96 *Inorg. Chem.* **1985**, *24*, 96-101

Contribution from the Chemistry Department and Energy and Mineral Resources Research Institute,
Iowa State University, Ames, Iowa 50011

Single-Crystal Polarized Spectra for the $\delta \rightarrow \delta^*$ Band of Tetrabutylammonium Octachlorodirhenate(III) and Tetrabutylammonium Octabromodirhenate(III). Crystal Structure of the Octabromo Salt

HEI WAI HUANG and DON S. MARTIN*

Received May 30, 1984

A crystal structure determination of tetrabutylammonium octabromodirhenate(III) by X-ray diffraction was solved for a $P2_1/n$ unit cell with $a{:}b{:}c$ = 14.328 (3):15.503 (3):11.381 Å (3), β = 97.10 (3)°, and Z = 2. There is a disorder in that the $Re_2Br_8^{2-}$ with a nearly cubic arrangement of the Br ligands has the Re–Re bond arranged with a Re near the center of two opposite faces of the cube in 62.1 (6)% of the cases and with the Re's near the centers of a different pair of faces of the cube in 37.9 (6)% of the cases. For both the octabromo and the octachloro salts, highly resolved vibrational structure in the polarized crystal spectra were recorded for the first observed electronic band at about 14 000 cm^{-1}. It was possible to resolve the Franck–Condon progressions for both the major and minor components of each compound with intensities consistent with the $\delta \rightarrow \delta^*$, ${}^1A_{1g} \rightarrow {}^1A_{2u}$ assignment. However, additional absorption features were observed that have been attributed to further defect components that have not been revealed by the X-ray diffraction structures. Spectra recorded for tan crystals found in the preparations of the green tetrabutylammonium octabromodirhenate(III) possessed the $\delta \rightarrow \delta^*$ band but with shifts of the vibrational lines that indicated a different crystal form.

Introduction

Both $Re_2Cl_8^{2-}$ and $Re_2Br_8^{2-}$, which contain quadruple metal–metal bonds, have absorption bands that peak about 14 000 cm^{-1}, which are the lowest observed electronic transitions. Cowman and Gray[1] reported polarized single-crystal spectra for tetrabutylammonium octachlorodirhenate(III), $(TBA)_2Re_2Cl_8$. At that time, the crystal structure of this compound had not been determined so the polarization ratio could not be used to indicate an unambiguous molecular polarization of the transition. However, they inferred from the temperature dependence of the transition and the MCD that it was a dipole-allowed transition to a nondegenerate state. It was also stated that the crystal spectra for the first band of $Re_2Cl_6[P(C_2H_5)_3]_2$, which was not published, indicated a z-polarized transition. They, therefore, concluded that this band was the spin-allowed $\delta \rightarrow \delta^*$ ($b_{2g} \rightarrow b_{1u}$) transition, which would be ${}^1A_{1g} \rightarrow {}^1A_{2u}$ for a D_{4h} $Re_2Cl_8^{2-}$ ion. In a subsequent crystal structure determinaion of $(TBA)_2Re_2Cl_8$, Cotton, Frenz, Stults, and Webb[2] found a disordered structure. The $Re_2Cl_8^{2-}$ ion consists of very nearly a cubic arrangement of eight chloride ligands with the two rhenium atoms very near the centers of two opposite pairs of faces of the cube. However, in 26.11% of the cubes the rhenium atoms occupied a different pair of the faces with a random distribution of this disorder. Cotton et al.[2] showed that a z-polarized transition for the two types of anions accounted quite well for the overall relative intensities of the two polarizations in Cowman and Gray's spectra.[1]

Information from crystal spectra for this band in $(TBA)_2Re_2Br_8$ is somewhat less complete. Cowman, Trogler, and Gray[3] publisehd a very small-scale pair of spectra, but these apparently were not the recorded crystal spectra. Instead, they denoted the curves as projections ∥ and ⊥ to the Re–Re molecular axes. We infer they used an inverse-matrix technique of the kind described by Piper[4] to prepare these curves. However, without the actual crystal structure information for the compound, it is not possible to judge their presentation. Cowman and Gray[1] did include wave numbers, $\tilde{\nu}$'s, for the first three vibrational components in the low-temperature band for the bromide salt.

We have been concerned about the vibrational assignments for this first band presented by Cowman and Gray[1] for $(TBA)_2Re_2Cl_8$. The lowest energy component of the band was quite weak, and they assigned it as the 0–0 line. There were then two strong progressions based on higher origins. Each progression had the same spacing. They assigned the spacing of the two progressions, $\tilde{\nu}_1$, to the totally symmetric metal–metal stretching frequency. Since this was a dipole–allowed transition, the distances of the origins of the two progressions above the 0–0 energy were assigned to ν_2 and ν_3, the other two totally symmetric vibrations of the $Re_2Cl_8^{2-}$ ions, viz., a Re–Cl stretch and Re–Re–Cl bends. Such an assignment requires that the v = 1 vibrational line of the ν_2 and the ν_3 Franck–Condon progressions be much more intense than all the other members of the progressions. This feature plus the feature that a progression of $\tilde{\nu}_1$ would be observed on a vibrational origin and not on the 0–0 origin of a dipole-allowed transition are most improbable.

In the present study, we are reporting spectra of $(TBA)_2Re_2Cl_8$ and $(TBA)_2Re_2Br_8$ for this band with considerably better resolution than those of the earlier work. These new spectra provide additional insight into the vibrational assignments of the first absorption band. In addition, an X-ray diffraction crystal structure determination has been performed for $(TBA)_2Re_2Br_8$ that indicates a disordered structure similar to that of $(TBA)_2Re_2Cl_8$.

Experimental Section

Both $(TBA)_2Re_2Cl_8$ and $(TBA)_2Re_2Br_8$ were prepared according to the procedure of Cotton et al.[5] by the reduction of $KReO_4$ by H_3PO_2. Each salt was recrystallized from a methanol solution containing a few drops of the concentrated hydrogen halide acid.

Among the dark blue crystals of $(TBA)_2Re_2Cl_8$ were a number of very thin platelets that were ideal for spectroscopy. The platelets under a polarizing microscope appeared blue-green at both extinctions although there was a distinct difference in the intensities of the absorption. Indices of refraction for Na–D light, indicated by the Becke line method, were found to be 1.546 (4) for the high-absorption extinction and 1.580 (4) for the low-absorption one.

