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Synthesis and Crystal Structure of Cobalt(III) Complex with Chiral Pentadentate Bis-Amide Ligand, 1,9-bis(S)-pyrrolidinyl-2,5,8-triazanonane-1,9-dione(S,S-prodienH₂)

Bae-Wook Lee, Chang-Eon Oh, and Myung-Ki Doh*

Department of Chemistry, Yeungnam University, Kyongsan 712-749, Korea
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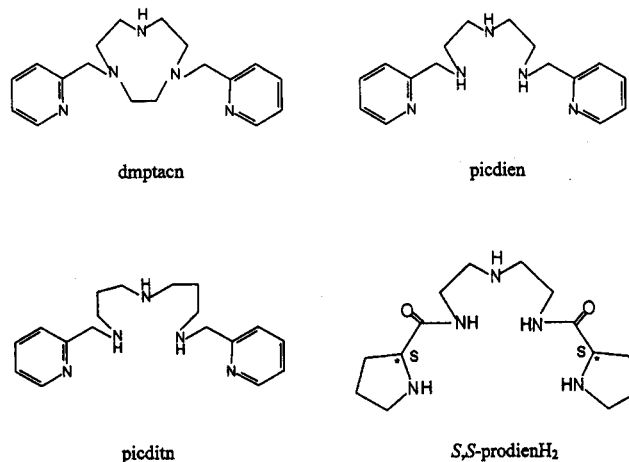
A chiral pentadentate bis-amide ligand, 1,9-bis(S)-pyrrolidinyl-2,5,8-triazanonane-1,9-dione(S,S-prodienH₂) has been synthesized from the reaction of bis(2-aminoethyl)amine(dien) and S-proline, and the structure of $[\text{Co}(\text{S},\text{S}\text{-prodien})\text{H}_2\text{O}]\text{ClO}_4$ has been determined by single crystal X-ray diffraction. The geometrical structure of the Co(III) complex has been an $\alpha\beta$ -form, where the dien moiety of ligand chelates to a facial in metal center, and the aqua ligand coordinates a *cis* site to the secondary nitrogen of dien. The Co-N(1), Co-N(3) distances of two amide moiety in S,S-prodien are shorter than the other Co-N(2), Co-N(4), and Co-N(5) distances because of the increased basicity of nitrogen in amide. The complex crystallizes in the monoclinic space group $\text{P}2_1(\#4)$, with $a=7.838(1)$, $b=12.675(1)$, $c=9.710(1)$ Å, $\beta=100.39(1)$ and $z=2$. Refinement gives the final R and R_w values of 0.045 and 0.057, respectively for 2130 observed reflections. Based upon the CD and X-ray data, it is identified that the absolute configuration of the $\alpha\beta$ - $[\text{Co}(\text{S},\text{S}\text{-prodien})\text{H}_2\text{O}]\text{ClO}_4$ has a Λ -form.

Introduction

Asymmetric synthesis and optical resolution of coordination compounds of multidentate ligands with nitrogen donor atoms are well known.¹ Particularly, chiral metal complexes with tetradentate ligands are well documented² but relatively few complexes have pentadentate ligands coordinated to metal ion. Recently, McLachlan *et al.*³ have reported the coordination chemistry of pentadentate ligands derived from the tripod ligand tris(2-aminoethyl)amine(tren) and 1,4,7-triazacyclononane(tacn). Pyridyl arms have been attached to tren forming the pentadentate ligands, 3-[4-(2-pyridyl)-3-azabut-3-enyl]-3-azapentane-1,5-diamine(L1) and 3-[4-(2-pyridyl)-3-azabutyl]-3-azapentane-1,5-diamine(L2), which have been applied in the synthesis of mononuclear and azido bridged binuclear nickel(II) complexes.⁴ The preparation and properties of Co(III) complexes with L1 and L2 ligand have been reported, along with the amide complex, $[\text{Co}(\text{HL}3)\text{Cl}]^{2+}$ (HL3=3-{2-[hydroxy(2-pyridyl)methylene-amino]ethyl}-3-azapentane-1,5-diamine) was obtained through oxidation of $[\text{Co}(\text{L}1)\text{Cl}]^{2+}$. Amed *et al.*⁵ have been reported the Co(III) complexes of pentadentate ligands, 1,9-bis(2'-pyridyl)-2,5,8-triazanonane(picdien) and 1,11-bis(2'-pyridyl)-2,6,10-triazaundecane(picdtn), which have pyridyl arms in dien[=bis(2-aminoethyl)amine] and ditn[=bis(3-aminopropyl)amine]. The geometrical structure of the Co(III) complexes of picdien and picdtn ligand have been an $\alpha\beta$ -form which the dien moiety of ligand chelates to a facial site in metal center, and aqua ligand coordinates a *cis* site to the secondary nitrogen of dien. In $\alpha\beta$ -Co(III) complexes

of picdien both *syn* and *anti* forms are found, while only the *anti* forms in the picdtn complexes have been isolated. The structures have been established by single-crystal X-ray diffraction. Also, Williams *et al.*⁶ have prepared and investigated the stereoselectivity of the Co(III) complex of pentadentate ligand, 3*S*-di(2-picolyl)-amino-N-(2-picolyl) hexahydroazepine(S-ahazterpy), with one chiral center. $[\text{Co}(\text{S-ahazterpy})\text{Cl}](\text{ClO}_4)_2 \cdot 2\text{H}_2\text{O}$ has been obtained to single isomer(*trans*-equatorial) that the tertiary amine has fixed stereochemistry by the *S*-chirality in the heterocyclic ring of the S-ahaz(3*S*-aminohexahydroazepine) unit.

