Coordinative Behaviour of the SNCN Ligand. Experimental and Density Functional Study of the Spectroscopic Properties of the Cr(CO)5CNCN Complexes

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Coordinative Behavior of the CNCN Ligand. Experimental and Density Functional Study of Spectroscopic Properties and Bonding in the Cr(CO)₅CNCN Complex

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The coordinative behavior of the CNCN ligand is investigated experimentally, by means of UV--Vis, UV–photoclectron, and IR spectra of the Cr(CO)₅CNCN complex and, theoretically, by means of density functional calculations on the same complex and on the free CNCN ligand. The density functional calculations give accurate results for the spectroscopic properties of these compounds. Special attention is paid to a comparison of the CO and CNCN ligands. First bond dissociation energies, and various components of this bond obtained by an energy decomposition, are compared for L = CO and L = CNCN in the Cr(CO)₅L complexes. It is found that the σ-base properties of CO and CNCN are quite similar, while CNCN is found to be an only slightly stronger π acid than CO in spite of a much lower lying π* LUMO. The π-acceptor capability of CNCN is not much larger than that of CO because the CNCN 3π* has lower amplitude than the CO 2π* at the coordinating C, leading to smaller overlap with the π-donor orbital of the metal fragment.

Introduction

The synergetic bonding mechanism of π-acceptor ligands when attached to transition metal atoms in low-positive, zero, or negative formal oxidation states has been recognized for a long time and has been used to explain the electronic structure of π complexes.1 These π-acceptor ligands have, in addition to σ lone pairs by which they can form the usual donative coordinate bond, low-lying vacant π orbitals that can act as acceptor orbitals in the π backdonation. Among the π-acceptor ligands the most well-known is carbon monoxide, but also N₂, CS, NO, isocyanides, and substituted phosphines, arsines, stibines, or sulfides are examples of this kind of ligand.

In 1988, Van der Does and Bickelhaupt2 synthesized the isocyanogen, CNCN, a new π-acceptor ligand of the group of the isocyanides, by pyrolyzing norbornadiene azine. Yamada et al.3a were also able to obtain CNCN as a pyrolysis product of n-cyano-2,3-diphenylcyclopropeneamine, while Blanch and McCluskey3b synthesized it by ambient light photolysis of gaseous BrCN. CICN, and ICN. Although originally reported as CNCNC, CNCN was unambiguously identified by Stroh and Winnewiser4 in the gas phase on the basis of its high-resolution Fourier transform infrared (FTIR) and microwave spectra. Later infrared spectra (IR),5 ultraviolet photoelectron (UV–PES) spectra,6 microwave,7 and ¹³C and ¹⁴N NMR spectral studies,8 as well as a number of theoretical investigations,9 have confirmed the CNCN molecule to be the main product of these pyrolyses. The mechanisms of these reactions have been discussed10,11 and the CNCN molecule was proposed to be formed by isomerization of CNNC.

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Although the synthesis of CNCN is quite recent, the first complex containing isocyanogen was reported in 1982. It was the Cr(CO)$_5$CNCN complex, synthesized by reaction of NET$_4$[Cr(CN)(CO)$_5$] with cyanogen chloride. In this work, the most intense IR bands of this complex were also reported. In a more recent study, the IR and Raman spectra of this complex were determined and interpreted. The authors concluded that the bonding properties remain practically unchanged when going from Cr(CO)$_5$ to Cr(CO)$_5$CNCN because of their very similar vibrational spectra and the absence of a dipole moment also in the latter case. These observations contradicted the earlier suggestion by other authors that CNCN is a much better $\pi$-acceptor ligand than CO.

This paper reports the experimental and calculated (density functional (DF)) UV−PES and UV−vis absorption spectra of the Cr(CO)$_5$CNCN complex. Also a comparison of the theoretical IR spectrum and the previously reported experimental\cite{12,13} one is performed. Since there is a large number of experimental\cite{14} and theoretical\cite{15} studies on the octahedral Cr(CO)$_6$ complex, this hexacarbonyl compound will be taken as a reference.

Experimental Section

Preparation. The Cr(CO)$_5$(CNCN) complex was synthesized according to a literature procedure\cite{12} by reaction of Cr(CO)$_5$(2-MeTHF) at −40 °C. This latter complex was obtained by irradiation of Cr(CO)$_5$ in 2-MeTHF at room temperature. Cr(CO)$_5$(CNCN) was isolated in moderate yield. After column chromatography on activated silica gel (Kieselgel 60, Merck, 70–230 mesh) with pentane as eluent, the compound had a purity of more than 97%.

Spectroscopic Measurements and Instrumentation.

