from a solution of tin(II) chloride containing hydrochloric acid.[26,27]

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[26] N. W. G. Debye and J. J. Zuckerman, unpublished results.

[27] Such extracts give Raman spectra which have been attributed to the pyramidal trichlorostannate(II) ion: L. S. Woodward and M. J. Taylor, *J. Chem. Soc.*, 407 (1962).

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Evidence for a Trigonal-Prismatic Activated Complex in the Solid-State Racemization of Tris(1,10-phenanthroline)nickel(II) Perchlorate Dihydrate

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In 1964 Schmulbach, *et al.*,[1] investigated the effect of pressure on the solid-state racemization of $[Fe(phen)_3](ClO_4)_2$ and $[Ni(phen)_3](ClO_4)_2$. A negative volume of activation was observed which was interpreted as being consistent with a Bailar twist[2] type of mechanism. The effect of water on the racemization process was not investigated, however, and activated complexes containing water could not be ruled out. Recently, evidence has been presented in support of a Bailar twist mechanism for the solid-state racemization of $K_3[Co(C_2O_4)_3]\cdot xH_2O$ at very high pressures.[3] An unusually small activation energy and frequency factor were found for this process. This communication reports the results of a further investigation of the activation parameters for the high-pressure solid-state racemization of tris(1,10-phenanthroline)nickel(II) perchlorate. It was hoped that a comparison of the results of such an investigation with the results previously reported for the $K_3[Co(C_2O_4)_3]$ system would shed some light on the general nature of the Bailar twist mechanism.

Experimental Section

Apparatus.—The high-pressure apparatus used here was similar to that described previously.[4] Pressures were maintained constant to within 1 or 2% using an air-driven hydraulic pump purchased from the High Pressure Equipment Co., Erie, Pa., and were measured with a Heise gauge accurate to *ca.* 0.5%. Samples were prepared as described in ref 3 and subjected to pressures ranging from 10,000 to 40,000 atm. Except for the determination of the volume of activation, temperatures were controlled to within ±0.5° with a thermistor–Wheatstone bridge assembly and were monitored with a Sargent SR recorder. Samples used for the determination of ΔV^* were run at room temperature which was 21 ± 2°. After their removal from the high-pressure apparatus, all of the samples were analyzed polarimetrically in 50 vol % acetone–water at 589 mμ on a Rudolph Model 80 polarimeter with Model 200 photoelectric attachments.

***d*-$[Ni(phen)_3](ClO_4)_2\cdot 2H_2O$.**—This complex was prepared and resolved according to the procedure of Kauffman and Takahashi[5] and kept in a desiccator over silica gel.

For the investigation of the effect of water on the racemization rate a portion of optically active material was divided into two parts. One part was stored over P_2O_5 while the other was placed in a desiccator over a saturated solution of KNO_2 (45% relative humidity). Analyses for Ni were done polarographically after wet-washing of the complex with H_2SO_4–HNO_3 and the water content of the samples was obtained as the difference between the actual sample weight and the weight of "anhydrous" $[Ni(phen)_3](ClO_4)_2$ calculated from the Ni analyses.

Results

The volume of activation, ΔV^*, is given by the equation[4]

$$\left[\frac{\partial \ln \ln ([\alpha_0]/[\alpha_t])^{1/2}}{\partial p}\right]_{t,T} = -\frac{\Delta V^*}{RT}$$

where $[\alpha_t]$ is the specific rotation of the sample subjected to a pressure p for a time period t and $[\alpha_0]$ is the specific rotation of a control sample which had not been subjected to pressure. No changes were observed in the specific rotation of the control samples over a period of several months. A plot of $\ln \ln ([\alpha_0]/[\alpha_t])^{1/2}$ *vs.* p should yield a straight line of slope $-\Delta V^*/RT$. The linear least-squares slope obtained from the data in Table I gives a value of -1.00 ± 0.13 cm^3 mol^{-1} for ΔV^*, in good agreement with the values -1.10 ± 0.14 and -1.08 ± 0.22 cm^3 mol^{-1} obtained by Schmulbach, *et al.*[1]

The activation energy for this reaction may be obtained from the equation[3]

$$\left[\frac{\partial \ln \ln ([\alpha_0]/[\alpha_t])^{1/2}}{\partial (1/T)}\right]_{p,t} = \frac{-E_a}{R}$$

A plot of $\ln \ln ([\alpha_0]/[\alpha_t])^{1/2}$ *vs.* $1/T$ should give a straight line of slope $-E_a/R$. A linear least-squares treatment of the data in Table II yields an activation energy of 2.40 ± 0.31 kcal mol^{-1}. The frequency factor, calculated from the least-squares intercept, has a value of *ca.* 3×10^{-5} sec^{-1}.

