

Synthesis and Equilibria of Octahedral and Tetrahedral Complexes of Cobalt(II) 2, 2'-Dipyridylamine

Myunghyun Paik Suh and Young-Hee Oh

Department of Chemical Education, Seoul National University, Seoul 151, Korea (Received July 28, 1981)

Reactions of cobalt(II) chloride with 2,2'-dipyridylamine (dpa) in alcoholic solutions afford the complex of octahedral $\text{Co}(\text{dpa})_2\text{Cl}_2 \cdot \text{CH}_3\text{OH}$. The octahedral complex is converted to tetrahedral $\text{Co}(\text{dpa})\text{Cl}_2$ in certain solvents or at the elevated temperature, and the tetrahedral complex is changed to the octahedral one with added dpa. The electronic spectra of the complexes in DMF, measured with various concentrations of 2,2'-dipyridylamine, establish the equilibrium; $\text{td-Co}(\text{dpa})\text{Cl}_2 + \text{dpa} \xrightleftharpoons{K} \text{oh-Co}(\text{dpa})_2\text{Cl}_2$. The equilibrium constants determined by the analysis of the visible spectra are 6.4, 3.6 and 2.0 M^{-1} , respectively, at 25.5, 38.0 and 49.0 °C, with ΔH° and ΔS° being -9.5 kcal/mole and -28 eu .

Introduction

Cobalt(II) forms numerous complexes mostly either octahedral or tetrahedral but five-coordinate and square planar species are also known. There are several cases in which cobalt(II) forms both tetrahedral and octahedral complexes with the same ligand. For example, the complex of stoichiometry CoPy_2Cl_2 has two structures. One is an octahedral chain (α -form) in which the chloride is bridged, and the other a discrete tetrahedral molecule (β -form). Moreover, the two forms are interconverted under certain conditions.¹

Equilibria between octahedral and tetrahedral configurations have also been observed in solution, with complexes such as CoL_4X_2 (L=pyridine or a substituted pyridine and $\text{X}=\text{Cl}^-$, Br^- , I^- , or SCN^-).²⁻⁶ In this case, the relative stabilities of the two configurations are determined not only by the crystal field stabilization energy, but also by the electronic properties, size, polarizability, and π -accepting capability of the ligand.

As for the cobalt (II) complexes of chelating heterocyclic ligands, however, such configurational interconversion has been found only in a few cases. The pseudo-octahedral complexes of $\text{Co}(\text{bipy})\text{Cl}_2$ ⁷ and $\text{Co}(4,4'\text{-bipy})(\text{NCS})_2$ ⁸ with bridging bidentate ligands are converted to tetrahedral geometry on thermolysis. Octahedral $\text{cis-Co}(\text{phen})_2\text{X}_2$ ⁹ and $\text{Co}(\text{dpk}_2\text{X})_2$ ¹⁰ disproportionate in solution giving rise to a mixture with the tetrahedral species depending on the temperature.

A chelating heterocyclic ligand 2,2'-dipyridylamine (dpa) has been reported to form tetrahedral $\text{Co}(\text{dpa})\text{Cl}_2$ with cobalt chloride,^{11,12} but octahedral $\text{Co}(\text{dpa})_2\text{Cl}_2$ and the equilibrium between octahedral and tetrahedral configurations are unknown.

In this article, the synthesis of the octahedral and the tetrahedral cobalt(II) complexes of 2,2'-dipyridylamine and the quantitative measurements of the thermodynamic data for the equilibrium between the two configurations in solution are reported.

Experimental Section

Synthesis. All solvents and chemicals were of reagent grade, and used without further purification.

oh-Co(dpa)₂Cl₂·CH₃OH. $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (1.91 g) dissolved in methanol (5ml) was slowly added to a methanol solution (10 ml) of 2,2'-dipyridylamine (2.74 g). The pink precipitates formed were filtered, washed with methanol, and dried in the air. The compound was recrystallized from methanol at room temperature, and the crystals were collected.

Anal. Calcd. for $\text{CoC}_{21}\text{H}_{22}\text{N}_6\text{Cl}_2\text{O}$: C, 49.95; H, 4.36; N, 16.65. Found: C, 48.81; H, 4.59; N, 16.36.

