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Steric hindrance in 2,6-disubstituted pyridines Part II. The crystal structures of *trans*-dichlorobis(2,6-dimethylpyridine)nickel(II) and *trans*-dichlorobis(2,4,6-trimethylpyridine)nickel(II)

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Abstract

trans-Dichlorobis(2,6-dimethylpyridine)nickel(II), $[NiCl_2(2,6\text{-}NC_5H_3(CH_3)_2]$ (I): $M=343.93$, triclinic, $P\bar{1}$, $a=7.611(2)$, $b=8.060(2)$, $c=8.115(2)$ Å, $\alpha=62.78(2)$, $\beta=86.02(3)$, $\gamma=114.02(3)°$, $V=383.8(2)$ Å^3, $Z=1$, $D=1.488$ g cm^{-3}, Mo Kα radiation, $\lambda=0.71069$ Å, $\mu=16.08$ cm^{-1}, $F(000)=178$, 296 K, $R=0.0328$ for 2937 observed reflections with $I>3\sigma(I)$. *trans*-Dichlorobis(2,4,6-trimethylpyridine)nickel(II), $[NiCl_2(2,4,6\text{-}NC_5H_2(CH_3)_3)]$ (**II**): $M=371.98$, monoclinic, $P2_1/c$, $a=7.523(2)$, $b=14.614(3)$, $c=7.959(2)$, $\beta=92.85(4)°$, $V=873.9(6)$ Å^3, $Z=2$, $D=1.413$ g cm^{-3}, Mo Kα radiation, $\lambda=0.71069$ Å, $\mu=14.18$ cm^{-1}, $F(000)=388$, 296 K, $R=0.0394$ for 1652 observed reflections with $I>3\sigma(I)$. The nickel, chloride and nitrogen donor atoms are strictly planar due to the siting of the molecule on a center of symmetry. Ni–Cl and Ni–N are 2.1940(8) and 1.935(1) Å for I and 2.1953(8) and 1.928(2) Å for II, respectively. The plane of the substituted pyridine ring in both cases is almost normal to the $NiCl_2N_2$ plane.

Introduction

Previously the synthesis and characterization of a series of square planar complexes of nickel(II) with 2,6-disubstituted pyridines of formula NiL_2X_2 was reported [1]. A unique feature of these complexes is their lack of solubility and chemical reactivity. The complexes are insoluble in most organic solvents and are not attacked by water or by aqueous solutions of strong chelating agents such as ethylenediamine or ethylenediaminetetraacetic acid (EDTA). Solutions of hydrochloric acid and nitric acid only react with the complexes after prolonged heating. It was concluded that this lack of chemical reactivity exhibited by the nickel complexes of doubly hindered methylpyridines is not due to electronic factors, since the *trans* square planar nickel(II) complexes of the mono-hindered 2,5-dimethylpyridine, although quite similar in their spectral properties to those of the doubly hindered pyridines, have completely different chemical behavior.

Thus steric hindrance was proposed as the reason for the inertness of the NiL_2X_2 complexes of doubly hindered pyridines. It was further postulated that the complexes were 'impenetrable' rather than 'unreactive' since their behavior is due to a blocking action, exerted by the (hydrophobic) CH_3 groups in the 2 and 6 positions of the ligands, on both the central nickel(II) ion and on the nitrogen atoms of the pyridine ring.

The IR spectra of the complexes NiL_2X_2 ($X=Cl^-$, Br^-, I^-, NCS^-; L=2,6-dimethylpyridine and 2,4,6-trimethylpyridine) have been systematically studied [1] and it was found that the values of the Ni–X and Ni–N (aromatic) stretching frequencies were anomalously high, exceeding the values commonly observed [2] for many known tetrahedral and octahedral 1:2 Ni(II)–pyridine complexes by as much as 100 cm^{-1}. For **I** and **II** the values of ν(Ni–N) were 340 and 330 cm^{-1} and ν(Ni–Cl) were 382 and 405 cm^{-1}, respectively.

