2. The stability of these five-coordinate platinum(II)–olefin complexes may be due to extensive π back-bonding by the anionic tridentate hydrotris(1-pyrazolyl)borate ligand.

Acknowledgment. The author thanks Mr. F. Davidson for running the ^{13}C spectra and Dr. D. W. Ovenall for obtaining the ^{19}F-decoupled ^{13}C spectrum.

Registry No. $Pt(CH_3)[HB(pz)_3](TFE)$, 51548-82-4; $Pt(CH_3)[HB(pz)_3](MA)$, 51607-50-2; $Pt(CH_3)[HB(pz)_3](FN)$, 59983-08-3; $Pt(CH_3)[HB(pz)_3](E)$, 59983-09-4; $Pt(CH_3)[HB(pz)_3](DEF)$, 51607-52-4; $Pt(CH_3)[HB(pz)_3](AN)$, 51607-38-6; $Pt(CH_3)[HB(pz)_3](MAC)$, 41982-15-4; $Pt(CH_3)[HB(pz)_3]$, 39395-33-0; ^{13}C, 14762-74-4.

References and Notes

(1) H. C. Clark and L. E. Manzer, *J. Am. Chem. Soc.*, **95**, 3812 (1973).
(2) H. C. Clark and L. E. Manzer, *Inorg. Chem.*, **13**, 1291 (1974).
(3) H. C. Clark and L. E. Manzer, *Inorg. Chem.* **13**, 1996 (1974).
(4) L. E. Manzer and P. Z. Meakin, to be submitted for publication in *Inorg. Chem.*
(5) H. C. Clark and L. E. Manzer, *J. Chem. Soc., Chem. Commun.*, 870 (1973).
(6) J. D. Oliver and N. C. Rice, submitted for publication.
(7) M. H. Chisholm, H. C. Clark, L. E. Manzer, and J. B. Stothers, *J. Am. Chem. Soc.*, **94**, 5087 (1972).
(8) D. G. Cooper, R. P. Hughes, and J. Powell, *J. Am. Chem. Soc.*, **94**, 9244 (1972).
(9) M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers, and J. E. H. Ward, *J. Am. Chem. Soc.*, **97**, 721 (1975).
(10) C. A. Tolman, A. D. English, and L. E. Manzer, *Inorg. Chem.*, **14**, 2353 (1975).
(11) M. H. Chisholm, H. C. Clark, L. E. Manzer, J. B. Stothers, and J. E. H. Ward, *J. Am. Chem. Soc.*, **97**, 721 (1975).
(12) D. G. Cooper, G. K. Hamer, J. Powell, and W. F. Reynolds, *J. Chem. Soc., Chem. Commun.*, 449 (1973).
(13) R. P. Hughes and J. Powell, *J. Organomet. Chem.*, **60**, 427 (1973).
(14) G. M. Bodner, B. N. Storhoff, D. Doddrell, and L. J. Todd, *Chem. Commun.*, 1530 (1970).
(15) W. J. Cherwinski, B. F. G. Johnson, and J. Lewis, *J. Chem. Soc., Dalton Trans.*, 1405 (1974).
(16) L. Kruczynski, J. L. Martin, and J. Takats, *J. Organomet. Chem.*, **80**, C9 (1974).
(17) R. G. Solomon and J. K. Kochi, *J. Organomet. Chem.*, **64**, 135 (1974).

Contribution from Webster Research Center,
Xerox Corporation, Rochester, New York 14644

Intermolecular Back-Bonding. 1. Stabilization of the Highly Conducting One-Dimensional Bis(oxalato)platinates

