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Synthesis and Characterization of Thallium (III) Complexes with Tetracyanoquinodimethane, $Tl(TCNQ)_3$ and $TlCl_2(TCNQ)_{2.5}$

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$TlCl_2(TCNQ)_{2.5}$ and $Tl(TCNQ)_3$ were obtained from the reaction of $LiTCNQ$ ($TCNQ$ =tetracyanoquinodimethane) and TlX_3 ($X=Cl$ and NO_3). These compounds were characterized by spectroscopic (IR, UV, EPR), electrochemical methods, and electrical conductivity measurements. Thermal analysis (TG, DSC) was also conducted. The room temperature electrical conductivities of these compounds are in the range of semiconductors. Spectroscopic studies indicate that $Tl(TCNQ)_3$ has fully ionized $TCNQ^-$ ions in a form of simple salt, whereas $TlCl_2(TCNQ)_{2.5}$ is consisted of $TCNQ^-$ and $TCNQ^0$ as a complex salt. EPR $\langle g \rangle$ values of $TCNQ^-$ radical anion are 1.999 in both compounds and the signal attributable to metal ion is not observed, suggesting that any unpaired electrons are localized on $TCNQ$ radicals, and metal atoms have diamagnetic state. Ligand decomposition and reduction process are simultaneously progressed in both compounds above at 200 °C. The endothermic activation energy of $TlCl_2(TCNQ)_{2.5}$ is shown somewhat larger than that of $Tl(TCNQ)_3$, it may be due to $Tl-Cl$ bond strength. The mid-peak potentials of these compounds are very similar to those of $TCNQ$ and the values of E_{pa} and E_{pc} are almost equal to 1. The wave of thallium ion is not detected in cyclic voltammogram, hence the redox processes of the complexes might be mainly localized to the $TCNQ$ ligand rather than thallium ion.

Introduction

The understanding of the electrical properties of purely organic compounds has been focused over past fifteen years. While most of known organic materials are electrical insulators, some of those exhibit high electrical conductivity comparable to metals.¹ Conducting organic compounds have been called as "organic metals" or "synmetals". Many researchers have performed in the studies of their designs, syntheses and physical properties as well as their potential technological applications.¹⁻⁹ Two paths of conducting organic charge transfer complexes are proposed as follows: One is the combination of various organic cations with $TCNQ$.²⁻⁶ But, the conductivities of these complexes are lower than that of tetrathiafulvalene-tetracyanoquinodimethane (TTF- $TCNQ$) com-

pound.² The others are focused on the electrical properties of TTF- $TCNQ$ and their relationship to the metallic state.

We have interested in incorporating inorganic materials with $TCNQ$. Shchegolov and coworkers⁶ first reported a 1:1 and a 1:2 complex between bis(benzene)-chromium and $TCNQ$. Siedle and coworkers⁷ also reported $V(TCNQ)_2$, $Cr(TCNQ)_2(CH_3CN)_2$, $Mo(TCNQ)(CO)_2$, $W(TCNQ)(CH_3CN)_2$, $Co(TCNQ)(CH_3CN)_2$, and $Ni(TCNQ)_2$. All of these complexes exhibited interesting properties, but none of them were conducting. $TCNQ$ molecule is a very interesting ligand;¹⁰ (i) stacking ligand to form aggregates *via* π/π interaction (ii) ambidentate and bridging ligand through one or more nitrile N lone pairs (iii) non-innocent ligand to be reduced to anionic radical and further to dianionic form exhibiting unusual conducting, optical, and magnetic properties.

Recently, tetranuclear pentaamineruthenium complexes with TCNQ were reported,¹¹ in which described that TCNQ was bridged in various oxidation states (TCNQ^{0/-1/-2}). The oxidation state of TCNQ as well as the crystal structure plays an important role to lead high conductivity. In this paper, thallium-TCNQ complexes were prepared from the reaction of LiTCNQ with TiX₃ (X=Cl, NO₃). The main question was the proper oxidation state formulation with respect to the TCNQ ligand. The simple salt with the formula, Ti(TCNQ)₃ and the complex (mixed) salt, TiCl₂(TCNQ)_{2.5} were evidenced from the spectroscopic properties. The compounds were characterized by electrical conductivity measurements, EPR, thermal analysis (TGA, DSC), and electrochemical methods.