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TABLE 1. Crystal data, data collection and structure solution and refinement for $NiCl_2(2,6\text{-diMepy})_2$ (**I**) and $NiCl_2(2,4,6\text{-triMepy})_2$ (**II**)

Parameter	**I**	**II**
Crystal data		
Empirical formula	$NiCl_2N_2C_{14}H_{18}$	$NiCl_2N_2C_{16}H_{22}$
Color (habit)	dark blue prisms	dark purple needles
Crystal size (mm)	0.35×0.30×0.23	0.15×0.17×0.35
Crystal system	triclinic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$
a (Å)	7.611(2)	7.523(2)
b (Å)	8.060(2)	14.614(3)
c (Å)	8.115(2)	7.959(2)
α (°)	62.78(2)	90
β (°)	86.02(2)	92.85(2)
γ (°)	114.02(2)	90
V (Å^3)	383.8(2)	873.9(6)
Z	1	2
Formula weight	343.93	371.98
Density (calc.) (g/cm^{-3})	1.488	1.413
Absorption coefficient (cm^{-1})	16.08	14.18
F(000)	178	388
Data collection		
Diffractometer used	Nicolet P3m	Nicolet P3m
Radiation used	Mo Kα (0.71069 Å)	Mo Kα (0.71069 Å)
Temperature (K)	296(1)	296(1)
Monochromator	highly oriented graphite crystal	
2θ range (°)	4–75	4–60
Scan type	θ–2θ	θ–2θ
Scan speed	variable; 3.97 to 29.3°/min in ω	
Scan range (ω)	1.0° plus Kα separation	1.0° plus Kα separation
Background measurement	Stationary crystal and stationary counter at beginning and end of scan, each for 50% of total scan time	
Standard reflections	4 every 96 reflections	4 every 96 reflections
Index ranges	$-12<h<12$, $-11<k<13$, $0<l<11$	$-10<h<10$, $0<k<20$; $0<l<13$
Independent reflections	3589	2832
Observed reflections	2937 ($>3\sigma$(I))	1652 ($>3\sigma$(I))
Absorption corrections	none	none
Solution and refinement		
System used	Texray-234 system based on a PDP 11/73	
Solution method	direct methods	direct methods
Refinement method	Full-matrix least-squares in both cases	
Quantity minimized	$\Sigma w(\lvert F_o\rvert-\lvert F_c\rvert)^2$	$\Sigma w(\lvert F_o\rvert-\lvert F_c\rvert)^2$
Weighting scheme	$w=1/[\sigma^2(F_o+p(F_o)^2]$ for both	
p factor	0.05	0.045
Hydrogen atoms	refined isotropically	refined isotropically
R^a (%)	3.28	3.94
$R_w{}^b$ (%)	4.41	4.80
Goodness-of-fit^c	1.308	1.364
Largest Δ/σ	0.03	0.02
Data to parameter radio	23.9:1	11.7:1
Largest difference peak (e Å^{-3})	0.53	0.69
Largest difference hole (e Å^{-3})	0.47	0.64

$^aR=\Sigma\{\lvert[F_o-F_c]\rvert\}/\Sigma(F_o)$. $^bR_w=\Sigma\{\lvert[F_o-F_c]\rvert(w)^{1/2}\}/\Sigma[(F_o)(w)^{1/2}]$. ^{c}Goodness-of-fit is defined as $s=\{[\Sigma(w\lvert[F_o-F_c]\rvert^2)]/[M-N]\}^{1/2}$, where M is the number of observed reflections and N is the number of parameters refined.

For the analogous copper complexes $Cu(2,6\text{-diMepy})_2Cl_2$ and $Cu(2,4,6\text{-triMepy})_2Cl_2$ the ν(Cu–N) values were 245 and 235 cm^{-1} and for ν(Cu–Cl) 318 and 310 cm^{-1}. This unexpected trend to lower metal ligand frequencies for the copper complexes must result from the relatively reduced stability of the copper–ligand bonds which has been ascribed to the presence of the additional 3d electron [1]. This should also be reflected in an increase in the metal–ligand bond lengths. Since the crystal structure of [Cu(2,6-diMepy)$_2$Cl$_2$] is known [3], comparisons can be made.

Therefore the structure determination of the complexes [NiCl$_2$L$_2$], L = 2,6 = dimethylpyridine (2,6-diMepy) (I), and 2,4,6-trimethylpyridine (2,4,6-triMepy) (II) has been undertaken in order to determine if the position and conformation of the methyl groups was indeed a factor in the apparent inertness of these complexes and to compare the results with those of analogous copper(II) complexes.