In this paper we present the preparation and structure of Co(III) complex with 1,9-bis(S)-pyrrolidinyl-2,5,8-triazanon-



ane-1,9-dione(*S,S*-prodien). The *S,S*-prodienH₂ is a linear chiral pentadentate bis-amide ligand that has not only two chiral center in *S*-proline moiety but also two amide group by the peptide bond between the dien and *S*-proline. Thus, *S,S*-prodien will provide a high stereoselectivity when coordinated to the Co(III) metal ion.

Experimental

Electronic absorption and CD spectra were measured using a HP 8452 spectrophotometer and Jasco J-715 spectropolarimeter, respectively. ¹³C NMR spectra were recorded with a Bruker (300 MHz) in D₂O, using DSS (sodium 2,2-dimethyl-2-silapentane sulfonate) as internal standard. Elemental analysis was carried out by Perkin Elmer 240-C. All materials were of reagent grade and were used without further purification.

Preparation of *S,S*-prodienH₂ ligand. Carbobenzoxy-(*S*)-proline was prepared from (*S*)-proline (0.2 mol, 23.0 g) and carbobenzoxy chloride (cbz-Cl) (0.24 mol, 40.9 g) according to the method of Corey et al.⁷ *N,N'*-bis(carbobenzoxy-(*S*)-prolyl)diethylenetriamine was prepared from the Carbobenzoxy-(*S*)-proline (0.12 mol, 30.0 g) and dien (0.24 mol, 24.8 g) by using of dicyclohexylcarbodiimide

(DCC) as coupling reagent in dichloromethane. The *S,S*-prodienH₂ was obtained from decarbobenzoylation⁸ of *N,N'*-bis(carbobenzoxy-(*S*)-prolyl)diethylenetriamine in methanol. Yield of oil phase was ca. 60%.

Preparation of Λ - $\alpha\beta$ -[Co(*S,S*-prodien)H₂O]ClO₄. *S,S*-prodienH₂ (5 mmol, 2.4 g) and CoCl₂·6H₂O (5 mmol, 1.2 g) were dissolved in 50 mL water and pH was maintained at 8.0, and then the mixture was oxidized by air bubbling for 24 hr. The solution was then diluted to 500 mL and adsorbed onto a cation exchange resin (SP Sephadex C 25) column. After the column was washed thoroughly with water, adsorption bands were separated with 0.1 M NaClO₄. The solution was evaporated to a volume of ca. 50 mL and on leaving overnight in a refrigerator, crude crystals of purple Λ - $\alpha\beta$ -[Co(*S,S*-prodien)H₂O]ClO₄ precipitated. A purple precipitate (1.15 g) was collected by filtration. Crystals suitable for single-crystal X-ray diffraction were recrystallized by dissolving in the minimum volume of hot water, yield 48%. Calc. for CoC₁₄H₂₇N₅O₇Cl ([Co(C₁₄H₂₅N₅O₂)OH₂]ClO₄): C, 35.64; H, 5.77; N, 14.84. Found: C, 35.32; H, 6.10; N, 14.59.

X-ray data collection. The preliminary experiments as well as unit cell parameters and intensity data collection were performed on a Enraf Nonius CAD4 TURBO dif-

Table 1. Summary of Crystallographic Data and Intensity Collection for Λ - $\alpha\beta$ -[Co(*S,S*-prodien)H₂O]ClO₄

Empirical formula	CoC ₁₄ H ₂₇ N ₅ O ₇ Cl
Formula weight	471.09
Crystal system	Monoclinic
Space group	<i>P</i> 2 ₁ (#4)
Z	2
Cell parameters	
<i>a</i> (Å)	7.838(1)
<i>b</i> (Å)	12.675(1)
<i>c</i> (Å)	9.710(1)
β (°)	100.39(1)
<i>V</i> (Å ³)	948.8(2)
D _{calc} (gcm ⁻³)	1.170
μ (cm ⁻¹ with Mo-Kα)	7.2
Transmission factor	88.0459-92.2743
Scan type	ω-2θ
Scan width(ω)(deg)	0.80+0.50tan(θ)
2θ _{max} (deg)	52.64
No. of reflections measured	2130
No. of reflections observed	1800
(<i>I</i> > 3σ(<i>I</i>))	
<i>F</i> (000)	486
No. of variable	252
Discrepancy indices	
<i>R</i> ^a	0.0446
<i>R</i> _w ^b	0.0565
Goodness of fit indicator ^c	1.74
Max. shift in final cycles	less than 0.01

^a $R = \sum |F_o - |F_c|| / \sum F_o$. ^b $R_w = [(\sum w(F_o - |F_c|)^2) / \sum w(F_o^2)]^{1/2}$, where, $w = [(\sigma(F^2))]^{-1}$. ^c Estimated standard deviation of an observation of unit weight: $[\sum w(F_o - |F_c|)^2 / (N_o - N_v)]^{1/2}$, where N_o = Number of observations and N_v = Number of variables. R^a , R_w^b = When the eta parameter is +1. (When the eta parameter is -1; R^a and R_w^b = 0.0464 and 0.0587).

