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An ESR Study of Monomeric Cobalt Oxygen Complexes in Solutions

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Several mononuclear cobalt oxygen complexes in solutions have been investigated by means of ESR measurements. When a pyridine (and also substituted pyridines, *N*,*N*-dimethylformamide, dimethyl sulfoxide, and hexamethylphosphoramide) solution of a bis-salicylaldehyde-imine cobalt(II) complex (*N*,*N*′-ethylene-bis(salicylideneiminato)cobalt(II), and *N*,*N*′-ethylene-bis(3-methoxysalicylideneiminato)cobalt(II)) was exposed to oxygen, there appeared a reversible ESR signal, in which a hf structure of eight lines caused by a mononuclear cobalt was observed. This spectrum could be analysed by considering the species to be essentially a superoxide cobalt(III). We tried to explain the deviations in the A_{Co} and the g values of the species from solvent to solvent by considering that the solvent coodinates to the cobalt complex in the *trans* position against the coodinated oxygen. As a comparative study, the mononuclear oxygen adduct of di(salicylal)-3,3′-diimino-di-*n*-propylamine-cobalt(II) was also studied in the above solvents.

Though cobalt complexes carrying molecular oxygen have long been known, most of these are 2 : 1 cobalt oxygen adducts. Only recently have several examples of 1 : 1 reversible O_2 adducts been reported;[1-8] these reports have kept pace with the study of the present authors, who have investigated the possibility of obtaining mononuclear cobalt oxygen complexes and the physico-chemical properties of the obtained complexes for the past several years. Some of these results have already been reported.[1-3]

In this paper, the authors wish to report an ESR study of mononuclear cobalt oxygen complexes which may exist equilibrially $(\mathrm{Co} \overset{O_2}{\rightleftharpoons} \mathrm{Co{-}O_2} \overset{\mathrm{Co}}{\rightleftharpoons} \mathrm{Co{-}O_2{-}Co})$ in some solutions. Several bis-salicylaldehyde-imine cobalt(II) complexes were dissolved in certain solvents under oxygen. The equilibrially-obtained mononuclear cobalt oxygen complexes were analysed by means of ESR measurements, though no reliable quantitative studies could be carried out because most of the solvents used were such as absorbed considerable microwave energies.

Results

The attempted complexes were *N*,*N*′-ethylene-bis(salicylideneiminato)cobalt(II) (Co(salen)), *N*,*N*′-ethylene-bis(3-methoxysalicylideneiminato) cobalt(II) (Co(3-MeOsalen)), bis(salicylaldimino)cobalt(II) (Co(sa)), and di(salicylal)-3,3′-diimino-di-*n*-propylamine-cobalt(II) (Co(salprtr)).

From the point of view of the solubility, Co(3-MeOsalen) was mainly investigated. When Co-(3-

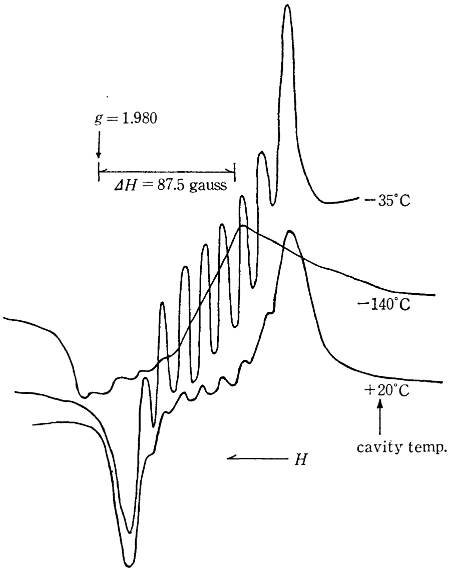

Fig. 1. ESR spectra of Co (3-MeOsalen) in pyridine under oxygen.
complex concn. $= 1.4 \times 10^{-2}$ mol/l
oxygen pressure = 1 atm

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[1] A. Misono, S. Koda and Y. Uchida, This Bulletin, **42**, 580 (1969).

[2] A. Misono, S. Koda and Y, Uchida, *ibid.*, **42**, 3470 (1969).

[3] A. Misono and S. Koda, This Bulletin, **42**, 3048 (1969).

[4] H. Kon and N. E. Sharpless, *Spectrosc. Lett.*, **1**, 49 (1968).

[5] J. H. Bayston, F. D. Looney and M. E. Winfield, *Aust. J. Chem.*, **16**, 557 (1963).

[6] J. H. Bayston, N. K. King, F. D. Looney and M. E. Winfield, *J. Amer. Chem. Soc.*, **91**, 2775 (1969).

[7] C. Floriani and F. Calderazzo, *J. Chem. Soc.*, *A*, **1969**, 946.

[8] A. L. Crumbliss and F. Basolo, *Science*, **164**, 1168 (1969).

MeOsalen) was dissolved in pyridine under nitrogen, a transparent red solution was obtained. The solution under nitrogen showed no ESR signal at room temperature.

