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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*-prodienH_2)

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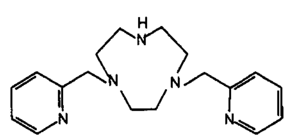
A chiral pentadentate bis-amide ligand, 1,9-bis(*S*)-pyrrolidinyl-2,5,8-triazanonane-1,9-dione(*S*,*S*-prodienH_2) has been synthesized from the reaction of bis(2-aminoethyl)amine(dien) and *S*-proline, and the structure of [Co(*S*,*S*-prodien)H_2O]ClO_4 has been determined by single crystal X-ray diffraction. The geometrical structure of the Co (III) complex has been an αβ-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 $P2_1$(#4), with a=7.838(1), b=12.675(1), c=9.710(1) Å, β=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 αβ-[Co(*S*,*S*-prodien)H_2O]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 documented[2] 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-azapen-tane-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, $[Co(HL3)Cl]^{2+}$(HL3=3-{2-[hydroxy(2-pyridyl)methyleneamino]ethyl}-3-azapentane-1,5-diamine) was obtained through oxidation of $[Co(L1)Cl]^{2+}$. 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(picditn), 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 pcdien and pcditn ligand have been an αβ-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 αβ-Co(III) complexes of picdien both *syn* and *anti* forms are found, while only the *anti* forms in the picditn 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. [Co(*S*-ahazterpy)Cl]$(ClO_4)_2 \cdot 2H_2O$ 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-



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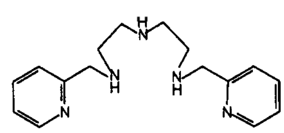

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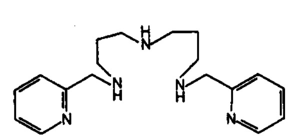

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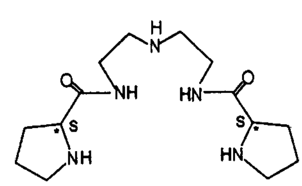


S,*S*-prodienH_2

ane-1,9-dione(*S,S*-prodien). The *S,S*-prodienH_2 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. ^{13}C NMR spectra were recorded with a Bruker (300 MHz) in D_2O, 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*-prodienH_2 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*-prodienH_2 was obtained from decarbobenzoxylation[8] of *N,N'*-bis(carbobenzoxy-(*S*)-prolyl)diethylenetriamine in methanol. Yield of oil phase was *ca*. 60%.

Preparation of Λ-αβ-[Co(*S,S*-prodien)H_2O]ClO_4. *S,S*-prodienH_2 (5 mmol, 2.4 g) and $CoCl_2 \cdot 6H_2O$ (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 $NaClO_4$. The solution was evaporated to a volume of *ca*. 50 mL and on leaving overnight in a refrigerator, crude crystals of purple Λ-αβ-[Co(*S,S*-prodien)H_2O]ClO_4 precipitated. A purple precipitate (1.15 g) was collected by filtration. Crystals suitable for single-crystal X-ray diffration were recrystallized by dissolving in the minimum volume of hot water. yield 48%. Calc. for $CoC_{14}H_{27}N_5O_7Cl$ ([Co($C_{14}H_{25}N_5O_2$)OH_2]ClO_4): 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-αβ-[Co(*S,S*-prodien)H_2O]ClO_4

Empirical formula	$CoC_{14}H_{27}N_5O_7Cl$
Formula weight	471.09
Crystal system	Monoclinic
Space group	$P2_1$(#4)
Z	2
Cell parameters	
a (Å)	7.838(1)
b (Å)	12.675(1)
c (Å)	9.710(1)
β (°)	100.39(1)
V (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)
$2\theta_{max}$ (deg)	52.64
No. of reflections measured	2130
No. of reflections observed (I > 3σ(I))	1800
F(000)	486
No. of variable	252
Discrepancy indices	
R^a	0.0446
R_w^b	0.0565
Goodness of fit indicator^c	1.74
Max. shift in final cycles	less than 0.01

