Investigations of Quadruple Bonds by Polarized Crystal Spectra. I. The Interpretation of the Spectrum of Tetra(*n*-butylammonium) Octachlorodirhenate. The Disordered Crystal Structure

F. Albert Cotton,*[1a] Bertram A. Frenz,[1b] B. Ray Stults,[1a] and Thomas R. Webb[1a]

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843, and the Molecular Structure Corporation, College Station, Texas 77840.

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Abstract: The crystal structure of the title compound is described in detail. It has a subtle but crucial form of disorder, such that 73.89% of the Re-Re units are aligned in one direction while 26.11% are aligned in a direction perpendicular to this. On the basis of this structural information it is now possible, for the first time, to determine the polarization relative to the molecular axis of the absorption band at ca. 700 nm. This band is found to be, within experimental error, entirely z polarized. This, in turn, virtually assures its assignment as the $\delta \rightarrow \delta^*$ ($A_{2u} \leftarrow A_{1g}$) transition. It is shown that the previous claim of experimental proof for z polarization is without any experimental foundation, being in fact only an assumption made in an unpublished thesis and later treated as a fact. The principal crystallographic data are: space group $P2_1/c$; $a = 10.933$ (5) Å; $b = 15.412$ (6) Å; $c = 16.435$ (5) Å; $\beta = 122.27$ (3)°; $V = 2341.6$ (8) Å^3; $Z = 2$; $d_{\text{calcd}} = 1.62$ g cm^{-3}. Using reflections for which $I > 3\sigma(I)$, the structure has been refined anisotropically to $R_1 = 0.034$ and $R_2 = 0.043$. This is the most precise structure yet available for an $Re_2Cl_8^{2-}$ compound. The Re-Re distance is 2.222 (2) Å. From an analysis of the effect of the disorder upon structure parameters, we conclude that the most probable values for the other independent parameters (averaged according to D_{4h} symmetry) are: Re-Cl, 2.32 ± 0.01 Å; ∠Re-Re-Cl = 103.9 ± 0.2°; ∠Cl-Re-Cl (cis) = 86.7 ± 0.1°; ∠Cl-Re-Cl (trans) = 152.2 ± 0.2°.

Introduction

A potentially powerful source of information on the detailed electronic structures of compounds containing quadruple bonds[2] is the polarization of their electronic absorption bands relative to the molecular axis. A knowledge of the polarization can be derived only from the combination of two experimental measurements: (1) the observed polarization relative to crystallographic axes and (2) an x-ray crystallographic determination of how the molecules are oriented in the unit cell. The former without the latter is at the very least useless and, if handled incompetently or illogically, misleading.

At the time the $Re_2Cl_8^{2-}$ ion was first correctly described and formulated as a species with a quadruple bond,[3-5] a suggestion was made as to the assignment of its visible spectrum,[5] according to which the absorption band at ca. 700 nm was considered too weak (the oscillator strength is ca. 10^{-2}) to qualify as the orbitally allowed ($A_{2u} \leftarrow A_{1g}$, z-polarized) $\delta \rightarrow \delta^*$ transition. It was therefore given a different assignment, consistent with its low intensity and, faute de mieux, the suggestion was made that one of the two strong bands, at ca. 305 nm and ca. 255 nm, with oscillator strengths of about 0.5, might be assigned as the $\delta \rightarrow \delta^*$ transition. Both of these, especially the latter, seemed to be of surprisingly high energy for such an assignment, and it was felt that only for the one of the lower energy was such an assignment credible.

In late 1967, Professor P. N. Schatz and Dr. A. J. McCaffery at the University of Virginia, at our request, measured the magnetic circular dichroism (MCD) spectrum of the $Re_2Cl_8^{2-}$ ion and reported that the band at ca. 305 nm shows an A term.[6] This positively rules out its assignment to the $\delta \rightarrow \delta^*$ transition since the observation of an A term requires that either the upper or lower state be degenerate. Since it seemed out of the question to attribute an even higher energy to the $\delta \rightarrow \delta^*$ transition, as would result from so assigning the other strong band at ca. 255 nm, we decided then that the band at ca. 700 nm might after all be the $\delta \rightarrow \delta^*$ band despite its weakness. We did not publish this conclusion at this time since there was no *positive* evidence to support it, but have since done so.[7]

Only recently have there appeared several publications attempting to deal directly with the assignments for $Re_2Cl_8^{2-}$ and related species.[8-10] Experimental evidence is presented in two preliminary communications[9,10] which is said to prove positively that the band at ca. 700 nm for the $Re_2Cl_8^{2-}$ ion must be assigned to the $\delta \rightarrow \delta^*$ transition. This evidence appears to consist of three parts.

(1) It is stated[9] that the intensity of this band "does not decrease on going from 300 to 5 K eliminating transition assignments which require vibronic intensity giving mechanisms". If the observation is quantitatively reliable, it constitutes good evidence since the activating vibrations[11] would have to be in the range below 360 cm^{-1}, and thus a decrease of at least 30% would be predicted using the approximate formula of McClure.[12]

(2) It is stated[9] that there is no A term for the ca. 700 nm band in the MCD spectrum. This proves nothing since A terms are very often unobserved even when present because they are masked by B and/or C terms.[6]

(3) It was stated[10] that crystal spectra show that this band is polarized along the fourfold rotation axis (z axis) of the $Re_2Cl_8^{2-}$ ion. Such a polarization would indeed afford strong—virtually conclusive—evidence for the δ-δ^* assignment. However, careful scrutiny shows that there is actually *no evidence* presented for such a polarization, as will be explained later. Thus, the experimental evidence favoring the assignment of the ca. 700 nm band of $Re_2Cl_8^{2-}$ to the $\delta \rightarrow \delta^*$ transition has, until now, consisted of nothing more positive than the reported[9] lack of any diminution of its intensity upon lowering the temperature from 300 to ca. 5 K.

