examples of this behavior have been reported in transition-metal chemistry in which substitution[39] or isomerization[40] at a transition-metal center occurs with no net current flow in an electrochemical experiment. In the present case, reduction requires two electrons and reoxidation provides one; thus, a net one-electron reduction from Mo(V) to Mo(IV) is observed. This combination of redox and coordination chemistry provides a link between the redox chemistries of higher oxidation state oxomolybdenum species and lower oxidation state nonoxo species. The structural change associated with this reaction allows formation of all four oxidation states to be compressed within an energetically narrow range of 0.45 V. Thus, it is possible to observe Mo(VI)–Mo(III) catechol complexes as stable monomeric entities in aqueous solution at pH >9.

Acknowledgment. Support of this research by the National Science Foundation (Grant No. CHE 76-18703) is gratefully acknowledged. We also wish to thank Drs. J. W. McDonald, W. E. Newton, and G. D. Watt of the Charles F. Kettering Research Laboratory, Yellow Springs, OH, for their assistance in obtaining and interpreting the EPR spectra described in this work. Sue Lahr performed additional helpful experiments.

Registry No. $MoO_2(cat)_2^{2-}$, 72985-79-6; $MoO(Hcat)(cat)_2^{2-}$, 79682-15-8; $Mo(cat)_3^{2-}$, 79682-16-9; $Mo(cat)_3^{3-}$, 79682-17-0.

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Applications of Magnetic Circular Dichroism Spectroscopy: Electronic Structure of the Thiotrithiazyl Cation, $S_4N_3^+$

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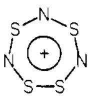
Received February 18, 1981

Magnetic circular dichroism of the $S_4N_3^+$ cation reveals the presence of four low-energy electronic transitions. Their number and properties are exactly those expected for $\pi^*-\pi^*$ excitations in a ten-π-electron system with cyclic delocalization, and they are assigned as the two L and two B bands in Platt's notation.

Introduction

The structure determination of the $S_4N_3^+$ cation[1] (**1**) showed



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it to be a planar ring and prompted studies of its electronic structure.[2-4] In these, primary importance was attached to the interpretation of the electronic spectrum. We now use the technique of magnetic circular dichroism[5] to demonstrate the presence of a larger number of low-energy transitions than previously assigned or even suspected and show that the observations are in perfect agreement for $\pi^*-\pi^*$ transitions in a delocalized "aromatic" system of ten π electrons in a seven-membered ring.

Experimental Section

A sample of S_4N_3Cl, prepared according to ref 6, was provided by Professor Chivers (Calgary). The solvent used was 11 N $HClO_4$. Absorption was measured on a Cary 17 spectrophotometer and MCD on a Jasco 500C spectropolarimeter equipped with a 15-kG electromagnet.

Oscillator strengths f and the B terms were evaluated from the formulas $f = 4.319 \times 10^{-9} \int \epsilon \, d\tilde{\nu}$ and $B = -33.53^{-1} \int d\tilde{\nu} \, [\Theta]_M/\tilde{\nu}$, where $\tilde{\nu}$ is wavenumber, ϵ is the decadic molar extinction coefficient, and $[\Theta]_M$ is molar ellipticity/unit magnetic field in deg L m^{-1} mol^{-1} G^{-1}.

Calculations were performed by using the semiempirical Pariser–Parr–Pople (PPP) method as described in ref 7, including all singly excited configurations and using standard parameter values,[8] I_N = 14.1 eV, A_N = 1.8 eV, I_{S+} = 20.27 eV, A_{S+} = 10.47 eV, and β_{SN} = −1.854 eV. The value of β_{SS} was varied over a wide range with little effect on the results; the results shown in Figure 1 were obtained with β_{SS} = −1.6 eV. In the calculation of magnetic moments the procedure "2" of ref 9 was used.

Results

The absorption and MCD spectra of $S_4N_3^+$ are shown in Figure 1. The absorption spectrum is in good agreement with the previous report although the integrated oscillator strengths deviate somewhat.[2] Whereas only two bands are apparent in the absorption spectrum, a weaker one near 29 500 cm^{-1} and a stronger one near 38 000 cm^{-1}, the MCD spectrum clearly reveals the presence of four bands located near 28 500, 30 500, 37 500, and 40 000 cm^{-1} and labeled L_1, L_2, B_1, and B_2, respectively, in Figure 1. The signs of their B terms are negative for L_1 and B_1 and positive for L_2 and B_2. The results thus show that each of the seemingly simple absorption bands consists of two nearly degenerate transitions. In the case of the first absorption band, this is actually also suggested by its unsymmetrical shape. The magnitudes of the B terms suggest that they are dominated by the mutual mixing of the L_1 and L_2 states and of the B_1 and B_2 states by the magnetic field, although the inequality of the magnitudes of $B(L_1)$ and $B(L_2)$ indicates that the situation is not quite so simple.

