Cobalt(III) Complexes of Salen Analog with Thioether Pendant Group. X-Ray Structure Analysis and Thioether Coordination Effects

Kaoru HORIUCHI, Masahiro MIKURIYA,†,§ Hisashi ŌKAWA,* and Sigeo KIDA†
Department of Chemistry, Faculty of Science, Kyushu University, Hakozaki, Higashiku, Fukuoka 812
†Laboratories of Coordination Chemistry, Institute for Molecular Science, Myodaiji, Okazaki 444
(Received May 29, 1987)

A pentadentate salen analog with a pendant thioether group, *N,N'*-disalicylidene-2-methyl-4-ethylthio-1,2-butanediamine (H_2L), formed two types of cobalt(III) complexes, $[Co(L)]ClO_4 \cdot H_2O$ (**1**) and $[Co(L)NH_3]PF_6 \cdot H_2O$ (**2**). Based on infrared and electronic spectra, the complex **1** was revealed to have a square-pyramidal configuration with the pendant sulfur coordination at the apex. The structure of the complex **2** was determined by single-crystal X-ray analysis. The molecule has a six-cooridnate structure with the coordination of the pendant sulfur and the ammonia molecule at the apical sites, the Co-S and Co-N(NH_3) distances being ca. 2.25 and 2.0 Å, respectively. Electrochemical measurements (CV and DPP) for **2** and $[Co(salen)(R\text{-}NH_2)_2]PF_6$ as the reference have revealed that the substitution of thioether sulfur for one of the apical amine ligands results in a positive shift of the Co^{III}/Co^{II} redox potential. It is also found that the Co^{III}/Co^{II} reduction of five-coordinate **1** occurs at a significantly high potential compared with six-coordinate **2** and $[Co(salen)(R\text{-}NH_2)_2]PF_6$.

Pentadentate salen analogs (H_2 salen=*N,N'*-disalicylidenethylenediamine) with a pendant group capable of axial coordination are of current interest because their metal complexes show some characteristics relevant to biological systems, such as formation of reversible oxygen-adducts[1-11] or alkylcobalt(III) complexes[12,13] and catalytic functions in substrate oxidation.[14-18] In a hope to elucidate the effect of the pendant donor atom on the electronic states and the reactivities of the complexes, pentadentate salen analogs with a pendant group of various kinds have been synthesized so far.[19-23] Salen analogs with a thioether in the pendant group, *N,N'*-disalicylidene-2-methyl-4-alkylthio-1,2-butanediamine and *N,N'*-disalicylidene-2-methyl-4-phenylthio-1,2-butanediamine (Fig. 1), were prepared in our laboratory.[22,23] It was shown that the cobalt(II) complexes of these ligands form dioxygen adducts in which the pendant thioether group is coordinated to the trans position to the dioxygen.[22] Further, these ligands form novel μ-oxodiiron(III,IV) complexes composed of high-spin iron(III) and low-spin iron(IV).[23] The unusual low-spin state of the iron(IV) presumably stems from the coordination of the pendant sulfur atom. These findings prompted us to examine the sulfur coordination effect in cobalt(III) complexes of these sulfur-containing salen analogs. This paper deals with synthesis, characterization, structure, and properties of five-coordinate cobalt(III) complex $[Co(L)]ClO_4 \cdot H_2O$ and six-coordinate complex $[Co(L)NH_3]PF_6 \cdot H_2O$ of *N,N'*-disalicylidene-2-methyl-4-ethylthio-1,2-butanediamine (H_2L: Fig. 1, R=C_2H_5).

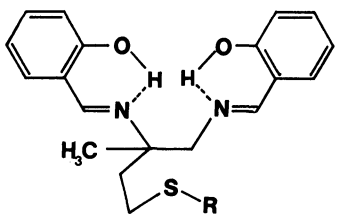

Fig. 1.

Experimental

Preparations. Synthesis of the ligand (H_2L) was described in the preceding paper.[23]

$[Co(L)]ClO_4 \cdot H_2O$ (**1**). Cobalt(II) perchlorate hexahydrate (0.25 g) and H_2L (0.25 g) were dissolved in methanol (30 cm^3), and the mixture was refluxed for 30 minutes to form brownish green solution. It was filtered and the filtrate was left stand in a refrigerator to give a dark green mass. It was crystallized from a chloroform-methanol (1:1) mixture.

