Presence of an isolated double bond in the second chelate loop of chromophore B is apparently of minor importance. However, if this double bond is conjugated with the α-diimine grouping (direct) electronic effects become operative. The large bathochromic

effect of such "intrachromophoric" conjugation strongly suggests that the π*-orbitals involved now become delocalized in the second chelate loop.

CONTRIBUTION FROM THE SCHOOL OF CHEMISTRY,
GEORGIA INSTITUTE OF TECHNOLOGY, ATLANTA, GEORGIA 30332

Cobalt(III) Complexes of *trans*-1,2-Cyclopentanediamine[1]

BY JOHN F. PHILLIPS AND DONALD J. ROYER

The cobalt(III) complexes of *trans*-1,2-cyclopentanediamine have been reinvestigated. The preparative methods used by the previous workers were found to be unsatisfactory, and more satisfactory procedures were developed. The ion previously reported to be [Co(cptdin)₃]³⁺ was found to be [Co₂(cptdin)₇(H₂O)₂]⁶⁺ and a structure which contains no chelate rings is proposed for this ion. This structure is consistent with the experimental data, and it explains the completely stereospecific character of this ion. During the course of the work a procedure was developed for the chemical determination of noncoordinated primary amine groups in an inert complex. A specialized procedure for the determination of the charge on a highly charged cation was also developed.

Introduction

Many years ago Jaeger and Blumendal[2] made one of the most significant of the early investigations of the stereochemical behavior of complex ions containing asymmetric ligands in which they studied the cobalt-(III) and rhodium(III) complexes of *trans*-1,2-cyclopentanediamine (cptdin). They prepared compounds which were reported to contain the ions [M(cptdin)₃]³⁺, [M(cptdin)₂Cl₂]⁺, [M(en)₂(cptdin)]³⁺, and [M(en)-(cptdin)₂]³⁺, where M is Co or Rh, and determined the optical configuration of the metal ion environment and of the ligands. Of the numerous possible isomers which could be postulated for these ions they were able to obtain evidence for the existence of only the following enantiomorphic pairs: D,L-[M(*l,d*-cptdin)₃]³⁺, D,L-*cis*-[M(*l,d*-cptdin)₂Cl₂]⁺, D,L-[M(en)(*l,d*-cptdin)₂]³⁺, and D- or L-[M(en)₂(*d*- or *l*-cptdin)]³⁺. On the basis of these findings and earlier investigations with other optically active bidentate ligands,[3-5] Jaeger attributed this drastic reduction in the number of isomers to the essentially exclusive formation of one preferred configuration, the complex tending to exist as the most symmetrical possible diastereoisomer.

Corey and Bailar[6] have considered the possible conformations of a tris-bidentate complex containing nonrigid five-membered ethylenediamine-type chelate rings. Their results indicate that while there is indeed a preferred diastereoisomer in these cases, it should be

only approximately 2 kcal./mole more stable than the remaining diastereoisomers.

Experimental support of the views of Corey and Bailar has been provided by Dwyer and co-workers,[7] who have prepared a number of additional isomers in which the optically active ligand is propylenediamine.

Implicit in all of the conclusions drawn from Jaeger's work, both by Jaeger and by later workers,[6] is the assumption that the cptdin molecule functions as a reasonably normal bidentate ligand. However, a consideration of the geometry of the cyclopentane ring and the steric requirements for chelate ring formation shows that this assumption may be incorrect. Assuming that the cyclopentane ring has the same conformation in the cptdin molecule as it has in cyclopentane itself,[8] the minimum nitrogen–nitrogen distance in an unstrained conformation of the free diamine molecule is 3.5 Å., and the angle formed by the projection of the two carbon–nitrogen bonds when viewed down the intervening carbon–carbon bond is 109°. The corresponding values in the Co(en) chelate ring are 2.75 Å. and 48.8°. Thus severe bond angle strain is introduced by the *trans* fusion of two five-membered rings which would be necessary if cptdin is to act as a bidentate ligand.

In view of the above considerations, a reinvestigation of the Co(III)–cptdin complexes was undertaken.

Experimental

Preparation of cptdin.—The cptdin was prepared by the

(1) This work was supported by National Science Foundation Grant NSF-G 11239. It is based in part on the Ph.D. thesis of J. F. P.

(2) F. M. Jaeger and H. B. Blumendal, *Z. anorg. allgem. chem.*, **175**, 161 (1928).

