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Syntheses and Spectroscopic Properties of Palladium(II) Complexes with Bidentate Aminophosphine of N,N-Dialkyl-N'-diphenylphosphinodi-aminoethane

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Several new palladium(II) complexes of aminophosphines, $(\text{Pd}(\text{L})\text{X}_2)$, ($\text{L} = \text{Ph}_2\text{PNH} \leftrightarrow \text{NR}_2$; $\text{R} = \text{CH}_3 (\text{L}_1)$, $\text{C}_2\text{H}_4 (\text{L}_2)$; $\text{X} = \text{Cl}$, Br , I , and NCS) that contain two different donor atoms of nitrogen and phosphorus as π -electron acceptor, were synthesized and characterized by conductivity measurement, ir, and UV/Vis-spectra. For the dithiocyanatopalladium(II) complexes with aminophosphines, it was confirmed that the thiocyanate group trans to phosphorus is coordinated as Pd-NCS mode and the one trans to nitrogen as Pd-SCN mode, and the aminophosphines form six-membered chelate ring. The spectra of dihalogenopalladium(II) complexes with aminophosphines show that the band maxima are shifted to the short wavelengths as the concentration is decreased.

Introduction

(N,N-dialkyl-N'-diphenylphosphino)diaminoethane can act as bidentate ligand with phosphorus and nitrogen donor atoms.

Bidentate ligands with two types of donor sites are well known and have been the subject of many reports. These ligands are of interest, because they can bridge dissimilar metals or, if one donor is easily replaced, yield complexes that readily provide a coordination site for incoming substrates.¹ For example, there are phosphines that contain a nitrogen or oxygen donor atom.²⁻⁹

Of the nitrogen containing phosphines, 2-(diphenylphosphino)pyridine,² 2-aminoalkylphosphine,³ 3-(diphenylphosphino)-N,N-dimethylpropylamine,^{4,6} 3-(diphenylphosphino)propionitrile,⁷ and o-(diphenylphosphino)benzotrile⁸ are the ligands that collectively function as chelate ligands.

In our previous work, the palladium(II) complexes, $\{\text{Pd}(\text{L})\text{X}_2\}$; $\{\text{L} = 1,2\text{-bis}((\text{diphenylphosphino})\text{amino})\text{alkane}; \text{X} = \text{Cl}, \text{Br}, \text{I}, \text{and NCS}\}$ have been synthesized and characterized, and we concluded that these complexes formed the seven-membered chelate ring.¹⁰

We have new synthesized several dihalogenopalladium (II) complexes with (N,N-dimethyl-N'-diphenylphosphino)di-

aminoethane (L_1) and (N,N-dimethyl-N'-diphenylphosphino)diaminoethane (L_2) and investigated the bonding characters of the ligands.

Experimental

General Information. Palladium chloride, chloro diphenylphosphine (Tykyo Kasei GR), N,N-dialkyl diaminoethane (Furker GR), and Triethylamine (Junsei GR) were purchased from the source indicated. $\text{Pd}(\text{PhCN})_2\text{Cl}_2$ ¹¹, $\text{Na}_2\text{Pd}(\text{NCS})_4$ ^{4c}, and LiX ($X = \text{Br}, \text{I}$) were prepared by literature's methods.

All solvents, including acetone, benzene, and dichloromethane were reagent grade and were purified.

All reactions were carried out under a nitrogen atmosphere.

Infra-red spectra ($4000\text{-}200\text{cm}^{-1}$) were recorded on Perkin-Elmer 1330 and Hitachi 270-50 model instrument. Ultra-violet-visible spectra (250-600nm) were recorded on Gilford Response and Hitachi 320 instrument. Melting points were measured by an electrothermal melting point apparatus. Elemental analyses were performed with Perkin-Elmer 240. Conductivities were measured with Suntex SC17-A model in acetone solutions.

Syntheses of Ligands. (N,N-dialkyl-N'-diphenylphosphino)diaminoethane, $\{R = \text{CH}_3 (L_1), \text{C}_2\text{H}_5 (L_2)\}$: To a solution of N,N-dialkylethylenediamine (0.02 mol, in 25ml benzene) were added triethylamine (0.02 mol) and chlorodiphenylphosphine (0.02 mol) with stirring under a nitrogen atmosphere over a period of 30 min. The mixture was continuously stirred for 1 hour at room temperature.

