with respect to the crystal axes as the perpendicular to the coordination plane, and this also was found to be the case.[4]

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Registry No. Ni[en(tfacac)$_2$], 40792-92-5.

Supplementary Material Available: listing of structure factor amplitudes (8 pages). Ordering information is given on any current masthead page.

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Crystal and Molecular Structure of Niobium Pentamethoxide—a Structure with Two Different Conformers in the Unit Cell

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Nb(OCH$_3$)$_5$ crystallizes in the triclinic system with $a = 8.684$ (3) Å, $b = 9.673$ (3) Å, $c = 12.543$ (3) Å, $\alpha = 69.33$ (2)°, $\beta = 85.84$ (2)°, and $\gamma = 86.46$ (3)° and with 4 formula units per unit cell, space group $P\bar{1}$. The structure was refined to $R = 0.04$; the esd's of the distances Nb–O and O–C are 0.007 and 0.01 Å and those of the bond angles O–Nb–O and Nb–O–C are 0.3 and 0.7°, respectively. The unit cell is pronouncedly pseudo body centered and contains two crystallographically different centrosymmetric dimeric molecules which have different conformations. Both forms consist of two approximately octahedral units with a shared edge, differentiated by a cis or trans arrangement of the equatorial methyl groups with respect to the equatorial plane. The evidence for a π contribution to the Nb–O bond and the absence of any significant trans effect is discussed.

Introduction

The preparation and solution properties of numerous transition metal alkoxides have been the subject of many publications and reviews.[2] By contrast there are very few data concerning their structures in the solid state. To our knowledge, the only x-ray structure determinations reported to date are those of the polymeric vanadium oxyalkoxide (VO(OCH$_3$)$_3$)$_n$[3] and the tetrameric titanium alkoxides Ti$_4$(OCH$_3$)$_{16}$,[4] Ti$_4$(OC$_2$H$_5$)$_{16}$,[5] and Ti$_4$(OCH$_3$)$_4$(OC$_2$H$_5$)$_{12}$.[6]

In the case of the vanadium and the methoxy titanium compounds, the precision of the structures which were determined from film data ($R = 0.17$ and 0.14, respectively) does not allow one to discuss the bonding parameters with any certainty; in the latter molecule two of the methoxy groups were presumed to be largely hydrolyzed in the sample which was analyzed. In the other two titanium alkoxides, only the metal and oxygen coordinates were reported.

This lack of existing data may well be attributable to the difficulty in obtaining suitable good-quality crystals for an x-ray study due to the extreme air sensitivity of these compounds.

The coordination chemistry,[7] stereolability,[8] and solvation[9] of niobium pentamethoxide Nb(OCH$_3$)$_5$ have been extensively studied. The compound was found to be dimeric in nonpolar solvents[8a,b] and in noncomplexing polar solvents.[8d] The dimeric unit has been shown to be retained in the vapor phase by mass spectrometry.[10] A precise knowledge of its molecular structure was expected to shed some light on its solvation properties, structural dynamics, and chemical behavior and also on the question of a trans effect, or inequivalence in d_π–p_π contribution between the axial and equatorial metal–oxygen bonds.

The crystal and molecular structure of Nb(OCH$_3$)$_5$ is reported herein. It presents the interesting feature of the existence of two conformers of the same molecule in the unit cell.

Experimental Section

Niobium pentamethoxide[11] readily forms monocrystals by slow sublimation when stored at 47 °C in an evacuated tube. However, the transfer of these extremely air-sensitive crystals to Lindemann tubes proved impossible with the equipment at our disposal. Suitable crystals were therefore prepared in the following manner. The alkoxide (~50 mg) was sealed into an evacuated 0.5-ml Pyrex glass ampule with one end drawn out into a fine capillary. The ampule was kept at 47 ± 0.5 °C for 4 weeks. After this time, several suitable crystals had formed in the capillary which was then sealed off from the ampule. In this manner, we were able to store the crystals in vacuo and without change for many weeks at room temperature. The rather thick walls of the capillary, however, led to a higher background of the x-ray intensities than normal, especially for the low-order reflections.

