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The Lowest-Energy Ligand to Metal Charge-Transfer Absorption Band of *trans*-$[OsO_2(Malonate)_2]^{2-}$

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The resolved structure of the lowest-energy oxo to osmium charge-transfer absorption band of *trans*-$[OsO_2(malonate)_2]^{2-}$ is analyzed on the basis of the exact molecular C_i symmetry determined from the structure of a crystal used for spectroscopy. The multiple progressions observed in the polarized spectra are rationalized in terms of the deviations from idealized D_{4h} point group symmetry and compared to the spectra observed for complexes with D_{2h} symmetry such as *trans*-$[OsO_2(oxalate)_2]^{2-}$ that show only a single dominant progression for this transition.

Introduction

trans-Dioxo complexes of metals with the [Kr]$5d^2$ electron configuration are a class of compounds with interesting structural, spectroscopic, photochemical, and electrochemical properties.[1−11] The most striking aspect of the absorption spectra of *trans*-dioxo complexes of osmium(VI) are two charge-transfer bands in the visible spectral region with a structure that is partially resolved even at room temperature in solution.[2,4−6,9,10,13,14]

We report polarized absorption spectra of the title complex at temperatures between 10 and 295 K and the structure of the $(Bu_4N)_2[(OsO_2(malonate)_2]$ crystals used for spectroscopy. The unpolarized spectra correspond to those in the literature,[2] but the distinct polarization effects are essential to rationalize the resolved structure in the absorption spectra. Our crystal structure shows only a single site for the *trans*-$OsO_2(malonate)_2{}^{2-}$ chromophore, in agreement with a recent literature structure.[12] We determine a space group different from ref 12 owing to the packing of the *tert*-butylammonium cations. This result underlines the importance of crystal structure determinations on samples used for spectroscopy.

Experimental Section

Both $(Bu_4N)_2[OsO_2(malonate)_2]$ and $(Bu_4N)_2[OsO_2(oxalate)_2]$ were prepared according to literature methods from $K_2OsO_4 \cdot 2\ H_2O$ (Strem Chemicals).[2] The malonate complex crystallizes as yellow needles with optical extinction directions parallel and perpendicular to the needle axis. The purity of all samples was checked by IR, Raman, and electronic spectroscopy, and a crystal of $(Bu_4N)_2[OsO_2(malonate)]_2$ was examined by X-ray diffraction.

Polarized absorption spectra of crystals were measured on a Varian Cary 5E spectrometer with the sample in a helium gas flow cryostat (Oxford Instruments CF-1204). The instrumentation for Raman and luminescence spectroscopy has been described elsewhere.[15,16]

The X-ray diffraction work was carried out at room temperature on an Enraf-Nonius CAD-4 diffractometer using graphite monochromatized Cu Kα radiation. The reduced cell deduced from 25 reflections observed on a rotation photograph indicated a primitive monoclinic lattice with the crystallographic *a* axis parallel to the needle axis of the sample crystal. The $2/m$ Laue symmetry was subsequently checked from the full data set, and the space group $P2_1/n$ was determined unambiguously from the systematic absences. The crystallographic data are collected in Table 1.

A whole sphere of data (16 779 reflections) were collected and corrected for absorption (NRCVAX package).[17] Equivalent reflections were averaged and corrected for the effects of Lorentz and polarization. The final data set consisted of 4295 independent hkl and $\bar{h}kl$ reflections, of which 2575 with $I > 2\sigma(I)$ were used for the structure determination.

The structure was solved by the direct methods of SHELXS-86[18] and ΔF syntheses. Least-squares refinement was done on F^2 with SHELXL-96.[19] The non-hydrogen atoms were refined anisotropically. Hydrogens were placed at idealized positions and refined as riding atoms, with isotropic thermal parameters 20% (methylene) or 50% (methyl) greater than for the connected atom. The terminal portion of chains 3 and 4 in the Bu_4N^+ ion showed disorder or very high thermal motion, and the refined coordinates are not totally reliable. Attempts to describe this portion as superimposed disordered individuals failed. The final ΔF map was featureless except for a few residuals of $\pm|0.4-0.6|$ e/Å^3 near the Os atom or in the disordered part of the Bu_4N^+ ion.

