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Chemical bonding and electronic structure in the ionic species $CrNO^{2+}$ and $[Cr(H_2O)_5NO]^{2+}$ by all electron ab initio multi configuration self consistent field calculations ☆

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Abstract

In the present work we present results of all electron ab initio multi configuration self consistent field (CASSCF) calculations of six electronic states of the linear ion $CrNO^{2+}$ and of eight electronic states of the ion $[Cr(H_2O)_5NO]^{2+}$. The predicted electronic ground state of $CrNO^{2+}$ is $^4\Pi$ and that of the $[Cr(H_2O)_5NO]^{2+}$ ion is $^2A_2$. For both ions the electronic ground state is well separated from the higher lying electronic states. For both ions and for all the electronic states investigated the net charge on chromium is in the range $+1.65e$ to $+1.84e$. This indicates that the oxidation state of chromium is approximately +2 in both $CrNO^{2+}$ and $[Cr(H_2O)_5NO]^{2+}$. In both ions a covalent chemical bond has been formed in between the Cr^{2+} ion and the NO ligand. The chemical bonds in both ions are due to the formation of bonding and antibonding molecular orbitals particularly in between the orbitals Cr $3d\pi$ and NO $p\pi^*$. The bond order is approximately one in between Cr and N in the $^4\Pi$ ground state of $CrNO^{2+}$, and it is approximately one and a half in the $^2A_2$ ground state of the $[Cr(H_2O)_5NO]^{2+}$ ion. The low spin ground state, $^2A_2$, of $[Cr(H_2O)_5NO]^{2+}$ as compared to the high spin ground state, $^4\Pi$, of $CrNO^{2+}$ is ascribed to a substantial energy splitting between the Cr $3d\delta$ partners caused by the H_2O ligand molecules.

Keywords: Chemical bonding; Electronic structure; Chromium complexes; Nitrosyl complexes; Aquo complexes

1. Introduction

Recently Ardon and Cohen [1] have for the first time determined the crystal structure of $[Cr(H_2O)_5NO]SO_4$. They interpret their structural data as support of a residual charge on the chromium atom in $[Cr(H_2O)_5NO]^{2+}$ similar to that in complexes with a formal oxidation state of +3. This is in agreement with the original assignment by Ardon and Herman [2]. An alternative formulation of the complex $[Cr(H_2O)_5NO]^{2+}$ assumes an oxidation state of +1 for the chromium atom. This interpretation was based on the observed N–O stretching frequency, $\nu = 1747$ cm^{-1}, and the magnetic moment, $\mu = 2.2\ \mu_B$ [3]. This latter formulation had been accepted by others [4].

The aim of the present work is to shed further light on the bonding in the complex $[Cr(H_2O)_5NO]^{2+}$, especially with respect to the chemical bond in between the chromium atom and the NO ligand. For this purpose we have performed all electron ab initio multi configuration self consistent field (CASSCF) calculations both for the linear ion $CrNO^{2+}$ that results when the $[Cr(H_2O)_5NO]^{2+}$ ion is stripped of its H_2O ligand molecules, and also for the entire ionic complex $[Cr(H_2O)_5NO]^{2+}$.

2. Calculational details

All electron ab initio multi configuration self consistent field calculations of the complete active space type (CASSCF) have been performed for the ionic species $CrNO^{2+}$ and $[Cr(H_2O)_5NO]^{2+}$ using the MOLCAS version 2 program system [5].

The molecular orbitals have been expanded in basis sets consisting of Gaussian type functions centered on the various nuclei. The basis set used for the Cr atom is identical to that used in our previous investigations of the CrC molecule [6,7]. It is essentially Wachters'

☆ Dedicated to Professor F. Albert Cotton on the occasion of his 65th birthday.

