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MO Studies for Transition Metal Complexes with Polydentate Ligands. III. Planar Bisdimethylglyoximato Complexes of Fe^{II}, Co^{II}, Co^{III}, Ni^{II}, Cu^{II}, Pd^{II}, and Pt^{II}

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A MO investigation on the bonding and energy levels, using the SCCC–MO method, for planar bisdimethylglyoximato complexes of several transition metals is presented. For the iso-electronic series Ni, Pd and Pt a linear correlation is found between the total ($\sigma+\pi$) overlap population and the stretching force constant of the M–N bond; in addition, the stability constant is found to be inversely related to the net charge carried by the metal atom. The spectroscopic g factors of the Cu^{II} and Co^{II} derivatives are evaluated and discussed . Qualitative considerations about the electronic spectra are also given.

Introduction

Dimethylglyoxime is well known to form readily stable complexes with a number of transition metal ions. Recently there has been a growing interest in the physical and chemical properties of such complexes. In particular, the electronic structure and related properties of bisdimethylglyoximato complexes of Fe^{II} and Co^{III} with nitrogen-containing axial ligands[1,2] and of bisdimethylglyoximato complexes of Ni^{II} [3] and Cu^{II} [4] have been extensively studied from the MO point of view. The main aim of this report is to give a theoretical insight into the electronic structure and bonding of several other fully planar bisdimethylglyoximato complexes of Fe^{II}, Co^{II}, Co^{III}, Ni^{II}, Cu^{II}, Pd^{II} and Pt^{II}. The Ni^{II} and Cu^{II} compounds have been here reinvestigated in order to correlate results obtained with the same theoretical approach, (*i.e.* the SCCC–MO formalism), and parameterisation. A simple interpretation of the electronic spectra is also given based on the theoretical one-electron transitions. Finally, the spectroscopic g factors are evaluated for the Co^{II} and Cu^{II} complexes.

Method of calculation. The molecules are taken to be fully planar and to have D_{2h} symmetry with the

bond containing rings and the y axis bisecting the other N–M–N angles. Bond distances and angles are deduced from the X-ray structures for Ni,[5] Cu,[6] Pd,[5] and Pt[7] complexes. The structural data for the Fe^{II}, Co^{II} and Co^{III} derivatives are assumed to be the same as in the $Co^{III}(Dmg)_2(NH_3)_2$ complexes.[8]

The computational procedure follows the Wolfsberg-Helmholz[9] semiempirical method in the SCCC–MO modification developed by Ballhausen and Gray.[10]

Twentyfive atomic orbitals are used as basis functions, with no hypothesis on their hydridization: nine metal orbitals (nd, (n+1)s, (n+1)p), one 2pσ for each nitrogen and one 2pπ orbital for each nitrogen, carbon and oxygen atom. The metal orbitals are taken as linear combinations of Slater-type orbitals relative to the state M^{+} with the exponents and coefficients proposed by Richardson *et al.*[11] for Fe, Co, Ni and Cu and by Basch and Gray[12] for Pd and Pt. Analytical functions for the ligand atomic orbitals are taken from the tabulation of Clementi and Raimond.[13]

VSIE's for Fe, Co and Ni are derived from Tables of Basch *et al.*,[14] while those for Pd and Pt are assumed to be equal to the respective VSIE's of Ni minus 10 kK, as suggested by Basch and Gray.[15] The VSIE's for ligand atom orbitals are taken from spectral data on appropriate valence state of the neutral atoms[16] and are assumed to be charge-independent.

The treatment for the Cu compound is not carried out by means of the Ballhausen-Gray procedure but following the extended Hückel method. The energies of the d, s and p copper orbitals are assumed to be dependent on charge through a linear relationship as suggested by Zerner and Gouterman.[16]

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Table I. Electronic Population of Metal Orbitals and Atomic net Charges

Complex	Fe^{II}	Co^{III}	Co^{II}	Ni^{II}	Cu^{II}	Ni^{II}	Pd^{II}	Pt^{II}
nd	6.9020	7.8169	7.9093	8.8228	9.4425	8.8228	8.7609	8.6905
(n+1)s	0.5518	0.6193	0.5816	0.6370	0.7198	0.6370	0.7034	0.7487
(n+1)p	0.2163	0.2440	0.2178	0.2995	0.4665	0.2995	0.4891	0.5336
Metal	0.3299	0.3198	0.2913	0.2407	0.3712	0.2407	0.0466	0.0272
N	0.0956	0.2504	0.1182	0.1540	0.1042	0.1540	0.2261	0.2539
C	0.2386	0.2863	0.2281	0.1930	0.2169	0.1930	0.1960	0.1738
O	−0.4166	−0.3666	−0.4192	−0.4072	−0.4149	−0.4072	−0.4338	−0.4345

