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Bis(bipyridine)[N,O-2-hydroxyiminopropionato(2-)] cobalt(III) Ion. Racemization Kinetics, Bipyridine Catalysed Racemization and Exchange with Tritium Labelled Bipyridine

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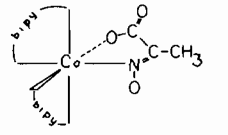
The kinetics of racemization of $(+)_{589}$-$[Co(bipy)_2paox]NO_3$ *(paox is the dianion of 2-ketopropionic acid oxime) have been measured in 0.1* M $NaNO_3$ *with 0.05* M *pH7 phosphate buffer between 70° and 98 °C. For the first order reaction at 98 °C,* $k = (4.2 \pm 0.4) \times 10^{-6}\ s^{-1}$, *with* $\Delta H^{\ddagger} = 22.7 \pm 0.7$ *kcal* mol^{-1} *and* $\Delta S^{\ddagger} = -22.6 \pm 2.0$ *cal* $deg^{-1}\ mol^{-1}$. *The reaction is accelerated in the presence of uncomplexed bipyridine, but the further addition of* Co^{2+} *does not increase the rate. The exchange of coordinated bipyridine with tritium labelled bipyridine, the synthesis of which is described, occurs more rapidly than racemization under the same conditions. This observation excludes any inferences about possible intramolecular racemization mechanisms.*

Introduction

The mechanisms of isomerisation and of racemization of metal complexes are of continuing interest in coordination chemistry [1]. Some time ago the optical resolution and some kinetics of racemization were reported [2] for the complex ion bis(bipyridine)[N,O-2-hydroxyiminopropionato(2-)] cobalt(III), $[Co(bipy)_2paox]^+$, (I);



(I)

(the dianionic oxime ligand can be written in different canonical forms). Because of the nature of the ligands and the possibility of an intramolecular mechanism for racemization, we undertook an investigation of the racemization process. To our surprise, this revealed an exchange reaction between the complexed bipyridine and free bipyridine in solution.

Experimental

Synthesis of $(+)_{589}$-$[Co(bipy)_2paox]NO_3$

cis-$[Co(bipy)_2Cl_2]Cl$ was prepared using the procedure of Jaeger and van Dijk [3]. Starting with 24 g of $CoCl_2 \cdot 6H_2O$ and 31.2 g of bipyridine, fractional crystallization gave 28 g of a green crystalline substance. The remaining viscous product was extracted with boiling absolute ethanol to yield 10 g of the desired violet product in addition to 19 g of the green substance.

The oxime of pyruvic acid, 2-hydroxyiminopropanoic acid, was prepared by adding to a solution of 19 g of $NH_2OH \cdot HCl$ in 35 ml of H_2O 19 ml of pyruvic acid dropwise with stirring. A precipitate formed and after stirring for 5 hrs at room temperature 4.5 g of pale yellow crystals were collected by filtration (m.p. 162 °C, dec.). After recrystallisation from dioxane, 2.5 g of white crystals were obtained, m.p. 170 °C (lit. 182°). *Anal.* Calcd. for $C_3H_5NO_3$: C, 35.0; H, 4.9; N, 13.6. Found: C, 35.4; H, 4.8; N, 13.1.

Racemic $[Co(bipy)_2paox]Cl \cdot 4H_2O$ was prepared [4] by dissolving 7.4 g of *cis*-$[Co(bipy)_2Cl_2]Cl$ in 85 ml of 1:1 ethanol:water and adding a solution of 1.9 g of $paoxH_2$ and 1.6 g of $NaHCO_3$ in 20 ml of H_2O. An additional 0.8 g of $NaHCO_3$ was added to the solution until evolution of CO_2 ceased and the solution was heated at 50 °C for 4 hr. Several gm of yellow-brown crystals were obtained from the solution after standing in a refrigerator overnight. The filtrate was evaporated to dryness and the residue extracted with portions of boiling absolute ethanol. A combined yield of 7.8 g of complex was obtained (m.p. 215 °C). *Anal.* Calcd. for $CoC_{23}H_{27}N_5O_7Cl$: C, 47.5; H, 4.7; N, 12.2; Cl, 6.1. Found: C, 47.8; H, 4.8; N, 11.9; Cl, 6.0. The nitrate salt, $[Co(bipy)_2paox]NO_3 \cdot 2H_2O$, was obtained as golden crystals (m.p. 242 °C, dec.) by metathesis with $AgNO_3$ in aqueous ethanol. *Anal.* Calcd. for $CoC_{23}H_{23}N_6O_8$: C, 48.5; H, 4.0; N, 14.7. Found: C, 48.5; H, 3.8; N, 14.5.

