November, 1973]   BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 46, 3453—3457 (1973)   3453

Trimethylenediamine Complexes. III.[1] *cis-trans* Isomeric Pairs of Diazido- and Dicyano-bis(trimethylenediamine)cobalt(III) Complexes

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(Received June 20, 1973)

trans-Diazido- and dicyano-bis(trimethylenediamine)cobalt(III) complexes have been prepared by the ligand substitution reactions of *trans*-dichlorobis(trimethylenediamine)cobalt(III) complexes in methanol. The corresponding *cis* isomers were obtained by similar reactions in aqueous solutions. The structural assignment of these isomeric pairs was made on the basis of electronic, infrared and nuclear magnetic resonance spectra.

As an extension of our synthetic studies on the diacidobis(trimethylenediamine)cobalt(III) complexes,[1] we have prepared the *cis-trans* isomeric pairs of diazido- and dicyano-complexes. The corresponding *cis*- and *trans*-diazidobis(ethylenediamine)cobalt(III) complexes were reported by Staples and Tobe.[2] The *cis*-dicyanobis(ethylenediamine)cobalt(III) salt was synthesized by Rây and Sharma as early as 1951,[3] but the *trans* isomer has long been unknown. Muto, Baba, and Yoneda[4] succeeded in preparing *trans*-$[Co(CN)_2en_2]Cl$ by the reaction of *trans*-$[CoCl_2en_2]NO_3$ or *cis*-$[CoCl_2en_2]Cl$ with potassium cyanide in dimethyl sulfoxide. Konya, Nishikawa, and Shibata[5] also obtained both *cis*- and *trans*-$[Co(CN)_2en_2]Cl$ by the reaction of $[Coen_3]Cl_3$ with potassium cyanide in a cold aqueous solution containing activated charcoal.

Various diacidobis(trimethylenediamine)cobalt(III) complexes were derived from *trans*-$[CoCl_2tn_2]Cl$ by the ligand substitution reactions in methanol and all of them were shown to have the *trans* configuration.[6] The method has been successfully extended to the preparation of *trans*-$[Co(N_3)_2tn_2]NO_3$ and *trans*-$[Co(CN)_2tn_2]Cl$ in the present study. The corresponding *cis* isomers were afforded by similar reactions in aqueous solutions.

Experimental

trans-*Diazidobis(trimethylenediamine)cobalt(III) Nitrate.* *trans*-$[CoCl_2tn_2]NO_3$ (1.7 g) was dissolved in a minimum quantity of hot methanol. To this was added a methanol solution of twice as many moles of sodium azide (0.75 g), and the mixture was heated to 40 °C or above for an hour, and left to stand overnight. Very dark green crystals were filtered, washed with a small quantity of methanol, and dried in air.

Found: C, 20.63; H, 5.87; N, 43.43%. Calcd for $C_6H_{20}N_{11}O_3Co=[Co(N_3)_2tn_2]NO_3$: C, 20.40; H, 5.71; N, 43.62%.

cis-*Diazidobis(trimethylenediamine)cobalt(III) Nitrate.* Two grams of *trans*-$[Co(NO_3)_2tn_2]NO_3$ were dissolved in 10—13 ml of water. To this was added at 0 °C an aqueous solution (5 ml) of sodium azide (0.6 g) and the mixture was kept standing in ice for 2 hr. A small quantity of the precipitated *trans* isomer was filtered, and a few ml of cold water was added to the filtrate, which was stored overnight in a refrigerator. Very dark violet crystals were filtered, washed with methanol and dried (ca. 0.5 g). The finely powdered compound was dissolved again in a minimum quantity of water, and the insoluble portion was filtered off. The solution was saturated with ammonium nitrate and kept standing overnight in ice. The recrystallized pure compound was filtered, washed successively with cold water and methanol and air-dried.

