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Crystal Absorption Spectra for Potassium Octachlorodimolybdate(II) Dihydrate

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Partial polarized crystal spectra are reported for $K_4Mo_2Cl_8{\cdot}2H_2O$ for both *b* and *c* polarization at 300 and 3.7 K. The intense band in the visible region, ca. 19 000 cm^{-1}, has been shown to possess molecular z–π polarization. This band was therefore assigned $^1A_{2u} \leftarrow {}^1A_{1g}$ $(\delta^* \leftarrow \delta)$. It is sufficiently intense that only the absorption due to a minority fraction could be recorded. At 3.7 K, vibrational structure to the band can be resolved, but there are irregularities in the observed progression. A dipole-allowed but low-intensity transition was observed at 28 800 cm^{-1} with higher intensity in z-π polarization. It has been assigned as the $A_2' \leftarrow A_1'$ component of a $^3E_u \leftarrow {}^1A_{1g}$ transition. This is a transition to the triplet state associated with the $^1E_u \leftarrow {}^1A_{1g}$ transition seen at 31 400 cm^{-1} in pellet and mull spectra, which was shown to be polarized x, y-σ. Weak absorptions at 22 000–24 000 cm^{-1} appeared to be vibronic bands.

Introduction

The red color of the $Mo_2Cl_8^{4-}$ ion is the consequence of an electronic absorption band with a maximum at 530 nm which has been reported[2,3] for mineral oil mulls of amorphous $K_4Mo_2Cl_8$ and crystalline $K_4Mo_2Cl_8{\cdot}2H_2O$. This color is seen in freshly prepared HCl solutions of $K_4Mo_2Cl_8$, but it fades rapidly. Compounds which contain the $Re_2Cl_8^{2-}$ ion (with a $5d^8$ rather than $4d^8$ configuration) have a band at ca. 700 nm which imparts a blue color to them. Cowman and Gray[3] published the polarized crystal spectra for $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ in the visible region and with Mortola et al.[4] have presented extended spectra into the ultraviolet region. With the crystal structure for this compound of Cotton et al.[5] it appears clear that this transition in $Re_2Cl_8^{2-}$ is polarized in the direction of the molecular *z* axis, i.e., along the metal–metal bond which is aligned with the tetragonal axis of the D_{4h} molecular point group. Such polarization justifies the transition assignment as $^1A_{2u} \leftarrow {}^1A_{1g}$ $(\delta^* \leftarrow \delta)$ for $Re_2Cl_8^{2-}$. Recently, Xα scattered-wave computations[2,4] for $Re_2Cl_8^{2-}$ and for $Mo_2Cl_8^{4-}$ have been performed. The ground-state ordering of the electronic orbitals for the $Mo_2Cl_8^{4-}$ ion, prepared by Norman and Kolari,[2] presented in Figure 1, implies that the lowest energy spin-allowed electronic transition should be $^1A_{2u} \leftarrow {}^1A_{1g}$ $(\delta^* \leftarrow \delta)$. The calculated value for this transition in $Mo_2Cl_8^{4-}$ was 13 700 cm^{-1}, well below the observed peak at 18 900 cm^{-1}. Cowman and Gray[3] reported that the spectrum of $K_4Mo_2Cl_8$ had a richly structured band with an origin at 17 897 cm^{-1} and vibrational spacing of about 351 cm^{-1}, but they were not able to report the polarization, since they used a pellet type of multioriented sample. The present work was undertaken to determine the polarization of bands from single-crystal spectra for $K_4Mo_2Cl_8{\cdot}2H_2O$ in the visible and near-ultraviolet regions.

Experimental Section

Amorphous $K_4Mo_2Cl_8$ was prepared by the method of Brencic and Cotton.[6] Small portions of this amorphous powder were placed on a fused silica plate, and a few drops of constant-boiling (under nitrogen) HCl was added. A second plate was placed over the first plate to give a film of the HCl. The plates were then stored under H_2O-saturated nitrogen for several days until crystals of $K_4Mo_2Cl_8{\cdot}2H_2O$ had developed between the plates. Examinations of the crystals under a polarizing microscope indicated that the technique produced many diamond-shaped crystals with four-twinned quadrants and rectangular plates which gave sharp total extinctions. These rectangular plates were strongly dichroic, and the high absorption was along the long dimension of the faces.