Experimental

Dark blue crystals of **I** and dark purple crystals of **II** were obtained from the reaction of NiCl$_2$ with the respective parent ligands [1]. Unit cell dimensions were determined by standard methods [4] from a least-squares fit of the angular parameters of 15 reflections, in the range $30 < 2\theta < 35°$, centered in the counter aperture of a Nicolet P3m four circle diffractometer. A unique data set was collected in the range $4 < 2\theta < 75°$ for **I** and $4 < 2\theta < 60°$ for **II** yielding 3589 (I) and 2832 (II) unique reflections of which 2937 (I) and 1652 (II) with $I > 3\sigma(I)$ (where $\sigma(I)$ is estimated from counting statistics) were considered observed and used in the structure solution and refinement. Absorption corrections were not applied due to the low linear absorption coefficient and regular shape of the crystal. Monochromatic Mo Kα radiation was used throughout; T was maintained at 296(1) K. Details of the determination of crystal data, collection of reflection data and solution and refinement of the structure are gathered together in Table 1.

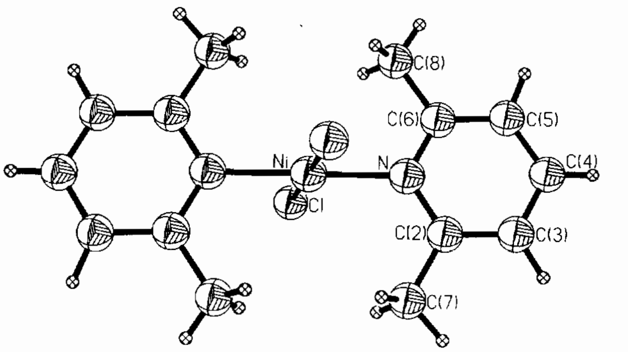

Fig. 1. Molecular diagram of *trans*-dichlorobis(2,6-dimethylpyridine)nickel(II).

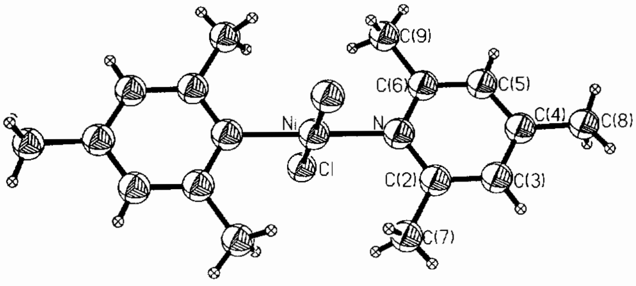

Fig. 2. Molecular diagram of *trans*-dichlorobis(2,4,6-trimethylpyridine)nickel(II).

TABLE 2. Bond distances (Å) in NiCl$_2$(2,6-diMepy)$_2$ (I) and NiCl$_2$(2,4,6-triMepy)$_2$ (II)

Bond	I	II
Ni–Cl	2.1940(6)	2.1953(8)
Ni–N	1.935(1)	1.928(2)
N–C2	1.352(1)	1.353(3)
C2–C3	1.390(2)	1.379(4)
C2–C7	1.493(2)	1.501(4)
C3–C4	1.379(2)	1.382(4)
C4–C5	1.381(2)	1.378(4)
C4–C8	–	1.501(4)
C5–C6	1.387(2)	1.379(4)
C6–N	1.356(1)	1.361(3)
C6–C9(C9)	1.496(2)	1.486(4)

TABLE 3. Bond angles (°) for NiCl$_2$(2,4-diMepy)$_2$ (I) and NiCl$_2$(2,4,6-triMepy)$_2$ (II)

Angle	I	II
Cl–Ni–N	90.49(3)	90.78(7)
Cl–Ni–N′	89.51(3)	89.22(7)
Ni–N–C2	120.57(7)	122.2(2)
Ni–N–C6	119.96(8)	118.9(2)
C2–N–C6	119.4(1)	118.9(2)
N–C2–C3	121.1(1)	121.1(3)
N–C2–C7	118.0(1)	117.4(2)
C3–C2–C7	120.9(1)	121.5(3)
C2–C3–C4	119.7(1)	121.1(3)
C3–C4–C5	118.9(1)	116.8(3)
C4–C5–C6	119.7(1)	121.5(3)
N–C6–C5	121.1(1)	120.6(3)
N–C6–C8(C9)	118.1(1)	117.9(2)
C5–C6–C8(C9)	120.8(1)	121.5(3)

