Electronic Structure of Tetracyanonickelate(II)

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ABSTRACT: Tetracyanonickelate(II) has been a poster child of ligand field theory for several decades. We have revisited the literature assignments of the absorption spectrum of $[Ni(CN)_4]^{2-}$ and the calculated ordering of orbitals with metal d character. Using low-temperature single crystal absorption spectroscopy and accurate ab initio and density functional quantum mechanical methods (NEVPT2-CASSCF, EOM-CCSD, TD-DFT), we find an ordering of the frontier d- and p-orbitals of $xy < xz, yz < z^2 < z < x^2\text{-}y^2 < x, y$ and assign the d-d bands in the absorption spectrum to ${}^1A_{1g} \rightarrow {}^3B_{1g} < {}^3E_g < {}^3A_{2g} < {}^1B_{1g} < {}^1E_g < {}^1A_{2g}$. While differing from all previous interpretations, our assignments accord with an MO model in which strong π-backbonding in the plane of the molecule stabilizes d_{xy} more than out of plane bonding stabilizes d_{xz} and d_{yz}.

1. INTRODUCTION

The electronic structures of both ground and excited states of octahedral (O_h) and tetrahedral (T_d) transition metal complexes are well described by ligand field theory.[1] Ambiguity can arise in the distortions of the electronic structure upon descents in symmetry, a problem that has long plagued analysis of the electronic absorption spectrum of $[Ni(CN)_4]^{2-}$, the prototypal square planar complex. Indeed, the ordering of the d-d excited states of this complex anion are still not agreed upon, and different electronic structures have been predicted by various calculations (including ligand field theory, crystal field theory, self-consistent field-linear combination of atomic-molecular orbital (SCF-LCAO-MO), Zerner's intermediate neglect of differential overlap (ZINDO), and time-dependent density functional theory (TD-DFT)).[1-5] Experimental methods (polarized absorption and magnetic circular dichroism spectroscopy) have had limited success,[6-8] owing in part to the poor resolution of weak absorptions that most likely are due to spin-forbidden ligand field transitions.

We decided to have a fresh look at the problem, with the goal of assigning transitions from the ${}^1A_{1g}$ ground state to all six d-d and the two allowed d-p excited states (**Figure 1**). As we knew that the positions of all three spin-forbidden d-d absorptions would be needed before we could attempt to make these assignments, we obtained a single crystal of tetraphenylarsonium tetracyanonickelate(II) for absorption spectroscopic measurements. We then analyzed these and other experimental data employing both ab initio and density functional quantum mechanics calculations. Here we report a full interpretation of the electronic spectrum of $[Ni(CN)_4]^{2-}$.

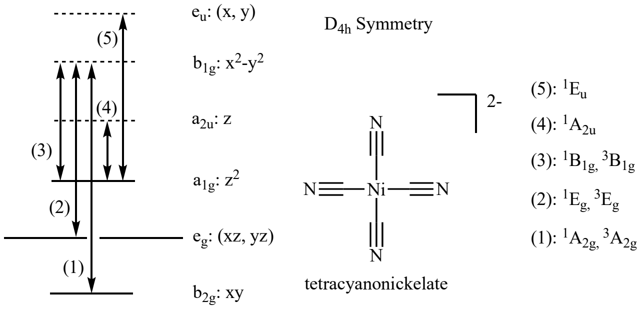

Figure 1. Relative d/p-orbital energies and d-d/d-p excited states [(1)-(5)] for D_{4h} $[Ni(CN)_4]^{2-}$; the ground state is ${}^1A_{1g}$. Dashed lines represent empty orbitals and bold lines represent doubly occupied orbitals in the ground state.

2. Experimental Section

Computational Details. All computations were performed in ORCA 4.1.0.[9] All time-dependent density functional theory (TD-DFT), complete active space self-consistent field (CASSCF), and strongly contracted N-electron valence state perturbation theory (SC-NEVPT2) calculations were performed with the ma-def2-TZVPP[10,11] basis and with CPCM[12] solvation with a dielectric constant of 37.5[13]. All TD-DFT calculations were made assuming the Tamm-Dancoff approximation with 25 roots. Calculations with the functionals B3LYP[14], PBE0[15], M06[16], X3LYP[17], and B97[18] are included. However, calculations with the M06-2X[16] flavor are not included as this functional greatly underestimates the energy of all excitations. The CASSCF and SC-NEVPT2 calculations included 10 orbitals and 10 electrons in the active space (x^2-y^2 σ-bonding, xy, z^2, xz, and yz occupied orbitals and the x^2-y^2 σ-antibonding, xy π-backbonding, z^2, xz π-backbonding, and yz π-backbonding virtual orbitals). The equation of motion-coupled cluster (EOM-CCSD) calculations were performed with the ma-def2-SVP basis set with no implicit solvation.[10,11] All TD-DFT calculations used complex anion geometries that were optimized with the same method. The *ab initio* calculations assumed a Ni-C bond of 1.87 Å and C-N bond length of 1.16 Å.[19]