Found: C, 46.03; H, 4.99; N, 5.13%. Calcd for $C_{21}H_{26}ClCoN_2O_7S$: C, 46.29; H, 4.81; N, 5.14%.

$[Co(L)NH_3]PF_6 \cdot H_2O$ (**2**). A methanolic solution of cobalt(II) acetate tetrahydrate (0.17 g) and H_2L (0.25 g) was refluxed for two hours. To the resulted deep brown solution was added a methanolic solution of ammonium hexafluorophosphate (excess) to give brown crystals. They were recrystallized from methanol.

Found: C, 41.28; H, 5.00; N, 6.65%. Calcd for $C_{21}H_{29}CoF_6N_3O_3PS$: C, 41.52; H, 4.81; N, 6.92%.

Single-Crystal X-Ray Analysis of 2. On prolonged standing the filtrate of the recrystallization of the complex **2**, the second crop of the complexes was obtained as crystals. From this crop a crystal was picked up and used for the X-ray analysis.

$[Co(L)NH_3]PF_6 \cdot H_2O = C_{21}H_{29}CoSPF_6O_3N_3$, M=607.44, dark brown plates, crystal dimensions 0.15×0.29×0.54 mm, triclinic, a=17.001(2), b=21.388(3), c=11.280(2) Å, α=102.57 (1), β=96.71(1), γ=94.38(1)°, V=3954 Å^3, space group $P\bar{1}$ (C_i, No. 2), Z=6, D_m (floatation)=1.53, D_c=1.53 g cm^{-3}, μ(Mo $K\alpha$)=8.52 cm^{-1}, F(000)=1872.

Data collection and processing: RIGAKU AFC-5 diffractometer, $\omega/2\theta$ mode with ω scan width=1.1+0.5 tanθ, ω scan speed 3 deg min^{-1} graphite-monochromated Mo $K\alpha$ radia-

§Present address: School of Science, Kwanseigakuin University, Uegahara, Nishinomiya 663.

Table 1. Atomic Postional Parameters ($\times 10^4$)