Experimental

Synthesis. TiCl₂(TCNQ)_{2.5} was prepared from the reaction of LiTCNQ (1 mmol) with TiCl₃·2H₂O (0.3 mmol) in ethanol under argon atmosphere. LiTCNQ was prepared according to the literature method using LiI and TCNQ in acetonitrile.¹² The resulting mixture was stirred for ca. 4 hours at room temperature and then was kept in a refrigerator for overnight. The dark-green microcrystalline precipitates were collected on a filter paper, washed several times with absolute ethanol, and dried under vacuum. Ti(TCNQ)₃ was synthesized in a similar way using Ti(NO₃)₃·3H₂O (0.3 mmol) in ethanol. The resulted complexes were moderately air-stable. Elemental analysis was performed by Korea Basic Science Center, Seoul, Korea.

Anal. Calc. for TiCl₂(TCNQ)_{2.5}: C, 45.86; H, 1.28; N, 17.83. Found: C, 45.86; H, 1.26; N, 17.82%. Calc. for Ti(TCNQ)₃: C, 52.92; H, 1.48; N, 20.57. Found: C, 52.93; H, 1.46; N, 20.57%.

Physical Measurements. The electrical conductivities of these complexes were determined using the compressed pellets in a two electrode system at room temperature.¹³ Infrared spectra were obtained with standard KBr pelleting techniques by a Mattson Instruments Polaris FT-IR Spectrometer. The resolution was 4 cm⁻¹. Electronic absorption spectra were taken by a Shimadzu UV-265 Spectrophotometer on solution or solid/nujol mulls between quartz plates. EPR spectra were acquired on powdered and solution samples at 77 K and at room temperature using a Bruker Instruments ESP-300S ESR Spectrometer at X-band frequency (9.35 GHz). The complexes were dissolved in CH₂Cl₂/DMF (1 : 1) and then immediately frozen in liquid N₂. The field modulation frequency was 100 kHz. Thermal analysis were carried out by Rigaku thermal analyzer TAS 100 system. DSC (Differential Scanning Calorimetry) and TGA (Thermogravimetric Analysis) were used in argon atmosphere for measuring thermal properties. α-Al₂O₃ was used as a standard material. DSC and TGA range was 10 mcal/F.S. and 5 mg/F.S., respectively. The heating rate used was 5, 10, 15 and 20 °C/min and the chart speed was 2.5 mm/min. Cyclic voltammetry was performed using a conventional three electrode system. The working electrode was a Pt disk of 1 mm in diameter. The working electrode was first polished with an alumina powder (0.3 micron) on a polishing cloth attached to a glass plate and rinsed thoroughly in an ultrasonic bath. A Pt wire

was used as a auxiliary electrode. The reference electrode was a Ag wire immersed in 0.1 M AgNO₃ in acetonitrile. All the electrode potentials were reported relative to the Ag/Ag⁺ electrode for a non-aqueous system. All the electrochemical measurements were made with a BAS CV-50W Voltammetric Analyzer and computer controlled with 50W Electrochemical Software (version : 1.0). The cell solution was made from 0.1 M tetraethylammonium perchlorate (TEAP)/DMF, where TEAP was as a supporting electrolyte.

Results and Discussion

Organic semiconductors can be formed by the combination of TCNQ radical anion with a large number of cations. For example, the conductivities of Li⁺ and N-methylquinolinium (NMQN⁺) salts with TCNQ were 3×10⁻⁵ and ~10⁻⁶ S·cm⁻¹ at room temperature, respectively.² The electrical conductivities of TiCl₂(TCNQ)_{2.5} and Ti(TCNQ)₃ are 2.30×10⁻⁶ and 1.40×10⁻⁶ S·cm⁻¹, respectively. It will be shown from the spectroscopic study that Ti(TCNQ)₃ is a simple salt of TCNQ whereas a complex salt in TiCl₂(TCNQ)_{2.5}. The observed electrical conductivities are similar to the literature values of LiTCNQ, [NMPy]TCNQ and [NMQN]TCNQ compound.¹⁴ The electrical conductivity of Ti(TCNQ)₃ lies in the range of semiconductors and also similar to those of simple alkali TCNQ salts (σ_{RT}=10⁻⁴~10⁻⁶ S·cm⁻¹) which have regular TCNQ stacks.¹⁵ This implies that the regular TCNQ stacks are formed in Ti(TCNQ)₃ and this inter-stack interactions between TCNQ molecules are significant. The electrical conductivity always exhibits much higher for the complex salts with low-dimensional TCNQ stacks than for the simple ones. In case of TCNQ salt of bis(arene)chromium cations gave a conductivity of 2 S·cm⁻¹, whereas the simple salt were 5×10⁻⁶ S·cm⁻¹ at room temperature.¹⁶ Moreover, in other case of a complex salt, the conductivity of TiCl₂(TCNQ)_{2.5} is comparable to that of Ti(TCNQ)₃ in this work. This means that TiCl₂(TCNQ)_{2.5} may be consisted of isolated units such as dimer etc.¹⁷ Therefore, the stacking between TCNQ's is not effective. Keller and co-workers¹⁵ prepared [Pt(NH₃)₂](TCNQ)₂ and a series of compounds [Pt(a-a)₂](TCNQ)_x, where a-a denoted a bidentate amine ligand and x was ranged from 2 to 4. They reported that these compounds had stacks of dimers, but without overlap between dimers and the electrical conductivities ranged from 7×10⁻² to 10⁻⁶ S·cm⁻¹.

