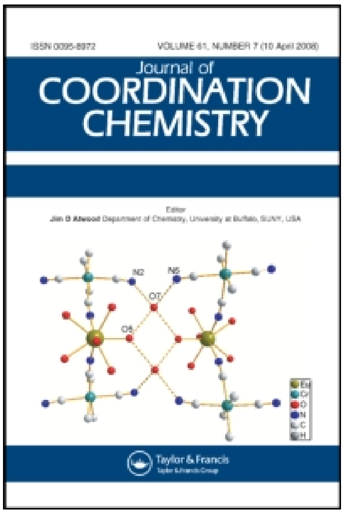

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Preparation and Properties of *trans*-[CoCl$_2$(tmd>)$_2$]Cl, and *trans*- and *cis*-[Co(NCS)$_2$(tmd)$_2$]NO$_3$ (tmd: Tetramethylenediamine)

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PREPARATION AND PROPERTIES OF *TRANS*-[$CoCl_2(tmd)_2$]Cl, AND *TRANS*- AND *CIS*-[$Co(NCS)_2(tmd)_2$]NO_3 (tmd: TETRAMETHYLENEDIAMINE)

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The cobalt(III) complexes $[CoX_2(tmd)_2]^+$ (X: Cl^- or NCS^-, tmd: tetramethylenediamine), in which tmd forms a seven-membered chelate ring, have been prepared. *Trans*-[$CoCl_2(tmd)_2$]Cl was derived from [$Co(NO_2)_2(tmd)_2$]NO_3 in a fairly good yield. Two geometrical isomers, *trans* and *cis*, of [$Co(NCS)_2$-$(tmd)_2$]NO_3 were independently synthesized from *trans*-[$CoCl_2(tmd)_2$]Cl by different methods. The geometrical configurations of the isomeric pair of the NCS complex have been determined based on chromatographic behavior, electronic absorption spectra, and vibrational spectra. The *d–d* and CT absorption maxima of the NCS complex ($18.7 \times 10^3\,cm^{-1}$ ($\varepsilon = 275$) and $30.9 \times 10^3\,cm^{-1}$ ($\varepsilon = 3630$) for the *trans* isomer, $19.3 \times 10^3\,cm^{-1}$ ($\varepsilon = 302$) and $31.0 \times 10^3\,cm^{-1}$ ($\varepsilon = 4070$) for the *cis* isomer) and the Co–N(amine) stretching frequency of *trans*-[$CoCl_2(tmd)_2$]Cl ($418\,cm^{-1}$) have been compared with those of the corresponding ethylenediamine and trimethylenediamine complexes.

Keywords: Tetramethylenediamine; Cobalt(III); Seven-membered chelate ring; Geometrical isomers

INTRODUCTION

Tetramethylenediamine (tmd; putrescin or 1,4-diaminobutane) is a biogenic diamine occurring in practically all types of cells and interacts with biomolecules such as nucleic acids in biological systems. In this regard, the copper (II)/nucleoside or nucleotide/tmd system has been recently studied [1,2].

Tmd is distinct from ethylenediamine (en) and trimethylenediamine (tn) with regard to its coordination mode to transition metals. While en and tn act mainly as chelating ligands, tmd tends to act as a bridging or a monodentate ligand rather than a chelating ligand (see Scheme 1) [3,4]. As a result, little is known about the stability and ligand field strength of a tmd chelate, though it is of importance to know such properties of a tmd chelate in order to better understand the behavior of tmd in biological systems.