When oxygen was added to the solution (oxygen was bubbled in or the nitrogen atmosphere above the solution was purged by pure oxygen), the red color of the solution under nitrogen was strengthened to some degree. The solution under oxygen showed an ESR signal which had an eight-line structure, as is shown in Fig. 1. The eight-line structure, all the lines of which had almost the same strength, could be considered to be caused by a certain interaction of a free spin with one cobalt nucleus, because the nuclear spin of ^{59}Co is 7/2. Spectra which were a little more resolved were observed at lower temperatures. When the solution was frozen, the spectrum changed to an anisotropic spectrum, but it was not so well resolved. This signal was observed to be rather stable. In fact, the strength of the signal did not decrease very much within several hours under oxygen at room temperature.

The ESR signal decreased when the solution was exposed to nitrogen, and increased again when the solution was again exposed to oxygen. The signal was suspected, therefore, to be due to a certain oxygen complex which was formed reversibly in the solution from oxygen and the cobalt complex.

Similar spectra could be observed in substituted pyridines, *N*,*N*-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and hexamethylphosphoramide (HMPT).

Table 1. ESR spectra of the complexes in several solvents under oxygen

Complex	Solvent (10^{-2} mol/*l*)	g_{sol}	A_{sol} (gauss)	Cavity temp. (°C)
Co(salen)	pyridine (2.3)	2.023	12.9	−37
Co(3-MeO-salen)	pyridine (1.4)	2.023	12.8	−35
	4-Mepyridine (1.7)	2.022*	13*	+20
	4-Etpyridine (1.7)	2.022	12.8	−10
	DMF (1.4)	2.028	17.0	−15
	DMSO (1.7)	2.028	17.3	+20
	HMPT (2.0)	2.022	19.0	+20
	toluene-PPh_3 (2.2, PPh_3/Co=17/1)	2.024	15.3	−35
Co(salprtr)	pyridine (1.6)	2.033	14.4	+20
	DMF (2.5)	2.033	14.4	+10
	HMPT (2.0)	2.030*	13.6*	+20

*: not well resolved, $P_{O_2}=1$ atm

The ESR characteristics are summarized in Table 1. The A_{sol} caused by a cobalt nucleus is the mean interval between two adjacent lines among the eight lines (observed in solutions). The best resolved isotropic spectra were observed in the neighborhood of the cavity temperature described in the table. Some observed results in mixed solvents are shown in Table 2. In these mixed solvents, similar spectra were observed.

Table 2. ESR spectra of Co(3-MeOsalen) in mixed (1/1 vol) solvents under oxygen

Solvent (10^{-2} mol/*l*)	g_{sol}	A_{sol} (gauss)	Cavity temp. (°C)
pyridine - DMF (0.9)	2.023	12.8	−10
pyridine - HMPT (2.2)	2.023	13.2	− 5
DMF - HMPT (1.6)	2.026	17.7	+ 7
cf.			
pyridine (1.4)	2.023	12.8	−35
DMF (1.4)	2.028	17.0	−15
HMPT (2.0)	2.022	19.0	+20

$P_{O_2}=1$ atm

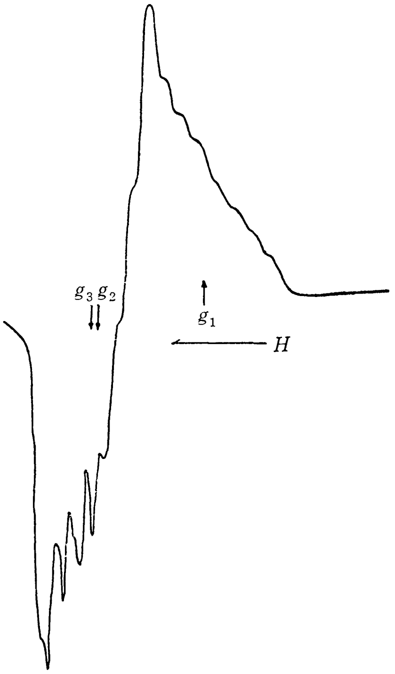

Fig. 2. Co(3-MeOsalen)–O_2 in frozen pyridine-HMPT (about −160°C).

$g_1=2.076$ $A_1=16.0$ gauss
$g_2=2.008$ $A_2=14.7$
$g_3=2.004$ $A_3=14.7$
cf. $g_{sol}=2.023$ $A_{sol}=13.2$

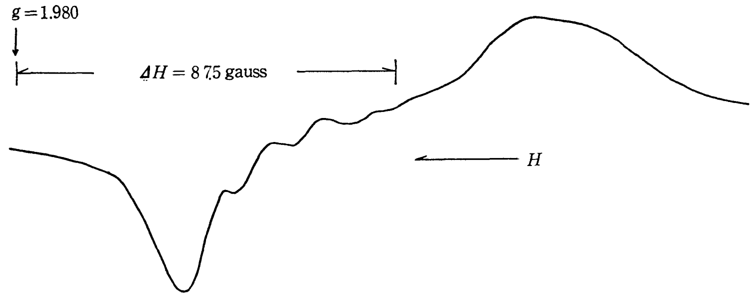

Fig. 3. ESR spectrum of Co(salprtr) in HMPT under oxygen (20°C). complex conc. $=2.0\times10^{-2}$ mol/l oxygen pressure = 1 atm

