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Review

# Strikingly similar electronic structures of $[Mn(N)(CN)_5]^{3-}$ and $[Mn(NO)(CN)_5]^{3-}$

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## Contents

## Abstract

The standard oxidation states of manganese in $[Mn(N)(CN)_5]^{3-}$ and $[Mn(NO)(CN)_5]^{3-}$ differ by four units, as the former complex is Mn(V), but the latter is Mn(I). Employing density functional theory and time-dependent density functional theory calculations, we show that the electronic structures of the ground and lowest excited states of these complexes are virtually the same. Thus we suggest that $Mn(V)[b_2(xy)]^2$ is a more appropriate formulation of the ground state of $[Mn(NO)(CN)_5]^{3-}$ than $Mn(I)[b_2(xy)]^2[e(xz,yz)]^4$.

*Keywords:* Density functional theory; Time-dependent density functional theory; Nitrido; Nitric oxide; Cyanide

## 1. Introduction

The oxidation state of manganese in $[Mn(NO)(CN)_5]^{3-}$ is commonly assigned as Mn(I), with the nitric oxide taken to be $NO^+$ [1,2]. By contrast, in the nitrido ($N^{3-}$) complex, $[Mn(N)(CN)_5]^{3-}$, the formal oxidation state of the metal is Mn(V).

Assigned oxidation states in complexes containing very strong donors or acceptors have no physical meaning. As Bendix et al. have pointed out, the situation for nitrido and nitrosyl complexes is extreme, as the observed $\nu$(CN) stretching frequencies in $[Mn(N)(CN)_5]^{3-}$ and $[Mn(NO)(CN)_5]^{3-}$ are very similar [2], suggesting that the ground state is $[b_2(xy)]^2$ in both cases. Assigning Mn(V) to the nitrido complex and Mn(I) to the nitrosyl makes little sense.

Here we investigate metal–nitrido and metal–nitrosyl bonding by using density functional theory (DFT) and time-dependent density functional theory (TDDFT) to calculate properties of the ground and lowest excited states of $[Mn(N)(CN)_5]^{3-}$ and $[Mn(NO)(CN)_5]^{3-}$. We find that the metal oxidation state in the latter complex is closer to Mn(V) than to Mn(I), and like $[Mn(N)(CN)_5]^{3-}$, $[Mn(NO)(CN)_5]^{3-}$ has a $[b_2(xy)]^2$ ground state.

## 2. Computational methods

All calculations reported herein were performed with the TURBOMOLE program package for ab initio electronic structure calculations [3]. We used the TZVP basis set [4] for all

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atoms in calculating the properties of these complexes. We performed four different DFT calculations for each complex, each using a different exchange-correlation functional selected from B3LYP, PBE, BP86, and BLYP [5–13]. The calculations were done using the COSMO continuum solvation model [14] with dielectric constant 37.5. Each calculation was performed with an $m^3$ gridsize [15]. The geometry of each complex was optimized using TURBOMOLE's JOBEX program with generalized internal coordinates [16] and the corresponding STATPT module. Energies of well-converged ground-state molecular orbitals were calculated with the DSCF module for semi-direct self-consistent-field evaluation. We then used these ground-state molecular orbitals to calculate the charges of the atoms with the MOLOCH program for population analysis and the energies of the lowest-lying singlet → singlet transitions with the ESCF package for full TDDFT calculations [17,18]. Similar methods in TURBOMOLE have previously been used to investigate the electronic structures and absorption spectra of various inorganic complexes [19–21].

## 3. Results

We have calculated the ground-state properties and the energies of the lowest electronic excitations of $[Mn(N)(CN)_5]^{3-}$ and $[Mn(NO)(CN)_5]^{3-}$ with each of four exchange-correlation functionals (Table 1). The calculated ground-state structures are in reasonable agreement with experimental crystal structures [22,23].

