We theorize that the N and S atoms, rather than Co, function as the base site toward the Hg atom. A chainlike structure in which the mercury atom has a coordination number of at least 4 could form. It is well-known[2] that the atoms of 1,2-dithiolenes are able to act as nucleophilic sites. Some Lewis acid behavior is exhibited by the catechol complex of IV, which reacts with $NH_2CH_2C_6H_5$ in hexane to produce a brown solid. Again, dissociation to the reactants occurs in solvents that dissolve the complex. None of the other complexes in Table I react with benzylamine. Apparently, the oxygen atoms of $(\eta^5-C_5H_5)CoO_2C_6H_4$ withdraw enough electron density from the cobalt center to allow for weak coordination by the amine.

Contribution from the Departamento de Quimica-Fisica, Facultat de Quimica, Universitat de Barcelona, Tarragona, Spain, and Department of Chemistry, University of Michigan, Ann Arbor, Michigan 48109

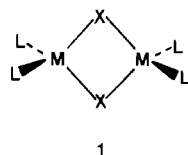# Polymeric One-Dimensional [CoXL₂]ₙ vs. Dimeric [CoXL₂]₂. Theoretical Analysis of the Factors Favoring Each Form

E. CANADELL*[†] and O. EISENSTEIN*[‡]

Received November 24, 1982

The polymeric one-dimensional structure of [CoI(NO)₂]ₙ and dimeric structure of [CoCl(NO₂)]₂ are analyzed by band structure and extended Hückel calculations, and the factors favoring the dimer vs. the polymer are discussed. It is shown that d¹⁰ metal atoms that are linked by an electropositive atom and carry strong π-acceptor groups will prefer a polymeric over a dimeric structure.

Electronic factors favoring polymeric over dimeric structures in oligomeric systems are not well-known. This dichotomy between dimers and polymers is commonly found in inorganic systems. Molecular orbital and band structure calculations are attempted to clarify this problem for the first time.

Numerous tetrahedral M_2L_6 transition-metal dimers are known. While most dimers with d¹⁰ metal centers have the general edge-sharing tetrahedral structure of type **1**, a few exist

1

as polymeric one-dimensional chain structures of type **2**. This
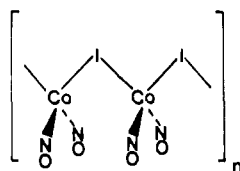
2

is the case for [CoX(NO)₂]ₙ with X = I[1] or Br.[2] The structure is made up of a zigzag chain of CoX in which the cobalt atom is tetrahedrally coordinated and no Co–Co bond is present as evidenced by the long Co–Co distance (3.86 Å, X = I). The polymer of type **2** does not exist for X = Cl. On the other hand, the dimer [CoCl(NO)₂]₂ of type **1** is well characterized.[3] To our knowledge, no polymer of type **2** is known for a transition-metal center with an incompletely filled d shell. In this paper, we present an analysis of the electronic structures of dimer **1** and polymer **2** and describe the conditions that favor one form over the other.

Theoretical Procedure

The tight-binding method[4] of band structure calculation obtained by the extended Hückel method has been used. Given a set of basis atomic orbitals {χ_μ} for the atoms of a unit cell, the set of the Bloch basis orbitals {$b_\mu(k)$} are formed as

$$b_\mu(\mathbf{k}) = N^{-1/2}\sum_l e^{i\mathbf{k}\cdot\mathbf{R}_l}\chi_\mu(r - \mathbf{R}_l) \qquad (1)$$

where **k** is the wave vector and $\mathbf{R}_l = l\cdot\mathbf{d}$, with **d** being the primitive vector. With these Bloch basis orbitals the extended Hückel method leads to the eigenvalue equation

$$H(\mathbf{k})\ C(\mathbf{k}) = S(\mathbf{k})\ C(\mathbf{k})\ e(\mathbf{k}) \qquad (2)$$