A rather well-resolved anisotropic ESR spectrum was observed for the species in a frozen mixed solvent of pyridine and HMPT (Fig. 2). The anisotropic g values and the corresponding A_{Co} values were roughly estimated, according to the method for randomly-orientated particles in a fixed position.[9]

The solution of Co(3-MeOsalen) in toluene (and benzene) showed no ESR signal under nitrogen; the situation was the same under oxygen at room temperature (the solubility of the complex in these solvents was not very large). When triphenylphosphine (PPh_3) was added to the solution (17 moles of PPh_3 *vs.* 1 mole of Co(3-MeOsalen)), however, a similar spectrum with an eight-line structure could be observed under oxygen.

Co(salen) behaved much like Co(3-MeOsalen) (investigated in a pyridine solution).

Kon *et al.*[4] have already reported on the ESR spectra of Co(salprtr) coordinated with oxygen in several solvents. The present authors investigated them in some other solvents (Fig. 3) in order to compare the spectra with those of Co(3-MeOsalen) (and Co(salen)) under oxygen. The signal shapes did not fully resemble those of Co(3-MeOsalen) under oxygen. This might well indicate the existence of some differences in geometrical structures and in electronic structures between the two kinds of cobalt mononuclear oxygen complexes.

When a red-colored solution of Co(sa) in pyridine was exposed to oxygen, the solution turned brown instantly. On the other hand, no ESR signal could be observed at room temperature several minutes after the exposure to oxygen. For comparison, it may be noted that no ESR spectra were observed when Co(3-MeOsalen) was dissolved in a mixed solvent of pyridine and methanol under oxygen at room temperature.

Discussion

It is naturally expected that some interactions may exist between such complexes as Co(salen), Co(3-MeOsalen), and Co(salprtr) and oxygen in some solvents. Calvin *et al.*[10] reported that two moles of activated Co(salen) absorbed one mole of oxygen and that one mole of Co(salprtr) absorbed one mole of oxygen in the solid state. The present authors have previously reported a reversible formation of mononuclear cobalt oxygen adducts from these complexes mixed in poly(4-vinylpyridine).[1,2] Floriani *et al.*[7] tried to isolate some oxygen complexes derived from these cobalt complexes which might be formed in some solvents. They isolated some binuclear oxygen adducts, such as [Co(salen)·DMF]$_2$·O_2, [Co(salen)·DMSO]$_2$·O_2, [Co(salen)·pyridine]$_2$·O_2, and [Co(3-MeOsalen)]$_2$·O_2·DMSO. Moreover, they could isolate [Co(3-MeOsalen)]·pyridine·O_2. The 1 : 1 oxygen adduct was isolated in only this case.

On the other hand, the present authors observed an ESR signal with an eight-line structure in both Co(3-MeOsalen) and Co(salen) solution (pyridine, DMF, DMSO, and HMPT) under oxygen, though no quantitative studies were pursued. The ESR signal at the position of a g_{sol} value of about 2 with an eight-line structure showed that the paramagnetic species was a certain radical containing one unpaired electron which interacted with one cobalt nucleus, because the nuclear spin of ^{59}Co is 7/2. In fact, a paramagnetic binuclear cobalt complex bridged by oxygen shows an ESR spectrum with a fifteen-line structure.[*1, 11–14]

In view of the facts that the ESR signal appeared reversibly under oxygen, and that the A_{sol} value of the signal and that of a paramagnetic binuclear

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[9] F. K. Kneubühl, *J. Chem. Phys.*, **33**, 1074 (1960).

[10] A. E. Martell and M. Calvin, "Chemistry of the Metal Chelate Compounds," Prentice Hall, N. J. (1956), p. 337.

[*1] $2\times2\times(7/2)+1\rightarrow15$ lines.

[11] E. A. V. Ebsworth and J. A. Weil, *J. Phys. Chem.*, **63**, 1890 (1959).

[12] M. Mori, J. A. Weil and J. K. Kinnaird, *ibid.*, **71**, 103 (1967).

[13] J. A. Weil and J. K. Kinnaird, *ibid.*, **71**, 3341 (1967).