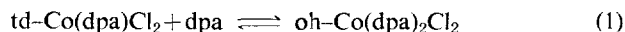
td-Co(dpa)Cl₂. This compound can be synthesized according to the published methods,^{11,12} but new convenient methods have been developed starting from oh-Co(dpa)₂Cl₂ in this study. **Method I.** The crystals of oh-Co(dpa)₂Cl₂·CH₃OH were dissolved in a minimum amount of methanol, and a few milliliters of CH_3CN , CH_3NO_2 , CHCl_3 , ethylether, THF, or acetone were added into the solution. Deep blue crystals formed from the solution. **Method II.** As a methanol solution of oh-Co(dpa)₂Cl₂·CH₃OH was heated at near the boiling temperature, blue crystals slowly precipitated from the solution. **Method III.** The pink crystals of oh-Co(dpa)₂Cl₂·CH₃OH were dissolved in water to give an orange-colored solution. The evaporation of water from this solution resulted in deep-blue precipitates. The deep blue precipitates obtained by the various methods were filtered, washed with methanol, and dried.

Anal. Calcd. for $\text{CoC}_{10}\text{H}_9\text{N}_3\text{Cl}_2$: C, 39.84; H, 2.98; N, 13.94. Found: C, 39.98; H, 3.05; N, 13.99.

Physical Measurements. Infrared spectra were recorded on a Perkin-Elmer 283 infrared spectrophotometer. Samples were prepared as nujol mulls. Visible electronic absorption spectra were measured with a Beckman Model 25 spectrophotometer. The conductivities of the complexes were obtained using an Industrial Instruments Model RC 16B conductivity bridge. Magnetic susceptibilities were measured by the nmr method¹³ by using a Wilmad coaxial sample unit. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tennessee, U.S.A.

Measurement of Thermodynamic Data. Dimethylformamide

was used as solvent and purified as described in the literature.¹⁴ To obtain the equilibrium constants, a series of solutions of known cobalt(II) concentrations ($2-3 \times 10^{-3} M$) were prepared containing different known amounts of 2,2'-dipyridylamine (0.05–0.35 *M*), and the spectra of the solutions were measured. The equilibrium constant for the reaction

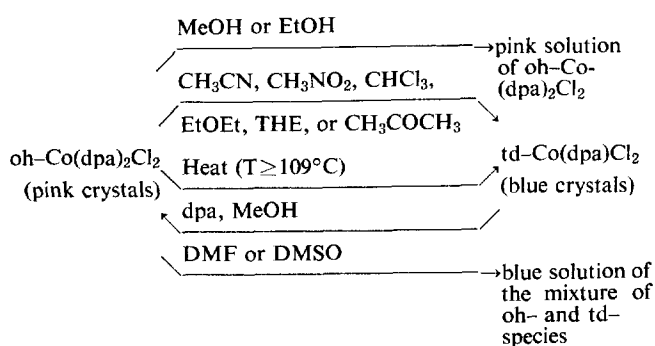


is given by $K = (A_0 - [\text{Td}]_{\text{eq}})/[\text{Td}]_{\text{eq}}\{B_0 - (A_0 - [\text{Td}]_{\text{eq}})\}$ where A_0 and B_0 are the initial concentration of the td-Co(dpa)Cl₂ and 2,2'-dipyridylamine, respectively, and $[\text{Td}]_{\text{eq}}$ is the equilibrium concentration of td-Co(dpa)Cl₂. $[\text{Td}]_{\text{eq}}$ was obtained from a previously determined calibration curve relating the concentration of Co(dpa)Cl₂ to absorbance in DMF where it was assumed that only td-Co(dpa)Cl₂ was present. Equilibrium constants were measured at 25.5, 38.0, and 49.0°C. ΔH^0 values were obtained from the plot of $\ln k$ vs. $1/T$, and ΔS^0 at 25°C according to $\Delta S^0_{25^\circ} = (\Delta H^0 - G^0_{25^\circ})/T$.

Results and Discussion

Characterization of Co(II) 2,2'-Dipyridylamine Complexes

oh-Co(dpa)₂Cl₂·CH₃OH The complex has a pink color in the solid state, and is soluble in methanol, ethanol, DMSO, and DMF. When it is dissolved in alcohol, it gives a pink solution whose electronic spectrum shows a maximum peak at 491 nm [$^4T_{1g}(F) \rightarrow ^4T_{1g}(P)$], characteristic of the octahedral Co(II) complexes. On the other hand, the DMF or DMSO solution of the complex gives an intense blue solution whose spectrum shows multicomponent absorption at 520–650 nm, indicating a large portion of the complex rearranged to the tetrahedral configuration on dissolution. The complex also turns blue when it is heated in the crystalline



Scheme 1. Configurational changes of octahedral and tetrahedral complexes of cobalt(II) 2,2'-dipyridylamine.

state ($T \geq 109^\circ\text{C}$) or in a methanol solution, or when it is mixed with CH_3CN , CH_3NO_2 , CHCl_3 , EtOEt, THF, or acetone. The phenomena of this configurational change of the complex are summarized in Scheme 1.

