A series of broad peaks increasing in frequency from 215 cm^{-1} for the Mn(II) complex to 246 cm^{-1} for Ni(II) can be seen in Figure 3. These may be M–O–S angle deformations; if so, the weak band at 291 cm^{-1} in the Cr(III) spectrum is the same vibration and its low intensity is puzzling. An alternative explanation is that the 215–246-cm^{-1} bands in the M(II) complexes represent lattice vibrations, all at approximately the same frequency (since the M(II) complexes are expected to be isostructural) but increasing slightly as the shorter M–O bonds allow tighter packing in the lattice. The Cr(III) complex cannot be isostructural with the M(II) complexes and the corresponding lattice vibration may well be below 200 cm^{-1}. If this is true, the angle deformations may be the very weak, diffuse features seen around 280 cm^{-1} for all of the M(II) complexes in Figure 3.

The results of this study may be compared with an infrared study of the quasi-octahedral pyridine N-oxide–metal perchlorate complexes by Kakiuti, Kida, and Quagliano.[12] The positions (in cm^{-1}) of the peaks assigned to M–O stretching vibrations by these authors[12] for complexes analogous to those we have studied are as follows: Fe(II), 320 s, ~304 w, sh; Mn(II), 311 s; Zn(II), 319 s; Co(II), 331 s; Ni(II), 342 s; Cr(III), 431 vs, 402 w. Not only is there excellent agreement in the order of the metals with respect to the strength of the M–O bond (judged by the frequency of ν_{MO}), but other spectral features such as the appearance of shoulders or splitting for Fe(II) and Cr(III) are reproduced. This is strong evidence for the validity of the assignments. The relative M–O bond strength in six-coordinate DMSO complexes is: Ni(II) > Co(II) > Zn(II) > Fe(II) > Mn(II). The order in the six-coordinate pyridine N-oxide series is: Cu(II) > Ni(II) > Co(II) > Zn(II) > Fe(II) ~ Mn(II). In both series the order is in agreement with the usual stability order toward oxygen donors. We also note that the ratio ν_{MO}(DMSO)/ν_{MO}(pyridine N-oxide) is 1.30–1.35 for corresponding M(II) complexes and is 1.23 for the Cr(III) complexes. If the M–O stretching force constant were the same for both types of complexes, the maximum value possible for this ratio would be 1.12. We can thus make the qualitative statement that pyridine N-oxide is a weaker ligand than DMSO for the metals included in this study (a quantitative statement would require knowledge of the quasi-F_{1u} bending frequencies). This conclusion is in conflict with the results of ligand field studies.[13] In nickel(II) and cobalt(II) complexes of the form $[ML_6](ClO_4)_n$ pyridine N-oxide has the larger Δ_0 value, but DMSO has the larger value in chromium(III) complexes. The conflict between the infrared and ligand field results merits further study.

Acknowledgment.—C. V. B. wishes to thank the Army Materials and Mechanics Research Center, Watertown, Mass., for hospitality during the summer of 1967, when much of the analysis presented here was carried out. We are grateful to Dr. Homer F. Priest for his encouragement.

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CONTRIBUTION FROM THE PENNSYLVANIA STATE UNIVERSITY,
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Evidence for a Trigonal-Prismatic Activated Complex in the Solid-State Racemization of Potassium Trioxalatocobaltate(III)[1]

BY C. D. SCHMULBACH, J. BRADY,[2] AND F. DACHILLE

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The volume of activation, ΔV^*, and the energy of activation were determined for the racemization of crystalline potassium trioxalatocobaltate(III) and found to be -1.66 ± 0.33 cm^3 $mole^{-1}$ and 1.9 ± 0.7 kcal $mole^{-1}$, respectively. The solid-state racemization was established to be first order with respect to the complex, and the specific rate constant for racemization at 34.0×10^3 atm and room temperature was determined to be 6.4×10^{-7} sec^{-1}. Water of hydration was found to decrease the rate of racemization. A trigonal-prismatic structure for the activated complex is favored.

Introduction

In a previous communication it was reported that the rate of the solid-state racemization of several inorganic salts is increased by pressure.[3] A negative volume of activation for racemization was determined for potassium trioxalatocobaltate(III), and trigonal-prismatic structures, E and F in Figure 1, were considered the most likely for the activated complex in this racemization process. Structure C, or for that matter any structure containing water in the coordination sphere, could not be ruled out as possible structures for the activated complex. We report here the results of an extended investigation of the $K_3[Co(C_2O_4)_3]$ system which was undertaken in an attempt to provide further evidence for the existence of the trigonal-prismatic ac-

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[3] J. Brady, F. Dachille, and C. D. Schmulbach, *Inorg. Chem.*, **2**, 803 (1963).

