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Magnetic Circular Dichroism and Optical Spectroscopy of *trans*-$[RuX_4L_2]^-$

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Lowest energy electronic excitation bands of dominating, medium optical intensities (ca. 1 D^2) of three members of the title series of compounds (X = Cl, L = PPh_3, $AsPh_3$; X = Br, L = $AsPh_3$ (Ph = phenyl)) are shown to be primarily of ligand-to-metal charge-transfer origin. These excited states correspond to bands in the region 330–1200 nm and are assigned on the basis of their optical and Faraday *C*-term behaviors. This order of excited states is established: $^2A_{2u}(\sim\sigma L \rightarrow \sim Ru) < {}^2A_{2u}(\sim\pi X \rightarrow \sim Ru) < \Gamma_{7u}[^2E_u](\sim\pi X \rightarrow Ru) < \Gamma_{6u}[^2E_u](\sim\pi X \rightarrow Ru) < {}^2B_{2u}(\sim\pi X \rightarrow Ru)$.

Introduction

This study of the title series of compounds, of which there exist three members (X = Cl, L = PPh_3, $AsPh_3$; X = Br, L = $AsPh_3$ (Ph = phenyl)), was undertaken for several reasons. High-symmetry d^5 systems are of general interest due to the usual presence of charge-transfer bands most often accessible to optical and magnetic CD (MCD) instrumentation.[1-8] Molecules of this configuration are also of chemical importance because the order of excited states is expected to follow more closely the order of molecular orbitals than in systems having more than one open shell upon excitation from the ground state.

A previous room-temperature optical study[9] of one of the complexes, the chloro–arsine complex, or $[RuCl_4(AsPh_3)_2]^-$, assigned two bands of that species as d → d transitions, but these workers did not have access to MCD for additional characterization. Previous experience with ruthenium(III) complexes and the presence of reasonably large molar extinction coefficients associated with those bands (1000–3000 l./(mol cm)) of the chloro–arsine complex led us to subject this series[9,10] to MCD and variable-temperature optical studies.

Another reason for undertaking this study was to compare the state orders of these ruthenium(III) species with those of the similar $5d^5$ iridium(IV) species investigated by Rowe et al.[8] Ligand field theory can predict reliably that d → d state orders are the same for similar species of the two d^5 metals, but little can be said a priori of the relative orders of the charge-transfer states because of the lack of proven methods of complete multicenter energy calculations for ground and excited states of such large molecules.

Experimental Section

The compounds were prepared by methods of Stephenson and Wilkinson[11] and of Stephenson.[12,13] Electronic absorption spectra were taken with a Cary 14 spectrophotometer. The ca. 195 K spectra were obtained in solutions using dry ice–acetone cryogen and were carefully corrected for contraction. Temperatures were measured with a calibrated copper–constantan thermocouple.

Instrumentation for the MCD spectra was as previously described.[14]

Results and Discussion

We will first consider the question of whether the major bands of these complexes are d → d or charge transfer in nature. Figure 1 shows the temperature-independent nature of the intense bands of all three species in methanol solution. This behavior confirms the g ↔ u (not d → d) nature of the dominant bands. Additionally, this feature and the relative band positions of the three spectra collectively indicate that these intense transitions are halide-to-metal excitations; i.e., the band positions of the two chloro complexes are essentially the same, whereas the spectrum of the bromo species is shifted to the red as expected from the relative ease of removing electrons from bromine as compared to chlorine. Other evidence follows.

Upon comparison of these spectra (Figure 1) of $[RuX_4L_2]^-$ with those of similar Ir(IV) species,[8] there first arises the question of whether or not the lowest energy band (assigned to a L → Ir transition) observed in the iridium species is present in these ruthenium complexes. Careful examination of chloroform solution spectra (Figure 2) of each of the three complexes studied here showed a band of low energy and relatively low intensity similar to that seen by Rowe et al.[8] It was not possible to measure the temperature dependence of these red bands in chloroform solution due to the limited solubilities of the compounds in this solvent (10-cm cells were required). However, one of the complexes, $[RuBr_4(AsPh_3)_2]^-$, is quite soluble in acetone, and Figure 2 shows the approximate temperature independence of the peak and red side of this band.

The band positions of all three complexes (Figures 1 and 2) are solvent dependent, which is another indication that the transitions (350–600 nm) are of ligand–metal charge transfer origin.[15] Intra-d-shell transitions would not be expected to show such large changes in energy in different solvents.

