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Electrochemistry in Liquid Ammonia. 5. Electroreduction of Oxygen

FRANCISCO A. URIBE and ALLEN J. BARD*

The reduction of O_2 in liquid NH_3 at a Pt electrode has been investigated. Chemical and electrochemical measurements show that the first reduction of O_2 is a one-electron process producing $O_2^-\cdot$, which is a stable species in liquid NH_3 and precipitates as KO_2 in the presence of K^+. The solubility of O_2 in liquid NH_3 at temperatures between –60 and –40 °C was determined, and from these results, the diffusion coefficient of O_2 in liquid NH_3 was evaluated as 4.4×10^{-5} cm^2/s at –55 °C.

Introduction

The chemistry of the dioxygen species (e.g., O_2, $O_2^-\cdot$, O_2^{2-}, $HO_2\cdot$) and their roles in various processes such as corrosion, biological oxidation, and energy conversion has been the subject of many studies. Many electrochemical investigations of the reduction of oxygen in aqueous and nonaqueous solutions have also appeared. The electrochemical reduction of O_2 in a number of aprotic solvents such as *N,N*-dimethylformamide (DMF), MeCN, dimethyl sulfoxide (Me$_2$SO), and pyridine usually occurs with the formation of the stable superoxide ion, $O_2^-\cdot$; further reduction leads to production of O_2^{2-}, which reacts so rapidly with the solvent, electrolyte, or residual impurities (e.g., H_2O) that a reverse (anodic) voltammetric wave for O_2^{2-} oxidation is not observed.[1-4] However, the electrochemical behavior of O_2 in liquid ammonia has not been the subject of many studies. Until a very recent gas chromatographic determination,[5] even the solubility of O_2 in the liquid NH_3 had not been reported. In an early dc polarographic study of O_2 in NH_3 at a dropping-mercury electrode, rather distorted waves were obtained and no evidence of stepwise reduction of O_2 via superoxide was found.[6]

We describe here the electrochemical behavior of O_2 in liquid NH_3 and discuss the electrochemical synthesis of superoxide salts.[7] Moreover, because of the low impurity levels and acidity of NH_3, evidence for the intermediacy of the O_2^{2-} species could be obtained. Finally, we have determined solubility and diffusion coefficient data for O_2 in this medium.

Experimental Section

Chemicals. The ammonia used was Matheson (Anhydrous Grade, 99.99%); its handling and purification have been described previously.[8,9] Oxygen, obtained from Big Three Industries, Inc., was purified and dried by passing it through a 60-cm column containing (successively) soda lime and magnesium perchlorate to remove carbon dioxide and water, respectively. A mass spectrum of this purified oxygen showed only significant impurity peaks corresponding to nitrogen. Cyclic voltammograms found with this oxygen in liquid ammonia were identical with those obtained when pure oxygen from the thermal decomposition of potassium permanganate was used.[10] KI (Aldrich

Table I. Cyclic Voltammetric Results for the Reduction of O_2 $O_2^-\cdot$ at a Pt Electrode in Liquid Ammonia at $-50 \,^\circ C^a$

scan rate, V/s	$i_{pc}/v^{1/2}$, μA s$^{1/2}$ V$^{-1/2}$	$i_{pa}/i_{pc}{}^d$	$\Delta E_p,{}^b$ mV	$10^3 k^\circ,{}^c$ cm/s
0.020	57	1.21	123	2.2
0.050	49	1.30	158	2.1
0.100	42	1.32	197	1.8
0.200	42	1.35	213	2.0
0.500	39	1.33	308	0.9
1.00	37	1.35	360	0.6

^{a} Saturated (<0.025 M) MeBu$_3$NI. ^{b} $E_{pa} - E_{pc}$. ^{c} Standard heterogeneous rate constant with the assumption of a quasireversible electron-transfer reaction.[16] ^{d} The base line for determining i_{pa} was estimated by assuming diffusional decay of the cathodic current beyond the peak potential.

Chemical Co., 99.999%), KBr (MCB, reagent grade), and methyltri-*n*-butylammonium iodide (MeBu$_3$NI; Southwestern Analytical Chemical, Inc., polarographic grade) were used as supporting electrolytes and were dried at 110 °C for at least 24 h before each experiment.