The triethylamine hydrochloride precipitated was filtered off. The filtrate was evaporated under reduced pressure to give an oily product. Yield: 67% (L_1), 64% (L_2). These ligands were used for preparation of palladium(II) complexes with out further purification.

Preparation of Palladium(II) Complexes.

$\{\text{Pd}(L_1)\text{Cl}_2\}$ and $\{\text{Pd}(L_2)\text{Cl}_2\}$

A solution of aminophosphine (1 mmol, in 10ml benzene) was added to a solution of $\{\text{Pd}(\text{PhCN})_2\text{Cl}_2\}$ (1 mmol, in 10 ml of benzene) with stirring.

A precipitate formed immediately, but the reaction mixture was stirred for 2 hours to promote homogeneity.

The compound was collected on a sintered-glass filter, and washed with ethanol, and ether, and then recrystallized from dichloromethane and diethyl ether.

$\{\text{Pd}(L_1)\text{Cl}_2\}$: yield: 80%, m.p: 142-143°C, Calcd. for $\text{Pd}(\text{C}_{16}\text{H}_{21}\text{N}_2\text{P})\text{Cl}_2$: C, 44.09; H, 4.82; N, 6.43%. Found: C, 44.23; H, 5.01; N, 6.52%, Color: yellow.

$\{\text{Pd}(L_2)\text{Cl}_2\}$: yield: 85%, m.p: 140-141°C, Calcd. for $\text{Pd}(\text{C}_{18}\text{H}_{25}\text{N}_2\text{P})\text{Cl}_2$: C, 45.24; H, 5.24; N, 5.86%. Found: C, 45.30; H, 5.29; N, 5.93%, Color: yellow.

$\{\text{Pd}(L_1)\text{X}_2\}$ and $\{\text{Pd}(L_2)\text{X}_2\}$; $X = \text{Br}, \text{I}$:

Ethanol solution (10ml) of LiBr or LiI (1 mmol) was added to the dichloromethane solution (5 ml) of $\{\text{Pd}(L)\text{Cl}_2\}$ (1 mmol), and the solution was stirred vigorously for 30 min.

The dichloromethane layer was washed three times with water (10 ml), and was concentrated to 5 ml by passing nitrogen. Orange crystals were obtained by addition of ethanol and diethyl ether to the concentrated solution. The crystals were collected by filtration and washed with diethylether. Then, they were recrystallized from dichloromethane and

diethylether.

$\{\text{Pd}(L_1)\text{Br}_2\}$: Yield: 75%, m.p: 149-151°C, Color: orange yellow.

$\{\text{Pd}(L_2) \text{I}_2\}$: Yield: 70%, m.p: 149-151°C, Color: orange yellow.

$\{\text{Pd}(L_2)\text{Br}_2\}$: Yield: 70%, m.p: 150-152°C, Color: orange yellow.

$\{\text{Pd}(L_1) \text{I}_2\}$: Yield: 74%, m.p: 151-152°C, Color: orange yellow.

$\{\text{Pd}(L_1)(\text{NCS})_2\}$ and $\{\text{Pd}(L_2)(\text{NCS})_2\}$

Sodium tetrathiocyanopalladate (1mmol) dissolved in absolute ethanol (10 ml) was treated with ethanol solutions (10 ml) of aminophosphine.

The reaction mixture was stirred for 1 hour and the precipitate was collected, washed with distilled water, ethanol, and diethyl ether successively. Then, it was recrystallized from dichloromethane and diethylether.

$\{\text{Pd}(L_1)(\text{NCS})_2\}$: Yield: 68%, m.p: 158-160°C, Calcd. for $\text{Pd}(\text{C}_{16}\text{H}_{21}\text{N}_2\text{P}) (\text{NCS})_2 \cdot 1/2\text{CH}_2\text{Cl}_2$: C, 43.03; H, 4.26; N, 10.85%. Found: C, 43.27; H, 4.13; N, 10.65%, Color: pale yellow.