It is concluded that all the major bands seen in the visible region of the optical spectra of these complexes are of charge-transfer origin. This conclusion is based on the *combined* evidence of five observations: (i) the magnitude of extinction coefficients, (ii) the temperature independence of the optical band intensities, (iii) the red shifts of the bands as heavier ligands replace lighter ones, (iv) the solvent dependence of the band positions, and (v) the near invariance of positions of the visible bands as L is changed from PPh_3 to $AsPh_3$ in $[RuCl_4L_2]^-$. While some d–d bands are probably present, it can be concluded that the intensities of the visible peaks are dominated by the charge-transfer bands.

We now consider the band assignments, for which optical spectroscopy by itself is not sufficient. MCD[16] and the analysis of Faraday *C*-term behavior has proven to be a most valuable technique in identifications of this nature.[1-8] However, the band at lowest energy of each complex (Figure 2) is at the moment not accessible to our MCD apparatus. The identification of this red band is made on other evidence, therefore. The temperature independence of the band (Figure 2) indicates that it is a charge-transfer transition, and the shift toward the red of this band in the chloro–arsine as compared to the chloro–phosphine complex (Figure 2) strongly suggests that it is a L → Ru transition (vide supra). Semiempirical molecular orbital calculations previously shown to be reliable[17-20] predict a low-energy transition from a phosphine-(or arsine-)localized a_{2u} MO. These data are in agreement with the assignments for the similar Ir(IV) compounds,[8] and therefore the red band is assigned as the transition to $^2A_{2u}$($\sim\sigma$L) (see Figure 3).

The remaining bands of the complexes in the visible region of the spectra are assigned primarily on the basis of their MCD behavior. Figure 4 shows the temperature dependence of the MCD spectrum of $[RuBr_4(AsPh_3)_2]^-$ in an isotropic poly(methyl methacrylate)matrix. The major value of this spectrum is that it shows the Faraday *C*-term behavior of the bands in this region. Unfortunately, the two chloro complexes proved impossible to place in a matrix in which the MCD temperature dependence might be measured. However, we

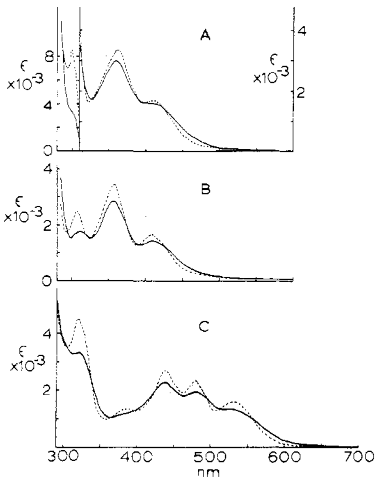

Figure 1. Effect of temperature on optical spectra of *trans*-$[RuX_4L_2]^-$ in methanol solution: A, X = Cl, L = PPh_3; B, X = Cl, L = $AsPh_3$; C, X = Br, L = $AsPh_3$; —— denotes ambient room temperature (ca. 295 K); - - - denotes *ca.* 195 K.

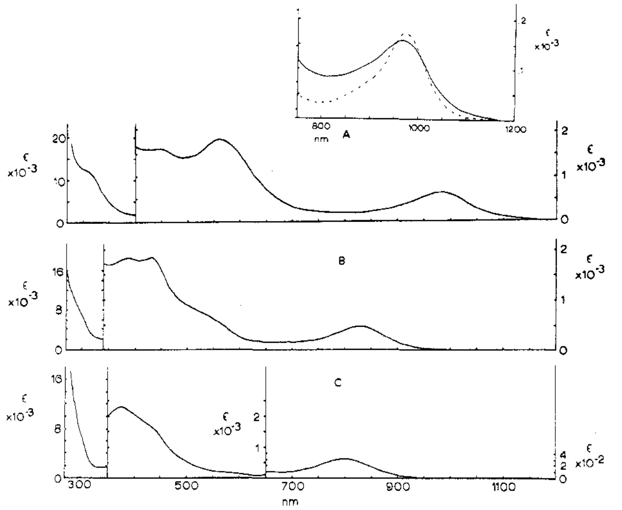

Figure 2. Room temperature optical spectra of *trans*-$[RuX_4L_2]^-$ in chloroform solution (10-cm path length): A, X = Br, L = $AsPh_3$; B, X = Cl, L = $AsPh_3$; C, X = Cl, L = PPh_3; A (insert), $([CH_3(CH_2)_3]_4N)[RuBr_4(AsPh_3)_2]$ in acetone solution.

