solved; however, two C–S frequencies are observed at 840 and 827 cm^{-1}.

Electronic Effects. Addition of $Cu(PPh_3)_2^+$ to the oxygen atoms of a SS-coordinated $S_2C_2O_2^{2-}$ ligand leads to a delocalization of charge away from the sulfur atoms. The anticipated decrease in $S \rightarrow M$ σ bonding and possibly a weaker M–S bond are not reflected in the M–S stretching vibrations which occur at *higher* frequencies in the adducts. These effects are very similar to those observed in the spectra of the SnX_4 adducts of the nickel(II) and palladium(II) dithiooxalates and their explanation follows closely the one given previously.[1] Specifically, the expected decrease in $L \rightarrow M$ σ bonding is accompanied by $M \rightarrow S$ backbonding to such an extent that a stronger M–S bond is observed in the adducts. Indirect evidence for the anticipated increase in the ligand field is found in the visible spectra (Table III) of the $M(S_2C_2O_2)_3((PPh_3)_2Cu)_3$ complexes (M = Co(III) and Cr(III)). Thus the $10Dq$ ($^4A_{2g} \rightarrow {}^4T_{2g}$) and ($^1A_{1g} \rightarrow {}^1T_{1g}$) transitions found at 17,000 and 17,700 cm^{-1} in the spectra of the Cr(III) and Co(III) parent complexes are not observed in the spectra of the adducts, presumably due to a hypschromic shift which brings them under the intense charge transfer absorptions (Table III).

Conclusions

The multifunctional nature of the dithiooxalate ligand is demonstrated by the existence of OO-bonded, SS-bonded, and OS-bonded complexes. As expected, the mode of coordination adopted by this ligand depends on the type of the metal ion and its relative affinity for "hard" *vs.* "soft" ligands. Substitution of the inert cations (K) by interacting $M(PPh_3)_2^+$ cations in the $K_nM(S_2C_2O_2)_n$ complexes results in adducts whose structures depend on (a) the kinetic characteristics of the parent complexes and (b) the intrinsic affinity of the metal ions involved for "hard" *vs.* "soft" ligands. It appears that in kinetically inert $M(S_2C_2O_2)_n^{n-}$ complexes the integrity of the $M(S_2C_2O_2)_n^{n-}$ unit is initially maintained and the interaction which takes place depends on the nature of the coinage metal and availability of bonding sites within the $M(S_2C_2O_2)_n^{n-}$ complex. Occasionally the resulting products are not the energetically most stable species. Such is the case with the $Cr(S_2C_2O_2)_3((PPh_3)_2M')_3$ complexes which slowly rearrange to the thermodynamically most stable linkage isomers. With kinetically labile $M(S_2C_2O_2)_n^{n-}$ complexes the relative thermodynamic stabilities of the $M-S_2C_2O_2$ *vs.* $(PPh_3)_2M'-S_2C_2O_2$ interactions determine the bridging mode adopted by the dithiooxalate ligand.

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Bonding, Spectra, and Geometry of the Tetrachlorocuprate Ion $CuCl_4^{2-}$. An *Ab Initio* LCAO–MO–SCF Calculation

J. Demuynck, A. Veillard,* and U. Wahlgren

Contribution from Equipe de Recherche No. 139 du CNRS,
Université Louis Pasteur, BP 296/R8, 67-Strasbourg, France, and the
Institute of Theoretical Physics, University of Stockholm, Sweden.
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Abstract: The description of the bonding for the ground state of the $CuCl_4^{2-}$ ion in the D_{4h} configuration is compared through the use of three different basis sets of Gaussian functions. It is concluded that a (12,8,5/10,6) set of Gaussian functions contracted to [5,4,2/3,3] gives a description of the ground state which is accurate enough. Doubly occupied MO's which are predominantly metal 3d orbitals are found at lower energy levels than the MO's which are mostly ligand 3p orbitals. Independent SCF calculations for the $CuCl_4^-$ ion (*in vacuo*) allow for electronic relaxation during the ionization process and lead to comparable ionization potentials (IP) for the ligand 3p and metal 3d orbitals. The effect of the crystal environment on the computed ionization potentials is represented by including the electrostatic potential of the crystal in the molecular SCF calculation. This results in a rather uniform increase of the computed IP's. The dependence of the results of a population analysis on the basis set used is exemplified by considering the three different basis sets and the effect of diffuse functions. Independent SCF calculations have been carried out for several excited states of the $CuCl_4^{2-}$ ion in the D_{4h} configuration. The lowest excitations correspond to d–d excitations in the order $^2B_{2g}(d_{xy} \rightarrow d_{x^2-y^2}) < {}^2E_g(d_{xz,yz} \rightarrow d_{x^2-y^2}) < {}^2A_{1g}(d_{z^2} \rightarrow d_{x^2-y^2})$ in agreement with experimental evidence from polarized spectra and magnetic circular dichroism for $PdCl_4^{2-}$ and $PtCl_4^{2-}$. The next excitations correspond to ligand to metal charge transfer. It is found by energy minimization that the most stable configuration of the $CuCl_4^{2-}$ ion corresponds to a flattened D_{2d} structure, with a predicted value of 120° for the Cl–Cu–Cl angle in good agreement with the experimental value of 124° in Cs_2CuCl_3. It is concluded that the distortion with respect to an ideal T_d geometry is an intrinsic property of the $CuCl_4^{2-}$ ion.

The *ab initio* LCAO–MO–SCF calculations of transition metal complexes and organometallics have become feasible in the last few years.[1-15] So far,

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* Author to whom correspondence should be addressed at the Universite L. Pasteur, France.

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(2) J. Demuynck, A. Veillard, and G. Vinot, *Chem. Phys. Lett.*, **10**, 522 (1971) ($Ni(CN)_4^{2-}$).

technical limitations have placed rather severe restrictions on the size of the systems which have been considered, ranging from simple oxoanions like MnO_4^- to simple organometallics like ferrocene. For the same reasons, these calculations have been carried usually with severe limitations on the basis set used, which is at best slightly better than a minimal basis set of Slater orbitals (with few exceptions like the rather refined work in NiF_6^{4-} [1]). Since this field will probably undergo some new development in the near future, it appears rather important to assess the effect of the basis set used on the results of the calculation. We report here a comparative work where LCAO-MO-SCF calculations are carried out with different basis sets for the square-planar $CuCl_4^{2-}$ complex. This is one of the simplest complexes with a metal of the first transition series, yet there are enough available experimental facts about it (*cf.* below) (NiF_4^{2-} and CuF_4^{2-} have been previously studied;[11,12] however, both are hypothetical compounds in the square-planar configuration). The choice of a planar compound reduces appreciably the computer time needed for the integral evaluation, since many integrals are zero by symmetry. $CuCl_4^{2-}$ is an open shell and this lends to some additional difficulties, but it also raises some interesting questions in connection with Koopmans' theorem and the significance of energy orbitals.

We report here additional calculations of the $CuCl_4^{2-}$ ion in the T_d and D_{2d} (flattened tetrahedron) configurations. Experimental work regarding the stereochemistry of coordination around Cu(II) raises some interesting problems. Experimentally, chloro complexes of Cu(II) have been found in a variety of coordinations: octahedral coordination with a strong tetragonal distortion in $CuCl_2$[16] and $CsCuCl_3$,[17] pentacoordination in $[Cr(NH_3)_6]CuCl_5$, with the Cu atom at the center of a trigonal bipyramid,[18] in a square-planar arrangement in $[Pt(NH_3)_4]CuCl_4$,[19] $(NH_4)_2CuCl_4$,[20] $(C_2H_5NH_3)_2CuCl_4$,[20,21] and $(CH_3NH_3)_2CuCl_4$,[21] at the center of a flattened tetrahedron in Cs_2CuCl_4[22,23] and $[N(CH_3)_4]_2CuCl_4$.[23] It is believed that $CuCl_4^{2-}$ in solution is nearly tetrahedral.[20-22] A detailed discussion of the stereochemical problem will be found at the beginning of the last section.

Previous theoretical work has been devoted either to the $CuCl_4^{2-}$ ion or to the more general class of MX_4^{2-} complexes (with M any transition metal), usually through the use of semiempirical methods. Gray and Ballhausen proposed a molecular orbital scheme for square-planar complexes and used it for a discussion of the corresponding electronic spectra.[24] This work was latter extended by Mason and Gray,[25] who relied on the molecular orbital calculations for $PtCl_4^{2-}$ and $PdCl_4^{2-}$ by Cotton and Harris using the extended Hückel theory[26] and by Basch and Gray with the SCCC-MO method.[27] Ros and Schuit have reported extended Hückel-type calculations for $CuCl_4^{2-}$ in the D_{4h} and T_d configurations.[28] Lohr and Lipscomb carried out a study of the static distortions for the VCl_4 molecule and the $CuCl_4^{2-}$ and $NiCl_4^{2-}$ ions through extended Hückel calculations.[29] More recently van der Lugt has calculated the transitions of a number of square-planar MX_4^{2-} complexes with an INDO procedure.[30,31] A Pariser–Parr–Pople-type calculation has been reported for the $PdCl_4^{2-}$ ion.[32] *Ab initio* LCAO-MO-SCF calculations have been carried for the hypothetical square-planar ions NiF_4^{2-} with a basis set of Gaussian functions[11] and CuF_4^{2-} with a basis set of Slater functions.[12] Excitation energies for both the d–d and charge-transfer states of NiF_4^{2-} were also computed in the virtual orbital approximation.[11] A preliminary account of this work with a small basis set has been reported earlier.[10]