$\{\text{Pd}(L_2)(\text{NCS})_2\}$: Yield: 70%, m.p: 160-162°C, Calcd. for $\text{Pd}(\text{C}_{18}\text{H}_{25}\text{N}_2\text{P}) (\text{NCS})_2 \cdot 0.7\text{H}_2\text{O}$: C, 42.69; H, 4.53; N, 9.62%. Found: C, 42.63; H, 4.67; N, 10.04%, Color: pale yellow.

Results and Discussion

Direct reaction of $\{\text{PdX}_4\}^{2-}$ with diphosphine, but not always, leads to the formation of insoluble Magnus-type salt, $\{\text{Pd}(\text{diphos})_2\} \cdot \{\text{PdX}_4\}$. It is possible to avoid formation of Magnus'salt by¹² using $\{\text{Pd}(\text{PhCN})_2\text{Cl}_2\}$ in place of $\{\text{PdX}_4\}^{2-}$ ¹³. The reaction of $\{\text{Pd}(\text{PhCN})_2\text{Cl}_2\}$ with equimolar aminophosphine in benzene yields a pale yellow precipitate of $\{\text{Pd}(L)\text{Cl}_2\}$ and for convenience, metathesis reactions between $\{\text{Pd}(L)\text{Cl}_2\}$ and LiX ($X = \text{Br}, \text{I}$) were used to obtain the analogous $\{\text{Pd}(L)\text{X}_2\}$ complexes, and also the thiocyanato complexes with aminophosphine were prepared from sodium tetrathiocyanatopalladate and aminophosphine.

All of these palladium(II) complexes are stable in air, and soluble in chlorinated hydrocarbons. These complexes are nonelectrolyte which was evidenced by conductance measurement of complexes in acetone ($\Lambda_M = \text{ca. } 1.3\text{cm}^2/\text{ohm mol}$).

The ir-spectra of (N,N-dimethyl-N'-diphenylphosphino)diaminoethane (L_1) and $\{\text{Pd}(L)\text{Cl}_2\}$ complex with L_1 are

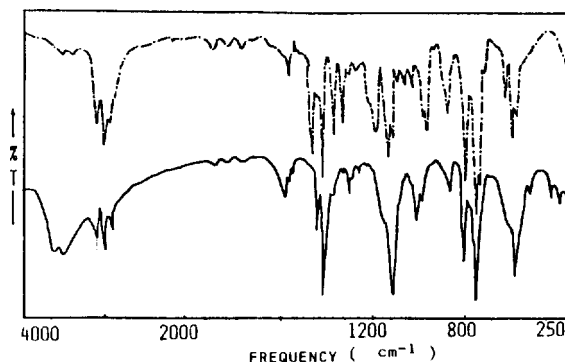


Figure 1. The ir spectra of N,N-dimethyl-N'-diphenylphosphinoethane (L_1) and $\{\text{Pd}(L_1)\text{Cl}_2\}$ $\text{Ph}_2\text{PNHCH}_2\text{CH}_2\text{N}(\text{CH}_3)_2$: ----, $\{\text{Pd}(L_1)\text{Cl}_2\}$: —.

Table 1. Selected ir Absorption Bands of Ligands and Complexes

Compounds	Characteristic absorption band (cm ⁻¹)				
	P-N	C-N	C=N	C-S	Pd-X
Ph ₂ PN + N(CH ₃) ₂ (L ₁)	1185s	1100s	.	.	.
Pd(L ₁)Cl ₂	1115sh	1100s	.	.	340, 300m
Pd(L ₁)Br ₂	1115sh	1100s	.	.	.
Pd(L ₁)(NCS)	1110sh	1100s	2100s	760w	.
(SCN)			2150	840w	.
Ph ₂ PN + N(C ₂ H ₅) ₂ (L ₂)	1180s	1100s	.	.	.
Pd(L ₂)Cl ₂	1115sh	1100s	.	.	340, 300m
Pd(L ₂)Br ₂	1120sh	1100s	.	.	.
Pd(L ₂)I ₂	1120sh	1100s	.	.	.
Pd(L ₂)(NCS)	1120sh	1100s	2050s	760w	.
(SCN)			2150	820	.

s: strong, sh; shoulder, m; medium, w; weak, d; doublet.

