five-membered ring OA's is not clear.

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Supplementary Material Available: Tables of 6-31G* optimized structures (6 pages). Ordering information is given on any current masthead page.

The Metal–Nitroxyl Interaction in MNO Metallacycles (M = Cu, Pd). An ab Initio SCF/CI Study

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Abstract: Ab initio SCF and CI calculations have been carried out on the isoelectronic and isostructural complexes $(CH_3)_2NOCuBr_2$ and $(CH_3)_2NOPdClPH_3$, where dimethyl nitroxide is a model for 2,2,6,6-tetramethylpiperidinyl-1-oxy (TMPO). Calculations show that the $CuBr_2$ and $PdClPH_3$ radicals have quite a different electronic structure, the magnetic orbital being delocalized with major weight on the ligands for $CuBr_2$ and mainly localized on the metal for $PdClPH_3$. The different nature of the metal fragments influences the η^2 coordination of the nitroxyl radical. In the copper complex, the bonding interaction is largely delocalized over the five atoms of the molecular plane. Through-space interactions between the bromine atoms and the nitroxide group contribute to stabilize the molecule. The net charge of the nitroxide is not significantly modified with respect to the free $(CH_3)_2NO$ radical. In the palladium complex, a significant charge transfer occurs from the metal to the NO π^* orbital, resulting in a strong, covalent interaction between these orbitals. The other ligands have little contribution in the bonding. Both the Cu and the Pd complexes are computed to be strongly diamagnetic, with respective singlet–triplet energy separations of 5000 and 17 000 cm^{-1}.

1. Introduction

The complexes of transition metals with nitroxyl ligands are the subject of a thorough physical and chemical investigation in relation with the design of new magnetic materials.[1-4] Concerning more specifically copper(II)–nitroxyl species, the magnetic properties have been shown to strongly depend upon the coordination geometry: an equatorial coordination of the nitroxyl ligand induces either strong antiferromagnetism or diamagnetism,[3] whereas an axial coordination generally yields complexes with a ferromagnetic behavior.[4] The importance of the metal–ligand distances and of the electronic structures of the metal and ligand have also been recognized.[2c] All copper(II)–nitroxyl complexes studied up to recent times were characterized by an η^1–O coordination mode. The only exception concerns the adduct of copper(II) bromide with 2,2,6,6-tetramethylpiperidinyl-1-oxy (TMPO) in which both the oxygen and the nitrogen atoms are at bonding distance from the metal (d_{Cu-O} = 1.860 Å, d_{Cu-N} = 1.998 Å).[5] The X-ray characterization of the geometrical structure has revealed some other remarkable features of the molecule: (i) planarity of the $CuBr_2(NO)$ moiety, corresponding to a distorted square-planar coordination for Cu, and (ii) a slight increase of the NO bond length and more pronounced pyramidalization of the nitrogen atom with respect to the geometry of the isolated TMPO.

Although these structural features are unprecedented with copper, they are reminiscent of the M–NO metallacycles characterized with various metals (M = V(III,V), Mo(II,IV,VI), U(VI), and Pd(II)).[6-8] Among these molecules the two complexes of palladium(II), $PdCl(PPh_3)TMPO$[7] and $Pd(C_5HF_6O_2)(C_9$-

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$H_{18}NO$),[8] appear very similar to the copper adduct with a somewhat longer NO distance (1.372 and 1.346 Å, respectively, compared to 1.304 Å in the Cu complex). The electronic structure of the palladium complexes has been interpreted in terms of a one-electron reduction of TMPO.[7] The possible occurrence of a similar redox process in $CuBr_2TMPO$ has been discussed, although the formal charge distribution assumed for copper(II)-nitroxyl systems does not require any charge transfer concerning TMPO. It has been noticed, however, that all redox processes characterized for copper(II)-nitroxyl systems correspond to an *oxidation* of the nitroxide.[9] Furthermore, the reactivity of $CuBr_2TMPO$ in solution toward benzyl alcohol suggests the presence of the nitrosonium ion as an oxidizing intermediate,[5] which seems uncompatible with the reduction of TMPO. However, the presence of oxidized TMPO in the complex could not be more seriously considered, since the structural characters of the nitrosonium ion (planarity of the C_2NO moiety, short NO distance of 1.22 Å),[9b,10] are in complete disagreement with those reported for the TMPO ligand in the Cu(II) complex.

To summarize, the M-N-O metallacycles in $CuBr_2TMPO$ (**1**) and $PdCl(PPh_3)TMPO$ (**2**) are isoelectronic and exhibit similar coordination mode and geometrical structures, but the formal charge of the NO fragment appears quite different in both molecules. According to the formal description of these molecules, the bonding in **1** and **2** should involve different mechanisms: an electron transfer from the metal to TMPO in the palladium complex leading to the coordinative interaction of two closed-shell fragments and the symmetry-allowed overlap of the magnetic orbitals of $CuBr_2$ and TMPO in the copper complex.

We therefore decided to check the validity of the formal description of both **1** and **2** by investigating the orbital interactions, the charge distributions in the metallacycles, and the role of the ancillary ligands through ab initio SCF and CI calculations. In view of the importance of the magnetic properties for the nitroxyl complexes, the origin of the reported diamagnetism of **1** has been investigated through a calculation at the CI level of the singlet-triplet energy separation.

