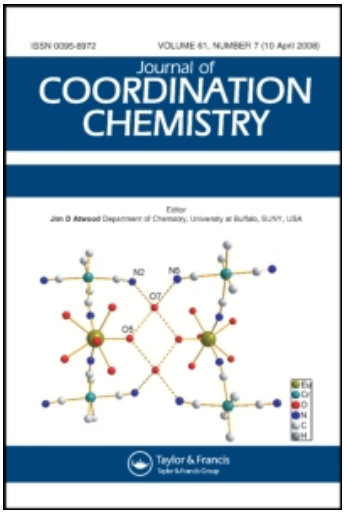

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

A Theoretical Study on the Structures and Spectra of Ni(II) Aquo Azides, Thiocyanates and Isothiocyanates

Rafie H. Abu-Eittah[a]; Ashraf T. Aly[a]
[a] Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt

Online publication date: 15 September 2010

To cite this Article Abu-Eittah, Rafie H. and Aly, Ashraf T.(2002) 'A Theoretical Study on the Structures and Spectra of Ni(II) Aquo Azides, Thiocyanates and Isothiocyanates', Journal of Coordination Chemistry, 55: 2, 129 — 151
To link to this Article: DOI: 10.1080/00958970211880
URL: http://dx.doi.org/10.1080/00958970211880

J. Coord. Chem., 2002, Vol. 55(2), pp. 129–151

Taylor & Francis
Taylor & Francis Group

A THEORETICAL STUDY ON THE STRUCTURES AND SPECTRA OF Ni(II) AQUO AZIDES, THIOCYANATES AND ISOTHIOCYANATES

RAFIE H. ABU-EITTAH* and ASHRAF T. ALY

Department of Chemistry, Faculty of Science, University of Cairo, Giza, Egypt

(Received 11 July 2000; In final form 1 November 2000)

A theoretical treatment of the formation and stability of some aquated nickel II azides, thiocyanates and isothiocyanates has been carried out. *Ab initio* molecular orbital calculations have been carried out using the DZ basis set and ^{3}F ground state for nickel and using the 3-21 G split valence basis set for H, C, N and O-atoms. For S-atom the 3-21 G basis set was augmented with 3*d*-function. Geometry optimization was carried out for each of the studied species; charge distribution and electron overlap population were calculated. The results of this work show that azide ion is a stronger ligand than isothiocyanate ion and the latter is stronger than thiocyanate ion with respect to bonding to nickel ion. The results of calculations indicated that the triplet state was the stable ground state for all the studied species. Calculations using ROHF procedure led to better results than calculations using UHF method.

Keywords: Theory; Nickel(II); Azide; Thiocyanate; Isothiocyanate

1. INTRODUCTION

Several attempts have been made to obtain a consistent theoretical description of the electronic states that arise from the s^2d^n, sd^{n+1} and d^{n+2} configurations of the transition metal atoms [1–3]. For nickel, the experimental results indicate that the $^3F(4s^23d^8)$ state lies 0.03 eV above the $^3D(4s3d^9)$ state whereas HF-calculations estimate the ^3F to lie 1.30 eV below the ^3D state. Botch *et al.* [4] could not predict this ordering; using MCSCF they calculated an excitation energy, $^3F \rightarrow {}^3D$ of 0.42 eV.

*Corresponding author. e-mail: rheittah@chem-sci.cairo.eun.eg

ISSN: 0095-8972 DOI: 10.1080/00958970290002108

Watchers [5] has published a fairly large basis set for transition metals and Schaefer *et al.* [6] optimized them. For nickel atom a nice collection of basis sets is reported, one of which is the fully re-optimized Watchers set while the other sets are of three different sizes: split valence (SV), ~split valence with 6-d-Gaussian functions (SV6D) and the double zeta (DZ). Each set was optimized for three possible ground states for nickel, the ^{3}F, ^{3}D and ^{1}S states.

In this work, several basis sets were tested in MO-calculations. The criterion was the prediction of the experimental parameters of the studied species. The basis set that produced results closest to the experiment was adopted.

Nickel(II) is a d^8 ion, the common geometry of its complexes is octahedral, distorted octahedral, tetrahedral or square planar depending on the crystal field imposed on the metal ion by the surrounding ligands. The ion $[NiL(H_2O)_5]^+$ and $[NiL_2(H_2O)_4]$ proved to have octahedral or distorted octahedral geometry and the triplet state is the ground state [7]. For an octahedral complex, the Orgel diagram indicates three expected transitions:

$$^3A_{2g} \rightarrow ^3T_{2g}; ^3A_{2g} \rightarrow ^3T_{1g}(F) \text{ and}$$
$$^3A_{2g} \rightarrow T_{1g}(P).$$

As the amount of tetragonal distortion increases, there, will be a continuous change in the energy levels.

The formation of azido nickel complexes in aqueous medium was studied by Egghart [8], while a study in non-aqueous media was performed by Gatmann and Bardy [9]. Both papers investigated the electronic absorption spectra of the complexes. Complexes of Ni^{2+} ion with SCN^- and CN^- ions were investigated in non-aqueous media and in the molten state [10]. In this work a comparative theoretical study is attempted on some aquated nickel (II) azido, thiocyanato and isothiocyanato complexes. The best basis set-ground state combination, DZ, ^{3}F, was used. The singlet states are calculated applying the RHF procedures whereas the triplet states are calculated applying both ROHF and UHF procedures.

2. COMPUTATIONAL METHODS

2.1. Electronic States of Ni

Computations in this work were carried out using the GAMESS program. Smaller programs were constructed for fine analysis of the output.

When dealing with a system of 2n electrons occupying n-double occupied molecular orbitals, the restricted Hartree-Fock state function is a product of the antisymmetrized spin orbitals

$$\psi^{\mathrm{RHF}} = |\phi_1\bar{\phi}_1, \ldots, \phi_n\bar{\phi}_n| \tag{1}$$

The LCAO approximation involves expanding ϕ_{i} as a finite series of simpler basis functions (which roughly corresponds to atomic orbitals), *i.e.*,

$$\Psi_i = \sum_{\mu=1}^{k} c_{ui}\phi_\mu \quad (\mathrm{i} = 1, 2, \ldots, k) \tag{2}$$

If the introduced set of k-known basis functions $\{\phi_\mu(\mathrm{r})|\mu = \mathrm{l}, 2, \ldots, \mathrm{k}$ this would be an exact expansion and an exact molecular orbital is obtained. For practical computation reasons, one is always restricted to finite k basis functions. Hence, it is important to choose a basis that will provide, as far as possible, a reasonably accurate expansion for the exact molecular orbitals $\{\Psi_{\mathrm{i}}\}$.

