otherwise very similar electronic properties of this polymer (vide infra) relative to those that are SHG active, we presume that this as yet structurally uncharacterized material crystallizes in a centrosymmetric space group.

Determination of the relative yield of SHG using standard techniques[13] shows that these polymers are 0.20–0.35 times as efficient as urea[14] (Table I). These efficiencies are surprisingly modest, in view of the facts that these compounds should, in principle, possess large molecular hyperpolarizabilities (β), as predicted from the $\beta \propto L^3$ dependence of this property on the conjugated chain length (L), and that, as d^0-configured species, their lower lying electronic excited states (including those of the $[\pi\pi^*]$ type) will be necessarily charge transfer in nature, which is important since the virtual excitation of such states induces large optical nonlinearities in conjugated organic species.[2c,10] The efficiencies do not appear to be intrinsically limited by crystallographic factors,[15] since the polymer dipoles are aligned parallel to one another in the solid state.[5]

In order to develop an electronic-structural framework through which to interpret the SHG properties of these polymers, and for the purpose of comparison to their calculated[8a] band structures, we have probed their lowest energy electronic excited states and found them to be highly emissive at low temperature. Crystals of all derivatives display broad and, for the molybdenum polymers, vibronically structured emission at 77 K (Figure 1). The extremely long excited-state lifetimes (Table I)—those for the molybdenum polymers are among the longest known for transition-metal complexes—indicate that the emission is a spin-forbidden process. In accord with this assignment, the emission excitation spectra of all polymers display a weak (and unstructured) band as the lowest energy feature.[16]

The emission energy of the $[MN(OR)_3]_n$ polymers is only moderately dependent upon the nature of the alkoxide ligand (Table I), which suggests that the orbital character of the emissive state derives largely from within the $[MN]_n$ backbone. This view is supported by the nature of the vibronic structure that is observed in the emission spectra of the molybdenum compounds. Although the vibronic transitions are irregularly spaced at higher quanta, the separation of the transitions near the electronic origin (where line broadening and coalescence effects are minimized) is ca. 1000 cm^{-1} (Figure 1), which is attributable to $\nu(Mo\equiv N)$ ($\bar{\nu} = 1020$ cm^{-1}).[5b] A simple Franck–Condon simulation of the vibronic intensity profile indicates that a ca. 0.2-Å distortion along the $M\equiv N$ coordinate is associated with the population of the emissive state, from which we infer that the orbital transition producing this state is strongly $M\equiv N$ bonding to antibonding in nature; by comparison, a 0.1-Å elongation of the $M\equiv N$ bond has been calculated for the $^3[\pi\pi^*]$ states of d^2 $[OsNX_4]^-$ (X = Cl, Br) ions).[17] Our interpretation of these data is consistent with the results of a band-structure calculation for $[WN(OH)_3]_n$,[8a] which indicates that the valence and conduction bands are $[WN]_n$ localized and correlate, respectively, with the $\pi(W\equiv N)/\sigma(W\equiv N:)$ and the $\pi^*(W\equiv N)$ orbitals of monomeric WN(OH)$_3$.[18] That such a large distortion should be associated with the band-gap excitation of an electron from the least $[MN]_n$-bonding orbital of the filled band to the least $[MN]_n$-antibonding orbital of the empty band indicates that the electron is not extensively delocalized

along the polymer chain, in accord with the small dispersion calculated[8a] for these bands.[19]

In view of these findings, we suggest that the effective conjugated chain length that controls the emission and SHG properties of these polymers is considerably less than the structural chain length. While this undoubtedly serves to limit $\chi^{(2)}$ for these materials, it also endows them with far greater optical transparency than more highly conjugated compounds, such that the 532-nm second-harmonic line in our SHG measurements is still ca. 1 eV below the onset of absorption. This contrasts with a number of recently reported transition-metal SHG complexes, which possess larger efficiencies but also strongly absorb visible light.[20] Optimizing this efficiency/transparency tradeoff is central to improving SHG materials and could be accomplished for these polymers by tuning the covalency of the polymer backbone through replacement of the nitrido bridges with other atoms or groups. We have succeeded in preparing complexes derived from these archetypal metal–nitrido polymers and will report on them shortly.

