be reflected in a weaker interaction between Sn and the "axial" oxygen atoms compared to the Sn–"equatorial" oxygen atom interaction; thus the ligand is, in fact, anisobidentate[18] with two distinct Sn–O bond distances, the former being larger than the latter. Such anisobidentate bonding has been observed in bis(N,N-diethyldithiocarbamato)tin(II),[19,20] and similar bonding anisotropies have been reported for a number of other analogous stannous compounds, including tin(II) bis(benzoylacetonate)[21], Sn[SnEDTA][22] and sulfatobis(thiourea)-tin(II).[23]

Finally, it is worth noting that the thermal parameters reported by Eriks et al.[12] in their crystallographic study of SnF_2 yield a mean-square amplitude which is ~5% larger in the direction perpendicular to the axis containing the lone-pair electrons than in the parallel direction. Thus the ellipsoid of vibration is inferred to be qualitatively similar in this inorganic compound without bidentate ligands to that inferred for $Sn^{II}(acac)_2$ from the Mössbauer results and may, in fact, be a rather general property of trigonal-pyramidally bonded stannous compounds.

Registry No. $Sn^{II}(acac)_2$, 16009-86-2; ^{119}Sn, 14314-35-3.

References and Notes

(1) I. Wakeshima and I. Kijima, *Chem. Lett.*, 1, 325 (1972).
(2) K. D. Bos, H. A. Budding, E. J. Bulten, and J. G. Noltes, *Inorg. Nucl. Chem. Lett.*, 9, 961 (1973).
(3) For a detailed review, see K. D. Bos, Ph.D. Thesis, University of Utrecht, 1976, and references therein.
(4) P. F. R. Ewings, D. E. Fenton, and P. G. Harrison, *Inorg. Nucl. Chem. Lett.*, 10, 43 (1974).
(5) P. F. R. Ewings, P. G. Harrison, and D. E. Fenton, *J. Chem. Soc., Dalton Trans.*, 821 (1975); A. B. Cornwell and P. G. Harrison, *ibid.*, 1722 (1975).
(6) R. H. Herber, M. F. Leahy, and Y. Hazony, *J. Chem. Phys.*, 60, 5070 (1974).
(7) G. A. Miller and E. O. Schlemper, *Inorg. Chem.*, 12, 677 (1973).
(8) A. J. Rein and R. H. Herber, *J. Chem. Phys.*, 63, 1021 (1975).
(9) J. J. Spijkerman, J. R. DeVoe, and J. C. Travis, *Natl. Bur. Stand. (U.S.), Spec. Publ.*, No. 260-20 (1970).
(10) V. I. Gol'danskii, E. F. Makarov, and V. V. Khrapov, *Zh. Eksp. Teor. Fiz.*, 44, 7521 (1963); *Phys. Lett.*, 3, 344 (1963).
(11) S. V. Karyagin, *Dokl. Akad. Nauk SSSR*, 148, 1102 (1963).
(12) R. C. McDonald, H. H.-K. Han, and K. Eriks, *Inorg. Chem.*, 15, 762 (1976).
(13) R. J. Gillespie, *Can. J. Chem.*, 39, 318 (1961).
(14) J. D. Donaldson, *Prog. Inorg. Chem.*, 8, 287 (1967), and references therein.
(15) R. H. Herber in "Mossbauer Spectroscopy and Its Applications", Publication 304, International Atomic Energy Agency, Vienna, 1972, and references therein.
(16) V. I. Gol'danskii and E. F. Makarov in "Chemical Applications of Mössbauer Spectroscopy", V. I. Gol'danskii and R. H. Herber, Ed., Academic Press, New York, N.Y., 1968, pp 102–107.
(17) P. S. Flinn, S. L. Ruby, and W. L. Kehl, *Science*, 143, 1434 (1964); see also Figure 1.33 of ref 16.
(18) J. L. K. F. deVries and R. H. Herber, *Inorg. Chem.*, 11, 2458 (1972).
(19) J. L. K. F. deVries, Ph.D. Thesis, University of Nijmegen, 1972; R. H. Herber and J. L. K. F. deVries, unpublished data.
(20) J. Potenza and D. Mastropaolo, *Acta Crystallogr., Sect. B*, 29, 1830 (1973).
(21) P. F. R. Ewings, P. G. Harrison, and T. J. King, *J. Chem. Soc., Dalton Trans.*, 1455 (1975).
(22) F. P. van Remoortere, J. J. Flynn, F. P. Boer, and P. P. North, *Inorg. Chem.*, 10, 1511 (1971).
(23) J. D. Donaldson, D. G. Nicholson, D. C. Puxley, and R. A. Howie, *J. Chem. Soc., Dalton Trans.*, 1810 (1973).