Results

For positional parameters and thermal parameters for **I** and **II**, see ‘Supplementary material’. Both compounds were solved by direct methods [5] which gave the positions of the nickel, chlorine and nitrogen atoms. The remaining non-hydrogen atoms were found from a difference Fourier synthesis based on refined positions for the atoms found from the direct methods solution. After anisotropic refinement (see ‘Supplementary material’) of all non-hydrogen atoms, the positions of all hydrogen atoms were determined from a difference Fourier synthesis. These were included in dampened

TABLE 4. Selected bond distances (Å) and angles (°) in planar MX_2L_2 (M = Cu, Ni, X = Cl, Br) compounds

Complex	M–X	M–N	X–M–N	Θ	Reference
$NiCl_2(2,6\text{-diMepy})_2$	2.1940(6)	1.935(1)	90.49(3)	88.7(2)	this work
$NiCl_2(2,4,6\text{-triMepy})_2$	2.1953(8)	1.928(2)	90.78(7)	88.8(3)	this work
$CuCl_2(2,6\text{-diMepy})_2$	2.264(2)	2.011(3)	90.6(2)	88.4(7)	3
$CuBr_2(2,6\text{-diMepy})_2$	2.425(1)	1.997(5)	90.4(2)	88.2(8)	3
$CuCl_2(dmp)_2$[a]	2.254(2)	1.977(6)	90.5(3)	57	9
$CuBr_2(dmp)_2$	2.392(2)	1.976(9)	90.4(4)	60	9

[a] dmp = 2,9-dimethyl-1,10-phenanthroline.

TABLE 5. Selected bond lengths (Å) and bond angles (°) for $NiCl_2(2,4\text{-diMepy})_2$ (**I**) and $NiCl_2(2,4,6\text{-triMepy})_2$ (**II**)

Parameter	**I**	**II**
C3–H3	0.97(2)	0.89(3)
C5–H5	1.00(2)	0.83(3)
C7–H71	0.93(2)	0.82(4)
C7–H72	0.99(2)	0.97(4)
C7–H73	0.89(2)	1.01(4)
C8–H81		0.95(7)
C8–H82		0.90(4)
C8–H83		0.90(6)
C9(C8)–H91(H81)	0.94(2)	0.95(3)
C9(C8)–H92(H82)	0.90(3)	0.85(4)
C9(C8)–H93(H83)	0.84(3)	0.93(3)
C2–C3–H3	119.(1)	119.(2)
C4–C3–H3	121.(1)	120.(2)
C3–C4–H4(C8)	119.(1)	121.9(3)
C5–C4–H4(C8)	123.(1)	121.4(3)
C4–C5–H5	125.(1)	121.(2)
C6–C5–H5	115.(1)	117.(2)
C2–C7–H71	112.(1)	110.(2)
C2–C7–H72	109.(1)	113.(2)
C2–C7–H73	112.(1)	111.(2)
H71–C7–H72	110.(2)	104.(4)
H71–C7–H73	106.(2)	109.(3)
H72–C7–H73	106.(2)	110.(3)
C4–C8–H81		107.(4)
C4–C8–H82		116.(3)
C4–C8–H83		114.(3)
H81–C8–H82		94.(5)
H81–C8–H83		98.(4)
H82–C8–H83		122.(4)
C6–C8(C9)–H81(H91)	111.(1)	111.(2)
C6–C8(C9)–H82(H92)	113.(2)	110.(2)
C6–C8(C9)–H93(H93)	109.(2)	111.(2)
H81(H91)–C8(C9)–H82(H92)	115.(2)	107.(3)
H81(H91)–C8(C9)–H83(H93)	109.(2)	107.(3)
H82(H92)–C8(C9)–H83(H93)	99.(2)	111.(3)

(0.75) least-squares refinement with isotropic temperature factors.