2. Computational Details

The calculations were carried out on model systems represented in Figure 1 and obtained from the replacement of TMPO by $(CH_3)_2NO$ and of PPh_3 by PH_3 in **2**. All CH distances were assumed to be equal to 1.09 Å. The CH bonds were oriented collinear to the three C-C bonds originating from C_1 in **1**, leading to H-H distances 1.758, 1.783, and 1.825 Å. The model phosphine ligand was characterized by P-H and H-H distances of 1.420 and 2.066 Å, respectively. All other geometrical parameters were taken from the X-ray characterization of **1** (Cu-Br = 2.272 Å, Cu-N = 2.021 Å, Cu-O = 1.864 Å, N-O = 1.308 Å, N-C = 1.508 Å, Cu-C = 2.937 Å) and of **2** (Pd-Cl = 2.321 Å, Pd-P = 2.256 Å, Pd-N = 2.093 Å, Pd-O = 2.023 Å, N-O = 1.372 Å, N-C = 1.530 Å). The original distances have been slightly modelized in order to ensure a perfect symmetry between the two methyl groups. A calculation has also been carried out on the hypothetical $CuCl_2$ fragment assuming the same X-M-X angle as for **1** (106.5°) and Cu-Cl distances of 2.191 Å.

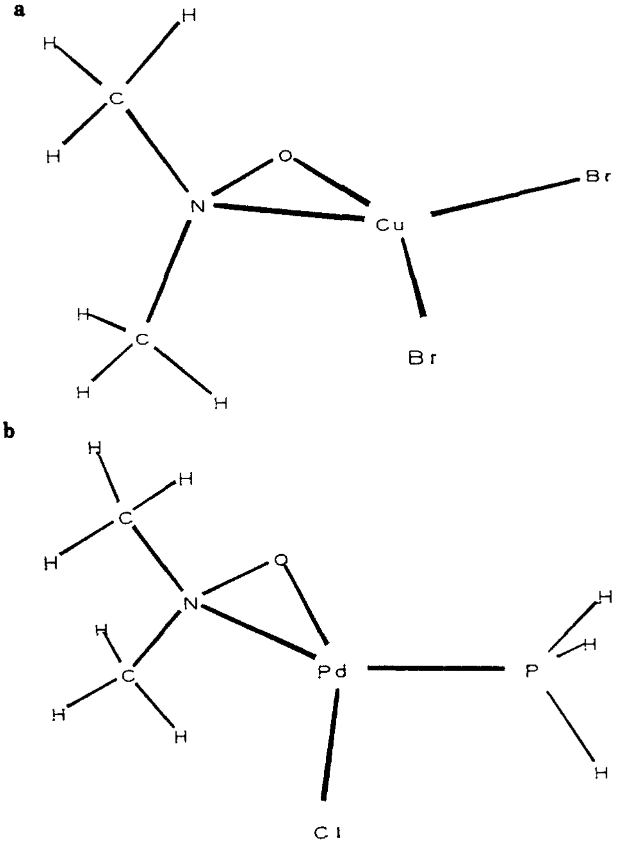

Figure 1. ORTEP plot of the model molecules used in the ab initio calculations: (a) $(CH_3)_2NOCuBr_2$ and (b) $(CH_3)_2NOPdClPH_3$. The M-N-O metallacycle lies in the *xOy* plane.

The ab initio MO SCF calculations have been carried out by using the ASTERIX system of programs (CRAY-2 version).[11] The basis sets were minimal for the inner shells and for the outer p shell of metal atoms and double-ζ for the other valence shells, except for the 3d shells of Cu and Br and for the 4d shell of Pd which are triple-ζ. The basis set for Cu was taken from Hyla-Kryspin et al.[12] and completed with a function of exponent 0.15 describing the 4p shell and a diffuse d function of exponent 0.12, thus yielding a (13,8,6) Gaussian contracted to [5,3,3]. For the Pd atom, the (15,9,8) set of primitives optimized by Veillard and Dedieu[13] was again supplemented with one p function of exponent 0.15 and then contracted to [6,4,4]. The basis sets for metal atoms were used in conjunction with the basis sets optimized by Huzinaga[14] for hydrogen ((4) contracted into [2]), first-row atoms ((9,5) contracted into [3,2]), and chlorine ((11,7) contracted into [4,3]). Finally, the (13,9,6) basis set used for bromine was taken from the (13,9,5) set of Dunning.[15] A d function of exponent 0.35 was added, and the obtained set was contracted to [5,4,3].

3. The Molecular Fragments

3.1. $(CH_3)_2NO$. Open-shell SCF calculations carried out on the dimethyl nitroxide radical confirm the NO π^* character of the semioccupied molecular orbital (SOMO). The pyramidal conformation of the N atom (with the same geometry as observed in the Cu complex) is preferred to the planar form, but the energy difference is no more than 0.3 kcal/mol. The deviation from planarity has not been further optimized, but the trend toward pyramidalization of the C_2NO group agrees with experiment[16] and with the results of previous ab initio calculations carried out for H_2NO.[17] The π^* orbital is mainly localized on oxygen (76%

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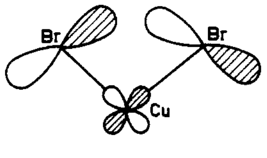
vs 22% on N), and the opposite polarization is obtained for the π orbital (see Figure 2). This π_{NO} orbital is split into two components due to a four-electron interaction with the occupied orbitals of the methyl groups. The Mulliken population analysis yields an overall negative charge of −0.57e on the NO moiety, almost equally distributed between nitrogen and oxygen.