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Table 1. Crystallographic Data

formula	$C_{38}H_{76}N_2O_{10}Os$
fw	911.20
space group	$P2_1/n$
a (Å)	9.667(3)
b (Å)	18.264(8)
c (Å)	13.163(6)
β(deg)	102.41(3)
V (Å^3)	2269.7(16)
Z	2
ρ_{calcd} (g/cm^3)	1.333
μ(mm^{-1})	5.715
temp (°C)	293(2)
λ(Å)	1.54056
R1^a	0.0289
wR2^a	0.0648

^{a} $R1 = \Sigma(||F_o| - |F_c||/\Sigma(|F_o|)$; $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$.

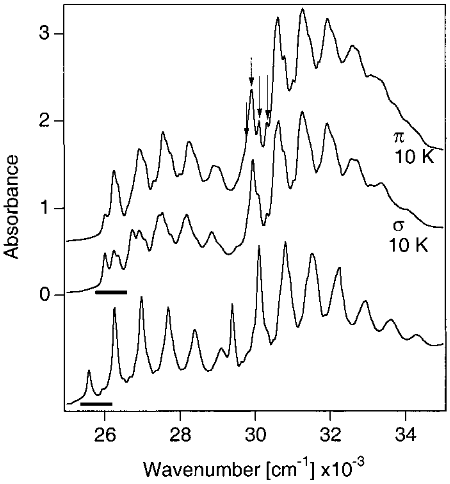

Figure 1. Top traces: overall single-crystal absorption spectra of $(Bu_4N)_2[OsO_2(malonate)_2]$ in the region of the lowest-energy charge-transfer bands measured with light polarized parallel (π) and perpendicular (σ) to the osmium−oxo bond. Bottom trace: absorption spectrum of $(Bu_4N)_2[OsO_2(oxalate)_2]$. Traces are offset along the ordinate axis for clarity. All spectra are measured at 10 K. The horizontal bars denote the wavenumber intervals shown in detail in Figures 2.

Results

Absorption Spectra. Figure 1 shows low-temperature single-crystal spectra of $(Bu_4N)_2[OsO_2(malonate)_2]$ at different temperatures and polarizations in comparison with the low-temperature spectrum of $(Bu_4N)_2[OsO_2(oxalate)_2]$[2,14] in the region of the two lowest-energy charge-transfer bands. The total intensity of the bands in Figure 1 is independent of temperature. The average spacing of the main progressions forming the lowest-energy band of the title compound in Figure 1 is 670 cm^{-1}; it is 705 cm^{-1} for the higher-energy band. The comparison of the low-temperature spectra shows overall similarities but a larger number of resolved peaks for the title compound than for the oxalate complex. An additional difference is that one set of resolved peaks forming the lowest-energy band of the title compound is predominantly π-polarized, in contrast to the oxalate complex where the shapes and relative intensities of the resolved peaks do not vary with polarization.[14]

A detailed view of the lowest-energy charge-transfer peaks of the title compound is given in Figure 2a. The polarized spectra in the main figure show that the middle peak is predominantly π-polarized (parallel to the crystallographic c axis and the osmium−oxo bond); all three transitions are weak with almost identical intensities in the perpendicular (σ) polarization. The temperature dependence of the spectrum in this polarization is shown in the inset to the figure. The peaks become broader as temperature increases, but the energies of the maxima are independent of temperature. We conclude that there is no structural phase transition in the temperature range examined. The energy differences between the bands are 230 and 100 cm^{-1}, significantly less than the average separation of 670 cm^{-1} between members of each progression. The onset of the lowest-energy band for the oxalate complex in Figure 2b shows a single intense peak and a very weak transition higher in energy by 380 cm^{-1}, a larger difference than between the resolved peaks of the title compound.

