Inorg. Chem. **1980**, *19*, 2779–2784

served if cycles were lying parallel to (00*l*) layer planes. These observations constitute a first direct experimental result which shows that the highest symmetry axis of guest cations lies parallel to the host lattice layers. A similar assumption has been drawn for the $TaS_2 \cdot 0.25CoCp_2$ compound from a wide-line NMR study.[23]

Conclusion

This vibrational study was centered around the interpretation of the spectra of the host lattice compounds with respect to their intercalates in order to afford new structural information and to study the dynamics of intercalated molecules.

Results of this study lead to the following conclusions:

Vibrational spectra of unintercalated MPX_3 compounds can be interpreted in terms of normal modes of PX_3 units weakly bonded through P–P interactions and of translational motions of metal cations.

Spectra of intercalated compounds are, in the first approximation, the superposition of those of the host lattice and of the guest species. This suggests that sandwiches and intercalated "molecules" are weakly interacting.

The guest molecules are intercalated under the cationic forms, $CoCp_2^+$ and $CrBz_2^+$, and from polarized infrared results we conclude that rings are perpendicular to layer planes.

The electron transfer, which occurs during the intercalation of a neutral molecule, does not modify the strength of the P–P interaction. However, the spectra show several perturbations of modes involving P–S bonds.

The main evidence of a different unit cell multiplicity for manganese intercalated compounds is afforded by the observation of new low-frequency intense absorptions.

From low-frequency Raman results, the guest $CoCp_2^+$ ions seem to be dynamically disordered at room temperature and can undergo rotational jumps around their principal axis.

Other layered chalcogenophosphates MPX_3, where M = Ni, Fe, ..., are currently under investigation, and the vibrational study of several new intercalates is in progress.

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Registry No. $CdPS_3$, 60495-79-6; $ZnPS_3$, 56172-70-4; $MnPS_3$, 59707-74-3; $MnPSe_3$, 69447-58-1; $CoCp_2^+$, 1277-43-6; $CrBz_2^+$, 11077-47-7.

Contribution from the Department of Chemistry,
The University of Chicago, Chicago, Illinois 60637

Internal Electron Transfer in Some Four- and Five-Coordinate Macrocyclic Complexes with Copper and Nickel

JEREMY K. BURDETT*[1] and P. DOUGLAS WILLIAMS

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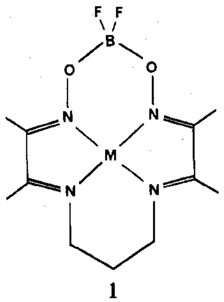
Molecular orbital calculations are presented for complexes of difluoro-3,3′-(trimethylenedinitrilo)bis(2-butanone oximato)borate (LBF_2) with copper and nickel in I and II oxidation states. In the approximately square-planar complexes $MLBF_2$ with M = Cu^I or Ni^I the $x^2 - y^2$ metal orbital lies above a normally unoccupied ligand π^* orbital. This leads to internal electron transfer to the ligand as witnessed experimentally via IR and EPR studies. For M = Cu^{II} or Ni^{II} or for the case where a ligand without conjugated CN groups is used, $x^2 - y^2$ lies below the ligand π^* orbitals and such a process does not occur. The presence of a small HOMO–LUMO gap in these species encourages a tetrahedral distortion experimentally observed in the crystal structure of Cu^ILBF_2. On CO coordination $x^2 - y^2$ always lies below these π^* orbitals. It is found that the CO is attached to the metal largely by interactions between ligand σ orbitals and metal 4s and 4p orbitals, augmented by stabilization via unoccupied CO π^* orbitals of two metal d orbitals (π back-donation). The contribution of the metal d orbitals to the metal–CO σ linkage is zero.

Introduction

There has been recent interest in the study of macrocyclic complexes containing copper atoms as possible models for biochemically important proteins and enzymes. One series of molecules,[2-4] which have been made, contain an apparently Cu^I atom trapped in a distorted square-planar environment (**1**) which readily add carbon monoxide to give the 20-electron species (**2**). There are an interesting series of observations concerning these complexes which we will rationalize in this paper during the development of their molecular orbital structure.



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(i) The free ligand LBF_2 has CN stretching vibrations in the region 1600–1650 cm^{-1}. In the $MLBF_2$ (**1**) species (M

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[1] Fellow of the Alfred P. Sloan Foundation and Henry and Camille Dreyfus Teacher-Scholar.

[2] (a) R. R. Gagné, *J. Am. Chem. Soc.*, **98**, 6709 (1976); (b) R. R. Gagné, J. L. Allison, and G. Lisensky, *Inorg. Chem.*, **17**, 3563 (1978).