A crystal in the form of a rectangular prism was mounted on a four-circle x-ray diffractometer and indexed using standard programs. The diffractometer indexed reflections of the crystal on the basis of orthorhombic axes $a{:}b{:}c$ = 8.019:13.302:8.053 Å, in good agreement with the structure determination of Brencic and Cotton.[7] In addition, the principal rectangular face was identified by the diffractometer as the 100 face for which the *c* axis was aligned with the long dimension of the face, i.e., with the direction of polarization for the high absorption.

The indices of refraction for the 100 face were measured by the Becke line method with a set of standard liquids supplied by the Cargille Co. The value of n_b (Na D) was 1.671 and n_c (Na D) was >1.700 (the highest index of refraction of standard set) and <1.742 (CH_2I_2).

One crystal was found with sufficiently good optical faces to provide marginal interference in the region of 664–615 nm for utilization in determination of the crystal thickness.[8] This crystal was found to be 17 ± 4 μ thick, and the thicknesses of other crystals were determined from this value and the ratio of the heights of an absorption band.

Techniques for recording spectra have been reported previously[9] with the exception that an Andonian Associates liquid-helium cryostat was employed for the low-temperature measurements. This cryostat provided He-vapor heat transfer and a germanium resistance thermometer attached to the sample mount to monitor the temperature. Temperatures below the atmospheric boiling point of He were obtained by pumping on the sample compartment.

Results and Discussion

The $Mo_2Cl_8^{4-}$ ion has the eight chlorine atoms in very nearly a cubic arrangement with the Mo–Mo bond along one of the fourfold axes of the cube, so the ion has essentially D_{4h} symmetry.[7] The $K_4Mo_2Cl_8{\cdot}2H_2O$ structure was found to be disordered in that a major fraction, 93% of the ions, have the Mo–Mo bond aligned exactly with the *c* orthorhombic axis while a minor fraction, 7%, have the Mo–Mo bond aligned at 90° to the *c* axis and 34.10° from the *b* axis.[10] the average unit cell therefore belongs to the *Pbam* space group with two $Mo_2Cl_8^{4-}$ ions per unit cell. For a transition with *z* or π molecular polarization, i.e., with polarization along the metal–metal bond, the crystal polarization for the majority fraction should be totally in the *c* direction for the 100 face. For the minority fraction, a π polarization will be forbidden in the *c* direction. The average square of the projection of a

Table I. Vibrational Structure in the 19 000-cm^{-1} Band for *b* Polarization of $K_4Mo_2Cl_8 \cdot 2H_2O$ and for KCl Pellets of $K_4Mo_2Cl_8 \cdot 2H_2O$ and for $K_4Mo_2Cl_8$ at Liquid-Helium Temperatures

Single crystal $K_4Mo_2Cl_8 \cdot 2H_2O$ 3.7 K		KCl pellet $K_4Mo_2Cl_8 \cdot 2H_2O$ 3.7 K		KCl pellet $K_4Mo_2Cl_8$ 15 K	
$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, cm^{-1}	$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, cm^{-1}	$\bar{\nu}$, cm^{-1}	$\Delta\bar{\nu}$, cm^{-1}
18 083 ± 6		17 912 ± 20		17 930 ± 15	
18 464 ± 6	381	18 280 ± 20	370	18 260 ± 15	330
18 804 ± 6	340	18 660 ± 20	380	18 620 ± 15	360
19 128 ± 6	324	19 000 ± 20	340	18 960 ± 15	340
19 445 ± 10	327	19 340 ± 20	340	19 280 ± 20	320
19 775 ± 15	320	19 660 ± 30	320	19 620 ± 20	340
20 101 ± 20	325	19 990 ± 30	330	19 920 ± 20	300
	Av 336		Av 346		Av 332