Table II. Partial and total bond orders for M—N bond

Complex	Fe^{II}	Co^{III}	Co^{II}	Ni^{II}	Cu^{II}	Ni^{II}	Pd^{II}	Pt^{II}
$d_{x^2-y^2}$	0.0020	0.0022	0.0020	0.0014	0.0022	0.0014	0.0032	0.0044
d_{z^2}	0.0156	0.0164	0.0160	0.0104	0.0164	0.0106	0.0250	0.0332
d_{xy}	0.3204	0.3368	0.3338	0.2912	0.0844	0.2912	0.3804	0.4252
s	0.3696	0.4142	0.3992	0.5382	0.4818	0.5382	0.4962	0.5100
p_y	0.0984	0.1128	0.1048	0.1350	0.2066	0.1350	0.2684	0.2978
p_x	0.0846	0.1368	0.1264	0.1662	0.2468	0.1662	0.3168	0.3494
σ-total	0.8906	1.0192	0.9826	1.0426	1.0382	0.9826	1.4900	1.6200
p_z	0.0482	0.0516	0.0454	0.0900	0.0696	0.0900	0.0312	0.0304
d_{xz}	0.1014	0.1082	0.0494	0.0010	−0.0010	0.0010	−0.0005	−0.0008
d_{yz}	0.1226	0.0546	0.0636	0.0740	0.0262	0.0740	0.0606	0.0904
π-total	0.2722	0.2144	0.1584	0.1650	0.0948	0.1650	0.0912	0.1200
σ+π total	1.1628	1.2336	1.1410	1.3076	1.1330	1.3076	1.5812	1.7400
				Bond order for N—C bond				
N—C	1.3846	1.3256	1.4418	1.5112	1.5052	1.5112	1.5118	1.5008

The off-diagonal matrix element H_{ij} is evaluated by means of the conventional Wolfsberg-Helmholz approximation, where the K parameter is given the value 2. Atomic orbital population analysis is performed according to Mulliken. The oscillator strengths of the one-electron transitions are calculated by taking into account only the diagonal elements of the transition moment matrix between the atomic orbitals.

In accord to the Ingraham's proposal,[3] the hydrogen atoms in hydrogen bridge between the two oxygen atoms are assumed to neutralize one-half negative charge on each oxygen so that the four oxygens are considered neutral with a total of six electrons.

The σ-type MO's span the irreducible representations a_g, b_{1g}, b_{2u} and b_{3u}. The π-type MO's transform as a_u, b_{1u}, b_{2g} and b_{3g}.

Electronic structures. The electronic configuration and charge of the metal atoms together with the charges of the ligand atoms are collected in Table I. The charge on metal decreases slightly on going along the series Fe, Co^{II}, and Ni, while a rather sharp lowering is observed from Ni to Pd and Pt, so that the last complex in each series should be considered the most covalent. This conclusion seems to be consistent with the hard-soft acid-base concept. In fact, in the isoelectronic series of Ni^{II}, Pd^{II} and Pt^{II} one expects Pt to be the softest one, owing to the greater size of the Pt ion in comparison with the Ni and Pd ions. The same argument can be applied to the series Fe^{II}, Co^{II} and N^{II} as well; then, among these complexes, that of Ni should be regarded as the softest.

The largest positive metal charge is computed for the Cu complex. This probably arises from the fact that the calculations on this compound have been performed using a different theoretical approach.

In all complexes the metal s and p electron densities are moderately increasing across both the series; the d population decreases slightly in the series Ni, Pd and Pt. Incidentally, it can be underlined that the metal electronic configurations predicted for the Pd and Pt complexes are not too different from those previously obtained for $PdCl_4^{2-}$ and $PtCl_4^{2-}$.[15] In Ni case, comparing the present results with Ingrahm's,[3] the metal charge is not very different, the s and p densities are rather lower and, on the contrary, the d density is moderately larger. For Cu derivative the charge carried by the metal is much lower than that obtained previously by Roos;[4] the p population is quite similar, while the s and d populations are moderately higher.