Table 2. Positional and Isotropic Equivalent Thermal Parameters (Å²) and Their Estimated Standard Deviations for Λ - $\alpha\beta$ -[Co(*S,S*-prodien)H₂O]ClO₄

Atom	x	y	z	B(Å ²) ^a
Co(1)	0.65503(9)	0.124	0.34312(7)	1.68(1)
Cl(1)	0.8051(3)	-0.4538(2)	0.0794(2)	4.07(4)
O(1)	0.4261(6)	0.560(4)	0.2796(5)	2.8(1)
O(2)	0.4117(7)	0.3590(5)	0.5020(6)	4.4(1)
O(3)	1.1660(5)	0.1113(7)	0.3921(5)	4.4(1)
O(4)	0.935(1)	-0.5274(9)	0.089(2)	13.4(5)
O(5)	0.644(1)	-0.4902(7)	0.0054(8)	7.7(2)
O(6)	0.800(1)	-0.445(1)	0.2167(9)	13.8(4)
O(7)	0.859(1)	-0.3641(7)	0.021(1)	9.5(2)
N(1)	0.5518(7)	0.2559(5)	0.3662(6)	2.6(1)
N(2)	0.6188(6)	0.0989(4)	0.5384(5)	2.0(1)
N(3)	0.8887(6)	0.1691(5)	0.3840(5)	2.5(1)
N(4)	0.7594(7)	-0.0166(5)	0.3314(5)	2.2(1)
N(5)	0.6656(7)	0.1842(5)	0.1517(6)	2.5(1)
C(1)	0.521(1)	0.2620(7)	0.1192(8)	3.9(2)
C(2)	0.515(1)	0.3283(7)	0.2469(7)	3.5(2)
C(3)	0.488(1)	0.2773(6)	0.4800(6)	2.6(1)
C(4)	0.5043(8)	0.1857(6)	0.5825(6)	2.4(1)
C(5)	0.588(1)	0.2181(7)	0.7349(7)	3.4(2)
C(6)	0.6946(9)	0.124(1)	0.7864(6)	3.5(1)
C(7)	0.770(1)	0.0870(7)	0.6591(7)	3.4(2)
C(8)	0.918(1)	0.2634(7)	0.3064(8)	3.7(2)
C(9)	0.839(1)	0.2345(7)	0.1548(7)	3.4(1)
C(10)	1.0063(8)	0.0954(7)	0.3971(7)	3.2(2)
C(11)	0.9433(8)	-0.0160(6)	0.4073(7)	2.9(1)
C(12)	1.043(1)	-0.0983(8)	0.3370(9)	4.4(2)
C(13)	0.898(1)	-0.1493(9)	0.222(1)	6.5(3)
C(14)	0.767(1)	-0.0658(7)	0.1921(8)	3.6(2)

^a Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as: $(4/3) * [a^{2*} \beta_{11} + b^{2*} \beta_{22} + c^{2*} \beta_{33} + ab(\cos \gamma) \beta_{12} + ac(\cos \beta) \beta_{13} + bc(\cos \alpha) \beta_{23}]$.

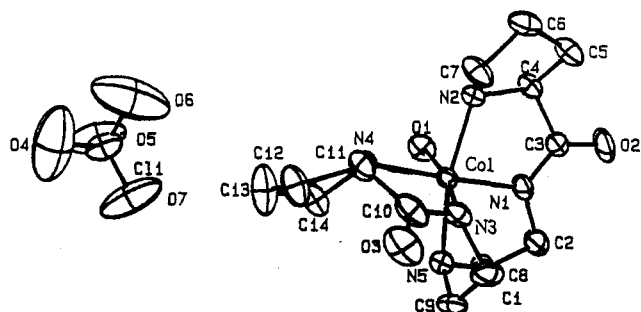


Figure 1. Perspective drawing and atomic numbering scheme for the Λ - $\alpha\beta$ - $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]\text{ClO}_4$.

fractometer with a graphite-monochromatized Mo- $K\alpha$ radiation ($\lambda=0.71069$ Å). The intensity data were collected by the ω - 2θ scan technique. A total of 2130 reflections up to $2\theta_{\text{max}}=60^\circ$ were collected, of which 1800 independent reflections with $I > 3\sigma(I)$ were used for the structure analysis. Crystallographic data and additional details of data collection and structure determination are summarized in Table 1. The structure was solved by MULTAN and refined by a full matrix least-squares refinement, using structure solution package MolEN.⁹ The neutral atomic scattering factors for all the non-hydrogen atoms were taken from the literature.¹⁰ The final error indices were $R=0.045$ and $R_w=0.057$, respectively. The final positional parameters are given in Table 2. Perspective drawing of the complex cation obtained is

Table 3. Bond Angle (deg) and Their Estimated Standard Deviations (in parentheses) for Λ - $\alpha\beta$ - $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]\text{ClO}_4$