A major conclusion from our preliminary work was that the copper 3d orbitals in the complex are at lower energies than the ligand 3p orbitals. This was in contrast to the results of the semiempirical calculations by Ros,[28] Basch,[27] and many others which predict the group of metal d orbitals to have the highest energy. Recently, Biloen and Prins have reported the X-ray photoelectron spectrum of $PtCl_4^{2-}$.[33] They claimed that, using Koopmans' theorem, they arrive at an orbital ordering which confirms the semiempirical calculations and thus contradicts our *ab initio* calculation.[10] They mention that reorganization and correlation effects (not included in Koopmans' theorem) are expected to depress the energy of the states corresponding to metal 3d ionization to a larger extent than the energy of the states corresponding to ligand 3p ionization. They also add that the lattice will tend to stabilize peripheral orbitals such as the ligand

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Table I. Atomic and Molecular Computed Energies (in au)

Basis set	Basis functions	Contracted functions	$E(\mathrm{Cu}^{2+}\ {}^2\mathrm{D})^a$	$E(\mathrm{Cl}^-\ {}^1\mathrm{S})^b$	$E(D_{4h})$	Binding energy (D_{4h})	$E(T_d)$	No. of two-electron integrals
BSI	10,6,3/8,4	5,3,2/3,3	−1622.033	−456.181	−3447.796	1.038		3.2×10^7
BSII	12,8,5/10,6	5,4,2/3,3	−1634.716	−458.731	−3470.577	0.937	−3470.606	1.3×10^8
BSIII	14,11,6/12,9	5,4,2/3,3	−1635.580	−458.935	−3472.284	0.965		4.1×10^8

[a] Hartree–Fock limit −1638.083 au: E. Clementi, *IBM J. Res. Develop., Suppl.*, **9**, 1 (1965). [b] Hartree-Fock limit −459.577 au: see footnote *a*.

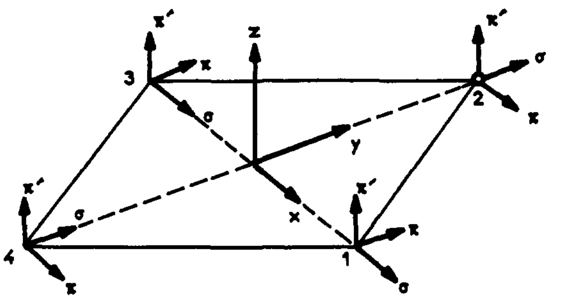

Figure 1. Choice of the coordinate axis and numbering of the atoms for the D_{4h} configuration.

ones relative to the central metal orbitals, but that this effect is too small to change the level ordering according to simple electrostatic calculations. In the present work, we have studied the influence of the electronic reorganization and of the lattice on the sequence of computed ionization potentials, in order to assess the validity of Koopmans' theorem and the validity of calculations for the ion *in vacuo*.

Computations

The present calculations are of the SCF–LCAO–MO type with a basis set of Gaussian functions. Three different basis sets have been used for the square-planar ion. The first one, denoted BSI, is a small set (10,6,3/8,4) contracted to [5,3,2/3,3] which has been described previously.[10] The second one, denoted BSII, is a medium-size basis set (12,8,5/10,6) contracted to [5,4,2/3,3]. This set is built from a (12,6,4) set with its exponents optimized for the ground state of Cu^0.[34] The lowest two exponents for the s functions (which may be considered as describing the 4s atomic orbital) are set equal to 0.32 and 0.08. Next this basis set is incremented with two p functions of exponents 0.32 and 0.08 in order to describe the 4p atomic orbital and one additional 3d function of exponent 0.2. The exponents for the chlorine atom were optimized for the ground state.[35] A large basis set (14,11,6/12,9) contracted to [5,4,2/3,3] and denoted BSIII is built from the (14,9,5) basis set of Wachters for the Cu atom[36] (with the lowest two s exponents substituted with the above values 0.32 and 0.08) equally incremented with two p functions of exponents 0.32 and 0.08 and one d function of exponent 0.15 and from the basis set of ref 37 for the chlorine atom. The number of two-electron integrals corresponding to these basis sets is reported in Table I. *Ab initio* calculations on transition metal complexes are usually carried out with the emphasis put on a better description of the valence shell.[38] For this reason the valence shells 3d, 4s, and 4p of Cu and 3p of Cl are described with two contracted functions, while only one contracted function is used for the inner shells and for the 3s shell of Cl (BSI has only one contracted function for the 4p shell of Cu). Calculations for the tetrahedral T_d and distorted D_{2d} ions were carried with the basis set BSII.

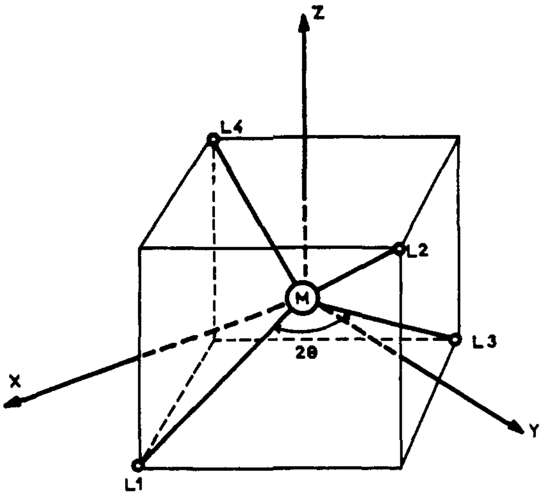

Figure 2. Choice of the coordinate axis and numbering of the atoms for the D_{2d} and T_d configurations.

The interatomic distance Cu–Cl was kept to the same value of 2.26 Å for the three configurations D_{4h}, T_d, and D_{2d}. This is an average of the experimental values reported for the square-planar configuration, 2.30 Å,[20] and the tetrahedral one, 2.22 Å.[22] Significant values of the energy differences among the three configurations can be only achieved either by keeping the same Cu–Cl bond length or by optimizing the energy with respect to the Cu–Cl bond length for each configuration. However, this latter procedure was beyond the scope of this work.

The choices of the coordinate axis are the ones given in Figures 1 and 2. For the T_d configuration (Figure 2) this choice leads to the simplest expressions for the symmetry adapted basis functions.[35] This ensures a minimization of the computation time needed for the transformation of the two-electron integrals from the basis of contracted functions to the basis of symmetry adapted functions.[39] Calculations for the D_{4h} and T_d configurations were carried out with symmetry-adapted functions. For the D_{2d} configurations, the

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Table II. SCF Wave Function for the Ground State $^2B_{1g}$ of the D_{4h} Configuration (subcase 1 of BSIII)

Orbital	Orbital energy, au	Cu–Cl overlap population	LCAO coefficients[a,b]
$6b_{1g}$	−0.461	−0.021	$0.25\ 3p_\sigma{}^2 - 0.98\ 3d_{x^2-y^2}$
$2a_{2g}$	−0.055	0.000	$-0.28\ 2p_\pi + 0.79\ 3p_\pi{}^1 + 0.31\ 3p_\pi{}^2$
$9e_u$	−0.084	0.007	$-0.38\ 3p_\sigma{}^1 - 0.20\ 3p_\sigma{}^2 + 0.24\ 2p_\pi - 0.66\ 3p_\pi{}^1 - 0.37\ 3p_\pi{}^2$
$2b_{2u}$	−0.091	0.000	$-0.27\ 2p_{\pi'} + 0.74\ 3p_{\pi'}{}^1 + 0.38\ 3p_{\pi'}{}^2$
$3e_g$	−0.104	−0.009	$-0.26\ 2p_{\pi'} + 0.72\ 3p_{\pi'}{}^1 + 0.41\ 3p_{\pi'}{}^2 - 0.11\ 3d_{xz,yz}$
$4a_{2u}$	−0.130	+0.009	$-0.25\ 2p_{\pi'} + 0.69\ 3p_{\pi'}{}^1 + 0.44\ 3p_{\pi'}{}^2$
$3b_{2g}$	−0.140	−0.007	$-0.25\ 2p_\pi + 0.70\ 3p_\pi{}^1 + 0.43\ 3p_\pi{}^2 - 0.14\ 3d_{xy}$
$5b_{1g}$	−0.141	+0.022	$-0.26\ 2p_\sigma + 0.73\ 3p_\sigma{}^1 + 0.34\ 3p_\sigma{}^2 + 0.23\ 3d_{x^2-y^2}$
$8e_u$	−0.157	+0.056	$0.22\ 2p_\sigma - 0.60\ 3p_\sigma{}^1 - 0.31\ 3p_\sigma{}^2 + 0.34\ 3p_\pi{}^1$
$9a_{1g}$	−0.188	+0.006	$0.24\ 3s_{Cu} - 0.10\ 4s_{Cu} + 0.24\ 3s + 0.23p_\sigma - 0.63\ 3p_\sigma{}^1 - 0.47\ 3p_\sigma{}^2 - 0.14\ 3d_{z^2}$
$8a_{1g}$	−0.447	−0.000	$-0.20\ 3s - 0.98\ 3d_{z^2}$
$2e_g$	−0.463	+0.006	$0.99\ 3d_{xz,yz}$
$2b_{2g}$	−0.504	+0.005	$0.99\ 3d_{xy}$
$4b_{1g}$	−0.644	+0.004	$-0.61\ 2s + 1.12\ 3s + 0.07\ 3d_{x^2-y^2}$
$7e_u$	−0.660	+0.028	$-0.60\ 2s + 1.10\ 3s + 0.07\ 4p_{Cu}$
$7a_{1g}$	−0.683	+0.012	$-0.58\ 2s + 1.08\ 3s - 0.12\ 3d_{z^2}$
Total		+0.117	

[a] Only the most significant terms in the expansion are reported. [b] The notations 2s, 3s, 2p, and 3p refer to symmetry-adapted orbitals of the ligands. The notations $3p^1$ and $3p^2$ refer to the split orbitals. The notations p_π and p_σ correspond to the conventions of Figure 1.

