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The Preparation and Some Properties of Cobalt(II) Schiff Base Complexes and Their Molecular Oxygen Adducts

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Seven new cobalt(II) complexes with a tetradentate Schiff base and their three oxygen adducts were synthesized. The adducts were stable at room temperature for several weeks. The isolated oxygen adducts showed intense new bands in the 1130—1150 cm^{-1} range characteristic of superoxide-like 1:1 oxygenated metal complexes. The ESR spectra of the adducts showed eight-lined, hyperfine structures with a very small splitting (10—20 G)** at 77 K. The adducts obtained were identified as monomeric 1:1 oxygen species, two complexes of which showed a reversible oxygenation in a 1,2-dichloroethane solution at 6 °C.

Cobalt(II) complexes with Schiff base have received considerable attention as biomimic model compounds for oxygen-carrying and storage proteins, such as hemoglobin and myoglobin.[1] Recently, many investigators have devoted their efforts to elucidate the mechanism of the oxygenation of the cobalt(II) complexes.[2–8] For instance, Basolo *et al.* reported that the electron density on a central cobalt(II) ion of the Schiff base complexes is an important factor in determining the oxygen affinity of the complexes.[3] The crystal structures of oxygen adducts of cobalt(II) Schiff base complexes with some peripheral groups in their ligand have also been determined by means of X-ray-diffraction analysis in order to elucidate the influence of the change in the substituents of the in-plane ligand on the cobalt-oxygen geometry.[9,10]

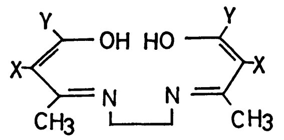
To date, many studies of the adducts of cobalt(II) Schiff base complexes have been published, but only a few monomeric 1:1 oxygen adducts are known to be stable at room temperature.[5,10–12] Therefore, it is of interest to elucidate the factors which determine the stability of the monomeric 1:1 oxygen adduct in the solid state; it is also important to prepare the adduct in order to improve the biomimic model system.

Seven new cobalt(II) complexes with a Schiff base derived from *N,N'*-bis(1-methyl-3-oxobutylidene)ethylenediamine (A-H) and *N,N'*-bis(1-methyl-3-oxo-3-phenylpropylidene)ethylenediamine (B-H) were synthesized; three of these complexes formed stable monomeric 1:1 oxygen adducts in the solid state. We wish to report here that the isolation of the stable oxygen adducts is affected by the kinds of peripheral groups and that the oxygen affinity of the complexes in solution is also dependent on the groups.

Experimental

Syntheses. *Schiff Base Ligands*: The ligands of A-Cl, A-succ, A-OPh, B-Cl, and B-succ were obtained by the elimination of metal with hydrogen sulfide from their copper(II) complexes, as has been described previously.[13,14] A-CONHPh and B-CONHPh were synthesized according to the method reported by Howells *et al.*[15]

Co(A-Cl): After A-Cl (1.2 g) had been suspended in 25 cm^3 of an ethanol solution saturated with potassium hydroxide, cobalt(II) acetate tetrahydrate (0.6 g) was added to the solution. Then, the solution was refluxed for 20 min under a nitrogen atmosphere, resulting in orange precipitates. The precipitates thus obtained were washed with ethanol and subsequently recrystallized from chloroform and small amounts of hexane. The other complexes were synthesized by a similar method.



	X =	Y =
A-H,	hydrogen	methyl
A-Cl,	chloro	methyl
A-succ,	succinimido	methyl
A-OPh,	phenoxy	methyl
A-CONHPh,	phenylcarbamoyl	methyl
B-H,	hydrogen·	phenyl
B-Cl,	chloro	phenyl
B-succ,	succinimido	phenyl
B-CONHPh,	phenylcarbamoyl	phenyl

Fig. 1. Abbreviation of Schiff base ligands.