The carbon 2pπ population increases slightly on passing from Fe to Pt. On the other side, the population resident on nitrogen atom is moderately decreasing. The oxygen charge remains nearly constant in all compounds, with the exception of the Pd and Pt cases, in which there is an increase of negative charge. These results seem then to indicate that some electronic charge is transferred from nitrogen to metal and carbon. This is possible only through a π delocalization.

In Co^{III} case the net charge predicted for the metal is not too different from the corresponding one in

Co^{II} case; the electronic structure is comparable too. In the last case, in order to achieve this result almost one electron must be withdrawn from adjacent atoms and this can be accomplished only through a π mechanism. This is apparent from the values of the charges on nitrogen, carbon and, especially, oxygen.

Some other features become apparent on looking at Table II, in which the Mulliken overlap populations are reported. The nd$_{xy}$ and (n+1)s orbitals account for most of the σ-bonding metal-nitrogen (M–N). In Cu case the 3d$_{xy}$ orbital makes a minor contribution because the unpaired electron occupies an antibonding MO which is essentially 3d$_{xy}$ in nature. Judging from the values of the overlap populations, the (n+1)p$_x$ and (n+1)p$_y$ orbitals are important especially in Cu, Pd and Pt cases. Looking now at the total σ overlap population of the metal-nitrogen bond, one can observe a moderate increase on going from Fe to Ni and a strong one from Ni to Pt. On the contrary, the total π population shows a rather irregular lowering. As a result the total $\sigma+\pi$ population as well as the total σ population rise across the series Ni, Pd and Pt, while display irregular trends in the other Concerning the C–N bond its π bond overlap population remains sensibly constant in the series Ni, Pd, Pt and Cu and increases in the series Fe, Co^{II} and Ni.

The stretching force constant (F_{M-N}) of the M–N bond obtained by recent normal coordinate analysis performed by the authors[17] shows the same trend as the *total* ($\sigma+\pi$) bond order (T.B.O.) along the isoelectronic series Ni, Pd Pt:

	Ni	Pd	Pt
$F_{(M-N)}$ (md/Å)	1.88	2.84	3.77
T.B.O.	1.31	1.58	1.74

No such a correlation is found between the stretching force constant and the π bond order of C–N bond, probably because no allowance is made for variation in σ bonding too.

Burger *et al.*[18] have suggested to ascribe the observed shift of the Infra-red frequency of the C–N bond to variation in the π-bond order. However, the normal coordinate treatment[17] indicates that the nature of the normal mode involving primarily the C–N bond is not preserved along the series, so that the comparison between the experimental frequency shift and the variation in force constant, and consequently in π or total ($\sigma+\pi$) bond order, is not justified.

The available data of stability constants are scarce for the investigated complexes.[19,20] However, for Ni and Pd derivatives is found an inverse relation between the stability constant and the net charge carried by the metal atom. The same correlation has been established previously for metal porphyrins,[16] the theoretical order of stability being in accord with that experimentally determined by Maley and Mellor[21] for metal complexes. Then, on this theoretical ground, the Pt complex is predicted to have the largest stability constant. Unfortunately it is not possible to extend this correlation to the Cu complex, for which too is available the stability constant,[22] because of the different method employed in the calculation of the electronic structure.

Energy diagrams. The energy levels are depicted in Figure 1, where the lowest bonding and the highest antibonding levels are not reported.

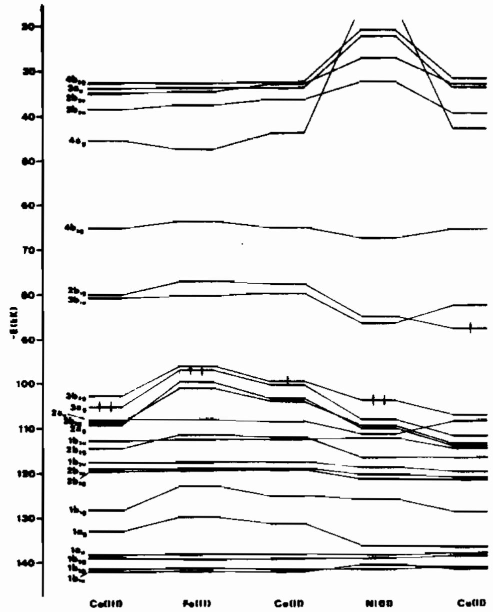

Figure 1a.