$^a R=\Sigma||F_0|-|F_c||/\Sigma|F_0|$. $^b R_w=[(\Sigma w(|F_0|-|F_c|)^2/\Sigma w(F_0^2)]^{1/2}$, where, $w=[\sigma(F^2)]^{-1}$. ^{c}Estimated standard deviation of an observation of unit weight: $[\Sigma w(|F_0|-|F_c|)^2/(N_0-N_v)]^{1/2}$, where N_0=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 (Å^2) and Their Estimated Standard Deviations for Λ-αβ-[Co(*S,S*-prodien)H_2O]ClO_4

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: $(4/3)*[a^2*\beta_{11}+b^2*\beta_{22}+c^2*\beta_{33}+ab(\cos\gamma)*\beta_{12}+ac(\cos\beta)*\beta_{13}+bc(\cos\alpha)*\beta_{23}]$.

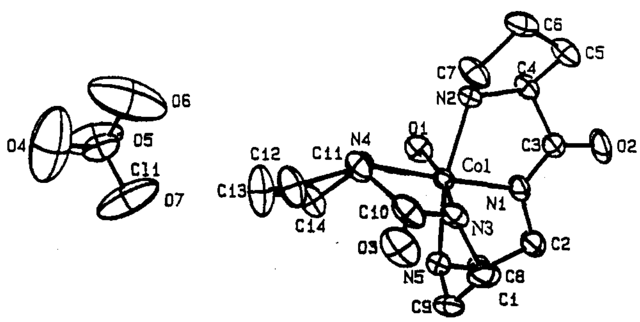


Figure 1. Perspective drawing and atomic numbering scheme for the Λ-αβ-[Co(*S,S*-prodien)H_2O]ClO_4.

fractometer with a graphite-monochromatized Mo-Kα radiation (λ=0.71069 Å). The intensity data were collected by the ω-2θ scan technique. A total of 2130 reflections up to $2\theta_{max}$=60° 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 shown in Figure 1. The bond angles and lengths with their estimated standard deviations in the complex are summarized in Table 3 and 4.

Table 3. Bond Angle (deg) and Their Estimated Standard Deviations (in parentheses) for Λ-αβ-[Co(*S,S*-prodien)H_2O]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-αβ-[Co(*S,S*-prodien)H_2O]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)

Results and Discussion

[Co(*S,S*-prodien)H_2O]ClO_4 was prepared in reasonable yield by the air oxidation of $CoCl_2\cdot 6H_2O$ and *S,S*-prodienH_2 mixtures in water. Elemental analysis indicated that the purple product was [Co(*S,S*-prodien)H_2O]ClO_4. The UV/Vis spectrum of [Co(*S,S*-prodien)H_2O]ClO_4 in water shows a similar absorption band of Co(III) complex with $Co^{III}N_5O$ chromophore (see Table 5).[11] Possible geometric isomers of [Co(*S,S*-prodien)H_2O]ClO_4 with linear pentadentate bis-amide ligand are shown in Figure 2. McLachlan *et al.*[3] have reported that tacn moiety in [Co(dmptacn)(H_2O)]$(ClO_4)_3$ of pentadentate ligands derived from tacn has coordinated to facial form. Amed *et al.*[5] have shown that complexes of [Co(picdien)X]$(ClO_4)_2$ and [Co(picditn)X]$(ClO_4)_2$ [picdien=1,9-bis(2'-pyridyl)-2,5,8-triazanonane, picditn=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 αβ configuration. The αβ, αα*-configuration indicated that amine backbones of ligands chelate to a facial form in the metal center. In this case, αβ indicates that the monodentate ligand coordinates *cis* site to the secondary nitrogens of dien and αα* coor-