[3] R. R. Gagné, J. L. Allison, S. Gall, and C. A. Kovac, *J. Am. Chem. Soc.*, **99**, 7170 (1977).

[4] R. R. Gagné, private communication.

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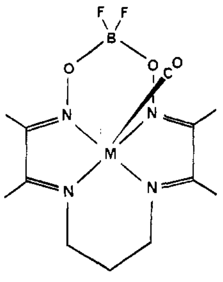

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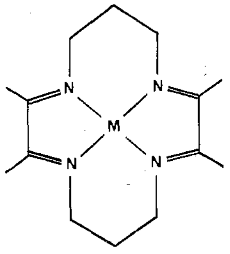
= Cu^I, Ni^I) these bands have disappeared and new absorptions (still apparently associated with the CN linkage) appear at a lower frequency (about 1250 cm^{-1}). In $MLBF_2{\cdot}CO$ complexes (**2**) with M = Cu^I or Ni^I these low-frequency bands are not present but the higher frequency absorptions around 1600 cm^{-1} have reappeared.

(ii) This behavior in result i is not found for M = Cu^{II} or Ni^{II} or for ML complexes (**4**) where L does not contain conjugated CN groups. In these species bands in the 1600-cm^{-1} region are found for free ligand L and both ML and ML·CO complexes.



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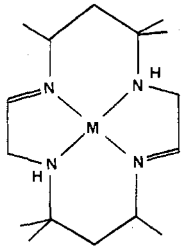

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(iii) EPR results for Ni^ILBF_2 indicate that the unpaired electron is ligand located and the species is best formulated as $(Ni^{II})^+(LBF_2)^-$. Analogous results for $Ni^ILBF_2{\cdot}CO$ show a largely metal d orbital located electron.

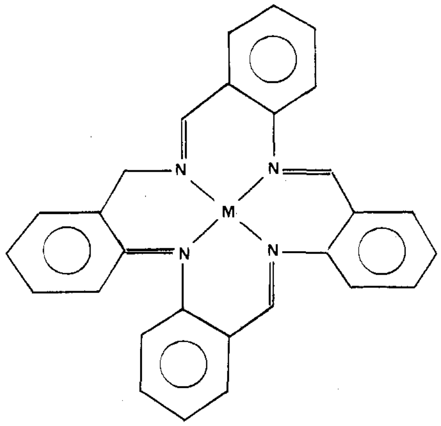
(iv) Cu^ILBF_2 species are basically square planar but with a significant tetrahedral distortion to a local D_{2d} geometry of the CuN_4 unit.

(v) $Cu^ILBF_2{\cdot}CO$ species contain a square-pyramidal $CuN_4{\cdot}CO$ unit with the metal atom very much displaced out of the N_4 plane (~0.94 Å) in a similar fashion to that of the iron atom in deoxyhemoglobin. The LBF_2 ligand adopts an interesting domed shape in this species.

(vi) $Ni^ILBF_2{\cdot}CO$ and $Cu^ILBF_2{\cdot}CO$ species are 19- and 20-electron species, respectively. The Cu–CO distance however is normal and the "CO stretching" frequency at 2080 cm^{-1} only a little higher than in $Ni(CO)_4$ (2054 cm^{-1}). Other than $W(PhC{\equiv}CPh)_3CO$ for which there is a simple explanation[5a] of its 20-electron count at the metal, there are no other carbonyl-containing species which violate the 18-electron rule.[5b]

Molecular Orbital Structure of the Complexes

Our molecular orbital calculations on species **1** through **5** (with the CH_3 groups attached to the diimine units replaced by H atoms for simplicity) have used the extended Hückel method with the parameters given in the Appendix. Figure 1c shows some of the important frontier orbitals of free ligand LBF_2 with a planar $(NCCN)_2$ skeleton.



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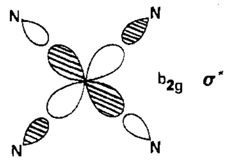
The orbital diagram is characterized by low-lying σ orbitals on the nitrogen atoms which point toward the center of the macrocycle and four pairs of π orbitals associated with the two conjugated NCCN chains. Inclusion of the metal to give $MLBF_2$ (**1**) leads to stabilization of these σ orbitals on interaction with the metal 3d, 4s, and 4p orbitals in the usual manner.[6] The most dramatic orbital energy change on complex formation is that of the Cu $x^2 - y^2$ orbital, strongly destabilized by metal d–ligand σ interactions (**6**).