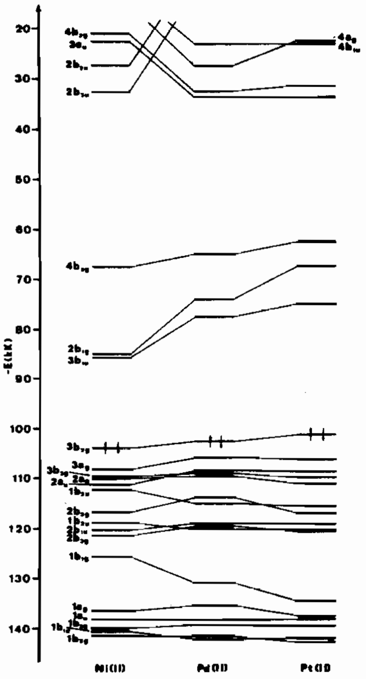

Figure 1b.

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For the considered complexes the MO's which consist mainly of metal d orbitals are:

$$2a_g \sim d_{x^2-y^2};\; 3a_g \sim d_{z^2};\; 2b_{1g} \sim d_{xy};\; 3b_{2g} \sim d_{xz};\; 3b_{3g} \sim d_{yz}$$

with the exception of Cu and Pt derivatives for which the $2b_{2g}$ instead of the $3b_{2g}$ should be regarded as the « d_{xz} » MO. As concerns the relative position of these levels, the $d_{x^2-y^2}$, d_{z^2}, d_{xz} and d_{yz} MO's are found to lie rather near each to other in a range not exceeding 10 kK, while the « d_{xy} » MO is some 20 kK higher in energy.

In view of the semiempirical, approximate nature of the computational approach, the very closely spaced d levels prevent one to regard the energy diagram as giving an unambiguous ordering of these levels. The present results indicate however that the energy splitting between the d_{xz} and d_{yz} levels, arising from rhombic distortion of the complex, should increase on going from Fe to Pt and that the d_{z^2} MO should be more destabilized than the $d_{x^2-y^2}$ MO. This latter result would be in agreement with that previously obtained by Zerner and Gouterman[16] for metal porphyrins, which display a similar tetradentate nitrogen-containing ligand.

In Fe^{II} and Co^{II} complexes the highest filled and the first virtual MO's are the $3a_g$ and $3b_{2g}$ respectively, both metal in character. The energy separation between these MO's is very small, of the order of about 1-2 kK. Then, for these until unknown compounds one could claim the possibility of a triplet as a ground electronic state.

g Factors. The EPR measurements on Cu derivative[23] show that the spectroscopic g factors are $g_{\parallel} = 2.15$ and $g_{\perp} = 2.05$, while copper hyperfine tensor components are $A_{\parallel} = 144 \times 10^{-4}$ cm^{-1} and $A_{\perp} = 14 \times 10^{-4}$ cm^{-1}. Following the computational method proposed by Abragam and Pryce[24] and further developed by Maki and McGarvey,[25] the spectroscopic g factors are predicted to be $g_{\parallel} = 2.13$ and $g_{\perp} = 2.03$, in rather good agreement with the experimental data. The calculated A components depend strongly upon the Fermi contact factor, which is rather hard to ascertain for the present complex. However, by assuming the value of 0.29 deduced from Wiersema and Windle data,[23] the evaluated components are $A_{\parallel} = 160 \times 10^{-4}$ cm^{-1} and $A_{\perp} = 41 \times 10^{-4}$ cm^{-1}. The agreement of these quantities with those experimentally found is not as satisfactory as that for the g factors. It is however worthwhile to recall that the 2s nitrogen orbitals are not taken into account in the considered basis orbital set. Moreover, despite of the very simple method employed, it is satisfying to remark that the present results compare well with those obtained by Roos[4] through a more sophisticated method.

