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Ab initio Calculation of the Charge Distribution and the Ligand Field Splitting in the Tetrahedral Halo Complexes $CuCl_4^{2-}$ and $NiCl_4^{2-}$

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The charge distribution and the ligand field splitting in the tetrachloro complexes $CuCl_4^{2-}$ and $NiCl_4^{2-}$ have been investigated by means of the restricted Hartree-Fock method. A rather large basis set of contracted Gaussian type orbitals has been employed. The charge distributions have been analysed by means of Mulliken population analyses. The ligand field splitting 10Dq has been compared with literature results known for the octahedral cluster NiF_6^{4-} occurring in $KNiF_3$. A detailed analysis has been carried out for $CuCl_4^{2-}$. From calculations on a selected number of states of $NiCl_4^{2-}$ the Racah parameters B and C have been obtained.

Key words: Ligand field splitting in transition metal complexes, *ab initio* HF calculation of ~ - Tetrachloro transition metal complexes, charge distribution of ~

1. Introduction

The advent of high-speed digital computers has made calculations on large inorganic systems containing transition metal atoms quite feasible within the Hartree-Fock LCAO-MO-SCF framework. Our aim is to make a contribution in this field by investigating the charge distribution and the ligand field splitting of the tetrahedral halo complexes $CuCl_4^{2-}$ and $NiCl_4^{2-}$. We expect that covalent bonding effects in the tetrachloro complexes will be more pronounced than in hexafluoro clusters like NiF_6^{4-}. Although the symmetry found in the experimentally observed MCl_4^{2-} units is not always perfectly tetrahedral [1], we neglect deviations from the ideal tetrahedral environment of the transition metal atom. The deformation of the $CuCl_4^{2-}$ tetrahedron has been the subject of a detailed study by Demuynck [2, 3]. It is well known that the principal features of the properties (spectral, magnetic, etc.) of transition metal ions in crystals or coordination compounds can be accounted for by means of the ligand field theory [4-6]. Quantitative investigations of ligand field phenomena starting from first principles have been carried out mainly for the octahedral NiF_6^{4-} cluster occurring in $KNiF_3$ [7-18]. In Ref. [18] a survey is given of the ligand field splittings and Racah parameters calculated by various authors. On the basis of these data it is argued that the SCF-MO level of approximation is sufficient to obtain about 75% of the experimentally observed ligand field splitting in $KNiF_3$. A simple picture of the ligand field splitting in ionic compounds like $KNiF_3$ has been suggested by considering the effect of orthogonalization of metal and ligand orbitals or, in other words, by considering the Pauli repulsion exerted on the metal *d*-electrons by the closed shell electrons of the ligands, as the dominant "mechanism" leading to the ligand field splitting. The experimentally observed reduction of the Racah parameters of the crystal with respect to the Ni^{2+} free ion values (about 10%) has not been obtained by the various authors. The computed reductions (only a few per cent) are generally too small. The explanations given for this discrepancy are only speculative. It has been suggested [18] that this discrepancy is not caused by inadequacies of the basis sets used in the calculations, but rather by inherent limitations of the Hartree-Fock approximation. Hence a treatment which includes correlation effects properly may be necessary in order to explain the observed "nephelauxetic" reductions of the metal *d*-electron repulsion parameters in $KNiF_3$. At this moment, however, such a treatment is still impractical. We continued the work on the ligand field splitting and the Racah parameters by studying complexes with a different geometry and a heavier ligand. For this purpose we investigated the tetrahedral complexes $CuCl_4^{2-}$ and $NiCl_4^{2-}$. Spin-orbit coupling, which is necessary for a precise interpretation of the experimentally observed ligand field spectra, is not taken into account. The results of the *ab initio* calculations performed on the octahedral NiF_6^{4-} cluster lead us to expect physically meaningful results for the tetrachloro clusters also.

