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REGULAR ARTICLE

Electronic structures of tetragonal nitrido and nitrosyl metal complexes

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Abstract The standard oxidation states of central metal atoms in C_{4v} nitrido ($[M(N)(L)_5]^z$) complexes are four units higher than those in corresponding nitrosyls ($[M(NO)(L)_5]^z$)(L = CN: $z = 3-$, M = Mn, Tc, Re; $z = 2-$, M = Fe, Ru, Os; L = NH_3: $z = 2+$, M = Mn, Tc, Re; $z = 3+$, M = Fe, Ru, Os). Recent work has suggested that $[Mn(NO)(CN)_5]^{3-}$ behaves electronically much closer to Mn(V)$[b_2(xy)]^2$, the ground state of $[Mn(N)(CN)_5]^{3-}$, than to Mn(I)$[b_2(xy)]^2[e(xz, yz)]^4$. We have employed density functional theory and time-dependent density functional theory to calculate the properties of the ground states and lowest-lying excitations of $[M(N)(L)_5]^z$ and $[M(NO)(L)_5]^z$. Our results show that $[M(N)(L)_5]^z$ and $[M(NO)(L)_5]^z$ complexes with the same z value have strikingly similar electronic structures.

Keywords Density functional theory · Time dependent density functional theory · Electronic structures · Nitrido · Nitric oxide

1 Introduction

The standard oxidation states of central metal atoms in $[M(N)(L)_5]^z$ are four units higher than those in the corresponding $[M(NO)(L)_5]^z$ complexes, as the nitrido is N^{3-}, but nitric oxide is assigned NO^+ [1,2]. Such widely differing oxidation states would suggest metal nitridos and metal nitrosyls have substantially different electronic structures, but at least in one notable pair they do not, as investigations of $[Mn(N)(CN)_5]^{3-}$ and $[Mn(NO)(CN)_5]^{3-}$ have shown that the ground states of both complexes have Mn(V)$[b_2(xy)]^2$ configurations [2,3].

We sought to determine whether it was generally true that the inner coordinate electronic structures of $C_{4v}[M(N)(L)_5]^z$ and $[M(NO)(L)_5]^z$ complexes (L = CN: $z = 3-$, M = Mn, Tc, Re; $z = 2-$, M = Fe, Ru, Os; L = NH_3: $z = 2+$, M = Mn, Tc, Re; $z = 3+$, M = Fe, Ru, Os) are virtually the same. In our work, we have employed density functional theory (DFT) and time-dependent density functional theory (TDDFT) to calculate the properties of the ground states and lowest excited states of these complexes. Our results show that in all cases the ground states of $[M(N)(L)_5]^z$ and $[M(NO)(L)_5]^z$ are both best described as derived primarily from $[b_2(xy)]^2$ electronic configurations.

Computational methods

All calculations reported herein were performed with the TURBOMOLE program package for *ab initio* electronic structure calculations [4]. We used the TZVP basis set [5] for all atoms in calculating the properties of these complexes. For Tc, Ru, Re, and Os complexes, we used the effective core potentials given by Andrae et al. [6] to account for relativistic effects. We performed four different DFT calculations, each using a different exchange-correlation functional selected from B3LYP, PBE, BP86, and BLYP [7–15]. The calculations were done using the COSMO continuum solvation model [16] for treatment of solvation effects with a dielectric constant equal to that of acetonitrile, 37.5. Each calculation

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was performed with an m3 gridsize [17]. The geometry of each complex was optimized using TURBOMOLE's JOBEX program with generalized internal coordinates [18] 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 Mulliken population analysis and the energies of the lowest-lying singlet → singlet transitions with the ESCF package for full TDDFT calculations [19,20]. Similar methods in TURBOMOLE have previously been used to successfully investigate the electronic structures and absorption spectra of other inorganic complexes [3,21–24].