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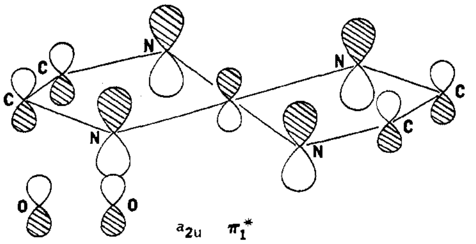
Although we call this orbital "$x^2 - y^2$", it does contain a heavy admixture of ligand σ character since the metal d and ligand σ orbitals of the free units are of very similar energy. The $x^2 - y^2$/ligand σ in-phase combination to lower energy also contains a large contribution from $x^2 - y^2$ but not quite as large as that in the higher energy combination. In square-planar geometry (for convenience we shall use D_{4h} labels for this species although even with a planar skeleton the point symmetry is C_{2v}) it is of the wrong symmetry to be stabilized by mixing with higher energy (4s, 4p) copper orbitals. There is virtually no destabilization of the ligand π* orbitals on complex formation, and thus π back-donation of the traditional sort, which has been suggested[2] to occur in these complexes, is probably not very important. One of these π* orbitals (π_1* of symmetry a_{2u}) is in fact depressed in energy compared to that of the free ligand by the admixture of some metal 4p character in a bonding fashion (**7**).



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Its partner π_2* in the free ligand (**8**) is of the wrong symmetry to interact with any metal orbital and remains unchanged in energy on complex formation. Of crucial importance in our discussion below is the relative ordering of these three orbitals (**6**–**8**) in the four- and five-coordinate complexes.

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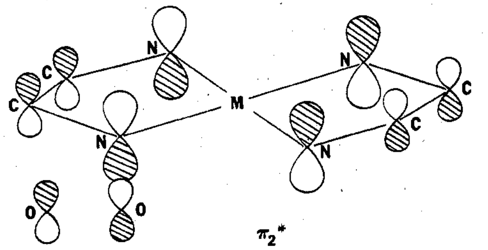
(5) (a) L. M. Laine, R. E. Moriaty, and R. Bau, *J. Am. Chem. Soc.*, **94**, 1401 (1972). (b) In $Cp_2W(CO)_2$ (G. Huttner, H. H. Brintzinger, L. G. Bell, P. Friedrich, V. Bejenke, and D. Neugebauer, *J. Organomet. Chem.*, **145**, 329 (1978)) and $Cp_2Mo(NO)(R)$ (J. L. Calderon, F. A. Cotton, and P. Legzdins, *J. Am. Chem. Soc.*, **91**, 2528 (1969)) which are apparently 20-electron systems the cyclopentadienyl rings have partially slipped off the metal with a concurrent decrease in η number to avoid the 20-electron problem.

(6) M. Elian and R. Hoffmann, *Inorg. Chem.*, **14**, 1058 (1975).



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On coordination of the CO ligand the square-planar pattern of d orbital energies is replaced by that corresponding to the square pyramid. Figure 2 shows the relationship between the orbitals of four- and five-coordinate species. In both cases the copper atom is restrained to lie in the plane of the four nitrogen atoms. The metal z^2 orbital is pushed to higher energy as a result of antibonding interactions with the carbonyl σ orbital and, in the reduced symmetry of the five-coordinate molecule, now contains an appreciable admixture of copper 4s and 4p character. Since both M–CO bonding and antibonding (metal "z^2") orbitals are occupied, a long apical bond might be expected (cf.[7] low-spin d^8 $Ni(CN)_5^{3-}$: $Ni-CN_{bas}$ = 1.838 Å, $Ni-CN_{ap}$ = 1.94 Å). This is not found in practice, and a population analysis of the $Cu^ILBF_2 \cdot CO$ complex (Table I) shows that the carbon monoxide is primarily attached to the metal by strong σ interactions with the copper 4s,4p orbitals, while interaction of the ligand σ and metal d orbitals leads overall to a negligible stabilization as expected. A smaller stabilizing effect is seen via interaction of CO π^* orbitals with filled metal xz,yz orbitals which gives rise to M–CO π back-donation of the conventional type. A similar mechanism for CO attachment is found with all the ligands mentioned above. The important σ interactions between $MLBF_2$ and CO are then very similar to those between the main group species BH_3 and CO. The major difference between the two systems is that in $CuLBF_2$, π back-donation is also possible, leading to a ν(CO) which is less (2070 cm^{-1}) than that in free CO (2148 cm^{-1}) rather than higher as in BH_3CO (2164 cm^{-1}). A similar domination of the population analysis by σ interactions with the copper 4s and 4p orbitals is found for the Cu–N linkages. The importance of $(n + 1)$s,p orbitals in these species has been noted earlier by Hoffmann and co-workers[8,9] in their studies on bonding interactions between the closed-shell species Cu^I/Cu^I and Pt^0/Pt^0. Their importance suggests that perhaps a useful analogue for these five-coordinate systems might be the main-group species square-pyramidal $SbPh_5$. If the Sb 4d electrons are included in the count, this is also a 20-electron species. The importance in general of higher orbitals in determining the properties of transition-metal complexes is still an open question. The present results, although parameter dependent, suggest that for these Cu^I complexes they are very important indeed.