For $(TBA)_2Re_2Br_8$, as with the chloride salt, a minority of the crystals were thin platelets. A large majority of these were clearly dichroic with a yellow-green absorption for one extinction and a tan for the other. The Na–D indices of refraction for these faces were 1.585 (4) and 1.632 (4) for the green and the tan extinctions, respectively. However, among the crystals were a very small fraction that appeared tan in both polarizations. These were apparently the type of crystal faces observed in a few instances by Cowman and Gray[1] and upon which in part they based their original assignment for a z-polarized transition for the band.[6]

X-ray Diffraction Methods. A thick plate of $(TBA)_2Re_2Cl_8$ was cemented to a glass fiber that was mounted on the goniometer head of a four-circle X-ray diffractometer interfaced with a PDP15 computer.

---

(1) Cowman, C. D.; Gray, H. B. *J. Am. Chem. Soc.* **1973**, *95*, 8177.

(2) Cotton, F. A.; Frenz, B. A.; Stults, B. R.; Webb, T. R. *J. Am. Chem. Soc.* **1976**, *98*, 2768.

(3) Cowman, C. D.; Trogler, W. C.; Gray, H. B. *Isr. J. Chem.* **1976/77**, *15*, 308.

(4) Piper, T. S. *J. Chem. Phys.* **1961**, *35*, 1240.

(5) Cotton, F. A.; Curtis, N. F.; Johnson, B. F. G.; Robinson, W. R. *Inorg. Chem.* **1965**, *4*, 326.

(6) Trogler, W. C.; Cowman, C. D.; Gray, H. B.; Cotton, F. A. *J. Am. Chem. Soc.* **1977**, *99*, 2993.

Table I. Crystallographic Parameters for $(TBA)_2Re_2Br_8$

space group	$P2_1/n$	β, deg	97.10 (3)
cryst syst	monoclinic	V, Å^3	2509 (1)
a, Å	14.328 (3)	Z	2
b, Å	15.503 (3)	R	0.090
c, Å	11.381 (3)	R_w	0.144

Automatic indexing was accomplished by an interactive program, ALICE, of Jacobson.[7] A transformation was applied to these axes to give a set that was tuned on four strong reflections with 2θ between 12 and 23° with $a{:}b{:}c$ = 10.95:15.32:16.30 Å and $\alpha{:}\beta{:}\gamma$ and 89.56:122.76:90.33°. This set was in quite satisfactory agreement with the monoclinic set from the structure determination by Cotton et al., viz., $a{:}b{:}c$ = 10.933 (5):15.412 (6):16:435 (5) Å and β = 122.27 (3)°. The face for this platelet was the 1,0,0. For this face the extinctions would lie along the b and c axes, and it was observed that the intense absorption or the 1.564 index of refraction applied to the b polarization. This was the same face indicated by Cowman and Gray[1] in the initial study. Since Bursten et al.[8] found a different face for crystals used in measurements of some of the weaker, higher energy absorption bands, the identification of our spectroscopic face was confirmed with a second crystal for which spectra had been recorded. However, this crystal was so thick that only the very weak first absorption feature was observable. The very thin crystals with which the full absorption band was collected did not provide sufficient diffracting intensity for X-ray confirmation of their axes.

A crystal plate of $(TBA)_2Re_2Br_8$ was selected for X-ray diffraction, which was 0.44 mm × 0.26 × 0.06 mm. This crystal was mounted on a Datex four-circle diffractometer, and axes were originally calculated from the diffraction angles of 16 reflections. Since α and γ were essentially 90° and a b-axis oscillation photograph exhibited the necessary mirror symmetry, the axes were finally computed from separately tuned values of $\pm 2\theta$ for 14 reflections with $24° < 2\theta < 37°$ by means of the program LATT.[9] These axes and other crystallographic properties are in Table I.

Intensity data were collected for 10075 reflections with $2\theta < 50°$ over four octants. From these data, 2439 independent reflections with intensities greater than 3σ were utilized for the structure determination. Graphite-monochromated Mo Kα X-radiation with λ = 0.71034 Å was utilized. The intensities were corrected for Lorentz–polarization with scattering factors from the ref 10 for non-hydrogen atoms and from Stewart et al.[11] for hydrogen. An empirical absorption correction was performed by means of diffractometer ϕ-scan data and the program ABSN.[12]

Estimated deviations in the observed structure factors were calculated by a finite-difference method.[13] The discrepancy factors were taken as $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$, where F_c was the calculated structure factor and $w = 1/\sigma^2(F_o)$, with $\sigma(F_o)$ indicating the estimated standard deviation in F_o. Locations of Re atoms were found from Patterson superposition techniques. A series of electron density maps provided locations of the non-hydrogen atoms. The 24 methylene hydrogen atoms were introduced at idealized positions and not refined. Positional parameters, the occupancy of the Re positions, and anisotropic thermal parameters of the non-hydrogen atoms were refined first by block-diagonal matrices and finally by full-matrix least squares. The observed and calculated values of the structure factors, thermal parameters, and unrefined calculated hydrogen positions have been deposited with the supplementary material.

Spectroscopic Measurements. The equipment and procedures for recording polarized crystal spectra have been described previously.[14,15]

Table II. Atom Fractional Coordinates for Re, Br, N, and C in $(TBA)_2Re_2Br_8$

atom	x	y	z
Re1 (62.1 (6)%)	0.0236 (1)	0.4375 (1)	0.5417 (2)
Re2 (37.9 (6)%)	0.0682 (2)	0.5058 (2)	0.4649 (3)
Br1	0.1139 (3)	0.6580 (2)	0.5056 (3)
Br2	0.02182 (3)	0.5528 (2)	0.2575 (3)
Br3	0.1858 (2)	0.4658 (2)	0.6340 (3)
Br4	0.0966 (2)	0.3600 (2)	0.3864 (3)
N	0.348 (2)	0.194 (1)	0.567 (2)
C1	0.365 (2)	0.294 (1)	0.600 (3)
C2	0.403 (3)	0.303 (2)	0.731 (3)
C3	0.439 (2)	0.399 (2)	0.743 (4)
C4	0.475 (3)	0.413 (3)	0.883 (4)
C5	0.442 (2)	0.141 (2)	0.579 (3)
C6	0.516 (2)	0.184 (2)	0.522 (3)
C7	0.605 (2)	0.126 (2)	0.540 (3)
C8	0.693 (2)	0.156 (3)	0.483 (5)
C9	0.287 (2)	0.156 (2)	0.646 (3)
C10	0.190 (2)	0.194 (2)	0.646 (3)
C11	0.131 (3)	0.142 (2)	0.724 (4)
C12	0.033 (2)	0.177 (2)	0.725 (4)
C13	0.300 (2)	0.198 (2)	0.432 (3)
C14	0.268 (2)	0.109 (3)	0.389 (3)
C15	0.226 (2)	0.116 (4)	0.256 (3)
C16	0.199 (3)	0.033 (3)	0.184 (5)