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basis [8], but slightly modified and extended. The charge densities due to the most diffuse s functions have been contracted by replacing the exponents 0.099511 and 0.037588 with 0.1953 and 0.06859, respectively. In order to represent the 4p orbital the basis set has been extended by addition of two p functions with exponents 0.197879 and 0.08208. Furthermore, a diffuse d function with exponent 0.13774 has been added. The resulting primitive basis set (14s, 11p, 6d) has been contracted to (8s, 6p, 3d) using a segmented contraction scheme. For the atoms N and O in the $CrNO^{2+}$ ion Huzinaga's (10s, 6p) basis sets [9] supplemented by addition of a d polarization function for each atom have been used. The exponents of the d polarization functions have been chosen as 0.95 for N and 1.05 for O. The resulting primitive basis sets (10s, 6p, 1d) have been contracted to (4s, 3p, 1d) using segmented contraction schemes. The results of the CASSCF calculations revealed that the d polarization functions of N and O in $CrNO^{2+}$ only acquired minor populations. Therefore we have chosen to use Huzinaga's (10s, 6p) basis [9] contracted to (4s, 3p) for N and O when performing the calculations for the $[Cr(H_2O)_5NO]^{2+}$ ion. Thus, compared to $CrNO^{2+}$ the d polarization functions for N and O have been omitted for $[Cr(H_2O)_5NO]^{2+}$. For the H atoms Huzinaga's (4s) primitive basis set [10] contracted to (2s) has been used.

For the $CrNO^{2+}$ ion the calculations have been performed for a linear configuration, symmetry group $C_{\infty v}$. The inter atomic distance Cr–N has been chosen as 3.18 a.u. = 1.682783 Å and that of N–O has been chosen as 2.23936 a.u. = 1.185018 Å. The N–O distance chosen is close to the inter atomic distance in the free NO molecule. Furthermore, both the Cr–N and the N–O distances are close to the corresponding distances measured for the $[Cr(H_2O)_5NO]^{2+}$ ion, i.e. 1.682 and 1.186 Å, respectively [1]. In the CASSCF calculations the core orbitals, i.e. the 1s, 2s, 3s, 2p and 3p of Cr and the 1s orbitals of N and O, have been kept fully occupied while selected valence orbitals derived from the 3d and 4s orbitals of Cr and from the 2s and 2p orbitals of the N and O atoms have been included in the active space. Altogether 11 orbitals consisting of three σ orbitals, two π orbitals, and one δ orbital have been included in the active space. The calculations have been performed for doublet, quartet and sextet states of Σ^+, Σ^-, Π and Δ symmetries. The calculations have been carried out in the subgroup C_{2v} of the full symmetry group, $C_{\infty v}$ of the $CrNO^{2+}$ ion. The number of configurations included in the CASSCF calculations reached 19 080 for the doublet states, 14 600 for the quartet states and 4095 for the sextet states.

The geometry of the $[Cr(H_2O)_5NO]^{2+}$ ion is pseudo-octahedral, but the C_{2v} symmetry has been imposed on the $[Cr(H_2O)_5NO]^{2+}$ ion when performing the CASSCF calculations. The geometry of $[Cr(H_2O)_5NO]^{2+}$, shown in Fig. 1, is based on the X-ray structure of $[Cr(H_2O)_5NO]SO_4$ [1]. The Cr and N atoms as well as the O atoms of NO and the O atom of the axial H_2O molecule are all placed along the *Z* axis. The Cr–N and N–O distances have been chosen as 1.682 and 1.186 Å, i.e. identical to those measured. The distance between the Cr atom and the O atom in the axial H_2O ligand molecule *trans* to the NO ligand has been chosen as 2.057 Å. The axial H_2O molecule is placed in the *XZ* plane. The $[Cr(H_2O)_5NO]^{2+}$ ion has four equatorial H_2O ligand molecules. The distance between the Cr atom and the O atom in the equatorial H_2O ligand molecules has been chosen as 1.998 Å, which is the average distance measured in $[Cr(H_2O)_5NO]SO_4$. The O atoms of the equatorial H_2O molecules are placed in a plane parallel to the *XY* plane, but shifted to $Z = -0.188028$ Å. This results in N–Cr–O angles of 95.4°. Two of the equatorial H_2O ligands are placed in the *YZ* plane, and the O atoms of the two remaining equatorial H_2O ligands are placed in the *XZ* plane. In all the ligand H_2O molecules the O–H distance is chosen as 0.957 Å and the H–O–H angle as 104.5°.

