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(9) Reaction of (*S*)-(+)-**1** ($[\alpha]^{25}$D +29.1° (*c* 6.37, CCl_4)) with $AgClO_4$ in CH_3OH at 25° afforded **2** having $[\alpha]^{25}$D −6.9° (*c* 3.60, CCl_4) after purification by GLC. At one-half reaction, the starting bromide **1** was collected by GLC and had lost only ~1% of its optical activity having $[\alpha]^{25}$D 28.7° (*c* 8.25, CCl_4).

(10) Kornblum reported[11] that conversion of (+)-2-octanol to (−)-**1** by PBr_3 is accompanied by 18% racemization and, at one-half reaction with $AgNO_2$–CH_3CN, **1** had racemized 19–21%.

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(12) A referee has suggested that the observed second-order dependence on silver ion could be only superficially related to the dissociation and/or aggregation of $AgClO_4$ and $AgOCH_3$ in methanol. Unfortunately, pertinent data on this question is not available, and our data do not prove any particular mechanism for this reaction. However, our preliminary results suggest that the reaction of **1** with excess $AgNO_3$ ($[Ag^+]/[RBr] \geq 3$) in CH_3OH is also second-order in silver ion. The reaction appears to be quite general for all alkyl bromides since the reaction of mono- and dibromocyclopropanes under typical preparative conditions with an excess of $AgClO_4$ in CH_3OH also exhibits second-order kinetic behavior in silver ion (unpublished results). It should also be emphasized that, under basic conditions, $AgOCH_3$ is unstable and rapidly affords elemental silver.

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Electronic Structure of Dioxygen in Cobalt(II) Oxygen Carriers, Singlet Oxygen or O_2^-?

Sir:

In a recent communication,[1] evidence was presented supporting the existence of magnetically equivalent oxygen atoms in the mononuclear cobalt complex Co(bzacen)pyO_2. The experimental results consisted of the solution ESR spectrum of the ^{17}O-enriched complex, which was interpreted in terms of two equal isotropic ^{17}O splittings of 21.6 G. The value is in the range to be expected for a_O in an O_2^- ion, and we implicitly assumed the oxygen molecule to be a modified O_2^- ion. This assumption is in line with that of most previous workers in the field. The previous ESR evidence in support of the O_2^- formulation has been summarized by Hoffman et al.[2]

Recently Tovrog and Drago[3] have brought forward experimental data which they use to argue against the O_2^- formulation. They suggest that there is very little electron transfer from metal to oxygen on complex formation, and that the oxygen molecule is best regarded as being in a singlet state. Their explanation of our ^{17}O results is that the O_2 molecule is jumping between two σ-bonded bent structures, the observed a_O being accounted for by overlap between cobalt d_{z^2} and oxygen sp^2 hybrids. In addition they dismiss the report of the ESR spectra of ^{17}O-labeled O_2 coordinated to a cobalt(II)-ammonia complex in a γ-Zeolite. The spectra of this system were interpreted by Vansant and Lunsford[4] in terms of an O_2^--type structure for oxygen. In support of an O_2 formulation they claim that CO, certainly a very weak electron acceptor, combines with their cobalt complexes to give ESR spectra indistinguishable from those in the presence of oxygen.

We do not accept Tovrog and Drago's conclusions. Before presenting further experimental evidence for the O_2^- picture, we wish to make some preliminary comments.

If the O_2 molecule is effectively in a singlet state carrying very little unpaired spin, it becomes difficult, if not impossible, to explain Vansant and Lunsford's spectra.[4] It is true, as Tovrog and Drago state, that the resolution is poor, as expected for a powder spectrum. However, the important point is the *spread* of the spectrum in the ^{17}O-labeled complex and the approximate values of the oxygen splittings (A_O). The minimum value that can be assigned to the sum of the splittings for the two oxygens is ~140 G, based on the total spread and the values of A_{Co}. Secondly, the values of ~60 and ~80 G for the two coupling constants are close to the figures of 60 and 88 G measured in a single crystal study of an unimpeachable bent peroxy group carrying one unpaired electron.[5] Incidentally, our value of 21.6 for a_O is almost exactly that to be predicted for the isotropic splitting due to an electron density of 0.5 in a pπ atomic orbital on oxygen,[6] and it would be an extraordinary coincidence if the same splitting were due to the mechanism that Tovrog and Drago propose.