From (2), one obtains the matrix equation for c_{ui} by substituting the linear expansion (2) into the Hartree-Fock equation

$$f(\mathbf{r}_1)\Psi_i(\mathbf{r}_1) = \varepsilon_i\Psi_i(\mathbf{r}_1) \tag{3}$$

to get, using the index ν,

$$f(1)\sum_\nu c_{\nu i}\phi_\nu(1) = \varepsilon_i\sum_\nu c_{\nu i}\phi_\nu(1) \tag{4}$$

Multiplying by $\phi_\mu^*(1)$

$$\sum_\nu c_{\nu i}\int d\boldsymbol{r}_1\phi_\mu^*(1)f(1)\phi_\nu(1) = \varepsilon_i\sum_\nu c_{\nu i}\int d\boldsymbol{r}_1\phi_\mu^*(1)\phi_\nu(1) \tag{5}$$

Define the overlap matrix **S** which has the elements

$$S_{\mu\nu} = \int d\boldsymbol{r}_1\phi_\mu^*(1)\phi_\nu(1) \tag{6}$$

and the Fock matrix **F** which has the elements

$$F_{\mu\nu} = \int d\boldsymbol{r}_1\phi_\mu^*(1)f(1)\phi_\nu(1) \tag{7}$$

With these definitions, the integrated Hartree-Fock equation (5) is written as

$$\sum_{\nu} F_{\mu\nu} C_{\nu i} = \varepsilon_i \sum_{\nu} S_{\mu\nu} C_{\nu i} \quad \mathrm{i} = 1, 2, \ldots, k \tag{8}$$

These are the Roothan equations, which can be written more compactly as the single matrix equation

$$\mathbf{FC} = \mathbf{SC}\boldsymbol{\varepsilon} \tag{9}$$

where **C** is a k × k square matrix of the expansion coefficients C_{ui} and $\boldsymbol{\varepsilon}$ is a diagonal matrix of the orbital energies ε_i. The Fock matrix **F** is the matrix representation of the Fock operator

$$f(1) = h(1) + \sum_{a}^{N/2} 2J_a(1) - k_a(1) \tag{10}$$

in the basis $\{\phi_\mu\}$, *i.e.*,

$$\begin{aligned} F_{\mu\nu} &= \int d\boldsymbol{r}_1 \phi_\mu^*(1) f(1) \phi_\nu(1) \\ &= \int d\boldsymbol{r}_1 \phi_\mu^*(1) h(1) \phi_\nu(1) + \sum_{a}^{N/2} \int d\boldsymbol{r}_1 \phi_\mu^*(1) [2J_a(1) - k_a(1)] \phi_\nu(1) \end{aligned} \tag{11}$$

Insert the linear expansion for molecular orbitals (1) into the two-electron terms giving

$$\begin{aligned} F_{\mu\nu} &= H_{\mu\nu}^{core} + \sum_{a}^{N/2} \sum_{\lambda\sigma} C_{\lambda a} C_{\sigma a}^* [2(\mu\nu/\sigma\lambda) - (\mu\lambda/\sigma\nu)] \\ &= H_{\mu\nu}^{core} + \sum_{\lambda\sigma} P_{\lambda\sigma} \left[(\mu\nu/\sigma\lambda) - \frac{1}{2} (\mu\lambda/\sigma\nu) \right] \\ &= H_{\mu\nu}^{core} + G\mu\nu \end{aligned} \tag{12}$$

where $G_{\mu\nu}$ is the two-electron part of the Fock matrix.

With an open shell system, two treatments will be used. The first is that proposed by Roothan [3] and called restricted open shell Hartree-Fock (ROHF) where the wave function is partitioned into a closed shell part describing the doubly occupied MOs and an open shell part for the rest of the occupied MOs. Thus, for a doublet system with 2n+1 electrons the ROHF wave function is

$$\psi^{\mathrm{RHF}} = |\phi_1 \bar{\phi}_1, \ldots, \phi_{\mathrm{n}} \bar{\phi}_{\mathrm{n}} \phi_{\mathrm{n+1}}| \tag{13}$$

The second treatment is that proposed by Pople *et al.* [14] and is called the unrestricted Hartree-Fock (UHF) method. It is based on the fact that, since the number of electrons of spin *a* differs from the number of electrons of spin, *b* and the repulsion between electrons depends on their spin, the state function for $2n+1$ electrons is

$$\psi^{\mathrm{UHF}} = |a_1(1), \ldots, a_n(n)a_{n+1}(n+1)b_1(1), \ldots, b_n(2n+1)| \qquad (14)$$

where the a_i and b_i are the α and β spin orbitals. The energy of this system is given by

$$E = \sum_{i}^{\alpha+\beta} h_i^N + \frac{1}{2}\sum_{i}^{\alpha+\beta}\sum_{j}^{\alpha+\beta} J_{ij} - \frac{1}{2}\left[\sum_{i}^{\alpha}\sum_{j}^{\alpha} + \sum_{i}^{\beta}\sum_{j}^{\beta}\right] K_{ij} \qquad (15)$$

where J_{ij} and K_{ij} are the conventional Coulomb and exchange integrals. The ψ^{UHF} is not an Eigen function of the spin operator $\hat{s}^2$ and the resulting states are spin contaminated and are difficult to interpret.

The success of a MO-calculation depends on the use of the appropriate basis set. In the LCAO method each MO is expressed as a finite sum of Slater-type orbitals (STO_s) or Gaussian-type functions (GTF_s). Contracted Gaussian type functions are used as basis functions instead of using individual Gaussian functions. The former consist of a linear combination of a small number of primitive Gaussians which are Cartesian Gaussians centered on the same atom but have different orbital exponents.

The partially filled and closely spaced *d*-orbitals allow the transition metals to have more than one ground state with little energy difference [5]. Several trials have been made to get a consistent theoretical description of the electronic states that arise from the s^2d^{n+1}, s^1d^{n+1} and d^{n+2} configurations of the transition metal atoms [1–3]. The generally accepted $s^2\,d^n$ configuration of the ground state is not always true. The Hartree-Fock calculations give inadequate results, a difference up to 1.3 eV is found between the experimental results and the Hartree-Fock calculations.

Botch *et al.* [4] considered the differential correlation effects within the lowest-lying states arising from s^2d^n, sd^{n+1} and d^{n+2} for the first-row transition metal atoms using multiconfiguration SCF and non-relativistic procedures. For nickel, experimental results indicate that the ^3F ($4s3d^8$) state lies 0.03 eV above the ^3D ($4s3d^9$) state [4]. The numerical HF calculations result in a ^3F state that is of 1.3 eV lower energy than the ^3D state. Using Watchers basis set Botch *et al.*, calculated the excitation energy $^3F \rightarrow {}^3D$ as 0.42 eV. It

turned out that a ^3F state is not a good ground state (lowest energy) for $Ni(CO)_4$ whereas a $^1S(3d^{10})$ is a good one. On the other hand a ^3D state is a good ground state for the nickel atom in NiH and Ni_2 [16].

2.2. Basis Sets

In a previous communication [17], the three possible ground states ^3F, ^3D and ^1S for nickel in $Ni(H_2O)_6^{2+}$ were considered using three different basis sets, namely, split-valence(SV), spilt-valence with six *d*-orbitals (SV6D) and double-zeta (DZ) basis sets for each ground state. The size of each basis set differs according to the electronic state under consideration. The results have indicated that the combination ^3F-DZ gives the best results, the nearest to the experimental value.