Table III. Bond Distances (Å) and Bond Angles (deg) for $Re_2Br_8^{2-}$

Re1–Re1	2.226 (4)	Re1–Br4	2.473 (4)
Re2–Re2	2.209 (6)	Re2–Br1	2.477 (4)
Re1–Br1	2.470 (4)	Re2–Br2	2.481 (5)
Re1–Br2	2.457 (4)	Re2–Br3	2.475 (5)
Re1–Br3	2.469 (4)	Re2–Br4	2.482 (4)

Re1–Re1–Br1	103.7 (1)	Br1–Re1–Br3	152.0 (1)
Re1–Re1–Br2	104.0 (1)	Br2–Re1–Br3	86.4 (1)
Re1–Re1–Br3	104.3 (1)	Br2–Re1–Br4	151.5 (1)
Re1–Re1–Br4	104.6 (1)	Br3–Re1–Br4	86.1 (1)
Re2–Re2–Br1	103.6 (2)	Br1–Re2–Br2	86.1 (2)
Re2–Re2–Br2	102.9 (2)	Br1–Re2–Br3	87.4 (2)
Re2–Re2–Br3	104.3 (2)	Br1–Re2–Br4	152.0 (2)
Re2–Re2–Br4	104.4 (2)	Br2–Re2–Br4	87.8 (1)
Br1–Re1–Br2	86.8 (1)	Br2–Re2–Br3	152.8 (2)
Br1–Re1–Br4	87.1 (1)	Br3–Re2–Br4	87.8 (1)

The spectra with resolved vibrational features were recorded with slits that provided dispersions of no more than 0.6 nm or 12 cm^{-1} at 700 nm. Plots for highly resolved spectra were recorded from digital output each 0.1 nm with a scan speed of 0.05 nm/s.

The thickness of a crystal of $(TBA)_2Re_2Cl_8$, 10 μm thick, was measured by observing the edge of a crystal with a calibrated scale in the eyepiece of a microscope. This thickness corresponded to 1.7 scale division, and limitations due to the focus and orientation usually limit the accuracy to about 20%. For $(TBA)_2Re_2Br_8$ an 8.8-μm-thick crystal was found with optical faces that provided interference maxima and minima in the transmitted light in the region of 626.8–534 nm for multiple internal reflections for the tan polarization. The thickness of the crystal was calculated from the wavelengths of these maxima and minima and from the measured index of refraction.[16] Neglect of the dispersion has been found to introduce an uncertainty of about 10% in the thickness. Thicknesses of other crystals were obtained by comparison of a band height with those of the measured crystal.

Results and Discussion

Structure of $(TBA)_2Re_2Br_8$. A b-oscillation photograph exhibited the mirror symmetry of a monoclinic lattice. Systematic extinctions for the set of axes in Table I occurred for k odd of $0k0$ reflections and for $h + l$ odd for $h0l$ reflections. The structure was refined in the space group $P2_1/n$. This space group is an alternative to $P2_1/c$, which was utilized by Cotton et al.[2] for

---

(7) Jacobson, R. A. "An Algorithm for Automatic Indexing on Bravais Lattice Selection: The Programs BLIND and ALICE", Report IS-3469; Ames Laboratory—USAEC: Iowa State University, Ames, IA, 1974.

(8) Bursten, B. E.; Cotton, F. A.; Fanwick, P. E.; Stanley, G. G. *J. Am. Chem. Soc.* **1983**, *105*, 3083.

(9) Takusagawa, F., unpublished results from Ames Laboratory of the USDOE, Iowa State University.

(10) Templeton, D. H. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1962; Vol. III, Table 3.3.2C, pp 215, 216.

(11) Stewart, R. F.; Davidson, E. R.; Simpson, W. T. *J. Chem. Phys.* **1965**, *42*, 3175.

(12) Karcher, B. A. Ph.D. Thesis, Iowa State University, 1961.

(13) Lawton, S. L.; Jacobson, R. A. *Inorg. Chem.* **1968**, *7*, 2124.

(14) Martin, D. S. *Inorg. Chim. Acta Rev.* **1971**, *5*, 107.

(15) Fanwick, P. E.; Martin, D. S.; Webb, T. R.; Robbins, G. A.; Newman, R. A. *Inorg. Chem.* **1978**, *17*, 2723.

(16) Martin, D. S., Jr.; Rush, R. M.; Kroening, R. F.; Fanwick, P. E. *Inorg. Chem.* **1973**, *12*, 301.

(17) Martin, D. S., Jr., Webb, T. R.; Robbins, G. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 475.

Table IV. Bond Distances (Å) and Bond Angles (deg) for the Tetra-*n*-butylammonium Ion

N-C1	1.61 (3)	C6-C7	1.55 (4)
N-C5	1.57 (4)	C7-C8	1.56 (5)
N-C9	1.45 (4)	C9-C10	1.51 (4)
N-C13	1.60 (4)	C10-C11	1.53 (5)
C1-C2	1.52 (5)	C11-C12	1.51 (5)
C2-C3	1.58 (5)	C13-C14	1.52 (5)
C3-C4	1.63 (6)	C14-C15	1.57 (5)
C5-C6	1.46 (4)	C15-C16	1.55 (7)
C1-N-C5	112 (2)	C2-C3-C4	106 (3)
C1-N-C9	109 (2)	C5-C6-C7	108 (3)
C1-N-C13	103 (2)	C6-C7-C8	118 (3)
C5-N-C9	108 (2)	C9-C10-C11	112 (3)
C5-N-C13	112 (2)	C10-C11-C12	113 (3)
C9-N-C13	113 (2)	C13-C14-C15	108 (3)
C1-C2-C3	104 (2)	C14-C15-C16	119 (4)

$(TBA)_2Re_2Cl_8$. However, $P2_1/n$ is somewhat more convenient to use since β is closer to 90°. The $P2_1/n$ axes in Table I can be transformed to the $P2_1/c$ values $a{:}b{:}c = 11.381{:}15.503{:}17.161$ Å and $\beta = 124.06°$, compared to the values $a{:}b{:}c = 10.933{:}15.412{:}16.435$ Å and $\beta = 122.27°$, reported for $(TBA)_2Re_2Cl_8$ by Cotton et al. An examination of the electron density maps indicated the presence of the type of disorder found in $(TBA)_2Re_2Cl_8$, viz., that quadruply bonded Re–Re dimers could randomly occupy alternate pairs of faces in a nearly cubic array of halides. Consequently, the occupancy of two alternate sites was included as a refinement parameter. The minor site indicated as Re_2 in Table II had a 37.9 (6)% occupancy, somewhat greater than the 26.11% for the minor Re of $(TBA)_2Re_2Cl_8$.