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

Complexes	λ_{max}/nm	Ref.
Λ-β-[Co(*R,R*-L)(*R*-ala)]$^+$	505	11(a)
Δ-α-[Co(*R,R*-L)(*S*-ala)]$^{2+}$	505	11(b)
Λ-α-[Co(*S,S*-picchxnMe$_2$)(*S*-pro)]$^{2+}$	508	11(c)
Λ-α-[Co(*S,S*-picchxnMe$_2$)(*rac*-ala)]$^{2+}$	500	11(c)
Λ-αβ-[Co(*S,S*-prodien)H_2O]$^+$	507	this study

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

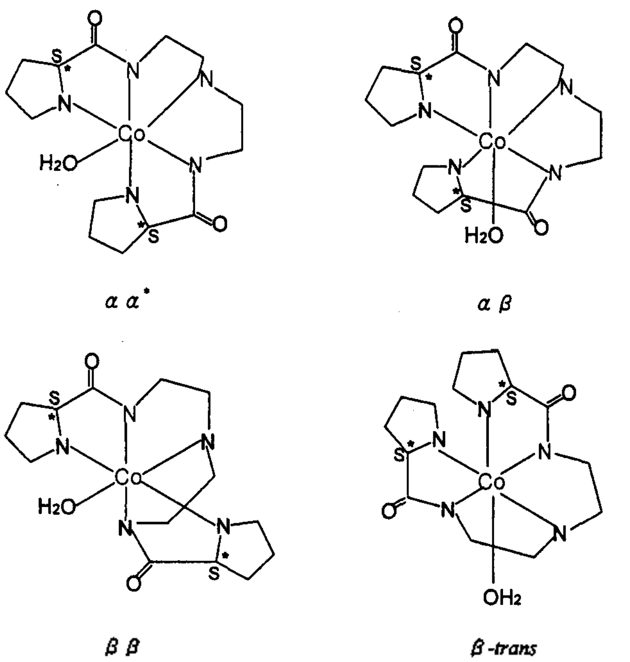


Figure 2. The possible isomers for [Co(*S,S*-prodien) H_2O]ClO_4.

dinates *trans* site. Based upon these results, it seems that [Co(*S,S*-prodien)H_2O]ClO_4 may be αα* or αβ configuration that dien moiety of ligand coordinates to facial as shown in Figure 2.

A feature of the ^{13}C NMR spectrum of [Co(*S,S*-prodien) H_2O]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 αα*-[Co(dmptacn)H_2O]ClO_4 [dmptacn=1,4-bis(2-pyridylmethyl)-1,4,7-triazacyclononane] shows only half the number of free ligand, but the αβ-[Co(dmptacn)H_2O]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 [Co(*S,S*-prodien)H_2O]ClO_4 shows all fourteen carbon resonances on the *S,S*-prodien ligand, the exact topology (αα* or αβ) of the complex was difficult to determine because of the puckered pyrrolidinyl ring.

The Circular Dichroism (CD) spectrum for the [Co(*S,S*-prodien)H_2O]ClO_4 is shown in Figure 4. The CD spectrum of [Co(*S,S*-prodien)H_2O]ClO_4 in visible absorption region shows two separated maximum bands for the $^1A_{1g} \rightarrow ^1T_{1g}$ (λ=554 nm, $\Delta\varepsilon_{max}$=+2.2 dm^2mol^{-1}) and $^1A_{1g} \rightarrow ^1T_{2g}$ (λ=479 nm, $\Delta\varepsilon_{max}$= − 1.76 dm^2mol^{-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 [Co(*S,S*-prodien)H_2O]ClO_4, asymmetry nitrogens in pyrrolydyl rings have a fixed stereochemistry as a consequence of the *S* chiral carbon in pyrrolydyl ring.