JOEL S. MILLER

Received April 5, 1976 AIC60257F

In order to rationalize the structure of the highly conducting one-dimensional bis(oxalato)platinates an *intermolecular back-bonding* model was formulated. The model involves overlap of a higher occupied molecular orbital (HOMO) on a molecular plane with a lower unoccupied molecular orbital (LUMO) on an adjacent molecular plane. Evaluation of the b_{3g} HOMO–b_{2g} LUMO interactions derived from the symmetric and antisymmetric molecular orbital combinations for the oxalato ligand for the bis(oxalato)platinate molecular planes results in eight ligand-centered intermolecular back-bonding overlaps when adjacent molecules are rotated by 60°. Rotation of a molecular plane will increase four back-bonding overlaps while breaking the remaining four overlaps. Thus a 60° relative rotation maximizes overlap. Similarly b_{1u} HOMO–a_u LUMO overlap gives rise to an additional net four back-bonding situations when adjacent molecular planes are rotated by 60°. These observations are in accord with the previously published structure of $Mg_{0.86}Pt(ox)_2{\cdot}5.3H_2O$. Thus, the intermolecular back-bonding contributes to the stabilization of the short intermolecular spacings ($\sim$2.85 Å) and provides an additional back-bonding mechanism to reduce the Coulomb repulsion of electrons in an a_g band.

In recent years there has been considerable interest in the chemical[1-7] and physical properties[1,3-5,9,10] of highly and poorly conducting one-dimensional (1-D) inorganic complexes comprised of equivalent molecules within a chain.[11] All of these chains are formed from d^8 square-planar complexes with small planar ligands which permit close approach of adjacent molecular planes. For the highly conducting partially oxidized materials close approach is an acute problem as strong overlap of the a_g (d_{z^2} like) orbitals is important in the stabilization of the system via band formation and subsequent partial oxidation.[1] In order to achieve the necessary strong overlap of the a_g metal orbitals several design criteria surface: (1) use of third-row d^8 complexes as the $5d_{z^2}$ orbital has the largest spatial extension; (2) use of transition metals with smaller nuclear charge as the larger nuclear charge will contract the spatial extension of the $5d_{z^2}$ orbital; (3) formation of a one-dimensional chain of negatively charged square-planar ions since net positive charges will contract the $5d_{z^2}$ orbital; (4) utilization of small nonbulky ligands in order to permit close approach of these ions; (5) use of strong-field ligands which are able to reduce the Coulomb repulsion of electrons on the metal through intramolecular d–π^* back-bonding (in order to achieve high conductivity); (6) optionally, hydrogen bonding between chains knitting together and stabilizing the one-dimensional strands. These general criteria for designing new highly conducting systems have been empirically extracted from evaluation of the known highly conducting one-dimensional complexes based on Ir^I, Pt^{II}, CO, CN^-, $O_2C_2O_2{}^{2-}$, and H_2O moieties.[1,2]

In the midst of the typical 1-D complexes[1,2,7] containing small monodentate ligands which presumably minimize steric interaction, e.g., $K_2Pt(CN)_4X_{0.3}{\cdot}3H_2O$ (X = Cl, Br), $K_{1.75}Pt(CN)_4{\cdot}1.5H_2O$, "$Ir(CO)_3Cl$", and (cation)$_{\sim 0.5}Ir(CO)_2Cl_2$, lies a series of partially oxidized complexes based upon the bis(oxalato)platinates,[7,12-17] e.g., (alkali$^+$)$_{\sim 1.64}Pt(ox)_2{\cdot}xH_2O$ [ox = oxalato = $O_2C_2O_2{}^{2-}$]. Although these complexes have not been characterized in detail, powder x-ray data indicate that all of these materials have short intermolecular spacings of $\sim$2.85 Å.[7,14,16] The room-temperature single-crystal conductivity of $K_{1.64}Pt(ox)_2{\cdot}xH_2O$ has been reported to be high,[13] i.e., 42 Ω^{-1} cm^{-1}, suggesting the possibility of a metallic state.[1] The single-crystal x-ray determination of $Mg_{0.86}Pt(ox)_2{\cdot}5.3H_2O$ reveals[12] that adjacent molecules are rotated by $\sim$60° and alternating molecules are eclipsed, Figure 1. The metal atoms form equivalently spaced 1-D chains with an interplanar separation of $\sim$2.85 Å. Thus, the bis(oxalato)platinates form a highly conducting 1-D chain with weak-field bidentate ligands,[18] which by virtue of the weak-field character does not remove electron density (reducing Coulomb repulsion between electrons on the metal[1]) from the metal to the same extent as of strong-field π-acceptor ligands.

