Ketones and exocyclic methylene groups are functional groups differing in type from those already considered. Double bonds prefer 0° and not 60° torsional angles to adjacent single bonds.[13] During *exo* attack on 2-norbornanones and 2-methylenenorbornanes, the dihedral angle between the C_2 exocyclic double bond and the C_1 bridgehead bond increases, which would be unfavorable except for the fact that during this process the double bond is becoming single. In this kind of situation torsional effects are in opposite directions and would tend to cancel. Processes involving the formation of exocyclic double bonds or the reverse should therefore be controlled stereochemically by nonbonded steric effects (Table I). It is probably for this reason that *exo*/*endo* ratios in reactions of this type in norbornane derivatives typically are low: ketal exchange (16);[19] ketone reductions by $NaBH_4$ (6.2,[20] 5)[21] and $LiAlH_4$(10)[21]; chromic acid alcohol oxidations (*exo*-H/*endo*-H = 2.5,[22] 6.5[23]). Reactions such as these should *not* be good models for the behavior of classical carbonium ions because of the expected difference in response toward torsional effects.

Still needed is quantitative evaluation of the importance of torsional, steric, and bridging effects in the various reactions involving norbornyl derivatives. However, it already seems likely that torsional effects are of appreciable magnitude.[24] The extent to which torsional effects (in conjunction with nonbonded interactions)[18] are involved in 2-norbornyl carbonium ion reactions reduces the need to ascribe observed behavior, such as high *exo*/*endo* rate ratios or the propensity toward *exo* attack, to bridging.[8,12a,18]

Acknowledgments. Exchanges of information and stimulating conversations with Professor H. C. Brown are gratefully acknowledged. This work was supported by grants from the National Science Foundation and the Petroleum Research Fund, administered by the American Chemical Society.

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(24) Recent oxymercuration results of Professor H. C. Brown, soon to be published, provide dramatic confirmation.

Paul von Rague Schleyer
Department of Chemistry, Princeton University
Princeton, New Jersey 08540

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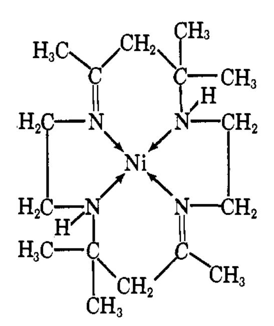
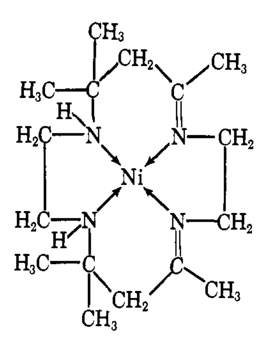
Stereochemistry of a Macrocyclic Complex. Chelate Ring Conformations and Unusual Isomers[1]

Sir:

In addition to the obvious position isomers (structures I and II) of the ligand in the planar nickel(II) complexes,[2] hexamethyl-1,4,8,11-tetraazacyclotetradecadienenickel(II), $Ni(CT)^{2+}$, more subtle forms of isomerism are possible. We report here two additional kinds of isomerism, one arising from the asymmetry of coordinated secondary amines, and the other

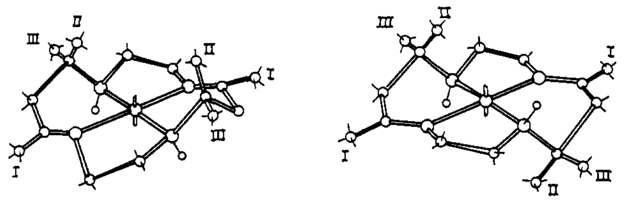

I
$Ni(1,7\text{-}CT)^{2+}$


II
$Ni(1,4\text{-}CT)^{2+}$

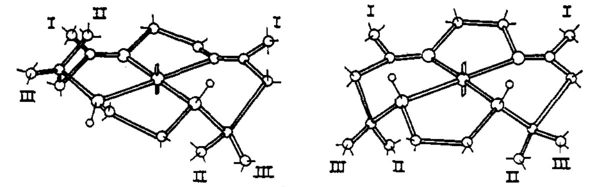
exemplifying the rare phenomenon of "coordination-number" isomerism. Studies on the pmr and visible spectra and other physical properties of these compounds have yielded detailed information on chelate ring conformations and conformational stability.

