Article

Electronic Structure of $Re_2(O_2CR)_4Cl_2$ Complexes (R = H, CMe$_3$) and Reassignment of the Electronic Absorption Spectrum of $Re_2(O_2CCMe_3)_4Cl_2$

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ABSTRACT: Electronic structure calculations on two dinuclear rhenium(III) carboxylate complexes, $Re_2(O_2CH)_4Cl_2$ and $Re_2(O_2CCMe_3)_4Cl_2$, are presented and discussed. Allowed electronic transitions for both molecules were calculated using time-dependent density functional theory (TDDFT). The results for the pivalate dimer, $Re_2(O_2CCMe_3)_4Cl_2$, are compared with previously reported single-crystal polarized absorption spectra obtained by Martin and co-workers (*Inorg. Chem.* **1984**, 23, 699−701). Several revisions to the previous spectral assignments are proposed.
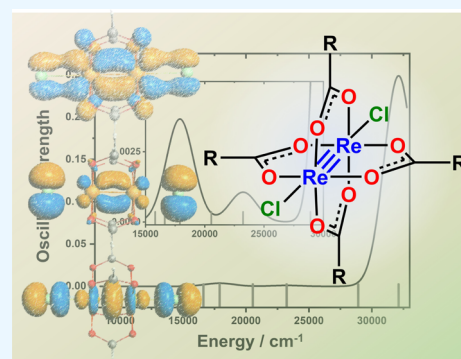
INTRODUCTION

Dinuclear rhenium(III) carboxylates of the type $Re_2(O_2CR)_4Cl_2$ with a classic "paddle-wheel" structure (Figure 1) are a well-known subclass of d^4–d^4 quadruply metal−metal
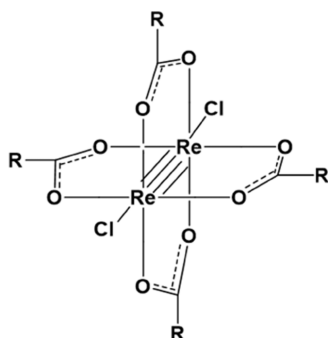
Figure 1. Structure of a generic quadruply metal−metal bonded $Re_2(O_2CR)_4Cl_2$ complex (R = H, alkyl, aryl).

bonded complexes.[1] Several preparative routes exist, but for the alkyl carboxylates, the simplest route is arguably the thermal reaction of the tetra-*n*-butyl ammonium salt of octachlorodirhenate, $(Bu_4N)_2[Re_2Cl_8]$,[2] with an alkyl carboxylic acid, usually admixed with the appropriate anhydride, under air- and moisture-free conditions (eq 1).[3] Under slightly different conditions, eq 1 is reversible and was offered as supporting evidence that the rhenium−rhenium quadruple bond

$$(Bu_4N)_2[Re_2Cl_8] + 4RCO_2H$$
$$\rightarrow Re_2(O_2CR)_4Cl_2 + 4HCl + 2Bu_4NCl \quad (1)$$
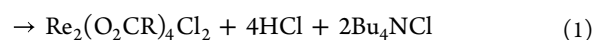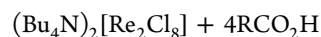
was maintained in $Re_2(O_2CR)_4Cl_2$ complexes.[4] Several of these dinuclear rhenium(III) carboxylate compounds have been structurally characterized,[1] including the pivalate derivative, $Re_2(O_2CCMe_3)_4Cl_2$.[5] The latter crystallizes in the tetragonal space group $I4/m$ with Z = 2. It has a Re−Re bond length of 2.234(1) Å and a Re−Cl bond length of 2.477(3) Å, and the molecules have crystallographically imposed $4/m$ (C_{4h}) symmetry. The Cl−Re−Re−Cl linkage (the molecular *z*-axis) is perfectly linear and parallel to the crystallographic *c*-axis. As Collins et al. recognized,[5] $Re_2(O_2CCMe_3)_4Cl_2$ is an ideal candidate for single-crystal polarized absorption spectroscopy, but it was several years before such an investigation was undertaken by Martin et al.[6] The latter authors collected single-crystal absorption data from 15 000 to 35 000 cm^{-1} and assigned a peak at 20 600 cm^{-1} with molecular *z* polarization as the electric-dipole-allowed $^1A_{1g} \rightarrow {}^1A_{2u}$ ($\delta \rightarrow \delta^*$) transition. Assignments for other absorption features were made, but the authors did not have access to electronic structure calculations on any $Re_2(O_2CR)_4Cl_2$ molecules and used the relativistic SCF-