In this paper we describe the partially disordered crystal structure of the compound $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$, which was first prepared by one of us,[4a] and then give an interpretation of the published crystal spectrum. The first positive evidence is thereby obtained that this band is z-polarized, thus strongly and positively supporting its assignment to the $\delta \rightarrow \delta^*$ transition. We shall also explain why the previous attribution of z polarization is actually devoid of experimental validity since (a) the argument used contains an egregious breach of logic and, (b) it attempts the impossible, namely, the interpretation of the crystal spectral data without adequate knowledge of the

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Re(1)	−0.02204 (3)	0.06325 (2)	0.02229 (2)	0.01027 (3)	0.00262 (1)	0.00400 (1)	−0.00085 (4)	0.00842 (2)	−0.00079 (2)
Re(2)	−0.10292 (8)	0.00453 (6)	−0.07081 (5)	0.00921 (8)	0.00301 (4)	0.00349 (3)	−0.00088 (10)	0.00691 (6)	−0.00050 (6)
Cl(1)	−0.2634 (2)	0.0506 (1)	−0.0254 (1)	0.0117 (1)	0.00479 (9)	0.00714 (7)	0.0008 (2)	0.0120 (1)	0.0000 (1)
Cl(2)	0.1991 (2)	0.1369 (1)	0.0927 (1)	0.0135 (2)	0.00408 (8)	0.00624 (7)	−0.0044 (2)	0.0112 (1)	−0.0028 (1)
Cl(3)	0.0355 (2)	0.0372 (1)	0.1783 (1)	0.0190 (2)	0.00536 (9)	0.00466 (6)	−0.0038 (2)	0.0132 (1)	−0.0021 (1)
Cl(4)	−0.1020 (2)	0.1504 (1)	−0.1128 (1)	0.0152 (2)	0.00408 (8)	0.00665 (7)	0.0016 (2)	0.0118 (2)	0.0031 (1)
N	0.2855 (5)	0.3057 (3)	0.3425 (3)	0.0121 (5)	0.0026 (2)	0.0055 (2)	−0.0005 (6)	0.0102 (4)	−0.0013 (4)
C(1)	0.3743 (6)	0.3098 (5)	0.2962 (4)	0.0129 (6)	0.0049 (3)	0.0064 (3)	−0.0022 (8)	0.0131 (5)	−0.0028 (5)
C(2)	0.3912 (7)	0.3968 (5)	0.2627 (5)	0.0138 (7)	0.0051 (4)	0.0058 (3)	−0.0041 (9)	0.0102 (6)	−0.0020 (6)
C(3)	0.4828 (7)	0.3900 (6)	0.2191 (5)	0.0155 (8)	0.0081 (5)	0.0055 (3)	−0.0058 (11)	0.0112 (7)	−0.0018 (7)
C(4)	0.5150 (9)	0.4759 (8)	0.1909 (6)	0.0254 (10)	0.0112 (6)	0.0097 (4)	−0.0149 (13)	0.0211 (8)	−0.0023 (10)
C(5)	0.3593 (7)	0.3549 (4)	0.4374 (4)	0.0162 (6)	0.0034 (3)	0.0064 (3)	−0.0024 (7)	0.0146 (5)	−0.0021 (5)
C(6)	0.4983 (7)	0.3170 (5)	0.5198 (4)	0.0153 (8)	0.0040 (3)	0.0058 (3)	−0.0030 (8)	0.0108 (7)	−0.0014 (6)
C(7)	0.5642 (7)	0.3766 (5)	0.6068 (5)	0.0151 (7)	0.0052 (4)	0.0063 (3)	−0.0019 (9)	0.0120 (6)	−0.0022 (6)
C(8)	0.7003 (11)	0.3449 (7)	0.6924 (7)	0.0235 (4)	0.0084 (6)	0.0082 (5)	0.0016 (16)	0.0104 (12)	−0.0039 (9)
C(9)	0.1372 (6)	0.3470 (4)	0.2796 (4)	0.0150 (6)	0.0032 (3)	0.0067 (3)	0.0008 (7)	0.0144 (5)	0.0003 (5)
C(10)	0.0418 (7)	0.3069 (5)	0.1805 (5)	0.0148 (7)	0.0039 (3)	0.0071 (3)	−0.0012 (8)	0.0123 (6)	−0.0009 (6)
C(11)	−0.1049 (9)	0.3531 (5)	0.1268 (6)	0.0179 (10)	0.0051 (4)	0.0082 (4)	0.0037 (11)	0.0105 (9)	−0.0007 (7)
C(12)	−0.2025 (9)	0.3226 (6)	0.0260 (6)	0.0170 (11)	0.0072 (5)	0.0083 (5)	−0.0036 (13)	0.0086 (11)	0.0003 (9)
C(13)	0.2685 (7)	0.2100 (4)	0.3585 (4)	0.0143 (7)	0.0024 (3)	0.0069 (3)	−0.0010 (7)	0.0121 (6)	−0.0016 (5)
C(14)	0.1791 (7)	0.1915 (5)	0.4011 (5)	0.0165 (7)	0.0038 (3)	0.0079 (3)	−0.0027 (8)	0.0145 (7)	−0.0013 (6)
C(15)	0.1979 (8)	0.1004 (5)	0.4359 (5)	0.0253 (9)	0.0038 (3)	0.0072 (3)	−0.0033 (10)	0.0182 (7)	−0.0016 (6)
C(16)	0.1025 (10)	0.0774 (6)	0.4717 (6)	0.0353 (11)	0.0058 (5)	0.0117 (4)	−0.0035 (12)	0.0310 (8)	0.0006 (7)