Curtis, Curtis, and Powell[3] have claimed that unpublished X-ray studies show that the $Ni(1,4\text{-}CT)^{2+}$ forms the least soluble isomer perchlorate. Our pmr studies confirm this conclusion. Further, Curtis reports that the $Ni(1,7\text{-}CT)^{2+}$ is separable into isomers of unspecified structures. Working with the fluoroborate and thiocyanate derivatives of $Ni(CT)^{2+}$, we had independently discovered the isomers[4] of $Ni(1,7\text{-}CT)^{2+}$ and can assign complete structures to them.

Figure 1 represents the structures of the four expected isomers of planar complexes containing either 1,4- or 1,7-CT. The optical activity of the two amine groups should yield a racemic isomer and a *meso* isomer in each case. Two distinct materials are readily obtained from $Ni(1,7\text{-}CT)(NCS)_2$, these being diamagnetic and appearing orange and yellow in color. The orange isomer can be resolved into enantiomers (Table I), thereby establishing it as the racemate. Best resolutions were obtained chromatographically using Fisher potato starch. All attempts to resolve the *meso* complex failed. In addition to serving as a structure



(a) $Ni(racemic\text{-}1,7\text{-}CT)^{2+}$ (b) $Ni(meso\text{-}1,7\text{-}CT)^{2+}$



(c) $Ni(racemic\text{-}1,4\text{-}CT)^{2+}$ (d) $Ni(meso\text{-}1,4\text{-}CT)^{2+}$

Figure 1. Idealized structures of the stereoisomers of $Ni(CT)^{2+}$.

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[1] Supported in part by U. S. Public Health Services Grant GM 10040 from the National Institute of General Medical Sciences.

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Table I. Partial Resolution[a] of Ni(*rac*-1,7-CT)(NCS)$_2$

Fraction	α_{obsd}, deg[b,c]	Concn, g/ml × 10^4 [d]	$[\alpha]_{546}$, deg[e]
1	+0.264	9.95	+133
2	+0.559	20.4	+137
3	+0.745	32.9	+113
5	+0.139	34.6	+ 20
7	−0.210	25.7	− 41
10	−0.102	5.9	− 87
13	−0.052	3.1	− 83
14	−0.069	3.8	− 90

[a] This resolution was achieved chromatographically using a column packed with potato starch and 0.01 *N* HCl as the eluent. [b] Readings taken with a Rudolph Model 80 polarimeter using a 2-dm tube. [c] Standard deviation of values ±0.008°. [d] Determined spectrophotometrically. [e] Uncertainty ~±5°.

proof, the resolution of *dl*-Ni(1,7-CT)(NCS)$_2$ is significant as a novel example of optical activity due to the nitrogens of coordinated secondary amines.[5]

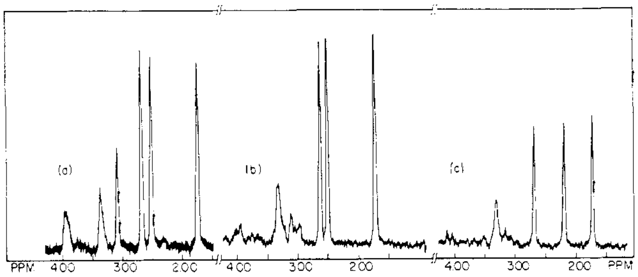

Figure 2. Pmr spectra of Ni(CT)(NCS)$_2$ isomers: (a) Ni(1,4-CT)(NCS)$_2$ in neutral D$_2$O; (b) Ni(*rac*-1,7-CT)(NCS)$_2$ in acidic D$_2$O; (c) Ni(*meso*-1,7-CT)(NCS)$_2$ in acidic D$_2$O. Spectra calibrated in ppm downfield from external TMS.

