Quantitative Evaluation of Lewis Acidity of Metal Ions Derived from the *g* Values of ESR Spectra of Superoxide: Metal Ion Complexes in Relation to the Promoting Effects in Electron Transfer Reactions

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Abstract: The *g* values of ESR spectra of superoxide – metal ion complexes ($O_2^{\bullet -}$ – M^{n+}, $n = 1, 2, 3$) are determined in acetonitrile at 143 K. The binding energies (ΔE) of metal ions with $O_2^{\bullet -}$ have been evaluated from deviation of the g_{zz} values from the free spin value. The ΔE values are well correlated with the catalytic reactivities of metal ions in electron transfer from cobalt(II) tetraphenylporphyrin to O_2 and *p*-benzoquinone, which does not occur in the absence of metal ions under otherwise the same experimental conditions. The ΔE values can thereby be used as the first quantitative measure for Lewis acidity of metal ions in relation with the catalytic reactivities in electron transfer reactions.

Keywords: electron transfer · EPR spectroscopy · Lewis acids · metal ions · superoxide ion

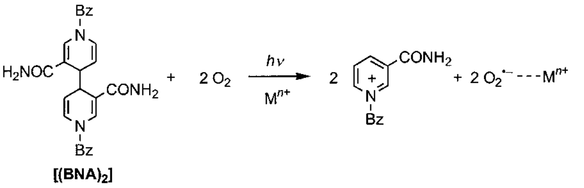
Introduction

Metal ions acting as Lewis acids has played a pivotal role in promoting various reactions of synthetic value because of the high reactivities and selectivities achieved under the mild reaction conditions.[1, 2] The Lewis acid promoted reactions are believed to proceed through the coordination of a Lewis acid to a lone pair of heteroatoms, such as oxygen of carbonyl compounds and a nitrogen atom of imines.[1, 2] The coordination of a Lewis acid to π-electrons of C–C multiple bonds has also been reported to be effective for the regio- and chemoselective reduction of aldehydes with an alkynyl group.[3] Metal ions and the salts acting as Lewis acids can also promote free radical reactions[4, 5] and electron transfer reactions.[6, 7] The promoting effects of metal ions are certainly related to the Lewis acidity of metal ion salts. Charges and ion radii are important factors to determine the Lewis acidity of metal ions. To the best of our knowledge, however, there has so far been no *quantitative* experimental measure to determine the Lewis acidity of a wide variety of metal ions in relation with the promoting effects, although limited number of formation constants for metal ion complexes with substrates are known.

We report herein that the g_{zz} values of ESR spectra of superoxide – metal ion complexes are highly sensitive to the Lewis acidity of a variety of metal ions and that the binding energies readily derived from the g_{zz} values provide the first quantitative experimental measure of Lewis acidity of a wide variety of metal ions, which are shown to be directly correlated to the promoting effects in electron transfer reactions.

Results and Discussion

Superoxide ion is formed by the photoinduced reduction of O_2 by the dimeric 1-benzyl-1,4-dihydronicotinamide [$(BNA)_2$] in acetonitrile (MeCN),[8] which can act as a unique two electron donor,[9] as shown in Equation (1).



(1)

When an oxygen-saturated MeCN solution containing $(BNA)_2$ (1.0×10^{-4} M) was irradiated with a high pressure mercury lamp, $O_2^{\bullet -}$ formed photochemically is detected by the ESR spectrum in frozen MeCN at 143 K. The ESR spectrum shows a typical anisotropic signal with $g_{\parallel} = 2.090$ and $g_{\perp} = 2.005$.[10] The ESR spectra of $O_2^{\bullet -}$ produced in the presence of a variety of closed shell metal ions were also measured at 143 K and the g_{zz} values are listed in Table 1.[11] The anisotropic ESR signals are changed significantly in the presence of each metal ion as compared to that in its absence.

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In particular, the g_{zz} values of $O_2^{\bullet -}$ in the presence of metal ions become significantly smaller than the value of $O_2^{\bullet -}$ due to the complexation of metal ions with $O_2^{\bullet -}$ ($O_2^{\bullet -}-M^{n+}$, $n=1-3$). Figure 1 shows typical examples of ESR spectra of $M^{2+}-O_2^{\bullet -}$ complexes ($M^{2+}=Mg^{2+}$, Ca^{2+}, Sr^{2+} and Ba^{2+}) measured in frozen MeCN at 143 K. The g_{zz} values of a series of metal ion–$O_2^{\bullet -}$ complexes are listed in Table 1.

