

magnetic bar was placed 0.699g (5 mmol) of (E)- β -phenylethylboronic acid, 0.688g (8 mmol) of methyl acrylate, 0.673g (5 mmol) of anhydrous cupric chloride and 25 ml of dry acetonitrile. 5 ml of 0.1 M LiPdCl₂ in acetonitrile was added to the flask and flushed with nitrogen and capped. The reaction mixture was stirred for 24 h at room temperature, and then diluted with 100 ml of ether and filtered. The filtrate was washed with water several times and dried over anhydrous magnesium sulfate. Remove solvent and the crude product was purified by column chromatography (silica gel, ethyl acetate/n-hexane = 1/10 (v/v)). 0.602g(64%) of pure (E,E)-methyl 2,4-pentadienoate (7) was obtained.

References

- (1) A.S. Onishchenko, *Diene Synthesis*, D. Davey, New York, 1964.
- (2) H.P. Dang and C. Linstrumelle, *Tetrahedron Lett.*, 191 (1978).
- (3) (a) E. Negishi, N. Okukado, A.O. King, D.E. Horn and B.I. Spiegel, *J. Amer. Chem. Soc.*, **100**, 2254 (1978); (b) E. Negishi, *Acc. Chem. Res.*, 340 (1982); (c) E. Negishi, *Pure Appl. Chem.*, **53**, 2333 (1981).
- (4) (a) K. Tamao, H. Matsumoto, T. Kakui and M. Kumada, *Tetrahedron Lett.*, 1141 (1978); (b) J. Yoshida, K. Tamao, T. Kakui and M. Kumada, *ibid.*, 1137 (1979).
- (5) (a) A. Commercon, J.F. Normant and J. Villieras, *Tetrahedron*, **36**, 1215 (1980); (b) N. Jabri, A. Alexakis and J.F. Normant, *Tetrahedron Lett.*, **22**, 959 (1981); (c) N. Jabri, A. Alexakis and J.F. Normant, *ibid.*, **23**, 1589 (1982).
- (6) G.M. Whitesides, C.P. Casey and J.K. Krieger, *J. Amer. Chem. Soc.*, **93**, 1379 (1971).
- (7) (a) R.C. Larock, *J. Org. Chem.*, **41**, 2241 (1976); (b) R.C. Larock and P. Riefling, *ibid.*, **43**, 1468 (1978).
- (8) N. Okukado, D.E. Van Horn, L.W. Klima and E. Negishi, *Tetrahedron Lett.*, 1027 (1978).
- (9) (a) G. Zweifel and N.L. Polston, *J. Amer. Chem. Soc.*, **92**, 4068 (1970); (b) E. Negishi and T. Yoshida, *J. Chem. Soc., Chem. Commun.*, 606 (1973); (c) Y. Yamamoto, H. Yatagai, K. Maruyama, S. Sonoda and S.I. Murahashi, *J. Amer. Chem. Soc.*, **99**, 5652 (1977); (d) J. Campbell and H.C. Brown, *J. Org. Chem.*, **45**, 549 (1980).
- (10) N. Miyaura, K. Yamada, H. Suginome and A. Suzuki, *J. Amer. Chem. Soc.*, **107**, 972 (1985).
- (11) R.F. Heck, *J. Amer. Chem. Soc.*, **90**, 5518 (1968).
- (12) R.F. Heck, *J. Amer. Chem. Soc.*, **90**, 5535 (1968).
- (13) R.F. Heck, *J. Amer. Chem. Soc.*, **93**, 6896 (1971).
- (14) W.P. Weber, R.A. Felix, A.K. Willard and K.E. Koenig, *Tetrahedron Lett.*, 4071 (1971).
- (15) H. Plaut and J.J. Ritter, *J. Amer. Chem. Soc.*, **73**, 4076 (1951).
- (16) H.C. Brown and S.K. Gupta, *J. Amer. Chem. Soc.*, **94**, 4371 (1972).
- (17) H.C. Brown and S.K. Gupta, *J. Amer. Chem. Soc.*, **97**, 5249 (1975).

The Stereochemistry of the Metal Complexes of Novel Stereospecific Quadridentate Ligands. Cobalt(III) Complexes of N,N'-Dimethylethylenediamine-N,N'-di- α -propionate and N,N'-Dimethylethylenediamine-N,N'-diacetate Ligands

Moo-Jin Jun[†], Jin-Seung Jung, and Chang Hwan Kim

Department of Chemistry, Yonsei University, Seoul 132 (Received August 7, 1985)

A new flexible quadridentate ligand, N,N'-dimethylethylenediamine-N,N'-di- α -propionic acid (dmedpa) has been synthesized, and diammine and ethylenediamine cobalt(III) complexes of dmedpa, [Co(dmedpa)(NH₃)₂]⁺ and [Co(dmedpa(en))]⁺, have been prepared. Only *s-cis* isomer has been yielded. A known N,N'-dimethylethylenediamine-N,N'-diacetic acid (dmedda) has also been prepared. Dichloro cobalt(III) complexes of both dmedda and dmedpa have been prepared. Only the *s-cis* isomer has been yielded in the [Co(dmedda)Cl₂]⁻ complex, while only the *uns-cis* isomer has been obtained for the [Co(dmedpa)Cl₂]⁻ complex.

