tuents,[24] vs. the frequency shifts of the 1637-cm^{-1} Raman line. Only the sterically hindered 5-nitro and phenyl derivatives lie off the line. The correlation with phen acceptor properties (Figure 1), together with a pattern of shifts in the Raman lines consistent with changes in π density, provides strong evidence for charge-transfer stabilization of the molecular complex.

Visible absorption spectral studies give a rough correlation between log K and the shift in frequency of the 1637-cm^{-1} Raman line. Charge transfer accounts for more than 1 order of magnitude in K or about 20% of the binding energy (ΔG). The tightness (log $K > 6$) of the methyl viologen dication complex is explained by the strong electrostatic interaction, which presumably induces an "unfavorable" charge transfer in the ground state, making viologen (normally a stronger acceptor then phen) a donor.

Recently, Shelnutt el al., observed that the O_2 affinity properties of hemoglobin[13] and myoglobin[25] correlate with the shifts in the π-electron density marker lines. A charge-transfer model for cooperative O_2 binding was suggested.[13,14] We also pointed out that nearby aromatic amino acid residues could form donor-acceptor complexes with the porphyrin. The present data shows for the first time that molecular complexes give shifts in the π-density marker lines like those observed in hemoglobin.[26]

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New Bonding Mode for a Bridging Dioxygen Ligand: Crystal and Molecular Structure of [K·dibenzo-18-crown-6][$Al_2(CH_3)_6O_2$]·1.5C_6H_6

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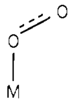
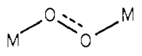
Dioxygen adduct complexes of metal ions have been the subject of many recent investigations.[1,2] Four types of structures have been observed (I–IV),[3] and correlations between the O–O bond length and the O–O symmetrical stretch have been made. I and II are formulated as the superoxide ion, O_2^-. With a bond order of 1.5, the bond distances for II fall in the range 1.10–1.30 Å, and ν_{O-O} 1075–1195 cm^{-1}.[4] For the bridged peroxo situation (IV), the lengths reside between 1.40 and 1.50 Å, and ν_{O-O} 790 and 930 cm^{-1}.[4] The ionic compounds KO_2 and Na_2O_2 exhibit values of 1.28 Å and 1145 cm^{-1}, and 1.49 Å and 842 cm^{-1}, respectively,[3] for bond distances and ν_{O-O}.


I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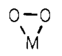
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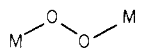

IV

In the course of our studies on high-oxygen content organoaluminum compounds, we have carried out the reaction of KO_2 and $Al(CH_3)_3$ according to

$$KO_2 + 2Al(CH_3)_3 + \text{dibenzo-18-crown-6 (V)} \xrightarrow{\text{aromatic}} [\text{K·dibenzo-18-crown-6}][Al_2(CH_3)_6O_2]$$

To our surprise the new complex is thermally stable for at least 24 h in refluxing toluene. More interesting, the single-crystal X-ray structure[5] has revealed a new type of coordination mode for the superoxide ion (See VI and Figure 1). The dioxygen moiety must be regarded as O_2^- for charge balance, but the O–O bond length is much longer than any previously found for a superoxide ion. Unfortunately, the distance is not known with great accuracy because of the high thermal motion of the nonbridging oxygen atom. The O–O value is 1.47 (2) Å. The weakness of the O–O linkage is also substantiated by the IR spectrum (Nujol mull) in which the ν_{O-O} is assigned to the band at 851 cm^{-1}.

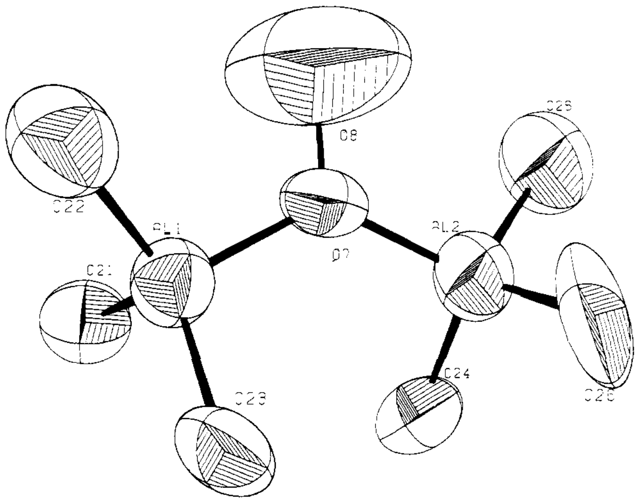
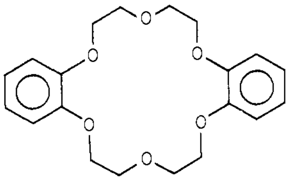
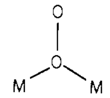
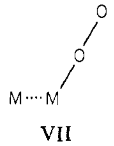