2. Basis Set and Procedure

Ab initio SCF-MO calculations have been performed on a number of states of the tetrahedral complexes $CuCl_4^{2-}$ and $NiCl_4^{2-}$ "*in vacuo*" within the framework of the restricted Hartree-Fock formalism [19] using the SYMOL program system [20]. For the metal atoms the basis set of Wachters for Cu, ^2S state, has been adopted [21]. This basis set, consisting of 14 *s*-type, 9 *p*-type and 5 *d*-type primitive Gaussian functions, was contracted to 9 *s*-type, 5 *p*-type and 3 *d*-type functions. In comparison with the uncontracted basis set of Watchers, in our contracted set three functions are used to describe the 1*s* atomic orbital and two for the 2*s*, 3*s* and 4*s* AO's respectively. The 2*p* AO is described by two functions, the 3*p* and 3*d* AO's each by three. Only the first function used to describe the 1*s*, 2*p* and 3*d* AO's respectively has been obtained by contraction. All other functions are primitive Gaussian functions. For chlorine Veillard's atomic basis set of Cl, ^2P state, has been adopted [22]. This basis set, consisting of 12 *s*-type and 9 *p*-type primitive Gaussian functions, was contracted to 7 *s*-type and 5 *p*-type functions following the same scheme and getting the same quality as obtained for the metal inner shells. One might question the adequacy of this basis set in molecular calculations. According to Roos and coworkers [23] the basis set of the transition metal atom has to be extended with appropriate functions which increase the capacity for the electron density to be built up in the region of chemical bonding. Specifically, the metal *d* basis set should be provided with an additional diffuse function to allow the 3*d* atomic orbitals to expand. Simultaneously the rather diffuse Gaussian functions representative of the neutral atom 4*s* AO should be replaced by more contracted functions with higher exponents. For a similar reason, basis functions describing the metal 4*p* AO cannot be inferred from the 4*p* orbital of the neutral atom optimized in some excited state configuration, but instead more contracted functions should be chosen in a way similar to the *s*-type basis functions of the 4*s* AO.

Actually we adopted two *s*-type functions with exponents 0.37 and 0.14 together with two *p*-type functions having exponents 0.31 and 0.12 to represent the metal 4*s* and 4*p* AO's respectively. These functions have been determined by extrapolation by plotting the logarithm of the orbital exponent versus the count number of the basis function for the metal *s*, *p* "core" basis set. Finally we added one diffuse *d*-type basis function to the metal atom with an exponent value of 0.2. The importance of 3*d* orbitals of second-row atoms in molecules had been studied rather systematically by Roos and Siegbahn [24]. Following their arguments, the main effect of these orbitals in MO-SCF calculations is to polarize *s* and *p* valence orbitals of the second-row atom in order to facilitate the formation of chemical bonds. Actually one should optimize these *d*-type functions in the molecule or complex under consideration along with the metal 3*d*, 4*s* and 4*p* functions. For reasons of economy we decided to use *d* function exponents with values of 1.0 and 0.3 respectively for the chlorine ligands without optimization. The final Gaussian basis set used in our calculations consisted of 9 *s*-type, 7 *p*-type and 4 *d*-type functions centred on the metal atom and 7 *s*-type, 5 *p*-type and 2 *d*-type functions on each chlorine ligand atom.

Table 1 demonstrates the flexibility of the resulting basis sets by comparing energy expectation values of Ni^{2+}, Cu^{2+} and Cl^- with Clementi's near Hartree-Fock results [25]. The metal–chlorine distance was kept fixed throughout our calculations at the value of 2.26 Å (4.27 a.u.). This value corresponds to the average distance found in several R_2CuCl_4 compounds [1]. As a result of the common basis set for both metal atoms and of the unique metal ligand distance, the two-electron integrals had to be computed only once for the tetrachloro complexes under consideration. All SCF iterations have been started by means of M^{2+} and Cl^- ionic trial vectors.

Table 1. Total energies and orbital energies of M^{2+} and Cl^- (a.u.)