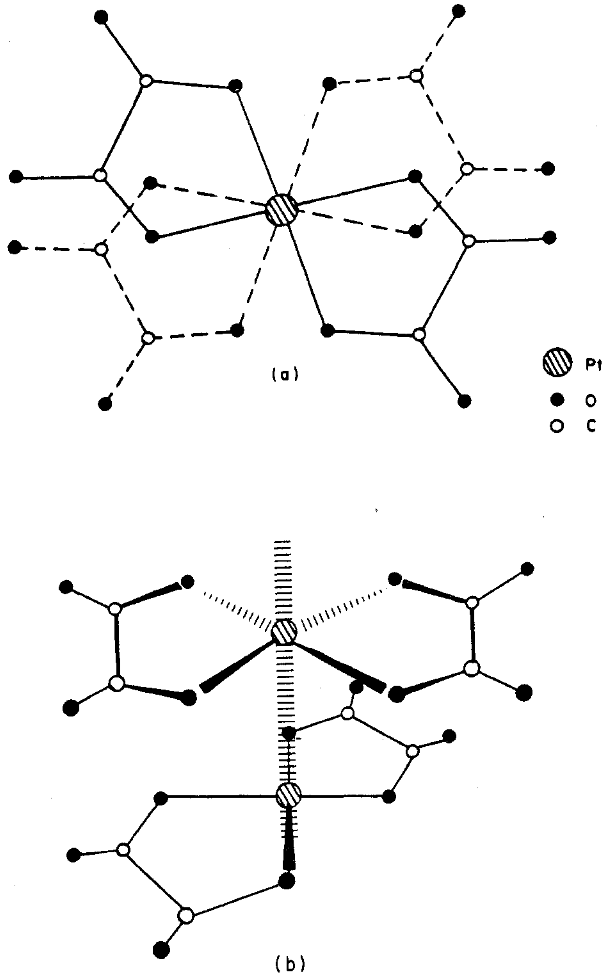


Figure 1. Crystal structure[12] of $Mg_{0.86}Pt(ox)_2{\cdot}5.3H_2O$: (a) top view; (b) side view.

The oxalato ligands require ligand–ligand molecular orbital interactions regardless of whether or not the donor atoms are eclipsed. In spite of the bidentate character of these oxalato ligands the molecular planes are ~2.85 Å apart, thus significantly closer than the sum of the van der Waals radii[19a] for an aromatic group (3.7 Å),[19b,20] a π-type oxygen (3.0 Å),[19a] or a π oxygen plus a π carbon (3.3 Å).[19a] Furthermore, the short interplanar spacings of 3.18 Å reported for $CaPt(ox)_2{\cdot}3H_2O$[24] are 12.5% larger than that reported for the partially oxidized $Ca_{0.84}Pt(ox)_2{\cdot}4H_2O$.[7] These atypical properties may in part be explained in terms of the stabilization of a highly conducting 1-D system by ***intermolecular back-bonding*** between the higher occupied molecular orbitals (HOMO) on one molecule and the lower lying unoccupied molecular orbitals (LUMO) on an adjacent molecule which have the correct symmetry to overlap.[25,26] Furthermore, the intermolecular back-bonding overlap provides an additional mechanism (besides intramolecular d–π^* back-bonding) of reducing the Coulomb repulsion of electrons on the metal. Thus, the relative arrangement of adjacent molecules will be described by the orientation that minimizes the free energy of the system via maximizing the van der Waals forces, the directional intermolecular back-bonding, as well as the electrostatic attraction and dipole interactions between atoms on the adjacent molecule.[27-29] Detailed calculations are necessary to understand the relative importance of each of these contributions.

In order to evaluate intermolecular HOMO–LUMO back-bonding available for the bis(oxalato)platinate system it is necessary to understand the electronic structure of the $Pt(O_2C_2O_2)_2{}^{2-}$ ion which has not been reported in the literature. However, the electronic absorption spectra of $Pt(S_2C_2O_2)_2{}^{2-}$ [30] and $Pt(O_2C_2O_2)_2{}^{2-}$ appear to be shifted with respect to each other. This suggests a similar electronic structure for both of these D_{2h} ions.[31] Thus, the electronic structure of the $Pt(S_2C_2O_2)_2{}^{2-}$ ion can, to a first approximation, be used as a model for evaluating intermolecular back-bonding in $Mg_{0.86}Pt(ox)_2{\cdot}5.3H_2O$.