where $H_{\mu\nu}(\mathbf{k}) = \langle b_\mu(\mathbf{k})|H_{eff}|b_\nu(\mathbf{k})\rangle$ and $S_{\mu\nu} = \langle b_\mu(\mathbf{k})|b_\nu(\mathbf{k})\rangle$. The solution of this eigenvalue problem results in LCAO crystal orbitals $\psi_n(\mathbf{k})$

$$\psi_n(\mathbf{k}) = \sum_\mu C_{n\mu}(\mathbf{k})\ b_\mu(\mathbf{k}) \qquad (3)$$

and eigenvalues $\epsilon_n(\mathbf{k})$. The band structure is then determined by performing the above calculation for various values of **k** (usually within the first Brillouin zone; $-0.5K \leq \mathbf{k} \leq 0.5K$ where $K = 2\pi/\mathbf{d}$). The parameters of the extended Hückel calculation and geometries are given in the Appendix.

A unit cell of **2** contains one CoI(NO)₂ unit. In our calculations, lattice sums were carried out to the third nearest neighbors (i.e., l = -3, -2, -1, 0, 1, 2, 3 in eq 1) and eq 2 was solved at **k** = 0.0K, 0.1K, 0.2K, 0.3K, 0.4K, and 0.5K.

Results and Discussion

The energy of the unit cell CoI(NO)₂ within polymer **2** can be compared to the energy of the same chemical fragment within the dimer of type **1**. The CoI(NO)₂ fragment is found to be 4.4 kcal/mol more stable inside the polymer than inside the dimer. The opposite is true for the CoCl(NO)₂ fragment,

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(1) Dahl, L. F.; de Gil, E. R.; Feltham, R. D. *J. Am. Chem. Soc.* **1969,** *91,* 1653.
(2) Bertinotti, F.; Corradini, P.; Diana, G.; Gamis, P.; Pedone, C. *Ric. Sci.,* *Parte 2: Sez. A* **1963,** *3,* 210.
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†Universitat de Barcelona.
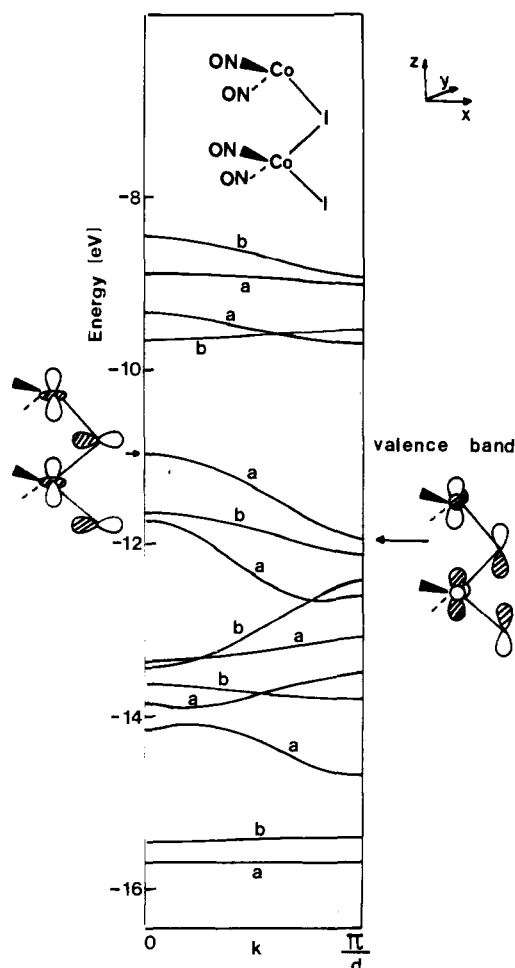‡University of Michigan.

Figure 1. One-dimensional band structure for the [CoI(NO)$_2$]$_n$ chain. The eight lower bands have been omitted.

which is 13.7 kcal/mol more stable within the dimer. In other words, according to these calculations the CoI(NO)$_2$ fragment prefers to polymerize while the CoCl(NO)$_2$ fragment prefers to dimerize, in excellent agreement with the observed result.