[14] D. L. Duffy, D. A. House and J. A. Weil, *J. Inorg. Nucl. Chem.*, **31**, 2053 (1969).

cobalt oxygen complex were in the same range (for example,12) $A_{\rm sol}$ of $[(NH_3)_5CoO_2Co(NH_3)_5](NO_3)_5$ in an acidic solution is 11.4 gauss), and also from a comparative consideration of the previously-published studies of similar complexes,*2,4–6) the signal which was observed under oxygen in the above solutions of Co(3-MeOsalen) (and Co(salen)) was considered to be due to some cobalt oxygen complexes. The ratio of 1 mole of cobalt *vs.* 1 mole of oxygen could also be said to be true, in view of the fact that the signal had an eight-line structure and by naturally assuming that the reversibly-produced binuclear cobalt oxygen complexes were diamagnetic. In fact, the binuclear complex, $[Co(salen)\cdot DMF]_2\cdot O_2$, and some similar complexes have been reported to be intrinsically diamagnetic, though with some temperature-independent paramagnetism.7) Apparently, a 1 : 2 adduct could be identified as Co(III)–O_2^{2-}–Co(III), which had no free spin, and a 1 : 1 adduct could be schematically considered to be Co(III)–O_2^- or Co(II)–O_2, each of which has one unpaired electron.

Therefore, a mononuclear cobalt oxygen complex has been proved to exist equilibrially in these Lewisbase solvents of Co(salen) and Co(3-MeOsalen).*3

The observation that no ESR signal could be found in a toluene solution of Co(3-MeOsalen) under oxygen agrees with the reports of Ueno *et al.*,7,15) who reported that oxygen could not interact to yield some stable oxygen adducts with Co(salen)'s in such solvents. That is, the coordination of a Lewis base such as pyridine may be necessary for the stable existence of mononuclear (and also binuclear) oxygen complexes. The idea is also supported by the experimental finding that an ESR signal appeared when PPh_3 was added to the solution.

Some decompositional reactions may proceed on the oxygen adducts when some protic solvents coexist. This seems to be a probable reason why no ESR signal could be observed in a pyridine solution of Co(3-MeOsalen) with some methanol under oxygen. In fact, Costa *et al.*16) supposed that Co(III)–OR^- might be produced from such systems. The same situation might hold in the case of Co(sa) in pyridine, because Co(sa) has protonic hydrogens in the ligands.

The Dependence of ESR Characteristics on Solvents. Let us now discuss the variation in $g_{\rm sol}$ and $A_{\rm sol}$ values from solvent to solvent.

The data in Table 1 show that the $g_{\rm sol}$ and $A_{\rm sol}$ values of the adducts of Co(3-MeOsalen) in pyridine, 4-methylpyridine, and 4-ethylpyridine are almost all the same. The $g_{\rm sol}$ and $A_{\rm sol}$ values of the adducts of Co(3-MeOsalen) are, however, considerably different in pyridine, DMF, DMSO, and HMPT. On the contrary, the difference are very small in the case of those of Co(salprtr), in which the *trans* position of the coordinated oxygen may not be occupied by the solvent (as a ligand) because of steric hindrances caused by the imine ligand. This situation is different from that of Co(3-MeOsalen). In fact, an X-ray analytical study of $[Co(salen)\cdot DMF]_2\cdot O_2$ by Calligaris *et al.*17) has shown that the DMF's exist in the *trans* positions of the bridge-oxygen.

On the basis of the above discussion, the variation in the $g_{\rm sol}$ and $A_{\rm sol}$ values of the adducts of Co(3-MeOsalen) (and Co(salen)) can be explained by considering that the solvent behaves as the fifth ligand in a *trans* position relative to the coordinated oxygen acting as the sixth ligand. The solvent might possibly affect the coordinated oxygen in a direct way, but the effect on $A_{\rm sol}$ and $g_{\rm sol}$ values may be quite small in comparison with the effect of the solvent in the *trans* position, judging from the observation that the $g_{\rm sol}$ and $A_{\rm sol}$ values of the adducts of Co(salprtr) are almost independent of the solvent.

The data of Table 2 show that the stabilities of the oxygen adduct are in this order: HMPT$\approx$DMF$<$pyridine.*4 On the other hand, the $A_{\rm sol}$ values are in this order: HMPT$>$DMF$>$pyridine, and the $g_{\rm sol}$ values are in this order: HMPT$\approx$pyridine$<$DMF.

The *Dq* values of the solvents may be considered

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*2 Recently, $[Co(BAE)\cdot pyridine]\cdot O_2$ and some similar oxygen adducts (Co(BAE)=bis(acetylacetone)-ethylenediiminecobalt(II)) were isolated.8) ESR studies were attempted on superoxocobalamines ($Co/O_2=1/1$)6) and also on $[Co(CN)_5O_2]^{3-}$.5) These ESR spectra very much resemble those in this paper.

*3 Of course, the non-oxygenated complex and the corresponding binuclear oxygen adduct may exist simultaneously; moreover, the amounts of the latter may be larger than those of the mononuclear adduct in many cases (*cf.* the lit.7)).

15) K. Ueno and A. E. Martell, *J. Phys. Chem.*, **60**, 1270 (1956).

16) G. Costa, G. Mestroni and G. Pellizer, *J. Organometal. Chem.*, **15**, 187 (1968).

17) M. Calligaris, G. Nardin and L. Randassio, *Chem. Commun.*, **1969**, 763.