Results and discussion

We have calculated the ground-state properties and the energies of the low-lying excitations for all complexes $[M(N)(L)_5]^z$ and $[M(NO)(L)_5]^z$ (L = CN: $z = 3-$, M = Mn, Tc, Re; $z = 2-$, M = Fe, Ru, Os; $L = NH_3$: $z = 2+$, M = Mn, Tc, Re; $z = 3+$, M = Fe, Ru, Os) using the B3LYP, BLYP, BP86, and PBE exchange-correlation functionals. The results are set out in Tables 1, 2, 3, 4, 5 and 6. We summarize the most important findings in the text that follows.

Table 1 Calculated M–L_{eq} bond distances (Å)

	B3LYP	B-LYP	BP86	PBE
$[Mn(N)(CN)_5]^{3-}$	2.008	2.009	1.979	1.977
$[Mn(NO)(CN)_5]^{3-}$	2.005	2.004	1.971	1.969
$[Fe(N)(CN)_5]^{2-}$	1.949	1.962	1.935	1.932
$[Fe(NO)(CN)_5]^{2-}$	1.958	1.968	1.938	1.935
$[Tc(N)(CN)_5]^{3-}$	2.132	2.137	2.110	2.109
$[Tc(NO)(CN)_5]^{3-}$	2.122	2.129	2.102	2.098
$[Ru(N)(CN)_5]^{2-}$	2.079	2.081	2.064	2.062
$[Ru(NO)(CN)_5]^{2-}$	2.079	2.091	2.066	2.061
$[Re(N)(CN)_5]^{3-}$	2.143	2.149	2.125	2.121
$[Re(NO)(CN)_5]^{3-}$	2.138	2.144	2.120	2.116
$[Os(N)(CN)_5]^{2-}$	2.101	2.110	2.087	2.084
$[Os(NO)(CN)_5]^{2-}$	2.102	2.113	2.090	2.087
$[Mn(N)(NH_3)_5]^{2+}$	2.073	2.092	2.064	2.063
$[Mn(NO)(NH_3)_5]^{2+}$	2.099	2.112	2.080	2.080
$[Fe(N)(NH_3)_5]^{3+}$	2.011	2.038	2.012	2.012
$[Fe(NO)(NH_3)_5]^{3+}$	2.030	2.053	2.023	2.023
$[Tc(N)(NH_3)_5]^{2+}$	2.201	2.219	2.191	2.190
$[Tc(NO)(NH_3)_5]^{2+}$	2.209	2.228	2.200	2.199
$[Ru(N)(NH_3)_5]^{3+}$	2.132	2.159	2.134	2.133
$[Ru(NO)(NH_3)_5]^{3+}$	2.143	2.166	2.142	2.140
$[Re(N)(NH_3)_5]^{2+}$	2.210	2.231	2.204	2.203
$[Re(NO)(NH_3)_5]^{2+}$	2.225	2.243	2.216	2.215
$[Os(N)(NH_3)_5]^{3+}$	2.164	2.188	2.162	2.161
$[Os(NO)(NH_3)_5]^{3+}$	2.153	2.177	2.153	2.152

Table 2 Calculated M–L_{ax} bond distances (Å)

