= 0.91). With consideration only of H_2Q-OH, H_2Q-OCH$_3$, H_2Q-Br, and H_2Q-CH$_3$, the fit to the Marcus equation is more satisfactory, with a correlation coefficient and slope of 0.98 and 0.54 ± 0.08, respectively. A range of only 1.0 kcal/mol in $\Delta G°_{12}$ is spanned by the reactions of these four substrates with Ce(IV), however, making it impossible to conclude safely that these reactions are outer-sphere or follow a different mechanism from the oxidations of H_2Q and H_2Q-SO$_3$H.

Excellent conformity to the Marcus relationship has been demonstrated in the reactions of substituted hydroquinones with numerous outer-sphere oxidants.[6] Free energy correlations based on reactions of ceric sulfate with outer-sphere reductants (i.e., iron(II)[13] and ruthenium(II)[14] phenanthroline complexes, Fe(CN)$_6^{4-}$,[15] Mo(CN)$_8^{4-}$,[15] W(CN)$_8^{4-}$ [15]) also accord well with Marcus theory. It appears likely, therefore, that an inner-sphere mechanism is employed in the reactions of H_2Q-X with cerium(IV) sulfate. A zeroth order hydroquinone dependence has been reported in the reaction with Ce(IV) in perchlorate media, suggesting the presence of a stable inner-sphere intermediate complex.[16] The first-order reductant dependences reported here also are consistent with an inner-sphere mechanism, considering the attenuation in precursor complex formation constants expected in sulfate media, where SO$_4^{2-}$ competes strongly for positions in the first coordination sphere of cerium (ca. 93% of the Ce(IV) in 1 N H_2SO_4 is present as Ce(SO$_4$)$_3^{2-}$, 7% as Ce(SO$_4$)$_2$).[17] The activation enthalpy of the hydroquinone–ceric sulfate reaction must reflect, for the most part, substitution of SO$_4^{2-}$ by H_2Q in the first coordination sphere of cerium, as the rate of electron transfer within the H_2Q–cerium(IV) perchlorate inner-sphere complex is independent of temperature ($\Delta H^\ddagger \approx 0$ kcal/mol).[16]

Rate constants for the one-electron oxidation of hydroquinone phosphate and hydroquinone sulfate by ceric sulfate are comparable to $k_{12}(H_2Q)$, being smaller by factors of only 2 and 3, respectively, at 25 °C. By contrast, the oxidations of HQ-P and HQ-S by periodic acid, a two-electron acceptor, in strongly acidic solution are much slower, by factors of 3 × 10^2 [18] and 2 × 10^3,[19] respectively, than the analogous oxidation of hydroquinone. Both of these substrates, HOC$_6$-H$_4$OPO$_3$H$_2$ (pK_1 = 1.5)[20] and HOC$_6$H$_4$OSO$_3$H (pK_1 = 2.9),[20] are fully protonated to the free acid forms in 1 N H_2SO_4. Irreversible two-electron oxidation waves have been reported in cyclic voltammetric studies of HQ-P and HQ-S in 1 M H_2SO_4.[20] An ECEC mechanism pertains in each case, with ester hydrolysis occurring only after loss of the second electron. The similarity of rate constants for reactions of ceric sulfate with hydroquinone, (4-hydroxyphenyl)phosphoric acid, and (4-hydroxyphenyl)sulfuric acid may be partially understood on this basis, as little stretching of the C–O (or P–O, S–O) bonds presumably is required in converting these reductants to the corresponding semiquinones. Substantial rate discrimination between hydroquinone and its esters (and among individual esters) will be observed only when ester hydrolysis accompanies the (two-electron) redox process.

The hydroquinone–ceric sulfate reaction exhibits a modest 2.5-fold rate increase as the hydrogen ion concentration is increased from 0.10 to 1.5 M at 25 °C, while the rate of the H_2Q–Ce(IV) reaction in perchlorate media is independent of acidity in the interval 0.2 ≤ [H$^+$] ≤ 2.0 M.[16] Protonation of hydroquinone, as monitored by proton NMR spectroscopy, is detected only in superacid media,[21] ruling this possibility out as a source of the kinetic hydrogen ion dependence. A plot of k_{12} vs. [H$^+$] based on the data in Table III is sigmoidal, reminiscent of a titration curve with an inflection point corresponding to a pK of ca. 0.1. The weak hydrogen ion dependence in the H_2Q–cerium(IV) sulfate system may be linked to the protonation of SO$_4^{2-}$ ions coordinated to Ce(IV) (pK-(HSO$_4^-$) = 0.43, 25 °C, I = 2.0 M; see Table III).

