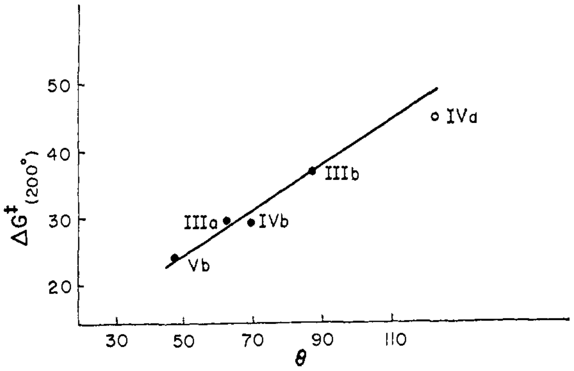

Figure 1. Plot of angle of skew (θ) *vs.* free energy of activation for ring closure ($\Delta G^{\ddagger}{}_{200°}$) of dienes. θ is defined as 0° for *s-cis* conformation. For comments on IVa, see footnote 10.

cisoid-skew rotamer F. This leads to a transition state for A $\rightleftharpoons$ B with the approximate geometry shown in G, and an estimated skew angle, θ, of ~45° from *s-cis*.[6] Accordingly, $\Delta G^{\ddagger}{}_{A \rightarrow B}$ for highly substituted dienes should reflect the attainability of G.[7]

To test this premise the ground-state molecular structure of dienes II–V have been investigated by single-crystal X-ray diffraction methods.[8] Table II lists unit-cell data and space-group constants for III–V. In all cases, an examination of the intra- and intermolecular contacts in the crystal structures leads to the conclusion that the particular configuration adopted by the butadiene backbone is a response to intramolecular interactions and is not noticeably affected by interactions with neighboring molecules in the crystal. Thus it is to be expected that the observed structures in the solid state closely resemble those found for the ground state of the molecule in solution. This assumption is strengthened by examination of the solution nmr spectra of the various isomers which may be categorized in a manner analogous to the crystallographic classification.

Table II. Unit Cell, Space Group, and Torsion Angles (θ) for the Substituted Tetraphenylbutadienes

Compd	*a*	*b*	*c*	β, deg	Space group	*Z*	θ, deg
Vb	14.34	11.68	14.08	106.0	C2/c	4	45[b]
IIIa	6.42	7.82	21.93	99.9	Pc	2	60[b]
IVb	12.14	9.47	19.61	98.0	P2₁/c	4	66 ± 3
IIIb	10.14	10.29	11.89	72.0[a]	P1	2	86 ± 4
IVa	11.03	20.24	9.74	98.9	P2₁/c	4	117 ± 4

[a] α = 96.7°, γ = 80.8°. [b] Error uncertain (probably ±7°) due to disorder.

Table II also lists θ, the angle of skew about the diene central bond. In contrast to unhindered dienes in which θ is invariably 180° (*i.e.*, *s-trans*),[9] the skew angle in III–V ranges from 45 to 120° and allo wsa decisive test of the premise that rates of diene ring closure are closely related to ground-state diene conformation. Figure 1, in which $\Delta G^{\ddagger}{}_{(200°)}$ is plotted *vs.* θ, demonstrates that such a relationship not only exists, but is reasonably quantitative.[10] Our assumption that $\Delta G^{\ddagger}$ is minimal when θ = 45° implies that $\Delta G^{\ddagger}$ will increase as θ approaches 0°. Though substantiation of this must await the availability of such a compound, we suspect that such *cis*, acyclic dienes will, as a consequence of severe steric interactions, be subject to an unusual amount of ground-state destabilization. This is not the case with dienes II–V, for which equilibration data clearly demonstrate that θ is of major influence on the transition rather than ground state.

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[6] A theoretical calculation of 40° for the optimum torsion angle (θ) has been reported by W. Th. A. M. van der Lugt and L. J. Oosterhoff, *J. Amer. Chem. Soc.*, **91**, 6042 (1969).