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Crystallographic Evidence for Multiple Coordinating Conformations in a Family of Macrocyclic Chelators

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Elucidating the relationship between a chelator's covalent structure and the strength with which that molecule binds metal ions remains an important goal in the domain of molecular recognition. A detailed mechanistic picture of the complexation process requires, among other things, information on the chelator's conformation in the final coordination complex. The most precise structural data are provided by single-crystal x-ray or neutron diffraction, but the binding processes of interest generally occur in solution, and the validity of extrapolation from the solid state to solution is unclear. In some cases, the relevance of crystallographically observed ligand conformations to solution behavior may be evaluated by NMR, but experimental parameters (e.g., paramagnetic ions or inconvenient exchange rates) are often not conducive to NMR spectroscopy. Even when NMR analysis is possible, this approach may provide only limited insight on ligand conformation.

Ni(II) complexation by **1–3** provides an example of divergent structural information obtained from crystallographic and solution spectroscopic studies. The X-ray crystal structure of **1**-Ni(BF$_4$)$_2$
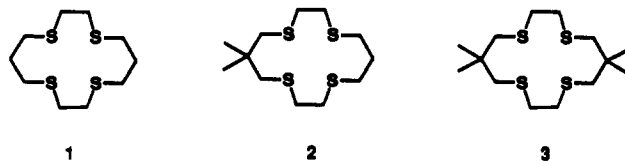
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(18) The location of the Fermi level for [WN(OH)$_3$]$_n$ is not apparent from ref 8a, since the calculated energies of the tops of the z and x,y bands are nearly identical. The large $M\equiv N$ distortion of the emissive state favors assignment of the band-gap excitation as $\pi \rightarrow \pi^*$; a $^3[e \rightarrow e]$ orbital transition such as this yields $^3A_1$, $^3A_2$, and ^3E excited states, for which there are two A$_1$, two A$_2$, and four E spin–orbit components. Although a detailed assignment of the emissive state is not available at present as a result of this complexity, the long emission lifetimes of [MoN(OR)$_3$]$_n$ may indicate that emission from an A$_2$ spin–orbit state predominates at 77 K, since the A$_2 \rightarrow A_1$ transition is dipole forbidden.

1   2   3

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shows only a single chelator conformation,[1] but ^{13}C NMR data on the complex dissolved in nitromethane reveal that there are two Ni(II)-bound macrocyclic conformations in slow exchange.[2] We recently reported that crystalline 2-Ni(ClO₄)₂ and 3-Ni(ClO₄)₂ display macrocycle conformations very similar to that seen for 1-Ni(BF₄)₂, but that ^{1}H NMR data for the Ni(ClO₄)₂ complexes of all three macrocycles in nitromethane implicate two chelating conformations,[3] which are present in roughly equal amounts. We now describe crystallographic and solution binding data for 2-Cu(ClO₄)₂ and 3-Cu(ClO₄)₂.[4] In the latter case, two very different chelator conformations are observed in the crystal lattice. The coexistence of multiple polydentate ligand conformations within a single crystal lattice is quite rare, particularly when the host cavity and the guest ion are well matched.[5] (Rorabacher et al. have shown that the 14-membered ring is the optimal tetrathioether macrocycle size for Cu(II) chelation.[6])

The previously reported crystal structure of 1-Cu(ClO₄)₂ shows only a single metal-bound macrocycle conformation,[7] which is very similar to that observed for the Ni(II) complexes of all three tetrathioethers 1-3.[1,3] This conformation of the 14-membered ring is also seen in the minor component we find in the crystal lattice of 3-Cu(ClO₄)₂ (Figure 1c). Cooper and Rawle have designated this conformation anti, on the basis of the fact that the two six-membered chelate rings extend out on opposite sides of the plane defined by the four sulfur atoms.[8] The central ion of the anti form of 3-Cu(ClO₄)₂ experiences four bonds of nearly equivalent length to sulfur (2.28 and 2.31 Å) and two long axial bonds to perchlorate oxygen atoms (2.53 Å). A very similar arrangement was observed for 1-Cu(ClO₄)₂ (Cu–S lengths 2.30 and 2.31 Å), although the Cu–O bonds were significantly longer (2.65 Å).[7]

The alternative folding pattern we observe for the Cu(II)-bound 14-membered ring has both six-membered rings on the same side of the approximate plane defined by the four sulfur atoms; this conformation has been previously designated syn.[8] Two slightly different versions of this backbone conformation are observed for 2-Cu(ClO₄)₂ (Figure 1a); disorder in one of the ethylene segments apparently results from roughly equal proportions of two different dispositions of the methylene groups in the crystal lattice.[9] The major ligand conformation observed in the crystal lattice of 3-Cu(ClO₄)₂ is also syn. The Cu–S bond lengths in the syn forms of 2-Cu(II) and 3-Cu(II) (2.29–2.31 Å) are similar to those seen for the anti conformations of 1-Cu(II) and 3-Cu(II), but in the syn structures, the Cu coordination environment is approximately