*4 The $g_{\rm sol}$ and $A_{\rm sol}$ values of the adduct in a mixed solvent of pyridine and DMF (and that of pyridine and HMPT) prove that the existing paramagnetic species in the mixed solvent is not a DMF (nor HMPT)-oxygen adduct, but a pyridine-oxygen adduct. The characteristic values of the paramagnetic species in the mixed solvent of DMF and HMPT (the volume ratio is 1/1; the mole ratio is, then, 2 moles of DMF *vs.* 1 mol of HMPT) may be explained if the species in the solvent is a mixture of a DMF-oxygen adduct and a HMPT-oxygen adduct (in the mole ratio of about 2/1). The observed $g_{\rm sol}$ (and also $A_{\rm sol}$) value in the mixed solvent is considered to be the weighted mean value of that of the DMF-oxygen adduct and that of the HMPT-oxygen adduct.

to be in this order: HMPT$\overset{?}{<}$DMF$<$pyridine.[*5]

The above comparison shows that close relationships may exist among the stability, the A_{sol} (caused by the cobalt nucleus) value, and the Dq value of the solvent.[*6]

It seems that the larger the crystal field strength of the *trans* ligand (the solvent), the more stable the oxygen adduct. The A_{sol} value seems to decrease with the increase in the Dq value. The changes in g_{sol} values seem to be more complicated than those in A_{sol} values. The description by Crumbliss[8] that the adduct [Co(BAE)·DMF]·O$_2$ is less stable than [Co(BAE)·pyridine]·O$_2$ also agrees with the above discussion.

The Properties of the Coordinated Oxygen. It is very important and interesting to clarify the electronic structure of the mononuclear oxygen complexes. The ESR characteristics shall be analysed from this point of view.

Such investigations as have been pursued on paramagnetic species formed on the surfaces of some metal oxides from molecular oxygen by means of ESR spectroscopies[23,24] may be worthy of attention. It is regretable that no ESR studies seem to have been made on the oxygen complexes of so-called low valent transition metal complexes, such as IrO$_2$X(CO)(PPh$_3$)$_2$,[25] because of their diamagnetism.

There are two ways of analysing the ESR signals of the mononuclear cobalt oxygen complexes. The first one is based on the electronic structure, Co(II)–O$_2$ (in this structure, the unpaired electron is considered to be localized in metal orbitals. A low-spin d^7 cobalt(II) is coordinated by a diamagnetic oxygen (for example, a $^1\Delta_g$ oxygen)), while the other is based on the electronic structure, Co(III)–O$_2^-$ (in this structure, the free spin is considered to be localized in an oxygen molecular orbital. A diamagnetic d^6 cobalt(III) is coordinated with a paramagnetic superoxide anion).

There are several low-spin cobalt(II) complexes which have been studied by means of ESR spectroscopy, for example, cobalt phthalocyanine (CoPc),[26,27] Co(CH$_3$NC)$_5^{2+}$,[28,29] and Co(CN)$_5^{3-}$.[28,29] These low-spin cobalt(II) complexes have g values which are relatively close to 2 (for example, $g_{||}=2.000$, and $g_{\perp}=2.117$ for Co(CH$_3$NC)$_5^{2+}$, and $g_{||}=1.992$, and $g_{\perp}=2.157$ for Co(CN)$_5^{3-}$). In general, however, the A values caused by the cobalt atom of these complexes are relatively large (for example, $A_{||}=78$ gauss and $A_{\perp}=57$ gauss for Co(CH$_3$NC)$_5^{2+}$, and $A_{||}=87$ gauss and $A_{\perp}=28$ gauss for Co(CN)$_5^{3-}$). From a consideration of these results, the A values of the oxygen cobalt complexes should be much larger than the measured values if the electronic structure of the adduct is considered to be mainly Co(II)–O$_2$. Of course, the smallness of the measured A_{sol} values does not mean necessarily the smallness of the individual anisotropic principal components of the A hf tensor (for example, $A_{||}$ and $A_{\perp}$). The individual anisotropic components are considered, however, not to be very large, as will be discussed later.

The finding that such small differences exist in the A_{sol} values of the adduct of Co(3-MeOsalen) in pyridine, 4-methylpyridine, and 4-ethylpyridine seems rather unacceptable if the unpaired electron exists mostly in the cobalt orbitals. For example, the $A_{||}$ value caused by the cobalt nucleus of a pyridine adduct of CoPc has been reported to be 78×10^{-4} cm^{-1}, and that of a 4-methylpyridine adduct of CoPc, 84×10^{-4} cm^{-1}.[27] If the situation is the same in the oxygen adduct of Co(3-MeOsalen), about 0.3 gauss[*7] is expected to be the difference

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[*5] This order seems to be true in view of the generally-accepted spectrochemical series[18] (Br$^-<$Cl$^-\sim$N$_3^-<$(NH$_2$)$_2$CO$<$H$_2$O$<$NH$_3\sim$pyridine) and the results of Donoghue *et al.*[19] (Cl$^-\sim$HMPT$<$N$_3^-$). The relation between HMPT and DMF is not clear, but the Dq of HMPT may be the smaller, for the Dq of DMF may be in the neighborhood of that of (NH$_2$)$_2$CO. Their donor ability against a protic species may be in this order: HMPT$>$DMF (by $\Delta\tau_{CHCl_3}$),[20] DMF$<$pyridine (by $\Delta\nu_D$)[21] ($\Delta\tau_{CHCl_3}$ is the deviation of the τ value of the proton signal of CHCl$_3$ in a given solvent from that in a reference solvent: $\Delta\nu_D$ is the deviation of the O–D stretching wave number of CH$_3$OD in the given solvent from that in a reference solvent). Which has the larger donor ability, HMPT or pyridine, is not clear.