The infrared spectrum of the nujol mull shows peaks at 3303 and 3202 cm^{-1} for N–H stretchings, at 3420 cm^{-1} for methanol, and at 1642 and 1583 cm^{-1} for pyridine ring. Elemental analyses as well as the conductance data (Table 1) and the spectra indicate that the complex has an octahedral geometry with two 2,2'-dipyridylamines coordinated to cobalt(II) in a bidentate fashion through the ring nitrogens. The complex may have either *cis* or *trans* configuration, but presumably with the *cis* configuration because of the possible severe steric hindrance in the *trans* structure. A complex of $\text{Co(phen)}_2\text{X}_2$ whose ligands are structurally similar to

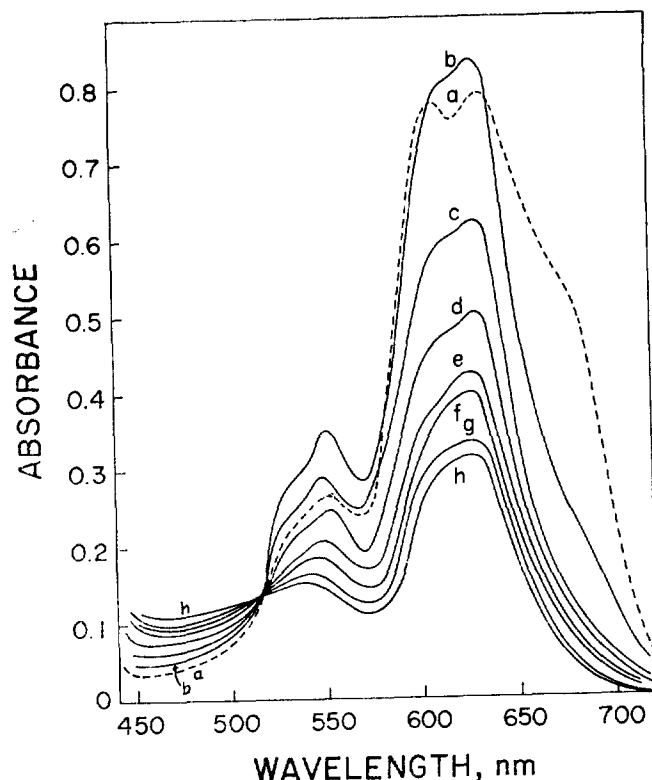


Figure 1. Electronic spectra of the equilibrium mixture of td-Co(dpa)Cl_2 and 2,2'-dipyridylamine in DMF at 25.5°C. $[\text{Co(dpa)Cl}_2]_0 = 2.75 \times 10^{-3} M$; a, with no added 2,2'-dipyridylamine, $[\text{dpa}]_0 = 0$; b, $[\text{dpa}]_0 = 6.7 \times 10^{-3} M$; c, $[\text{dpa}]_0 = 0.0508 M$; d, $[\text{dpa}]_0 = 0.0813 M$; e, $[\text{dpa}]_0 = 0.112 M$; f, $[\text{dpa}]_0 = 0.140 M$; g, $[\text{dpa}]_0 = 0.175 M$; h, $[\text{dpa}]_0 = 0.254 M$.

TABLE 1: Conductance and Electronic Spectral Data of the Co (II) 2,2'-Dipyridylamine Complexes

Complex	Solvent	Molar Conductance λ_M at 20°C ($\Omega^{-1}\text{cm}^2\text{mole}^{-1}$)	Electronic Spectrum, Kk (ϵ)
[Co(dpa) ₂ Cl ₂]·CH ₃ OH	CH ₃ OH	59.4 ^a	20.4(16.8)
	DMF	16.6 ^b	
[Co(dpa)Cl ₂]	DMF	17.9 ^c	18.7 sh(83), 18.0(97), 15.8(285), 14.7 sh(185)
	DMF	20.4 ^d	
	DMF	23.9 ^e	

^a [complex] = $1.14 \times 10^{-2} M$; ^b [complex] = $2.51 \times 10^{-3} M$; ^c [complex] = $2.00 \times 10^{-3} M$; ^d [complex] = $2.00 \times 10^{-3} M$, $[\text{dpa}]_0 = 0.013 M$;

^e [complex] = $2.00 \times 10^{-3} M$; $[\text{dpa}]_0 = 0.202 M$.