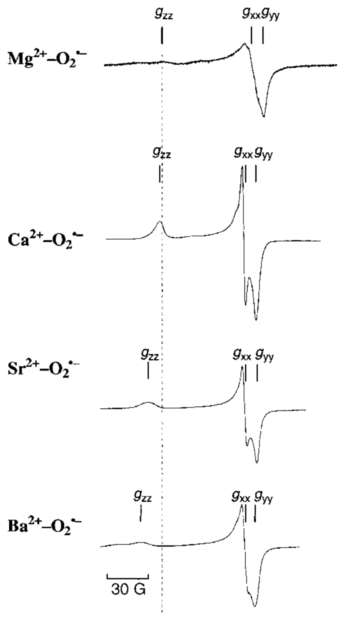


Figure 1. ESR spectra of $M^{2+}-O_2^{\bullet -}$ complexes ($M^{2+}=Mg^{2+}$, Ca^{2+}, Sr^{2+} and Ba^{2+}) in frozen MeCN at 143 K.

Table 1. g_{zz} Values of ESR spectra of $O_2^{\bullet -}-M^{n+}$, rate constants (k_{et}) for M^{n+}-promoted electron transfer from (TPP)Co to O_2 and *p*-benzoquinone (Q) and ionic radii (*r*) of M^{n+}.

M^{n+}	r/Å	g_{zz}	ΔE/eV	O_2	Q
				k_{et}/M^{-2} s^{-1}	
free	–	2.0900	0.32	[b]	[b]
Li^{+}[c]	0.92	2.0546	0.53	3.6×10^{-1}	1.6×10^{-1}
Na^{+}[c]	1.18	2.0841	0.34	[b]	[b]
Mg^{2+}[c]	0.89	2.0451	0.65	1.3×10	3.3
Ca^{2+}[c]	1.12	2.0499	0.58	1.1	7.0×10^{-1}
Sr^{2+}[c]	1.26	2.0558	0.52	1.0×10^{-1}	1.6×10^{-1}
Ba^{2+}[c]	1.42	2.0587	0.49	5.1×10^{-2}	3.0×10^{-2}
Sc^{3+}[d]	0.81	2.0304	1.00	1.9×10^{6}	2.7×10^{5}
Y^{3+}[d]	1.02	2.0349	0.85	1.2×10^{4}	2.7×10^{4}
La^{3+}[d]	1.16	2.0365	0.82	3.0×10^{3}	1.9×10^{3}
Eu^{3+}[d]	1.25	2.0362	0.82	7.0×10^{2}	1.1×10^{3}
Yb^{3+}[d]	1.14	2.0357	0.83	8.2×10^{2}	1.2×10^{3}
Lu^{3+}[d]	0.98	2.0358	0.83	1.1×10^{3}	8.2×10^{2}

[a] Effective ionic radii (coordination number = 8).[16] [b] No reaction or too slow to be determined accurately. [c] ClO_4^- salt. [d] $CF_3OSO_3^-$ salt.

The *g* tensor and in particular the g_{zz} value gives valuable information concerning the binding strength of $O_2^{\bullet -}-M^{n+}$. The deviation of the g_{zz} value from the free spin value ($g_e=2.0023$) is caused by the spin-orbit interaction as given by Equation (2):[12]