We have performed calculations on $MLBF_2Cl^-$ species to investigate the effect of coordination of a σ donor in the fifth site. From the population analysis (Table I) it is clear that this species is attached by analogous interactions between ligand σ orbitals and copper 4s,4p orbitals. The positive π(d) contribution found for the carbonyl case via π back-donation is absent and is in fact replaced by a negative (destabilizing) contribution to the overlap population. This π-antibonding effect resulting from occupation of both M–Cl bonding and antibonding orbitals has been noted[10] by Okawa and Busch in a recent study on related systems. Our results are consistent with the observations[11] of larger equilibrium constants K for reaction 1 when X is a π acceptor than when X is a σ donor.

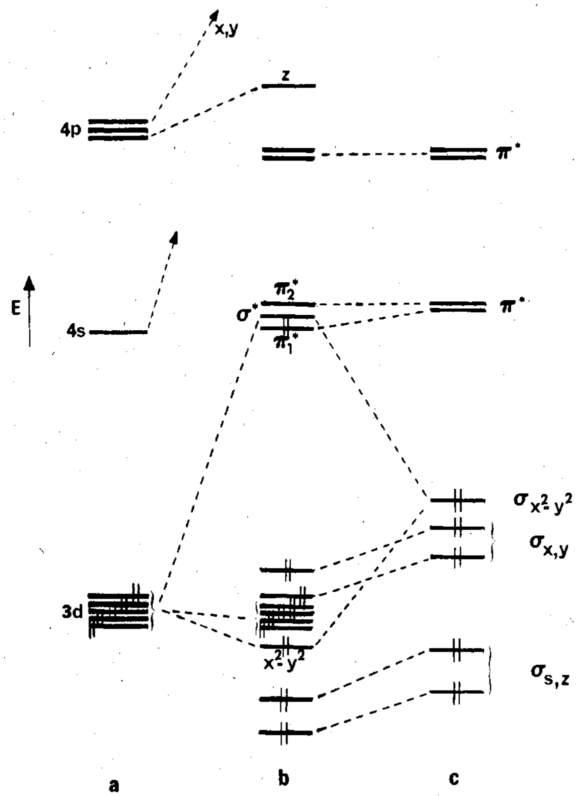

Figure 1. Molecular orbital diagram for the complex Cu^ILBF_2 (b) showing its assembly from the diagram for the free ligand (c) and the metal (a). The ligand has an idealized planar skeleton in parts b and c, and the metal lies in the ligand plane. Only the orbitals which change in energy significantly on complexation have been included. The ligand σ orbitals are labeled with subscripts to indicate with which central atom orbitals they predominantly interact. The orbital occupancies are for neutral ligand and Cu^I.

Table I. Cu–X Population Analysis in $Cu^ILBF_2 \cdot X$

	total	σ(s,p)	σ(d)	π(d)	π(p)
Cu–CO (sq planar)	0.55	0.45	0.02	0.07	0.01
Cu–CO (obsd geom)	0.66	0.54	0	0.09	0.02
Cu–Cl^- (sq planar)	0.34	0.41	0.01	−0.08	0

Table II. C–N Population Analysis

	total	σ	π
LBF_2	1.11	0.80	0.31
Cu^ILBF_2 (sq planar)	1.01	0.82	0.19
$Cu^ILBF_2 \cdot CO$ (pyramid)	1.11	0.82	0.29
$Cu^ILBF_2 \cdot CO$ (domed)	1.12	0.81	0.31

$$CuLBF_2 + X \rightleftharpoons CuLBF_2 \cdot X \qquad (1)$$

$$X = CO \qquad K = 1.2 \times 10^5\ M^{-1}$$

$$X = \text{1-methylimidazole} \qquad K = 1.6 \times 10\ M^{-1}$$

Very similar results are found from our calculations on **1** and **3** and their respective CO adducts. We are not in a position therefore to comment on the suggestion[4] that the presence of the BF_2 group aids CO binding.