$X\alpha$-SW calculations of Bursten et al. on $[Re_2Cl_8]^{2-}$ as a substitute guide.[7] Given the fact that rhenium(III) carboxylates are among the earliest examples of quadruply metal−metal bonded complexes,[1,8] it is surprising that the electronic structures of prototypical $Re_2(O_2CR)_4Cl_2$ compounds have not been thoroughly investigated by modern theoretical techniques[9] and used as an aid in verifying the assignments of the bands observed in the single-crystal spectrum of $Re_2(O_2CCMe_3)_4Cl_2$.[6] This and a continuing interest in the chemistry and spectroscopy of metal−metal multiply bonded complexes[10−12] motivate the work presented herein.

■ EXPERIMENTAL SECTION

Materials. $Re_2(O_2CCMe_3)_4Cl_2$ was prepared as described in the literature and purified by recrystallization from dichloromethane (DCM). Synthetic details, including slight modifications to the published route,[3] are provided in the Supporting Information. The modifications were superficial and made for convenience. The solution electronic absorption spectrum of $Re_2(O_2CCMe_3)_4Cl_2$ in DCM (see below) was in good agreement with that reported in the literature.[5,13]

Computational Methods. Calculations employed the Amsterdam Modeling Suite, ADF 2020.102.[14,15] The PBE0 functional[16] gave a good estimate of the Re−Re, Re−Cl, and Re−O distances (vide infra). Triple-zeta polarized (TZP) basis sets were used, with triple-zeta accuracy sets of Slater-type orbitals and with polarization functions added to all atoms.[17] Use of a hybrid functional necessitated inclusion of all core orbitals in the calculations. Scalar relativistic corrections were made using zero-order relativistic approximation (ZORA) formalism.[18] Geometries were optimized for $Re_2(O_2CR)_4Cl_2$, where R = H and CMe_3 with D_{4h} for the formate and C_{4v}, C_{2h}, and no symmetry for the pivalate.[19] A fragment calculation on $Re_2(O_2CH)_4Cl_2$ built the molecule using basis sets from hypothetical $Re_2(O_2CH)_4$ and Cl_2. Allowed transitions were calculated for the $Re_2(O_2CR)_4Cl_2$ molecules (R = H, CMe_3) using time-dependent density functional theory (TDDFT).[20] The energies of the lowest triplet excited states were calculated by unrestricted calculations with S = 1 using the optimized geometry of the parent singlet molecules.

■ RESULTS AND DISCUSSION

Cartesian coordinates for the optimized structures of $Re_2(O_2CH)_4Cl_2$ and $Re_2(O_2CCMe_3)_4Cl_2$ are provided in the Supporting Information. Both molecules adopt the paddle-wheel geometry with short metal−metal distances consistent with a Re−Re quadruple bond. The calculated Re−Re, Re−Cl, and Re−O distances of $Re_2(O_2CCMe_3)_4Cl_2$ are in good agreement with those reported in the literature (Table 1).[5] An X-ray crystal structure for the formate complex, $Re_2(O_2CH)_4Cl_2$,[21] has not been reported.