The experimental measurements[26] on Co^{II} derivative, made in solution of pyridine or in solid state, yield only two values of g factors, *i.e.* $g_{\parallel}$ and $g_{\perp}$. Whilst the observed ratio $g_{\parallel}/g_{\perp} > 1$ is monitoring the unpaired electron in an essentially d_{z^2} MO, the calculated electronic structure assigns the unpaired electron to the $3b_{2g}$ MO essentially d_{xz}. The latter attribution gives three different g factors, the evaluated values being $g_{xx} = 2.91$, $g_{yy} = 1.99$ and $g_{zz} = 2.05$. The discrepancy between this result and the experimental one is likely due to the incorrect theoretical ordering of the two very closely spaced levels $3b_{2g}(d_{xz})$ and $3a_g(d_{z^2})$, which could probably be inverted by adopting a slightly different parameterisation. (On the other hand, previous calculations[1,2] performed on $Co^{II}(Dmg)_2L_2$ indicate that the last filled MO is really an essentially d_{z^2} MO).

Electronic spectra. The spectra of Ni, Pd and Pt derivatives have been investigated both in chloroform solution and in nujol mull, while that of the Co^{II} compound has been recorded only in chloroform solution under oxygen-free nitrogen atmosphere. In the Tables III and IV the experimentals bands are reported together with the symmetry-allowed one-electron transitions which have a significant value of oscillator strength. The proposed assignments must however be regarded as purely tentative. Indeed the theoretical approach here adopted does not permit to make a confident attribution of the observed bands because the interelectronic repulsions and configuration interaction are not taken into account.

Looking at these Tables one can recognize four theoretical transitions peculiar to all compounds which seem to match rather well with the experimental bands. Thus they can be regarded as forming a sort of skeletal of the spectra. They are $3b_{2g} \rightarrow 3b_{1u}$, $3b_{3g} \rightarrow 3b_{1u}$, $2b_{2g} \rightarrow 3b_{1u}$, and $2a_u \rightarrow 4b_{3g}$. The first two transitions are mainly charge-transfer (CT) in nature, M→L. The last two are L→L. Attention must however be payed to the fact that the $3b_{1u}$ MO is essentially a ligand MO, but to it participates to a rather important extent also the p_z metal orbital, thus in the first three transitions there is a significant contribution of d→p transition (M→M).

The transition $2a_u \rightarrow 4b_{3g}$ must be considered a $\pi \rightarrow \pi^*$ transition of the Dmg ligand because the a_u MO's are built out only of Dmg orbitals and the d_{yz} metal orbital does not participate to the $4b_{3g}$ MO to a significant extent. This transition, predicted to lie around 43 kK and thus to be scarcely affected by the nature of the metal atom, can reasonably be attributed to the highest-energy band observed in the spectra. This assignment is supported by the fact that a band of the same character also occurs in the same range of frequency of free Dmg.

Interspersed between the mentioned transitions there are several others which are predicted to occur at very different wavelengths on going from one complex to another. These transitions could be responsible for the irregular behaviour shown by some experimental bands along both the series.

As regards the intensity it must be stressed that some transitions may become stronger as the molecular symmetry falls down. Indeed the real geometry of the complexes is slightly distorted from the square-

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Table III. Electronic Transitions (Energy in Kilokaysers)

		Ni^{II}					Pd^{II}					Pt^{II}		
Exp.	**Calcd.**	**Osc. Str.**	**Transition**	**Nature**	**Exp.**	**Calcd.**	**Osc. Str.**	**Transition**	**Nature**	**Exp.**	**Calcd.**	**Osc. Str.**	**Transition**	**Nature**
(21.1)	17.3	0.01	$3b_{2g} \rightarrow 3b_{1u}$	M—L										
23.2	22.9	0.13	$3b_{2g} \rightarrow 3b_{1u}$	M—L		24.8	0.05	$3b_{2g} \rightarrow 3b_{1u}$	M—L		23.7	0.04	$3b_{2g} \rightarrow 3b_{1u}$	M—L
26.7	27.2	0.39	$1b_{3u} \rightarrow 2b_{1g}$	L—M	27.0	31.4	0.14	$3b_{3g} \rightarrow 3b_{1u}$	M—L	28.6				
30.7	30.1	0.10	$2b_{2g} \rightarrow 3b_{1u}$	L—L										
	33.7	0.32	$1b_{2u} \rightarrow 2b_{1g}$	L—M						33.3	32.4	0.21	$3b_{3g} \rightarrow 3b_{1u}$	M—L
	34.7	0.03	$2b_{2g} \rightarrow 3b_{1u}$	L—L										
38.5	44.0	0.42	$2a_u \rightarrow 4b_{3g}$	$\pi \rightarrow \pi^*$	36.3	37.2	0.12	$2b_{2g} \rightarrow 3b_{1u}$	L—L	37.0	39.4	0.13	$2b_{2g} \rightarrow 3b_{1u}$	L—L
						40.9	0.59	$1b_{3u} \rightarrow 2b_{1g}$	L—M					
						42.1	0.02	$2b_{3g} \rightarrow 3b_{1u}$	L—L		43.1	0.01	$2b_{3g} \rightarrow 3b_{1u}$	L—L
					47.6	43.5	0.42	$2a_u \rightarrow 3b_{3g}$	π—π^*	45.4	46.2	0.46	$2a_u \rightarrow 4b_{3g}$	$\pi \rightarrow \pi^*$
						45.9	0.40	$1b_{2u} \rightarrow 2b_{1g}$	L—M		48.2	0.73	$1b_{3u} \rightarrow 2b_{1g}$	L—M
											53.1	0.49	$1b_{2u} \rightarrow 2b_{1g}$	L—M