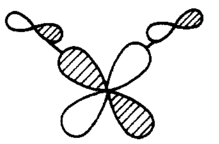
3.2. CuBr$_2$. The isolated monomeric transition-metal dihalides are generally believed to be linear ($D_{\infty h}$) and with essentially ionic bonds. The quantum chemical studies carried out on CuF$_2$ and CuCl$_2$ in the $D_{\infty h}$ conformation[18] agreed to assign the $^2\Sigma_g^+$ state as the ground state, with the σ_g open-shell orbital having major weight on the metal d_{x^2} orbital (assuming the x axis to contain the molecule). CuF$_2$ and CuCl$_2$ in their ground state—and in the lowest excited states—therefore correspond to a d^9 electronic configuration for copper. As noticed by Shaskin and Goddard,[18e] this formal ionic description is purely idealistic, and significant neutralization arises from the partial filling of 4s and and 4p orbitals. We obtained a similar description from a SCF calculation carried out on linear CuBr$_2$.

The bending of the copper dihalides in the xy plane completely modifies the electronic structure of these molecules. When copper bromide is considered with a Br–Cu–Br angle of 106.5°, the two bromine atoms are facing each other, separated by a relatively short distance of 3.2 Å. An important interaction therefore develops between the bromine p_x valence orbitals, and the out-of-phase combination $p_x(Br_1) + p_x(Br_2)$ is pushed up in energy. This orbital combination, slightly modified by some admixture of the bromine p_y orbitals, can interact with the copper d_{xy} level. The out-of-phase term of this interaction (metal–ligand antibonding) gives rise to the SOMO of the bent CuBr$_2$ system (**1**). At variance from what happens for the linear conformation, the destabilized $p_x + p_x$ bromine orbital combination has been sufficiently raised in energy to reach the level of the d copper orbitals and induce a real delocalization of the SOMO over the three atoms *with major weight on bromine and no more than 24% contribution from the metal.* The in-phase (metal–ligand bonding) term of the same interaction will therefore give rise to a doubly occupied orbital with major contribution (78%) from the metal d_{xy} orbital (**2**). As a consequence, the metal d_{xy} population in the bent CuBr$_2$ remains as high as 1.79e. *The bent CuBr$_2$ fragment can therefore neither be considered as a complex of Cu(I) nor of Cu(II) but as an intermediate entity due to the large delocalization of the SOMO over the copper and bromine atoms.* This representation of the CuBr$_2$ moiety rules out the interpretation of the stability of CuBr$_2$TMPO as exclusively coming from the overlap of the magnetic orbitals in the fragments. The capital and unsuspected role of the bromine ligands in the magnetic orbital of the CuBr$_2$ moiety explains why the tentative interpretation of the electronic structure and properties of CuBr$_2$TMPO in terms of the pure metal d and NO π^* orbitals has led to contradictions.[5]



SOMO

1



2

A qualitatively similar representation of the SOMO was obtained for the bent conformation of CuCl$_2$. In spite of the smaller X–X distance, the repulsive interaction between the less diffuse p_x orbitals of chlorine is not sufficient to localize the SOMO on the Cl atoms. A balanced, delocalized description was therefore obtained corresponding to 33% weight on each chlorine atom. The weight on the metal d_{xy} is therefore 34%, compared to 24% for CuBr$_2$.

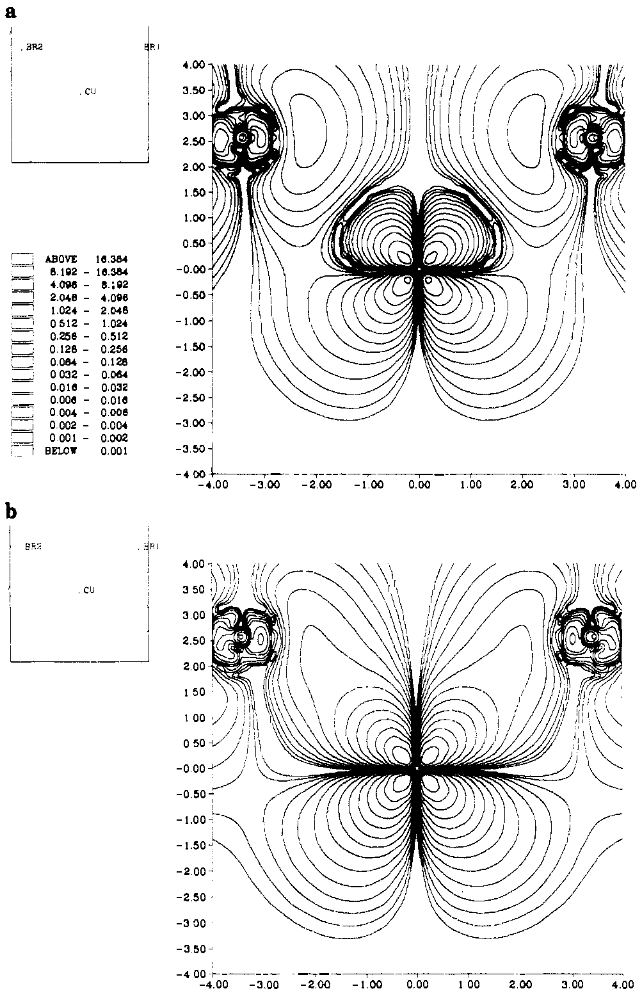


Figure 2. Plot of the electron densities associated with the SOMO (a) and with the doubly occupied orbital corresponding to the metal–ligand bonding interaction (b) in the CuBr$_2$ radical. Grid intervals are given in bohrs. The outermost contour corresponds to a density of 0.001 eÅ^{-3}. Thereafter successive contours differ by a factor of 2.