Cell and Electrodes. The three-compartment electrochemical cell was similar to the one described previously.[9] The working electrode for cyclic voltammetry and potential step experiments was a platinum disk sealed in soft glass. The Pt was polished with an alumina slurry (0.3-μm particle size) on a felt cloth, rinsed with deionized water and then with ethanol, and finally wiped with an absorbent tissue. In one experiment, a glassy carbon disk sealed in Teflon and pretreated in the same manner as the Pt disk was used. For coulometry, a Pt gauze ∼6 cm × 2 cm was used as a working electrode. This was soaked in warm 6 M HNO_3 for ∼10 min and then rinsed in the same manner as the disk electrodes. The reference electrode was a silver wire inserted into a glass tube containing supporting electrolyte and was separated from the test solution by a fine-porosity sintered-glass disk (AgRE). This electrode was pretreated by polishing it with an alumina slurry and then soaking it in concentrated HNO_3 for ∼10 s until the surface appeared white. Finally, it was rinsed successively with deionized water and ethanol and then wiped with an absorbent tissue. This pretreatment resulted in a stable potential of the reference electrode for at least 6 h. A cylindrical piece of reticulated vitreous carbon (0.6-cm diameter × 2.5 cm) was used as a counterelectrode for bulk electrolysis. Before insertion into the cell, it was allowed to stand in ethanol for 24 h and then dried at 110 °C for 2 h.

All electrochemical experiments were performed with a Princeton Applied Research (PAR) Model 173 potentiostat–galvanostat and a Model 179 digital coulometer–current to voltage converter equipped with positive feedback *IR* compensation. A PAR Model 175 universal programmer provided the desired potential or current programs. For scan rates up to 200 mV/s, a Houston Instrument Model 2000 X-Y recorder was used. For higher scan rates and other data acquisition, a Norland Model 3001 digital oscilloscope was employed.

Preparation of KO_2 and Controlled-Potential Coulometry (CPC). Potassium superoxide, which is insoluble in liquid NH_3, was prepared by controlled-potential coulometry at –0.35 V vs. AgRE of a 0.2 M

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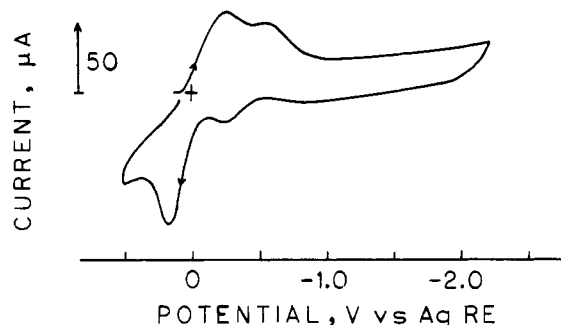
Figure 1. Cyclic voltammogram of O_2 (1 atm total pressure) in liquid $NH_3/0.1$ M KI (-55 °C) (scan rate 200 mV/s; Pt disk working electrode (0.039 cm²)).
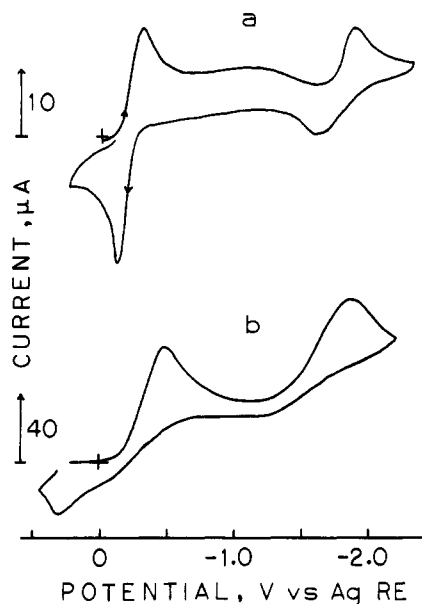
Table II. Controlled-Potential Coulometric Results of Reduction of O_2 and Reoxidation of $O_2^-\cdot$ in Liquid NH_3 at -55 °C

Q_f,[a] C	Q_b,[b] C	$|Q_b/Q_f|$	t,[c] min
	0.2 M KBr[d]		
-2.21	2.21	1.00	1
-5.00	4.93	0.986	1
-5.01	4.94	0.986	10
-7.00	6.92	0.989	15
-10.00	9.69	0.969	30
	Saturated MeBu₃NI		
-1.23	1.23	1.00	2
-2.50	2.41	0.964	15
-5.00	4.69	0.938	60