In an attempt to exclude, as possible mechanistic paths, transition states which contain water in the coordination sphere, the effect of water on the reaction rate was examined. Samples containing different amounts of water were subjected to the same conditions of pressure, temperature, and time under pressure. The results of these experiments are presented in Table III. It will be noted that in each case the sample con-

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[1] C. D. Schmulbach, F. Dachille, and M. E. Bunch, *Inorg. Chem.*, **3**, 808 (1964).

[2] J. C. Bailar, Jr., *J. Inorg. Nucl. Chem.*, **8**, 165 (1958). The term Bailar twist is used here to describe the paths leading to either trigonal-prismatic activated complex, B or C in Figure 1.

[3] C. D. Schmulbach, J. Brady, and F. Dachille, *Inorg. Chem.*, **7**, 287 (1968).

[4] J. Brady, F. Dachille, and C. D. Schmulbach, *ibid.*, **2**, 803 (1963).

[5] G. B. Kauffman and L. T. Takahashi, *J. Chem. Educ.*, **39**, 481 (1962).

Table I

Values Used for the Determination of $\Delta V^{\ddagger}$ for $[Ni(phen)_3](ClO_4)_2 \cdot 2H_2O$

$[\alpha_t]$,[a] deg	Ln ln $([\alpha_0]/[\alpha_t])^{1/2}$ [b]	Pressure × 10^{-3}, atm
1309	−3.96	10.2
1287	−3.59	13.6
1281	−3.51	17.0
1306	−3.89	17.0
1261	−3.28	19.7
1265	−3.32	24.8
1252	−3.19	27.6
1228	−2.97	27.9
1188	−2.69	37.8
1184	−2.67	41.5

[a] Time under pressure, 20.0 hr; temperature 21 ± 2°. [b] $[\alpha_0]$ = 1360°, average of 10 measurements.

Table II

Values for the Determination of E_a for $[Ni(phen)_3](ClO_4)_2 \cdot 2H_2O$

$[\alpha_t]$,[a] deg	Ln ln $([\alpha_0]/[\alpha_t])^{1/2}$ [b]	Temp, °C
1320	−3.26	26.8
1335	−3.42	31.5
1315	−3.21	36
1300	−3.08	46.7
1282	−2.93	55.3
1291	−3.01	50.6
1285	−2.96	57.5
1267	−2.83	65.4
1257	−2.77	82.5

[a] Pressure, 3.09 × 10^4 atm; time under pressure, 20.0 hr. [b] $[\alpha_0]$ = 1425°, average of nine measurements.

Table III

The Effect of Water on the Rate of Racemization

"Wet" sample, 8.84% H_2O		"Dry" Sample, 4.06% H_2O	
$[\alpha_t]$,[a] deg	Change in $[\alpha]$,[b] deg	$[\alpha_t]$,[a] deg	Change in $[\alpha]$,[b] deg
893	−50	854	−94
898	−45	847	−101
...	...	874	−74

[a] This represents the specific rotation calculated on the basis of "anhydrous" complex present in the sample. All runs were performed at a pressure of 3.06 × 10^4 atm for 20 hr. [b] Based on $[\alpha_0]$ = 943° (corrected for H_2O content).

taining the largest amount of water underwent the smallest change in optical rotation.

Discussion

Schmulbach, *et al.*,[1] eliminated as possibilities for the transition state in the solid-state racemization of $[Ni(phen)_3](ClO_4)_2$ those structures which involve bond breaking since at very high pressures bond stretching, which must precede bond breaking, would be suppressed. The remaining three possible structures which must be considered are shown in Figure 1. The results which are reported in Table III indicate that structure A, or for that matter any structure containing water in the coordination sphere, may also be eliminated. The fact that water retards the rate of racemization implies that the water concentration appears to some negative power in the rate law rather than to a positive power as would be expected for a structure containing water. While this evidence strongly supports the elimination of A, it has been pointed out[3] that the possibility exists that there may be some unknown lattice effect, dependent on lattice water, which would tend to retard the rate to the extent that a rate acceleration by water would be masked. Indeed, the existence of some such water-dependent rate retarding lattice effect is supported by our results since there does not seem to be any plausible reason to expect water to inhibit the racemization of this complex ion. These observations make the elimination of structure A on the *sole* basis of the effect of water on the rate somewhat uncertain.

