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Polarized Electronic Absorption Spectra of Dichlorotetrakis(μ-pivalato)dirhenium(III)

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Single-crystal polarized absorption spectra are reported for $Re_2[O_2CC(CH_3)_3]_4Cl_2$ from 15 000 to 35 000 cm^{-1}. A peak at 20 600 cm^{-1} with molecular *z* polarization is assigned as the electric-dipole-allowed ${}^1A_{1g} \rightarrow {}^1A_{2u}$ ($\delta \rightarrow \delta^*$) transition. A much weaker band at 16 500 cm^{-1} with *x,y* polarization can be the spin-forbidden ${}^1A_{1g} \rightarrow {}^3A_{2u}$ ($\delta \rightarrow \delta^*$) transition. Weak transitions are observed at 21 600, 24 700, 29 000, and 32 000 cm^{-1}. They appear to be electric-dipole-forbidden, vibronically allowed transitions. Their possible assignments are discussed.

Introduction

The dimeric complexes of molybdenum(II) and rhenium(III) possess the unusual quadruple bond between the transition-metal atoms. Recent theoretical treatments of these systems[1-6] have generally indicated that the lowest energy electronic excitation in such dimers should be $\delta \rightarrow \delta^*$ transitions. Many of these dimers have four ligands with square-planar coordination of the bonds to each metal atom. With an eclipsed configuration of equivalent bonds the dimers possess a local D_{4h} symmetry. The $\delta \rightarrow \delta^*$ transition can then be characterized as $A_{1g} \rightarrow A_{2u}$ ($b_{1g} \rightarrow b_{2u}$). Such a singlet–singlet transition ${}^1A_{1g} \rightarrow {}^1A_{2u}$ should be electric dipole allowed for light polarized along the molecular *z* axis, which lies along the metal–metal bond. Single-crystal polarized optical spectroscopy therefore offers the possibility of a definitive identification of this transition. From crystal spectra for the tetrabutylammonium salts of octachloro- and octabromodirhenate(III), Cowman and Gray,[7] Cowman et al.,[8] and Trogler et al.[9] have demonstrated that the polarization for the electronic band observed at the lowest energy in single crystals was consistent with the $\delta \rightarrow \delta^*$ assignment. Fanwick et al.[10] similarly showed that the lowest energy observed band in $K_4Mo_2Cl_8 \cdot 2H_2O$ possessed the *z* polarization and assigned the band as the spin-allowed $\delta \rightarrow \delta^*$ transition. The polarized spectra for $K_4Mo_2(SO_4)_4 \cdot 2H_2O$, which contains the $Mo_2(SO_4)_4{}^{4-}$ dimeric ion with four bridging sulfates, also indicated that the lowest electronic band had the *z* polarization expected for the $\delta \rightarrow \delta^*$ polarization.[11]

A number of polarized single-crystal spectra for compounds with tetrakis(μ-carboxylato)dimolybdenum(II) complexes have presented a more puzzling situation for the lowest energy absorption band. Crystals of these compounds have provided highly resolved, unusually rich vibrational structures for the band at liquid-helium temperatures. Vibrational lines with comparable intensities were observed that had strikingly different polarization ratios so overwhelming intensity could not be assigned to a *z* polarization as expected for a normal dipole-allowed transition, ${}^1A_{1g} \rightarrow {}^1A_{2u}$. The spectra have frequently been compromised by the low crystal site symmetries and by the presence of defect components. However, from the orientation of the transition moment and hot bands observed for crystals of dimolybdenum tetraacetate[14] it is demonstrated that the band was electric dipole allowed for molecular *z* polarization, but the transition moment was so low that vibronically excited lines contributed a substantial intensity to the band. Single-crystal spectra for a tetrakis(carboxylato)-bridged rhenium(III) complex have not been reported previously because of the difficulty of preparing suitable crystalline specimens, resulting from the low solubility of the compounds in convenient solvents. The present study provides the spectra for such a dimer, viz., $Re_2[O_2CC(CH_3)_3]_4Cl_2$.