In this work the combination ^3F-DZ is used in all calculations. The ^3F-DZ basis set (14s 9p 5d) contracted to [8s 5p 2d] = {62 111111/33 111/3 11}. The split-valence 3-21 G [18] basis set was used for carbon, nitrogen and hydrogen atoms. For sulfur atom an extra *d*-function was added to the 3-21 G.

3. RESULTS AND DISCUSSION

3.1. Pentaaquoazidonickel II Complex Ion: $[Ni(N_3)(H_2O)_5]^+$

In an aqueous mixture of Ni^{2+} and N_3^- ions, the monoazidopentaaquonickel II ion is the predominant species. Molecular orbital calculations give the geometry and energies of the gaseous species, yet a comparison of such results with the results of the same species existing in solution is a common procedure. In this work *ab initio* molecular orbital calculations were applied to a number of aquoazidonickel (II) complexes. The singlet states were calculated at the RHF-SCF level whereas the triplets were calculated at the ROHF and UHF-SCF levels. Geometry optimization of $[Ni(N_3)(H_2O)_5]^+$, was carried out using the gradient method optimization. The symmetry is reduced from $C_{4\nu}$ to $C_{2\nu}$ due to the positions of the two hydrogens of the axial water molecules. The appropriate symmetry was imposed on each structure of the studied species separately, this facilitates calculations and in some cases removes some orbital degeneracy. The values of bond lengths in the optimized geometry for the studied species are given in Table I.

The ROHF calculation on the triplet ground state of $[Ni(N_3)\ (H_2O)_5]^+$ gave a total energy of -2047.101845 au leading to a binding energy (Tab. II)

TABLE I Optimized geometry of aquated nickel(II) azides, thiocyanates and isothiocyanates

Ion	*Bond length, Å*				
Nickel azide	Ni—N_1	Ni—O_{ax}	Ni—N_{eq}	N_1—N_2	N_2—N_3
$[Ni(N_3)(H_2O)_5]^+$	2.312	2.247	1.928	1.230	1.123
$Ni(N_3)_2(H_2O)_4$	1.912	–	2.121	1.180	1.141
Nickel thiocyanate	Ni—S	Ni—O_{ax}	Ni—O_{eq}	S—C	C—N
$[Ni(SCN)(H_2O)_5]^+$	2.752	2.261	1.920	1.678	1.144
$Ni(SCN)_2(H_2O)_4$	2.698	–	1.899	1.677	1.146
Nickel isothiocyanate	Ni—S	Ni—O_a	Ni—O_{eq}	N—C	C—S
$[Ni(NCS)(H_2O)_5]^+$	2.198	2.306	1.942	1.169	1.621
$Ni(SCN)_2(H_2O)_4$	2.198	–	1.942	1.169	1.621

TABLE II Comparison between the binding energies of the studies compounds

Compound	*Binding energy, Kcal·mol*$^{-1}$	
	Singlet state	*Triplet state*
$[Ni(N_3)(H_2O)_5]^+$	−620	−678(ROHF) −679(UHF)
$[Ni(N_3)_2(H_2O)_4$	−719	−789(ROHF) −790(UHF)
$[Ni(SCN)(H_2O)_5]^+$	−500	−557(UHF)
$[Ni(SCN)_2(H_2O)_4$	−582	−628(ROHF) −629(UHF)
$[Ni(NCS)(H_2O)_5]^+$	−514	−584(ROHF) −585(UHF)
$[Ni(NCS)_2(H_2O)_4$	−620	−690(ROHF) −691(UHF)

of −1.080118 au (−678 Kcal · mol^{-1}) which indicates a significant stability of the ion. The triplet ground state configuration is:

$$1a_1^2 1a_2^2 1b_1^2 1b_2^2 2a_1^1 2a_2^1 3a_1 2b_1 2b_2$$

A MO-energy level diagram is shown in Figure 1 and the analysis of the different MO's are given in Table III.

Figure 1 and Table III indicate that the two highest singly occupied MO's are almost *d-orbital* over Ni^{2+} ion, also the lowest vacant MO is a *d*-metal orbital. Hence, the transitions: $2a_1 \rightarrow 2a_2$, $2a_2 \rightarrow 3a_1$ and $2a_1 \rightarrow 3a_1$ are all Laporte forbidden $d \rightarrow d$ transitions. On the other hand the $2a_2 \rightarrow 2b_1$

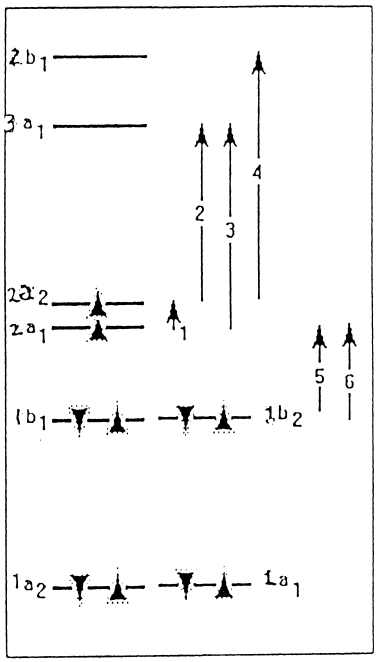

FIGURE 1 MO energy level diagram of $[Ni(N_3)(H_2O)_5]^+$ in the triplet ground state using ROHF SCF.

TABLE III Analysis of the wave functions of some of the MOs of $[Ni(N_3)(H_2O)_5]^+$ in the triplet ground state using ROHF SCF

Energy a.u.	*MO*	*% metal (type)*	
−0.6462	$1a_2$	0.01	
−0.6343	$1a_1$	62.95	
−0.4162	$1b_1$	0.14	
−0.4158	$1b_2$	0.12	
−0.2786	$2a_1$	95.04	d
−0.2460	$2a_2$	86.80	d
−0.0110	$3a_1$	92.84	d
0.1010	$2b_1$	0.10	
0.1032	$2b_2$	0.08	
0.1040	$4a_1$	29.76	s
0.1433	$3a_2$	0.13	

transition is a ligand to metal charge transfer transition and is expected to be much more intense than the forbidden $d-d$ transitions.

The above results agree with the UV-VIS absorptions of $[Ni(N_3)(H_2O)_5]^+$ reported before [19]. The spectrum shows a $d-d$ transition at 25,650 cm^{-1} in addition to a charge transfer transition around 34,483 cm^{-1}.

Mulliken population analysis gives the following result for nickel in $[Ni(N_3)(H_2O)_5]^+$

$$3d^{7.87}4s^{0.5}4p^{0.04}$$

which indicates the involvement of the 4s-atomic orbital in bonding instead of the 4p-orbitals. The charge distribution is given in Table IV.

Atomic overlap population is correlated to the type and extent of bonding. For the ROHF triplet ground state of $[Ni(N_3)(H_2O)_5]^+$ one gets the population: Ni—N = 0.0204; N_1—N_2 = 0.5106; N_2—N_3 = 0.4624; Ni—O_{eq} = 0.0594; Ni—O_{ax} = 0.1240 and O—H = 0.534 and 0.4654. These results indicate a weak, but existing covalent bonding between the metal ion and azide ion. Hence the complex ion, $[Ni(N_3)(H_2O)_5]^+$ is a covalent (sometimes called inner orbital) complex.