$$g_{zz}=g_e+2\sqrt{\frac{\lambda^2}{\lambda^2+\Delta E^2}} \tag{2}$$

where λ is the spin-orbit coupling constant of oxygen which is known as 0.014 eV,[13] and ΔE is the energy splitting of π_g levels due to the complex formation between $O_2^{\bullet -}$ and M^{n+}. Under the conditions that $\Delta E \gg \lambda$, [Eq. (2)] is reduced to a simple relation, $g_{zz}=g_e+2\lambda/\Delta E$. Thus, the ΔE values are readily determined from the deviation of the g_{zz} values from the g_e value as listed in Table 1.[14] It should be noted that the g_{zz} values can be determined quite accurately within experimental errors ±0.0001. The ΔE value increases generally with in order: monovalent cations (M^{+}) < divalent cations (M^{2+}) < trivalent cations (M^{3+}) except for Li^{+} which has the smallest ion radius.[15] The ΔE value also increases with decreasing the ion radius when the oxidation state of the metal ion is the same (Table 1). Thus, the ΔE value of a monovalent cation (Li^{+}) becomes larger than those of divalent cations (Ba^{2+} and Sr^{2+}) whose radii are significantly larger than that of Li^{+} (Table 1).[16] Scandium ion which has the smallest ion radius among the trivalent metal cations gives the largest ΔE value, and this indicates that the binding energy between Sc^{3+} and $O_2^{\bullet -}$ is the strongest. In the case of $O_2^{\bullet -}-Sc^{3+}$, an "end-on" coordination form of $^{\bullet}O{-}O^{-}-Sc^{3+}$ is indicated by the hyperfine splitting of two different ^{17}O atoms ($I=5/2$) in which the electron spin is more localized at the terminal oxygen (60 %).[8] This is confirmed by the DFT (density function theory) calculation using the spin-restricted B3LYP functional and the 6-311++G(3d,3p) basis set for the open shell $O_2^{\bullet -}-Sc^{3+}$, which gives more localized spin density at the terminal oxygen (65 %) (see Experimental Section).[17] The structures of $O_2^{\bullet -}$ and $O_2^{\bullet -}-M^{n+}$ ($M^{n+}=Li^{+}$, Mg^{2+}, and Sc^{3+} were also calculated. The O–O distance decreases in order: $O_2^{\bullet -}$ (1.343 Å) > $O_2^{\bullet -}-Li^{+}$ (1.309 Å) > $O_2^{\bullet -}-Mg^{2+}$ (1.297 Å) > $O_2^{\bullet -}-Sc^{3+}$ (1.211 Å) as the ΔE vlaue increases (Table 1).

Metal ions such as Mg^{2+} has been reported to promote electron transfer from (TPP)Co (TPP^{2-} = dianion of tetraphenylporphyrin) to *p*-benzoquinone, although no reaction between (TPP)Co and *p*-benzoquinone occurs in the absence of metal ions in MeCN.[7e] Such promoting effects of metal ions in electron transfer reduction of substrates have been ascribed to the binding of metal ions to the radical anions produced in the electron transfer reactions.[6] Thus, in order to assess a relation between the ΔE value and promoting effects of metal ions in electron transfer reduction of O_2, the rates of electron transfer from (TPP)Co to O_2 are determined in the presence of a series of metal ions (M^{n+}, $n=1-3$) by the UV/Vis spectral change for the decay of (TPP)Co ($\lambda_{max}=411$ nm) and the formation of $[(TPP)Co]^{+}$ ($\lambda_{max}=434$ nm) in MeCN at 298 K.

No electron transfer from (TPP)Co ($E^0_{ox}=0.35$ V versus SCE in MeCN)[18] to O_2 ($E^0_{red}=-0.86$ V versus SCE in MeCN)[19] has occurred in MeCN at 298 K. In the presence of M^{n+}, however, an efficient electron transfer from (TPP)Co to O_2 occurs to yield $[(TPP)Co]^{+}$ [Eq. (3)], as shown in Figure 2.

$$\mathrm{(TPP)Co} + O_2 \xrightarrow[k_{et}]{M^{n+}} [\mathrm{(TPP)Co}]^{+} + O_2^{\bullet -}{-}M^{n+} \tag{3}$$

The electron transfer rates obeyed second-order kinetics, showing a first-order dependence on the concentration of O_2 (Figure 3a). The observed second-order rate constant (k_{obs})

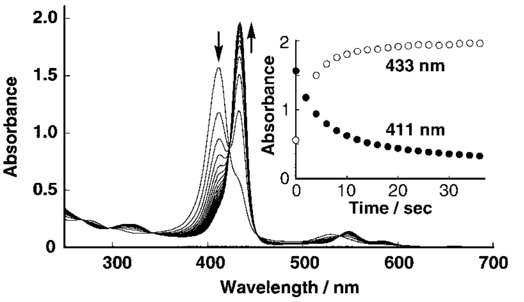


Figure 2. Electronic absorption spectra observed in electron transfer from (TPP)Co (1.0×10^{-5} M) to O_2 (air saturated, 2.6×10^{-3} M) in the presence of Sc^{3+} (1.7×10^{-5} M) in MeCN at 298 K.

