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Assignment of the Electronic Absorption Spectra of Bis(β-ketoenolate) Complexes of Copper(II) and Nickel(II)[1]

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The problem of the relative positions of the molecular orbitals which are mainly metal d orbitals in square bis(β-ketoenolato)-copper(II) complexes has been investigated by studying the polarizations of single-crystal spectra of $Cu(DPM)_2$ at 25°. (DPM represents the anion of 2,2,6,6-tetramethylheptane-3,5-dione, which has the common name dipivaloylmethane, DPM.) The orientation of the molecules in the unit cell of this compound permits the complete sorting out of the polarizations, something which is not possible in the prototype compound, bis(acetylacetonato)copper(II). The conclusion is that all four "d–d" transitions occur within a range of a few thousand wavenumbers as predicted earlier by our LCAO–MO calculation. This result is also in accord with though was not demanded by the esr data. A similar but less complete study of $Ni(DPM)_2$ indicates that also in that molecule the d_{xz}, d_{yz}, $d_{x^2-y^2}$, and d_{z^2} orbitals lie close together, some 20,000 cm^{-1} below the d_{xy} orbital. The observed polarizations for $Cu(DPM)_2$ are sufficient to rule out a magnetic dipole mechanism as the main source of intensity, but they do not, in themselves, provide a basis for assignment of the transitions if the intensity mechanism is taken to be a vibronic one. The assignment of the ultraviolet spectrum of $Cu(DPM)_2$ is reviewed. Assignments previously proposed by Fackler, Cotton, and Barnum are confirmed except that the band at 48,600 cm^{-1} is now postulated to be a metal to ligand charge-transfer band instead of a $\pi \rightarrow \pi^*$ band.

Introduction

The question of the d-orbital splittings in bis(acetylacetonato)copper(II) and hence the interpretation of the visible absorption spectrum of that and similar compounds (*e.g.*, salicylaldiminato complexes) have been the subject of several previous publications[2–9] but still no complete and definitive conclusions have been reached.

In view of the fact that bis(dipivaloylmethanido)-copper(II),[10] $Cu(DPM)_2$, has been found to have a crystal structure[11] which is favorable for polarization measurements, while its over-all electronic structure and metal–ligand bonding should be essentially the same as in the acetylacetonate,[12] a study of its visible spectrum at room temperature, including the measurement of polarizations, was undertaken. It was hoped that the results so obtained would help to resolve some of the existing uncertainties in the interpretation of the spectrum of the acetylacetonate. These stem from the facts that the components of the visible absorption of that compound are not well separated and the orientation of the molecules in the unit cell is decidedly unfavorable[6] for the interpretation of polarization measurements, as the molecular x axis of one molecule is nearly parallel to the molecular z axis of the other in the monoclinic unit cell.

In what follows, the data and particularly the projection drawings previously published[11] for the crystal structure of $Ni(DPM)_2$, with which $Cu(DPM)_2$ is isomorphous, will be utilized. Of course, it is possible that there may exist small differences in molecular orientation in the two different crystals, but it seems safe to assume that these differences will be small enough (perhaps a few degrees) that this is a satisfactory procedure. The polarized visible spectrum of $Ni(DPM)_2$ will also be briefly discussed.

The near-ultraviolet spectra of β-ketoenolate complexes have also been the subject of several previous experimental and theoretical investigations.[14–19] Assignments of the transitions down to about 200 mμ have been based on comparisons with the results of simple Hückel calculations,[14,16,17] on comparison with the results of somewhat more refined calculations for the acetylacetonate ion alone,[19] and on the effects of chelate ring substituents upon the transition energies,[17,18] particularly in complexes of Cu(II).

At present, there seems to be general agreement that a band usually found in the neighborhood of 270–300 mμ, with a molar extinction coefficient of around 10^4 per ring, is due to the lowest $\pi \rightarrow \pi^*$ transition of the ring system. Many of the complexes have additional absorption bands, whose assignments are as yet less certain. The copper(II) complexes, for example, have strong bands at ~205 and ~250 mμ and a shoulder

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[1] This work was supported by Contract No. AT(30-1)-1965 with the U. S. Atomic Energy Commission and by a Mobil Oil Corp. fellowship to John J. Wise.

[2] R. Belford, M. Calvin, and G. G. Belford, *J. Chem. Phys.*, **26**, 1165 (1957).

[3] J. Ferguson, *ibid.*, **34**, 1609 (1961).

[4] T. S. Piper and R. L. Belford, *Mol. Phys.*, **5**, 169 (1962).

[5] D. P. Graddon, *J. Inorg. Nucl. Chem.*, **14**, 161 (1960).

[6] J. Ferguson, R. L. Belford, and T. S. Piper, *J. Chem. Phys.*, **37**, 1569 (1962).

[7] C. Dijkgraaf, *Theoret. Chim. Acta*, **3**, 38 (1965).

[8] J. Ferguson, *ibid.*, **3**, 287 (1965).

[9] R. L. Belford and G. G. Belford, *ibid.*, **3**, 465 (1965).

[10] Dipivaloylmethane is a common semisystematic name for 2,2,6,6-tetramethylheptane-3,5-dione, which is a homolog of acetylacetone in which the methyl groups have been replaced by *t*-butyl groups. DPM^- is used as an abbreviation for the anionic ligand.

[11] F. A. Cotton and J. J. Wise, *Inorg. Chem.*, **5**, 1200 (1966).

[12] Aside from general reasons for expecting such similarity due to the close resemblance of the ligands, the single-crystal esr spectrum[13] of $Cu(DPM)_2$, especially the equality of g_x and g_y, clearly shows the close similarity.

[13] F. A. Cotton and J. J. Wise, *Inorg. Chem.*, **6**, 915 (1967).

[14] R. L. Belford, A. E. Martell, and M. Calvin, *J. Inorg. Nucl. Chem.*, **2**, 11 (1956).

[15] R. H. Holm and F. A. Cotton, *J. Am. Chem. Soc.*, **80**, 5658 (1958).

[16] D. W. Barnum, *J. Inorg. Nucl. Chem.*, **21**, 221 (1961); **22**, 183 (1961).

[17] J. P. Fackler, Jr., F. A. Cotton, and D. W. Barnum, *Inorg. Chem.*, **2**, 97 (1963).