It must be noted that configuration interaction is requested in order to obtain the correct ordering for the state energies of bent CuX$_2$ molecules. The SCF results are biased in favor of a metal-localized SOMO because of the symmetry constraints that force the weakly overlapping halogen atoms to share the unpaired electron. More specifically, two distinct doublet states of b$_1$ symmetry can be characterized for CuBr$_2$ from symmetry-adapted open-shell SCF calculations. The lowest in energy (−6771.303h) localizes the unpaired electron on the d_{xy} orbital of Cu (93%). The other $^2B_1$ state (−6771.280h) corresponds to a SOMO mainly localized (89%) on the destabilized bromine p_x combination. The results discussed above were obtained from CI expansions limited to single excitations from five reference states corresponding to a localization of the unpaired electron either on a p_x or p_y orbital combination of the halogen atoms or on the metal d_{xy} orbital. This "singles on multireference" CI expansion is expected to properly relocalize the unpaired electron in a symmetry-adapted formalism.[19] The energy associated to this CI expansion was −6771.380h for CuBr$_2$. Figure 2 displays the electron density associated with the SOMO of CuBr$_2$ and its doubly occupied metal–ligand

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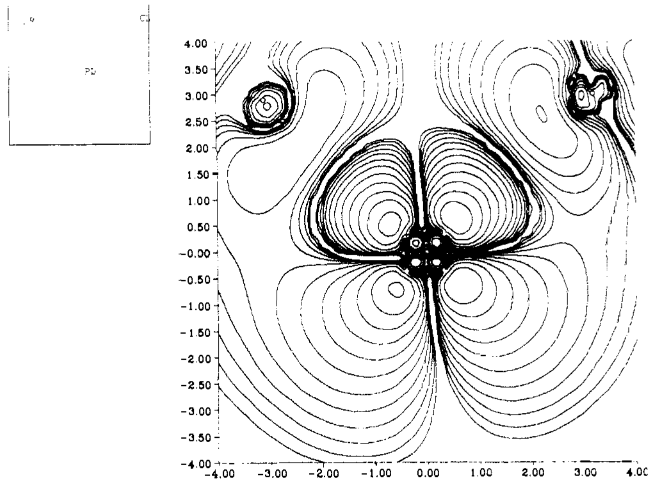

Figure 3. Plot of the electron densities associated with the SOMO of the $PdClPH_3$ radical. Contour intervals as in Figure 2.

bonding counterpart as obtained from the natural orbital analysis of the CI expansion.

3.3. $PdClPH_3$. At variance from CuX_2, the SOMO of the bent $PdClPH_3$ fragment remains mainly localized on the metal d_{xy} orbital at the same level of CI calculations. This is due to the combination of the following two effects: (i) The doubly occupied hybrid orbital of the PH_3 fragment is oriented toward the metal atom in order to ensure the σ donation. No other occupied orbital can combine with the p_x level of chlorine in order to raise its energy. (ii) The valence 4d levels of the palladium atom are more diffuse and higher in energy than the 3d levels of copper. This is reflected by the values currently taken in extended Hückel[20] calculations for the H_{ii} integrals describing the valence d shells of copper and palladium, which are, respectively, −14.0 and −12.02 eV.[21,22]

Contrary to the CuX_2 molecules, the high-energy d_{xy} orbital of palladium is not in competition with a ligand orbital combination destabilized because of a four-electron interaction. The density generated by the SOMO of $PdClPH_3$, computed at the CI level, is displayed in Figure 3. This orbital has its major weight on the metal (69%), with some contributions coming from the σ interactions with the Cl atom (19%) and with the phosphine ligand (12%).

4. The $CuBr_2$TMPO Complex

The formation of $CuBr_2$TMPO results from an intricate interaction involving the occupied and semioccupied orbitals of both electron-rich fragments. The interaction diagram is represented in Figure 4. The main terms of this interaction are (i) for the $CuBr_2$ fragment, the two molecular orbitals generated by the three-electron interaction discussed above (see Figure 2), and (ii) for the modelized TMPO fragment, the SOMO, which can be identified with the NO π^* orbital. This represents a four-electron/three-center interaction, the three centers involved being the NO π^* orbital, the metal d_{xy} orbital, and the $p_x + p_x$ antibonding combination of the bromine ligands.

As usual, this interaction will give rise to (i) an antibonding, destabilized orbital which in the present case becomes the LUMO (Figure 6), (ii) a nonbonding orbital with major weights on the bromine (82%) and the NO π^* (13%) centers (Figure 5d), and (iii) a stabilized component with both metal–Br_2 and metal–NO bonding characters. It can be noted from the interaction diagram (Figure 4) that this orbital is at the same time pushed up in energy due to the four-electron interaction with the underlying NO π orbital. The resulting level is split in the set of canonical SCF orbitals, and the associated electron density maps are represented in Figure 5 (parts a and b).

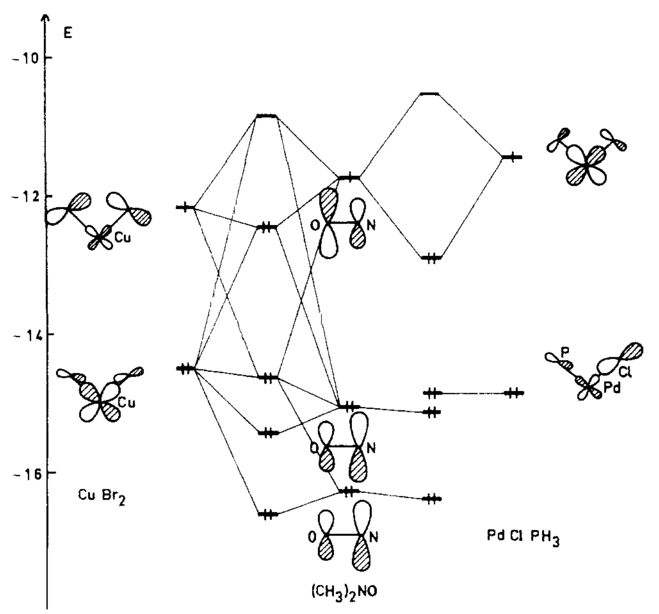

Figure 4. Orbital interaction diagram between the $(CH_3)_2NO$ radical and (i) the $CuBr_2$ fragment (left-hand side) and (ii) the $PdClPH_3$ fragment (right-hand side), from extended Hückel calculations.[20]

Other minor interactions could be pointed out. The most important one seems to be the stabilizing influence of direct, through-space interactions between the diffuse p_y orbitals of bromine and the NO π^* orbitals. This interaction is displayed in Figure 5c.

