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	10^4k, s^{-1}	Temp, °C	[Amine], M	10^4k, 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) × 10^{-3} OD unit/data point from least-squares line. [b] Runs with 1:1 Zn(II):N-CH_3TPP and with excess Zn(II). [c] Runs with Mn-N-CH_3TPP^+ concentrations of 9.0 × 10^{-5} and 2.0 × 10^{-4} M. [d] Runs with 1:1 Mn(II):N-CH_3TPP and with excess Mn(II).

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

M	$\Delta H^‡$, kcal/mol	$\Delta S^‡$(318 K), eu	$\Delta G^‡$, 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.

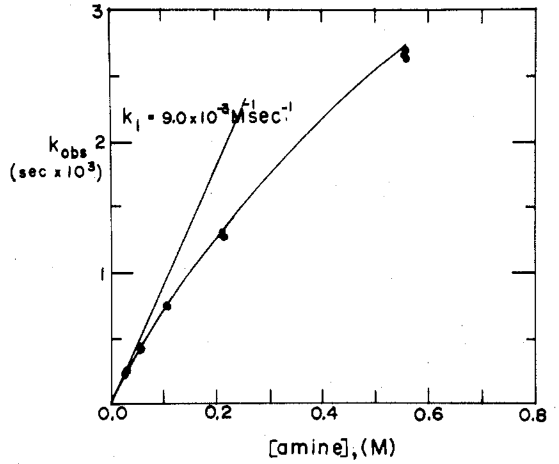

Figure 1. Plot of the observed first-order rate constant for the demethylation of the nickel(II) complex of *N*-methyltetraphenylporphyrin by di-*n*-butylamine at 65 °C as a function of the amine concentration. The curve is drawn for the fit $k_1 = 9.0 \times 10^{-3}$ M^{-1} s^{-1}, $k_2 = 3.6 \times 10^{-3}$ 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 $k_1 = (9.00 \pm 0.75) \times 10^{-3}$ M^{-1} s^{-1}, $k_2 = (3.65 \pm 0.45) \times 10^{-3}$ M^{-1} s^{-1}, and $K_{eq} = 6.0 \pm 3.0$.

For the purpose of comparison to planar porphyrin metalation parameters, the activation parameters of the second-order path for all four species are employed. It is evident from Table III that the activation parameters for the demethylation 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 $\Delta H^‡$ and $T\Delta S^‡$ 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.

Acknowledgment. We express gratitude to the Environmental Health Sciences Institute of the National Institutes of Health (Grant ES-00987) for support of this research.

Registry No. Ni^{II}-N-CH_3TPP^+, 61633-95-2; Zn^{II}-N-CH_3TPP^+, 61633-96-3; Mn^{II}-N-CH_3TPP^+, 61633-97-4; Cu^{II}-N-CH_3TPP^+, 57606-45-8; di-*n*-butylamine, 111-92-2.

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Xerox Corporation, Rochester, New York 14644

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

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Received September 7, 1976 AIC60671F

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

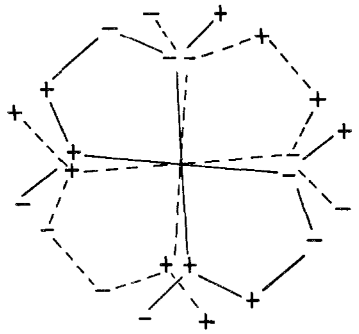
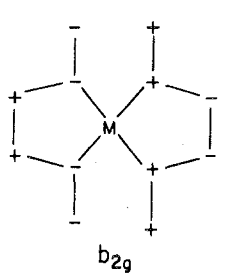


Figure 1. Intermolecular back-bonding overlap of the HOMO b_{2g}, **1** (dashed line), and LUMO b_{3g}, **2** (solid line), for $M^{II}(HDMG)_2$ giving rise to 12 back-bonding overlaps at a 90° relative rotation.