Bonding. A molecular orbital (MO) scheme for selected MOs of $Re_2(O_2CH)_4Cl_2$ is shown in Figure 2. The MO energies and % rhenium metal character for both $Re_2(O_2CR)_4Cl_2$

Table 1. Selected Bond Lengths (Å) for $Re_2(O_2CR)_4Cl_2$ (R = H, CMe_3)

	R = H, calc.	R = CMe₃, calc.	R = CMe₃, exp.[5]
Re−Re	2.241	2.224	2.236(1)
Re−Cl	2.435	2.460, 2.462	2.477(3)
Re−O	2.028	2.020, 2.025	2.025(4)

complexes are given in Table 2. The selection was made to show principally the orbitals with Re−Re bonding and antibonding character and includes all orbitals involved in the low-energy electronic transitions.

The ordering of molecular orbitals (MOs) is identical in the two compounds, and their composition is very similar. The MOs of the pivalate complex are higher in energy than the MOs of the formate complex. Most noteworthy is the fact that the top two occupied levels ($2a_{1g}$, $2e_u$ for R = H; $3a_1$, $3e$ for R = CMe_3) are predominantly halide in character. The genesis of these orbitals is σ overlap of the rhenium $5d_{z^2}$ orbitals with the Cl $3p_z$ orbitals and π overlap of the rhenium $5d_{xz}$ and $5d_{yz}$ orbitals with the chlorine $3p_x$ and $3p_y$ orbitals, respectively (Figure 2). The σ bonding manifold merits some additional comment. As noted above, the Re−Cl distance in $Re_2(O_2CCMe_3)_4Cl_2$ is ∼2.48 Å. In $[Re_2Cl_8]^{2-}$, the Re−Cl distance is ∼2.32 Å.[22] Thus, the axial Re−Cl interaction in $Re_2(O_2CCMe_3)_4Cl_2$ appears to be relatively weak. Bonding along the 4-fold axis is controlled principally by four orbitals, the two Re $5d_{z^2}$ orbitals and the two Cl $3p_z$ orbitals, the contributions from Re $6p_z$ orbitals being insignificant. Together, they form two bonding a_{1g} orbitals and two antibonding a_{2u} orbitals, as illustrated in Figure 3. These four orbitals hold a total of six electrons. The favorable Re−Cl σ-bonding interaction of the $1a_{1g}$ orbital is, to a certain extent, canceled by the occupation of the $2a_{1g}$ orbital, but a strong Re−Re σ-bond is maintained. The $1a_{2u}$ orbital is dominated by the Cl $3p_z$ orbitals, so the implied Re−Re antibonding interaction is minimized, and the two axial Re−Cl bonds may be considered "half-bonds."[23] We are unaware of any gas-phase photoelectron spectroscopic (PES) studies of $Re_2(O_2CR)_4Cl_2$ molecules, which could be used to benchmark the calculated MO diagram and the presence of the high-lying chloride-based orbitals. The dinuclear rhenium(III) trifluoroacetate complex, $Re_2(O_2CCF_3)_4Cl_2$, might be a good candidate for such measurements, but its synthesis and characterization have not been reported. Attempts to prepare this complex are underway in our laboratory.

The Re−Re δ bonding orbital lies third in the occupied orbital manifold of $Re_2(O_2CR)_4Cl_2$. In $[Re_2Cl_8]^{2-}$, the Re−Re δ orbital is the HOMO.[7] As an aside, we see no electronic reason why the electron-rich, triply bonded rhenium(II) carboxylates, $Re_2(O_2CR)_4$, with $\sigma^2\pi^4\delta^2\delta^{*2}$ ground states should not be isolable. However, none have been reported to date.

