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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Registry No. $Nb_2(OCH_3)_{10}$, 18533-43-2.

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

References and Notes

(1) (a) Laboratoire de Chimie Minérale Moléculaire, Nice. (b) Institut de Cristallographie, Université de Lausanne.

(2) (a) D. C. Bradley, *Adv. Inorg. Chem. Radiochem.*, **15** (1972); (b) D. L. Keppert, "The Early Transition Metals", Academic Press, London, 1972.

(3) C. N. Caughlan, H. M. Smith, and K. Watenpaugh, *Inorg. Chem.*, **5**, 2131 (1966).

(4) D. A. Wright and D. A. Williams, *Acta Crystallogr., Sect. B*, **24**, 1107 (1968).

(5) J. A. Ibers, *Nature (London)*, **197**, 686 (1963).

(6) R. D. Witters and C. N. Caughlan, *Nature (London)*, **205**, 1313 (1965).

(7) (a) L. G. Hubert-Pfalzgraf, J. Guion, and J. G. Riess, *Bull. Soc. Chim. Fr.*, 3855 (1971); (b) L. G. Hubert-Pfalzgraf, *Inorg. Chim. Acta*, 229 (1975).

(8) (a) D. C. Bradley and C. E. Holloway, *J. Chem. Soc. A*, 219 (1968); (b) L. G. Hubert-Pfalzgraf and J. G. Riess, *Bull. Soc. Chim. Fr.*, 2401 (1968); (c) L. G. Hubert-Pfalzgraf and J. G. Riess, *ibid.*, 4348 (1968); (d) L. G. Hubert-Pfalzgraf and J. G. Riess, *ibid.*, 1201 (1973); (e) C. E. Holloway, *J. Coord. Chem.*, **1**, 253 (1971).

(9) J. G. Riess and L. G. Hubert-Pfalzgraf, *J. Chim. Phys. Phys.-Chim. Biol.*, **70**, 646 (1973).

(10) (a) L. G. Hubert-Pfalzgraf, Thesis, Nice, 1970; (b) H. Preiss, *Z. Anorg. Allg. Chem.*, **389**, 293 (1972).

(11) D. C. Bradley, B. N. Chakravarti, and W. Wardlaw, *J. Chem. Soc.*, 2381 (1956).

(12) C. Cromer and J. Mann, *Acta Crystallogr., Sect. A*, **24**, 321 (1968).

(13) J. M. Stewart, F. A. Kundell, and J. C. Baldwin, "X-Ray 72" system, Technical Report TR-192, Computing Science Center, University of Maryland June 1972 (as modified by D. Schwarzenbach).

(14) C. K. Johnson, Report ORNL-3794, Oak Ridge National Laboratory Oak Ridge, Tenn., 1971.

(15) W. H. Zachariasen, *Acta Crystallogr.*, **23**, 558 (1967).

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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-

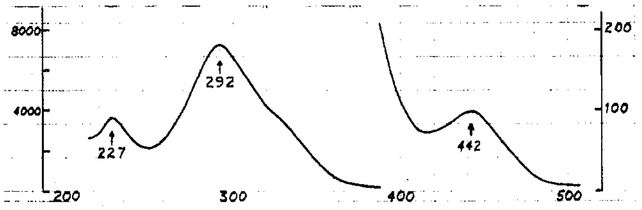

Figure 1. Absorption spectrum of the $Mo_2(O_2CCH_2NH_3)_4^{4+}$ ion in aqueous solution. The solution was prepared by dissolving $Mo_2(O_2CCH_2NH_3)_4Cl_4 \cdot xH_2O$ in 50 ml of 0.25 M HCl containing 1.0 g of glycine. Wavelengths are in nm; absorbance ϵ is in M^{-1} cm^{-1}.

formation on the assignment of the electronic spectra of compounds with M–M quadruple bonds under suitable circumstances could be the polarization of one or more of the electronic transitions. Such information is obtained by combining experimental measurement of the polarizations relative to crystal axes with an x-ray crystallographic determination of the orientation of the molecular axes relative to the crystal axes. Thus far, there have been only two such studies for quadruply bonded dirhenium compounds, namely, for $Re_2Cl_6(PEt_3)_2$[4] and for $[N(C_4H_9)_4]_2[Re_2Cl_8]$.[1]

In this paper we turn to a different type of molecule containing an M–M quadruple bond, namely, the $M_2(O_2CR)_4X_2$ type, which is also very common and important. Although a number of such compounds are known and there have been some studies of their spectra,[5,6] no polarization data have so far been published. This is doubtless due, at least in part, to the fact that none of the crystal structures so far determined for molybdenum[7–9] or rhenium[10,11] compounds of the $M_2(O_2CR)_4X_2$ type have had molecular orientations well suited to such measurements.