The refinement for $(TBA)_2Re_2Be_8$ was rather poor since the final value of R was only 0.090. However, it does provide a satisfactory description of the $Re_2Br_8^{2-}$ ion and the orientation of the Re–Re bonds that has not been available previously for a rational interpretation of the crystal spectra. The non-hydrogen atom positions are in Table II. Bond lengths and bond angles for $Re_2Br_8^{2-}$ ions are in Table III and for non-hydrogen atoms of $N(C_4H_9)_4^+$ ions in Table IV. The thermal parameters and calculated hydrogen positions are deposited in the supplementary material. The structure is obviously very similar to that reported for $(TBA)_2Re_2Cl_8$. With the larger bromide ligand, the Re–Br bonds average 0.132 Å longer than the Re–Cl. Also, the unit cell volume is 7% larger for the $Re_2Br_8^{2-}$ salt. The average of the Re–Re bond distance of 2.218 Å is virtually the same as for $(TBA)_2Re_2Cl_8$ (2.220 Å). The $Re_2Br_8^{2-}$ ion possesses only $\bar{1}$ site symmetry required by the space group. However, deviations from D_{4h} symmetry for the $Re_2Br_8^{2-}$ units are small.

Crystal Spectra. $(TBA)_2Re_2Cl_8$. Since the X-rays average the unit cell structures over the entire crystal, the transmission of polarized light with wavelengths long compared to cell dimensions will be established by the monoclinic crystal cell defined by the X-ray diffraction. The orientation of the electric vector of the two plane-polarized light waves transmitted for the 1, 0, 0 face will be along the *b* axis (*b* polarization) and along the *c* axis (*c* polarization). The optical examination of the crystals confirmed that the extinctions for the crystal occurred with these axes aligned with the crossed polarizers of the polarizing microscopes.

The relative intensities of absorptions can be calculated from the oriented molecule model. Under D_{4h} symmetry an absorption feature will have either molecular *z* polarization or molecular *x,y* polarizations for two degenerate transitions. The *z* axis lies along the metal–metal bond. For the major $Re_2Cl_8^{2-}$ anions (73.9% abundant), the *z* axis is oriented at an angle of $\theta_{1,b} = 28.77°$ from the *b* axis and an angle of $\theta_{1,c} = 63.57°$ from the *c* axis. The intensity of absorption[18] for a unit molecular *z*-polarization transition appearing in *b* polarization is $0.739 \cos^2 \theta_{1,b} = 0.567$ and appearing in *c* polarization is $0.739 \cos^2 \theta_{1,c} = 0.143$. The expected polarization ratio, $(I_b/I_c)_{1,z}$, is 3.88.

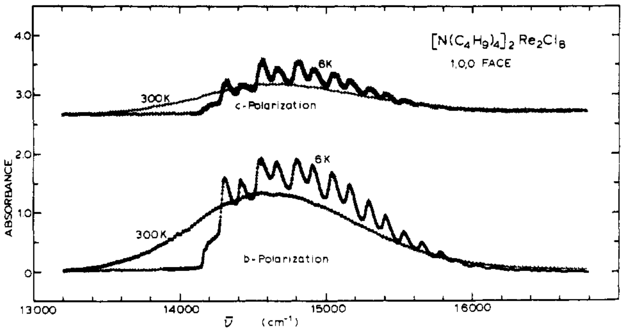

Figure 1. Polarized spectra of the entire band for a crystal of $(TBA)_2Re_2Cl_8$ that was 2.2 μm thick at 300 and 6 K.

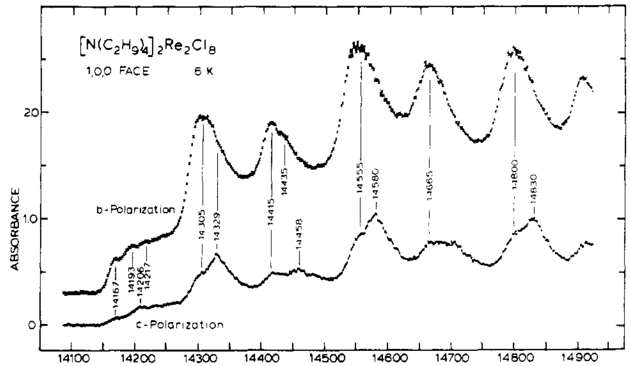

Figure 2. Polarized spectra in the low-energy region with an extended wavenumber scale for a crystal of $(TBA)_2Re_2Cl_8$ that was 2.2 μm thick at 6 K.

The intensity from the two *x*- and *y*-polarized unit transitions appearing in *b* polarization is $0.739 \sin^2 \theta_{1,b} = 0.171$ and appearing in *c* polarization is $0.739 \sin^2 \theta_{1,c} = 0.590$ with the polarization ratio of $(I_b/I_c)_{1,xy} = 0.289$.

For the minor $Re_2Cl_8^{2-}$ component (26.1%) the *z* axis is oriented at an angle $\theta_{2,b} = 86.39°$ with the *b* axis and at an angle $\theta_{2,c} = 59.45°$ with the respect to the *c* axis. Thus, the *b*-axis intensity is $0.261 \cos^2 \theta_{2,b} = 0.0010$, and the *c*-axis intensity is $0.261 \cos^2 \theta_{2,c} = 0.0674$ with the polarization ratio of $(I_b/I_c)_{2,z} = 0.015$. For *x,y*-polarized transitions, the *b*-axis intensity calculated from $0.261 \sin^2 \theta_{2,b} = 0.260$ and the *c*-axis intensity from $0.261 \sin^2 \theta_{2,c} = 0.194$ with the polarization ratio $(I_b/I_c)_{2,xy} = 1.34$.