2,2'-dipyridylamine also had *cis*-octahedral arrangement.⁹ *td*-Co(dpa)Cl. The complex is soluble only in DMF or DMSO leading to a deep blue solution. The addition of 2,2'-dipyridylamine into the DMF solution of the complex gives the pink *oh*-Co(dpa)₂Cl₂. The electronic spectrum of the DMF solution (Figure 1) shows λ_{\max} at 632 nm ($\epsilon=285$), 613 nm ($\epsilon=283$), and 555 nm ($\epsilon=97$) for the ${}^4A_2(F) \rightarrow {}^4T_1(P)$ transition, which is characteristic of the tetrahedral Co(II) complexes. The complex dissociates slightly in dilute DMF solution ($\sim 10^{-3}M$). This is evidenced by an increase in the intensity at 520–640 nm and a decrease at 680 nm when small amounts of free 2,2'-dipyridylamine ($1-6 \times 10^{-3} M$) are added. However, the difference is less than 5%, and the solution obeys Beer's law. The complexity of the ${}^4A_2(F) \rightarrow {}^4T_1(P)$ transition band may be interpreted by the tetragonal component caused by lowering the symmetry of the tetrahedral component.¹² With the assumption of its inter-electronic repulsion parameter $B \approx 700 \text{ cm}^{-1}$, the ligand field of the complex is estimated as about $10Dq \approx 5,000 \text{ cm}^{-1}$. By the comparison of the $10Dq$ value of $\sim 11,000 \text{ cm}^{-1}$ for the *oh*-Co(dpa)₃²⁺,¹¹ the $10Dq$ value of Co(dpa)Cl₂ indicate that the complex has tetrahedral configuration instead of square planar geometry. Measurement of magnetic susceptibility ($X_g = 32.7 \times 10^{-6}$ c.g.s. unit) by the nmr method gives the magnetic moment of 4.80 BM, and this also supports the tetrahedral structure of the complex with $S=3/2$.

Configurational Equilibrium between *td*-Co(dpa)Cl₂ and *oh*-Co(dpa)₂Cl₂ in DMF. In Figure 1, the electronic spectra of the DMF solution of *td*-Co(dpa)Cl₂ measured in the presence of various amounts (0.0067–0.254 M) of 2,2'-dipyridylamine are illustrated. Although slight dissociation of *td*-Co(dpa)Cl₂ occurs in the absence of added 2,2'-

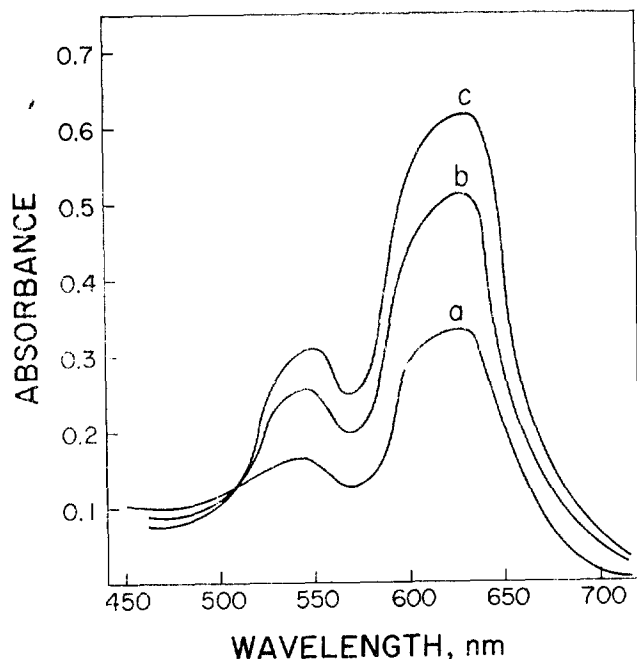


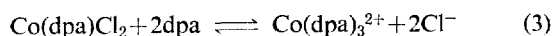
Figure 2. Electronic spectra of *td*-Co(dpa)Cl₂ in DMF at various temperatures. $[\text{Co(dpa)Cl}_2]_0 = 2.75 \times 10^{-3} M$, $[\text{dpa}]_0 = 0.175 M$; a, 25.5 °C; b, 38.0 °C; c, 49.0 °C.