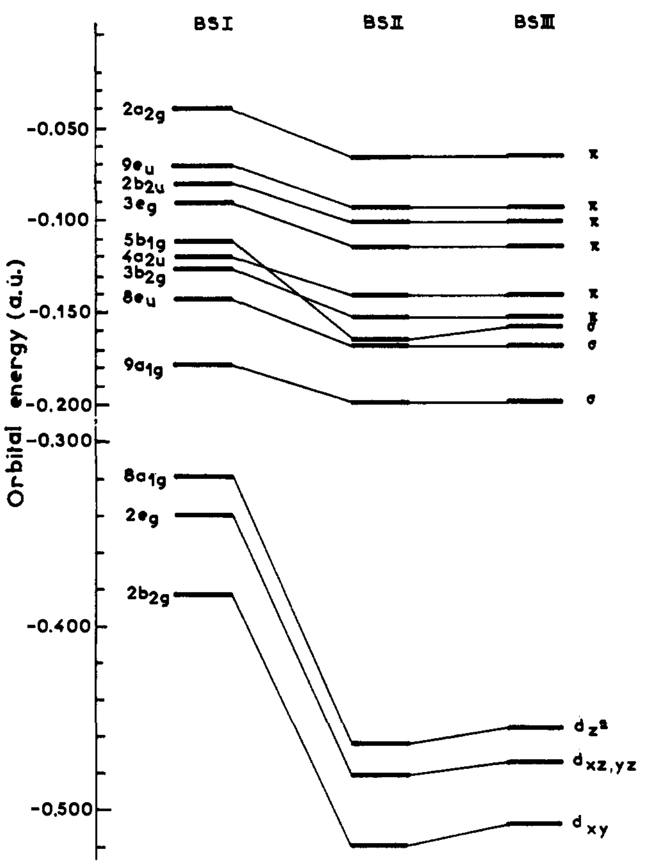

Figure 3. Orbital energies (in au) of the valence molecular orbitals for the D_{4h} configuration.

SCF calculation was carried out directly over the contracted functions.[40]

We have used the restricted Hartree–Fock formalism as given by Roothaan, with the closed- and open-shell orbital solutions of two distinct eigenvalue equations.[41] The corresponding vector coupling coefficients for the various states may be found in ref 35.

Results and Discussion

The Ground State for the D_{4h} and T_d Configurations. The total energy computed for the D_{4h} and T_d configurations are reported in Table I with the corresponding values for the ions Cu^{2+} and Cl^-. The relative stability of the two configurations will be discussed below in conjunction with the D_{2d} configuration.

No experimental result is available regarding the enthalpy of the reaction

$$Cu^{2+}(g) + 4Cl^-(g) = CuCl_4{}^{2-}(g)$$

Only relative values have been reported for the $MCl_4{}^{2-}$ ion in solution.[42] The electrostatic energy released by a set of five point charges +2 and −1 taken from infinity to the above interatomic distances is 0.977 au and may be compared with the computed binding energy reported in Table I for the D_{4h} configuration. The decrease in this binding energy when going from BSI to BSII points probably to the inadequacy of BSI, with the individual atom basis sets artificially serving as additional basis functions in describing the purely atomic parts of the molecular wave function of neighboring atoms in the complex. On the contrary, the close binding energies obtained with BSII and BSIII give some indication that BSII is probably accurate enough for a satisfactory description of the valence shells and that the improvement with BSIII is mostly at the level of the inner shells.

The sequence of orbital energies associated with the valence orbitals are compared for the three calculations relative to the D_{4h} configuration in Figure 3. The wave function with BSIII for the configuration D_{4h} and the wave function for the configuration T_d (both limited to the valence molecular orbitals) are reported in Tables II and III. For the D_{4h} configuration, the sequence of orbital energies is found to be the same in the three calculations (the exact meaning of these orbital energies is discussed below), $3d_{xy}(2b_{2g}) < 3d_{xz,yz}(2e_g) < 3d_{z^2}(8a_{1g}) < 3p_\sigma(9a_{1g}, 8e_u, 5b_{1g}) < 3p_\pi(3b_{2g}, 4a_{2u}, 3e_g, 2b_{2u}, 9e_u, 2a_{2g})$, except for an interversion of the $5b_{1g}$ orbital with respect to the $4a_{2u}$ and $3b_{2g}$ orbitals when going from BSI to BSII or

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Table III. SCF Wave Function for the Ground State $^2T_2$ of the T_d Configuration (subcase 1 of BSII)

Orbital	Orbital energy	Cu–Cl overlap population	LCAO coefficients[a,b]
$10t_2$	−0.443	−0.024	$0.99\ d_{xz,yz,x^2-y^2}$
$2t_1$	−0.112	0.000	$-0.26\ 2p + 0.54\ 3p^1 + 0.62\ 3p^2$
3e	−0.132	−0.010	$-0.25\ 2p + 0.51\ 3p^1 + 0.64\ 3p^2 + 0.13\ 3d_{xy,z^2}$
$9t_2$	−0.137	+0.011	$-0.25\ 2p + 0.51\ 3p^1 + 0.60\ 3p^2$
$8t_2$	−0.169	+0.069	$-0.24\ 2p + 0.48\ 3p^1 + 0.61\ 3p^2$
$8a_1$	−0.205	+0.009	$-0.23\ 3s(Cu) - 0.20\ 3s + 0.23\ 2p - 0.45\ 3p^1 - 0.68\ 3p^2$
2e	−0.469	+0.008	$0.99\ d_{z^2,xy}$
$7t_2$	−0.684	+0.022	$0.58\ 2s - 1.10\ 3s$
$7a_1$	−0.699	+0.005	$-0.57\ 2s + 1.09\ 3s$
Total		+0.088	

[a] Only the most significant terms in the expansion are reported. [b] The notations 2s, 3s, 2p, and 3p refer to symmetry-adapted orbitals of the ligands. The notations $3p^1$ and $3p^2$ refer to the split orbitals.

Table IV. Orbital Energies and Computed Ionization Energies in the D_{4h} Configuration (BSII)

Electronic configuration of the $CuCl_4^-$ ion	State	Free ion			Ion with lattice	
		Orbital energy	Computed IP[a]	Computed IP[b]	Orbital energy	Computed IP[b]
$6b_{1g}^0$	$^1A_{1g}$	0.476	0.476	0.110	0.794	0.437
$2a_{2g}^1$	$^1B_{2g}$	0.065	0.067	0.056	0.392	0.381
$9e_u^3$	^1E_u	0.091			0.418	
$2b_{2u}^1$	$^1A_{2u}$	0.099	0.101	0.091	0.424	0.416
$3e_g^3$	^1E_g	0.112			0.437	
$4a_{2u}^1$	$^1B_{2u}$	0.139	0.141	0.132	0.461	0.453
$3b_{2g}^1$	$^1A_{2g}$	0.150	0.152	0.143	0.478	0.470
$5b_{1g}^1$	$^1A_{1g}$	0.163			0.480	
$8e_u^3$	^1E_u	0.165			0.488	
$9a_{1g}^1$	$^1B_{1g}$	0.197	0.218	0.197	0.515	0.514
$8a_{1g}^1$	$^1B_{1g}$	0.465	0.528	0.110	0.769	0.422
$2e_g^3$	^1E_g	0.482		0.108	0.784	0.425
$2b_{2g}^1$	$^1A_{2g}$	0.522	0.553	0.103	0.829	0.424

[a] IP computed according to Koopmans' theorem (negative of the orbital energy for the open shell, formula I for the closed shells). [b] IP computed as the difference of the total energies for $CuCl_4^{2-}$ and $CuCl_4^-$.