Level Ordering in $MLBF_2$ and $MLBF_2 \cdot CO$

The diagrams of Figures 1 and 2 show that three orbitals, $x^2 - y^2$ (σ^*) and a pair of ligand π^* orbitals (π_1^* and π_2^*),

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(7) K. N. Raymond, P. W. R. Corfield, and J. A. Ibers, *Inorg. Chem.*, **7**, 842 (1968).

(8) P. K. Mehrota and R. Hoffmann, *Inorg. Chem.*, **17**, 2187 (1978).

(9) A. Dedieu and R. Hoffmann, *J. Am. Chem. Soc.*, **100**, 2074 (1978).

(10) H. Okawa and D. H. Busch, *Inorg. Chem.*, **18**, 1555 (1979).

(11) R. R. Gagné, J. L. Allison, and D. M. Ingle, to be submitted for publication.

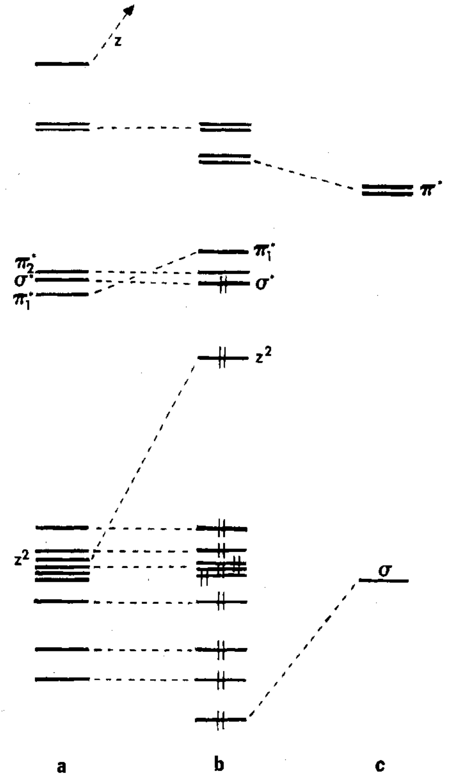
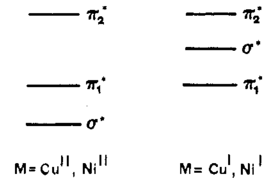


Figure 2. Molecular orbital diagram for the complex $Cu^ILBF_2{\cdot}CO$ (b) showing its assembly from the diagram for the complex Cu^ILBF_2 (a) and free CO (c). The ligand has an idealized planar skeleton in parts b and c and the metal atom lies in the ligand plane.

lie close in energy in the HOMO–LUMO region. In Cu^I, Ni^I (Cu^{II}), and Ni^{II} systems, 2, 1, and 0 electrons, respectively, are associated with this group of orbitals. Two different level orderings are found from the results of the molecular orbital calculations (**9**). Because the d orbitals are more contracted



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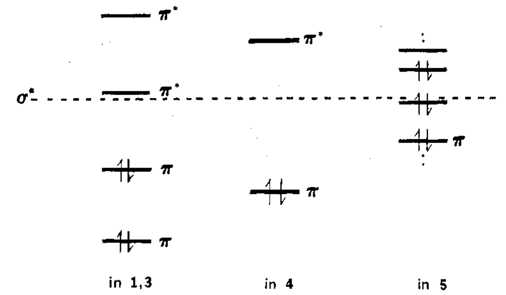
in M^{II} compared to those in M^I, the overlap with the ligand σ orbitals in $M^{II}LBF_2$ is less than in M^ILBF_2. Correspondingly $x^2 - y^2$ lies to a lower energy (less M–N antibonding) in the higher oxidation state.[12] Our calculations indicate therefore that in $MLBF_2$ species (M = Cu^I, Ni^I) the HOMO is a ligand π^* orbital. Experimentally this is suggested by results i and iii above and is clearly shown in the CN population analysis of Table II where occupation of a CN π^* orbital in the four-coordinate complex leads to a drop of about 10%. Our results are in accord with observation ii that this behavior is not found for Cu^{II}. For Ni^{II} this trio of orbitals is empty and effects of this type do not need to be considered (and indeed are not observed). For ligands where the CN groups are not conjugated (in **4**, for example) the π-orbital structure is very different (**10**) with the π^* orbital of each separated CN unit lying very much higher in energy than orbital **7** of the conjugated C_2N_2 system. Thus this internal electron transfer from metal to ligand is not predicted to occur with nonconjugated macrocycles, and indeed experimentally[4] these species are found to behave normally. This ligand reduction process has been suggested[13] to occur in the species Cu^ITAAB. (But the vibrational frequency shifts on reduction on which such a suggestion was made are considerably smaller than in the present case with LBF_2 as a ligand.) Our molecular orbital calculations on the free ligand show that the π-orbital structure contains a cluster of occupied ligand orbitals which straddle the energy of $x^2 - y^2$ (**10**). Thus in Cu^I species no electron transfer to the ligand should occur. Of interest however is the possibility in the Ni^I, Cu^{II}, or Ni^{II} analogues of the reverse process, namely, electron transfer *from* the ligand to the metal. One possibility which we are unable to test by using our one-electron molecular orbital model is the likelihood of a triplet Cu^ILBF_2 species with the configuration (**9**) $(\sigma_1{}^*)^1(\pi^*)^1$. In the square-planar complex these two orbitals lie close in energy. In the (experimentally observed) tetrahedrally distorted system they move further apart in energy as we show below. In the triplet of course only one electron resides in a predominantly ligand-located orbital.