18) F. Basolo and R. G. Peason, "Mechanisms of Inorganic Reactions," Second Ed., John Wiley & Sons. Inc., New York (1967), p. 67.

19) J. T. Donoghue and D. S. Drago, *Inorg. Chem.*, **1**, 866 (1962).

20) H. Normant, *Angew. Chem., Int. Ed.*, **6**, 1046 (1967).

21) T. Kagiya, Y. Sumida and T. Inoue, This Bulletin, **41**, 767 (1968).

[*6] PPh$_3$ should be omitted, because the properties of this ligand are rather complicated because of the existence of a strong π-ability. The DMSO seems not to be very different from DMF.[22]

22) D. W. Meek, "The Chemistry of Non-Aqueous Solvents," ed. by J. J. Lagowski, Academic Press, New York (1966), p. 1.

23) P. H. Kasai, *J. Chem. Phys.*, **43**, 3322 (1965).

24) K. M. Wang and J. H. Lunsford, *J. Phys. Chem.*, **73**, 2069 (1969).

25) Y. Saito, *Yuki Gosei Kagaku Kyokai Shi*, **26**, 943 (1968).

26) J. M. Assour and W. K. Kahn, *J. Amer. Chem. Soc.*, **87**, 207 (1965).

27) J. M. Assour, *ibid.*, **87**, 4701 (1965).

28) M. E. Kimball, D. W. Pratt and W. C. Kaska, *Inorg. Chem.*, **7**, 2006 (1967).

29) J. J. Alexander and H. B. Gray, *J. Amer. Chem. Soc.*, **89**, 3356 (1967).

[*7] 0.3 gauss$\fallingdotseq(84\times10^{-4}\text{ cm}^{-1}-78\times10^{-4}\text{ cm}^{-1})\times(13\text{ gauss}/84\times10^{-4}\text{ cm}^{-1})\times(1/3)$; the contribution of the $A_{||}$ to the A_{sol} may be one-third of the total.

between the A_{sol} value of the cobalt oxygen complex in pyridine and that in 4-methylpyridine. Therefore, we suspect that the unpaired electron does not interact with the cobalt nucleus in a direct way. Very small differences were also observed between the signal characteristics of Co(3-MeOsalen) and that of Co(salen) in pyridine.

In due course, the analytical method based on the Co(III)–O_2^- electronic structure is expected to be more fruitful. This idea is also compatible with the fact that the A_{sol} value of the paramagnetic binuclear complex, $[(NH_3)_4Co(\mu\text{-}O_2)(\mu\text{-}NH_2)Co(NH_3)_4]^{4+}$,[12] the oxygen of which is considered to be superoxide-like as a result of analysing the $A_{O^{17}}$ values,[13] is in the neighborhood of those of the mononuclear oxygen complexes.

The superoxide anion can be analysed as having the following g values, according to Känzig *et al.*,[30,31] who derived the equations for superoxides of alkali metal ions:

$$g_1 = g_e + 2\left(\frac{\lambda^2}{\lambda^2+\Delta^2}\right)^{1/2} l$$

$$g_2 = g_e\left(\frac{\Delta^2}{\lambda^2+\Delta^2}\right)^{1/2} - \left(\frac{\lambda}{E}\right)\left[-\left(\frac{\lambda^2}{\lambda^2+\Delta^2}\right)^{1/2} - \frac{\Delta}{(\lambda^2+\Delta^2)^{1/2}} + 1\right]$$

$$g_3 = g_e\left(\frac{\Delta^2}{\lambda^2+\Delta^2}\right)^{1/2} - \left(\frac{\lambda}{E}\right)\left[\left(\frac{\lambda^2}{\lambda^2+\Delta^2}\right)^{1/2} - \frac{\Delta}{(\lambda^2+\Delta^2)^{1/2}} - 1\right]$$

The E and Δ values are shown in Fig. 4. The splitting, Δ, is caused by the crystal field constructed by surrounding ions. l is a correction to the angular momentum about the oxygen molecular axis caused by the crystal field. λ is the spin-orbit coupling constant. It has been reported that some superoxide anions adsorbed on metal oxides can be analysed by the above equations.[23,24] Theoretically speaking, these equations can be used in the case of the mononuclear cobalt oxygen complex, Co(III)–O_2^-, as the first approximation. The splitting, Δ, may be caused by the parent cobalt chelate (the parent cobalt chelate means the part of the cobalt oxygen adduct except the coordinated oxygen), which serves as a certain crystal field against the superoxide anion.