Materials. Solvents were obtained from an in-house solvent purification system. Potassium tetracyanonickelate(II) and tetraphenylarsonium chloride (Sigma Aldrich) were used as received.

Tetraphenylarsonium tetracyanonickelate(II). Tetraphenylarsonium chloride (1.83 g, 8.72 mmol) was added to a concentrated aqueous solution of potassium tetracyanonickelate(II) hydrate (0.50 g, 4.15 mmol). The solution was extracted with chloroform, washed with dichloromethane, and dried overnight on a vacuum line. A yellow powder was recovered (1.14 g, 65%).

Spectroscopy. Low temperature crystal spectra were taken on an Ocean Optics QE Pro UV-Vis spectrometer. A 0.2 mm thick single crystal of tetraphenylarsonium tetracyanonickelate(II) was grown from a concentrated solution of acetonitrile, mounted on a copper disc, and masked with copper grease. The disc was cooled in a close-cycle refrigerator (Brooks CTI-Cryogenics Cryodyne) under vacuum, and spectra were collected at 21 K.

3. Results

Spectroscopy. The low temperature (21 K) visible absorption spectrum of a tetraphenylarsonium tetracyanonickelate(II) crystal is shown in **Figure 2**. In accord with the work of Perumareddi et al., a weak band around 23,000 cm^{-1} is observed.[20] Of special interest is the partially resolved absorption band around 18,000 cm^{-1}.

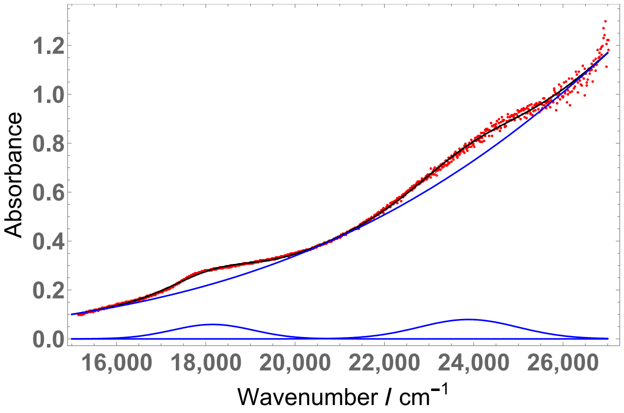

Figure 2. The 21 K absorption spectrum of tetraphenylarsonium tetracyanonickelate(II) (red) and Gaussian fit (black and blue). Prominent features are at ~18,154 and ~23,844 cm^{-1}.

Both bands are obscured in solution spectra by tailing absorptions attributable to spin-allowed transitions.

CFT. The energy levels were calculated for a transition metal ion surrounded by four point charges in a square planar (D_{4h}) geometry. The electrostatic interaction matrices were taken from Perumareddi (1972) and solved assuming no spin-orbit coupling (**Figure 3**).[21]