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Recent XPS studies[14] on Cu^ILBF_2 revealed a Cu 2p binding energy in the region associated with Cu^I. *Formally* the description suggested above is $Cu^{III}(LBF_2)^{2-}$ and is at variance with these results. However, first, the heavy mixing between Cu $x^2 - y^2$ and the ligand σ orbitals means that the σ^* orbital **6** does contain a large contribution from the latter and the filled bonding combination, a significant amount of metal character. Second, the distorted four-coordinate geometry (vide infra) involves mixing of the HOMO and LUMO of the square-planar structure, and as a result some metal character is mixed into the $\pi_1{}^*$ orbital. These two effects mean that this charge transfer is nowhere near being complete and thus experiment and theory are not as far apart as appears at first sight.[15]

Geometries of $MLBF_2$ and $MLBF_2{\cdot}CO$

The square-planar d^9,d^{10} molecules $MLBF_2$ have a rather small HOMO–LUMO gap associated with the orbitals of symmetry b_{2g} and a_{2u}. Perturbation theory arguments or the application of the second order Jahn–Teller theorem leads to

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[12] Our calculations used the same values of the VSIP's for all $M^{I,II}$. In fact higher values probably apply for M^{II} compared to M^I. The use of a deeper lying d orbital basis will mean that $x^2 - y^2$ will lie even lower in energy in the divalent systems and reinforce the effect we see here from the radial wave function contraction alone.

[13] (a) V. Katovic, L. T. Taylor, F. L. Urbach, W. H. White, and D. H. Busch, *Inorg. Chem.*, **11**, 479 (1972). (b) More conclusive evidence for ligand reduction has recently been found in some Fe^I–tetraphenylporphyrin systems where abnormally long CN distances are found (W. R. Scheidt, private communication).

[14] R. R. Gagné, J. L. Allison, C. A. Kovac, W. S. Mialki, T. J. Smith, and R. A. Walton, to be submitted for publication.

[15] The detailed numerical correlation between XPS binding energies and the molecular orbital structure of the system is a rather murky area. In addition to the electronic structure of the neutral molecule, the relaxation energy and Madelung corrections also need to be included. From the EHMO charges associated with two electrons in the $\pi_1{}^*$ orbital (located close to the Cu), we calculate a Madelung correction to the binding energy of about 2 eV. This is of the right order of magnitude to make distinction between a formally Cu^{III} species (but with a large Madelung correction from the electrons in $\pi_1{}^*$) and a Cu^I species (with no such correction) difficult.

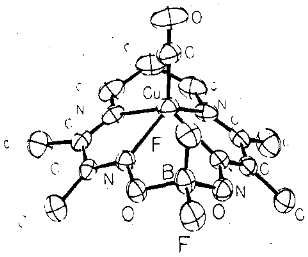
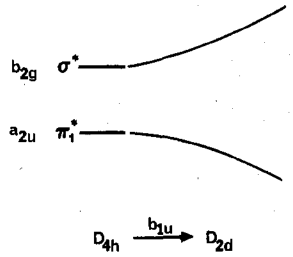


Figure 3. Crystal structure of $Cu^ILBF_2 \cdot CO$ from ref 2.