	Ni^{2+}, ^3F [a]	Ni^{2+}, ^3F [c]	Cu^{2+}, ^2D [a]	Cu^{2+}, ^2D [c]	Cl^-, ^1S [b]	Cl^-, ^1S [c]
$\epsilon\ 1s$	−306.27	−306.33	−329.78	−329.77	−104.48	−104.51
$\epsilon\ 2s$	−38.600	−38.618	−41.802	−41.806	−10.199	−10.229
$\epsilon\ 3s$	−5.5900	−5.5894	−5.9831	−5.9829	−0.71353	−0.73290
$\epsilon\ 2p$	−33.644	−33.646	−36.621	−36.604	−7.6723	−7.6953
$\epsilon\ 3p$	−3.9860	−3.9873	−4.2892	−4.2873	−0.13309	−0.14988
$\epsilon\ 3d$	−1.4182	−1.4177	−1.4703	−1.4716	–	–
E_{tot}	−1505.8	−1506.0	−1637.9	−1638.1	−459.55	−459.58

[a] Cu ^2S contr. basis set of Wachters [21] extended with polarization functions (9*s*/7*p*/4*d*).
[b] Cl ^2P contr. basis set of Veillard [22] (7*s*/5*p*).
[c] STO basis set of Clementi [25]: near Hartree-Fock limit.

3. Orbital Energies and Charge Distributions of $CuCl_4^{2-}$ and $NiCl_4^{2-}$

Tables 2, 3 show the ground-state orbital energies and the gross populations on the metal atom and the chlorine ligands along with the metal ligand overlap populations.

Table 2. Orbital energies and charge distributions

$NiCl_4^{2-}$	$^3T_1$ state $e^4t_2^4$ configuration			
MO	Ni pop	Cl Pop	Ni–Cl Ovl. Pop	ϵ (a.u.)
$7a_1$ Cl^- $3s$	0.067	1.933	0.107	−0.72022
$8a_1$ Cl^- $3p_\sigma$	0.155	1.845	0.178	−0.20225
Σa_1	6.226	9.774	0.280	
$2e$ Ni^{2+} $3d$	1.943	0.057	0.043	−0.36355
$3e$ Cl^- $3p_\pi$	0.061	1.939	−0.026	−0.11453
Σe	2.004	3.996	0.017	
$7t_2$ Cl^- $3s$	0.051	1.949	0.085	−0.70755
$8t_2$ Cl^-3p_σ	0.079	1.921	0.090	−0.15578
$9t_2$ Cl^- $3p_\pi$	0.043	1.957	0.051	−0.12459
$10t_2$ [a] Ni^{2+} $3d$	1.296	0.037	−0.047	−0.36019
Σt_2	5.469	13.864	0.184	
Total	26.642	71.358	0.867	

[a] Open shell orbital. Charge on Ni +1.358, Charge on each Cl −0.840.

Table 3. Orbital energies and charge distributions

$CuCl_4^{2-}$	$^2T_2$ state	$e^4t_2^5$ configuration		
MO	Cu Pop	Cl Pop	Cu–Cl Ovl. Pop	ϵ (a.u.)
$7a_1$ Cl^- $3s$	0.071	1.929	0.113	−0.72065
$8a_1$ Cl^- $3p_\sigma$	0.180	1.820	0.215	−0.20671
Σa_1	6.254	9.746	0.326	
$2e$ Cu^{2+} $3d$	1.967	0.033	0.029	−0.42377
$3e$ Cl^- $3p_\pi$	0.040	1.960	−0.007	−0.11711
Σe	2.006	3.994	0.022	
$7t_2$ Cl^- $3s$	0.051	1.949	0.086	−0.70767
$8t_2$ Cl^- $3p_\sigma$	0.089	1.911	0.104	−0.15816
$9t_2$ Cl^- $3p_\pi$	0.042	1.958	0.047	−0.12610
$10t_2$ [a] Cu^{2+} $3d$	1.618	0.049	−0.052	−0.39502
Σt_2	5.801	13.866	0.191	
Total	27.669	71.331	0.944	

[a] Open shell orbital. Charge on Cu + 1.331, Charge on each Cl −0.883.