	x	y	z	β_{11}	Atom	x	y	z	β_{11}
H(1.1)	0.332 (6)	0.274 (4)	0.244 (4)	5.0000 (0)	H(9.1)	0.098 (6)	0.345 (4)	0.317 (4)	5.0000 (0)
H(1.2)	0.462 (6)	0.298 (4)	0.339 (4)	5.0000 (0)	H(9.2)	0.156 (6)	0.401 (5)	0.274 (4)	5.0000 (0)
H(2.1)	0.302 (6)	0.413 (5)	0.217 (4)	5.0000 (0)	H(10.1)	0.094 (6)	0.312 (4)	0.154 (4)	5.0000 (0)
H(2.2)	0.431 (6)	0.430 (4)	0.316 (4)	5.0000 (0)	H(10.2)	0.032 (6)	0.246 (4)	0.186 (4)	5.0000 (0)
H(3.1)	0.431 (6)	0.346 (4)	0.163 (4)	5.0000 (0)	H(11.1)	−0.090 (6)	0.405 (5)	0.140 (4)	5.0000 (0)
H(3.2)	0.566 (6)	0.358 (4)	0.261 (4)	5.0000 (0)	H(11.2)	−0.161 (6)	0.350 (4)	0.149 (4)	5.0000 (0)
H(4.1)	0.559 (6)	0.470 (5)	0.160 (4)	5.0000 (0)	H(12.1)	−0.238 (6)	0.264 (4)	0.005 (4)	5.0000 (0)
H(4.2)	0.414 (6)	0.507 (5)	0.148 (4)	5.0000 (0)	H(12.2)	−0.154 (6)	0.338 (4)	−0.007 (4)	5.0000 (0)
H(4.3)	0.578 (6)	0.517 (5)	0.256 (4)	5.0000 (0)	H(12.3)	−0.312 (6)	0.350 (4)	0.003 (4)	5.0000 (0)
H(5.1)	0.293 (6)	0.363 (4)	0.451 (4)	5.0000 (0)	H(13.1)	0.370 (6)	0.184 (4)	0.397 (4)	5.0000 (0)
H(5.2)	0.374 (6)	0.396 (5)	0.421 (4)	5.0000 (0)	H(13.2)	0.219 (6)	0.183 (5)	0.297 (4)	5.0000 (0)
H(6.1)	0.472 (6)	0.257 (5)	0.537 (4)	5.0000 (0)	H(14.1)	0.204 (6)	0.274 (5)	−0.055 (4)	5.0000 (0)
H(6.2)	0.563 (6)	0.310 (4)	0.495 (4)	5.0000 (0)	H(14.2)	0.076 (6)	0.198 (4)	0.353 (4)	5.0000 (0)
H(7.1)	0.496 (6)	0.395 (5)	0.626 (4)	5.0000 (0)	H(15.1)	0.316 (6)	0.095 (5)	0.496 (4)	5.0000 (0)
H(7.2)	0.576 (7)	0.437 (4)	0.583 (4)	5.0000 (0)	H(15.2)	0.199 (6)	0.063 (4)	0.398 (4)	5.0000 (0)
H(8.1)	0.738 (6)	0.387 (5)	0.750 (4)	5.0000.(0)	H(16.1)	−0.016 (6)	0.057 (4)	0.411 (4)	5.0000 (0)
H(8.2)	0.761 (6)	0.326 (4)	0.676 (4)	5.0000 (0)	H(16.2)	0.083 (6)	0.113 (5)	0.494 (4)	5.0000 (0)
H(8.3)	0.694 (6)	0.279 (4)	0.711 (4)	5.0000 (0)	H(16.3)	0.120 (6)	0.021 (5)	0.501 (4)	5.0000 (0)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

crystal structure. The space group and unit cell dimensions[9] do *not* constitute adequate knowledge for a system with two formula units in space group $P2_1/c$ *even for an ordered crystal*—which this one is not.

Experimental Section

The compound $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ was prepared by Mr. L. W. Shive as previously described[3] by reduction of $KReO_4$ with H_3PO_2. Large crystals were obtained by slow evaporation of a methanol/HCl solution of the crude product.

Two crystals were mounted on glass fibers and examined on a Syntex P$\bar{1}$ autodiffractometer. The ω scans of several intense reflections had peak widths at half-height of ca. 0.15°. Cell constants and an orientation matrix for the monoclinic unit cell were obtained by least-squares refinement of the setting angles of 15 computer-centered reflections, giving $a = 10.933$ (5) Å, $b = 15.412$ (6) Å, $c = 16.435$ (5) Å, $\beta = 122.27$ (3)°, and $V = 2341.6$ (8) Å^3. For $Z = 2$ and mol wt 1141, the calculated density is 1.623 g cm^{-3}. Systematic absences in the data set ($0k0$ for k odd, $h0l$ for l odd) identify the space group as $P2_1/c$, as reported earlier.[9] A considerably more practical option would have been to use the more nearly orthogonal cell in space group $P2_1/n$ with 10.932 (5) Å, 15.412 (6) Å, 14.062 (5) Å, $\beta = 98.83$ (3)°, but we have kept to the earlier choice[9] to minimize confusion.

Data were collected at 23 °C using Mo Kα radiation monochromated by a graphite crystal. The θ-2θ scan technique with a scan varying from 3 to 24°/min was used to collect 3223 unique reflections (2407 with $F_o^2 > 3\sigma(F_o^2)$) in the range $0 < 2\theta \leq 45°$ on the first crystal and later 4136 unique reflections (2829 with $F_o^2 > 3\sigma(F_o^2)$) in the range $0 < 2\theta \leq 50°$ on the second crystal. The scan range was from 0.7° below the Kα_1 peak to 0.7° above the Kα_2 peak. Four standard reflections were remeasured every 100 reflections; the intensity of one standard in the second data set increased by ca. 10% during collection of the data set. No correction was applied. Additional details of data collection have been given elsewhere.[13]

The absorption coefficient for Mo Kα radiation is 59.6 cm^{-1}, and a numerical absorption correction was applied to the data set from a second crystal having the dimensions 0.09 × 0.17 × 0.22 mm. Calculated transmission factors ranged from 0.375 to 0.617 with an average of 0.546. The standard deviations of the observed intensities, $\sigma(F_o^2)$, were calculated[14] using a value of 0.06 for the parameter p. No correction for secondary extinction was deemed necessary.