Discussion

The planar cyclic structure of $S_4N_3^+$, which guarantees considerable π overlaps, and a simple electron count invite the thought that this cation must be a rare representative of a delocalized ten-π-electron seven-membered ring system, iso-

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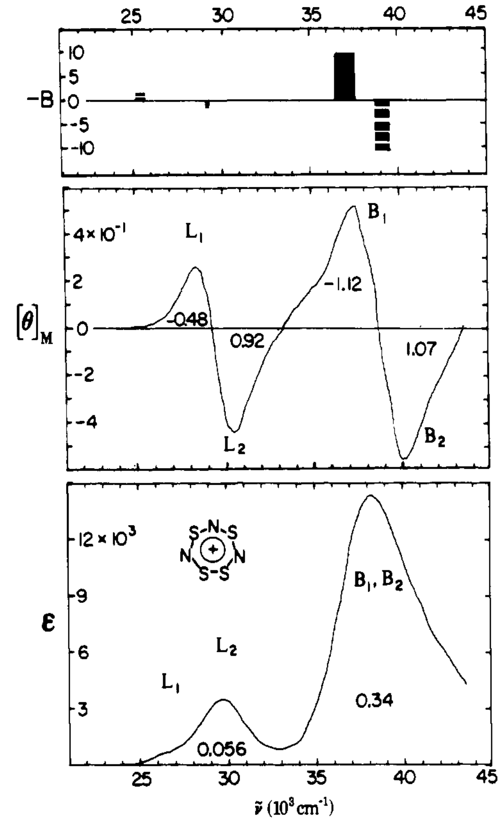

Figure 1. Thiotrithiazyl cation: bottom, absorption (oscillator strength given); center, MCD (B terms in units of 10^{-3} μ_B D/cm^{-1}); top, calculation. Full bars indicate vertical polarization and a broken bar indicates horizontal polarization with respect to the formula shown. The thickness of the bar indicates intensity: thin line, $f \leq 0.05$; medium line, $0.05 < f < 0.5$; thick line, $f \geq 0.5$.

electronic with the hypothetical [7]annulenide trianion, $C_7H_7^{3-}$. A previous attempt[3] to predict the electronic spectrum from such a picture, using essentially the same PPP model as used presently, but without configuration interaction, led to the prediction of three transitions of about equal intensity in the region of interest, in definite disagreement with the presently available experimental results. We shall now show that this discrepancy does not reflect on the model of bonding used but is entirely due to the fact that configuration interaction is essential to the proper description of electronic states of cyclic conjugated systems when molecular orbital theory is used.

The simplest reasonable representation of the electronic structure of π-electron systems derived by a perturbation of a $(4N + 2)$-π-electron [n]-center delocalized cyclic perimeter of D_{nh} symmetry is the perimeter model originally devised by Platt[10] and recently summarized in a form suitable for our present purpose.[11-13] The parent perimeter is characterized by an array of molecular orbitals (Figure 2). The most stable among these is nondegenerate and totally symmetrical (a) in the C_n subgroup, while all others come in degenerate pairs and are of symmetries ϵ_k, ϵ_{-k} in the C_n subgroup, with $k = 1, 2, ..., (n-1)/2$. Their energy increases with increasing k. If n is even, the highest energy orbital is nondegenerate and of symmetry b. Except for the rare case $N = 0$, the highest occupied molecular orbital is doubly degenerate (ϵ_N, ϵ_{-N}), and except for the rare case $N = (n/2) - 1$, the lowest unoccupied molecular orbital is also degenerate (ϵ_{N+1}, ϵ_{-N-1}). Four single excitations from the former to the latter result and lead one to expect four low-lying electronic transitions. If $n \neq 4N + 2$, as is the case of interest here, these occur in two degenerate pairs.