[18] J. P. Fackler, Jr., and F. A. Cotton, *ibid.*, **2**, 102 (1963).

[19] L. S. Forster, *J. Am. Chem. Soc.*, **86**, 3001 (1964).

of medium to low intensity around 400 mμ in addition to the $\pi \rightarrow \pi^*$ band at ~300 mμ. In the case of Cu(DPM)$_2$, the 300-mμ band shows definite evidence of splitting though the two components are not well resolved (*cf.* Figure 3 of this paper).

The ultraviolet spectra of bis(β-ketoenolato)nickel(II) complexes have not previously been discussed in any detail. For most of them, such as the acetylacetonate itself, such discussion would be greatly complicated by the fact that the compounds exist wholly, or at least partially, as polymers in solution[20,21] and in the solid.[22] However, Ni(DPM)$_2$ has been shown to be a planar monomer both in solution[20] and in the crystal,[11] and its spectrum, which is reported here for the first time, can be discussed in the same way as that of Cu(DPM)$_2$ with which it is isostructural.[11]

Experimental Section

Single crystals measuring about 3 × 3 × 0.1 mm were grown by allowing acetonitrile to diffuse slowly into a benzene solution of the complex. The two main crystal habits were those in which the 001 and the 110 faces were most prominent. The 100 face was obtained by carefully splitting one of the thicker crystals with a razor blade. The identity of the faces used was in every case verified by X-ray photographs.

The crystals were fastened to quartz plates using Apiezon Q putty which also served as a mask for the portion of the beam not passing through the crystal. The quartz plate was mounted in the sample beam of a Cary Model 11 spectrophotometer which was equipped with a condensing lens which reduced the effective beam cross section to about 12 mm^2 at the center of the compartment. A polarizing device mounted so that it could be rotated through 360° was placed just before the crystal mount. Both Polaroid film and a Glan-Thompson prism were found to be satisfactory, giving essentially the same results.

The polarization measurements were successful only for the relatively weak visible bands. Because of the high intensities of the ultraviolet bands, extremely thin specimens (~10^{-2} mm) would be required. All attempts to cut sections anywhere nearly this thin, using a biological microtome and imbedding crystals in plastic, failed, owing to the friable character of the crystals. It was found that crystals having hopper-shaped indentations often formed and sometimes these indentations extended nearly all the way through the crystal leaving a very thin section parallel to a crystal face. Attempts were made to utilize the thinnest of these sections to measure the ultraviolet spectra. Some indications of reproducible polarization effects were observed and we tended earlier[23] to attach some significance to these indications. However, the spectra also show such evident effects of stray and scattered light that we think it safer to omit the results of the attempted polarization measurements in the ultraviolet region from consideration. We are indebted to a referee for his persuasive arguments in this respect.

Solution spectra were measured in the usual way using the Cary 11 spectrophotometer.

Results

Visible Spectra.—The results are shown in Figure 1A, B, and C for Cu(DPM)$_2$. The fraction of light polarized along the various molecular axes is given in Table I (calculated from the crystallographic data[11]) and the magnitude of the major molecular polarization is given on each spectrum for convenience. The molecular axes are defined with z perpendicular to the mean molecular plane, x bisecting the O–Cu–O angles within chelate rings, and y bisecting the O–Cu–O angles between chelate rings. The molecular symmetry is taken to be D_{2h}.

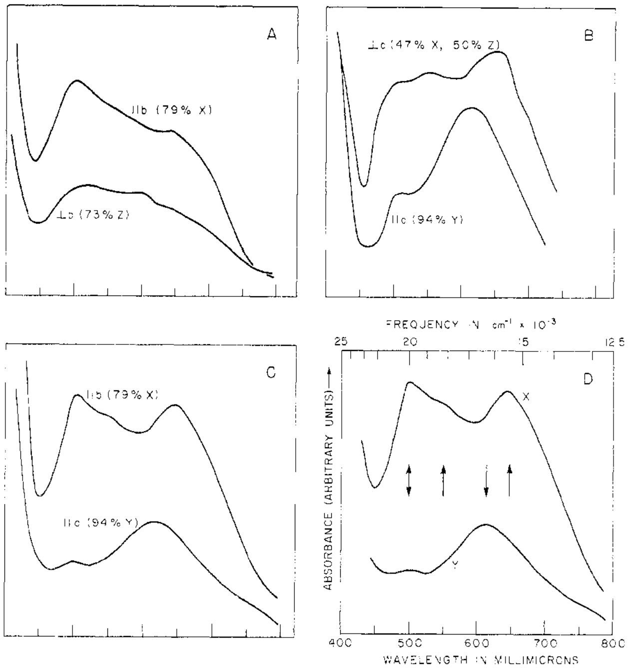

Figure 1.—Polarized crystal spectra of Cu(DPM)$_2$: (A) with light normal to the 001 face; (B) with light normal to the 110 face; (C) with light normal to the 100 face; (D) resolution of the spectra from the 100 face into pure x and y molecular components.

Table I

Resolution of Polarized Spectra into Molecular Bases for Various Crystal Faces

Crystal face	Polarization	Fraction of light polarized parallel to molecular axes[a]		
		x	y	z
b,a (001)	$\parallel b$	0.794	0.058	0.148
	$\perp b$	0.061	0.207	0.732
$\perp c,c$ (110)	$\perp c$	0.468	0.030	0.501
	$\parallel c$	0.065	0.935	0.000
b,c (100)	$\parallel b$	0.794	0.058	0.148
	$\parallel c$	0.065	0.935	0.000

[a] Molecular axes are defined in the text.

The solution spectrum of Cu(DPM)$_2$ in the visible region and also the spectra of some other bis(β-ketoenolate)copper(II) complexes, including the acetylacetonate, have previously been reported.[17] The Cu(DPM)$_2$ spectrum is quite similar to the others except that it is spread over a somewhat larger energy range. Indeed it was this observation which initially prompted the present study since it suggested that for Cu(DPM)$_2$ there might be the best chance of sorting out all of the component absorption bands contributing to the observed envelope.