To see the effect of spin function normalization on the energetics of $[Ni(N)_3(H_2O)_5]^+$, the UHF procedures were adopted for MO-calculations on $[Ni(N_3)(H_2O)_5]^+$. The total energy obtained was -2047.103850 au giving a binding energy of $\sim 679\,\text{Kcal}\cdot\text{mol}^{-1}$ which is almost equal to that obtained from ROHF calculations. A molecular orbital energy level diagram is given in Figure 2 and the orbital analysis is given in Table V Both Figure 2 and Table V indicate that the lowest electronic transitions are not d–d transitions but rather charge transfer transitions from the ligand to the metal, this result does not agree with the spectral results of $[Ni(N_3)(H_2O)_5]^+$. Hence, the ROHF procedures give a better description of the triplet ground state of $[Ni(N_3)(H_2O)_5]^+$ than the UHF procedures in spite of the fact that the values of charge distribution and binding energy did not differ significantly from one procedure to the other.

The singlet ground state of $[Ni(N_3)(H_2O)_5]^+$ was calculated using the RHF procedure, total energy of -2047.002090 au was obtained and the binding energy was $-620\,\text{Kcal}\cdot\text{mol}^{-1}$, less binding than in the case of the triplet state, $-678\,\text{Kcal}\cdot\text{mol}^{-1}$. The low-energy electronic transitions are:

$$2b_2 \rightarrow 3a_1 : \text{ligand} \rightarrow \text{metal}$$
$$2b_2 \rightarrow 2a_2 : \text{ligand} \rightarrow \text{ligand}$$
$$2b_1 \rightarrow 3a_1 : \text{ligand} \rightarrow \text{metal}$$
$$2b_1 \rightarrow 2a_2 : \text{ligand} \rightarrow \text{ligand}$$

Thus, the lowest-energy four electronic transitions are either charge transfer or localized ligand → ligand transitions. All these transitions should be rather intense which experimentally is not the case. Another result is that the calculated overlap population between Ni and the nearest N is only 0.0014

TABLE IV Distribution of charge density in aquated nickel azides

Species	*G. state*	*Ni*	N_1	$O_{ax,eq}$	$H_{ax,eq}$	N_2	N_3
$[Ni(N_3)(H_2O)_5]^+$	Trip. (ROHF)	1.5431	−0.6438	−0.8694	0.4556	−0.0441	−0.0929
				−0.7833	0.4568		
	Trip. (UHF)	1.5981	−0.6549	−0.8734	0.4476	−0.0436	−0.0817
				−0.7941	0.4514		
	Sing. (RHF)	1.5728	−0.5786	−0.7852	0.4114	−0.0912	−0.1918
$[Ni(N_3)_2(H_2O)_4]$	Trip. (ROHF)	1.6139	−0.5863	−0.7946	0.4163	−0.0935	−0.2032

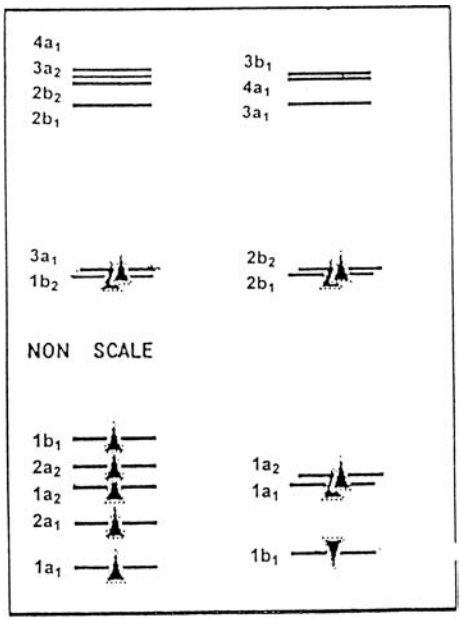

FIGURE 2 MO energy level diagram of $[Ni(N_3)(H_2O)_5]^+$ in the triplet ground state using UHF SCF.

TABLE V Analysis of the wave functions of some of the MOs of $[Ni(N_3)(H_2O)_5]^+$ in the triplet ground state using UHF SCF

Energy a.u.	*MO*	*%metal* (*type*)	
α-set			
−0.7166	$1a_1$	16.43	d
−0.6622	$2a_1$	6.41	
−0.6578	$1a_2$	16.42	d
−0.6431	$2a_2$	11.14	
−0.4173	$1b_1$	0.07	
−0.4169	$1b_2$	0.06	
−0.0106	$3a_1$	92.98	s
0 1005	$2b_1$	0.09	
0.1026	$2b_2$	0.07	
0.1049	$3a_2$	28.59	s
0.1451	$4a_1$	0.14	
0.1553	$2b_2$	0.04	
β-set			
−0.6661	$1b_1$	0.96	
−0.6486	$1a_1$	52.17	d
−0.6468	$1a_2$	0.01	
−0.4165	$2b_1$	0.12	
−0.4162	$2b_2$	0.11	
−0.0101	$3a_1$	92.95	d
0.0991	$4a_1$	38.51	s
0.1029	$3b_1$	0.09	
0.1050	$3b_2$	0.07	
0.1293	$4a_2$	1.72	
0.1564	$4b_2$	0.03	

in the singlet state which is much less than in the triplet ground state. The formation of $[Ni(N_3)(H_2O)_5]^+$ has been confirmed and its stability constant was calculated [20]. Thus, the singlet state is not a good description of the ground state for $[Ni(N_3)(H_2O)_5]^+$. The calculated binding energy, Table III, indicates that the computed ground states are all triplet and not singlet.

3.2. Tetraaquodiazidonickel II: $[Ni(N_3)_2(H_2O)_4]$

Several *ab initio* MO-calculations were performed on the above mentioned complex using the DZ-^{3}F combination for nickel and 3-21 G basis set for H, O, C and N-atoms and considering a D_{4h} symmetry point group. Singlet and triplet ground states were considered, the optimized geometry bond lengths are given in Table I.

The total energy for the singlet ground state of $[Ni(N_3)_2(H_2O)_4]$ is -2133.860567 au, leading to a binding energy of $-719\,\text{Kcal}\cdot\text{mol}^{-1}$ which indicates extra stability of the complex.

The distribution of charge density is shown in Table IV and Mulliken population analysis gives:

$$\ldots 3d^{7.95}4s^{0.44}4p^{0.03}$$

a result which indicates the involvement of the 4s orbital in bonding. The charge density has increased on nickel in $[Ni(N_3)_2(H_2O)_4]$ compared to its value in $[Ni(N_3)(H_2O)_5]^+$, Table IV. Calculated atomic overlap gives, Ni—N = 0.1306; Ni—O = 0.0580; N_1—N_2 = 0.7660, N_2—N_3 = 0.3984, and O—H = 0.5176 which indicate stronger covalent bonding between Ni^{2+} and N_3^- than in the case of $[Ni(N_3)(H_2O)_5]^+$. Analysis of the orbital overlap between Ni^{2+} and N_3^- gives 0.1455 for σ-overlap and -0.00149 for π-overlap which accounts for the absence of π-bonding between Ni^{2+} and the adjacent nitrogen.