[a] Number of coulombs for reducing O_2 at $E = -0.35$ V. [b] Number of coulombs for oxidizing $O_2^-\cdot$ at $E = +0.25$ V. [c] Time elapsed between the end of the reduction and the beginning of the oxidation. [d] Q_b was obtained by reoxidation of a suspended KO_2 precipitate, under constant stirring.
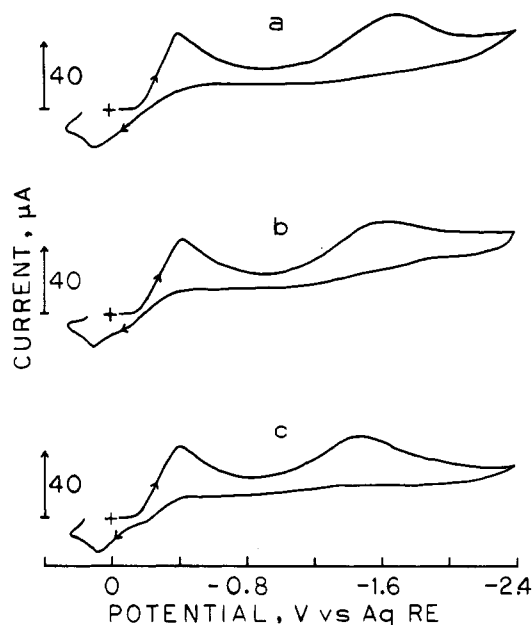

Figure 2. Cyclic voltammograms of O_2 (1 atm total pressure) in liquid NH_3 saturated with MeBu₃NI (-55 °C): (a) at Pt disk electrode (0.039 cm²), 50 mV/s; (b) at glassy carbon electrode (0.071 cm²), 200 mV/s.

Figure 3. Cyclic voltammograms of O_2 (1 atm total pressure) in liquid NH_3 saturated with MeBu₃NI (-52 °C). The solutions contained H_2O: (a) 0.28 M; (b) 0.56 M; (c) 1.12 M (glassy carbon electrode; scan rate 100 mV/s).

KBr/liquid NH_3 solution, with constant bubbling of gaseous O_2 into the solution. After 80 C (0.83 mmol KO_2) had passed, the electrolysis was stopped and the solvent was allowed to evaporate. The remaining mixture of KBr and KO_2 was dried in the cell at room temperature under vacuum for 24 h. The potassium superoxide was determined by the decomposition of KO_2 to gaseous O_2 by the action of acetic acid in diethyl phthalate.[11] A 20.0-mL sample of a mixture of these compounds was injected into the cell through the rubber septum via a syringe. After the reaction, 10.2 ± 0.2 mL of gaseous O_2 was recovered (25.0 °C, 751.8 mmHg, ~0.41 mmol of O_2).

Results and Discussion

Cyclic Voltammetry. Tetraalkylammonium Electrolyte. Cyclic voltammetry (CV) of O_2 in NH_3 yields different voltammograms, which depend on the nature of the supporting electrolyte cation (K^+ or MeBu₃N⁺; Figures 1 and 2). With MeBu₃NI, two well-separated reduction waves were observed. The first wave is quite similar to the one obtained in other aprotic solvents[1–4,12,13] and represents a quasi-reversible one-electron reduction to superoxide ion, eq 1. Typical CV data

$$O_2 + e^- \rightarrow O_2^-\cdot \qquad (1)$$

are given in Table I. Controlled-potential coulometric (CPC) reduction of a solution (saturated MeBu₃NI) and subsequent reoxidation (reversal coulometry) show that the $O_2^-\cdot$ is stable

for at least 1 h (Table II). In MeBu₃NI a second CV wave at ~-1.8 V vs. AgRE appears. This second reduction step for O_2 has been attributed to formation of peroxide anion, eq 2, and is irreversible in other aprotic solvents because of the