(3) P. Pfeiffer and T. H. Gassmann, *Ann.*, **346**, 59 (1906).

(4) L. Tschugaeff and W. Sokoloff, *Ber.*, **42**, 55 (1909).

(5) A. Smirnoff, *Helv. Chim. Acta*, **3**, 59 (1920).

(6) E. J. Corey and J. C. Bailar, *J. Am. Chem. Soc.*, **81**, 2620 (1959).

(7) (a) F. P. Dwyer, F. L. Garvan, and A. Shulman, *ibid.*, **81**, 290 (1959); (b) F. P. Dwyer and F. L. Garvan, *ibid.*, **81**, 1043 (1959); (c) F. P. Dwyer and A. M. Sargeson, *ibid.*, **81**, 5269 (1959); (d) F. P. Dwyer and A. M. Sargeson, *ibid.*, **81**, 5272 (1959); (e) F. P. Dwyer, A. M. Sargeson, and L. B. James, *ibid.*, **86**, 590 (1964).

(8) K. S. Pitzer, J. E. Kilpatrick, and R. Spitzer, *ibid.*, **69**, 2481 (1947).

following reaction sequence: diethyl adipate → 2-carbethoxy-cyclopentanone → 1,2-cyclopentanedionemonooxime → 1,2-cyclopentanedioxime → 1,2-cyclopentanediamine. The 2-carbethoxycyclopentanone was prepared by Dieckmann ring closure.[9] The series of reactions used to convert 2-carbethoxycyclopentanone to 1,2-cyclopentanedioxime were carried out using the procedure of Cope, *et al.*[10]

The 1,2-cyclopentanedioxime was then converted to the desired 1,2-cyclopentanediamine by the following modification of the method of Jaeger and Blumendal.[2]

1,2-Cyclopentanedioxime (10 g.) and absolute ethanol (2 l.) were placed in a 3-l. flask and 180 g. of sodium, cut into small pieces, was added over a period of several hours. The solution was then heated under reflux until all of the sodium had reacted. The alcohol was then steam distilled away and the remaining amine–water mixture was continuously extracted with diethyl ether for 48 hr. The ether was then stripped off and the crude amine distilled at reduced pressure through a column having about five theoretical plates and stored in a sealed glass vial. This procedure was repeated numerous times with an average yield of 30% of theoretical.

Attempts were made to reduce the 1,2-cyclopentanedioxime by catalytic hydrogenation and by the use of lithium aluminum hydride but the results proved to be less satisfactory than the sodium in ethanol reduction.

An attempt was also made to prepare cptdin by the preparation and Curtius rearrangement of 1,2-cyclopentanedicarboxylic acid, but only a very low yield was obtained.

Purification of cptdin.—The crude diamine was fractionally distilled at a pressure of 60 mm. The distilling column, 1 cm. in diameter and 90 cm. long, was packed with glass helices and the reflux ratio was kept greater than 40. Under these conditions approximately the first 25% of the distillate contained a significant amount of the somewhat lower boiling *cis* isomer of the amine. The remaining 75% of the material distilled at an essentially constant temperature and was used in the preparation of the metal complexes; b.p. (uncor.) 103° (60 mm.).

Anal. Calcd. for $C_5H_{12}N_2 \cdot 2HCl$: C, 34.7; H, 8.0; N, 16.2. Found: C, 34.8; H, 8.5; N, 16.4.

Constant boiling *cis*-cptdin was then obtained by redistilling that portion of the distillate which contained a significant amount of the *cis* isomer through a completely vacuum-jacketed distillation column of the type described by Ray[11]; b.p. (uncor.) 99° (60 mm.).

The two isomeric amines may be differentiated by means of their n.m.r. spectra in D_2O. The center of the triplet arising from the protons attached to carbons 1 and 2 occurs at τ 7.28 in the *trans* amine and at τ 7.23 in the *cis* amine (external tetramethylsilane standard). This previously unreported *cis* isomer of the amine amounted to approximately 10% of the crude diamine mixture.

Preparation of $Co_2(cptdin)_7Cl_6 \cdot 4H_2O$.—The general preparative procedure of Bauer and Drinkard[12] was used.

cptdin·2HCl (5–10 g.) was dissolved in a minimum amount of water. Sodium triscarbonatocobaltate(III) trihydrate was added in the ratio of 1 mole of cobalt to 6 moles of amine, and the mixture was heated on a steam bath for 30 min. The product was cooled, 5 ml. of absolute ethanol was added, and the resulting precipitate was filtered off, washed with alcohol and ether, and recrystallized once from water.