The spectra shown in Figure 1A, B, and C lead to the conclusion that there are four components to the visible absorption of Cu(DPM)$_2$, with maxima at about 500, 550, 610, and 640 mμ (20,000, 18,200, 16,400, and 15,600 cm^{-1}). The band at 610 mμ appears to be polarized

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[20] F. A. Cotton and J. P. Fackler, *J. Am. Chem. Soc.*, **83**, 2818 (1961).
[21] J. P. Fackler and F. A. Cotton, *ibid.*, **83**, 3775 (1961).
[22] G. J. Bullen, R. Mason, and P. Pauling, *Inorg. Chem.*, **4**, 456 (1965).
[23] F. A. Cotton and J. J. Wise, *J. Am. Chem. Soc.*, **88**, 3451 (1966).

principally in the y direction while the other three are principally x polarized. The 500-mμ band also seems to have a weak y polarization. The spectrum of the (100) face, which contains mainly x and y molecular components is resolved into its molecular contributions in Figure 1D. The $||c$ spectrum contains no z component (*cf.* Table I) while the $||b$ spectrum could have a small z-polarized contribution (14.8%). Since no prominent z polarizations appear elsewhere, however, the $||b$ spectrum was assumed to be composed entirely of x- and y-polarized contributions when calculating the curves of Figure 1D.

In summary, the most notable results for $Cu(DPM)_2$ are: (1) there are definitely four (or more) components to the visible absorption; (2) all components are x and/or y polarized, there being no prominent z polarization detected.

The visible spectrum of $Ni(DPM)_2$ is shown in Figure 2.

Ultraviolet Spectra.—The solution spectra for both compounds are shown in Figure 3.

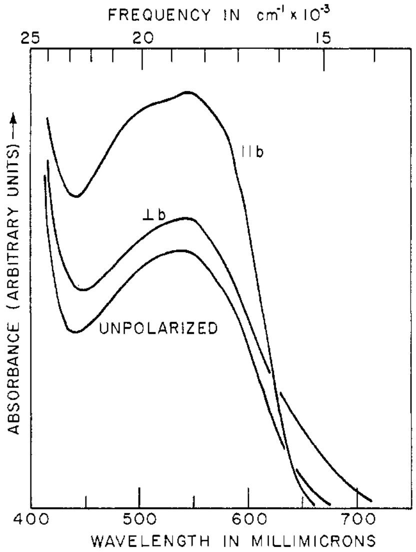

Figure 2.—Unpolarized visible spectrum of $Ni(DPM)_2$ and the polarized spectra taken with radiation normal to the 001 face. The $||b$ spectrum is mainly (79%) x polarized while the $\perp b$ spectrum is mainly (73%) z polarized.

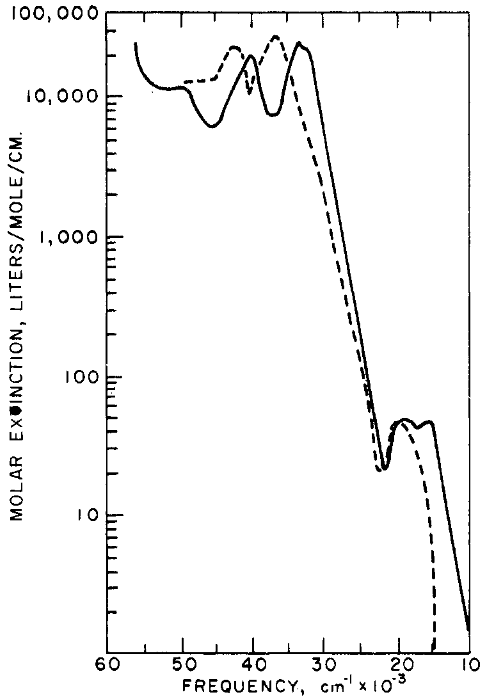

Figure 3.—The visible and ultraviolet spectra of $Cu(DPM)_2$ (———) and $Ni(DPM)_2$ (- - - -) measured at 25° in cyclohexane.

Discussion

The d-Orbital Splitting Pattern.—We have shown previously[24] that over a wide range of reasonable values for the disposable parameters, an LCAO–MO calculation on a generalized bis(β-ketoenolate)copper(II) or -nickel(II) complex leads to a pattern of "d" orbitals[25] in which d_{xy} lies some 20,000 cm^{-1} higher than the other four, which lie relatively close together, in an order which the calculation suggests should be $d_{z^2} > d_{xz} > d_{x^2-y^2} > d_{yz}$ for the Cu(II) complex. Owing to the approximate nature of the MO calculation and the small calculated differences in the energies of these orbitals, this sequence, except perhaps in regard to d_{yz} lying lowest, cannot be taken too seriously, although it was invariant over considerable ranges in the parameters of the calculation.

The experimental observations reported here, namely, that the d_{z^2}, d_{yz}, $d_{x^2-y^2}$, and d_{yz} MO's are relatively close together, with d_{xy} being 15,000–20,000 cm^{-1} higher in energy, are in good agreement with the major result of the calculation. It may also be recalled that the esr results[13] showed that the d_{xz}, d_{yz}, and $d_{x^2-y^2}$ MO's lie close together, some 20,000 cm^{-1} below d_{xy}.

Thus, in summary, the polarized crystal spectrum, together with the LCAO–MO and esr results show conclusively that the absorption in the region from ~500 to ~650 mμ for $Cu(DPM)_2$ is due to the four d–d transitions, $d_{xy} \rightarrow d_{z^2}, d_{x^2-y^2}, d_{xz}, d_{yz}$.

Comparison to $Cu(acac)_2$.—The polarization of the copper acetylacetonate crystal spectrum has been measured twice.[3,6,7] Ferguson reported only three distinct bands in the visible region, whereas Dijkgraaf claimed to find four. The presence of four bands in the spectra of $Cu(DPM)_2$ lends some support to Dijkgraaf's observations.

A band at 26,000 cm^{-1} in the near-ultraviolet region has been assigned previously[3,5] to a d–d transition. The appearance of four visible bands in $Cu(acac)_2$ and $Cu(DPM)_2$ now makes that assignment untenable. The assignment has also been challenged[4,26] on the basis of solvent effects.[26,27]

As noted earlier, owing to the unfortunate orienta-

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[24] F. A. Cotton, C. B. Harris, and J. J. Wise, *Inorg. Chem.*, **6**, 909 (1967).

[25] In this discussion we shall use the expressions for d orbitals, *e.g.*, d_{xy}, to represent those molecular orbitals of the complex which consist predominantly of the corresponding d orbital. This is done only to save cumbersome phraseology and to avoid more arcane or complicated notation, not to obscure the fact of ligand orbital–metal orbital admixture.