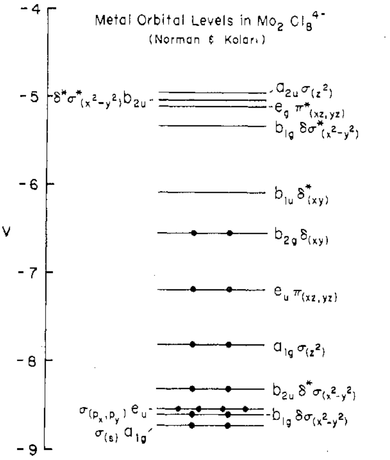

Figure 1. Ground-state energies of orbitals for the $Mo_2Cl_8^{4-}$ ion computed by the $X\alpha$ scattered-wave method.[2]

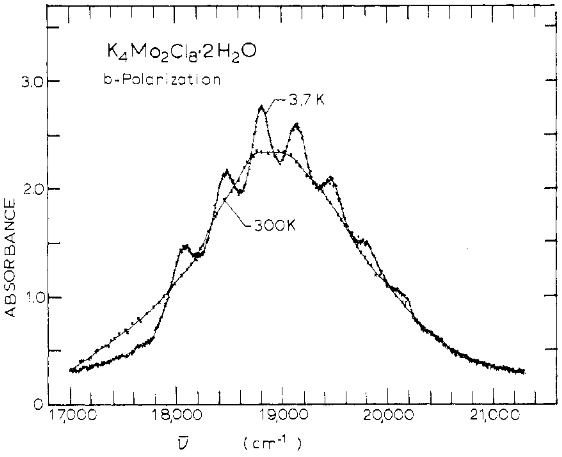

Figure 2. Absorption spectra for *b* polarization for the 100 face of a crystal of $K_4Mo_2Cl_8 \cdot 2H_2O$ at temperatures of 3.7 and 300 K. Crystal thickness was 12 ± 3 μ. Absorbance can be converted to molar absorptivity by multiplying by a factor of 215 ± 50 cm^{-1} M^{-1}.

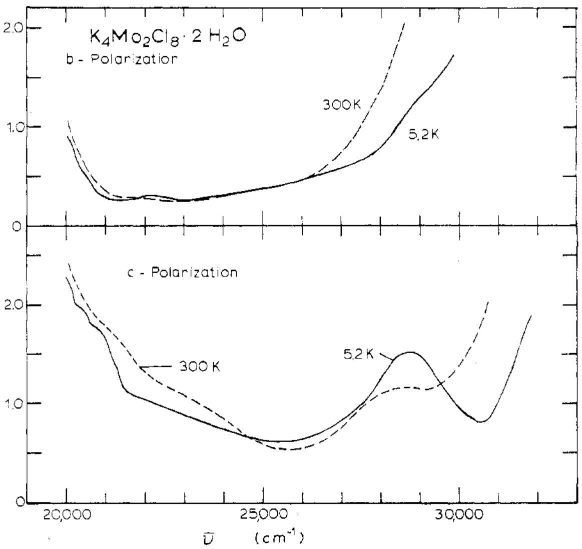

Figure 3. Absorption spectra for *b* and *c* polarization for a crystal of $K_4Mo_2Cl_8 \cdot 2H_2O$ at temperatures of 5.2 and 300 K. Crystal thickness was 12 ± 3 μ. (This was the same crystal used to obtain Figure 1.)

unit z-π transition moment of the minority fraction upon the *b* axis for the two sites is 0.68, so the polarization ratio of intensities is estimated to be $c{:}b = 0.93/(0.07 \times 0.68) = 19.7$.

The observation that the high absorption in the visible region is along the orthorhombic *c* axis confirms that the band with a maximum at ca. 19 000 cm^{-1} is polarized along the ionic *z* or π axis. Indeed, for all the crystals inspected, the measurement of this band in *c* polarization was beyond the capabilities of our technique. It was possible to record good *b*-polarized spectra, and these have been presented for this band in Figure 2 for 300 and for 3.7 K. This then is considered to represent the z-π polarization of the minority fraction.[11] The spectra for both polarizations at higher energies are shown in Figure 3.