This preparation was repeated several times. The yield was rather erratic with an average of approximately 50%.

Anal. Calcd. for $[Co_2(C_5H_{12}N_2)_7(H_2O)_2]Cl_6 \cdot 2H_2O$: C, 38.1; H, 8.3; N, 17.6; Co, 10.68; Cl, 19.3. Found: C, 37.9; H, 8.2; N, 17.8; Co, 10.75; Cl, 19.6.

Preparation of Other Complexes.—When the cptdin to cobalt ratio in the above preparation was reduced to 3:1, the principal

product was found to have the formula $Co(cptdin)_3(CO_3)Cl \cdot 1.5H_2O$.

Anal. Calcd. for $Co(C_5H_{12}N_2)_3(CO_3)Cl \cdot 1.5H_2O$: C, 40.4; H, 8.2; N, 17.7; Co, 12.4; Cl, 7.5. Found: C, 40.1; H, 8.2; N, 18.0; Co, 12.7; Cl, 7.7.

This material, which is lavender in color, seems to contain coordinated carbonate ions (as indicated by its very slow reaction with acid).

Treatment of this material with HCl gives what appears to be a pair of typical praseo–violeo isomers of the dichlorotetraammine type. Work is continuing on these compounds, and while we have not definitely established their composition, we have gathered enough information about them that we definitely say that they do not contain simple monomeric $[Co(cptdin)_2Cl_2]^+$ ions.

Optical Resolutions.—The cobalt complexes were resolved as the *d*-tartrate chloride double salts which were prepared by adding enough silver *d*-tartrate to a solution of the chloride salt to precipitate two-thirds of the chloride present. The resolution was then carried out by standard fractional crystallization until constant rotation was achieved. The material was then converted back to the chloride salt by means of an anion-exchange resin, and the final rotation was measured in dilute aqueous solution.

The resolution of the free diamine was attempted using the *d*-tartrate, *l*-malate, *d*-10-camphorsulfonate, and *d*-bromocamphorsulfonate salts, but no really satisfactory procedure was found. The resolution was eventually carried out using the *d*-tartrate salt, but 30 cycles of fractional crystallization were required to obtain a constant rotation. The final rotation of the free diamine in dry benzene was $[\alpha]D$ −42 ±1°. The rotation in water solution was $[\alpha]D$ −39 ± 1°.

The amine was recovered from the resolved cobalt complexes by dissolving the complexes in concentrated sodium hydroxide solution and extracting with benzene. All of the complexes react rapidly with concentrated base at room temperature in contrast to the very slow reaction of $[Co(en)_3]^{3+}$ and similar complexes under these conditions. The benzene extract was then dried over magnesium sulfate, the rotation determined, and the amount of amine present determined by titration.

Determination of the Charge to Cobalt Ratio.—The cationic charge to cobalt ratio was determined in the usual way by adsorbing a weighed sample of complex on a large excess of Dowex 50X2 resin in the hydrogen form and titrating the liberated acid.

Chromatographic Separation of the Isomers of $[Co_2(cptdin)_7(H_2O)_2]^{6+}$.—These materials were separated using Amberlite CG-50 chromatographic grade carboxylic acid resin of 400–600 mesh. Approximately 250 mg. of the complex was adsorbed on a column of the hydrogen form of the resin which was 3 cm. in diameter and 80 cm. high. The material was then eluted with hydrochloric acid solution of pH 2.1 at a flow rate of 5 ml./hr. Fractions of 40 ml. were collected and the optical density was measured at 490 mμ using 10-cm. spectrophotometer cells.

The three materials separated in this way were all found to have essentially the same analysis as the starting material.

Anal. Found—first band: C, 38.0; H, 8.0; N, 17.7; Co, 10.7; Cl, 19.4. Second band: C, 37.4; H, 8.2; N, 17.7; Co, 10.6; Cl, 19.4. Third band: C, 38.0; H, 8.1; N, 17.8; Co, 10.7; Cl, 19.5.

The analyses reported for the second and third bands were determined after the separation of these two materials was completed by fractional crystallization.

Solubility Studies.—An excess of the solid nitrate salt of the complex was added to a series of solutions of known potassium nitrate concentration. The solutions were placed in a mechanical shaker for 48 hr. at 25° (no changes in concentration were observed after 24 hr.). The solutions were then filtered and the concentration of cobalt in solution was measured spectrophotometrically. The known salts were determined in exactly the same way.