Electronic Excitations. Singlet-to-singlet, symmetry-allowed transitions were calculated for both molecules using TDDFT.[20] Table 3 gives the excitation energies and the orbital character of the transitions.
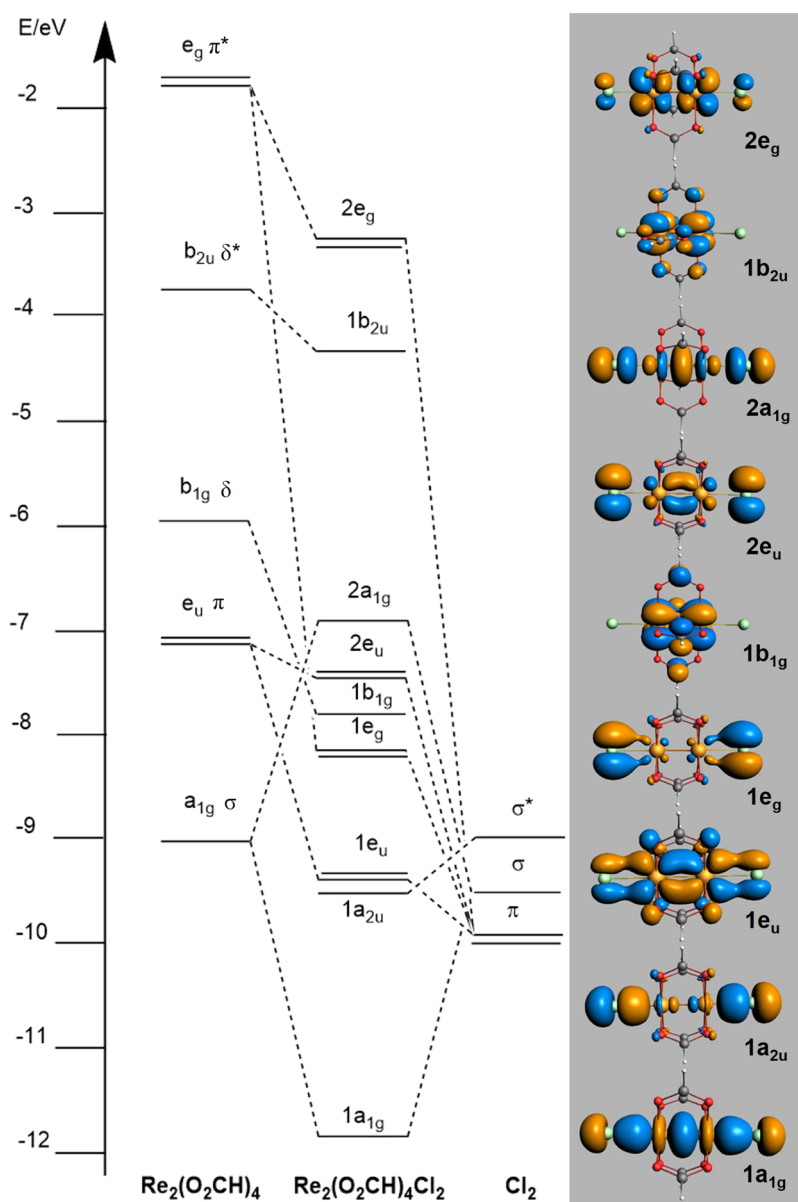
The calculated spectrum of $Re_2(O_2CCMe_3)_4Cl_2$ in the low-energy region is shown in Figure 4a.

The pivalate complex, being of lower symmetry, has more allowed transitions than the formate complex, those of g → g and u → u symmetry in the latter being now formally allowed in the former but of lower intensity. It should be noted that even symmetry-forbidden transitions may be evident as a consequence of vibronic coupling. The lowest energy transition for the pivalate complex is of $Cl(\pi^*) \rightarrow \delta^*$ character, whereas in the formate complex, this transition lies at higher energy than the $\delta \rightarrow \delta^*$ excitation.

As noted above, single-crystal polarized electronic absorption spectra have been recorded for $Re_2(O_2CCMe_3)_4Cl_2$.[6] The orientation of the crystal and use of polarized light enable transitions of A_1 and E symmetry to be distinguished, A_1 transitions being excited by z-polarized light and E transitions

Figure 2. MO scheme for $Re_2(O_2CH)_4Cl_2$ built from $Re_2(O_2CH)_4$ and Cl_2. $Re_2(O_2CH)_4Cl_2$ molecular orbitals are occupied up to the $2a_{1g}$ level. For the e-type orbitals, only one orientation is pictured.