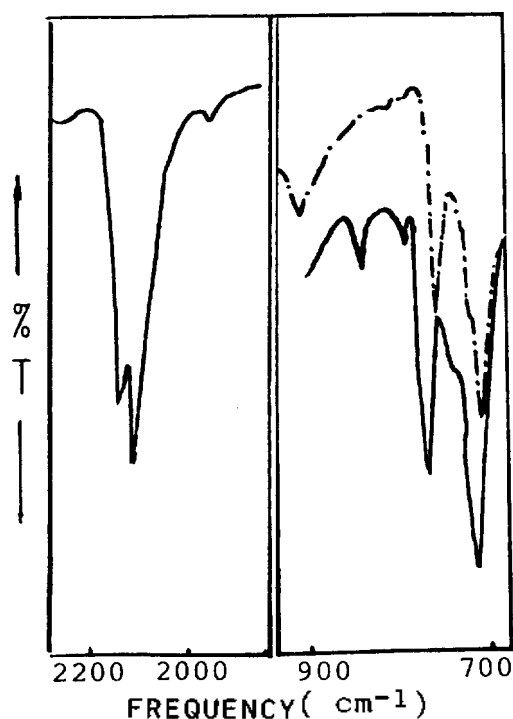


Figure 2. The C≡N stretching (2000-2200cm⁻¹) and C-S stretching (700-900 cm⁻¹) region of the infrared spectra. {Pd(L₁)Cl₂}: - - - - -; {Pd(L₁)(NCS)(SCN)}: —.

shown in Figure 1, and the characteristic absorption bands of the ir-spectral data for {Pd(L)X₂} are summarized in table 1.

As shown in Figure 1 and Table 1, the ν(C-N) peaks of uncomplexed aminophosphine are observed at or near ca. 1100 cm⁻¹¹⁰ for the complexes.

Although the ν(P-N) peaks are observed¹⁴ at 1185cm⁻¹ for L₁ and 1180cm⁻¹ for L₂, these peaks were shifted about 70cm⁻¹ toward the lower frequency (from 1115 to 1120cm⁻¹) for the complexes, and might be overlapped with the ν(C-N) peak at ca. 1110cm⁻¹.

The free ligand has partially double bond character of the P-N bond (p_π-d_π), which is resulted from the overlap of P_π

Table 2. Electronic Spectral Data for the Complexes in CH₂Cl₂

X	Pd(L ₁)X ₂		Pd(L ₂)X ₂	
	λ _{max}	ν	λ _{max}	ν
NCS	372	2090	371	1950
	358	2180	355	2182
Cl	351	2140	343	2150
	312	2050	310	2030
Br	420sh		420sh	
	335	2100	335	2110
I	310	2055	310	2030
	420		240sh	
	340	2050	335	2100
	315	2200	317	2250

orbital of the nitrogen atom with empty 3d-orbital on phosphorus atom.¹⁵ However, when the phosphorus atom of aminophosphine was coordinated to palladium, the p-competition occurs between palladium and the P-N bond. Accordingly, ν(P-N) peak is shifted about 70cm⁻¹ toward the lower frequency.

Much structural informations can often be presented from a study of the vibrational spectra of other ligand present in the complex, and stereochemical assignments are frequently made on the basis of metal-halogen stretching frequencies which occur in the far infrared region.¹⁶

The two ν(Pd-X) peaks are observed at 350 and 270cm⁻¹ for the chlorine containing complexes with aminophosphine. This result is in a good agreement with bond order¹⁷ (reduced overlap population) calculated by the extended Hückel molecular orbital method.¹⁸

The C≡N stretching (2000-2200cm⁻¹) and the C-S stretching frequency aminophosphine are shown in Figure 2 and compared with the ir-spectrum of the dichloropalladium(II) complex. The ir-spectra (Figure 2) of the dithiocyanatopalladium(II) complex with aminophosphine displays a strong and sharp peak at about 2100cm⁻¹ and relatively broader peak at about 2000cm⁻¹ indicating the presence of two different types of coordinated thiocyanate ions.^{19,40} Also the weak absorption band at 840cm⁻¹ in the spectrum of the thiocyanato complexes is assigned to the C-S stretching frequency of N-bonded thiocyanate to palladium(II) ion. Intense absorptions of organic ligand preclude location of the C-S stretching frequency of the S-bonded thiocyanate to palladium(II) ion.