Found: C, 20.42; H, 5.78; N, 43.39%.

trans-*Dicyanobis(trimethylenediamine)cobalt(III) Chloride Monohydrate.* One gram of *trans*-$[CoCl_2tn_2]Cl$ and 3g of silver oxide were suspended in methanol (40 ml) and stirred at room temperature for about 2 hr. The initial green color finally turned to violet. Precipitates of silver chloride and remaining silver oxide were filtered off. Three times as many moles of potassium cyanide were added and dissolved with stirring for about 1 hr. The solution, warmed on a hot water bath for a while, turned brownish, and a small amount of precipitate was separated out. The mixture was concentrated to half its volume by evaporation under reduced pressure. The crude product (3 g) was purified with a cation-exchange resin (Dowex 50 W-X8, 110—200 mesh) in the lithium form. A 0.2 M solution of lithium chloride was used as an eluent, and the effluent was evaporated under reduced pressure until crystals began to appear. Ethyl alcohol was added to the concentrate to precipitate more crystals, which were filtered, washed with ethanol and dried over calcium chloride. The final yield was 1.8 g.

Found: C, 30.81; H, 6.99; N, 26.26%. Calcd for $C_8H_{22}N_6OClCo=[Co(CN)_2tn_2]Cl\cdot H_2O$: C, 30.73; H, 7.09; N, 26.88%. When a concentrated solution of this compound was gradually cooled, crystals of $[Co(CN)_2tn_2]Cl\cdot 3H_2O$ were separated out. These crystals were subjected to X-ray analysis.

cis-*Dicyanobis(trimethylenediamine)cobalt(III) Chloride.* *cis*-$[Co(CN)_2tn_2]_2S_2O_3$ was prepared by the method of Ohkawa *et al.*,[7] and was transformed into the chloride by means of anion exchange chromatography.

Found: C, 31.61; H, 6.88; N, 28.33%. Calcd for $C_8H_{20}N_6ClCo=[Co(CN)_2tn_2]Cl$: C, 32.61; H, 6.84; N, 28.54%.

Measurements. Electronic absorption spectra were measured with Hitachi EPS-2 and Shimadzu QV-50 spectrophotometers. Infrared absorption spectra in the 4000—650

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[1] Part II: H. Kawaguchi and S. Kawaguchi, This Bulletin, **43**, 2103 (1970).

[2] J. P. Staples and M. L. Tobe, *J. Chem. Soc.*, **1960**, 4812.

[3] P. Rây and B. Sharma, *J. Indian Chem. Soc.*, **28**, 59 (1951).

[4] M. Muto, T. Baba, and H. Yoneda, This Bulletin, **41**, 2981 (1968).

[5] K. Konya, H. Nishikawa, and M. Shibata, *Inorg. Chem.*, **7**, 1165 (1968).

[6] H. Kawaguchi, N. Yano, and S. Kawaguchi, This Bulletin, **42**, 136 (1969).

[7] K. Ohkawa, J. Fujita, and Y. Shimura, *ibid.*, **38**, 66 (1965).

cm^{-1} region were measured with a Hitachi infrared spectrophotometer EPI-2, and those in the 700—200 cm^{-1} region with a Hitachi grating infrared spectrophotometer EPI-L. The NMR spectra were recorded at 60 MHz with TMS as the external reference on a JEOL C-60 HL spectrometer.

Results and Discussion

Diazidobis(trimethylenediamine)cobalt(III) Complexes. From the analytical data the identical empirical formula $[Co(N_3)_2tn_2]NO_3$ was found to be valid for both the very dark green crystals prepared by the reaction of *trans*-$[CoCl_2tn_2]NO_3$ with sodium azide in methanol, and the very dark violet crystals derived from *trans*-$[Co(NO_3)_2tn_2]NO_3$ in aqueous solutions. Thus, the two compounds are isomeric with each other, and two possibilities can be considered: ionization isomerism or geometrical isomerism. If the nitrate group is coordinated to the cobalt atom, the mode of linkage must be clarified.

The structural aspects of coordinated nitrate groups have been studied extensively,[8] and the vibrational spectra are useful for distinguishing between ionic and coordinated nitrate groups.[9] Both *trans*-$[CoCl(NO_3)tn_2]NO_3$[6] and *trans*-$[Co(NO_3)_2tn_2]NO_3$[10] exhibit very strong absorptions in the IR around 1500, 1260, and 990 cm^{-1} which are assignable to the coordinated nitrate group. Neither of the present complexes, however, shows such absorptions, indicating non-ligation of the nitrate group. They can thus be considered to be a pair of *cis-trans* isomers.