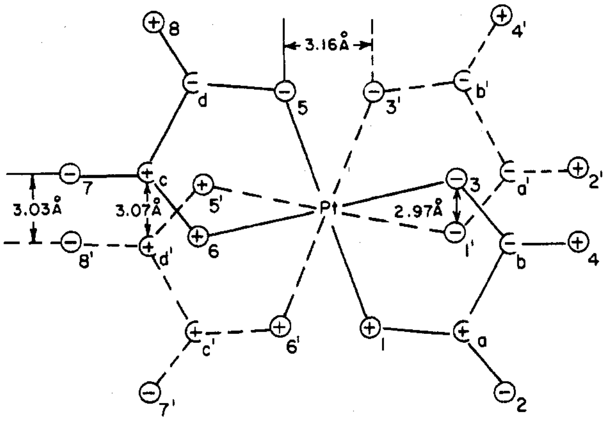


Figure 2. Eight intermolecular back-bonding overlaps between the HOMO (**1**) and LUMO (**3**) of b_{2g} and b_{3g} symmetries, respectively, for the bis(oxalato)platinates. The primed atoms represent the HOMO.

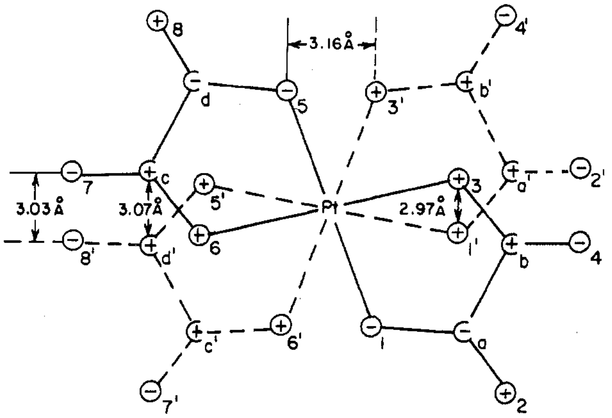
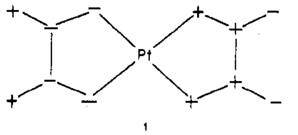
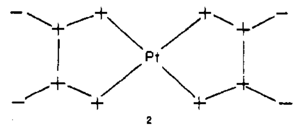


Figure 3. Six intermolecular back-bonding and two intermolecular anti-back-bonding overlaps between the HOMO (**2**) and LUMO (**4**) of b_{1u} and a_u symmetries, respectively. The primed atoms represent the HOMO.

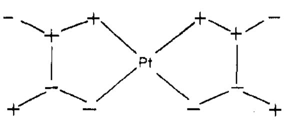
The lower unoccupied out-of-plane ligand π^* orbitals are of b_{2g} (**1**) and b_{1u} (**2**) symmetries whereas the higher occupied orbitals are of b_{3g} (**3**), a_u (**4**), and b_{1u} symmetries.[30]



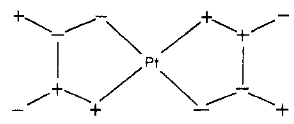
1



2



3



4

Thus, for intermolecular back-bonding the HOMO donates electron density to the LUMO stabilizing the system. This is accomplished through maximum overlap of **1** and **3** (eight back-bonding overlaps) (Figure 2) and additionally via overlap of **2** and **4** (six back-bonding and two anti-back-bonding overlaps) (Figure 3). The overlap of the gerade and ungerade HOMO–LUMO's does not give rise to a net back-bonding situation. Figure 2 depicts the HOMO–LUMO overlap arising from **1** and **3**. The O_3–O_1', O_4–O_2', O_6–O_5', O_7–O_8', O_5–O_3', O_1–O_6', C_b–C_a', and C_c–C_d' orbitals are of the correct symmetry to overlap. The molecular geometry can be described by these overlaps. Rotation of the bottom molecule (primed atoms) counterclockwise increases the overlap of the O_3–O_1', O_5–O_3', O_6–O_5', and O_1–O_6' orbitals but decreases the overlap of the orbitals of O_7–O_8', O_4–O_2', C_b–C_a', C_c–C_d'. Clockwise rotation reverses this situation. Thus, an energy minimum is reached by the structure with a relative 60° rotation between adjacent molecules. This is in accord with the observed structure,[12] Figure 1.