Oxygen Adducts of Co(A-Cl): By bubbling air through 10 cm^3 of an acetone solution of Co(A-Cl) (0.2 g) in the presence of small amounts of pyridine at 0 °C for several min, a dark-red oxygenated compound was precipitated. The precipitates were subsequently washed with ether and dried in air. The adducts of Co(A-succ) and Co(B-succ) were also obtained by a similar method. In the case of the other complexes, no oxygenated adducts were isolated.

Measurements. The ^1H-NMR spectra were recorded with a JEOL-MH 100 spectrophotometer at a frequency of 100 MHz. The chemical shifts were determined in ppm, using TMS as the internal standard. The electronic spectra in solution and the infrared spectra using Nujol-mull methods were measured on a Hitachi 124 spectrophotometer and a Hitachi 215 spectrophotometer respectively. The ESR spectra (X-band) were measured with a JEOL-1X spectrometer. The reversible oxygenation in a 1,2-dichloroethane solution was observed by means of the method reported by Kubokura *et al.*[5]

Results and Discussion

^1H-NMR Spectra of Ligands. The ^1H-NMR spectra of the ligands obtained are shown in Table 1.

** 1 G = 10^{-4} T.

TABLE 1. ^{1}H-NHR SPECTRA OF FREE LIGANDS IN 1,2-DICHLOROETHANE-d_4 (ppm)

Ligand	δ_{succ}	δ_{CH_3}	δ_{CH_2}	δ_{CH}	δ_{Ph}	δ_{CHN}
A-H		1.86(d, 12H)	3.30(s, 4H)	4.92(s, 2H)		
A-Cl		2.16(d, 12H)	3.36(s, 4H)			
A-succ	2.84(s, 8H)	1.80(d, 12H)	3.52(br s, 4H)			
A-OPh		1.79(d, 12H)	3.42(m, 4H)		7.17(t, 16H) 7.53(t, 14H)	
A-CONHPh[a)]		2.10(s, 12H)	3.63(s, 4H)		7.11—7.77 (m, 10H)	10.20(s, 2H)
B-H		2.13(s, 6H)	3.63(br s, 4H)	5.85(s, 2H)	7.59(s, 6H) 8.04(s, 4H)	
B-Cl		2.34(s, 6H)	3.69(m, 4H)		7.59(m, 6H) 7.74(m, 4H)	
B-succ	1.96(s, 8H)	2.50(m, 6H)	3.68(br s, 4H)		7.24(br s, 10H)	
B-CONHPh[a)]		2.25(br s, 6H)	3.78(br s, 4H)		7.32(m, 20H)	10.02(s, 2H)

a) In dimethyl-d_6 sulfoxide. s = Singlet, d = doublet, t = triplet, m = multiplet, and br = broad.

TABLE 2. ELEMENTAL ANALYSES AND YIELDS OF THE COBALT(II) COMPLEXES AND THEIR OXYGEN ADDUCTS

Compound	Found(%)			Calcd(%)			Yield	Absorption	
	C	H	N	C	H	N	%	λ_{max}/nm (log ε)	
Co(A-Cl)	40.95	4.44	8.18	40.93	5.15	7.96	24	392(3.30)	475^{sh} (2.41)
Co(A-succ)	49.94	5.22	11.05	50.53	5.09	11.79	88	382(3.58)	455^{sh} (3.02)
Co(A-OPh)	62.17	5.55	6.16	61.94	5.63	6.02	90	396(3.44)	460^{sh} (2.40)
Co(A-CONHPh)	59.85	5.56	10.90	60.11	5.54	10.79	32	390^{sh} (3.32)	450^{sh} (3.01)
Co(B-Cl)	55.73	4.13	6.02	55.72	4.25	5.91	27	411(3.48)	490^{sh} (2.72)
Co(B-succ)	59.36	4.67	9.45	60.10	4.71	9.35	93	394(3.83)	455^{sh} (3.38)
Co(B-CONHPh)	65.50	4.65	8.27	65.15	4.87	8.44	45	360^{sh} (4.04)	450^{sh} (3.20)
Co(A-Cl)pyO$_2$	44.43	4.50	8.97	44.27	4.59	9.14	26	370	
Co(A-succ)pyO$_2$	51.09	5.25	11.26	51.21	4.98	11.94	56	355, 525	
Co(B-succ)pyO$_2$	58.88	5.02	9.25	59.15	4.68	9.86	65	360, 525	

py = Pyridine. Yields are mole percentages. sh = Shoulder.