The lowest possible electronic transitions assuming a singlet ground state for $[Ni(N_3)_2(H_2O)_4]$ are:

$$1e_g \rightarrow 1a_g : \text{ligand} \rightarrow \text{metal} : \text{charge transfer transition}$$
$$1e_g \rightarrow 2e_u : \text{ligand} \rightarrow \text{ligand} : \text{localized transition}$$
$$1e_u \rightarrow 1a_g : \text{ligand} \rightarrow \text{metal} : \text{charge transfer transition}$$

It is known that g → g and u → u transitions are Laport forbidden but charge transfer transitions are allowed. The above analysis does not agree with the experimental results which show that d–d, metal → metal, transitions are the lowest electronic transitions in the spectrum of the

complex $[Ni(N_3)_2(H_2O)_4]$. This result leads to the conclusion that the singlet state is not a good description of the ground state of $[Ni(N_3)_2(H_2O)_4]$ in aqueous solution.

Molecular orbital calculations on the ground triplet state of $[Ni(N_3)_2(H_2O)_4]$ were carried out using the ROHF procedures. The binding energy of the complex is 789 Kcal · mol^{-1} greater by 70 Kcal · mol^{-1} than in the singlet state. The charge distribution is given in Table IV and the Mulliken population of nickel in the triplet ground state of $[Ni(N_3)_2(H_2O)_4]$ is:

$$\ldots 3d^{7.89}4s^{0.46}p^{0.03}$$

which indicates the involvement of the 4s-atomic orbital on nickel ion in bonding with the surrounding ligands.

Atomic overlap population between bonded atoms in $[Ni(N_3)_2(H_2O)_4]$ gives: Ni—N = 0.0908, Ni—O = 0.0676, N_1—N_2 = 0.06866, N_2—N_3 = 0.04068, O—H = 0.5192.

A molecular orbital energy level diagram is given in Figure 3 and the analysis of the wave functions corresponding to these orbitals is given in

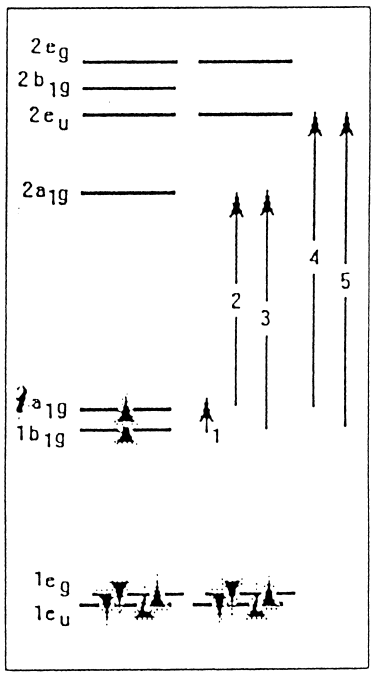

FIGURE 3 MO energy level diagram of $[Ni(N_3)_2(H_2O)_4]$ in the triplet ground state using ROHF SCF.

TABLE VI Analysis of the wave functions of some of the MOs of $[Ni(N_3)_2(H_2O)_4]$ in the triplet ground state using ROHF SCF

Energy a.u.	*MO*	*%metal* (*type*)	
−0.2761	$1e_u$	0.08	
−0.2647	$1e_g$	3.79	
−0.0900	$1b_{1g}$	95.41	d
−0.0702	$1a_{1g}$	89.82	d
0.1491	$2a_{1g}$	93.00	s
0.2297	$2e_u$	0.14	
0.2578	$2b_{1g}$	0.13	
0.2878	$2e_g$	0.43	

Table VI. Starting with the triplet ground state of $[Ni(N_3)_2(H_2O)_4]$ the following electronic transitions are predicted:

$1b_{1g} \rightarrow la_{1g}$, both Laporte and symmetry forbidden $d-d$ transition.
$1a_{1g} \rightarrow 2a_{1g}$, both Laporte and symmetry forbidden $d \rightarrow s$, metal $\rightarrow$ metal transition.
$1b_{1g} \rightarrow 2a_{1g}$, Laporte and symmetry forbidden metal $\rightarrow$ metal transition.
$1a_{1g} \rightarrow 2e_u$ and $lb_{1g} \rightarrow 2e_u$ are metal $\rightarrow$ ligand, charge transfer allowed transitions.

The above predictions agree completely with the experimental spectral behavior of nickel(II) aquo azido complex [19, 20].

Calculations on the triplet state of $[Ni(N_3)_2(H_2O)_4]$ were repeated using the UHF procedure but the results were less satisfactory than the results using ROHF procedures.

3.3. Pentaaquothiocyanatonickel(II): $[Ni(SCN)(H_2O)_5]^+$

In spite of the fact that the ion is a distorted octahedron, a C_{2v} symmetry point group was imposed on the ion and *ab initio* MO-calculations were carried out using a DZ basis set for nickel and the split valence 3-21 G basis set for carbon, nitrogen, oxygen and hydrogen atoms. For sulfur the 3-21 G basis set was augmented with an extra *d*-function.

The optimized geometry is given in Table I. The results of RHF-calculations on the singlet ground state of $[Ni(SCN)(H_2O)_5]^+$ gave $\approx -500\,\text{Kcal} \cdot \text{mol}^{-1}$ for the binding energy. Table VII gives the values of charge density on different atoms of the complex ion.

Mulliken atomic overlap population for $[Ni(SCN)(H_2O)_5]^+$ gives: Ni—S = −0.0180, C—N = 1.6788, Ni—O_{eq} = 0.1076, Nj—O_{ax} = 0.0938 and S—C = 0.2464. Analysis of Ni—S overlap gives −0.0166 for σ-overlap and 0.0014 for π-overlap. Such results indicate the absence of any covalent

TABLE VII Distribution of charge density in aquated nickel thiocyanates and isothiocyanates

Species	*G. state*	*Ni*	*S*	$O_{ax,\ eq}$	$H_{ax,\ eq}$	*C*	*N*
$[Ni(SCN)(H_2O)_5]^+$	Sing. (RHF)	1.5378	−0.5881	−0.8661 −0.7904	0.4622 0.4892	0.1265	−0.4830
	Sing. (RHF)	1.5973	−0.5646	−0.8589	0.4747	0.1211	−0.5361
$[Ni(SCN)_2(H_2O)_4]$	Trip. (ROHF)	1.6777	−0.5734	−0.8667	0.4665	0.1309	−0.5290
	Trip. (UHF)	1.6747	−0.5732	−0.8661	0.4665	0.1310	−0.5290
$[Ni(NCS)(H_2O)_5]^+$	Sing. (RHF)	1.5505	−0.1822	−0.8485 −0.7833	0.4551 0.4668	0.2457	−0.9668
$Ni(NCS)_2(H_2O)_4$	Sing. (RHF)	1.5519	−0.2333	−0.7936	0.4202	0.3223	−0.9586

bonding between Ni^{2+} and SCN^- ions and weak bonding between nickel and water molecules; the complex ion is an outer orbital complex.