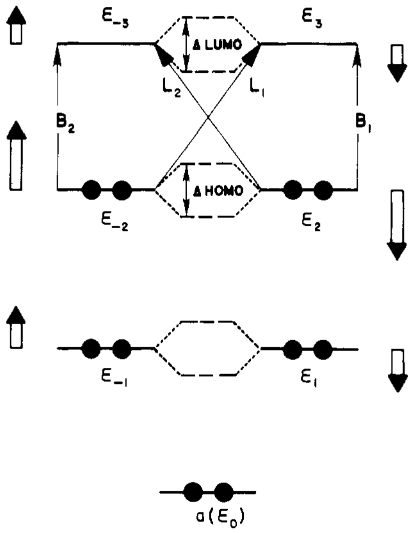

Figure 2. Schematic MO level diagram for a ten-π-electron [7]-membered-ring parent perimeter. Orbital magnetic moments are indicated by double arrows. The four excitations of L and B types are indicated by single arrows. The splitting introduced upon conversion of the idealized symmetrical perimeter to the $S_4N_3^+$ ion is indicated by dotted lines in the center.

The two components of the lower energy pair are $\epsilon_{-N} \rightarrow \epsilon_{N+1}$ and $\epsilon_N \rightarrow \epsilon_{-N-1}$ and are referred to as L_1 and L_2 (E_{2N+1} in C_n). Electric dipole transition from the ground state into this L state is forbidden, and observed intensity is due solely to vibronic interactions. The magnetic moment of the L_1 state, μ^+, is negative and is given by the sum of the magnetic moment of an electron in the orbital of symmetry ϵ_{N+1} and that of an electron in the orbital of symmetry ϵ_N. For a ten-π-electron cyclic system of seven centers this has been estimated[11] at 2 μ_B in the case of an all-carbon ring, and there is reason to believe that the value will be similar in an S–N ring.[14]

The two components of the higher energy pair are $\epsilon_N \rightarrow \epsilon_{N+1}$ and $\epsilon_{-N} \rightarrow \epsilon_{-N-1}$, referred to as B_1 and B_2 (E_1 in C_n). Electric dipole transition from the ground state into this degenerate B state is strongly allowed and in-plane polarized. The magnetic moment of the B_1 state, μ^-, is given by the magnetic moment of an electron in the orbital of symmetry ϵ_{N+1} minus that of an electron in the orbital of symmetry ϵ_N. It is a small negative quantity for most combinations of N and n, but it is positive if N is relatively large for a given n. For $C_7H_7^{3-}$, it is positive and has been estimated[11] at $+0.6$ μ_B. A roughly similar value can be expected for the corresponding S–N heterocycles.

The basic pattern of two low-energy forbidden excitations of type L, with a large magnetic moment, and two high-energy allowed excitations of type B, with a small magnetic moment, is preserved when the regular D_{nh} perimeter is perturbed into the actual molecule of interest. In the low-symmetry C_{2v} case of interest here, all degeneracies are removed (Figure 2). The model then predicts the presence of two weak low-energy transitions L_1 and L_2 (the predicted intensity of L_2 is at most equal to that of L_1 and may actually be vanishingly small) and two strong high-energy transitions B_1 and B_2.

The absence of degeneracies in molecules of C_{2v} group permitted us to rule out the presence of A bands in the MCD spectrum of **1**. The B terms of the four transitions of the perturbed annulene contain contributions proportional to μ^- and those proportional to μ^+. For L_1 and L_2, each of the

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contributions in turn contains a part due to the L_1–L_2 magnetic mixing and a part due to the L–B magnetic mixing. If $n \neq 4N + 2$, the former part is expected to predominate.[12] The signs of the μ^- contributions to *B* terms are then equal to the sign of μ^- for L_2 and B_2 and opposite to it for L_1 and B_1. In our case, μ^- is positive, and since a positive *B* term corresponds to a negative MCD peak, the expected MCD signs due to μ^- contributions alone are +, −, +, − in the order of increasing energy.

The μ^+ contributions to the four *B* terms are more sensitive to the nature of the perturbation that produced the molecule of interest from the parent perimeter. This perturbation splits the originally degenerate pair of highest occupied molecular orbitals by an amount that we refer to as ΔHOMO. Similarly, it splits the original pair of lowest unoccupied molecular orbitals by an amount ΔLUMO (Figure 2). If ΔHOMO = ΔLUMO, the μ^+ contributions to *B* terms vanish. If ΔHOMO > ΔLUMO, their signs are +, −, +, − in the order of increasing energy, and if ΔHOMO < ΔLUMO, they are −, +, −, +.