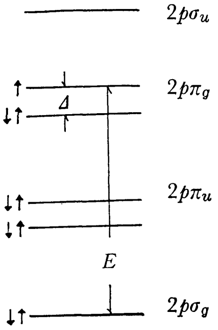

Fig. 4. The electronic levels of O_2^-.

Providing that l is equal to 1.00, that λ/E is negligibly small (the energy internal between $2p\pi_g$ and $2p\sigma_g$ is calculated to be 2.25 Rdg[32]), and that λ is 223 cm^{-1} [30] (or 115 cm^{-1} [24])),[*8] the g_1 value of the 2.076 of the oxygen adduct in the mixed solvent of pyridine and HMPT (in Fig. 2; also, g_2, $g_3 \fallingdotseq 2.00$—2.01) is explainable if Δ is 6100 cm^{-1} (or 3050 cm^{-1}). The actual λ value is thought to be between the above two values.[33] This value of Δ (several thousand cm^{-1}) is comparable with those of adsorbed superoxide anions on some metal oxides;[24] it is also comparable with the theoretically-calculated value for an oxygen coordinated with iron phthalocyanine (with its molecular axis parallel to the complex plain).[34]

The g_{sol} value may be also calculated by using the relation:

$$g_{\mathrm{sol}} = (1/3)(g_1+g_2+g_3)$$

The derivation in g_{sol} values of the adducts of Co(3-MeOsalen) from solvent to solvent seems not to correspond to the change in the Dq values of the solvent (acting as the *trans* ligand). There may be some complicated mechanism in the transport of the crystal-field effect of the *trans*-position ligand to the coordinated oxygen. It is also probable that there is some deviation of the individual l value from 1.00 and a change in the λ values.

As a summary of the preceding discussions about g values, it can be claimed that the coordinated oxygens in the mononuclear cobalt oxygen complexes can be considered to be rather superoxide-like.

An analysis of the A_{sol} and anisotropic components of the hf tensor is expected to clarify the electronic structure of the oxygen adduct more precisely. An exact analysis based only on the observed results is now, however, very difficult, because of our little knowledge about the geometrical structure and because of the probable disagreement of the directions of the g tensor with those of the A tensor. Therefore, only a rough analysis was attempted according to the method used by Kon *et al.*,[4] by assuming the geometrical structure to

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[30] W. Känzig and M. H. Cohen, *Phys. Rev. Lett.*, **3**, 509 (1959).

[31] R. T. Shuey and H. R. Zeller, *Helv. Phys. Acta*, **40**, 873 (1967).

[32] T. Shimanouchi, "Kozo-Kagaku Kogi-Shiryo," Shokabo Co,. Ltd., Tokyo (1965), p. 35.

[*8] The value of 223 cm^{-1} was used in the first report of Känzig *et al.*[30]; the value of 115 cm^{-1} was used by Wang *et al.*[24]

[33] H. R. Zeller and W. Känzig, *Helv. Phys. Acta*, **40**, 845 (1967).

[34] M. Zerner, M. Gouterman an H. Kobayashi, *Theoret. Chim. Acta*, **6**, 363 (1966).

be the one in which the oxygen molecule is coordinated to the parent chelate with its molecular axis oblique (the angle is θ; θ was assumed to be 60°) against the principal axis of the parent cobalt chelate.*[9] The A characters used were: $|A_{\mathrm{sol}}|=13.2$ gauss, $|A_1|=16.0$ gauss, and $|A_2|=|A_3|=14.7$ guass (for the oxygen adduct in the mixed solvent of pyridine and HMPT).

When it was assumed that the unpaired electron was in d_{z^2} and that $A \fallingdotseq -P(\kappa-4/7)$, $B \fallingdotseq -P(\kappa+2/7)$ (A and B are the probable principal components of the hf tensor under an axis symmetry. These equations are quite rough[36)]). The dipolar part, $|A_d|$, was estimated to be 10.4 gauss.

When it was assumed that the unpaired electron was in d_{xz} (or d_{yz}) and that $A \fallingdotseq -P(\kappa+4/7)$, $B \fallingdotseq -(\kappa-2/7)$;[36)] the $|A_d|$ was calculated to be 18 gauss.

Though the above assumptions and calculations are quite rough and insufficient, it may be possible to state that the unpaired electron density in the cobalt d orbital (ρ) is rather small, considering that $|A_d|=(4/7)P\rho$ and that the P value for cobalt is 0.022—0.025 cm^{-1}.[4,37)]

The above conclusion agrees well with the intended analysis based on the Co(III)–O_2^- structure. It is likely that the larger the A_{sol} value (though it is not necessarily parallel to the A_d value), the more the spin density in cobalt d orbitals.