In analogy with the investigation performed for the $CrNO^{2+}$ ion the core orbitals, i.e. 1s, 2s, 3s and 3p of Cr as well as the 1s orbitals of N and O in the NO ligand, have been kept fully occupied when performing the CASSCF calculations on the $[Cr(H_2O)_5NO]^{2+}$ ion. Furthermore, all the orbitals, i.e. core as well as valence orbitals of the H_2O ligand molecules, have also been kept fully occupied. Thus, the orbitals included into the active space consist of three σ orbitals, two π orbitals and one δ orbital derived from the 3d and 4s orbitals of Cr and from the 2s and 2p orbitals of the N and O atoms belonging to the NO ligand molecule. The CASSCF calculations performed for the $[Cr(H_2O)_5NO]^{2+}$ ion have been carried out for doublet and quartet states of the symmetries A_1, A_2, B_1 and B_2. The calculations performed for the $[Cr(H_2O)_5NO]^{2+}$

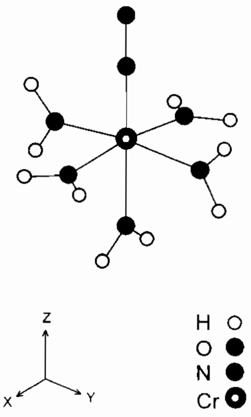

Fig. 1. The idealized C_{2v} geometry of the $[Cr(H_2O)_5NO]^{2+}$ ion as used for performing the CASSCF calculations.

ion are equivalent to those performed for the CrNO^{2+} ion. Thus, the number of configurations reached 19 080 for the doublet states and 14 600 for the quartet states. For both ions 13 electrons have been correlated by allowing all rearrangements within 11 orbitals.

2.1. The CrNO^{2+} ion

When the complex [Cr(H$_2$O)$_2$NO]$^{2+}$ ion is stripped of its H$_2$O ligand molecules the CrNO^{2+} ion remains. In order to gain insight into the nature of the bonding in the [Cr(H$_2$O)$_5$NO]$^{2+}$ ion, particularly in between the chromium atom and the NO ligand, we have carried out extensive CASSCF calculations for selected electronic states of the CrNO^{2+} ion.

Tables 1 and 2 show selected results of the CASSCF calculations performed for CrNO^{2+}. Table 1 presents the relative energies of the low-lying electronic states. In addition this Table also shows the charges associated with the individual nuclei as well as the populations of the 3dσ, 3dπ and 3dδ orbitals of Cr. Table 2 shows the populations resulting from the CASSCF calculations of the valence orbitals that have been included in the active space for the electronic states investigated.

The electronic ground state of CrNO^{2+} has been determined as $^4\Pi$. The leading configuration of the $^4\Pi$ ground state wave function is $(9\sigma)^2(10\sigma)^2(3\pi)^4(4\pi)^3(1\delta)^2$ with a weight of 62.3%. The lowest lying doublet state, $^2\Delta$, has the leading configuration $(9\sigma)^2(10\sigma)^2(3\pi)^4(4\pi)^4(1\delta)^1$ with a weight of 71.0%.

Table 1
The relative energies of the low-lying electronic states of the CrNO^{2+} ion. Also shown are the charges on Cr, N and O as well as the populations in the 3dσ, 3dπ and 3dδ orbitals of Cr

State	Relative energy (eV)	Charge on			Population of Cr 3d		
		Cr	N	O	3dσ	3dπ	3dδ
$^4\Pi$	0.00	+1.72	−0.02	+0.30	0.13	2.07	2.00
$^6\Pi$	0.99	+1.78	−0.11	+0.33	0.13	1.99	2.00
$^2\Delta$	1.48	+1.68	+0.04	+0.28	0.13	2.96	1.12
$^6\Sigma^+$	1.52	+1.65	0.00	+0.35	1.01	1.10	2.00
$^2\Pi$	2.42	+1.68	0.00	+0.31	0.14	2.09	2.00
$^4\Delta$	2.51	+1.75	−0.06	+0.31	1.01	1.10	2.00