[7] We note that this conclusion is applicable only to those dienes with a substantial barrier to rotation about the central single bond; moderately substituted dienes which lack this barrier lack also the driving force necessary for conrotatory orbital overlap and will ineffectually pass through conformation F.

[8] Structural details and methodology will be reported independently by R. F. Bryan, Department of Chemistry, University of Virginia, Charlottesville.

[9] *Cf.* W. Haugen and M. Traetteberg, *Acta. Chem. Scand.*, **20**, 1726 (1966); A. Almenningen, O. Bastiansen, and M. Traetteberg, *ibid.*, **12**, 1221 (1958); R. A. Beaudet, *J. Amer. Chem. Soc.*, **87**, 1390 (1965); R. M. Conrad and D. A. Dows, *Spectrochem. Acta*, **21**, 1039 (1965).

[10] Compound IVa was excluded from the least-squares analysis of Figure 1 inasmuch as it represents an estimated minimum value for $\Delta G^{\ddagger}$(200°). Correlation of this point with the line predicts that cyclization of IVa will require a $\Delta G^{\ddagger}$ of ~50 kcal and is probably not attainable relative to other thermal processes. X-Ray investigation of II, currently in progress by R. F. B., will further test the validity of the relationship between $\Delta G^{\ddagger}$ and θ; Figure 1 predicts a skew angle of ~50° for II, a value not obvious from a consideration of intramolecular contacts based on space-filling models.

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Mutual Ligand–Metal Ion Oxidation State Stabilization in a System Containing a Quadridentate Macrocycle Analogous to the Porphyrin Ring

Sir:

Metal complexes of certain quadridentate macrocyclic ligands, which may serve as models for similar naturally occurring systems,[1] are expected to exhibit unusual redox behavior. Notable interdependence between ligand and metal ion in the electrochemistry of such complexes may be of particular importance in providing the basic foundations that are necessary in order to understand the more complicated native systems. Earlier work shows promise in this regard. The studies of Endicott, *et al.*,[2] show that polarographic reduction of the $[\mathrm{Cu^{II}}(trans\text{-}[14]\mathrm{diene})]^{2+}$ ion yields the Cu(I) complex of essentially unchanged coordination geometry, despite the contrary stereochemical proclivity of the product ion. Olson and Vasilevskis[3] have reported Ni(I) and Ni(III) in similar studies.

We report here the presence of unusual oxidation states together with evidence for extensive ligand–metal ion interdependence in the polarographic studies of the Co, Ni, and Cu complexes of tetrabenzo[*b,f,j,n*,]-[1,5,9,13]tetraazacyclohexadecine, structure I, hereafter called TAAB.[4] The most dramatic characteristic of

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[1] D. H. Busch, "Fasciculus Extraordinarius Alfred Werner, 1866–1919," Verlag Helvetica Chimica Acta, Basel, 1967, p 174.

[2] J. M. Palmer, E. Papaconstantinou, and J. F. Endicott, *Inorg. Chem.*, **8**, 1516 (1969).

[3] D. C. Olson and J. Vasilevskis, *ibid.*, **8**, 1611 (1969).

[4] G. A. Melson and D. H. Busch, *J. Amer. Chem. Soc.*, **86**, 4834 (1964).

Table I. Half-Wave Potentials for Polarography of the Complexes[a]