Introduction

Octahedral cobalt(III) complexes of a linear flexible edda-type ligand (edda is ethylenediaminediacetic acid, HOOCCH₂NHCH₂CH₂NHCH₂COOH) can have three geometric isomers, *s-cis* (symmetric *cis*), *uns-cis* (unsymmetric *cis*), and *trans*, as depicted in Figure 1. The cobalt(III) complexes of edda were prepared by Mori *et al.*,¹ who have observed that the carbonate, diaqua, and dinitro complexes yielded the *s-cis* isomer only. On the other hand, Legg and Cooke² isolated both *s-cis* and *uns-cis* isomers for the [Co(edda)(am)]⁺

(am is ethylenediamine or (NH₃)₂). *Uns-cis* isomer of the cobalt(III) complexes of edda has also been observed by other workers.³⁻⁶

Liu and coworkers⁷ have prepared the first C-alkyl-substituted analogue of edda, ethylenediamine-N,N'-di-S- α -propionic acid (SS-eddp). Both *s-cis* and *uns-cis* isomers of [Co(SS-eddp)(L)]⁺ (L is en or R-pn) were isolated. Other C-alkyl-substituted edda ligands include S-stilbenediamine-N,N'-diacetate (S-sdda),⁸ ethylenediamine-N,N'-di-S- α -isovalerate (ven),^{9,10} and 2S, 2'S-1,1'-ethane-1,2-diylbis (pyrrolidine-2-carboxylate) (pren).^{11,12}

The N-alkyl substituted analogue of edda was first prepared by Maricondi and Douglas^{13,14} who have synthesized N,N'-diethylethylenediamine-N,N'-diacetic acid (dmedda) and N,N'-diethylethylenediamine-N,N'-diacetic acid (deedda). Cobalt(III) complexes of both dmedda have yielded only the *s-cis* isomer.

While the cobalt(III) complexes of the N-alkyl substituted analogue of edda (dmedda and deedda) have yielded the *s-cis* isomer only, the cobalt(III) complexes of edda and C-alkyl-substituted analogue of edda (eddp, sdda, and ven) have given both *s-cis* and *uns-cis* isomers. It will be of interest to see what isomers would be obtained from the preparation of cobalt(III) complexes of a new edda-type ligand containing both C-alkyl and N-alkyl substitution at, respectively, α -carbon and nitrogen donor atom, if such new ligand be successfully obtained. In this work we have designed and synthesized such new ligand containing methyl groups at both α -carbon and nitrogen donor atom: N,N'-dimethylethylenediamine-N,N'-di- α -propionic acid (dmedpa). We report here the synthesis of dmedpa and the preparation of diammine and ethylenediamine cobalt(III) complexes of dmedpa. The known ligand of dmedda has also been prepared. Although some cobalt(III) complexes of dmedda are known, the dichloro complex of dmedda has not been reported. In this paper the dichloro cobalt(III) complexes of both dmedda and dmedpa ligands are also described.

Experimental

Chemical Reagents. N,N'-dimethylethylenediamine was purchased from Aldrich Chemical Co. and α -chloropropionic acid was obtained from Tokyo Kasei Kogyo Co., both of which were used without further purification.

Physical Measurements. Electronic absorption spectra were obtained with a Shimadzu UV-240 Spectrophotometer. Pmr spectra were recorded on a Varian EM 360L Spectrometer. Infrared spectra were taken with a Shimadzu IR-435 Spectrophotometer. Elemental analyses were performed by Micro-Tech Analytical Laboratories, Skokie, Illinois, U.S.A.

Preparation of Barium N,N'-dimethylethylenediamine-N,N'-di- α -propionate (Badmedpa). A cold solution of 20.0g of sodium hydroxide in 40ml of water was carefully added to a cold solution 59.0g of α -chloropropionic acid in 40ml of water with stirring at such a rate that the temperature might not rise above 20°C. To this solution 22.0g of N,N'-dimethylethylenediamine was added dropwise over a period of 90 min while stirring and then 20.0g of sodium hydroxide in 40ml of water was added. The temperature was kept between 90°C and 100°C during this addition. After a 90 min. of standing, 65.0g of barium chloride dihydrate dissolved in 120ml of boiling water was added rapidly, and the solution was shaken. The cloudy suspension of Ba(dmedpa) formed was heated at 60°C for 30min with occasional stirring, filtered from the hot solution, and washed. The product was purified by stirring in 100ml of water at about 90°C for 10min and filtered while hot. The product was washed with acetone and dried for 2h at 80°C. Yield: 15.2g (8.3%). *Anal.* Calcd. for BaC₁₀H₁₈N₂O₄: C, 32.67; H, 4.94; N, 7.62. Found: C, 32.60; H, 5.02; N, 7.49.