Experimental Section

The compound was prepared by the procedure of Collins, Cotton, and Gage.[15] They reported from an X-ray diffraction study the crystal structure with a tetragonal cell, *I*4/*m*, *Z* = 2, *a*:*c* = 11.469 (4):10.733

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Table I. Electronic Transitions, Polarized Intensities, and Proposed Assignments for $Re_2[O_2CC(CH_3)_3]_4Cl_2$

z polarizn		*x,y* polarizn		
band max ($\bar{\nu}$), cm^{-1}	osc str,[a] *f*	band max ($\bar{\nu}$), cm^{-1}	osc str,[a] *f*	proposed assgnt
		16 500	5×10^{-5}	$^1A_{1g} \rightarrow {}^3A_{2u}$, $\delta \rightarrow \delta^*$
20 200	3×10^{-3}	20 600	7×10^{-4}	$^1A_{1g} \rightarrow {}^3A_{2u}$, $\delta \rightarrow \delta^*$
b	*b*	21 600	1×10^{-5}	$^1A_{1g} \rightarrow {}^3E_g$, $\pi \rightarrow \delta^*$
24 700	1.5×10^{-4}	24 700	7×10^{-4}	$^1A_{1g} \rightarrow {}^1E_g$, $\pi \rightarrow \delta^*$
29 000	8×10^{-4}	29 000	$<2 \times 10^{-4}$	$^1A_{1g} \rightarrow {}^1E_g$, $\delta \rightarrow \pi^*$
c	*c*	32 000	1.6×10^{-3}	spin-forbidden $\pi \rightarrow \pi^*$ or CT

[a] Oscillator strengths at 6 K calculated by the expression $f = 4.32 \times 10^{-9} \int \epsilon \, d\bar{\nu}$. [b] Not resolved. [c] Beyond range.

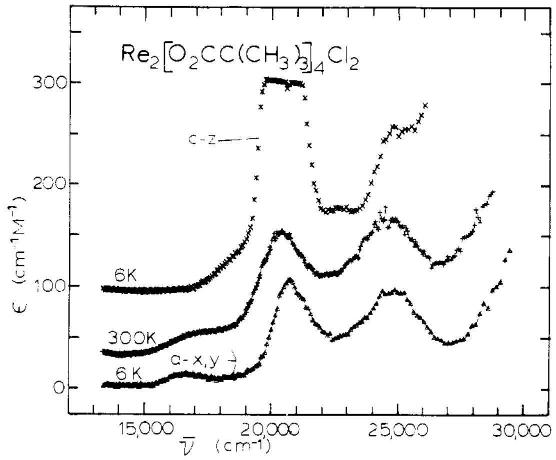

Figure 1. Polarized spectra for a $Re_2[O_2CC(CH_3)_3]_4Cl_2$ crystal that was 41 μm thick.

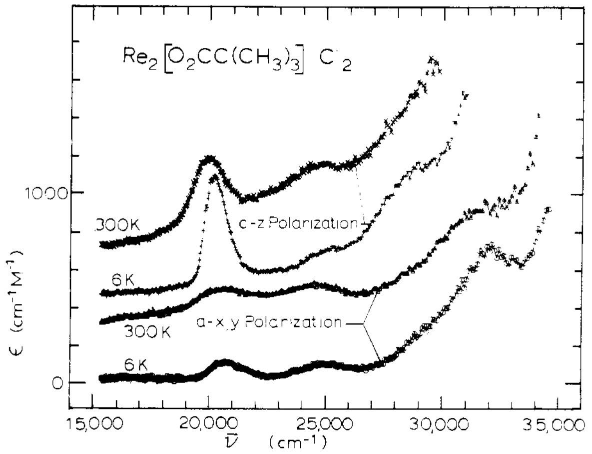

Figure 2. Polarized spectra for a $Re_2[O_2CC(CH_3)_3]_4Cl_2$ crystal that was 2.3 μm thick.