Table 2
Occupation of selected valence orbitals of the CrNO^{2+} ion in its $^4\Pi$ electronic ground state as well as in the low-lying excited states

Orbital	Occupation					
	$^4\Pi$	$^6\Pi$	$^2\Delta$	$^6\Sigma^+$	$^2\Pi$	$^4\Delta$
9σ	1.99	1.99	1.99	1.99	1.99	1.99
10σ – N–O pσ	1.97	1.97	1.97	2.00	1.97	2.00
11σ – N–O pσ*	0.03	0.03	0.03		0.03	
11σ – Cr dσ				1.00		1.00
3π – N–O pπ	3.87	3.87	3.88	3.85	3.85	3.84
4π – Cr dπ+N–O pπ*	2.54	2.03	3.52	1.85	2.69	1.66
5π – Cr dπ−N–O pπ*	0.60	1.10	0.48	0.31	0.46	0.51
1δ – Cr dδ	2.00	2.00	1.12	2.00	2.00	2.00

From Table 1 it is noted that for all the states investigated the charge on Cr is in the range +1.65*e* to +1.78*e* while that on O is in the range +0.28*e* to +0.35*e*. This indicates that the formation of the chemical bond has resulted in charge transfer from the NO molecule to the Cr^{2+} ion. Specifically, in the $^4\Pi$ ground state of CrNO^{2+} the charge on Cr amounts to +1.72*e* and that on O and N to +0.30*e* and −0.02*e*, respectively. This indicates that the formation of the chemical bond gives rise to a charge transfer of 0.28*e* from the NO molecule to the Cr^{2+} ion.

As noted from Table 2 the 9σ orbital is practically fully occupied. This orbital is a linear combination of an spdσ hybrid of Cr, an spσ hybrid of N polarized away from Cr and of the 2s orbital of O. For all the states investigated the 10σ orbital is essentially the NO pσ bonding molecular orbital. The 11σ orbital is either the NO pσ* antibonding molecular orbital with a population of only 0.03*e* or it is the Cr dσ non-bonding orbital with a population of 1.00*e*. For all the states investigated the 3π molecular orbitals are essentially the NO pπ bonding molecular orbitals. The 4π and 5π orbitals are respectively the bonding and antibonding combinations of the Cr 3dπ orbital with the NO 2pπ* antibonding orbitals. Finally, the 1δ orbitals are almost entirely the Cr 3dδ non-bonding orbitals.

Thus, the results of the CASSCF calculations on CrNO^{2+} reveal strong interactions between the 3d orbitals of Cr and the antibonding valence orbitals of the NO ligand, and this gives rise to charge transfer as well as to formation of the covalent chemical bond.

From Table 1 it is recognized that the configuration of the Cr^{2+} ion as part of the CrNO^{2+} ion in all the states $^4\Pi$, $^6\Pi$ and $^2\Pi$ is approximately (3dπ)^2(3dδ)^2. Furthermore, Table 2 shows that the number of electrons in the bonding relative to the antibonding molecular orbitals arising from the Cr 3dπ and the NO 2pπ* amounts to 1.94*e*, 0.93*e* and 2.23*e* in the states $^4\Pi$, $^6\Pi$ and $^2\Pi$, respectively. This can be interpreted as the CrNO^{2+} ion having approximately one covalent bond between Cr and the NO ligand in the electronic state $^4\Pi$, and approximately half a covalent bond between Cr and NO in the state $^6\Pi$. In the $^2\Pi$ state the bond order between Cr and NO is slightly larger than one. The higher energy of the $^2\Pi$ state as compared to the states $^4\Pi$ and $^6\Pi$ is presumably due to antiparallel coupling of the spins of the 3d electrons located on Cr. In the states $^4\Pi$ and $^6\Pi$ the 3d electrons located on Cr have parallel coupled spins. However, it is not possible to keep the spins of all the 3d electrons located on Cr parallel coupled in a doublet state; some 3d electrons have to have antiparallel coupled spins. This is presumably the reason for the much higher energy, 2.42 eV, of the $^2\Pi$ state as compared to the $^4\Pi$ electronic ground state although the bond order in the $^2\Pi$ state is larger than that in the $^4\Pi$ ground state.

