COOH
|
(CH₂)₁₀
|
H—C—OH
|
(CH₂)₆
|
CH₃

D-12-hydroxy
stearic acid

$\xrightarrow[H_2SO_4]{CH_3OH}$

COOCH₃
|
(CH₂)₁₀
|
H—C—OH
|
(CH₂)₆
|
CH₃

$\xrightarrow{\quad H_3C-\!\!\langle\quad\rangle\!\!-SO_2Cl \atop \text{in pyridine}}$

COOCH₃
|
(CH₂)₁₀
|
H—C—O—SO₂—⟨ ⟩—CH₃
|
(CH₂)₆
|
CH₃

$\xrightarrow[\text{in }\{\text{acetic acid} + \atop \text{acetic anhydrous}\}]{CH_3COONa}$

COOCH₃
|
(CH₂)₁₀
|
CH₃COO—C—H
|
(CH₂)₆
|
CH₃

$\xrightarrow[\text{in ethanol}]{KOH}$

COOH
|
(CH₂)₁₀
|
HO—C—H
|
(CH₂)₆
|
CH₃

L-12-hydroxy-
stearic acid
$[\alpha]^{15}D +0.40 \pm 0.05°$
(pyridine)

Figure 2. Preparation of L-12-hydroxystearic acid by Walden inversion.

form were used without sufficient purification, this did not affect the result.

As is well known, single crystals of optically active antipodes exhibit the phenomenon of enantiomorphism. It is interesting to note that the enantiomorphism has been found to occur in the crystalline aggregate when the optical isomer aggregates to possess helical symmetry.

Acknowledgment. Sincere thanks of the authors are due to the Central Technical Research Laboratory of Nippon Oil Co. for providing the necessary facilities.

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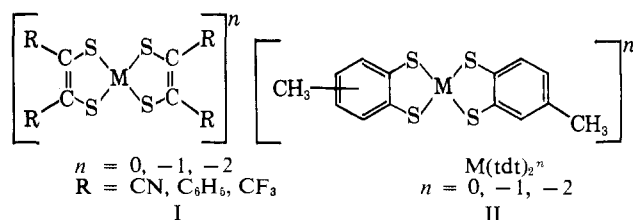*Bunkyoku, Tokyo*
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The Myth of Nickel(III) and Nickel(IV) in Planar Complexes[1]

Sir:

Recent work[2] has firmly established the existence of planar metal complexes of general formulas I and II in which one of the significant features is the stability of the electronically unusual systems with $n = 0, -1$. Although the $n = -2$ complexes can be successfully formulated in the usual fashion as containing dianionic ligands and divalent metal ions, the $n = -1, 0$ complexes show chemical and physical properties inconsistent with the classical M(III) ($n = -1$) and M(IV)
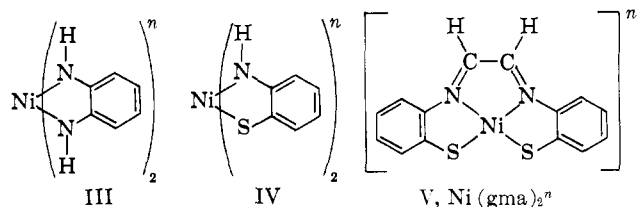
(1) Acknowledgment is made to the National Science Foundation for support of this research.
(2) S. I. Shupack, E. Billig, R. J. H. Clark, R. Williams, and H. B. Gray, *J. Am. Chem. Soc.*, **86**, 4594 (1964), and references contained therein.

$\left[\begin{array}{c} R-C-S\quad S-C-R \\ \|\quad M\quad\| \\ R-C-S\quad S-C-R \end{array}\right]^n$

$n = 0, -1, -2$
$R = CN, C_6H_5, CF_3$

I

$\left[CH_3-\langle\rangle\begin{array}{c}S\quad S\\M\\S\quad S\end{array}\langle\rangle-CH_3\right]^n$

M(tdt)₂ⁿ
$n = 0, -1, -2$

II

($n = 0$) formulations. In fact, evidence indicates that these complexes are more acceptably assigned as "metal-stabilized radical-ligand" systems.[2]

Our interest in the two possible formulations for these systems has led us to investigate the electronic structures of complexes containing nitrogen as well as sulfur as donor atom; certain of these complexes have been cited as authentic examples of Ni(IV).[3] In this communication, we report results on nickel complexes in series II, III, IV, and V.