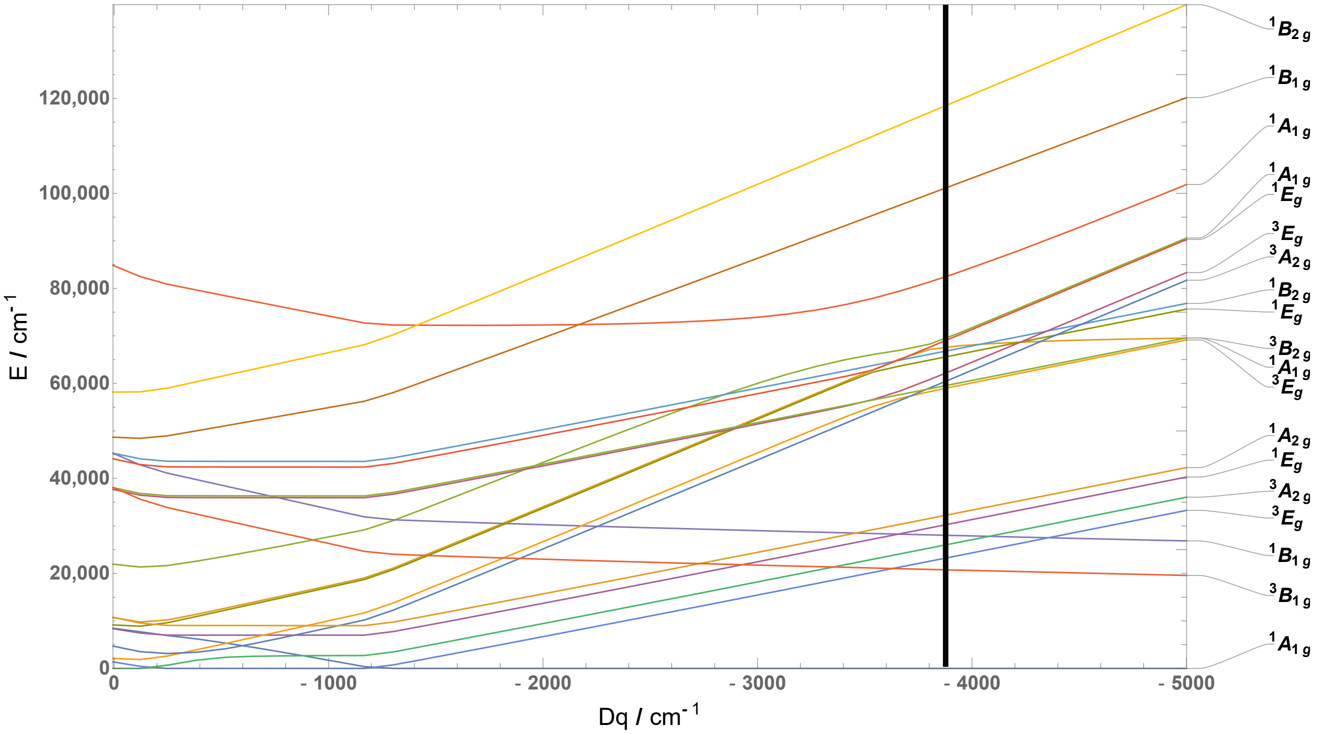

Figure 3. Tanabe-Sugano diagram for a d^8 system in a tetragonal crystal field. The vertical line represents the best fit to experimental data. The CFT parameters for Fit 1 are unrealistic (B = 131 cm^{-1}, C = 3,106 cm^{-1}, Dq = -3,885 cm^{-1}, Dt = 3,190 cm^{-1}, Ds = 4,786 cm^{-1}).

By fitting literature experimental excitation energies to

this model, the calculated crystal field parameters are B = 131 cm^{-1}, C = 3,106 cm^{-1}, Dq = -3,885 cm^{-1}, Dt = 3,190 cm^{-1}, and Ds = 4,786 cm^{-1} (Fit 1). However, using our measurement of the $^3B_{1g}$ excitation at 18,153 cm^{-1} and ^3E_g excitation at 23,844 cm^{-1}, we obtain more reasonable parameter values: B = 466 cm^{-1}, C = 2,428 cm^{-1}, Dq = -3,810 cm^{-1}, Dt = 3,121 cm^{-1}, and Ds = 5,028 cm^{-1} (Fit 2). As the system is overdetermined (with six LF excitation energy constraints and five variables), fitting was performed by fixing the spin-allowed transition energies and allowing one quadratic degree of freedom for fluctuations about the spin-forbidden transitions. The B value varies significantly depending on the energy of the $^3B_{1g}$ state. Racah parameters B and C indicate the degree of electrostatic repulsion between d-orbital electrons, Dq is the parameter related to the one-electron energy associated with the splitting between octahedral t_{2g} and e_g levels, and Dt and Ds are axial energy splitting parameters ($3Ds - 5Dt = E(d_{xy}) - E(d_{xz}/d_{yz})$ and $4Ds + 5Dt = E(d_{x2-y2}) - E(d_{z2})$). With these fitted parameters, we find $E(d_{xy}) < E(d_{xz}/d_{yz}) < E(d_{z2}) < E(d_{x2-y2})$; however, these fits are not unique. Note that the nephelauxetic parameter $\beta = B / B_o = 0.45$ (Fit 2 – assuming a free ion Racah parameter B_o = 1042 cm^{-1}) is small,[22] consistent with high ligand polarizability, which weakly correlates with covalency.[23]