	x	y	z		x	y	z	
CoA	3569(1)	−166(1)	8916(2)	C14A	5748(10)	−371(9)	5887(15)	
CoB	5726(1)	4316(1)	6253(2)	C15A	5431(9)	−22(8)	6899(15)	
CoC	9284(1)	7251(1)	1535(2)	C16A	4701(9)	−258(8)	7211(14)	
SA	2773(3)	485(2)	8110(4)	C17A	2064(11)	−1820(9)	6963(18)	
SB	5785(3)	4290(3)	8243(5)	C18A	1740(10)	−687(9)	7068(17)	
SC	8099(3)	7616(2)	1149(4)	C19A	1779(10)	30(9)	7761(18)	
PA	0	0	0	C20A	3042(11)	505(10)	6591(16)	
PB	2274(3)	8617(3)	2945(6)	C21A	2522(14)	959(12)	6029(21)	
PC	5914(4)	2836(3)	1636(6)	C1B	4034(11)	3992(9)	6324(16)	
F1A	−429(7)	565(5)	737(11)	C2B	3298(11)	4190(12)	6561(16)	
F2A	−312(10)	196(6)	−1221(11)	C3B	2637(14)	3756(12)	6630(20)	
F3A	759(7)	490(6)	114(13)	C4B	2730(13)	3131(16)	6493(22)	
F1B	1667(9)	8956(10)	2249(20)	C5B	3461(15)	2856(11)	6210(19)	
F2B	1568(10)	8269(11)	3404(22)	C6B	4149(12)	3317(10)	6118(17)	
F3B	2839(10)	8228(9)	3583(20)	C7B	4893(12)	3053(9)	5833(17)	
F4B	2902(10)	8963(11)	2481(23)	C8B	6318(11)	3083(9)	5622(19)	
F5B	2246(21)	9096(12)	4031(20)	C9B	7017(12)	3539(8)	6379(17)	
F6B	2128(19)	8060(13)	1878(22)	C10B	7415(11)	4633(9)	6263(17)	
F1C	5276(10)	2987(9)	2487(16)	C11B	7307(10)	5317(9)	6321(16)	
F2C	6569(10)	3183(9)	2734(14)	C12B	7994(12)	5703(9)	6209(18)	
F3C	6598(11)	2703(11)	796(17)	C13B	7970(12)	6331(10)	6359(19)	
F4C	5248(12)	2462(12)	603(17)	C14B	7277(12)	6626(9)	6639(18)	
F5C	6011(11)	2202(8)	1996(20)	C15B	6598(12)	6252(9)	6727(17)	
F6C	5807(17)	3452(11)	1266(24)	C16B	6601(11)	5573(8)	6550(15)	
O1A	3977(6)	537(5)	10237(10)	C17B	7779(12)	3323(10)	5869(21)	
O2A	4434(6)	102(5)	8165(9)	C18B	7140(13)	3528(11)	7775(19)	
O1B	4614(7)	4420(6)	6211(11)	C19B	6413(16)	3589(10)	8387(19)	
O2B	5900(7)	5232(5)	6635(10)	C20B	6518(16)	4982(11)	9100(19)	
O1C	9171(7)	7425(5)	3223(10)	C21B	6514(29)	7985(8)	3999(15)	
O2C	8822(7)	6414(6)	1473(11)	C1C	9313(10)	7985(8)	3999(15)	
OWA	4500(17)	1497(13)	8509(28)	C2C	9112(11)	8028(9)	5194(16)	
OWB	5571(17)	2008(11)	7498(22)	C3C	9264(11)	8599(10)	6077(16)	
OWC	8509(11)	3033(10)	−25(20)	C4C	9623(12)	9166(10)	5800(18)	
N1A	2699(8)	−423(7)	9706(12)	C5C	9828(12)	9143(10)	4619(16)	
N2A	3143(7)	−859(6)	7581(12)	C6C	9659(10)	8549(8)	3730(15)	
N3A	4251(7)	−728(6)	9675(12)	C7C	9897(10)	8562(9)	2512(15)	
N1B	5565(9)	3411(7)	5867(13)	C8C	10080(10)	8152(8)	469(15)	
N2B	6836(8)	4201(7)	6281(12)	C9C	9553(10)	7678(8)	−615(16)	
N3B	5622(8)	4329(7)	4460(12)	C10C	9392(11)	6515(9)	−886(18)	
N1C	9782(7)	8078(6)	1596(11)	C11C	9190(11)	5923(9)	−487(17)	
N2C	9408(8)	7072(6)	−148(12)	C12C	9268(12)	5353(9)	−1394(21)	
N3C	10343(9)	6958(7)	1959(14)	C13C	9063(13)	4748(10)	−1118(24)	
C1A	3578(10)	818(8)	11092(14)	C14C	8764(12)	4723(10)	66(23)	
C2A	3917(10)	1421(8)	11839(15)	C15C	8690(11)	5297(9)	891(21)	
C3A	3504(12)	1727(9)	12787(15)	C16C	8911(11)	5902(8)	627(18)	
C4A	2774(11)	1435(10)	13030(17)	C17C	9983(11)	7569(10)	−1766(16)	
C5A	2446(11)	846(9)	12322(15)	C18C	8735(10)	7906(9)	−946(15)	
C6A	2837(10)	519(8)	11348(15)	C19C	8272(10)	8154(9)	107(16)	
C7A	2455(10)	−109(9)	10653(15)	C20C	7444(12)	6939(10)	207(19)	
C8A	2260(10)	−1060(8)	9027(16)	C21C	6592(13)	7135(13)	66(24)	
C9A	2293(9)	−1103(9)	7655(15)	PD1	116(33)	6057(27)	6238(51)	0.1[a]
C10A	3509(9)	−1096(8)	6663(15)	PD2	784(34)	5805(28)	6162(52)	0.1
C11A	4279(9)	−833(8)	6504(15)	PD3	785(49)	5571(40)	4942(74)	0.07
C12A	4616(11)	−1160(9)	5464(16)	PD4	232(22)	5851(18)	5130(34)	0.13
C13A	5328(10)	−941(9)	5181(16)	PD5	−186(30)	6217(25)	3885(46)	0.1

a) Occupancy factor.

tion; 14641 reflections measured ($2.0 \leqslant 2\theta \leqslant 50.0°$), giving 7623 with $F > 3\sigma(F)$.