the prediction of a b_{1u} distortion of this geometry to a D_{2d} point group of the MN_4 entity (a tetrahedral distortion). This is experimentally observed in the crystal structure[2] of Cu^ILBF_2 and the numerical results of our molecular orbital calculations show that the total energy decreases on such a distortion, dominated by rapid stabilization of the HOMO (**11**). The driving force for the distortion is the stabilization of $x^2 - y^2$ on moving from the square plane to the tetrahedron. (Cu^I species in the absence of a restrictive ligand are usually tetrahedral.) If $x^2 - y^2$ lies higher in energy than $\pi_1{}^*$ in $MLBF_2$ (as for $M = Cu^I$), then there is an avoided crossing on distortion. In this case the HOMO of the distorted species contains a sizable contribution from the metal $x^2 - y^2$ orbital as the $x^2 - y^2$ orbital and $\pi_1{}^*$ orbitals of the square plane mix on distortion. During this process therefore in the Cu^I and Ni^I species some of the ligand-located charge in the square-planar structure returns to the metal. We would therefore predict a correlation between the vibrational CN stretching frequencies and the degree of distortion away from the square-planar structure. By suitable macrocycle choice Gagné and co-workers have succeeded[4] in being able to study an equilibrium of the type shown in eq 2 but no structural data are available, on either of these two distinctly different entities.



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$$Ni^IL \rightleftharpoons (Ni^{II})^+(L)^- \qquad (2)$$

The five-coordinate $MLBF_2 \cdot CO$ species exhibits an interesting domed geometry[3] where (i) the metal atom is 0.96 Å out of the plane of the N atoms with an average (O)CCuN angle of 117°, (ii) the side flaps of the ligand have folded down about the line joining the two nitrogen atoms (Figure 3), and (iii) the O_2BF_2 and $(CH_2)_3$ units remain in approximately the same position as in the square-planar complex. This out-of-plane distortion is probably the largest known. Deoxyhemoglobin[16] has an analogous angle of 110°; most species with more than six d electrons have angles of 96–101°. Our calculations reproduce the direction of the observed distortion. (Since the Cu–N distances change significantly (~0.20 Å) on moving from planar four-coordinate to domed five-coordinate structures, we do not trust our extended Hückel calculations to accurately predict the size of the distortion. EHMO calculations are much more reliable when we look at bond angle rather than bond distance changes.) The system is strongly stabilized when the copper atom moves out of the plane of the four N atoms with the other atoms fixed. An additional but somewhat smaller stabilization is found as the C_2N_2 "flaps" are folded down. The "punch bowl" geometry where in addition the O_2BF_2 and $(CH_2)_3$ units are folded down is found to be strongly disfavored as a distortion mode.

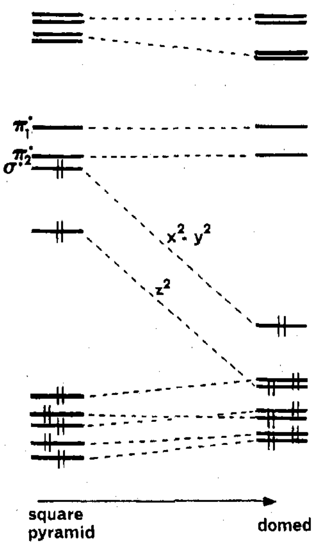

Figure 4. Behavior of the orbitals of $Cu^I \cdot BF_2CO$ on distorting the molecule of Figure 2b to the experimentally observed geometry of Figure 3.

Table III. Extended Hückel Parameters

atom	orbital	exponent	H_{ii}, eV
H	1s	1.300	−13.60
B	2s	1.300	−15.20
B	2p	1.300	−8.50
C	2s	1.625	−21.40
C	2p	1.625	−11.40
N	2s	1.950	−26.00
N	2p	1.950	−13.40
O	2s	2.275	−32.30
O	2p	2.275	−14.80
F	2s	2.425	−40.00
F	2p	2.425	−18.10
Cl	3s	2.033	−30.00
Cl	3p	2.033	−15.00
M	4s	2.200	−11.40
M	4p	2.200	−6.06
Cu^I	3d	5.95 (0.5933),[a] 2.30 (0.5744)	−14.00
Cu^{II}	3d	5.95 (0.6062), 2.50 (0.5371)	−14.00
Ni^I	3d	5.75 (0.5817), 2.20 (0.5890)	−14.00
Ni^{II}	3d	5.75 (0.5959), 2.40 (0.5497)	−14.00

[a] The 3d orbitals are in double-ζ form with expansion coefficients in parentheses.