for the M^{n+}-promoted electron transfer increases linearly with increasing the metal ion concentration (Figure 3b). The M^{n+}-promoted electron transfer rate constants (k_{et}) determined from the slope of the linear plot of k_{obs} versus $[M^{n+}]$ are also listed in Table 1.

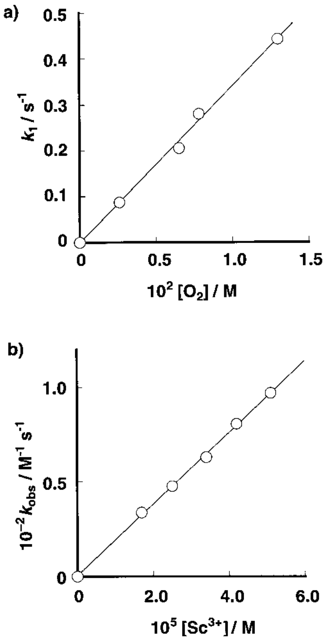


Figure 3. a) Plot of pseudo-first-order rate constants (k_1) versus $[O_2]$ in the presence of Sc^{3+} (1.7×10^{-5} M) in MeCN at 298 K. b) Plot of k_{obs} versus $[Sc^{3+}]$ in MeCN at 298 K.

There is a *striking* linear correlation between log k_{et} and ΔE of $O_2^{\bullet -}-M^{n+}$ derived from the g_{zz} values as shown in Figure 4. The remarkable correlation spans a range of almost 10^7 in the rate constant. The slope of the linear correlation between logk_{et} and ΔE is obtained as 14.0 which is close to the value of $1/2.3kT$ (= 16.9, where k is the Boltzmann constant and T = 298 K).[20] This means that the variation of ΔE is well reflected in the difference in the activation free energy for the M^{n+}-promoted electron transfer from (TPP)Co to O_2. The stronger the binding of M^{n+} with $O_2^{\bullet -}$, the larger will be the promoting effects of M^{n+}. Thus, ΔE can be regarded as good measure of the binding energies in the $O_2^{\bullet -}-M^{n+}$ complexes.

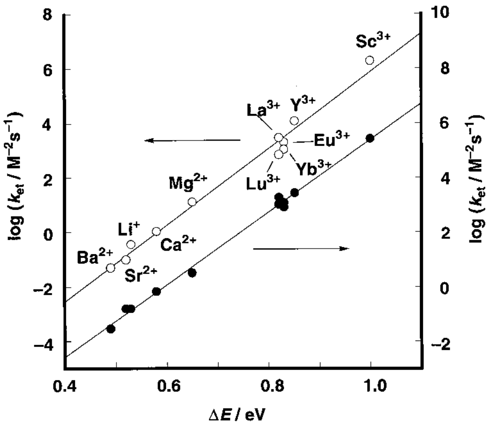
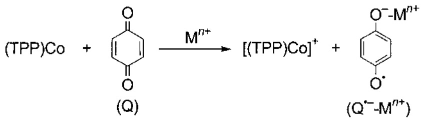


Figure 4. Plots of log k_{et} versus ΔE in M^{n+}-promoted electron transfer from (TPP)Co to O_2 (○) and p-benzoquinone(●).

The applicability of ΔE to predict the reactivities in M^{n+}-promoted electron transfer reactions is also examined in M^{n+}-promoted electron transfer from (TPP)Co to p-benzoquinone (Q) [Eq. (4)].



(4)

It should be noted that no electron transfer occurred from (TPP)Co to Q ($E^0_{red} = -0.51$ V versus SCE) in the absence of M^{n+}. The M^{n+}-promoted electron transfer rate constants (k_{et}) determined from the slopes of the linear plots of k_{obs} versus $[M^{n+}]$ for Q are also listed in Table 1. There is also an excellent linear correlation between log k_{et} and ΔE as shown in Figure 4 (closed circles). More importantly the slope (13.3) for Q (closed circles) is nearly the same as the slope (14.0) for O_2 (open circles). Such an agreement indicates that the ΔE values of $O_2^{\bullet -}-M^{n+}$ are parallel to those of $Q^{\bullet -}-M^{n+}$.