The Mulliken population analysis [26] has been displayed only for those molecular orbitals which show a significant delocalized behaviour. Table 4 shows the total gross populations of the different function types together with the total energies of $CuCl_4^{2-}$ and $NiCl_4^{2-}$. The MO's obtained bear a distinct relation to the free ion orbitals of M^{2+} and Cl^- and have been designated according to these orbitals. The greatest part of the

Table 4. Total gross populations of the different function types

	$NiCl_4^{2-}$	$CuCl_4^{2-}$
M s	6.226	6.254
M p	12.321	12.348
M d	8.094	9.067
Cl s	23.805	23.805
Cl p_σ	15.613	15.585
Cl p_π	31.888	31.892
Cl d	0.051	0.049
Total Energies (a.u.)	$NiCl_4^{2-}$	$CuCl_4^{2-}$
E_{tot} (orthog.)	−3344.753	−3476.912
E_{tot} (SCF)	−3344.901	−3477.060
E binding (orthog.)	0.754	0.786
E binding (SCF)	0.902	0.934
E binding (point charge model) = 1.013		

MO's are essentially unaltered core orbitals of the M^{2+} and Cl^- ions. The tabulated overlap populations suggest that the covalent interaction is dominated by the chlorine $3s$ and $3p_\sigma$ AO's. These orbitals are mixed predominantly with the metal $4s$ AO in the MO's belonging to the a_1 representation. In the MO's of the t_2 representation the chlorine valence orbitals mix with the metal $4p$ AO's and with the metal d orbitals. The chlorine $3p_\pi$ AO's mainly interact with the metal d orbitals. The covalent interactions of these orbitals are less important. In the e representation (π-interaction) the closed shell metal $3d$ MO's have weakly bonding properties. In the t_2 representation, however, the open shell $3d$ MO's are antibonding. There is only a slight "p–d mixing" on the metal atom. The overlap populations show that the bonding and antibonding properties of the metal $3d$ MO's are largely compensating each other. It is found that the metal $3d$ orbitals in the complexes have a lower orbital energy than the ligand $3p$ orbitals. This apparent disagreement with experiment has been discussed by Demuynck [2, 3, 27, 28, 29].

The total SCF energies of the complexes (Table 4) have been compared with the results obtained with ionic M^{2+} and Cl^- orthogonalized vectors. Subtracting the ground state SCF energies of the isolated constituent ions, referring to the same basis set, gives an impression of the ionic and covalent part of the bonding energy. The SCF bonding energies have been compared with the value resulting from a simple point charge model. The results show the tetrachloro complexes to be fairly ionic species, the SCF procedure contributing about 16% to the total computed SCF bonding energies.

By considering the bonding energies more carefully it turns out that the SCF procedure causes a lowering of the bonding energies obtained with orthogonal ionic orbitals with approximately the same amount (0.149 a.u.). The population analyses suggest that this is due mainly to the interaction of the occupied Cl^- $3s$, $3p_\sigma$ orbitals with the vacant M^{2+} $4s$, $4p$ orbitals.

4. Ligand Field Splitting in $CuCl_4^{2-}$ and $NiCl_4^{2-}$

According to ligand field theory [4-6], the differences of the energy levels of transition metal ions in cubic crystalline fields can be expressed in general as linear combinations of the crystal field strength parameter Dq and the Racah parameters B and C if spin-orbit coupling is neglected. Looking at these expressions [6] for the manifold of states resulting from the d-orbital configuration $t_2^x e^y$ with $x + y = 8$ ($NiCl_4^{2-}$) and $x + y = 9$ ($CuCl_4^{2-}$), an easy way can be found to define 10 Dq, the crystal field splitting, for both tetrachloro complexes considered:

$$CuCl_4^{2-} \quad 10\,\mathrm{Dq} = E(t_2^6 e^3;\, {}^2E) - E(t_2^5 e^4;\, {}^2T_2) \tag{1}$$

$$NiCl_4^{2-} \quad 10\,\mathrm{Dq} = E(t_2^6 e^2;\, {}^3A_2) - E(t_2^5 e^3;\, {}^3T_2) \tag{2}$$