The preparation of complexes containing a tmd chelate is more difficult than the en and tn complexes. [$Co(tmd)_3$]Br_3 has been prepared from cobalt(II) nitrate and tmd in

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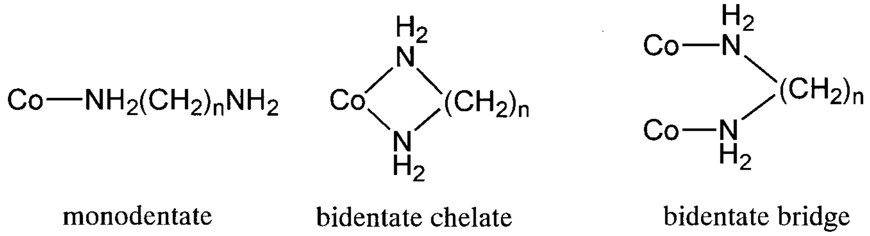


SCHEME 1

dimethylsulfoxide by air oxidation [5]. However, the major product obtained by this method was polymeric complexes that might contain bridging tmd ligands, while the yield of the desired chelate complex was only 6% [5]. Many complexes of [$CoX_2(N\text{–}N)_2$]-type (X: monodentate ligand; N–N = en or tn) have been synthesized using *trans*-$[CoCl_2(N\text{–}N)_2]^+$ as the starting material. However, *trans*-$[CoCl_2(tmd)_2]^+$ has been prepared only as a by-product of $[Co(tmd)_3]^{3+}$ in a very low yield [5]. As a consequence, only a few bis(tmd) complexes have been fully characterized [6].

We have briefly communicated that $[Co(NO_2)_2(tmd)_2]NO_3$ was synthesized in 16% yield (total of *trans* and *cis* isomers) and *trans*-$[CoCl_2(tmd)_2]Cl$ could be derived from $[Co(NO_2)_2(tmd)_2]NO_3$ in a fairly good yield [7]. We now report the preparation, characterization, and some properties of *trans*- and *cis*-$[Co(NCS)_2(tmd)_2]NO_3$.

EXPERIMENTAL

Instrumentation

The electronic absorption spectra were recorded on a Hitachi 220 spectrophotometer. The Raman spectra were records on a JASCO R-800 Laser Raman spectrophotometer using a He-Ne laser as the excitation source. A spinning sample cell was employed to avoid decomposition of the solid sample induced by laser illumination. The infrared spectra were measured as Nujol mulls and an aqueous solution between KRS-5 plates using a JASCO A-3 spectrophotometer.

Preparation of Complexes

Trans-[CoCl₂(tmd)₂]Cl *Trans*- and/or *cis*-$[Co(NO_2)_2(tmd)_2]NO_3^7$ (0.5 g; 1.3 mmol) was dissolved in 3 mL of conc. H_2SO_4. The color of the solution turned violet with the evolution of nitrogen dioxide. (*Caution*! Nitrogen dioxide is toxic. This procedure should be done in a well-ventilated chamber.) After evolution of the NO_2 gas ceased, the solution was added to 1 L of water. The diluted solution was poured onto a cation-exchange column (SP-Sephadex C-25, H^+ form, ϕ 4 cm × 20 cm). The column was then washed with water. The purple complex was eluted with 0.3 M of HCl. The purple eluate was evaporated to dryness to give green *trans*-$[CoCl_2(tmd)_2]Cl\cdot H_2O$ [5]. The crude product was dissolved in minimum 0.3 M HCl. The pure product precipitated upon the addition of conc. HCl. The deposited green crystals were collected by filtration, washed with ether, and air-dried. The yield was 0.29 g (62.5%).

Trans-[Co(NCS)$_2$(tmd)$_2$]NO$_3$ (isomer 1) *Trans*-[CoCl$_2$(tmd)$_2$]Cl · H$_2$O (0.14 g; 0.39 mmol) was added to 30 mL of methanol. To the mixture was immediately added an excess of KSCN (1.3 g; 13 mmol) with stirring. The color of the solution turned from green to gray, and finally to purple. A reddish-purple precipitate appeared after 2 h. Stirring was continued for an additional half hour. The precipitate was collected by filtration, and dissolved in 20 mL of 0.01 M HNO$_3$. The solution was passed through an anion-exchange column (Dowex 1 × 8, 200–400 mesh NO_3^--type, ϕ 4 cm × 10 cm) for exchange to the nitrate salt. The elute was concentrated to 5 mL, and kept in a refrigerator. The finely deposited purple crystals were collected by filtration, washed with ethanol and ether, and air-dried. The yield was 0.0017 g (10.5%). Anal. Calcd. for $C_{10}H_{24}N_7ClCoO_3S_2$(%): C, 29.1, H, 5.9, N, 23.7: Found: C, 29.1, H, 6.2, N, 23.5.