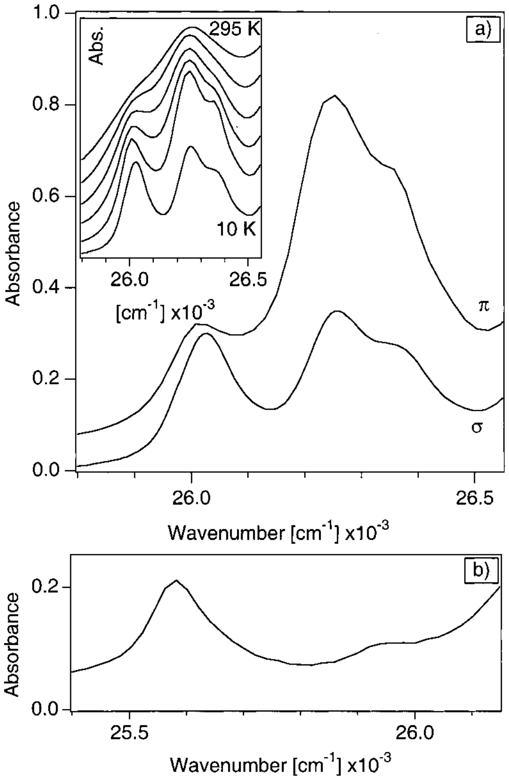

Figure 2. (a) Detailed view of the resolved lowest-energy charge-transfer peaks of $(Bu_4N)_2[OsO_2(malonate)_2]$. The main figure shows polarized spectra measured at 10 K; the inset shows σ-polarized spectra at temperatures of (top to bottom) 295, 230, 180, 130, 80, and 10 K. Traces are offset along the ordinate axis for clarity. (b) Detailed view of the lowest-energy charge-transfer peaks of $(Bu_4N)_2[OsO_2(oxalate)_2]$ at 10 K. The ordinates in both (a) and (b) cover a wavenumber range of 750 cm^{-1} given as horizontal bars in Figure 1.

We observe a superposition of four progressions forming the second band of the title compound, as indicated by the arrows in Figure 1. Their lowest energy maxima are at −95, 195, and 430 cm^{-1} relative to the maximum of the first peak of the most intense progression at 29 914 cm^{-1}. A similar pattern of four progressions is reported in the literature[2] with band maxima that differ by less than 100 cm^{-1} from our values, a difference that could be due to the polymorphism of the title compound, discussed in the following section.

Crystal Structure of $(Bu_4N)_2[OsO_2(malonate)_2]$. The unit cell contains well-separated Bu_4N^+ and *trans*-$[OsO_2(malonate)_2]^{2-}$ ions (Figure 3). The $[OsO_2(mal)_2]^{2-}$ ion sits on a crystallographic inversion center. Its bond lengths and angles in Table 2 are very similar to those reported recently for a different polymorph of the same compound.[12] The Os−O single bonds (mean 2.032(3) Å) compare well with those found for other carboxylates.[20−23] As expected, increased double-bond character makes the free C−O bonds (1.219(5) and 1.205(6) Å) shorter

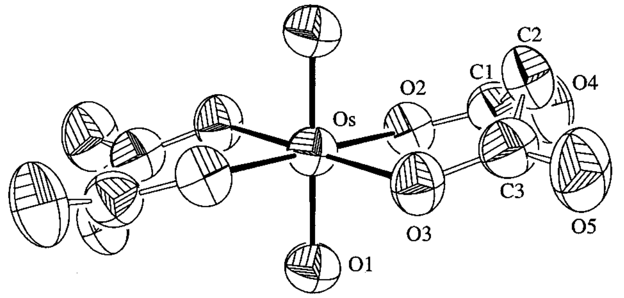

Figure 3. ORTEP view of the *trans*-[OsO$_2$(malonate)$_2$]$^{2-}$ ion. The Os atom lies on a crystallographic inversion center. Ellipsoids correspond to 50% probability. Hydrogen atoms are omitted for clarity.

Table 2. Bond Lengths (Å) and Angles (deg)

Os−O(1)	1.716(3)	Os−O(2)	2.031(3)
Os−O(3)	2.034(3)	O(2)−C(1)	1.295(6)
O(3)−C(3)	1.289(6)	O(4)−C(1)	1.205(6)
O(5)−C(3)	1.219(5)	C(1)−C(2)	1.521(7)
C(2)−C(3)	1.521(7)		
O(1)−Os−O(1)^a	180.0	O(1)−Os−O(2)^a	88.69(14)
O(1)−Os−O(2)	91.31(14)	O(1)−Os−O(3)^a	88.79(14)
O(1)−Os−O(3)	91.21(14)	O(2)−Os−O(2)^a	180.0
O(2)−Os−O(3)^a	88.07(13)	O(2)−Os−O(3)	91.93(13)
O(3)a−Os−O(3)	180.0	C(1)−O(2)−Os	123.6(3)
C(3)−O(3)−Os	123.9(3)	O(4)−C(1)−O(2)	122.5(5)
O(4)−C(1)−C(2)	119.4(5)	O(2)−C(1)−C(2)	118.0(5)
C(3)−C(2)−C(1)	117.5(4)	O(5)−C(3)−O(3)	122.5(5)
O(5)−C(3)−C(2)	119.0(5)	O(3)−C(3)−C(2)	118.4(4)