Besides overlap between **1** and **3**, overlap of **2** and **4** is also of the correct symmetry to contribute to intermolecular overlap, Figure 3. The bonding of O_3–O_1', O_4–O_2', O_6–O_5', O_7–O_8', C_b–C_a', and C_c–C_d' is the same as outlined in Figure 2, but in contrast to the **1–3** overlap, anti-back-bonding overlap occurs for O_1–O_6' and O_5–O_3'. Due to the larger O_1–O_6' (and O_5–O_3') interatomic spacings [3.15 Å][12,32] for the anti-back-bonding overlap with respect to the bonding O_3–O_1' (and O_6–O_5') [2.97 Å],[12] O_4–O_2' (and O_7–O_8') [3.03 Å],[12] and C_b–C_a' (and C_c–C_d') [3.07 Å][12] overlaps, net back-bonding occurs. Detailed molecular orbital calculations are necessary to establish the importance of these overlaps as the bonding stabilization is inversely proportional to the energy separation and orbital coefficients. The HOMO–LUMO ligand back-bonding does not significantly alter the observed intramolecular distances of bis(oxalato)platinate in $K_2Pt(ox)_2{\cdot}2H_2O$[33] and in $Mg_{0.86}Pt(ox)_2{\cdot}5.3H_2O$.[12] However, the small differences in the intramolecular distances that are observed[34] are consistent with the back-donation of electron density into the LUMO, but these changes are of the order of those reported for coordinated and noncoordinated CO[19b] and are of the magnitude of typical standard deviations.

This description of intermolecular ligand-bonding stabilization of the 1-D bis(oxalato)platinate system suggests that highly conducting 1-D materials may be prepared from platinum(II) complexes with isoelectronic and isostructural ligand systems. For example, the bis(1,2-dithiooxalato) complex of platinum(II)[35] is an appropriate candidate for observing high conductivity.[1] To date attempts to partially oxidize $Pt(S_2C_2O_2)_2^{2-}$ have not succeeded.[36] It may be that the larger van der Waals radius of sulfur as compared with that of oxygen prevents the necessary close approach,[19] but short intermolecular sulfur interactions have previously been reported, e.g., 3.059 Å for $[Pt(S_2C_2H_2)_2]_2$,[37] suggesting that highly conducting chains with sulfur donor atoms are conceptually feasible.[38] Furthermore, upon oxidation $Pt(S_2C_2O_2)_2^{2-}$ may break the C–C bonds and liberate carbonyl sulfide.[39]

A chain structure where intermolecular planes are separated by less than the van der Waals radii requires a stabilization force to overcome the van der Waals forces. The primary bonding force which contributes to the stabilization of the chain structure is band formation; however, intermolecular HOMO–LUMO back-bonding, dipole–dipole type interactions, and electrostatic attractions are important in stabilizing the close approach of intermolecular planes and in defining the relative orientation of the planes. Where unsaturated chelated complexes form a 1-D chain with close interplanar separations molecular orbital overlaps must be maximized to account (along with dipole interactions which may in some cases alter) for the relative orientation of molecules in a chain.[40] Thus, deviations from geometries predicted for such HOMO–LUMO overlap would not be surprising; however, evaluation of the HOMO–LUMO interactions as well as the other cohesive forces should reveal insight into the binding of one-dimensional complexes and futhermore give insight into the design of new 1-D materials.

Acknowledgment. The author wishes to acknowledge the helpful and stimulating discussions with Drs. G. P. Ceasar, C. B. Duke, R. Eisenberg, A. J. Epstein, J. Kuder, N. O. Lipari, W. A. Little, and G. D. Stucky. A special acknowledgment is made to the Webster Research Center for its introduction of a short course on organic molecular orbital theory ably given by Professor M. J. S. Dewar and to Professor M. J. S. Dewar for his stimulating discussions pertaining to extensions of organic molecular orbital theory to inorganic molecules.

Registry No. $Pt(O_2C_2O_2)_2^{2-}$, 36444-17-4.