structure of the highly conducting one-dimensional $Mg_{0.86}Pt(O_2C_2O_2)_2{\cdot}5.3H_2O$ complex.[1] The model is also applicable to poorly conducting chain complexes[2-4] containing unsaturated ligands with interplanar spacings less than the sum of the van der Waals radii.[5] When these conditions are met, the higher occupied molecular orbitals (HOMO) on one molecular plane overlap with the low-lying unoccupied molecular orbitals [LUMO (or POMO if the HOMO is partially occupied)] on an adjacent molecular plane. This intermolecular back-bonding model is qualitatively similar to Mulliken's *overlap and orientation principle*[1,6] and the intramolecular $d \rightarrow \pi^*$ back-bonding used to describe the bonding for transition metal carbonyl (etc.) complexes.[7]

A variety of poorly conducting glyoximato[2,8] and phthalocyanine[2,9,10] complexes exhibit a chain structure with equivalent intermolecular spacings $\lesssim 3.5$ Å. The best characterized system is based on glyoxime ligands.[8] The bis(dimethylglyoximato)nickel(II) triad complexes, $M(HDMG)_2$ (M = Ni, Pd, Pt), exhibit a chain structure with relatively short equivalent interplanar spacings.[11-14]

Evaluation of the available *intermolecular back-bonding* available for this glyoxime system requires knowledge of the electronic structure of $M^{II}(HDMG)_2$ (M = Ni,[15,16] Pd,[15,16] Pt[16]). The reported MO calculations are inconsistent with each other and, as the state-of-art improves, certainly deserve a reevaluation. However, these MO calculations suggest the existence of both higher occupied and lower unoccupied ligand-centered MO's of b_{2g} (**1**) and b_{3g} (**2**) symmetries, respectively. HOMO-LUMO intermolecular back-bonding can only be effected through a 90° rotation between adjacent molecules via overlap of the b_{2g} HOMO, **1**, and b_{3g} LUMO, **2**. This results in 12 symmetry-allowed back-bonding interactions,[17] Figure 1. This conformation has been reported for the $M(HDMG)_2$ (M = Ni,[11,12] Pd,[12] Pt[13]) and $[Rh^{II}(HDMG)_2PPh_3]_2$[19] complexes.



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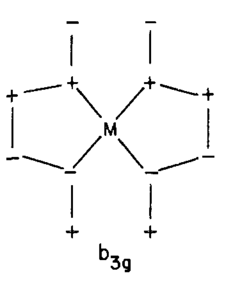

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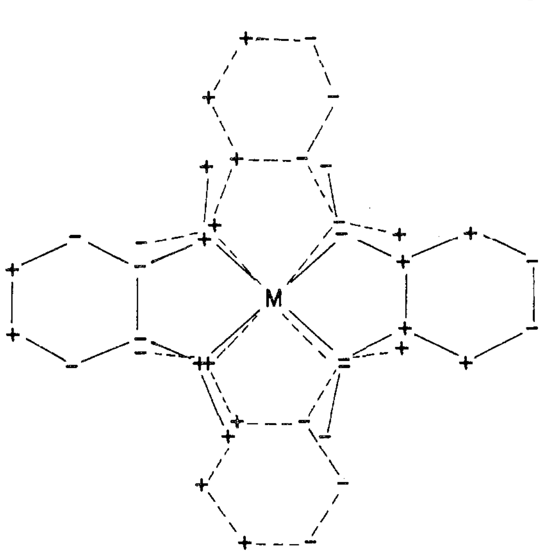
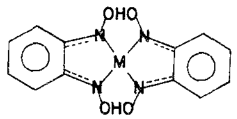


Figure 2. Intermolecular back-bonding overlap of the b_{2g} HOMO, **4** (solid line), and b_{3g} LUMO, **5** (dashed line), for $M^{II}(HBQD)_2$ giving rise to 12 back-bonding overlaps at a 90° relative rotation.