To understand why each system behaves the way it does, we then turned our attention to the interactions of a CoX(CO)$_2$ unit with its neighbor(s) in the polymer and in the dimer. This fragment analysis has been widely used by Hoffmann,[5] Whangbo,[6] and Burdett[7] for the understanding of crystalline systems.

The band structure of [CoI(NO)$_2$]$_n$ is shown in Figure 1. Because of a very large participation of the iodine orbitals in the frontier orbitals, it is impossible to sort out only d-block bands in the system. The bands have been labeled according to their symmetry with respect to the CoICo plane, i.e., a for symmetrical and b for antisymmetrical. There is a gap of 1.22 eV between the highest occupied band and the lowest empty band.

The valence (highest occupied) band shows significant dispersion composed as it is of z^2 on the cobalt and p$_x$ on the iodine. This valence band is made in a transparent fashion of the HOMO **3** and LUMO **4** of each CoI(NO)$_2$. Both the HOMO (Figure 2a) and the LUMO (Figure 2b) are CoI antibonding and have large contributions on both atoms. Therefore, at the center of the zone (k = 0), where the valence

band is made of the in-phase combination of the frontier orbitals of the unit cells, the energy of the valence band goes through a maximum (I and Co orbitals are in a strong out-of-phase interaction). The out-of-phase combination of the frontier orbitals at the edge of the zone (**k** = $\pi/\mathbf{d}$) results in the net Co–I interaction being slightly bonding (Figure 1).

Consider now the bridged dimer [CoI(NO)$_2$]$_2$. Dimeric M$_2$L$_6$ has been examined in detail by Summerville and Hoffmann.[8] For our purpose, it is convenient to consider the dimers as made of two CoI(NO)$_2$ fragments. The interaction diagram limited to the frontier orbitals is shown in Figure 3. The overlap between the two HOMOs is large, 0.114, because the large lobe of z^2 overlaps with p$_x$ of iodine. In contrast, the overlap of the LUMO of one fragment with the HOMO of the other one is negligible, 0.006. Consequently, the HOMO of the dimer is the antibonding combination of the two HOMOs without any noticeable stabilization provided by the LUMO of each fragment. Therefore, occupancy of the HOMO of the dimer results in a strong destabilization of the whole system.

The overlaps between the orbitals of each CoI(NO)$_2$ unit are different inside the polymer. Consider part of polymer **5**. The central unit B is attached to two fragments A and

	Overlap
HOMO$_A$ HOMO$_B$	= 0.0570
LUMO$_A$ HOMO$_B$	= 0.0327
LUMO$_C$ HOMO$_B$	= 0.0137
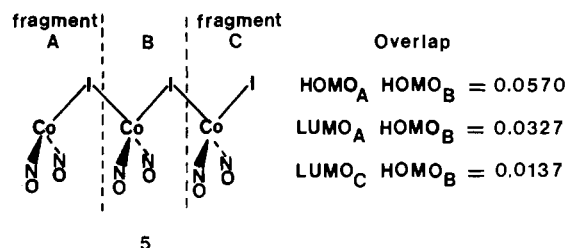
C. The overlap between HOMO$_A$ and HOMO$_B$ (which is equal to the overlap HOMO$_B$–HOMO$_C$) is 0.057. The overlap between LUMO$_A$ and HOMO$_B$ is 0.0327 while the overlap between LUMO$_C$ and HOMO$_B$ is 0.0137.

If one compares the overlap in the polymer to that in the bridge dimer, two conclusions appear. (1) The interaction between the HOMOs is approximately equivalent in the polymer and in the dimer (overlap 0.114 on the dimer and 0.057 with each neighbor in the polymer). (2) The stabilizing influence of the LUMO of each CoI(NO)$_2$ upon the HOMO of each neighbor is larger inside the polymer than in the dimer (the HOMO–LUMO overlap is much larger in the polymer).

The comparison of relative energy values of the valence band and the HOMO of the bridge dimer supports this qualitative analysis. The top of the valence band, –11 eV, which occurs at **k** = 0, is lower in energy than the HOMO of the bridge dimer, –10.75 eV. Although it is certain that the difference in stability of the two systems is not entirely contained in one band or one orbital and that our analysis is a simplified view of the reality, it has been often observed that the energy of the highest orbital is directly related to the stability of the system in question.