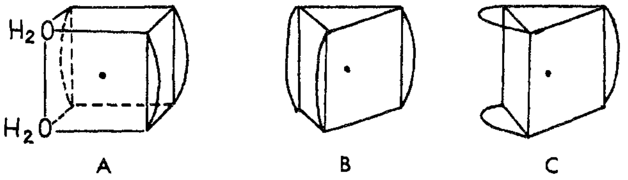

Figure 1.—Transition states for the solid-state racemization of $[Ni(phen)_3](ClO_4)_2 \cdot 2H_2O$.

The strongest support for the Bailar twist mechanism, and hence the elimination of structure A, is found in the activation energy and frequency factor for this reaction. The unusually small values for these quantities have been shown to be completely consistent with a twist mechanism involving the production of structure B or C in Figure 1.[3] The values for the activation energy and frequency factor observed for the racemization of $K_3[Co(C_2O_4)_3] \cdot xH_2O$ were 1.9 ± 0.7 kcal mol^{-1} and 1.5 × 10^{-5} sec^{-1}, respectively. The preponderance of evidence for this oxalato complex points to a Bailar twist mechanism. The identical (to within experimental error) values of the energy of activation and frequency factor obtained for the $[Ni(phen)_3](ClO_4)_2$ complex suggest that structures B and C are also involved in the racemization of the nickel salt.

By far the most interesting and significant result of the present work is the implication which it contains concerning the nature of the Bailar twist mechanism. In the two solid-state racemization reactions which have been studied in detail, for $K_3[Co(C_2O_4)_3] \cdot xH_2O$ and $[Ni(phen)_3](ClO_4)_2 \cdot 2H_2O$, the activation energies and frequency factors are virtually identical. We have here a comparison between two systems which are quite different in many ways: in one the complex is an anion while the other contains a complex cation; one possesses a metal with a d^6 electronic configuration while the other has a metal with a d^8 configuration. In general, the characteristics of the ligands are also very dissimilar, yet, despite the rather large number of differences between these two systems, the activation energies and frequency factors are remarkably alike. If the small activation energy, which may be characteristic of the high-pressure solid-state mechanism, is characteristic of the Bailar twist mechanism in general, then it is not at all surprising that a number of stable trigonal-prismatic coordination complexes have been found to exist.[6-9] It

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(6) R. Eisenberg and J. A. Ibers, *J. Am. Chem. Soc.*, **87**, 3776 (1965).

(7) R. Eisenberg and J. A. Ibers, *Inorg. Chem.*, **5**, 411 (1966).

(8) A. E. Smith, G. N. Schrauzer, V. P. Mayweg, and W. Heinrich, *J. Am. Chem. Soc.*, **87**, 5798 (1965).

(9) R. Eisenberg, E. I. Stiefel, R. C. Rosenberg, and H. B. Gray, *ibid.*, **88**, 2874 (1966).

could well be that the energy difference between the octahedron and the trigonal prism is small in a very large number of cases and that the reason the Bailar twist mechanism is not generally observed is due, not to its unfavorable activation energy, as suggested by some authors,[10,11] but rather to its unusually low frequency factor.

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[10] R. E. Hamm, R. Kollrack, G. L. Welch, and R. H. Perkins, *J. Am. Chem. Soc.*, **83**, 340 (1961).

[11] E. L. Muetterties, *ibid.*, **90**, 5097 (1968).

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Metal Complexes of Octamethylmethylenediphosphonic Diamide

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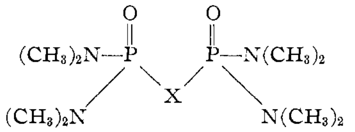
Octamethylpyrophosphoramide (OMPA) has been found to form complexes with a large number of metal ions.[1–5] X-Ray and infrared studies have shown OMPA to be a bidentate ligand with the phosphoryl oxygens as the donor sites.[6] This results in the formation of six-membered chelate rings which are essentially planar in the tris-OMPA complexes of cobalt(II),[7] magnesium(II),[7] and copper(II).[6] Since the bridging oxygen has two lone pairs of electrons available for delocalization into the chelate ring by dπ–pπ bonding with the phosphorus atoms, it was decided to see what effect replacing the bridging oxygen by groups with one or no lone pairs of electrons would have on the coordinating ability of the ligand.

The oxygen bridge was first replaced by a methyl-substituted nitrogen which had only one lone pair of electrons available for delocalization into the chelate ring.[8] This ligand is nonamethylimidodiphosphoramide (NIPA). Essentially no difference was noted in its coordinating properties compared to those of OMPA.