Atomic population for nickel in the ground singlet state of $[Ni(SCN)(H_2O)_5]^+$ gives

$$\ldots 3d^{7.93}4s^{0.49}4p^{0.04}$$

that is a *d*-orbital population almost equal to its value in a free Ni^{2+} ion.

For the singlet ground state the HOMO is localized on the SCN^- ion and the LUMO is a pure metal ion, orbital $4s(2a_1)$ whereas the next vacant MOs, $2a_2$ and $3b_1$ are almost localized on the SCN^- ion. As a result the lowest electronic transitions in $[Ni(SCN)(H_2O)_5]^+$, $2b_2 \rightarrow 2a_1$ is a charge transfer transition and the next two or three electronic transitions are ligand $\rightarrow$ ligand localized transitions. The spectrum, as now predicted, would not show any metal–metal, *d*–*d*, transitions.

To confirm the above results, MO-calculations were repeated on $[Ni(SCN)(H_2O)_5]^+$. Assuming a triplet ground state using the UHF procedures, the ROHF procedures did not converge. The results were very similar to those of the singlet state, especially the prediction of the absence of covalent bonding between Ni^{2+} and SCN^- ions and only weak bonding between Ni^{2+} and water molecules. Hence, $[Ni(SCN)(H_2O)_5]^+$ is not a coordination complex ion in the usual sense and the *d*-orbitals of the metal ion are not split in the usual manner in an O_h or distorted O_h field. This result explains the electronic transitions predicted for the $[Ni(SCN)(H_2O)_5]^+$ ion. The behavior of $[Ni(N_3)\ (H_2O)_5]^+$ differs from the corresponding thiocyanate complex. For the azide complex, calculations show the extent of Ni^{2+} and azide ion overlap and the predicted electronic transitions agree with the experimental results. Moreover, the azide complex is much more stable than the thiocyanate one.

3.4. Tetraaquodithiocyanatonickel(II): $[Ni(SCN)_2(H_2O)_4]$

MO-calculations on $[Ni(SCN)(H_2O)_5]^+$ showed that the complex ion is an ionic compound. It is instructive to investigate the situation for $[Ni(SCN)_2(H_2O)_4]$. Assuming D_{4h} symmetry, the optimized geometry of the molecule is given in Table I and the charge distribution is given in Table VII. The heat of formation of the molecule, in the singlet ground state is $-582\,\text{Kcal}\cdot\text{mol}^{-1}$ which is large enough to account for extra stability. The population of nickel in $[Ni(SCN)_2(H_2O)_4]$ is $3d^{7.95}\ 4s^{0.42}\ 4p^{0.03}$.

Atomic overlap population is correlated to bonding between atoms. For $[Ni(SCN)_2(H_2O)_4]$ the following results were obtained: Ni—S = −0.0162, Ni—O = 0.1140, S—C = 0.2742, C—N = 1.6930 and O—H = 0.5170. The data reveal weak overlap, weak bonding, between the metal ion and water molecules and a rather weak or no overlap between the metal ion and SCN^- ion in $[Ni(SCN)_2(H_2O)_4]$. The same behavior was observed in $[Ni(SCN)(H_2O)_5]^+$ and led to the suggestion that it is an ionic rather than a covalent complex ion. Hence, one concludes similarly, that the complex molecule tetraaquodithiocyanatonickel II is an ionic compound.

A confirmation of the above result is obtained by considering the plausible electronic transitions. The electronic configuration of the singlet ground state of tetraaquoithiocyanatonickel II is

$$1e_g^4 1e_u^4 2e_g^4 1a_{1g} 1b_{1g} 2e_u 2a_{1g} 1a_{2u}$$

Hence, the lowest electronic transitions are either charge transfer or L → L ($SCN^- \rightarrow SCN^-$) localized transitions. Complex ions of nickel (II) are expected to show $d \rightarrow d$ as well as charge transfer transitions. Consequently, one concludes that the singlet state is not a good description of the ground state of tetraaquodithiocyanatonickel II.

Computations were repeated using the ROHF procedures and adopting a triplet ground state for $[Ni(SCN)_2(H_2O)_4]$. The calculated heat of formation of this molecule is $-628\,\text{Kcal} \cdot \text{mol}^{-1}$ *i.e.*, more negative by $\sim 100\,\text{Kcal} \cdot \text{mol}^{-1}$ than the singlet state. Atomic overlap population is Ni—S = −0.0080, Ni—O = 0.0618, S—C = 0.3244 and C—N = 1.6916. The Ni—S overlap is slightly negative, almost zero, indicating very weak or no covalent bonding between Ni^{2+} and SCN^-, the analysis of the overlap population is −0.0114 for sigma overlap and 0.0034 for pi-overlap. Again, no evidence for covalent bonding between Ni^{2+} and SCN^-. The electronic configuration of the ground triplet state of $[Ni(SCN)_2(H_2O)_4]$ is

$$1e_u^4 1e_g^4 1a_{1g}^1 1b_{1g}^1 2a_{1g} 2e_u 3a_{1g} 2b_{1g}$$

A molecular orbital energy level diagram is shown in Figure 4 and analysis of the orbitals is given in Table VIII. The singly occupied MOs are mainly *d*-orbitals and a low-energy $d-d$ transition is possible. This result was not obtained with a singlet ground state of $Ni(H_2O)_4(SCN)_2$ hence, the triplet ground state is a better representation for the complex. Calculations on the triplet state using UHF procedures led to less satisfactory results.

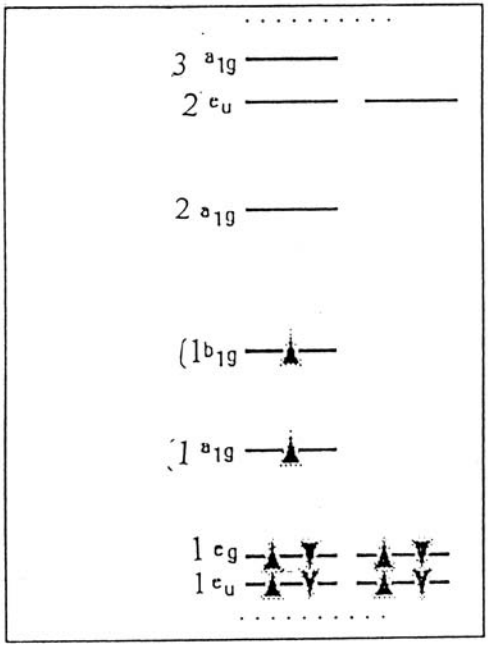

FIGURE 4 MO energy level diagram of $[Ni(SCN)_2(H_2O)_4]$ in the triplet ground state using ROHF SCF.