Table 2. Molecular Orbital (MO) Energies and % Re Character for $Re_2(O_2CR)_4Cl_2$ (R = H, CMe_3)

| MO type[a]	$Re_2(O_2CH)_4Cl_2$			$Re_2(O_2CCMe_3)_4Cl_2$		
	symmetry	energy, eV	% Re	symmetry	energy, eV	% Re
π^*	$2e_g$	−3.39	87	4e	−2.74	88
δ^*	$1b_{2u}$	−4.33	79	$2b_1$	−3.64	77
$Cl(\sigma)$	$2a_{1g}$	−6.94	34	$3a_1$	−6.46	34
$Cl(\pi)$	$2e_u$	−7.47	21	3e	−7.00	19
δ	$1b_{1g}$	−7.84	77	$1b_1$	−7.03	72
$Cl(\pi^*)$	$1e_g$	−8.17	11	2e	−7.62	8
π	$1e_u$	−9.42	57	1e	−8.87	53
$Cl(\sigma^*)$	$1a_{2u}$	−9.49	19	$2a_1$	−8.88	17
σ	$1a_{1g}$	−11.86	66	$1a_1$	−11.26	64

[a]MOs are labeled by their principal character and symmetry, either Cl or Re−Re bonding character. The $2a_{1g}$ and $3a_1$ orbitals are the highest filled for $Re_2(O_2CH)_4Cl_2$ and $Re_2(O_2CCMe_3)_4Cl_2$, respectively.

by x,y-polarized light. A summary of the experimental transition energies and their symmetries is given in Table 4.

A solution spectrum of the pivalate dimer in DCM has been reported[5,13] with band maxima at ca. 20 000 cm^{-1}, ca. 25 000 cm^{-1}, and ca. 35 970 cm^{-1}. The trace of the solution spectrum suggests that additional excitations may also be present at around 17 500 and 29 400 cm^{-1}. The spectrum has been reproduced in this work (Figure 4b), and band maxima are included in Table 4.

Proposed assignments by Martin, Huang, and Newman were confined to transitions between the occupied metal-based π and δ levels and the unoccupied π^* and δ^* levels. Thus, to account for the number of observed transitions, singlet-to-triplet transitions were also proposed. Notably, the x,y-polarized transition at 16 500 cm^{-1} was assigned to the $\delta \rightarrow \delta^*$ singlet-to-triplet transition. Calculations of the lowest energy triplet of $Re_2(O_2CCMe_3)_4Cl_2$ place the energy of this state 0.80 eV above the singlet ground state; hence, one would predict a transition
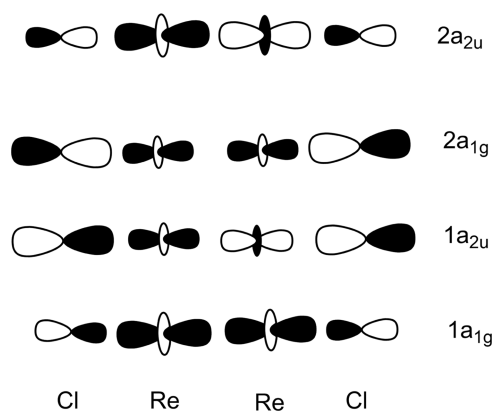
Figure 3. Diagrammatic representation of bonding along the 4-fold axis of $Re_2(O_2CCMe_3)_4Cl_2$ showing the phase combinations in the four relevant orbitals. They are occupied up to the $2a_{1g}$ level. The energies for the $1a_{1g}$, $1a_{2u}$, and $2a_{1g}$ MOs are given in Table 1. The energy of the $2a_{2u}$ orbital is much higher in energy (0.15 eV).