Table I. Atomic Parameters for $Nb_2(OCH_3)_{10}$ with Standard Deviations in Parentheses

Atom	10^4x	10^4y	10^4z	10^4U_{11}	10^4U_{22}	10^4U_{33}	10^4U_{12}	10^4U_{13}	10^4U_{23}
Nb1	−378 (1)	1152 (1)	795 (1)	356 (8)	441 (6)	429 (6)	−26 (6)	3 (5)	−181 (6)
Nb2	4564 (1)	6482 (1)	5471 (1)	350 (8)	401 (6)	470 (6)	−19 (6)	−9 (5)	−166 (6)
O11	1387 (7)	181 (7)	−35 (5)	275 (45)	482 (40)	469 (36)	−16 (35)	−20 (32)	−173 (33)
O21	6366 (7)	4982 (6)	5224 (5)	340 (47)	380 (36)	546 (41)	1 (35)	−10 (34)	−202 (34)
O12	−58 (8)	−496 (7)	2155 (5)	606 (54)	658 (46)	422 (39)	−48 (41)	−14 (36)	−166 (35)
O22	4263 (8)	5030 (7)	6955 (5)	587 (54)	737 (48)	483 (40)	7 (42)	−3 (37)	−209 (37)
O13	−2326 (7)	1735 (7)	1286 (5)	471 (50)	602 (45)	600 (42)	3 (39)	19 (37)	−259 (36)
O23	2605 (8)	7424 (7)	5569 (5)	483 (50)	532 (42)	692 (44)	75 (38)	21 (37)	−287 (36)
O14	1082 (9)	2108 (8)	1344 (6)	572 (60)	685 (48)	855 (50)	−53 (44)	9 (43)	−458 (43)
O24	5877 (9)	7397 (8)	6159 (6)	495 (58)	744 (51)	1090 (57)	9 (45)	−155 (46)	−539 (47)
O15	−392 (8)	2763 (7)	−618 (5)	584 (54)	434 (40)	702 (45)	49 (38)	42 (39)	−144 (36)
O25	5140 (8)	7805 (6)	4017 (5)	576 (53)	373 (38)	664 (45)	−42 (37)	122 (39)	−71 (36)
C11	2959 (13)	−54 (14)	328 (9)	270 (79)	1184 (96)	909 (84)	61 (70)	−198 (63)	−613 (77)
C21	8011 (13)	5354 (13)	5074 (11)	254 (80)	745 (82)	1338 (98)	−88 (64)	−22 (71)	−387 (78)
C12	892 (15)	−1256 (15)	3073 (9)	744 (97)	1263 (112)	717 (82)	63 (85)	−506 (74)	106 (80)
C22	5261 (15)	4194 (12)	7861 (8)	935 (106)	824 (85)	646 (76)	228 (76)	−401 (72)	−156 (67)
C13	−3514 (15)	2824 (12)	1071 (10)	495 (95)	700 (82)	1276 (102)	241 (72)	−114 (78)	−309 (80)
C23	1351 (14)	7559 (14)	6275 (8)	582 (97)	1121 (99)	603 (71)	86 (79)	172 (63)	−428 (71)
C14	1854 (18)	3463 (13)	1009 (11)	908 (128)	609 (83)	1530 (119)	−70 (85)	−185 (99)	−320 (88)
C24	6752 (16)	8666 (12)	5887 (11)	649 (105)	629 (78)	1493 (109)	−283 (74)	−195 (86)	−494 (81)
C15	512 (15)	3552 (12)	−1640 (9)	951 (112)	750 (86)	704 (79)	−247 (77)	219 (76)	−44 (69)
C25	6068 (15)	8641 (13)	3070 (9)	741 (97)	947 (97)	776 (83)	−230 (78)	304 (73)	121 (76)