Refinement converged with maximum parameter shifts for the non-hydrogen atoms being less than $0.03\Delta/\sigma$ giving $R = 0.0328$ (**I**), and 0.0394 (**II**) and $R = 0.0441$ (**I**) and 0.0480 (**II**). Neutral atom scattering factors were used throughout; Ni, Cl, N and C being corrected for anomalous dispersion [6]. Computation was carried out using supplied programs [7] implemented on a PDP 11/73.

Discussion

As can be seen from their molecular diagrams (Figs. 1 and 2) both molecules consist of a central nickel atom surrounded by two *trans* chloride and two *trans* nitrogen donor atoms from the substituted pyridine rings, the nickel atoms being sited on a center of symmetry. The asymmetric unit comprises one-half of the molecule in each case, and the nickel environments are necessarily planar. The N–Ni–Cl angles only deviate trivially from 90° (90.49(3)° **I**, 90.78(7)° **II**). The angle between the NiN_2Cl_2 and the ligand planes is 88.7(2)° for **I** and 88.8(3)° for **II**. In each case the e.s.d.s of the defining atoms was less than or equal to 0.002 Å and the nickel deviations were 0.196(1) and 0.201(1) Å, respectively.

Table 2 gives bond distances and Table 3 gives bond angles for **I** and **II**, while Table 4 gives values for other planar MX_2L_2 compounds (M = Cu, Ni, X = Cl, Br). It can be seen from Tables 2 and 3 that the bond distances and angles in the two structures, without exception, agree within experimental errors. In both cases the plane of the aromatic ring is approximately perpendicular to the plane made up of the four donor atoms. Because of the steric bulk of the methyl groups in **I** and **II** there are no close halide approaches from adjacent molecules to the vacant octahedral sites of the nickel atoms.

It can also be clearly seen from Figs. 1 and 2 that the 2- and 6-methyl groups, in both cases, have adopted a conformation which projects the two protons from each methyl group into the area above and below the nickel atoms thus creating a hydrophobic pocket in the region where attack by potential donors might be expected to occur. In fact, an examination of the angles subtended by the 2- and 6-methyl groups to the pyridine moiety shows that these groups are slightly tilted towards the vacant area above and below the NiN_2Cl_2 plane

(118.1(1)°, 118.0(1)° for **I** and 117.9(3)°, 117.4(3)° for **II**). Thus this conformation effectively shields the nickel atoms completely and explains the total lack of reactivity of these molecules (except to prolonged heating in strong acid solutions).

An examination of the bond lengths and bond angles found in the substituted pyridine ligands themselves reveals the usual pattern of short C–N lengths (av. 1.355 Å) and short C–C bond lengths (av. 1.384 Å for **I**, 1.379 Å for **II**) compared with values of 1.399 Å found in aromatic rings. Additionally, it can be seen that the orientation of the ring in the 2,6-disubstituted pyridine derivatives is approximately normal to the MN_2X_2 plane for both the nickel and copper [3] complexes (88.7(2)° for **I**, 88.8(3)° for **II**, 88.4(7)° for $CuCl_2$(2,6-diMepy)$_2$ and 88.2(8)° for $CuBr_2$(2,6-diMepy)$_2$ while for the analogous CuX_2(dmp)$_2$ complexes the aromatic ring makes an angle of only 57 and 60° to the CuN_2X_2 plane for the chloro and bromo derivatives, respectively. It is this perpendicular orientation that projects the methyl groups in positions directly above and below the metal atoms and thus makes them chemically unreactive.

From Table 4 it can be seen that the metal ligand bond lengths found for the nickel complex of 2,6-dimethylpyridine are significantly shorter than that found for the analogous copper complex (2.1940(6) Å Ni–Cl, 1.935(1) Å Ni–N: 2.264(2) Å Cu–Cl, 2.011(3) Å Cu–N). This explains the fact that the ν(Ni–N) and ν(Ni–X) stretching frequencies for the nickel complexes of these sterically hindered ligands occur at lower wavelengths than do the corresponding ν(Cu–N) and ν(Cu–X) for the corresponding copper complexes.

Supplementary material

Positional parameters, thermal parameters, selected metrical parameters involving hydrogen, F_o and F_c lists are available from the authors on request.

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