The He I photoelectron spectrum was recorded on a Perkin-Elmer PS-18 photoelectron spectrometer with a Heelectron Development hollow cathode He I/He II light source.


in the complex and the interaction energy ($\Delta E_{\text{int}}$). This interaction energy is explicitly split up in the steric repulsion ($\Delta E^{\text{el}}$) and orbital interaction ($\Delta E_{\text{elstat}}$) parts. The steric repulsion between two interacting systems A and B is the energy difference between the wave function

$$\Psi_0 = NA[\Psi_A^0 \Psi_B^0]$$

and the isolated systems A and B. $\Psi_0$ is the normalized (operator N) and antisymmetrized (operator A) product of the monomer wave functions. It comprises both the classical electrostatic interaction ($\Delta E_{\text{elstat}}$) between the unperturbed charge distributions of the fragments and (in an orbital method like Kohn–Sham) the four-electron destabilizing interactions between occupied orbitals (Pauli repulsion, $\Delta E_{\text{Pauli}}$). The orbital interaction, $\Delta E_{\text{elstat}}$, accounts for charge transfer (interaction between occupied orbitals in one moiety with unoccupied orbitals of the other, including the HOMO–LUMO interactions) and polarization (empty/occupied orbital mixing on one fragment). The $\Delta E_{\text{elstat}}$ has, however, not been decomposed into these terms but it has been decomposed, according to the extended transition-state method (ETS) into contributions from the different irreducible representations in which the orbital interactions occur. This means that in the pertinent $C_4v$ symmetry the $A_1$ energy component is associated with the $\sigma$ component of the bond between Cr(CO)$_5$ and CNCN, while the $E$ component reflects the strength of the $\pi$ (back)bonding.

### Results and Discussion

#### 1. Experimental Spectra.

The UV–vis absorption spectrum of the complex was recorded in dimethylbutane/pentane (8:3) at room temperature (---) and 77 K (---).

Figure 1. Experimental UV–vis spectrum of the Cr(CO)$_5$(CNCN) complex in dimethylbutane/pentane (8:3) at room temperature (---) and 77 K (---).

The UV–PES spectrum of Cr(CO)$_5$(CNCN), obtained by He I excitation, is presented in Figure 2. The ionization energies derived from this spectrum are collected in Table 7 together with the theoretical data. The assignments and correlations between experiment and theory will be discussed hereafter.

In a previous article on the IR and Raman spectra of the complex, a band at 1950 cm$^{-1}$ was tentatively assigned to a different complex, possibly the isomer Cr(CO)$_5$(NCNC). In order to find out whether we are dealing here with an equilibrium between these two complexes, IR spectra were recorded in 2-MeTHF in the temperature range 170–290 K and in pentane between 190 and 290 K. These experiments did not give evidence for such an equilibrium since the intensity of the 1950 cm$^{-1}$ band did not change with respect to those of the bands assigned to Cr(CO)$_5$(CNCN).

#### 2. Theoretical Results.

In this section we present the results of the calculations, starting with the geometries and IR spectra of the CO and CNCN ligands. Next, the geometry of the Cr(CO)$_5$(CNCN) complex is analyzed followed by the first bond dissociation energies of the two ligands for which an energy decomposition is performed. Finally the UV–vis, UV–PES, and IR spectra of Cr(CO)$_5$(CNCN) are calculated and the results are compared with the experimental data.

(a) Preliminary Study of the Ligands.

The purpose of this section is twofold. The first goal is to collect the geometry and the IR spectra of the free CO and CNCN ligands. The pur- treatment of the ligands as a reference for studying the changes undergone by these ligands in the Cr(CO)$_5$(CNCN) complex. We will also compare the density functional results with previously reported ab initio calculations for the free ligands.

Tables 1 and 2 report the geometry, dipole moment, and harmonic frequencies of CO and CNCN molecules, respectively. Experimental frequencies for the CNCN molecule in Table 2 are the observed frequencies which contain nonharmonic contributions.

It has been already noted that in DFT calculations of organic molecules the single bonds between non-
hydrogen atoms are too short by 0.01–0.02 Å, while triple bonds are too long by ∼0.01 Å. This trend is also observed in the CO and CNCN systems for both the LDA and LDA-NL approaches. The CN–CN single bond length is found 0.019 Å shorter and the CO and CN triple bonds are found 0.008–0.013 Å longer than the experimental values. Nevertheless, the bond length accuracy obtained with the DFT approach is comparable to, actually slightly better than, that obtained with second-order Møller–Plesset perturbation theory (MP2).

As previously shown for the CO and NO molecule, DFT is successful in computing the sign of dipole moments with values close to zero. On the other hand, it is well-known that CO is predicted to have the wrong sign in Hartree–Fock (HF) calculations. Interestingly, the values obtained for the dipole moments of the CO and CNCN molecules using the DFT approach are the most precise among the different methodologies compared.

For vibrational frequencies, the HF results are well-known to be systematically large by ∼10–15%. Again, DFT calculations at LDA and LDA-NL levels show the characteristics of a correlated electronic structure, and their predicted frequencies are closer to the experimental ones than MP2 frequencies. In fact, only CEPA calculations are found to be in slightly better agreement with experiment. Interestingly, LDA and LDA-NL harmonic frequencies are very similar, i.e., nonlocal corrections have a rather modest influence in calculated frequencies, their main effect being to decrease the frequencies by ∼10–15 cm⁻¹. A similar result was reported by Bérces and Ziegler, who found that differences between LDA and LDA-NL harmonic frequencies are mainly related to the differences in optimized geometries. If we restrict ourselves to the LDA results, which will be used for the complex, we observe that for CO the calculated harmonic frequency of 2152 cm⁻¹ is somewhat higher (∼10 cm⁻¹) than the measured fundamental at 2143 cm⁻¹. The anharmonicity correction being close to +30 cm⁻¹, the calculated harmonic frequency is still 20 cm⁻¹ lower than the experimental ν₁. For the high-frequency modes of CNCN, ν₁ and ν₂, we find that the calculated harmonic ones are also higher than the measured fundamentals (some 20 cm⁻¹), but if the anharmonicity correction for the CNCN triple bonds is similar to that for the CO triple bond, the calculated harmonic frequencies are probably still a bit too low. The largest disagreement between theoretical and experimental frequencies is found for the ν₃ and ν₄ frequencies. This is likely to be the result of a Fermi resonance between ν₂ and 2ν₄, as pointed out by Botschwina and Sebald. This interaction would increase the observed ν₂ frequency and decrease ν₄. On the whole, one can conclude that the DFT/DZP scheme seems quite appropriate to undertake a study of the Cr(CO)₅CNCN spectroscopic properties at reasonable computing cost.