The compound $Mo_2(O_2CCH_2NH_3)_4(SO_4)_2 \cdot 4H_2O$ was recently prepared and found to have a crystal structure ideally suited to the measurement of polarized spectra since all Mo_2^{4+} units are crystallographically equivalent and aligned parallel to the crystallographic *c* axis.[12] In this paper we report our observations on the crystal spectra in the region 20 000–25 000 cm^{-1} for this compound and suggest an interpretation of the very detailed vibrational–electronic absorptions that can be seen at 15 K.

Experimental Section

The absorption spectrum of an aqueous solution of $Mo_2(O_2CCH_2NH_3)_4Cl_4 \cdot xH_2O$ in the visible and near-ultraviolet regions is shown in Figure 1.

The method for recording the polarized single-crystal absorption spectra has been described previously.[13] The refractive indices for the crystals were determined by the observation of the Becke line of crystals under a set of certified refractive index liquids prepared by the Cargille Co. Values for the refractive indices (Na D) were $n_O = 1.604 \pm 0.002$; $n_E = 1.620 \pm 0.002$. The spectrum of a crystal which exhibited a second-order green interference color between crossed polarizers was recorded at room temperature to serve as a standard. With a birefringence of 0.016 the thickness of this crystal was calculated to be 50 ± 5 μ. This thickness was confirmed approximately by the comparison of its thickness with a calibrated scale in a microscope eyepiece.

The absorption spectra for a crystal in a liquid helium cryostat with conductive cooling, taken at a nominal temperature of 15 K, are shown in Figures 2 and 3. The thickness of this crystal determined by comparison of its absorption to that of the standard crystal at room temperature was 45 μ ± 10%.

Results and Discussion

The lowest energy visible absorption band for solutions of $Mo_2(O_2CCH_2NH_3)_4^{4+}$, Figure 1, occurs at 442 nm with a molar extinction coefficient of about 95 cm^{-1} M^{-1}. This spectrum is quite similar to that previously reported for $Mo_2(O_2CCH_3)_4$ in ethanol by Dubicki and Martin,[6] who also reported similar bands for several tetracarboxylatodimolybdenum(II) complexes. It is apparently representative of $Mo_2(O_2CR)_4$ systems in general.

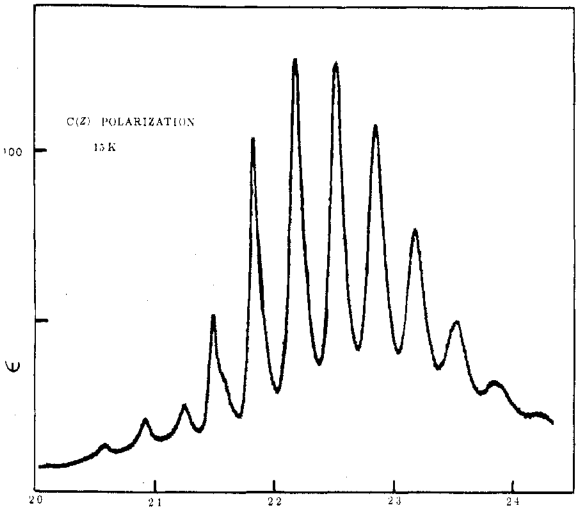

Figure 2. Crystal spectrum at about 15 K of $Mo_2(O_2CCH_2NH_3)_4(SO_4)_2 \cdot 4H_2O$ with light polarized parallel to the *c* axis of the crystal. The abscissa is in units of 10^3 cm^{-1}.