The structure was solved by direct method and Fourier technique, and refined by block-diagonal least-squares method. This gave the positions of six $[Co(L)NH_3]^+$ cations, five PF_6^- anions, and six lattice water molecules in the unit cell. At this stage, no remaining peaks as intense as those of a PF_6^- anion could be found. The remaining peaks were eventually assigned to five sites for disordered PF_6^- ion. It was not possible to locate the fluorine atoms of the PF_6^- ion. No attempts were made to locate hydrogen atoms. The weighting scheme was $w=[\sigma_{count}^2+(0.015|F_o|)^2]^{-1}$. Final R and R_w values are 0.093 and 0.167, respectively. The final difference Fourier synthesis showed no peaks higher than 1.3

e Å^{-3}. All the calculations were performed on HITAC M-680H computer of the Computer Centre of the Institute for Molecular Science with the UNICS-III, MULTAN 78, and ORTEP programs. The final atomic parameters are given in Table 1. The anisotropic thermal parameters and the F_o—F_c tables have been deposited as a Document No. 8759 at the Office of the Editor of Bull. Chem. Soc. Jpn.

Other Physical Measurements. Electronic spectra were recorded on a Shimadzu Multipurpose Spectrometer Model MPS-5000 in acetonitrile. Infrared spectra were recorded on a JASCO Infrared Spectrometer Model IR-810 on KBr disks or Nujol mulls. Cyclic voltammograms and differential pulse polarograms were obtained with a Yanagimoto P-1000 voltammetric analyzer in freshly distilled dichloromethane, using a three-electrode cell equipped with a glassy-carbon working electrode, a platinum coil auxiliary electrode, and a calomel electrode as the reference electrode. Tetrabutylammonium perchlorate (0.1 mol dm^{-3}) was added as the supporting electrode. All the potentials were normalized relative to the ferrocenium/ferrocene potential[24] added as the internal standard.

Results and Discussion

Electronic spectra of the complexes in acetonitrile are shown in Fig. 2. The spectrum of **1** is characterized by an absorption ($\varepsilon \approx 700$ dm^3 mol^{-1} cm^{-1}) at 16.9×10^3 cm^{-1}. A similar absorption is observed for five-coordinated salen-cobalt(III) complexes with a soft donor group such as an alkyl anion,[12,25-27] cyanide ion,[18] or triphenylphosphine[28] at the apical site. The spectrum, therefore, suggests the configuration of this complex to be of square-pyramid with the coordination of the pendant sulfur at the apex. The infrared spectrum of the complex indicates non-coordination of the perchlorate ion to the metal ($\nu(ClO_4) \approx 1100$ cm^{-1}).[29] The O-H stretching mode appears near 3400 cm^{-1} when measured on Nujol mulls. This implies that the water molecule is not coordinated but combined in the crystal lattice.[30] It is evident that the complex **1** retains the five-coordinate structure in solid state.

The crystal structure of **2** was determined by single crystal X-ray structure analysis in this study. The crystal contains three crystallographically independent $[Co(L)NH_3]^+$ cations (represented as **A**, **B**, and **C**) which show the essentially same structure. The molecular structure of A is shown in Fig. 3. Selected interatomic distances and bond angles of the cations are given in Table 2. The coordination geometry around the cobalt ion is a distorted octahedron with the thioether sulfur and the ammonia molecule at the apical positions. The in-plane Co-N and Co-O distances are in the range 1.880—1.917 Å, and are comparable to those of salen-complexes.[31] The ethylene chain of the salen skeleton adopts a gauche conformation with the pendant group at the axial orientation so as to allow the sulfur coordination to the metal ion with the Co-S distance of 2.244—2.268 Å. The S-Co-O(1), S-Co-O(2), S-Co-N(1), and S-Co-N(2) angles all are close to 90°, demonstrating that the Co-S bond

