B_5H_{11}, 18433-84-6; B_6H_{10}, 23777-80-2; $B_{10}H_{14}$, 17702-41-9.

Acknowledgments. We thank W. N. Lipscomb, E. Tolpin, K. Kustin, and S. Hermanek for reading and commenting on the manuscript. This work was supported in part by grants from the Research Corp., the National Institutes of Health (Biomedical Grant RR 7044-06), and the Petroleum Research Fund, administered by the American Chemical Society.

Department of Chemistry,
Brandeis University
Waltham, Massachusetts 02154
Irving R. Epstein

Received June 12, 1972

Antisymbiosis and the Trans Effect

Sir:

The concept of chemical symbiosis was introduced by Jorgensen in 1964[1] and has proved useful in understanding a number of chemical facts. The interpretation of symbiosis is very simple: hard bases (electronegative donor atoms) retain their valence electrons when attached to a given central atom, hence keeping the positive charge of that atom high and making it a hard Lewis acid. Soft bases (donor atoms of low electronegativity) substantially give up their valence electrons to the same central atom, reducing its positive charge and making it a softer Lewis acid.

Despite this elementary interpretation and its obvious predictions, it has been known for some time that class b metal ions, more often than not, behave in an antisymbiotic manner.[2] That is, soft bases attached to an already soft Lewis acid can lower the affinity for another soft base. An example would be the synthesis of *trans*-$Ir[P(C_6H_5)_3]_2(CO)NCS$, which is the N-bonded, rather than the S-bonded, linkage isomer expected for the soft iridium(I) acceptor atom.[2]

The purpose of this note is to point out a number of examples of antisymbiosis for class b metal ions and to show that a simple explanation exists based on the trans effect or trans influence.[3] The examples show that far reaching consequences exist for the structure, stability, and reactivity of complexes of the class b metal ions.

In 1968, Chatt and Heaton pointed out "that groups of high trans effect, as ethylene in $Pt(C_2H_4)Cl_3^-$, render the position in mutual trans position more susceptible to bonding by what are now known as hard bases."[4] They also pointed out that this result was a natural consequence of the theory of the trans effect. Whether a trans activating group is a σ donor or a π acceptor is of little consequence.[5] In either case it is advantageous to have an ionic ligand trans to a strongly covalent ligand.

The evidence of Chatt and Heaton dealt with the kinds of coligands that would stabilize hydroxo complexes of platinum(II). Tobias discussed the stabilities and structures of alkyl derivatives of the transition metals.[6] He pointed out that all dialkyl derivatives of gold(III) had cis structures, virtually all dialkyl derivatives of platinum(II) and platinum(IV) also had cis structures, and all trialkyl complexes of Pt(IV) had fac structures. An explanation was given in terms of the trans influence of one alkyl ligand on another, leading to mutual repulsion. Alkyl groups are known to have a high trans influence.

Since ligands of large trans influence are invariably soft bases, we can put the rules of Chatt and Heaton, and of Tobias, into a more compact form: *two soft ligands in mutual trans position will have a destabilizing effect on each other when attached to class b metal atoms.* That is, they will show antisymbiotic behavior. This rule explains many otherwise puzzling phenomena.

For example, it has been found that *cis*-$Rh(CO)_2Cl_2^-$ is formed in preference to $Rh(CO)_2I_2^-$ and that the thermodynamically stable form of *cis*-$Ir(CO)_2X_4^-$ is $Ir(CO)_2Cl_2I_2^-$ with Cl trans to CO.[7] Since Rh(I) is normally a soft metal ion, the preference for Cl^- over I^- must be due to the CO ligand trans to halogen.

Dimethylmercury is readily cleaved by dilute acid to form $CH_3HgH_2O^+$. However, this cation resists cleavage even by a strong mineral acid.[8] While the methylmercury cation is often regarded as the prototype soft acid, it must now be borne in mind that its affinity for soft bases is markedly reduced by virtue of the CH_3^- ligand in the trans position.

The Pd(II) and Pt(II) ions in dimethyl sulfoxide solution form a solvate with two S-bonded and two O-bonded solvent molecules, in mutual cis positions.[9] There are a number of chelate complexes containing ligands with both S and O donors, or S and N donors. The structures of these always show that each S-donor atom has an O- or N-donor atom trans to it for planar Pd(II) and Pt(II) and for octahedral Co(III) and V(III) complexes.[10] This is not true for planar Ni(II), nor is it necessarily expected, since Ni(II) is not a class b metal ion.