The wave functions for the above-mentioned states, being in general symmetry adapted linear combinations of Slater determinants, may be found in standard text books [5, 6]. From these wave functions energy expressions can be obtained which are needed to construct appropriate open shell HF operators [14]. These expressions can be used directly in conjunction with the SYMOL program system [20]. The total SCF energy of the states involved in the definition of 10 Dq in the case of $CuCl_4^{2-}$ and $NiCl_4^{2-}$ (Eqs. (1) and (2)) can be decomposed into a number of contributions originating respectively from the kinetic energy, the nuclear electron attraction energy and the two-electron repulsion energy. The ligand field splitting can accordingly be expressed in terms of these contributions. Table 5 shows numerical values obtained for $NiCl_4^{2-}$ and $CuCl_4^{2-}$. Results for NiF_6^{4-} [18] are also shown for comparison along with the experimental data available. The magnitude of the calculated ligand field splitting of $NiCl_4^{2-}$, amounting to at least 60% of the experimental value, looks reasonable. In Refs. [17, 18] it has been pointed out that a major contribution to the ligand field splitting in $KNiF_3$ results from the orthogonalization of the Ni^{2+} and F^- ionic orbitals, its contribution to the theoretical and experimental 10 Dq value being 71% and 55% respectively. The orthogonalized ionic orbitals represent the correct quantum description of the purely ionic situation since the Pauli principle has been fulfilled. The effect of orthogonalization is dominated by an increase of the kinetic energy which is, as may be seen from Table 5, the sign determining contribution to be calculated ligand field splitting of the NiF_6^{4-} cluster. The SCF procedure allows for the rearrangement of the charge distribution with respect to the ionic situation. Our data collected in Table 5 show that compared with the NiF_6^{4-} results, the contribution of the ionic orthogonalized vectors to the calculated 10 Dq value has decreased to 51% in the case of $NiCl_4^{2-}$ and 43% in the case of the $CuCl_4^{2-}$ complex. Obviously rearrangement effects are becoming more important for the tetrachloro complexes. This conclusion is supported by the observation that the kinetic energy is no longer the only sign determining contribution to the computed ligand field splitting, instead, the contribution of the nuclear electron attraction energy has changed sign compared to the NiF_6^{4-} cluster and exceeds the kinetic energy contribution to the calculated 10 Dq value of the tetrachloro complexes.

In Table 6 the effect is shown of successively including the contributions to ΔKE and ΔNAE due to the valence electrons. The analysis of the contributions to ΔKE and

Table 5. Contributions to the ligand field splitting 10 Dq of NiF_6^{4-}, $NiCl_4^{2-}$ and $CuCl_4^{2-}$ (in cm^{-1})

	NiF_6^{4-} (see [17, 18])	$NiCl_4^{2-}$	$CuCl_4^{2-}$
Ionic orthog. vectors	3890	1171	951
ΔKE	+25330	+10147	+10082
ΔNAE	−9130	+17677	+23687
ΔERE	−10760	−25519	−31569
Total SCF	5440	2305	2200
Experiment	7250 [7, 8]	3540, 3850 [30]	–

The SCF ligand field splitting has been decomposed into the following contributions: a) kinetic energy ΔKE, b) nuclear el. attraction energy ΔNAE, c) two-el. repulsion energy ΔERE.

Table 6. Ligand field splitting of $CuCl_4^{2-}$

Contributions of		ΔKE (a.u.)	ΔNAE (a.u.)
Cu $3d$ electrons	e, t_2 sym.	−1.79449	+5.78034
+ Cl $3p_\pi$ electrons		+0.29862	−1.52904
+ Cl $3s$, $3p_\sigma$ electrons		+0.04325	+0.14590
All electrons		+0.04594	+ 0.10793

ΔNAE shows that all valence electrons occupying MO's with e and t_2 symmetry have to be taken into account in order to obtain the correct sign and orders of magnitude of ΔKE and ΔNAE. Hence the computed ligand field splitting involves rearrangment effects of all valence electrons belonging to MO's with the same symmetry as the metal $3d$ orbitals.