The ^{1}H-NMR signals arising from the methine protons of the parent ligands, A-H and B-H, disappear in their derivatives, indicating the displacement of the methine protons in the derivatives. The ^{1}H-NMR signals of the succinimido groups in A-succ appear at lower magnetic fields than those of its methyl groups. On the other hand, the signals of the succinimido groups in B-succ are shifted to higher magnetic fields compared with those of its methyl groups. This may result from the effect of a ring current of phenyl groups in B-succ. The inductive effects of chloro and phenylcarbamoyl groups in A-Cl, A-CONHPh, B-Cl, and B-CONHPh shift ^{1}H-NMR signals of their methine and methyl protons to lower magnetic fields compared with their parent ligands.

Cobalt(II) Complexes and Their Oxygen Adducts. While Co(A-Cl) and Co(B-Cl) were dark reddish crystals, the other complexes were yellow or yellowish orange. The yellow Co(A-OPh) complex gradually changed to dark brown in polar-solvent moistures. The molecular oxygen adducts of the cobalt(II) complexes with A-Cl, A-succ, and B-succ were isolated and were stable at room temperature for several weeks (the stability was checked by means of the IR spectra). These adducts are sparingly soluble in common organic solvents. On the other hand, the adducts of the other cobalt(II) complexes could not be isolated, not even below 0 °C. When *N*-methylimidazole was employed instead of pyridine, no adducts were isolated. That is, the acetone solution of the complexes containing small amounts of the bases turned dark red when air bubbled in. Subsequently, reddish, tarry substances were formed by the condensation of the solution under reduced pressure or by the addition of hexane to the solution, but no adducts were isolated. The suitable solubility of a complex into a solution containing small amounts of the base seems to be one of the key factors for isolating the oxygen adduct. The results of elemental analyses, the yields, and the electronic spectra of the cobalt(II) complexes and some of their adducts are listed in Table 2.

The infrared spectra of the isolated adducts are shown in Fig. 2. The adducts show intense new bands arising from O–O stretching vibrations in the 1130—1150 cm^{-1} range characteristic of superoxide-like 1:1 oxygenated metal complexes.[1)] The oxygenated complexes with succinimide-substituted, Schiff base complexes, Co(A-succ)pyO$_2$ and Co(B-succ)pyO$_2$, each show two ν_{O_2} bands. Such an appearance of the doublet of ν_{O_2} was also found in the oxygen adduct of cobalt(II) picket-fence porphirin with 1-tritylimidazole; it was due to two different conformers of molecular oxygen and to the base orientations.[16)] In the case of the succinimide derivatives, the carbonyl groups

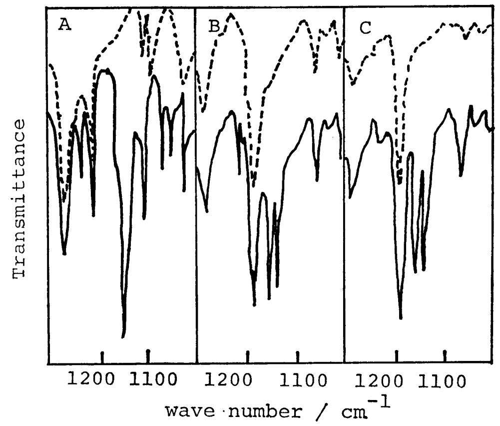


Fig. 2. IR spectra of the complexes and their oxygen adducts.
A: Co(A-Cl), B: Co(A-succ), C: Co(B-succ), ----: complex, ——: oxygen adduct.

vicinal to the imide residues might fix the plane of pyridine with dipole-dipole interactions, resulting in the two conformers.