[26] D. S. McClure, "Electronic Spectra of Molecules and Ions in Crystals," Academic Press Inc., New York, N. Y., 1959.

[27] D. P. Graddon, *Nature*, **183**, 1610 (1959).

Table II

Possible Assignment of Visible Transitions in $Cu(DPM)_2$ and $Cu(acac)_2$

Transition		Calcd[a] energy, cm^{-1}	Observed energy					
MO designation	"d orbital" designation		$Cu(DPM)_2$		$Cu(acac)_2$[c]		$Cu(acac)_2$[d]	
			Cm^{-1}	Polarization[e]	Cm^{-1}	Polarization	Cm^{-1}	Polarization
ψ_{24} to ψ_{23}	d_{z^2} to d_{xy}	19,180	15,600	x	14,500	x and/or z	15,600	x and/or z
ψ_{25} to ψ_{23}	d_{xz} to d_{xy}	19,490	16,400	y	15,600	y and x or z	16,100	y
ψ_{26} to ψ_{23}	$d_{x^2-y^2}$ to d_{xy}	19,870	18,200	x	(~16,800)[b]	(x and/or z)	18,000	x and/or z
ψ_{27} to ψ_{23}	d_{yz} to d_{xy}	21,290	20,000	x (y)	18,000	x and/or z	18,500	y

[a] See ref 15. [b] Estimated position, see text. [c] See ref 4 and 6. [d] See ref 7. [e] Principal polarization; weaker polarization in parentheses.

tion of the two molecules in the unit cell of $Cu(acac)_2$, the x components could not be separated from the z components. However, in $Cu(DPM)_2$ no band was found to be principally z polarized. It would be reasonable to presume that the same would be true for $Cu(acac)_2$. We would then conclude that the polarizations found by Ferguson should be x, xy, and x for the three bands he observed. As shown in Table II, these polarizations are the same as those found for $Cu(DPM)_2$, if we assume that the 16,000-cm^{-1} band in $Cu(acac)_2$ contains both the d_{xz} and $d_{x^2-y^2}$ to d_{xy} transitions. The $d_{x^2-y^2}$ to d_{xy} transition is estimated by comparison with the $Cu(DPM)_2$ results to be at about 16,800 cm^{-1} and should be x polarized.

The results of Dijkgraaf[7] are similar to those of Ferguson. Assuming no z polarizations, the polarizations observed by Dijkgraaf, as shown in Table II, would be similar to those observed in $Cu(DPM)_2$. To be equivalent, however, the highest energy band, which Dijkgraaf reports to be polarized perpendicular to b, should also appear in the parallel to b spectrum. Apparently it was not resolved from the peak near 18,000 cm^{-1}.

Dijkgraaf[7] claims that the four bands observed in the crystal spectra are the result of factor-group splitting. Factor-group splitting is the splitting of transitions due to intermolecular crystal forces. For two molecules in the unit cell, each band would be split into two bands. One band of each pair would be polarized parallel to the extinction axis and the other perpendicular to it.[28] Dijkgraaf claims that there are only two d–d transitions and that they are split by factor-group splitting into four bands in the crystal spectra. In $Cu(DPM)_2$ the appearance of three bands in the same polarization rules out the possibility of factor-group splitting of two d–d transitions as claimed by Dijkgraaf. Other grounds for discarding Dijkgraaf's analysis have also been given.[8,9]

Belford, *et al.*,[2] have carried out an extensive analysis of the solvent effects on the visible bands of $Cu(acac)_2$ and its 3-ethyl variant. Their analysis, in crystal-field theory terms, of the solvent effect on the spectrum is based on the following considerations. As basic ligands (pyridine solvent) are added to the axial positions, the xy and $x^2 - y^2$ levels should undergo identical shifts. This axial addition should result in the z^2, xz, and yz levels approaching the xy level. The net result should be a shift of all d–d transitions, except the $d_{x^2-y^2}$ to d_{xy}, to lower energy, the latter remaining unchanged. The results of Belford, *et al.*, analyzed on the basis of three visible bands, show that the bands near 14,000 and 18,000 cm^{-1} shift to lower energy upon the addition of basic solvent. The band near 16,000 cm^{-1} remains unchanged. This result indicates that the band near 16,000 cm^{-1} in $Cu(acac)_2$ must contain the $d_{x^2-y^2}$ to d_{xy} transition since there was no shift on solvent addition. This is consistent with the assumption made above that the $d_{x^2-y^2}$ to d_{xy} transition is not resolved from the 16,000-cm^{-1} band in $Cu(acac)_2$.

Comparison with Planar Copper Salicylaldiminato Complexes.—Ferguson[29] has measured the polarized spectra of bis(N-methylsalicylaldiminato)copper(II). Although the determination of polarizations is made difficult by overlap with higher energy bands, the polarized spectra appear to be similar to those of $Cu(acac)_2$ and $Cu(DPM)_2$. Three distinct bands were found in the visible spectrum, near 15,000, 17,000, and 20,500 cm^{-1}. The broad band at 15,000 cm^{-1} shows both x and y polarizations. It is probable that this band corresponds to the two low-energy bands observed in the β-ketoenolates. The band at 17,000 cm^{-1} is x polarized. The highest energy band at 20,500 cm^{-1} is not resolved from the rising ultraviolet absorption but appears to be mainly x polarized, with a weak z component. If our assumption that the band near 15,000 cm^{-1} contains two transitions is correct, then the pattern is similar to that observed for the β-ketoenolates.

Polarized spectra of copper acetate and propionate[30] as well as bis(tropolonato)copper(II), bis(hinokiliolato)-copper(II), and bis(salicylaldehydato)copper(II)[31] have shown that the visible bands are primarily in-plane polarized. It appears that in-plane polarization of the visible bands is common in planar four-coordinate chelates of copper(II).

The $Ni(DPM)_2$ Spectrum.—The visible absorption is shown in Figure 2. Although the unpolarized spectrum has a rather smooth and symmetrical envelope, the polarized spectra suggest that at least three bands are present, namely, those with maxima as follows: ~16,000 cm^{-1}, y and/or z polarized; ~18,500 cm^{-1}, mainly x polarized; ~20,000 cm^{-1}, mainly x polarized.