### (b) Geometry of the Cr(CO)₅CNCN Complex

The LDA, LDA-NL, and experimental geometries of the Cr(CO)₅CNCN complex are reported in Table 3. The geometry parameters used in this table are described in Figure 3. The dipole moment for this complex is found to be 2.377 and 2.470 D at the LDA and LDA-NL levels, respectively.

The values of Table 3 show that LDA metal–ligand bond lengths are shorter than experimental by 0.02–0.03 Å. Inclusion of nonlocal corrections tends to elongate these bonds and improves the agreement between theory and experiment. At the LDA-NL level, the remaining differences between calculated and experimental metal–ligand bond lengths range from 0.01 (Cr–COeq and Cr–CNCN) to 0.03 Å (Cr–COex). The mean square deviations of calculated bond lengths from the experimental ones are 0.029 Å for LDA and 0.026 Å for NLD, respectively. Here too we find that the CN and CO calculated triple bond lengths are too long, by 0.02–0.04 Å, i.e., slightly more so than in the free ligands. As expected, the backbonding mechanism of π complexes leads to a lengthening of the calculated CO and CN triple bonds as compared to those found in the CO and CNCN free ligands. Surprisingly, this is not reproduced by the experimental data either for CNCN or for CO. For instance, the experimental C–NCN and CNC–N bond lengths in the CNCN molecule are 1.175 and 1.158 Å, whereas in the complex they are found to be 1.167 and 1.132 Å. Also, the C–O bond length in the CO free molecule is 1.128 Å and is reported to be 1.125 Å for the C–Oex in the Cr(CO)₅CNCN complex. More often a slight contraction of the triple CO bond in carbonyl complexes is observed, in contrast to the expected bond weakening and lengthening. The latter is always calculated and fits in with the generally observed IR frequency lowering of the CO stretch vibration. We have not been able to find an explanation for this discrepancy.

The optimized Cr–C and C–O bond lengths for the Cr(CO)₅ complex with the basis set used in this study are 1.869 and 1.151 Å at the LDA level and 1.910 and 1.152 Å when nonlocal corrections are added to the exchange-correlation functional. When these Cr–C and C–O bond lengths in the Cr(CO)₅ complex are compared to those of the Cr(CO)₅CNCN system, it is found that substitution of a CO by a CNCN molecule in the Cr(CO)₅ complex has virtually no effect on the C–O bond distance and slightly increases the Cr–C bond length by ∼0.01 Å.

The theoretically derived lengthening of the C–NCN and CNC–N triple bonds and the shortening of the CN–CN single bond in the complex, as compared to the free CNCN molecule, can be understood by taking into account the shape of the LUMO orbital of the CNCN ligand and the effects of the π-backbonding mechanism. The LUMO orbital of CNCN is a 3π* orbital which has

### Table 3. Bond Length (R_C-O in Å), Dipole Moment (µ in D), and Harmonic Frequency (ν in cm⁻¹) for the CO Molecule

<table>
<thead>
<tr>
<th>Method</th>
<th>R_C-O</th>
<th>µ</th>
<th>ν</th>
</tr>
</thead>
<tbody>
<tr>
<td>LDA</td>
<td>1.136</td>
<td>-0.150</td>
<td>2151.6</td>
</tr>
<tr>
<td>LDA-NL</td>
<td>1.136</td>
<td>-0.089</td>
<td>2137.2</td>
</tr>
<tr>
<td>6-31G*</td>
<td>1.114</td>
<td>+0.264</td>
<td>2439</td>
</tr>
<tr>
<td>MP2/6-31G*</td>
<td>1.150</td>
<td>-0.192</td>
<td>2125</td>
</tr>
<tr>
<td>QCISD/6-31G*</td>
<td>1.145</td>
<td>+0.011</td>
<td>2176</td>
</tr>
<tr>
<td>QCISD/6-311G*</td>
<td>1.134</td>
<td>-0.082</td>
<td></td>
</tr>
<tr>
<td>exp*</td>
<td>1.128</td>
<td>-0.122</td>
<td>2170.2</td>
</tr>
</tbody>
</table>

* A negative dipole means the positive end of the dipole is toward oxygen. From ref 29. From ref 38. From ref 18. The fundamental frequency is 2143 cm⁻¹ (ref 1b).


antibonding character in the triple bonds and bonding character in the single bond. Therefore, any supply of charge from the 3d orbitals of Cr to the 3π* orbital of the CNCN molecule is expected to result in larger CN triple bond lengths and a shorter CN–CN single bond distance, as indeed found in the calculations. Experimentally there appears to be an overall shortening of all ligand bonds of 0.02–0.03 Å compared to the calculations, yielding an extremely short CN–CN single bond and slightly shortened rather than lengthened triple bonds.