In previous papers,[1,6] Baldwin's criterion[11] of using the CH_2-rocking vibration for distinguishing geometrical isomers was shown to be helpful in many cases. However, it is not applicalbe to the present diazido complexes, since both show a single peak at 890 or 895 cm^{-1}. The IR spectra in the lower frequency region are shown in Fig. 1. The spectrum (1) of the dark-violet isomer prepared in aqueous solutions is more complicated than that (2) of the dark-green isomer obtained in methanol. The former exhibits three peaks while the latter only one in the diagnostic ν(Co–N(tn)) region[12] (490—540 cm^{-1}). The absorption band around 590 cm^{-1} which is assignable to the δ(NNN) is also different. The dark-violet isomer can thus be concluded to have a *cis* configuration.

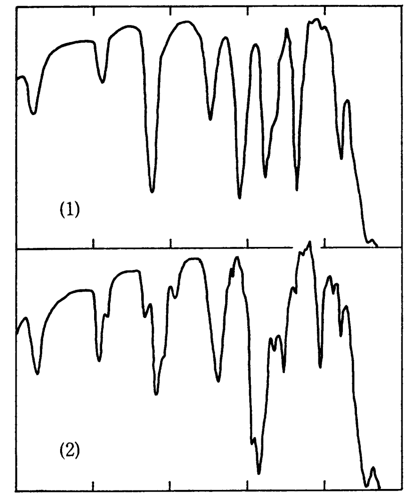

Fig. 1. Infrared spectra of *trans*(1)- and *cis*(2)-$[Co(N_3)_2tn_2]NO_3$ in the 700—200 cm^{-1} region (Nujol mull).

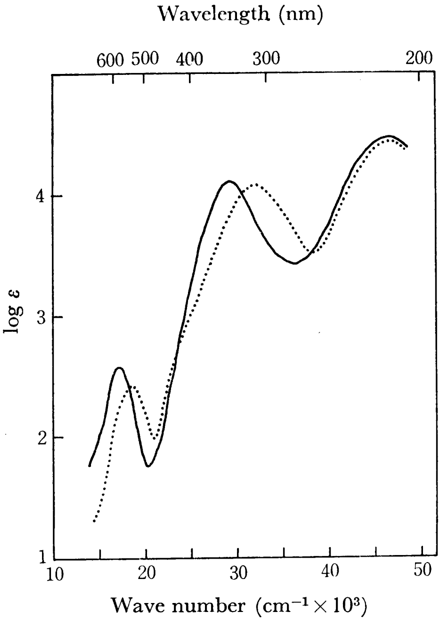

Fig. 2. Absorption spectra of *trans*(——)- and *cis*(······)-$[Co(N_3)_2tn_2]NO_3$ in aqueous solutions.

The electronic spectra of $[Co(N_3)_2tn_2]NO_3$ in aqueous solutions are shown in Fig. 2. Both *cis* and *trans* isomers are not entirely inert, but gradually undergo the aquation reaction. However, addition of sodium azide to the complex solutions in concentration of 3 M or 6 M did not alter the spectra at all, revealing that the solutions are not contaminated with aquated species during the course of spectral measurements. In the case of $[Co(N_3)_2en_2]ClO_4$, the intensity of the first absorption band is nearly equal for *cis* and *trans* isomers.[2] In contrast, *cis*-$[Co(N_3)_2tn_2]NO_3$ exhibits a weaker peak at the shorter wavelength region than the *trans* isomer. A similar feature was also observed for *cis*- and *trans*-$[Co(NCS)_2tn_2]SCN$.[1]

cis-$[Co(N_3)_2tn_2]NO_3$ is quite stable in the solid state at room temperature, but if its aqueous solution is evaporated upon heating, crystals of the *trans* isomer are separated out. This is the reason why cold aqueous solutions were employed for preparation of the *cis* isomers.

Dicyanobis(trimethylenediamine)cobalt(III) Complexes. The *cis*-$[Co(CN)_2tn_2]^+$ complex was first prepared by Ohkawa, Fujita, and Shimura, the *cis*-assignment being

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[8] C. C. Addison, N. Logan, S. C. Wallwork, and C. D. Garner, *Quart. Rev.*, **25**, 289 (1971).

[9] B. M. Gatehouse, S. E. Livingstone, and R. S. Nyholm, *J. Chem. Soc.*, **1957**. 4222,

[10] E. Yasaki, I. Oonishi, H. Kawaguchi, S. Kawaguchi, and Y. Komiyama, This Bulletin, **43**, 1354 (1970).

