been carried out on the related Fe system showing that it is isostructural (Forster & Dahm, 1972).

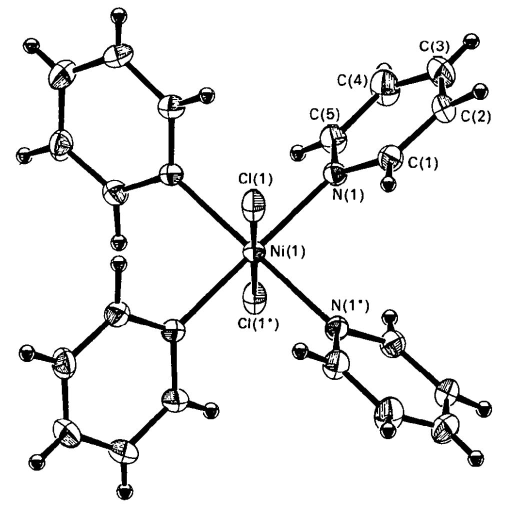

Fig. 1. *ORTEP*II (Johnson, 1976) representation showing the coordination of the central Ni atom and the atomic numbering scheme.

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Structure of the μ-Azido-dichloro(η^5-methylcyclopentadienyl)titanium(IV) Dimer

By Kristin Kirschbaum and Dean M. Giolando

Department of Chemistry, University of Toledo, Toledo, OH 43606, *USA*

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Abstract. Di-μ-azido-N:N-bis[dichloro(η^5-methylcyclopentadienyl)titanium(IV)], $[TiCl_2(N_3)(C_6H_7)]_2$, $M_r = 479.90$, monoclinic, $P2_1/c$, $a = 7.101$ (2), $b =$ 13.920 (3), $c = 19.050$ (4) Å, $\beta = 98.47$ (2)°, $V =$ 1863 (5) Å^3, $Z = 4$, $D_x = 1.71$ g cm^{-3}, λ(Mo $K\alpha$) = 0.71073 Å, $\mu = 14.4$ cm^{-1}, $F(000) = 960$, $T =$

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