In such an electron-rich complex, the LUMO is the only low-energy unoccupied orbital of the valence-shell. The nature of this unique orbital provides, as a photographic negative, a clear, though reversed information about the bonding in the molecule. This is in contrast with the various frontier orbitals of the occupied set, most of them being altered by four-electron interactions. A sketch of the density generated by the LUMO in the molecular plane is displayed in Figure 6. The main features of this orbital are as follows: (i) The first feature is an antibonding Br–Br and metal–bromine character, reminiscent of the SOMO of $CuBr_2$. At variance from this latter orbital, however, the weight of d_{xy}(Cu) is balanced with the dibromine contribution (24% Cu, 24% Br_2) due to the contribution from the low-lying copper orbital in the three-center interaction. The complexation of $(CH_3)_2NO$ therefore results in the transfer of the Br–Br and Cu–Br antibonding contributions from a singly occupied to an unoccupied orbital, thus stabilizing the bent conformation of $CuBr_2$. (ii) The second feature is an antibonding interaction between the NO π^* and the metal d_{xy} orbitals. The NO weight is about 47%, equally distributed between N and O. This balance of the virtual π^* component and, as a consequence, the similar balance of the π^* contribution to the occupied space are at variance from the polarization of the π^* orbital toward oxygen in the SOMO of the isolated nitroxyl radical. The antibonding interactions of the LUMO, largely delocalized over the five atoms of the coordination plane, are sufficient to explain the stability, the diamagnetism, and the structural properties of the complex. The atomic net charges of the nitroxide ligand are quite similar to those computed in the free radical: −0.33e on oxygen and −0.28e on nitrogen (SCF values), compared to −0.30e and −0.27e, respectively, in $(CH_3)_2NO$. This global stability conceals some reorganization of the density between the π and the σ systems of the nitroxide, and a small positive charge of +0.21e, localized in the methyl groups, appears in the complexed nitroxide moiety. In spite of these minor changes, the Mulliken analysis globally rules out the possibility for an electron transfer either from or to the nitroxyl radical. This conclusion appears in agreement with the structural parameters of the complex, particularly with the reported NO

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[20] (a) Hoffmann, R. *J. Chem. Phys.* **1963**, *39*, 1397–1412. (b) Hoffmann, R.; Lipscomb, W. N. *Ibid.* **1962**, *36*, 2179–2189, 3489–3493; *37*, 2872–2883.

[21] The difference is ~2 eV from the parameters currently used for extended Hückel calculations.[22]

[22] (a) Tatsumi, K.; Hoffmann, R.; Yamamoto, A.; Stille, J. K. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 1857–1867. (b) Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884–4899.