O(1)—Co(1)—N(1)	92.2(2)	Co(1)—N(1)—C(3)	121.0(5)
O(1)—Co(1)—N(2)	87.1(2)	C(2)—N(1)—C(3)	119.0(6)
O(1)—Co(1)—N(3)	169.4(2)	Co(1)—N(2)—C(4)	110.1(4)
O(1)—Co(1)—N(4)	87.1(2)	Co(1)—N(2)—C(7)	121.7(4)
O(1)—Co(1)—N(5)	93.6(2)	C(4)—N(2)—C(7)	105.8(5)
N(1)—Co(1)—N(2)	83.8(2)	Co(1)—N(3)—C(8)	112.2(4)
N(1)—Co(1)—N(3)	97.3(3)	Co(1)—N(3)—C(10)	116.5(4)
N(1)—Co(1)—N(4)	176.1(2)	C(8)—N(3)—C(10)	117.7(6)
N(1)—Co(1)—N(5)	82.2(2)	Co(1)—N(4)—C(11)	109.8(4)
N(2)—Co(1)—N(3)	82.2(2)	Co(1)—N(4)—C(14)	120.8(4)
N(2)—Co(1)—N(4)	92.4(2)	C(11)—N(4)—C(14)	104.8(5)
N(2)—Co(1)—N(5)	166.0(2)	Co(1)—N(5)—C(1)	106.8(5)
N(3)—Co(1)—N(4)	83.6(2)	Co(1)—N(5)—C(9)	109.3(4)
N(3)—Co(1)—N(5)	83.1(2)	C(1)—N(5)—C(9)	111.9(6)
N(4)—Co(1)—N(5)	101.6(2)	N(5)—C(1)—C(2)	109.2(6)
O(4)—Cl(1)—O(5)	113.3(6)	N(1)—C(2)—C(1)	105.8(6)
O(4)—Cl(1)—O(6)	98.6(9)	O(2)—C(3)—N(1)	125.8(7)
O(4)—Cl(1)—O(7)	108.0(7)	O(2)—C(3)—C(4)	120.9(7)
O(5)—Cl(1)—O(6)	110.3(6)	N(1)—C(3)—C(4)	113.1(6)
O(5)—Cl(1)—O(7)	112.0(5)	N(2)—C(4)—C(3)	110.5(5)
O(6)—Cl(1)—O(7)	114.0(7)	N(2)—C(4)—C(5)	106.8(5)
Co(1)—N(1)—C(2)	119.1(5)	C(3)—C(4)—C(5)	113.0(6)
C(4)—C(5)—C(6)	102.8(6)	N(3)—C(10)—C(11)	116.4(6)
C(5)—C(6)—C(7)	104.5(6)	N(4)—C(11)—C(10)	105.7(5)
N(2)—C(7)—C(6)	103.3(5)	N(4)—C(11)—C(12)	107.3(6)
N(3)—C(8)—C(9)	103.1(6)	C(10)—C(11)—C(12)	114.2(6)
N(5)—C(9)—C(8)	109.3(6)	C(11)—C(12)—C(13)	103.7(7)
O(3)—C(10)—N(3)	124.4(8)	C(12)—C(13)—C(14)	103.3(8)
O(3)—C(10)—C(11)	119.1(7)	N(4)—C(14)—C(13)	105.3(7)

Table 4. Bond Distances (Å) and Their Estimated Standard Deviations (in parentheses) for Λ - $\alpha\beta$ - $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]\text{ClO}_4$

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Co(1)—O(1)	1.986(4)	N(3)—C(8)	1.45(1)		
Co(1)—N(1)	1.888(6)	N(3)—C(10)	1.303(9)		
Co(1)—N(2)	1.993(5)	N(4)—C(11)	1.496(8)		
Co(1)—N(3)	1.891(5)	N(4)—C(14)	1.50(1)		
Co(1)—N(4)	1.974(6)	N(5)—C(1)	1.49(1)		
Co(1)—N(5)	2.024(6)	N(5)—C(9)	1.49(1)		
Cl(1)—O(4)	1.37(1)	C(1)—C(2)	1.51(1)		
Cl(1)—O(5)	1.414(7)	C(3)—C(4)	1.52(1)		
Cl(1)—O(6)	1.346(9)	C(4)—C(5)	1.561(9)		
Cl(1)—O(7)	1.37(1)	C(5)—C(6)	1.49(1)		
O(2)—C(3)	1.23(1)	C(6)—C(7)	1.54(1)		
O(3)—C(10)	1.277(8)	C(8)—C(9)	1.54(1)		
N(1)—C(2)	1.464(9)	C(10)—C(11)	1.50(1)		
N(1)—C(3)	1.320(9)	C(11)—C(12)	1.53(1)		
N(2)—C(4)	1.529(9)	C(12)—C(13)	1.58(1)		
N(2)—C(7)	1.517(8)	C(13)—C(14)	1.46(1)		

shown in Figure 1. The bond angles and lengths with their estimated standard deviations in the complex are summarized in Table 3 and 4.