As already mentioned, soft ligands can make a soft metal ion invert its normal preference for S over N in thiocyanate complexes.[2,11] The explanation offered here is that the inversion results when the thiocyanate ligand binds trans to a soft ligand. This may not cover every case since steric factors can also enter in. Very few structures are known. A fascinating example is PdL(NCS)(SCN), where L is 1-diphenylphosphino-3-dimethylaminopropane. The structure is as predicted: the N-bonded thiocyanate is trans to P and the S-bonded thiocyanate is trans to N.[12]

The classic example of $Pt[P(C_2H_5)_3]_2(NCS)_2$ reported by Turco and Pecile[13] is thus predicted to be the cis isomer. From kinetic behavior, it is clear that *trans*-$Pt[P(C_2H_5)_3]_2Cl_2$ reacts with thiocyanate ion to form the S-bonded isomer, at least initially.[14]

Table I shows some data for the first and second formation constants of complexes of Cu(I), Ag(I), Hg(II), and Cd(II)

---

[1] C. K. Jorgensen, *Inorg. Chem.*, 3, 1201 (1964).

[2] N. J. DeStefano and J. Burmeister, *Inorg. Chem.*, 10, 998 (1971).

[3] "Trans effect" refers to rate phenomena and "trans influence" to ground-state phenomena: A. Pidcock, R. E. Richards, and L. Venanzi, *J. Chem. Soc. A*, 1707 (1966).

[4] J. Chatt and B. T. Heaton, *J. Chem. Soc. A*, 2745 (1968).

[5] C. H. Langford and H. B. Gray, "Ligand Substitution Processes," W. A. Benjamin, New York, N. Y., 1965, Chapter 2.

[6] R. S. Tobias, *Inorg. Chem.*, 9, 1296 (1970).

[7] D. Forster, *Inorg. Chem.*, 11, 1686 (1972).

[8] G. Schwarzenbach and M. Schellenberg, *Helv. Chim. Acta*, 48, 28 (1965).

[9] J. H. Price, A. N. Williamson, R. F. Schramm, and B. B. Wayland, *Inorg. Chem.*, 11, 1280 (1972).

[10] R. H. Holm, *Progr. Inorg. Chem.*, 14, 241 (1972); J. S. Gordon, M. J. O'Connor, and R. H. Holm, *Inorg. Chim. Acta*, 5, 381 (1971); S. E. Livingstone, *Coord. Chem. Rev.*, 7, 59 (1971).

[11] J. L. Burmeister, *Coord. Chem. Rev.*, 1, 205 (1966); 3, 225 (1968).

[12] G. R. Clark and G. J. Palenik, *Inorg. Chem.*, 9, 2754 (1970).

[13] A. Turco and C. Pecile, *Nature (London)*, 191, 66 (1961).

[14] U. Belluco, L. Cattalini, F. Basolo, R. G. Pearson, and A. Turco, *J. Amer. Chem. Soc.*, 87, 241 (1965). However see C. Pecile, *Inorg. Chem.*, 5, 210 (1966).

Table I. Stability Constants for Formation of ML (K_1) and ML_2 (K_2) in Water at 25°[a]

		DOP	DPM	NH_3
Cu^+	$\log K_1$	12.60		5.93
	$\log K_2$	7.74		5.93
Ag^+	$\log K_1$	11.53		3.39
	$\log K_2$	9.02		3.92
Hg^{2+}	$\log K_1$		14.3	8.8
	$\log K_2$		10.3	8.7
Cd^{2+}	$\log K_1$	3.94	0.90	2.65
	$\log K_2$	3.75	2.48	2.10

[a] DOP = $P(C_2H_5)_2(C_2H_4OH)$; DPM = $P(C_6H_5)_2(C_6H_4SO_3)^-$. Data from ref 15.

with monodentate phosphine and ammine ligands.[15] For the first three metal ions, which should form linear bis complexes, there is obviously a reluctance to add the second phosphine ligand, but not the second ammine ligand. Cadmium ion, which should form a pseudotetrahedral complex, does not show this antisymbiotic behavior.

Cobalt(III) is a metal ion subject to symbiotic effects. For example, the corrin ring or porphyrin rings as cis ligands convert the normally hard Co(III) center into a relatively soft center. However, an alkyl group attached to cobalt in these complexes has an antisymbiotic effect on the position trans to it.[16]

A great deal of rate data on platinum(II) complexes has been accumulated.[14,17] A very strong symbiotic effect is found in the rates when soft ligands are in the cis position to the leaving group. Thus *trans*-$Pt[P(C_2H_5)_3]_2Cl_2$ reacts very slowly with hard bases and very rapidly with soft bases, compared to *trans*-$Pt(py)_2Cl_2$. The same is true for Pt(bipy)-SCNCl, compared to $Pt(bipy)Cl_2$. However, *trans*-$Pt(py)_2$-CH_3Cl shows an antisymbiotic effect.[18]

Metal carbonyls of the formula $M(CO)_nL$, where $n = 4$ or 5, are activated toward substitution when L is a halogen or an N or O atom donor but not when L is a C, S, P, or As atom donor.[19] This behavior represents a normal symbiotic effect, the complex containing mixed hard and soft ligands being destabilized. However it is always a CO group trans to another CO group which is replaced.