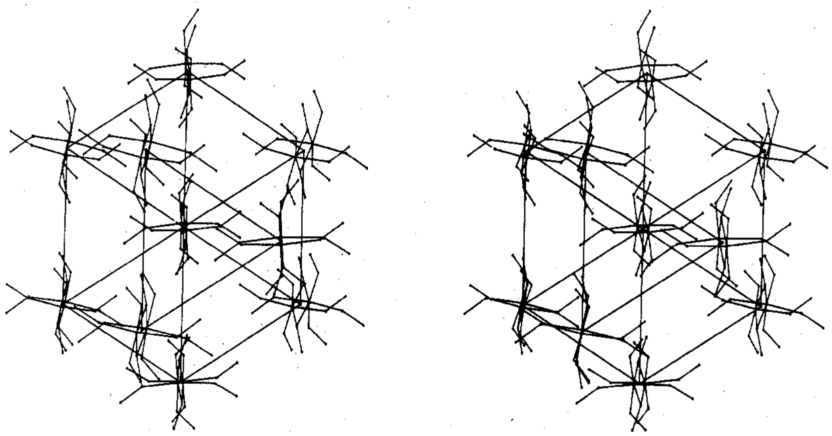

Figure 1. Stereoscopic view of the packing of $Nb_2(OCH_3)_{10}$ projected onto the (011) plane. *a* is directed from the top to the bottom of the page; $[01\bar{1}]$, from left to right.

The dimensions of the chosen crystal were 0.073 × 0.123 × 0.143 mm. The unit cell was determined to be triclinic having cell dimensions $a = 8.864$ (3) Å, $b = 9.673$ (3) Å, $c = 12.543$ (3) Å, $\alpha = 69.33$ (2)°, $\beta = 85.84$ (2)°, $\gamma = 86.46$ (3)° and containing 4 formula units. The density, $d = 1.62$ g cm^{-3}, was measured by flotation in a mixture of $C_8F_{17}CH{=}CH_2$ and $CFCl_2CF_2Cl$ ($d_{calcd} = 1.68$ for $z = 4$). The structure was subsequently solved in the centrosymmetric space group, $P\bar{1}$.

The intensities of 2594 unique reflections, 1556 of which were above the 3σ limit, were measured with a Syntex $P2_1$ automated four-circle diffractometer using graphite-monochromatized Mo Kα radiation and the 2θ scan method to a maximum of $(\sin\theta)/\lambda = 0.540$. The intensities were corrected for absorption using a crystal form which was accurately measured with a special telescope mounted on the 2θ arm of the diffractometer ($\mu_{MoK\alpha} = 11.79$ cm^{-1}). Scattering factors for the neutral atoms were taken from Cromer and Mann.[12] All computer programs were taken from the X-Ray 72 program system as modified by Schwarzenbach.[13] The stereoscopic drawings were prepared by the program ORTEP.[14]

Solution of the Structure

The reflections with $h + k + l$ even are systematically much stronger than those with $h + k + l$ odd. This indicates a pseudo-body-centered cell. Knowing the compound to be dimeric in solution[8a,b] and as a vapor[10] and assuming a centrosymmetric cell, two types of possible structures can be envisaged: one contains an unsymmetrical molecule centered near $^1/_4$, $^1/_4$, $^1/_4$; the other is formed by two crystallographically unrelated but centrosymmetric molecules centered at 0, 0, 0 and $^1/_2$, $^1/_2$, $^1/_2$. The Patterson map did not allow us to distinguish between these models. The necessarily centrosymmetric mean Nb position in an exactly body-centered cell and the mean orientation of the molecules, however, were easily obtained and indicated indeed a dimeric species with an Nb–Nb distance of about 3.5 Å.

The structure was therefore first solved using only the reflections with $h + k + l$ even. To this end, a new primitive reduced cell with $a' = {}^1/_2\,(a + b - c)$, $b' = b$, and $c' = {}^1/_2(a - b + c)$ was chosen. All of the nonhydrogen atoms were found from two difference Fourier maps. The resulting structure was refined by full-matrix least squares with anisotropic temperature factors to $R = 0.07$. The thermal ellipsoids of Nb, the terminal oxygens, and three carbon atoms were strongly anisotropic, each showing one long axis.

The model was desymmetrized by splitting these atoms by two rms amplitudes along their long thermal vibration axes. Inspection of an ORTEP[14] plot indicated how these split atoms had to be connected to form two similar but independent $Nb(OC)_5$ units. After transforming back to the true cell and using all reflections and an overall temperature factor, R values were calculated to distinguish between the two possible types of models referred to above. The one with two independent centrosymmetrical molecules was chosen since it gave $R = 0.16$, as opposed to $R = 0.25$ for the structure with one unsymmetrical molecule. This model was easily refined on the structure factors $|F|$ to a final residual $R = 0.04$ by block-diagonal least squares, each block containing the parameters of two atoms connected by a pseudotranslation. The weights used were $1/\sigma^2$, where the esd's (σ) of the structure factors were derived from counting statistics and the variations of the intensities of periodically measured check reflections. The number of observations per refined parameter was 13; the goodness of fit was 1.89. Isotropic extinction[15] was refined in a final cycle and shown to be negligible. [A compilation of observed and calculated structure factors is available as supplementary material.]