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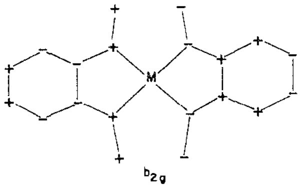

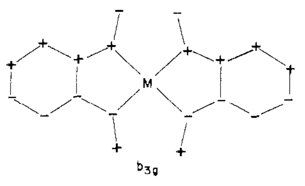

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Evaluation of the overlap of the ligand b_{2g} HOMO[20] and b_{3g} LUMO[20] for the bis diphenylglyoximato ($HDPG^-$) and bis 1,2-benzoquinone dioximato ($HBQD^-$) complexes of the nickel triad, **3** (**4** and **5**, respectively), suggests that these divalent complexes will be isomorphous to $M^{II}(HDMG)_2$, Figure 2. Preliminary crystallographic data for $M^{II}(HDPG)_2$[21] and $M^{II}(HBQD)_2$ (M = Pd, Pt)[22] suggest that these divalent complexes are isomorphous to $M^{II}(HDMG)_2$.

Upon oxidation an electron is lost from the highest occupied molecular orbital which may be either an a_{1g} (d_{z^2}-like) molecular orbital or a ligand-centered molecular orbital. The former situation is clearly observed for various highly conducting species,[2] e.g., bis(oxalato)platinates[1] or tetracyanoplatinates;[1] i.e., the relative orientation of adjacent molecular planes does not change upon oxidation. However, if oxidation removes an electron from a ligand-centered molecular orbital, intermolecular back-bonding will occur through a POMO-POMO overlap;[23] consequently, the relative rotation of adjacent planes may differ for the oxidized and reduced species. However, in either case shorter interplanar spacings would be anticipated. Since close approach of adjacent molecular planes along the M-M axis will tetragonally distort the electronic structure of the square-planar complex, the a_{1g} (d_{z^2}) orbital is expected to be the HOMO;[2,25] thus, oxidation will not change the relative orientation between adjacent planes. It is possible that in some situations the a_{1g} orbital will be of greater energy in the 1-D complex than in the isolated molecule but lower in energy than a ligand centered HOMO such that upon oxidation an electron will be lost from the π-ligand MO and a different relative orientation may be expected.[26] The prediction cannot be tested at the present time as a detailed understanding of the binding forces and electronic structure for a series of 1-D complexes is not available for oxidized and nonoxidized chain complexes. However, structural data supporting this supposition have recently been published.

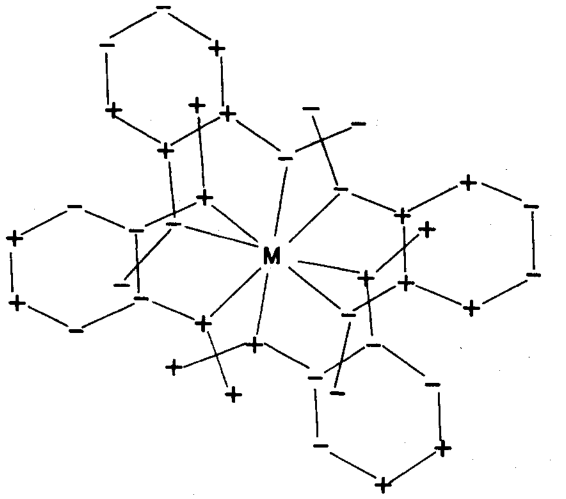


Figure 3. Intermolecular back-bonding overlap of the partially filled b_{2g} HOMO, **4**, with the b_{2g} HOMO on an adjacent molecule giving rise to six back-bonding overlaps at a 60° relative rotation.

The $M^{II}(HDPG)_2$[21] and $M^{II}(HBQD)_2$, **3** (M = Pd, Pt),[22] complexes have been shown to be isomorphous to $M(HDMG)_2$; thus, they possess a 90° relative rotation between adjacent planes. This 90° rotation is also observed in the recent x-ray analysis of the iodine oxidation product of $Ni^{II}(HDPG)_2$,[28,29] i.e., $Ni(HDPG)_2I$.[30] Similarly, the iodine oxidation product of $Pd^{II}(HG)_2$ (H_2G = glyoxime), i.e., $Pd(HG)_2I$, exhibits a relative 90° rotation between adjacent molecular planes.[14,31] Thus, oxidation effects the loss of electrons from the a_g band.