The results of the MO calculation suggest that the "d–d" transitions should occur at the energies shown in Table III. As for $Cu(DPM)_2$, these results are not to be taken literally, but only as showing that the four transitions should occur close together and in approxi-

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[28] *Cf.* ref 26, p 13.

[29] J. Ferguson, *J. Chem. Phys.*, **35**, 1612 (1961).

[30] R. Tsuchida and S. Yamada, *Nature*, **176**, 1171 (1955).

[31] S. Yamada and R. Tsuchida, *Bull. Chem. Soc. Japan*, **29**, 694 (1957).

TABLE III

CALCULATED "d–d" TRANSITIONS IN Ni(DPM)$_2$

Calculated transitions		Energy, cm^{-1}
ψ_{24} to ψ_{21}	d_{z^2} to d_{xy}	15,900
ψ_{25} to ψ_{21}	$d_{x^2-y^2}$ to d_{xy}	16,300
ψ_{26} to ψ_{21}	d_{xz} to d_{xy}	16,400
ψ_{27} to ψ_{21}	d_{yz} to d_{xy}	18,100

mately the indicated energy range. Apparently three or all four are within the envelope of the band at ~525 mμ.

Vibronic Coupling.—The intensity of "d–d" transitions in centrosymmetric complexes is usually (though not invariably) ascribed to electric dipole allowed transitions between vibronic energy levels of appropriate symmetries. The only alternative explanation which might merit consideration is that the transitions are purely electronic ones which are magnetic dipole allowed. This alternative is ruled out for the molecules being considered here for several reasons.

First the components of the magnetic dipole operator transform as rotations, whence it can readily be shown that two transitions, *viz.*, $d_{z^2} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{xy}$, should be z polarized. This is contrary to the fact that none of the observed d–d intensity has principally z polarization. Second, the observed reduction in band intensity for the visible spectrum of Cu(acac)$_2$ upon cooling[6,7] points to vibronic coupling as the intensity mechanism.

The u-type normal modes of vibration of an MO$_4$ group having D$_{2h}$ symmetry are of the following types: two M–O stretching modes of b$_{2u}$ and b$_{3u}$ symmetries; two in-plane bending modes of b$_{2u}$ and b$_{3u}$ symmetries; two out-of-plane bending modes of b$_{1u}$ and a$_u$ symmetries. These are sufficient to make all vibronic "d–d" transitions allowed in all polarizations and thus the polarization data do not *a priori* lead to an assignment of any of the four transitions. Ferguson, Belford, and Piper[6] have speculated from the reduction in band intensities upon cooling that the vibrations which are efficient in conferring intensity have frequencies ≤200 cm^{-1}. This would suggest then that only the bending modes need be considered. However, since the u-type in-plane bends have the same symmetry types as the stretches, there is still no way to make an assignment from the experimental data alone.

If one assumes that the level order given by the MO calculation[24] and supported for all but one (d_{z^2}) of the d orbitals by the esr data is correct, one can make an assignment and then determine which types of vibration are most effective in conferring intensity. This is done in Table IV, whence it follows that the b$_{3u}$ bending mode is ineffectual, the a$_u$ mode nearly so, with the b$_{1u}$ and b$_{2u}$ modes being the potent ones. Since the validity of the assignment is open to question, this conclusion can be only very tentative, however.

Ultraviolet Spectra.—The solution spectrum of Cu(DPM)$_2$ consists of bands occurring at 48,600, 40,000, 32,300, and 34,600 cm^{-1}, the last two being poorly resolved from each other, with a shoulder (not clearly evident in Figure 3, but quite distinct in spectra displayed on a more extended frequency scale) at about 26,500 cm^{-1}.

TABLE IV

OBSERVED AND CALCULATED POLARIZATIONS OF d–d TRANSITIONS IN Cu(DPM)$_2$

Transition			Calculated polarizations for activation by each of the bending modes			
Frequency, cm^{-1}	Assignment (from MO calculation and esr)	Obsd polarization	a$_u$	b$_{1u}$	b$_{2u}$	b$_{3u}$
15,600	$d_{z^2} \rightarrow d_{xy}$	x	z	...	x	y
16,400	$d_{xz} \rightarrow d_{xy}$	y	x	y	z	...
18,200	$d_{x^2-y^2} \rightarrow d_{xy}$	x	z	...	x	y
20,000	$d_{yz} \rightarrow d_{xy}$	x (y?)	y	x	...	z

The solution spectrum of Ni(DPM)$_2$ shows two well-resolved peaks at 42,700 and 37,300 cm^{-1} and a shoulder at ~29,000 cm^{-1}.

Oscillator strengths were estimated from the solution spectra. Because of the lack of separation of the bands these estimates are necessarily inaccurate. They are perhaps uncertain to about a factor of 2.

From the results of the extended Hückel calculations reported earlier,[24] transition moments, polarizations, and energies of possible transitions can be estimated. The transition moments were estimated by decomposing the integrals $\langle\psi_i|\vec{r}|\psi_j\rangle$ (in which ψ_i and ψ_j are two MO wave functions and $\vec{r}$ is the dipole vector) into three components, $\langle\varphi_M|\vec{r}|\varphi_M\rangle$, $\langle\varphi_M|\vec{r}|\varphi_L\rangle$, and $\langle\varphi_L|\vec{r}|\varphi_L\rangle$, where φ_M is a metal atomic orbital and φ_L is a linear combination of ligand orbitals. The first two are relatively small, of the order of overlaps. Those of the third type can be divided into two classes, $\langle\varphi_{L_i}|\vec{r}|\varphi_{L_j}\rangle$ and $\langle\varphi_{L_i}|\vec{r}|\varphi_{L_i}\rangle$. The first ones are again relatively small, being of the order of overlaps, while the second ones represent the major part of the transition moments. The operator $\vec{r}$ can be written as $\vec{r}_o + \vec{r}\,'$, where $\vec{r}_o$ is an average distance from the origin and $\vec{r}\,'$ is an integration variable. The first of these makes the main contribution, and $\vec{r}\,'$ was therefore neglected. The resulting integrals are rather easy to evaluate and probably give about 80% of the full value of the transition moment, M. The oscillator strengths were then taken as $1.09 \times 10^{-5}\nu M^2$. Those transitions which are expected to occur in or close to the near-ultraviolet region (200–400 mμ) are listed, together with their energies, oscillator strengths, and polarizations, in Tables V and VI.