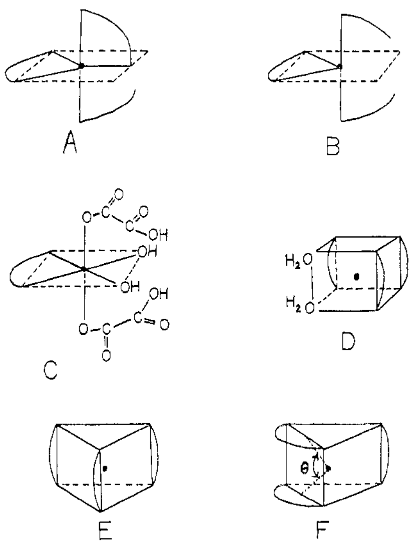

Figure 1.—Possible structures for the activated complex for intramolecular rearrangement of octahedral coordination compounds.

tivated complex. The results of this work take on additional significance in light of recent successes in the search for stable complexes with trigonal-prismatic coordination.[4]

Experimental Section

Potassium Trioxalatocobaltate(III).—The preparation and resolution of this compound has been described previously.[3] The degree of hydration of the crystalline, optically active material was found to vary over a wide range depending upon the conditions used for drying. Freshly prepared samples, precipitated from aqueous solution by addition of ethanol and thoroughly air dried after filtration, were found to contain as many as six waters of hydration while samples dried in a desiccator for several days contained as few as 1.56 waters of hydration. All optically active material used for a given determination of ΔV^* or E_a was from the same lot and contained the same quantity of water of hydration.

High-Pressure Apparatus and Temperature Control.—A modified Bridgman opposed-anvil, high-pressure apparatus was used in this study.[5]

For experiments designed to measure the effect of temperature on the rate of racemization, two different temperature-controlling devices were employed. The first of these is described in detail elsewhere[6] and was used for temperature control between 25 and 36°. It was capable of controlling temperature to within ±0.2°. Above 35° a second device was used which could control temperature to within ±0.5°. This regulator was made up of three chromel–alumel thermocouples in series coupled to a Minneapolis–Honeywell–Brown Pyr-O-Vane temperature controller. The three hot junctions were taped to the sample assembly and the cold junctions maintained at 0° in an ice bath. The controller was connected through a relay to a vertical combustion-tube furnace, which completely surrounded the sample assembly. The voltage across the heater coils was regulated with a powerstat so that the temperature could not increase beyond the point where the current would be shut off by the controller. The temperature of the sample was measured with a separate chromel–alumel thermocouple in conjunction with a Leeds and Northrup Model 1012624 potentiometer.

Procedure.—Samples of crystalline, optically active complex were pelletized at pressures of approximately 60,000 psi. This operation was shown to have no effect on the optical activity of the sample.

Myers, Dachille, and Roy[7] have demonstrated that the diameter to thickness ratio of the sample is the most important factor affecting the pressure which is exerted on the sample in the opposed-anvil pressure apparatus. Limited studies on our system have also shown the importance of this variable.

At diameter–thickness ratios ranging from about 17 to 20 the pressure gradient on the sample was very small and the pressure on the sample was very nearly equal to the applied load pressure. Whereas our initial experiments were carried out on samples encased in nickel rings of $^3/_8$ in. outside diameter and $^1/_4$ in. inside diameter and being 0.010 in. thick (diameter to thickness ratio of 37.5), all data in this paper are for samples contained in nickel rings of the same diameter but 0.020 in. thick (diameter to thickness ratio of 18.8). Sample weights of 0.0340 g gave sample thicknesses within ±0.0005 in. of the desired value of 0.020 in. As a result of this sample geometry the experimentally derived values of ΔV^* and E_a are considered valid.

