

reaction it can be said that this change must occur at or after the slow rate-determining step. Spectral data indicate that the reaction does not occur *via* the process of isomerization followed by anation.

We are continuing our investigation of this system in both acidic and slightly basic media. In the pH range 7-9 we hope to obtain individual values for k_1 and K_6 . Anation experiments conducted at pH 1 or below indicate that no geometry

change occurs and that the product of the reaction is α -*cis*-Co(EDDA)(C₂O₄)⁻.

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Registry No. α -*cis*[Co(EDDA)(OH₂)₂]ClO₄, 32715-40-5; H₂C₂O₄, 144-62-7; β -*cis*-Co(EDDA)(C₂O₄)⁻, 26135-71-7.

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Stereochemistry of β -Diketone Complexes of Cobalt(III). XII. Kinetics and Mechanism of the Isomerization of Some *trans*-Anionopyridinebis(acetylacetonato)cobalt(III) Complexes

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Kinetic studies have been carried out in CDCl₃ on the *trans*-*cis* isomerization of [Co(acac)₂(X)(py)] where X⁻ = N₃⁻, NO₂⁻, CN⁻, and NCO⁻. Rate constants were determined over a temperature range of 29-60° by pmr methods, and activation and equilibrium parameters were obtained. At 29°, the first-order rate constants are (1.92 ± 0.13) × 10⁻⁴ sec⁻¹ for X⁻ = N₃⁻, (1.75 ± 0.20) × 10⁻⁵ sec⁻¹ for X⁻ = NCO⁻, and (1.06 ± 0.05) × 10⁻⁶ sec⁻¹ for X⁻ = NO₂⁻. The enthalpies and entropies of activation, ΔH^* and ΔS^* , are as follows: 26.7 ± 2.7 kcal/mol and 13.1 ± 9.1 eu for X⁻ = N₃⁻; 33.2 ± 2.9 kcal/mol and 29.8 ± 9.9 eu for X = NCO⁻; 38.8 ± 1.0 kcal/mol and 42.9 ± 3.4 eu for X⁻ = NO₂⁻. The corresponding complex where X⁻ = CN⁻ does not isomerize in CDCl₃. The isomerization rate order is N₃⁻ > NCO⁻ > NO₂⁻ > CN⁻. Several dissociative mechanisms involving a trigonal-bipyramidal intermediate are suggested. The trend in the rates may be attributed to the π -donor ability of X⁻ to stabilize the intermediate. The synthesis of *trans*-[Co(acac)₂(NCO)(py)] is described.

In previous work involving the synthesis and characterization of a number of new bis(acetylacetonato)cobalt(III) complexes,^{1,2} marked differences were noted in the reactivity of the complexes in solution. Such changes appeared to be correlated with changes in the anions bound to the cobalt. For example, while *cis*-[Co(acac)₂(CN)₂]⁻ is completely inert in aqueous solution, *cis*-[Co(acac)₂(N₃)₂]⁻ rapidly undergoes a complex series of solvolyses and isomerizations under the same conditions. *cis*-[Co(acac)₂(NO₂)₂]⁻ also undergoes isomerization and subsequent solvolysis in aqueous solution,³ but at a much slower rate than the *cis*-diazide.

In an effort to determine the nature of the effect exerted by the anions on the reactivity of the cobalt(III) acetylacetonates, a kinetic study of the *trans* → *cis* isomerization of [Co(acac)₂(X)(py)] in chloroform, where X⁻ = N₃⁻, NCO⁻, CN⁻, and NO₂⁻, was undertaken. The neutral complexes may be studied in a nonpolar, noncoordinating solvent which eliminates the possibility of solvolysis as well as ion-pair effects. The isomerization of the acetylacetonates is easily monitored by means of nmr spectroscopy.

Experimental Section

Materials. The *trans* isomers of [Co(acac)₂(N₃)(py)]¹, [Co(acac)₂(CN)(py)]², and [Co(acac)₂(NO₂)(py)]⁴ were prepared as previously described. The solvent used in the kinetic runs was chloroform-*d*, 99.8% purity, containing 1% TMS (Diaprep, Inc.).