Infrared spectra were obtained using standard KBr pelleting techniques. Both the C≡N and C=C stretching bands of TCNQ can give informations on the oxidation states of TCNQ within the complexes, that is, the vibrational frequencies (ν_{C≡N} and ν_{C=C}) are going down from neutral molecules to fully charged molecular ions. IR spectra were successfully applied to the determination of the charge density distribution in the TCNQ molecule¹⁸ and semiconducting salts, such as Cs₂(TCNQ)₃¹⁹ and Cu(TCNQ).¹⁶ The spectra assignments are listed in Table 1. The assignments were carried out by comparing the data of TCNQ reported by Girlando *et al.*²⁰ The ν₂, ν₁₉ and ν₃₃ vibrational mode are associated with the stretching of C≡N band. The ν₃ and ν₂₀ mode are contributed from -C=C(CN)₂ and C=C ring stretching bands, respectively. The ν₅₀ band is arisen from the out-of-plane bending

Table 1. Physical properties of Tl-TCNQ compounds

Compound	σ_{RT} ($S \cdot cm^{-1}$)	Vibrational frequencies (cm^{-1})	Electronic frequencies (λ_{max} , nm)	EPR parameter ($\langle g \rangle$) (Gauss)	Mid-peak potentials ($E_{1/2}$)
$TlCl_2(TCNQ)_{2.5}$	2.30×10^{-6}	$\nu_{C=N}$: 2226(s), 2196 (m), 2182, 2168(w) $\nu_{C=C}$: 1544(s), 1508(w) ν_{C-H} : 811(w), 824(m)	340, 409, 422, 574, 668, 684, 749, 767 (in DMF) 246, 290, 346, 408, 436, 610, 758 (solid/nujol)	1.999	$-0.70(TCNQ^{\cdot-}/TCNQ^{2-})$ $-0.12(TCNQ^0/TCNQ^{\cdot-})$
$Tl(TCNQ)_3$	1.40×10^{-6}	$\nu_{C=N}$: 2226(w), 2195(s), 2180, 2152(s) $\nu_{C=C}$: 1569, 1544(s), 1504(s) β_{C-H} : 825(s)	340, 411, 422, 498, 617, 632, 670, 685, 749, 767 (in DMF) 234, 288, 348, 412, 434, 607, 775 (solid/nujol)	1.999	$-0.71(TCNQ^{\cdot-}/TCNQ^{2-})$ $-0.11(TCNQ^0/TCNQ^{\cdot-})$

of the C-H bonds. Extensive infrared spectroscopy studies of TCNQ salts have provided significant information on charge occupation and intermolecular interaction.¹²

In $TlCl_2(TCNQ)_{2.5}$ complex, the ν_{CN} stretching frequency is splitted into a very strong peak at 2226 cm^{-1} and a medium peak at 2196 cm^{-1} . This splitting can be explained by assuming that the nitrile group are inequivalent.¹² There are relevant bands which can be attributed either to $TCNQ^0$ or to $TCNQ^{\cdot-}$. The 2226 cm^{-1} peak at the high wavenumber is assigned to the ν_2 mode of $TCNQ^0$, and the other at 2196 cm^{-1} is attributed to the ν_{19} mode of $TCNQ^{\cdot-}$. Also, ν_{20} (1508 cm^{-1}) band may be due to the $TCNQ^{\cdot-}$, although the choice of assignments is difficult. These results indicate that both $TCNQ^{\cdot-}$ and $TCNQ^0$ states are existed in $TlCl_2(TCNQ)_{2.5}$ complex.