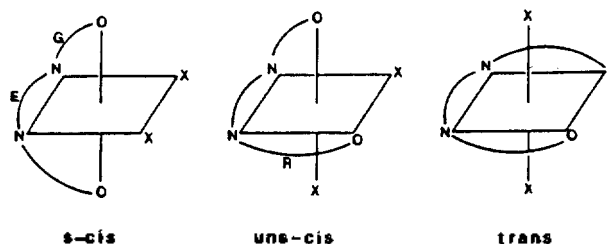


Figure 1. The possible geometric isomers of the $[Co(edda)X_2]^{n+}$ complexes.

Preparation of S-cis-N,N'-dimethylethylenediamine-N,N'-di-propionatoethylenediaminecobalt(III) Nitrate, S-cis-[Co(dmedpa)(en)]NO₃. To a rapidly stirred suspension of Ba(dmedpa)(3.68g, 0.01 mole) dissolved in 20ml of water at about 60°C, 2.81g (0.01 mole) of cobaltousulfate heptahydrate dissolved in 20ml of water was added over a period of 20 min. After heating at 60°C for 30 min, the solution was filtered. The precipitate was washed with 15ml of hot water. To the combined filtrate and washings were added successively 5 ml of 2.0N nitric acid, 1.0g of activated charcoal, and 0.61g (0.01 mole) of ethylenediamine in 4ml of water. The oxidation reaction was carried out by the dropwise addition of 1.1g 30% H₂O₂ in 15ml of water to the stirred solution. After stirring several more minutes, air was bubbled through the solution for 8hrs. The resulting wine-red solution was filtered away from the charcoal. It was then added to an ion-exchange column full of 200-400 mesh Dowex 50W-X4 cation-exchange resin in the H⁺ form. The mixture of complexes formed a red band at the top. Washing with water removed a purplish material that was not adsorbed on the column. Only one fraction was obtained by elution with 0.2N HCl with a flow rate of about 0.5cm³ min⁻¹. The dark red product was then obtained by evaporating the solution to dryness on a water bath. Yield: 0.3g (7.1%). *Anal.* Calcd. for CoC₁₀H₂₄O₇N₃: C, 35.22; H, 5.91; N, 14.40. Found: C, 34.80; H, 5.93; N, 14.52.

Preparation of S-cis-Diammine-N,N'-dimethylethylenediamine-N,N'-di- α -propionatocobalt(III) Chloride, S-cis-[Co(dmedpa)(NH₃)₂]Cl. A mixture of 1.84g (5.0×10^{-3} mole) of Ba(dmedpa) and 1.4g (5.0×10^{-3} mole) of CoSO₄·7H₂O in 20ml of water was stirred at 60°C for 20 min and then filtered. To the hot filtrate were added 0.24g of NH₄Cl and 10ml of 3% H₂O₂ dropwise, and then air was bubbled through the solution for 8 hrs. To the violet solution were added 1.0ml of concentrated ammonia and 1.0g of activated charcoal. After allowing the solution to stand for several hours at room temperature, it was filtered to remove the charcoal. The resulting violet solution was added to an ion-exchange column full of 200-400 mesh Dowex 50W-X4 cation-exchange resin in the H⁺ form. The mixture of complexes formed a red band at the top. Elution with 0.1N HCl at a rate of about 0.5cm³min⁻¹ caused essentially one band. The product was then obtained by evaporating the solution to dryness on a water bath. Yield: 0.23g (13%). *Anal.* Calcd. for CoC₁₀H₂₄N₄ClO₄: C, 33.48; H, 6.74; N, 15.62. Found: C, 33.58; H, 6.70; N, 15.70.

Preparation of Barium N,N'-dimethylethylenediamine-N,N'-diacetate (Badmedda). This was prepared essentially by the method of Legg² with the following modifications. 47.5g

of monochloroacetic acid dissolved in 40 ml of water was placed in a 500 ml round-bottom flask in an ice-bath. While the temperature was maintained below 10°C, 41.0 g of sodium hydroxide dissolved in 120 ml of water was carefully added over two hours. Then 22.0 g of *N,N'*-dimethylethylenediamine was added to this solution for 90 min and the temperature was kept below 45°C. 65.0 g of barium chloride dihydrate dissolved in 125 ml of boiling water was slowly added to this reaction mixture with stirring, while the temperature was kept at about 60°C. The solid product was filtered while hot and washed several times with hot water.

Preparation of Potassium Dichloro-*N,N'*-dimethylethylenediamine-*N,N'*-diacetatocobaltate(III), $K[Co(dmedpa)Cl_2]$.