Synthesis of *trans*-[Co(acac)₂(NCO)(py)]. Two grams of [Co-

(acac)₂] (0.0078 mol) was dissolved in 100 ml of water. After the addition of 1.25 g of potassium cyanate (0.0156 mol) and 2 ml of pyridine (0.0248 mol), 2 ml of 30% hydrogen peroxide solution (0.0176 mol) was added dropwise. The reaction mixture was stirred at 25° for 4 hr, at which point the crude product was filtered and air-dried. The green-brown product was dissolved in a minimum of chloroform and deposited on a 2.5-cm column packed to a height of 30 cm with 60-100 mesh Florisil (Floridin Co.). Elution with benzene-10% methanol resulted in the rapid movement of a single concentrated green band down the column. This component, the pure product, was collected and evaporated to dryness. The impurities in the reaction mixture remain on the top of the column. The product was recrystallized from chloroform-petroleum ether and air-dried. The yield was 0.23 g (8%). *Anal.*⁵ Calcd for C₁₆H₁₉N₂O₅Co, [Co(acac)₂(NCO)(py)]: C, 50.79; H, 5.03; N, 7.41. Found: C, 50.49; H, 4.97; N, 7.22; mp 160°. The pmr spectrum of this compound in CDCl₃ exhibits methyl resonance at -2.22 ppm downfield from TMS and a single methine resonance at -5.38 ppm. The asymmetric stretch of the coordinated cyanate gives a single band at 2230 cm⁻¹ in the ir spectrum.

Kinetic Measurements. The kinetic measurements of the *trans* → *cis* isomerization were made using a Varian HA-100 high-resolution 100-MHz nmr spectrometer equipped with a Varian Model V-4343 variable-temperature controller. The temperature of the probe prior to each run was determined (±0.1°) by measuring the methylene coupling constant of an ethylene glycol sample. Each complex was measured at five different temperatures with three runs being made at each temperature and averaged. In each case, 15 mg of complex was dissolved in 400 μ l of deuteriochloroform, giving a 0.1 M solution. Spectra were recorded in the methyl region of the spectra at 50-Hz sweep width at various time intervals (Figure 1) until the sample reached equilibrium (~4 half-lives). For cases in which the time required for attainment of equilibrium prohibited the run being carried out in the variable-temperature probe, the samples were kept in a thermostated bath of ±0.01° and prior to each measurement the sample was transferred to the nmr probe which was preset to the bath temperature.

Concentrations of *trans* and *cis* isomers were determined by

(5) Elemental analysis performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

(1) L. J. Boucher and D. R. Herrington, *Inorg. Chem.*, **11**, 1772 (1972).

(2) L. J. Boucher, C. G. Coe, and D. R. Herrington, *Inorg. Chim. Acta*, in press.

(3) R. J. York, Ph.D. Thesis, University of Massachusetts, 1969; *Diss. Abstr. B*, **30**, 4031 (1970).

(4) L. J. Boucher and J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **27**, 1093 (1965).

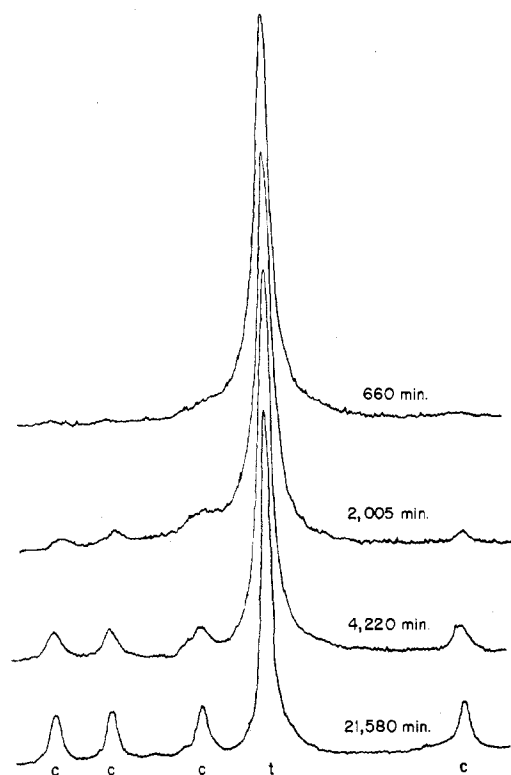
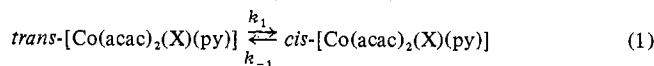