Cis-[Co(NCS)$_2$(tmd)$_2$]NO$_3$ (isomer 2) *Trans*-[CoCl$_2$(tmd)$_2$]Cl · H$_2$O (0.20 g; 0.57 mmol) was dissolved in 15 mL of 0.001 M HNO$_3$. To the resulting red solution was added silver nitrate (0.29 g; 1.7 mmol). The solution was stirred for half an hour in a dark place. The precipitated silver chloride was filtered out. To the filtrate was added an excess of KSCN (1.2 g; 12 mmol) with stirring. The reddish-purple powder began to precipitate after 10 min. After stirring for 1 h, the reddish purple precipitate was collected by filtration. The precipitate was dissolved in 30 mL of 0.01 M HNO$_3$. The solution was passed through an anion-exchange column (Dowex 1 × 8, 200–400 mesh NO_3^--type, ϕ 4 cm × 10 cm) for exchange to the nitrate salt. The eluate was concentrated to 5 mL, and kept in a refrigerator overnight. The deposited reddish-purple fine crystals were filtered, washed with ethanol and ether, and air-dried. The yield was 0.12 g (49%). Anal. Calcd. for $C_{10}H_{24}N_7ClCoO_3S_2$(%): C, 29.1, H, 5.9, N, 23.7. Found: C, 29.0, H, 6.1, N, 23.7.

RESULTS AND DISCUSSION

Preparation, Assignment of Geometrical Isomers, and Some Spectroscopic Characteristics

We have prepared the two geometrical isomers of [Co(NCS)$_2$(tmd)$_2$]NO$_3$ (isomers **1** and **2**) by two different methods (see Experimental section). In order to examine the isomeric purity of the complexes, the column-chromatographic behavior of each complex was examined.

The solution of each complex was poured onto a column containing a cation-exchange resin (SP-Sephadex C-25, Na$^+$ form) and eluted with 0.05 M NaClO$_4$. Only one band was eluted in each case, indicating that each complex obtained by the different preparation methods was isomerically pure, and thus each geometrical isomer was selectively synthesized.

For the [CoX$_2$(en)$_2$]$^+$-type complexes (X: monodentate anion), the *trans* isomer is generally eluted earlier than the corresponding *cis* isomer, since the *trans* isomer has a lower dipole moment than the *cis* counterpart. We dissolved the separately prepared two isomers of [Co(NCS)$_2$(tmd)$_2$]NO$_3$ in water and chromatographed them over the cation-exchange resin. Isomer **1** was first eluted, followed by isomer **2**. This chromatographical behavior suggests that isomer **1** has the *trans* configuration, and therefore isomer **2** has the *cis* configuration.

It is well known that the electronic absorption spectra of $[CoX_2(N–N)_2]$ ($X = NO_2^-, NCS^-$–, or N_3^-) complexes are diagnostic for the geometrical configurations. As shown in Table I, the *d–d* band in the visible region as well as the intense LMCT (or specific) bands in the UV region of the *trans* isomers lie in the lower energy region than those of the *cis* counterparts for the ethylenediamine [8] and trimethylenediamine complexes [9,10].

Figure 1 shows the electronic absorption spectra of isomers **1** and **2** and the observed absorption maxima are listed in Table I. The *d–d* band as well as the CT band of isomer **1** is situated in a lower energy region than those of isomer **2**, though the difference in the CT region is very small. This observation suggests that isomer **1** has the *trans* configuration and isomer **2** the *cis* configuration in agreement with the assignment based on the chromatographic behavior.

