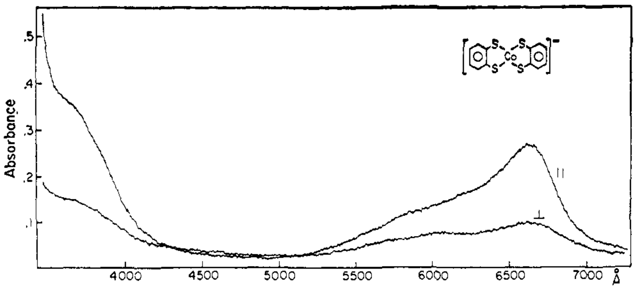

Figure 4. Polarized spectra of 8 × 10^{-3} *M* nematic solution of *n*-tetrabutylammonium bis(benzene-1,2-dithiolato)cobaltate. The electric vector of light is polarized parallel and perpendicular to the long axis of the solvent molecules.

Figures 1 and 2 show that $(\epsilon_{||} - \epsilon_{\perp})$ is positive for the long-wavelength absorption bands of β-carotene and *p*-azoxyanisole. On the basis of eq 1 and the above discussion, we interpret this to mean that the electronic transitions in question are polarized along the long molecular axis $(\epsilon_x \gg \epsilon_y, \epsilon_z)$. This interpretation is in accord with other experiments.[2,8-10] As shown in Figure 3, $(\epsilon_{||} - \epsilon_{\perp})$ for the lowest energy band system in anthracene is negative. Since ϵ_z for anthracene is expected to be nearly zero, the data indicate short-axis (*y*) polarization. Again, our interpretation agrees with previous work.[11-13] Thus it may be concluded that in the spectra studied here our generalizations concerning solute orientation are valid and that the technique is capable of reliable polarization information.

Figure 4 represents the first measurement of the polarizations of the lowest allowed bands in planar inorganic complexes of the monoanionic bis(benzenedithiolato)-metalate system. Both the 15,200- and 27,800-cm^{-1} bands in the $Co(bdt)_2^-$ complex are long-axis polarized. We have also measured the 25,400-cm^{-1} band in $Cu(bdt)_2^-$ and find it similarly polarized. These results provide strong support for a recent theoretical analysis[14] of the electronic structures of these complexes in which the bands are assigned to L → M charge-transfer transitions. For example, the assignment of the 25,400-cm^{-1} band in $Cu(bdt)_2^-$ as $b_{2u}L \rightarrow b_{1g}d\sigma^*$ is consistent with the *x* polarization.

As the above examples show, electronic spectroscopy in oriented nematic liquids provides a quick, simple method for obtaining band polarizations for both inorganic and organic molecules. The method perhaps will be most useful in studying intense bands, because it is not always possible to find a suitable host in single crystal work. We are presently investigating several representative metal complexes to test further the range of applicability of this technique.

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Magnetism and Structure of $[Cr_4(OH)_6(en)_6]^{6+}$ [1]

Sir:

The structure of Pfeiffer's cation,[2] $[Cr_4(OH)_6(en)_6]^{6+}$, has been a subject of recent interest. In an interpretation of magnetic susceptibility measurements on $[Cr_4(OH)_6(en)_6]I_6 \cdot 4H_2O$ from room temperature to liquid nitrogen temperature (77°K), Wentworth and Saillant[3] logically assumed that the arrangement of the four metals in the tetrameric complex is the same as in Werner's optically active inorganic ion,[4] $Co[(OH)_2Co(NH_3)_4]_3^{6+}$, namely, three metal(III) atoms surrounding a central metal(III) to form a trigonal planar array. Later it was pointed out[5] that a tetrahedral $[Cr(III)]_4$ unit is in better accord with the observed temperature dependence of the magnetic susceptibility than is the "Werner structure."

We have made magnetic susceptibility measurements on $[Cr_4(OH)_6(en)_6]I_6 \cdot 4H_2O$ and $[Cr_4(OH)_6(en)_6](N_3)_6 \cdot 4H_2O$ down to 4.2°K using a vibrating sample magnetometer with liquid helium dewar and found that neither of the above models is adequate over the wider temperature range. Theoretical curves[5] of μ_{eff}^2 *vs.* *T* for the tetrahedral and trigonal planar models are compared in Figure 1 with the experimental results for $[Cr_4(OH)_6(en)_6](N_3)_6 \cdot 4H_2O$. The calculated curve for trigonal planar structure is clearly in complete variance with experiment. And the theoretical curve for tetrahedral structure falls well below the experimental points starting at about 80°K.

