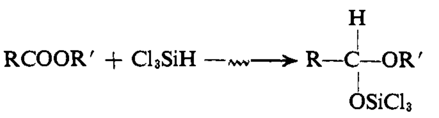
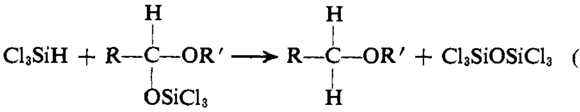
values (plotted in Figure 1) suggest the possible existence of an intermediate.

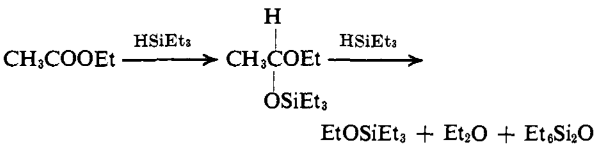
Analogy with the reaction of trichlorosilane with ketone suggests that the first step of the present reduction may be written as in eq 1. Although the intermediate could not be isolated, it is considered to react further with another molecule of trichlorosilane (eq 2). The reduction[3] of ethyl acetate with triethylsilane catalyzed by nickel chloride treated with triethylsilane proceeds as in eq 3. In this sequence, hexaethyldisiloxane corresponds to hexachlorodisiloxane in our reaction, but the yield of diethyl ether is much lower than ours, because of the side reaction producing triethylethoxysilane. In the present study, hexachlorodisiloxane expected in eq 2 was separated by distillation (8.3 g) from an irradiated (6.1 MR at 0.125 MR/hr) mixture of 70.4 g of ethyl acetate and 239 g of trichlorosilane (1:2.2 molar ratio) and identified by glpc after it was converted to hexamethoxydisiloxane.[4] The authentic hexamethoxydisiloxane was prepared *via* hexachlorodisiloxane, which was synthesized by partial hydrolysis of tetrachlorosilane.[5] Besides hexachlorodisiloxane, distillation of the irradiated mixture yielded tetrachlorosilane, 43 g (bp 58°, lit.[6] bp 58°), octachlorotrisiloxane, $Cl_3SiOSiCl_2OSiCl_3$, 5.6 g (bp 75–77° (15 mm), lit.[5] bp 76° (15 mm)), and higher boiling fraction, 91.5 g, which was considered a mixture of higher siloxanes. Since Chambers and Wilkins[6] reported that hexachlorodisiloxane was decomposed to a mixture of higher chlorosiloxanes and tetrachlorosilane by heat, hexachlorodisiloxane produced in eq 2 might be rearranged also by γ irradiation.



$$\mathrm{RCOOR' + Cl_3SiH \rightsquigarrow R{-}\overset{H}{\underset{OSiCl_3}{C}}{-}OR'} \qquad (1)$$

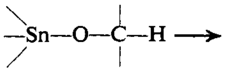


$$\mathrm{Cl_3SiH + R{-}\overset{H}{\underset{OSiCl_3}{C}}{-}OR' \longrightarrow R{-}\overset{H}{\underset{H}{C}}{-}OR' + Cl_3SiOSiCl_3} \qquad (2)$$

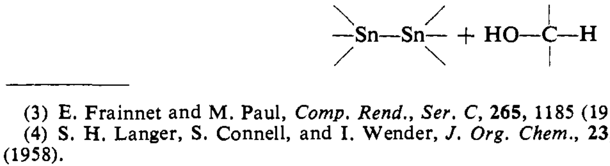


$$\mathrm{CH_3COOEt \xrightarrow{HSiEt_3} CH_3\overset{H}{\underset{OSiEt_3}{C}}OEt \xrightarrow{HSiEt_3} EtOSiEt_3 + Et_2O + Et_6Si_2O} \qquad (3)$$