TABLE VIII Analysis of the wave functions of some of the MOs of $[Ni(SCN)_2(H_2O)_4]$ in the triplet ground state using ROHF SCF

Energy a.u.	*MO*	*%metal(type)*	
−0.3204	$1e_u$	0.00	
−0.3169	$1e_g$	0.25	
−0.2233	$1a_{1g}$	96.12	d
−0.1634	$1b_{1g}$	89.11	d
0.1033	$2a_{1g}$	89.66	s
0.1924	$2e_u$	0.08	
0.1973	$2a_{1g}$	74.75	s
0.2217	$2b_{1g}$	0.20	

3.5. Pentaaquoisothiocyanatonickel II: $[Ni(NCS)(H_2O)_5]^+$

It is important to compare the structure, geometry and energetics of the thiocyanato complex $[Ni(SCN)_n(H_2O)_{6-n}]^{2-n}$ with the corresponding isothiocyanate one, $[Ni(NCS)_n(H_2O)_{6-n}]^{2-n}$. Calculations have shown that the binding energy, Table II, varies as:

$Ni(N_3)(H_2O)_5^+ \gg Ni(NCS)(H_2O)_5^+ > Ni(SCN)(H_2O)_5^+$ for both singlet and triplet ground states. The order reflects the order of binding of N_3^+,

NCS^- and SCN^- to the metal ion. It is important to note that the same order holds for the tetraaquo ion. The binding energy (heat of formation) varies as $Ni(N_3)_2(H_2O)_4 \gg Ni(NCS)_2(H_2O)_4 > Ni(SCN)_2(H_2O)_4$. The optimized geometry of $[Ni(NCS)(H_2O)_5]^+$ is given in Table I and MO-calculations were carried out on both the singlet and the triplet ground states. The charge distribution on each atom in $[Ni(NCS)(H_2O)_5]^+$ in the ground triplet state is given in Table VII.

The electronic configuration of the ground singlet state of $[Ni(NCS)(H_2O)_5]^+$ is

$$1b_1^2 1b_2^2 2b_1^2 2b_2^2 2a_1 3b_1 3b_2 3a_1 4b_1$$

The lowest electronic transitions are: $2b_2 \rightarrow 3a_1$ and represent a charge transfer, $L \rightarrow M$, transition; $1b_1 \rightarrow 3a_1$, and also represent a charge transfer transition, the $2b_2 \rightarrow 3a_2$ and $2b_2 \rightarrow 3b_1$ are both the $L \rightarrow L$ localized transitions. As is seen no low-energy $d-d$ transition is predicted, a result that leads to the conclusion that the ground singlet state is not a good description for $[Ni(NCS)(H_2O)_5]^+$.

The atomic overlap populations are: Ni—N = 0.0160, Ni—O_{eq} = 0.1038 Ni—O_{ax} = 0.0894, N—C = 1.4946, C—S = 0.4090 and O—H = 0.5330 and 0.5082. The values are highly comparable to the corresponding ones in $[Ni(SCN)(H_2O)_5]^+$.

Calculations of the triplet state of $[Ni(NCS)(H_2O)_5]^+$ were performed using the ROHF procedures, the total energy is -2372.292399 au and the heat of formation is $-584\,\text{Kcal} \cdot \text{mol}^{-1}$. A molecular orbital energy level diagram is shown in Figure 5 and MO-analysis is gives in Table IX. The electronic configuration of this triplet state is:

$$1b_1^2 1b_2^2 2b_1^2 2b_2^2 1a_1^1 1a_2^1 2a_1 3b_1 3b_2 3a_1$$

and the predicted low-energy transitions are: $1a_1 \rightarrow 1a_2$ which represents a $d-d$ transition, whereas $1a_2 \rightarrow 2a_1$ and $1a_1 \rightarrow 2a_1$ both represent $d-s$ transitions and are theoretically forbidden.

The atomic overlap populations in the triplet ground state of $[Ni(NCS)(H_2O)_5]^+$ are: Ni—N = 0.0286, Ni—O_{eq} = 0.064, Ni—O_{eq} = 0.116, N—C = 1.4816, C—S = 0.4228 and O—H = 0.5324 and 0.5100. Partitioning of the metal-nitrogen atomic overlap leads to 0.0152 for σ-overlap and 0.0134 for π-overlap. The evidence for covalent bonding between Ni^{2+} and NCS^- is not nil as was the case between Ni^{2+} and SCN^- in $[Ni(SCN)(H_2O)_5]^+$. Hence, the isothiocyanato complex is stronger than the thiocyanato one. The triplet ground state of $[Ni(NCS)(H_2O)_5]^+$ is more

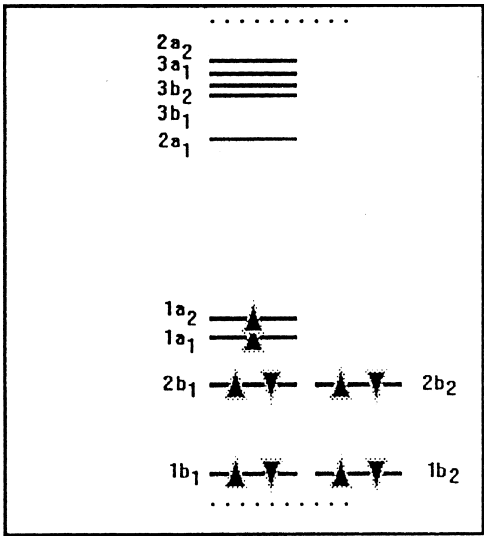

FIGURE 5 MO energy level diagram of $[Ni(NCS)(H_2O)_5]^+$ in the triplet ground state using ROHF SCF.

TABLE IX Analysis of the wave functions of some of the MOs of $[Ni(NCS)(H_2O)_5]^+$ in the triplet ground state using ROHF SCF

Energy a. u.	*MO*	*% metal(type)*	
−0.6023	$1b_1$	1.76	
−0.6019	$1b_2$	1.63	
−0.3863	$2b_1$	0.11	
−0.3861	$2b_2$	0.11	
−0.2770	$1a_1$	95.06	d
−0.2523	$1a_2$	87.13	d
−0.0212	$2a_1$	92.37	s
0.0855	$3b_1$	0.12	
0.0880	$3b_2$	0.10	
0.0930	$3a_1$	29.07	s
0.1221	$2a_2$	0.13	

acceptable than the singlet state. Calculations on the triplet state of $[Ni(NCS)(H_2O)_5]^+$ using the UHF procedure gave less satisfactory results.

3.6. Tetraaquodiisothiocyanatonickel II $[Ni(NCS)_2(H_2O)_4]$

The complex has D_{4h} symmetry and the parameters of the optimized geometry, in the singlet ground state, are given in Table I. The electronic configuration and the arrangement of the MOs lead to low-lying charge transfer and L−L localized transitions, the atomic-overlap population

between the metal and NCS^- is rather large: Ni—N = 0.1336. The results of calculations assuming a triplet ground state of $[Ni(NCS)_2(H_2O)_4]^+$ lead to low-lying $d-d$ transition in addition to charge transfer transitions, Figure 6 and Table X. The overlap Ni—N = 0.0622 is partitioned to 0.0398 σ and 0.0223 π-overlap. Similar to the previously studied complexes, the triplet state is a better description of the ground state than is the singlet state. Also, the results obtained with ROHF treatment are better than those obtained with the UHF procedures.