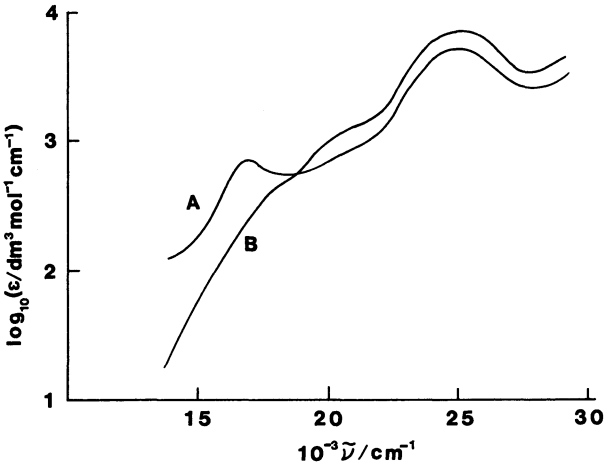

Fig. 2. Electronic spectra of (A) $[Co(L)]ClO_4 \cdot H_2O$ and (B) $[Co(L)NH_3]PF_6 \cdot H_2O$ in acetonitrile.

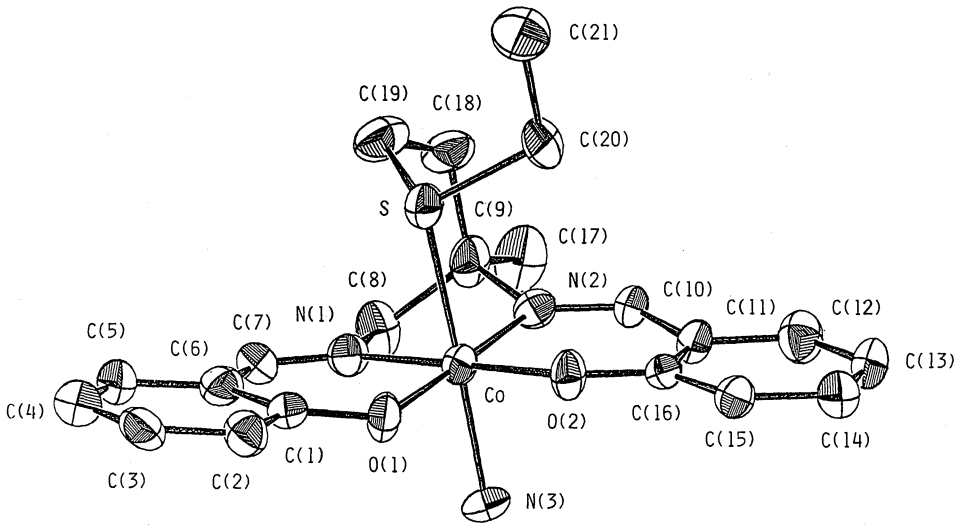

Fig. 3. ORTEP view of the cation **A** with the atomic numbering scheme.

Table 2. Selected Interatomic Distances (l/Å) and Bond Angles with Their Estimated Standard Deviations in Parentheses

	A	B	C
Co-S	2.269(6)	2.248(6)	2.244(6)
Co-O1	1.894(10)	1.915(12)	1.895(12)
Co-O2	1.893(11)	1.904(11)	1.883(12)
Co-N1	1.919(14)	1.881(15)	1.885(13)
Co-N2	1.897(11)	1.921(15)	1.893(14)
Co-N3	1.988(14)	2.016(14)	1.993(15)
S-Co-O1	89.5(4)	89.1(4)	89.1(4)
S-Co-O2	91.7(4)	92.2(4)	93.1(4)
S-Co-N1	88.3(5)	88.2(5)	88.9(4)
S-Co-N2	89.3(4)	91.2(5)	91.6(4)
S-Co-N3	178.1(4)	177.6(4)	177.1(4)
O1-Co-O2	84.8(5)	86.4(5)	85.7(5)
O1-Co-N1	94.0(5)	94.2(6)	94.8(5)
O1-Co-N2	178.8(6)	179.2(5)	179.2(6)
O1-Co-N3	89.4(5)	88.6(6)	88.4(6)
O2-Co-N1	178.8(5)	179.3(6)	178.0(6)
O2-Co-N2	95.4(5)	94.3(6)	94.2(6)
O2-Co-N3	89.7(5)	88.6(6)	88.2(6)
N1-Co-N2	85.8(6)	85.1(6)	85.4(6)
N1-Co-N3	90.3(6)	91.1(6)	89.9(6)
N2-Co-N3	91.8(5)	91.1(6)	90.9(6)