Kuivila[7] proposed a free-radical mechanism for the addition of organotin hydride to carbonyl group, and proposed the sequence in eq 4 and 5 for the over-all reduction of carbonyl group to alcohol. In the present study eq 1 seems to proceed by a radical mechanism, because uv irradiation of a mixture of ethyl acetate and trichlorosilane confirms the formation of diethyl ether, although qualitatively.[8] The comparatively high *G* value of 435 which was calculated from the run for 24-hr irradiation under 0.15 MR/hr in Figure 1 suggests a radical-chain mechanism for eq 1. As mentioned above, RCOOR′, either R or R′ aryl, was not reduced by this method. The probable reason may consist in eq 1 not applying for esters of this type similarly to the case for ketone.[2] Our experiments also confirm that acetophenone and benzophenone were recovered almost quantitatively after γ irradiation (9.6 MR) of the mixture with trichlorosilane (1:6 molar ratio). The reason that when either R or R′ was a benzyl group the reduction does not occur is obscure at present. Equation 2 seems to proceed without γ irradiation. Because of the affinity of Si for an O atom, disiloxane is formed instead of catenated compound as in the case of tin hydride.



$$\mathrm{{-}\overset{\diagdown}{\underset{\diagup}{Sn}}H + \overset{\diagdown}{\underset{\diagup}{}}C{=}O \longrightarrow {-}\overset{\diagdown}{\underset{\diagup}{Sn}}{-}O{-}\overset{|}{\underset{|}{C}}{-}H} \qquad (4)$$



$$\mathrm{{-}\overset{\diagdown}{\underset{\diagup}{Sn}}H + {-}\overset{\diagdown}{\underset{\diagup}{Sn}}{-}O{-}\overset{|}{\underset{|}{C}}{-}H \longrightarrow {-}\overset{\diagdown}{\underset{\diagup}{Sn}}{-}\overset{\diagup}{\underset{\diagdown}{Sn}}{-} + HO{-}\overset{|}{\underset{|}{C}}{-}H} \qquad (5)$$

---

[3] E. Frainnet and M. Paul, *Comp. Rend., Ser. C*, **265**, 1185 (1967).

[4] S. H. Langer, S. Connell, and I. Wender, *J. Org. Chem.*, **23**, 50 (1958).

[5] W C. Schumb and A. J. Stevens, *J. Amer. Chem. Soc.*, **72**, 3178 (1950).

[6] D. W. S. Chambers and C. J. Wilkins, *J. Chem. Soc.*, 5088 (1960).

[7] H. G. Kuivila, *Advan. Organometal. Chem.*, **1**, 70 (1964).

(8) Mechanistic study by uv irradiation is now carrying out at our laboratory.

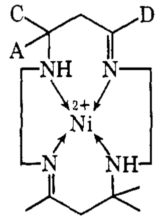
Jitsuo Tsurugi, Ren Nakao, Tsugio Fukumoto
Radiation Center of Osaka Prefecture
Shinke-cho, Sakai, Osaka, Japan

Received June 2, 1969

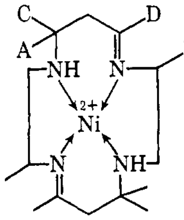
Isomerism of Some Octamethyl-1,5,8,12-tetraazacyclotetradecadiene Complexes of Nickel(II) and Copper(II)

Sir:

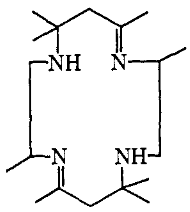
Tris[(±)-1,2-diaminopropane)]nickel(II) perchlorate reacts with acetone to form two noninterconvertible isomeric octamethyl-1,5,8,12-tetraazacyclotetradecadienenickel(II) complexes.[1] The site of the isomerism was unknown, three possibilities being (i) the positions of the imino groups *cis* (1,11) or *trans* (1,8) with respect to the nickel ion, as observed for the hexamethyl analogs, *trans*, I, and *cis*, similarly formed with diaminoethane;[2] (ii) racemic or *meso* modifications associated with the two asymmetric carbon centers of the diaminopropane residues (any isomers associated



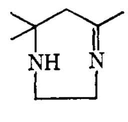
I



II



III



IV

---

[1] M. M. Blight and N. F. Curtis, *J. Chem. Soc.*, 1204 (1962).

