between 3,6-dihydronicotinic acid and an *N*-methyl-Δ^1-pyrrolinium salt.

(8) Prepared from [1-^{14}C]aniline (ICN, Calif.) by the method of D. Gros, A. Felge, and H. R. Schütte, *Z. Chem.*, **5**, 21 (1965).

(9) Absolute incorporation is defined as the total activity found in the isolated alkaloid divided by the total activity fed.

(10) This method has been used to elucidate pathways for the biosynthesis of numerous microbial metabolites derived from [1,2-^{13}C$_2$]acetate,[11] tropic acid[11] and tenellin[12] derived from [1,3-^{13}C$_2$]phenylalanine, ovalicin derived from [3,4-^{13}C$_2$]mevalonate,[13] and porphyrins derived from [2,11-^{13}C$_2$] porphobilinogen.[14] Since the natural abundance of contiguous carbon-13 atoms is only 0.01%, quite low specific incorporations of such labeled precursors can be detected.

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(15) Prepared by the sequence: [^{14}C]methyl iodide + [^{13}C]methyl iodide → [^{14}C,^{13}C]nitromethane[16] → [2,3-^{14}C,^{13}C]-3-aminoquinoline[17] → [2,3-^{14}C,^{13}C]quinoline → [5,6-^{14}C,^{13}C]nicotinic acid. Analysis by mass spectrometry indicated the presence of 55% [5,6-^{13}C$_2$]-, 19% [5-^{13}C]-, 19% [6-^{13}C]-, and 7% unlabeled nicotinic acid.

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(18) The Fourier transform ^{13}C NMR spectra were determined in either CDCl$_3$ or benzene-d_6 in a Varian XL 100 spectrometer (25.2 MHz). The enriched dioscorine (240 mg in 0.3 ml of C$_6$D$_6$ in a 5-mm tube) was run with an acquisition time of 2.0 s (0.5 Hz/data point), only 5000 transients being required to observe the satellites at C-1 and C-7.

(19) This is the expected ^{13}C–^{13}C coupling constant for an sp^3–sp^3 bond, cf. J. B. Stothers, "Carbon-13 NMR Spectroscopy", Academic Press, New York, N.Y., 1972, p 327.

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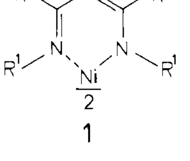
Stereochemistry of Tetrahedral Nickel Complexes. Configurational Rigidity and Stereochemical Analyses

Sir:

We wish to demonstrate that paramagnetic, (pseudo)tetrahedral nickel complexes of the chelate type **1** can be chiral and configurationally stable on the NMR time scale. We observed two ^{1}H NMR signals of equal intensity for the β-hydrogen atoms of the ethyl group in **2**. This nonequivalence indicates a chiral environment for the β-protons. Ethyl rotation is not sufficiently restricted[1,2] as the β-shifts of all such complexes are similar.[1] Since signal coalescence does not occur in **2** below 147 °C, configurational inversion at nickel requires $\Delta G^{\ddagger} \geqslant 21.8$ kcal/mol (420 K in (Cl$_2$CD)$_2$). The analogous β-splitting in **1a** yields $\Delta G^{\ddagger} > 20$ kcal/mol (407 K in (Cl$_2$CD)$_2$). Its counterparts **1b** and **1c**[1] do not show any nonequivalence because of their D_{2d} symmetry.



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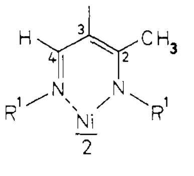


	R^1	R^2	R^3	R^4
1a	C$_6$H$_5$	*n*-C$_3$H$_7$	C$_2$H$_5$	H
b	C$_6$H$_5$	*n*-C$_3$H$_7$	C$_2$H$_5$	*n*-C$_3$H$_7$
c	C$_6$H$_5$	H	C$_2$H$_5$	H
d	H	CH$_3$	H	CH$_3$

2, R^1 = C$_6$H$_5$

3, R^1 = CH$_3$

Complex **3** with NCH$_3$ instead of phenyl substituents exhibits similar β-splitting (and full paramagnetism) with $\Delta G^{\ddagger} = 17.3$ kcal/mol (358 K in cyclohexane) and $\Delta S^{\ddagger}$ = about −30 eu. As usual, the tetrahedral ground state is favored by entropy factors. Only **1d** accommodates a diamagnetic (planar) ground state.[3]