Metal Ion Promoted Demethylation of N-Methyltetraphenylporphyrin by Nickel(II), Zinc(II), and Manganese(II)

David K. Lavallee

Reactions of metal complexes of N-methylporphyrins that result in demethylation have been observed to follow two very different mechanisms. Cobalt(I) and rhodium(I) N-methylporphyrin complexes can undergo an oxidative addition to give cobalt(III) and rhodium(III) organometallic porphyrin products.[1,2] The product analysis and presence of a term first order in nucleophile for demethylation of chloro-N-methyl-$\alpha,\beta,\gamma,\delta$-tetraphenylporphinatocopper(II) by di-n-butylamine, diethylamine, and pyridine, however, demonstrate simple abstraction of $-CH_3^+$.[3] The production of etioporphinato-zinc(II) from chloro-N-methyletioporphinatozinc(II) in refluxing pyridine, observed by Hambright,[4] also likely involves dissociation of $-CH_3^+$. This reaction, in which a metal ion assists in the dissociation of an electrophile bound to one of the pyrrolic nitrogen atoms of the porphyrin, may be viewed as an analogue of the collapse of a "sitting-atop" complex.[5] Although the existence of such complexes as isolated species has been disputed,[6] such species are consistent with porphyrin metalation kinetics.[7] The very facile cleavage of a pyrrolic nitrogen–carbon bond in this reaction is also of interest.

In this report, it is shown that chloro-N-methyltetraphenylporphinatonickel(II) reacts similarly to the corresponding copper(II) complex, which shows a two-path mechanism in which each path involves removal of $-CH_3^+$ by a nucleophile. The reactions of the corresponding zinc(II) and manganese(II) complexes involve nucleophilic attack of the methyl group but the data only require postulation of a single-path mechanism.

Experimental Section

Preparation of the Complexes. The preparation and characterization of N-methyl-$\alpha,\beta,\gamma,\delta$-tetraphenylporphyrin ($N$-$CH_3TPP$)[8] and the chloromanganese(II) and chlorozinc(II) complexes[9] of this ligand have been described previously. The more reactive nickel and copper complexes were prepared in situ from the appropriate chloride salt, as reported previously for the copper complex.[3] Complexes prepared from the hydrated perchlorate salts behaved identically with complexes prepared from the chloride salts. The visible absorption spectra are very similar to those found for other N-CH_3TPP complexes of 2+ metal ions.[9]

Product Analysis and Stoichiometry. The products of demethylation reactions caused by di-n-butylamine are the planar porphyrin complexes and methyldi-n-butylamine. The planar porphyrin complexes were quantitatively identified from their visible absorption spectra.[10] The methylated amine product was identified quantitatively by gas chromatographic techniques for the nickel(II) and copper(II) reactions, as described previously.[3] The reactions of the manganese(II) and zinc(II) complexes were much too slow to employ concentrations of amine sufficiently low for relative GC peak height determination. The first-order dependence on amine concentration is taken as evidence of the similarity of the manganese(II) and zinc(II) reactions with the well-defined nickel(II) and copper(II) reactions. The NMR spectra of the diamagnetic planar porphyrins ZnTPP and NiTPP show that no methylation of the porphyrin ring system has occurred.

The stoichiometry of these reactions is given by

M-N-CH_3TPP^+ + di-n-butylamine → MTPP
    + methyldi-n-butylamine
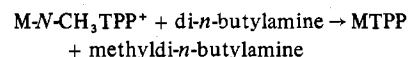
Kinetic Measurements. The measurements and results for the copper(II) reaction have been reported.[3] Similar conditions were used for obtaining kinetic information on the nickel(II) reaction. Stock solutions of the nickel(II) N-methyltetraphenylporphyrin complex varied in nickel(II) concentration from 10^{-4} to 10^{-3} M while the

Table I. First-Order Rate Constants for the Reactions of N-Methyltetraphenylporphinatonickel(II) Cation with Di-n-butylamine[a]