	B3LYP	B-LYP	BP86	PBE
$[Mn(N)(CN)_5]^{3-}$	2.304	2.316	2.250	2.248
$[Mn(NO)(CN)_5]^{3-}$	2.054	2.052	2.010	2.010
$[Fe(N)(CN)_5]^{2-}$	2.141	2.171	2.132	2.123
$[Fe(NO)(CN)_5]^{2-}$	1.954	1.965	1.940	1.936
$[Tc(N)(CN)_5]^{3-}$	2.495	2.511	2.447	2.424
$[Tc(NO)(CN)_5]^{3-}$	2.187	2.186	2.150	2.150
$[Ru(N)(CN)_5]^{2-}$	2.325	2.351	2.311	2.310
$[Ru(NO)(CN)_5]^{2-}$	2.073	2.085	2.058	2.055
$[Re(N)(CN)_5]^{3-}$	2.496	2.510	2.460	2.454
$[Re(NO)(CN)_5]^{3-}$	2.213	2.210	2.176	2.175
$[Os(N)(CN)_5]^{2-}$	2.360	2.382	2.347	2.344
$[Os(NO)(CN)_5]^{2-}$	2.109	2.144	2.092	2.089
$[Mn(N)(NH_3)_5]^{2+}$	2.425	2.440	2.394	2.394
$[Mn(NO)(NH_3)_5]^{2+}$	2.128	2.143	2.113	2.113
$[Fe(N)(NH_3)_5]^{3+}$	2.170	2.241	2.218	2.218
$[Fe(NO)(NH_3)_5]^{3+}$	2.020	2.046	2.018	2.017
$[Tc(N)(NH_3)_5]^{2+}$	2.551	2.579	2.534	2.534
$[Tc(NO)(NH_3)_5]^{2+}$	2.262	2.270	2.235	2.235
$[Ru(N)(NH_3)_5]^{3+}$	2.379	2.411	2.368	2.368
$[Ru(NO)(NH_3)_5]^{3+}$	2.135	2.161	2.136	2.135
$[Re(N)(NH_3)_5]^{2+}$	2.548	2.580	2.538	2.538
$[Re(NO)(NH_3)_5]^{2+}$	2.274	2.292	2.254	2.254
$[Os(N)(NH_3)_5]^{3+}$	2.394	2.422	2.393	2.393
$[Os(NO)(NH_3)_5]^{3+}$	2.168	2.186	2.161	2.160

Table 3 Calculated M–N bond distances (Å)

	B3LYP	B-LYP	BP86	PBE
$[Mn(N)(CN)_5]^{3-}$	1.526	1.556	1.552	1.551
$[Mn(NO)(CN)_5]^{3-}$	1.640	1.669	1.659	1.658
$[Fe(N)(CN)_5]^{2-}$	1.516	1.547	1.539	1.540
$[Fe(NO)(CN)_5]^{2-}$	1.656	1.677	1.663	1.660
$[Tc(N)(CN)_5]^{3-}$	1.647	1.671	1.669	1.669
$[Tc(NO)(CN)_5]^{3-}$	1.768	1.796	1.789	1.788
$[Ru(N)(CN)_5]^{2-}$	1.631	1.658	1.654	1.653
$[Ru(NO)(CN)_5]^{2-}$	1.788	1.811	1.800	1.798
$[Re(N)(CN)_5]^{3-}$	1.687	1.708	1.706	1.705
$[Re(NO)(CN)_5]^{3-}$	1.790	1.817	1.813	1.810
$[Os(N)(CN)_5]^{2-}$	1.668	1.692	1.687	1.687
$[Os(NO)(CN)_5]^{2-}$	1.807	1.829	1.820	1.818
$[Mn(N)(NH_3)_5]^{2+}$	1.497	1.528	1.520	1.520
$[Mn(NO)(NH_3)_5]^{2+}$	1.633	1.653	1.640	1.639
$[Fe(N)(NH_3)_5]^{3+}$	1.490	1.520	1.511	1.511
$[Fe(NO)(NH_3)_5]^{3+}$	1.672	1.675	1.658	1.657
$[Tc(N)(NH_3)_5]^{2+}$	1.619	1.641	1.635	1.634
$[Tc(NO)(NH_3)_5]^{2+}$	1.742	1.763	1.752	1.751
$[Ru(N)(NH_3)_5]^{3+}$	1.600	1.624	1.617	1.616
$[Ru(NO)(NH_3)_5]^{3+}$	1.771	1.784	1.769	1.767
$[Re(N)(NH_3)_5]^{2+}$	1.660	1.680	1.674	1.673
$[Re(NO)(NH_3)_5]^{2+}$	1.759	1.780	1.771	1.770
$[Os(N)(NH_3)_5]^{3+}$	1.638	1.660	1.654	1.653
$[Os(NO)(NH_3)_5]^{3+}$	1.781	1.797	1.786	1.784

Table 4 Calculated N–O bond distances (Å)