(1) Å. An examination of our crystals indicated they were mostly small square prisms. Faces containing the prism needle axis were distinctly dichroic, appearing red-orange for light polarized along the needle axis and yellowish for light polarized perpendicular to the axis. A prism was cemented to a glass fiber and mounted in the goniometer head of a computer-controlled four-circle X-ray diffractometer. From a series of oscillation photographs, coordinates of 12 reflections were entered into the computer program that tuned on the reflections and by means of standard programs computed cell constants to be a:b:c = 11.461:11.461:10.714 Å; α:β:γ = 89.96:90.00:90.00°. The needle faces were 100 with c directed along the needle axis. These values are in very good agreement with the values from the structure determination of Collins et al.[15] Indices of refraction for the 100 face were determined to be n_c = 1.674 and n_a = 1.572 by means of the Becke line method[16] with a set of standards prepared by the Cargille Laboratory.

Procedures and equipment for obtaining single-crystal spectra have been described previously.[17,18] A crystal whose thickness was 41 μm, measured by a calibrated scale in a microscope eyepiece, was mounted over a pinhole in a metal plate to provide the spectra of Figure 1. An attempt to recrystallize the material from chloroform yielded mostly amorphous powder. However, an examination of the product between crossed polarizers revealed a few flakes that were single crystals. One flake whose thickness was estimated to be 2.3 μm from its interference color and the birefringence was mounted over an oval pinhole of 40 × 50 μm dimensions, and the spectra recorded have been reproduced in Figure 2.

Results and Discussion

As Collins et al.[15] indicated, the structure of $Re_2[O_2CC(CH_3)_3]_4Cl_2$ is ideal for crystal spectroscopy. There is only one molecule in a primitive cell, and the site symmetry is $4/m$. The molecular z axis is directed along the crystallographic c axis so the c- and a-polarization absorptions give directly the molecular z and x,y absorptions, respectively. The locations of the maxima for the bands of the experimental spectra in Figures 1 and 2 together with the indicated intensities, polarizations, and proposed assignments are listed in Table I.

In the thick-crystal spectra, Figure 1, the most intense feature is a band in z polarization whose intensity was well beyond the capabilities of the instrumentation. However, with the thin crystal, Figure 2, it was possible to scan over this peak with a maximum of ca. 600 cm^{-1} M^{-1} at 20 200 cm^{-1} and 6 K. The peak height at 6 K in z polarization for this 20 200-cm^{-1} band is distinctly higher than at 300 K. This band is clearly electric dipole allowed in this polarization since the higher peak height implies that the intensity does not fall off significantly at low temperatures as should that for a vibronically allowed but dipole-forbidden band. It seems appropriate to assign this band to the $^1A_{1g} \rightarrow {}^1A_{2u}$ ($\delta \rightarrow \delta^*$), which is electric dipole allowed in the z direction. The absorption in x,y polarization peaking at 20 500 cm^{-1} would then be attributed to vibronic excitation of this electronic transition that would require an E_g degenerate pair of vibrations under D_{4h} symmetry. In this case the vibronic intensity is about 15% that of the electric-dipole-allowed portion seen in z polarization. For $Mo_2(O_2CCH_3)_4$, which has a comparable electronic configuration, the first observed band has been demonstrated to be dipole allowed in z polarization. It occurs with a maximum at ca. 23 000 cm^{-1}, some 3000 cm^{-1} higher energy. At 300 K the corresponding $Mo_2(O_2CCH_3)_4$ band had an oscillator strength of ca. 1×10^{-3} or only one-fourth of that for $Re_2[O_2CC(CH_3)_3]_4Cl_2$.[14] For the molybdenum compound the vibronic contribution was a considerably higher fraction of the intensity.