Table 3. Calculated Allowed Transitions for $Re_2(O_2CR)_4Cl_2$ (R = H, CMe₃) Giving the Symmetry of Each Transition, Orbital Character, Transition Energy (cm⁻¹), and Oscillator Strength

symmetry	orbital character		energy, cm⁻¹	oscillator strength
		$Re_2(O_2CH)_4Cl_2$		
A_{2u}	$\delta \to \delta^*$	$1b_{1g} \to 1b_{2u}$	18 512	0.0068
E_u	$Cl(\pi^*) \to \delta^*$	$1e_{1g} \to 1b_{2u}$	21 975	0.0002
A_{2u}	$Cl(\pi) \to \pi^*$	$2e_u \to 2e_g$	31 595	0.3195
		$Re_2(O_2CCMe_3)_4Cl_2$		
E	$Cl(\pi^*) \to \delta^*$	$3e \to 2b_1$	15 825	0.0000
E	$Cl(\sigma) \to \pi^*$	$3a_1 \to 4e$	16 631	0.0016
A_1	$\delta \to \delta^*$	$1b_1 \to 2b_1$	17 904	0.0037
E	$\delta \to \pi^*$	$1b_1 \to 4e$	20 551	0.0000
E	$Cl(\pi^*) \to \delta^*$	$2e \to 2b_1$	23 233	0.0011
E	$\pi \to \delta^*$	$1e \to 2b_1$	28 911	0.0000
A_1	$Cl(\pi) \to \pi^*$	$3e \to 4e$	32 121	0.2489

energy of ~6500 cm⁻¹ for the $^1A_{1g} \to {}^3A_{2u}$ transition.[24] This value is not dissimilar to that found (0.37 eV, ~3000 cm⁻¹) by Gagliardi and Roos for the energy of the $\delta \to \delta^*$ singlet-to-triplet transition of $Re_2Cl_8^{2-}$.[25] Gagliardi and Roos point out that the effective bond order of $Re_2Cl_8^{2-}$ is close to three, the δ bond

being weak. A good conceptual model is that the δ symmetry electrons on each metal center interact only weakly and that the $\delta \to \delta^*$ triplet transition reflects the energy of one of the electrons flipping its spin. Considering the presence of high-lying orbitals of dominant Cl character, our calculations suggest that the band at 16 500 cm⁻¹ is associated with the $3a_1 \to 4e$ or $3e \to 2b_1$ transition or both.

The assignment of the z-polarized band at 20 200 to the singlet $\delta \to \delta^*$ transition (mislabeled in Table 1 of ref 6 but not in the text) is supported by the calculated oscillator strength. The calculated energy of 17 904 cm⁻¹ gives a measure of the present calculation's accuracy. The presence of this transition in the experimental x,y-polarized crystal spectrum,[6] at much weaker oscillator strength, is accounted for by vibronic coupling.

One can also make plausible assignments of higher energy bands as given in Table 4, thus accounting for all but one of the bands noted in the single-crystal spectroscopic work. Although numerical agreement is not close for all bands, the predicted relative intensities correspond quite well with those observed. The crystal spectroscopy band at 24 700 cm⁻¹ (23 233 cm⁻¹ calc.) is assigned to the $2e \to 2b_1$ transition and has elements of $Cl(\pi^*) \to \delta^*$ character. In solution, this band shifts from 24 940 to 23 980 cm⁻¹ in the spectrum of $Re_2(O_2CCMe_3)_4Br_2$.[5,13] The weak x,y-polarized crystal spectroscopy band at 32 000 cm⁻¹ is assigned to the triplet $Cl(\pi) \to \pi^*$ transition. In solution, the singlet $Cl(\pi) \to \pi^*$ band is located at ~35 970 cm⁻¹ with an $\varepsilon \sim$ 20 000 M⁻¹cm⁻¹. This band is z-polarized but is beyond the range of the instrumentation used in the single-crystal experiments.[6] Our calculated energy for this transition is 32 121 cm⁻¹. It shifts to ~31 850 cm⁻¹ in the solution spectrum of $Re_2(O_2CCMe_3)_4Br_2$.[5,13]