Here a last remark must be made. In the experimental work, it was found that the CNCN moiety bends considerably (CNC angle, 168.5°). Further geometry optimization of the Cr(CO)₅CNCN complex without symmetry constraints has not lead to an appreciable distortion of the CNCN linearity. Moreover, we do not see any electronic reason for the CNCN bending. We have calculated the energy of a structure with a CNC angle of 165.5°, which is only 0.41 kcal/mol above the linear structure. Therefore, we have concluded that a crystal effect can be responsible for the observed considerable deviation from linearity of the CNCN moiety in the Cr(CO)₅CNCN complex.

(c) Energetics and Fragment Analysis. The main objective of this section is to compare the first bond dissociation energy (FBDE) of the CNCN ligand in the Cr(CO)₅CNCN complex, and its components, to those of CO in the Cr(CO)₅ complex. The latter has also been determined experimentally. All FBDEs were decomposed into their components according to the ETS method. The results are collected in Tables 4 and 5. Thermal corrections and contributions to the vibrational zero-point energy correction are not included but are expected to be small on the basis of previous studies. Deformation energies from free fragments to the structures of the fragments in the complex were computed from the energy of the geometry-optimized structures of the fragments. Optimization of the Cr(CO)₅ fragment has been performed keeping the C₄ᵥ symmetry of a square pyramidal structure, since previous experimental studies have shown that Cr(CO)₅ possesses C₄ᵥ symmetry. Furthermore, it was theoretically reported that the D₃h structure of a trigonal bipyramid for...
Coordinative Behavior of the CNCN Ligand

Table 5. Overlaps between Frontier Orbitals, Mulliken Populations of the Frontier Orbitals, and Contributions to the Bond Energy (eV) between the Cr(CO)₅ and CNCN Fragments

<table>
<thead>
<tr>
<th></th>
<th>LDA</th>
<th>LDA-NL</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Overlaps</td>
<td></td>
<td></td>
</tr>
<tr>
<td>(9π, 10a₁)</td>
<td>0.462</td>
<td>0.440</td>
</tr>
<tr>
<td>(3π⁺, 8e)</td>
<td>0.141</td>
<td>0.138</td>
</tr>
<tr>
<td>Populations</td>
<td></td>
<td></td>
</tr>
<tr>
<td>10a₁</td>
<td>0.371</td>
<td>0.323</td>
</tr>
<tr>
<td>8e</td>
<td>1.776</td>
<td>1.776</td>
</tr>
<tr>
<td>9σ</td>
<td>1.558</td>
<td>1.629</td>
</tr>
<tr>
<td>3π⁺</td>
<td>0.225</td>
<td>0.223</td>
</tr>
<tr>
<td>Energies</td>
<td></td>
<td></td>
</tr>
<tr>
<td>∆E Pauli</td>
<td>5.371</td>
<td>5.129</td>
</tr>
<tr>
<td>∆E stat</td>
<td>-4.261</td>
<td>-3.908</td>
</tr>
<tr>
<td>∆E σ</td>
<td>1.110</td>
<td>1.421</td>
</tr>
<tr>
<td>∆E π</td>
<td>-4.030</td>
<td>-3.698</td>
</tr>
<tr>
<td>A₁</td>
<td>-1.973</td>
<td>-1.734</td>
</tr>
<tr>
<td>E</td>
<td>-2.043</td>
<td>-1.974</td>
</tr>
<tr>
<td>A₂, B₁, B₂</td>
<td>-0.010</td>
<td>-0.005</td>
</tr>
<tr>
<td>∆E stat²</td>
<td>-0.004</td>
<td>0.015</td>
</tr>
<tr>
<td>∆E int</td>
<td>-2.920</td>
<td>-2.777</td>
</tr>
<tr>
<td>∆E def</td>
<td>0.072</td>
<td>0.127</td>
</tr>
<tr>
<td>∆E total</td>
<td>-2.848</td>
<td>-2.150</td>
</tr>
</tbody>
</table>

a Error due to the use of the fitted density instead of exact one in energy decomposition.

Cr(CO)₅ was ∼9 kcal/mol higher in energy than the square pyramidal structure for the same complex.

In order to gain more insight into the nature of the nonlocal corrections, we have calculated the energy contributions to the FBDEs at the LDA and LDA-NL levels. Most trends when going from LDA to LDA-NL are the same for the CO (Table 4) and CNCN (Table 5) ligands. When nonlocal corrections are included in the exchange-correlation functional, we have found, for the two cases, a decrease in the Pauli repulsion term and a quantitatively more important reduction of the electrostatic interaction. As a result, the LDA-NL total steric repulsion energies ∆E⁰ become larger than the LDA ones. The effect of the nonlocal corrections is rather intricate, since both the Pauli repulsion and the electrostatic attraction are quite sensitive to the bond length, and the observed changes from LDA to LDA-NL are primarily caused by the larger Cr—L bond length at the LDA-NL level. Similarly, the LDA-NL orbital interaction energy is smaller than the LDA one, mostly due to smaller overlaps due to larger bond lengths. As a whole, the final LDA-NL interaction energies are smaller than the LDA ones.