Conclusion

In summary, these results establish that the ΔE values of $O_2^{\bullet -}-M^{n+}$ readily derived from the g_{zz} values of the ESR spectra can be utilized as the first quantitative experimental measure to determine the Lewis acidity of metal ions in relation with the promoting effects in electron transfer reactions.[21]

Experimental Section

Materials: Cobalt(II) tetraphenylporphyrin, (TPP)Co, was prepared as described in the literature.[22] p-Benzoquinone was purchased from Tokyo Kasei Organic Chemicals, and purified by the standard methods.[23] The dimeric 1-benzyl-1,4-dihydronicotinamide [$(BNA)_2$] was prepared according to the literature.[24] Scandium triflate [$Sc(OTf)_3$] was purchased from Pacific Metals Co., Ltd. (Taiheiyo Kinzoku). Lanthanum triflate [$La(OTf)_3$] was obtained from Aldrich as hexahydrate form. Yttrium triflate [$Y(OTf)_3$], europium triflate [$Eu(OTf)_3$], ytterbium triflate [$Yb(OTf)_3$] and lutetium triflate [$Lu(OTf)_3$] were prepared as follows.[25] A deionized aqueous solution was mixed (1:1 v/v) with trifluoromethanesulfonic acid (>99.5%, 10.6 mL) obtained from Central Glass, Co., Ltd., Japan. The trifluoromethanesulfonic acid solution was slowly added to a flask which contained the corresponding metal oxide (>99.9%, 30 mmol).

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The mixture was refluxed at 100 °C for 3 d. After centrifugation of the reaction mixture, the solution containing the metal triflate was separated and water was removed by vacuum evaporation. Yttrium oxide, europium oxide, and ytterbium triflate were supplied by Shin Etsu Chemical, Co., Ltd., Japan. Lutetium oxide was supplied by Nichia Corporation, Japan. Metal triflates were dried under vacuum evacuation at 403 K for 40 h prior to use. Magnesium perchlorate [$Mg(ClO_4)_2$] and sodium perchlorate ($NaClO_4$) were obtained from Wako Pure Chemical Ind. Ltd., Japan. Calcium perchlorate [$Ca(ClO_4)_2$], strontium perchlorate [$Sr(ClO_4)_2$], barium perchlorate [$Ba(ClO_4)_2$], and lithium perchlorate ($LiClO_4$) were obtained from Nacalai Tesque, Japan. Acetonitrile (MeCN) used as solvent was purified and dried by the standard procedure.[23]

ESR measurements: A quartz ESR tube (4.5 mm ID) containing an oxygen-saturated MeCN solution of $(BNA)_2$ (1.0×10^{-4} M) and a metal ion (1.0×10^{-3} M) was irradiated in the cavity of the ESR spectrometer with the focused light of a 1000 W high-pressure Hg lamp through an aqueous filter. The ESR spectra of $O_2^{\bullet -}-M^{n+}$ in frozen MeCN were measured at 143 K with a JEOL X-band spectrometer (JES-RE1XE) using an attached VT (Variable Temperature) apparatus under nonsaturating microwave power conditions. The g values were calibrated precisely with a Mn^{2+} marker which was used as a reference.

Spectral and kinetic measurements: Kinetic measurements for electron transfer from (TPP)Co to oxygen and p-benzoquinone were carried out using a Hewlett–Packard 8453 photodiode array spectrophotometer or a Shimadzu UV-3100PC spectrophotometer at 298 K. The rates of the electron transfer were followed by spectrally monitoring an increase or decrease in absorbance due to $[(TPP)Co]^+$ or (TPP)Co. The rate constants of electron transfer (k_{et}) were determined by the pseudo-first-order plots for the electron transfer reactions in the presence of a large excess oxygen and metal ions. It was confirmed that the pseudo-first-order rate constant was proportional to the oxygen (or p-benzoquinone) and metal ion concentrations. The pseudo-first-order rate constants were determined by a least-squares curve fit using a Macintosh microcomputer. The pseudo-first-order plots were linear for three or more half-lives with the correlation coefficient $\rho > 0.999$. The k_{et} values in Table 1 were determined within an experimental error of ±5%.