1.6 g of barium *N,N'*-dimethylethylenediamine-*N,N'*-diacetate was dissolved in 20 ml of water. 1.4 g of cobaltous sulfate heptahydrate dissolved in 20 ml of water was added to this solution and the reaction mixture was maintained at 50°C for 30 min. Barium sulfate was removed from the reaction mixture by filtration. 2.0 ml of 30% H_2O_2 was carefully added to the filtrate. 30 ml of concentrated hydrochloric acid was added to this solution and then the resulting solution was concentrated to a volume of 20 ml, which was added to an ion-exchange column full of 200-500 mesh Dowex 1-8X anion exchange resin. The eluent was 0.1N KCl solution. The first band showed a purple color, which turned out to be the $[Co(dmedda)ClH_2O]$ complex, and the second band showed a green color which was the $K[Co(dmedda)Cl_2]$ complex. Such band identification was later confirmed by the observation that, when the water solution of $K[Co(dmedda)Cl_2]$ was allowed to stand several hours, the color changed from green to purple. The purple and green solutions were evaporated to dryness and the solid products were immediately subjected to the electronic absorption and nmr spectroscopy, because they were highly hygroscopic.

Preparation of Potassium Dichloro-*N,N'*-dimethylethylenediamine-*N,N'*-di- α -propionatocobaltate(III), $K[Co(dmedpa)Cl_2]$. This was prepared *via* the same method as that used to prepare $K[Co(dmedda)Cl_2]$ using *dmedpa* in place of *dmedda*. As observed in the case of $K[Co(dmedda)Cl_2]$, the ion-exchange chromatography of $K[Co(dmedpa)Cl_2]$ showed two bands, one purple and the other green, which were turned out to be, respectively, $[Co(dmedpa)(Cl)H_2O]$ and $K[Co(dmedpa)Cl_2]$. The electronic absorption and nmr spectra showed that these are not the different geometrical isomers but the same *uns-cis* isomer.

Results and Discussion

The *dmedpa* ligand, *N,N'*-dimethylethylenediamine-*N,N'*-di- α -propionic acid, has been prepared as a barium salt from the reaction between *N,N'*-dimethylethylenediamine and α -chloropropionic acid. Figure 2 shows the pmr spectrum of the *dmedpa* ligand. The α -carbon proton (marked a) is shown at 3.2 ppm as a quartet, the α -methyl protons (marked d) at 1.2 ppm as a doublet, the *N*-methyl protons (marked c) at 2.3 ppm, and the methylene protons between the two nitrogen donor atoms (marked b) at 2.6 ppm as a singlet.

Diammine and ethylenediamine cobalt(III) complexes of *dmedpa* have been prepared in this work, and only one isomer,

s-cis isomer, has been obtained during the course of our preparation. The infrared spectrum of the *dmedpa* ligand showed the free unionized $-COOH$ group at 1730cm^{-1} while the infrared spectra of the complexes indicated the coordinated carboxyl group at 1650cm^{-1} . The electronic absorption spectra of these complexes are shown in Figure 3. The Band I and Band II which are due to the *d-d* transitions in the octahedral CoN_4O_2 crystal field, appear, respectively, at 530 nm and 370 nm. The shape of the first band is nearly symmetrical, although a small deformation in the high energy side of the band is observable. If the complex has the *trans* configuration (*trans* in Figure 1), a split of the band I would have been observed in the diammine complex.^{11,15,16} The ethylenediamine cobalt(III) complex of *dmedpa* cannot have a *trans* geometry. Therefore, the possibility of the *trans* geometric configuration is eliminated. If any of the complexes prepared in this work is the *uns-cis*

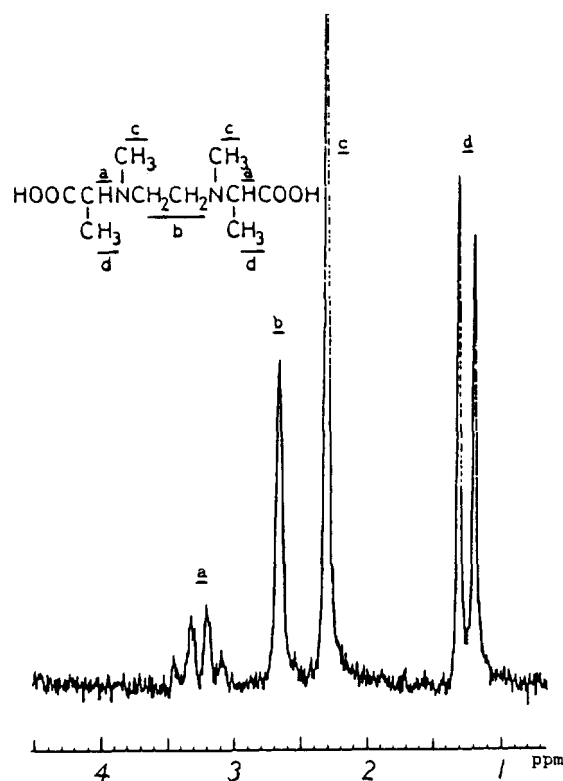


Figure 2. Pmr spectrum of *N,N'*-dimethylethylenediamine-*N,N'*-di- α -propionic acid.