$Ni\left(\begin{array}{c}/H\\N\\\langle\rangle\\N\\H\end{array}\right)_2^n$
III

$Ni\left(\begin{array}{c}/H\\N\\\langle\rangle\\S\end{array}\right)_2^n$
IV

$\left[\begin{array}{c}H\quad H\\C=C\\N\quad N\\ \langle\rangle Ni \langle\rangle\\S\quad S\end{array}\right]^n$
V, Ni(gma)₂ⁿ

The $n = -1$ member of series II is reduced by BH_4^- to $n = -2$ and oxidized by iodine to $n = 0$. Both the neutral complex Ni(tdt)₂ and $[(n\text{-}C_4H_9)_4N]_2[Ni(tdt)_2]^4$ have been characterized. This demonstrates that electron-transfer reactions occur readily in series II, as they do in series I.

The $n = 0$ III complex was originally claimed by Feigl and Fürth,[5] but doubt has since been expressed[6] concerning the number of hydrogens attached to nitrogens. Our analytical and molecular weight results, including a mass spectrum with parent peak at m/e 270, on a sample prepared by the published method[5] agree with the original formulation III ($n = 0$). The $n = 0$ complex undergoes two reversible one-electron reductions to give the $n = -1$ and -2 complexes.

Complex IV ($n = 0$) was prepared by a published method.[7] Analytical and molecular weight data, including a mass spectrum with parent peak at m/e 304, establish formula IV ($n = 0$) and are inconsistent with the original formulation as a binuclear oxygen-bridged Ni(IV) complex. Complex IV ($n = 0$) shows two reversible reduction waves, indicating the existence of the $n = -1$ and -2 complexes. Complex IV ($n = -1$), prepared by BH_4^- reduction of IV ($n = 0$), shows an e.s.r. spectrum with $\langle g \rangle = 2.055$ (DMF, DMSO, THF). The behavior of systems III and IV suggests that the electron-transfer reactions common to the sulfur systems may be a more general phenomenon.

Complexes of Zn(II) and Cd(II) with glyoxal bis-(2-mercaptoanil) (gma) have been prepared recently.[8]

(3) See, for example, F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Division, John Wiley and Sons, Inc., New York, N. Y., 1962, pp. 744, 745.
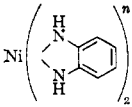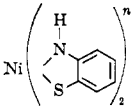(4) R. Williams, unpublished results.
(5) F. Feigl and M. Fürth, *Monatsh.*, **48**, 445 (1927).
(6) Z. Bardoděj, *Collection Czech. Chem. Commun.*, **20**, 176 (1955), prefers two less hydrogens on the nitrogens and formulates this as a nickel(II) species with oxidized ligands.
(7) W. Hieber and R. Bruck, *Z. anorg. allgem. Chem.*, **269**, 13 (1952).
(8) H. Jadamus, Q. Fernando, and H. Freiser, *J. Am. Chem. Soc.*, **86**, 3056 (1964).

Table I. Polarographic and Electron Spin Resonance Results

Complex	$E_{1/2}{}^a$ for $n = 0 \to n = -1$	$n = -1 \to n = -2$	g values^c for $n = -1$ $\langle g \rangle$	g_1	g_2	g_3
Ni(tdt)$_2{}^n$	b	-1.068^d	2.082	2.016	2.048	2.183
Ni(mnt)$_2{}^n$	b	-0.218^d	2.063	1.996^e	2.043^e	2.140^e
Ni(NH/NH-benzene)$_2{}^n$	-1.404	-2.075	2.034^f	b	b	b
Ni(NH/S-benzene)$_2{}^n$	-0.720	-1.573	2.055	2.006	2.030	2.123
Ni(gma)^n	-0.823	-1.605	2.051	2.009	2.027	2.119

^{a} Potentials in volts measured in DMF using a dropping Hg electrode with a Ag–AgClO$_4$ reference electrode. Oscillopolarography was used to establish that all waves are due to reversible electron transfers. We thank R. Williams, B. Werden, and M. J. Baker for assistance. ^{b} Accurate value not available. ^{c} $\langle g \rangle$ normally obtained in several solvents; g_1, g_2, and g_3 obtained from DMF–CHCl$_3$ glass at 77°K. unless otherwise noted. ^{d} From ref. 4. ^{e} A. Davison, N. Edelstein, R. H. Holm, and A. H. Maki, *J. Am. Chem. Soc.*, **85**, 2029 (1963); glass at 100°K. ^{f} Obtained in DMSO only.

Using precisely the same synthetic procedure, we have prepared the Ni(II) complex, Ni(gma) = V ($n = 0$). The Ni(gma) complex shows two polarographic reduction waves, indicating the existence of Ni(gma)$^-$ and Ni(gma)$^{2-}$.