The pelletized samples were then subjected to high pressures ranging from 8000 to 46,000 atm. After removal of the samples from the pressure apparatus, the optical rotation was measured in the conventional manner using aqueous solutions of the samples. A Rudolph Model No. 80 high-precision polarimeter fitted with a No. 200 photoelectric attachment was used for the purpose. The optical densities of the solutions studied on the polarimeter were measured at 4225 Å with a Cary Model 14 spectrophotometer. From the optical density and the measured extinction coefficient at this wavelength, ϵ 222 (ϵ 220 reported),[8] the concentration of *anhydrous* $K_3[Co(C_2O_4)_3]$ in each solution was calculated. This value was used in the calculation of the specific rotation for that sample. The specific rotation of the pressurized sample was compared to that of a control which had not been subjected to high pressure.

Infrared Spectra.—All infrared spectra were obtained for dispersions of solid samples in Nujol on a Beckman IR8 infrared spectrophotometer.

Results

It was discovered that samples of $K_3[Co(C_2O_4)_3]\cdot xH_2O$ that had been subjected to high pressure underwent partial decomposition. Solutions of pressurized samples for which the initial $K_3[Co(C_2O_4)_3]$ content was known were analyzed spectrophotometrically at 4225 Å. Invariably the optical density was less than that required for the initial concentration of the complex. The extent of the decomposition, which never exceeded more than 6%, was dependent upon the pressure. The decomposition is essentially complete in the first 10–15 min the sample is under pressure. The exact nature of the decomposition is unknown although its existence is firmly established. Presumably, reactions of the following type occur

$$2K_3[Co(C_2O_4)_3] \longrightarrow 3K_2C_2O_4 + 2CoC_2O_4 + 2CO_2$$

The large initial change in optical rotation and the scatter in the data at short time intervals that were observed in the early attempts to determine the rate law (see Figure 1 of ref 3) were due in large measure to partial decomposition of the samples. The values for ΔV^* and E_a reported herein have been corrected for decomposition.

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That the racemization reaction occurs by a first-order (or at least pseudo-first-order) process with respect to the complex anion was shown by a conventional plot of ln $[\alpha_t]$ at 34.0 × 10^3 atm *vs.* time as shown in Figure 2. The equation $\ln([\alpha_0]/[\alpha_t]) = k't = 2kt$ therefore applies, where k' is the rate constant for racemization, k is the rate constant for the disappearance of d or l ions, $[\alpha_0]$ is the specific rotation of the control sample, and $[\alpha_t]$ is the specific rotation of the sample subjected to a pressure p for a time period t.

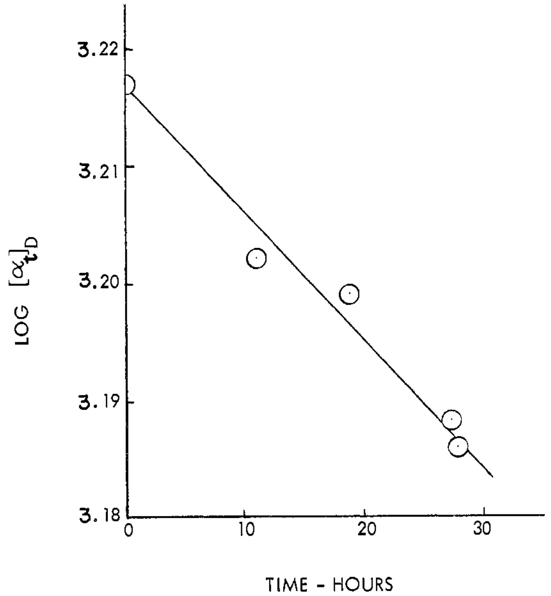

Figure 2.—Racemization of solid l-$K_3[Co(C_2O_4)_3]$ at 34.0 × 10^3 atm and 23–28°.

Since the racemization is indeed first order with respect to $[\alpha]$, the relationship[3]

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

permits the determination of ΔV^* from a plot of ln ln $([\alpha_0]/[\alpha_t])^{1/2}$ *vs.* pressure. A linear least-squares treatment of the data collected in Table I for two different determinations gave values for ΔV^* of −1.54 ± 0.49 and −1.79 ± 0.46 cm^3 $mole^{-1}$ (reported uncertainties are standard deviations). From this least-squares treatment, values for k' at 34.0 × 10^3 atm of 4.7 × 10^{-7} and 7.5 × 10^{-7} sec^{-1} were obtained which are in good agreement with the value 6.9 × 10^{-7} sec^{-1} derived graphically from Figure 2.