The 19 000-cm^{-1} band exhibits vibrational structure at 3.7 K which is almost but not wholly lost at room temperature. In a cursory inspection, the band at 3.7 K appears to comprise a single progression of components with increasing intensity up to the third peak at 18 804 cm^{-1}. The sixth–eighth components are discernible only as shoulders. Now the $\delta^* \leftarrow \delta$ ($^1A_{2u} \leftarrow {}^1A_{1g}$) transition is expected to exhibit the 0–0 transition with Franck–Condon progressions based upon this transition for the three A_{1g} vibrations. These three vibrations involve the metal–metal stretch, the metal–chloride stretch and a Mo–Mo–Cl bending mode. Since the $^1A_{2u}$ state provides a relaxation in the metal–metal bond, the progression based on the metal–metal stretch might be expected to have the greatest intensity. The separation of the peaks would then be the wavenumber of the stretching vibration in the excited state which is expected to be smaller than that for the ground state. The ν's for each of the components in the band, which were read directly from the recorder chart, are presented in Table I. With the peak at 18 083 cm^{-1} assigned as the 0–0 transition the first separation of peaks is 381 cm^{-1} whereas the average of the final five separations is only 327 cm^{-1}. The metal–metal stretch for the gound state was established as 345 cm^{-1} by resonance Raman techniques.[12] The Raman spectra also contained a peak at 275 cm^{-1} which was apparently primarily the metal–chloride stretch. The high values of 381 cm^{-1} for the separation of the first and second peaks imply that this is not just a progression due to the single metal–metal stretching vibration since this separation is higher than the 345 cm^{-1} for metal–metal stretch of the ground state. The separation of 347 cm^{-1} between the second and third peaks

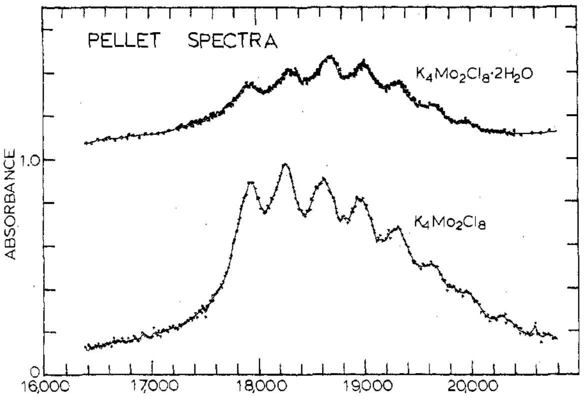

Figure 4. Absorption spectra for KCl pellets containing finely ground $K_4Mo_2Cl_8 \cdot 2H_2O$ and containing amorphous $K_4Mo_2Cl_8$. The $K_4Mo_2Cl_8 \cdot 2H_2O$ pellet was at 3.7 K whereas the $K_4Mo_2Cl_8$ was in a liquid-helium cryostat without a temperature sensor and was almost certainly below 15 K.

may be considered abnormally high as well. The separation of succeeding peaks is perhaps reasonable for the metal–metal stretching frequency. The exceptionally high value for the separation between the first two peaks was observed in the low-temperature spectra of several crystals and appears too large to be ascribed to the experimental uncertainty. It seems likely that the irregularity in the separations is due to the contribution from more than just the one totally symmetric vibration. Vibrational structure in the spectra of $[(n\text{-}C_4H_9)_4N]_2Re_2Cl_8$ of Cowman and Gray[3] perhaps indicated a similar effect more clearly in that there were two progressions with identical separations for both progressions.

The spectrum of $Mo_2Cl_8^{2-}$ in KCl pellets is somewhat different from the single-crystal *b*-polarized spectrum. Pellets were prepared from samples of both $K_4Mo_2Cl_8$ powder and from crushed crystals of the hydrate $K_4Mo_2Cl_8 \cdot 2H_2O$. Spectra of these pellets are shown in Figure 4 and the wavenumbers for the vibrational peaks and separations are tabulated in Table I. Differences in the peak wavenumbers for the two pellet spectra were not greatly different in view of the uncertainties. There were significant differences however in the relative intensities of the various components. The pellet spectrum for the $K_4Mo_2Cl_8 \cdot 2H_2O$ agrees quite satisfactorily with the reported value of 17 897 cm^{-1} for the first peak and vibrational spacing of 351 cm^{-1} reported by Cowman and Gray.[3]