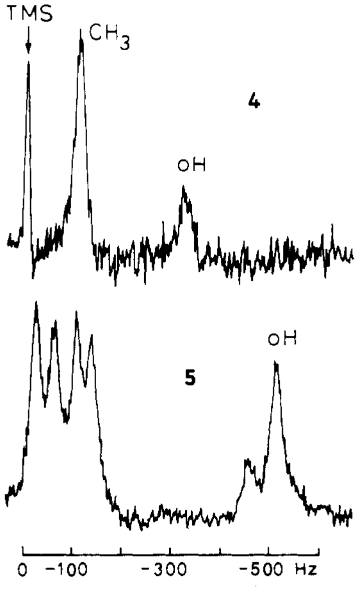
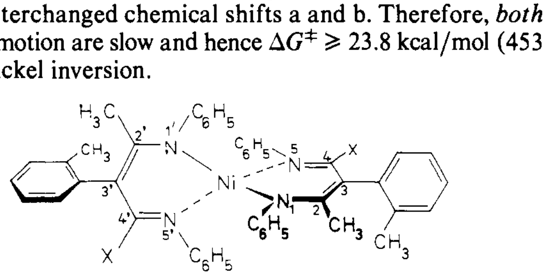


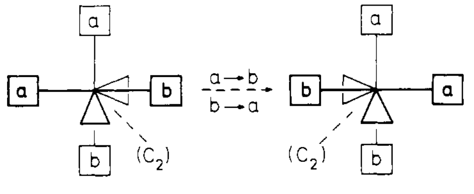
Figure 1. Ortho methyl and ortho hydrogen NMR signals (tolyl group of **4** and **5**) at 60 MHz and −39 °C in DCCl$_3$.

A different case with symmetric ligands is presented with full geometry in **4** (X = CH$_3$). The axis C^{3}NiC$^{3\prime}$ constitutes the only chirality element here. Projection **6** with *R* configuration[4,5] results by viewing **4** along this axis from the right. The front chelate ring shows up as a horizontal bar, with the asymmetric arrangement of its *o*-tolyl substituent at C^3 represented as a wedge below the bar.[6] The more distant chelate ring projects vertically in **6** with its *o*-tolyl at C$^{3\prime}$ as a wedge to the right. Methyl groups at C^2, C$^{2\prime}$, C^4, and C$^{4\prime}$, or else the four anilino moieties, are presented as squares. A C_2 axis, passing through Ni, bisects the distances N^{1}N$^{1\prime}$ and N^{5}N$^{5\prime}$. Therefore, only one ^{1}H NMR signal is found in the upper trace of Figure 1 for the two *o*-CH$_3$ substituents (◁). The para hydrogen atoms of the anilino groups show two equally intense signals (a and b) in tetralin up to 180 °C. Rotations by 180° of the rear tolyl substituent or of the rear ligand as a whole (i.e., nickel inversion) would produce enantiomer **7** from **6** with interchanged chemical shifts a and b. Therefore, *both* kinds of motion are slow and hence $\Delta G^{\ddagger} \geqslant 23.8$ kcal/mol (453 K) for nickel inversion.



4, X = CH$_3$

5, X = H



6, R

7, S

Complex **5** (X = H) may be used to examine the stereochemical consequences more generally; all its possible isomerizations are symbolized in Figure 2. Projection **8** results as before by viewing **5** from the right. Circles were drawn for X = H, all other notations being taken over from **6**.[6] For sym-

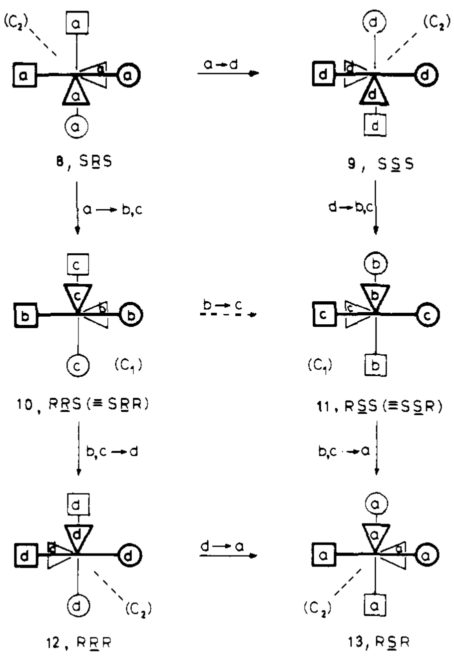


Figure 2. Symbolic representation of nickel inversion (horizontal transitions) and of substituent inversions (vertical) in **5**: diastereomerizations (→) and enantiomerizations (⇢).