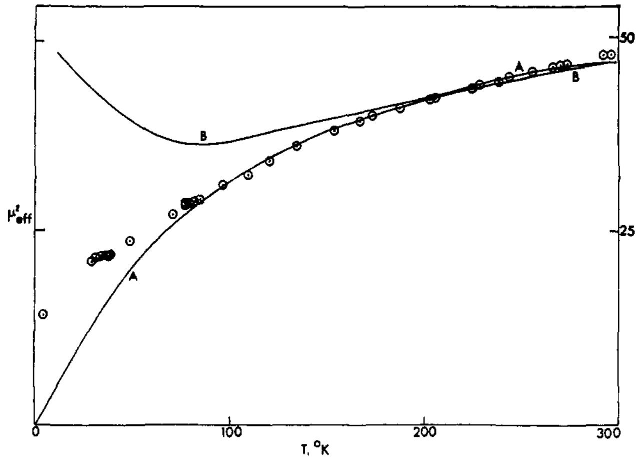

Figure 1. Plots of μ_{eff}^2 *vs.* *T*: (A) theoretical curve for a tetrahedral model with $S = ^3/_2, g = 2.00, J = -10k$; (B) theoretical curve for a trigonal planar model with $S = ^3/_2$, $g = 2.00$, $J = -5k$; (⊙) observed data for $[Cr_4(OH)_6(en)_6](N_3)_6 \cdot 4H_2O$.

We have resolved this question by determining the crystal and molecular structure of $[Cr_4(OH)_6(en)_6](N_3)_6 \cdot 4H_2O$. The structure was determined by conventional heavy-atom methods from data obtained from Cu Kα radiation and a Datex-automated General Electric

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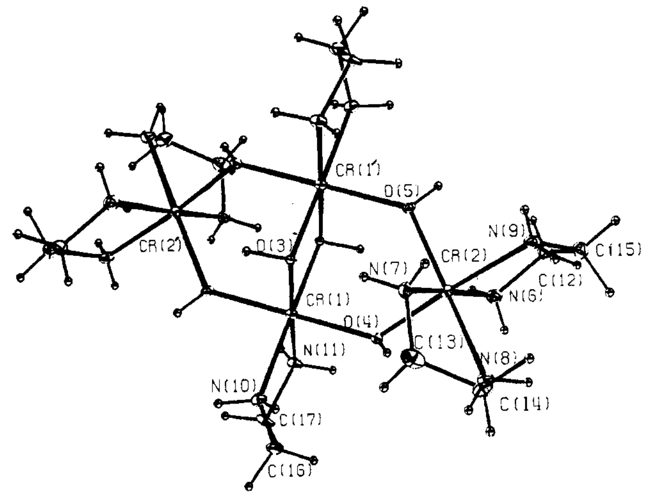

Figure 2. A view of the $[Cr_4(OH)_6(en)_6]^{6+}$ cation. The atoms are represented by ellipsoids whose principal axes were derived from the final values of the anisotropic temperature parameters. A crystallographic center of symmetry relates the primed and unprimed atoms.

XRD-6 diffractometer using 2155 reflections of which 252 were considered to have zero intensity. The compound crystallizes with four formula units in the orthorhombic space group D_{2h}^{15}-Pbca with unit cell dimensions $a = 12.608$ (0.002) Å, $b = 24.038$ (0.003) Å, $c = 13.528$ (0.014) Å. The calculated density of the crystal is 1.612 g/cm^3; the observed density (flotation) is 1.597 g/cm^3. The structure was refined by least squares to an R value $[R = (k|F_o| - |F_c||/\Sigma k|F_o|)]$ of 0.092 and a goodness of fit $(\Sigma w(F_o^2 - F_c^2/k^2)^2/(m - s))^{1/2}$ of 1.80.