Solution of the Structure.[14] The coordinates of one rhenium atom and one chlorine atom were recovered from the three-dimensional Patterson map. The positions of these atoms were varied in two cycles of least-squares refinement to give $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.406$ and $R_2 = (\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2)^{1/2} = 0.496$. The remaining chlorine atoms were located in a difference map. Isotropic refinement

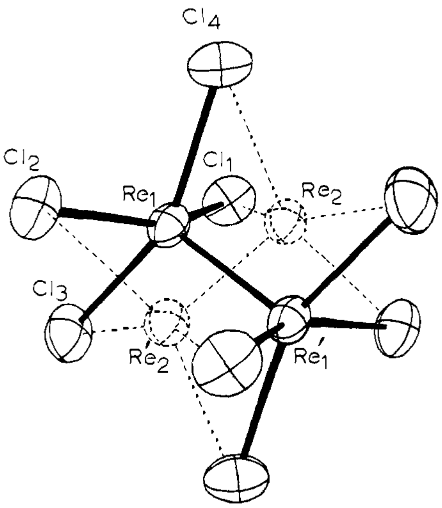

Figure 1. The $Re_2Cl_8^{2-}$ ion. Re_1 and Re_1' represent the Re positions with an occupation number of 73.89% while Re_2 and Re_2' are those with an occupation number of 26.11%. The common midpoint of the two Re-Re lines is a crystallographic center of inversion. Ellipsoids enclose half the electron density for the Cl atoms, and also for the Re atoms if the latter positions are treated as fully occupied.

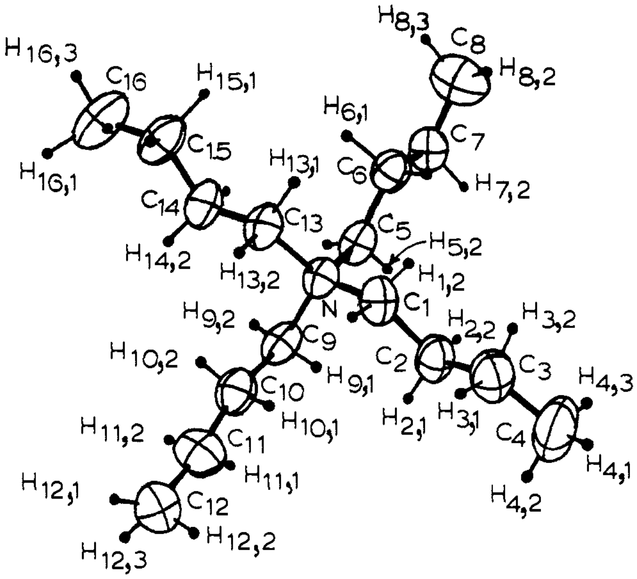

Figure 2. The $(C_4H_9)_4N^+$ ion showing the atom numbering scheme.

Table II. Bond Distances (Å) in $[(\eta\text{-}C_4H_9)_4N]_2Re_2Cl_8$[a,b]

Re(1)-(1)'	2.224 (1)	C(1)-H(1,1)	0.91 (8)
Re(2)-Re(2)'	2.215 (2)	-H(1,2)	0.85 (8)
Re(1)-Cl(1)	2.325 (2)	C(2)-H(2,1)	0.89 (8)
-Cl(2)	2.342 (2)	-H(2,2)	0.91 (9)
-Cl(3)	2.325 (2)	C(3)-H(3,1)	1.03 (8)
-Cl(4)	2.328 (2)	-H(3,2)	0.94 (8)
Re(2)-Cl(1)	2.353 (2)	C(4)-H(4,1)	0.87 (9)
-Cl(2)	2.363 (2)	-H(4,2)	1.09 (8)
-Cl(3)	2.338 (2)	-H(4,3)	1.10 (8)
-Cl(4)	2.352 (2)	C(5)-H(5,1)	0.87 (8)
N-C(1)	1.522 (9)	-H(5,2)	0.74 (9)
N-C(5)	1.521 (10)	C(6)-H(6,1)	1.06 (8)
N-C(9)	1.520 (10)	-H(6,2)	1.00 (8)
N-C(13)	1.527 (9)	C(7)-H(7,1)	1.00 (8)
C(1)-C(2)	1.498 (12)	-H(7,2)	1.05 (8)
C(2)-C(3)	1.515 (12)	C(8)-H(8,1)	1.01 (8)
C(3)-C(4)	1.505 (16)	-H(8,2)	0.96 (8)
C(5)-C(6)	1.513 (12)	-H(8,3)	1.09 (8)
C(6)-C(7)	1.520 (11)	C(9)-H(9,1)	0.92 (8)
C(7)-C(8)	1.485 (15)	-H(9,2)	0.86 (9)
C(9)-C(10)	1.520 (12)	C(10)-H(10,1)	0.90 (8)
C(10)-C(11)	1.532 (13)	-H(10,2)	0.96 (8)
C(11)-C(12)	1.489 (15)	C(11)-H(11,1)	0.83 (9)
C(13)-C(14)	1.503 (11)	-H(11,2)	0.86 (8)
C(14)-C(15)	1.488 (12)	C(12)-H(12,1)	0.97 (8)
C(15)-C(16)	1.486 (14)	-H(12,2)	0.97 (8)
		-H(12,3)	1.13 (8)
		C(13)-H(13,1)	1.03 (8)
		-H(13,2)	0.96 (8)
		C(14)-H(14,1)	0.82 (8)
		-H(14,2)	0.97 (8)
		C(15)-H(15,1)	1.14 (8)
		-H(15,2)	0.85 (8)
		C(16)-H(16,1)	1.18 (8)
		-H(16,2)	0.73 (9)
		-H(16,3)	0.95 (8)

[a] Figures in parentheses are the estimated standard deviations in the least significant figures. [b] Atoms labeled with primes (′) are symmetry related to the corresponding atoms without primes. See Figure 1.

of the unique $ReCl_4$ group gave $R_1 = 0.318$ and $R_2 = 0.408$. A succession of difference maps and least-squares refinements located the Bu_4N^+ ion, but refinement produced $R_1 = 0.283$ and $R_2 = 0.369$. Most of the temperature factors were unreasonable. The structure was solved again by direct methods. The most intense peak in the resulting E map corresponded to the rhenium atom peak in the original Patterson solution. Several weaker peaks also appeared around the Re atom; an examination of earlier results indicated that one of these weaker peaks, located about 1.5 Å from the Re atom, had appeared in earlier difference maps and that cross vectors between it and the original Re atom appeared in the Patterson map. A disordered model, consisting of two Re_2 units, with occupancy factors of ca. 0.75 and 0.25, occupying two of the local fourfold axes of a cube defined by the chlorine atoms, was assumed. Refinement of the disordered model produced $R_1 = 0.107$ and $R_2 = 0.130$, and all temperature factors appeared reasonable. No further use was made of the data set from the first crystal.