As noted previously [2], the Mn–$C_{eq}$ bond distances are very similar in the two complexes. A strong axial trans effect is observed only in the nitrido complex [24], as the Mn–$C_{ax}$ bond distance is much longer than the Mn–$C_{eq}$ bond distance in

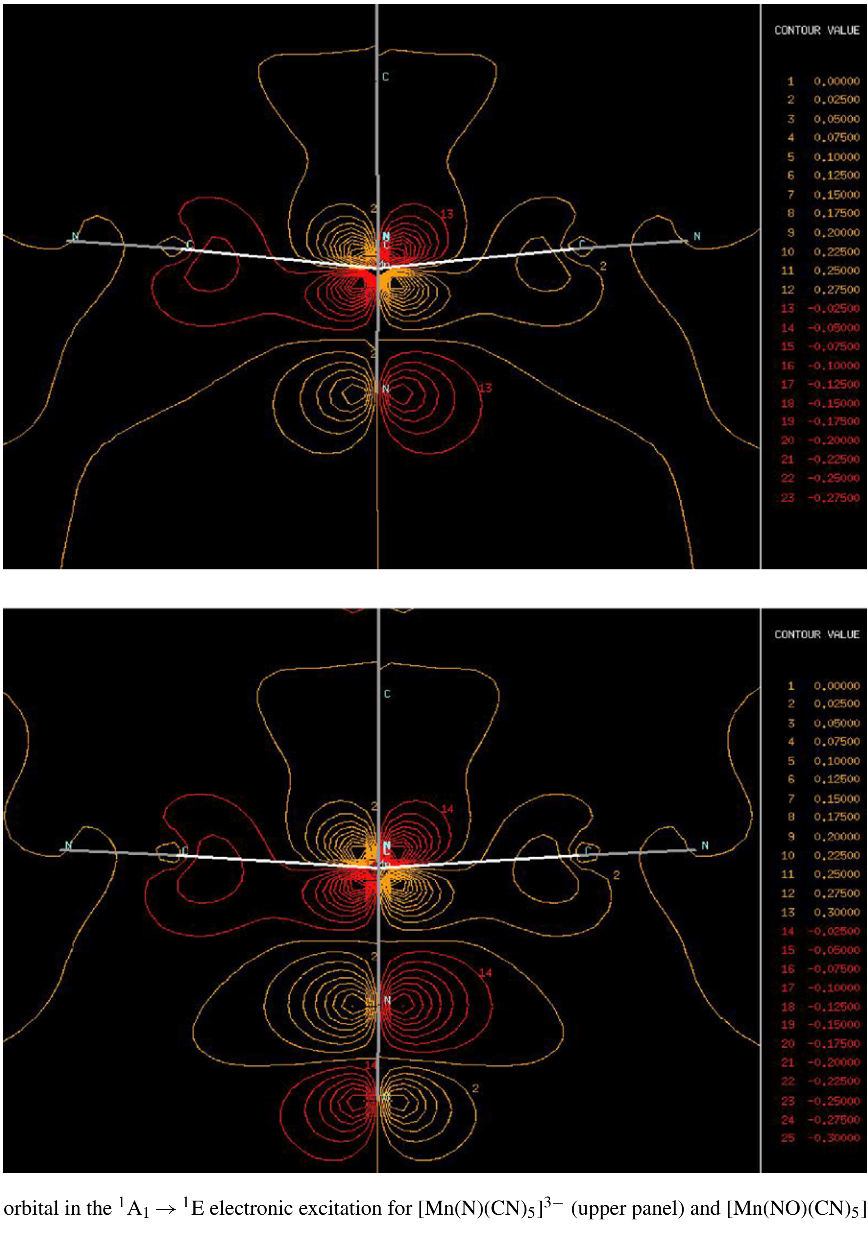

Fig. 1. Acceptor orbital in the $^1A_1 \rightarrow {}^1E$ electronic excitation for $[Mn(N)(CN)_5]^{3-}$ (upper panel) and $[Mn(NO)(CN)_5]^{3-}$ (lower panel).