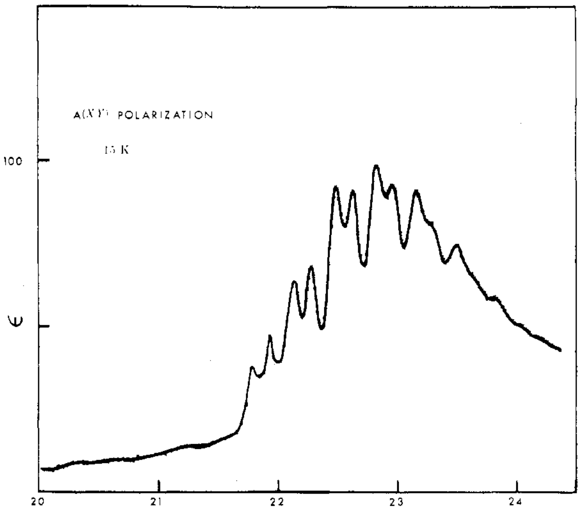

Figure 3. Crystal spectrum at about 15 K of $Mo_2(O_2CCH_2NH_3)_4(SO_4)_2 \cdot 4H_2O$ with light polarized perpendicular to the *c* axis of the crystal. The abscissa is in units of 10^3 cm^{-1}.

$Mo_2(O_2CCH_2NH_3)_4(SO_4)_2 \cdot 4H_2O$ crystallizes in space group $I\bar{4}$. In the primitive cell there is only one Mo_2^{4+} unit and the Mo–Mo bond, which establishes the molecular *z* axis, is aligned with the crystallographic *c* axis. Although the true site symmetry for the Mo_2^{4+} unit is S_4, there is no significant degradation of virtual D_{4h} symmetry in the $Mo_2(O_2CCH_2NH_3)_4^{4+}$ unit until the orientation of the $-NH_3$ groups is considered.

The single crystal spectra in the region 20 000–25 000 cm^{-1} at liquid helium temperatures for *c*(*z*) and *a*(*x*, *y*) polarization, shown in Figures 2 and 3, respectively, exhibit very well-resolved vibrational structure. Table I gives accurate wavenumbers for the maxima and the peak separations.

In *z* polarization two progressions are observed. A weak one begins at 20 570 cm^{-1} and consists of four lines with a mean separation of 343 ± 9 cm^{-1}. A second, considerably more intense, progression begins at 21 510 cm^{-1} and consists of nine lines with a mean separation of 345 ± 10 cm^{-1}. The fourth member of the weak progression and possibly a fifth appear as shoulders on the high-energy side of the first and second members of the more intense progressions. In *x*, *y* polarization there are also two overlapping progressions. Each

Table I. Vibrational Structures for $Mo_2(gly)_4(SO_4)_2 \cdot 4H_2O$ (cm^{-1})

c polarization		*a* polarization				
ν	$\Delta\nu$	ν_1	$\Delta\nu_1$	ν_2	$\Delta\nu_2$	$\nu_2 - \nu_1$
1st Series						
20 570		21 790		21 930		140
	350		350		350	
20 920		22 140		22 280		140
	350		350		350	
21 270		22 490		22 630		140
	(330)		340		330	
(21 600)		22 830		22 960		130
			340		340	
2nd Series						
		23 170		23 300		130
			350		350	
21 510		23 520		(23 650)		130
	360		320			
21 870		(23 840)				
	360					
22 230						
	340					
22 570						
	340					
22 910						
	350					
23 260						
	340					
23 600						
	330					
23 930						
	340					
24 270						

$21\,510 - 20\,570 = 940$
$21\,790 - 20\,570 = 1220$
$21\,930 - 20\,570 = 1360$

is an order of magnitude more intense than the weak progression in *z* polarization but somewhat weaker than the intense lines in *z*. The first progression in *x*, *y* begins at 21 790 cm^{-1} and consists of seven lines with an average separation of 342 ± 11 cm^{-1} while the second begins at 21 930 cm^{-1} and six lines can be discerned with an average separation of 344 ± 8 cm^{-1}.

We propose to assign the first, weak progression in *z* polarization to an electronic transition, forbidden in D_{4h} symmetry but allowed in the S_4 symmetry of the crystal field. Since the deviation from D_{4h} is small, this progression is weak. The peak at 20 570 cm^{-1} is presumably the 0–0 line. The other progression in *z* polarization and the progression in *x*, *y* polarization are attributed to vibronic transitions involving the same electronic excitation having asymmetric vibrations, under D_{4h}, with frequencies in the excited electronic state of 940, 1220, and 1360 cm^{-1}, respectively. That such a simple spectral picture occurs in an extended polyatomic ion with its many vibrational modes imples that the electronic excitation is quite localized. It probably involves orbitals concentrated on the molybdenum atoms. The vibrational spacings of the progressions averaging 340–345 cm^{-1} are attributed to that normal mode which consists chiefly of Mo–Mo stretching. Since this mode has a frequency of 393 cm^{-1} in the ground state, the transition presumably involves a transition from an Mo–Mo bonding orbital or into an Mo–Mo antibonding orbital or both. The exciting frequencies are probably those of vibrations within the $Mo_2(O_2C-)_4$ tetracyclic core.