	B3LYP	B-LYP	BP86	PBE
$[\mathrm{Mn(NO)(CN)_5}]^{3-}$	1.171	1.192	1.185	1.184
$[\mathrm{Fe(NO)(CN)_5}]^{2-}$	1.125	1.152	1.147	1.147
$[\mathrm{Tc(NO)(CN)_5}]^{3-}$	1.177	1.196	1.187	1.186
$[\mathrm{Ru(NO)(CN)_5}]^{2-}$	1.130	1.153	1.148	1.148
$[\mathrm{Re(NO)(CN)_5}]^{3-}$	1.186	1.203	1.194	1.192
$[\mathrm{Os(NO)(CN)_5}]^{2-}$	1.139	1.160	1.154	1.154
$[\mathrm{Mn(NO)(NH_3)_5}]^{2+}$	1.162	1.187	1.184	1.183
$[\mathrm{Fe(NO)(NH_3)_5}]^{3+}$	1.110	1.139	1.137	1.137
$[\mathrm{Tc(NO)(NH_3)_5}]^{2+}$	1.176	1.195	1.190	1.189
$[\mathrm{Ru(NO)(NH_3)_5}]^{3+}$	1.122	1.145	1.142	1.141
$[\mathrm{Re(NO)(NH_3)_5}]^{2+}$	1.188	1.206	1.198	1.198
$[\mathrm{Os(NO)(NH_3)_5}]^{3+}$	1.132	1.153	1.149	1.148

Table 5 Calculated metal atomic charges

	B3LYP	B-LYP	BP86	PBE
$[\mathrm{Mn(N)(CN)_5}]^{3-}$	−0.422	−0.475	−0.622	−0.713
$[\mathrm{Mn(NO)(CN)_5}]^{3-}$	−0.752	−0.843	−0.997	−1.114
$[\mathrm{Fe(N)(CN)_5}]^{2-}$	−0.788	−0.758	−0.904	−0.980
$[\mathrm{Fe(NO)(CN)_5}]^{2-}$	−0.999	−1.025	−1.175	−1.276
$[\mathrm{Tc(N)(CN)_5}]^{3-}$	0.083	−0.031	−0.091	−0.199
$[\mathrm{Tc(NO)(CN)_5}]^{3-}$	−0.293	−0.397	−0.470	−0.584
$[\mathrm{Ru(N)(CN)_5}]^{2-}$	0.050	−0.029	−0.092	−0.173
$[\mathrm{Ru(NO)(CN)_5}]^{2-}$	−0.302	−0.362	−0.429	−0.524
$[\mathrm{Re(N)(CN)_5}]^{3-}$	0.604	0.467	0.439	0.313
$[\mathrm{Re(NO)(CN)_5}]^{3-}$	0.349	0.219	0.179	0.043
$[\mathrm{Os(N)(CN)_5}]^{2-}$	0.608	0.483	0.467	0.326
$[\mathrm{Os(NO)(CN)_5}]^{2-}$	0.300	0.204	0.178	0.021
$[\mathrm{Mn(N)(NH_3)_5}]^{2+}$	0.567	0.569	0.450	0.422
$[\mathrm{Mn(NO)(NH_3)_5}]^{2+}$	0.477	0.457	0.333	0.294
$[\mathrm{Fe(N)(NH_3)_5}]^{3+}$	0.137	0.181	0.046	0.025
$[\mathrm{Fe(NO)(NH_3)_5}]^{3+}$	0.106	0.106	−0.032	−0.063
$[\mathrm{Tc(N)(NH_3)_5}]^{2+}$	0.789	0.734	0.637	0.599
$[\mathrm{Tc(NO)(NH_3)_5}]^{2+}$	0.490	0.450	0.333	0.285
$[\mathrm{Ru(N)(NH_3)_5}]^{3+}$	0.579	0.552	0.449	0.423
$[\mathrm{Ru(NO)(NH_3)_5}]^{3+}$	0.286	0.272	0.166	0.130
$[\mathrm{Re(N)(NH_3)_5}]^{2+}$	1.089	0.996	0.945	0.876
$[\mathrm{Re(NO)(NH_3)_5}]^{2+}$	0.881	0.806	0.723	0.655
$[\mathrm{Os(N)(NH_3)_5}]^{3+}$	1.067	0.978	0.951	0.872
$[\mathrm{Os(NO)(NH_3)_5}]^{3+}$	0.818	0.761	0.708	0.637