dipyridylamine, it is suppressed by the addition of the amine. As the concentration of 2,2'-dipyridylamine is increased, the spectra at 520–680 nm remain unchanged in peak position and profile, corresponding well to the solid spectrum of *td*-Co(dpa)Cl₂, and only a decrease in intensity is observed. The figure discloses that the addition of the amine leads to a less amount of the tetrahedral complex. The spectra at various temperatures are presented in Figure 2. It indicates that the concentration of the tetrahedral complex increases as the temperature is raised. These establish well the equilibrium of Eq. (1) in DMF solution.

However, it is necessary to consider other possible equilibria before estimating the thermodynamic data for the equilibrium of Eq. (1). Other possibilities are the reaction



and, in the presence of an excess ligand



These equilibria are excluded, however, on the basis of following reasons. (i) The spectra at 520–680 nm of *td*-Co(dpa)Cl₂ with various concentrations of 2,2'-dipyridylamine correspond well to that of the solid state (as nujol mull). The absorption of *td*-Co(dpa)Cl₂ in DMF obeys Beer's law, and distinctly differs from the known spectra of the CoCl₄²⁻ species.¹⁵ (ii) The molar conductance of the DMF solution of *oh*-Co(dpa)₂Cl₂ or *td*-Co(dpa)Cl₂ was essentially that of a nonelectrolyte. Moreover, when various amounts (0.01–0.20M) of 2,2'-dipyridylamine were added to a DMF

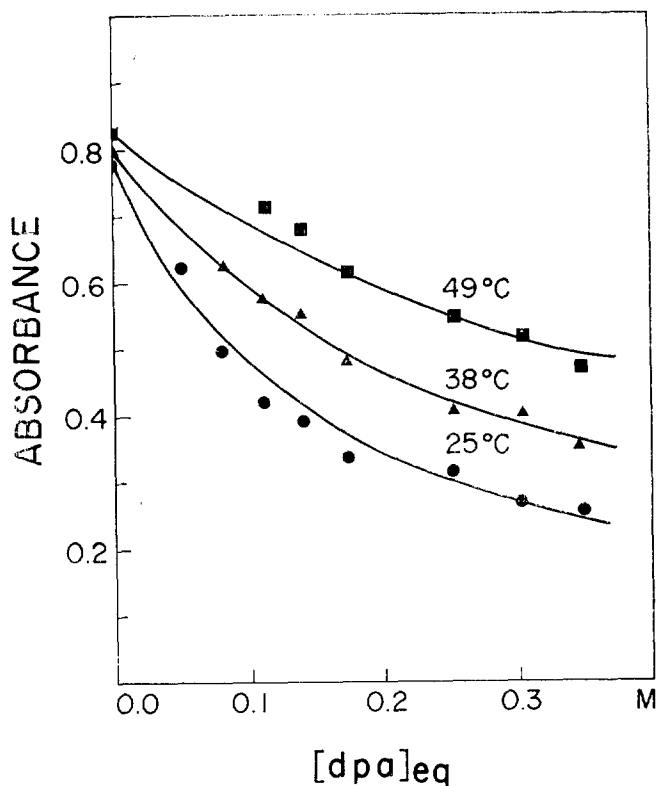


Figure 3. Plot of the absorbances at 632 nm of the equilibrium mixtures obtained with $[\text{Co(dpa)Cl}_2]_0 = 2.75 \times 10^{-3} M$ against the equilibrium concentration of 2,2'-dipyridylamine at various temperatures.

TABLE 2: Thermodynamic Data for Tetrahedral-Octahedral Equilibria of Cobalt(II) Complexes

System	Solvent	Temp.(°C)	K (M^{-1}) ^a , (M^{-2}) ^b	$[L]_{1/2}$ ^c (M)	ΔG^0 (kcal·mole ⁻¹)	ΔH^0 (kcal·mole ⁻¹)	ΔS^0 (cal·deg ⁻¹ mole ⁻¹)		
Co(dpa)Cl ₂	DMF	25.5	6.37±0.27	0.157	-1.10	-9.47	-28.0		
		38.0	3.55±0.10	0.282	-0.75				
		49.0	1.98±0.09	0.505	-0.41				
Copy ₂ Cl ₂	CH ₃ NO ₂ ^d	20	0.40	1.58		-11.2	-38.3		
		25	0.71	1.18					
	CH ₃ NO ₂ ^e	39	0.28	1.87					
		48	0.17	2.41					
		48	0.17	2.41					
	Pyridine ^e	25	0.21	2.17				-13.3	-48.0
		38	0.16	2.47					
Pyridine ^f	38	0.435	1.52		-13.0	-43.4			