Temp, °C	[Amine], M	$10^3 k$, s^{-1}	Temp, °C	[Amine], M	$10^3 k$, s^{-1}
65	1.12	4.92 ± 0.14	45	0.226	0.370 ± 0.037
	0.562	2.71 ± 0.08		0.113	0.195 ± 0.020
	0.216	1.30 ± 0.03		0.057	0.090 ± 0.004
	0.108	0.762 ± 0.017	25	1.19	0.213 ± 0.011
	0.054	0.424 ± 0.004		0.593	0.124 ± 0.005
	0.027	0.221 ± 0.004		0.233	0.055 ± 0.001
45	1.16	1.36 ± 0.04		0.116	0.032 ± 0.002
	0.578	0.790 ± 0.015			

[a] Error limits are the standard deviations of the two to four independent determinations of each rate constant. Internal variance of curve fitting for each determination was (1.0–3.0) × 10^{-3} OD unit/data point. For several amine concentrations, different Ni(II) concentrations were used. Data were accumulated for 3–6 half-lives.

porphyrin concentration was 10^{-5} to 5 × 10^{-5} M. Stock solutions 5 × 10^{-5} to 5 × 10^{-4} M in chloro-N-methyl-$\alpha,\beta,\gamma,\delta$-tetraphenyl-porphinatomanganese(II) or the corresponding zinc(II) complex were used. Some reactions were run in each case with an excess of metal ion. Dried, distilled di-n-butylamine (Eastman) was used in pseu-do-first-order excess in the range of 10^2–10^4-fold.

The reaction of the Ni(II) complex was monitored like the reaction of the Cu(II) complex.[3] For measurements of the extent of reaction of the Mn(II) and Zn(II) complexes, the complex was dissolved in 50 mL of CH$_3$CN and brought to temperature in a flask with a condenser attached. After 0.5 h the amine (at the same temperature) was added. The reaction was monitored by withdrawal of aliquots, quenching by cooling, and recording of the visible absorption spectrum.

Results

The demethylations of the Mn(II), Ni(II), Cu(II), and Zn(II) complexes of N-CH$_3$TPP by di-n-butylamine show several similar characteristics. In all of these reactions, there is a first-order disappearance of the N-CH$_3$TPP complex which has the same rate as the appearance of the corresponding TPP complex. The data show excellent fits for several half-lives. Isosbestic points are evident in each reaction, indicating no observed uncomplexed N-CH$_3$TPP. There is no dependence of the rate constant on porphyrin concentration (10^{-5} to 2 × 10^{-4} M) and no changes in rate are apparent when excess metal salt is present.

The kinetic results for the reaction of the Ni^{II}-N-CH$_3$TPP$^+$ complex are summarized in Table I. A plot of the observed rate constants as a function of di-n-butylamine concentration is illustrated in Figure 1. The data in Table II for the reactions of the Zn(II) and Mn(II) complexes indicate that there is no evident deviation from first-order dependence on amine concentration at high amine concentrations whereas such deviation is pronounced for the Cu(II) and Ni(II) reactions.
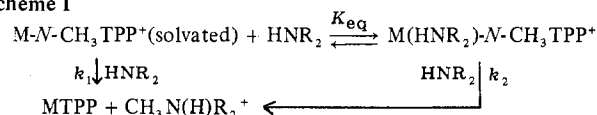
The activation parameters for the demethylation reactions listed in Table III refer to the first-order portion of the plot of observed rate constant vs. amine concentration.

Discussion

Although many reports of kinetic studies of the binding of metal atoms to porphyrins have appeared in the literature,[7] important features of the intimate mechanism still remain undefined. The determination of kinetics and mechanisms of related macrocyclic species are of interest in this regard. The demethylation of N-methylporphyrins bears a resemblance to the collapse of a "sitting-atop" type intermediate and factors that are important in this reaction may also be of importance in reactions of nonmethyl porphyrins in which a metal atom proceeds from a highly out-of-plane to an "in-plane" position.