Figure 1. Structure of the anion [$Al_2(CH_3)_6O_2$]$^-$, with the atoms represented by their 50% probability ellipsoids for thermal motion.


V


VI

The importance of the new bonding mode is underscored by a consideration of the hemerythrins, a group of oxygen-carrying proteins. The resonance Raman spectrum of oxyhemerythrin shows an assigned O–O stretch at 844 cm^{-1}.[6] The two oxygen atoms have also been shown to exist in two different environments. Structures VI and VIII were proposed.[6] Our investigation demonstrates that a low ν_{O-O} and long O–O length may be associated with not only a peroxo group but also with the superoxo


VII

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(5) The space group is the triclinic $P\bar{1}$ with unit cell parameters $a = 13.210$ (8), $b = 13.671$ (8), $c = 14.090$ (8) Å; $\alpha = 68.11$ (4), $\beta = 65.46$ (4), $\gamma = 87.42$ (4)°; $D_c = 1.08$ g cm^{-3} for $Z = 2$; $\lambda = 0.71069$ Å, and $T = 22$ °C. Least-squares refinement based on 1509 observed reflections led to a final R value of 0.084. The hydrogen atoms of the crown ether were included with fixed contributions and those of the anion were located on a difference Fourier map, but their parameters were not refined. The nonhydrogen atoms of the crown, the anion, and the potassium ion were refined with anisotropic thermal parameters. The overall accuracy of the structure is impaired by the disorder (or high thermal motion) associated with the benzene molecules.

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ligand in the single oyxgen bridge mode VI.

The Al-O lengths, 1.852(9) and 1.868(9) Å, are normal,[7] and the overall geometry of the anion conforms closely to that found in related complexes such as $K[Al_2(CH_3)_6N_3]$[8] [i.e., Al-O-Al = 128.3 (7)° vs. Al-N-Al = 128.0 (3)°].

Acknowledgment. We are grateful to the National Science Foundation and the University of Alabama School of Mines and Energy Development for support of this work.

Supplementary Material Available: Tables of bond distances, angles, final fractional coordinates, themal parameters, and observed and calculated structure factors are available (14 pages). Ordering information is given on any current masthead page.

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Enantioselective Aldol Reactions with High Threo or Erythro Selectivity Using Boron Azaenolates