Raman spectra in the skeletal vibration (vibration related to the coordination bonds) region have been successfully applied to determine the geometrical configuration of $[Co(NO_2)_2(tmd)_2]NO_3$ [7]. If the molecular symmetry of *trans*-$[Co(NCS)_2(tmd)_2]^+$ is

TABLE I Maxima ($10^3\,cm^{-1}$) and molar absorbance of the electronic absorption bands of bis(isothiocyanato)bis(diamine) cobalt(III) complexes

Diamine	*Configuration*	*d–d band* $\nu_{max}, (\varepsilon)$	*CT band* $\nu_{max}, (\varepsilon)$	*Ref.*
en	*trans*	19.7 (275)	31.6 (3090)	8
	cis	20.4 (347)	32.5 (2880)	8
tn	*trans*	18.2 (331)	28.7 (3290)	9
	cis	19.2 (319)	29.4 (2750)	10
tmd	*trans* (isomer **1**)	18.7 (275)	30.9 (3630)	This work
	cis (isomer **2**)	19.3 (302)	31.0 (4070)	This work

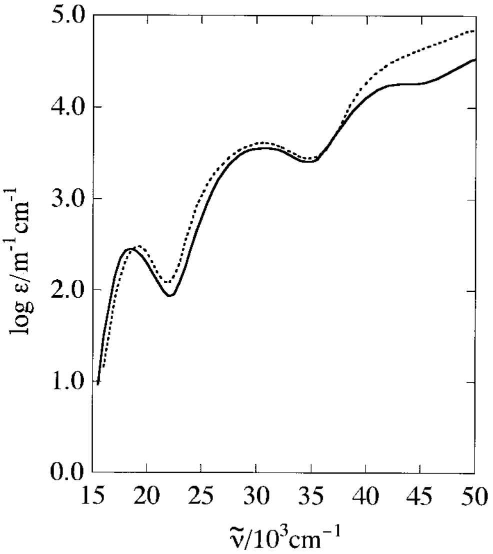


FIGURE 1 Electronic absorption spectra of $[Co(NCS)_2(tmd)_2]NO_3$ (isomer **1**, solid line; isomer **2**, broken line).

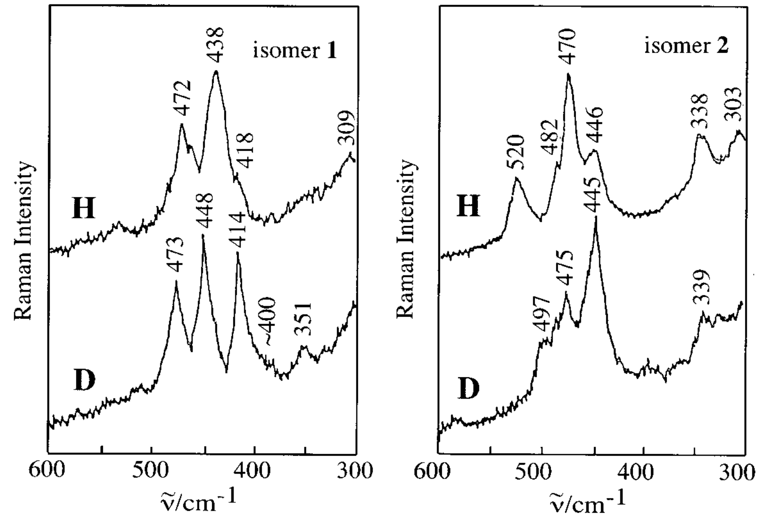


FIGURE 2 Raman spectra of the isomeric pair of $[Co(NCS)_2(tmd)_2]NO_3$ in the skeletal vibration region (upper, normal complex; lower, N-deuterated complex).

assumed to be D_{2h}, two Co–N(amine) stretching vibrations (A_g and B_{1g} modes) are Raman active. On the other hand, four Co–N(amine) stretching vibrations ($2A + 2B$) are expected to be observed in the Raman spectrum of *cis*-$[Co(NCS)_2(tmd)_2]^+$ based on the assumption of C_2 symmetry.