^{a} $-x$, $1 - y$, $1 - z$.

than the coordinated ones (1.295(6) and 1.289(6) Å). The Os=O(1) distance (1.716(3) Å) is 0.015 Å shorter than the mean value based on 37 *trans*-O=Os=O units found in the Cambridge Crystallographic Database.[24] Three dianionic structures have been determined; in [OsO$_2$Cl$_4$]$^{2-}$, the Os=O distances are only slightly greater (1.718(4), 1.728(4) Å),[25] but in the two [OsO$_2$L^4]^2 complexes with macrocyclic tetraamide ligands (L^4), the distances are definitely greater ($\geq$1.735 Å).[26] In general, O donors (or R$^-$ groups) in the equatorial plane tend to keep the Os=O bonds shorter than average, whereas N donors have the opposite effect. For instance, Os=O bonds only slightly longer than ours were observed in the OsO$_4$N$_2$ systems [OsO$_2$(glycinate)$_2$] (1.731(3) Å)[20] and [OsO$_2$py$_2$(oxalate)] (1.729(5) Å),[23] whereas longer bonds are found for OsO$_2$N$_4$ systems such as [OsO$_2$en$_2$]$^{2+}$ (1.74(1) Å)[13] and various [OsO$_2$L^4] macrocyclic complexes (1.735−1.745 Å).[6,26−28]

The OsO$_6$ octahedron is remarkably regular, considering that two chelate rings are present. The trans angles are rigorously equal to 180° by crystallographic symmetry, whereas the cis angles range from 88.1(1) to 91.9(1)°. Flexibility introduced by the methylene group allows the malonate to coordinate with minimal distortion around metal centers. The chelate ring adopts a flattened boat conformation commonly found in nonbridging malonate ligands.[29] The O2−C1−C3−O3 atoms are coplanar within 0.024(2) Å. Os and C2 are displaced from this plane, on the same side, by 0.497(6) and 0.553(8) Å, respectively, whereas planarity at C1 and C3 requires that O4 and O5 be displaced on the opposite side (0.454(8) and 0.305(9) Å, respectively). In this flattened boat, the O2−Os−O3 and C1−C2−C3 sections make dihedral angles of 20.6(3) and 44.5(5)°, respectively, with the O2−C1−C3−O3 part. The main structural difference between this compound and the other polymorph described earlier[12] lies in the conformation of the Bu$_4$N$^+$ counterion. According to Figure 4 in ref 12, the four butyl groups adopt a stretched conformation, whereas in our polymorph we determine a gauche arrangement in one of the butyl chains (about the C11−C12 bond). This leads to an appreciably different van der Waals envelope of the cation and induces a different packing pattern.

Discussion

Electronic States. The electronic states of 5d^2 configured *trans*-dioxo complexes have been described in detail before in idealized D_{4h} symmetry with the z axis parallel to the Os=O double bond.[3,11] The orbital excitation of an electron from the π_{nb} (e$_\text{u}$) orbitals localized on the oxo ligands to the doubly degenerate LUMO (e$_\text{g}$) orbitals with predominant d$_{xz}$, d$_{yz}$ character leads to ^{1,3}(A$_{1\text{u}}$, A$_{2\text{u}}$, B$_{1\text{u}}$, B$_{2\text{u}}$) excited states in the D_{4h} point group. These states become ^{1,3}(A$_\text{u}$, B$_{1\text{u}}$, A$_\text{u}$, B$_{1\text{u}}$) in the D_{2h} point group of the *trans*-[OsO$_2$(ox)$_2$]$^{2-}$ complex and finally ^{1,3}(A$_\text{u}$, A$_\text{u}$, A$_\text{u}$, A$_\text{u}$) in the C_i point group of the title compound.[30]