Refinement was continued using the data set from the second crystal, which had been corrected for absorption effects. Refinement of the 23 nonhydrogen atoms employing, first, isotropic and then anisotropic thermal parameters resulted in $R_1 = 0.042$ and $R_2 = 0.056$. In the preceding and all subsequent least-squares refinement cycles the multiplicity factors for the disordered rhenium atoms, Re(1) and Re(2), were treated as variables, subject to the constraint that the sum of the two must be unity.

Scattering factors for the neutral atoms were obtained from Cromer and Waber.[15] Anomalous dispersion effects were included in calculated structure factors for the rhenium and chloride atoms.[16]

Two difference Fourier maps, each following the least-squares refinement of the atoms previously located, resulted in the location of the 36 hydrogen atoms of the Bu_4N^+ ion. The structural model was refined to convergence in four cycles of full-matrix least-squares refinement employing anisotropic temperature factors for all nonhydrogen atoms and isotropic temperature factors for the 36 hydrogen atoms (a value of 5.0 was chosen and not refined) to give the final residuals $R_1 = 0.034$ and $R_2 = 0.043$ for the 2829 reflections having $2\theta \leq 50.0°$ and $I > 3\sigma(I)$. A table of the observed and calculated structure factor amplitudes is available.[17] The final value for the error in an observation of unit weight is 1.023.

The final, refined occupancy factors for the disordered rhenium atoms are 0.7389 (2) and 0.2611 for Re(1) and Re(2), respectively.

During the final cycle of refinement the average parameter shifts were less than 0.06 times their esd's with the largest shift of 0.6σ being observed for H(16,2). An examination of the final values of F_o and F_c showed no trends in Miller indices, reflection number, or $\sin\theta/\lambda$. A final difference Fourier map showed no features of significance. An examination of the final correlation coefficients showed that for all atoms the coefficients for x and z and β_{11} and β_{13} averaged to 0.6 ± 0.1, these values being within ±10% of the values expected having a β angle of 122.27°. This could have been avoided had the cell with the n glide and $\beta \approx 99°$ been chosen, instead of the unfortunate choice already adopted.[9] As already noted, we considered it best to continue in $P2_1/c$ in order to facilitate the interpretation of the polarization measurements in relation to the structure.

Polarization Calculation. The polarization ratios were calculated

Table III. Bond Angles (Degrees) in $[(\eta\text{-}C_4H_9)_4N]_2Re_2Cl_8$[a,b]

Re(1)′-Re(1)-Cl(1)	102.82 (5)
-Cl(2)	103.87 (5)
-Cl(3)	103.50 (5)
-Cl(4)	103.21 (5)
Re(2)′-Re(2)-Cl(1)	101.37 (8)
-Cl(2)	102.79 (8)
-Cl(3)	102.90 (8)
-Cl(4)	101.97 (8)
Cl(1)-Re(1)-Cl(2)	153.31 (7)
-Cl(3)	87.01 (8)
-Cl(4)	86.89 (7)
Cl(3)-Re(1)-Cl(4)	153.29 (8)
Cl(2)-Re(1)-Cl(3)	86.48 (7)
-Cl(4)	87.39 (7)
Cl(1)-Re(2)-Cl(2)	88.87 (7)
-Cl(3)	155.73 (9)
-Cl(4)	85.70 (8)
Cl(2)-Re(2)-Cl(3)	85.70 (7)
-Cl(4)	155.23 (8)
Cl(3)-Re(2)-Cl(4)	89.39 (8)
N-C(1)-H(1,1)	108 (5)
-H(1,2)	108 (6)
C(2)-C(1)-H(1,1)	107 (5)
-H(1,2)	101 (6)
H(1,1)-C(1)-H(1,2)	116 (8)
C(1)-C(2)-H(2,1)	105 (5)
-H(2,2)	104 (5)
C(3)-C(2)-H(2,1)	109 (5)
-H(2,2)	114 (5)
H(2,1)-C(2)-H(2,2)	114 (8)
C(2)-C(3)-H(3,1)	107 (4)
-H(3,2)	108 (5)
C(4)-C(3)-H(3,1)	114 (4)
-H(3,2)	113 (5)
H(3,1)-C(3)-H(3,2)	99 (7)
C(3)-C(4)-H(4,1)	113 (6)
-H(4,2)	106 (4)
-H(4,3)	109 (4)
H(4,1)-C(4)-H(4,2)	111 (8)
-H(4,3)	112 (7)
C(1)-N-C(5)	111.1 (6)
-C(9)	112.1 (6)
-C(13)	107.1 (5)
C(5)-N-C(9)	106.1 (6)
-C(13)	110.6 (6)
C(9)-N-C(13)	109.8 (6)
N-C(1)-C(2)	117.2 (6)
N-C(5)-C(6)	117.1 (6)
N-C(9)-C(10)	115.5 (6)
N-C(13)-C(14)	115.6 (6)
C(1)-C(2)-C(3)	110.8 (8)
C(2)-C(3)-C(4)	114.0 (10)
C(5)-C(6)-C(7)	110.7 (7)
C(6)-C(7)-C(8)	114.9 (8)
C(9)-C(10)-C(11)	109.6 (7)
C(10)-C(11)-C(12)	113.7 (9)
C(13)-C(14)-C(15)	111.5 (7)
C(14)-C(15)-C(16)	113.4 (9)
N-C(5)-H(5,1)	106 (5)
-H(5,2)	99 (7)
C(6)-C(5)-H(5,1)	114 (5)
-H(5,2)	111 (7)
H(5,1)-C(5)-H(5,2)	109 (8)
C(5)-C(6)-H(6,1)	107 (4)
-H(6,2)	106 (4)
C(7)-C(6)-H(6,1)	110 (4)
-H(6,2)	112 (4)
H(6,1)-C(6)-H(6,2)	111 (6)
C(6)-C(7)-H(7,1)	114 (5)
-H(7,2)	106 (4)
C(8)-C(7)-H(8,1)	110 (4)
-H(8,2)	112 (5)
H(7,1)-C(7)-H(7,2)	98 (6)
C(7)-C(8)-H(8,1)	112 (4)
-H(8,2)	110 (5)
-H(8,3)	113 (4)
H(8,1)-C(8)-H(8,2)	117 (7)
-H(8,3)	111 (6)
H(8,2)-C(8)-H(8,3)	92 (7)
H(4,2)-C(4)-H(4,3)	106 (4)
N-C(9)-H(9,1)	104 (5)
-H(9,2)	104 (6)
C(10)-C(9)-H(9,1)	114 (5)
-H(9,2)	110 (6)
H(9,1)-C(9)-H(9,2)	108 (7)
C(9)-C(10)-H(10,1)	105 (5)
-H(10,2)	110 (5)
C(11)-C(10)-H(10,1)	115 (5)
C(11)-C(10)-H(10,2)	112 (5)
H(10,1)-C(10)-H(10,2)	104 (7)
C(10)-C(11)-H(11,1)	108 (6)
-H(11,2)	119 (6)
C(12)-C(11)-H(11,1)	122 (6)
-H(11,2)	100 (6)
H(11,1)-C(11)-H(11,2)	94 (8)
C(11)-C(12)-H(12,1)	127 (5)
-H(12,2)	105 (5)
-H(12,3)	104 (4)
H(12,1)-C(12)-H(12,2)	105 (7)
-H(12,3)	94 (6)
H(12,2)-C(12)-H(12,3)	122 (6)
N-C(13)-H(13,1)	107 (4)
-H(13,2)	107 (5)
C(14)-C(13)-H(13,1)	113 (4)
-H(13,2)	106 (5)
H(13,1)-C(13)-H(13,2)	107 (6)
C(13)-C(14)-H(14,1)	107 (5)
-H(14,2)	111 (5)
C(15)-C(14)-H(14,1)	111 (5)
-H(14,2)	106 (5)
H(14,1)-C(14)-H(14,2)	110 (5)
C(14)-C(15)-H(15,1)	105 (4)
-H(15,2)	114 (6)
C(16)-C(15)-H(15,1)	110 (4)
-H(15,2)	114 (6)
H(15,1)-C(15)-H(15,2)	98 (7)
C(15)-C(16)-H(16,1)	114 (4)
-H(16,2)	119 (8)
-H(16,3)	114 (5)
H(16,1)-C(16)-H(16,2)	88 (9)
-H(16,3)	92 (6)
H(16,2)-C(16)- -H(16,3)	121 (9)