The configuration of the Cr^{2+} ion as part of $CrNO^{2+}$ in the lowest lying doublet state, $^2\Delta$, located 1.48 eV above the $^4\Pi$ ground state, is $(3d\pi)^3(3d\delta)^1$. It is noted from Table 2 that the bond order in the $^2\Delta$ state amounts to approximately one and a half which is appreciably higher than that of the $^4\Pi$ electronic ground state. The higher energy of the $^2\Delta$ state as compared to the $^4\Pi$ ground state is presumably basically due to the different configurations of Cr, i.e. $(3d\pi)^3(3d\delta)^1$ in $^2\Delta$ and $(3d\pi)^2(3d\delta)^2$ in $^4\Pi$.

In both the states $^6\Sigma^+$ and $^4\Delta$ of $CrNO^{2+}$ the configuration of Cr^{2+} is approximately $(3d\sigma)^1(3d\pi)^1(3d\delta)^2$. The energies of the $^6\Sigma^+$ and $^4\Delta$ states are 1.52 and 2.51 eV, respectively, above the $^4\Pi$ ground state. The high energies of these states are presumably due to the occupancy of the Cr 3dσ orbital, since this orbital has a loop pointing directly towards the electron rich NO ligand.

Relative to the $^4\Pi$ electronic ground state of $CrNO^{2+}$, the excited states investigated, $^2\Delta$, $^6\Sigma^+$ and $^4\Delta$, can be considered as arising from d–d transitions.

The electronic ground state of the $CrNO^{2+}$ ion has been determined as the high spin $^4\Pi$ state. In this state a covalent bond with the bond order of approximately one has been formed between the Cr^{2+} ion and the NO ligand molecule. In the lowest lying doublet state identified for the $CrNO^{2+}$ ion, $^2\Delta$, the covalent bond formed has the approximate bond order of one and a half. In all the electronic states investigated for $CrNO^{2+}$, the ion is stabilized by delocalization of the positive charge. The resulting charge on Cr is in the range $+1.65e$ to $+1.78e$. This indicates that chromium has an oxidation state close to +2 as part of the $CrNO^{2+}$ ion.

The work by Ardon and Cohen [1] on the complex $[Cr(H_2O)_5NO]SO_4$ has indicated that the complex has a low spin ground state. Thus, the electronic structure of $CrNO^{2+}$ deviates from that of the complex $[Cr(H_2O)_5NO]^{2+}$, and the present investigation of the chemical bond in the $CrNO^{2+}$ ion does not explain fully the chemical bonding between Cr and NO in the complex $[Cr(H_2O)_5NO]^{2+}$. On this background we decided to perform CASSCF calculations also for the full complex $[Cr(H_2O)_5NO]^{2+}$.

2.2. The $[Cr(H_2O)_5NO]^{2+}$ ion

The $[Cr(H_2O)_5NO]^{2+}$ ion has been investigated by performing extensive CASSCF calculations analogous to those performed for the $CrNO^{2+}$ ion.

Table 3
Correlation between symmetries of the point groups C_{2v} and $C_{\infty v}$

C_{2v}	$C_{\infty v}$
A_1	Σ^+, Δ,...
B_1	Π, Φ,...
B_2	Π, Φ,...
A_2	Σ^-, Δ,...

Table 4
The relative energies of the low-lying electronic states of the $[Cr(H_2O)_5NO]^{2+}$ ion. Also shown are the charges on Cr and on the NO unit as well as the populations in the 3dσ, 3dπ and 3dδ orbitals of Cr

State	Relative energy (eV)	Charge on		Population of Cr 3d		
		Cr	NO	3dσ	3dπ	3dδ
$^2A_2$	0.00	+1.70	−0.04	0.30	2.60	1.13
$^4B_2$	1.76	+1.75	+0.05	0.27	1.89	1.94
$^4B_1$	1.85	+1.75	+0.05	0.40	1.89	1.81
$^2B_1$	1.87	+1.65	+0.06	0.25	1.81	2.08
$^4A_2$	1.93	+1.84	−0.22	0.34	2.38	1.14
$^2B_2$	2.03	+1.66	+0.06	0.25	1.80	2.08
$^2A_1$	2.39	+1.78	−0.07	0.23	2.64	1.11
$^4A_1$	2.61	+1.76	−0.09	0.29	2.58	1.13