Table 4 gives the components of the FBDE for the Cr(CO)₅ + CO fragments in the Cr(CO)₅O₆ complex at the LDA and LDA-NL levels. The experimental gas-phase FBDE obtained using pulsed laser pyrolysis techniques is ∼36.8 ± 2 kcal/mol.¹⁴ Our calculated FBDEs are ∼56.9 and ∼42.2 kcal/mol at the LDA and LDA-NL levels of theory, respectively. As expected, the LDA approach overestimates the binding energy by ∼20 kcal/mol. The best estimate computed at the LDA-NL level with a more extended basis set and including corrections for the basis set superposition error (BSSE) yields ∼41.5 kcal/mol,¹⁵i slightly too high as compared to the experimental value but quite close to the value found here. Interestingly, the A₁ and E contributions to the orbital interaction energy are very similar. The stabilizing ∆Eᵣ reflects the π backbonding, but in A₁ symmetry there are, apart from the σ donation, considerable polarization effects, presumably due to the large amplitude of the 5π orbital toward the metal fragment, which induces electrostatic polarization effects.

The results gathered in Tables 4 and 5 allow a comparison to be made between the CO and the CNCN ligands. As a preliminary, it is worth noting that at the LDA level the HOMO (5σ) and LUMO (2π⁺) energies of the CO molecule are ∼8.725 and ∼1.809 eV, respectively. For the CNCN, the HOMO (9σ) and LUMO (3π⁺) have energies of ∼8.616 and ∼3.395 eV. Therefore, from the energy values of the HOMO and LUMO of CO and CNCN, one can expect that the CNCN molecule is likely to have a similar σ-base character but a much better π-acceptor character than CO, as previously suggested.¹²

The CNCN is indeed found to have a larger FBDE to the Cr(CO)₅ fragment than the CO ligand, both at the LDA and LDA-NL levels, but not very much so. In particular, at the LDA-NL scheme the CNCN molecule binds 0.32 eV (7.4 kcal/mol) stronger than CO. This is due to a somewhat more favorable σ bond (∆Eₐ₁) and a clearly stronger π bond (∆Eₚ), which together more than compensate the slightly more repulsive ∆E⁰. The individual contributions to ∆E exhibit larger differences, which demonstrates the generally occurring compensating effects of more positive Pauli repulsion and more negative electrostatic attraction when the metal—ligand bond becomes somewhat shorter, and when there are more occupied orbitals, as for CNCN as compared to CO. The σ bond (∆Eₐ₁) is only slightly stronger for CNCN, and indeed also the σ donation (depletion of 5σ and 9σ, respectively, and population of 10a₁), is remarkably similar for CO and CNCN. As noted above, one expects the π bonding (∆Eₚ) to be stronger in CNCN because of the relatively low position of the π-acceptor LUMO 3π⁺, and this effect does occur but it is rather moderate. Also, the π-backdonation (population of 2π⁺ and 3π⁺, respectively, depletion of 8e) is somewhat larger for CNCN, but not much. In this respect, it should be noted that in spite of the smaller Cr—C bond distance for the CNCN ligand, the π overlap (between the π acceptor on the ligand (2π⁺ respectively 3π⁺) and the 8e π donor on Cr(CO)₅) is actually smaller for the CNCN than for the CO ligand. This can be rationalized by taking into account the fact that the 2pπ atomic orbital of the coordinating C has a larger contribution in the 2π⁺ orbital of CO (1.020) than in the 3π⁺ orbital of CNCN (0.831). The lower 3π⁺ energy makes the π bond nevertheless stronger, and accordingly, there is somewhat more π backdonation toward CNCN and somewhat stronger π (back)bonding.

In summary, one can conclude that the σ-base properties of CO and CNCN ligands are very similar but that the CNCN ligand is a somewhat stronger π-acid ligand. This was expected from the relative HOMO and LUMO energies of the CNCN and CO ligands, but we have noted that the effect remains moderate due to the smaller π overlap with the metal in the CNCN case.

(d) UV–vis Spectrum. The lowest singlet excitation energies present in the Cr(CO)₅CNCN complex are given in Table 6. To visualize the energetic order of the highest occupied and lowest unoccupied orbitals, we give an orbital energy diagram in Figure 4 that contains, apart from the highest occupied “t₂g” derived levels, all

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CO $2\pi^*$ derived levels, including the antibonding "t$_{2g}^*$" counterparts of the occupied t$_{2g}$ levels, as well as the CNCN $3\pi^*$ (the LUMO 11e) and the nominally 3d$_e$ type levels 6b$_1$ and 16a$_1$, which contain a considerable amount of antibonding CO 5$\sigma$. The procedure used here for calculating multiplet energies and in particular singlet excitation energies was put forward by Ziegler et al.$^{27}$ These authors have argued that it is not possible to use the up- and down-spin densities of an arbitrary configuration state function, or of the average of configuration, in the currently used exchange-correlation functionals, since the effective exchange hole in these energy expressions may violate certain conditions that enter the derivation of the model functionals. These conditions are always met by single-determinant wave functions, and the up- and down-spin densities are given in Table 6. The intensity of this transition seems too low for assignment to an MLCT transition, but the calculations offer no alternative and the presence of this band in the experimental spectrum of Cr(CO)$_5$CNCN and absence in Cr(CO)$_6$ is in agreement with this assignment.