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Magnetic Circular Dichroism of Cyclic π-Electron Systems. 22.[1a] Derivatives of the Trisulfur Trinitride Anion

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Magnetic circular dichroism (MCD) of low-energy transitions in molecules derived from ($4N + 2$)-electron cyclic conjugated perimeters can be interpreted simply by using the perimeter model.[2-4] Of the three categories of parent perimeters [two π electrons, $N = 0$, two π holes, $N = (n/2) - 1$, and the rest, $N \neq 0$, $N \neq (n/2) - 1$], the third category is the largest and the predicted signs are a sensitive yet usually simply predictable function of molecular structure. The first two categories provide an interesting contrast to the third in that the MCD signs are predicted to be structure independent.

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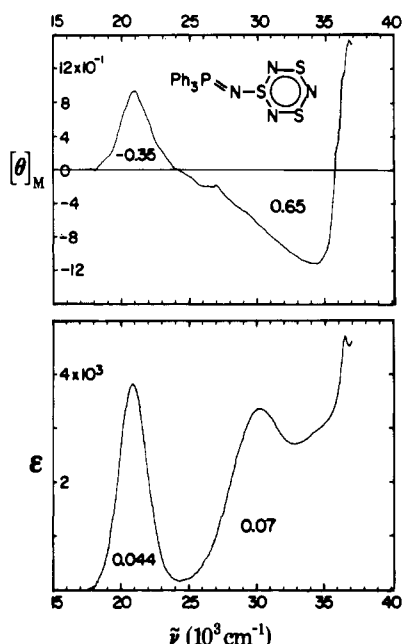(4) J. Michl, *J. Am. Chem. Soc.,* **100,** 6819 (1978).

Figure 1. Spectra of **1** in acetonitrile: top, MCD (*B* terms in units of 10^{-3} D^2 μ_B/cm^{-1}); bottom, absorption (oscillator strength given). The values for **2** are very similar (*B* terms −0.32 and 0.38, oscillator strengths 0.040 and 0.07).

In the order of increasing energy, they are −, + if $N = 0$ and +, − if $N = (n/2) - 1$ [i.e., in the usual terminology, $A > 0$ or $B_1 > 0$, $B_2 < 0$ if $N = 0$ and $A < 0$ or $B_1 < 0$, $B_2 > 0$ if $N = (n/2) - 1$]. In the present note, we report the MCD spectra of two derivatives of the ten-π-electron six-atom $S_3N_3^-$ perimeter [$N = (n/2) - 1$], **1** and **2**.
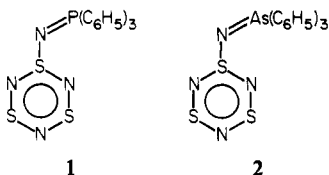
Experimental Section

Preparation[5] of **1** and **2** and spectral procedures (absorption,[1a] MCD,[1a] linear dichroism[6]) have been described elsewhere.

Results

The spectra of **1** are shown in Figure 1; those of **2** are very similar. Both show a transition near 20 500 cm^{-1} ($f \simeq 0.04$, $D \simeq 4.2$ D^2) and a second transition near 30 000 cm^{-1}, which overlaps with higher energy absorptions. Its oscillator strength appears to be comparable to that of the first transition. The *B* term of the first transition is negative, $B_1 = -(3.5 \pm 0.3)$ × 10^{-4} D^2 μ_B/cm^{-1}, where μ_B is the Bohr magneton. The *B* term of the second transition, B_2, is positive and appears to be comparable to B_1 in magnitude.

Due to the poor solubility of **1** in polyethylene, linear dichroism was obtained only for the first transition. It was positive, with the dichroic ratio 1.13. Since the alignment of solutes in stretched polyethylene is dictated primarily by their shape[7] and since the heterocyclic substituent on phosphorus is larger than the phenyl moiety, it is much more likely that the transition moment of the visible transition lies approximately along the P=N bond rather than approximately perpendicular to it.

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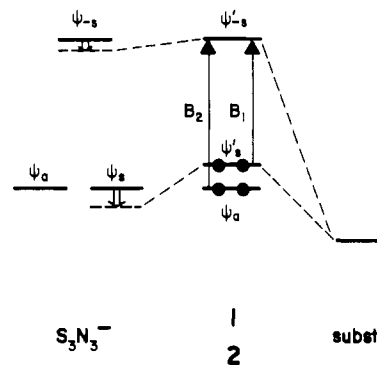
Figure 2. Schematic representation of the frontier π MOs of **1** and **2** (center) as resulting from those of $S_3N_3^-$ (left) by the effects of increased electronegativity of the tricoordinate sulfur atom (double arrows) and of the interaction with "π-symmetry" orbitals of the substituent (right). The B_1 and B_2 transitions are indicated by single arrows.