According to 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 yield a straight line, the slope of which is $-E_a/R$. The Arrhenius activation energy, E_a, determined in this manner for three different pressures, 25.2 × 10^3, 34.0 × 10^3, and 39.5 × 10^3 atm, was 2.1 ± 1.0, 2.1 ± 0.5, and 1.5 ± 0.2 kcal $mole^{-1}$, respectively. A linear least-squares treatment was applied to the data given in Table II.

TABLE I

VALUES USED FOR THE DETERMINATION OF ΔV^* CORRECTED FOR DECOMPOSITION

$[\alpha_t]$, deg	$\ln \ln ([\alpha_0]/[\alpha_t])^{1/2}$	Pressure $\times 10^{-3}$, atm
	Sample 1[a]	
−1824	−6.41	7.9
−1804	−4.94	9.5
−1795	−4.64	20.4
−1775	−4.18	24.7
−1816	−5.56	27.2
−1777	−4.22	30.2
−1731	−3.58	36.3
−1730	−3.57	43.8
	Sample 2[b]	
−1794	−4.61	15.9
−1815	−5.49	19.0
−1778	−4.24	25.8
−1776	−4.20	27.2
−1775	−4.18	30.6
−1784	−4.36	34.0
−1593	−2.67	46.0

[a] Time under pressure, 20.0 hr; $[\alpha_0]$ = 1830°; temperature 23–28°. [b] Time under pressure, 16.0 hr; $[\alpha_0]$ = 1830°; temperature 23–28°. Stoichiometry of both samples, $K_3[Co(C_2O_4)_3] \cdot 4.5H_2O$.

TABLE II

EFFECT OF TEMPERATURE ON THE RACEMIZATION OF l-$K_3[Co(C_2O_4)_3] \cdot xH_2O$

$[\alpha_t]$, deg	Temp, °C	$\ln \ln ([\alpha_0]/[\alpha_t])^{1/2}$	$[\alpha_t]$, deg	Temp, °C	$\ln \ln ([\alpha_0]/[\alpha_t])^{1/2}$
	Sample 3[a]			Sample 5[c]	
−1780	25.5	−3.63	−1634	23.5	−3.06
−1762	38.3	−3.45	−1639	35.0	−3.10
−1782	41.8	−3.65	−1589	50.0	−2.80
−1759	50.3	−3.43	−1601	51.2	−2.87
−1763	54.0	−3.46	−1585	60.0	−2.78
−1725	57.3	−3.16	−1593	64.3	−2.82
			−1528	67.8	−2.52
	Sample 4[b]				
−1666	30.5	−2.68			
−1665	36.0	−2.68			
−1652	44.0	−2.62			
−1612	61.0	−2.47			

[a] Pressure, 25.2 × 10^3 atm; time under pressure, 20.0 hr; $[\alpha_0]$ = −1877°. [b] Pressure, 34.0 × 10^3 atm; time under pressure, 20.0 hr; $[\alpha_0]$ = −1910°. [c] Pressure, 39.5 × 10^3 atm; time under pressure, 20.0 hr; $[\alpha_0]$ = −1794°.

Experiments were undertaken to determine the influence of water of hydration on the rate of solid-state racemization. It was found that when samples of $K_3[Co(C_2O_4)_3]$, containing different amounts of water but having approximately the same initial optical activity, were subjected to the same conditions of pressure and time-under-pressure, the greatest loss of optical activity occurred with the samples containing the least amount of water. The results are given in Table III.

Discussion

It is necessary, in light of experimental evidence on salts similar to $K_3[Co(C_2O_4)_3]$, to reexamine each of the possible structures for the activated complex before eliminating them as structures for the activated com-

TABLE III

EFFECT OF H_2O ON THE RATE OF RACEMIZATION OF l-$K_3[Co(C_2O_4)_3]$[a]

Pressure $\times 10^{-3}$, atm	"Water of hydration"	$[\alpha_0]$, deg	$[\alpha_t]$, deg	Change in $[\alpha]$, deg
30.6	4.46	−1806	−1527	−279
30.6	6.01	−1921	−1737	−182
34.0	4.46	−1806	−1469	−337
34.0	6.01	−1921	−1703	−218
40.8	4.46	−1806	−1457	−349
40.8	6.01	−1921	−1663	−258

[a] Time under pressure, 24.0 hr; temperature 23–28°.

plex. Structures similar to A or B in Figure 1, which do not contain water of hydration in the coordination sphere, may be eliminated on the grounds that during their formation an expansion of the metal–ligand bond distance accompanied by a twisting of either the ligand or complex through the solid would be required. Such an expansion and twisting would certainly be suppressed by an increase in pressure, leading to a decrease in rate with increase in pressure.

