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# Resonance Raman Spectra of Electronically Excited $M_2(dppm)_3$ Complexes (M = Pd, Pt)

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The resonance Raman spectra of $d^{10}$–$d^{10}$ $M_2(dppm)_3$ (M = Pd, Pt; dppm = bis(diphenylphosphino)methane) complexes have been investigated by CW and time-resolved resonance Raman spectroscopy. The $^3$(dσ*pσ) excited-state frequencies are 152 (Pd–Pd) and 120 $cm^{-1}$ (Pt–Pt); ground-state frequencies are 120 and 102 $cm^{-1}$, respectively. The increase in ν(M–M) upon excitation confirms that there is a stronger metal–metal bond with a correspondingly greater force constant in the excited state. The M–M force constant in each case indicates that the metal–metal bond shortens by ~0.1 Å upon electronic excitation.

Spectroscopic investigations have shown that $d^8$–$d^8$ $M_2$ complexes (M = $Rh^I$, $Ir^I$, $Pt^{II}$) exhibit enhanced M–M bonding interactions in their singlet and triplet dσ*pσ states.[2–6] The spectroscopic and photophysical properties of a number of $d^{10}$–$d^{10}$ $Pd_2$ and $Pt_2$ complexes have also been reported, and assignments for the lowest $^{1,3}$(dσ*pσ) excited states have been proposed.[7,8] The $d_{x^2-y^2}$ and $d_{xy}$ orbitals in $d^{10}$ $MP_3$ units interact weakly in $d^{10}$–$d^{10}$ $M_2(dppm)_3$ species (M = Pd, Pt; dppm = bis(diphenylphosphino)methane)[7–9] to form dδ and dδ* molecular orbitals, and it appears from absorption and emission spectroscopic experiments that the energy gap between dδ (dδ*) and dσ* is relatively small (~2000 $cm^{-1}$).[8] Contrary to the $^{1,3}$(dσ*pσ) situation, metal–metal bonding interactions in the $^{1,3}$(dδpσ) and $^{1,3}$(dδ*pσ) states are weak and are not expected to be very different from those in the ground state; excited-state distortions, ΔQ, are very small. We have extended our work on $d^{10}$–$d^{10}$ $M_2L_3$ complexes[10] to include time-resolved resonance Raman ($TR^3$)[11] experiments, and the results have shed new light on the nature of the metal–metal interactions in the lowest triplet excited states.

The transient difference absorption spectrum (370–600 nm) of $Pd_2(dppm)_3$ in acetone (Figure 1) exhibits a bleaching of the intense singlet dσ* → pσ band[8] at ~430 nm (τ = 5.5 μs).[12] Isosbestic points are evident in the Δ(absorbance) spectrum at λ ~390 and ~460 nm. The broad absorption centered at 500 nm cannot be definitively assigned solely from this experiment;[13] triplet–triplet absorptions arising from dδpσ, dδ*pσ, and dσ*pσ excited states are all reasonable possibilities. The transient difference spectrum of $Pt_2(dppm)_3$ has not been obtained; a ~40-nm red shift is expected from Pd to Pt.

The following "pump-probe" $TR^3$ experiments were attempted: (a) $\lambda_{pump}$ = 355 and 396 nm and $\lambda_{probe}$ = 532 nm for $M_2(dppm)_3$ (M = Pd, Pt), (b) $\lambda_{pump} = \lambda_{probe}$ = 532 nm for $Pt_2(dppm)_3$, (c) $\lambda_{pump} = \lambda_{probe}$ = 396 nm for $Pd_2(dppm)_3$, and (d) $\lambda_{pump} = \lambda_{probe}$ = 355 nm for $Pt_2(dppm)_3$. The excitation lines were those of a Quanta-Ray DCR-1A Nd:YAG laser (fwhm = 7 ns; 355 and 532 nm) and a Quanta-Ray RS-1 $H_2$(g) Raman shifter cell pumped by the 355-nm line (producing the 396-nm line). A delay of 1 ns was optically induced between the pump and probe pulses.[11] The best results were obtained when procedures c and d were employed, and there was no effect of $\lambda_{exc}$ on the shapes and frequencies of the Raman peaks.