The polarographic and e.s.r. data pertinent to this discussion are set out in Table I. The important point is the obvious electronic similarity of complexes IV ($n = -1$) and Ni(gma)$^-$. Their polarography, $\langle g \rangle$ values, and anisotropic g-values are almost identical. The lack of axial symmetry in the g-tensor rules against the d^9 Ni(I) formulation[9] for Ni(gma)$^-$, and the electronic similarity of IV ($n = -1$) with Ni(gma)$^-$, rules out the d^7, Ni(III) formulation for IV ($n = -1$). The $n = -1$ complexes are both consistently formulated as Ni(II)–radical-ligand complexes. In this scheme, the $n = 0$ complexes are assigned as Ni(II)–radical-ligand complexes with both spin-singlet and spin-triplet ground states as possibilities in a molecular orbital system for the planar geometry. The difference in the three possible members of each series I–V is then understood as a change in oxidation state of the ligand.

Examination of anisotropic g-values for Ni(mnt)$_2{}^-$ and Ni(tdt)$_2{}^-$, obtained on oxidation of the classical Ni(II) complexes Ni(mnt)$_2{}^{2-}$ and Ni(tdt)$_2{}^{2-}$, reveals that these complexes are electronically similar to IV ($n = -1$) and Ni(gma)$^-$. Thus again the Ni(II)–radical-ligand formulation is applicable.

We wish to emphasize that although Ni(II)–radical-ligand is a more consistent formalism than Ni(II), Ni(III), or Ni(IV) for this series of related complexes, it is in no way a substitute for a complete molecular orbital description of electronic structure. The detailed MO calculations of the Ni(mnt)$_2{}^n$ system are fully consistent with the Ni(II)–radical-ligand formulation for the $n = -1$ and 0 complexes.[2]

The present results are inconsistent with the conclusion of Maki, Edelstein, Davison, and Holm[10] that Ni(mnt)$_2{}^-$ is correctly d^7, Ni(III). Their conclusion was based on an analysis of single crystal e.s.r. results,

using a basis set of pure 3d-functions. It seems clear, however, that not only are the highest-filled levels in these systems *not* pure d-levels, they *are* in fact much closer to pure ligand levels. These e.s.r. spectra[10] must be reinterpreted in terms of a complete molecular orbital basis set.

(11) Alfred P. Sloan Research Fellow.

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Crystalline 1,2-Polyallene

Sir:

Allene has been polymerized by Ziegler-type catalysts containing VOCl$_3$ and other metals,[1] but the polymer was not of regular structure. We wish to report here a successful synthesis of 1,2-polyallene by use of transition metal π-complex catalysts.

Polymerization of Allene. Typical catalysts which control the microstructure satisfactorily are π-complexes of nickel such as bis(1,5-cyclooctadiene)nickel[2] (I), (π-C$_8$H$_{12}$)$_2$Ni; bis(π-allyl)nickel[3] (II), (π-C$_3$H$_5$)$_2$Ni; π-allylnickel bromide[4] (III), (π-C$_3$H$_5$NiBr)$_2$; bis(acrylonitrile) nickel,[5] (CH$_2$=CH CN)$_2$Ni.

Results of some polymerization runs using nickel catalysts are summarized in Table I. If one regards π-allyl ligand as a formal three-electron donor,[6] the formal oxidation state of nickel in II and III will be zero- and univalent, respectively. As shown in Table I divalent nickel complexes were inactive. Thus it appears that low valency states of nickel are important electronic structure for the catalysis.

If, however, nickel(II) acetylacetonate was reduced by 2 moles of triethylaluminum, the allene polymer

(9) Planar complexes in which d^9 is an acceptable assignment have axial or near axial symmetry: see, for example, H. R. Gersmann and J. D. Swalen, *J. Chem. Phys.*, **36**, 3221 (1962).

(10) A. H. Maki, N. Edelstein, A. Davison, and R. H. Holm, *J. Am. Chem. Soc.*, **86**, 4580 (1964).

(1) W. P. Baker, Jr., *J. Polymer Sci.*, **A1**, 655 (1963).

(2) G. Wilke, *Angew. Chem.*, **72**, 581 (1960).

(3) G. Wilke and B. Bogdanovic, *ibid.*, **73**, 756 (1961).

(4) E. O. Fischer and G. Burger, *Z. Naturforsch.*, **16b**, 77 (1961).

(5) G. N. Schrauzer, *J. Am. Chem. Soc.*, **81**, 5310 (1959); *Chem. Ber.*, **94**, 642, 650 (1961).

(6) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, Inc., New York, N. Y., 1962, p. 654.