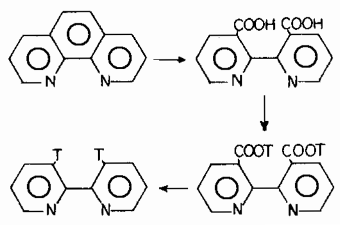
Silver antimonyl tartrate was prepared by the double decomposition of potassium antimonyl tartrate with silver nitrate (yield 95%) [4].

Diastereomeric $[Co(bipy)_2paox]SbOC_4H_4O_6$ was prepared [4] by mixing a solution containing 8.4 g of racemic $[Co(bipy)_2paox]Cl \cdot 4H_2O$ in 84 ml of water with a suspension of 6 g of $AgSbOC_4H_4O_6$ in 280 ml of hot water (50–55 °C), and shaking the resulting mixture for about 4 hr. The precipitate was filtered off and the filtrate was evaporated to dryness at a temperature below 60 °C under reduced pressure. The residue was treated with 33 ml of 1:1 ethanol:water mixture at 60 °C, and the supernatant solution filtered and left at room temperature. The resulting orange crystals were filtered off and to the filtrate 170 ml of ethanol was added, causing the deposition of an additional amount of the crystals. After recrystallization from aqueous ethanol, 4.2 g of orange needlelike crystals were obtained (m.p. 98 °C, dec., $[\alpha]^{33}_{D} = +238°$). *Anal.* Calcd. for $CoC_{27}H_{23}N_5O_{10}Sb$: C, 42.7, H, 2.9; N, 9.2. Found: C, 42.6; H, 2.9; N, 9.0.

The $(+)_{589}$-$[Co(bipy)_2paox]NO_3$ *enantiomer* was obtained by mixing the solutions of 4.8 g of $(+)_{589}$-$[Co(bipy)_2paox]SbOC_4H_4O_6$ in diluted ethanol (60 ml of ethanol and 30 ml of water) and 1.1 g of silver nitrate (in 5 ml of water). The $AgSbOC_4H_4O_6$ was filtered off and the filtrate was evaporated under reduced pressure (at 35 °C) to dryness. The residue was extracted by absolute ethanol at 55–60 °C. A combined yield of 1.9 g of dark orange crystalline enantiomer was obtained (m.p. 243 °C, dec., $[\alpha]^{30}_{D} = +382°$). *Anal.* Calcd. for $CoC_{23}H_{19}N_6O_6$: C, 51.7; H, 3.6; N, 15.7. Found: C, 51.5; H, 3.6; N, 15.5.

Preparation of Tritium Labelled Bipyridine

Labelled bipyridine was prepared by the following route:



Oxidation of 1,10-phenanthroline (Baker Analysed Reagent) to binicotinic acid was accomplished by alkaline potassium permanganate [5]. The binicotinic acid (0.1 g) was exchanged with tritiated water by refluxing for 3 hr. During this time freshly precipitated copper [6] (0.06 g dried) was covered with tritiated water. The copper–water suspension was then added to the binicotinic acid solution and the water removed by distillation at atmospheric pressure. The dry mixture thus obtained was heated for 30 min in a sublimation vessel under nitrogen. The sublimate was dissolved in ether to which was added 1 g of bipyridine (Matheson, Coleman and Bell, m.p. 70–71 °C). The solution was evaporated to dryness from an open beaker.

Procedures for the Exchange Experiment

It was established that the tritiated bipyridine does not exchange with water in a pH 7 phosphate buffer solution during 190 hr of heating at 98 °C in a sealed ampoule.

For the exchange experiment, a 25 ml solution was prepared of 2.07×10^{-3} *M* resolved Co(III) complex and 4.14×10^{-3} *M* tritiated bipyridine in pH 7 phosphate buffer containing 0.1 *M* $NaNO_3$. Aliquots (3.3 ml) of this solution were heated in sealed ampoules at 98 °C and the reactions then quenched by cooling.

The free bipyridine was separated from the coordinated bipyridine by extraction with 5 ml of benzene. The aqueous solution was then treated with a solution of Na_2S. After removing the cobalt sulfide precipitate by centrifugation, the liberated bipyridine was extracted with benzene.