$$O_2^-\cdot + e^- \rightarrow O_2^{2-} \qquad (2)$$
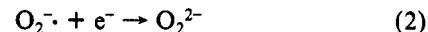
reaction of O_2^{2-} with the solvent, electrolyte, or impurities. However, in NH_3 at a Pt electrode this reduction shows some degree of reversibility, probably because NH_3 can be more highly purified than other aprotic solvents, the temperature is low, and NH_3 is a very weak acid. When crystals of NH_4Cl are dissolved in the solution, the second wave becomes totally irreversible. The nature of the electrode, however, also plays some role in the reversibility of this wave, because at a glassy carbon electrode this wave shows no reversibility (Figure 2b). This can probably be attributed to reaction of the O_2^{2-} with carbon. There are also differences between Pt and C in the nature of the current decay following the first wave. At a Pt electrode the current at potentials 300 mV beyond E_{pc} of the first wave does not show diffusion-controlled decay but rather a plateau suggestive of several small waves. These might be caused by some reaction of $O_2^-\cdot$ with the Pt surface or by a

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reaction of O_2^-· catalyzed by Pt. Reactions of O_2^-· with Pt also occur in other aprotic solvents.[14] At a glassy carbon electrode the current shows diffusion-controlled decay beyond the first peak potential. Even significant amounts of water do not appreciably affect the nature of the wave for electro-generation of O_2^-·. E_{pc} and i_{pc} for the first wave are almost the same, either in water-free solutions or in those containing various concentrations of water up to 1.12 M (Figure 3). However, the second reduction step is strongly affected; the wave becomes irreversible and shifts to more positive potentials with an increase in the water concentration. This suggests rapid reaction of O_2^{2-} (probably protonation and dispropor-tionation). An attempt to fit the CV results for the first reduction to a simple quasi-reversible one-electron-transfer reaction (Table I)[15] also suggests some reaction of O_2^-· with the Pt surface. Although ΔE_p, the separation of anodic and cathodic peak potentials, is a function of the scan rate, v, and the standard rate constant for the electron transfer, $k°$, evaluated from the variation of ΔE_p with v,[15] yields a constant value of $k°$ for v between 0.020 and 0.200 V/s of 2.0 × 10^{-3} cm/s, at larger v the apparent value of $k°$ decreases. Some of this might be attributed to increased, uncompensated iR drop for the larger currents at higher v; the resistance of NH_3 solutions with the more soluble tetraalkylammonium salt supporting electrolyte, $MeBu_3NI$, is still rather high, since a saturated solution has a concentration of less than 0.025 M. The ratio i_{pa}/i_{pc} is constant but slightly larger than 1. This may be caused by the difficulty in correcting for the decaying cathodic current base line in determining i_{pa} because of the current leveling shown in Figure 2a but might also involve some adsorption or precipitation of the reduced species, as happens to a larger extent with KI or KBr supporting elec-trolyte (see below). Moreover, $i_p/v^{1/2}$ shows some decrease with v, as is characteristic of a quasi-reversible reaction.

Cyclic Voltammetry. KBr or KI Electrolyte. When the supporting electrolyte contains K^+, the CV behavior is very different (Figure 1). The value of i_{pa}/i_{pc} for the first wave is large, a small peak follows the first wave, and the reduction peak at -1.8 V is absent. This can be attributed to the pre-cipitation of potassium superoxide, KO_2, which is highly in-soluble in NH_3. This is clearly demonstrated in coulometry experiments, where precipitation during the first reduction step is observed. That this is indeed KO_2 was demonstrated by collection of the precipitate and treatment of it with acetic acid to cause liberation of O_2 via the reaction

$$2KO_2 + 2HOAc \rightarrow 2KOAc + H_2O_2 + O_2 \qquad (3)$$

as described in the Experimental Section. The experimental number of faradays used in the reduction step and the number of moles of O_2 recovered by reaction 3 satisfied the predicted stoichiometric ratio of 2:1. If part of the current involved in the electrolysis had been used to generate a more highly re-duced species, the amount of $O_2(g)$ recovered would have been smaller because the decomposition with acetic acid occurs only with superoxides.[11]