In $Tl(TCNQ)_3$ compound, three bands due to $TCNQ^{\cdot-}$ are exhibited in the $C\equiv N$ stretching region. A strong peak at 2195 cm^{-1} band is assigned to the ν_{19} mode of $TCNQ^{\cdot-}$ and very strong peak at 2180 and 2152 cm^{-1} to the ν_{33} mode of $TCNQ^{\cdot-}$.

As pointed out by Lunelli *et al.*,²¹ it is possible to determine whether $TCNQ^{2-}$, $TCNQ^{\cdot-}$, $TCNQ^{\delta-}$ ($0 < \delta < 1$), or $TCNQ^0$ (or a combination of these possibilities) is present in a certain compound by examining in the region of $800\text{--}880\text{ cm}^{-1}$ in the infrared spectra. The ν_{50} mode of TCNQ and $LiTCNQ$ are assigned at 811 and 827 cm^{-1} , respectively. Thus, the absorption at 811 cm^{-1} and at 824 cm^{-1} in $TlCl_2(TCNQ)_{2.5}$ indicates that $TCNQ^0$ and $TCNQ^{\cdot-}$ states are present.¹² The absorption at 825 cm^{-1} in $Tl(TCNQ)_3$ supposes that $TCNQ^{\cdot-}$ state exists.¹²

Additionally, the solution conductivity for thallium-TCNQ complexes prepared in this work was obtained on Conduct Meter Model CM-2A (TOA Electronic Ltd.). The solution conductivity for $1.25 \times 10^{-4}\text{ M}$ $Tl(TCNQ)_3$ of $103\text{ }\mu\text{S/cm}$ is similar to the value of $110\text{ }\mu\text{S/cm}$ for $TlCl_3$. This means that the formula of $Tl(TCNQ)_3$ can be presumed as $Tl^{III}(TCNQ^{\cdot-})_3$. But the solution conductivity for $TlCl_2(TCNQ)_{2.5}$ of $51.7\text{ }\mu\text{S/cm}$ was much smaller than that of $Tl(TCNQ)_3$. This difference may be come out from environmental condition, such as structural oxidation, equilibrium in solution etc.

The electronic spectra were recorded in the range of $200\text{--}800\text{ nm}$ in both solution and solid state. The results are also summarized in Table 1. The maxima absorbance (λ_{max})

of the neutral TCNQ was existed at 407 nm in DMF, whereas that of the $LiTCNQ$ was splitted at 410 and 422 nm . In both $Tl(TCNQ)_3$ and $TlCl_2(TCNQ)_{2.5}$, the λ_{max} was exhibited around at 410 and 422 nm , indicating that the presence of $TCNQ^{\cdot-}$ radical anion. However, in case of $TlCl_2(TCNQ)_{2.5}$ complex, unusual peak at 574 nm is shown, but this peak has not been assigned as yet.

The EPR spectra of $TlCl_2(TCNQ)_{2.5}$ and $Tl(TCNQ)_3$ in $CHCl_3/DMF$ at 77 K exhibited a symmetric signal centered in the same value, $\langle g \rangle = 1.999$. A signal related to Tl ion in both compounds was not detected. The observed g values and the absence of metal ion signals clearly propose that any unpaired electrons are localized on TCNQ radicals and the metal atoms have diamagnetic $Tl(III)$ (d^{10}) electronic state. The g values of $TlCl_2(TCNQ)_{2.5}$ and $Tl(TCNQ)_3$ are similar to the value of 2.003 for $TCNQ^{\cdot-}$.²² This supports that $TlCl_2(TCNQ)_{2.5}$ and $Tl(TCNQ)_3$ complexes contain $TCNQ^{\cdot-}$ radical anion.

Thermal properties were obtained by DSC and TGA. TG thermogram of $TlCl_2(TCNQ)_{2.5}$ shows that decomposition has occurred by two steps. The first endothermic peak at $206\text{--}269\text{ }^\circ\text{C}$ may be attributed to the loss of two chlorides and two TCNQ molecules, and the second exothermic peak at $351\text{--}426\text{ }^\circ\text{C}$ to the loss of 0.5 mole TCNQ molecules. TG thermogram of $Tl(TCNQ)_3$ complex was different from that of $TlCl_2(TCNQ)_{2.5}$ and observed three steps of decomposition: in the first and second steps, together two moles of TCNQ were lost around $207\text{--}355\text{ }^\circ\text{C}$ and the last step was attributed to the loss of one mole of TCNQ.