The upper part of Fig. 2 shows the Raman spectra of the two geometrical isomers of $[Co(NCS)_2(tmd)_2]NO_3$ in the 300–600 cm^{-1} region. The Co–N(amine) stretching vibrations are expected to lie in the 400–550 cm^{-1} region [11,12]. In the present NCS complexes, however, the NCS bending vibrations are also expected to lie in the same region [13]. In order to discriminate the Co–N(amine) stretching and the NCS bending vibrations, the Raman spectra of the N-deuterated complexes of $[Co(NCS)_2(tmd)_2]NO_3$ were measured. In spite of the N-deuteration experiment, the assignment of the Raman bands was still difficult because of the serious band overlapping between the Co–N(amine) stretching and the NCS bending vibrations as shown in the lower part of Fig. 2. A similar difficulty in the assignment of the infrared and Raman spectra has been noted for $[Co(NCS)_2(NH_3)_4]Cl$ [14]. The polarization Raman measurement of a solution sample is sometimes useful to assign the symmetry of the vibrational modes. The Raman spectrum of the solution $[Co(NCS)_2(tmd)_2]NO_3$ could not be obtained due to the low solubility of the complex.

The infrared spectra of the CN stretching region has been applied to distinguish the geometrical isomers of $[Co(NCS)_2(en)_2]Cl \cdot H_2O$, i.e., the *trans* isomer exhibits one band at 2136 cm^{-1}, while the *cis* one has two bands at 2122 and 2110 cm^{-1} [15]. The infrared and Raman spectra of isomers **1** and **2** in the solid state are shown in Fig. 3 (solid line). Both isomers exhibit two infrared bands and two Raman bands in the CN stretching region. The positions of the infrared bands do not coincide with those of the Raman bands. The above facts indicate that both isomers exhibit four bands that can be assigned to the CN stretching. Thus, the vibrational spectra of the solid sample in the CN stretching region were not useful to differentiate the geometrical isomers of the present tmd complexes. The appearance of the additional bands for the solid sample is considered to be a result of the lowering of the molecular symmetry in the solid state as found for $[Co(NCS)_2(NH_3)_4]Cl$ [14].

Contrary to the solid state spectra, the infrared spectra of a saturated D_2O solution of isomers **1** and **2** (broken line) show the distinct differences between the two isomers. Isomer **1** exhibits one band at $2117\,cm^{-1}$ while isomer **2** has two bands at 2101 and $2132\,cm^{-1}$. These infrared characteristics confirm the geometrical configuration of isomers **1** and **2**.

On the basis of the above assignment of the geometrical configurations, the selective preparation of the geometrical isomers of $[Co(NCS)_2(tmd)_2]^+$ can be explained as shown in Scheme 2. The methanolic solution of *trans*-$[CoCl_2(tmd)_2]Cl$ kept its original green color, indicating that the isomerization did not occur in methanol at least during the preparation procedures. Then, *trans*-$[Co(NCS)_2(tmd)_2]SCN$ can be prepared exclusively by substitution of the chloro ligands with NCS^-. On the other hand, aquation of *trans*-$[CoCl_2(tmd)_2]Cl$ is considered to be accompanied by complete isomerization to *cis* configuration. This consideration would be reasonable since the isomer of $[Co(OH_2)_2(en)_2]^{3+}$ obtained is *cis*. The substitution of the aqua ligands by NCS^-, then, exclusively yields *cis*-$[Co(NCS)_2(tmd)_2](SCN)$.