The experimental excitation energies represent rather broad bands in the UV--vis spectra, cf. Figure 1. The UV--vis experimental spectrum of the octahedral Cr(CO)$_6$ complex shows two bands at 4.44 and 5.48 eV$^{14f}$ corresponding to the transitions from the 2b$_2$ to the lowest unoccupied orbitals, the 6b$_1$, LUMO (mostly CO $2\pi^*$) and 2t$_{1u}$ LUMO$+1$ (purely CO $2\pi^*$). These transition energies are calculated at 4.43 and 4.85 eV within the LDA scheme. Gray has assigned a weak shoulder at 335 nm (3.70 eV) to a LF transition, but we do not find such a low-lying LF transition in Cr(CO)$_6$. As a matter of fact, as in the Cr(CO)$_5$CNCN complex (Figure 4), we find the e$_g^*$ levels in Cr(CO)$_6$ rather high up in the CO $2\pi^*$ spectrum of levels, even above the t$_{2g}^*$. Therefore, we cannot assign the low-energy shoulder to the LF transition. Comparing these data to those of the Cr(CO)$_5$CNCN complex, one may expect two features. First, the low-lying CNCN $3\pi^*$ is introduced into the virtual spectrum (11e), and we may expect low-energy transitions from "t$_{2g}^*" (2b$_2$,10e) to this orbital. According to the calculations, such low-energy excitations do occur, and these transitions should fall under the extended low-intensity band at low energy (330--360 nm) in the experimental spectrum (the experimental band at 3.68 eV (337 nm) in Table 6). The intensity of this transition seems too low for assignment to an MLCT transition, but the calculations offer no alternative and the presence of this band in the experimental spectrum of Cr(CO)$_5$CNCN and absence in Cr(CO)$_6$ is in agreement with this assignment. The second change expected in Cr(CO)$_5$CNCN is that orbitals will split due to the symmetry lowering from Oh to C$_4$, and there will be a larger number of transitions (more excitations to fall under the experimental bands). However, due to the large similarity in the coordinative behavior of CNCN and CO, the splittings are usually not large. For instance, the HOMO 2t$_{2g}$ orbital of Cr(CO)$_6$ is decomposed into the quite close-lying 2b$_2$ (HOMO) and 10e orbitals of Cr(CO)$_5$CNCN (Figure 4). As one can see from Table 6, these two orbitals lead to transitions of almost the same energy, which will reduce the total number of observed bands. It is difficult to make a definitive assignment. We can tentatively assume that the bands due to transitions to the 12e and 5b$_1$ overlap, because of the small calculated difference in excitation energy, and similarly for the transitions to the 13e and 3b$_2$. These transitions would then give rise to the 4.64 and 5.34 eV observed bands, respectively. Finally, the transitions to the 15a$_1$ explain the experimental band at 4.19 eV. All transitions, except those to the 11e CNCN $3\pi^*$ orbital, are transitions from the metal to the $2\pi^*$ system of CO. Rather than putting too much emphasis on the individual assignments above, we note...
The experimental frequencies (which are fundamentals, i.e., contain anharmonic contributions) for the Cr(CO)$_5$CNCN complex in cyclohexane.

Since calculations of LDA-NL frequencies are computationally very demanding and given that it has been pointed out$^{32,36,37}$ that nonlocal corrections do not introduce important improvements in the calculated harmonic frequencies (see also Tables 1 and 2), at least when they are computed at the same reference geometry,$^{32}$ only LDA frequencies are reported in Table 8. The experimental frequencies are all lower than the calculated harmonic frequencies. As a matter of fact, it has been found$^{38}$ that the corrections to be applied to the fundamental frequencies so as to obtain the harmonic frequencies amount in the case of Cr(CO)$_6$ to values between +20 (A$_{1g}$, E$_g$) and +40 (T$_{1u}$) cm$^{-1}$. For the free CO molecule, the correction is also $\sim$+30 cm$^{-1}$ (see Table 1). We note that applying a similar correction of 20–40 cm$^{-1}$ to the corresponding experimental frequencies of Cr(CO)$_5$CNCN (the Cr(CO)$_6$ “parentage” of the modes is indicated in Table 8) shows that the calculations agree very well with experiment. As a matter of fact, for Cr(CO)$_6$ we found with the present basis set very good agreement between calculated and experimental harmonic frequencies (for A$_{1g}$, E$_g$, and T$_{1u}$: 2139, 2043, and 2023 cm$^{-1}$ calculated, 2139.2, 2045.2, and 2043.7 experimental$^{39}$). A slightly larger difference, probably too large to be covered by anharmonicity corrections, is found for the highest A$_1$ mode in Cr(CO)$_5$CNCN, at 2310 cm$^{-1}$, which is basically the symmetric stretch mode of the CNCN triple bonds. Apart from anharmonicity effects, a further tendency to too-high calculated frequencies in these LDA calculations will arise from the too-short metal–ligand bond distances at the LDA level, as pointed out by Bérces and Ziegler.$^{32}$