The relative rates of planar porphyrin metalation have been determined by a number of workers using a large variety of metal salts and solvents. Of note are the studies of Hambright and Chock[11] and of Lowe and Phillips,[12] who studied the incorporation of metal ions into tetrakis(4-N-methylpyridyl)porphyrin in aqueous solution. At 22 °C with pH 4.0 for all ions except Cu^{2+} (pH 2.1), the order of rates found by Hambright and Chock is Cu^{2+} > Mn^{2+} $\simeq$ Co^{2+} > Ni^{2+}. At 55 °C and pH 4.0, Lowe and Phillips determined the order

Scheme I

$$\text{M-}N\text{-CH}_3\text{TPP}^+\text{(solvated)} + \text{HNR}_2 \xrightleftharpoons{K_{eq}} \text{M(HNR}_2)\text{-}N\text{-CH}_3\text{TPP}^+$$

$$k_1 \downarrow \text{HNR}_2 \qquad\qquad\qquad\qquad \text{HNR}_2 \Big| k_2$$

$$\text{MTPP} + \text{CH}_3\text{N(H)R}_2{}^+ \longleftarrow$$

to be Cu^{2+} > Zn^{2+} > Co^{2+} $\simeq$ Mn^{2+} > Ni^{2+}. The order of reaction is consistent with the order of solvent dissociation from the aquated ions.[13] Activation parameters for the series were not reported.

The most comprehensive series of metal ions and porphyrins was reported by Longo and co-workers for reactions of chloride salts, with 15 different porphyrins in dimethylformamide.[14] The order of reaction with the porphyrins was found to be Cu(II) > Cd(II) > Zn(II) > Co(II) > Ni(II) > Mn(II). In this case, comparison with ligand dissociation rates is inappropriate since the reactive metal-containing species were not determined. Of interest, however, is the finding of an isokinetic effect for activation parameters determined for the series of metal chlorides with tetraphenylporphyrin. The compensation for larger $\Delta H^{\ddagger}$ values by more favorable $\Delta S^{\ddagger}$ values has been found in a number of cases of reactions that likely go via the same mechanism.[15–17] In such cases, the $\Delta H^{\ddagger}$ and $T\Delta S^{\ddagger}$ changes may be highly influenced by solute–solvent interactions such that comparisons of rates or of $\Delta G^{\ddagger}$ are of more value than comparisons of the separate activation parameters.

We wish to compare these results with the kinetic parameters for the demethylation reactions of the complexes of N-CH$_3$TPP. The demethylation reactions for the Cu(II) and Ni(II) complexes are explained by a two-path reaction scheme, as postulated earlier for the Cu(II) reaction.[3] The two-path mechanism illustrated by Scheme I leads to the rate equation

$$\frac{d[\text{MTPP}]}{dt} = \frac{k_1 + k_2 K_{eq}[\text{HNR}_2]}{1 + K_{eq}[\text{HNR}_2]}[\text{HNR}_2][\text{M-}N\text{-CH}_3\text{TPP}^+]$$

Good fits to the data were achieved within the ranges $k_1 = (9.00 \pm 0.75) \times 10^{-3}$ M^{-1} s^{-1}, $k_2 = (3.56 \pm 0.45) \times 10^{-3}$ M^{-1} s^{-1}, and $K_{eq} = 6.0 \pm 3.0$. At low amine concentration, the rate equation reduces to a simple second-order rate law, as found. The data for the reactions of the Zn(II) and Mn(II) porphyrins do not require the second path invoked for Cu(II) and Ni(II).

Some complexity is introduced in the manganese(II) reaction due to the production of Mn^{III}TPP$^+$ as product rather than Mn^{II}TPP. The high potential for oxidation of Mn^{II}-N-CH$_3$TPP$^+$ (0.77 V vs. Ag/AgCl in CH$_3$CN)[18] and its stability in refluxing CH$_3$CN for days rule against oxidation of Mn^{II}-N-CH$_3$TPP$^+$ before insertion. On the other hand, Mn^{II}TPP is very readily oxidized ($E_{1/2}$ of –0.23 V vs. Ag/AgCl in CH$_3$CN, with rapid oxidation in air).[19] The good isosbestic point leads to the formulation of the reaction scheme as

$$\text{Mn}^{II}\text{-}N\text{-CH}_3\text{TPP}^+ + \text{HNR}_2 \xrightarrow{\text{slow}} \text{Mn}^{II}\text{TPP} + \text{CH}_3\text{N(H)R}_2{}^+$$

$$\text{O}_2 \Big| \text{rapid}$$

$$\downarrow$$

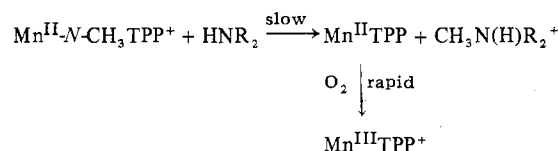$$\text{Mn}^{III}\text{TPP}^+$$

Table II. First-Order Rate Constants for the Reactions of *N*-Methyltetraphenylporphinatozinc(II) and
N-Methyltetraphenylporphinatomanganese(II) with Di-*n*-butylamine[a]