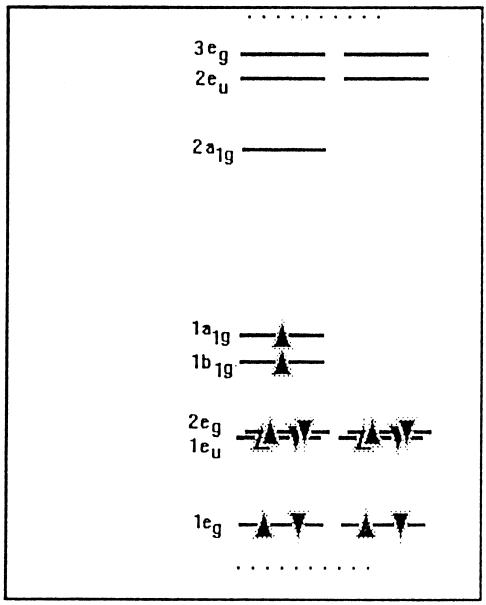

FIGURE 6 MO energy level diagram of $[Ni(NCS)_2(H_2O)_4]$ in the triplet ground state using ROHF SCF.

TABLE X Analysis of the wave functions of some of the MOs of $[Ni(NCS)_2(H_2O)_4]$ in the triplet ground state using ROHF SCF

Energy a. u.	*MO*	*% metal(type)*	
−0.4879	e_g	32.79	d
−0.2979	e_u	0.02	
−0.2941	e_g	1.29	
−0.1272	b_{1g}	95.43	d
−0.1028	a_{1g}	91.27	d
0.1293	a_{1g}	94.04	s
0.2031	e_u	0.20	
0.2381	e_g	0.53	

4. CONCLUSIONS

For all the complexes studied in this work the triplet ground state is a better description than the singlet ground state and the results obtained using the ROHF procedures are more reliable than those when using the UHF procedures.

Calculations on $[Ni(SCN)(H_2O)_5]^+$ gave negative values for both σ and π-overlap between the metal ion and thiocyanate ion and led to the conclusion that the complex $[Ni(H_2O)_5]^{++}[SCN]^-$, an outer sphere one, the same result was obtained with the bi-isocyanato complex and the suggested structure is $[Ni(H_2O)_4]^{++}[SCN]_2^{2-}$. Considering the isothiocyanato complex the situation was different. In the ground triplet state of $[Ni(NCS)(H_2O)_5]^+$ the atomic overlap between Ni^{2+} and NCS^- was small but not zero. A stronger atomic overlap, σ, was calculated in the case of $[Ni(NCS)_2(H_2O)_4]$. These results indicate that the ability of the thiocyanate ion for bonding through nitrogen is much stronger than its ability for bonding through sulfur. Similar results were previously reported [21–24].

The results of this work have shown that the binding energy, heat of formation, varies in the order $[Ni(N_3)(H_2O)_5]^+ \gg [Ni(NCS)(H_2O)_5]^+ > [Ni(SCN)(H_2O)_5]^+$ for both singlet and triplet ground states. For tetraaquocomplex ions, the heat of formation varies as $[Ni(N_3)_2(H_20)_4] \gg [Ni(NCS)_2(H_2O)_4] > [Ni(SCN)_2(H_2O)_4]$. This result indicates that N_3^- group is a stronger ligand than NCS^- and the latter is stronger than the SCN^- group. The values calculated for the atomic overlap population between the metal ion and the ligand confirm the results obtained for the binding energies of the complexes.

References

[1] T. H. Dunning, Jr., B. H. Botch and J. F. Harrison, *J. Chem. Phys.* **72**, 3491 (1980).
[2] R. L. Martin, *Chem. Phys. Lett.* **75**, 290 (1980).
[3] M. Guse, N. S. Ostlund and G. D. Blyholder, *Chem. Phys. Lett.* **61**, 526 (1979).
[4] B. H. Botch, T. H. Dunning, Jr. and J. F. Harrison, *J. Chem. Phys.* **75**, 3466 (1981).
[5] A. J. H. Watcher, *J. Chem. Phys.* **52**, 1033 (1970).
[6] A. Schaefer, H. Horn and R. Ahlrichs, *J. Chem. Phys.* **97**, 2571 (1992).
[7] C. J. Ballhausen, *Molecular Structure of Transition Metal Complexes*, McGraw-Hill (1979).
[8] H. C. Egghart, *Inorg. Nucl. Chem.* **31**, 1538 (1969).
[9] V. Gutmann and H. Bardy, *Z Inorg. Allg. Chem.* **361**, 1213 (1968).
[10] G. Tridot, J. Nicol, J. Hennion and R. Pelleriaux, *C. R. Acad. Sci. Ser.* **269**, 1290 (1969); C.A. **72**(12), 59845u (1970).
[11] M. W. Schmidt, K. K. Baldridge, J. A. Boatz, S. T. Elbert, M. S. Gordon, J. H. Jensen, S. Koseki, N. Matsunaga, K. A. Nguyen, S. J. Su and T. L. Windus, Together With M. Dupuis, J. A. Mo'ntgomery, *J. Comput. Chem.* **14**, 1347 (1993).

[12] C. C. J. Roothan, *Rev. Mod. Phys.* **23**, 69 (1951).
[13] C. C. J. Roothan, *Rev. Mod. Phys.* **32**, 179 (1960).
[14] J. A. Pople and R. K. Nebest, *J. Chem. Phys.* **22**, 571 (1954).
[15] M. Goodgame, D. M. L. Goodgame and F. A. Cotton, *J. Am. Chem. Soc.* **83**, 4161 (1961).
[16] C. F. Melius, B. D. Olufson and W. A. Goddard III, *Chem. Phys. Lett.* **28**, 457 (1974).
[17] R. H. Abu-Eittah, M. El-Esawy, N. Ghoneim and A. T. Aly, *Can. J. Chem.* **76**, 1006–10014 (1998).
[18] For H, C, N: J. S. Binkley, J. A. Pople and W. J. Hehre, *J. Am. Chem. Soc.* p. 102939 (1980); for S: M. S. Gordon, J. S. Binkley, J. A. Pople, W. J. Pietro and W. J. Hehre, *J. Am. Chem. Soc.* **104**, 2797 (1982); W. J. Pietro, M. M. Francl, W. J. Hehre, D. J. Defrees, J. A. Pople and J. S. Binkley, *J. Am. Chem. Soc.* **104**, 5039 (1982).
[19] R. H. Abu-Eittah and S. El-Makabaty, *Bull. Chem. Soc. Jpn.* **46**, 3427 (1973).
[20] T. T. Bamgboye and D. B. Sowergy, *Polyhedron* **5**, 1487 (1986).
[21] J. Dillen, A. T. H. Lenstra, J. G. Haasnoot and J. Reedijk, *Polyhedron* **2**, 195 (1983).
[22] P. P. Singh and D. S. Gupta, *Polyhedron* **5**, 1941 (1986).
[23] C. W. G. Ansell, M. Mcpartlin and P. A. Tasker, *Polyhedron* **2**, 83 (1983).
[24] K. W. Hipps and Mazur, *J. Phys. Chem.* **91**, 5218 (1978).