is nearly perpendicular to the least-squares plane defined by the Co, O(1), O(2), N(1), and N(2) atoms (N_2O_2 plane). The Co atom resides on the equatorial plane, the deviation of the cobalt atom from the N_2O_2 least square plane being less than 0.03 Å. The Co-N (NH_3) distance (1.987—2.012 Å) is essentially equivalent to the Co-N (pyridine) distance (2.031 Å) of [CH_3OCo(salen)py][32] and Co-N (amine) distance (2.01 Å) of [Co(salen)(n-BuNH_2)$_2$]$^+$ (n-BuNH_2=butylamine),[33] but significantly short compared with the Co-N (pyridine) bond (2.15 Å) of [Co(salen)py].[34]

In the related cobalt(II)[20,35] and iron(II)[35] complexes of *N,N'*-disalicylidene-4-(2-pyridyl)-1,2-butanediamine, the coordination of the pendant pyridyl group induces distortions of the MN_2O_2 moiety from square-plane to trigonal bipyramid. Because of this distortion the cobalt complex is high-spin. The cobalt(II) complex of H_2L ([Co(L)]), on the other hand, was revealed to be low-spin based on EPR spectra.[22] In the six-coordinate O_2-adduct, [*N,N'*-disalicylidene-4-(2-pyridyl)-1,2-butanediaminato]superoxocobalt(III),[36] the cobalt atom is still displaced towards the pendant pyridyl nitrogen from the equatorial plane. All these facts suggest that in metal complexes of H_2L the pendant sulfur can occupy the apical position without any significant strain when the salen skeleton coordinates to a metal in the usual planar manner.[31]

Cyclic voltammograms (CV) and differential pulse polarograms (DPP) of **1** and **2** were obtained in order to examine the sulfur coordination effect on their electrochemical properties. Both complexes showed two reduction waves but no oxidation wave up to +1.0 V (see Fig. 4). It is reasonable to assign the reduction

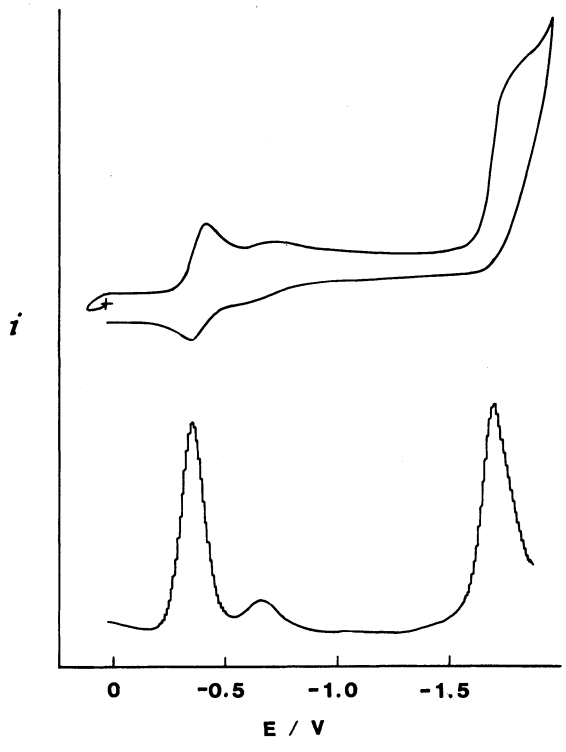

Fig. 4. Cyclic voltammogram (above) and differential pulse polarogram (below) of [Co(L)]$ClO_4 \cdot H_2O$ in dichloromethane ($\approx 1 \times 10^{-3}$ mol dm^{-3}); scan rate 0.1 V s^{-1} for both CV and DPP.

waves to the Co^{III}/Co^{II} and Co^{II}/Co^{I} processes, respectively.[37] The reduction potentials determined by DPP are given in Table 3. The Co^{III}/Co^{II} process of **1** is quasi-reversible: The separation between the anodic and cathodic peaks is 65 mV. On the other hand, the