Theoretical calculations: Density functional calculations were performed on a COMPAQ DS20E computer using the spin-restricted B3LYP functional for the open shell $O_2^{\bullet -}-M^{n+}$.[17] B3LYP geometries for $O_2^{\bullet -}-M^{n+}$ were determined using the 6-311++G(3d,3p) basis and the Gaussian 98 program.[26] The S^2 value was determined to range from 0.755 to 0.762 for $O_2^{\bullet -}$ and $O_2^{\bullet -}-M^{n+}$ ($M^{n+} = Li^+$, Mg^{2+} and Sc^{3+}), indicating a good representation of the doublet state.

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[1] a) H. Yamamoto, *Lewis Acid Chemistry: A Practical Approach*, Oxford University Press, Oxford, **1999**; b) *Selectivities in Lewis Acid Promoted Reactions* (Ed.: D. Schinzer), Kluwer, Dordrecht, The Netherlands, **1989**; c) M. Santelli, J.-M. Pons, *Lewis Acids and Selectivity in Organic Synthesis*, CRC Press, Boca Raton, FL, **1995**; d) M. T. Reetz, *Angew. Chem.* **1984**, *98*, 542–555; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 556–569.

[2] a) S. V. Kessar, P. Singh, *Chem. Rev.* **1997**, *97*, 721–737; b) R. Mahrwald, *Chem. Rev.* **1999**, *99*, 1095–1120.

[3] N. Asao, T. Asano, T. Ohishi, Y. Yamamoto, *J. Am. Chem. Soc.* **2000**, *122*, 4817–4818.

[4] a) P. Renaud, M. Gerster, *Angew. Chem.* **1998**, *110*, 2704–2722; *Angew. Chem. Int. Ed. Engl.* **1998**, *37*, 2562–2579; b) Y. Guindon, B. Guerin, J. Rancourt, C. Chabot, N. Mackintosh, W. W. Ogilvie, *Pure Appl. Chem.* **1996**, *68*, 89–96.

[5] a) C. L. Mero, N. A. Porter, *J. Am. Chem. Soc.* **1999**, *121*, 5155–5160; b) M. P. Sibi, J. Ji, J. B. Sausker, C. P. Jasperse, *J. Am. Chem. Soc.* **1999**, *121*, 7517–7526; c) M. P. Sibi, J. Ji, *Angew. Chem.* **1997**, *109*, 266–268; *Angew. Chem. Int. Ed. Engl.* **1997**, *36*, 274–276; d) Y. Yamamoto, S. Onuki, M. Yumoto, N. Asao, *J. Am. Chem. Soc.* **1994**, *116*, 421–422; e) J. H. Wu, R. Radinov, N. A. Porter, *J. Am. Chem. Soc.* **1995**, *117*, 11029–11030.

[6] a) S. Fukuzumi, *Adv. Electron Transfer Chem.* **1992**, *Vol. 2*, pp. 67–175; b) S. Fukuzumi, *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1–28; c) S. Fukuzumi, S. Itoh, *Advances in Photochemistry*, *Vol. 25* (Eds: D. C. Neckers, D. H. Volman, G. von Bünau), Wiley, New York, **1998**, pp. 107–172; d) S. Fukuzumi, *Electron Transfer in Chemistry*, *Vol. 5* (Ed.: V. Balzani), Wiley-VCH, Weinheim, **2000**, in press.

[7] a) H. Ohtsu, Y. Shimazaki, A. Odani, O. Yamauchi, W. Mori, S. Itoh, S. Fukuzumi, *J. Am. Chem. Soc.* **2000**, *122*, 5733–5741; b) S. Fukuzumi, T. Okamoto, J. Otera, *J. Am. Chem. Soc.* **1994**, *116*, 5503–5504; c) S. Fukuzumi, T. Okamoto, *J. Chem. Soc. Chem. Commun.* **1994**, 521–522; d) S. Fukuzumi, Y. Tokuda, Y. Chiba, L. Gereci, P. Carloni, E. Damiani, *J. Chem. Soc. Chem. Commun.* **1993**, 1575–1577; e) S. Fukuzumi, T. Okamoto, *J. Am. Chem. Soc.* **1993**, *115*, 11600–11601; f) S. Fukuzumi, S. Kuroda, T. Tanaka, *J. Am. Chem. Soc.* **1985**, *107*, 3020–3027.