In case of $TlCl_2(TCNQ)_{2.5}$, IR spectra were investigated after decomposing at $350\text{ }^\circ\text{C}$. The IR intensity of $TlCl_2(TCNQ)_{2.5}$ decomposed at $350\text{ }^\circ\text{C}$ almost disappeared. However, the CN stretching frequencies after the decomposition at $350\text{ }^\circ\text{C}$ were shifted from 2226 cm^{-1} to 2206 and 2179 cm^{-1} , indicating that the neutral $TCNQ^0$ is not exist in $Tl(TCNQ)_{0.5}$. Considering the above results, we propose that the oxidation state of $TlCl_2(TCNQ)_{2.5}$ compound is changed from $Tl(III)$ to $Tl(I)$ during decomposition process. It is well known that the oxidation state of Tl is quite stable; in aqueous solution $Tl(I)$ is distinctly stable than $Tl(III)$ with the value of the standard reduction potential of $+1.25\text{ V}$ ($Tl(III) \rightarrow Tl(I)$).²³

In the study of DSC in $Tl(TCNQ)_3$, endothermic peak and 1st exothermic peak were appeared continuously in the range

of 254-291 °C. An identical phenomenon was observed in sparteine-CuCl₂ complex,²⁴ and it was concluded that the exothermic peak was due to the evolution of HCl resulting from the decomposition of sparteine ligand and the reduction of Cu(II) to Cu(I). In sparteine-ZnCl₂ complex,²⁴ the exothermic peak was not present because of the difficulty of the reduction of the Zn metal. Therefore, we suggest that the endothermic peak of Tl(TCNQ)₃ complex may be caused by the dissociation of Tl-TCNQ bond resulting from the reduction from Tl(III) to Tl(I), while the consecutive 1st exothermic peak may be related to the evolution of HCN. The evidence of HCN evolution were identified with a manual test using AgNO₃ solution.

The following Ozawa equation²⁵ may be used to determine an apparent activation energies.

$$\log \Psi + 0.4567E_a/RT_m = \text{constant}$$

, where Ψ : heating rate, T_m : maximum deflection temperature

The maximum deflection temperature increases as increasing the heating rate. The Ozawa plot ($\log \Psi$ vs. $1/T_m$) should

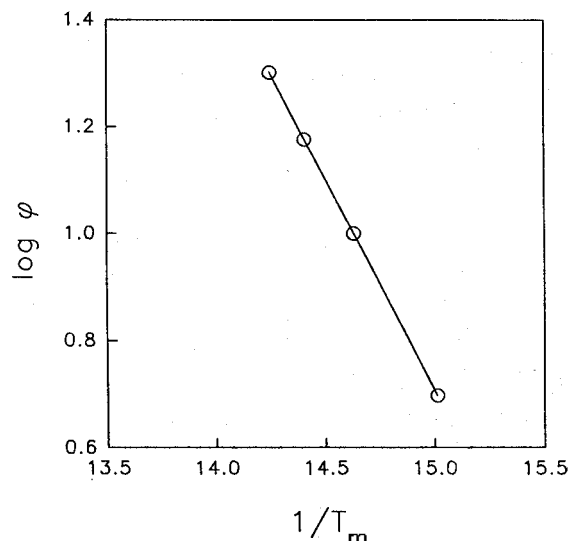


Figure 1. The Ozawa's plot of TlCl₂(TCNQ)_{2.5}.

be linear, as shown in Figure 1. The activation energy are evaluated from the slope and the results are listed in Table 2. Endothermic activation energy (119.7 kJ/mol) of Tl(TCNQ)₃ is somewhat smaller than that of TlCl₂(TCNQ)_{2.5} (122.7 kJ/mol). This result may be come from the stronger Tl-Cl bond strength than Tl-TCNQ.

Cyclic voltammograms of TCNQ, LiTCNQ and thallium-TCNQ complexes were recorded in 0.1 M TEAP/DMF on a Ag/Ag⁺ non-aqueous reference electrode. The observed mid-peak potential ($E_{1/2}$) values of TCNQ are -0.74 V (TCNQ⁻/TCNQ²⁻) and -0.14 V (TCNQ⁰/TCNQ⁻) and those of LiTCNQ are -0.73 V and -0.14 V, respectively. Moreover, similar values were observed for thallium-TCNQ complexes and are listed in Table 1. The peak related to thallium ion was not detected, hence redox processes of these complexes may be localized to the ligands rather than metal center. The value of E_{pa} and E_{pc} should be identical for simple reversible couple, $E_{pa}/E_{pc}=1$.²⁶ The mid-peak potentials of these compounds indicate that the values of E_{pa}/E_{pc} are nearly equal to 1. This result means that the redox processes are quite reversible.