Results and Discussion

$[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]\text{ClO}_4$ was prepared in reasonable yield by the air oxidation of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ and S,S-prodienH_2 mixtures in water. Elemental analysis indicated that the purple product was $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]\text{ClO}_4$. The UV/Vis spectrum of $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]\text{ClO}_4$ in water shows a similar absorption band of Co(III) complex with $\text{Co}^{\text{III}}\text{N}_5\text{O}$ chromophore (see Table 5).¹¹ Possible geometric isomers of $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]\text{ClO}_4$ with linear pentadentate bis-amide ligand are shown in Figure 2. McLachlan *et al.*³ have reported that tacn moiety in $[\text{Co}(\text{dmptacn})(\text{H}_2\text{O})](\text{ClO}_4)_3$ of pentadentate ligands derived from tacn has coordinated to facial form. Amed *et al.*⁵ have shown that complexes of $[\text{Co}(\text{picdien})\text{X}](\text{ClO}_4)_2$ and $[\text{Co}(\text{picditm})\text{X}](\text{ClO}_4)_2$ [picdien=1,9-bis(2'-pyridyl)-2,5,8-triazanonane, picditm=1,11-bis(2'-pyridyl)-2,6,10-triazaundecane; X=Cl, Br, NO_2 , NCS, N_3 , MeCO_2 , or H_2O] have only the $\alpha\beta$ configuration. The $\alpha\beta$, $\alpha\alpha^*$ -configuration indicated that amine backbones of ligands chelate to a facial form in the metal center. In this case, $\alpha\beta$ indicates that the monodentate ligand coordinates *cis* site to the secondary nitrogens of dien and $\alpha\alpha^*$ coor-

Table 5. UV/Vis spectral data for N_5O type Co^{III} complexes

Complexes	$\lambda_{\text{max}}/\text{nm}$	Ref.
Λ - β - $[\text{Co}(\text{R,R-L})(\text{R-ala})]^+$	505	11(a)
Δ - α - $[\text{Co}(\text{R,R-L})(\text{S-ala})]^{2+}$	505	11(b)
Λ - α - $[\text{Co}(\text{S,S-picchxnMe}_2)(\text{S-pro})]^{2+}$	508	11(c)
Λ - α - $[\text{Co}(\text{S,S-picchxnMe}_2)(\text{rac-ala})]^{2+}$	500	11(c)
Λ - $\alpha\beta$ - $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]^+$	507	this study

$\text{R,R-L}=3\text{R},4\text{R}$ -diphenyl-1,6-di(2-pyridyl)-2,5-diazahexane. $\text{R-L}=\text{N,N}'$ -dimethyl-3R-methyl-1,6-di(2-pyridyl)-2,5-diazahexane. $\text{S,S-picchxnMe}_2=\text{N,N}'$ -dimethyl-N,N'-di(2-picolyl)-1S,2S-diaminocyclohexane.

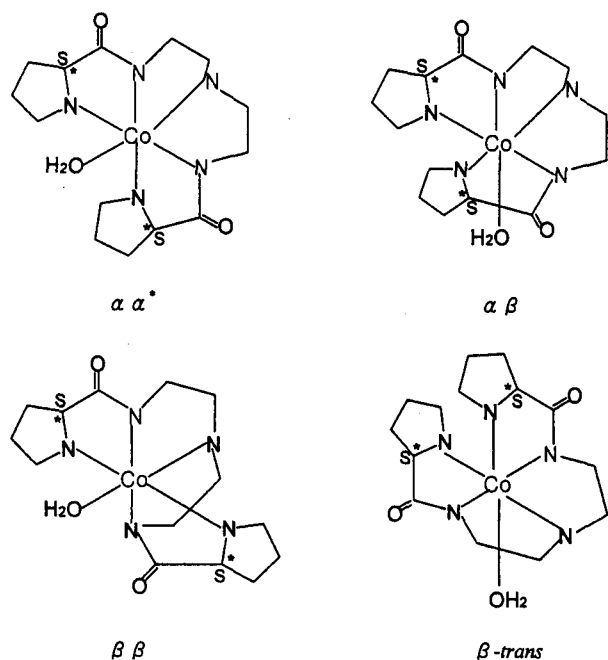


Figure 2. The possible isomers for $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]\text{ClO}_4$.

dinates *trans* site. Based upon these results, it seems that $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]\text{ClO}_4$ may be $\alpha\alpha^*$ or $\alpha\beta$ configuration that dien moiety of ligand coordinates to facial as shown in Figure 2.

A feature of the ^{13}C NMR spectrum of $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]\text{ClO}_4$ is that distinct signals are observed for each carbon on the ligand. There are ten resonances between δ 27.0–58.5 for the methylene carbons, two resonances at δ 67.0, 70.0 for the chiral carbon on the pendant pyrrolidinyl group, two resonances at δ 182.5, and 188.9 for the carbonyl carbon on the *S,S*-prodien ligand. But the ^{13}C NMR spectrum of the free ligand shows only half the number of resonances, which indicates that the ligand has C_2 symmetry (see Figure 3). McLachlan *et al.*³ reported that ^{13}C NMR spectrum of $\alpha\alpha^*[\text{Co}(\text{dmptacn})\text{H}_2\text{O}]\text{ClO}_4$ [dmptacn=1,4-bis(2-pyridylmethyl)-1,4,7-triazacyclononane] shows only half the number of free ligand, but the $\alpha\beta[\text{Co}(\text{dmptacn})\text{H}_2\text{O}]\text{ClO}_4$ shows as same as the free ligand. The fact that this symmetry is lost in the Co^{III} complex indicates that the aqua ligand coordinates *cis* to the secondary amine on the tacn ring. Although ^{13}C NMR spectrum of $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]\text{ClO}_4$ shows all fourteen carbon resonances on the *S,S*-prodien ligand, the exact topology ($\alpha\alpha^*$ or $\alpha\beta$) of the complex was difficult to determine because of the puckered pyrrolidinyl ring.