[2] N. F. Curtis, Y. M. Curtis, and H. K. J. Powell, *ibid.*, *A*, 1015 (1966); M. F. Bailey and I. E. Maxwell, *Chem. Commun.*, 908 (1966); R. R. Ryan, B. T. Kilbourn, and J. D. Dunitz, *ibid.*, 910 (1966).

with the two asymmetric nitrogen centers should be interconvertible, as observed for I[2,3]); and (iii) isomerism associated with the position of the methyl groups of the diaminopropane residues, which could be *cis* or *trans* with respect to the nickel ion and/or adjacent to amino or imino groups.

A full X-ray structural investigation of the "yellow" isomer[1] as the perchlorate[4] has revealed the molecular structure II, with *trans* (1,8) imino groups, with both the asymmetric carbon and nitrogen centers racemic, with the adjacent C–H and N–H of the asymmetric centers on opposite sides of the molecular plane, and with the methyl groups of the diaminopropane residues in "axial" (2,9) positions adjacent to the imino groups.

The space group of the "orange" isomer[1] perchlorate, requires the nickel ion to be on a center of symmetry; *i.e.*, both the asymmetric carbon and nitrogen centers must be *meso*, the imino groups *trans* (7,14), and the diaminopropane residue methyl groups *trans* in 2,9 or 3,10 positions. Since the two isomeric products are formed in approximately equal amounts when tris(diaminopropane)nickel(II) reacts with acetone, it is reasonable to conclude that they are the C-*rac* and C-*meso* isomers of II. Two configurations are possible, with the hydrogen atoms of the adjacent asymmetric carbon and nitrogen centers on the same, or opposite, sides of the "molecular plane."

Confirmation of these structural assignments is provided by pmr spectra. The pmr spectra of the "orange" and "yellow" isomers (Table I) closely resemble those of the N-*meso* and N-*rac* isomers of I,[3] with in each case an additional doublet assigned to equivalent diaminopropane residue methyl groups. For the "yellow" C-*rac* isomer this methyl group is in an axial site, insofar as this terminology is appropriate to the imine end of the diaminoethane chelate ring. Deshielding by the nickel(II)[3] ion is less than for the axial geminal methyl group, and is obviously dependent on details of conformation. The similar σ value observed for the "orange" C-*meso* isomer supports assignment of these methyl groups to axial sites for this compound also.

Table I. Pmr Spectra, Methyl Group Resonances[a]

	A^b	B^c	C^d	D^e
"Orange" isomer[f]	1.22	1.29, 1.40	2.68	2.25
N-*meso*-I[g]	1.25	...	2.71	2.19
"Yellow" isomer[f]	1.18	1.48, 1.59	2.13	2.20
N-*rac*-I[g]	1.25	...	2.02	2.17

[a] Measured in acidified D_2O using a Varian HR60 spectrometer and with NaTPS as internal standard, σ values in ppm. [b] Equatorial component of *gem*-dimethyl group. [c] Diaminopropane residue methyl group. [d] Axial component of *gem*-dimethyl group. [e] Imine methyl group. [f] As tetrachlorozincate. [g] As thiocyanate. Values from ref 3 relative to an external TMS standard have been adjusted (−0.5 ppm) for convenience in comparison.