However, from the integrated absorption values of two different C≡N bands in the coordinated thiocyanate ligand, it is confirmed that one thiocyanato group trans to the nitrogen donor atom of aminophosphine is S-bonded, but the other thiocyanate group trans to the π-bonding phosphorus donor atom is N-bonded. Such a form was found in isothiocyanatothiocyanato(1-diphenylphosphino-3-dimethylamino)propane palladium(II) complex⁴⁰ having one strong and one weak π-bonds. These phenomena are indicative of π-bonding competition between donor atom of ligand and d_π-orbital of a palladium(II) ion.

In view of the ir spectral data presented above it is proposed that the aminophosphines of these {Pd(L)X₂} complexes consist of six-membered chelate ring.

Electronic absorption spectral data for the {Pd(L)X₂}

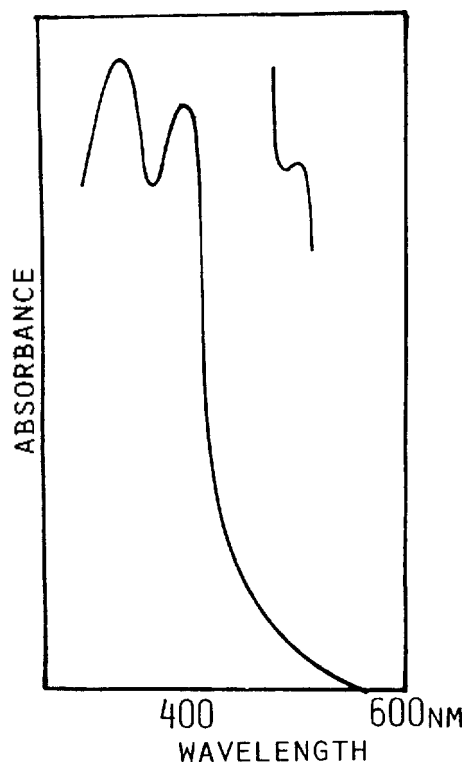


Figure 3. UV-Visible spectra of $\{Pd(L_1)Cl_2\}$ in CH_2Cl_2 solutions.

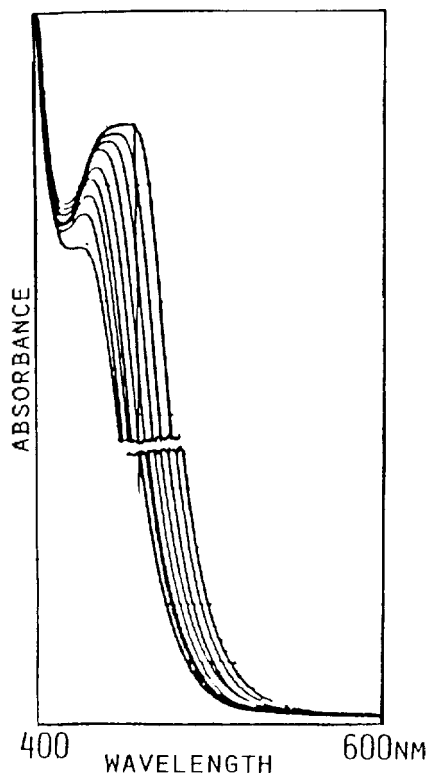


Figure 4. UV-Visible spectra of $\{Pd(L_1)Cl_2\}$ with various concentration range from $2 \times 10^{-2} M$ to $2 \times 10^{-3} M$ in CH_2Cl_2 solutions.

complexes are summarized in Table 2, and the spectra of $\{Pd(L_1)Cl_2\}$ are shown in Figure 3. As shown in Figure 3, the bands for $\{Pd(L)Cl_2\}$ have been assigned on the bases of the assignments for $\{Pd(en)Cl_2\}$.²⁰ The first band at visible