The Circular Dichroism (CD) spectrum for the $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]\text{ClO}_4$ is shown in Figure 4. The CD spectrum of $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]\text{ClO}_4$ in visible absorption region shows two separated maximum bands for the $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ ($\lambda=554$ nm, $\Delta\epsilon_{\text{max}}=+2.2$ $\text{dm}^2\text{mol}^{-1}$) and $^1\text{A}_{1g} \rightarrow ^1\text{T}_{2g}$ ($\lambda=479$ nm, $\Delta\epsilon_{\text{max}}=-1.76$ $\text{dm}^2\text{mol}^{-1}$) transition. These split in octahedral parentage indicates the loss of degeneracy in the excited states expected for a low symmetry species such as the present complex. In $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]\text{ClO}_4$, asymmetry nitrogens in pyrrolydyl rings have a fixed stereochemistry as a consequence of the *S* chiral carbon in pyrrolydyl ring.

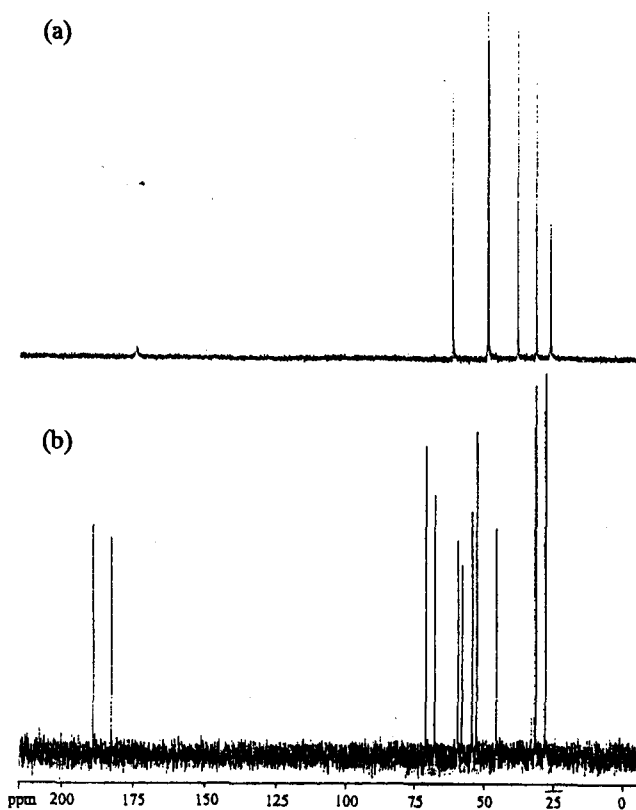


Figure 3. (a) ^{13}C NMR spectrum of *S,S*-prodien ligand. (b) ^{13}C NMR spectrum of $\Lambda\text{-}\alpha\beta\text{-}[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]\text{ClO}_4$.

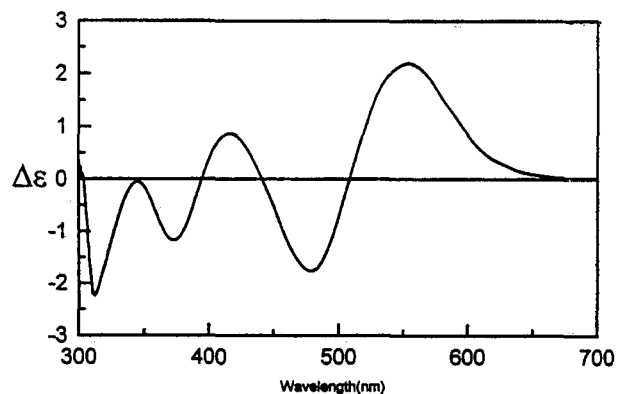


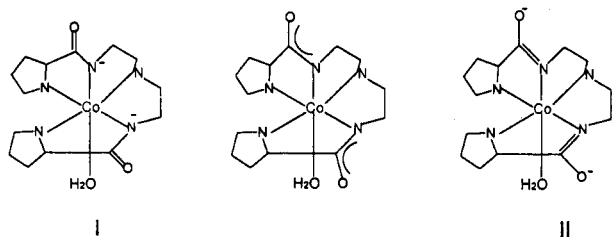
Figure 4. The CD spectrum of $\Lambda\text{-}\alpha\beta\text{-}[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]\text{ClO}_4$.