Table 3 shows the correlation between the symmetries of the symmetry group for the complex $[Cr(H_2O)_5NO]^{2+}$, C_{2v}, and that of the ion $CrNO^{2+}$, $C_{\infty v}$. Tables 4 and 5 present selected results of the CASSCF calculations for the $[Cr(H_2O)_5NO]^{2+}$ ion corresponding to those presented in Tables 1 and 2 for the $CrNO^{2+}$ ion. Thus, Table 4 shows the relative energies of the low-lying electronic states of the $[Cr(H_2O)_5NO]^{2+}$ ion together with the charges attributed to the Cr and the NO units, respectively. Also included are the populations in the 3dσ, 3dπ and 3dδ orbitals of Cr. Table 5 presents the occupations of the valence orbitals that have been included in the active space for all the electronic states of $[Cr(H_2O)_5NO]^{2+}$ investigated.

From Table 4 it is noted that the electronic ground state of the complex $[Cr(H_2O)_5NO]^{2+}$ has been determined as a doublet, i.e. $^2A_2$. The leading configuration in the wave function of the $^2A_2$ ground state, $(20a_1)^2(21a_1)^2(9b_1)^2(10b_1)^2(9b_2)^2(10b_2)^2(3a_2)^1$, has a weight of 72.1%. The lowest lying excited state, $^4B_2$, is separated from the $^2A_2$ electronic ground state by 1.76 eV. The leading configuration of the wave function of the $^4B_2$ state is $(20a_1)^2(21a_1)^2(23a_1)^1(9b_1)^2(10b_1)^1(9b_2)^2(10b_2)^2(3a_2)^1$ with a weight of 65.5%.

According to Table 3 the $^2A_2$ electronic ground state of $[Cr(H_2O)_5NO]^{2+}$ correlates with the excited state $^2\Delta$ of the $CrNO^{2+}$ ion. The lowest lying excited state $^4B_2$ of the $[Cr(H_2O)_5NO]^{2+}$ ion correlates with the electronic ground state, $^4\Pi$, of $CrNO^{2+}$. The interchange of the quartet and doublet states of $[Cr(H_2O)_5NO]^{2+}$ relative to those of $CrNO^{2+}$ is due to the energy splittings

Table 5
Occupation of selected valence orbitals of the $[Cr(H_2O)_5NO]^{2+}$ ion in its $^2A_2$ electronic ground state as well as in the low-lying excited states

Orbital	Occupation							
	$^2A_2$	$^4B_2$	$^4B_1$	$^2B_1$	$^4A_2$	$^2B_2$	$^2A_1$	$^2A_1$
$20a_1$	1.98	1.99	1.99	1.98	1.98	1.98	1.99	1.98
$21a_1$ – N–O pσ	1.96	1.97	1.97	1.96	1.96	1.96	1.97	1.96
$22a_1$ – Cr pdσ+N–O pσ*	0.04				0.04	0.04		0.04
$22a_1$ – N–O pσ*		0.03	0.03	0.04			0.03	
$23a_1$ – Cr pdσ−N–O pσ*	0.02			0.02	0.02	0.02		0.02
$23a_1$ – Cr dδ_{x2-y2}		1.00	1.00				1.00	
$9b_1$ – N–O pπ_x	1.96	1.91	1.97	1.91	1.96	1.97	1.96	1.91
$10b_1$ – Cr dπ_{xz}+N–O pπ_x*	1.78	0.98	1.58	0.97	1.23	1.76	1.78	1.02
$11b_1$ – Cr dπ_{xz}−N–O pπ_x*	0.26	0.11	0.45	0.14	0.80	0.27	0.25	0.15
$9b_2$ – N–O pπ_y	1.96	1.97	1.91	1.97	1.96	1.91	1.96	1.98
$10b_2$ – Cr dπ_{yz}+N–O pπ_y*	1.79	1.60	0.98	1.77	1.57	0.98	1.79	1.92
$11b_2$ – Cr dπ_{yz}−N–O pπ_y*	0.25	0.43	0.12	0.26	0.47	0.14	0.24	1.01
$3a_2$ – Cr dδ_{xy}	1.00	1.00	1.00	1.97	1.00	1.97	0.03	1.00