The arguments which can be presented for the elimination of structures C and D are not as convincing as those presented above. There is evidence[9] from nmr studies that the trioxalatorhodate(III) ion in $K_3[Rh(C_2O_4)_3]\cdot 4.5H_2O$ exists partly in the form shown in Figure 3. In order for a species of this type to be involved in the racemization process an additional molecule of water must enter the coordination sphere to displace one end of another oxalate ligand so as to yield structure C during rearrangement. Such a path would require that some positive power of the water "concentration" within the crystal be involved in the rate expression. The fact that water retards the rate of racemization suggests that structure C, or for that matter any structure containing water in the coordination sphere, may be eliminated. Because of the possibility that the addition of water to the crystal lattice may be accompanied by lattice variations that retard the racemization process and that these lattice variations may predominate over the "concentration" effect, elimination of structures C and D is still equivocal.

The negative dependence on H_2O "concentration," if in fact it is a true concentration dependence, can be accounted for on the basis of infrared spectral measurements. Samples of $K_3[Co(C_2O_4)_3]\cdot xH_2O$ were dehydrated over phosphorus pentoxide. Investigation of the infrared spectra of samples of anhydrous and hydrated $K_3[Co(C_2O_4)_3]$ revealed that an absorption band at 1240 cm^{-1} in the anhydrous material shifted to longer wavelength by about 8 cm^{-1} in the hydrated complex. A similar shift of *ca.* 10–20 cm^{-1} was observed in the carbonyl stretching frequency at 1750 cm^{-1} in going from the anhydrous salt to the hydrate. The band at 1240 cm^{-1} has been assigned to the O–C–O symmetric stretching frequency in the oxalate ligand.[10] These results suggest hydrogen bonding of water molecules to the carbonyl oxygen of the complex ion. Owing to the close-packed nature of the solid matrix, the complete anion, hydrogen bonded to water, would encounter considerable resistance during reorientation. Thus the presence of water molecules might well be expected to inhibit racemization *via* transition states E or F. The apparent negative dependence on water concentration is therefore consistent with racemization *via* structure E or F.

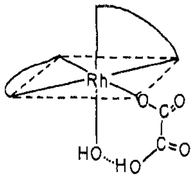

Figure 3.—Proposed structure for hydrated trioxalatorhodate ion in the solid state.[9]

A frequency factor of 1.5 × 10^{-5} sec^{-1} for the solid-state racemization was computed from the average value for k' at 34.0 × 10^3 atm, 6.4 × 10^{-7} sec^{-1}, and the average value for the activation energy, 1.9 ± 0.7 kcal mole^{-1}. For racemization of this complex in aqueous solution, the values for the frequency factor and energy of activation are 1.92 × 10^{16} sec^{-1} and 26.0 kcal mole^{-1}, respectively.[11] The vast difference between these quantities for racemization in the solid state and in solution (*viz.* about 10^{21} sec^{-1} for the frequency factor and about 24 kcal mole^{-1} for the activation energy) definitely show that the same mechanism is not operative in both cases. This adds support to the elimination of a mechanism involving structures A through D since studies of the mechanism of racemization of the trioxalato complexes of chromium(III) and cobalt(III) in aqueous solution indicate that a one-ended dissociation of an oxalate ligand is involved.[12,13]

It is still necessary to justify the very small activation energy and frequency factor in terms of a trigonal-prismatic activated complex. The activation energy in this case can be considered to arise from two contributions—changes in electrostatic energy and crystal field stabilization energy. The rhombic twist mechanism proposed by Ray and Dutt[14] can be considered to give rise to a structure corresponding to F in Figure 1. It has been shown[6,15] that increasing the angle θ to approximately 115° leads to a decrease in energy over the more rigid trigonal prism E. This energy decrease results from a weakening of the ligand–ligand repulsions in the distorted trigonal prism. Fay and Piper[15] report an electrostatic activation energy for this distorted structure of $0.144q^2/R$ where q is the number of electronic charges on each oxygen ligand and R is the metal–oxygen bond distance. A reasonable value of R = 1.90 Å for the Co–O distance in the $[Co(C_2O_4)_3]^{3-}$ ion may be obtained from the known Co–O distance in the $[Co(EDTA)]^-$ complex.[16] With this value of R and a