DFT and *Ab Initio* QM Calculations. The vertical excitation energies of $[Ni(CN)_4]^{2-}$ were investigated with both ab initio and density functional methods. The CASSCF calculation with 10 electrons and 10 orbitals with the SC-NEVPT2 perturbation agrees well with the EOM-CCSD energies (and relative ordering) of the lowest three spin-allowed excited states (Table 1). Each CASSCF state is well described by a single configuration function that accounts for more than 94% of the wavefunction. While CASSCF is not in agreement with other calculations, the addition of electron correlation with SC-NEVPT2 greatly improves accuracy. The excited states have B_{1g}, E_g, and A_{2g} symmetries, which correspond to transitions from d_{z2}, d_{xz}/d_{yz}, and d_{xy} orbitals to the d_{x2-y2} orbital, respectively. As only d-orbital states are included in the active space, excitations to the p_z orbital cannot be identified using the CASSCF method. The algorithms implemented for EOM-CCSD cannot account for spin-forbidden transitions and the roots containing the excitations to the p_z based orbitals could not be located due to poor convergence. The DFT energies and relative ordering of these low-lying spin-allowed and spin-forbidden excited states agree well with ab initio methods (noting that the M06 density functional predicts a reversal of the relative ordering of the ^1E_g and $^1A_{2g}$ excited states). These results indicate that density functional methods can be employed to obtain accurate energies for the low-lying electronic excited states of tetracyanonickelate(II). We find, in order of increasing energy: $^3B_{1g}$, ^3E_g, $^3A_{2g}$, $^1B_{1g}$, ^1E_g, $^1A_{2g}$, $^1A_{2u}$, ^1E_u, with an orbital ordering of $d_{xy} < d_{xz,yz} < d_{z2} < p_z < d_{x2-y2} < p_{x,y}$.

4. DISCUSSION

Tetracyanonickelate was first synthesized early in the 19th century by Joseph Proust during studies on the simple prussiates of various metals.[24] In investigations over the next few decades, the compound was found to have the empirical formula $K_2[Ni(CN)_4] \cdot x H_2O$.[25-29]

Table 1. Calculated vertical excitation energies (cm^{-1}) of the lowest excited states of $[Ni(CN)_4]^{2-}$. Experimental data (absorption energies and molar extinction coefficients (ε) [cm^{-1}M^{-1}]) are from Perumareddi et al.[21]

Method	$^3B_{1g}$	^3E_g	$^3A_{2g}$	$^1B_{1g}$	^1E_g	$^1A_{2g}$	$^1A_{2u}$	^1E_u
Ab initio								
CASSCF(10,10)	19,656	22,045	28,128	34,524	35,747	36,760	-	-
SC-NEVPT2	18,491	20,799	25,845	30,119	31,224	32,700	-	-
EOM-CCSD	-	-	-	31,788	31,917	33,319	-	-
TD-DFT								
B3LYP	18,215	21,455	27,010	28,194	30,011	31,925	37,964	40,233
PBE0	18,587	21,943	27,288	29,188	31,136	32,948	39,393	41,850
M06	19,298	23,023	26,402	28,013	30,341	29,810	40,511	41,730
X3LYP	17,864	21,114	26,717	27,979	29,823	31,735	38,728	40,837
B97	18,704	22,023	27,558	28,541	30,359	32,239	37,533	40,064
Experiment								
Peak Abs (this study)	18,154	23,844	-	-	-	-	-	-
Peak Abs (Lit)	20,580	23,470	25,900	28,010	30,310	32,300	35,220	37,590
ε	0.75	2	7.8	49	409	770	4,820	16,150