Solid-state resonance Raman spectra of $M_2(dppm)_3$ complexes have been reported previously.[8] Part of the $Pt_2(dppm)_3$ ground-state spectrum has been reproduced in Figure 2. The ground-state ν(Pd–Pd) and ν(Pt–Pt) values are 120 and 102 $cm^{-1}$, respectively; they have been assigned on the basis of their relative intensities and close resemblance in frequencies with $d^8$–$d^8$ species.[3,6] The $TR^3$ spectrum of $Pt_2(dppm)_3$ is shown in Figure 2. Features are seen in this spectrum at 102 and 120 $cm^{-1}$; the former is attributable to ν(Pt–Pt) of ground-state $Pt_2(dppm)_3$, owing to incomplete excitation of all of the complexes in the pump/probe region. A saturation experiment was not attempted, so the relative ground- and excited-state ν(M–M) intensities are not meaningful. The new Raman feature at 120 $cm^{-1}$ is ν(Pt–Pt) of the electronically excited complex. The $TR^3$ spectrum of $Pd_2(dppm)_3$ shows a feature at 152 $cm^{-1}$ that is assigned to the excited-state ν(Pd–Pd).[14] These vibrational assignments are based upon the close similarities

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(10) The $M_2(dppm)_3$ complexes were synthesized according to standard procedures and were purified by triple recrystallization in benzene/ethanol or benzene/propanol. See: Grossel, M. C.; Brown, M. P.; Nelson, C. D.; Yavari, A.; Kallas, E.; Moulding, R. P.; Seddon, K. R. *J. Organomet. Chem.* **1982**, *232*, C13. Stern, E. W.; Maples, P. K. *J. Catal.* **1972**, *27*, 120. Note that the reduction of $M(PPh_3)_3Cl_2$ by $NaBH_4$ in the presence of dppm gives strongly emissive $M(PPh_3)_3$ as a residual impurity. The starting material $M(dppm)Cl_2$ is preferred. Purity was checked by elemental analysis and $^{31}P$ and $^1H$ NMR spectroscopy (500 MHz; 2000 scans). All complexes are air-sensitive; they were stored in an oxygen-free drybox when not in use. Tetrahydrofuran (THF) was purified according to: Gordon, A. J.; Ford, R. A. *The Chemist's Companion, A Handbook of Practical Data, Techniques, and References*; John Wiley and Sons: New York, 1972; p 436. Fresh THF and acetone solutions of the $M_2(dppm)_3$ complexes were freeze–pump–thaw-degassed prior to the measurements.

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(13) The 500-nm feature in the $Pd_2(dppm)_3$ transient difference spectrum probably represents the spin-allowed dσ* ← dσ transition in $^3Pd_2^*$. This assignment is based upon a comparison of the spectroscopic properties of $Pd_2(dppm)_3$ with previously reported data for the triplet excited state of $Pt_2(P_2O_5H_2)_4^{4-}$ (see ref 5d); bandwidths for the dσ* ← dσ bands (fwhm ~ 4600 $cm^{-1}$) and the relative intensity ratios of the dσ* ← dσ and bleached pσ ← dσ* bands are similar for both binuclear ($^3M_2^*$) systems. Moreover, this interpretation is consistent with the relative $^3M_2^*$ dσ* ← dσ transition energies ($\lambda_{max}(Pt_2(P_2O_5H_2)_4^{4-})$ = 320 nm and $\lambda_{max}(Pd_2(dppm)_3)$ = 500 nm), because the dσ*–dσ splitting decreases with increasing M–M bond length (the M–M separations are 2.73 ($Pt_2$)[6] and 2.92 Å ($Pd_2$) in the $^3M_2^*$ states).

(14) Two-color $TR^3$ experiments ($\lambda_{pump}$ = 355 nm; $\lambda_{probe}$ = 532 nm; delay time ~ 1 ns) were not successful. The $TR^3$ spectrum was obtained by using 396-nm excitation (where Δ(absorbance) ~ 0). In this spectrum, the ground-state ν(Pd–Pd) is obscured by an artifact generated by the $H_2$(g) shift cell.