BSIII (the case of the open-shell orbital $6b_{1g}$ is discussed below). The $5b_{1g}$ orbital is a bonding Cu–Cl orbital built mostly from $3p_\sigma$ functions of the chlorine atoms with a small admixture of Cu $3d_{x^2-y^2}$ orbital. With BSI, the lowest exponent of the 3d function on the Cu atom is 1.02, *vs.* 0.2 or 0.15 with BSII or BSIII. As a consequence, there is little bonding in the wave function corresponding to BSI (*cf.* below the negative Cu–Cl overlap population with BSI compared with a positive population with BSII and BSIII, Table V). On the contrary the metal–ligand bonding stabilizes the $5b_{1g}$ orbital with BSII or BSIII. BSI is shown not to be appropriate to describe the ligand–metal bonding, while BSII and BSIII are rather equivalent with this respect.[43,44]

The concept of orbital energy has a physical meaning only through Koopmans' theorem which states that, for a closed-shell system, the ionization potential (IP) is equal to the negative of the orbital energy (this theorem neglects the electronic relaxation in the ionized system and the effect of electronic correlation).[45] One may show easily (see ref 35) that, of the eigenvalues (η) associated with the Roothaan open-shell SCF equations, only the eigenvalue associated with the half-filled orbital in the D_{4h} structure satisfies Koopmans' theorem. With the same approximations, the ionization potential of the closed-shell orbitals is given by[35]

$$\begin{aligned} IP_l &= -\eta_l - {}^1/_2 K_{lm}\ \text{(triplet)} \\ IP_l &= -\eta_l + {}^3/_2 K_{lm}\ \text{(singlet)} \end{aligned} \qquad \text{(I)}$$

depending on the singlet or triplet character of the electronic state obtained through the ionization of an electron in a nondegenerate orbital φ_l (m stands for the open-shell orbital $6b_{1g}$ and K is the exchange integral). We have reported in column 4 of Table IV the ionization potentials computed according to this formula for the singlet states of the $CuCl_4^-$ ion. It turns out that, with the approximations of Koopmans' theorem, the lowest computed IP's are associated with molecular orbitals which are mostly chlorine 3p orbitals (from $2a_{2g}$ to $9a_{1g}$ with computed ionization potentials in the range 0.06–0.21 au) and not with molecular orbitals which are mostly Cu 3d orbitals ($6b_{1g}$, $8a_{1g}$, and $2b_{2g}$, with computed ionization poten-

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(43) A few levels ($2b_{2g}$, $2e_g$, $8a_{1g}$, and $5b_{1g}$) are slightly shifted to higher energies on going from BSII to BSIII (Figure 3). These MO's involve the metal 3d orbitals. Despite the fact that a lower energy is achieved with BSIII probably as the result of a better description of the inner shells, it may be that BSIII provides a less satisfactory description of these valence MO's, as the result of somewhat less appropriate values for the exponents of the 3d functions. A similar situation has been reported by Roos for the SH_2 and SO_2 molecules.[44] Roos observed that the overall agreement with experimental values of molecular properties was better with a medium size basis set than with a large size basis. A possible explanation according to this author is that the valence orbital exponents from the medium size basis are closer to exponents which would be optimal in the molecules (valence orbital exponents become smaller when the size of the basis set increases) (*cf.* below a similar dependance on the basis set for the computed electronic excitations).

(44) B. Roos and P. Siegbahn, *Theor. Chim. Acta*, 21, 368 (1971).

(45) T. Koopmans, *Physica* (*Utrecht*), 1, 104 (1933).

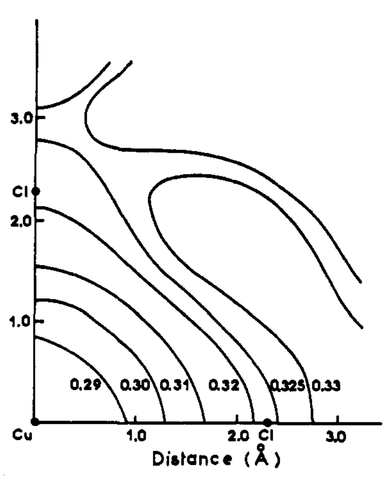

Figure 4. Plot of the crystal potential (in au) at the site of the $CuCl_4^{2-}$ ion.

tials in the range 0.47–0.55 au). A similar situation, with the lowest IP associated to ligand orbitals on the basis of Koopmans' theorem, has been found previously for both the $Ni(CN)_4^{2-}$ ion and the ferrocene molecule.[3,15] However, it was shown that this situation was a consequence of the assumptions inherent in Koopmans' theorem and that different conclusions, more in agreement with the experimental facts for ferrocene, were reached when the electronic relaxation was taken into account by carrying separate calculations for the molecule and the ion. For this reason, we have also reported in Table IV the IP's computed as the difference of the SCF energies for the two systems $CuCl_4^{2-}$ and $CuCl_4^-$.[46] The ionization potentials for the ligand and metal orbitals become now comparable (0.110 au for the $6b_{1g}$ orbital and 0.056 au for the $2a_{2g}$ orbital) when electronic relaxation is allowed during the ionization process and the difference between these two values is probably beyond the accuracy of this calculation.

The above calculations have been carried out for the free ions $CuCl_4^{2-}$ and $CuCl_4^-$ *in vacuo* and the low values of the computed IP's are directly connected to the dinegative charge of the anion $CuCl_4^{2-}$. However, since the experimental measurements for this ion refer to crystal structures, one should take into account the effect of the crystal environment on the properties of the ion. Crystal effects on ions have been calculated by Brown, *et al.*, who have included crystal potentials in CNDO-type calculations on various ions.[47]

A large part of the effect of an ionic crystal on a complex ion may be calculated by including the electrostatic potential of the crystal in the molecular SCF calculation. The potential is evaluated following the method proposed by Ewald.[48] The crystal is assumed to be built up from point charges occupying the positions of atomic nuclei or groups of atomic nuclei. These point charges were taken as +1 on the Cu atom and −0.75 on the Cl atoms (these are rather close to the results of the population analysis for the wave function using BSII, *cf.* below). We have considered the crystal $(NH_4)_2CuCl_4$ where the planar copper tetrachloride is only approximately squared, being part of a strongly distorted $CuCl_6^{4-}$ octahedron with two long (2.79 Å) and four short (2.33 and 2.30 Å) copper–chlorine bonds, with the space group of the $(NH_4)_2CuCl_4$ crystal being *Cmca* or *C2ca* and the $CuCl_4^{2-}$ ion in D_{2h} symmetry.[20] However, the deviations from D_{4h} point symmetry are small both for the ion and for the potential field at the site of the ion, as seen from a plot of the potential in Figure 4. The potential was calculated in 8000 points within the van der Waals radius of $CuCl_4^{2-}$ and then simulated by 44 point charges, the size of which were found by a least-square procedure. These point charges were included in the final SCF calculations. The corresponding results are reported in Table IV, under the heading "Ion with lattice."

The inclusion of the crystal potential results in a stabilization of the molecular orbitals; the orbital energy shifts from Table IV are in the range from 0.302 to 0.327 au. This is in agreement with the fact that the potential in the region of the ion ranges from 0.29 au at the site of the Cu atom to 0.33 au at the boundaries of the ion (see Figure 4). Inner-shell orbitals on Cu are shifted by about 0.303 au and inner-shell orbitals on Cl by about 0.323 au, while the energy shifts of valence orbitals vary between 0.307 and 0.327 au. For instance the $5b_{1g}$ and $6b_{1g}$ orbitals, which are bonding and antibonding combinations of the $3p_\sigma$ and $3d_{x^2-y^2}$ orbitals, are stabilized by 0.317 and 0.318 au. The orbital energy shifts give a clue to the density distribution of the different molecular orbitals.

One will notice from Table IV that the inclusion of the crystal potential does not affect the sequence of computed IP's. The lowest IP computed as the difference of the energies for the two ions is associated with the molecular orbital $2a_{2g}$. Furthermore, there are not less than eight molecular orbitals with a computed IP in the range 0.38–0.43 au, a difference less than 1.5 eV, so that any prediction concerning the exact sequence of IP is probably beyond the scope of this work.

The results of Table IV deserve some additional comments. First the orbital energies associated with the closed-shell orbitals and the IP computed according to I are very close, owing to the small value of the K_{lm} integral as long as the closed-shell orbital is predominantly a ligand orbital (for instance $2a_{2g}$, $2b_{2u}$, and $4a_{2u}$). We may consider the K_{lm} integral as negligible; then Koopmans' theorem may be extended to these orbitals. Next, it turns out that Koopmans' theorem is approximately valid for these same orbitals; namely, the IP computed as the difference of two energies is very close to the orbital energy (or to the value given by (I)) for the orbitals from $2a_{2g}$ to $9a_{1g}$. But Koopmans' theorem turns out to be not valid for the orbitals which are predominantly metal 3d orbitals (compare the two computed IP's for the orbitals $6b_{1g}$, $8a_{1g}$, $2e_g$, and $2b_{2g}$ of the free ion and note that these conclusions are not changed for the ion in the crystal). The same conclusions regarding the limits of validity for Koopmans' theorem have been reached previously for the Ni-

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(46) SCF calculations for the $CuCl_4^-$ ion have been carried out in the restricted Hartree–Fock scheme with the same geometry used for the $CuCl_4^{2-}$ ion (vertical ionization).

(47) R. D. Brown, B. H. James, and M. F. O'Dwyer, *Theor. Chim. Acta*, **19**, 45 (1970).

(48) P. P. Ewald, *Ann. Phys. (Leipzig)*, **64**, 253 (1921).

Table V. Atomic and Orbital Populations for the D_{4h} Configuration (ground state)

Populations	BSI		BSII		BSIII	
	Subcase 1[a]	Subcase 2[b]	Subcase 1[c]	Subcase 2[b]	Subcase 1[c]	Subcase 2[b]
Cu s	6.00	6.34	6.09	6.32	6.10	6.42
p_x, p_y	4.00	4.15	4.10	4.19	4.13	4.30
p_z	4.00	4.10	4.02	4.12	4.02	4.11
$d_{x^2-y^2}$	1.04	1.04	1.07	1.30	1.08	1.39
d_{xy}	2.00	2.00	2.00	2.03	2.00	2.06
$d_{xz,yz}$	2.00	2.00	2.00	2.02	2.00	2.04
d_{z^2}	2.00	1.96	2.00	2.03	2.00	2.03
Formal charge	+1.96	+1.28	+1.62	+0.78	+1.54	+0.28
Cl s	6.00	5.96	5.99	5.90	5.97	5.78
p_σ	3.99	3.89	3.92	3.85	3.92	3.86
p_π	4.00	3.99	4.00	3.98	4.00	3.97
$p_\pi{}'$	4.00	3.97	4.00	3.96	3.99	3.95
Formal charge	−0.99	−0.82	−0.91	−0.69	−0.88	−0.57
Cu-Cl overlap population	−0.015	+0.213	+0.095	+0.406	+0.117	+0.576

[a] 4s and 4p functions of Cu deleted. [b] No functions deleted. [c] s, p, and d functions of lowest exponent deleted.