Table 6 Calculated $^1\mathrm{A}_1 \rightarrow ^1\mathrm{E}$ transition energies (cm^{-1})

	B3LYP	B-LYP	BP86	PBE
$[\mathrm{Mn(N)(CN)_5}]^{3-}$	19,860	18,930	19,550	19,570
$[\mathrm{Mn(NO)(CN)_5}]^{3-}$	19,180	17,600	18,560	18,670
$[\mathrm{Fe(N)(CN)_5}]^{2-}$	20,560	17,950	18,640	18,690
$[\mathrm{Fe(NO)(CN)_5}]^{2-}$	20,920	17,830	18,920	19,050
$[\mathrm{Tc(N)(CN)_5}]^{3-}$	24,580	22,310	22,730	22,640
$[\mathrm{Tc(NO)(CN)_5}]^{3-}$	21,970	19,070	19,690	19,790
$[\mathrm{Ru(N)(CN)_5}]^{2-}$	24,780	21,070	21,780	21,900
$[\mathrm{Ru(NO)(CN)_5}]^{2-}$	22,880	18,900	19,720	19,820
$[\mathrm{Re(N)(CN)_5}]^{3-}$	24,860	22,500	22,750	22,800
$[\mathrm{Re(NO)(CN)_5}]^{3-}$	22,080	19,120	19540	19,650
$[\mathrm{Os(N)(CN)_5}]^{2-}$	25,660	22,090	22,650	22,770
$[\mathrm{Os(NO)(CN)_5}]^{2-}$	23,110	19,200	19,860	19,960
$[\mathrm{Mn(N)(NH_3)_5}]^{2+}$	19,070	17,430	17,460	17,250
$[\mathrm{Mn(NO)(NH_3)_5}]^{2+}$	17,940	15,800	16,270	16,190
$[\mathrm{Fe(N)(NH_3)_5}]^{3+}$	21,600	19,050	19,310	19,110
$[\mathrm{Fe(NO)(NH_3)_5}]^{3+}$	21,380	18,000	18,620	18,580
$[\mathrm{Tc(N)(NH_3)_5}]^{2+}$	23,980	22,140	22,430	22,300
$[\mathrm{Tc(NO)(NH_3)_5}]^{2+}$	21,890	19,570	20,090	20,100
$[\mathrm{Ru(N)(NH_3)_5}]^{3+}$	26,660	24,400	24,800	24,720
$[\mathrm{Ru(NO)(NH_3)_5}]^{3+}$	24,810	21,560	22,310	22,330
$[\mathrm{Re(N)(NH_3)_5}]^{2+}$	24,540	22,840	23,140	23,030
$[\mathrm{Re(NO)(NH_3)_5}]^{2+}$	22,660	20,400	20,870	20,880
$[\mathrm{Os(N)(NH_3)_5}]^{3+}$	27,910	25,530	25,870	25,850
$[\mathrm{Os(NO)(NH_3)_5}]^{3+}$	25,630	22,520	23,110	23,240

Our calculations are in excellent agreement with metrical parameters from the available crystal structures for $[\mathrm{Mn(N)(CN)_5}]^{3-}$ (Mn-N = 1.499 Å), $[\mathrm{Mn(NO)(CN)_5}]^{3-}$ (Mn-N = 1.651 Å), and $[\mathrm{Fe(NO)(CN)_5}]^{2-}$ (Fe–N=1.620 Å) [25–27]. The M–$\mathrm{L_{eq}}$ bond distances are virtually the same for any pair of complexes $[\mathrm{M(N)(L)_5}]^z$ and $[\mathrm{M(NO)(L)_5}]^z$. All nitrido complexes exhibit strong axial *trans* effects; the nitrosyl complexes do not. The M–N distances are all very short in the $[\mathrm{M(N)(L)_5}]^z$ complexes; these distances are slightly longer in the corresponding metal nitrosyls, but still within the M–N triple bond range (under 1.8 Å) [28]. Our conclusions are not affected by the choice of exchange-correlation functional.