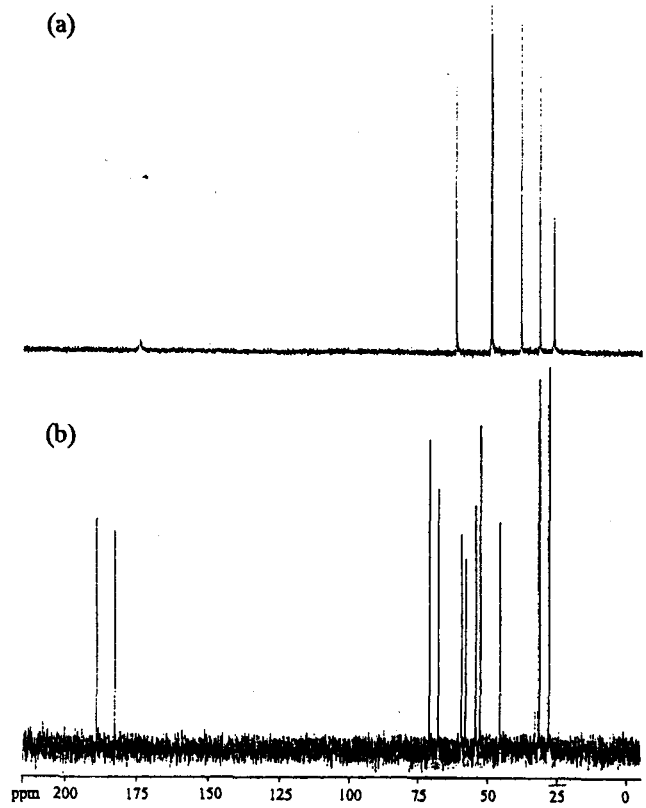


Figure 3. (a) ^{13}C NMR spectrum of *S,S*-prodien ligand. (b) ^{13}C NMR spectrum of Λ-αβ-[Co(*S,S*-prodien)H_2O]ClO_4.

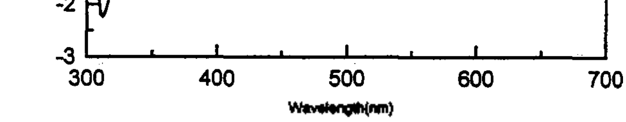


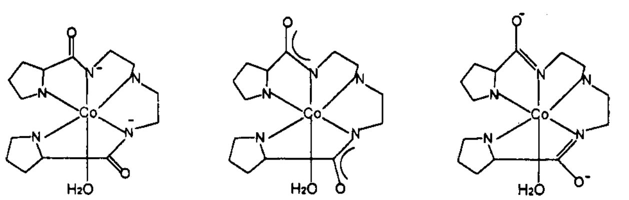
Figure 4. The CD spectrum of Λ-αβ-[Co(*S,S*-prodien)H_2O]ClO_4.

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 stereospecifity of *S,S*-prodien. Based upon the eta parameter (Table 1) of the X-ray analysis data, we confirmed that the [Co(*S,S*-prodien)H_2O] has the Λ configuration by chelate ring method.[13]

Figure 1. shows a perspective drawing of the [Co(*S,S*-prodien)H_2O]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 αβ-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 αβ-$[Co(picdien)Cl]^{2+}$ with significantly distorted octahedral geometry.

The Co-N(1), N(3), N(5), Co-N(2), N(4) and Co-OH_2 bond distances (Table 4) in $[Co(S,S\text{-prodien})H_2O]^+$ are different to the corresponding distances[5] in $[Co(picdien)H_2O]^{3+}$ [average; 1.938, 1.954 and 1.951 Å] and $[Co(dmptacn)H_2O]^{3+}$ [average; 1.930, 1.921 and 1.945 Å] respectively. Also, the Co-N(5) (2.024 Å) bond length in $[Co(S,S\text{-prodien})H_2O]^+$ is similar to the corresponding distances in some other Co^{III} complexes of pendant arm ligands derived from tacn, *viz.* $[Co(daptacn)Cl]^{2+}$ [1.987(7) Å] and $[Co(taptacn)Cl]^{3+}$ [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 $[Co(picdien)H_2O]^{3+}$, $[Co(daptacn)Cl]^{2+}$ and $[Co(taptacn)Cl]^{3+}$.[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 bis-amide moiety of *S,S*-prodien is increased. On the other hand, the bond lengths of two amide portion in $[Co(S,S\text{-prodien})H_2O]^+$ 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 $[Co(S,S\text{-prodien})H_2O]ClO_4$, the amide C-N and C-O bond