References and Notes

(1) J. S. Miller and A. J. Epstein, *Prog. Inorg. Chem.*, **20**, 1 (1976), and references therein.
(2) J. S. Miller, *Adv. Chem. Ser.*, **No. 150**, 18 (1976).
(3) H. J. Keller, Ed., *NATO Adv. Study Inst. Ser., Ser. B*, **7** (1975).
(4) L. V. Interrante, Ed., *ACS Symp. Ser.*, **No. 5** (1975).
(5) H. G. Schuster, Ed., *Lect. Notes Phys.*, **34** (1975).
(6) T. W. Thomas and A. E. Underhill, *Chem. Soc. Rev.*, **1**, 99 (1972).
(7) K. Krogmann, *Angew. Chem., Int. Ed. Engl.*, **8**, 35 (1969).
(8) I. F. Shchegolev, *Phys. Status Solidi A*, **12**, 9 (1972).
(9) H. R. Zeller, *Festkörperprobleme*, **13**, 31 (1973).
(10) W. Gläser, *Festkörperprobleme*, **14**, 205 (1974).
(11) Chain complexes comprised of alternating cations and anions or alternating complexes in different oxidation states have also been the focus of recent study.[1]
(12) K. Krogmann, *Z. Anorg. Allg. Chem.*, **358**, 97 (1968).
(13) F. N. Lecrone, M. J. Minot, and J. H. Perlstein, *Inorg. Nucl. Chem. Lett.*, **8**, 173 (1972).
(14) A. Bertinotti, C. Bertinotti, and G. Jehanno, *C. R. Hebd. Seances Acad. Sci., Ser. B*, **278**, 45 (1974).
(15) K. Krogmann, *NATO Adv. Study Inst. Ser., Ser. B*, **7**, 277 (1975).
(16) K. Krogmann, *ACS Symp. Ser.*, **No. 5**, 350 (1974).
(17) K. Krogmann and P. Dodel, *Chem. Ber.*, **99**, 3402, 3408 (1966).
(18) C. K. Jorgensen, "Modern Aspects of Ligand Field Theory", North-Holland Publishing Co., Amsterdam, 1971, Chapter 26.
(19) (a) A. Bondi, *J. Phys. Chem.*, **68**, 441 (1964); (b) F. A. Cotton and G. Wilkinson, "Advances in Inorganic Chemistry", 3d ed, Wiley, New York, N.Y., 1972.
(20) Planar aromatic organic molecules with some bonding interaction between molecules typically are separated by greater than 3.1 Å [e.g., graphite (3.35 Å),[19] TCNQ in (TTF)(TCNQ) (3.17 Å),[21] TTF in (TTF)(TCNQ) (3.47 Å),[21] $(TCNQ)_2^{2-}$ in $Nb_3Cl_6(C_6Me_6)_3(TCNQ)_2$ (3.10 Å)[22]]. The interplanar spacings in the α and β forms of charge-transfer quinhydrone complex are 3.22[23a] and 3.19 Å,[23b] considerably larger than observed for the bis(oxalato)platinate chain.[12]
(21) T. J. Kistenmacher, T. E. Phillips, and D. O. Cowan, *Acta Crystallogr., Sect. B*, **30**, 763 (1974); T. E. Phillips, T. J. Kistenmacher, J. P. Ferraris, and D. O. Cowan, *J. Chem. Soc., Chem. Commun.*, 471 (1973).
(22) S. Z. Goldberg, B. Spivack, G. Stanley, R. Eisenberg, D. M. Braitsch, J. S. Miller, and M. Abkowitz, submitted for publication.
(23) (a) T. Sakurai, *Acta Crystallogr.*, **19**, 320 (1965); (b) T. Sakurai, *Acta Crystallogr., Sect. B*, **24**, 403 (1968).
(24) K. Krogmann, *Z. Naturforsch., B*, **23**, 1012 (1968).
(25) The primary stabilization force for the 1-D chain arises from band formation; however, since the intermolecular planes are typically less than the sum of the van der Waals radii, the relative orientation must be described by several attractive components to the binding energy.
(26) Beside band formation a molecule in an infinite chain would gain twice as much intermolecular back-bonding stabilization per molecule than would occur in a dimer.
(27) HOMO–LUMO donor–acceptor charge-transfer overlap interactions are the basis of Mulliken's "overlap and orientation principle" [R. S. Mulliken, *Recl. Trav. Chim. Pays-Bas*, **75**, 845 (1956)] which, along with excited-state HOMO–LUMO interactions, van der Waals interactions, and dipole interactions, describe the relative orientation of parallel molecular planes separated by less than 3.5 Å [B. Mayoh and C. K. Prout, *J. Chem. Soc., Faraday Trans. 2*, 1072 (1972); see also I. Goldberg, *Theor. Chim. Acta*, **40**, 271 (1975)].
(28) Overlap of the partially filled b_{2g} HOMO orbitals on adjacent segregated molecular planes of 7,7,8,8-tetracyano-*p*-quinodimethanide ($TCNQ^-$) has been used to describe the structures found for various structures of conducting charge-transfer TCNQ salts [A. F. Garito and A. J. Heeger, *Acc. Chem. Res.*, **7**, 232 (1974)].
(29) A directed structural arrangement involving HOMO–LUMO interactions at ~3.5 Å has been reported for the interaction between ClF and Ar [S. J. Harris, S. E. Novick, W. Klemperer, and W. E. Falconer, *J. Chem. Phys.*, **61**, 193 (1974)]. Likewise, intermolecular back-bonding has also been reported for trigonal Se and Te [R. M. Martin, G. Lucovsky, and K. Helliwell, *Phys. Rev.*, **13**, 1383 (1976)]. Furthermore, similar