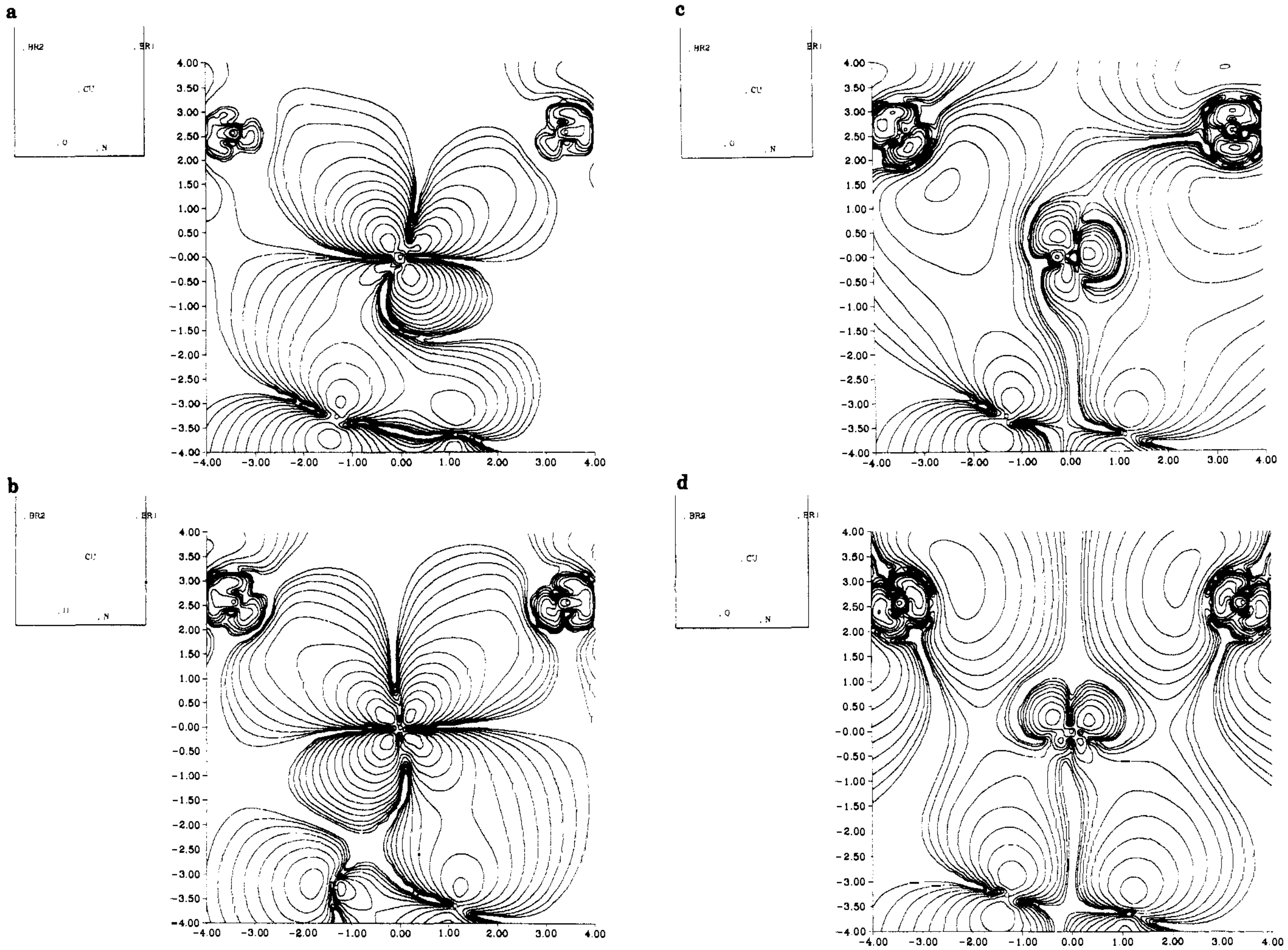

Figure 5. Plot of the electron densities associated with some doubly occupied molecular orbitals from the SCF wave function of $(CH_3)_2NOCuBr_2$, namely (a) orbital 1.41 (e = −0.605h), (b) orbital 1.42 (e = −0.552h), (c) orbital 1.44 (e = −0.398h), and (d) orbital 1.46 (HOMO; e = −0.348h). Contour intervals as in Figure 2.

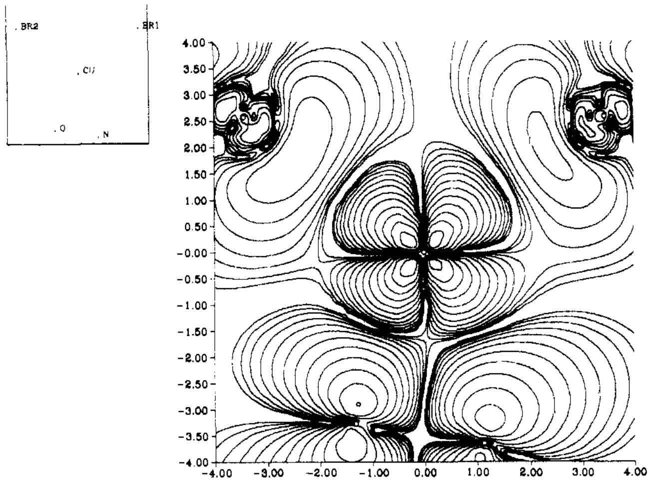

Figure 6. Plot of the electron density associated with the LUMO of $(CH_3)_2NOCuBr_2$, as obtained from SCF calculations: orbital 1.47, e = −0.075h. Contour intervals as in Figure 2.

distance of 1.304 Å barely modified with respect to the distance observed in the free TMPO (1.283 Å). In the $CuBr_2$ moiety, the population of the metal d_{xy} orbital has decreased from 1.79e in the fragment to 1.51e in the complex, to the benefit of the bromine population. The CI expansion defined in the next section allows further reorganization of the density in the $CuBr_2$ triangle, without significantly affecting the nitroxyl ligand. The metal population at the CI level is $(sp)^{0.64}(d)^{9.42}$ with a population of 1.34e for the d_{xy} orbital (Table I). These populations support the covalent concept of an spd hybridization of the metal orbital involved in the bonding with bromine. In terms of electron density, the complexation of TMPO repels the charge from the metal back to the bromine ligands, giving rise to a delocalized interaction that globally corresponds to the bonding counterpart of the LUMO.

5. Singlet-Triplet Energy Separation

The magnetic coupling in transition-metal-nitroxyl complexes has been the subject of detailed investigations.[1-4] Little is known however on the influence of the η^2 coordination of NO on the magnetic properties of the complex. The reported diamagnetism of $CuBr_2TMPO$ therefore needs to be interpreted in relation with the unusual bonding proposed for this system.

It appears obvious from the above discussion that the diamagnetism is a direct consequence of the multicentered linkage delocalized over the five atoms of the coordination plane. Since no significant charge transfer does occur, the complex cannot be considered as resulting from the interaction of two closed-shell moieties. It is therefore of interest to estimate the order of magnitude of the singlet-triplet energy separation. SCF-level calculations are of little help for this purpose. As a matter of fact, the lowest triplet state characterized from open-shell SCF calculations is found *lower* in energy than the singlet ground state by as much as 1.44 eV (−6979.5433h vs −6979.4907h). It is well-known however that the energy comparison is biased in favor of the triplet state due to the neglect of correlation effects.