$(CN)_4^{2-}$ ion[3] and the ferrocene molecule.[15,49] Finally the lowest IP is not associated with the open-shell orbital, as would be expected on the basis of the aufbau principle. However, this is not a requirement and a similar situation has already been encountered for the CrO_8^{3-} ion.[8,51]

van der Lugt has reported recently a semiempirical calculation for $CuCl_4^{2-}$ which reproduces the sequence of orbital energies from our *ab initio* calculation; namely, the orbitals which are mainly metal 3d orbitals are at a lower energy level than the orbitals built from the ligand 3p orbitals.[31] He states that, if Koopmans' theorem can be applied, the IP's in the lowest energy range may be expected to be due to the ionization of electrons in ligand orbitals. We would like to emphasize again that Koopmans' theorem is not valid for these types of compounds, and therefore it is not possible to make any prediction regarding the sequence of IP from the sequence of energy levels and *vice versa*. Biloen and Prins have assigned the lowest ionization energy in the X-ray photoelectron spectrum of $PtCl_4^{2-}$ to the removal of metal 3d electrons.[33] They state that, using Koopmans' theorem, one may infer from the photoelectron spectrum an orbital ordering which confirms the semiempirical calculations and thus contradicts the *ab initio* ones. However, this conclusion is unacceptable in the light of our results regarding the lack of validity of Koopmans' theorem. Furthermore, the assignment from the X-ray photoelectron spectrum may not be so straightforward as reported by Biloen and Prins. These authors state that the valence band in the spectrum consists of two separate subbands corresponding respectively to the group of metal orbitals and to the group of ligand orbitals. However, the experimental spectrum given in Figure 1 of ref 33 shows in fact a broad band with one sharp maximum and a second, less distinct, maximum which reduces to a shoulder for Na_2PtCl_4. If one refers to Table IV, it is found that the computed IP's for the ligand 3p orbitals are spread over 0.13 au (from 0.381 to 0.514 au), while the IP's associated with the metal 3d orbitals are concentrated on a narrow range of about 0.015 au (from 0.422 to 0.437 au). Besides the fact that the sequence of IP's may be slightly different in $CuCl_4^{2-}$ and $PtCl_4^{2-}$, the valence band in the experimental spectrum of $PtCl_4^{2-}$ could as well be interpreted as the superposition of a broad band corresponding to the ligand 3p orbitals and a sharp maximum for the metal 3d orbitals, with the possibility that the broad band extends to slightly lower IP (or comparable IP) than the sharp maximum.

Some clue to the nature of the bonding in the ion may be obtained from a comparison of the orbital energies reported above with the ones for the atomic species Cu^{2+} and Cl^-. The orbital energies for the 3d orbitals of the Cu^{2+} ion and the 3p orbitals of the Cl^- ion are respectively −1.53 and −0.12 au (with BSIII).[52] Upon coordination, there is a strong destabilization of the Cu 3d orbitals and a slight stabilization of the Cl $3p_\sigma$ orbitals. This may be rationalized on the basis of a σ-electron transfer from the ligand to the metal, electron transfer which is also evidenced from the results of a population analysis.

Orbital populations are reported in Table V for the D_{4h} configuration with the three basis sets, together with the overlap population Cu-Cl. Two subcases have been considered for each basis set, in order to exemplify the dependence of the population analysis on the basis set used (this point has been discussed at length by Mulliken[53]). For BSI, we have reported the results of a subcase with the basis functions corresponding to the 4s and 4p orbitals of Cu (*i.e.*, the ones corresponding to the lowest two exponents) deleted from the basis set. For BSII and BSIII we have reported the results corresponding to the deletion from the SCF calculation of the s, p, and d functions on Cu with the lowest exponents (d function of

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(49) When we say that Koopmans' theorem is not valid for a molecule, we mean that the sequence of orbital energies (or the substitutes of eq I) does not parallel the sequence of experimental IP's. When we say that Koopmans' theorem is not valid for a given orbital, we mean that the orbital energy differs appreciably (by more than 1 or 2 eV) from the IP's computed as the difference of the energy for the molecule and the ion. Koopmans' theorem is known to fail for as simple a molecule as N_2 and, for this molecule, the calculation of the three lowest IP's as differences of total energies leads to the wrong sequence in the Hartree–Fock approximation.[50] Then the failure of Koopmans' theorem should be traced to the neglect of correlation energy. However, results for the ferrocene molecule[15] and for the $Ni(CN)_4^{2-}$ ion[3] indicate that the failure of Koopmans' theorem should be traced for these molecules to the neglect of the electronic relaxation upon ionization.

(50) P. E. Cade, K. D. Sales, and A. C. Wahl, *J. Chem. Phys.*, **44**, 1973 (1966).

(51) J. Demuynck and A. Veillard, unpublished results.

(52) The corresponding values reported by Clementi with an extended basis set of Slater functions are −1.47 and −0.15 au.[39]

(53) R. S. Mulliken, *J. Chem. Phys.*, **36**, 3428 (1970).

exponent 0.2 or 0.15, s and p functions of exponent 0.08). The net charge on the Cu atom is found to vary from +1.96 (BSI, subcase 1) to +0.28 (BSIII, subcase 2). This dependence on the basis set is easily rationalized in terms of the more or less diffuse character of the basis functions. In the subcase 1 of BSI, there is no function of appropriate exponent to describe the Cu-Cl bonding, and the picture given through the population analysis corresponds to an assembly of ions. Subcase 2 of BSI introduces some possibility of bonding only through the 4s and 4p orbitals of Cu, a description which is probably not very appropriate. On the contrary, subcase 2 of BSII and BSIII is characterized by the use of diffuse functions, d, s, and p, on the Cu atom resulting in lower values of the energy but at the cost of less significance for the population analysis. Careful analysis of the wave function shows that diffuse functions on the Cu atom are used to improve the description of the chlorine orbitals (essentially the 3s orbitals), probably as the result of a slight lack of balance between the atomic basis sets.[54] For these reasons, we will consider that significant population analysis has been achieved only in subcase 1 of BSII and BSIII.

With this restriction in mind, it is apparent from Table V that the bonding in $CuCl_4^{2-}$ involves a small electronic transfer from the chlorine $3p_\sigma$ filled atomic orbitals to the copper $3d_{x^2-y^2}$ half-filled and 4s, $4p_x$, and $4p_y$ empty orbitals. This transfer amounts to 0.09 e for each Cl atom in subcase 1 of BSII and to 0.11 e in subcase 1 of BSIII, most of it coming from the $3p_\sigma$ orbital. The total charge transfer is equally distributed between the four orbitals of Cu (in subcase 1 of BSII, 0.07 e goes to the orbital $3d_{x^2-y^2}$, 0.09 e to 4s, and 0.10 to the $4p_x$ and $4p_y$ orbitals). This is somewhat reminiscent of a dsp^2 hybridization.

We have reported in Table VI the populations in the T_d configuration with subcase 1 of BSII (this should be compared with column 4 of Table V). It is apparent that the charge transfer and the Cu-Cl overlap population are very much the same in the two configurations, with a slightly higher population of the 3d orbitals in the D_{4h} configuration.

Table VI. Atomic and Orbital Populations for the T_d Configuration (subcase 1 of BSII)

	Population		Population
Cu s	6.09	Cl s	5.99
p_x, p_y, p_z[a]	4.08	$p_x(\sigma + \pi)$	3.95
$3d(t_2)$[a]	1.67	$p_y(\pi)$	4.00
3d(e)[a]	2.00	$p_z(\sigma + \pi)$	3.98
Formal charge	+1.66	Formal charge	−0.92
		Cu–Cl overlap population	+0.088

[a] For each.

The chlorine hyperfine coupling in single crystals of $CsCuCl_3$ has been derived from ^{35}Cl nmr measurements and analyzed in terms of $CuCl_4^{2-}$ square-planar anions.[55] We have computed the isotropic part, A_s, of the hyperfine interaction, and the results are reported in Table VII. The agreement with the experimental value is better than expected, since the wave function used is of the RHF type and contributes to A_s only through the half-filled molecular orbital.[56] Nevertheless, this indicates that the approximation of analyzing the results in $CsCuCl_3$ in terms of a square-planar anion is probably acceptable. Again the results obtained from the two basis sets BSII and BSIII are rather close, further substantiating the conclusion that these two basis sets are of comparable accuracy in the description of the valence shells, at least for the ground state.

Table VII. Computed Isotropic Part A_s of the Hyperfine Interaction for the D_{4h} Configuration (in 10^{-4} cm^{-1})

	BSI	BSII	BSIII	Exptl[a]
A_s	3.67	10.28	10.73	9.1

[a] Reference 55.

The Excited States and Electronic Transitions for the D_{4h} Configuration. Independent SCF calculations have been carried out in the restricted Hartree–Fock scheme for several excited states of the $CuCl_4^{2-}$ ion in the D_{4h} configuration. We have assumed that the geometry used for the ground state is retained in the excited states. The excitations which we have considered may be classified as: ligand field or d–d excitations of an electron from the $2b_{2g}$, $2e_g$, and $8a_{1g}$ orbitals to the $6b_{1g}$ orbital; ligand to metal charge-transfer excitations from the orbitals $8e_u$, $4a_{2u}$, $2b_{2u}$, $9e_u$, and $2a_{2g}$ to the $6b_{1g}$ orbital; "atomic" excitations from the $6b_{1g}$ orbital to the orbitals $10a_{1g}$, $5a_{2u}$, and $10e_u$ which are not occupied in the ground-state wave function (these are nearly pure 4s and 4p atomic orbitals of Cu).