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**Table I.** Structural and Spectroscopic Parameters for $d^{10}$–$d^{10}$ and $d^8$–$d^8$ Complexes

| | $\nu$(M–M)/Å | $r$(M–M)/Å | $\nu$(M–M)*/cm$^{-1}$ | $r$(M–M)*/Å[a] | $\Delta A$/Å |
|---|---|---|---|---|---|
| $Pd_2(dppm)_3$ | 120[b] | 3.04[a] | 152 | 2.92 | 0.12 |
| $Pt_2(dppm)_3$ | 102[b] | 3.025[c] | 120 | 2.93 | 0.10 |
| $Pt_2(pop)_4^{4-}$[d] | 118[e] | 2.925[f] | 156[e] | 2.73 | 0.20 |
| $Rh_2b_4^{2+}$[g] | 79[h] | 3.242[i] | 144[h] | 2.96 | 0.28 |
| $[Rh(CNPh)_4]_2^{2+}$ | 60[h] | 3.193[j] | 162[h] | 2.89 | 0.30 |

[a] Calculated by using eq 1 and 2; (M–M)* refers to the $^3(d\sigma^*p\sigma)$ state. [b] From ref 8. [c] From ref 17. [d] pop = $P_2O_5H_2$. [e] From ref 6. [f] From: Filomena Dos Remedios Pinto, M. A.; Sadler, P. J.; Neidle, S.; Sanderson, M. R.; Subbiah, A.; Kuroda, R. *J. Chem. Soc., Chem. Commun.* **1980**, 13. Marsh, R. E.; Herbstein, F. H. *Acta Crystallogr.* **1983**, *B39*, 280. [g] b = $CN(CH_2)_3NC$. [h] From ref 3. [i] From: Mann, K. R.; Thich, J. L.; Bell, R. A.; Coyle, C. L.; Gray, H. B. *Inorg. Chem.* **1980**, *19*, 2462. [j] From: Mann, K. R.; Lewis, N. S.; Williams, R. M.; Gray, H. B.; Gordon, J. G., II *Inorg. Chem.* **1978**, *17*, 828.

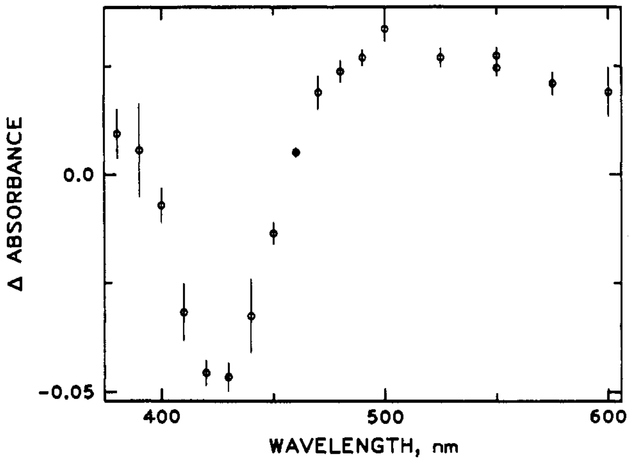

**Figure 1.** Transient difference absorption spectrum of $Pd_2(dppm)_3$ in acetone at room temperature. Experimental conditions: $\lambda_{exc}$ = 355 nm (Nd:YAG laser; typically 50 mJ/pulse; 1.5-ns delay after each pulse), OD = 1.0.

of the $\nu$(M–M) values to those of other excited binuclear species.[3,6] Moreover, $\tau_F$ of the $d\sigma^*p\sigma$ singlet state is very short (estimated to be ~8 ps) from the oscillator strength of the singlet–singlet $d\sigma^* \rightarrow p\sigma$ transition; a short-lived singlet also accords with the experimentally measured $\tau_F$ for $Pt_2(P_2O_5H_2)_4^{4-}$.[5a] Thus, the Raman peaks are due only to triplet species.[15] No other Raman peaks were observed.