Discussion

The highest occupied molecular orbital (HOMO) of π symmetry in $S_3N_3^-$ is doubly degenerate ($2e''$) and the lowest unoccupied molecular orbital (LUMO) of π symmetry is nondegenerate ($2a_2''$).[1a,8] The HOMO → LUMO excitation at ca. 28 000 cm^{-1} produces a doubly degenerate excited state of E′ symmetry and has the expected negative *A* term. Substitution on one of the sulfur atoms should have two effects (Figure 2): (i) the tricoordinate sulfur will have a formal positive charge and increased effective electronegativity and (ii) the π system will be extended by interaction with "π-symmetry" orbitals of the substituent.[9] One of the HOMOs, with a node at the position of substitution (ψ_a), will be insensitive to either effect. The other will have an antinode there (ψ_s), as will LUMO (ψ_{-s}), and these will react to substitution, which will convert them into more delocalized orbitals ψ_s' and ψ_{-s}', respectively. The $N^--P^+(C_6H_5)_3$ and $N^--As^+(C_6H_5)_3$ substituents will act as quite strong π donors, and their conjugative effect will destabilize ψ_s relative to ψ_a. It is not immediately obvious whether this effect will prevail over the stabilizing effect of the increased electronegativity of the tricoordinate sulfur atom. If it does, the $\psi_s' \rightarrow \psi_{-s}'$ transition, polarized along the substitutent–ring bond, will be shifted to lower energies from the 28 000 cm^{-1} found in $S_3N_3^-$. The effect of π-electron substituents on the energy of the LUMO (ψ_{-s}), which will be converted into ψ_{-s}', is likely to be of only sec-

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(9) The geometry of the S_3N_3 ring in **1** and **2** is not fully planar. In **1** the tricoordinate sulfur lies 139° out of the plane of the other five ring atoms [E. M. Holt and S. L. Holt, *J. Chem. Soc., Dalton Trans.* 1990 (1974)]; in **2** the angle is 140° [E. M. Holt and K. J. Watson, *J. Chem. Soc., Dalton Trans.*, 514 (1977)]. The substituent-carrying ring sulfur atom is somewhat pyramidal and its "lone-pair" hybrid atomic orbital overlaps in the π fashion with a 2p atomic orbital of each of the two neighboring ring nitrogens and with a hybrid atomic orbital of the exocyclic nitrogen. Thus, cyclic conjugation survives, though probably somewhat diminished relative to $S_3N_3^-$ (this probably reduces the magnetic moments of the ring orbitals somewhat), and the delocalized orbital system of the ring is in interaction with an orbital of the substituent which, in turn, will be in further interaction with atomic orbital or orbitals of the neighboring phosphorus or arsenic atom. In order to estimate the spectral effects of substitution on the $S_3N_3^-$ ring in a qualitative fashion, it is essential to identify all those atomic orbitals that are in strong interaction with the delocalized "π" orbitals of the ring. We refer to these loosely as forming the "π system" and to electrons in them as π electrons, although strictly speaking, a σ–π separation is impossible in nonplanar molecules. The π system defined in this manner consists of eight atomic orbitals (3 × S, 4 × N, and P or As) and contains ten electrons provided by the ring chromophore and two more provided by the substituent, altogether twelve electrons. The treatment of the phosphorus (arsenic) atoms as providing a single vacant orbital and the neglect of the three phenyl rings it carries are arbitrary but appear acceptable for qualitative purposes.

ondary importance, since the donor π orbital of the substituent is too far removed in energy from ψ_{-s} for efficient interaction and its π^* orbital is primarily localized on the phosphorus or arsenic rather than the nitrogen attached to the ring. The transition $\psi_a \rightarrow \psi_{-s}$, polarized perpendicular to the substituent–ring bond, should thus occur roughly at the same energy as in $S_3N_3^-$ itself.

Inspection of Figure 1 suggests that ψ_s' is indeed destabilized considerably relative to ψ_a and that the 20 500 cm^{-1} transition corresponds to the $\psi_s' \rightarrow \psi_{-s}'$ transition, in agreement with our tentative assignment of its polarization direction from the stretched-sheet measurement. The second transition (30 000 cm^{-1}), which occurs at almost the same energy as in $S_3N_3^-$ itself, is then assigned to the $\psi_a \rightarrow \psi_{-s}'$ excitation.