[a] Figures in parentheses are the estimated standard deviations in the least significant figures. [b] Atoms labeled with primes (′) are symmetry related to the corresponding atoms without primes. See Figure 1.

by modifying Piper's equations.[18] In a complex with axial symmetry, the parallel and perpendicular absorbances ($A_{\parallel}$ and $A_{\perp}$) relative to the crystal axes are functions of the parallel and perpendicular absorbances (A_z and A_x) relative to the molecular axes. If absorbances obey Beer's law, and are identical for both orientations, we have for a disordered crystal

$$A_{\parallel} = \sum_i f_i A_{\parallel_i}$$

$$A_{\perp} = \sum_i f_i A_{\perp_i}$$

where f_i is the occupancy factor of the ith orientation of the disordered chromophore ($\Sigma f_i = 1$) and $A_{\parallel_i}$ and $A_{\perp_i}$ are the parallel and perpendicular absorbances for the ith orientation. Piper's equations for $A_{\parallel}$ and $A_{\perp}$ were written in the form

$$A_{\parallel} = \Sigma f_i (A_z \cos^2 \theta_i + A_x \sin^2 \theta_i)$$

$$A_{\perp} = \Sigma f_i (A_z \cos^2 \gamma_i + A_x \sin^2 \gamma_i)$$

Polarization ratios $A_{\parallel}/A_{\perp}$ were calculated by varying A_z and A_x subject to the constraint $A_z + A_x = 1$. Under this constraint, a transition allowed only in z polarization would have $A_x = 0$; an $x(y)$-allowed transition would have $A_z = 0$; for a transition having some allowed character in both directions (a vibronic band), neither A_z nor A_x would be 0.

Results

The final positional parameters and thermal vibration parameters are listed in Table I. Anisotropic thermal parameters are given for all atoms except hydrogen atoms. An isotropic thermal parameter, fixed at 5.0 Å^2, was used for each hydrogen atom.

The $Re_2Cl_8{}^{2-}$ ion and the $(C_4H_9)_4N^+$ ion are shown in Figures 1 and 2, respectively. The $Re_2Cl_8{}^{2-}$ ion occupies a crystallographic center of inversion, and thus there are only four crystallographically independent chlorine atoms. Re(1) and Re(1)′ are the related pair of rhenium atoms which have the larger occupation factor, while Re(2) and Re(2)′ are those with the smaller occupation factor. In Figure 1, Re(1) and Re(1)′ are shown in heavy outline while Re(2) and Re(2)′ are shown with broken lines. The atom numbering scheme is defined in the figures.

Numerical values of the individual bond distances and bond angles are listed in Tables II and III, respectively.

Table IV gives average values of bond distances and angles. For the $Re_2Cl_8{}^{2-}$ ion, the averages were computed assuming ideal D_{4h} symmetry for each orientation. The values are listed separately for each orientation. As will be shown later, an average of the dimensions for the two orientations does *not* correspond to the true dimensions of the $Re_2Cl_8{}^{2-}$ ion. The problem is a little more subtle and it will be dealt with in the Discussion section.