The atomic coordinates are listed in Table I, and the calculated bond lengths and angles for the two molecules, in Table II. A

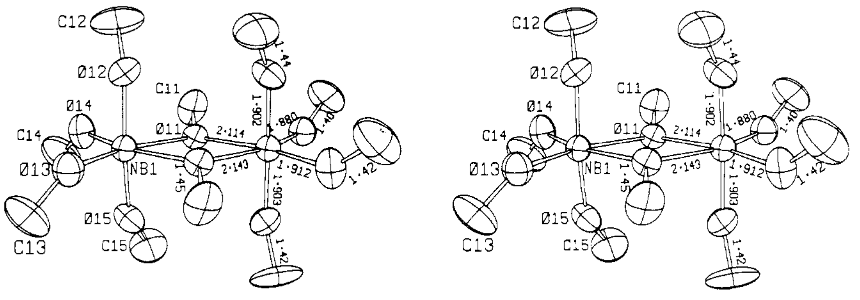

Figure 2. Stereoscopic view of $Nb_2(OCH_3)_{10}$–conformer I.

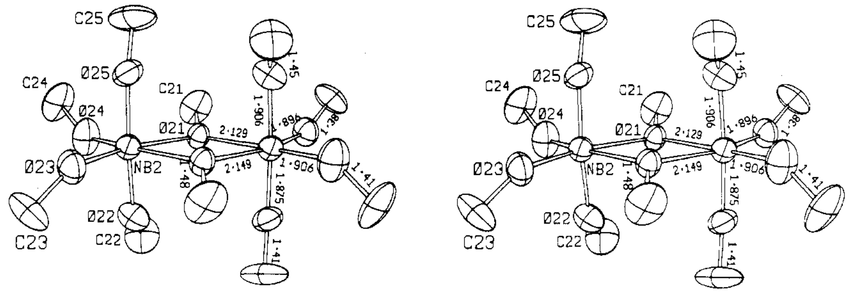

Figure 3. Stereoscopic view of $Nb_2(OCH_3)_{10}$–conformer II.

stereoplot of the packing projected on the (011) plane is shown in Figure 1. The stereoplots of molecules I and II are shown in Figures 2 and 3.

Discussion

As expected from previous observations, the alkoxide is dimeric,[8a,b] the niobium atoms being essentially octahedrally surrounded by six oxygen atoms with two bridging alkoxide groups. In contrast to the previously reported alkoxides,[3,4] we are in the fortunate position of having obtained accurate structural data for *two conformers*, both molecules being required to be centrosymmetric. Conformer I (Figure 2) is characterized by a cis arrangement of the equatorial terminal methyl groups, and conformer II (Figure 3), by a trans configuration with respect to the equatorial plane. As the transformation of I into II may be accomplished by a simple rotation around a metal–oxygen bond, the observation of an average molecule in solution is not unexpected (by ^{1}H NMR down to −95 °C). Examination of the structural parameters (Table II) and the intramolecular distances for each conformer does not show important differences and suggests a similar stability for the two structures. In addition to the very different arrangements of the equatorial methoxy groups, there is a significant difference in the axial methoxy groups between the two isomers. Whereas the angles at nonbridging oxygens in conformer I are essentially equal (140.2–148.7°) conformer II has an important distortion. The Nb2–O25–C25 angle is abnormally large (160.0°), and, conversely, the angle observed for the other axial methoxy group is small (135.2°).