^a For Co(dpa)Cl₂ system; ^b For Copy₂Cl₂ system. ^c Concentration of dpa or py at which [td]/[Oh] = 1; ^d The data were taken from reference 2; ^e The data were taken from reference 3; ^f The data were taken from reference 6.

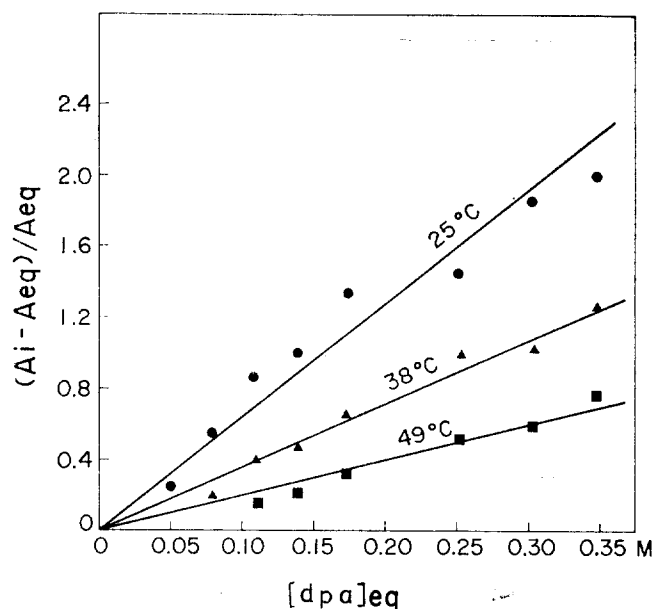


Figure 4. Linear Plot of the Data of Figure 3 according to Eq. (7).

solution of td-Co(dpa)Cl₂ (2×10^{-3} M), the conductance of the solution did not vary appreciably (Table 1).

In an attempt to obtain the thermodynamic properties of Eq. (1), the spectral changes of the DMF solutions of td-Co(dpa)Cl₂ upon the addition of 2,2'-dipyridylamine were measured at various temperatures. The absorbance readings at 632 nm under various conditions are illustrated in Figure 3. At this wavelength, the molar extinction coefficient of oh-Co(dpa)₂Cl₂ is negligible compared with that (ϵ_{td}) of td-Co(dpa)Cl₂.

Thus, the absorbance reading produces directly the equilibrium concentration (Eqs. 4-6).

$$[Td]_{eq} = \frac{A_{eq}}{\epsilon_{td}} \quad (4)$$

$$[Oh]_{eq} = \frac{A_i - A_{eq}}{\epsilon_{td}} \quad (5)$$

$$[B]_{eq} = B_0 - [oh]_{eq} \quad (6)$$

Here, A_i and A_{eq} are the absorbance readings of td-Co(dpa)Cl₂ solution in the absence of the added 2,2'-dipyridylamine, and at equilibrium in the presence of

added amine, respectively. Eqs. 4-6 lead to

$$\frac{A_i - A_{eq}}{A_{eq}} = K[B]_{eq} \quad (7)$$

In Figure 4, the plots of $(A_i - A_{eq})/A_{eq}$ against $[B]_{eq}$ are illustrated. The equilibrium constants obtained from the slopes are summarized in Table 2. The solid lines drawn for the plots of A_{eq} against $[B]_{eq}$ (Figure 3) are constructed using these values of K . The values of ΔG^0 , ΔH^0 and ΔS^0 at 25°C obtained from the temperature dependence of K are also presented in Table 2.