The spectra of $S_4N_3^+$ (Figure 1) are in perfect qualitative agreement with expectations for a perturbed ten-π-electron seven-center perimeter, except that the order of the nearly degenerate transitions L_1 and L_2 seems to be interchanged, since L_1 has lower absorption intensity than L_2. This could be confirmed by a determination of polarization directions, which are presently unknown. According to the simple perimeter model, the stronger transition should be polarized along the S–S bond and the weaker transition perpendicular to it. In order to account for this possible interchange, additional configurations would have to be considered in the perimeter model.

In view of the expected positive sign and sizable magnitude of the magnetic moment μ^-, it is tempting to assign the observed *B* term sequence (−, +, −, +) entirely to the μ^- contribution. Although this appears to account for the bulk of the observed effect and agrees with our PPP calculations, which suggest that ΔHOMO and ΔLUMO are of similar size, a simple check suggests that the μ^+ contribution is probably not totally negligible and that ΔHOMO actually is smaller than ΔLUMO,[15] so that the μ^- and μ^+ contributions reinforce each other. If the magnitude of the transition magnetic moment μ between two nearly degenerate states is estimated by treating their contribution to MCD as an *A* term and using the relation $\mu = -2A/D$, where *D* is the dipole strength, the values 1.0 and 0.46 μ_B are obtained for the L pair and B pair, respectively. Although these are only crude estimates, the value for the L pair is sufficiently in excess of the expected value of about 0.6 μ_B that one strongly suspects that a contribution of the μ^+ type is also present. This suspicion is reinforced by the results of ab initio calculations on the $S_4N_3^+$ cation,[16] which lead to the order ΔHOMO < ΔLUMO.

Whatever the detailed origin of the numerical magnitudes of the observed *B* terms, it is clear that the observed absorption and MCD spectra are in perfect agreement with the notion that a delocalized ten-π-electron system is present in $S_4N_3^+$. This is not in contradiction to the absence of any spectacular shortening of the S–S bond (2.06 Å) in the equilibrium ground-state geometry. The fact that the bond order calculated for this bond in the ground state is quite low (about 0.3 in our calculations) does not mean that there is no interaction between the 3p-type orbitals on the two adjacent sulfur atoms, only that it is not particularly stabilizing in the ground state, so that there is little driving force for making this bond shorter in this state of the cation.

Acknowledgment. This research was supported by U.S. Public Health Service (Grant No. GM-21153). We are indebted to Professor T. Chivers (Department of Chemistry, University of Calgary, Calgary, Alberta, Canada) for the kind gift of a sample of S_4N_3Cl and for comments on the manuscript and to Professor W. G. Laidlaw of the same Department for informing us about his unpublished calculations.

Registry No. 1, 29631-23-0.

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(15) More accurately: the 2 → −1 configuration is lower in energy than the 1 → −2 configuration, where the occupied MOs are labeled 1, 2, ... in the order of decreasing energy and the vacant MOs are labeled −1, −2, ... in the order of increasing energy. If the π-electron system in question does not deviate too strongly from the parent perimeter, this condition is equivalent to the condition ΔHOMO < ΔLUMO.[12]

(16) W. G. Laidlaw, personal communication.

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ESCA Investigation of Perfluoromethylated Germanium Halides

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Received March 5, 1981

Core-level binding energies have been recorded for all atoms in the series of compounds $(CF_3)_{4-n}GeX_n$, where $n = 0$–3 and X = F, Cl, Br, and I. The binding energy shifts are compared with those observed in the corresponding methyl series and are discussed in terms of estimated atomic charges derived from CNDO/2 and electronegativity-equalization procedures. The inclusion of potential and relaxation terms is also investigated.

Introduction

Bonding in trifluoromethyl derivatives of group 4 elements, especially in relation to analogous methyl compounds, has become a subject of both experimental and theoretical investigations. The preparation of several (trifluoromethyl)germanes[2] makes it possible to undertake a systematic study of their properties. An electron diffraction study of $(CF_3)_4Ge$[3] confirms the conclusion, based on the vibrational spectra[4] of the complete series $(CF_3)_{4-n}GeX_n$, $n = 1$–4, X = F, Cl, Br, I, that the Ge–C bond is weakened relative to that in the methyl analogues, and that the CF_3 group, in terms of second-order effects, behaves in a manner similar to the chlorine atom.

We report an ESCA investigation of the complete series of perfluoromethyl(halo)germanes. Earlier work on the methylhalogermanes[5,6] has shown that, in the gas phase, the

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