The above calculated values can only serve as guides rather than as precise predictions because of crystal field perturbations that may significantly lower the site symmetry from D_{4h}. a relative minor crystal field might alter the polarization ratio by moving the transition moment of a molecular *z*-polarized transition away from the metal–metal bond. A major perturbation might break the degeneracy of the two *x*–*y* transitions to give two bands with very different intensities and polarization ratios.

The first absorption band is predicted from Xα–SW calculations[8] to be the $\delta \rightarrow \delta^*$ transition, $^1A_{1g} \rightarrow {}^1A_{2u}$, which will have *z* polarization. However, on a microscopic scale the two ions in the disordered crystal constitute different sites and the transitions of the two different sites can possibly have different energies. Since a *z*-polarized transition of the minority site has a very high *c*-polarized intensity compared to *b* and whereas the predicted $(I_b/I_c)_{1,z}$ was 3.88, the spectra were examined carefully for evidence of vibrational lines for the minority sites.

Scans of the complete band for a crystal 2.2 μm thick at 300 and 6 K for the *b* and *c* polarizations are shown in Figure 1. It can be seen that although the band has sharpened and vibrational structure appeared in the low-temperature spectra, the integrated intensity of the band is virtually identical at the two temperatures.

---

(18) Martin, D. S.; Newman, R. E.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 2511.

This feature indicates an electric dipole-allowed transition. The relative intensities of the general features are in very good agreement with those of Cowman and Gray.[1] However, a plot of the 6 K spectra with an extended wavenumber scale reveals a good deal more detail than they were able to resolve. For one thing, they did not scan to sufficiently long wavelengths where the absorbance falls to zero. Hence, they placed the lowest energy feature as a shoulder at 14 183 cm^{-1}. Our spectra show as the lowest energy feature a component at 14 167 cm^{-1}. This is followed by a rather broad region of absorption in which at least two weak maxima can be discerned in each polarization. This absorption lies on a rising absorption associated with much more intense features at 14 305 cm^{-1}. (Cowman and Gray placed these intense lines at 14 298 cm^{-1}.) It is noted that at 14 417 cm^{-1} in each polarization, just 250 cm^{-1} above the first feature, there is a sharp peak followed by a broad area of absorption in each polarization. The average separation of 249 (2) cm^{-1} occurs between all successive major elements in the Franck–Condon progression in the band. Such detailed features less well resolved but still recognizable are in the peak 14 650–14 770 cm^{-1}. Therefore, we have concluded that the feature at 14 150–14 270 cm^{-1} is really the origin of the long progression that continues 14 440–14 520, 14 650–14 770 cm^{-1}, etc., and not a separate origin. The difference in the shape of the first feature arises from the fact that it lies on the rising absorption of the major component at 14 305 cm^{-1} whereas the later members of the progression each lie between much more intense components. The polarization ratio of the members of this progression, I_b/I_c, can be estimated to be about 3 with considerably uncertainty. This might be considered consistent with a z-polarized absorption of the major component. However, at 14 206 cm^{-1} there is clearly a weak maximum in c polarization just where there is a minimum b polarization. Hence, there is probably a contribution from the minor component as well.

In b polarization there is the intense peak at 14 305 cm^{-1} with subsequent members of a Franck–Condon progression based on this peak at the indicated spacings of 249 ± 2 cm^{-1}. However, in c polarization a rather sharp maximum is at 14 329 cm^{-1}, 24 cm^{-1} higher than the b-polarization peak; and there is clearly a shoulder at 14 305 cm^{-1}. There is no discernible component at 14 329 cm^{-1} in b polarization. We, therefore, propose that 14 305 cm^{-1} is the origin of a z-polarized progression for the major component, whereas 14 329 cm^{-1} is the origin for the minor component. The predicted c-polarized intensity for the major site is 0.143, whereas it is 0.067 for the minor site. However, the 14 329-cm^{-1} feature appears somewhat sharper than the 14 305-cm^{-1} band, and the higher peak at 14 329 cm^{-1} may be a consequence of a smaller width even though its integrated intensity is lower. The feature of a shoulder on a narrow peak is evident in the higher members of the Franck–Condon progression as well.

The progressions with origins at 14 305and 14 329 cm^{-1} therefore are consistent with the spin-allowed δ–δ^* transition, i.e., electric dipole allowed, z polarized for the major and minor sites, respectively, indicated by the crystal structure and with a site splitting of 24 cm^{-1}.

The source of the additional progression based on the broad, multiple-component origin, 14 150–14 270 cm^{-1}, is not evident from the crystal structure. We propose that it must arise from site differences resulting from additional disorder in the crystal. The intensity of this alternative progression appears to be 20–30% of the more intense progression. It is disturbing that no such alternative disorder was evident from the crystal structure where the refinement produced an R of 0.042.[2] Of course, the crystal structure was performed with a different crystal from that used for the spectra. However, we have observed consistent spectra with at least eight different crystals, and the results of Cowman and Gray[1] are consistent with ours as well. Since the site difference with the alternative metal–metal bond orientation shifted the origin by only 24 cm^{-1}, the shift of up to 138 cm^{-1} indicates a much larger crystal field shift. We believe that it must be caused by a difference in orientation or positioning of parts of the cations, which could have significant electrostatic effects on the Re orbitals. The breadth and complexity of the origin indicate that there are a number of different disordered perturbations each of which might have such a low occupancy that none were identified in the averaging by the X-ray diffraction. A comparison of the chloride and bromide compounds (see below) is relevant to the consideration of such disorder.

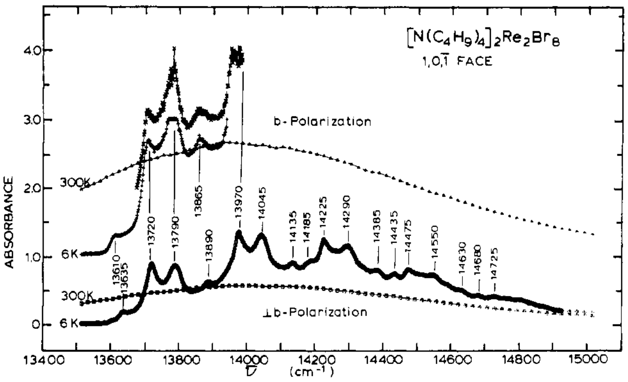

Figure 3. Polarized spectra in the low-energy region with an extended wavenumber scale for a crystal of $(TBA)_2Re_2Br_8$ 3.4 μm thick at 6 K. The short segment above the b polarization was obtained with a higher range extender setting that increased the noise.