From a comparison of the observed energies, polarizations, and oscillator strengths with the calculated values, the assignments of the observed spectra were made. Most molecular orbitals (ψ) are made up of both metal and ligand orbitals. In all cases one or the other is the dominant constituent. For brevity, an MO made up primarily of a metal atomic orbital will be referred to by the metal orbital designation. An MO made up primarily of ligand atomic orbitals will be described as a π_L or σ_L molecular orbital depending upon the symmetry. π_L refers to out-of-plane symmetry while σ_L refers to in-plane symmetry.

The Cu(DPM)$_2$ Spectrum, Band I.—The band at 48,600 cm^{-1} is assigned as a metal d_{yz} to π^*_L (MO ψ_{25}

TABLE V

CALCULATED SYMMETRY-ALLOWED TRANSITIONS[a] FOR Cu(DPM)$_2$

Symmetry-allowed transition	Energy, cm^{-1}	Polarization	Oscillator strength
σ_{ligand} to Cu 3d$_{xy}$			
ψ_{28} (b$_{2u}$) to ψ_{23} (b$_{1g}$)	21,500	x	0.53
ψ_{32} (b$_{3u}$) to ψ_{23} (b$_{1g}$)	42,350	y	0.74
ψ_{34} (b$_{3u}$) to ψ_{23} (b$_{1g}$)	46,765	y	0.13
ψ_{37} (b$_{2u}$) to ψ_{23} (b$_{1g}$)	64,950	x	0.40
π_{ligand} to π^*_{ligand}			
ψ_{31} (b$_{1u}$) to ψ_{22} (b$_{3g}$)	32,380	y	0.36
ψ_{30} (b$_{2g}$) to ψ_{21} (a$_u$)	32,880	y	0.34
ψ_{30} (b$_{2g}$) to ψ_{20} (b$_{1u}$)	60,410	x	0.17
ψ_{31} (b$_{1u}$) to ψ_{19} (b$_{1g}$)	65,170	x	0.06
Cu 3d to π^*			
ψ_{25} (b$_{2g}$) to ψ_{21} (a$_u$)	23,200	y	0.03
ψ_{27} (b$_{3g}$) to ψ_{21} (a$_u$)	25,100	x	0.10
ψ_{25} (b$_{2g}$) to ψ_{20} (b$_{1u}$)	50,600	x	0.12
ψ_{27} (b$_{3g}$) to ψ_{20} (b$_{1u}$)	52,700	y	0.03
σ_{ligand} to π_{ligand}			
ψ_{28} (b$_{2u}$) to ψ_{22} (b$_{3g}$)	23,300	z	~0.0
ψ_{29} (b$_{1g}$) to ψ_{21} (a$_u$)	29,300	z	~0.0

[a] Numbering of MO's follows ref 24.

TABLE VI

CALCULATED SYMMETRY-ALLOWED TRANSITIONS[a] FOR Ni(DPM)$_2$

Symmetry-allowed transition	Energy, cm^{-1}	Polarization	Oscillator strength
σ_{ligand} to Ni 3d$_{xy}$			
ψ_{28} (b$_{2u}$) to ψ_{21} (b$_{1g}$)	27,370	x	0.41
ψ_{32} (b$_{3u}$) to ψ_{21} (b$_{1g}$)	48,220	y	0.31
ψ_{34} (b$_{2u}$) to ψ_{21} (b$_{1g}$)	52,500	y	0.09
ψ_{37} (b$_{2u}$) to ψ_{21} (b$_{1g}$)	70,820	x	0.09
π_{ligand} to π^*_{ligand}			
ψ_{30} (b$_{1g}$) to ψ_{22} (a$_u$)	32,230	y	0.44
ψ_{31} (b$_{1u}$) to ψ_{23} (b$_{3g}$)	32,910	y	0.35
ψ_{30} (b$_{1g}$) to ψ_{20} (b$_{1u}$)	59,700	x	0.23
ψ_{31} (b$_{1u}$) to ψ_{19} (b$_{2g}$)	65,200	x	0.02
Ni 3d to π^*			
ψ_{26} (b$_{2g}$) to ψ_{22} (a$_u$)	14,300	y	0.002
ψ_{27} (b$_{3g}$) to ψ_{22} (a$_u$)	16,000	x	0.16
ψ_{26} (b$_{2g}$) to ψ_{20} (b$_{1u}$)	41,800	x	0.06
ψ_{27} (b$_{3g}$) to ψ_{20} (b$_{1u}$)	43,600	y	0.07
σ_{ligand} to π^*_{ligand}			
ψ_{28} (b$_{2u}$) to ψ_{23} (b$_{3g}$)	24,400	z	~0.0
ψ_{29} (b$_{1g}$) to ψ_{22} (a$_u$)	27,400	z	~0.0

[a] Numbering of MO's follows ref 24.

TABLE VII

ULTRAVIOLET TRANSITIONS IN Cu(DPM)$_2$

	Obsd		Calcd			
Band	Cm^{-1}	Oscillator strength	Cm^{-1}	Polarization	Oscillator strength	Assignment
I	48,600	~0.1	50,600	x	0.12	ψ_{25} to ψ_{20} (d$_{yz}$ to π^*)
II	40,000	~0.3	42,350	y	0.74	ψ_{32} to ψ_{23} (σ_L to 3d$_{xy}$)
III	32,300 34,600	~0.4	32,400 32,900	y y	0.36 0.34	ψ_{31} to ψ_{22} ψ_{30} to ψ_{21} (π_L to π^*_L)
	~26,600 (sh)	. . .	21,500	x	0.53	ψ_{28} to ψ_{23} (σ_L to Cu 3d$_{xy}$)

to ψ_{20}) transition. As shown in Table VII, the observed energy and oscillator strength correspond within acceptable limits to the calculated values. Fackler, *et al.*,[17,18] have previously measured the shift in band energies with changes in α and γ substitution. Their premise was that α substitution would lower the energy of bands originating in the oxygen σ system as a function of the inductive character of the substituent. The changing of γ substituents would be expected primarily to shift the transitions originating in the π system. With γ substituents of increasing *ortho–para* directing (in benzene) capacity, π_L–π^*_L type transitions would be expected to be lowered in energy. Their study of band I indicated no consistent shift with either α or γ substitution. To verify that the position of the band was not a function of the α substituent, band positions of Cu(DPM)$_2$ and Cu(acac)$_2$ were carefully remeasured in this study. Measurements were made in deoxygenated spectral grade cyclohexane on a Cary Model 14 spectrophotometer in a nitrogen atmosphere. The band positions found were 205.9 mμ for Cu(DPM)$_2$ and 206.4 mμ for Cu(acac)$_2$. The peaks were well defined. Since the accuracy of the measurement is no better than ±0.5 mμ, the bands can be considered to be at the same position.[32] It would be expected that substitution would have little effect on the energies of metal π orbitals. Since it is known[33] that substituents do not perturb greatly the vacant π levels in aromatic systems, it is reasonable to assume that substituents would not substantially perturb the vacant ligand π levels in the β-diketone complexes. One might expect, therefore, that ring substitution would have little effect on a band assigned as a d$_{yz}$ to π^*_L transition, in accord with the observations.