It is interesting to observe that CNCN distinguishes itself from CO in that there are two CNCN triple bond vibrations, the symmetric and asymmetric ones. The symmetric one has calculated frequency 2321 cm$^{-1}$ (see Table 2) clearly distinct from the CO stretch of 2152 cm$^{-1}$ (calculated), but the asymmetric CNCN triple bond vibration is calculated to be rather close (at 2082 cm$^{-1}$) to the CO stretch vibration (70 cm$^{-1}$ difference; experimentally the difference between the fundamental frequencies, which are the only ones known for CNCN, is 10 cm$^{-1}$ larger). The asymmetric CNCN triple bond vibration rather than the symmetric one is therefore expected to mix with CO vibrations in the complex. Indeed, we find in Cr(CO)$_5$CNCN that the 2306 cm$^{-1}$ harmonic frequency of symmetry A$_1$ can be assigned basically to the CNCN triple bond symmetric stretching mode, which shows very little mixing with the CO vibrations. Since this vibration was 2321 cm$^{-1}$ (see Table 2) in the free CNCN ligand, the computed lowering for this frequency is only 15 cm$^{-1}$. The next A$_1$ harmonic frequency of 2122 cm$^{-1}$ in the complex involves both CO stretch vibrations and the CNCN asymmetric stretch. In this mode, the CNCN vibrates “as the CO it replaces”, as previously suggested on the basis of the experimental results.$^{13}$ As a matter of fact,

### Table 7. Vertical LDA-NL Ionization Energies (from Unrestricted Kohn–Sham (UKS) Calculations on the Ions) and Experimental Photoelectron Spectra

<table>
<thead>
<tr>
<th>E, eV</th>
<th>LDA-NL/UKS</th>
<th>exp</th>
</tr>
</thead>
<tbody>
<tr>
<td>10e</td>
<td>9.28</td>
<td>8.4</td>
</tr>
<tr>
<td>2b$_2$</td>
<td>9.39</td>
<td>8.4</td>
</tr>
<tr>
<td>9e</td>
<td>11.86</td>
<td>11.4–11.5</td>
</tr>
<tr>
<td>14a$_1$</td>
<td>12.73</td>
<td>&gt;13</td>
</tr>
<tr>
<td>8e</td>
<td>13.29</td>
<td>&gt;13</td>
</tr>
<tr>
<td>13a$_1$</td>
<td>13.26</td>
<td>&gt;13</td>
</tr>
</tbody>
</table>

*a Energies are given in electronvolts.

### Table 8. LDA and Experimental Infrared Spectra of the Cr(CO)$_5$CNCN Complex

<table>
<thead>
<tr>
<th>Type</th>
<th>LDA</th>
<th>exp$^c$</th>
<th>exp$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A$_1$</td>
<td>ν$_A$ C≡N=C≡N</td>
<td>2306</td>
<td>2246</td>
</tr>
<tr>
<td>A$_1$</td>
<td>ν$_{A2}$</td>
<td>2122</td>
<td>2102</td>
</tr>
<tr>
<td>A$_1$</td>
<td>ν$_{E(g),C≡N=C≡N}$</td>
<td>2051</td>
<td>2019</td>
</tr>
<tr>
<td>B$_1$</td>
<td>ν$_{E(g)}$</td>
<td>2036</td>
<td></td>
</tr>
<tr>
<td>A$_1$</td>
<td>ν$<em>{T</em>{1u}}$</td>
<td>2032</td>
<td>1992</td>
</tr>
<tr>
<td>E</td>
<td>ν$<em>{T</em>{1u}}$</td>
<td>2015</td>
<td>1952</td>
</tr>
</tbody>
</table>

*a Spectra were measured in cyclohexane and frequencies are given in reciprocal centimeters. b The symmetries of the parent Cr(CO)$_6$ vibrational modes are given within quotes. c Reference 12. d Reference 13.

### Table 2

The CNCN–CN vibration is calculated to be rather close (at 2082 cm$^{-1}$) to the CO stretch vibration (70 cm$^{-1}$ difference; experimentally the difference between the fundamental frequencies, which are the only ones known for CNCN, is 10 cm$^{-1}$ larger). The asymmetric CNCN triple bond vibration rather than the symmetric one is therefore expected to mix with CO vibrations in the complex. Indeed, we find in Cr(CO)$_5$CNCN that the 2306 cm$^{-1}$ harmonic frequency of symmetry A$_1$ can be assigned basically to the CNCN triple bond symmetric stretching mode, which shows very little mixing with the CO vibrations. Since this vibration was 2321 cm$^{-1}$ (see Table 2) in the free CNCN ligand, the computed lowering for this frequency is only 15 cm$^{-1}$. The next A$_1$ harmonic frequency of 2122 cm$^{-1}$ in the complex involves both CO stretch vibrations and the CNCN asymmetric stretch. In this mode, the CNCN vibrates “as the CO it replaces”, as previously suggested on the basis of the experimental results.$^{13}$ As a matter of fact,

### Table 8

- UV Photoelectron Spectrum. The values of the experimental and calculated ionization energies (IEs) for the Cr(CO)$_5$CNCN are gathered in Table 7. The experimental UV–PES spectrum of Cr(CO)$_5$CNCN is shown in Figure 2. The geometry of the Cr(CO)$_5$CNCN$^+$ complex has been kept frozen at the LDA-NL Cr(CO)$_5$CNCN-optimized geometry given in Table 3. All theoretical IEs have been computed within the spin-unrestricted formalism (unrestricted Kohn–Sham, UKS) including nonlocal corrections (LDA-NL/UKS).