Vibrational structure was poorly resolved on the z-polarized peak of $Re_2[O_2CC(CH_3)_3]4Cl_2$ at 20 200 cm^{-1}. The plots in Figure 3 show this band with an extended scale where three maxima are clearly seen. A fourth component, a shoulder at 19 640 cm^{-1}, is barely discernible but was more evident in the larger scale recorder plots. The separation of the components is 200 cm^{-1}. This behavior is certainly different from the dimolybdenum tetracarboxylate crystal spectra at liquid-helium temperature where very sharply resovled vibration lines

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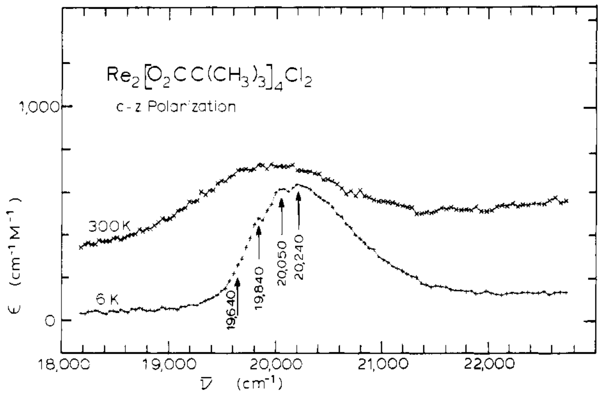

Figure 3. Expanded scale plot of the 20 200-cm^{-1} peak in *c* polarization for the $Re_2[O_2CC(CH_3)_3]_4Cl_2$ crystal that was 2.3 μm thick.

form progressions not only on the 0–0 but on several vibronic origins. The slit for the spectrum in Figure 3 was sufficiently narrow to provide a dispersion of 25 cm^{-1} so the lack of resolution was not instrumental. The progressions for the molybdenum(II) carboxylate spectra are generally based on a single vibration assigned as the metal–metal stretching mode in the excited state. The $\bar{\nu}$ for this mode is typically about 330–370 cm^{-1} and generally about 10% below the metal–metal stretching wavenumber for the ground state assigned from the Raman spectra. The value of 200 cm^{-1} is 31% below the 289 cm^{-1} assigned as the ground-state Re–Re stretch by Bratton et al.[19] and indeed is very close to their value of 199 cm^{-1} assigned to the Re–Cl stretch. It may well be that this progression is an example of the missing mode effect (MIME). Tutt, Tannor, Heller, and Zink[20] demonstrated this effect in a spectrum of $W(CO)_5(C_5H_5N)$ where they found that an electronic band, observed in emission, with poor resolution of vibrational structure could exhibit, as a consequence of two totally symmetric modes, a single apparent Franck–Condon progression with the separation of maxima corresponding to a wavenumber intermediate to those of the two normal modes. The separation indicated in the progression in Figure 3 lies between the expected Re–Re and Re–Cl stretches for the excited state.

The 20 600-cm^{-1} band in *x,y* polarization had a very weak shoulder on the high-energy side, indicated at 21 600 cm^{-1} in Table I. This shoulder was evident in scans of several crystals. It has been assigned as a spin-forbidden transition corresponding to one of the spin-allowed bands at higher energy. The intensity of the $\delta \rightarrow \delta^*$ transition in *z* polarization would obscure any component in that polarization.

The *x,y* spectrum, Figure 1, shows a weak band at 16 300 cm, below the spin-allowed $\delta \rightarrow \delta^*$ transition. This band is missing in *z* polarization. A $^1A_{1g} \rightarrow {}^3A_{2u}$ transition would by spin–orbit coupling be electric dipole forbidden in *z* polarization but allowed in *x,y* polarization under D_4' symmetry. We are therefore assigning it as the spin-forbidden $\delta \rightarrow \delta^*$ transition. In this case the separation of the $^3A_{2u}$ and $^1A_{2u}$ states would be 3800 cm^{-1}. This is a rather normal separation for a transition-metal complex. No corresponding spin-forbidden band has been found below the band that is dipole allowed with *z* polarization for any of the molybdenum(II) dimeric complexes. However, rhenium with the higher atomic number than molybdenum is expected to have a considerably high spin–orbit coupling and consequently higher intensity for the spin-forbidden bands. However, no spin-forbidden band has been reported for $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$. *z*-Polarized dipole-allowed transitions for those complexes are seen at 14 600 and 14 100 cm^{-1}, respectively.[7,8] In his theoretical treatment of the $Re_2Cl_8^{2-}$, Hay[6] suggested that the spin-forbidden band might be at very low energies, perhaps about 3000 cm^{-1}.