Additional conclusions and extrapolations can be drawn. (1) If no electrons occupy the HOMO of the bridge dimer, one particular destabilizing factor of the system is removed. It

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(8) Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 7240.
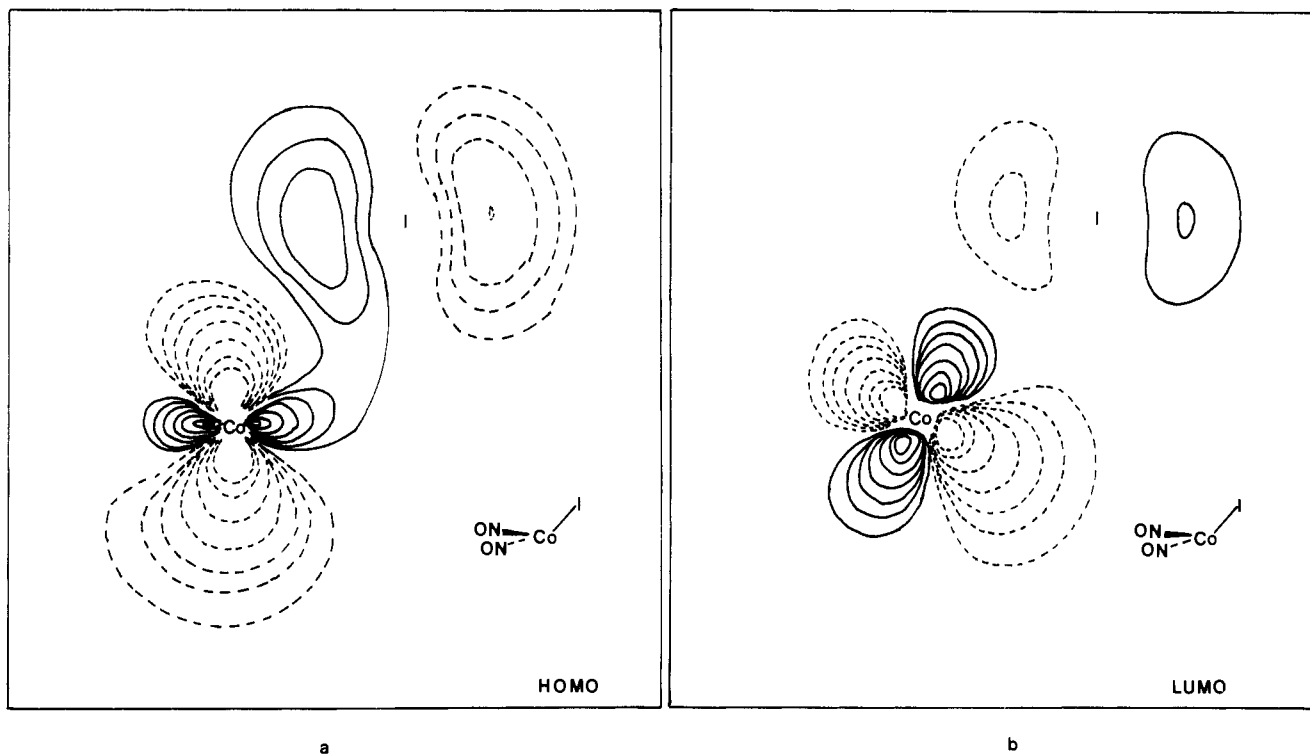
a