- IR Spectrum. Table 8 contains the LDA harmonic theoretical frequencies together with the observed
the LDA harmonic frequency for the equivalent $A_{1g}$ mode in Cr(CO)$_6$ is calculated to be 2139 cm$^{-1}$, i.e., only 17 cm$^{-1}$ of difference. Since in the free CO the calculated stretch frequency is 2152 cm$^{-1}$ (see Table 1), the harmonic frequency of this (still mostly CO) vibration is calculated to be lowered by 30 cm$^{-1}$. These frequency lowerings of 15 and 30 cm$^{-1}$ assigned to CNCN and CO, respectively, within the limitations that should be clear from the above, are smaller than those deduced from experimental data. Actually, the observed lowering of the “CNCN symmetric stretching” is 51 cm$^{-1}$ (2302–2251 cm$^{-1}$), whereas for the “CO stretching”, the frequency is found to be lowered by 40 cm$^{-1}$ (2143$^{1b}$–2103 cm$^{-1}$). Most of the difference between the calculated lowering for the harmonic frequencies and observed lowering for the fundamentals can most likely (for CO certainly) be attributed to the too-low calculated harmonic frequencies of the free ligands; see section 2a. We return to the rather similar frequency lowerings for CNCN and for CO below.

The $E_g$ mode in $O_h$ Cr(CO)$_6$, which is computed at 2043 cm$^{-1}$ at the LDA level, is split up in the $A_1$ and $B_1$ frequency modes with calculated frequencies 2051 and 2036 cm$^{-1}$. The 2036 cm$^{-1}$ vibration is the $B_1$ equatorial CO stretching, which has zero intensity by symmetry. The CNCN triple bond asymmetric stretching vibration can only occur in the $A_1$ component, which in fact is again very much like the “$A_1$-type” of the degenerate set of $E_g$ modes in Cr(CO)$_6$ with one axial CO stretch replaced by $v_{as}$ (CNCN). Note that the measured fundamental frequency (2020 cm$^{-1}$) is also very close to the $E_g$ fundamental of Cr(CO)$_6$ (2026.7 cm$^{-1}$). The $T_{1u}$ frequency of $O_h$ Cr(CO)$_6$, which is 2023 cm$^{-1}$ within the LDA approach, decomposes with very little shift into the closely spaced $A_1$ of 2032 cm$^{-1}$ and the $E$ of 2015 cm$^{-1}$. The observed fundamentals at 1993 and 1951 cm$^{-1}$ are close to the $T_{1u}$ fundamental of Cr(CO)$_6$ at 2000.4 and show a bit more spread and shift than the calculated harmonic frequencies.

The experimentally observed frequencies of 1962 and 1925 cm$^{-1}$ were assigned to the Cr(CO)$_5$NCNC complex in the experimental work. We have not attempted to assign them here.

Finally, the $A_1$ mode of 1062 cm$^{-1}$ corresponds to the CN–CN single bond stretching. This vibration is 975 cm$^{-1}$ in the free ligand and it has increased as a result of the Cr 3d backdonation. As previously mentioned, the $\pi$ backbonding of Cr to CNCN decreases the strength of the CN triple bonds and increases the CN–CN single bond strength. This fact is well reproduced by the LDA-computed harmonic frequencies.

Summarizing, we note that the substitution of one CO by CNCN distorts the IR spectrum remarkably little, both the calculated and the experimental spectra. This can be attributed to the presence of an asymmetric CNCN triple bond stretching mode that is close to the CO stretch and also couples to the CO vibrations very much like the stretch vibrations of the replaced CO would. These IR data indicate that electronically CNCN is similar to, and not a much better $\pi$ acceptor, than CO. The similarity to CO is more striking than the difference. This gives support to our earlier finding that the relatively low position of the 3$\pi^*$ LUMO of CNCN does not lead to much stronger $\pi^*$ acceptor behavior.

**Conclusions**

The coordinative behavior of CNCN is found to be remarkably similar to that of CO, in spite of a clearly much lower lying $\pi$ acceptor LUMO on CNCN (the C lone pair $\sigma$ donor orbitals of CO and CNCN are very similar in spatial extent and energy). The low position of the 3$\pi^*$ LUMO of CNCN does lead to calculated low-lying transitions in the Cr(CO)$_5$CNCN UV–vis absorption spectrum, which are, however, only observed with very low intensity. Nevertheless, although the calculated first bond dissociation energy of CNCN is somewhat larger than for CO, the difference is modest. The low 3$\pi^*$ does not lead to much stronger $\pi$-acceptor behavior of CNCN, as is also apparent from the very similar lowering of the CNCN stretch frequency compared to that of CO and to the fact that the CNCN stretch vibration (the asymmetric one) couples to the other CO stretches very much like the CO stretch it replaces. We have also observed in the decomposition of the bond energy that the $\sigma$ and $\pi$ components of the bond to the metal fragment are similar for CNCN and CO, the $\pi$ bond being only some 20% stronger in the case of CNCN. The analysis of the bonding shows that the low position of the 3$\pi^*$ is counteracted by a smaller overlap (hence smaller interaction matrix element) with the $\sigma$-donor orbital of the metal fragment, due to the less pronounced C $\pi$ character of the CNCN 3$\pi^*$ LUMO than the CO 2$\pi^*$ LUMO.

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