The configurations of the bridging oxygen atoms are not quite planar, the sums of the angles around O11 and O21 being 354.5 and 355.0°, respectively. The geometry of the bridge may be considered to be moderately strained. The oxygen to niobium angles at the oxygen bridges have been reduced from the pure sp^2 angle (120°) to the sp^3 angle (109.7° average), although the other two angles (C–O–Nb) remain large (122.6° average). Further strain in the bridge is evident from the reduction of the bridge angle at niobium (70.4° average) from the ideal octahedral angle of 90° and the long Nb–O bridge bonds (2.134 Å average vs. 2.07 Å from the sum of the covalent radii). These bond lengths and angles for the bridge are in agreement with those found for the analogous bridge in the vanadium oxyalkoxide $(VO(OCH_3)_3)^3{}_n$ allowing for the increased size of the metal atom. The difference in the two systems lies in the planarity of the four-membered ring. In the case of niobium the bridge is required to be planar crystallographically, whereas the vanadium compound is bent, but with angles comparable to those in the present structure.

Table II. Bond Lengths (Å) and Angles (deg) in $Nb_2(OCH_3)_{10}$ with Standard Deviations in Parentheses

Conformer I

Distances

Nb1-O11	2.143 (7)	O11–C11	1.45 (1)
Nb1-O12	1.903 (5)	O12–C12	1.42 (1)
Nb1-O13	1.880 (7)	O13–C13	1.40 (1)
Nb1-O14	1.912 (8)	O14–C14	1.42 (2)
Nb1-O15	1.902 (5)	O15–C15	1.44 (1)
Nb1-O11	2.114 (7)		

Angles

O11-Nb1-O12	87.6 (2)	O13-Nb1-O11	91.8 (3)
O11-Nb1-O13	161.7 (3)	O14-Nb1-O15	90.6 (3)
O11-Nb1-O14	93.0 (3)	O14-Nb1-O11	163.0 (3)
O11-Nb1-O15	85.4 (3)	O15-Nb1-O11	90.0 (3)
O11-Nb1-O11	70.1 (3)	Nb1-O11-Nb1	109.9 (3)
O12-Nb1-O13	95.5 (3)	Nb1-O11–C11	121.2 (7)
O12-Nb1-O14	85.5 (3)	Nb1-O12–C12	148.7 (7)
O12-Nb1-O15	171.8 (3)	Nb1-O13–C13	146.4 (6)
O12-Nb1-O11	91.7 (3)	Nb1-O14–C14	140.2 (7)
O13-Nb1-O14	105.1 (3)	Nb1-O15–C15	144.9 (7)
O13-Nb1-O15	92.5 (3)	Nb1-O11–C11	123.4 (7)

Conformer II

Distances

Nb2-O21	2.149 (6)	O21–C21	1.48 (1)
Nb2-O22	1.906 (5)	O22–C22	1.45 (1)
Nb2-O23	1.896 (7)	O23–C23	1.38 (1)
Nb2-O24	1.906 (9)	O24–C24	1.41 (1)
Nb2-O25	1.875 (5)	O25–C25	1.41 (1)
Nb2-O21	2.129 (7)		

Angles

O21-Nb2-O22	85.0 (3)	O23-Nb2-O21	92.3 (3)
O21-Nb2-O23	162.8 (3)	O24-Nb2-O25	90.8 (3)
O21-Nb2-O24	93.5 (3)	O24-Nb2-O21	163.7 (3)
O21-Nb2-O25	87.9 (2)	O25-Nb2-O21	92.0 (3)
O21-Nb2-O21	70.6 (3)	Nb2-O21-Nb2	109.4 (3)
O22-Nb2-O23	92.5 (3)	Nb2-O21–C21	122.0 (6)
O22-Nb2-O24	86.2 (3)	Nb2-O22–C22	135.2 (6)
O22-Nb2-O25	172.1 (3)	Nb2-O23–C23	146.1 (6)
O22-Nb2-O21	88.9 (3)	Nb2-O24–C24	140.6 (7)
O23-Nb2-O24	103.4 (3)	Nb2-O25–C25	160.6 (7)
O23-Nb2-O25	95.1 (3)	Nb2-O21–C21	123.6 (7)

The other angles around niobium (Table II) are consistent with normal steric requirements which lead to a distorted octahedron for each conformer. Only the angles between the equatorial terminal oxygen atoms (104.2°) are very significantly larger than 90°.