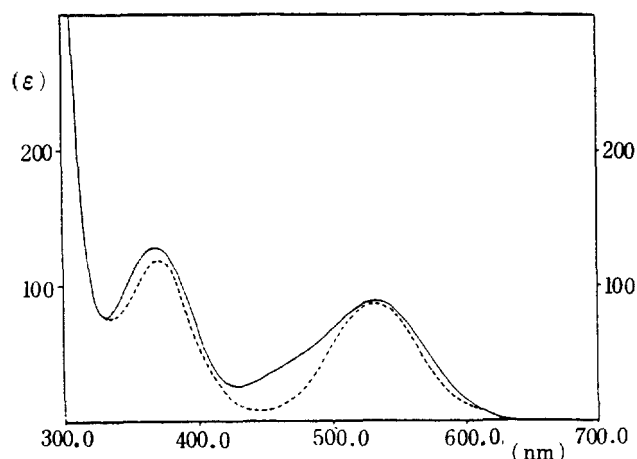


Figure 3. Electronic absorption spectra of *s-cis*- $[Co(dmedpa)(en)]NO_3$ (—) and *s-cis*- $[Co(dmedpa)(NH_3)_3]Cl$ (---)

isomer (Figure 1), two atoms of the same kind (N-N, O-O) are at the *cis* positions, and a very intense absorption could be observed, since the ligand field around the central metal atom is highly unsymmetrical. The *s-cis* configuration, though the evidence from the electronic absorption spectrum alone is not conclusive, is the most reasonable assignment, and the small deformation mentioned above may be attributed to the *trans* (O-O) component of the coordination mode.^{17, 18}

The fact that the cobalt(III) complexes of dmedpa prepared in this work has the *s-cis* configuration is clearly shown in the pmr spectra of those complexes shown in Figure 4 and 5. Figure 4 shows the pmr spectrum of $[\text{Co}(\text{dmedpa})(\text{en})]^+$. The methyl protons at the α -carbon atom (marked b) are shown as a doublet at 1.3 ppm, the proton at the α -carbon atom (marked a) is nicely shown as a quartet at 3.8 ppm, and the methylene protons present between the two nitrogen donor atoms of dmedpa (marked f) at near 2.7 ppm. In Figure 5, which shows the pmr spectrum of $[\text{Co}(\text{dmedpa})(\text{NH}_3)_2]^+$, the methyl protons at the α -carbon atom (marked a) are shown at 1.5 ppm as a doublet and the proton at the α -carbon atom (marked b) is shown as a quartet at 4.0 ppm. If the complexes have the *uns-cis* configuration,

the same methyl protons would have shown two doublets and the CH (a) proton should have shown two quartets. The *uns-cis* isomer has only C_1 symmetry and the two propionato arms are no longer equivalent in the *uns-cis* geometry. The CH (a) proton and the methyl protons (b) in the planar carboxylate arm in the *uns-cis* geometry no longer lie in the same shielding area of the C-N bond, and such loss of shielding would cause the CH proton and methyl protons to resonate at lower fields with, respectively, two quartets and two doublets. The *s-cis* configuration is, therefore, assigned to each of the two complexes obtained in this work.

Although the *s-cis* isomer appears to have been mostly formed in the CoN_2O_2 systems so far reported,^{1, 6, 14-19} it is quite interesting to observe that the cobalt(III) complexes of our new ligand dmedpa have yielded only *s-cis* isomer. Severe ring strain totally prevents the formation of the *trans* isomer. Because of the tetrahedral nature of the nitrogen atom, the puckered chelate rings in the *uns-cis* isomer are somewhat strained and slightly distorted from the plane containing the nitrogen atoms so that the *uns-cis* isomer is expected to be less stable than the *s-cis* isomer.¹⁹⁻²¹ In the cobalt(III) complexes of edda it has been postulated that non-bonding interactions between the sterically restricted amine protons and edda prevented the formation of substantial amounts of the *uns-cis* isomers.^{19, 21}

From our experimental observation the dmedpa ligand, like edda, appears to favor an *s-cis* configuration due to such increased steric interactions observed in the *uns-cis* isomer. The dmedpa ligand has a methyl substituent at each of the two α -carbon atoms as well as a methyl substituent at each of the two nitrogen donor atoms. Because of such methyl groups, the steric interaction would be greater for the in-plane chelate rings if an *uns-cis* isomer were to be formed. It was pointed out earlier that, while the cobalt(III) complexes of the N-alkyl substituted analogues of edda gave only the *s-cis* isomer, those of the C-alkyl substituted analogues of edda have yielded both *s-cis* and *uns-cis* isomers. Although our new ligand dmedpa contains both N-methyl and C-methyl (at α -carbon) groups, it has behaved just like an N-alkyl substituted analogue of edda and has yielded only *s-cis* isomer when it was coordinated to cobalt(III) ion. From our experimental observation it appears that the N-alkyl substituent has shown a greater impact than the C-alkyl substituent upon the formation of the *s-cis* isomer. It is, however,