M = Zn(II)			M = Mn(II)		
Temp, °C	[Amine], M	$10^4 k$, s^{-1}	Temp, °C	[Amine], M	$10^4 k$, s^{-1}
79	0.99	4.81	79	0.52[c]	0.13 ± 0.01
	0.54	3.23[b] ± 0.27		0.32[d]	0.086 ± 0.001
	0.23	1.25 ± 0.02		0.11	0.029
	0.12	0.47	70	0.52	<0.019
70	0.54	0.53 ± 0.01			
60	0.54	0.102 ± 0.004			

[a] Data accumulated for 2–5 half-lives. Internal variance of $(1.0–10.0) \times 10^{-3}$ OD unit/data point from least-squares line. [b] Runs with
1:1 Zn(II):*N*-CH$_3$TPP and with excess Zn(II). [c] Runs with Mn-*N*-CH$_3$TPP$^+$ concentrations of 9.0×10^{-5} and 2.0×10^{-4} M. [d] Runs
with 1:1 Mn(II):*N*-CH$_3$TPP and with excess Mn(II).

Table III. Activation Parameters for the Demethylation of
N-Methyltetraphenylporphyrin Complexes[a]

M	$\Delta H^\ddagger$, kcal/mol	$\Delta S^\ddagger$(318 K), eu	$\Delta G^\ddagger$, kcal/mol
Cu(II)	16.9 ± 1.0	−13.1 ± 2.9	21
Ni(II)	18.0 ± 1.0	−14.0 ± 3.0	23
Zn(II)	41.6 ± 2.0	54.6 ± 6.2	26
Mn(II)	>51	>65	

[a] Error limits are the standard deviations from least-squares
best-fit line of ln *k* vs. 1/*T*. Eyring activation parameters are
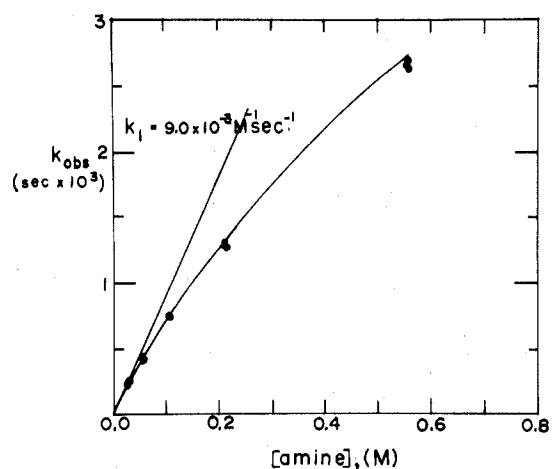specified.

Figure 1. Plot of the observed first-order rate constant for the de-
methylation of the nickel(II) complex of *N*-methyltetraphenylporphyrin
by di-*n*-butylamine at 65 °C as a function of the amine concentration.
The curve is drawn for the fit $k_1 = 9.0 \times 10^{-3}$ M^{-1} s^{-1}, $k_2 = 3.6 \times 10^{-3}$ M^{-1} s^{-1}, and $K_{eq} = 5.4$. For this k_1 value, the standard deviation
of the fit of k_2 is 5% and of K_{eq} is 9%. The variance for the fit becomes
significantly poorer (over threefold difference) outside the range $k_1 = (9.00 ± 0.75) \times 10^{-3}$ M^{-1} s^{-1}, $k_2 = (3.65 ± 0.45) \times 10^{-3}$ M^{-1} s^{-1},
and $K_{eq} = 6.0 ± 3.0$.

For the purpose of comparison to planar porphyrin met-
alation parameters, the activation parameters of the sec-
ond-order path for all four species are employed. It is evident
from Table III that the activation parameters for the de-
methylation of the Ni(II) and Cu(II) complexes are essentially
the same. The zinc(II) and manganese(II) reactions show
much higher enthalpies of activation. The entropy of activation
of the zinc(II) reaction compensates to a large degree. The
reactivity order Cu(II) ≈ Ni(II) > Zn(II) > Mn(II) is in
reasonable agreement with the stability order of the planar
porphyrin products.[20] It is possible that a simple electrostatic
promotion of CH$_3$$^+$ dissociation is operative, however, since
the ionic radii are in the order Ni(II) (0.69 Å) ≈ Cu(II) (0.69
Å) > Zn(II) (0.74 Å) > Mn(II) (0.80 Å).[21] The order found
for the demethylation reaction is certainly quite different from
that found by Hambright and Chock and by Lowe and Phillips
for metalation reactions.