The ESR data of the adducts were obtained in a 1,2-dichloromethane solution by the use of the X band at 77 K (Table 3). The spectra indicate two signals of $g_{//}$ and $g_{\perp}$, and each signal consistents of eight lines due to the hyperfine splitting of ^{59}Co nucleus. The eight-lined hyperfine structures with the very small splitting indicate that the 1:1 oxygen adducts are isolated; this is consistent with the results of the IR data.

Reversible Oxygenation. Spectral changes were recorded for a 1,2-dichloroethane solution of Co(A-succ) containing 1% pyridine at different partial pressures of oxygen at 6.0±0.4 °C in order to estimate the oxygen uptake (1):

$$\text{Co(A-succ)py} + O_2 \overset{K_{O_2}}{\rightleftharpoons} \text{Co(A-succ)py}O_2. \qquad (1)$$

A new absorption was observed at 525 nm when the complex was oxygenated. The intensity of the band increased with an increase in the partial pressure of oxygen. Subsequently, the original spectrum was recovered by bubbling a nitrogen gas through the solution. The stability constant for oxygenation, K_{O_2} is given by this relation:

$$P_{O_2} = -1/K_{O_2} + (\varepsilon_2 - \varepsilon_1)[\text{Co(A-succ)}]_t P_{O_2}/A - A_0, \qquad (2)$$

where A and A_0 are the absorbances at 525 nm in the absence of oxygen and at the proper partial pressure of oxygen; ε_1 and ε_2 are the molar absorption coefficients of Co(A-succ)py and Co(A-succ)pyO_2; P_{O_2} is the partial pressure of oxygen; [Co(A-succ)]$_t$ is the total concentration of the complex. The plot of P_{O_2} against $P_{O_2}/A-A_0$ gave a straight line with a slope nearly equal to 1 (Fig. 3). This indicates that the monomeric oxygen adduct is formed in the solution, consistent with the isolation of the monomeric oxygen adduct. The value of $\log K_{O_2}$ (-2.48 ± 0.01/Torr^{-1}) (1 Torr=133.322 Pa) was also obtained from the intercept of the line. In a similar manner, the value of $\log K_{O_2}$ (-2.85 ± 0.02/Torr^{-1}) for Co(B-succ) was obtained. In spite of the isolation of the oxygen adduct, the reversibility of Co(A-Cl) was not confirmed under the present conditions.

Table 3. The results of IR and ESR spectral data for the oxygen adducts

Adduct	ν_{O_2}/cm^{-1} (Nujol mull)	$g_{//}$	$g_{\perp}$	$A_{//}$/G	$A_{\perp}$/G
Co(A-Cl)pyO_2	1141	2.079	1.999	17.5	13.8
Co(A-succ)pyO_2	1136, 1152	2.079	1.999	18.8	13.0
Co(B-succ)pyO_2	1132, 1150	2.079	1.996	17.5	12.5

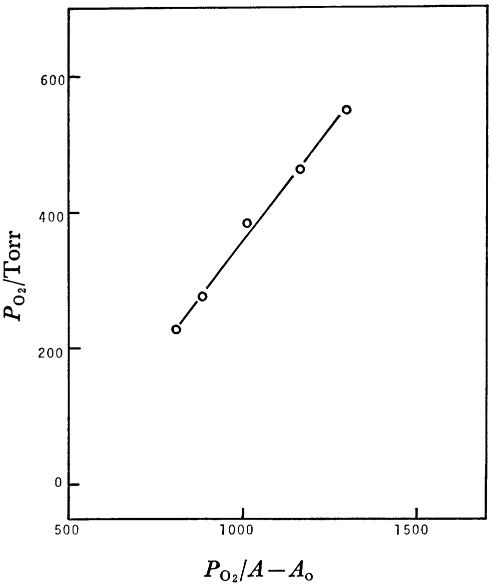


Fig. 3. Plots of P_{O_2} *versus* $P_{O_2}/A-A_0$ for the reversible oxygenation of Co(A-succ) (3.4×10^{-4} mol dm^{-3}) in a 1,2-dichloroethane solution containing 1% pyridine at 6.0±0.4 °C.