The subject of this paper is the preparation of metal complexes from octamethylmethylenediphosphonic diamide (PCP). In PCP the oxygen bridge of OMPA is replaced by a methylene group. The methylene group has no lone pairs of electrons or orbitals of suitable energy to participate in dπ–pπ bonding within the chelate ring. The methylene bridge would be expected to be somewhat more rigid than the oxygen or nitrogen bridges of OMPA and NIPA. Complexes of selected metal ions with PCP have been prepared and will be discussed in this paper. The structure of the ligand is



OMPA, X = O
NIPA, X = NCH_3
PCP, X = CH_2

Experimental Section

Preparation of the Ligand.—The preparation of PCP has not been reported. The compound was prepared by first making tetraisopropylmethylene diphosphonate by a Michaelis–Arbuzov reaction from triisopropyl phosphite and methylene bromide.[9]

$$2(RO)_3P + CH_2Br_2 \longrightarrow [(RO)_2P(O)]_2CH_2 + 2RBr$$

The ester was then converted to the acid by refluxing for several hours with concentrated hydrochloric acid.[9] An equimolar mixture of methylenediphosphonic acid and tetraisopropylmethylene diphosphonate was then treated with PCl_5 to form the acid chloride–methylenediphosphonic dichloride[10]

$$[(RO)_2P(O)]_2CH_2 + 4HCl \longrightarrow [(HO)_2P(O)]_2CH_2 + 4RCl$$

$$[(RO)_2P(O)]_2CH_2 + [(HO)_2P(O)]_2CH_2 + PCl_5 \longrightarrow 2[Cl_2P(O)]_2CH_2 + 4HCl + 4RCl + 8POCl_3$$

A solution of 75 g (0.3 mol) of methylenediphosphonic dichloride in 1.5 l. of dry benzene was placed in a 2-l. flask fitted with a condenser, a stirrer, and a gas-bubbling tube. The gas-inlet tube should have an opening of approximately 1 cm so that it will not become stopped up with the amine hydrochloride formed during the reaction. The reaction flask was cooled in an ice bath and dimethylamine was bubbled in for about 8–10 hr. At the end of this time, the hydrochloride salt was removed by filtering and the benzene was removed on a rotoevaporator connected to a water aspirator. The oily residue was then shaken with ether to give a milky white dispersion and brown solid. The ether was removed on a rotoevaporator and the oily liquid was vacuum distilled. The main fraction was collected at 147° at 0.25 mm ($n_{25\mathrm{D}}$ 1.4888). After standing for 1 hr, the liquid solidified. The solid was very hygroscopic and melted over the range 47–60°.

$$[Cl_2P(O)]_2CH_2 + 8(CH_3)_2NH \longrightarrow \{[(CH_3)_2N]_2P(O)\}_2CH_2 + 4(CH_3)_2NH_2Cl$$

The nmr of a chloroform solution of PCP has a methyl hydrogen doublet at 2.66 ppm. This agrees with the value of 2.58 ppm reported for $[(CH_3)_2N]_3PO$.[11] A triplet is expected for the methylene protons in the 2.40-ppm region.[12] This region is partially obscured by the methyl protons but it appears that the middle peak of the triplet occurs at 2.38 ppm.

The mass spectrum of PCP shows a parent peak at 284 mass units which agrees well with the calculated value of 284.3.

The triisopropyl phosphite and the dibromomethane were obtained from Aldrich Chemical Co. and used without further purification.

Preparation of Complexes.—The complexes of PCP were prepared by allowing an acetone solution of the hydrated metal perchlorate and excess PCP to evaporate slowly in a desiccator until crystals formed. The crystals were removed from the solution, washed once with ether, and dried *in vacuo*. Analytical data for the complexes are presented in Table I.

Conductance Measurements.—A conductance bridge (Industrial Instruments, Inc.) was used to measure the conductivities

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[1] M. D. Joesten and K. M. Nykerk, *Inorg. Chem.*, **3**, 548 (1964).

[2] C. J. Popp and M. D. Joesten, *ibid.*, **4**, 1418 (1965).

[3] M. D. Joesten and J. F. Forbes, *J. Am. Chem. Soc.*, **88**, 5465 (1966).

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[10] J. J. Richard, K. E. Burke, J. W. O'Laughlin, and C. V. Banks, *J. Am. Chem. Soc.*, **83**, 1722 (1961).

[11] A. H. Cowley and R. P. Pinnell, *ibid.*, **87**, 4454 (1965).

[12] T. H. Siddall and C. A. Prohaska, *Inorg. Chem.*, **4**, 783 (1965).