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2-Cu(ClO₄)₂
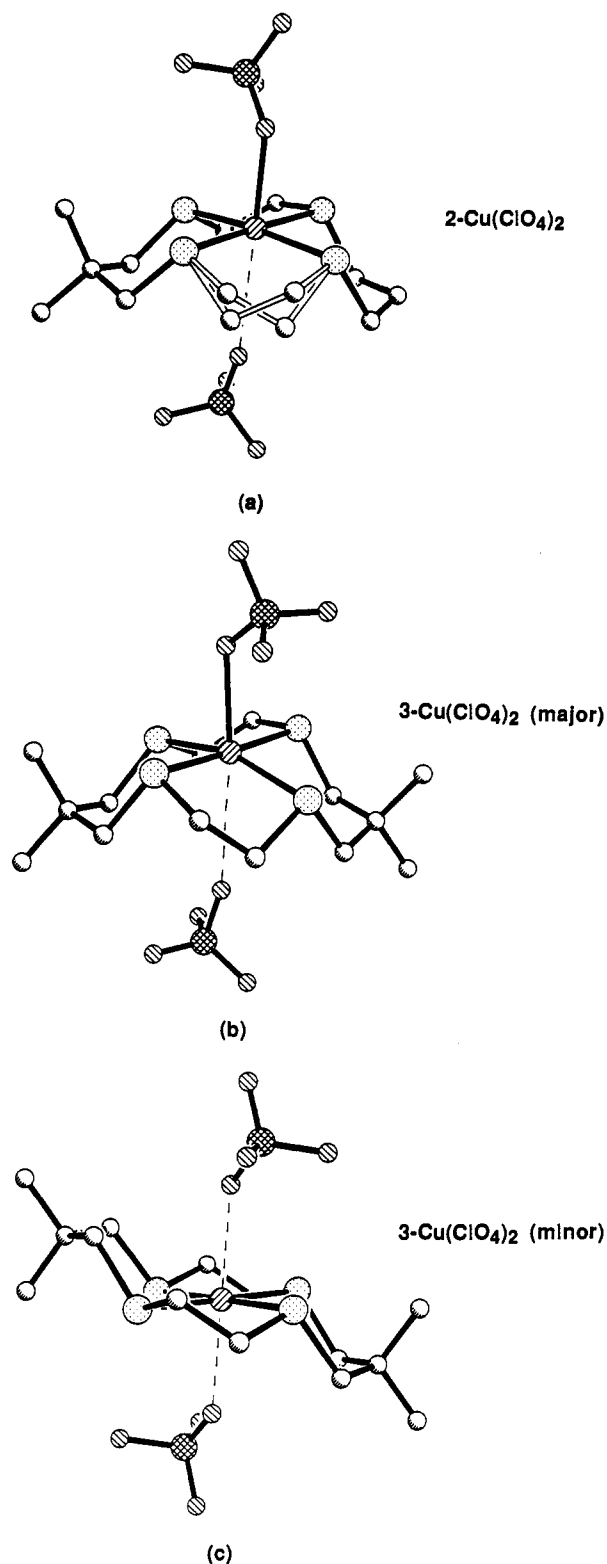
(a)

3-Cu(ClO₄)₂ (major)

(b)

3-Cu(ClO₄)₂ (minor)

(c)

Figure 1. Ball-and-stick representation of the crystallographically observed Cu(II)–tetrathioether complexes; hydrogen atoms omitted for clarity. (a) 2-Cu(ClO₄)₂; disorder in one of the ethylene segments could be accounted for as an approximately 1:1 mixture of the two conformations shown. (b) Major form of 3-Cu(ClO₄)₂ (one per asymmetric unit). (c) Minor form of 3-Cu(ClO₄)₂ (one-half per asymmetric unit); the perchlorate ions are crystallographically equivalent. Short bonds between Cu and perchlorate O (<2.4 Å) are indicated by a heavy line; longer Cu–O distances are indicated by a dotted line.

square pyramidal, with a single short Cu–O bond to a perchlorate (2.33–2.37 Å). (The other perchlorate is quite distant from the metal center, Cu--O distance 3.10–3.34 Å.)

Each CS–CC bond in the anti Cu(II) chelates (e.g., Figure 1c) displays an anti torsion angle, while all SC–CC and SC–CS bonds in these structures are gauche. The major conformational difference in the syn complexes (Figure 1, parts a and b) is that two of the eight CS–CC bonds are gauche.