Results

Racemization Kinetics

The rate of racemization of a 2×10^{-3} *M* solution of $(+)_{589}$-$[Co(bipy)_2paox]NO_3$ was measured by polarimetry in 0.05 *M* pH 7.0 phosphate buffer containing 0.10 *M* $NaNO_3$ at temperatures between 70 and 98 °C. Most of the experiments were performed at 98 °C, where the half-life is 45 hr. The decrease in optical activity is linear for at least the two half-lives observed. At 70° the half-live is about 600 hr and the decay in optical activity was linear over this period. Preliminary experiments indicated that the rate is strongly pH dependent, being about ten times more rapid at pH 6 than at pH 7. A number of experiments attempted in water without any buffer gave optical activity changes which deviated from a first order decrease after about one half-life. Consequently, the results reported below were obtained in a buffered solution at pH 7.0. At pH 9.0 some decomposition occurred on heating for longer than a day, as indicated by a change in the visible

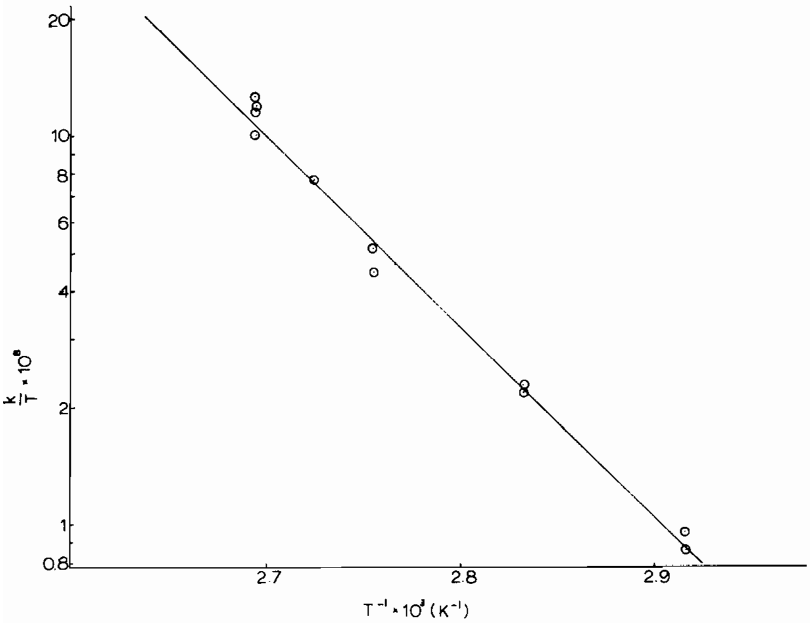


Fig. 1. Eyring plot of observed racemization rate constants.

TABLE I. Observed First-Order Racemization Rate Constants.

T (°C)		k (×10^{-6} s^{-1})
98		3.7
		4.3
		4.7
		3.7
		4.4
	Av.	4.2
94		2.6
		2.8
		2.6
	Av.	2.7
90		1.8
		1.9
		1.6
	Av.	1.8
80		0.76
		0.80
	Av.	0.78
70		0.29
		0.32
	Av.	0.30

absorption spectrum. Similarly, a change in the spectrum resulted if the complex were heated with a tenfold excess (2 × 10^{-2} *M*) of the oxime ligand. However, no change in the visible absorption spectrum occurred when the complex was heated with a two-fold excess (4 × 10^{-3} *M*) of bipyridine. Furthermore, the complex was reisolated and displayed an IR spectrum identical with that of the untreated complex, except for additional bands due to the excess bipy.

The rate constants for the racemization process are given in Table I. The activation enthalpy and entropy parameters derived from these rate constants using a linear least squares fit to the Eyring equation are 22.7 ± 0.7 kcal mol^{-1} and −22.6 ± 2.0 cal deg^{-1} mol^{-1}, as illustrated in Fig. 1.

In order to test whether the racemization reaction were intramolecular, its rate was measured in the presence of tritium labelled bipyridine. The addition of free, unlabelled bipyridine greatly accelerates the racemization rate, as illustrated in Fig. 2. Furthermore, *incorporation* of the labelled bipyridine proceeds even more rapidly than does the racemization. By using tritium labelled free bipyridine and measuring both the incorporation of tritium in the complex and the loss of label in the uncomplexed bipyridine, the exchange of the bipyridine ligands with free bipyridine was observed. In the first of two experiments the unexpected acceleration of racemization by free bipyridine led to incomplete data. The limiting extent of incorporation in both experiments, however, indicated that a single bipyridine on the cobalt complex