In the period 1962-1963, Perumareddi et al. studied the electronic structure of tetracyanonickelate(II) using LFT, which accounted for mixing between metal and ligand valence orbitals.[20,21] These workers measured the absorption spectrum of the complex anion (presumably in solution, although not stated), extracted the energy of each ligand field (LF) band, and fit the one-electron molecular orbital parameters by assuming a relationship between two-electron Slater-Condon parameters (F_2 = 770 cm^{-1}, F_4 = 77 cm^{-1}). In this seminal work, they found that the energies of LF excited states increased in the order ${}^1A_{1g} \rightarrow {}^3B_{1g} < {}^3E_g < {}^3A_{2g} < {}^1B_{1g} < {}^1A_{2g} < {}^1E_g$. It was not immediately evident why the ${}^3A_{2g}$ state would be higher in energy than the ${}^3E_g$ state, while the ${}^1A_{2g}$ state was assigned to lie below the ${}^1E_g$ state. Without any constraints on values of the Slater-Condon parameters, we find F_2 = 575 cm^{-1}, F_4 = 88.5 cm^{-1} (Fit 1). In a parallel study, one of us (HBG) and Ballhausen employed LF theory in an attempt to assign the absorption spectrum of aqueous $[Ni(CN)_4]^{2-}$.[30] However, we underestimated the group overlap between the d-orbital electrons and π* ligand wavefunctions with b_{2g} symmetry, resulting in the energy of the d_{xy} orbital being too high. In our work, an unresolved band in the 22,500 cm^{-1} region (extinction coefficient of 2 cm^{-1} M^{-1}) was assigned to the ${}^1A_{1g} \rightarrow {}^1A_{2g}$ transition. Clearly, this was sheer stupidity on our part, as bands with such low extinction coefficients in the spectra of covalent complexes more likely arise from spin-forbidden transitions. Although the same LF method was employed for analysis of the spectrum, we and Perumareddi arrived at different conclusions. To further complicate matters, there were other d-orbital orderings for square-planar complexes in the literature (Table 2).[2] Surely one was correct for $[Ni(CN)_4]^{2-}$, but sadly, that was not the case! The problem: we and others had greatly underestimated the strength of π-backbonding from nickel to cyanide.

In 1965, Ballhausen et al. reported polarized absorption spectra of various $[Ni(CN)_4]^{2-}$ crystals (as K, Na, Ca, Sr, and Ba salts) from 19,000 to 30,000 cm^{-1}.[31] These workers resolved a weak parallel-polarized band at 20,000 cm^{-1}, a broad parallel-polarized band at 23,000 cm^{-1}, and a perpendicular-polarized band at 27,000 cm^{-1} (directions with respect to the c-axis of the crystal) in all spectra. Finding that D_{4h} vibronic selection rules could not account for the observed polarizations, these investigators proposed that there must be substantial excited state distortions from square planar to D_{2d} geometry (we question this proposal, as our TD-DFT optimizations did not require such large D_{2d} excited-state distortions).

Table 2. Proposed d-orbital orderings for $[Ni(CN)_4]^{2-}$ and $[PtCl_4]^{2-}$ as of 1964. [a]

Perumareddi et al. (1963)[20] $[Ni(CN)_4]^{2-}$	Gray and Ballhausen (1965)[30] $[Ni(CN)_4]^{2-}$	Martin et al. (1962)[2] $[PtCl_4]^{2-}$	Chatt et al. (1958)[2] $[PtCl_4]^{2-}$
x^2-y^2	x^2-y^2	x^2-y^2	x^2-y^2
z^2	xy	xy	xy
xy	z^2	z^2	xz, yz
xz, yz	xz, yz	xz, yz	z^2

[a] None of the orderings had d_{xy} as the lowest energy orbital.

In 1968, Stephens et al. studied the magnetic circular dichroism (MCD) of $K_2[Ni(CN)_4]$ from ~20,000 to 50,000 cm^{-1} in solution at room temperature.[6] The MCD spectrum unambiguously revealed that ${}^1A_{2u}$ and ${}^1E_u$ states are above the LF excited states. The authors were unable to assign any of the LF transitions in the poorly resolved spectrum, although with the same data, Piepho et al. (ignoring LF transitions) proposed a d-p excited state order of ${}^3B_{1u} < {}^3A_{2u} < {}^1B_{1u} < {}^3E_u < {}^1A_{2u} < {}^1E_u$ (or $d_{xy} < d_{z2} < d_{xz,\,yz} < d_{x2\text{-}y2}$).[32] A more highly resolved MCD spectrum was analyzed by Mason in 1989, who supported the Piepho d-p assignments with a d-orbital ordering based on a qualitative bonding model.[7]