The average values of the parameters for the $(C_4H_9)_4N^+$ ion are all satisfactorily close to the standard values for such distances and angles. The mean C–H distance, 0.96 (8) Å, is no exception, appearances to the contrary, since it is well known

Table IV. Average Structure Parameters

A. For $Re_2Cl_8^{2-}$	Major orientation	Minor orientation
Re-Re	2.224 (1)	2.215 (2)
Re-Cl	2.330 (2)	2.352 (2)
Re-Re-Cl	103.35 (5)	102.26 (8)
Cl-Re-Cl(trans)	153.30 (8)	155.48 (9)
Cl-Re-Cl(cis)	86.94 (7)	87.42 (8)

B. For $(n\text{-}C_4H_9)_4N^+$

N-C	1.52 (1)	C-C-C	112.3 (8)
C-C	1.50 (1)	N-C-H	105 (5)
C-H	0.96 (8)	C-C-H	110 (5)
C-N-C	109.5 (6)	H-C-H	106 (7)
N-C-C	116.4 (6)		

Table V. Deviations from Cubic Shape of Some $M_2X_8^{n-}$ Ions

Compound	D_v, Å	D_b, Å	% dev	Ref
$K_3Tc_2Cl_8 \cdot 2H_2O$	3.32	3.23	2.7	*a*
$K_2Re_2Cl_8 \cdot 2H_2O$	3.32	3.1t	t.3	*b*
$CsRe_2Br_8$	3.48	3.39	2.6	*c*
$K_4Mo_2Cl_8 \cdot 2H_2O$	3.42	3.35	2.1	*d*
$(enH_2)_2Mo_2Cl_9 \cdot 2H_2O$	3.41	3.35	1.8	*e*
$(NH_4)_5Mo_2Cl_9 \cdot H_2O$	3.43	3.38	1.5	*f*

[a] F. A. Cotton and L. W. Shive, *Inorg. Chem.*, **14**, 2032 (1975). [b] F. A. Cotton and C. B. Harris, *ibid.*, **4**, 330 (1965). [c] F. A. Cotton, B. G. DeBoer, and M. Jeremic, *ibid.*, **9**, 2143 (1970). [d] J. V. Brencic and F. A. Cotton, *ibid.*, **8**, 7 (1969). [e] J. V. Brencic and F. A. Cotton, *ibid.*, **8**, 2698 (1969). [f] J. V. Brencic and F. A. Cotton, *ibid.*, **9**, 346 (1970).

that x-ray crystallographic results consistently underestimate C-H distances by about 0.1 Å. It is very common for the alkyl chains of tetra-*n*-alkylammonium ions, or even the entire ion, to be disordered. This compound constitutes one of the rare examples of a well-ordered structure.

Discussion

The work reported here provides new and significant results on three points: (1) the polarization of the absorption band at ca. 700 nm; (2) the tendency of $M_2X_8^{2-}$ ions to be disordered in crystals; (3) the interpretation of the experimental results on this disordered crystal to provide the best values of structure parameters for the $Re_2Cl_8^{2-}$ ion.

Polarization of the 700 nm Absorption Band. Crystals of $[(n\text{-}C_4H_9)_4N]_2[Re_2Cl_8]$ characteristically grow as plates with well-developed {100} faces. Using such a crystal it was shown[9,10] that the 700 nm band is stronger for radiation polarized parallel to the *b* axis than perpendicular to the *b* axis. It is obvious from the published[9,10] spectra that the intensity ratio is approximately 2, and in Cowman's Ph.D. thesis[19] the value 2.203 is given. It was then stated[10] that the polarization relative to the molecular axes was deduced from the measured polarization relative to the crystal axis and found to be along the molecular *z* axis. The equations relating crystal polarizations ($A_{\parallel}$, $A_{\perp}$) to molecular absorption coefficients (A_z, A_{xy}) were presented.[10] These included direction cosines for the Re-Re axis, and the source of this necessary information was stated to be "C. D. Cowman, Ph.D. Thesis, California Institute of Technology".

Since no crystal structure had ever been published[20] for the compound in question, it was not evident how the crystal data could have been related to the molecular coordinates and absorption coefficients, as was done in the equations. Cowman's thesis[19] was therefore consulted. According to that document no crystal structure analysis was ever done, and the equations quoted in the publication[10] were obtained (see p 121, ref 19) *"assuming that the transition at 700 nm is z polarized"*. In short, there is no logical nexus between any experimental datum and the subsequent statement that "The *z* polarization of the 14,180 cm^{-1} band is consistent with its assignment . . .". Therefore, prior to the study now being reported by us, there has been *no* experimental determination of how the ca. 700 nm transition in the $Re_2Cl_8^{2-}$ ion is polarized relative to the molecular axes. We can now report that important datum on the basis of the necessary experimental facts.

Using the structural data we have presented above and the equations we have given earlier, one can calculate, for any given polarization relative to molecular axes, the observed polarization ratio relative to crystal axes. For a transition which has a nonzero value of A_z but $A_{xy} = 0$ (i.e., is *z* polarized), the calculated ratio is 2.158 (4), where the esd is derived from the esd in the occupation factors omitting the esd's in the positional parameters. Clearly, this value is in close agreement with the measured value of 2.203 (no error limits are stated[19] for the measured ratio) and allows us to conclude that the ca. 700 nm transition of $Re_2Cl_8^{2-}$ is *z*-polarized. This, in turn, as indicated in the introduction, provides, for the first time, strong experimental support for assigning this band to the $\delta \rightarrow \delta^*$ ($A_{2u} \leftarrow A_{1g}$) transition.

Disordering of $M_2X_8^{n-}$ Ions. Disordering of the type found here has been observed before and is not entirely surprising when the shape of the $M_2X_8^{n-}$ ions is considered. As was emphasized some time ago,[21] the eight X atoms in these ions lie approximately at the vertices of a cube, the edges of which approximate to the sum of packing radii for the X atoms. There are, however, small deviations from cubic shape, namely, elongations in the direction of the M-M bond. Thus, these ions are square parallelepipeds with $D_v > D_b$, where D_v is the length of the "vertical" edge (parallel to M-M) and D_b is the length of the basal edge. Table V gives values of D_v, D_b, and the percentage difference between them for six structures.