Complex	Solvent, electrolyte, electrode	$E_{1/2}^1$, V	n_1	$E_{1/2}^2$, V	n_2	$E_{1/2}^3$, V	n_3	$E_{1/2}^{b}$, V	n_b	No. of electrons added to ligand
$Cu^{II}(TAAB)^{2+}$	CH_3OH, KNO_3, DME	+0.057 (II → I)	1					−1.004 −1.138	2.5	2.5
$Ni^{II}(TAAB)^{2+}$	CH_3OH, KCl, DME	−0.432 (II → I)	1	−0.624 (I → 0)	1			−1.568	8	8
$Co^{II}(TAAB)^{2+}$	CH_3OH, Bu_4NI, DME	−0.497 (II → I)	1	−0.840 (I → 0)	1	−1.025 (0 → −I)	1	−1.300	8	8
$Cu^{I}(TAAB)^{+}$	CH_3OH, KNO_3, DME	+0.052 (I → II)	1					−0.971 −1.533	8	8
$Ni^{I}(TAAB)^{+}$ [c]	CH_3CN, Et_4NClO_4, RPE	−0.640 (I → II)	1	−0.930 (I → 0)	1					
$Ni^{II}(TAAB)^{2+}$ [c]	CH_3CN, Et_4NClO_4, RPE	−0.640 (II → I)	1	−0.930 (I → 0)	1			−2.035	1	1
$Co^{III}(TAAB)(NO_3)_2^{+}$ [d]	CH_3OH, Et_4NClO_4, RPE	−0.550 (II → I)	1	−0.887 (I → 0)	1	−1.066 (0 → −I)	1	−1.470 −1.650	8	8
$Ni^{II}(H_8TAAB)^{2+}$	CH_3OH, KCl, DME	−0.973 (II → 0)	2						0	0
$Cu^{II}[(TAAB)(OMe)_2]$[e]	CH_3OH, KCl, DME	−0.195 (II → I)	1					−1.004 −1.283 −1.500	4	4
$Ni^{II}[(TAAB)(OMe)_2]$[e]	CH_3OH, KCl, DME	−0.496 (II → I)	1					−1.543	5	4

[a] [Complex] = 5×10^{-4} *M*, 25°, $E_{1/2}$ *vs.* sce. The following complexes were investigated: (1) $Cu^{II}(TAAB)(NO_3)_2$, (2) $Ni^{II}(TAAB)Cl_2 \cdot H_2O$, (3) $Co^{II}(TAAB)Br_2 \cdot H_2O$, (4) $Cu^{I}(TAAB)PF_6$, (5) $Ni^{I}(TAAB)ClO_4$, (6) $Co^{III}(TAAB)(NO_3)_3$, (7) $Ni^{II}(H_8TAAB)Cl_2$, (8) $Cu^{II}[(TAAB)(OMe)_2]$, (9) $Ni^{II}[(TAAB)(OMe)_2]$. [b] $E_{1/2}$ of ligand reduction. [c] Reference electrode, $Ag|Ag^+$ (0.1 *M*) in acetonitrile. [d] $Co^{III} \rightarrow Co^{II}$, $E_{1/2}$ at +0.508. [e] [Complex] = 1×10^{-4} *M*.

these reductions is the existence of an electron saturation effect, which occurs when the metal ion *formally* achieves the d^{10} configuration within the TAAB complex (*i.e.*, additional stability apparently is conferred on these particular reduced ligand–metal ion species when the sum of the number of ligand π electrons plus the number of metal ion d electrons is 42). These reductions occur stepwise, as is illustrated by the polarogram of Co(II) in Figure 1, adding one electron in each successive step, until the number of electrons added, *n*, equals 10 minus the number of d electrons in the metal ion of the starting material (Table I).

At more cathodic potentials in methanol, the ligand double bonds are reduced in a broad ill-defined wave involving 2*r* electrons where *r* is the number of carbon–nitrogen double bonds. In the best behaved examples, these waves correspond very closely to expectation; however, they derive from very complicated processes and, in some instances, are so broadened that the final diffusion currents cannot be readily observed. In general, the number of equivalents of reduction has been determined by the comparison of the diffusion current with those of well-known electrode reactions as standards, and by coulometry in critical cases.