An apparent discrepancy from the HOMO–LUMO predictions occurs for the iodine oxidation product of $Ni(HBQD)_2$.[32,33] The structure of the oxidation production reveals a relative ~60° rotation between adjacent molecular planes.[33-35] This can be reconciled by the removal of an electron from the highest occupied ligand-centered molecular orbital,[20] **4**. Thus, intermolecular back-bonding is effected through a POMO–POMO (**4**–**4**) overlap and a different conformation is predicted for the oxidized and the nonoxidized species. Figure 3 illustrates the POMO–POMO[24] (**4**–**4**) overlap for oxidized $Ni(HBQD)_2$.

Therefore, the intermolecular back-bonding model is consistent with a ligand-centered HOMO. This has not been established; however it is in accord with the ESR data obtained from $Ni(HDPG)_2X$ (X = Br, I) which show that in defect sites the unpaired electrons reside on the ligand and not on the metal.[36] The $Ni(HDPG)_2I$ structure suggests that the a_{1g} is the HOMO; however, since the ESR data suggests a low-lying filled ligand-centered orbital, complexes with somewhat different ligand systems may have the ordering of levels reversed. Further work is necessary to fully understand the detailed electronic structure of the halogen-oxidized bis(glyoximato) complexes.[28]

Similar to the bis(1,2-benzoquinone dioxime) complexes of the nickel triad are the bis(*o*-phenylenediamine) complexes of the nickel triad,[38] **6**, $M(o\text{-phen})_2$. Due to the absence of oxygen atoms on **6** (with respect to **3**) the latter complexes possess a different electronic structure where 12 back-bonding overlaps are not available for back-bonding. Thus, it is not surprising that $Ni(o\text{-phen})_2$ does not form a chain structure with parallel modular planes.[37]

Oxidation[37] may remove an electron from either the a_{1g} orbital or a π-ligand MO permitting the formation of a chain via overlap of the partially occupied orbitals. If an electron is lost from the a_{1g} orbital, a 90° relative rotation between adjacent planes is predicted on the basis of ligand calculations.[20] However, if the electron is lost from the highest occupied ligand orbital, then the POMO–POMO overlap, electrostatic, van der Waals, and dipole–dipole interactions will govern the resultant structure. The structure of $M(o\text{-phen})_2I$ has not been reported.[39]

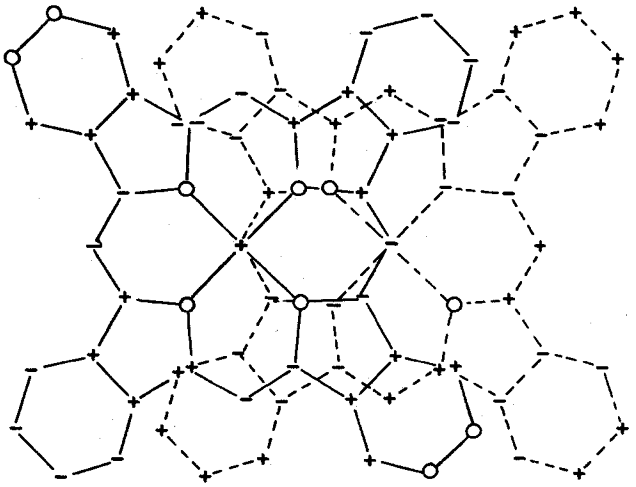
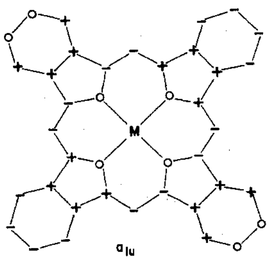


Figure 4. Intermolecular back-bonding overlap of the a_{1u} HOMO, **7** (solid line), and the b_{3g} LUMO, **8** (dashed line), for metal phthalocyanine complexes.