of the 3dδ orbitals of Cr caused by the presence of the H_2O ligand molecules. As shown in Table 4 the states $^2A_2$ and $^2A_1$ both have approximately one electron in the Cr 3dδ orbitals, and according to Table 3 both states correlate with the $^2\Delta$ state of $CrNO^{2+}$. In the $^2A_2$ ground state of $[Cr(H_2O)_5NO]^{2+}$ the 3dδ_{xy} orbital of Cr is approximately singly occupied while the 3d$\delta_{x^2-y^2}$ is approximately singly occupied in the $^2A_1$ excited state. The energy difference between the states $^2A_2$ and $^2A_1$ is 2.39 eV, and this value provides a measure of the energy splitting between the two 3dδ partners of chromium in the $[Cr(H_2O)_5NO]^{2+}$ ion. The lower energy of the $^2A_2$ ground state as compared to that of the $^2A_1$ excited state is consistent with the fact that the loops in the 3dδ_{xy} orbital of Cr point in between the H_2O ligands while the loops in the 3d$_{x^2-y^2}$ orbital point directly towards the O lone pairs in the H_2O ligands. Thus, the H_2O ligand molecules cause large energy splitting between the two 3dδ orbitals of Cr in the $[Cr(H_2O)_5NO]^{2+}$ ion.

The electronic ground state of $CrNO^{2+}$, $^4\Pi$, correlates with the excited states $^4B_2$ and $^4B_1$ of the $[Cr(H_2O)_5NO]^{2+}$ ion. The energy splitting between these states amounts to only 0.09 eV. This energy difference can be considered as a measure of the energy splitting between the Cr 3dπ_x and 3dπ_y orbitals arising from the lower symmetry of the $[Cr(H_2O)_5NO]^{2+}$ ion as compared to that of the $CrNO^{2+}$ ion. The energy splitting of the 3dπ_x and 3dπ_y orbitals of chromium is small because the x and y directions in the $[Cr(H_2O)_5NO]^{2+}$ complex only differ due to the orientations of the H_2O ligand molecules. This is also recognized by considering the states $^2B_1$ and $^2B_2$ both correlating with the $^2\Pi$ state of the $CrNO^{2+}$ ion. The energy separation between these states amounts to 0.16 eV.

Table 4 shows that the charge on chromium in all the low-lying states of the $[Cr(H_2O)_5NO]^{2+}$ ion is in the range $+1.65e$ to $+1.84e$. This indicates that the $[Cr(H_2O)_5NO]^{2+}$ ion has been stabilized by delocalization of the positive charge as is also the case for the $CrNO^{2+}$ ion. However, Table 4 shows that for all the states investigated, except for the state $^4A_2$, the charge associated with the NO ligand in $[Cr(H_2O)_5NO]^{2+}$ is considerably smaller than that of NO as part of $CrNO^{2+}$. Examination of the population analyses of the wave functions for the $[Cr(H_2O)_5NO]^{2+}$ ion show that the charge has been transferred from the H atoms of the H_2O ligand molecules to the Cr^{2+} ion rather than from the NO ligand to the Cr^{2+} ion as is the case for the $CrNO^{2+}$ ion. Analogous to the results obtained for the $CrNO^{2+}$ ion the residual charge on chromium as part of the ion $[Cr(H_2O)_5NO]^{2+}$ indicates that the oxidation state of chromium is approximately +2.