We have reported in Table VIII the excitation energies computed with BSII and BSIII. The lowest excitations are found to be the d–d excitations, next the charge-transfer excitations. This would be unexpected on the basis of the sequence of energy orbitals, since the orbitals $2b_{2g}$, $2e_g$, and $8a_{1g}$ which are mostly metal 3d orbitals have higher orbital energies than the ligand orbitals from $8e_u$ to $2a_{2g}$. It has been shown previously for the $Ni(CN)_4^{2-}$ ion that one should not expect any relationship between the sequence of orbital energies and the sequence of excitation energies, due to the importance of both the Coulomb and exchange terms and the electronic reorganization upon excitation.[3] The computed excitation energies depend somewhat on the basis set used; the d–d excitation energies are shifted down by approximately 500 cm^{-1} from BSII to BSIII while the charge-transfer excitations are shifted to higher energies by about 5000 cm^{-1}. These shifts may be understood on the basis of the changes in the electronic distribution which are induced by the electronic excitation. On the charge-transfer excitation, the configuration of the metal gets close to $3d^{10}$ (*cf.* Table X)

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(54) This point could be checked by performing atomic calculations for the Cl atom with both basis sets of Cl and Cu (while keeping the molecular interatomic distance). However, we have not carried such calculations.

(55) H. Rinneberg, H. Haas, and H. Hartmann, *J. Chem. Phys.*, **50**, 3064 (1969).

(56) With BSI incremented with one 3d function of exponent 0.3[10], the isotropic constant A_s is computed as 8.51×10^{-4} cm^{-1} with a RHF-SCF wave function and as 15.37×10^{-4} cm^{-1} with a UHF-SCF wave function. It has been pointed out that the value predicted from a UHF-SCF wave function is generally too high.[57]

(57) B. T. Sutcliffe, *J. Chem. Phys.*, **39**, 3322 (1963).

Table VIII. Computed Excitation Energies (in cm^{-1}) for the D_{4h} Configuration

Excited state and transition[a]	BSIII	BSII	Nature of the transition	Type of transition
$^2B_{2g}$ ($2b_{2g} \rightarrow 6b_{1g}$)	7,500	8,100	$d_{xy} \rightarrow d_{x^2-y^2}$	d → d
^2E_g ($2e_g \rightarrow 6b_{1g}$)	9,400	9,900	$d_{xz,yz} \rightarrow d_{x^2-y^2}$	
$^2A_{1g}$ ($8a_{1g} \rightarrow 6b_{1g}$)	10,100	10,500	$d_{z^2} \rightarrow d_{x^2-y^2}$	
$^2A_{2g}$ ($2a_{2g} \rightarrow 6b_{1g}$)	37,000	32,200	$\pi_L \rightarrow d_{x^2-y^2}$	Charge transfer
^2E_u* ($9e_u \rightarrow 6b_{1g}$)	42,500	37,700	$\pi_L \rightarrow d_{x^2-y^2}$	
$^2B_{2u}$* ($2b_{2u} \rightarrow 6b_{1g}$)	44,900	40,400	$\pi_L \rightarrow d_{x^2-y^2}$	
^2A_u ($4a_{2u} \rightarrow 6b_{1g}$)	53,800	48,100	$\pi_L \rightarrow d_{x^2-y^2}$	
^2E_u* ($8e_u \rightarrow 6b_{1g}$)	56,200	50,900	$\sigma_L \rightarrow d_{x^2-y^2}$	
$^2A_{2u}$ ($6b_{1g} \rightarrow 5a_{2u}$)	81,900		$d_{x^2-y^2} \rightarrow 4p_z$	Cu → Cu
$^2A_{1g}$ ($6b_{1g} \rightarrow 10a_{1g}$)	89,900		$d_{x^2-y^2} \rightarrow 4s$	
^2E_u* ($6b_{1g} \rightarrow 10e_u$)	129,600		$d_{x^2-y^2} \rightarrow 4p_x, 4p_y$	

[a] (*) excited states corresponding to allowed transitions.

and one should expect an expansion of the 3d orbitals in the excited state.[58] It turns out that this expansion is probably better described with BSII than with BSIII, due to the fact that the second 3d contracted function is too diffuse in BSIII (exponent 0.15 *vs.* 0.2 in BSII). Upon a d–d excitation, the population of the $3d_{x^2-y^2}$ orbital is raised from about one to two (*cf.* Tables V and X). As a result, the ligand to metal electronic transfer is diminished and the formal charge of the Cl is slightly raised (from −0.88 to −0.90). The corresponding expansion in the 3p orbital is more accurately described with BSIII (which has three gaussian functions to describe the 3p orbital) than with BSII (which has only two Gaussian functions). Besides the inclusion of correlation effects, accurate calculations of the excitation energies may require more flexible basis sets than the ones used here, in order to give a balanced description of both the ground and excited states. However, in the present case the sequence of excitation energies is not affected by the basis set used.

There is little experimental information regarding the electronic absorption spectrum of the square-planar $CuCl_4^{2-}$ ion, except for the work of Hatfield and Piper on $[Pt(NH_3)_4]$ $[CuCl_4]$[59] and the work of Willet, *et al.*, on $(RNH_3)_2CuCl_4$.[21] Their results are reported in Table IX. Comparison with Table VIII indicates that the computed d–d excitation energies are too low by about 3000 cm^{-1}, while the first computed charge-transfer excitation energy is too high. However, one should be reminded that, on the one hand, this calculation suffers from the use of a limited basis set and does not account for the correlation energy but also that the experimental spectrum refers to the solid state with experimental evidence for ionic interactions, with the charge-transfer bands the most affected by these interactions.[21] The assignment of the experimental d–d excitations reported in Table IX from ref 21 was based on crystal field calculations.[59] Our calculation leads to a different assignment,[60] $^2B_{2g}(d_{xy} \rightarrow d_{x^2-y^2}) < {}^2E_g(d_{xz,yz} \rightarrow d_{x^2-y^2}) < {}^2A_{1g}(d_{z^2} \rightarrow d_{x^2-y^2})$, which is probably more reliable. As already mentioned, it does not seem to depend on the basis set. Further confirmation is provided by the extensive available literature regarding the electronic spectra of square-planar complexes MX_4^{2-} with M a d^8 metal (Pd, Pt) and X a halogen.[25,61] Experimental evidence from polarized spectra and magnetic circular dichroism (MCD) has supported the following assignment for $PdCl_4^{2-}$ and $PtCl_4^{2-}$:[25,61] $^1A_{2g}(d_{xy} \rightarrow d_{x^2-y^2}) < {}^1E_g(d_{xz,yz} \rightarrow d_{x^2-y^2}) < {}^1B_{1g}(d_{z^2} \rightarrow d_{x^2-y^2})$ (the position of the $^1A_{1g} \rightarrow {}^1B_{1g}$ transition is less firmly established) which is similar to the one which we propose for $CuCl_4^{2-}$.

Table IX. Experimental Transitions (in cm^{-1}) and Assignments for the Square-Planar $CuCl_4^{2-}$ Ion

Assignment	$Pt(NH_3)_4$-$CuCl_4$[a]	$(CH_3NH_3)_2$-$CuCl_4$[b]	$(C_2H_5NH_3)_2$-$CuCl_4$[b]
$\sigma \rightarrow d_{x^2-y^2}$		49,000	49,000
$\pi \rightarrow d_{x^2-y^2}$		38,500	38,500
$\pi \rightarrow d_{x^2-y^2}$		33,300	33,300
$\pi \rightarrow d_{x^2-y^2}$	24,900	24,000	24,000
$d_{xz,yz} \rightarrow d_{x^2-y^2}$	14,3000	13,000	12,800
$d_{xy} \rightarrow d_{x^2-y^2}$	13,1000		
$d_{z^2} \rightarrow d_{x^2-y^2}$	10,900	10,700	10,500

[a] Reference 59. [b] Reference 21.

The same MX_4^{2-} complexes usually display one or two bands with a high intensity, which are generally referred to as ligand to metal charge-transfer bands, although they could also be due to transitions from the *n*d shell to a mainly metal (*n* + 1)p orbital.[61] The transition $^2B_{1g} \rightarrow {}^2A_{2u}$ ($d_{x^2-y^2} \rightarrow 4p_z$) is computed to be above 80,000 cm^{-1}, giving further support to the hypothesis that they are charge-transfer bands. It has been inferred from the polarized spectra and the MCD spectra that in $PtCl_4^{2-}$ and $PdCl_4^{2-}$ the excitation energies to the $^1A_{2u}$ ($\pi b_{2u} \rightarrow b_{1g}$) and to the ^1E_u ($\pi e_u \rightarrow b_{1g}$) states are extremely close, with the following sequences: in $PtBr_4^{2-}$,[25] $^1A_{2u}(\pi b_{2u} \rightarrow b_{1g}) < a^1E_u(\pi e_u \rightarrow b_{1g}) < b^1E_u(\sigma e_u \rightarrow b_{1g})$; and in Pd halides,[61] $^1A_{2u}(\pi b_{2u} \rightarrow b_{1g}) \sim a^1E_u(\pi e_u \rightarrow b_{1g}) < b^1E_u(\sigma e_u \rightarrow b_{1g})$. This gives a strong support to the conclusions which we have reached for the charge-transfer excitation energies of $CuCl_4^{2-}$. Our computed excitation energies for the two allowed transitions to the states $^2E_u(\pi 9e_u \rightarrow 6b_{1g})$ and $^2B_{2u}(2b_{2u} \rightarrow 6b_{1g})$ are very close with a difference of about 2500 cm^{-1} and fall at longer wavelengths than the excitation to the state $^2E_u(\sigma 8e_u \rightarrow 6b_{1g})$. It should be emphasized that our predictions are not very different from the ones proposed previously by several authors on the basis of

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(58) This is supported by an examination of the optimized orbital exponents reported by Wachters for the Cu atom in the two states $3d^{10}$ $4s^1$ (^2S) and $3d^9$ $4s^2$ (^2D); the exponents associated with the 3d orbital are lower for the ^2S state.