HOMO–LUMO arguments have been used to describe the Ag^+–benzene and Ag^+–ethylene interactions [R. S. Mulliken and W. B. Person, "Molecular Complexes", Wiley-Interscience, New York, N.Y., 1969, Chapter 17].

(30) (a) A. R. Latham, V. C. Hascall, and H. B. Gray, *Inorg. Chem.*, **4**, 788 (1965); (b) D. Coucouvanis, N. C. Baenziger, and S. M. Johnson, *J. Am. Chem. Soc.*, **95**, 3875 (1973).

(31) J. S. Miller, D. G. Marsh, and J. W. Lewicki, unpublished results.

(32) The larger spacings of O_5–O_3' and O_1–O_6' can be rationalized by the weighted contribution of both back-bonding overlaps depicted in Figures 2 and 3.

(33) R. Mattes and K. Krogmann, *Z. Anorg. Allg. Chem.*, **332**, 247 (1964).

(34) Unfortunately the standard deviations for the bond lengths and angles are not reported.

(35) E. G. Cox, W. Wardlow, and K. C. Webster, *J. Chem. Soc.*, 1475 (1935).

(36) J. H. Perlstein, private communication.

(37) K. W. Browall, T. Bursh, L. V. Interrante, and J. S. Kasper, *Inorg. Chem.*, **11**, 1800 (1972); K. W. Browall, L. V. Interrante, and J. S. Kasper, *J. Am. Chem. Soc.*, **93**, 6289 (1971).

(38) Although close approach of sulfur atoms (~3.0 Å) has been characterized,[37] smaller interplanar separations (<2.9 Å) appear to be necessary for allowing strong overlap and band formation.[1]

(39) D. Coucouvanis, private communication.

(40) HOMO–LUMO intermolecular back-bonding considerations have also revealed 12 back-bonding overlaps for $M(HDMG)_2$ (M = Ni, Pd, Pt; H_2DMG = dimethylglyoxime) when adjacent planes are rotated by 90° and a maximum number of four back-bonding overlaps when adjacent molecular planes are rotated by 180° for $M(CO)_2(acac)$ (M = Rh, Ir; Hacac = acetylacetone). These and other results will be discussed in subsequent papers.