[11] M. E. Baldwin, *J. Chem. Soc.*, **1960**, 4369.

[12] M. N. Hughes and W. R. McWhinnie, *J. Inorg. Nucl. Chem.* **28**, 1659 (1966).

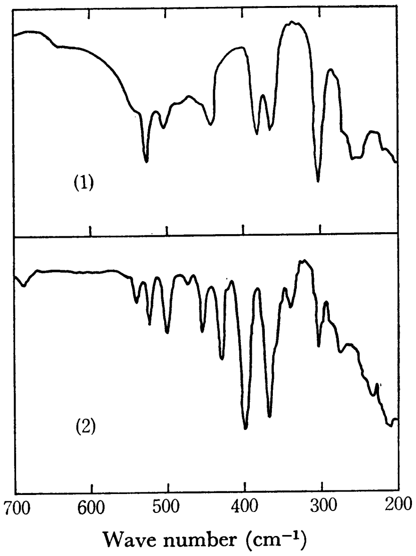

Fig. 3. Infrared spectra of *trans*-$[Co(CN)_2tn_2]Cl\cdot H_2O$(1) and *cis*-$[Co(CN)_2tn_2]Cl$(2) in the 700—200 cm^{-1} region (Nujol mull).

made on the splitting of the C≡N stretching band.[7] No corresponding *trans* isomer could be prepared by the direct reaction of *trans*-$[CoCl_2tn_2]Cl$ with potassium cyanide in methanol, but it could be obtained by a similar reaction after the action of silver oxide. A yellow plate of *trans*-$[Co(CN)_2tn_2]Cl\cdot 3H_2O$ was subjected to X-ray crystal analysis.[13] Crystal data: monoclinic, $a=17.906(5)$, $b=10.753(6)$, $c=8.575(5)$ Å, $\beta=95.74(5)°$, $Z=4$, $D_c=1.33$, $D_m=1.31$ $g\cdot cm^{-3}$, $\mu(Ni-K_\alpha)=38.5$ cm^{-1}; space group C_c. The *trans* configuration was ascertained, and the linear orientation of Co–C–N and the chair conformation of the six-membered chelate rings were clarified (R=0.121).

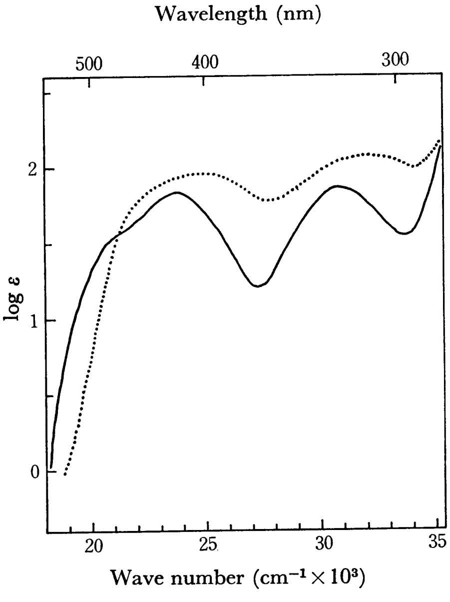

Fig. 4. Absorption spectra of *trans*-$[Co(CN)_2tn_2]Cl$ (——) and *cis*-$[Co(CN)_2tn_2](S_2O_3)_{1/2}$ (······) in aqueous solutions.

The IR spectra of the two isomers in the low-frequency region are shown in Fig. 3. The curve for the *cis* isomer is a little more complicated than that for the *trans* isomer. In the CH_2-rocking region the *cis* isomer exhibits a distinct shoulder at the lower frequency side of a rather sharp peak at 898 cm^{-1}, while the *trans* compound shows a broad symmetric band at 892 cm^{-1}. Their electronic spectra are shown in Fig. 4. Just as in the case of the corresponding ethylenediamine complexes,[4,5] the *trans* isomer has a remarkable shoulder in the longer wavelength side of the first band.

The present synthetic method for the *trans*-$Co(CN)_2tn_2^+$ complex was also applied to the preparation of *trans*-$Co(CN)_2en_2^+$ and a satisfactory yield was attained; 1 g of *trans*-$[Co(CN)_2en_2]Cl$ was obtained from 4 g of *trans*-$[CoCl_2en_2]Cl$.