(59) W. E. Hatfield and T. S. Piper, *Inorg. Chem.*, 3, 841 (1964).

(60) One will notice that, even for the d–d excitations, the sequence of excitation energies does not parallel the sequence of orbital energies, with the $2b_{2g}$ (d_{xy}) the deepest one and the excitation to the state $^2B_{2g}$ the easiest one.

(61) A. J. McCaffery, P. N. Schatz, and P. J. Stephens, *J. Amer. Chem. Soc.*, 90, 5730 (1968).

Table X. Atomic and Orbital Populations for the Excited States of the D_{4h} Configuration (subcase 1 of BSIII)

Excited state	$^2B_{1g}$		$^2B_{2g}$		^2E_g		$^2A_{1g}$		$^2A_{2g}$		^2E_u		$^2B_{2u}$		$^2A_{2u}$		^2E_u	
transition	ground state		$2b_{2g} \rightarrow 6b_{1g}$		$2e_g \rightarrow 6b_{1g}$		$8a_{1g} \rightarrow 6b_{1g}$		$2a_{2g} \rightarrow 6b_{1g}$		$9e_u \rightarrow 6b_{1g}$		$2b_{2u} \rightarrow 6b_{1g}$		$4a_{2u} \rightarrow 6b_{1g}$		$8e_u \rightarrow 6b_{1g}$	
	Cu	Cl	Cu	Cl	Cu	Cl	Cu	Cl	Cu	Cl	Cu	Cl	Cu	Cl	Cu	Cl	Cu	Cl
4s/3s	0.10	1.97	0.11	1.98	0.11	1.98	0.10	1.98	0.02	1.98	0.02	1.98	0.02	1.98	0.02	1.98	0.03	1.98
$4p_x/3p\sigma$	0.13	1.92	0.13	1.93	0.13	1.93	0.13	1.93	0.04	1.99	0.04	1.91	0.04	1.99	0.04	1.99	0.04	1.78
$4p_y/3p\pi$	0.13	2.00	0.13	2.00	0.13	2.00	0.13	2.00	0.04	1.75	0.04	1.83	0.04	2.00	0.04	2.00	0.04	1.96
$4p_z/3p\pi'$	0.02	2.00	0.03	1.99	0.03	1.99	0.03	1.99	0.01	2.00	0.01	2.00	0.01	1.75	0.00	1.75	0.01	2.00
$3d_{xy}$	2.00		1.01		2.00		2.00		1.99		1.99		1.99		1.99		1.99	
$3d_{xz,yz}$	2.00		2.00		1.50		2.00		1.99		1.99		1.99		1.99		1.99	
$3d_{x^2-y^2}$	1.08		2.00		2.00		2.00		2.00		2.00		2.00		2.00		2.00	
$3d_{z^2}$	2.00		1.99		1.99		1.01		1.99		1.98		1.98		1.98		1.98	
Total 3d	9.08		9.00		8.99		9.01		9.96		9.96		9.96		9.96		9.96	
Formal charge	+1.54	−0.88	+1.59	−0.90	+1.60	−0.90	+1.60	−0.90	+0.93	−0.73	+0.93	−0.73	+0.93	−0.73	+0.93	−0.73	+0.92	−0.73
Cu–Cl overlap population	+0.117		+0.105		+0.102		+0.102		−0.015		−0.013		−0.013		−0.013		−0.011	

Table XI. Components of the Total Energy (in au) for the D_{4h} and T_d Configurations (with BSII)

Geometry	Electronic state	T	V_{ne}	V_{ee}	V_{nn}	E
D_{4h}	$^2B_{1g}$	3597.7927	−9893.8818	2104.7106	720.8014	−3470.5770
T_d	$^2T_2$	3597.7905	−9871.5727	2092.8090	710.3675	−3470.6057[a]

[a] With symmetry-adapted functions and symmetrical occupancy.

either a "reasonable" energy level diagram or a semiempirical calculation.[25,27] However, this is achieved with a sequence of molecular orbitals which is drastically different in our *ab initio* calculation from the ones previously proposed. Using a semiempirical method of the SCF type with the INDO approximation, van der Lugt has recently reached similar conclusions regarding the charge-transfer transitions of $PdCl_4^{2-}$ and $PtCl_4^{2-}$ with a similar sequence of energy levels.[30,31]

The results of a population analysis for some excited states are compared in Table X with the results for the ground state. Upon the d-d excitations, the electronic transfer from the chlorine orbitals to the metal $3d_{x^2-y^2}$ orbital vanishes since the $3d_{x^2-y^2}$ orbital is now filled. As a result, the formal charge on the metal is slightly increased and the Cu-Cl overlap population is slightly diminished. A different situation prevails in the charge-transfer excited states. The formal charge on the metal is decreased to a rather uniform value of +0.93, the electronic transfer to the metal 4s and 4p orbitals are very much decreased, and the Cu-Cl overlap population turns out to be negative (with a rather uniform value close to −0.013), partly as the result of the double occupancy of the antibonding orbital $6b_{1g}$.

The Relative Stabilities of the Various Configurations for the $CuCl_4^{2-}$ Ion. The D_{4h} configuration for the $CuCl_4^{2-}$ ion is considered to result from a strong tetragonal distortion of the octahedral coordination, due to the Jahn-Teller effect, as in $(NH_4)_2CuCl_4$. It has been argued that the case of square coordination as found in many complexes of Cu^{II} should be regarded as the extreme of the Jahn-Teller effect rather than as a different type of coordination.[62] The tetracoordinated species $CuCl_4^{2-}$ is expected to achieve a tetrahedral configuration. Experimentally, the M_2CuCl_4 compounds like Cs_2CuCl_4 and $[N(CH_3)_4]_2CuCl_4$, where the cations are large, contain CuX_4^{2-} ions which are squashed tetrahedra. The Cu^{2+} d^9 ion in a tetrahedral surrounding is subject to a Jahn-Teller effect; however, it has been shown that the orbital degeneracy of the tetrahedral $CuCl_4^{2-}$ is removed by spin-orbit coupling without recourse to distortion from T_d symmetry.[29]

In the present study, we first compare the relative stabilities of the D_{4h} and T_d configurations, since it has been stated that the factors governing the stability of the tetrahedral configuration relative to the planar one are not fully understood.[63] Next we have attempted to find, by energy minimization with respect to the angle θ of Figure 2, what is the distortion associated with the stable configuration of the free ion, compared with a tetrahedral stereochemistry. Since distortions of a complex in a crystal may arise from packing considerations, it appears important to have an estimate of the distortion associated with the free ion. This parallels the work of Lohr and Lipscomb[29] using the extended Hückel method, with the energy defined as the sum of the one-electron energies (thus neglecting the nuclear repulsion energy and counting twice the electron-repulsion terms). These authors found that the T_d structure is more stable than the D_{4h} structure by 27.6 kcal/mol and that the most stable geometry is the tetragonally compressed D_{2d} structure with a Cl-Cu-Cl

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(62) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience, New York, N. Y., 1968, p 898 and following.

(63) Reference 62, p 131.

angle of 120° ($\theta = 60°$) and a stabilization energy of 4.6 kcal/mol compared with the T_d structure (a second minimum corresponds to a Cl–Cu–Cl angle of 100° but with a stabilization of only 0.2 kcal/mol compared with the T_d). Given the importance of these results with respect to the stereochemistry of the MX_4^{2-} ions, we have found worthwhile to reinvestigate this problem through *ab initio* calculations with the total energy correctly defined.

We have reported in Table XI the components of the energy values for the D_{4h} and T_d configurations. The T_d structure is more stable than the D_{4h} structure by 18 kcal/mol, as the result of a large cancellation between the nucleus–nucleus V_{nn} and electron–electron V_{ee} repulsion energies which favor the tetrahedral structure and the nuclear attraction energy V_{ne} which favors the planar structure (the Cl–Cl distance is 3.20 Å in the D_{4h} and 3.69 Å in the T_d structures). The kinetic energy (T) remains practically the same in the two structures.