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choice of $q = 1.0$, the charge on one end of an oxalate ion, the electrostatic contribution to the activation energy is +25 kcal/mole. The electrostatic contribution to the activation energy will be counterbalanced by an increase in crystal field stabilization energy (CFSE)[6,15] on forming a trigonal-prismatic structure such as E in Figure 1. Fay and Piper[15] estimated this quantity to be between 21 and 30 kcal/mole^{-1} for the tris(trifluoroacetylacetonato)cobalt(III) complex. We have estimated the increase in CFSE for the $[Co(C_2O_4)_3]^{3-}$ ion to be approximately 54 kcal/mole^{-1}.[6] Even with a considerable loss of CFSE in the distortion of the rigid trigonal prism, as suggested by Fay and Piper, the gain in CFSE will very nearly compensate for the increase in electrostatic repulsion and the net activation energy would be expected to be very small. The unusually small activation energy observed for the racemization of $[Co(C_2O_4)_3]^{3-}$ in the solid state is certainly consistent with a trigonal-prismatic activated complex of structure E or F in Figure 1. It is, however, not possible to distinguish between these two choices since the more rigid structure will have a greater CFSE and also a greater electrostatic energy of activation than the distorted structure. The energy difference between structure E and a distorted structure similar to F would therefore probably not be large.

Finally, the very small frequency factor observed in this reaction may be accounted for by the same argument advanced by Ray and Dutt.[14] This argument suggests that the activation energy can be readily lost by an ion through deactivation before it has found its way into the rather improbable twisting motion required for racemization. This would lead to a low probability for passage through the transition state and hence a small frequency factor.

In summary, the experimental evidence presented here is consistent with a trigonal-prismatic activated complex being responsible for the solid-state racemization of $K_3[Co(C_2O_4)_3]\cdot xH_2O$. A stronger claim for support of this mechanism is made difficult, however, by problems inherent in the interpretation of results obtained from kinetic measurements on solid-state reactions. In addition to the uncertainty associated with the interpretation of the effect of waters of hydration on the rate of racemization, it should be pointed out also that lattice distortions over large distances, which may accompany local volume changes in the complex ion, make it difficult to interpret volumes of activation in terms of volume changes of the complex ion alone.[17]

Acknowledgment.—The support of the National Science Foundation is gratefully acknowledged.

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[17] The authors wish to thank a referee for drawing our attention to the limitations in interpreting solid-state kinetic results because of unknown lattice effects.

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Tetraphenyldiphosphine Complexes of Nickel(II) and Cobalt(II)

BY L. SACCONI AND J. GELSOMINI

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The ligands 1,4-bis(diphenylphosphino)butane (PC_4P), 1,5-bis(diphenylphosphino)pentane (PC_5P), and bis(diphenylphosphinoethyl) oxide (POP) form complexes of the general formula $M(PC_nP)X_2$ and $M(POP)X_2$ with the halides and thiocyanates of nickel(II) and cobalt(II). All of the ligands are bidentate and complexes with tetrahedral or planar stereochemistry are obtained depending on the nature of the anion.

Introduction

Many complexes of ditertiary diphosphines with the formula $M(ligand)X_2$, where ligand = $R_2P-(CH_2)_n-PR_2$ and X = halogen or NCS, have been prepared and characterized.[1-3] When R is a cyclohexyl group and M = Co(II), the complexes are generally tetrahedral;[4,5] when M = Ni(II), the complexes formed are planar and independent of the length of the chain and of the nature of the ligand X. The complexes with $n = 2$ or 3 are *cis* planar while those with $n = 5$ are *trans* planar.[4] When R = phenyl the complexes are *cis* planar if n = 1 or 2 presumably both in the solid state and in solution;[1,2] if $n = 3$ the complexes are planar in the solid state but give rise to an equilibrium of planar and tetrahedral forms in solution.[3] However if a donor atom like sulfur is introduced into the alkyl chain forming, for example, the potentially tridentate ligand $(C_6H_5)_2P(CH_2)_2S(CH_2)_2P(C_6H_5)_2$ (PSP), the ligand behaves as tridentate and forms the pentacoordinated complex $Ni(PSP)I_2$[6] which has been reported to dissociate partially in solution to form planar species.

In order to study the effect of lengthening the alkyl chain and of introducing an oxygen atom into it, of the donor ability of these ligands, and thus of the stereochemistry of the metal complexes formed from them

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