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Isolation and Characterization of a Reversible Dimeric Paramagnetic Cobalt–Dioxygen Complex from a High Spin Cobalt(II) Precursor

R. H. NISWANDER and L. T. TAYLOR

Department of Chemistry, Virginia Polytechnic Institute and State University, Blacksburg, Virginia 24061, U.S.A.

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In two recent communications,[1,2] considerable attention has been given to the reaction of dioxygen with the *high spin* 5-coordinate cobalt(II) complexes Co(SALDPT) and Co(SALMeDPT).[3] The two reports were concerned with 1:1 dioxygen adducts, but no complexes were isolated in either case. Characterization of the 1:1 adducts was accomplished via esr and nmr spectroscopy below –50 °C. Prior to these studies the isolation of a compound from THF surmised to be Co(SALDPT)O_2 was reported;[4] however, this irreversible oxygenated compound was not subjected to extensive characterization.

We would like to report the isolation and characterization of a reversible dioxygen adduct of Co(SALMeDPT). This compound, produced by bubbling oxygen through a filtered benzene solution of gold colored Co(SALMeDPT), is a black crystalline material which we formulate as $[Co(SALMeDPT)]_2O_2 \cdot 2C_6H_6$. The repeatedly consistent analyses from two different analytical laboratories (calcd: C, 64.28; H, 6.15; N, 8.33; Co, 11.71. Found: C, 64.11; H, 6.27; N, 8.33; Co, 11.80) are supported by thermogravimetric weight loss data at 50 °C (weight loss observed: 18.0%; weight loss calculated for removal of mass equivalent to one O_2 and two C_6H_6 per dimer: 18.65%). This loss in weight is accompanied by a color change from black to gold. An elemental analysis and a magnetic moment of the recovered gold colored material is that of Co(SALMeDPT). Deoxygenated species can be repeatedly oxygenated–deoxygenated with very little loss of compound due to irreversible oxidation. Volumetric O_2 uptake experiments in solution as a function of pressure further support the 2:1 stoichiometry (n_{O_2}/n_{Co} found: 0.34 at 750 torr; 0.49 at 810 torr). Infrared analysis of the oxygen complex via Nujol mull and KBr pellet techniques showed only one additional band in comparison with the precursor corresponding to the benzene solvate. No vibrational modes involving O_2 were observed; however, the compound readily deoxygenated upon crushing. Attempts to observe a laser Raman spectrum of the compound resulted in sample decomposition. Mass spectral analysis of the oxygen complex also resulted in its decomposition producing peaks corresponding to oxygen, benzene, and Co(SALMeDPT).

It is interesting to compare $[Co(SALMeDPT)]_2O_2 \cdot 2C_6H_6$ with a similarly formulated, closely related oxygen complex, $[Co(SALDPT)]_2O_2 \cdot C_6H_5CH_3$.[5] The latter compound is a fairly stable μ-peroxo dimer which loses both oxygen and solvate upon heating to 110 °C *in vacuo.*[6] $[Co(SALMeDPT)]_2O_2 \cdot 2C_6H_5$, on the other hand, loses both oxygen and benzene within 48 hours after placing the compound *in vacuo* (10^{-1}–10^{-2} torr) at room temperature. Heating the compound results in rapid deoxygenation. The volume of oxygen given off, corrected for benzene, corresponds again to a 2:1 adduct (n_{O_2}/n_{Co} found = 0.50). The compound also vigorously evolves O_2 when placed in several non-coordinating organic solvents. $[Co(SALDPT)]_2O_2 \cdot C_6H_5CH_3$, however, is relatively stable in the same organic solvents. If $[Co(SALMeDPT)]_2O_2 \cdot C_6H_6$ is placed in deoxygenated toluene–methylene chloride, an esr spectrum is observed which is that of the previously reported 1:1 adduct plus Co(SALMeDPT). These observations can be rationalized in terms of the following equilibria:

$$[Co(SALMeDPT)]_2O_2 \cdot 2C_6H_6 \rightleftharpoons Co(SALMeDPT)O_2 + Co(SALMeDPT)$$