Two conclusions concerning the present study are (1) the
dependence on nucleophile concentration and the compensation
of $\Delta H^\ddagger$ and $T\Delta S^\ddagger$ point to the same mechanism and (2) the
tendency to promote demethylation does not correspond to
relative rates of nonmethyl porphyrin metallation, suggesting
that the rate-determining steps of these two reactions are
affected differently by the various metal ions studied.

Registry No. Ni^{II}-*N*-CH$_3$TPP$^+$, 61633-95-2; Zn^{II}-*N*-CH$_3$TPP$^+$,
61633-96-3; Mn^{II}-*N*-CH$_3$TPP$^+$, 61633-97-4; Cu^{II}-*N*-CH$_3$TPP$^+$,
57606-45-8; di-*n*-butylamine, 111-92-2.

References and Notes

(1) H. Ogoshi, E. Watanabe, N. Kaketsu, and Z. Yoshida, *J. Chem. Soc.,
Chem. Commun.*, 943 (1974).
(2) H. Ogoshi, J. Setsume, T. Omura, and Z. Yoshida, *J. Am. Chem. Soc.*,
97, 6461 (1975).
(3) D. K. Lavallee, *Inorg. Chem.*, **15**, 691 (1976).
(4) B. Shears and P. Hambright, *Inorg. Nucl. Chem. Lett.*, **6**, 679 (1970).
(5) E. B. Fleischer and J. H. Wang, *J. Am. Chem. Soc.*, **82**, 3498 (1960).
(6) (a) J. E. Falk, R. Lemberg, and R. K. Morton, Ed., "Haematin Enzymes",
Pergamon Press, London, 1961; (b) B. F. Burnham and J. J. Zuckerman,
J. Am. Chem. Soc., **92**, 1547 (1970); (c) C. H. Baker, P. Hambright,
and L. Wagner, *ibid.*, **95**, 5942 (1973).
(7) W. E. Schneider, *Struct. Bonding (Berlin)*, **23**, 123 (1975).
(8) D. K. Lavallee and A. E. Gebala, *Inorg. Chem.*, **13**, 2004 (1974).
(9) D. K. Lavallee, *Bioinorg. Chem.*, **6**, 219 (1976).
(10) A. Wohlberg and J. Manassen, *J. Am. Chem. Soc.*, **92**, 2982 (1970).
(11) P. Hambright and P. B. Chock, *J. Am. Chem. Soc.*, **96**, 3122 (1974).
(12) M. B. Lowe and J. N. Phillips, "Progress in Coordination Chemistry",
Butterworths, London, 1968, p 16.
(13) (a) M. Eigen, W. Kruse, G. Maass, and L. W. DeMaeyer, *Prog. React.
Kinet.*, **2**, 286 (1964); (b) G. Geier, *Ber. Bunsenges. Phys. Chem.*, **69**,
617 (1965).
(14) F. R. Longo, E. M. Brown, D. J. Quimby, A. D. Adler, and M. Neot-Mer,
Ann. N.Y. Acad. Sci., **206**, 420 (1973).
(15) J. D. Miller and R. H. Prince, *J. Chem. Soc. A*, 1048 (1966).
(16) D. Thusius, *Inorg. Chem.*, **10**, 1106 (1971).
(17) H. P. Bennitto, *J. Chem. Soc. A*, 2211 (1971).
(18) D. K. Lavallee and M. J. Bain, *Inorg. Chem.*, **15**, 2090 (1976).
(19) L. J. Boucher, *Coord. Chem. Rev.*, **7**, 289 (1972).
(20) J. W. Buchler in "Porphyrins and Metalloporphyrins", K. M. Smith,
Ed., Elsevier, New York, N.Y., 1975, pp 157–231.
(21) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", 3rd
ed, Interscience, New York, N.Y., 1972, p 52.

**Intermolecular Back-Bonding. 2. Stabilization of the
Poorly Conducting One-Dimensional Inorganic
Complexes Containing Unsaturated Chelate Ligands**

Joel S. Miller

As previously described, the ligand-centered intermolecular
back-bonding model has been successful in describing the