Figure 1. Methyl region of the *trans*-[Co(acac)₂(NO₂)(py)] pmr spectra at 50-Hz sweep width at various times during isomerization in CDCl₃ at 29°. The spectrum at *t* = 21,580 min represents the equilibrium composition.

measuring the areas under the nmr peaks with a polar planimeter, taking the average of five determinations for each peak area. Since some of the samples take several hours or even several days to reach equilibrium, changes in instrument response over the course of several spectra could produce errors in the determination of concentrations by absolute area measurements. Therefore, amounts of *cis* and *trans* isomers were represented by percentages rather than absolute concentrations. Thus at time *t*, the amount of *cis* isomer present is designated by $\chi(C)$, the area under the *cis* methyl resonances divided by the total area under all the methyl resonances of that scan times 100. The resulting data⁶ were fit to the appropriate rate equation by a least-squares program.

Results and Discussion

Kinetic Data. The system being measured is one involving two opposing reactions, both of which are first order (eq 1).



The expression for the forward rate constant can be written as

$$k_1 = \frac{\chi(C_{eq})}{\chi(T_0)t} \ln \frac{\chi(C_{eq})}{\chi(C_{eq}) - \chi(C)} \quad (2)$$

where $\chi(C_{eq})$ is the per cent *cis* isomer at equilibrium, $\chi(C)$ is the per cent *cis* isomer at time *t*, and $\chi(T_0)$ is the per cent *trans* isomer at *t* = 0 (100%). Treatment of the experimental data *via* (2) results in linear rate plots such as those in Figure 2, and the resulting kinetic data are contained in Table I.

Arrhenius plots for the *trans* → *cis* isomerization of [Co(acac)₂(X)(py)] are shown in Figure 3. The activation energies derived from these, together with the activation enthalpies, entropies, and free energies, are contained in Table II. The values of ΔS^* were obtained from eq 3. The

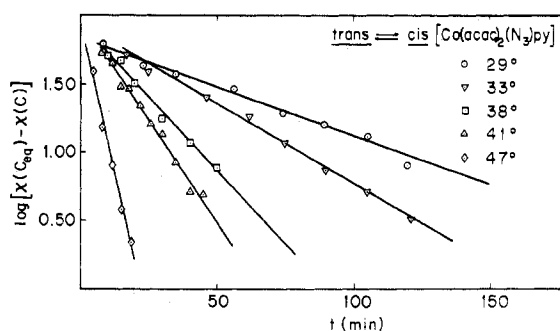


Figure 2. First-order rate plots for *trans* → *cis*-[Co(acac)₂(N₃)(py)] isomerization in CDCl₃.

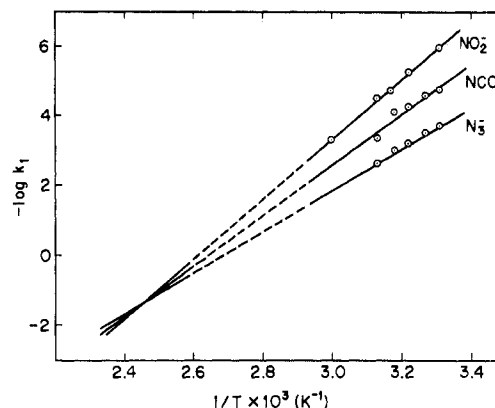


Figure 3. Arrhenius plots for *trans* → *cis*-[Co(acac)₂(X)(py)] isomerization in CDCl₃, extrapolated to the isokinetic temperature.

Table I. Kinetic Data for *trans* → *cis*-[Co(acac)₂(X)(py)] Isomerization in CDCl₃