The signs of the observed B terms agree with the assignment of the two transitions in question to the two perimeter MO excitations ($\psi_a \rightarrow \psi_{-s}'$ and $\psi_s' \rightarrow \psi_{-s}'$). The B term of the first transition is given approximately[2] by

$$B_1/D_1 = -[\mu^-(2N + 2, N)](W_2 - W_1)^{-1}$$

where the magnetic moment $\mu^-(2N + 2, N)$ is characteristic of the $S_3N_3^-$ ring and $W_2 - W_1$ is the energy difference of the two transition energies. Using the experimental values of B_1, D_1, and $W_2 - W_1$, we find $\mu^- \simeq 0.8 \ \mu_B$. In $S_3N_3^-$ we found[1a] $\mu^- = 0.98 \ \mu_B$. To the extent that the excited state is represented by the pure $\psi_a \rightarrow \psi_{-s}$, $\psi_s \rightarrow \psi_{-s}$ pair of configurations, this is equal to the magnetic moment of an electron in the complex HOMO of $S_3N_3^-$. Alternatively, it can be viewed as the magnetic dipole transition moment between ψ_a and ψ_s. In **1** and **2**, the physical significance of μ^- is magnetic transition dipole moment between the first and second excited states. As long as these are each reasonably represented by a single configuration, this is equal to the magnetic dipole transition moment between orbitals ψ_a and ψ_s'. Since ψ_s' is somewhat delocalized onto the substituent and since only that part of it that lies on the ring contributes significantly to magnetic moments, it is quite reasonable that μ^- should be a little smaller in **1** and **2** than in $S_3N_3^-$ itself, as is found.[9]

In conclusion, we believe to have identified the lowest two perimeter states[2,10] in **1** and **2**, B_1 and B_2, and we find that the signs and magnitudes of their B terms agree with expectations based on the perimeter model.

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Linkage Isomers of 5-Methyl- and 5-Phenyltetrazolato(1-) Complexes of Pentaamminecobalt(III) and Their Isomerization Reactions

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Tetrazoles and substituted tetrazoles have been investigated as the ligands of transition-metal complexes for several years. The cyclic tetrazolato(1-) anion, HCN_4^-, is isoelectronic with the cyclopentadienyl anion and the imidazolato anion. Thus, several potential bonding modes exist for the ligand in coordination compounds. First, the anion could function as an η^5 π-bonding ligand. However, despite early realization of this

possibility[1] no evidence for such a bonding mode exists for complexes prepared to date. Numerous σ-bonding possibilities exist for the ligand as well. The carbon atom of the ring, ring position 5, has been shown to function as the σ donor with
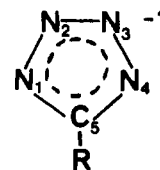
tetrazolato ring and numbering scheme

Au(III).[2] However, with 5-substituted tetrazoles, which are the topic of this study, this potential binding site is eliminated. Finally, the nonequivalent ring nitrogens may serve as the donor atom. For 5-substituted tetrazolato complexes, both N_1-[3] and N_2-bonded[4] complexes have been verified for complexes of coordination number 4 or less. Nevertheless, linkage isomers of a particular complex have never been isolated although equilibrium mixtures of the N_1- and N_2-bonded forms have been detected in solution for several Pt(II) and Pd(II) complexes.[5] Six-coordinate Co(III) complexes of 5-substituted tetrazoles have been recently reported[6] with bonding occurring exclusively via the N_2 donor. Although the N_1 nitrogens of 5-substituted tetrazolato anions are more nucleophilic than the N_2 nitrogens,[6a] it has been suggested that steric crowding of the substituent at ring position 5 with the four groups cis to the tetrazole ligand, especially if the cis groups are sterically demanding, obviates N_1 coordination in octahedral complexes.[6a]

Tetrazoles with substituents at ring position 5 are conveniently prepared from organonitriles via nucleophilic attack of azide ion by a 1,3-dipolar cycloaddition reaction.[7] Coordination of organonitriles to the pentaamminecobalt(III) moiety is known to enhance the susceptibility of the nitrile carbon to nucleophilic attack by hydroxide ion[8] and cyanide ion.[9] Therefore, we have explored the possible reactions of organonitriles coordinated to cobalt(III) with azide ion in aqueous solution. Given the well-known substitution inertness of low-spin cobalt(III), an N_1-bonded tetrazolato complex would be expected if such attack were to occur. Direct substitution of 5-substituted tetrazoles for water in the aquopentaamminecobalt(III) complex has been shown by Lieberman et al.[6b] to yield N_2-substituted tetrazoles exclusively. Therefore, the synthetic approach employing formation of the 5-substituted

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