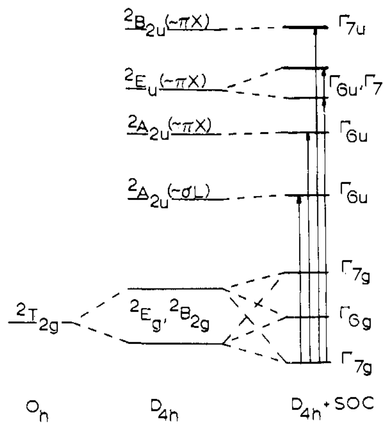

Figure 3. Energy levels of *trans*-$[RuX_4L_2]$ (see text).

interpret the room-temperature MCD spectra of the three complexes by analogy on the basis of *C* terms, this being the usual dominating MCD effect in Ru(III) systems[1,6] and there being no reason to expect the chloro complexes to behave very differently from the bromo member of the series.

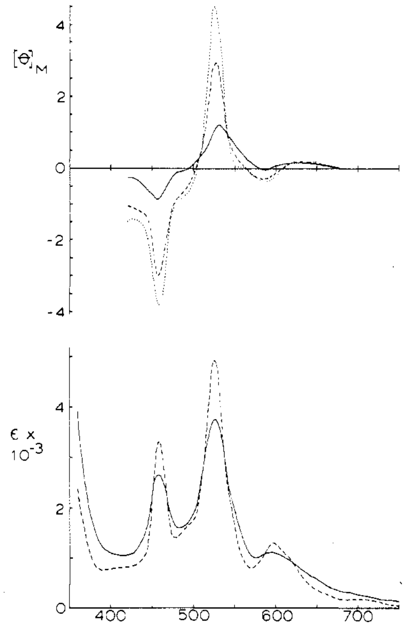

Figure 4. Effect of temperature on MCD and optical spectra of *trans*-$[RuBr_4(AsPh_3)_2]^-$ in polymethylmethacrylate. MCD: ——, 295 K; - - - -, 204 K; · · · ·, 143 K. Abs: ——, 299 K; - - - -, 84 K.

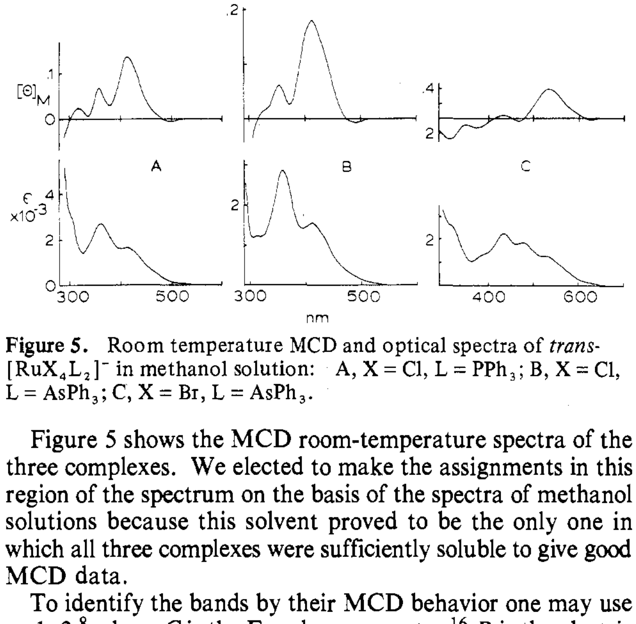

Figure 5. Room temperature MCD and optical spectra of *trans*-$[RuX_4L_2]^-$ in methanol solution: A, X = Cl, L = PPh_3; B, X = Cl, L = $AsPh_3$; C, X = Br, L = $AsPh_3$.

Figure 5 shows the MCD room-temperature spectra of the three complexes. We elected to make the assignments in this region of the spectrum on the basis of the spectra of methanol solutions because this solvent proved to be the only one in which all three complexes were sufficiently soluble to give good MCD data.