The locations of the peaks in the single-crystal *b*-polarized spectrum are definitely different from the pellet spectrum. Each peak of the single crystal lies 150–200 cm^{-1} higher than the corresponding peak in a pellet spectrum. It seems likely that the pellet spectrum reflects accurately the transitions for the majority fraction which provides the intense absorption in *c* polarization and that there has been an energy shift 150–200 cm^{-1} for the minority fraction because of the different site conditions. On the other hand, the possibility also exists that the inclusion of the K_4MoCl_8 in the pelleted KCl modifies the spectra somewhat. The differing orientation of neighbors about a site as a consequence of the disorder may be responsible for some of the broadening of the peaks and loss of resolution.

There is an increase in absorption for *b* polarization in the region of 17 200–17 800 cm^{-1} before the rise associated with the first vibrational peak. The absorption in this region might be merely a low-energy tail for the band. It does seem possible however that absorption in this region might be due to the $^3A_{2u} \leftarrow {}^1A_{1g}$ transitions. Clark and Franks[13] reported a band with vibrational structure at 6250 cm^{-1} in the diffuse-reflectance spectrum at room temperature of several but not all salts containing the $Mo_2Cl_8^{4-}$ ion; it was not observed for $K_4Mo_2Cl_8$. They assigned this band to the $^3A_{2u} \leftarrow {}^1A_{1g}$ transition. However, a separation of nearly 12 000 cm^{-1} for the triplet and singlet states would be unexpectedly high. Also, since the band was not seen in all $Mo_2Cl_8^{4-}$ salts there would seem to be the distinct possibility that it might be due to a minor impurity component in the preparation. The spin-orbit coupling of Mo is sufficiently low that spin-forbidden transitions are expected to be quite weak. However, a spin-orbit induced transition, $^3A_{2u} \leftarrow {}^1A_{1g}$, is dipole-allowed in the *x,y* polarizations. Therefore, absorption with *b* polarization in the single crystal would be associated primarily with the major orientation, and the intensity observed in the 17 200–17 800-cm^{-1} region might be reasonable for it. It must be stated that the separation of only 1000 cm^{-1} between the $^3A_{2u}$ and $^1A_{2u}$ states seems quite low and, in the absence of vibrational structure in this region, an assignment of a $^3A_{2u}$ transition here is only problematical.

The pellet spectrum for $K_4Mo_2Cl_8$ at higher energies showed an absorption band at 31 400 cm^{-1}. The crystal spectrum for *c* polarization could be recorded up to 31 800 cm^{-1} whereas the *b* polarized spectrum was off-scale at 28 600 cm^{-1}. Since the $x,y\text{-}\sigma$ component for the major fraction of $Mo_2Cl_8^{2-}$ would be forbidden in *c* polarization, the 31 400 cm^{-1} must be an $^1E_u \leftarrow {}^1A_{1g}$, in agreement with the assignment of $d_{x^2-y^2} \leftarrow \pi$ proposed by Norman and Kolari.[2]