Reaction of tris[(+)-1,2-diaminopropane)]nickel(II) perchlorate or tris[(−)-1,2-diaminopropane)]nickel(II) perchlorate with acetone yields the enantiomorphs of the "yellow" racemate (product from (+)-1,2-diaminopropane, α_D +151°; product from (−)-1,2-diaminopropane, α_D −150.6°)

The monohydroperchlorate of (±)-1,2-diaminopropane reacts with acetone, diacetone alcohol, or mesityl oxide to form crystalline $\mathrm{III\cdot 2HClO_4}$[5] analogous to the compound formed with diaminoethane.[6] This product reacts with nickel(II) to form C-*meso*-II, and therefore III is assigned the C-*meso* configuration. Failure to isolate any C-*rac* isomer apparently results from a higher solubility of the C-*rac* salt, (−)-1,2-diaminopropane hydroperchlorate yielding no crystalline product under these conditions. The formation of C-*meso*-II from $\mathrm{III\cdot 2HClO_4}$ confirms the tetraazacyclotetrodecadiene structure for III, rather than the possible dihydrodiazapene IV, which would be expected to form a mixture of C-*meso*- and C-*rac*-II.[7]

Reaction of bis(diaminopropane)copper(II) perchlorate with acetone at 110° is reported[8] to form a macrocyclic copper(II) complex analogous to II, in low yield. At room temperature tris(diaminopropane)copper(II) perchlorate reacts slowly with acetone to form this compound and an isomeric product. The previously reported compound is also formed from $\mathrm{III\cdot 2HClO_4}$ and is therefore assigned the C-*meso* configuration. The new compound crystallizes with cell dimensions similar to C-*rac*-$\mathrm{II\cdot 2ClO_4}$, supporting assignment as the C-*rac* isomer.

Crystal Data. C-*rac*-(2,4,4,7,9,11,11,14-Octamethyl-1,5,8,12-tetraazacyclotetradeca-1,8-diene)nickel(II) perchlorate[9] ("yellow" isomer): monoclinic, $P2_1/c$, a = 16.55, b = 10.90, c = 15.10 Å; β = 90° 55′; for Z = 4, D_c = 1.42; D_m = 1.45 g cm^{-3}.

C-*meso*-(2,4,4,7,9,11,11,14-Octamethyl-1,5,8,12-tetraazacyclotetradeca-1,8-diene)nickel(II) perchlorate ("orange" isomer): monoclinic, $P2_1/c$; a = 10.13, b = 8.37, c = 14.38 Å; β = 100° 5′; for Z = 2, D_c = 1.56; D_m = 1.52 g cm^{-3}.

C-*rac*-(2,4,4,7,9,11,11,14-Octamethyl-1,5,8,12,tetraazacyclotetradeca-1,8-diene)copper(II) perchlorate: orthorhombic, Pbcm or $Pbc2_1$; a = 15.80, b = 15.28, c = 10.41 Å; for Z = 4, D_c = 1.47; D_m = 1.50 g cm^{-3}.

---

(3) L. G. Warner, N. J. Rose, and D. H. Busch, *J. Amer. Chem. Soc.*, **89**, 703 (1967); 90, 6938 (1968).

(4) Approximately 2600 independent reflections; current R index of 0.15.

(5) *Anal.* Calcd for $C_{18}H_{36}Cl_2N_4O_8$: C, 42.7; H, 7.2. Found: C, 42.3; H, 7.4.

(6) N. F. Curtis and R. W. Hay, *Chem. Commun.*, 524 (1966).

(7) Further support has been presented elsewhere: N. F. Curtis, *Coord. Chem. Rev.*, 3, 21 (1968).

(8) M. M. Blight and N. F. Curtis, *J. Chem. Soc.*, 3016 (1962).

(9) Since the original preparation,[1] a hydrate has nucleated, and the anhydrous salt no longer crystallizes. Failure to notice this change resulted in some incorrect deductions about the structures of these compounds (ref 7, p 10).

N. F. Curtis
Chemistry Department, Victoria University
Wellington, New Zealand

D. A. Swann and T. N. Waters
Chemistry Department, University of Auckland
Auckland, New Zealand

I. E. Maxwell
Chemistry Division, Scientific & Industrial Research Department
Wellington, New Zealand

Received May 3, 1969

Measurement of Optical Activity in Racemic Mixtures

Sir:

Chiral molecules absorb left and right circularly polarized light to a different extent. A measure for this effect is the dissymmetry factor g.