metry reasons, only one signal (a) is expected for each of the three homotopic pairs □, O, and ◁ (*o*-methyl groups). The central chirality at nickel will be labeled ***R*** and ***S***; in **8**, its configuration is ***R***.[7] Both bidentate ligands of **5**/**8** possess axial chirality and *S* configuration.[4,5] Hence **8** may be denoted at *S**R**S*. Its mirror image is **13** with *R**S**R* configuration.

If only the front tolyl group rotates by 180°, the ligand chirality changes to *R*, producing a totally asymmetric[11] (C_1) isomer **10** (*R**R**S*). Therefore, structurally equivalent substituents are diastereotopic and may have different NMR signals b and c. Further rotation of the rear tolyl group leads to the third diastereomer **12** (*R**R**R* with shifts d). When the rear ligand of **8** is rotated as a whole, only the nickel configuration will be inverted to the diastereomer **9** (*S**S**S*). The same rotation in **10** to yield **11** constitutes an enantiomerization.

Consequently, up to *four* NMR signals a-d (b and c must be equally intense) are expected. As shown in the lower part of Figure 1, we detected all four methyl absorptions (◁) at −20, −60, −105, and −135 Hz upfield from Me_4Si (60 MHz). Intensities were close to a molar ratio 1:2:1 for (**8** + **13**):(**10** + **11**):(**9** + **12**). Signal coalescences yielded $\Delta G^{\ddagger} = 17.7$ kcal/mol (380 K in tetralin), corresponding to easier tolyl rotation in **5** than in **4**.

Whereas chiral tetrahedral complexes are known of transition metals with four different ligands[12] and with bidentate ligands,[13,14] compounds **1a** and **2-5** appear to be the first clear-cut examples of the paramagnetic, open-shell type.[8,10,14,15] Chirality is normally not preserved even with similar ligands.[8-10,14] The nickel in an O_2N_2-tetrahedron could only be forced into stable chirality by a nonracemizing ligand cage[8] or by the bulky adamantyl substituent.[17] It is, however, quite possible that more examples of chirality went unrecognized.[18-22]

The old explanation of signal splitting by some conformational preference of the *N*-aryl substituents (but rapid nickel inversion) is vitiated by the NCH_3 groups of **3** and also incompatible with **1a**, **2**, **4**, and **5**. Such conformations should relax after one nickel inversion to produce the enantiomer and hence coalescence. Furthermore, *N*-phenyl rotation in **5** is quite fast with $\Delta G^{\ddagger} = 13.1$ kcal/mol (253 K).

We intend to report on additional chiral complexes, on the reasons for their rigidity, and on the mechanism of inversion in due course.

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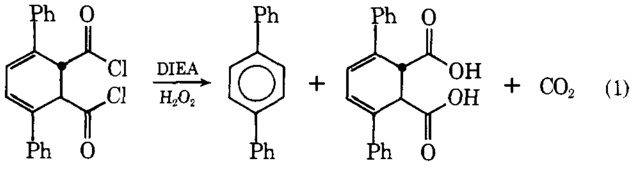
New Chemiluminescent Reaction Systems. Light Formation from the Reaction of a Vicinal Diacid Chloride

Sir:

We wish to report the observation of a new, remarkably efficient, chemiluminescent processes.[1] It was found that 3,6-diphenyl-3,5-cyclohexadiene-1,2-*trans*-dicarboxylic acid chloride (**1**) reacts with diisopropylethylamine (DIEA) and hydrogen peroxide in THF to produce an easily detected emission of light from the singlet state (^1L_A) of *p*-terphenyl (**2**).[2-4] This reaction represents one of the most energetic organic chemiluminescent systems and one of the first examples



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