I II

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 $[Co(S,S\text{-prodien})H_2O]ClO_4$ 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 $[Co(S,S\text{-prodien})H_2O]ClO_4$ with chiral pentadentate bis-amide ligand, *S,S*-prodien has αβ-form, in which the dien moiety of ligand chelates 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 αβ-$[Co(S,S\text{-prodien})H_2O]ClO_4$ 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-αβ-$[Co(S,S\text{-prodien})H_2O]ClO_4$ 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, (η^5-MeCp)Mn(CO)$_2$Mn(CO)$_5$·M$^+$ (M$^+$=Na$^+$, PPN^{+a}) by PR$_3$ (R=C$_6$H$_5$, C$_2$H$_5$, OCH$_3$)

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The homobimetallic anion, (η^5-MeCp)Mn(CO)$_2$Mn(CO)$_5^-$M$^+$ (M$^+$=Na$^+$, PPN$^+$) was disrupted by PR$_3$ (R=C$_6$H$_5$, C$_2$H$_5$, OCH$_3$) in THF at various temperatures (r.t. ~65°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 PPN$^+$Mn(CO)$_5^-$ and (η^5-MeCp)Mn(CO)$_2$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 Mn(CO)$_5$ moiety on to the (η^5-MeCp)Mn(CO)$_2$ of the corresponding homobimetallic complex, eventually resulting in Na$^+$Mn(CO)$_4$PR$_3^-$ and (η^5-MeCp)Mn(CO)$_3$. This reaction is of overall first order with respect to [homobimetallic complex] with the activation parameters ($\Delta H^{\neq}$=23.0±0.7 kcal/mol, $\Delta S^{\neq}$=−8.7±0.8 e.u. for Na$^+$ analog; $\Delta H^{\neq}$=28.8±0.4 kcal/mol, $\Delta S^{\neq}$=15.7±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 (OC)$_5$CrMn(CO)$_5$M$^+$ (M$^+$=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]

$$\mathrm{(OC)_5CrMn(CO)_5 \;+ RX \rightarrow XCr(CO)_5^- + RMn(CO)_5} \quad (1)$$

$$\mathrm{(OC)_5CrMn(CO)_5^- + PR_3 \rightarrow Cr(CO)_5(PR_3) + Mn(CO)_5^-} \quad (2)$$

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

$$\mathrm{(\eta^5\text{-}MeCp)Mn(CO)_2(THF) + Mn(CO)_5^-M^+ \rightarrow (\eta^5\text{-}MeCp)Mn(CO)_2Mn(CO)_5^-M^+ + THF} \quad (3)$$

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 heterobimetallics 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).

$$\mathrm{PPN^+(\eta^5\text{-}MeCp)Mn(CO)_2Mn(CO)_5^- + PR_3 \rightarrow (\eta^5\text{-}MeCp)Mn(CO)_2PR_3 + Mn(CO)_5^-PPN^+} \quad (4)$$

$$\mathrm{Na^+(\eta^5\text{-}MeCp)Mn(CO)_2Mn(CO)_5^- + PR_3 \rightarrow (\eta^5\text{-}MeCp)Mn(CO)_3 + Mn(CO)_4PR_3^-Na^+} \quad (5)$$

For the last two decades much effort has been directed to elucidate the counter ion effects on those reactions involving mononuclear carbonylates such as HFe(CO)$_4^-$,[5] Mn(CO)$_5^-$,[6] Co(CO)$_4^-$,[7] CpMo(CO)$_3^-$,[8] and CpW(CO)$_3^-$;[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 (η^5-MeCp)Mn(CO)$_2$Mn(CO)$_5^-$M$^+$ (M$^+$=Na$^+$, PPN$^+$) disrupted by PR$_3$ (R=C$_6$H$_5$, C$_2$H$_5$, 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-

[a] PPN$^+$=bis(triphenylphosphine)iminium cation.