The discussion about the electronic structure of $CuBr_2TMPO$ has already shown that this electron-crowded complex should be considered as a reverse image of most currently investigated molecules. The bonding interactions are distributed among a large number of doubly occupied orbitals and blurred because of in-

Table I. Net Charges (Electrons) of Atoms and Fragments in $(CH_3)_2NOCuBr_2$ and $(CH_3)_2NOPdClPH_3$, from the Mulliken Population Analysis of the ab Initio CI Wave Functions (SCF for the Nitroxyl Fragment)[a]

	$(CH_3)_2NO$ fragment	$CuBr_2$ fragment	$PdClPH_3$ fragment	$(CH_3)_2NOCuBr_2$	$(CH_3)_2NOPdClPH_3$
N	−0.27			−0.29 (1.37)	−0.35 (1.55)
O	−0.30			−0.32 (1.34)	−0.46 (1.51)
$(CH_3)_2NO$	0			+0.20	−0.17
X (Br, Cl)		−0.32	−0.52	−0.57[b]	−0.55
metal		+0.64 (1.79)	+0.36 (1.38)	+0.94 (1.34)	+0.46 (1.03)
d_{NO} (Å)	1.283[16]			1.304[5]	1.372[7]

[a] Values in parentheses correspond to the populations of the orbitals involved in bonding (p_y for N and O, d_{xy} for the metal atom). Observed NO distances (Å) are displayed. [b] Average charge.

tricate four-electron destabilizing interactions. The stabilization of the complex is much more easily interpreted by considering a hypothetical bonding counterpart to the unique valence virtual orbital.

The same is true for the definition of the "nondynamic correlation", i.e., the account of the most important correlation effects arising in the space of valence orbitals. Nondynamic correlation is usually accounted for through CI or MCSCF expansions involving a small set of doubly occupied bonding orbitals and, at the very least, an equal number of unoccupied counterparts. In the present case, the LUMO is the unique unoccupied orbital that has to be included in the valence CI. On the opposite way, *all* occupied valence orbitals are expected to "correlate" this unoccupied level. The CI expansion for the singlet state has therefore been designed on such grounds.

In spite of the small number of generated configurations, the correlation energy for the singlet state was 0.0755h, thus yielding a total energy of −6979.5662h. Since the energy of the lowest triplet remains unaffected by a similar expansion because of the Brillouin theorem, the singlet–triplet energy separation can be estimated to 0.023h, that is about 5000 cm^{-1}. This energy gap is obviously too large for the triplet state to be thermally populated even at room temperature. This result confirms that the diamagnetism of the present complex is the consequence of a strong interaction with covalent character.

6. Comparison with PdCl(PPh₃)TMPO

Dickman and Doedens[7] have reported in 1982 the structure of the complex of the TMPO nitroxide free radical with chlorine(triphenylphosphine)palladium. This molecule is isoelectronic with the copper–nitroxyl complex investigated in the present work. It is also characterized by a similar "side-on" coordination of the nitroxide radical. The NO distance however appears significantly longer than in the copper complex (1.372 Å compared to 1.304 Å).

The frontier orbitals of the $PdCl(PPh_3)$ moiety are closely related to those analyzed for the copper complex (Figure 4). The nature of the bonding with $(CH_3)_2NO$ is however modified due to the much higher energy of the palladium d levels[21] and to the lack of electron repulsion between the chlorine and phosphine ligands. At variance from $CuBr_2$, the SOMO of the $PdClPR_3$ fragment has now major metal character (Figure 4). The destabilization of this SOMO due to σ donation interactions with the phosphine and the chlorine ligands raises the palladium d_{xy} orbital *above* the semioccupied π^* orbital of $(CH_3)_2NO$ (Figure 4). The balance of the orbital interactions discussed for the copper complex and leading to the delocalization of the LUMO now favors *a charge transfer from the metal to the NO* π^* *orbital.* This expected increase of the NO π^* population can be characterized from the Mulliken population analysis of the CI wave function. The NO net charge is −0.8e in the Pd complex, compared to −0.6e in the Cu complex and approximately the same in the isolated $(CH_3)_2NO$ radical. A salient feature related to this electron transfer is the reversal of the nitroxyl radical net charge: −0.17e in the Pd complex vs +0.20e in the Cu complex (Table I). Another striking change with respect to the copper complex is the difference in the metal valence d_{xy} population: 1.03e for palladium, compared to 1.34e for copper.

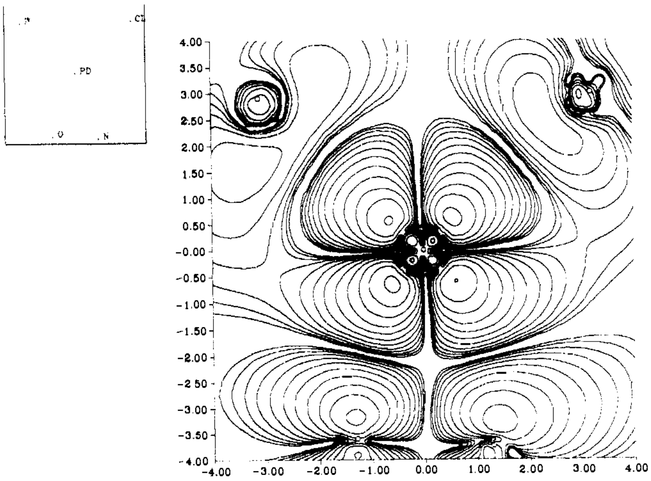

Figure 7. Plot of the electron density associated with the LUMO of $(CH_3)_2NOPdClPH_3$, as obtained from SCF calculations: orbital 1.58, e = +0.062h. Contour intervals as in Figure 2.