The increase in band height at 28 800 cm^{-1} (*c* polarization) has been attributed to the narrowing of the band for a transition whose intensity was essentially unchanged when the temperature was lowered. This temperature behavior is characteristic of a static dipole-allowed transition rather than of one excited by a vibronic perturbation. It therefore appears to be a weak but static dipole-allowed transition with molecular $z\text{-}\pi$ polarization. Norman and Kolari's calculation has placed the second $^1A_{2u}$ state ($\pi^*(e_g) \leftarrow \pi(e_u)$) at some 5300 cm^{-1} above the lowest ^1E_u state. This $\pi^* \leftarrow \pi$ transition is expected to be more intense than the $\delta^* \leftarrow \delta$ because of higher orbital overlap. A third $^1A_{2u}$ state ($\delta_{x^2-y^2}(b_{1g}) \leftarrow$ Cl-$\pi(b_{2u})$) might be expected to have a relative low intensity since it results from the promotion of an electron from a chlorine 3p orbital with pure π character with respect to the Mo–Cl bond into an antibonding Mo–Cl orbital with pure σ character. Jorgensen[14] has commented on the low intensities of such charge-transfer transitions. However, Norman's[15] calculations place this some 34 300 cm^{-1} above the $\delta^* \leftarrow \delta$ transition. He has suggested that the transition at 28 800 cm^{-1} is likely to be due to the spin-forbidden transitions $^3E_u \leftarrow {}^1A_{1g}$ associated with the spin-allowed $^1E_u \leftarrow {}^1A_{1g}$ band seen at 31 400 cm^{-1}. One of the spin-forbidden transitions, $A_2' \leftarrow A_1'$, in the D_4' double group will have a nonzero static transition dipole by virtue of spin–orbit coupling. The relatively low intensity would be consistent with the relatively low spin–orbit coupling parameter of Mo, and the band in *c* polarization would apply to the majority component. Other spin-forbidden transitions to the ^3E_u state include $E_1' \leftarrow A_1'$, which are dipole allowed in the molecular $x,y\text{–}\sigma$ polarization. This transition would give a component in *b* polarization. The shoulder which is apparent at 28 800 cm^{-1} in the 5.2 K *b* polarization might be attributed to this transition although its weakness is somewhat disturbing. It would also include a contribution from the $A_2' \leftarrow A_1'$ transition for the minority component.

Like the pellets and mulls, the crystal spectra reveal some very weak absorptions in the region of 22 000–24 000 cm^{-1}. Norman and Kolari[2] have assigned this absorption to vibronic bands, $^1E_g \leftarrow A_{1g}$ ($\delta^* \leftarrow \pi$) or $^1A_{2g} \leftarrow A_{1g}$ ($d_{x^2-y^2} \leftarrow \delta$), which appears reasonable.

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Registry No. $K_4Mo_2Cl_8$, 25448-39-9; $K_4Mo_2Cl_8{\cdot}2H_2O$, 22239-46-9.

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(10) It should be kept in mind that there is no evidence to show whether the extent of disordering (7%) found in the crystal used to collect x-ray data for the structure determination will be found in other crystals. If this is the thermodynamic equilibrium value and crystals from other sources are also obtained under equilibrium conditions, the extent of disordering should be the same. We have tentatively assumed this although, provided the value is small, it could be different (not zero, however) without affecting our interpretation of conclusions. The calculation of molar absorptivity (Figure 1) would, of course, be affected.

(11) From Figure 1 it is possible to estimate the oscillator strength of the $\delta \rightarrow \delta^*$ transition. Using the conversion factor given in the caption one obtains 540 ± 135 for ϵ, but account must be taken of the fact that only a fraction (presumably 7%, but see footnote 10) of the molecules are in the correct orientation to absorb. The width at half-height of the peak is about 1600 cm^{-1}. With these data we calculate that $f = (4.6 \times 10^{-9})(\epsilon/0.07)(1600) = (57 \pm 14) \times 10^{-3}$. As is well-known, solutions of $Mo_2Cl_8^{4-}$ are extremely unstable. The nature and kinetics of the decomposition are under study at Texas A&M University by Mr. L. D. Gage. From his data it is possible to obtain by extrapolation the "spectrum at $t = 0$" and this shows a symmetrical band with its maximum at 524 nm, ϵ 1000 ± 50 cm^{-1} M^{-1}, and $\Delta\nu_{1/2} = 2020$ cm^{-1}. From these data we get $f = (4.6 \times 10^{-9})(1000 \pm 50)(2020) = (9.3 \pm 0.5) \times 10^{-3}$. These two results actually agree within a factor of 2 since it is necessary to divide the former by a factor of 3, giving $(19 \pm 4) \times 10^{-3}$, when making the comparison, to account for the random orientation characteristic of the solution.