To identify the bands by their MCD behavior one may use eq 1–3,[8] where *C* is the Faraday parameter,[16] *D* is the electric

$$\frac{C}{D}[\Gamma_{7g} \rightarrow \Gamma_{6u}(^2A_{2u})] = -{}^1/_4 g_z \text{ BM} \tag{1}$$

$$\frac{C}{D}[\Gamma_{7g} \rightarrow \Gamma_{7u}(^2B_{2u})] = +{}^1/_4 g_z \text{ BM} \tag{2}$$

$$\frac{C}{D}[\Gamma_{7g} \rightarrow (\Gamma_{6u} + \Gamma_{7u})(^2E_u)] = \frac{-AZg_y}{2(A^2 + Z^2)} \text{ BM} \tag{3}$$

dipole strength of the band, Γ_{7g} is the spin–orbit coupled (SOC) ground state (octahedral $^2T_{2g}$ parentage—see Figure 3), Γ_{6u} and Γ_{7u} are the SOC excited states deriving from the D_{4h} parents in parentheses, g_y and g_z are the principal-axis ESR *g* values, and *A* and *Z* are defined as in

$$g_y = 2[2AZk + Z^2] \text{ BM} \tag{4}$$

$$g_z = 2[2A^2(k + 1) - Z^2] \text{ BM} \tag{5}$$

Table I. Calculated Faraday *C*/*D* Ratios[a] from Experimental ESR Parameters[b]

	$[RuCl_4(PPh_3)_2]^-$	$[RuCl_4(AsPh_3)_2]^-$	$[RuBr_4(AsPh_3)_2]^-$
g_y	−2.43	−2.47	−2.57
g_z	1.78	1.74	1.68
$(C/D)(\Gamma_{7g} \rightarrow A_{2u})$	−0.445	−0.435	−0.420
$(C/D)(\Gamma_{7g} \rightarrow {}^2B_{2u})$	+0.445	+0.435	+0.420
$(C/D)(\Gamma_{7g} \rightarrow {}^2E_u)$	+0.166 (net)	+0.183 (net)	+0.208 (net)

[a] Units of BM. [b] Values from ref 10.

Table II. Positions,[a] Intensities,[a] and Assignments of Charge-Transfer Bands of *trans*-$[RuX_4L_2]^-$

	Position				
	Wavelength[b]	Energy[c]	ϵ_{max}[d]	Sign of *C* parameter	Excited-state assignment
I[f]	797[e]	12.5[e]	310[e]		$^2A_{2u}(\sim\sigma L)$
II[g]	828[e]	12.1[e]	463[e]		
III[h]	982[e]	10.2[e]	682[e]		
I	410	24.4	1490	−	$^2A_{2u}(\sim\pi X)$
II	410	24.4	1420	−	
III	530	18.9	1420	−	
I	361	27.7	2981	−	
II	357	28.0	2894	−	$^2E_u(\sim\pi X)$
III	480	20.8	1960	+ (Γ_{7u})	
	436	22.9	2270	− (Γ_{6u})	
III	385	26.0	1160	+	$^2B_{2u}(\sim\pi X)$
I	302	33.1	3320	−	
II	310	32.3	2034	−	
III	322	31.1	3815	+	

[a] In methanol solution except as noted (see Figures 1 and 5). [b] Units of nm (1 nm = 10 Å). [c] Units of kK (1 kK = 1000 cm^{-1}). [d] Units of l./(mol cm). [e] Chloroform solution. [f] $[RuCl_4(PPh_3)_2]^-$. [g] $[RuCl_4(AsPh_3)_2]^-$. [h] $[RuBr_4(AsPh_3)_2]^-$.

where *k* is the orbital reduction factor. Values of g_y, g_z, and *k* are given by DeSimone and Drago.[10] Table I reproduces those values and the values of *C*/*D* which we derived from the above equations.

Bearing in mind that dispersion due to a *C* term is opposite in sign to the *C* parameter itself, i.e., a *negative C*/*D* ratio would denote a *positive* $[\Theta]_M$ value, the assignments of the bands are given in Table II. The red band (800–1000 nm) identified as L → Ru, or $^2A_{2u}(\sim\sigma L)$, was discussed above. The lowest energy visible band is assigned as the first halogen → Ru transition, $^2A_{2u}(\sim\pi X)$, as its MCD dispersion has the correct sign, and the MCD band (Table II) maximizes at the same energy as the optical band, thereby fixing the assignment.