For the four $M_2Cl_8^{n-}$ ions in which M is from the second transition series (Tc or Mo) and the M-M bond is fairly short (2.12-2.15 Å), the elongation is about 2%. For $Re_2Br_8^{2-}$, the elongation is not significantly greater since the larger size of the Br atoms allows the X_8 cube to accommodate the larger M_2 unit without a great increase in distortion. With $Re_2Cl_8^{2-}$, however, there is a significantly greater elongation since the rather large Re_2 unit forces the opposite square faces of the cube apart. Nevertheless, even for $Re_2Cl_8^{2-}$, and especially for the others, an $M_2X_8^{n-}$ unit can probably fit into its crystal environment almost as well in a perpendicular orientation (i.e., tipped, in either of two ways, by 90°) as it can in its proper, or parallel, orientation. It can thus be anticipated that there will, occasionally, be cases where the parallel orientation and at least one of the perpendicular orientations will be similar enough energetically that, at equilibrium, some of the units lie perpendicular.

This phenomenon was first observed some years ago in $K_4Mo_2Cl_8 \cdot 2H_2O$ (see Table V for the reference), where 7% of the $Mo_2Cl_8^{4-}$ ions are in a perpendicular orientation. It is also pertinent to note here that in $Re_2Cl_4(PEt_3)_4$ there is a disorder of the same type which attains the limit of randomness: three equivalent, mutually perpendicular orientation are equally populated.[22]

In the present case, despite the fact that the $Re_2Cl_8^{2-}$ ion is somewhat more elongated than $Mo_2Cl_8^{4-}$, we find 26.1% of the ions in a perpendicular orientation. It must be noted that the tendency to this sort of disorder will depend not only on the extent to which the shape of the $M_2X_8^{n-}$ ion approaches a cube but also on the extent to which the surroundings will tolerate the tipping of the nearly cubic parallelepiped in a perpendicular orientation. It does not appear possible to make a priori predictions of the latter, and thus we suggest that this type of disorder is always a possibility to be considered in the crystal

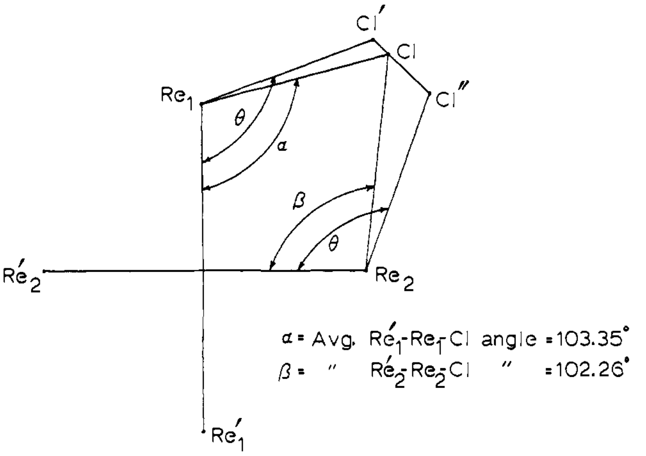

Figure 3. A diagram showing how the best approximation to the Re-Re-Cl angle, θ, was calculated from the apparent values, α and β, for the two orientations of the molecule.

structures of $M_2X_8{}^{n-}$ compounds and other related ones.

Structure of the $Re_2Cl_8{}^{2-}$ Ion. Since this ion has the historical distinction of being the species in which the existence of quadruple bonds was discovered,[3-5] it is ironic that its structure has heretofore not been determined with precision. Unfortunately, the present study, despite the high state of refinement attained according to the conventional figures of merit, also gives most of the parameters with relatively low precision because of the disorder.

The occurrence of the disorder does not affect the accuracy of the Re-Re distance in any direct manner, as is the case for other distances and angles. The weighted average of Re(1)-Re(1)′ and Re(2)-Re(2)′, namely 2.222(2) Å, differs insignificantly from Re(1)-Re(1)′. We shall take the weighted average as the nominal "true" Re-Re distance.

For all dimensions involving the Cl atoms, we analyze the influence of the disorder as follows. We assume that the apparent Cl positions are a compromise, or weighted average, of the actual positions for Cl atoms in the separate orientations. This results from the fact that the Cl positions for the two orientations are so close that it is impossible to resolve them. The apparent positions should be smeared a little but this will be absorbed in the thermal vibration tensor. The question then is: How should we extract from these average positions the bond lengths and angles applicable to the individual orientations of the molecule? We note first that the apparent Cl positions are such as to give a less elongated $Re_2Cl_8{}^{2-}$ ion in *each* orientation. Each $Re_2Cl_8{}^{2-}$ ion is distorted *in the same way*, though to different degrees by the effect of the other one on the apparent Cl positions. Thus, averaging the dimensions for the two, as they appear in Table IV, does *not* produce an approximation to the correct set.

The correct approach can be most easily explained by considering the case of the Re-Re-Cl angle. Figure 3 shows, approximately, the considerations involved. We assume that the apparent position of a Cl atom lies one-quarter of the way between the actual positions for the two orientations, in each of which we have the true Re-Re-Cl angle, θ. The observed angles α (for the main orientation) and β (for the minor orientation) are both smaller. The relation between α, β, and θ is

$$3(\theta - \alpha) = \theta - \beta$$

Table VI. Estimated Best Values for Structure Parameters of $Re_2Cl_8{}^{2-}$

Re-Re,	Å 2.222 (2)	∠Re-Re-Cl, deg	103.9 ± 0.02
Re-Cl,	Å 2.32 ± 0.01	∠Cl-Re-Cl(cis), deg	86.7 ± 0.1
		∠Cl-Re-Cl(trans), deg	152.2 ± 0.2

from which it is easy to calculate that $\theta = 103.9°$. Taking account of the esd's in α and β as well as the fact that our argument is not perfectly rigorous, we feel that an uncertainty of ±0.2° can reasonably be assigned to this value. Note that the true value of θ is larger than either α or β and that, as already stated, the average $(3\alpha + \beta)/4$ does not correspond to the true value of θ.

Proceeding in a similar way, we estimate the true values of other structure parameters which involve the Cl atoms, and assign them reasonable uncertainties. These final results are collected in Table VI.

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Supplementary Material Available: A listing of structure factor amplitudes (13 pp). Ordering information is given on any current masthead page.

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