$(TBA)_2Re_2Br_8$. The large well-developed face for the crystal used for the structure determination of $(TBA)_2Re_2Br_8$, presumably the spectroscopic face for the thinner crystals, was identified from the diffractometer angles as the 1, 0, $\bar{1}$ face for the $P2_1/n$ cell. This is the same face indicated in the $P2_1/c$ space group that was found for our $(TBA)_2Re_2Cl_8$ crystals. One optical extinction is required to be parallel to the b axis and the other perpendicular to the b axis. Since this latter direction is not that of the crystallographic c axis, these two crystal polarizations for the spectra are designated as the b and $\perp b$. For the major site, indicated by the crystal structure to have an occupancy of 62.1%, the z axis is oriented at an angle of $\theta_{1,b}$ = 29.47° with respect to the b axis and with an angle of $\theta_{1,\perp b}$ = 62.13° with respect to the $\perp b$ direction for the 1, 0, $\bar{1}$ face. The predicted intensity of a unit molecular z-polarized transition appearing in b polarization is $0.621 \cos^2\theta_{1,b} = 0.471$ and appearing in $\perp b$ polarization is $0.621 \cos^2\theta_{1,\perp b} = 0.136$. The predicted polarization ratio, $(I_b/I_{\perp b})_{1,z} = 3.46$. The intensity from the two x- and y-polarized unit transitions appearing in b polarization is $0.621 \sin^2 \theta_{1,b} = 0.150$ and appearing in $\perp b$ polarization is $0.621 \sin^2 \theta_{1,\perp b} = 0.485$ with the polarization ratio $(I_b/I_{\perp b})_{1,x,y} = 0.309$. For the minor $Re_2Br_8{}^{2-}$ component (37.9%) the z axis is oriented at an angle, $\theta_{2,b}$ = 85.34°, with the b axis and at angle, $\theta_{2,\perp b}$ = 62.37°, with the $\perp b$ extinction direction. Thus, for a z polarization, the b-axis intensity is $0.379 \cos^2 \theta_{2,b} = 0.0025$, and the $\perp b$ intensity is $0.379 \cos^2 \theta_{2,\perp b} = 0.0815$ with the polarization ratio $(I_b/I_{\perp b})_{2,z} = 0.031$. For the x,y polarization, the b intensity is calculated from $0.379 \sin^2 \theta_{2,b} = 0.376$ and the $\perp b$ intensity from $0.379 \sin^2 \theta_{2\perp b} = 0.297$ with the predicted polarization ratio, $(I_b/I_{\perp b})_{2,x,y} = 1.28$.

A search of the crystals of $(TBA)_2Re_2Br_8$ failed to uncover any as thin as those that were available for $(TBA)_2Re_2Cl_8$. Polarized spectra for our thinnest spectroscopic crystal, viz. 3.4 μm thick, is shown in Figure 3. Even so, the intensity of the band was so great that it was not possible to scan over the highest peaks for b polarization. The short section above the longer scan was obtained with a higher range-extender setting for the Model 14 Cary spectrophotometer that produced considerably higher noise level.

In the $\perp b$ polarization, four members of two strong progressions are clearly resolved with origins at 13 720 and 13 790 cm^{-1}, respectively, a splitting of 70 cm^{-1}. Only the first member of each

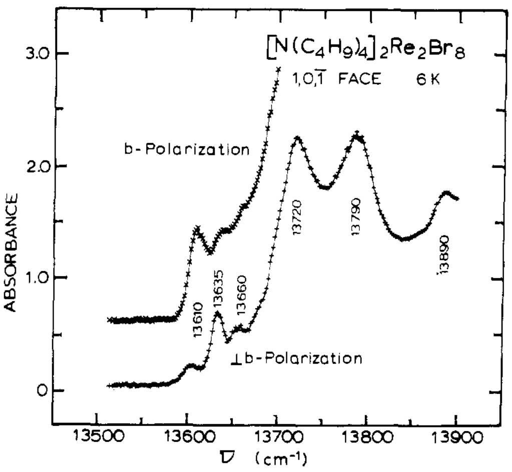

Figure 4. Polarized spectra for a $(TBA)_2Re_2Br_8$ crystal that is 8.5 μm thick.

progression was observable in *b* polarization. The *b*-polarized component at 13 720 cm^{-1} was considerably less intense than the ⊥*b*-polarized component, whereas the *b*-polarized peak at 13 790 cm^{-1} is at least three times as intense as the ⊥*b* component. We are therefore assigning the 13 790-cm^{-1} line as the 0–0 line of a *z*-polarized transition for a major component. The relative $b/\perp b$ polarization ratio appears quite compatible with this assignment. We then assign the 13 720-cm^{-1} line as the 0–0 line for a *z*-polarized transition in the minority component. The intensity of this line in *b* polarization is obviously higher than that predicted from the oriented-ion theory. This feature can well be due to a moderate deviation of the transition moment vector from the molecular *z* axis caused by the crystal fields. The theory also predicts that the 13 720-cm^{-1} line should be less intense than the 13 790-cm^{-1} line in ⊥*b* polarization. The 13 720-cm^{-1} component is slightly higher although this may be in part due to the fact that it is somewhat narrower. Again, it is probably partly another consequence of the crystal field on the transition moment alignment. If our assignment is correct, it indicates that the origin of the *z*-polarized band, presumably the $\delta \rightarrow \delta^*$ transition, has been red shifted by 70 cm^{-1} in the minority component.

Below the two intense origins there is evident some absorption in the region of 13 570–13 680 cm^{-1}. Higher progression terms based on the origins in this region are clearly seen in both polarizations. We attribute these origins to the same sorts of unspecified disorder that also occurred in $(TBA)_2Re_2Cl_8$. In the case of the bromide salt, the disorder must be clearly 1 order of magnitude less abundant, because these progressions are such minor features in the spectra. A very minor origin was also noted to occur at 14 185 cm^{-1} in the ⊥*b* spectrum. This is 395 cm^{-1} above the 13 790-cm^{-1} origin and appears to be too high to be a vibronic origin. It may indicate a further minor disorder.

There is some vibrational structure in the region 13 570–13 680 cm^{-1} that is more clearly seen in the spectra for a thicker crystal in Figure 4. Thus, the two peaks, 13 610 and 13 643 cm^{-1} which are much more intense in *b* polarization, can be attributed to orientation of the major site, and the peaks at 13 635 and 13 660 cm^{-1}, which are much more intense in ⊥*b*, can be attributed to the orientation of the minor site.