$$Co(SALMeDPT)O_2 \rightleftharpoons Co(SALMeDPT) + O_2$$

One striking difference between $[Co(SALDPT)]_2O_2 \cdot C_6H_5CH_3$ and $[Co(SALMeDPT)]_2O_2 \cdot 2C_6H_6$ is in their magnetic susceptibilities. The former is diamagnetic but the latter is paramagnetic with $\mu_{eff} = 3.26$ B.M. for each cobalt atom at 22 °C. Low temperature magnetic susceptibility measurements are consistent with those at room temperature. No spin pairing is observed down to 2.7 °K. After removing oxygen and benzene solvate, the magnetic moment increases to the value found for Co(SALMeDPT) ($\mu_{eff} = 4.20$ B.M.). The magnetic moment of the oxygen adduct also changes with time, increasing gradually over a period of several months. This, together with elemental analyses and a corresponding color change indicates that the complex is somewhat unstable even at room temperature and atmospheric pressure. The magnetic moment of 3.26 B.M. is that of freshly prepared samples. Only slight paramagnetism (< 0.8 B.M.) is observed in μ-peroxo complexes of Co(SALDPT) and its derivatives.[7] Models show that a dimeric oxygen complex of $[Co(SALMeDPT)]_2O_2 \cdot 2C_6H_6$ may not have the same solid state structure as these μ-peroxo compounds because of steric

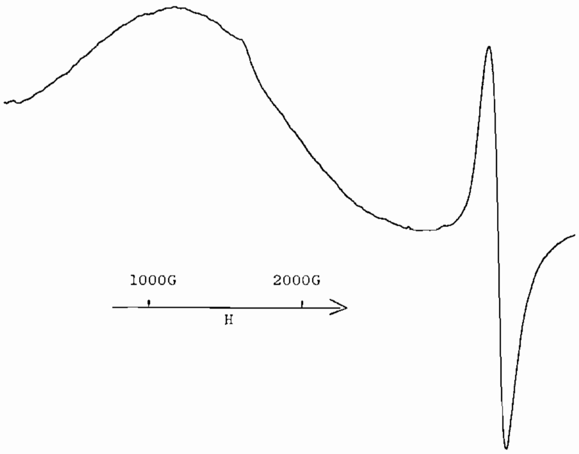

Figure 1. Esr spectrum of $[Co(SALMeDPT)]_2O_2 \cdot 2C_6H_6$; solid state at −140 °C.

crowding produced by the methyl groups. If this steric interaction were great enough, it could prevent dimerization of the type observed in $[Co(SALDPT)]_2O_2 \cdot C_6H_5CH_3$. The usual magnetic moment (4.62 B.M. per dimer) could be explained in terms of a superoxo compound which is associated, through the superoxo ligand, with a high spin cobalt(II) complex by a dipole–dipole interaction. Essentially, this could be thought of as a dimer with non-equivalent halves: $[(SALMeDPT)Co^{III}–O_2^-–––Co^{II}(SALMeDPT)]$.

Although the above explanation is only tentative until a structural analysis is completed, an esr spectrum of $[Co(SALMeDPT)]_2O_2 \cdot 2C_6H_6$ in the solid state can be interpreted in terms of a 1:1 adduct plus a high spin Co(II) species (see Fig. 1). A physical mixture of 1:1 adduct and unreacted Co(II) is ruled out based on the homogeneous quality of the repeatedly obtained crystalline material and its consistent analyses which indicate no deoxygenation before or soon after the magnetic measurements are made. Furthermore, low temperature magnetic data on the starting compound, Co(SALMeDPT), shows spin pairing starting to occur at 15 °K. No spin state change is observed in $[Co(SALMeDPT)]_2O_2 \cdot 2C_6H_6$ indicating that the high spin cobalt(II) compound is not present as a discrete complex. A dipolar interaction could perturb the system enough to prevent spin pairing. This further substantiates an associated species, however it must be realized that association could occur without involving the superoxo ligand.[8]

Since the major difference between the dimeric oxygen adduct of Co(SALDPT) and Co(SALMeDPT) is their magnetic susceptibility and reversibility, these physico-chemical properties may be related. Surprisingly, and again unlike Co(SALDPT), an oxygen adduct could not be isolated from any other solvent, including toluene. Attempts to isolate an oxygen complex with various derivatives (5-CH_3O, 3-CH_3O, 5-Cl, 5-NO_2) were unsuccessful even in benzene. However, all derivatives form 1:1 adducts with oxygen in solution as evidenced by their esr spectra. We also prepared Co(SALi-PropylDPT) and Co(SALi-ButylDPT) but no isolable adducts were obtained. These results suggest that perhaps additional factors are important other than the steric hindrance imposed by the methyl group. The ultimate interpretation of the bonding in $[Co(SALMeDPT)]_2O_2 \cdot 2C_6H_6$ will probably depend on the X-ray analysis. This work is currently in progress.

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