Tentative assignments of the higher energy bands in the spectra are based on the earlier studies[3,7–9] of $Re_2Cl_8^{2-}$ and a paper by Bursten, Cotton, Fanwick, and Stanley,[21] which we received recently prior to its publication. This latter paper describes a SCF–Xα–scattered wave calculation for $Re_2Cl_8^{2-}$ that includes inner-shell and valence relativistic effects. This calculation indicated that the first orbital excitation above the $\delta \rightarrow \delta^*$ should be the $\pi \rightarrow \delta^*$. Accordingly we have assigned the band at 24 700 cm^{-1} with about the same intensity in *z* as in *x,y* polarization as the spin-allowed $^1A_{1g} \rightarrow {}^1E_g$ ($\pi \rightarrow \delta^*$) with the spin-forbidden $^1A_{1g} \rightarrow {}^3E_g$ ($\pi \rightarrow \delta^*$) as the shoulder seen at 21 600 cm^{-1} in *x,y*. This places the $^1A_{1g} \rightarrow {}^1E_g$ at 4100 cm^{-1} above the $\delta \rightarrow \delta^*$, comparable to the 3800-cm^{-1} difference between the corresponding bands assigned by Bursten et al.[21] The peak at 29 000 cm^{-1} some 8500 cm^{-1} above the $\delta \rightarrow \delta^*$ band apparently does not correspond to the peak in $Re_2Cl_8^{2-}$ that lies 7000 cm^{-1} above the $\delta \rightarrow \delta^*$ since the latter had a much higher intensity in *x,y* polarization than in *z*. Hence, we are assigning the 29 000-cm^{-1} transition as $^1A_{1g} \rightarrow {}^1E_g$ ($\delta \rightarrow \pi^*$). Finally, the band at 32 000 cm^{-1} is likely a spin-forbidden $\pi \rightarrow \pi^*$ or charge-transfer transition. Since the computations of Norman and Ryan[5] indicate that in $Mo_2Cl_8^{4-}$ and $Mo(O_2CH)_4$ the carboxylate stabilizes both the π and π^* orbitals with respect to the δ and δ^*, there is the possibility that the $\delta \rightarrow \pi^*$ and $\pi \rightarrow \delta^*$ assignments are reversed.

If this compound had been the first quadruply bonded d^8 dimer to have had its polarized single-crystal electronic spectra determined, there would have been no question but that it confirmed theoretical expectations of a lowest $\delta \rightarrow \delta^*$ transitions for these systems. The spin-forbidden transition below the spin-allowed transition, each with the correct polarization would have been accepted as an unambiguous justification for the assignment. The crystal field perturbations on the low symmetry sites and the low intensities of the first band in the molybdenum(II) carboxylates have introduced considerable uncertainty into their assignment as the $\delta \rightarrow \delta^*$ transitions despite the beautiful vibrational structure they exhibit at liquid-helium temperatures. There is also the disturbing feature that no band corresponding to a spin-forbidden $\delta \rightarrow \delta^*$ has been discerned for any molybdenum or rhenium dimer previously. There is always the possibility that a weak feature such as the band at 16 500 cm^{-1} is due to a minor impurity component in a crystal. However, the band was observed reproducibly in several crystals whose spectra were measured. It would be a helpful confirmation if spectra for other rhenium carboxylate dimers could be measured. However, they generally form such insoluble compounds that it has not yet been possible to prepare spectroscopic quality crystals.

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