Trogler et al.[6] and Bursten et al.[8] described a very weak absorption, designated by them as band I, in $(TBA)_2Re_2Cl_8$ in the vicinity of 16 000–18 500 cm^{-1}. This absorption, above the $\delta \rightarrow \delta^*$ transition, had well-resolved vibrational structure for which Bursten et al. tabulated wavenumbers for four Franck–Condon progressions. Since the origin of their fourth progression, designated d, was 1 687 cmm^{-1} above the first origin, they concluded that there were two transitions in this band. Our measurements in this region were essentially in agreement with their results, so we have not presented spectral plots for them. Our observations were made with a 1, 0, 0 face, whereas they had a 1, 1, 0 face. This probably accounts for the fact that our *b*:*c* peak height ratio was about 4.0 whereas their ⊥*c*:*c* ratio was reported as 2.6. We presume they confirmed their extinction directions since for the 1, 1, 0 face of a monoclinic crystal the extinction directions are not fixed by the crystal symmetry. We concur that their a, b, and d progressions would correspond to a *z* polarization of the majority site. However, the c progression might correspond to the *x*,*y* polarization of the majority site but alternatively might equally well respresent the *z* polarization of the minority site. In view of the site differences that were apparent in the $\delta \rightarrow \delta^*$ band, we are less confident that this absorption does necessarily represent two transitions; however, the 1687 cm^{-1} of their d origin above the a origin is much greater than any difference seen in the $\delta \rightarrow \delta^*$ transition.

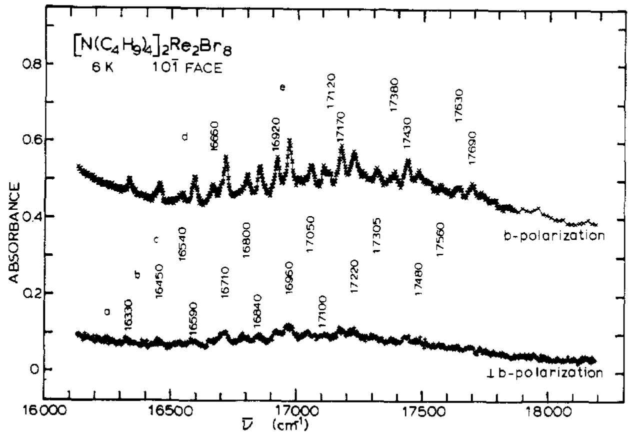

Figure 5. Polarized spectra for a 37 μm thick $(TBA)_2Re_2Br_8$ crystal in the region of the weak band, 16 000–18 000 cm^{-1}.

We are not aware of any reports for absorption by $(TBA)_2$-Re_2Br_8 in this region. We did observe in a crystal 37 μm thick an absorption in this same region that is shown in Figure 5. Generally, thicker specimens than this consisted of clumps of crystals that did not provide satisfactory spectra. Wavenumbers for the vibrational lines are included in Figure 5. There are clearly at least five progressions discernible in *b* polarizations. Peaks are much weaker in ⊥*b* polarization. There are weak lines in ⊥*b* polarization coincident with the stronger components in *b* polarization. The intensities are consistent with a *z*-polarized line in the majority sites with no evidence for *x*,*y* polarizations or *z* polarizations of minority sites that have been shifted in wavenumber from those of the majority sites. The average of all the separations in the progressions is 256 (5) cm^{-1}, which is very similar to the separations in the lower energy $\delta \rightarrow \delta^*$ band. This feature is somewhat different from the chloride salt where the separations for this band averaged 22 cm^{-1} below those for the $\delta \rightarrow \delta^*$ band.

The origins of the b, c, d, and e progression lie 130, 210, 330, and 790 cm^{-1} above the a origin, respectively. Hence, the d and e progressions clearly must originate from either site splittings or different transitions. They are greater than the highest vibrational frequency for $Re_2Be_8^{2-}$, viz., the metal–metal stretch that can be placed at 275 cm^{-1} in the ground state according to the resonance Raman study of Clark and Franks[19] and in the $\delta \rightarrow \delta^*$ excited state corresponds to the 252-cm^{-1} splitting. Even the 210-cm^{-1} origin of the b-progression here is suspect if the a progression is also a vibronic origin for an orbitally forbidden $\pi \rightarrow \delta^*$ or $\delta \rightarrow \pi^*$ ($^1A_{1g} \rightarrow {}^1E_g$) as Bursten et al. have proposed for this band in the $Re_2Cl_8^{2-}$ salt. Since the lowest origin of the bromide salt lies only 305 cm^{-1} below the weak band I in $(TBA)_2Re_2Cl_8$, such an assignment to one or both of these transitions does appear reasonable.

---

(19) Clark, R. J. H.; Franks, M. L. *J. Am. Chem. Soc.* **1976**, *98*, 2763.

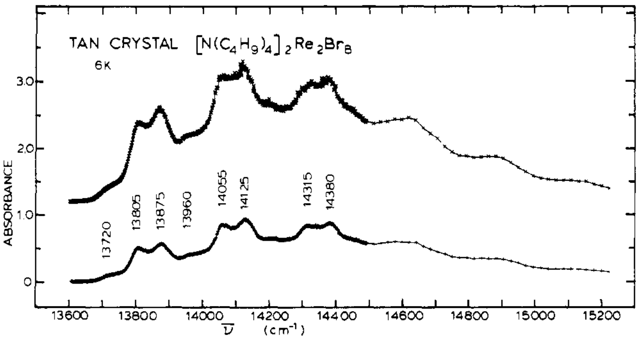

Figure 6. Polarized spectra of a tan crystal found in the preparation of (TBA)$_2$Re$_2$Br$_8$.

Trogler et al.[6] commented that in their sample of (TBA)$_2$Re$_2$Br$_8$ they observed some thin tan crystals that they attributed to a different face from the normal specimens. They indicated it was partially due to this observation that they concluded the 14 000-cm^{-1} band must be z polarized since, if the green color was due to an x,y polarization, there would be no face where this component would not be seen in at least one polarization. We also found a limited number of tan crystals, some of which were suitable for spectroscopic measurements. Polarized spectra for the 14 000-cm^{-1} band of such a crystal are shown in Figure 6. There are two intense progressions seen in each polarization and a third weaker progression based on an origin below the other two. The pattern is clearly similar to the bands in Figure 3 for (TBA)$_2$Re$_2$Br$_8$. However, lines in the tan crystals are some 90 cm^{-1} higher in energy than in the green crystals. This result has been confirmed with a second crystal as well. We are, therefore, forced to conclude that the tan crystals represent a different crystal structure from the green, which does contain the Re$_2$Br$_8$$^{2-}$ anion, and that the 90-cm^{-1} shift of the vibrational lines results from the different crystal environment.