CONCLUSIONS

The electronic structures of $Re_2(O_2CH)_4Cl_2$ and $Re_2(O_2CCMe_3)_4Cl_2$ have been investigated in detail for the first time. In both cases, the highest occupied molecular orbitals are halide-based orbitals associated with the Cl–Re–Re–Cl σ- and π-bonding interactions. Allowed electronic transitions for both molecules were calculated using time-dependent density functional theory (TDDFT). The agreement between the calculated and observed electronic transitions for $Re_2(O_2CCMe_3)_4Cl_2$ is quite good. Perhaps the main benefit of the calculations is to demonstrate that invoking singlet-to-triplet transitions to account for the experimental spectrum is unnecessary for most of the transitions and that the calculated

Table 4. Energies (cm⁻¹), Oscillator Strengths, and Polarizations of Electronic Transitions Observed for Crystalline[6] and Solution[a] $Re_2(O_2CCMe_3)_4Cl_2$

z polarization		x,y polarization			
band max	oscillator strength	band max	oscillator strength	previous assignment[6]	calc. assignment
		16 500	5×10^{-5}	$^1A_{1g} \to {}^3A_{2u}(\delta \to \delta^*)$	$Cl(\sigma) \to \pi^*$
20 200	3×10^{-3}	20 600	7×10^{-4}	$^1A_{1g} \to {}^1A_{2u}(\delta \to \delta^*)$	$\delta \to \delta^*$
20 000					
not resolved		21 600	1×10^{-5}	$^1A_{1g} \to {}^3E_g(\pi \to \delta^*)$	$\delta \to \pi^*$
24 700	1.5×10^{-4}	24 700	7×10^{-4}	$^1A_{1g} \to {}^1E_g(\pi \to \delta^*)$	$Cl(\pi^*) \to \delta^*$
24 900					
29 000	8×10^{-4}	29 000	$<2 \times 10^{-4}$	$^1A_{1g} \to {}^1E_g(\delta \to \pi^*)$	$\pi \to \delta^*$
29 400 (sh)[b]					
beyond range	beyond range	32 000	1.6×10^{-3}	spin-forbidden$\pi \to \pi^*$ or CT	spin-forbidden$Cl(\pi) \to \pi^*$
36 000				unassigned	spin-allowed$Cl(\pi) \to \pi^*$