Inspection of Table V shows that there is one other plausible assignment. A σ_L to d$_{xy}$ (MO ψ_{34} to ψ_{23}) transition could also be considered. The energy and intensity would be about that expected. Since the observed band did not show a shift on variation of the α substituent, this possibility was ruled out as a major contributor to this band in the solution spectrum. A d$_{xz}$ to π^*_L transition (ψ_{27} to ψ_{20}) could also occur in this region. However, the calculated transition moment is only one-fourth that for the d$_{yz}$ to π^*_L transition. Although it may contribute to the observed band, it is unlikely that this transition is the major contribution.

It was earlier suggested[17] that this band might be a component of a high-energy π_L to π^*_L transition. There is, however, little shift in the band position upon γ substitution. The results of our MO calculation[24] indicate that this π_L to π^*_L transition should occur be-

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[32] The actual peak positions reported previously[17] were slightly different from those measured in the present study but were nearly identical for the two compounds.

[33] *Cf.* F. A. Matsen in "Technique of Organic Chemistry," Vol. IX, "Chemical Applications of Spectroscopy," W. West, Ed., Interscience Publishers, New York, N. Y., 1956, pp 671–677.

yond 60,000 cm^{-1}. Forster[19] in his calculation on the acetylacetonate anion indicates that this transition should be and is generally found beyond 51,000 cm^{-1}. Moreover, if band I were a π_L–π^*_L transition, one would expect it to be in substantially the same position in the nickel complex. No band was observed in Ni(DPM)$_2$ near 205 mμ. Since measurements were made only down to 205 mμ, it is possible that the band was shifted slightly and occurs just beyond the range of measurement, but there is no indication of this.

Band II.—This strong band, observed at 40,000 cm^{-1}, is assigned as a σ_L to Cu 3d$_{xy}$ (MO ψ_{32} to ψ_{23}) transition. As shown in Table VII, the calculated and observed energies and oscillator strengths are in reasonable agreement. The particular σ_L orbital is composed primarily of oxygen p$_y$ orbitals. The band energy is sensitive to α substitution but not to γ substitution.[17,18] It was concluded, therefore, that this band originates in the σ system. A similar band is observed in Cu(H$_2$O)$_6^{2+}$ between 40,300 and 47,000 cm^{-1}, which is attributed to electron transfer.[34] This spectroscopic evidence is, therefore, in accord with this assignment as a σ_L to Cu 3d$_{xy}$ transition.

Band III.—This is observed as an intense absorption near 300 mμ which is slightly split. The results of the molecular orbital calculation indicate that there should be two slightly separated, strong transitions at about this energy. This split peak is assigned as the two π_L to π^*_L transitions (ψ_{31} (b$_{1u}$) to ψ_{22} (b$_{3g}$) and ψ_{30} (b$_{2g}$) to ψ_{21} (a$_u$)) predicted by the MO calculation. The predicted oscillator strength and band positions agree reasonably well with the calculated values as shown in Table VII.

Fackler, *et al.*,[17,18] have assigned this band as a π_L–π^*_L transition on the basis of a simple Hückel MO calculation in which only the π orbitals were considered. Their assignment was supported by spectroscopic results which indicated band shift on γ substitution. Measurements of shifts in this band with changes in ligand have also been made for Cr^{3+} complexes with β-ketoenolates. The shifts were shown to support the assignment of this band as a π_L–π^*_L transition.

A large number of metal acetylacetonates have been examined by Holm and Cotton[15] in the 240–400-mμ region. Acetylacetone and the lithium, potassium, and sodium salts of acetylacetone all show a strong symmetrical peak near 290 mμ. Since, in these cases, there is little likelihood of metal interaction and no low-lying vacant σ levels, it is most probable that this transition is a π_L–π^*_L type. The same can be said for Al(acac)$_3$ which has been shown[35] to have a strong absorption with a lower energy shoulder in this region. The splitting of this band, which is observed in the more covalent metal compounds, has been attributed[35] to interaction with metal orbitals or to effective overlap between rings. In the case of the copper complex, it is probably the result of the metal π (d$_{xz}$, d$_{yz}$) orbitals mixing with the ligand π orbitals. This removes a degeneracy and splits the peak.

Shoulder on Band III.—A weak shoulder is observed at ~26,600 cm^{-1}. As noted earlier, the possibility of assigning this to a d–d transition has frequently been considered by previous workers, but this is now ruled out by the evidence that all four d–d transitions occur in the visible.

Referring to Table V, we see that there remain five symmetry-allowed transitions, all estimated to occur near 26,000 cm^{-1}, none of which has yet been discussed. Four of these, ψ_{25} to ψ_{21}, ψ_{27} to ψ_{21}, ψ_{28} to ψ_{22}, and ψ_{29} to ψ_{21}, have calculated intensities in the range 0–0.1 and are thus compatible with the experimental data. There is no basis for selecting any particular one to be assigned to the observed absorption, and quite possibly several may be involved. The calculated oscillator strengths would favor either or both of the 3d → π^*_L assignments rather than the $\sigma_L \rightarrow \pi_L$ possibilities, and we therefore suggest these as the likely candidates.