Contribution from the Department of Chemistry,
Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061

Structural Changes in Cobalt(II) Complexes Resulting from Nonsteric Substituent Effects with Potentially Five-Coordinate Ligands[1]

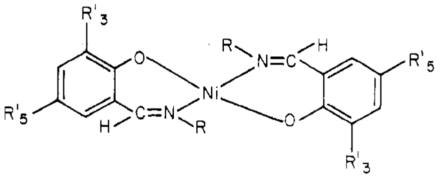
R. H. NISWANDER and L. T. TAYLOR*

Received November 20, 1975 AIC508421

Linear, potentially pentadentate Schiff base ligands derived from various salicylaldehydes (*R*-SAL) and bis(3-aminopropyl) ether (DAPE), bis(3-aminopropyl) sulfide (DAPS), or bis(3-aminopropyl)phenylamine (PhDPT) represent a series of chelate compounds in which the central donor atom is varied. Cobalt(II) complexes of these ligands have been isolated and characterized via elemental analysis, infrared–visible spectra, and magnetic susceptibility. The structure of these complexes depends upon the aromatic substituents in the molecule. This is the first report of structural changes in complexes of this type resulting from nonsteric substituent effects. The results are discussed in terms of the electronic effect of the substituents.

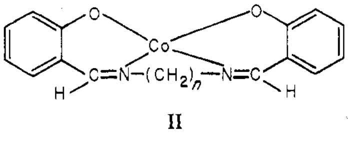
Introduction

The stereochemical and structural features imposed on a metal complex by Schiff base ligands have been the subject of numerous studies.[2a] Most of the systematic studies that have been carried out have investigated the steric effects of ligand substituents. Many of these studies have dealt with the coordination of nickel(II) and cobalt(II) ions. A good example of these investigations is illustrated by the nickel(II) salicylaldimine complexes shown in structure I. Upon increasing the bulkiness of the R group, the complex stereochemistry in the solid state changes from a diamagnetic square-planar structure to a paramagnetic tetrahedral arrangement. In general the effect of a benzene ring substituent, R′, on the stereochemistry of these complexes is minimal[2b] (R′ = H, 3-CH_3, 5-CH_3, 3-Cl, 3-Br, 3-NO_2, 3,5-benzo, 5-NO_2, 3,4-benzo).

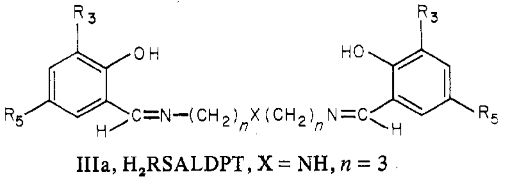


I

A ligand-promoted configurational change has also been observed with linear tetradentate ligands derived from salicylaldehyde and long-chain diamines bound to cobalt(II)[3] (structure II). With increasing chain length joining azomethine linkages, tetrahedral geometries become favored over square-planar ones. The effect of ring substitution on the resulting complex stereochemistry was not investigated, though it might be concluded that the stereochemical effect of electron-withdrawing and electron-donating groups on these salicyladehyde-related ligands is negligible. This conclusion is supported by the fact that Zn(II), Cu(II), Ni(II), Co(II), and Mn(II) complexes incorporating linear pentadentate ligands derived from variously substituted salicylaldehydes and either bis(3-aminopropyl)amine, $H_2RSALDPT$ (IIIa), or bis(3-aminopropyl)methylamine, $H_2RSALMeDPT$ (IIIb), have been shown to be isomorphous[4] (R = H, 5-CH_3, 5-C_2H_5, 3,4-benzo, 5,6-benzo, 5-Cl, 3-Cl, 3,5-Cl_2, 5-Br). Also, $H_2RSALDAES$ (IIId), a potentially pentadentate ligand, was shown to produce four-coordinate complexes with cobalt(II) regardless of the substituent[5] (R = H, 5-NO_2, 5-Br, 5-CH_3, 3-$(CH_3)_2CH$). Studying a related group of potentially pentadentate ligands we have noticed differences in the solid-state structure of cobalt(II) complexes which appear to depend on the coordinating properties of the central donor.[6] If the central donor is P-CH_3 (IIIc, R = H) or N-C_6H_5 (IVc, R and R′ = H), five-coordinate cobalt complexes are observed, while ether (IVb, R = H) and thioether (IVa, R = H) donors result in cobalt(II) complexes which are four-coordinate



II



IIIa, $H_2RSALDPT$, X = NH, *n* = 3
b, $H_2RSALMeDPT$, X = NCH_3, *n* = 3
c, $H_2RSALDAPP$, X = PCH_3, *n* = 3
d, $H_2RSALDAES$, X = S, *n* = 2