Both pmr and visible spectra demonstrate that both pure Ni(*meso*-1,7-CT)$^{2+}$ and pure Ni(*rac*-1,7-CT)$^{2+}$ convert to the same equilibrium mixture of isomers in neutral aqueous solution or in acetone. However, if the solutions are distinctly acidic, the isomerization process is stopped. This is consistent with the long known pH dependence of hydrogen-exchange reactions involving coordinated amine groups.[6]

When separated from chloroform, Ni(*meso*-1,7-CT)(NCS)$_2$ crystallizes with coordinated thiocyanates. Its spectrum and magnetic moment (3.2 BM) are typical of pseudo-octahedral nickel(II).[7] It is apparent (Figure 1) that the two extraplanar coordination sites are equivalent in the Ni(*meso*-1,7-CT)$^{2+}$, but not in the *rac*-1,7-CT complex. The paramagnetic violet isomer is unstable and readily converts into the yellow diamagnetic form.

It is instructive to consider the only known (diamagnetic) isomer of Ni(1,4-CT)$^{2+}$ along with the Ni(1,7-CT)$^{2+}$ isomers. Three equally intense methyl resonances are most prominent in the pmr spectra (Figure 2) of all isomers: for NCS$^-$ salts, Ni(*rac*-1,7-CT)$^{2+}$, 2.67, 2.52, and 1.75 ppm; Ni(*meso*-1,7-CT)$^{2+}$, at 2.69, 2.21, and 1.75 ppm; and Ni(1,4-CT)$^{2+}$, 2.70, 2.54, and 1.75 ppm. Three resonances require the six methyl groups to be pairwise equivalent, a result easily accommodated if the two six-membered chelate rings with a given isomer have identical conformations and if the secondary amines are configurationally stable toward inversion. This produces an axial *vs.* equatorial distinction between the *gem*-methyl groups.

Under conditions for rapid proton exchange (basic D$_2$O), the pmr spectra show that rapid flexing of the chelate rings occurs for both position isomers. At 35° the *gem*-methyl proton resonances of Ni(1,4-CT)$^{2+}$ are merely broadened, but the bands collapse into a single resonance at 100°.

The imine methyl and the methylene protons of the six-membered chelate ring are readily identified by deuteration experiments. The proximity of these protons to the imine function[8,9] causes them to exchange for deuterium in basic D$_2$O.

The remainder of each pmr spectrum is assignable to the dimethylenic protons. This region provides a convenient and trustworthy method for distinguishing between the position isomers in this and similar systems. For Ni(1,4-CT)$^{2+}$ the two dimethylene chains are different, but each has its two extremities identical. As a result, the most complex pattern expected would be two A$_2$B$_2$ patterns.[10,11] In the limit of slight distinction between the axial and equatorial hydrogens, the patterns would merely produce two distinct peaks, each of intensity 4. Figure 2 shows this to be the case: amine dimethylene, line at 3.11 ppm; imine dimethylene, A$_2$B$_2$ pattern at 3.92 ppm. In contrast, the two dimethylene chains are alike in either Ni(1,7-CT)$^{2+}$ isomer, but the two ends of each chain are different. Conformational effects then cause each of the four protons to be distinct. This produces a complicated unsymmetrical ABCD pattern (Figure 2).

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Larry G. Warner, Norman J. Rose,[12] Daryle H. Busch
Department of Chemistry, The Ohio State University
Columbus, Ohio 43210

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Reaction of Diazomethane with Silyl Ketones

Sir:

The reaction of diazomethane with ketones to give homologous ketones or epoxides is well documented.[1] It appeared of interest to investigate how the spectrally

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