Table 3. Redox Potentials of Cobalt(III) Complexes

	Co^{III}/Co^{II}	Co^{II}/Co^{I}
$[Co(L)]ClO_4$	−0.36	−1.70
$[Co(L)NH_3]PF_6$	−0.87	−1.77
$[Co(salen)(CH_3NH_2)_2]PF_6$	−1.03	−1.66
$[Co(salen)(C_2H_5NH_2)_2]PF_6$	−1.06	−1.64
$[Co(salen)(n\text{-}C_3H_7NH_2)_2]PF_6$	−1.00	−1.63

Determined by DPP in dichloromethane and given by V vs. $E(F_c^+/F_c)$.

corresponding process of **2** is irreversible where only anodic peak was observed in the CV spectrum. The Co^{II}/Co^{I} process is irreversible for both **1** and **2**. Esr investigations[2,7] have revealed that the cobalt(II) complexes of salen and its homologs adopt five-coordinate structure even in donative solvents such as pyridine. Such five-coordination has been proved for [Co(salen)py] by single-crystal X-ray analysis.[34] In the case of five-coordinate **1**, no structural change is necessitated to be reduced to the cobalt(II) species [Co(L)]. On the other hand, one of the apical donors (NH_3 or thioether) should be removed in the case of the reduction of **2** to the cobalt(II) species,[38] and such a structural change must be associated with the irreversible Co^{III}/Co^{II} process. The structure of the cobalt(I) species is presumably square planar because of its d^8-electronic configuration. Agin, the structural change on going from the five-coordinate cobalt(II) species to the four-coordinate cobalt(I) species must be the reason for the irreversibility of the Co^{II}/Co^{I} process. It is seen that the Co^{III}/Co^{II} potential of five-coordinate **1** is considerably high relative to the corresponding potential of six-coordinate **2**.

For comparison electrochemical measurements were also made for diamine(*N,N'*-disalicylideneethylenediaminato)cobalt(III) hexafluorophosphate, $[Co(salen)(R\text{-}NH_2)_2]PF_6$,[33] whose structures were shown to be pseudo-octahedral with the coordination of the amine molecules at the apical sites. They also showed two irreversible reductions waves. The reduction potentials determined by DPP are included in Table 3. Inspection of the electrochemical data of **2** and $[Co(salen)(R\text{-}NH_2)_2]PF_6$ indicates that the substitution of the thioether sulfur for the axial amine gives rise to a significant positive shift of the Co^{III}/Co^{II} potential. This is particularly interesting in view of redox potentials of cytochromes, where axial donor groups play an important role in controlling the redox potential required for the enzymes. It is generally known that the redox potential of cytochromes with two histidinyl residues as axial ligands is lower than that of cytochromes with one histidinyl and one methionyl axial ligands.[39]