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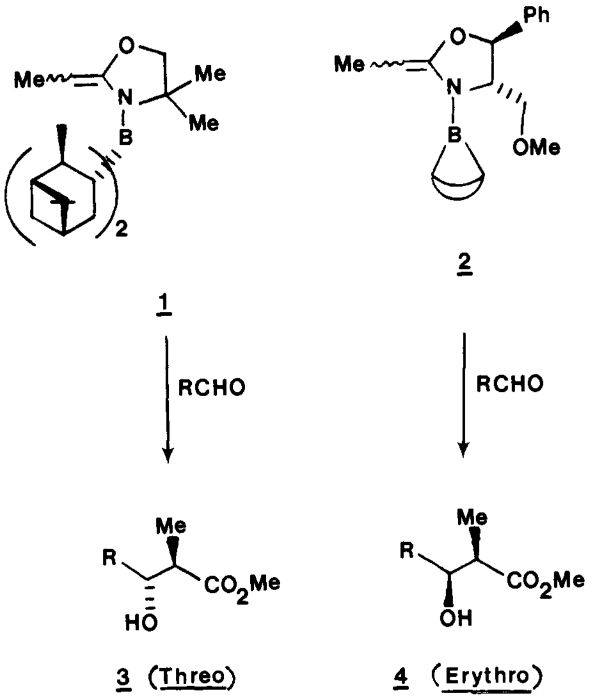
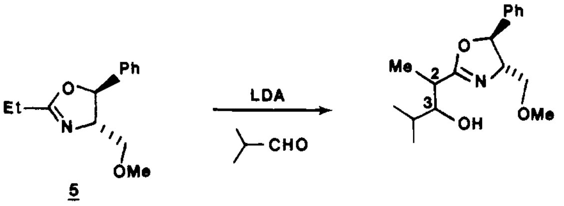
The extensive activity in recent years to control acyclic stereochemistry has resulted in a number of reports dealing with diastereoselection and/or enantioselection. A few of these have reached very impressive levels of success by using boron enolates.[1] We wish to report that our studies using the boron azaenolates, **1** and **2**, derived from achiral[2] and chiral oxazolines[3] has led to some useful and surprising results in the area of acyclic stereochemistry, particularly for the rarely reached threo isomers. Thus, by exchanging the chiral auxiliary from boron (**1**) to the heterocycle (**2**), we have been successful in altering the stereochemical course of the aldol process from threo to erythro products with enantioselectivities of ~90% (77–85% ee) in the former and ~70–80% (40–60% ee) in the latter. Table I depicts the results obtained by using boron azaenolate **1**[4-6] with several representative aldehydes. The reactions were carried out by adding 1.0 equiv of the aldehyde to preformed boron azaenolate **1** in ether at −78 °C, stirring for 2 h, and then warming to −20 °C for 1 h. Phosphate buffer (pH 7) was added along with methanol and 30% hydrogen peroxide at 0 °C. Usual extraction and drying procedures gave the alkylated oxazoline which was hydrolyzed to the β-hydroxy acid by heating (12 h) in 3 N sulfuric acid. The crude acids were transformed into the methyl esters **3** by treatment with diazomethane. The five-step sequence from 2-ethyloxazoline to the hydroxy ester was carried out without any isolation and purification of intermediates. None of these steps have been as yet optimized. The threo configuration was assigned on the basis of ^1H NMR data which showed the α proton as a quintet at δ 2.6–2.7 with J = 7 Hz.[7] In order to assign absolute stereochemistry to threo-**3**, the chiral oxazoline **5** was metalated and treated with isobutyraldehyde to give four diastereoisomers as previously reported;[7b] **6a** and **6b** were correlated to (−)-and (+)-*threo*-**3**,





(2R,3R)-6A }
(2S,3S)-6B } Threo, 82%

(2S,3R)-6C }
(2R,3S)-6D } Erythro, 18%

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[2] Meyers, A. I.; Temple, D. L.; Nolen, R. L.; Mihelich, E. D. *J. Org. Chm.* **1974**, *39*, 2778.

[3] Meyers, A. I.; Knaus, G.; Kamata, K.; Ford, M. E. *J. Am. Chem. Soc.* **1976**, *98*, 567.

[4] The boron azaenolates **1** and **2** were prepared from the oxazolines by using boryl triflates as reported by Mukaiyama.[5] Preparation of **1**: Borane in THF (1 M, 57 mL), (+)-α-pinene (17.8 g, $[\alpha]_D$ 41.1°) was added together under nitrogen and stored at 0 °C for 3 days upon which a precipitate appeared. After cooling the solution to −30 °C, the precipitate was collected, giving diisopinocampheylborane of 99.8% optical purity as described by Brown.[6] After drying in vacuo (13.5 g, 83%), the borane was dissolved in hexane (250 mL) and trifluoromethanesulfonic acid (7.1 g) was added at 0 °C (hydrogen evolution!). After stirring overnight, the solution was filtered and evaporated and the residue (diisopinocampheylboryl triflate) was used without further purification. Addition of 2-ethyl-4,4-dimethyloxazoline (0.72 g) to 2.5 g of the boryl triflate in 42 mL of ether and addition of 0.73 g diisopropylethylamine at −78 °C gave a mixture which was stirred for 1 h (amine triflate precipitated). The solution and precipitate were used as such for the aldol reactions. Preparation of **2**: this was accomplished by using 0.88 g of (4*S*,5*S*)-2-ethyl-4-(methoxymethyl)-5-phenyloxazoline, 1.08 g of 9-borabicyclononane triflate,[5] and 0.52 g of diisopropylethylamine in the manner described above.

[5] Inoue, T.; Uchimaru, T.; Mukaiyama, T. *Chem. Lett.* **1977**, 153.

[6] Brown, H. C.; Yoon, N. M.*Israel J. Chem.* **1976**, *15*, 12.