b

Figure 2. (a) Plot of the HOMO of $CoI(NO)_2$. The contour values of ψ are ± 0.3, ± 0.225, ± 0.15, ± 0.1, ± 0.07, ± 0.05, ± 0.03. (b) Plot of the LUMO of $CoI(NO)_2$. Contour values are the same.
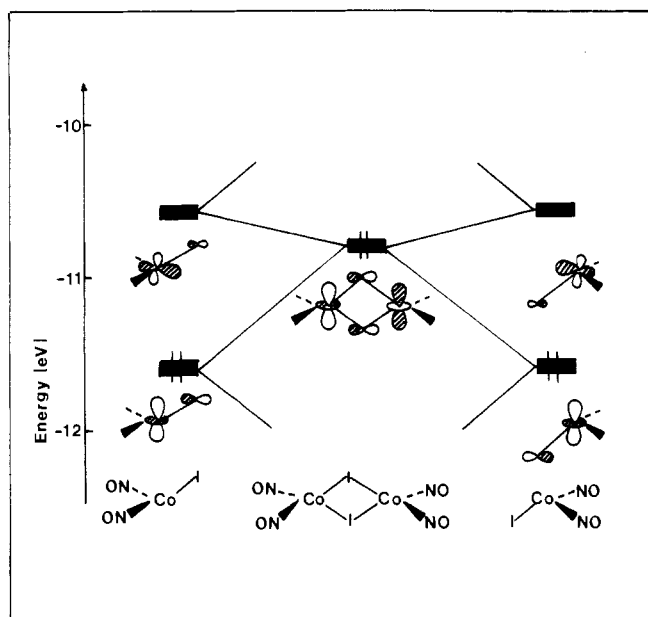

Figure 3. Partial interaction diagram for the dimeric structure $[CoI(NO)_2]_2$. Only frontier orbitals are shown.

is therefore not surprising to find that the d^9d^9 $[FeI(NO)_2]_2$ is a bridge dimer. (2) By modifying the linking atom, one can expect to reverse the preference of the polymeric form over the dimeric structure. We have seen that the stability of the polymer is in part due to the influence of the LUMO of each $CoI(NO)_2$, which mixes into the valence band. In contrast, the role of the LUMO of $CoI(NO)_2$ in the stability of the bridge dimer is negligible. Therefore, decreasing the participation of the LUMO disfavors the polymer more than the dimer. The replacement of the iodine atom by a chlorine whose orbitals are much deeper in energy diminishes the amount of halogen orbitals in the frontier orbital of the cobalt fragment. The overlaps between the orbitals of adjacent fragments are much smaller for Cl than for I. In addition,

the calculations show that the HOMO-LUMO gap of CoX-$(NO)_2$ is larger for X = Cl than for X = I. Both effects contribute to a smaller influence of the LUMO of $CoCl(NO)_2$. The bridge dimer is therefore preferred as we mentioned earlier. (3) Another way to reverse the preference of the polymer over the dimer is to replace the two NO groups by groups which are not good π acceptors. The reasoning is analogous to the one just developed. The strong π-acceptor character of the NO groups causes the LUMO of $CoI(NO)_2$, which has a large π^*_{NO} character, to be of low energy. The replacement of the NO groups by poorer acceptors raises the LUMO and consequently disfavors the polymer more than the dimer. A model calculation replacing the NO groups by terminal iodines and adjusting the charges to keep d^{10} centers indicates the polymer to be less stable than the dimer by 3.2 kcal/mol. Our arguments are consistent with the known dimeric Cu $d^{10}d^{10}$ structure **6**, which contains iodides and chelating ligands in place of the NO group.[9]

6
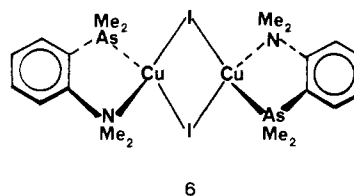
In conclusion, the polymeric one-dimensional structure **2** is preferred over the bridged dimer of type **1** if the bridging groups are not electronegative and the nonbridging groups are good π acceptors. Iodine is certainly the best candidate as a linking atom for the polymer. A systematic replacement of the other ligands, for instance from phosphines where the dimer may be preferred to phosphites where the polymer may be observed, would be worthwhile pursuing experimentally.