X ⁻	Temp, °C	k ₁ , sec ⁻¹	t _{1/2} ^a , min	K _{eq} ^b
NO ₂ ⁻	29	(1.06 ± 0.05) × 10 ⁻⁶ ^c	5133 ± 133	0.59 ± 0.05
	38	(5.54 ± 0.44) × 10 ⁻⁶	1060 ± 70	0.77 ± 0.06
	43	(1.79 ± 0.15) × 10 ⁻⁵	402 ± 28	0.83 ± 0.11
	47	(3.14 ± 0.42) × 10 ⁻⁵	201 ± 30	0.81 ± 0.03
	60	(5.02 ± 0.17) × 10 ⁻⁴	13 ± 2	1.03 ± 0.06
NCO ⁻	29	(1.75 ± 0.20) × 10 ⁻⁵	530 ± 170	3.69 ± 0.32
	33	(2.54 ± 0.22) × 10 ⁻⁵	350 ± 50	3.87 ± 0.11
	38	(5.43 ± 0.67) × 10 ⁻⁵	178 ± 50	2.67 ± 0.33
	41	(7.56 ± 0.81) × 10 ⁻⁵	137 ± 27	2.75 ± 0.45
	47	(4.43 ± 0.40) × 10 ⁻⁴	34 ± 2	2.36 ± 0.53
N ₃ ⁻	29	(1.92 ± 0.13) × 10 ⁻⁴	39 ± 3	2.49 ± 0.09
	33	(3.12 ± 0.14) × 10 ⁻⁴	35 ± 1	2.68 ± 0.35
	38	(6.38 ± 0.06) × 10 ⁻⁴	15 ± 1	3.92 ± 0.08
	41	(9.78 ± 1.05) × 10 ⁻⁴	13 ± 1	3.02 ± 0.23
	47	(2.39 ± 0.43) × 10 ⁻³	4 ± 1	3.32 ± 0.42
	29 ^d	(1.97 ± 0.13) × 10 ⁻⁴		2.91 ± 0.25
29 ^e	(2.13 ± 0.14) × 10 ⁻⁴		2.48 ± 0.08	

^a Time at which $\chi(C) = \chi(C_{eq})/2$. ^b $K_{eq} = \chi(C_{eq})/(100 - \chi(C_{eq}))$. ^c The error limits reflect the range of the three measurements at each temperature. ^d Contains excess pyridine (1:1 pyridine-d₅: complex). ^e Contains excess pyridine (2:1 pyridine-d₅: complex).

$$\Delta S^* = R [\ln k_1 - \ln (kT/h)] + \Delta H^*/T \quad (3)$$

standard free energy change, as well as the standard enthalpies and entropies, were obtained from the equilibrium constants.

Reactivity. The isomerization of cobalt(III) acetylacetonates may proceed *via* a number of possible mechanisms. Intramolecular pathways would include a twist mechanism⁷ or a ring-opening process involving an axial trigonal-bipyramidal intermediate or transition state. An intermolecular mechanism for the isomerization of [Co(acac)₂(X)(py)] would involve loss of X⁻ or pyridine in the rate-determining

(6) Complete tabulation of all experimental data is contained in the Ph.D. thesis of D. R. Herrington, Carnegie-Mellon University, Nov 1972.

(7) J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, 8, 165 (1958).

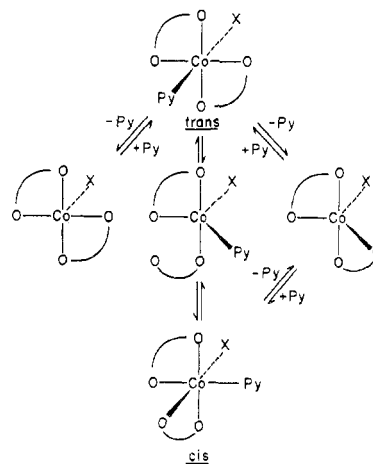
Table II. Activation Parameters and Thermodynamic data for *trans*- → *cis*-[Co(acac)₂(X)(py)] in CDCl₃ at 29°

X ⁻	E _a , kcal/mol	ΔH [‡] , kcal/mol	ΔS [‡] , eu	ΔG [‡] , kcal/mol	ΔH [°] , kcal/mol	ΔS [°] , eu	ΔG [°] , kcal/mol
N ₃ ⁻	27.3 ± 2.7	26.7 ± 2.7	13.1 ± 9.1	22.7 ± 5.5	-3.1 ± 2.1	-8.3 ± 7.0	-0.54 ± 0.03
NCO ⁻	33.8 ± 2.9	33.2 ± 2.9	29.8 ± 9.9	24.2 ± 5.9	-5.5 ± 3.3	-20.8 ± 11.1	-0.78 ± 0.05
NO ₂ ⁻	39.4 ± 1.0	38.8 ± 1.0	42.9 ± 3.4	25.8 ± 2.1	-3.3 ± 0.9	-12.0 ± 3.2	0.31 ± 0.05