[8] S. Fukuzumi, M. Patz, T. Suenobu, Y. Kuwahara, S. Itoh, *J. Am. Chem. Soc.* **1999**, *121*, 1605–1606.

[9] a) S. Fukuzumi, T. Suenobu, M. Patz, T. Hirasaka, S. Itoh, M. Fujitsuka, O. Ito, *J. Am. Chem. Soc.* **1998**, *120*, 8060–8068; b) M. Patz, Y. Kuwahara, T. Suenobu, S. Fukuzumi, *Chem. Lett.* **1997**, 567–568.

[10] R. N. Bagchi, A. M. Bond, F. Scholz, R. Stösser, *J. Am. Chem. Soc.* **1989**, *111*, 8270–8271.

[11] Since open shell metal ion complexes with $O_2^{\bullet -}$ are ESR silent, determination of ΔE values are limited to closed shell metal ions.

[12] a) W. Känzig, M. H. Cohen, *Phys. Rev. Lett.* **1959**, *3*, 509–510; b) H. R. Zeller, W. Kanzig, *Helv. Phys. Acta* **1967**, *40*, 845.

[13] P. H. Kasai, *J. Chem. Phys.* **1965**, *43*, 3322–3327.

[14] The ΔE values can also be derived from g_{xx}- and g_{yy} values.[12] However, the g_{zz} values are used to determine the ΔE values since they are the most sensitive to the ΔE values.

[15] The same trend has been reported for $O_2^{\bullet -}$ adsorbed on the surface of various metal oxides; see: a) J. H. Lunsford, *Catal. Rev.* **1973**, *8*, 135–157; b) M. Che, *Chem. Rev.* **1997**, *97*, 305–331.

[16] R. D. Shannon, *Acta Crystallogr.* **1976**, *A32*, 751.

[17] A. D. Becke, *J. Chem. Phys.* **1993**, *98*, 5648–5652.

[18] S. Fukuzumi, S. Mochizuki, T. Tanaka, *Inorg. Chem.* **1989**, *28*, 2459–2465.

[19] D. T. Sawyer, T. S. Calderwood, K. Yamaguchi, C. T. Angelis, *Inorg. Chem.* **1983**, *22*, 2577–2583.

[20] The value is obtained from $1/2.3kT = (1.602 \times 10^{-19}\,\mathrm{J})/[2.3(1.381 \times 10^{-23}\,\mathrm{J\,K^{-1}})(298\,\mathrm{K})] = 16.9$.

[21] The ΔE values may also be applied to predict the reactivities of metal ions in a variety of metal ion-promoted reactions, although more general applicability of the ΔE values has yet to be examined.

[22] A. D. Adler, F. R. Longo, V. Váradi, *Inorg. Synth.* **1976**, *16*, 213.

[23] D. D. Perrin, W. L. F. Armarego in *Purification of Laboratory Chemicals*, Butterworth-Heinemann, Oxford, **1988**.

[24] a) K. Wallenfels, M. Gellerich, *Chem. Ber.* **1959**, *92*, 1406; M. Patz, Y. Kuwahara, T. Suenobu, S. Fukuzumi, *Chem. Lett.* **1997**, 567–568.

[25] a) J. H. Forsberg, V. T. Spaziano, T. M. Balasubramanian, G. K. Liu, S. A. Kinsley, C. A. Duckworth, J. J. Poteruca, P. S. Brown, J. L. Miller, *J. Org. Chem.* **1987**, *52*, 1017–1021; b) S. Kobayashi, I. Hachiya, *J. Org. Chem.* **1994**, *59*, 3590–3596.

[26] *Gaussian 98* (*Revision A.7*), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, Jr., R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, A. G. Baboul, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, J. L. Andres, C. Gonzalez, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh PA, **1998**.

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