Striking similarities of all electronic properties lead us to conclude that both $[\mathrm{M(N)(L)_5}]^z$ and $[\mathrm{M(NO)(L)_5}]^z$ complexes are well described by $[b_2(xy)]^2$ ground-state configurations. The calculated atomic charges on the central metal atoms are generally 0.10 to 0.40 units greater in $[\mathrm{M(N)(L)_5}]^z$ than in the corresponding $[\mathrm{M(NO)(L)_5}]^z$ complexes. Even more compelling is our finding that the lowest-lying spin-allowed transition is a $^1\mathrm{A}_1 \rightarrow {}^1\mathrm{E}([b_2(xy)] \rightarrow [e(xz, yz)])$ excitation in every case, and that the calculated excitation energies are typically no more than 3,000 cm^{-1} higher for $[\mathrm{M(N)(L)_5}]^z$ than for the corresponding nitrosyl complex. These calculated excitation energies are within 1,000 cm^{-1} of the peaks of lowest energy in the absorption spectra for $[\mathrm{Mn(N)(CN)_5}]^{3-}$, $[\mathrm{Mn(NO)(CN)_5}]^{3-}$, $[\mathrm{Fe(NO)(CN)_5}]^{2-}$, and $[\mathrm{Ru(NO)(NH_3)_5}]^{2-}$ (at 19,380, 18,520, 20,080, and 22,000 cm^{-1} respectively) [2,29,30]. The 10–40 $\mathrm{M}^{-1}\ \mathrm{cm}^{-1}$ extinction coefficients of these lowest-lying peaks support our assignment to $^1\mathrm{A}_1 \rightarrow {}^1\mathrm{E}([b_2(xy)] \rightarrow [e(xz,\ yz)])$ excitations.

It would be infelicitous to assert that the electronic structures of the $[\mathrm{M(N)(L)_5}]^z$ and $[\mathrm{M(NO)(L)_5}]^z$ complexes are exactly the same. In each of the $[\mathrm{M(NO)(L)_5}]^z$ complexes, the N–O bond distances are not long enough to be classified as single bonds. It thus would be more reasonable to describe the ground state of $[M(NO)(L)_5]^z$ as a resonance hybrid of $[b_2(xy)]^2$ and $[b_2(xy)]^2[e(xz,yz)]^4$ configurations, with the electronic structure much closer to the first resonance structure than the second.

Although the correct ground-state formalisms are not affected by the choice of L, the ancillary ligand does affect the properties of the complexes in other ways. For L = CN, the energies of the $^1A_1 \rightarrow ^1E$ excitations do not have a marked dependence on z. But for $L = NH_3$, these excitation energies increase with increasing z. Following our explanation of similar trends for *trans*-dioxometal complexes with high metal oxidation states [22], we suggest that the increase in electronic excitation energies in $[M(N)(NH_3)_5]^z$ and $[M(NO)(NH_3)_5]^z$ complexes can be attributed to enhanced π-donor interactions from the nitrido and nitric oxide groups. But, in $[M(N)(CN)_5]^z$ and $[M(NO)(CN)_5]^z$ complexes, increased π-donation from the π(CN) orbitals destabilizes the $b_2(xy)$ orbital by as much as the $e(xz,yz)$ orbitals are destabilized by increased π-donation from the π(N) or π(NO) orbitals.

Importantly, our work shows clearly that the limiting low-oxidation-state-metal/NO^+ formulation of metal nitrosyls is incorrect. Assignments of oxidation states in metal nitrosyls can be very misleading, as noted over 30 years ago by Enemark and Feltham [1], and much more recently by Bendix, Wieghardt and coworkers [2].

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