Table 1
Distances, angles, central atom charges, and excitation energies for $[Mn(N)(CN)_5]^{3-}$ and $[Mn(NO)(CN)_5]^{3-}$ from experiment [2,22,23,25] and calculations with B3LYP

| Property | $[Mn(N)(CN)_5]^{3-}$ | | $[Mn(NO)(CN)_5]^{3-}$ | |
|---|---|---|---|---|
| | Calculated | Experimental | Calculated | Experimental |
| Mn–$C_{eq}$ (Å) | 2.008 | 1.990 | 2.005 | 1.974 |
| Mn–$C_{ax}$ (Å) | 2.304 | 2.243 | 2.054 | 2.016 |
| Mn–N (Å) | 1.526 | 1.499 | 1.640 | 1.651 |
| $C_{eq}$–N (Å) | 1.162 | 1.146 | 1.164 | 1.145 |
| $C_{ax}$–N (Å) | 1.164 | 1.146 | 1.162 | 1.144 |
| N–O (Å) | – | – | 1.171 | 1.174 |
| N–M–$C_{eq}$ (°) | 97.1 | 95.2 | 94.6 | 94.4 |
| Mn charge | −0.422 | – | −0.752 | – |
| $^1A_1 \rightarrow {}^1E$ ($cm^{-1}$) | 19860 | 19380 | 19180 | 18520 |

$[Mn(N)(CN)_5]^{3-}$, but not in $[Mn(NO)(CN)_5]^{3-}$. The calculated Mn–N bond distance in $[Mn(N)(CN)_5]^{3-}$ is extremely short, consistent with expectation for a triple bond; the corresponding Mn–N bond distance in $[Mn(NO)(CN)_5]^{3-}$ is only about 0.1 Å longer. Atomic charges on the central metal atom are found to differ by less than 0.4 units of charge in $[Mn(N)(CN)_5]^{3-}$ and $[Mn(NO)(CN)_5]^{3-}$.

The calculated energies of the lowest spin-allowed ($^1A_1 \rightarrow {}^1E$) electronic excitations for $[Mn(N)(CN)_5]^{3-}$ and $[Mn(NO)(CN)_5]^{3-}$ are virtually the same. In both cases the calculations agree very closely with the results from spectroscopic experiments [2,25]. The observed band intensities ($\varepsilon$ values in the 20–40 $M^{-1}\,cm^{-1}$ range) are best interpreted in terms of $[b_2(xy)] \rightarrow [e(xz,yz)]$ transitions for both $[Mn(N)(CN)_5]^{3-}$ and $[Mn(NO)(CN)_5]^{3-}$. Depictions of the e-symmetry acceptor orbitals are in Fig. 1 (generated with MOLDEN [26]), as calculated with B3LYP. Others are similar. As seen in Fig. 1, the e-symmetry orbitals are primarily Mn(xz,yz). The energy of the $^1A_1 \rightarrow {}^1E$ excitation was found to be much lower than the energy of the next higher electronic excitation in each case.

## 4. Conclusions

The above results confirm that the inner coordination electronic structures of $[Mn(N)(CN)_5]^{3-}$ and $[Mn(NO)(CN)_5]^{3-}$ are virtually the same, both in the ground state and in the lowest excited state. The Mn–N triple bonds are not quite as strong in $[Mn(NO)(CN)_5]^{3-}$ as in $[Mn(N)(CN)_5]^{3-}$, so the nitric oxide complex does have fractional Mn–N single bond character. We also recognize that the short N–O bond distance in $[Mn(NO)(CN)_5]^{3-}$ suggests the N–O bond has some multiple bond character. But this does not change the finding that $[Mn(NO)(CN)_5]^{3-}$ behaves electronically much closer to Mn(V) than to Mn(I).

## Supplementary material

Our table in the main body of the manuscript contains only the values calculated with B3LYP. The values calculated with PBE, BP86, and BLYP can be found in the supplementary material. These values are fairly close to those calculated with B3LYP.

## Acknowledgments

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## Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ccr.2006.04.008.

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