Table I presents polarographic data for a number of the complexes of TAAB and related macrocyclic ligands. Most of these data have been obtained with the dropping mercury electrode in methanol solvent. More specific indications of conditions are given in Table I and the footnotes thereto. Three of the reduction products, TAAB derivatives of formally monovalent Cu and Ni and zerovalent Ni, have been isolated and characterized as pure materials. Polarograms of these reduced compounds are essentially identical with those of their oxidized congeners except, of course, that one-electron anodic waves appear in lieu of the appropriate cathodic waves of the parent compounds. Similarly, the reduction behavior of the complex ion $Co^{III}TAAB(NO_3)_2^{+}$ corresponds closely to that of $Co^{II}TAAB^{2+}$ (compare lines 3 and 7 of Table I). The actual Co(III)–Co(II) couple is anodic with respect to the decomposition potential of mercury, but has been observed with the rotating platinum electrode, rpe, to occur at +0.508 V *vs.* sce.

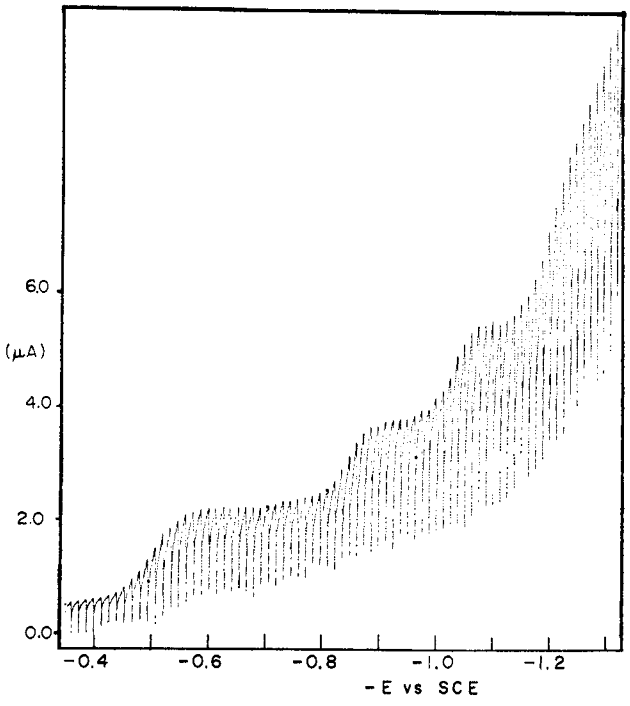
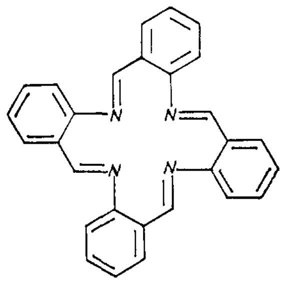
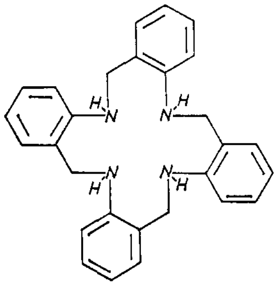


Figure 1.

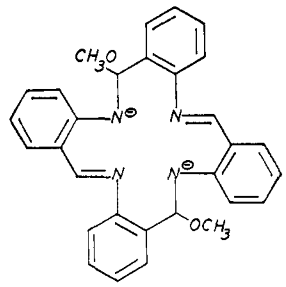
The degree of ligand unsaturation has a profound effect on the polarographic behavior observed. This is clearly shown by polarograms of the Ni(II) complexes of H_8TAAB, structure II, the fully hydrogenated de-



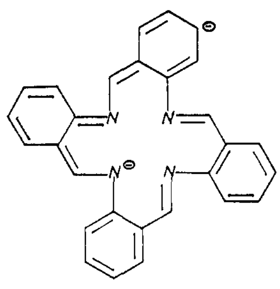
I



II



III



IV

rivative of TAAB, and TAAB(OMe)$_2$$^{2-}$, structure III, which has two azomethine linkages. The first complex gives a single two-electron wave at -0.970 V *vs.* sce, similar to waves observed for Ni(bipy)$_3$$^{2+}$.[5] No ligand reduction wave is observed in the region more negative than -1.000 V. By contrast, the first one-electron reduction wave of the methoxy derivative appears at -0.470 V *vs.* sce, very close to the first wave for Ni-TAAB^{2+}. No further reduction is observed until -1.500 V, where five electrons are transferred, enough to hydrogenate both double bonds (4) and to reduce the metal ion itself to Ni(0).