step or ligand exchange with loss of a chelate ring. While a twist mechanism cannot be ruled out for the [Co(acac)₂(X)(py)] system, such a process appears to be unlikely, particularly in view of the high ΔS[‡] values observed. This twist mechanism involves a trigonal-prismatic intermediate which would result in a low ΔS[‡].⁸ To date, no cobalt(III) β-diketone complexes have been found to isomerize *via* a twist mechanism. An intermolecular process involving dissociation of X⁻ is also unlikely in a nonpolar solvent such as chloroform.

Other likely dissociative pathways for [Co(acac)₂(X)(py)] isomerization are presented in Figure 4. Previous qualitative nmr work⁹ indicates that pyridine exchange without isomerization is rapid. For example, 4-*tert*-butylpyridine resonances of the free pyridine and [Co(acac)₂(NO₂)(Bu-py)] undergo coalescence at 85° in nitrobenzene. This pyridine-loss pathway most likely occurs for the complexes discussed here. It involves a square-pyramidal intermediate and does not typically lead to isomerization. There is a possibility that the square pyramid rearranges *via* a trigonal bipyramid to a square pyramid that forms the *cis* isomer.¹⁰ The formation of a trigonal bipyramid may occur *via* chelate ring opening or pyridine dissociation. Preliminary results on the rates of *trans*- → *cis*-[Co(acac)₂(NO₂)(L)] isomerization, where L = a series of amines, indicate only slight dependence of the rate on L.⁹ This is contrary to what would be expected if the rate-determining step were the breaking of a cobalt-amine bond. Finally, the isomerization rates and equilibria at least for the N₃⁻ case (see Table I) are unaffected by the presence of excess pyridine at the 1:1 and 2:1 pyridine:complex level. Of course this latter result and the other arguments do not rule out a pyridine-exchange mechanism for isomerization. Further work with unsymmetrical β-diketones and optical isomers may help clarify this point.

Studies conducted on the isomerization of various tris(β-diketonato)cobalt(III) complexes, including [Co(acac)₃], have indicated that the mechanism involved is chelate ring opening *via* the formation of a trigonal-bipyramidal intermediate.¹⁰⁻¹⁵ A comparison of the activation parameters for the [Co(β-dik)₃] and [Co(acac)₂(X)(py)] systems shows the same order of magnitude for the activation energies, but the activation entropies are higher in the latter case. If a chelate ring opening mechanism is operable in the [Co(acac)₂(X)(py)] system, these results are reasonable. In each case, the rate-determining step is the breaking of a cobalt-β-di-

**Figure 4.** Possible mechanisms for the reactions of [Co(acac)₂(X)(py)] in CDCl₃.

ketone chelate bond, and therefore the activation energies should be similar.

The variation in the activation energies of the [Co(acac)₂(X)(py)] species can be attributed to the effect of X⁻ on the stability of the trigonal bipyramid. If such an intermediate were formed in the [Co(acac)₂(X)(py)] system, it would be stabilized by a good π donor in the trigonal plane. Studies of the acid hydrolysis of *trans*-[Co(en)₂(X)(Cl)]⁺ have shown that this will proceed *via* a trigonal bipyramid if X⁻ is a good π donor.¹⁶ π bonding between a filled p_x orbital of the ligand and the empty d_{x²-y²} orbital of the metal results in a net lowering of the energy of the trigonal bipyramid. Conversely, a good π acceptor in the trigonal plane will destabilize such an intermediate, raising the activation energy. The observed rate order for the [Co(acac)₂(X)(py)] series is consistent with such an effect. Experiments with the *trans*-[Co(acac)₂(CN)(py)] complex in chloroform show no isomerization at 60° after 30 hr.² Thus the rate order for the *trans* → *cis* isomerization of [Co(acac)₂(X)(py)] is N₃⁻ > NCO⁻ > NO₂⁻ > CN⁻. Both NO₂⁻ and CN⁻ are good π acceptors while N₃⁻ can act as a π donor,¹⁷ and thus the observed rate order may be explained by the ability of X⁻ to stabilize the intermediate. The activation energy for the racemization of [Co(acac)₃] is 34.8 ± 0.6 kcal/mol.¹¹ The similarity of this E_a to that found for the isomerization of *trans*-[Co(acac)₂(NCO)(py)] (33.8 ± 2.9 kcal/mol) indicates that acetylacetonate has about the same ability to stabilize this intermediate as py-NCO⁻. The entropies of activation for the [Co(β-dik)₃] system are 2-14 eu, whereas the values of ΔS[‡] for [Co(acac)₂(X)(py)] are 13-43 eu. This large difference in the activation entropies may be attributed to the differences in the intermediates or transition states of the two processes, *i.e.*, the extent to which the trigonal bipyramid is formed.¹⁸ It is also likely that the fact that different solvents were used in the two studies (chloroben-