Solubility of O_2 in Liquid NH_3. The determination of the diffusion coefficient for O_2 in NH_3 and evaluation of the CPC n_{app} values depend upon a knowledge of the concentration of O_2 in NH_3 at a given temperature and partial pressure of O_2. The solubility of O_2 in a number of aprotic solvents is avail-able,[16,17] but data for NH_3 under the conditions of these ex-periments are not available. Therefore, we determined the
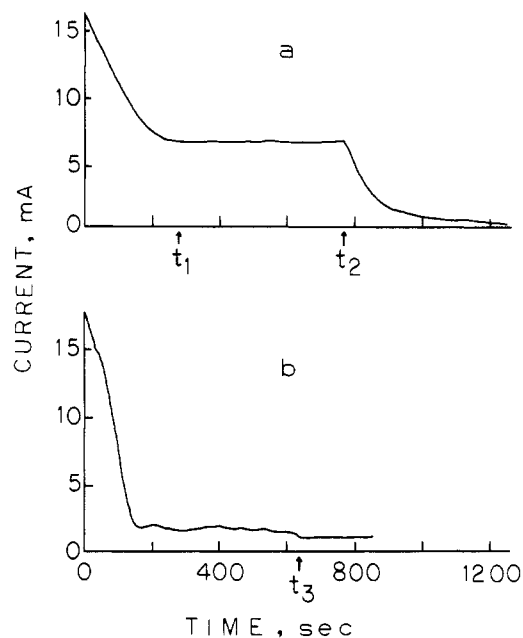
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Figure 4. Current–time curves for controlled-potential coulometry of O_2 in liquid $NH_3/0.2$ M KBr at -40 °C. The potential was set at -0.35 V vs. AgRE: (a) saturated oxygen solution (1 atm total pressure); (b) O_2 from gaseous phase swept out of the cell with N_2, before starting the coulometry.

solubility of O_2 at three temperatures by means of CPC of a stirred solution of O_2 in liquid ammonia (0.1 M KBr) initially at equilibrium with $O_2(g)$ (total pressure 1 atm). The current decreases to a stationary value, as shown by curve a of Figure 4. As soon as the electrochemical reduction started, dissolved O_2 was rapidly consumed by the reaction at the large surface area electrode. Oxygen in the gas phase then dissolved into the liquid. When the steady-state current, at time t_1, was reached, the current depended upon the rate at which gaseous O_2 dissolved into the liquid NH_3. The current dropped to near zero very quickly when the oxygen in the gaseous phase in the electrochemical cell was swept out with $N_2(g)$ (time t_2). Since the reduction of O_2 is a one-electron process, the number of coulombs recorded until time t_1 is slightly greater than the number of moles of O_2 in liquid NH_3 at equilibrium. The coulometry was repeated under the same conditions, except that, after the equilibration between the gaseous and liquid phases was attained, the O_2 in the gaseous phase was rapidly swept out of the cell with $N_2(g)$ and then the electrolysis was immediately started (curve b, Figure 4). At the beginning, the current–time curves are similar for both experiments, indicating that the rate of loss of O_2 from solution into the gas phase does not change significantly the initial concentration of O_2 in solution. In this experiment, however, the current dropped almost to zero (indicated by t_3 in curve b, Figure 4). The O_2 that was being reduced was no longer replaced by dissolution from the gas phase. The number of coulombs recorded up to t_3 should be slightly smaller than the actual number of moles of dissolved O_2 at equilibrium. Therefore the amount of O_2 dissolved in liquid ammonia must correspond to an extent of electrolysis represented by a number between the number of coulombs recorded to t_1 and those registered to t_3. These two values differ by about 10% as shown in Table III. Recently the determination of the O_2 in the liquid NH_3 at various pressures by gas chromatography has been reported.[5] Although values at temperatures lower than 253 K were not given, the enthalpy of solution estimated from these results allowed us to estimate the solubility between 213 and 233 K, corresponding to the range of our own data. The experimental values determined electrochemically are 25–40% smaller than

Table III. Controlled-Potential Coulometric Determination of Solubility of O_2 in Liquid NH_3 (0.1 M KBr)

temp, °C	Q_a,[a] C	Q_b,[b] C	concn,[c] mol/L	solubility,[d] mol/L
−60	−7.20	−6.20	0.0034	0.0045
−50	−5.20	−4.75	0.0022	0.0038
−40	−2.88	−2.54	0.0012	0.0039