The next higher energy band in the chloro complexes (I and II in Table II) also has a net positive MCD dispersion (negative *C*). This is surprising at first sight, since the theory based on linear combinations of octahedral ground-state wave functions (ref 8, eq 1–3, and Table I) predicts only *one net* positive *C* term among the π halogen-to-ruthenium transitions (Figure 3). This dilemma is resolved by remembering that the $^2E_u(\sim\pi X)$ excited state actually has two spin–orbit components (Figure 3); viz., since the MCD dispersion seen for the transition to ^2E_u must be the sum of oppositely signed spin–orbit components (known from *C*-term theoretical analysis in the D_{4h} point group), it *appears* that by using eq 3 with the negative value of g_y[10] one predicts the wrong *net* sign for this transition. However, the band is assigned to $^2E_u(\sim\pi X)$ (Table II) because (i) it has been shown to be charge transfer in nature (vide supra), (ii) it cannot be either $^2A_{2u}(\sim\pi X)$ (already assigned) or $^2B_{2u}(\sim\pi X)$ (wrong *C*-term sign) and yet by its position in the spectra must originate from π halogen MO's, (iii) these MCD maxima do not coincide with the absorption maxima in the chloro complexes, and (iv) the analogous second band of $[RuBr_4(AsPh_3)_2]^-$ is split by about the Br spin–orbit coupling constant (~2400 cm^{-1}) into two oppositely signed MCD components. Points (iii) and (iv) are important because the magnitude of splitting (Figure 3) of the $^2E_u(\sim\pi X)$ excited state upon spin–orbit coupling is predicted to be $\sim\zeta_X$, the halogen spin–orbit coupling constant. Since ζ_{Cl} (~590 cm^{-1}) is much smaller than ζ_{Br}, it is expected that splitting in the chloro complexes would be much less than in the bromo species. It is also worthwhile to point out now that the Γ_{6u} component of ^2E_u is at higher energies in each of the three species. This observation follows from the knowledge that all spin–orbit components of the same symmetry must have the same-signed *C* terms and therefore Γ_{6u} of ^2E_u must have the same sign as $\Gamma_{6u}(^2A_{2u})$; on comparing MCD and optical band positions near 360 nm (Figure 5) of $[RuCl_4L_2]^-$, it can be noted that the positive MCD maximum is somewhat on the blue side of the optical band, which is consistent with the contents of this paragraph, e.g., $\Gamma_{6u} > \Gamma_{7u}$.

It is curious that the d^5 perturbation theory should appear not to predict the proper *net* sign of these transitions to $^2E_u(\sim\pi X)$, since similar transitions to spatially degenerate excited states of other complexes are predicted correctly.[1,8] The sign of the ESR g_y component also appears to have been extracted properly.[10] However, the unusual narrowness of the blue half of the $^2A_{2u}(\sim\pi Cl)$ MCD band at 410 nm for $[RuCl_4L_2]^-$ (Figure 5) and the noncoincidence (vide supra) of optical and MCD maxima of the ca. 360-nm band (Figure 5) strongly suggest that negative MCD activity of the proposed $^2E_u(\sim\pi Cl)$ state for the 360-nm optical band has been canceled by the positive $^2A_{2u}(\sim\pi Cl)$ band.

The bromo complex has a negative dispersion minimizing at 385 nm (Figure 5, Table II) coincident with a maximum of the optical spectrum. That band is assigned to the excitation to $^2B_{2u}(\sim\pi Br)$ of $[RuBr_4(AsPh_3)_2]^-$; it is the last of the π halogen → Ru transitions. However, the chloro complexes do not exhibit a positive *C* parameter (negative dispersion) for any of these charge-transfer bands, so that it must be concluded that the transitions to the $^2B_{2u}(\sim\pi X)$ excited states are covered by the other bands.

Each of the three species shows a high-energy (300–320 nm) transition in which the MCD maxima ($[RuCl_4L_2]^-$) or minimum ($[RuBr_4L_2]^-$) do not correspond to the optical maxima. The close proximity of very intense phenyl transitions, along with the possible presence of d–d and parity-forbidden charge-transfer transitions, makes a firm analysis not possible here.

In conclusion, present experiments and data analysis led to the assignment of five charge-transfer transitions in the spectral region of 330–1200 nm.

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Registry No. $[RuCl_4(PPh_3)_2]^-$, 47841-10-1; $[RuCl_4(AsPh_3)_2]^-$, 47841-03-2; $[RuBr_4(AsPh_3)_2]^-$, 47841-01-0.