(8) N. Serpone and D. G. Bickley, *Progr. Inorg. Chem.*, **17**, 391 (1972).

(9) L. J. Boucher and N. G. Paez, *Inorg. Chem.*, **10**, 1680 (1971).

(10) J. G. Gordon, II, and R. H. Holm, *J. Amer. Chem. Soc.*, **92**, 5319 (1970).

(11) R. C. Fay, A. Y. Girgis, and U. Klabunde, *J. Amer. Chem. Soc.*, **92**, 7056 (1970).

(12) A. Y. Girgis and R. C. Fay, *J. Amer. Chem. Soc.*, **92**, 7061 (1970).

(13) R. C. Fay and T. S. Piper, *J. Amer. Chem. Soc.*, **85**, 500 (1963).

(14) R. C. Fay and T. S. Piper, *Inorg. Chem.*, **3**, 348 (1964).

(15) U. Klabunde and R. C. Fay, Abstracts, 156th National Meeting of the American Chemical Society, Atlantic City, N. J., Sept 1968, No. INOR 37.

(16) R. G. Pearson and F. Basolo, *J. Amer. Chem. Soc.*, **78**, 4878 (1956).

(17) D. F. Gutterman and H. B. Gray, *J. Amer. Chem. Soc.*, **93**, 3364 (1971).

(18) M. L. Tobe, *Inorg. Chem.*, **7**, 1260 (1968).

zene vs. CDCl_3) makes some contribution to the entropy differences.

A change in the nature of X^- results in rather marked changes in both the enthalpies and entropies of activation for $[\text{Co}(\text{acac})_2(\text{X})(\text{py})]$ isomerization. In fact, a linear relationship is observed between ΔH^* and ΔS^* . Such an isokinetic relationship is indicative of a common mechanism for the three processes.^{19,20} The slope of the isokinetic plot is 406 K (133°C). This is the isokinetic temperature, *i.e.* the temperature at which the rates of all three processes become equal. Verification of the validity of this relationship comes from the Arrhenius plots (Figure 3), which do in fact intersect at this isokinetic temperature. Such verification is necessary, since systematic errors in ΔH^* measurements can result in an apparent linear relationship between ΔH^* and ΔS^* .²¹ The trend in activation energies can be attributed to the effect of X^- on the stability of the trigonal bipyramid. Similar reasoning may be invoked to rationalize the trends in the activation entropies. With a π acceptor such as nitrite destabilizing the intermediate, it may be that the intermediate is not a true trigonal bipyramid but distorted to something between this and a square-pyramidal intermediate. That the same effect is acting upon both the ΔH^* and ΔS^* would account for the linear relationship which is observed.

It is interesting to note the change in ΔH^* with non-leaving groups for the aquation of $\text{trans-}[\text{Co}(\text{en})_2(\text{X})(\text{Cl})]^+$. The spread between the extreme values, $\text{X}^- = \text{NO}_2^-$ to $\text{X}^- = \text{OH}^-$, is $\sim 5 \text{ kcal/mol}$.¹⁸ This is in marked contrast to the spread of $\sim 14 \text{ kcal/mol}$ for $\text{trans-}[\text{Co}(\text{acac})_2(\text{X})(\text{py})]$ when going from $\text{X}^- = \text{CN}^-$ to $\text{X}^- = \text{N}_3^-$. The increased sensitivity of the activation parameters to the nonleaving anion in the acetylacetonate complexes may be related to weaker σ bonding of the chelate ring. In other words the cobalt atom's ability to respond to change in other ligands is damp-

ened by strong donor chelates like ethylenediamine.