Conclusion

Thallium-TCNQ compounds were characterized by spectroscopic (IR, UV, EPR), electrochemical methods, electrical conductivity measurements, and thermal analysis. In case of TlCl₂(TCNQ)_{2.5}, both TCNQ⁻ radical anion and TCNQ⁰ neutral state are existed as a complex salt, while Tl(TCNQ)₃ complex contains TCNQ⁻ radical anion. The electrical conductivities of these compounds are in the range of semiconductor at room temperature. This result forces the conclusion that Tl(TCNQ)₃ consists of segregated stacks of the TCNQ⁻ anion, thereby providing a pathway for inter-stack interaction, whereas TlCl₂(TCNQ)_{2.5} is existed as an isolated unit. This suggestion could be evidenced from a structure determination by x-ray crystallography. However, we have not yet obtained the single crystal suitable for the experiment.

Thermal analysis results of TlCl₂(TCNQ)_{2.5} and Tl(TCNQ)₃ were different from each other. Metal-ligand decomposition and reduction process were progressed simultaneously in both compounds above at 200 °C. The endothermic activation energy of TlCl₂(TCNQ)_{2.5} was shown somewhat larger than

Table 2. Thermal analytical data of Tl-TCNQ compounds

Compound	Temperature range of decomposition (°C)	% loss (calc.)	Probable composition of		DSC	E_a (kJ/mol) ^a
			expelled group	residual		
TlCl ₂ (TCNQ) _{2.5}	206-269	60.61 (61.00)	Cl ₂ (TCNQ) ₂	Tl(TCNQ) _{0.5}	endothermic (263.2 °C)	122.7
	351-426	12.33 (12.99)	(TCNQ) _{0.5}	Tl	exothermic (426.2 °C)	143.2
Tl(TCNQ) ₃	207-355	49.63 (49.99)	(TCNQ) ₂	Tl(TCNQ) ₁	endothermic (247.5 °C)	119.7
	382-471	26.77 (24.99)	(TCNQ) ₁	Tl	exothermic (275.0 °C) exothermic (446.7 °C)	108.9 167.0

^a Activation energy (E_a) was obtained by Ozawa method, $\log \Psi + 0.4567 E_a/RT_m = \text{const.}$ (where Ψ : heating rate, T_m : maximum deflection temp. of DSC peak)

that of $Tl(TCNQ)_3$, it may be closely related to Tl-Cl bond strength.

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Cobalt(III) Complexes of N_4 and N_2O_2 System Tetradentate Ligands: Amino Acid Cobalt(III) Complexes of 1,3-Diaminopropane- N,N' -Di- α -(β -methyl)-Pentanoic Acid

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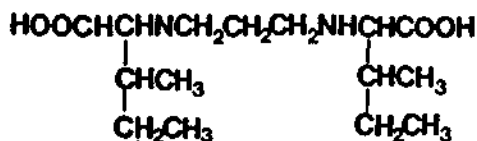
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Amino acid cobalt(III) complexes of 1,3-diaminopropane- N,N' -di- α -(β -methyl)-pentanoic acid (H_2dpdmp), *uns-cis*-[Co(dpmp)(aa)] (aa = glycine, S-alanine, R-aspartic acid, sarcosine) have been prepared from the reaction between the *uns-cis*-[Co(dpmp)Cl₂]⁻ complex and the corresponding amino acid. In the reaction with the *uns-cis*-[Co(dpmp)Cl₂]⁻ complex, glycine and S-alanine have yielded both meridional and facial isomers, while R-aspartic acid and sarcosine, only meridional isomers. The stereospecific substitution reaction of R-aspartic acid to racemic *uns-cis*-[Co(dpmp)Cl₂]⁻ complex has yielded two meridional diastereomers; ΔR -*uns-cis*- and ΔR -*uns-cis*-[Co(dpmp)(R-asp)]. It is of interest to note that this is one of the few Co^{III}(ONNO)(aa) type complex preparations, which gives only one isomer with stereospecificity. On the other hand, two meridional products obtained from the reaction of sarcosine with racemic *uns-cis*-[Co(dpmp)Cl₂]⁻ are turned out to be mixtures of optical isomers.

Introduction

1,3-diaminopropane-di- α -(β -methyl)-pentanoic acid (H_2dp -



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