The data indicate that the enthalpy change is favored for the formation of the octahedral complex, but the entropy change is disfavored. In view of the bond energy and the crystal field stabilization energy, the octahedral complex is expected to have lower energy than the tetrahedral one¹⁶. π -Backbonding which is possible in octahedral geometry by the overlap of metal nonbonding orbitals with vacant anti-bonding π -orbitals of 2,2'-dipyridylamine stabilizes octahedral complex better leading to a more negative ΔH . However, change in bond energies and crystal field stabilization energy are not the only factors that determine the net enthalpy change. Solvation of the complexes and entering ligands would also play a part. Negative entropy change similar to the observed value is expected in the system.¹⁷ On formation of octahedral complex, 2,2'-dipyridylamine loses translational freedom. In addition, the ligand loses rotational entropy also when the ligand chelates to the metal atom in bidentate fashion, and the partial double bond character of the metal-ligand bond due to π -bonding restricts its rotation severely. Solvation accounts in part for the ΔS^0 value, but would be relatively unimportant for the complexes because they are not charged. Of the three molecular species involved in the reaction, 2,2'-dipyridylamine would be solvated most strongly in DMF solution probably as a result of hydrogen bonding. This solvation would be broken once 2,3'-dipyridylamine is coordinated to the complex and makes positive contribution to the ΔS value, but this effect would be minor compared with the loss of translational and rotational entropy.

In Table 2, thermodynamic data for the equilibrium of Eq. (1) is compared with those for the corresponding

equilibrium for $\text{Co(dpa)}_2\text{Cl}_2$ system. Half conversion of $\text{td-Co(dpa)}_2\text{Cl}_2$ to $\text{oh-Co(dpa)}_2\text{Cl}_2$ occurs with 0.157 M of 2,2'-dipyridylamine at 25°C, while that of $\text{td-Copy}_2\text{Cl}_2$ occurs with 1.18 M (in CH_3NO_2) or 1.52–2.17 M (in pyridine) of pyridine. Although the effect of different solvents on the equilibria is uncertain, binding of 2,2'-dipyridylamine, a chelating ligand, appears to result in 4–7 times (with statistical correction) more effective formation of the octahedral complex than binding of a nonchelating ligand, pyridine. The "chelate effect"^{18,19} is further supported by the values of ΔH° and ΔS° . The greater ΔH° for $\text{Co(dpa)}_2\text{Cl}_2$ system may be attributed to the greater steric strain resulting from the presence of two chelate rings in $\text{Co(dpa)}_2\text{Cl}_2$. On the other hand, the greater ΔS° for $\text{Co(dpa)}_2\text{Cl}_2$ system reflects the smaller number of the reacting ligand. Thus, the more favorable formation of $\text{oh-Co(dpa)}_2\text{Cl}_2$ compared with $\text{oh-Copy}_2\text{Cl}_2$ is caused by the greater ΔS° value.

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- (16) As the values of $\Delta_{\text{td}} = \sim 5,000 \text{ cm}^{-1}$ and $\Delta_{\text{oh}} = \sim 11,000 \text{ cm}^{-1}$ are assumed, the enthalpy change caused by crystal field stabilization is estimated to be about -5.7 kcal/mole .
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The Crystal and Molecular Structures of Sulfametrole

Chung Hoe Koo and Yong Je Chung

Department of Chemistry, Seoul National University, Seoul 151, Korea

Hyun So Shin

Department of Chemical Engineering, Dongguk University, Seoul 100, Korea

Jung Sun Suh

Department of Chemical Engineering, Myong Ji University, Seoul 122, Korea (Received August 13, 1981)

Sulfametrole, $\text{C}_9\text{H}_{10}\text{N}_4\text{O}_3\text{S}_2$, crystallizes in the monoclinic system, space group $P2_1/n$, with $a=8.145(2)$, $b=16.505(4)$, $c=9.637(1) \text{ \AA}$, $\beta=103.72(1)^\circ$, $D_m=1.52 \text{ gcm}^{-3}$, $Z=4$. Intensities for 3594(2143 observed) unique reflections were measured on a four-circle diffractometer with $\text{Mo } K_\alpha$ radiation ($\lambda=0.71069 \text{ \AA}$). The structure was solved by direct method and refined by full-matrix least squares to a final R of 0.070. The geometrical features of the thiaziazole ring indicate some π -electron delocalization inside the ring. The least squares planes defined by the benzene and thiaziazole rings are nearly perpendicular to each other (dihedral angle; 93.9°). All the potential hydrogen-bond donor atoms in the molecule, N(1) and N(2), are included in the hydrogen bonding. The molecules through hydrogen bonding form three dimensional network.

Introduction

The study of sulfametrole was undertaken as a part of

a program of structure analysis of the therapeutically useful, sulfonyl-group containing compounds being pursued in this