If there were no thermodynamic difference between the trans and cis isomers of $[\text{Co}(\text{acac})_2(\text{X})(\text{py})]$, the distribution of the two at equilibrium would be purely statistical and K_{eq} would be 4. This corresponds to a ΔG° of -0.83 kcal/mol , at 29° , which is equal within experimental limits to that observed for $[\text{Co}(\text{acac})_2(\text{NCO})(\text{py})]$. In the case of the other two complexes, ΔG° is more positive than the statistical value by a small amount, 0.2–1.0 kcal/mol. In order to discuss the apparent differences in stability of the isomeric forms of the complexes, it is useful to consider the other thermodynamic parameters. The ΔH° values, -3 kcal/mol , are equal for N_3^- and NO_2^- , while the value for NCO^- is more positive by some 8 kcal/mol. The negative ΔH° for $[\text{Co}(\text{acac})_2(\text{NO}_2)(\text{py})]$ and $[\text{Co}(\text{acac})_2(\text{N}_3)(\text{py})]$ indicates that the bonding is stronger and the complex more stable for the cis isomer. This would be the case if the complex preferred to have the two strongest σ donors, X^- and py , cis to one another. Trans effect arguments reason that a good σ -donor group would prefer a weaker donor (*i.e.*, an acetylacetonate oxygen) trans to it.²² The positive ΔH° for $[\text{Co}(\text{acac})_2(\text{NCO})(\text{py})]$ may indicate that NCO^- is the weakest of the three X^- ligands in terms of its bonding to the cobalt.

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Registry No. $\text{Co}(\text{acac})_2$, 14024-48-7; py , 110-86-1; $\text{trans-}[\text{Co}(\text{acac})_2(\text{N}_3)(\text{py})]$, 37646-79-0; $\text{trans-}[\text{Co}(\text{acac})_2(\text{CN})(\text{py})]$, 40864-82-2; $\text{trans-}[\text{Co}(\text{acac})_2(\text{NO}_2)(\text{py})]$, 14220-10-1; $\text{trans-}[\text{Co}(\text{acac})_2(\text{NCO})(\text{py})]$, 40864-84-4.

(22) J. M. Pratt and R. G. Thorp, *Advan. Inorg. Chem. Radiochem.*, **12**, 375 (1969).

(19) J. E. Leffler, *J. Org. Chem.*, **20**, 1202 (1955).

(20) G. C. Lalor, *J. Inorg. Nucl. Chem.*, **31**, 1206 (1969).

(21) R. C. Petersen, *J. Org. Chem.*, **29**, 3133 (1964).

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A Voltammetric Study of the Coordinative Reactions of Pyridine with Bis(maleonitriledithiolate)cobalt Complexes

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Stationary electrode voltammetry (voltage scan rates, 0.01 – 500 V sec^{-1}) is used to determine the dynamic characteristics in acetonitrile solution of the coordination of pyridine to bis(maleonitriledithiolate)cobalt complexes, $[\text{Co}(\text{mnt})_2]^z$, in two oxidation states, $z = 1-$, $2-$. Peaks due to the reduction of $[\text{Co}(\text{mnt})_2\text{py}]^-$ and $[\text{Co}(\text{mnt})_2\text{py}_2]^{2-}$ and the oxidation of $[\text{Co}(\text{mnt})_2\text{py}]^{2-}$ are identified; $[\text{Co}(\text{mnt})_2\text{py}_2]^{2-}$ was not detected at room temperature. The rate and equilibrium constants for the formation of the mono- and bispyridine adducts of the oxidized complex are evaluated, and an order of magnitude estimate is obtained for the formation of $[\text{Co}(\text{mnt})_2\text{py}]^{2-}$. A brief exposition of the pertinent voltammetric theory is appended.

Introduction

Electrochemical studies of the electron-transfer reactions characteristic of transition metal dithiolene complexes¹

have been directed mainly toward establishment of the existence of electron-transfer series of complexes, determination of the number of electrons transferred, assessment of the lifetimes of highly reduced or oxidized species, determination of comparative redox potentials, and analysis for com-

(1) J. A. McCleverty, *Progr. Inorg. Chem.*, **10**, 49 (1968).