In 1968, Mason reported absorption spectra of tetrabutylammonium tetracyanonickelate(II) in H_2O, EPA (at 300 K and 77 K), CH_3CN, and in a crystal.[33] Finding that the transition energies are weakly dependent on temperature and solvent, he proposed that energetic LF excited states ${}^3A_{2g} < {}^1A_{2g}$ would fall below the lowest d-p states, ${}^1B_{1u} < {}^1A_{2u}$.[33] A few years later, Cowman and colleagues reported polarized electronic spectra of tetrabutylammonium tetracyanonickelate(II) films at 5 K.[8] With these results along with Piepho's MCD data, it was clear that the two intense UV bands must be due to allowed d-p transitions. But the weak σ-polarized band at 31,650 cm^{-1} was reassigned (from d-p) to a LF transition. It also was suggested that the energies of LF excited states increased in the order ${}^1B_2 < {}^1A_{2g} < {}^1E$ (based on a calculation that did not account for π-backbonding effects involving the d_{xy} orbital). Shortly before Cowman's work, Demuynck et al. (1971) had performed the first ground state ab initio SCF-LCAO-MO calculation on $[Ni(CN)_4]^{2-}$.[3] Importantly, π-backbonding between the d_{xy} and cyanide orbitals was included, giving a d-orbital energy order xy < xz, yz < z^2 < x^2-y^2. In 1982, employing SCF-LCAO-MO calculations, Sano et al. arrived at the same conclusion.[34]

Although the 3d-orbital order had been settled (*vide supra*), the energies of the Ni 4p orbitals relative to the most energetic 3d level had not. In 2002, Mantz and Musselman performed LCAO-MO-SCF and ZINDO calculations that gave an orbital ordering of $d_{xy} < d_{xz}, d_{yz}, < d_{z2} < p_z < d_{x2-y2} < p_{x,y}$.[4] Of interest is that, according to their calculation, the p_z orbital energy is below that of d_{x2-y2}, as was found for the 5d cyano complex, $[Pt(CN)_4]^{2-}$.[32]

Finally, we have a definitive interpretation of the $[Ni(CN)_4]^{2-}$ absorption spectrum. The transition assignments that are in accord with all experimental data collected so far are set out in Table 3. Note that Orhan and O'Regan have a different view, based on Hubbard U corrected linear-response time-dependent DFT (TD-DFT+U) calculations on the complex anion;[5] they proposed the incorrect orbital energy order yz, xz < xy < z^2 < x^2-y^2.

Table 3. Assignments of the absorption spectrum of $[Ni(CN)_4]^{2-}$.

Experimental Band Energy (cm^{-1})	Excitation
18,154[a]	$^1A_{1g} \rightarrow {}^3B_{1g}$ ($a_{1g} \rightarrow b_{1g}$)
23,844[a]	$^1A_{1g} \rightarrow {}^3E_g$ ($e_g \rightarrow b_{1g}$)
25,900[b]	$^1A_{1g} \rightarrow {}^3A_{2g}$ ($b_{2g} \rightarrow b_{1g}$)
28,010[b]	$^1A_{1g} \rightarrow {}^1B_{1g}$ ($a_{1g} \rightarrow b_{1g}$)
30,310[b]	$^1A_{1g} \rightarrow {}^1E_g$ ($e_g \rightarrow b_{1g}$)
32,300[b]	$^1A_{1g} \rightarrow {}^1A_{2g}$ ($b_{2g} \rightarrow b_{1g}$)
35,220[b]	$^1A_{1g} \rightarrow {}^1A_{2u}$ ($a_{1g} \rightarrow a_{2u}$)
37,590[b]	$^1A_{1g} \rightarrow {}^1E_u$ ($e_g \rightarrow a_{2u}$)

[a] This work. [b] Reference 20.

5. CONCLUSION

We have obtained single crystal absorption data and performed ab initio and density functional calculations of the electronic structures of the ground and LF excited states of $[Ni(CN)_4]^{2-}$. We have established that the energies of the Ni 3d and 4p orbitals increase as follows: $d_{xy} < d_{xz}, d_{yz} < d_{z2} < p_z < d_{x2-y2} < p_x, p_y$. Our results are consistent with previous density functional calculations but differ from earlier ones based on LF and ZINDO theories. Importantly, the original 3d to 4p assignments[30,33] of the intense absorptions at 35,220 and 37,590 cm^{-1} are in accord with TD-DFT and other calculations:[3,13,34] and we emphasize that the correct order of d-orbital energies was found only after *ab initio* calculations by theorists showed that backbonding between d_{xy}, d_{xz}, and d_{yz} metal orbitals and ligand π* orbitals could not be ignored.

ASSOCIATED CONTENT

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Notes

The authors declare no competing financial interest.

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