Empirical relationships between force constants and bond distances for $M_2$ species have recently been formulated.[16] These relationships are similar to Badger's rules but are more accurate for molecules exhibiting $M_2$ bond orders between 0 and 1.[16b] For $M_2$ complexes containing a 4d or a 5d metal, the M–M separation, $r$ (Å), is

$$r(4d) = 1.83 + 1.45 \exp(-F/2.53) \qquad (1)$$

$$r(5d) = 2.01 + 1.31 \exp(F/2.36) \qquad (2)$$

where $F$ (mdyn Å$^{-1}$) is the M–M force constant. By use of the diatomic approximation to extract $F$(M–M) from $\nu$(M–M) for $Pt_2(dppm)_3$ in the ground state, a calculated value of $r$(Pt–Pt) = 3.03 Å is obtained. This value is, within experimental uncertainties, identical with the $r$(M–M) obtained by single-crystal X-ray diffraction.[17] Application of eq 1 and 2 to estimate $r$(M–M) values for the $M_2(dppm)_3$ complexes in their excited states is reasonably justified. From the TR$^3$ experiments, the estimated excited-state $F$(M–M) values are 0.72 (Pd) and 0.83 mdyn Å$^{-1}$ (Pt); $r$(M–M)'s are 2.92 (Pd) and 2.93 Å (Pt). The excited-state M–M contractions, $\Delta Q$, are ~0.12 ($Pd_2(dppm)_3$) and 0.10 Å ($Pt_2(dppm)_3$), consistent with the $^3(d\sigma^*p\sigma)$ assignment.

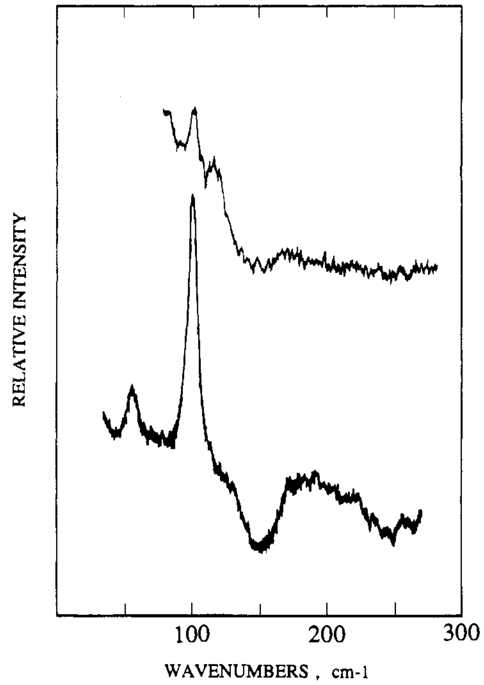

**Figure 2.** Lower trace: Ground-state resonance Raman spectrum of solid $Pt_2(dppm)_3$ at room temperature obtained by CW excitation. Experimental conditions: $\lambda_{exc}$ = 514.5 nm, 10 mW laser power at the sample. Upper trace: TR$^3$ spectrum of $Pt_2(dppm)_3$ in THF solution at room temperature. Experimental conditions: $\lambda_{exc}$ = 355 nm (Nd:YAG laser; 5 mJ/pulse), OD = 1.4 mm$^{-1}$, resolution = 4 cm$^{-1}$, 10 scans.

The ground-state electronic configurations of $d^8$–$d^8$ and $d^{10}$–$d^{10}$ complexes are similar; importantly, in each case the HOMO is $d\sigma^*$ and the LUMO is $p\sigma$. Upon excitation, the lowest excited states are a singlet and a triplet derived from the $(d\sigma^*)^1(p\sigma)^1$ configuration. While the ground state is formally nonbonding, the excited-state electronic configuration possesses less antibonding M–M character (i.e., bonding metal–metal interactions increase in the excited states). This is clearly demonstrated in the $d^8$–$d^8$ systems (see Table I) where large increases in $\nu$(M–M) are observed upon photoexcitation. The corresponding $\Delta Q$ values are larger than 0.2 Å. An interesting finding is that $\Delta Q(d^8\text{–}d^8) > \Delta Q(d^{10}\text{–}d^{10})$. The smaller effect for $d^{10}$–$d^{10}$ complexes may be explained by the mixing[8] of $^3(d\sigma^*p\sigma)$ with nearby states such as $^3(d\delta p\sigma)$ and $^3(d\delta^*p\sigma)$ (energy gap ~ 2000 cm$^{-1}$). The poor overlap between the $d_{x^2-y^2}$ and $d_{xy}$ orbitals that make up the $d\delta$ and $d\delta^*$ molecular orbitals in $M_2$ complexes produces only weak interactions between the M atoms both in the ground state and in the $^{1,3}(d\delta p\sigma)$ and $^{1,3}(d\delta^*p\sigma)$ states. Photoexcitation of $M_2$ into $d\delta p\sigma$ and $d\delta^*p\sigma$ states will not lead to a measurable increase (or decrease) in $\nu$(M–M)*; i.e., $\Delta Q$ ~ 0. A mixture of triplets [$(d\delta p\sigma)$, $(d\delta^*p\sigma)$, and $(d\sigma^*p\sigma)$] would produce an intermediate situation among pure $(d\delta p\sigma)$, $(d\delta^*p\sigma)$ ($\Delta Q$ ~ 0), and $(d\sigma^*p\sigma)$ ($\Delta Q$ > 0.2 Å) excited states. Mixing of this type is probably