The $\sigma_L \rightarrow$ d$_{xy}$ transition, ψ_{28} to ψ_{23}, for which the calculated energy and oscillator strength are 21,500 cm^{-1} and ~0.5, poses something of a problem. Its calculated intensity is much too high for it to be assigned to the shoulder under discussion. We tentatively suggest that the position of this transition may be badly misrepresented by the MO calculation and that it may actually lie at some energy above 30,000 cm^{-1}. It would thus contribute to the strong absorption which was earlier assigned to the lowest π_L–π^*_L transitions. The consistency between theory and experimental observation for this transition is certainly a conspicuous and disappointing shortcoming in the present analysis. It should not be glossed over and we wish to avoid any suggestion of doing so.

It is consistent with our proposed assignments (ψ_{25} to ψ_{21} and/or ψ_{27} to ψ_{21}) that no band is observed around 26,000 cm^{-1} in Al(acac)$_3$, in acetylacetone, or in alkali metal acetylacetonates,[15] since no occupied metal d orbitals are present in these cases.

The Ni(DPM)$_2$ Spectrum, Band I.—The highest energy band observed in the Ni(DPM)$_2$ solution spectrum is at 42,700 cm^{-1}. No higher energy bands were observed although observations were made down to 205 mμ. As shown in Table VI, transitions from 3d$_{yz}$ to π^*_L (MO ψ_{26} to ψ_{20}) and 3d$_{xz}$ to π^*_L (MO ψ_{27} to ψ_{20}) are predicted to occur at 41,800 and 43,600 cm^{-1}, respectively. A transition from σ_L to 3d$_{xy}$ (MO ψ_{32} to ψ_{21}) is predicted at 48,220 cm^{-1}. The observed band at 43,900 cm^{-1} may be assigned as one or more of these transitions. It is probable that the σ_L to 3d$_{xy}$ transition is the major contributor to this band based on its higher calculated oscillator strength. The calculated and observed oscillator strengths are compared in Table VIII. A study of the effect of α and γ substitution on this band might resolve this assignment, but it would be complicated by the tendency of the β-ketoenolates of nickel to form polymeric species.

Band II.—The band at 37,300 cm^{-1} may be assigned as the two strong π_L to π^*_L transitions predicted [MO ψ_{30} (b$_{1g}$) to ψ_{22} (a$_u$) and MO ψ_{31} (b$_{1u}$) to ψ_{22} (b$_{3g}$)]

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(34) J. Halpern and A. C. Harkness, *J. Chem. Phys.*, **31**, 1147 (1959).

(35) K. DeArmond and L. S. Forster *Spectrochim. Acta*, **19**, 1393 (1963).

TABLE VIII

ULTRAVIOLET TRANSITIONS IN $Ni(DPM)_2$

Band	Obsd		Calcd			Assignment
	Cm^{-1}	Oscillator strength	Cm^{-1}	Polarization	Oscillator strength	
I	42,700	~0.2	48,220	y	0.31	ψ_{32} to ψ_{21} (σ_L to $3d_{xy}$)
II	37,300	~0.4	32,230	y	0.44	ψ_{30} to ψ_{22} (π_L to π^*_L)
			32,910	y	0.35	ψ_{31} to ψ_{23}
	~29,000 (sh)	. . .	27,370	x	0.41	ψ_{28} to ψ_{21} (σ_L to $3d_{xy}$)

and corresponds to band III in the copper complex. Calculated and observed energies and oscillator strengths compare well as shown in Table VIII.

Shoulder on Band II.—A lower energy band representing a σ_L to Ni $3d_{xy}$ transition would be expected on the basis of the MO calculations (see Table VI). A transition with a calculated oscillator strength of 0.41 and x polarization is predicted to occur near 27,000 cm^{-1}. However, as in the corresponding region of the $Cu(DPM)_2$ spectrum, the consistency between calculated and observed spectra is poor and further discussion is not warranted.

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Molecular Orbital Calculations for Complexes of Heavier Transition Elements. III. The Metal–Metal Bonding and Electronic Structure of $Re_2Cl_8^{2-}$ [1]

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The metal–metal and metal–chlorine bonding in $(Re_2Cl_8)^{2-}$ are treated by "extended" Hückel molecular orbital theory. The calculation suggests that the π-bonding contribution to the Re–Re bond is five times that of the δ bonding and almost three times that of the σ bonding. The Re–Re bond stabilization and the rotational barrier in $(Re_2Cl_8)^{2-}$ are calculated as 366 and 51 kcal, respectively, by comparing a hypothetical $(ReCl_4)^-$ anion (C_{4v}) with the $(Re_2Cl_8)^{2-}$ anion (D_{4h}). The ordering of the molecular orbitals is discussed with respect to the magnetic properties and the observed and calculated spectral properties.

Introduction

The preparation[3] and structure[4] of the $[Re_2Cl_8]^{2-}$ anion have been discussed. Its chemistry[5] appears to be consistent with the proposed[6] quadruple metal–metal bond. It therefore provides an excellent opportunity to study the effects of the various factors contributing to metal–metal bonding. This approach, however, requires a detailed knowledge of the individual orbital contributions to the metal–metal bond; therefore, an extensive molecular orbital calculation for $[Re_2Cl_8]^{2-}$ has been undertaken. All Re–Re, Re–Cl, and Cl–Cl interactions have been considered in a semiempirical approach of the type generally called an extended Hückel calculation. It is recognized that for various reasons, to be discussed in detail below, such a calculation cannot provide results which can be taken literally. It is our belief, however, that the results obtained, when interpreted properly, do provide a semiquantitative picture of the main features of the metal–metal bonding and their relative importance. For this reason, we believe that the study reported here provides a useful advance beyond the level of the simple overlap treatment which has already been given[6] for $Re_2Cl_8^{2-}$.

Method of Calculation

Choice of the Basis Set.—A basis set of fifty atomic orbitals, χ_i (i = 1, 2, . . ., 50), was used to construct the molecular orbitals ψ^j (j = 1, 2, . . ., 50), in the LCAO–MO approximation[7] (eq 1). This basis set included the 5d, 6s, and 6p orbitals of each Re atom and the 3s and 3p orbitals of each Cl atom. It was assumed that the nonvalence atomic orbitals on both Re atoms and the eight Cl atoms did not participate in bonding, but formed a core potential that was unaltered by interactions of the valence electrons. The atomic orbitals, χ_i's, were expressed as single term Slater-type orbitals[8] (STO's) as given in eq 2, where α_i is the shielding parameter, N is the normalization co-

$$\psi^j = \sum_i C_i^j \chi_i \qquad (1)$$

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