[a]This work. [b]sh = shoulder.
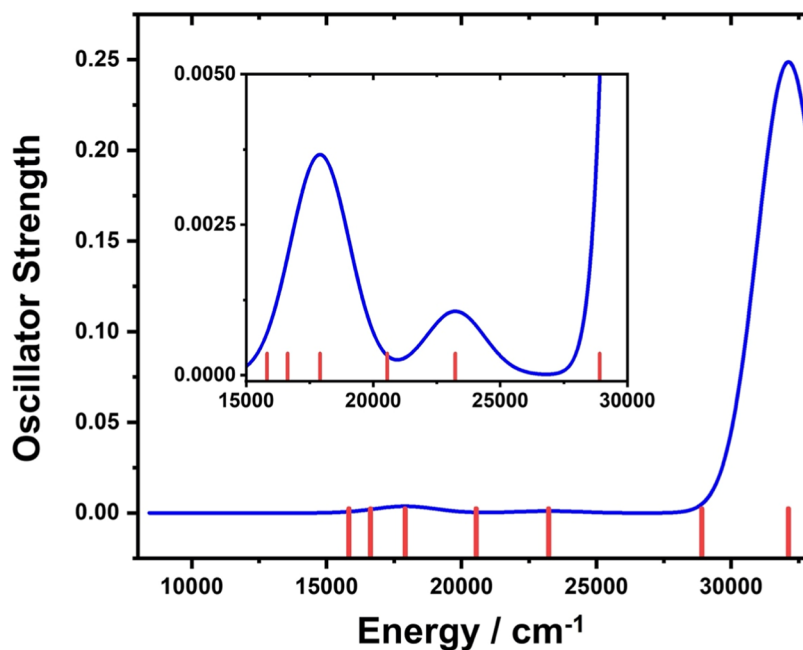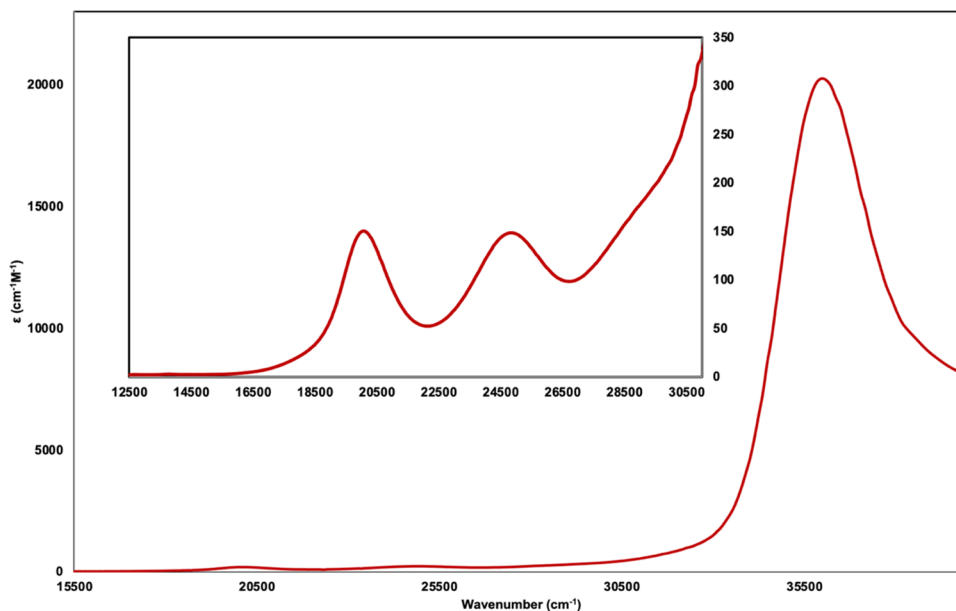
Figure 4. (a) Calculated electronic excitation spectrum of $Re_2(O_2CCMe_3)_4Cl_2$. (b) UV−vis spectrum of $Re_2(O_2CCMe_3)_4Cl_2$ in dichloromethane (DCM). The inset is a blowup of the low-energy region.

energy of the triplet $\delta \rightarrow \delta^*$ excited state relative to the ground state is similar to that found for $Re_2Cl_8^{2-}$.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsomega.2c07334.

> Experimental section, fractional coordinates for $Re_2(O_2CH)_4Cl_2$ and $Re_2(O_2CCMe_3)_4Cl_2$, and calculated.xyz files for $Re_2(O_2CH)_4Cl_2$ and $Re_2(O_2CCMe_3)_4Cl_2$ (PDF)

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Notes
The authors declare no competing financial interest.

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(9) (a) We are aware of two earlier papers on the electronic structures of rhenium(III) carboxylate compounds. One reports on $[Re_2(O_2CCF_3)Cl_6]^{1-}$, $Re_2[O_2CCCHCo_2(CO)_6]_4Cl_2$ and $Re_2(O_2CCMe_3)_4Cl_2$,[9b] and the second describes $Re_2(dppm)_2(O_2CC_6H_4)_2Cl_2$ and $Re_2(O_2CC_6H_4NO_2)_4Cl_2$, where dppm = $Ph_2PCH_2PPh_2$.[9c] There is some overlap between the work reported here and that described in ref 9b. However, the authors of the latter paper, as their title suggests, had a very different focus and did not address the optical spectroscopy described in refs 5 and 6. (b) Vega, A.; Calvo, V.; Manzur, J.; Spodine, E.; Saillard, J-Y. New Dirhenium(III) Compounds Bridged by Carboxylate Ligands: N-$(C_4H_9)_4[Re_2(OOCCF_3)Cl_6]$ and $Re_2(OOCCCHCo_2(CO)_6)_4Cl_2$. *Inorg. Chem.* **2002**, *41*, 5382−5387. (c) Alberding, B. G.; Chisholm,

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