[a] Number of coulombs recorded until current dropped to a constant value, with O_2 in the gas phase. [b] Q without O_2 in the gas phase. [c] 1 atm total pressure ($O_2 + NH_3$). [d] 1 atm O_2 partial pressure.
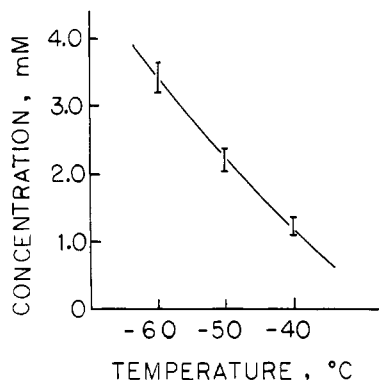
Figure 5. Concentration of O_2 in liquid NH_3 (M) vs. temperature (1 atm total pressure).

those calculated from data given by Ahrens and Heusler.[5] These differences are not too large in light of the uncertainty of the enthalpy of solution and the uncertainties of our experimental determination.

Diffusion Coefficient of O_2. Potential step chronoamperometry was employed to determine the diffusion coefficient, D,

for O_2 in NH_3 at −55 °C.[18] A potential step from +0.10 to −0.35 V vs. AgRE for 5 s was employed and the slope of the plot of i vs. $t^{-1/2}$ was determined to be 14.1 ± 0.7 μA $s^{-1/2}$. From the known area of the electrode (0.0145 cm²) and the solution concentration determined from the coulometric measurements (2.7 mM) a value of D in saturated $MeBu_3NI$ of 4.4×10^{-5} cm²/s was obtained. This value is generally of the order of that expected on the basis of diffusion coefficients found in other nonaqueous solvents[2,4a,16] when account is taken of the low viscosity of NH_3 (0.317 cP at −50 °C).[19] The diffusion coefficient estimated from the Stokes–Einstein equation[20] with a radius for O_2 of 1.4 Å and T = 223 K is 3.6×10^{-5} cm²/s.

Conclusions

The results presented here suggest that the electroreduction of O_2 in liquid ammonia provides a convenient procedure for preparing stable solutions or precipitates of O_2^-. Liquid ammonia may also be a useful solvent for carrying out and studying reactions of O_2^-, since NH_3 is a good solvent for both organic and inorganic compounds, provides a very low proton availability, and has a wide low-temperature liquid range. Studies of reactions of O_2^{2-} may also be possible since this species shows some stability in this medium.

Registry No. O_2, 7782-44-7; NH_3, 7664-41-7; KO_2, 12030-88-5.

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Effect of Two Ligands on Ternary Complex Stability

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The formation constants for the complexes of the type [CuAL], where A = 2,2′-bipyridyl, 1,10-phenanthroline, 2-(2-pyridyl)benzimidazole, or 2-(2-pyridyl)imidazoline and L = ethylenediamine, 1,2-diaminopropane, N-methylethylenediamine, N-ethylethylenediamine, glycine, α-alanine, or malonate, have been determined in dioxane–water (1:1 v/v) solutions and 0.2 mol dm⁻³ $NaClO_4$ at 30 °C. The formation constant values have been determined by a graphical method and further refined by using a computer program. The value of $\Delta \log K = \log K^{MA}_{MAL} - \log K^{M}_{ML}$ is small negative or positive showing astatisticality, and an increase in the value of mixed-ligand complexes is due to a lowering in repulsion between metal $d\pi$ electrons and the ligand electrons in the mixed-ligand complex.

Introduction

In the study of mixed-ligand complexes of the type [MAL], where A is a heteroaromatic N base, it has been observed that the stability constant of the ternary complex is higher than expected from statistical consideration.[1,2] This has been explained to be due to a M → bpy π interaction.[3–6] Sigel has

shown that the complex [MA] shows discrimination toward secondary ligands L with coordinating atoms N–N, N–O⁻, and O⁻–O⁻.[7,8] In cases of ternary complexes in which L coordinates through two nitrogen atoms or one nitrogen and one oxygen atom, $\Delta \log K = \log K^{MA}_{MAL} - \log K^{M}_{ML}$ is a small negative quantity. However, when L coordinates through two oxygen atoms, $\Delta \log K$ in [CuAL] complexes is positive. Sigel extended this observation to explain the greater stability of mixed-ligand complexes in biological systems involving the imidazole ring.[9,10] However, in a recent publication Abbott

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