We have reported in Table XII the energy of the $CuCl_4^{2-}$ ion as a function of the angle θ. Calculations were carried out for three values of the angle $\theta = 54° 44'$[64] (T_d), $\theta = 60°$ (D_{2d}), and $\theta = 65°$ (D_{2d}). For economy reasons, we have not looked at the second minimum reported by Lohr and Lipscomb for θ less than 54° 44′ (elongated bisphenoid). The minimum of the total energy is achieved for a value of θ close to 60°, the stabilization with respect to the T_d structure being of the order of 0.003 au or about 2 kcal/mol. The value of 120° predicted for the Cl–Cu–Cl angle is the same as the one reported by Lohr and Lipscomb, with a stabilization energy slightly smaller in our calculation. It is close to the experimental value of 124° in Cs_2CuCl_4.[23] We conclude that the distortion with respect to an ideal T_d geometry is an intrinsic property of the free ion. The same conclusion has been reached previously on the basis of the similitude between the spectrum of the crystal and that of the ion in solution.[67,68]

Table XII. Energy of the $CuCl_4^{2-}$ Ion as a Function of the Angle θ

θ	Point group	Electronic state	Total energy[a]
54° 44′	T_d	$^2T_2$	−3470.6053[b]
60°	D_{2d}	$^2B_2$	−3470.6082
65°	D_{2d}	$^2B_2$	−3470.6050

[a] In au. [b] Without symmetry-adapted functions and with forced occupancy.

The computed stabilization of 2 kcal/mol for the D_{2d} structure compared with the T_d structure is a very small fraction (of the order of 10^{-6}) of the total energy. This raises the question of how significant is this energy difference. The corresponding error should be the sum of the error introduced by the use of a limited basis set plus the change in the correlation energy between the two structures. The computed energy for the $CuCl_4^{2-}$ ion is well above the Hartree–Fock limit by a few atomic units (1 au = 628 kcal/mol). However, most of the error is at the level of the atomic inner shells, since our calculation has put the emphasis on the description of the valence shells. There is hope that improving the wave function in the Hartree–Fock scheme will not alter significantly the above value (*i.e.*, will not change it by a factor of 10 or reverse the order of stability of the T_d and D_{2d} structures). Any estimation of the change in correlation energy is difficult. However, one is reminded that the corresponding change for the ammonia molecule, when going from the pyramidal to the planar conformation, is probably less than 1 kcal/mol.[71] The change in the $CuCl_4^{2-}$ ion, when going from the T_d to the close D_{2d} structure, is probably minor compared with the one in ammonia when passing from the C_{3v} to the D_{3h} conformation.

Conclusion

We have reported LCAO–MO–SCF calculations for the $CuCl_4^{2-}$ ion in a variety of geometries (D_{4h}, T_d, D_{2d}). For the D_{4h} structure, three different basis sets have been used with the conclusion that a medium size set provides a description of the bonding which is accurate enough. The lowest IP's computed according to Koopmans' theorem are associated with molecular orbitals which are mostly chlorine 3p orbitals. When electronic relaxation is allowed during the ionization process, the ionization potentials for the ligand 3p and metal 3d orbitals become comparable. The inclusion of the crystal potential results in a stabilization of the molecular orbitals which is slightly larger for the ligand orbitals but which does not affect the sequence of computed ionization potentials. The conclusion of Biloen and Prins,[33] that one may infer from the photoelectron spectrum an orbital ordering which confirms the semiempirical calculations and thus contradicts the *ab initio* one, appears unacceptable in the light of the above results, because of the failure of Koopmans' theorem. Furthermore, the interpretation given by these authors of the experimental photoelectron spectrum of $PtCl_4^{2-}$ may be questioned on the basis of the large spread associated with the IP's of the ligand 3p orbitals compared with the IP's of the metal 3d orbitals.

We have found that the net charge on the Cu atom from a population analysis may vary from +1.96 to +0.28. This exemplifies the dependence of the population analysis on the basis set used. Significant population analysis is achieved only if diffuse functions are deleted from the Cu atom; then the bonding in $CuCl_4^{2-}$

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(64) Calculations for the T_d structure have been carried either in the configuration $t_x^{5/3}$ $t_y^{5/3}$ $t_z^{5/3}$ (symmetrical occupancy) or in the configuration t_x^2 t_y^2 t_z^1 (forced occupancy).[65,66] D_{2d} structures have electronic configurations analogous to the forced occupancy and are thus best compared to it. The two calculations for the T_d structure lead to energy values which differ by 0.0004 au probably as a consequence of different round-off errors (only the calculation with symmetrical occupancy used symmetry-adapted functions).

(65) J. Arents and L. C. Allen, *J. Chem. Phys.*, **53**, 73 (1970).

(66) R. N. Dixon, *Mol. Phys.*, 20, 113 (1971).

(67) J. Ferguson, *J. Chem. Phys.*, 40, 3406 (1964).

(68) We have carried out similar calculations for the $NiCl_4^{2-}$ ion, with the same basis set of Gaussian functions used for the Ni atom as for the Cu atom in $CuCl_4^{2-}$ (as a way to avoid additional computation of two-electron integrals). Only one-electron integrals had to be recomputed to account for the change in the nuclear charge. For the T_d structure, the high-spin state $^3T_1$ is found more stable than the low-spin state by 0.104 au or 65 kcal/mol, in agreement with the fact that $NiCl_4^{2-}$ is a high-spin complex.[69] The low-spin D_{4h} structure is now found more stable than the low-spin T_d structure by 5 kcal/mol. This is qualitatively in agreement with the fact that the low-spin D_{4h} structure may compete with the high-spin T_d structure for some four-coordinated complexes of Ni(II).[70]

(69) Reference 62, p 883.

(70) Reference 62, p 889.

(71) A. Rauk, L. C. Allen, and E. Clementi, *J. Chem. Phys.*, **52**, 4133 (1970).

involves a small charge transfer from the chlorine $3p_\sigma$ atomic orbitals to the Cu $3d_{x^2-y^2}$ (half-filled) and 4s, $4p_x$, and $4p_y$ (empty) orbitals.

From independent SCF calculations, the lowest excitations are found to be d–d excitations followed by ligand to metal charge-transfer excitations, a result unexpected on the basis of the sequence of energy orbitals. The assignment from our calculation for both the d–d excitations $^2B_{2g}(d_{xy} \rightarrow d_{x^2-y^2}) < {}^2E_g(d_{xz,yz} \rightarrow d_{x^2-y^2}) < {}^2A_{1g}(d_{z^2} \rightarrow d_{x^2-y^2})$, and the charge-transfer excitations are in qualitative agreement with the experimental evidence from the polarized spectrum and magnetic circular dichroism for complex halides of Pd and Pt.

Finally, the T_d structure is computed to be more stable than the D_{4h} structure by 18 kcal/mol. However, it is found by energy minimization with respect to the Cl–Cu–Cl angle that the most stable configuration of the $CuCl_4^{2-}$ ion corresponds to a flattened D_{2d} structure, with a value of 120° for the Cl–Cu–Cl angle close to the experimental value of 124° in Cs_2CuCl_3. The distortion with respect to an ideal T_d geometry appears as an intrinsic property of the $CuCl_4^{2-}$ ion, not as a consequence of packing effects.

The wave function which we have reported for the ground state of the $CuCl_4^{2-}$ ion in the D_{4h} structure is somewhat different from the ones obtained previously from semiempirical calculations by other authors. It should be emphasized that these semiempirical wave functions were used in conjunction with either Koopmans' theorem or with the assumption that the excitation energies may be represented as a difference of orbital energies. We have made the calculation at one level more sophisticated (independent SCF calculations for the ionized and excited states). The good agreement with experimental properties achieved for the electronic spectrum, the hyperfine interaction, and the equilibrium configuration gives some confidence in the reported wave functions.

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Electronic Structure of Phosphorus Pentafluoride and Polytopal Rearrangement in Phosphoranes

A. Strich and A. Veillard*

Contribution from Equipe de Recherche No. 139 du CNRS,
Université Louis Pasteur. BP 296/R8,
67-Strasbourg, France. *Received March 12, 1973*

Abstract: The electronic structure of PF_5 is discussed through *ab initio* LCAO–MO–SCF calculations with a medium size basis set. It is shown that d functions on the phosphorus atom play a significant role through d_π–p_π bonding. Computed energy differences between the D_{3h}, C_{4v}, and C_s structures support Berry's pseudorotation mechanism as the mechanism of ligand interchange for PF_5 and seem to rule out the mechanism of turnstile rotation. The ease of ligand exchange in substituted phosphoranes $PR_nF_{(5-n)}$ is discussed in terms of the computed energy differences between the trigonal bipyramid (TBP) and the square pyramid (SP) together with the energy differences between the TBP isomeric structures. The slow exchange limit found experimentally for the amino- and thiotetrafluorophosphoranes is accounted for by a relatively high barrier to Berry's pseudorotation. The corresponding barriers to rotation around the P–N or the P–S bond are computed, and it is found that the rotation process around the P–N bond is coupled to the inversion process at the N atom.

Stereochemical nonrigidity is common in five-coordinate chemistry and has been extensively studied for pentacoordinate compounds of phosphorus.[1,2] The Berry mechanism, which accounts for most experimental observations relating to intramolecular rearrangements of phosphoranes, has been initially proposed for the PF_5 molecule.[3] Other mechanisms have been proposed since.[4] It has been pointed out that information concerning the mechanism is usually inferential, although the corresponding potential surfaces can be obtained from nonempirical quantum mechanical calculations.[5]

Quantum mechanical *ab initio* calculations have been fairly successful in the prediction of the stereochemistry for small molecules and in the calculation of rotation and inversion barriers.[6] However, there has been no attempt so far to investigate nonrigid structures through *ab initio* quantum mechanical calculations, except for model studies by Rauk, *et al.*, of the intramolecular ligand exchange in phosphoranes.[7] Only semiempirical calculations have been reported for PF_5, with some controversy regarding the importance of d orbitals in the bonding.[8–12] We report here non-

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