While the phenyl groups in Co(B-succ) withdraw an electron from the chelate ring, resulting in a decrease in the electron density on the cobalt(II) ion, the methyl groups in Co(A-succ) increase the electron density on the cobalt(II) ion and stabilize the binding between the cobalt(II) ion and molecular oxygen. This may stabilize the adduct of Co(A-succ) more strongly than that of Co(B-succ) in solution.

Although the stability of the adduct of Co(A-H) in solution ($\log K_{O_2}=-2.08\pm0.03$/Torr^{-1} in a toluene solution at 0 °C) is larger than those of Co(A-succ) and Co(B-succ), the adduct of Co(A-H) releases molecular oxygen in the solid state above 0 °C.[17] On the other hand, the adduct of Co(B-H) is relatively stable in the solid state in spite of its low oxygen affinity in solution.[18] This has been explained by means of the coplanarity of the phenyl substituents with the Schiff base cobalt(II) system in the solid state; a π electron donation to the cobalt(II) ion from the π system in the phenyl groups stabilizes the binding between the cobalt(II) ion and molecular oxygen.[19]

However, judging from the fact that the oxygen adducts of Co(A-Cl), Co(A-succ), and Co(B-succ) are stable in the solid state at room temperature, there seem to be predominant factors for stabilizing the adducts in the solid state other than the electronic factor. More detailed studies will be performed in order to elucidate these factors.

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References

1) R. D. Jones, D. A. Summerville, and F. Basolo, *Chem. Rev.*, **96**, 139 (1979).

2) B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Am. Chem. Soc.*, **92**, 61 (1970).

3) M. J. Carter, D. P. Rillema, and F. Basolo, *J. Am. Chem. Soc.*, **96**, 392 (1974).

4) B. S. Torrog, D. J. Kitko, and R. S. Drago, *J. Am. Chem. Soc.*, **98**, 5144 (1976).

5) K. Kubokura, H. Okawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **51**, 2036 (1978).

6) L. S. Chen, M. K. Koehler, C. P. Pestel, and S. C. Cummings, *J. Am. Chem. Soc.*, **100**, 7243 (1978).

7) K. Miyokawa and I. Matsuda, *J. Inorg. Nucl. Chem.*, **43**, 1495 (1981).

8) M. Suzuki, T. Ishiguro, M. Kozuka, and K. Nakamoto, *Inorg. Chem.*, **20**, 1993 (1981).

9) W. P. Schaefer, B. T. Huie, M. G. Kurilla, and S. E. Ealick, *Inorg. Chem.*, **19**, 340 (1980).

10) B. T. Huie, R. M. Leyden, and W. P. Schaefer, *Inorg. Chem.*, **18**, 125 (1979), and the articles cited therein.

11) C. Floriani and F. Calderazzo, *J. Chem. Soc., A*, **1969**, 946.

12) J. D. Landels and G. A. Rodley, *Synth. Inorg. Metal-Org. Chem.*, **2**, 65 (1972).

13) T. Nagahara, K. Kasuga, and Y. Yamamoto, *Inorg. Chim. Acta*, **47**, 37 (1981).

14) T. Nagahara, K. Kasuga, and Y. Yamamoto, *Inorg. Nucl. Chem. Lett.*, **17**, 235 (1981).

15) P. N. Howells, J. W. Kenny, J. H. Nelson, and R. A. Henry, *Inorg. Chem.*, **15**, 124 (1976).

16) J. P. Collman, J. I. Brauman, T. R. Halbert, and K. S. Suslick, *Proc. Natl. Acad. Sci. U.S.A.*, **73**, 3333 (1976).

17) A. L. Crumbliss and F. Basolo, *J. Am. Chem. Soc.*, **92**, 55 (1970).

18) M. J. Carter, D. P. Rillema, and F. Basolo, *J. Am. Chem. Soc.*, **96**, 392 (1974).

19) G. A. Rodley and W. T. Robinson, *Nature*, **235**, 438 (1972).