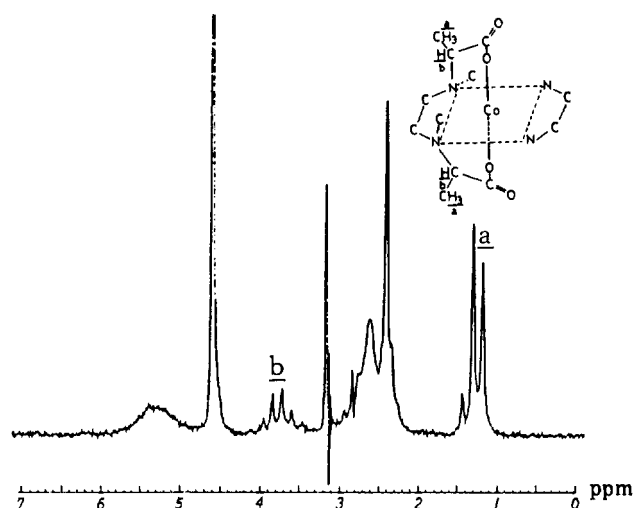


Figure 4. Pmr spectrum of *s-cis*- $[\text{Co}(\text{dmedpa})(\text{en})]\text{NO}_3$ in D_2O

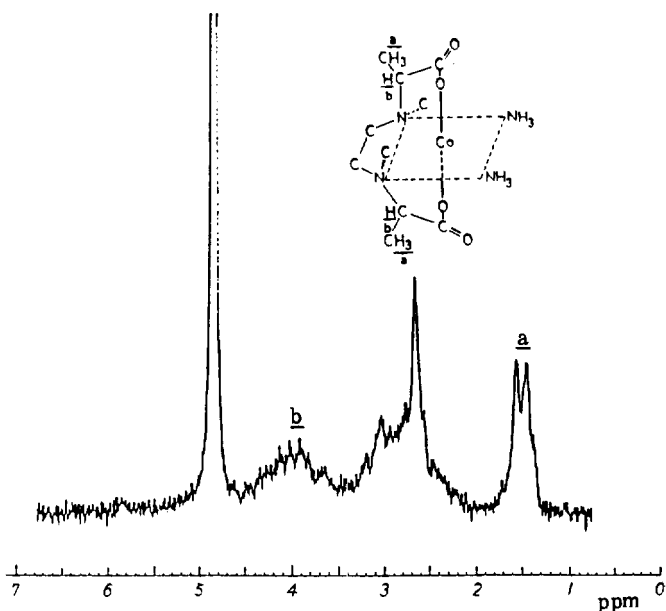


Figure 5. Pmr spectrum of *s-cis*- $[\text{Co}(\text{dmedpa})(\text{NH}_3)_2]\text{Cl}$ in D_2O

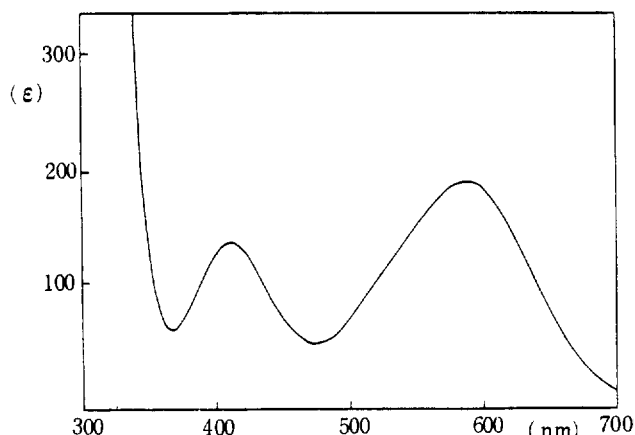


Figure 6. Electronic absorption spectrum of *s-cis*- $\text{K}[\text{Co}(\text{dmedpa})\text{Cl}_2]$

not clear at this point why the N-alkyl substituent has a greater impact than the C-alkyl substituent and further works are to be accomplished to clarify the effect of the N-alkyl and C-alkyl substituents on the formation of certain geometric isomers.

Even though some complexes of the dmedda ligand are known for quite some time, the dichloro cobalt(III) complex of dmedda has not been reported. The electronic absorption spectrum of $[\text{Co}(\text{dmedda})\text{Cl}_2]^-$ (Figure 6) shows that this complex has a *cis* configuration. The fact that the $[\text{Co}(\text{dmedda})\text{Cl}_2]^-$ complex has the *s-cis* configuration is clearly shown in its nmr spectrum (Figure 7). The N-methyl protons are shown at near 2.5 ppm and the methylene protons between the two nitrogen donor atoms are shown at about 3.0 ppm. If the complex has the *uns-cis* configuration, those nmr peaks would have shown more complicated chemical shifts. The H_a protons are shown at near 4.2 ppm, while the H_b protons are shown at near 3.3 ppm due to the magnetic anisotropy of the C-N bond.^{7,22,23}