The observations that such a small deviation exists in the A_{sol} values of the adducts of Co(3-MeOsalen) in pyridine, 4-methylpyridine, and 4-ethylpyridine, and that the ESR characteristics of the oxygen adduct of Co(salen) are almost the same as those of Co(3-MeOsalen), seem to be acceptable in view of the fact that a small part of the unpaired electron is considered to exist in the cobalt orbitals.

Though many considerations should be pursued further, if we are to understand the electronic structure of the individual oxygen adduct exactly (for example, by drawing the molecular orbital energy diagram quantitatively), the coordinated oxygen in these mononuclear cobalt oxygen complexes can be safely stated to be a kind of superoxide anion which is modified by the parent cobalt chelate, and the properties of these oxygens can be changed in some degree by selecting the solvent (or the *trans* ligand). The deviation can be estimated according to the character of the solvent.

Experimental

Reagents. *N,N′-Ethylene-bis(salicylideneiminato)cobalt(II).* This chelate was obtained according to the method in the literature[38)] and was recrystallized from methanol.

Found: C, 58.85; H, 4.08; N, 8.62%. Calcd for $C_{16}H_{14}CoN_2O_2$: C, 59.10; H, 4.30; N, 8.63%.

N,N′-Ethylene-bis(3-methoxysalicylideneiminato)cobalt(II). This chelate was synthesized as a monohydrate by mixing cobalt(II) acetate tetrahydrate (commercially obtained, and recrystallized from aqueous acetic acid) and *N,N′*-ethylene-bis(3-methoxysalicylideneimine) (synthesized from ethylenediamine and 3-methoxysalicylaldehyde) in the mole ratio of 1/1 in a mixed solvent of DMF and water at 60°C.

Found: C, 53.41; H, 5.33; N, 7.07.% Calcd for $C_{18}H_{18}CoN_2O_4 \cdot H_2O$: C, 53.61; H, 5.00; N, 6.95%.

The monohydrate was dehydrated at 170—185°C for 1.5 hr *in vacuo*. The decrease in the weight: Found: 4.1%. Theoretical: 4.4%. The chelate was stored in dried nitrogen.

Bis(salicylaldimino)cobalt(II). This chelate was synthesized according to the method of Endo.[39)] At first as a dihydrate:

Found: C, 50.94; H, 4.86; N, 7.91%. Calcd for $C_{14}H_{12}CoN_2O_2 \cdot 2H_2O$: C, 50.16; H, 4.81; N, 8.36%.

Then, it was dehydrated at 130°C for 2.5 hr *in vacuo*.

Found: C, 56.18; H, 3.93%. Calcd for $C_{14}H_{12}CoN_2O_2$: C, 56.20; H, 4.04%.

As for this complex, *cf.* the literature.[1,2)]

Di(salicylal)-3,3′-diimino-di-n-propylamine-cobalt(II). This chelate was synthesized according to the method in the literature[38)] and was purified by reprecipitating it, by water from an ethanol solution, as a monohydrate.

Found: C, 57.81; H, 6.21; N, 10.21%. Calcd for $C_{20}H_{23}CoN_3O_2 \cdot H_2O$: C, 58.00; H, 6.09; N, 10.14%.

Pyridine, 4-Methylpyridine, 4-Ethylpyridine, DMF, DMSO, and HMPT. Commercially obtained solvents were distilled under purified nitrogen or under reduced pressure, and were stored under purified nitrogen.

Methanol, Benzene and Toluene. Commercially obtained solvents were dehydrated by appropriate methods and were distilled under purified nitrogen.

Triphenylphosphine. The commercial product of a guaranteed reagent grade was used without further purification.

The Measurements of the ESR Spectra. In general, a cobalt complex was dissolved in a given solvent under purified nitrogen. A part of the solution was then injected into a slender tube ($\phi=1$ mm), and the ESR spectrum was measured under purified nitrogen. The remaining solution was then exposed to oxygen (from a commercially obtained bomb), and a part of it was injected into a tube which was kept under oxygen. The oxygen atmosphere above the solution could be changed to nitrogen, and *vice versa.*

The ESR spectra were observed with a Japan Optics Laboratory Co., Ltd., ESR spectrometer, Model JES-3BS-X. A manganese marker was used for the calibration. The cavity temperature could be changed over a wide range by means of an attached apparatus for the temperature control.

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*[9] Similar structures are common in the cases of binuclear cobalt oxygen complexes.[35)] A similar structure has been also claimed in the case of [Co(BAE)·ligand]·O_2's, on the basis of their infrared spectra.[8)]

35) Lit. 20, p. 641.

36) A. H. Maki, N. Edelstein, A. Davison and R. H. Holm, *J. Amer. Chem. Soc.*, **86**, 4580 (1964).

37) J. M. Assour, *J. Chem. Phys.*, **43**, 2477 (1965).

38) R. H. Bailes and M. Calvin, *J. Amer. Chem. Soc.*, **69**, 1886 (1947).

39) J. Endo, *Nippon Kwagaku Kwaisi*, **65**, 424 (1944).