The position of the first reduction wave for a given dipositive metal ion also appears to reflect the degree of unsaturation of the ligand to which it is complexed. As the number of azomethine groups increases, the first electron addition becomes easier (more anodic). During addition of a second and third electron, when charge repulsion becomes a significant factor, the correlation of $E_{1/2}$ with degree of unsaturation is less clear. Except in the special case of complexes of TAAB itself, addition of a second electron is simultaneous with hydrogenation of the ligand. Obviously, the ligand TAAB has a special ability to stabilize the products of addition of two, three and, perhaps, even more electrons.

Ignoring changes in the ligand for the moment, the stepwise reductions lead formally to the following species, all of which have d^{10} configurations (number of electrons added is shown in parentheses): Cu$^+$ (1), Ni^0 (2), Co$^-$ (3). It is considered to be unlikely that the actual degree of oxidation of the metal ion is properly reflected by the formal oxidation state. It is known that the d^{10} configuration is unfavorable to planar coordination, and crystallographic studies[6] have confirmed earlier suggestions[4] that TAAB complexes tend toward square-planar coordination. It is more reasonable that the electrons are added to molecular orbitals that have significant ligand character. TAAB itself is an analog of the nonaromatic alternating hydrocarbon, tetrabenzo[16]annulene,[7] but the addition of two electrons would produce an analog (presumably planar) of the aromatic porphyrin dianion (one canonical form is given in structure IV). In this extreme model, the stabilized reduction products would be most simply described as d^8 ions (Cu^{3+}, Ni^{2+}, and Co$^+$) bound to the ligand dianion. The real situation must be intermediate, but the delocalization in the ligand–metal ion π orbitals must be such that charge density is decreased at the metal ion, thereby making the square-planar configuration energetically more favorable. However, electron density must remain sufficiently low at all points on the ligand to make hydrogen addition to the double bonds energetically and/or kinetically unfavorable.

These conclusions find some support in the contrasting chemical behavior of Cu(TAAB)$^{2+}$ and Ni(TAAB)$^{2+}$ when exposed to several atmospheres of hydrogen over PtO$_2$ in methanol. The copper complex is merely reduced to Cu(TAAB)$^+$, while the major product obtained from workup in the nickel(II) case is Ni(H$_8$-TAAB)$^{2+}$. The apparent combined stability of the reduced ligand–metal ion system, Cu(TAAB)$^+$, may result, then, from its energetically favored aromatic character combined with a relatively low electron density at all points on the pseudo-porphyrin ring. The unusual stabilities of the electronically saturated substrates, as well as the occurrence of multiple one-electron reduction sequences, may serve as models for the co-involvement of ligand and metal ion in important naturally occurring redox systems containing such macrocycles as the porphyrin ring.

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(6) S. W. Hawkinson and E. B. Fleischer, Winter Meeting, American Crystal Association, Tucson, Ariz., Feb 1968.

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The Reaction of Aryl and Vinyl Halides with Nickel(0) Complexes

Sir:

Recently, the importance of oxidative-addition reactions of low-valent transition metal complexes has been recognized, particularly in relationship to transition-metal catalysis.[1] Numerous examples of oxidative additions of organic halides to zerovalent d^{10} complexes of Pd and Pt affording products possessing stable carbon–metal σ bonds have been reported.[2] The corresponding reactions with nickel(0) complexes remain almost unexplored. The only example reported in which a stable carbon–metal σ bond is formed is the addition of tetrachloroethylene to (Et$_3$P)$_2$Ni(C$_2$H$_4$), affording

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