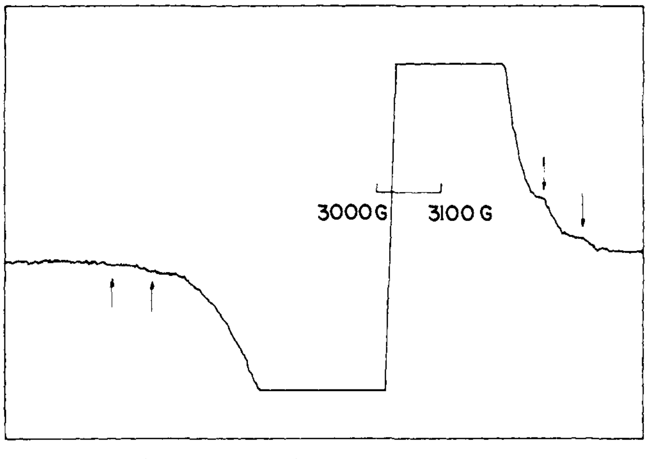

Figure 1. First derivative X-band ESR spectrum of a frozen solution of Co(bzacen)py-$^{17}O_2$ (~40 atom %) complex in CH_2Cl_2 at −100°. The two extreme ^{17}O satellites at high and low field are indicated by arrows.

In the present report, we describe the frozen solution ESR spectrum of ^{17}O-enriched Co(bzacen)pyO_2 complex. The results show unambiguously that the bound oxygen molecule is effectively an O_2^- ion, *at least in this complex.*

Co(bzacen)pyO_2 was synthesized with O_2 gas enriched to 40 atom % ^{17}O. Solutions in methylene chloride were frozen and the ESR spectra recorded at −100°. The first and second derivative spectra respectively are shown in Figures 1 and 2. Despite the heavy overlapping in the central part of the spectrum there are easily distinguishable ^{17}O satellites at the two extremes of the first derivative spectrum. The second derivative spectrum shows considerably better resolution, and the ^{17}O satellites are clearly visible. The separation between the outermost satellites is ~60 G. The total spread of the spectrum is ~740 Gauss which implies that $\Sigma A_O \sim 148$ G, and therefore that the two oxygen hyperfine splittings are ~60 and ~88 G. Despite the probable error of ±10 G in these figures, there is absolutely no doubt that they arise from the combined isotropic and anisotropic contributions due to a single unpaired electron in the π system of an unsymmetrically bound O_2^- group. The observed splittings can be simply rationalized in terms of pπ-spin densities of approximately 0.40 and 0.60 on the two oxygens, as explained previously.[5]

The addition of carefully purified oxygen-free CO had no detectable effect on the solution or ESR spectrum of Co(bzacen)py.

The complex studied here differs from that used by Tovrog and Drago, both in the nature of the Schiff base and in the fact that their Co(II) complexes are high spin. The relevance of our results to their complexes might therefore be questioned. After the submission of our original manu-

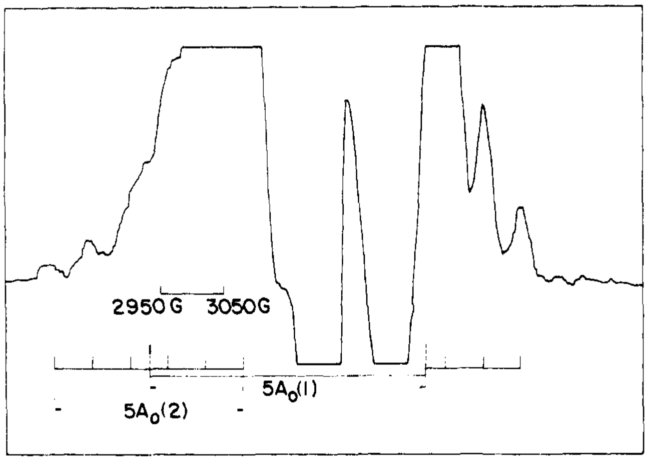

Figure 2. Second derivative X-band ESR spectrum of a frozen solution of Co(bzacen)py-$^{17}O_2$ (~40 atom %) complex in CH_2Cl_2 at −100°.

script, the work of Hoffman, Szymanski, and Basolo[7] became available to us. These workers have carefully repeated parts of Tovrog and Drago's ESR and NMR experiments and conclude that "the observations are artefacts caused by the presence of O_2".