Energy separations of the d$_{xz}$, d$_{yz}$ (e$_\text{g}$), and π_{nb} (e$_\text{u}$) molecular orbitals that are degenerate in D_{4h} symmetry can be estimated from EHMO calculations[31] based on the structures of both *trans*-[OsO$_2$(malonate)$_2$$^{2-}$] and *trans*-[OsO$_2$(oxalate)$_2$$^{2-}$][12] and literature parameters for the osmium atom.[32] Our structure of the title compound leads to separations of 60 and 120 cm^{-1} for the d$_{xz}$, d$_{yz}$ and π_{nb} orbitals, respectively. The corresponding energy differences calculated from the literature structure[12] of the title compound are 20 and 100 cm^{-1}. For *trans*-[OsO$_2$(oxalate)$_2$$^{2-}$] we calculate energy differences of 290 and 510 cm^{-1} between the d$_{xz}$, d$_{yz}$ and π_{nb} orbitals, respectively. The calculated splittings are in qualitative agreement with the observed energy differences in Figure 2, which are larger for *trans*-[OsO$_2$(oxalate)$_2$]$^{2-}$ than for the title compound, but they do not account for the higher number of resolved peaks for the title compound in Figure 2a compared to the oxalate complex in Figure 2b. Selection rules are essential to rationalize the observed spectra, as is shown in the following section.

Electronic Transitions. Selection rules in the two relevant point group symmetries for *trans*-[OsO$_2$(oxalate)$_2$$^{2-}$] ($D_{2h}$) and *trans*-[OsO$_2$(malonate)$_2$$^{2-}$] ($C_i$) are used to estimate transition intensities. The ground state is ^{1}A$_{1\text{g}}$ in D_{2h} and ^{1}A$_\text{g}$ in C_i. In D_{2h} symmetry, the only allowed transition is the π-polarized ^{1}A$_\text{g}$ $\rightarrow$ ^{1}B$_{1\text{u}}$ band. Transitions to both ^{1}B$_{1\text{u}}$ states give rise to the broad peaks with shoulders forming the higher-energy band for the oxalate complex in Figure 1. The transitions to the lower-energy triplet states of the same symmetry can borrow intensity

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through spin−orbit coupling, and two progressions are expected for the lowest-energy charge-transfer band. It is likely that the two resolved peaks in Figure 2b correspond to the origins of these two forbidden bands, with the transition that is allowed in the D_{4h} parent symmetry being more intense. We cannot rule out the alternative that the weak higher energy peak in Figure 2b is a vibronic sideband, but its energy separation from the intense peak is smaller than the vibrational frequencies with predominant Os−oxalate character.[2,12] Single dominant progressions are observed in several complexes with D_{2h} point group symmetry such as *trans*-[OsO_2(oxalate)$_2$$^{2-}$][12,14] or *trans*-[$OsO_2(en)_2$$^{2+}$],[33] resulting in spectra similar to those expected for the higher D_{4h} point group, where only a single π-polarized transition is allowed.

The situation is different for the title compound with C_i point group symmetry. The charge-transfer transitions to all four ^1A_u states are fully allowed, and four progressions are observed for the higher-energy band, as indicated by the arrows in Figure 1. Transitions to all four triplet excited states can have nonzero intensities, and three resolved peaks are observed in Figure 2a. The transition to the fourth triplet state is most likely too close in energy to one of the other bands to be resolved. We observe one predominant transition polarized along the osmium−oxo axis (π polarization, Figure 2), as expected for the idealized D_{4h} symmetry. An assignment of the two higher-energy resolved peaks as vibronic sidebands of the lowest-energy resolved peak is unlikely because of the intensity distribution, which does not correspond to a Poisson envelope. In addition, we expect any low-frequency progressions to be in modes with significant osmium−malonate character, which have ground-state vibrational frequencies of approximately 550 cm^{-1},[2,12] values higher by more than a factor of 2 than the observed splittings in the absorption spectrum of Figure 2. In view of the electron configuration of the lowest charge-transfer excited state a reduction of the vibrational frequencies by a factor of 2 is not likely and a vibronic assignment can be ruled out on the basis of both the experimental energy differences and intensities. Polarized electronic transitions in absorption spectra can therefore provide detailed information even on small deviations from an idealized point group symmetry.

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Supporting Information Available: Complete crystallographic results for $(Bu_4N)_2[OsO_2(malonate)_2]$ in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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