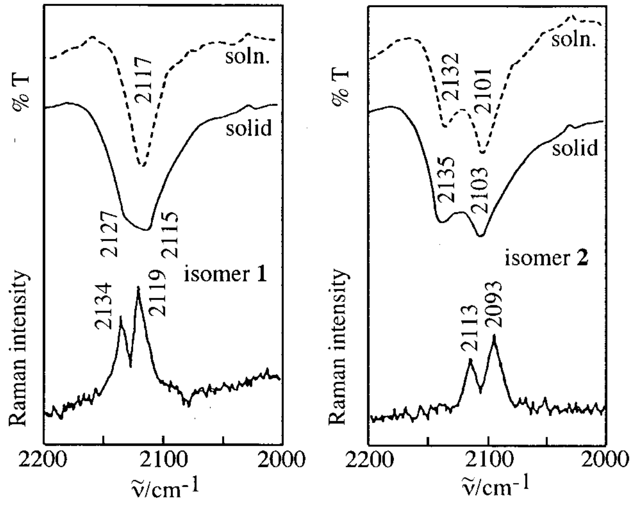
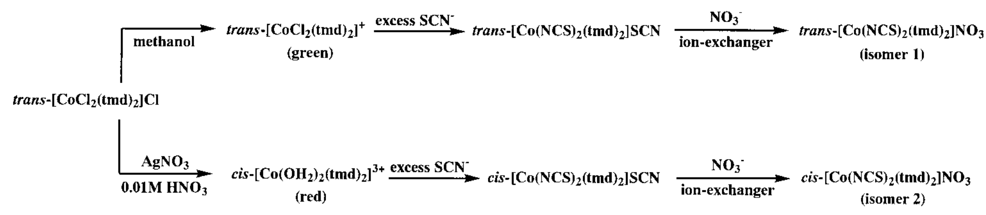


FIGURE 3 Infrared and Raman spectra of the isomeric pair of $[Co(NCS)_2(tmd)_2]NO_3$ in the CN stretching vibration region (solid sample, solid line; D_2O solution, broken line).



SCHEME 2

The present tmd complexes are relatively stable in aqueous solution at room temperature similar to the tn counterparts, but heating above 50°C caused decomposition of the complexes accompanying the reduction to cobalt(II).

Ligand Field Strength of a tmd Chelate

In the tris(diamine) complexes, the *d–d* absorption positions continuously shift to lower energy with the expansion of the chelate ring size (21.3 ($\varepsilon = 95.5$) and 29.4×10^3 ($\varepsilon = 155$) cm^{-1} for en, 20.5 ($\varepsilon = 75.9$) and 28.6×10^3 ($\varepsilon = 75.9$) cm^{-1} for tn, and 19.9 ($\varepsilon = 77.8$) and 27.9×10^3 ($\varepsilon = 70.4$) cm^{-1} for tmd) [5]. This indicates that the ligand field strength of the diamine decreases in this order in the tris(diamine) complexes.

The *d–d* band positions of $[\mathrm{Co(NCS)_2(N{-}N)_2}]$ complexes (N–N: en, tn, and tmd) are compared in Table I. The *d-d* band positions of $[\mathrm{Co(NCS)_2(tn)_2}]^+$ lie lower in energy compared to $[\mathrm{Co(NCS)_2(en)_2}]^+$, consistent with the tendency observed for the tris(diamine) type complexes. Interestingly, the *d–d* band maximum of *cis*-$[\mathrm{Co(NCS)_2(tmd)_2}]^+$ lies at almost the same position as that of the corresponding tn complex. Furthermore, *trans*-$[\mathrm{Co(NCS)_2(tmd)_2}]^+$ exhibits *d–d* band in a slightly higher energy region than the corresponding tn complex. These observations indicate that the ligand field strength of the tmd chelate of cobalt(III) is similar to that of the tn chelate in the bis(NCS) complexes. Then, in the $[\mathrm{Co(tmd)_3}]^{3+}$ complex, the steric interactions among the three flexible seven-membered chelate rings would reduce the ligand field strength of the tmd chelate.