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[15] In steady state, the relative ([triplet]/[singlet]) excited-state population is the same as the ratio of their lifetimes. For $M_2(dppm)_3$ species, [triplet]/[singlet] ~ $10^6$.

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unimportant in $d^8$–$d^8$ complexes,[2-6] as the spacing between $^3(d\sigma^*p\sigma)$ and the $d\delta p\sigma$ excited states is relatively large (energy gap > 4800 $cm^{-1}$).

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# Electronic Spectra of the $d^6$ Binary Carbonyl Complexes $Mn(CO)_6^+$, $Cr(CO)_6$, and $V(CO)_6^-$: An ab Initio Analysis

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The UV–visible spectra of the isoelectronic series $Mn(CO)_6^+$, $Cr(CO)_6$, and $V(CO)_6^-$ have been reinvestigated by using the Hartree–Fock–Roothaan method. The calculations do confirm the classical assignment of the two intense absorption peaks as MLCT transitions. For the weak bands, however, an alternative assignment has been proposed. It is essentially based on the observation that the calculated spectrochemical strength $10Dq$ *increases* in the order $Mn(CO)_6^+ < Cr(CO)_6 < V(CO)_6^-$; this result is in conflict with earlier assignments.

## I. Introduction

The electronic spectra of the neutral and ionic $d^6$ binary carbonyls have been known for a long time. In 1963, Gray and Beach were the first to report the vapor-phase spectra for the hexacarbonyls of the group VIB metals Cr–Mo–W.[1] In a more recent paper, the same authors[2] also include the ionic species $Mn(CO)_6^+$, $V(CO)_6^-$, and $Re(CO)_6^+$.

As one would expect, the electronic spectra of these series of complexes are very similar. Each one of them contains two intense absorption bands, which were identified as metal-to-ligand charge-transfer transitions ($d\pi \rightarrow L\pi^*$), in addition to a number of weaker bands, assigned as d–d transitions.

The assignment of the two larger peaks in the spectra is straightforward, since in these $d^6$ species only two metal-to-ligand excitations are orbitally allowed, namely $^1A_{1g}(t_{2g}^6) \rightarrow {}^1T_{1u}(t_{2g}^5t_{1u}^1)$ and the $^1A_{1g}(t_{2g}^6) \rightarrow {}^1T_{1u}(t_{2g}^5t_{2u}^1)$ transition. The weaker bands present a more difficult problem, and a number of slightly different assignments have been proposed.[1-6] Eventually however, the original assignment of Beach and Gray became rather widely accepted.[7] It is shown in Table I for the isoelectronic series $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$.