(9) Graziani, R.; Bombieri, G.; Forsellini, E. *J. Chem. Soc. A* **1971**, 2331.

of the band program. They are grateful to Dr. T. Hughbanks, Dr. L. Messerle, and Dr. S. Wijeyesekera for their comments. O.E. thanks Du Pont for a summer salary, and E.C. thanks the University of Michigan for its hospitality during the summer.

Appendix

The exponents and parameters for iodine and chlorine were taken from Clementi and Roetti[10] and from Hinze and Jaffe,[11] respectively. The exponents and parameters of the cobalt are those of ref 12. The modified weighted Wolfsberg–Helmholtz

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(11) Hinze, J.; Jaffe, H. H. *J. Phys. Chem.* **1963**, *67*, 1501.
(12) Lauher, J. W.; Elian, M.; Summerville, R. H.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 3219.

formula was used.[13] Experimental structural data were used for the polymer. In the bridge dimer, bond distances and angles at the iodine (96.2°) were kept as in the polymer.

atom	orbitals	H_{ii}, eV	ζ
Co	4s	−10.2	1.700
	4p	−6.11	1.050
	3d	−12.84	5.55 (0.5551)
			1.9 (0.6461)
I	5s	−18.0	2.679
	5p	−12.7	2.322
Cl	3s	−24.2	2.356
	3p	−15.0	2.039

Registry No. 1, 13931-93-6; **2**, 28986-75-6.

(13) Ammeter, J. H.; Burgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686.

Contribution from the Department of Chemistry, Brigham Young University, Provo, Utah 84602

A New Electrostatic Model of Molecular Shapes

JAMES L. BILLS* and S. PAUL STEED

Rationale and procedure are presented for a formal distribution of valence electrons that makes each ligand electrically neutral. Ligands are classified according to the number of bonding electrons thus assigned to each ligand. The valence electrons remaining on the central atom are treated as point charges with interorbital repulsions given by Coulomb's law. This approach is called the neutral-ligand electron-repulsion (NLER) model. The NLER model correctly predicts the main features of most molecular shapes, including relative energies of bond–bond, bond–lone, and lone–lone repulsions, and the tendency of the bond orbitals to remain stationary as the bonds bend. A few cases are considered where isomers are possible, and the NLER model predicts the energetically favored isomer for every case where experiment has shown a clearly favored isomer to exist.

Introduction

Various models and theories have been proposed to enable chemists to correlate, and possibly to predict, the shapes of molecules and polyatomic ions. Approximate solutions of the Schrödinger equation give molecular shapes that are in good agreement with experiment, whether the approximation is in the valence bond (VB) or molecular orbital (MO) form.[1] When canonical MO's are transformed to localized MO's (LMO's), the results support the chemist's concepts of electron-pair bonds and lone pairs.[2] Because the computations of VB and LMO theories are difficult, there remains a need for simpler models that every chemist can use.

A currently popular approach is to follow the rules of the valence-shell-electron-pair repulsion scheme (VSEPR).[3] The amazing success of those rules has stimulated much work aimed at discovering their theoretical basis.[4] A point worthy of emphasis, however, is that those rules were derived from

experiment[5] and are still regarded as largely empirical.[6] The indiscriminate inclusion of the empirical rules under the heading of "VSEPR theory" tends to give the *theory* credit for the success of the *rules*. As a result, the theory appears to be better substantiated than it really is. However, criticism of the theory is likely to be construed as criticism of the rules, about which many chemists are justifiably defensive. In this paper, disagreement with the VSEPR theory does not extend to the empirical rules, which are fully supported by our work. Moreover, the proponents of the VSEPR theory have contributed many of the ideas incorporated in our model, and we acknowledge our indebtedness to them.

Unfortunately, there is some ambiguity as to what the VSEPR theory is. Some authors have described the VSEPR theory as an electrostatic model,[4c,7] but this attribute has been repudiated.[8] Indeed, one account of VSEPR claimed that molecular shapes can be deduced from the Pauli exclusion principle even when electrostatic forces are neglected.[9] Other statements, which must not be taken literally, are recent claims that screened one-electron models have "no electron–electron repulsions"[4f] and that another model "omits electrostatic

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