The driving force for pyramidalization is the stabilization of $x^2 - y^2$ and z^2 orbitals (Figure 4) on moving the metal atom out of the plane as metal–ligand antibonding effects are relieved (thus ensuring incidentally that the $x^2 - y^2$ orbital always lies below the $\pi_1{}^*$ orbital of the ligand in the $MLBF_2 \cdot CO$ complexes). An analogous effect is responsible for the out-of-plane/in-plane behavior of hemoglobin on moving from the high-spin to the low-spin form. In the present system the smaller out-of-plane displacement found experimentally for the Cu^{II} species is understandable. With the $x^2 - y^2$ orbital half-occupied, the driving force for pyramidalization is less. A detailed dissection of this molecular orbital result is given elsewhere.[6]

Discussion

We have suggested that the nature of the HOMO in some of these copper-containing systems changes in nature from being ligand located to being metal located as a function of

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the oxidation state of the metal, its coordination number, the nature of the macrocyclic ligand, and indeed the finer details of its geometry. In molecular orbital terms the reasons for such behavior lie first with the presence of low-lying (usually π-type) orbitals in the macrocycles and second with relatively deep-lying metal d orbitals at this end of the periodic table. (For gallium, two elements further along in the periodic table, we seldom consider the 3d orbitals when looking at its chemistry: they are usually considered to be buried in the core.) It is interesting to speculate that this internal electron-transfer process, which may be tailored by adjustment of the variables, we have just mentioned plays an important role in the molecular mechanism for electron transport in copper-containing proteins. Unfortunately at present there is no detailed description of the role of the copper site available to examine this idea further.

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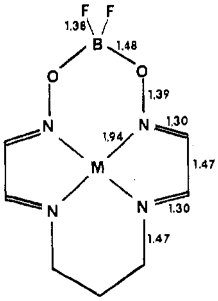
Appendix



12

Our calculations were carried out on molecule **12** with the dimensions given. It differs from the ligand used in the experimental work by replacement of some terminal alkyl groups by H atoms. The parameters of the extended Hückel calculations[17] are given in Table III. The calculations are of course rather crude ones, and the position of the $x^2 - y^2$ orbital will be sensitive to the actual choice of exponents and coefficients as in any calculation. Use of an arbitrary single-ζ radial 3d function gave an orbital description qualitatively similar to that described in the paper. The $x^2 - y^2$ orbital dropped in energy as the (single) exponent increased in these calculations. The Richardson et al. double-ζ functions,[18] with which we obtained the results described, needed to be employed to distinguish quantitatively, for example, between isoelectronic Ni^I and Cu^{II}. Values of the metal 4s and 4p orbital exponents and s, p, and d VSIP's are those used by Hoffmann and Mehrota.[9] Bond lengths for the other molecules studied were similar to those of **12**. In the carbonyl adducts M–CO = 1.78 Å and C–O = 1.12 Å.

Registry No. LBF_2, 74219-94-6; Cu, 7440-50-8; Ni, 7440-02-0.

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Stability and Kinetics of a Macrocyclic Tetrapeptide Complex, Tetradeprotonated (*cyclo*-(β-Alanylglycyl-β-alanylglycyl))cuprate(II)

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The 14-membered macrocyclic ligand *cyclo*-(β-alanylglycyl-β-alanylglycyl) (C) reacts with copper(II) and releases four protons in base to form $Cu(H_{-4}C)^{2-}$. The ESR spectrum at room temperature shows a finely resolved nitrogen fine structure and is consistent with a structure having four deprotonated peptide nitrogens in a planar arrangement about copper(II). A stability constant of log $^*K = -25.1$ (for the reaction $Cu^{2+} + C \rightleftarrows Cu(H_{-4}C)^{2-} + 4H^+$) is determined by competition with triethylenetetramine (trien). The rate of reaction of $Cu(H_{-4}C)^{2-}$ with trien is many orders of magnitude slower than that of other copper(II)-peptide complexes. The kinetics of the trien reaction corresponds to a reaction sequence in which protonation by solvent, coordination by trien, and a second protonation by solvent are required to displace the macrocyclic ligand. The acid-dissociation rates are also relatively slow. The rate-determining step is proton transfer to a peptide nitrogen with a rate constant of 6.2×10^5 M^{-1} s^{-1} for H_3O^+ and 4.6×10^3 M^{-1} s^{-1} for CH_3COOH. Above pH 5 a higher order hydrogen ion dependence is observed.

Introduction

Oligopeptides react with copper(II) ion to form complexes in which the peptide nitrogen atoms deprotonate and coordinate to the metal. Potentiometric,[1-3] spectrophotometric,[3] and crystallographic[4] methods have been used to establish the structure and thermodynamic stabilities of these complexes. The kinetics and mechanisms have been studied for many copper–peptide reactions.[5-11]

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