As can be seen from Table I, in each spectrum five bands were identified. For $V(CO)_6^-$ and $Cr(CO)_6$ the energetic sequence of the two strong and three weaker bands is identical, and therefore, in both cases, the strong bands were assigned as MLCT transitions, the weak signal between these bands was assigned as a ligand field transition to $^1T_{2g}$, and the two lowest weak bands were assigned as vibrational components of the ligand field transition to $^1T_{1g}$. The latter assignment was partially substantiated by the fact that the separation between the two signals nearly equals the CO stretching frequence.[2]

**Table I.** Electronic Spectral data for $V(CO)_6^-$, $Cr(CO)_6$, and $Mn(CO)_6^+$ in Acetonitrile Solution and Assignment According to Reference 2

| complex | $\bar{\nu}$, $cm^{-1}$ | $\epsilon$, $cm^{-1}$ | $10^2f$ | assignment |
|---|---|---|---|---|
| $[n\text{-}B_4N][V(CO)_6]$ | $\{$23 200 | 300 | 0.28 | vibrational components |
| | 25 100 | 1 640 | 2.0 | of $^1A_{1g} \rightarrow {}^1T_{1g}$ (d–d) |
| | 28 400 | 6 240 | 8.0 | $^1A_{1g} \rightarrow {}^1T_{1u}(d\text{–}t_{1u})$ |
| | ~31 100 | 3 300 | ~3.2 | $^1A_{1g} \rightarrow {}^1T_{2g}(d\text{–}d)$ |
| | 37 550 | 60 900 | 120 | $^1A_{1g} \rightarrow {}^1T_{1u}(d\text{–}t_{2u})$ |
| | 41 200 | 21 200 | 29 | |
| | 43 700 | 13 700 | 16 | |
| $Cr(CO)_6$ | $\{$29 500 | 700 | 0.61 | vibrational components |
| | 31 550 | 2 670 | 3.3 | of $^1A_{1g} \rightarrow {}^1T_{1g}(d\text{–}d)$ |
| | 35 700 | 13 100 | 24 | $^1A_{1g} \rightarrow {}^1T_{1u}(d\text{–}t_{1u})$ |
| | 38 850 | 3 500 | 4.0 | $^1A_{1g} \rightarrow {}^1T_{2g}(d\text{–}d)$ |
| | 43 600 | 85 100 | 227 | $^1A_{1g} \rightarrow {}^1T_{1u}(d\text{–}t_{2u})$ |
| | >50 000 | | | |
| $[Mn(CO)_6][BF_4]$ | ~33 250 | 600 | 1 | $^1A_{1g} \rightarrow {}^3T_{1g}(d\text{–}d)$ |
| | $\{$~37 300 | 1 100 | 2 | vibrational components |
| | ~39 600 | 2 200 | 2 | of $^1A_{1g} \rightarrow {}^1T_{1g}(d\text{–}d)$ |
| | 44 500 | 16 000 | 34 | $^1A_{1g} \rightarrow {}^1T_{1u}(d\text{–}t_{1u})$ |
| | 49 900 | 27 000 | 61 | $^1A_{1g} \rightarrow {}^1T_{1u}(d\text{–}t_{2u})$ |

The $Mn(CO)_6^+$ spectrum is slightly different. The $^1T_{2g}$ band between the two MLCT signals turned out to be undetectable, but instead of a new weak signal appeared below the two $^1T_{1g}$ bands. The latter signal was assigned as a spin-forbidden ligand field transition to $^3T_{1g}$.

According to these assignments, the different transitions all move to higher energies in the order $V(CO)_6^- < Cr(CO)_6 < Mn(CO)_6^+$. For the M → L charge-transfer bands, this behavior is to be expected since the d-orbital energy must decrease, and therefore, the $\pi^*$–d energy difference must increase as the charge on the central metal becomes more positive. The simultaneous increase of the ligand field transition energies however is less obvious. Starting from the assignments in Table I, the following $10Dq$ values were calculated for the three complexes:[2]

$$V(CO)_6^-:\ 10Dq = 25\,500\ cm^{-1}$$

$$Cr(CO)_6:\ 10Dq = 32\,200\ cm^{-1}$$

$$Mn(CO)_6^+:\ 10Dq = 41\,050\ cm^{-1}$$

Now according to the traditional MO picture, the ligand field separation $10Dq$ between the $e_g$ and $t_{2g}$ orbitals in these carbonyl complexes arises from two mechanisms: on the one hand, the CO to metal $\sigma$-donation causes a destabilization of the $e_g$ orbitals, while on the other hand the $t_{2g}$ orbitals are stabilized due to $\pi$-back-donation into the empty $\pi^*(CO)$ orbitals. During the last decades

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