References

1) T. Tsumaki, *Bull. Chem. Soc. Jpn.*, **13**, 252 (1938).
2) M. J. Carter, D. P. Rillema, and F. Basolo, *J. Am. Chem. Soc.*, **96**, 392 (1974).
3) D. Diemente, B. M. Hoffman, and F. Basolo, *J. Chem. Soc., Chem. Commun.*, **1970**, 467; B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Am. Chem. Soc.*, **92**, 61 (1970).
4) G. Amiconi, M. Brunori, E. Antonini, G. Tauzher, and G. Costa, *Nature (London)*, **228**, 549 (1970).
5) C. Floriani and F. Calderazzo, *J. Chem. Soc. A*, **1969**, 946.
6) A. Misono and S. Koda, *Bull. Chem. Soc. Jpn.*, **42**, 3048 (1969).
7) E. I. Ochiai, *J. Inorg. Nucl. Chem.*, **35**, 1727 (1973).
8) C. Busetto, C. Neri, N. Palladino, and E. Perrotti, *Inorg. Chim. Acta*, **5**, 129 (1971).
9) R. S. Gall and W. P. Schaefer, *Inorg. Chem.*, **15**, 2758 (1976).
10) A. Avdeef and W. P. Schaefer, *J. Am. Chem. Soc.*, **98** 5153 (1976).
11) E. Cesarotti, M. Gullotti, A. Pasini, and R. Ugo, *J. Chem. Soc., Dalton Trans.*, **1977**, 757.
12) G. Costa, G. Mestroni, and L. Stefani, *J. Organomet. Chem.*, **7**, 493 (1967).
13) G. Costa, G. Mestroni, and G. Pellizer, *J. Organomet. Chem.*, **11**, 333 (1968).
14) L. H. Vogt, Jr., J. G. Wirth, and H. L. Finkbeiner, *J. Org. Chem.*, **34**, 273 (1969).
15) T. J. Fullerton and S. P. Ahern, *Tetrahedron Lett.*, **1976**, 139.
16) A. Nishinaga, K. Watanabe, and T. Matsuura, *Tetrahedron Lett.*, **1974**, 1291.
17) A. Nishinaga, *Chem. Lett.*, **1975**, 273.
18) Y. Aimoto, W. Kanda, S. Megura, Y. Miyahara, H. Ōkawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **58**, 646 (1985).
19) A. R. Amundsen, J. Whelan, and B. Bosnich, *Inorg. Chem.*, **18**, 206 (1979).
20) J. P. Collman, H. Takaya, B. Winkler, L. Libit, S. S. Koon, G. A. Rodley, and W. T. Robinson, *J. Am. Chem. Soc.*, **95**, 1656 (1973).
21) W. Kanda, H. Ōkawa, and S. Kida, *Bull. Chem. Soc. Jpn.*, **56**, 3268 (1983).
22) K. Nakamoto, H. Oshio, H. Ōkawa, W. Kanda, K. Horiuchi, and S. Kida, *Inorg. Chim. Acta*, **108**, 231 (1985).
23) H. Ōkawa, K. Horiuchi, W. Kanda, H. Oshio, and S. Kida, *Bull. Chem. Soc. Jpn.*, **59**, 2795 (1986).
24) R. R. Gagne, C. A. Koval, and G. C. Lisensky, *Inorg. Chem.*, **19**, 2854 (1980).
25) M. Calvin, R. H. Bailes, and W. K. Wilmarth, *J. Am. Chem. Soc.*, **68**, 2254 (1946).
26) R. H. Bailes and M. Calvin, *J. Am. Chem. Soc.*, **69**, 1886 (1947).
27) M. Calvin and C. H. Barkelew, *J. Am. Chem. Soc.*, **68**, 2267 (1946).
28) C. W. Smith, G. W. Van Loon, and M. C. Baird, *Can. J. Chem.*, **54**, 1875 (1976).
29) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, John-Wiley & Sons, New York (1970), p. 176.
30) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, John-Wiley & Sons, New York (1970), p. 166.
31) M. Calligaris, G. Nardin, and L. Randaccio, *Coord. Chem. Rev.*, **7**, 385 (1972).
32) M. Cesari, C. Neri, G. Perego, E. Perrotti, and A. Zazzetta, *J. Chem. Soc., Chem. Commun.*, **1970**, 276.

33) S. Maeda, M. Nakamura, M. Mikuriya, T. Shinmyozu, H. Ōkawa, and S. Kida, *Mem. Fac. Sci., Kyushu Univ., Ser. C*, **15(1)**, 63 (1985).
34) M. Calligaris, D. Minichelli, G. Nardin, and L. Randaccio, *J. Chem. Soc. A*, **1970**, 2411.
35) G. B. Jameson, F. C. March, W. T. Robinson, and S. S. Koon, *J. Chem. Soc., Dalton Trans.*, **1978**, 185.
36) G. B. Jameson, W. T. Robinson, and G. A. Rodley, *J. Chem. Soc., Dalton Trans.*, **1978**, 191.
37) D. F. Averill and R. F. Broman, *Inorg. Chem.*, **17**, 3389 (1978).
38) J. Hanzlik, A. Puxeddu, and G. Costa, *J. Chem. Soc., Dalton Trans.*, **1977**, 542.
39) A. V. Xavier, "The Coordination Chemistry of Metalloenzymes," ed by I. Bertini, R. S. Drago, and C. Luchinat, D. Reidel Publishing Co., Holland (1983), p. 291.