Table 5 reveals that the occupations and the orbital characters of the valence orbitals of the $[Cr(H_2O)_5NO]^{2+}$ ion resemble those of the $CrNO^{2+}$ ion considerably. Thus, the orbitals $20a_1$ through $23a_1$ of $[Cr(H_2O)_5NO]^{2+}$ correspond to the orbitals 9σ through 11σ and 1δ of $CrNO^{2+}$. Likewise, the orbitals $9b_1$ through $11b_1$ and $9b_2$ through $11b_2$ of $[Cr(H_2O)_5NO]^{2+}$ correspond to the orbitals 3π through 5π of $CrNO^{2+}$. It is especially noted that bonding and antibonding molecular orbitals have been formed in between the Cr 3dπ and the NO 2pπ* orbitals in the complex $[Cr(H_2O)_5NO]^{2+}$ as is also the case for the $CrNO^{2+}$ ion. Table 5 shows that the excess of electrons in the bonding relative to the antibonding π orbitals originating from the Cr 3dπ and NO 2pπ* orbitals amounts to 3.06e for the $^2A_2$ electronic ground state and to 2.04e for the $^4B_2$ lowest lying excited state. This is in accordance with our findings for the states $^2\Delta$ and $^4\Pi$ of $CrNO^{2+}$ which correlate with the states $^2A_2$ and

$^4B_2$ of $[Cr(H_2O)_5NO]^{2+}$, respectively. Thus, in the $^2A_2$ electronic ground state of the $[Cr(H_2O)_5NO]^{2+}$ ion the chemical bond in between Cr and NO is covalent similar to that identified in the $^2\Delta$ electronic excited state of the $CrNO^{2+}$ ion. The bound order in the $^2A_2$ electronic ground state of the complex $[Cr(H_2O)_5NO]^{2+}$ is approximately one and a half while it is approximately one in the $^4B_2$ lowest lying excited state. The bond order larger than one determined in the $^2A_2$ electronic ground state of $[Cr(H_2O)_5NO]^{2+}$ is in agreement with the short bond distance measured in between Cr and N [1]. Finally, the low spin of the electronic ground state of the ion $[Cr(H_2O)_5NO]^{2+}$ is in reasonable agreement with the experimentally measured magnetic moment $\mu = 2.2\ \mu_B$ [1].

3. Conclusions

The $CrNO^{2+}$ ion has a $^4\Pi$ high spin electronic ground state with approximately two electrons in the Cr 3dδ orbitals. The $[Cr(H_2O)_5NO]^{2+}$ ion has a low spin $^2A_2$ electronic ground state with only one electron in the Cr 3dδ orbitals. The H_2O ligand molecules in the ion $[Cr(H_2O)_5NO]^{2+}$ cause large energy splittings between the two 3dδ partners of Cr, and this gives rise to the low spin ground state of the $[Cr(H_2O)_5NO]^{2+}$ ion as compared to the high spin ground state of the $CrNO^{2+}$ ion. In each ion a covalent chemical bond has been formed between the Cr^{2+} ion and the NO ligand molecule. This chemical bond originates from the formation of bonding and antibonding linear combinations of the Cr 3dπ orbitals with the NO 2pπ^* antibonding molecular orbitals. The bond order between Cr and N amounts to approximately one and a half in the $^2A_2$ ground state of the $[Cr(H_2O)_5NO]^{2+}$ ion while it is approximately one for the $^4\Pi$ ground state of $CrNO^{2+}$.

Both ions, $CrNO^{2+}$ and $[Cr(H_2O)_5NO]^{2+}$, have been stabilized by delocalization of the positive charge. This gives rise to a net charge on Cr of $+1.72e$ in the $^4\Pi$ ground state of $CrNO^{2+}$ and to $+1.70e$ in the $^2A_2$ ground state of $[Cr(H_2O)_5NO]^{2+}$. For the $CrNO^{2+}$ ion the charge has been transferred from the O atom of the NO ligand to the Cr^{2+} ion, while for the $[Cr(H_2O)_5NO]^{2+}$ ion the charge has been transferred from the H atoms of the H_2O ligand molecules to Cr^{2+}. The results indicate that the oxidation state of chromium is approximately +2 in both ions, $CrNO^{2+}$ and $[Cr(H_2O)_5NO]^{2+}$.

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