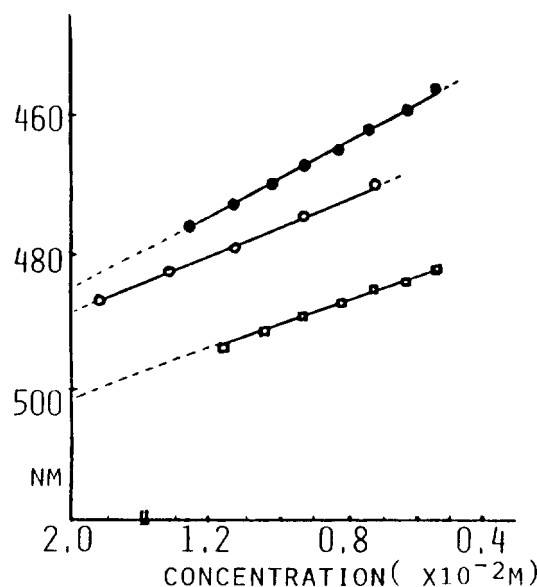


Figure 5. Plot of absorption maxima vs concentration of $\{Pd(L_1)Cl_2\}$ in CH_2Cl_2 solutions $Pd(L_1)Cl_2$: $\bullet\bullet\bullet\bullet$, $Pd(L_1)Br_2$: $\square\square\square\square$, $Pd(L_1)I_2$: $\circ\circ\circ\circ$ L = $Ph_2PNHCH(CH_3)CH_2NHPh_2$.

region may be interpreted $^1A_{2g} \leftarrow ^1A_{1g}$ transition band, and the other band are charge transfer of Pd(II)-Ligand.²¹

The spectrochemical series that is derived from the electronic spectra of the $\{Pd(L)X_2\}$ complexes with the monodentate ligand is $Cl > NCS > Br > I$.

Figure 4 shows the variation of the absorption maxima and extinction coefficient of spectra with various concentrations.

The band maxima and the extinction coefficient increase as the concentration increases (see Figure 5). The deviation from Beer's law for $\{Pd(L)X_2\}$ complexes were considerable, and spectra obtained in acetonitrile solutions and those in dichloromethane solutions were similar type.

The spectrum was changed systematically as the concentration of complex increased and exhibited isosbestic point. Finally, when a solution was evaporated to dryness and the solids were redissolved in dichloromethane, the spectrum was the same as that was initially prepared.

These results correspond to the spectra of dihalogenopalladium(II) complex with $Ph_2PNHCH(CH_3)CH_2NHPh_2$.²²

The presence of such variation in the spectra of each complex may be considered as an inter-molecular interaction between the filled $d(\pi)$ -orbital of metal and the filled anti-bonding p-orbital of halogen atom in high concentration of complexes.

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Oligomerization State of the Plasma Membrane Proteolipid Apoprotein Purified from the Bovine Kidney, Probed by the Fluorescence Polarization

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In order to investigate the oligomerization state of the plasma membrane proteolipid apoprotein purified from the bovine kidney, fluorescence polarization experiment was carried out in the two different solvent systems, i.e., water and organic solvent (chloroform-methanol). The molecular volumes of the proteins estimated from the Perrin equation, were to be $45,258\text{\AA}^3$ and $17,608\text{\AA}^3$ in water and organic solvent, respectively. These values indicate that a trimerization is possibly occurring in the aqueous environment. As an auxiliary experiment for the calculation of the molecular volume using Perrin equation, fluorescence quenching constants (K_q) with the quencher acrylamide and fluorescence lifetimes (τ_f) of the intrinsic fluorophore tryptophan residue were estimated in the two different solvent systems. K_q in water was 18.21M^{-1} and it was 46.24M^{-1} in organic solvent. Fluorescence lifetimes of tryptophan residue were calculated to be 2.80 nsec. in water and 3.81 nsec. in organic solvent, respectively.

Introduction

Proteolipid is a kind of hydrophobic membrane-bound proteins. They are characterized by their solubility in chloroform-methanol, and contain covalently bound fatty acid residues, probably attached in ester linkage to serine or threonine hydroxyl groups. By the way, the apoprotein whose lipid components are almost removed can be obtained by the routine methods. The extraction of proteolipids is possible

by the chloroform-methanol solvent mixture. They are readily soluble in chloroform-methanol (2:1, v/v) solvent system and insoluble in water, but a water soluble form can be prepared by several methods¹⁻³. The organic solvent soluble form of proteolipid and the water soluble one can be interconvertible each other.

The proteolipids in the plasma membrane have all been related with the ion channel formation for transporting K^+ ions. To understand the structure-function relationship of these proteins, a few physico-chemical studies have been carried out. Circular dichroic analysis for these proteins must be

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