NMR Studies. The proton NMR spectra of diamagnetic tris(diamine)metal complexes have been studied extensively in recent years. The ethylenediamine chelate rings in these complexes have *gauche* conformations[14] with either δ or λ chirality. It has been established theoretically[15] and experimentally[16] that the Men_3 complexes undergo rapid ring inversion at room temperature. Appleton, Hall, and Hawkins[17] pointed out, however, that the methylene protons of the ethylenediamine ligand can not be equivalent even if the rapid conformational equilibration is attained, since the environment of an axial proton in a δ conformer is not identical with that of an axial proton in a λ conformer due to the presence of the other two chelate rings.

Although there is no environmental difference among NH_2 and CH_2 protons respectively in *trans*-MX_2en_2 complexes, there exists some additional complexity in the case of *cis*-MX_2en_2 in comparison with Men_3. The NH_2 protons situated in the *cis* position to both the X groups are inherently nonequivalent to the other NH_2 protons which are *cis* to one X and *trans* to the other X. A similar discrimination should be extended to the adjacent α-CH_2 groups. The different patterns of NH_2 proton signals in *cis*- and *trans*-CoX_2en_2 complexes have frequently been exemplified since the original work of Clifton and Pratt.[18] Distinct splitting of CH_2 bands is also observed for *cis*-$[Co(H_2O)_2en_2](ClO_4)_3$ in 1.8 M D_2SO_4.[19]

A six-membered chelate ring, on the other hand, is capable of existing in several conformational types such as "chair," "boat," and "skew boat" or "twist" conformations. An optically active trimethylenediamine complex $(-)_D$-$[Cotn_3]Br_3\cdot H_2O$ was shown to have the tris-chair conformation.[20] However, the tris-chair con-

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13) H. Hasegawa, K. Matsumoto, H. Kuroya, H. Kawaguchi, and S. Kawaguchi, Presented at the 20th Symposium on the Coordination Compounds of the Chemical Society of Japan, 18A18, Tokyo, November, 1970.

14) Y. Saito, K. Nakatsu, M. Shiro, and H. Kuroya, This Bulletin, **30**, 795 (1957); J. K. Beattie and H. Elsbernd, *J. Amer. Chem. Soc.*, **92**, 1946 (1970).

15) J. R. Gollogly, C. J. Hawkins, and J. K. Beattie, *Inorg. Chem.*, **10**, 317 (1971).

16) J. K. Beattie, *Accounts Chem. Res.*, **4**, 253 (1971).

17) T. G. Appleton, J. R. Hall, and C. J. Hawkins, *Inorg. Chem.*, **9**, 1299 (1970).

18) P. Clifton and L. Pratt, *Proc. Chem. Soc.*, **1963**, 339.

19) D. A. Buckingham, L. Durham, and A. M. Sargeson, *Aust. J. Chem.*, **20**, 257 (1967).

20) T. Nomura, F. Marumo, and Y. Saito, This Bulletin, **42**, 1016 (1969).

formation seems to be only slightly more stable than the tris-skew-boat conformation.[21] The CD spectra of $Cotn_3^{3+}$ ions in solutions were interpreted to indicate the equilibrium between these two conformers.[22] The conformational inversion is quite rapid as evidenced by the observation that the NMR spectra of $Pdtn_2^{2+}$ and $Pttn_2^{2+}$ complexes are no more complicated than the spectrum of $tn(HCl)_2$.[23]

The six-membered chelate rings in several diacidobis(trimethylenediamine)cobalt(III) complexes have also been revealed to have the chair form in crystals,[10,24] but seem to undergo rapid conformational interconversion in solutions. Figure 5-(1) shows the NMR spectra of *trans*-$[Co(CN)_2tn_2]Cl$ in D_2O containing *ca.* 1 M DCl. Three peaks are observed at 6.15, 7.25, and 8.25 τ with the relative integral intensities 2: 2: 1. The broad lowest-field band disappears in solutions without acid as is illustrated in Fig. 6-(1), and can thus be attributed to the amine protons. The remaining two peaks which are not influenced by pH of the solution may be assigned to the methylene protons. The observed area ratio unequivocally indicates that the lower-field signal is due to the α-CH_2 and the higher-field one to the β-CH_2 protons. Here the methylene protons are designated as: NH_2–$CH_2(\alpha)$–$CH_2(\beta)$–$CH_2(\alpha)$–NH_2. The α-CH_2 signal in Fig. 5-(1) reveals the characteristic five-line pattern, but that in Fig. 6-(1) is essentially a triplet because of the quenching of coupling with NH_2 protons by deuteration. These features indicate the magnetic equivalence of methylene protons in trimethylenediamine ligands by virtue of the rapid conformational interchange as discussed above.