The structure of the cation is shown in Figure 2. It is centrosymmetric and features a planar, rhomboid array of chromium atoms held together by oxygen atoms of four bridging hydroxo groups; the bridging angle Cr(1)–O(4)–Cr(2) is 131°, which is a large valence angle for three-coordinate oxygen. Furthermore, Cr(1) and Cr(1′) are brought into close contact by O(3) and O(3′) atoms of two more bridging hydroxo groups. The chromium–chromium distances are: Cr(1)–Cr(1′), 2.929 Å; Cr(1)–Cr(2), 3.606 Å; Cr(2)–Cr(2′), 6.554 Å. Each chromium atom is approximately octahedrally coordinated. The O(3)–Cr(1)–O(3′) angle is 85.1°, whereas the O(4)–Cr(2)–O(5) angle is 95.1°.

Kambe's method[6] can be extended to derive an expression for the temperature dependence of the magnetism for the observed rhomboid structure of the four chromiums. Using this model and including all Cr(III)–Cr(III) interactions except Cr(2)–Cr(2′), we have been able to fit satisfactorily the experimental data points shown in Figure 1. Details of this treatment and further electronic structural interpretation will be the subject of a subsequent paper.[7]

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Structures of $B_{20}H_{18}^{2-}$ and $B_{20}H_{18}NO^{3-}$ and Conformations of the Triethylammonium Ion

Sir:

Polyhedral[1] $B_{10}H_{10}^{2-}$ is oxidized by Fe^{3+} to yield[2,3] $B_{20}H_{18}^{2-}$, in which we have located H atoms, and by NO_2 to yield[4] a product called $B_{14}H_{12}NO^{2-}$, but which we show here to be $B_{20}H_{18}NO^{3-}$. Solutions of the disordered crystal structures of the triethylammonium salts of these ions also yield six conformations of this positive ion and precise interatomic distances for the B_{10} units in the negative ions (Figures 1 and 2).

Crystals of $(Et_3NH)_2B_{20}H_{18}$ are monoclinic, in the space group P2$_1$/a, and have unit cell parameters $a = 17.52 \pm 0.02$, $b = 7.60 \pm 0.01$, $c = 11.72 \pm 0.01$ Å and $\beta = 109.7 \pm 0.2°$. Two formula weights in the unit cell yield the calculated density of 0.991 g/cm^3 (observed 0.982). The Sayre method[5] as programmed by Long[6] provided a recognizable E map once the twofold disorders of both $B_{20}H_{18}^{2-}$ and Et_3NH^+ were recognized. Least-squares refinement of the 1874 intensities, measured on the Buerger automated diffractometer, has reached $R = \Sigma||F_o| - |F_c||/\Sigma|F_o| = 0.106$. Hydrogen atoms of interest, located and refined in both disordered orientations, are 1.13 and 1.25 Å from apices near the center of the ion, but 2.34 and 2.27 Å to the nearest boron atoms of the opposite B_{10} units, respectively. This direct location of these H atoms thus supports the indications of the nuclear magnetic resonance study[7] in which the B_{10} units were linked by two three-center B–B–B bonds rather than by two hydrogen bridges. The B_{20} unit is similar to that found in Babcock's study[8] of $[(CH_3)_3S]_2B_{20}H_{18}$ in which H atoms were not located and B–B distances have not yet appeared.

The intense purple crystals of $(Et_3NH)_3B_{20}H_{18}NO$ are monoclinic in the space group P2$_1$/n and have unit cell parameters of $a = 24.44 \pm 0.04$, $b = 16.68 \pm 0.03$, $c = 9.65 \pm 0.02$ Å, and $\beta = 97.0 \pm 0.1°$. The four molecules per unit cell yield a calculated density of 0.972 g/cm^3 (observed 0.986). The structure was recognized in an E map after application of G. N. Reeke's direct methods program, and the largest 4555 independent reflections have been refined so far to $R = 0.144$. One Et_3NH^+ ion has a twofold disorder. The N–O distance of 1.28 Å and B–N distances of 1.51 and 1.46 Å compare with values of N–O = 1.28 and 1.23 and of C–N = 1.51 and 1.44 Å in, respectively, the radicals di-*t*-butyl nitroxide[9] and di-*p*-anisyl nitroxide.[10] Although not a radical, the $B_{20}H_{18}NO^{3-}$ ion appears to have a more satisfactory charge distribution if the N–O distance is between single- and double-bond distances, and if the B–N bonds have a bit more than single-bond character.

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