The asymmetry of the O_2^- group in frozen solution is not inconsistent with the equivalence of the oxygen atoms in solution. As we suggested earlier, it seems probable that the O_2^- group is jumping between two equivalent bent conformations in solution, and that this motion is frozen in the solid. In single crystals, the O–O group is known, from X-ray studies, to be bent.[8] In this connection it is of significance that Collman et al.[9] have explained the temperature dependence of the line width of the O_2 stretching frequency in an Fe(II) porphyrin dioxygen complex as due to a rapid thermal equilibrium between several rotomeric states. "Lowering the temperature apparently brings about an increase in the population of the most stable conformer". In our case we postulate two energetically equivalent conformations in solution. In the solid state, the degeneracy is split by the local environment of each molecule in the rigid lattice.

In conclusion we feel that, at least for Co(bzacen), the description of bound oxygen in terms of an O_2^- structure is unambiguously proved, by our own and other workers results, and that such a structure occurs in most if not all cobalt(II) adducts of dioxygen.

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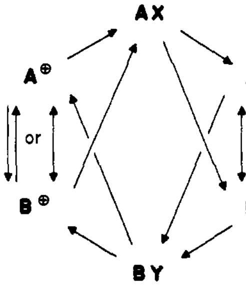
Reversible Charge Control. The Barbaralyl–Bicyclo[3.2.2]nonatrienyl Example

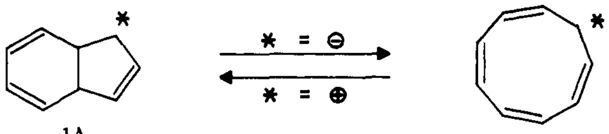
Sir:

Rational synthetic methodology has long recognized the technique of deliberately shifting thermodynamic control from the ultimate product to a chemical intermediate. For example, "contrathermodynamic" alkene isomerizations are achieved through the greater thermodynamic stability of the primary alkalboranes.[1] Alkylaromatic isomerizations can be made highly selective through the greater thermodynamic stability of the tertiary carbonium ion.[2]

It has apparently not been recognized that cyclic conjugated and homoconjugated topologies allow extending this strategy to the *reversible charge control* of a desired carbon skeleton.[3] In detail, such control would (a) select anionic conditions to transform a derivative of one structural isomer, more stable as the cation (AX in Scheme I), into a derivative of the second (BY), more stable as the anion. Then (b) it would select cationic conditions to achieve the reverse transformation. **1A** ⇌ **1B** provides a (still incompletely realized)[4] pericyclic example.

Scheme I



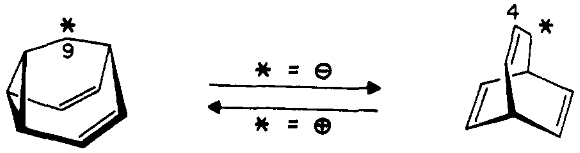


1A

1B

Two further experimental criteria protect this strategy from mechanistic and theoretical distraction: (c) AX must retain its structural integrity under cationic conditions and (d) BY must do the same under anionic ones. No experimental system that we know has yet satisfied all four criteria.

Previous studies of the 9-barbaralyl (**2A**) ⇌ 4-bicyclo[3.2.2]nonatrienyl (**2B**) transformations did, however, satisfy three. (b) Aqueous acetone hydrolysis of 4-bicyclo[3.2.2]nonatrienyl *p*-nitrobenzoate[5a] or 3,5-dinitrobenzoate[5b] provides 9-barbaralol as the exclusive alcohol product. (c) 9-Barbaralyl tosylate also provides no other alcohol under similar conditions.[5c] (d) Potassium *tert*-butoxide catalyzed hydrogen exchange of bicyclo[3.2.2]nonatriene proceeds without rearrangement.[5a,d] So too does Na/K transformation of 4-methoxybicyclo[3.2.2]nonatriene to the anion followed by methanol[5a] or *tert*-butyl alcohol[5d] protonation.



2A

2B

We here complete the last formal requirement by reporting the first unambiguous synthesis of 9-halobarbara-