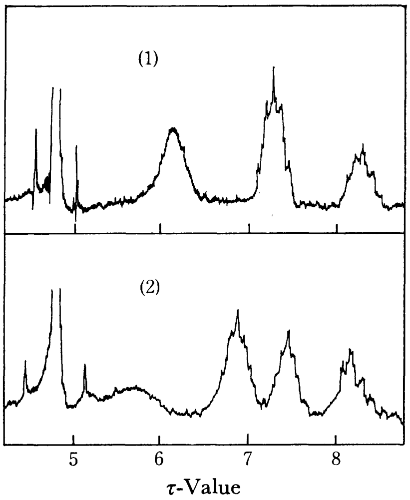

Fig. 5. Proton NMR spectra of *trans*(1)- and *cis*(2)-$[Co(CN)_2tn_2]Cl$ in acidic D_2O solutions.

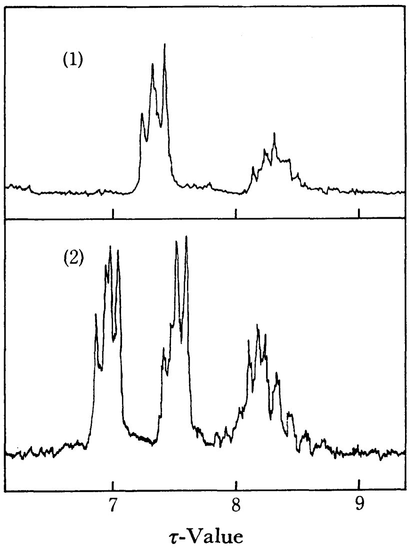

Fig. 6. Proton NMR spectra of *trans*(1)- and *cis*(2)-$[Co(CN)_2tn_2]Cl$ in neutral D_2O solutions.

On the other hand, the spectra of *cis*-$[Co(CN)_2tn_2]Cl$ give three methylene signals at 6.87, 7.44, and 8.14 τ both in acidic and neutral D_2O solutions, and their area ratios are about 1.9: 1: 1 (Fig. 5-(2)) and 1: 1: 1 (Fig. 6-(2)), respectively. These features indicate that there exist two kinds of nonequivalent protons in the α-CH_2 groups, which are distinctly differentiated under the strong influence of cyanide ligands.

The very broad signal of NH_2 protons around 5.7 τ has about one half of the expected area (Fig. 5-(2)). It seems improbable on the basis of the following that 50% of the NH_2 protons was exchanged with D_2O immediately after dissolution. (1) The rate data of base-catalyzed hydrogen exchange of ammine and ethylenediamine cobalt(III) complexes in D_2O[25] suggest that the exchange reaction of the trimethylenediamine complex in the present solution containing 1 M DCl can not be so rapid. (2) The observed NMR spectrum shows no change at all even after one-day standing. Thus it seems appropriate to consider that the NH_2

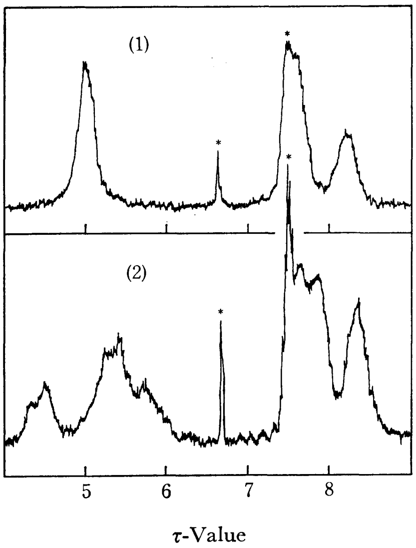

Fig. 7. Proton NMR spectra of *trans*(1)- and *cis*(2)-$[Co(NCS)_2tn_2]SCN$ in dimethylsulfoxide-d_6 solutions, asterisk denoting impurity bands.

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[21] J. R. Gollogly and C. J. Hawkins, *Inorg. Chem.*, **11**, 156 (1972).