The electronic absorption spectra of $[\text{Co}(\text{dmedpa})\text{ClH}_2\text{O}]$ and $[\text{Co}(\text{dmedpa})\text{Cl}_2]^-$ shown in Figure 8 indicate that these complexes have the *cis* configuration. Unlike the *s-cis*- $[\text{Co}(\text{dmedda})\text{Cl}_2]^-$ complex, the $[\text{Co}(\text{dmedpa})\text{Cl}_2]^-$ complex has the

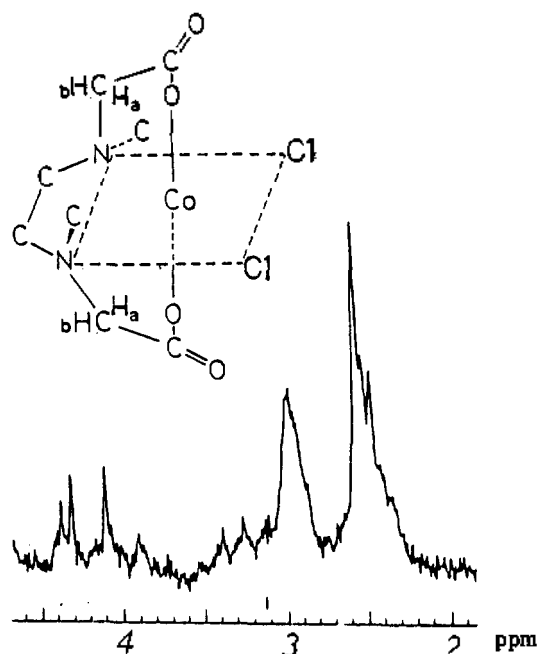


Figure 7. Pmr spectrum of *s-cis*- $[\text{Co}(\text{dmedda})\text{Cl}_2]^-$.

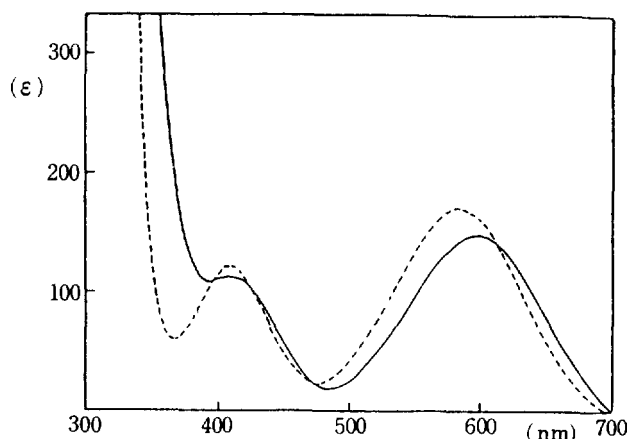


Figure 8. Electronic absorption spectra of *s-cis*- $[\text{Co}(\text{dmedpa})\text{ClH}_2\text{O}]$ (—) and *s-cis*- $[\text{Co}(\text{dmedpa})\text{Cl}_2]^-$ (---).

uns-cis configuration, which is shown by its nmr spectrum in Figure 9. The methyl protons (marked a) show two doublets at near 1.3 ppm and the H_b protons show two quartets (marked b) at near 4.0 ppm. It is quite interesting to note that, while the ethylenediamine and diammine cobalt(III) complexes of dmedpa have yielded the *s-cis* isomer only, the dichloro cobalt(III) complex of dmedpa has yielded only the *uns-cis* isomer in this work. Legg and Cooke² obtained mostly the *s-cis* isomer from their preparation of $[\text{Co}(\text{edda})(\text{am})]^+$, $[\text{Co}(\text{dmedda})(\text{am})]^+$, and $[\text{Co}(\text{deedda})(\text{am})]^+$ when am was en or 2NH_3 . Later, Legg and coworkers²³⁻²⁶ showed that, when steric interaction between the ligands postulated for the diamine analogues in the *uns-cis* isomers was eliminated by employing unidentate ligands such as H_2O and Cl^- , substantial quantities of the *uns-cis* isomers were obtained. Our experimental results are strikingly similar to those of Legg and coworkers. When the two chloro ligands replace the ethylenediamine in the $[\text{Co}(\text{dmedpa})(\text{en})]^+$ in the *uns-cis* geometry, the nonbonded interaction existed between dmedpa and en ligands is mostly eliminated, thereby facilitating the formation of the *uns-cis* isomer. Although the exact reason why the *uns-cis* isomer is the predominant product during the preparation of the $[\text{Co}(\text{dmedpa})\text{Cl}_2]^-$ complex could not be determined from the data obtained in this work alone, it is seen that the steric interaction is the decisive factor in determining the favored geometrical isomer and should be minimized in the *uns-cis* configuration in the case of the $[\text{Co}(\text{dmedpa})\text{Cl}_2]^-$ complex. The only difference between dmedda and dmedpa is that the dmedpa ligand has two C-methyl groups, one each at each of the two α -carbon atoms. The C-methyl group should have some role in determining the geometrical isomer considering from our observation that, while the $[\text{Co}(\text{dmedpa})\text{Cl}_2]^-$ has yielded only the *uns-cis* isomer, the $[\text{Co}(\text{dmedda})\text{Cl}_2]^-$ complex has given only the *s-cis* isomer. It is thought that the influence of the C-methyl group is more pronounced in the case of the $[\text{Co}(\text{dmedpa})\text{Cl}_2]^-$