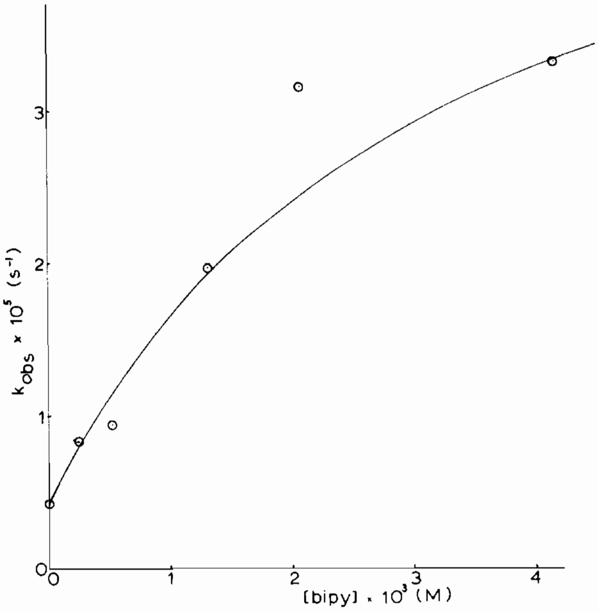


Fig. 2. Dependence of observed rate of racemization on the concentration of added bipyridine.

undergoes exchange during the period of observation. The rate law for the incorporation of labelled bipyridine was not established and consequently rate constants cannot be calculated from the McKay equation [7]. The rates of racemization and incorporation were measured under one set of identical conditions, however, namely 2×10^{-3} *M* $[Co(bipy)_2paox]^+$ and 4×10^{-3} *M* bipy. In these experiments the half-life for ligand exchange was about 1.2 hr, while the half-life for racemization was 5.8 hr.

The racemization is not accelerated by the addition of 2×10^{-5} *M* $CoCl_2 \cdot 6H_2O$ in the presence of 4×10^{-3} *M* bipyridine.

Discussion

The racemization of $(+)_{589}$-$[Co(bipy)_2paox]^+$ is first order in buffered solution at pH 7, in contrast to non-first-order kinetics observed previously [2], apparently in non-buffered solutions. This could indicate that the complex decomposes in non-buffered solution [8] in accord with our observations of decomposition in pH 9 solution. It may only reflect, however, the strong pH dependence of the racemization, which suggests that the process may be acid catalysed. In our preliminary experiments in unbuffered solutions the racemization rate decreased with time, whereas in the previous Japanese work [2] it increased with time.

A significant observation is that the reaction is catalysed by free bipyridine. A superficial inspection of Fig. 2 raises the question whether an uncatalysed racemization reaction occurs at all. Consideration of the concentration of bipyridine required for catalysis indicates that an uncatalysed reaction does occur. Catalysis requires approximately a stoichiometric concentration of free bipyridine. The characterization and analysis of $(+)_{589}$-$[Co(bipy)_2paox]$-NO_3 does not suggest the possibility of contamination with bipyridine at the 5–10% mol ratio level required to account for the uncatalysed rate.

The catalysed racemization appears not to proceed by an optically labile cobalt(II) electron transfer mechanism. For addition of 1 mol per cent of cobalt(II) in the presence of excess bipyridine did not accelerate the racemization.

This observation, together with the indication from the limited data that the acceleration due to excess bipyridine may saturate at a ratio of 1 bipyridine:1 complex, suggests that the bipyridine plays a stoichiometric role in the process, perhaps by forming an outer-sphere complex or even by participating in a substitution reaction.

This hypothesis is consistent with the further unexpected observation that free bipyridine exchanges with coordinated bipyridine significantly more rapidly than the catalysed racemization reaction. This observation suggests that it will be difficult to reach conclusions about the intramolecular or intermolecular mechanism of the racemization reaction. It does indicate, however, that coordinated bipyridine ligands cannot be ignored but must be considered as participants in possible mechanisms, even for substitution inert cobalt(III) complexes.

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References

1 N. Serpone and D. G. Bickley, *Prog. Inorg. Chem., 17,* 391 (1972).
2 M. Murakami, S. Senoh, N. Matsusato, H. Itatani and J. W. Kang, *Nippon Kagaku Zasshi, 83,* 819 (1962).
3 F. M. Jaeger and J. A. van Dijk, *Z. anorg. Chemie, 227,* 273 (1936).
4 M. Murakami, S. Senoh, N. Matsusato, H. Itatani and J. W. Kang, *Nippon Kagaku Zasshi, 83,* 737 (1962).
5 G. E. Inglett and G. F. Smith, *J. Am. Chem. Soc., 72,* 842 (1950).
6 Organic Syntheses, Collective Volume 2,ed. A. H. Blatt, Wiley, N.Y., 1943, p. 446.
7 A. A. Frost and R. G. Pearson, 'Kinetics and Mechanisms', 2nd ed., Wiley, N.Y., 1961, p. 192.
8 R. J. Mureinik and M. Spiro, *J. Chem. Soc. Dalton Trans.,* 2493 (1974).
9 M. Yamamoto and Y. Yamamoto, *Inorg. Nucl. Chem. Letters, 11,* 691 (1975).