It was surprising to note that there was a considerable intensity difference in the two polarizations of the tan crystals. The intensity ratio at room temperature appeared to be approximately 2 whereas in the green crystal it was estimated to be only a little greater than 3. In examination of the extended spectra for the tan crystals, which are presented in Figure 7, it was noted that a band peaking at 21 100 cm^{-1} with equal intensity in each polarization is about the same intensity as the 14 000-cm^{-1} band in the polarization with lower intensity. The room-temperature scans for the green crystal, whose 14 000-cm^{-1} band at 6 K is shown in Figure 4, are also in Figure 7, and they show a 21 000-cm^{-1} peak that is only 10–20% of the $\perp b$ polarization of the 14 000-cm^{-1} band. Since there is such a difference in the relative intensity of these bands, it seems likely that the 21 000-cm^{-1} band may be due to an impurity component. In any event, the 21 000-cm^{-1} band appears to play an important role in establishing the color of the tan crystals. For the green crystals, the relative intensity of the 14 000-cm^{-1} band, primarily with little absorption at 21 000 cm^{-1} serves to provide the responses that the eye interprets as green and tan colors for the different polarizations.

Comparison of (TBA)$_2$Re$_2$Cl$_8$ and (TBA)$_2$Re$_2$Br$_8$. In summary, we enumerate the striking similarities in the first band of these two compounds but also note some distinct differences as well. First of all, the bands have nearly the same energies with maxima in the region of 14 000–14 500 cm^{-1}. Room-temperature oscillator strengths calculated for a particular polarization from the equation

$$f = 4.32 \times 10^{-9} \int \epsilon \, d\bar{\nu}$$

were quite similar as well. For (TBA)$_2$Re$_2$Cl$_8$, $f_b = 2.6 \times 10^{-2}$ and $f_c = 9.5 \times 10^{-3}$. For (TBA)$_2$Re$_2$Br$_8$, $f_b = 2.0 \times 10^{-2}$ and $f_{\perp b} = 6.8 \times 10^{-3}$. However, since the thinnest crystal of (TBA)$_2$Re$_2$Br$_8$ was nearly 50% thicker than that of (TBA)$_2$Re$_2$Cl$_8$ in Figure 5 and because the vibrational components in (TBA)$_2$Re$_2$Br$_8$ were somewhat better resolved and higher, it was not possible to scan over the b-polarized spectra of this compound.

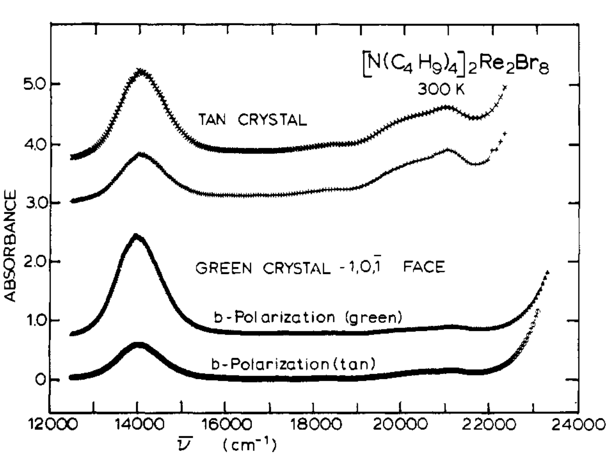

Figure 7. Room-temperature polarized crystal spectra for tan and green crystals of (TBA)$_2$Re$_2$Br$_8$.

The average separations in Franck–Condon progressions were nearly equal for each compound, 249 (2) cm^{-1} for (TBA)$_2$Re$_2$Cl$_8$ and 252 (4) cm^{-1} for (TBA)$_2$Re$_2$Br$_8$. This indicates that the progression in each compound is due to the relaxation of the Re–Re bond in the excited state, as expected for the $\delta \rightarrow \delta^*$ transition, rather than on Re–X bond relaxation. These values are very reasonable in view of the corresponding stretching frequencies for the ground state of 271.9 and 275.4 cm^{-1} reported by Clark and Franks[19] from their resonance Raman study of these compounds.

The most intense progression of each compound is based on an origin that can be considered the 0–0 line of a dipole-allowed, z-polarized transition of the majority component in the disordered crystals. This line for (TBA)$_2$Re$_2$Br$_8$ was 515 cm^{-1} below the corresponding line for the (TBA)$_2$Re$_2$Cl$_8$. The corresponding 0–0 line of the minority component in the crystal of (TBA)$_2$Re$_2$Cl$_8$ was blue shifted only 25 cm^{-1} above that for the major component, and the two lines were barely resolvable. On the other hand, this line for the minor component of (TBA)$_2$Re$_2$Be$_8$ was red shifted by 70 cm^{-1} so the two progressions were clearly resolved. A complex pattern of absorption below these 0–0 lines occurred for both compounds that we have attributed to a disorder not revealed by the X-ray diffraction. The considerable difference in the relative intensities for these additional absorptions and the progression based on them are consistent with their assignment to such a disorder component. They indicate a much lower occurrence of such an anomalous component in the bromide compound. This feature may well account for the better resolution of the major vibrational components in (TBA)$_2$Re$_2$Br$_8$.

Because of the complexity of the spectra observed for these compounds, it should be worthwhile to expend some effort on seeking salts of these anions with other cations that might have a more definitive symmetry and would also provide somewhat simpler spectra.

Acknowledgment. The authors acknowledge the assistance of Professor R. A. Jacobsen in the crystal structure determination, who also provided the equipment for the X-ray diffraction. The support of this work by NSF Grants CHE 76-83665 and CHE 80-007442 is gratefully acknowledged.

Registry No. (TBA)$_2$Re$_2$Br$_8$, 14049-60-6; (TBA)$_2$Re$_2$Cl$_8$, 14023-10-0; Re, 7440-15-5.

Supplementary Material Available: Complete tables of anisotropic thermal parameters, observed and calculated structure factor parameters, and calculated hydrogen positions (9 pages). Ordering information is given on any current masthead page.