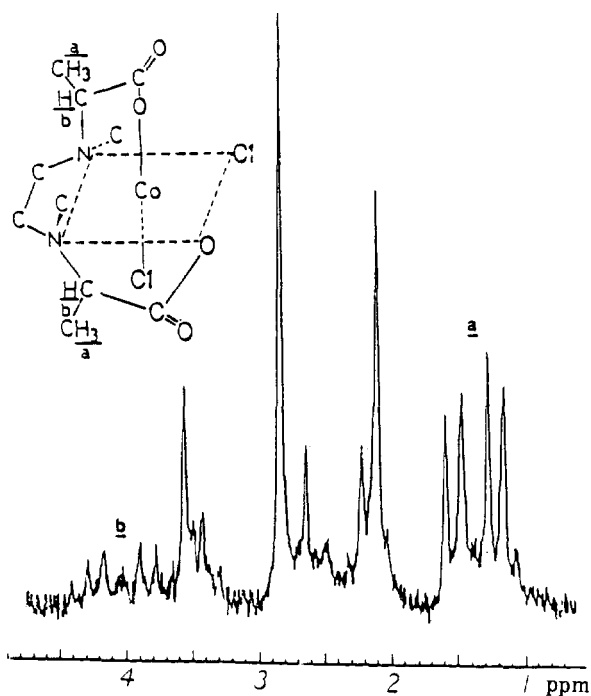


Figure 9. Pmr spectrum of *uns-cis*- $[\text{Co}(\text{dmedpa})\text{Cl}_2]^-$.

complex. Further work is to be done to clarify the steric influence of such C-methyl group.

Acknowledgments. Authors wish to express their thanks to Professor C.F. Liu at Department of Chemistry, University of Illinois at Chicago for technical assistance and to the Korea Science and Engineering Foundation for financial support for this work.

References

1. M. Mori, M. Shibata, E. Kyuno, and F. Maruyama, *Bull. Chem. Soc. Jpn.*, **35**, 75 (1962).
2. J. Legg and D. Cooke, *Inorg. Chem.*, **4**, 1576 (1965).
3. K. Kuroda and K. Watanabe, *Bull. Chem. Soc. Jpn.*, **44**, 1034, 2520 (1971); *ibid.*, **45**, 2176 (1972).
4. L. Halloran and J. Legg, *Inorg. Chem.*, **13**, 2193 (1974).
5. J. Dabrowski and D. Cooke, *J. Am. Chem. Soc.*, **92**, 1097 (1970).
6. W. Jordan and J. Legg, *Inorg. Chem.*, **13**, 955 (1974).
7. L. Schoenberg, D. Cooke, and C. Liu, *ibid.*, **7**, 2386 (1968).
8. G. Hawn, C. Maricondi, and B. Douglas, *ibid.*, **18**, 2542 (1979).
9. M. Strasak and J. Majer, *Inorg. Chim. Acta*, **70**, 231 (1983).
10. M. Strasak, F. Bachraty, and J. Majer, *Coll. Czech. Chem. Comm.*, **47**, 210 (1982).
11. T. Woon and M. O'Connor, *Aust. J. Chem.*, **32**, 1661 (1979).
12. M. Strasak and F. Bachraty, *J. Coord. Chem.*, **13**, 105 (1984).
13. C. Maricondi and B. Douglas, *Inorg. Chem.*, **11**, 688 (1972).
14. W. Jordan and B. Douglas, *ibid.*, **12**, 403 (1973).
15. H. Yamatera, *Bull. Chem. Soc., Jpn.*, **31**, 95 (1968).
16. F. Basolo, C. Ballhausen, and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955).
17. K. Nakamoto and P. McCarthy, "Spectroscopy and Structure of Metal Chelate Compounds," Ch. 2, p. 103-113, Wiley & Sons, 1968.
18. J. Legg, D. Cooke, and B. Douglas, *Inorg. Chem.*, **6**, 700 (1967).
19. D. Radanovic, *Coord. Chem. Rev.*, **54**, 159 (1984).
20. M. Jun and C. Liu, *J. Chem. Soc. (Dalton)* 1031 (1976).
21. P. Harrington, S. Linke, and M. Alexander, *Inorg. Chem.*, **12**, 168 (1973).
22. W. Freeman, *J. Coord. Chem.*, **7**, 197 (1978).
23. P. Coleman, J. Legg, and J. Steele, *Inorg. Chem.*, **9**, 937 (1970).
24. J. Legg and D. Cooke, *ibid.*, **5**, 594 (1966).
25. J. Sudmeier, A. Senzel, and G. Blackiner, *ibid.*, **10**, 90 (1971).
26. P. Garnett, D. Watts, and J. Legg, *ibid.*, **8**, 2534 (1969).