Table IV. Electronic Transitions (Energy in Kilokaysers)

		Co^{II}					Ni^{II}					Cu^{II}		
Exp.	**Calcd.**	**Osc. Str.**	**Transition**	**Nature**	**Exp.**	**Calcd.**	**Osc. Str.**	**Transition**	**Nature**	**Exp.**	**Calcd.**	**Osc. Str.**	**Transition**	**Nature**
21.0	19.7	0.14	$2a_u \rightarrow 3b_{2g}$	L—M										
	9.0	0.09	$3b_{2g} \rightarrow 3b_{1u}$	M—L	(21.1)	17.3	0.01	$3b_{2g} \rightarrow 3b_{1u}$	M—L	21.0	24.0	0.05	$3b_{2g} \rightarrow 3b_{1u}$	L—L
	19.5	0.01	$2b_{1u} \rightarrow 3b_{2g}$	L—M										
	24.0	0.11	$3b_{3g} \rightarrow 3b_{1u}$	M—L	23.2	22.9	0.13	$3b_{3g} \rightarrow 3b_{1u}$	M—L	27.5	26.8	0.41	$1b_{3u} \rightarrow 2b_{1g}$	L—M
					26.7	27.2	0.39	$1b_{3u} \rightarrow 2b_{1g}$	L—M					
33.3	32.2	0.12	$2b_{2g} \rightarrow 3b_{1u}$	L—L		30.0	0.10	$2b_{2g} \rightarrow 3b_{1u}$	L—L		30.7	0.07	$3b_{3g} \rightarrow 3b_{1u}$	M—L
	34.9	0.49	$1b_{3u} \rightarrow 2b_{1g}$	L—M	30.7	33.7	0.32	$1b_{2u} \rightarrow 2b_{1g}$	L—M	30.0	31.9	0.29	$1b_{2u} \rightarrow 2b_{1g}$	L—M
						34.7	0.03	$2b_{3g} \rightarrow 3b_{1u}$	L—L		33.9	0.06	$2b_{2g} \rightarrow 3b_{1u}$	M—L
	38.8	0.01	$1a_u \rightarrow 3b_{2g}$	L—M						35.4	38.8	0.04	$2b_{3g} \rightarrow 3b_{1u}$	L—L
38.5	39.3	0.04	$2b_{1g} \rightarrow 3b_{1u}$	L—L	38.5	44.0	0.42	$2a_u \rightarrow 4b_{3g}$	$\pi \rightarrow \pi^*$					
	39.7	0.35	$1b_{2u} \rightarrow 2b_{1g}$	L—M										
48.0	43.4	0.41	$2a_u \rightarrow 4b_{3g}$	$\pi \rightarrow \pi^*$						42.2	42.9	0.47	$2a_u \rightarrow 4b_{3g}$	$\pi \rightarrow \pi^*$
											48.3	0.19	$2b_{1g} \rightarrow 2b_{3u}$	M—L

planar structure and in the Cu case the metal atom is out of the molecular plane.

Finally, the symmetry-forbidden d→d transitions are expected to fall in the region of about 20-30 kK for all complexes and are probably obscured by the more intense symmetry-allowed $3b_{2g} \rightarrow 3b_{1u}$ transition.

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