[22] P. G. Beddoe, M. J. Harding, S. F. Mason, and B. J. Peart, *Chem. Commun.*, **1971**, 1283.

[23] T. G. Appleton and J. R. Hall, *Inorg. Chem.*, **9**, 1807 (1970).

[24] K. Matsumoto, M. Yonezawa, H. Kuroya, H. Kawaguchi, and S. Kawaguchi, This Bulletin, **43**, 1269 (1970); R. J. Geue and M. R. Snow, *J. Chem. Soc. A*, **1971**, 2981.

[25] F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," 2nd ed., J. Wiley and Sons, New York (1967), p. 185.

proton signal is split into two bands in the case of *cis*-$Co(CN)_2tn_2^+$, one appearing around 5.7 τ and the other overlapping with the lowest-field methylene peak. The observed larger integral intensity of the latter peak supports this interpretation.

The spectra of *trans*- and *cis*-$[Co(NCS)_2tn_2]SCN$ in dimethyl sulfoxide-d_6 are shown in Fig. 7. The configurational assignments of these complexes have already been reported.[1,24] The spectrum of the *trans* isomer gives three signals at 5.00, 7.60, and 8.20 τ, which are assigned to NH_2, α-CH_2, and β-CH_2 protons, respectively. A sharp peak at 6.70 τ and an overlapping peak at 7.50 τ are attributed to impurities in the solvent. The α-CH_2 absorption in *cis*-$[Co(NCS)_2tn_2]SCN$ is partially split into two bands at 7.65 and 7.85 τ, although the separation is not so complete as in the case of *cis*-$Co(CN)_2tn_2^+$. This might suggest that the thiocyanate anion does not exert so strong an influence as the cyanide anion. A similar degree of splitting of the α-CH_2 absorption was also noticed in the spectrum of $CoCO_3tn_2^+$ in neutral D_2O.[26] The NH_2 absorption in *cis*-$[Co(NCS)_2tn_2]SCN$ shows a very complicated pattern and can not be interpreted, especially in reference to the rather simple pattern exhibited by NH_2 protons of *cis*-$[Co(N_3)_2tn_2]NO_3$.

The spectra of *trans*- and *cis*-$[Co(N_3)_2tn_2]NO_3$ in DMSO-d_6 are shown in Fig. 8. The α-CH_2 signal is not split in this *cis* isomer. The azide group may exert a weaker effect on the α-CH_2 protons than the thiocyanate ligand. Buckingham, Durham, and Sargeson[19] also observed no splitting of the CH_2 signals in the CoX_2en_2 complexes where both of the coordinating atoms of X are nitrogen, *i.e.* $X{=}NH_3$, N_3^-, NO_2^-, or 1/2en. However, the NH_2 signal of *cis*-$Co(N_3)_2tn_2^+$ is split into two bands quite remarkably, permitting the differentiation from the *trans* isomer. The minor NH_2 band observed at 6.05 τ in the spectrum of *trans*-$[Co(N_3)_2tn_2]NO_3$ (Fig. 8-(1)) is not explicable at present. It might be due to the partial solvolysis.

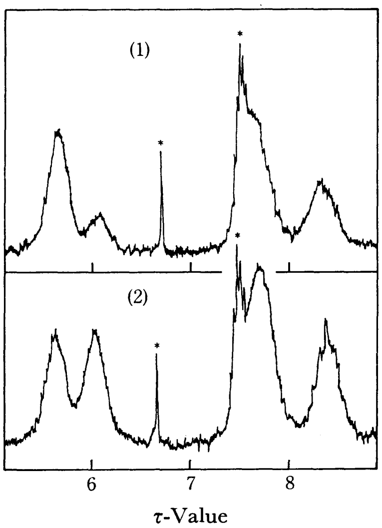

Fig. 8. Proton NMR spectra of *trans*(1)- and *cis*(2)-$[Co(N_3)_2tn_2]NO_3$ in dimethyl sulfoxide-d_6 solutions, asterisks denoting impurity bands.

We are indebted to Mr. J. Gohda and Miss M. Iwao for the elemental analyses and NMR measurements. Financial aid by the Ministry of Education is also acknowledged.

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[26] I. R. Jonasson, S. F. Lincoln, and D. R. Stranks, *Aust. J. Chem.*, **23**, 2267 (1970).