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Mutual Influence of Ligands in Main Group Element Coordination Compounds

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The mutual influence of ligands (MIL) in main group element coordination compounds AL_n has been analyzed on the basis of the orbitally deficient scheme of the structure of these compounds. It is shown that the directing influence of ligand X in quasi-octahedral and quasi-square complexes AXL_m depends on the oxidation state of the central atom A. If A is not of the highest oxidation state (formally preserving ns^2 "lone pair"), in complexes AXL_m the trans influence must always take place. If A is of the highest oxidation state, the MIL regularities are of more complicated character. In particular, contrary to transition metal complexes MXL_m, a strong σ donor X (of the H or CH_3 type) can cause the strengthening of the $A-L_{trans}$ bond at the expense of the weakening of the $A-L_{cis}$ bonds, a multiply bonded ligand X (of the terminal oxygen type) can cause the relative cis weakening, a decrease of the A–F bond strength can be accompanied by an increase of spin–spin coupling constant $|J(A-F)|$, etc. The results obtained agree with the experimental data and permit a number of predictions to be made. The reasons for both similarity and difference in the displays of the MIL in transition metal MXL_m and main group AXL_m complexes are discussed.

Trans and Cis Influence. The mutual influence of ligands (MIL) in complexes is considered to be a fundamental problem in coordination chemistry. Here we shall be interested only in the directing influence of ligands, the most important display of which is the trans influence. As the term "trans influence" is used to describe rather heterogeneous things (see, for example, the latest relevant reviews[1–4]) it is useful to clarify the terminology.

Generally speaking, the substitution of ligand X in complexes EXL_m (E is a transition metal atom M or a main group element atom A) influences the properties of *all* E–L bonds. In this sense one can speak about both the trans and the cis influence in any coordination compound EXL_m containing trans and cis ligands.[1–3] However, if we want to find out the peculiarities of the directing influence of ligands (first of all, the differences between the MIL in complexes of transition and main group elements), it is much better to consider the trans or cis influence as a relative characteristic. That is, we deal with the trans influence in a EXL_m complex (where positions of formally identical ligands L are nonequivalent) if the influence of the ligand X on equilibrium properties of the $E-L_{trans}$ bond is stronger than that on properties of the $E-L_{cis}$ bond. Similarly, in the case of the cis influence the properties of the $E-L_{cis}$ bond are more sensitive to the influence of the X ligand. It is of importance that in the framework of such a definition the trans (or cis) influence can result in both weakening and strengthening of the $E-L_{trans}$ ($E-L_{cis}$) bond; the only thing that would matter is that the corresponding changes of the $E-L_{cis}$ ($E-L_{trans}$) bond are less significant.

Really, the seeming chaotic displays of the MIL in transition metal complexes can be described as the trans influence only in the framework of the definition above when the trans influence is considered as a relative characteristic.[4,5]

Now we comment on the determination of the trans influence by means of quantum chemical computations of concrete complexes. The trans influence itself has various manifestations for each compound (depending on what property of the E–L bond is under consideration) and there exist hundreds of such compounds. Even if one takes only the geometric manifestations of trans influence, there should be performed enough accurate calculations with the variation of all internuclear distances and valence angles. At present such calculations on coordination compounds are beyond our possibilities (they become possible only for molecules containing light atoms in the framework of the MINDO/3 method[6]). In any case, all attempts that had been made to solve the MIL problem by quantitative calculations had rather limited success.[1,4]

All this makes it necessary to look for general qualitative models of the MIL. Recently we have developed such a model[4,7] based upon such fundamental properties of molecular orbitals as their nodal structure and symmetry (which determines bonding or antibonding character of MO's). In addition, the differences between covalent (due to unpaired electrons), donor–acceptor, and back-donation interactions are taken into account. On this basis we could obtain the trans-weakening series in complexes MXL_m (depending on X, M, and L) which permits the x-ray data for a great number of compounds to be explained, especially in those cases with multiple M–X bonds, where the trans influence is displayed most distinctly.[4]

The usefulness of this consideration prompted us to use a similar approach (based on the nodal structure and symmetry of LCAO MO's) for the analysis of the MIL in the main group element complexes.

Peculiarities of Chemical Bonding in Complexes of Transition and Main Group Elements. Any realistic MIL model must take into account the main differences in chemical bonding in transition metal coordination compounds MXL_m compared to main group element compounds AXL_m. In complexes ML_n the ligand valence σ orbitals are usually of lower energy than all metal valence ($(n-1)$d, ns, and np) orbitals. In complexes AL_n the typical picture is that the ligand valence σ orbital lies