An examination of the structures of transition metal hydrides shows a remarkably consistent pattern of behavior.[20] There are some hundreds of structures available for compounds of the general formula $ML_l(CO)_mX_nH_o$ where L is a phosphine or arsine and X is a halogen or an O- or N-type donor ligand. With only two or three exceptions, all hydrides are cis to each other and not trans. H and CO usually avoid being trans to each other. The relatively hard ligand X is always trans to either H or CO and never trans to L, unless $n > 1$. The same pattern of behavior is found for alkyl complexes of the heavier transition metals.[21]

We can understand these structural features in terms of the instability of two soft ligands trans to one another, if the order of decreasing softness is $R^-, H^- > CO > L > X$. The structures of the adducts formed when H_2, RX, HX, etc., undergo oxidative addition to $IrL_2(CO)X$ and related molecules are also seen to fall into a logical pattern.[22]

Antisymbiotic behavior has been related in the previous examples to the operation of trans influences. It is well known that the trans effect diminishes in ascending a group in the periodic table. Thus *trans*-dialkyl or -diaryl complexes are quite rare for Pt(II) and more common for Pd(II) and Ni(II).[21b] The rule of mutual destabilization of two soft ligands trans to one another is weaker for the first transition series than for the third. This shows up in the structures of chelates containing S and O donors, or S and N donors, as mentioned earlier.

The trans influence is undoubtedly a result of strong covalent bonding. Thus it is not expected in complexes where the bonding is primarily ionic, as is usually true for class a metal ions.[23] For such metal ions *trans*-dialkyl or -diaryl ligands are common.

Tetrahedral complexes should show diminished antisymbiotic effects, since no true trans positions exist. Nevertheless, a similar competition for orbitals is still present, though diluted. For example, $Cu(NH_3)_2(SCN)$ contains S-bonded thiocyanate, as expected for Cu(I). But Cu-(DPPA)(NCS), where DPPA is $(C_6H_5)_2PCCP(C_6H_5)_2$, contains N-bonded thiocyanate.[24]

Finally it should be noted that any factors not included in the simple explanation for symbiosis given initially can also produce opposing effects. These include steric factors, solvation phenomena, and strong ligand to metal π bonding. Such π bonding may account for the fact that symbiosis is very pronounced in organic chemistry (carbon as central atom) but is weak or nonexistent in the remaining group IV elements (Si, Ge, Sn, Pb).[25]

Acknowledgment. This work was partly supported by the National Science Foundation under Grant GP31060X.

---

[15] M. Meier, Dissertation, ETH, Zurich, 1967.

[16] R. A. Firth, H. A. O. Hill, J. M. Pratt, R. G. Thorp, and R. J. P. Williams, *Chem. Commun.*, 400 (1967).

[17] L. Cattalini and M. Martelli, *Inorg. Chim. Acta*, **1**, 189 (1967).

[18] U. Belluco, M. Graziani, and P. Rigo, *Inorg. Chem.*, **5**, 1123 (1966).

[19] J. J. Graham and R. J. Angelici, *Inorg. Chem.*, **6**, 988 (1967). A special mechanism, ligand migration, probably operates when $L^- = H^-$.

[20] J. P. Jesson in "Transition Metal Hydrides," E. L. Muetterties, Ed., Marcel Dekker, New York, N. Y., 1971, Chapter 4.

[21] (a) J. D. Ruddick and B. L. Shaw, *J. Chem. Soc. A*, 2801 (1969); (b) G. E. Coates, M. L. H. Green, and K. Wade, "Organometallic Compounds," Vol. II, Methuen, London, 1968, Chapter 7.

[22] D. M. Blake and M. Kubota, *Inorg. Chem.*, **9**, 989 (1970); L. M. Haines, *ibid.*, **10**, 1693 (1971).

[23] Covalent bonding may also be related to the use of d orbitals, and ionic bonding to the use of p orbitals of the metal, as suggested by Tobias.[6]

[24] A. J. Carty and A. Efraty, *Inorg. Chem.*, **8**, 543 (1969). See also A. P. Gaughan, R. F. Ziolo, and Z. Dori, *Inorg. Chim. Acta*, **4**, 640 (1971).

[25] R. G. Pearson and J. Songstad, *J. Amer. Chem. Soc.*, **89**, 1827 (1967); J. C. Lockhart, *Chem. Rev.*, **65**, 131 (1965).

Department of Chemistry
Northwestern University
Evanston, Illinois 60201

Ralph G. Pearson

Received August 15, 1972

Computer Generation of Cubic Molecular Symmetry Orbitals

Sir:

It is well known that the use of symmetry in molecular orbital studies of moderately large molecules greatly reduces the amount of calculation required and helps to classify the results in a very convenient manner. A starting point in such calculations is the deduction of a basis set of symmetry-adapted linear combination of atomic orbitals (SA-LCAO). Often such a step is accomplished by inspection,[1] sometimes

---

[1] (a) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962; (b) C. J. Ballhausen and H. B. Gray, "Molecular Orbital Theory," W. A. Benjamin, New York, N. Y., 1965; (c) F. A. Cotton, "Chemical Applications of Group Theory," 2nd ed, Interscience, New York, N. Y., 1971, Chapter 6.