5. Racah Parameters of $NiCl_4^{2-}$

The Racah parameters of Ni^{2+} coordinated tetrahedrally to four Cl^- ions, have been obtained from the SCF energies of a (limited) number of states of the $NiCl_4^{2-}$ complex, arising from the configurations $t_2^x e^y$ with $x + y = 8$. Configuration interaction between these states has not been taken into account. Besides this, we have computed, also within the restricted Hartree-Fock formalism, the energies of all terms resulting from the $3d^8$ configuration of the gaseous Ni^{2+} ion, using for Ni^{2+} the same basis set as for the metal centre in $NiCl_4^{2-}$. The separations between these free ion term energies are expressed as linear combinations of the (free ion) Racah parameters B_0 and C_0. In Table 7 the SCF energies of the considered states of $NiCl_4^{2-}$ are displayed along with the energies obtained with orthogonalized ionic vectors. The energies of the Ni^{2+} free ion terms have also been given in Table 7. Energy differences between states of $NiCl_4^{2-}$ are shown in Table 8 together with data for the Ni^{2+} ion. By matching the computed

Table 7. Energies of different states of $NiCl_4^{2-}$ and Ni^{2+}

State of $NiCl_4^{2-}$	Config. $t_2^x e^y$	$E_{\text{orth. ionic}}$ vectors (a.u.)	E_{SCF} (a.u.)
^1E	$t_2^4 e^4$	−3344.67220	−3344.82663
$^3A_2$	$t_2^6 e^2$	−3344.76026	−3344.89838
$^3T_2$	$t_2^5 e^3$	−3344.76559	−3344.90888
$^3T_1$	$t_2^4 e^4$	−3344.75267	−3344.90149

State of Ni^{2+}	E_{SCF} (a.u.)
^1S	−1505.52927
^1G	−1505.69918
^3P	−1505.72539
^1D	−1505.74124
^3F	−1505.81567

energy differences with the corresponding expressions (Table 7) the (theoretical) Racah parameters B, C of the $NiCl_4^{2-}$ complex together with B_0, C_0 of the free Ni^{2+} ion can be obtained. The quantity 10 Dq has been discussed previously. The results regarding the Racah parameters are displayed in Table 9.

From the tabulated data several conclusions can be drawn. It is observed that the B, C parameters of $NiCl_4^{2-}$, obtained with orthogonalized ionic vectors, have hardly changed with respect to the corresponding parameters B_0, C_0 of the gaseous Ni^{2+} ion.

Table 8. Energy differences between states of $NiCl_4^{2-}$ and Ni^{2+}

Energy differences ($NiCl_4^{2-}$)	Crystal Field Th.[a]	ΔE Ionic Orth. Vect. (a.u.)	ΔE SCF (a.u.)
$E(^3A_2) - E(^3T_2)$	10 Dq	+0.005335	+0.010502
$E(^3A_2) - E(^3T_1)$	20 Dq − 3B	−0.007585	+0.003118
$E(^1E) - E(^3A_2)$	−20 Dq + 9B + 2C	+0.088061	+0.071743

Energy Differences Ni^{2+}	Expression	ΔE SCF (a.u.)
$E(^1D) - E(^3F)$	$5B_0 + 2C_0$	0.074440
$E(^3P) - E(^3F)$	$15B_0$	0.090276
$E(^1G) - E(^3F)$	$12B_0 + 2C_0$	0.116487
$E(^1S) - E(^3F)$	$22B_0 + 7C_0$	0.286405

[a] See Griffith A27 [6]. No diagonalization of CI matrices.

Table 9. Racah parameters

Gaseous Ni^{2+} Ion	B_0 (cm^{-1})	C_0 (cm^{-1})
SCF	1321	4831
Exp. [12]	1030	4850
$NiCl_4^{2-}$ Complex	B (cm^{-1})	C (cm^{-1})
Orthog. ionic vectors	1335	4825
SCF	1308	4289
Exp. Ref. [30]	734	2907
Exp.	725	3263

Not until allowance is made for the rearrangement of the charge distribution by the SCF procedure do reductions of the Racah parameters occur. The calculated "nephelauxetic" reductions, being only 1% for the B parameter and amounting to about 11% for the C parameter, are significantly smaller than the reductions obtainable from the experimental data, being at least 30% for both Racah parameters [30].

The calculated reductions of the Racah parameters of the $NiCl_4^{2-}$ complex are, however, larger than in the case of the more ionic NiF_6^{4-} cluster [18].

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