Still in contrast with the complex of copper, the nature of the SOMO of the palladium fragment, mainly centered on the metal, makes the bonding interaction less delocalized over the chlorine and especially over the phosphine ligands, as can be seen from the density map associated with the LUMO of $(CH_3)_2NOPdClPH_3$ (Figure 7). The low-lying component of the three-electron interaction in $PdClPH_3$ has now little metal character, and its interaction with either the π or π^* levels of NO becomes negligible (Figure 4). On the opposite way, the overlap between the SOMOs of the two fragments is enhanced, and, since the energy difference between these orbitals remains moderate, the HOMO–LUMO gap in the palladium complex becomes larger. Moreover the charge transfer evidenced from the metal to the NO moiety diminishes the radical character of the fragments and is therefore expected to drastically increase the singlet–triplet energy separation. This trend is confirmed by a calculation carried out on the lowest triplet state of $(CH_3)_2NOPdClPH_3$. At variance from the copper complex, the SCF energy corresponding to the lowest triplet is ***higher*** than that of the singlet ground state (−5936.754h compared to −5936.808h). Although the correction due to CI is somewhat reduced with respect to the copper complex (0.025h), it still increases the singlet–triplet energy gap. This energy difference therefore reaches 0.079h, that is about 17 000 cm^{-1}, more than three times as much as the splitting obtained for the $(CH_3)_2CuBr_2$.

The electronic structure of palladium complexes cannot be properly rationalized without making reference to the influence of the ligand field on the electronic configuration of the metal. The ground state of the palladium atom is d^{10}, but the lowest d^9s^1 state is higher by no more than 22 kcal/mol.[23] Ab initio studies carried out on oxidative addition and reductive elimination[24] and

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other reactions catalyzed by palladium[25] have lead to the conclusion that the metal atom should be given a large perturbation in order to activate the d^9s^1 state only capable of giving strong bonds with an incoming ligand. The localization of the SOMO of $PdClPH_3$ on the d metal orbital is indicative of such a promotion of the bonding state. The Mulliken population obtained for palladium in the fragment, $(sp)^{0.36}(d)^{9.28}$, is not quite characteristic however of a d^9s^1 complex. The presence of a phosphine ligand which tends to destabilize the metal bonding orbitals and to favor the d^{10} state[24a,b] is at the origin of this intermediate situation. The incoming of the nitroxyl ligand achieves the metal activation, evidenced by the rise of the sp population from 0.36e to 0.59e and the concomitant decrease of the overall d population to 8.96e.

The evolution of these populations shows that the resonance between the d^{10} and the d^9s^1 configurations is a key point for describing the energetics of the nitroxyl ligand approach along the reaction path and the bond energy between the two fragments. This would require a careful MCSCF and CI treatment which has not been carried out since this point was beyond the scope of the present study.

7. Conclusion

The bonding in $CuBr_2TMPO$ and $PdCl(PPh_3)TMPO$ has been interpreted in terms of the interactions between the π^* and π orbitals of NO on the one hand and the two combinations involving the metal d_{xy} orbitals on the other hand. The balance of these interactions depends on the nature of the SOMO in the bent ML_1L_2 fragment, conditioned itself by the energy of the d levels in the free metal. The low energy of the copper d levels yields for CuX_2 a SOMO with main halogen character. The contribution of this SOMO to the interaction with the NO π^* orbital extends the bonding interactions to the halogen ligands, without any significant change of the NO π^* orbital population. At variance from that, the high energy of the valence d levels of palladium gives rise to a SOMO with major metal character for $PdCl(PR_3)$. This SOMO is higher in energy than the NO π^* orbital, and the interaction of the magnetic orbitals induces some charge transfer from the metal to the nitroxyl radical. This interpretation agrees with the NO distances characterized for the free TMPO radical and for the two complexes investigated in the present study. We expect the synthesis and characterization of other electron-rich nitroxyl complexes with η^2 coordination to help in refining the present analysis.

Acknowledgment. All calculations have been carried out on the CRAY-2 computer of the Centre de Calcul Vectoriel de la Recherche (Palaiseau, France) through a grant of computer time from the CCVR.

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Ge-Ge Bonding in the High-Pressure Modification of Lithium Germanide: A Near-Zintl Phase

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Abstract: The Zintl-phase LiGe has recently been shown to undergo a transformation at elevated temperature and pressure to a metastable modification, which differs markedly from the normal-pressure form in the bonding between the Ge atoms. In the normal form the Ge net is exclusively three-connected, but in the high pressure (HP) form there is a mixture of Ge environments. One-third are approximately tetrahedrally four-connected, while the remainder have two short bonds (to the four-connected atoms) and two longer contacts (to other atoms of the same type), arranged in a distorted square plane. Whether or not the longer contacts are ignored, the HP form no longer obeys the electron-counting principles of Zintl or Klemm. In this paper we examine the bonding between the planar four-coordinated atoms and discuss the way the deviation from the Zintl counting rules can be seen to be consistent with the observed structure.

The Zintl phases[1] are one group of binary materials in which the simplest theories of covalent bonding in molecules have proved most useful. In these compounds the large difference in electronegativity between the two component elements enables a principally ionic model to be used for the distribution of valence electrons between the two atom types A and B; the electropositive atoms A (usually alkali-metal or alkaline-earth elements) are considered to give up their valence electrons to the more electronegative element B (generally from one of the groups 13-16). However, because of the stoichiometries, the resulting anions do not achieve closed-shell (or octet) configurations, as in simple ionic complexes (e.g., NaCl). They are isoelectronic not with the noble gases, but with other p-block elements (e.g., S or P), and so form bonds yielding anionic networks and clusters. The number of bonds expected between the non-metal atoms is easily anticipated from the total valence electron count, including the electrons donated by the cations.[2] The cations are distributed among these networks and clusters.

As noted by Schäfer and Eisenmann,[3] the Zintl phases may be considered to be intermediate between simple ionic salts and the intermetallic phases. The boundary between phases for which the Zintl concept works well, and those in which there is important metallic bonding between the two components, is not distinct. A number of factors affect the importance of these two types of bonding. Intermetallic character increases as the electronegativity difference between A and B decreases. For a given binary system the intermetallic character also becomes more important as the mole fraction of the electropositive element A increases. This is clearly expected, as in the limit pure A would have a metallic

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