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Crystal and Molecular Structure of a Mercaptide-Bridged Dinickel(II) Complex: Bis-μ-[2-[(2-pyridylethyl)amino]ethylthiolato]-dinickel(II) Perchlorate

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The crystal structure of bis-μ-[2-[(2-pyridylethyl)amino]ethylthiolato]-dinickel(II) perchlorate, $[Ni(C_9H_{13}N_2S)ClO_4]_2$, was determined by single-crystal x-ray diffraction techniques and was refined by full-matrix least-squares methods to a final conventional R index of 0.023. The dark violet crystals form as prisms in space group $P2_12_12$ with a = 14.896 (4), b = 12.861 (4), and c = 6.631 (1) Å at 20 °C. The binuclear molecules of symmetry 2 (C_2 in Schönflies notation) have a mercaptide-bridged structure with a central four-membered $\overline{\mathrm{NiSNiS}}$ ring which is severely folded to 110° at its S^-–S^- diagonal to give a Ni(II)–Ni(II) distance of 2.739 (1) Å. Each Ni(II) ion has distorted square-planar coordination involving an amino nitrogen, a pyridyl nitrogen, and two bridging mercaptide ions.

Introduction

The redox equilibrium between organic disulfide, RSSR, and mercaptide, RS^-, in neutral aqueous solution in the presence of O_2 can be shifted by complexation to Ni(II). (The mercaptide is oxidized slowly by O_2 or more rapidly by H_2O_2.) The direction of the shift depends upon the bidentate R groups studied.[1] When R is 2-[(2-pyridylmethyl)amino]ethyl, the equilibrium shifts to the disulfide, and disulfide complexes of Ni(II) can be isolated.[1] The structures of two of these, chloro[bis[2-[(2-pyridylmethyl)amino]ethyl] disulfide]nickel(II) perchlorate and its isostructural bromide derivative, have been reported.[2,3] In these disulfide complexes, a five-membered chelate ring is formed by each R group with Ni(II). The corresponding six-membered ring does not appear in an isolatable complex and may be considered a disfavoring feature.

When R is 2-[(2-pyridylethyl)amino]ethyl, which is one methylene group larger, the equilibrium favors the mercaptide complex, and a disulfide complex could not be isolated. Apparently a six-membered chelate ring is better accommodated by the mercaptide complex.

This work was undertaken to understand better the dependence of the disulfide–mercaptide Ni(II) complex equilibrium on the chelate ring sizes and orientations and to observe the structural relationship between the disulfide and mercaptide complexes. Perhaps the Ni(II) ion is coordinated to the ligands during the redox process, and a mechanism involving the complexes would be apparent.

Experimental Section

Preparation Section. Ethylene monothiocarbonate and 2-(β-aminoethyl)pyridine were obtained from Eastman Kodak Co. and Chemicals Procurement Laboratories, respectively. Reagent grade $NiClO_4{\cdot}6H_2O$ and $NaClO_4$ were obtained from G. Frederich Smith Chemical Co. All other chemicals were of reagent grade quality. The infrared spectrum was obtained using a Beckman IR-10 instrument. Elemental analysis was performed by Galbraith Laboratories.

Preparation of 2-[(2-Pyridylethyl)amino]ethanethiol, $pyCH_2CH_2NHCH_2CH_2SH$. A 43.8-g (0.36 mol) sample of distilled 2-(β-aminoethyl)pyridine was dissolved in 75 mL of toluene (distilled over Na) and brought to reflux. Ethylene monothiocarbonate (18.7 g, 0.18 mol) dissolved in 25 mL of anhydrous toluene was added dropwise with stirring to the refluxing solution. After 2 h of refluxing, an additional 9 g of ethylene monothiocarbonate was added; heating continued for 4 h more at 120 °C, just below reflux temperature. Toluene was distilled away at atmospheric pressure; the remainder was fractionally vacuum distilled. The desired product had a boiling point range of 106–110 °C at 0.15 Torr.

Preparation of Bis-μ-[2-[(2-pyridylethyl)amino]ethylthiolato]-dinickel(II) Perchlorate, $Ni_2(pyCH_2CH_2NHCH_2CH_2S)_2(ClO_4)_2$. Following the procedure of Gavino,[1] a 0.18-g (0.001 mol) sample of $pyCH_2CH_2NHCH_2CH_2SH$, dissolved in 15 mL of acetone was added to an acetone solution of $NiClO_4{\cdot}6H_2O$ (0.37 g or 0.001 mol in 75