It is impossible to use ^{1}H or ^{13}C NMR to examine the multiplicity of Cu(II)-bound conformations of 1–3 in solution because the ion is paramagnetic. However, the fact that both anti and syn conformations of the 14-membered tetrathioether macrocycle can be observed crystallographically for Cu(II) complexes, even within a single crystal lattice, strongly suggests that both types of backbone conformation are energetically accessible in solution. Because of the similarity of Cu(II)–S and Ni(II)–S bond lengths (average lengths: 2.30 and 2.18 Å, respectively), the present structural data indirectly support the hypothesis of Moore et al. that the two forms of 1-Ni(II) observed by ^{13}C NMR in nitromethane solution are the anti and syn conformational isomers.[2]

It has been suggested, on the basis of a survey of crystallographic data on tetracoordinated transition metal ion complexes of 1, that the chelated ligand's conformation depends upon the size of the ion, with smaller ions that fit well into the ligand cavity tending toward the anti coordination mode.[8] In contrast, our observations with 1–3 in solution and in the solid state imply that for ions well matched in size to the 14-membered ring, like Ni(II)[3] and Cu(II), there is no strong energetic preference for anti over syn. The fact that the syn ligand conformation has not previously been crystallographically observed for the Ni(II) complexes of 1–3 or the Cu(II) complex of 1 is presumably an accident of crystal packing.

We examined the Cu(II) binding strengths of 1–3 in 4:1 MeOH/H$_2$O containing 0.1 M HClO$_4$ (room temperature) using the UV-based methodology of Rorabacher et al.[6] The association constant for 1 and Cu(II) we measured under these conditions, 3.2×10^3 M^{-1}, was similar to the reported value (3.0×10^3 M^{-1}). For 2, we found $K_a = 1.6 \times 10^4$ M^{-1}, and for 3, we found $K_a = 7.4 \times 10^4$ M^{-1} (each value is the average of several determinations). Accordingly, 2 binds Cu(II) 5 times more strongly than does 1, and 3 binds Cu(II) 23 times more strongly than does 1. Thus, each additional gem-dimethyl pair produces an incremental improvement of approximately 5-fold in Cu(II) binding strength, which is analogous to our previous observations for Ni(II) complexation by 1–3 in nitromethane (an approximately 7-fold gem-dimethyl effect was observed in the latter case).[3]

It is not yet clear why the gem-dimethyl pairs enhance the binding strength of the macrocyclic tetrathioether array for Ni(II) and Cu(II). Our previously reported crystal structures for metal-free 2 and 3,[3] in conjunction with data for metal-free 1,[10] show that each gem-dimethyl pair progressively biases the 14-membered ring toward the chelating conformations. In 1, all 14 backbone bonds must be altered for formation of a tetradentate complex,[11] but in 2 and 3, smaller numbers of alterations are required, for adoption of either an anti or a syn coordination stereochemistry.[3] These observations suggest that the gem-dimethyl pairs may reduce the enthalpic cost of chelation, a cost that arises because covalent bonds in the macrocyclic polythioether skeleton must be distorted from their inherent torsional preferences to allow tetradentate coordination. An alternative but nonexclusive possibility is that the gem-dimethyl substituents rigidify the metal-free macrocycle, diminishing the conformational entropic cost of complexation. Experiments designed to dissect the entropic and enthalpic components of this gem-dimethyl effect are underway.

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A Molecular Constraint That Generates a Cis Peptide Bond

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The peptide bond in proteins generally assumes the trans configuration, since its cis counterpart induces unfavorable interresidue steric interactions.[1] In those instances where the cis isomer is present, a proline residue is almost invariably a participant in the peptide linkage.[2–3] In short conformationally flexible peptides, a proline-generated cis amide configurational isomer generally accounts for 10–30% of the total cis/trans population.[4] There have been a few reports of cis amide bonds in cyclic peptides containing N-substituted amino acids other than that of proline.[5,6] Recently, Goodman and his colleagues observed this phenomenon in cyclic peptides that do not possess any N-substituted amino acid residues.[7] Additionally, Peggion et al. have described a linear heptadecapeptide (bombolitin) composed only of non-proline L-amino acid residues that contains a cis amide bond when the peptide is incorporated into a micelle.[8] We report herein that the peptide bond in a Cys-Cys dyad, in which the adjacent cysteine residues are connected via both amide and disulfide linkages (abbreviated as Cys⇔Cys), exists predominantly in the cis configuration in a simple heptapeptide.

In 1969, Chandrasekaran and Balasubramanian predicted that the strain inherent in the eight-membered ring of a Cys⇔Cys dyad would compel the peptide linkage to adopt the cis arrangement.[9–11]

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