The Co–N(amine) stretching frequency (or more strictly, the force constant) can be regarded as a measure of the strength of the coordination bond. The totally symmetric stretching vibration of the Co–N(amine) bonds, ν_S(Co–N(amine)), of the *trans*-$[\mathrm{CoX_2(N{-}N)_2}]$-type complexes, which is Raman active, but infrared inactive under D_{2h} symmetry, is considered to be a reliable indication of the Co–N(amine) stretching frequency for the following reasons. The mechanical coupling of ν_S(Co–N(amine)) with ν_S(Co–a) is negligible as the displacement vectors of the two stretching modes are at right angles to each other in the *trans* geometry. Therefore, the observed band is considered to be due to a fairly pure Co–N(amine) stretching vibration. The Raman band due to ν_S(Co–N(amine)) generally appears as an intense band and hence is easily assignable in most cases. Unfortunately, we could not clearly assign the ν_S(Co–N(amine)) for *trans*-$[\mathrm{Co(NCS)_2(tmd)_2}]\mathrm{NO_3}$ because of band overlap. Therefore, we compare ν_S(Co–N(amine)) for the *trans*-$[\mathrm{CoCl_2(N{-}N)_2}]^+$ complexes (N–N: en, tn, and tmd).

Figure 4 shows the Raman spectrum of *trans*-$[\mathrm{CoCl_2(tmd)_2}]\mathrm{Cl}$ in the 200–500 cm^{-1} region. The band at 418 cm^{-1} can be assigned to the ν_S(Co–N(amine)). The band at 445 cm^{-1} is assignable to the B_{1g} mode of the Co–N(amine) stretching. The very intense band at 271 cm^{-1} is due to ν_S(Co–Cl) [11]. Table II summarizes the observed Raman frequencies of ν_S(Co–N(amine)) and ν_S(Co–Cl) for the *trans*-$[\mathrm{CoCl_2(N{-}N)_2}]^+$ complexes. The ν_S(Co–Cl) frequency is only slightly affected by the coexisting diamine, suggesting that the mechanical coupling between ν_S(Co–N(amine)) and ν_S(Co–Cl) is rather small.

The ν_S(Co–N(amine)) frequency of the tn complex decreases by 76 cm^{-1} compared to that of the en complex. However, the difference in the ν_S(Co–N(amine)) frequency between the tn and tmd complexes is only 25 cm^{-1}. Therefore, the ν_S(Co-N(tmd)) frequency also indicates that the strength of the coordination bond in the tmd chelate is not so weak compared to that of the tn chelate.

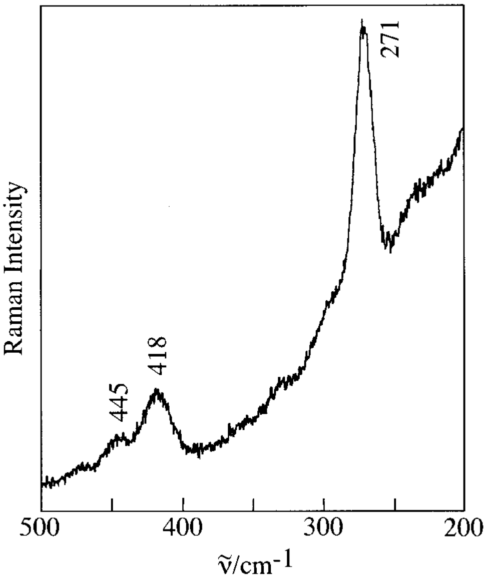


FIGURE 4 Raman spectrum of *trans*-[$CoCl_2(tmd)_2$]Cl in the skeletal vibration region.

TABLE II Vibrational frequencies (cm^{-1}) of Co–N(amine) and Co–Cl stretching vibrations for *trans*-[$CoCl_2(N\text{–}N)_2$]$^+$ complexes

Diamine	ν_S*(Co–N)*	ν_S*(Co–Cl)*	*Ref.*
en	519	281	13
tn	443	274	14
tmd	418	271	This work

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