This is assumed to dominate the visible CD spectrum. The absolute configurations of the optically active isomers with polydentate ligands have been assigned according to the sign of the dominant CD component at the first absorption band region, that is, the plus sign to the Λ configuration.¹² In this complex, although it is difficult to assign the correct absolute configuration from only the CD spectrum, which has been a Λ configuration is expected due to the stereospecificity of *S,S*-prodien. Based upon the eta parameter (Table 1) of the X-ray analysis data, we confirmed that the $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]$ has the Λ configuration by chelate ring method.¹³

Figure 1. shows a perspective drawing of the $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]\text{ClO}_4$ which is the major constituent for the molecular cation, together with the atom labelling scheme.

In this figure the cobalt atom has distorted octahedral coordination with the *S,S*-prodien adopting a $\alpha\beta$ -topology, and with an aqua ligand is a *cis* site to the secondary amines of dien moiety. Bond angles (Table 3) of *trans* position in this complex, N(2)-Co-N(5); 166.0° , O(1)-Co-N(3); 169.4° and N(4)-Co-N(1); 176.1° are smaller than those of a normal octahedral complexes. The structure is thus similar to that of $\alpha\beta$ - $[\text{Co}(\text{picdien})\text{Cl}]^{2+}$ with significantly distorted octahedral geometry.

The Co-N(1), N(3), N(5), Co-N(2), N(4) and Co-OH₂ bond distances (Table 4) in $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]^+$ are different to the corresponding distances⁵ in $[\text{Co}(\text{picdien})\text{H}_2\text{O}]^{3+}$ [average; 1.938, 1.954 and 1.951 Å] and $[\text{Co}(\text{dmptacn})\text{H}_2\text{O}]^{3+}$ [average; 1.930, 1.921 and 1.945 Å] respectively. Also, the Co-N(5) (2.024 Å) bond length in $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]^+$ is similar to the corresponding distances in some other Co^{III} complexes of pendant arm ligands derived from tacn, viz. $[\text{Co}(\text{daptacn})\text{Cl}]^{2+}$ [1.987(7) Å] and $[\text{Co}(\text{taptacn})\text{Cl}]^{3+}$ [2.025(7) Å] [daptacn=1,4-bis(3-aminopropyl)-1,4,7-triazacyclononane, taptacn=1,4,7-tris(3-aminopropyl)-1,4,7-triazacyclononane], but the Co-N(1), (3) (1.888, 1.891 Å) bond lengths are significantly shorter than those in $[\text{Co}(\text{picdien})\text{H}_2\text{O}]^{3+}$, $[\text{Co}(\text{daptacn})\text{Cl}]^{2+}$ and $[\text{Co}(\text{taptacn})\text{Cl}]^{3+}$.^{5,14,15} The large difference in bond distances of Co-N(5) and Co-N(1), N(3) suggest that the basicity of nitrogen in the bisamide moiety of *S,S*-prodien is increased. On the other hand, the bond lengths of two amide portion in $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]^+$ are N(1)-C(3); 1.320, N(3)-C(10); 1.303, C(3)-O(2); 1.230, C(10)-O(3); 1.277 Å and Co-N(1); 1.888, Co-N(3); 1.891 Å. If hydrogen in amide-N is deprotonated, amide group is expected to the negative charge that would be delocalized along the amide C-N and C-O bonds. In this case, two resonance forms have different C-N and C-O bond length.¹⁶ In the resonance form I, C-N has single bond character, C-O double bond character and the Co-N (amide) bond is relatively short. Conversely, in the resonance form II, C-N has double bond character, C-O single bond character and the Co-N (amide) bond is longer. These bonds can also be intermediate between double and single bonds. In a $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]\text{ClO}_4$, the amide C-N and C-O bond



lengths are not consistent with either of these resonance forms. However, the amide C(3)-O(2), C(10)-O(3) bond lengths, 1.230, 1.277 Å, are close to that expected for a normal value of C=O (≈ 1.20 Å) bond length.¹⁷ Thus, Co-N(1), N(3) bond lengths in a $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]\text{ClO}_4$ are much shorter than the other Co-N bonds indicating significant contribution from resonance form I. From this result, we could identify that the charge of Co(III) complex with *S,S*-prodien is +1 cation.

Therefore, the geometrical structure of $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]\text{ClO}_4$ with chiral pentadentate bis-amide ligand, *S,S*-prodien has $\alpha\beta$ -form, in which the dien moiety of ligand che-

lates to a facial form in metal center, while the aqua ligand coordinates a *cis* site to the secondary nitrogen of dien. The absolute configuration of the $\alpha\beta$ - $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]\text{ClO}_4$ is identified to a Λ -form by the single crystal X-ray diffraction and CD spectral data. And, in this complex the Co-N (amide) distances are shorter than the other Co-N distances because the basicity of nitrogen in amide moiety of *S,S*-prodien is increased. This fact indicates that the charge of the Λ - $\alpha\beta$ - $[\text{Co}(\text{S,S-prodien})\text{H}_2\text{O}]\text{ClO}_4$ is +1 cation via the contribution of the resonance form I.