Possible assignments for this transition, forbidden in D_{4h} and allowed in *z* polarization under S_4, in accordance with the spectra are $^1A_{1g} \rightarrow {}^1A_{1u}$, $^1B_{1g}$ and $^1B_{2g}$. The most significant point, however, is that the observations reported here are inconsistent with an assignment of this absorption band to the $\delta \rightarrow \delta^*$ transition which would be electric dipole allowed under D_{4h} symmetry.[14]

Registry No. $Mo_2(O_2CCH_2NH_3)_4(SO_4)_2 \cdot 4H_2O$, 57214-97-8.

References and Notes

(1) Part 1: F. A. Cotton, B. A. Frenz, B. R. Stults, and T. R. Webb, *J. Am. Chem. Soc.*, in press.
(2) (a) Texas A&M University, with support from the National Science Foundation under Grant No. 33142X. (b) Iowa State University of Science and Technology, under U.S. Energy and Research Development Administration Contract No. W-7405-eng-82.
(3) F. A. Cotton, *Chem. Soc. Rev.*, **4**, 27 (1975).
(4) C. D. Cowman and H. B. Gray, *J. Am. Chem. Soc.*, **95**, 8177 (1973).
(5) F. A. Cotton, C. Oldham, and W. R. Robinson, *Inorg. Chem.*, **5**, 1708 (1966).
(6) L. Dubicki and R. L. Martin, *Aust. J. Chem.*, **22**, 1571 (1969).
(7) (a) D. Lawton and R. Mason, *J. Am. Chem. Soc.*, **87**, 921 (1965); (b) F. A. Cotton, Z. C. Mester, and T. R. Webb, *Acta Crystallogr., Sect. B*, **30**, 2768 (1974).
(8) F. A. Cotton and J. G. Norman, Jr., *J. Coord. Chem.*, **1**, 161 (1971).
(9) F. A. Cotton, J. G. Norman, Jr., and T. R. Webb, unpublished studies of $Mo_2(O_2CH)_4$.
(10) M. J. Bennett, W. K. Bratton, F. A. Cotton, and W. R. Robinson, *Inorg. Chem.*, **7**, 1570 (1968).
(11) C. Calvo, N. C. Jayadevay, C. J. L. Lock, and R. Restivo, *Can. J. Chem.*, **48**, 219 (1970).
(12) F. A. Cotton and T. R. Webb, *Inorg. Chem.*, **15**, 68 (1976).
(13) D. S. Martin, *Inorg. Chim. Acta, Rev.*, **5**, 107 (1971).
(14) A referee has raised the possibility of an assignment in which the weak progression in *z* polarization is assigned to a singlet–triplet $\delta \rightarrow \delta^*$ transition. It is then not at all evident why the singlet–singlet transition should be present in both *z* and *x*, *y* polarization. More serious is the fact that a $^1A_{1g} \rightarrow {}^3A_{2u}$ transition would not be *z* polarized! It would be *x*, *y* polarized.

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High-Yield Synthesis of 1,1,3,3-Tetramethyl-1,3-diazonia-2,4-diboratocyclopentane and Syntheses of Some Halo Derivatives

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The reduction of bis(trimethylamine)dihydroboronium iodide $[[(CH_3)_3N]_2BH_2^+][I^-]$ with potassium metal in 1,2-dimethoxyethane produced a 74% yield of 1,1,3,3-tetramethyl-1,3-diazonia-2,4-diboratocyclopentane ($B_2N_2C_5H_{18}$). The reactivity of this new small-ring heterocycle was briefly investigated with most of the attention centered on its reactivity toward some halogenating agents (HCl, HBr, HI, Cl_2, Br_2, I_2). A clear-cut halogenation sequence was observed. The hydrogen halides monohalogenated 1,1,3,3-tetramethyl-1,3-diazonia-2,4-diboratocyclopentane at the boron atom in ring position 4.

This new small-ring boron heterocycle 1,1,3,3-tetramethyl-1,3-diazonia-2,4-diboratocyclopentane ($B_2N_2C_5H_{18}$),[1] I, is the missing link between the six-membered ring II produced by Miller and Muetterties[2] and the four-membered ring formed by the dimerization of $(CH_3)_2NBH_2$, III.

The purpose of this research was to improve the yield and find a more convenient procedure to obtain I from the reaction

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