Similarly, the relative orientation of adjacent phthalocyanine metal complexes can be rationalized. The phthalocyanine a_{1u} HOMO,[40] **7**, and either of the low-lying b_{3g}, **8**, and b_{2g} MO's[40] maximize HOMO–LUMO overlaps when adjacent molecular planes are translated by the metal–noncoordinated nitrogen distance.[41] Thus, adjacent phthalocyanine planes form a one-dimensional chain containing alternating collinear metal noncoordinating nitrogen atoms, Figure 4. This is in good agreement with the reported structure for various phthalocyanine complexes.[9,10,42]



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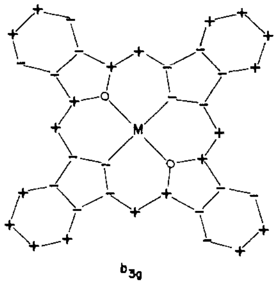

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Halogen oxidation of various phthalocyanine complexes of the first-row transition metals yields complexes containing variable amounts of halogen which exhibit high room-temperature conductivities.[43] It is unlikely that an a_{1g} band could form from the overlap of first-row transition metal complexes containing conjugated macrocyclic ligands as the spatial extension of the $3d_{z^2}$ orbital is significantly shorter than that of π-ligand MO's.[44] Thus, oxidation could remove an electron from localized a_{1g} orbitals on the metals, or if the HOMO was π-ligand in character, oxidation would remove a ligand-centered electron. The latter case would allow for POMO–POMO overlap (i.e., a_{1u}–a_{1u}, **7**–**7**) and subsequently band formation of the type used to describe the electronic structure and electrical properties of $TCNQ^{-}\cdot$.[45]

Evaluation of the a_{1u}–a_{1u} overlap suggests two possible relative orientations, i.e., an eclipsed structure (collinear metal atoms) or the staggered structure previously reported.[42] Thus, this suggests that upon oxidation the 1-D phthalocyanine structure may not be altered although the formation of a conduction band may arise through overlap of the a_{1u} orbital, to account for the observed high conductivity.[45]

Thus, the intermolecular back-bonding model is useful in describing the solid-state structures of various types of poorly conducting chain complexes. Intermolecular back-bonding provides a mechanism for stabilization of chain complexes and may contribute to the binding energy observed for $Ni^{II}(HDMG)_2$; however, evaluation of the other contributing binding forces is necessary. Oxidation of a chain complex removes an electron either from an a_{1g} band (and not altering the structure except for permitting a stronger a_{1g} overlap and shorter M–M spacing) or from a ligand-centered MO (permitting POMO–POMO overlap and the possibility of a different relative rotation as well as shorter intermolecular spacings). Utilization of the model may reveal information about the electronic structure of chain complexes and may stimulate further study into the operative binding forces in chain complexes.

Acknowledgment. The author wishes to acknowledge the helpful and stimulating discussions with Drs. G. P. Ceasar, M. J. S. Dewar, C. B. Duke, R. Eisenberg, A. J. Epstein, J. E. Kuder, N. O. Lipari, W. A. Little, and G. D. Stucky.

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Reaction of Cationic Group 7B Metal Carbonyl Derivatives with Sodium Hydrogen Sulfide. Production of Metal Hydrides

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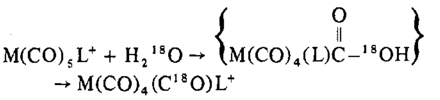
Received September 10, 1976 AIC60676C

Recently we reported on the stereospecific incorporation of oxygen-18 into manganese and rhenium pentacarbonyl derivatives via exchange reactions with $H_2{}^{18}O$.[1,2] The equatorial CO sites were observed to be preferentially enriched in oxygen-18 over the axial CO group. This process was proposed to proceed through the intermediacy of a hydroxycarbonyl species, resulting from hydroxide attack at a carbonyl carbon site, which is in chemical equilibrium with the starting material and where proton exchange readily occurs between the two oxygens (eq 1). That these cationic species are susceptible



$$M(CO)_5L^+ + H_2{}^{18}O \rightarrow \left\{M(CO)_4(L)\overset{\overset{\displaystyle O}{\|}}{C}-{}^{18}OH\right\} \rightarrow M(CO)_4(C^{18}O)L^+ \qquad (1)$$

M = Mn, Re; L = phosphines, pyridine, CH_3CN