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Novel Counter Ion Effect on the Disruption of the Homobimetallic Anion, $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5\text{-M}^+$ ($\text{M}^+=\text{Na}^+$, PPN^+) by PR_3 ($\text{R}=\text{C}_6\text{H}_5$, C_2H_5 , OCH_3)

Yong Kwang Park*, Seon Joong Kim, and Chang Hwan Rhee

Department of Chemistry, Kangwon National University, Chuncheon 200-701, Korea

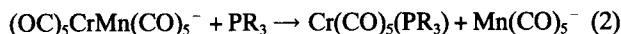
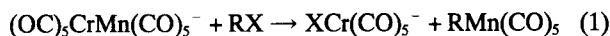
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The homobimetallic anion, $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5\text{-M}^+$ ($\text{M}^+=\text{Na}^+$, PPN^+) was disrupted by PR_3 ($\text{R}=\text{C}_6\text{H}_5$, C_2H_5 , OCH_3) in THF at various temperatures (r.t. $\sim 65^\circ\text{C}$) under the pseudo first order reaction conditions where excess of PR_3 was employed under a nitrogen atmosphere. For the reaction involving PPN^+ analog, Mn-Mn heterolytic cleavage occurred, leading to $\text{PPN}^+\text{Mn}(\text{CO})_5\text{-}$ and $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{PR}_3$ as products; however, in case of Na^+ analog, Na^+ seems to play a novel counter ion effect on the disruption reaction by transferring one terminal CO from the $\text{Mn}(\text{CO})_5$ moiety on to the $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2$ of the corresponding homobimetallic complex, eventually resulting in $\text{Na}^+\text{Mn}(\text{CO})_4\text{PR}_3\text{-}$ and $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_3$. This reaction is of overall first order with respect to [homobimetallic complex] with the activation parameters ($\Delta H^\ddagger=23.0\pm 0.7$ kcal/mol, $\Delta S^\ddagger=-8.7\pm 0.8$ e.u. for Na^+ analog; $\Delta H^\ddagger=28.8\pm 0.4$ kcal/mol, $\Delta S^\ddagger=15.7\pm 0.6$ e.u. for PPN^+ analog reaction).

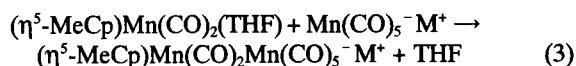
Introduction

Interest in heterobimetallics is growing due to their usefulness as homogeneous catalysts.¹ These complexes are often a combination of an electron-rich and an electron-deficient metal moiety. The metal-metal bond of this type in the heterobimetallic complex may be described as a donor-acceptor bond or dative metal-metal bond.²

Recently we have been interested in the reactions involving $(\text{OC})_5\text{CrMn}(\text{CO})_5\text{-M}^+$ ($\text{M}^+=\text{Na}^+$, PPN^+). This heterobimetallic anion reacts either with organic halides or with PR_3 as shown in the following equations (eq. 1 and eq. 2).³



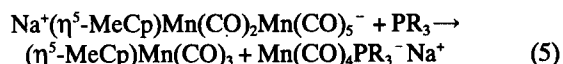
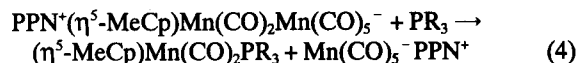
Recently we have prepared $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5\text{-M}^+$ ($\text{M}^+=\text{Na}^+$, PPN^+) from the reaction of $\text{Mn}(\text{CO})_5\text{-M}^+$ ($\text{M}^+=\text{Na}^+$, PPN^+) with $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2(\text{THF})_4$ in the same fashion as the above-mentioned heterobimetallics were made (eq. 3).³



Usually it is widely accepted that most of homobimetallics may have rather covalent character in their metal-metal bond; however, this homobimetallic anion is likely to have a donor-acceptor metal-metal bond character as usual het-

erobimetallics would have.

Such a Lewis acid-base relationship in Mn-Mn bond may be in part evidenced by the following disruption reactions (eq. 4 and eq. 5).



For the last two decades much effort has been directed to elucidate the counter ion effects on those reactions involving mononuclear carbonylates such as $\text{HfFe}(\text{CO})_4\text{-}$,⁵ $\text{Mn}(\text{CO})_5\text{-}$,⁶ $\text{Co}(\text{CO})_4\text{-}$,⁷ $\text{CpMo}(\text{CO})_3\text{-}$,⁸ and $\text{CpW}(\text{CO})_3\text{-}$,⁹ however, not much work has been done to understand the counter ion effect on the reactions of anionic bimetallics.

Here we report some unusual kinetic results from the $(\eta^5\text{-MeCp})\text{Mn}(\text{CO})_2\text{Mn}(\text{CO})_5\text{-M}^+$ ($\text{M}^+=\text{Na}^+$, PPN^+) disrupted by PR_3 ($\text{R}=\text{C}_6\text{H}_5$, C_2H_5 , OCH_3).

Experimental

An inert-atmosphere glove box, Schlenk wares and high vacuum line were employed for most of sample transfers and manipulations. Infrared spectra were recorded on a Perkin-Elmer 238B spectrophotometer using 0.10 mm sealed CaF_2 , KBr or NaCl solution cells.

Photoreactions were performed using a 550 watt Hg vapor lamp covering a rather broad range of UV-VIS wavelengths. Solvents were distilled and degassed under a N_2 at-

* PPN^+ =bis(triphenylphosphine)iminium cation.