The large bond angles at the terminal oxygen atoms (145.3° average) coupled with the short terminal niobium–oxygen bonds (1.898 Å average vs. 2.07 Å, from the sum of their covalent radii) may be taken to indicate a significant π contribution to the bonding. The character of the terminal oxygen atoms may be described as between sp^2 and sp which leaves two pairs of electrons in orbitals with a significant amount of p character which may interact with the empty metal t_{2g} orbitals. We note that there are potentially 16 electrons available for π bonding but only three available metal orbitals; hence we expect the bond order to be between 1 and 2 for the terminal Nb–O bonds. We have excluded the possibility of a π interaction with the bridge oxygen atoms due to the long bonds and presume that the remaining pair of electrons on each of these atoms is nonbonding. A π contribution to the terminal metal–oxygen bond was proposed from previous structural data.[2a]

It is noteworthy that we have found no significant difference between the axial and equatorial terminal Nb–O bond lengths for either conformer. This is not in agreement with the results of Caughlan et al.[3] and Wright et al.,[4] who found an important range of metal–terminal oxygen bond lengths for $(VO(OCH_3)_3)_n$ and $(Ti(OCH_3)_4)_4$. For example the V–O bonds trans to the bridge are 1.74–1.86 Å while the Ti–O bonds trans to the bridging methoxy groups have lengths varying from 1.78 to 2.08 Å. On this basis, Bradley[2a] predicted that there would be a trans effect in $Nb_2(OCH_3)_{10}$ leading to equatorial Nb–O bond lengths shorter than the axial ones. This prediction is not borne out by our results.

The packing of the molecules (Figure 1) may be described as a pseudocubic close-packed arrangement (stacking sequence ABC) of cylindrical molecules, with their long axes approximately perpendicular to (011).

The smallest intermolecular contacts are observed between O25 and O13 (3.35 Å, van der Waals contact 2.85 Å), between C25 and O13, and between C12 and O23 (3.35 Å, van der Waals contact 3.40 Å). The closest carbon–carbon interaction occurs between C22 and C13 (3.78 Å). Thus the presence of two conformers is probably derived from the most efficient packing of the methyl groups.

In the light of the disagreement between our results and those already reported in the literature we suggest that further examination of the previous structures and the determination of the structures of other metal alkoxides is warranted.

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Supplementary Material Available: listing of observed and calculated structure factors (3 pages). Ordering information is given on any current masthead page.

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Investigations of Quadruple Bonds by Polarized Crystal Spectra. 2. Quadruply Bonded Tetra-μ-glycine-dimolybdenum(II) Sulfate Tetrahydrate[1]

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Polarized single crystal spectra have been recorded for the compound $Mo_2(O_2CCH_2NH_3)_4(SO_4)_2 \cdot 4H_2O$ over the first absorption band through the region 20 000–25 000 cm^{-1}. The crystal spectra at 15 K have revealed the vibrational structure for this band in each of the two polarizations with respect to the molecular axes. For z polarization (parallel to the Mo–Mo bond) a weak progression of four lines begins at 20 570 cm^{-1}. A more intense progression consisting of nine lines begins at 21 510 cm^{-1}. For x, y polarization two intense progressions are seen: one beginning at 21 790 cm^{-1} has seven lines, and one beginning at 21 930 cm^{-1} has six lines. The average separation of lines in each progression is about 343 cm^{-1}. It is concluded that the transition is forbidden under the local symmetry of D_{4h}. The weak band in z polarization is attributed to degradation of the local D_{4h} symmetry to the crystallographic site symmetry of S_4. The more intense progression in z and the two progressions in x, y polarization are attributed to vibronic excitation by asymmetric vibrations under the D_{4h} symmetry. Accordingly, the absorption band cannot be assigned to the $\delta \rightarrow \delta^*$ ($^1A_{1g} \rightarrow {}^1A_{2u}$) transition under D_{4h} symmetry.

Introduction

Although a great deal is known about the chemical and structural properties of molecules with quadruple bonds,[3] quantitative knowledge of the quadruple bond itself and detailed interpretations of electronic spectra are still areas in which much remains to be done. A point of particular interest is the assignment of the $\delta \rightarrow \delta^*$ transition, which is orbitally $b_{2g} \rightarrow b_{2u}$, and of overall molecular symmetry $A_{1g} \rightarrow A_{2u}$. Such a transition is electric dipole allowed and polarized along the M–M axis of the molecule. A powerful source of in-