Determination of Noncoordinated Amine.—The standard Van Slyke apparatus could not be used because of the slowness

(9) P. S. Pinkney, "Organic Syntheses," Coll. Vol. II, John Wiley and Sons, Inc., New York, N. Y., 1943, p. 116.

(10) A. C. Cope, L. L. Ester, J. R. Emery, and A. C. Haven, *J. Am. Chem. Soc.*, **73**, 1199 (1951).

(11) J. D. Ray, *Rev. Sci. Instr.*, **28**, 200 (1957).

(12) H. F. Bauer and W. C. Drinkard, *J. Am. Chem. Soc.*, **82**, 5031 (1960).

of the reaction and the consequent large volume of nitrous oxide produced. The apparatus used consisted of two gas burets fitted with mercury leveling bulbs. The tops of the two burets were connected through an inverted Y of capillary tubing fitted with a three-way stopcock in such a fashion that gas could be transferred quantitatively from one buret to the other and material added to or removed from each buret independently.

In a typical determination, 3 ml. of dilute complex solution, 5 ml. of sodium nitrite solution (800 g./l.), and 1 ml. of glacial acetic acid were placed in one of the burets. After about 10 min., most of the gas was forced into the other buret and washed with concentrated ferrous sulfate solution to remove nitrous oxide. The remaining gas was then forced back into the original buret and the spent ferrous sulfate solution removed from the system. This procedure was repeated as necessary for 18 hr. In several runs, fresh nitrous acid solution was introduced after 18 hr. and the reaction allowed to continue for another 18 hr., and no additional nitrogen was produced.

Blank runs were made, using no complex and using tris(ethylenediamine)cobalt(III). These runs gave a small relatively constant blank of nitrogen which was subtracted from the amount found when the cptdin complex was used.

Analyses.—Cobalt was determined by EDTA titration after destruction of the complex with base, and chloride was determined potentiometrically. The C, H, and N analyses were by Galbraith Laboratories Inc., Knoxville, Tenn.

Physical Measurements.—Electronic spectra were recorded, using a Cary Model 14 spectrophotometer or a Bausch and Lomb 505 spectrophotometer. Infrared spectra were taken with a Perkin-Elmer Infracord Model 137, using the Nujol mull technique. N.m.r. spectra were recorded using a Varian A-60 spectrometer. The ORD spectra were taken using a Cary Model 14 spectrophotometer fitted with a Perkin-Elmer ORD attachment, using 1-cm. quartz cells. Optical rotations at the sodium D-line were determined using a Bellingham and Stanley manual polarimeter. The crystal measurements were made with a conventional reflecting goniometer.

Results

Preparation of Cobalt(III) Complexes of cptdin.—

Repeated attempts to prepare cobalt(III) complexes of cptdin following the procedures given by the previous workers[2] gave negative results. In our hands the procedures given for the production of these compounds gave complete oxidation of the amine and led to a quantitative recovery of cobalt(II) chloride. We can only suggest that this failure can probably be attributed to unavoidable differences between our reagents and the reagents available to the previous workers 35 years ago.

Using the entirely different preparative procedures outlined in the Experimental section, compounds bearing a superficial resemblance (color and crystal habit) to the compound reported to be $Cp(cptdin)_3Cl_3 \cdot 3H_2O$ and the two isomeric compounds reported to be $[Co(cptdin)_2Cl_2]Cl \cdot H_2O$ were prepared. However, our elementary analyses of these compounds are more in accord with the formulas $Co_2(cptdin)_7Cl_6 \cdot 4H_2O$ and $Co_2(cptdin)_{5-6}Cl_6 \cdot HCl$, respectively.

The previous workers reported the results of a crystallographic examination of their compounds, and thus it is possible to compare the material to which we assign the formula $Co_2(cptdin)_7Cl_6 \cdot 4H_2O$ with the compound to which the previous workers assigned the formula $Co(cptdin)_3Cl_3 \cdot 3H_2O$. The results of a crystallographic examination of our material in both the racemic and

TABLE I
CRYSTALLOGRAPHIC COMPARISON

	This work	Previous work[2]
Formula	$rac\text{-}Co_2(cptdin)_7\text{-}$ $Cl_6 \cdot 4H_2O$	"$rac\text{-}Co(cptdin)_3\text{-}$ $Cl_3 \cdot 3H_2O$"
Axial ratio	$a:b:c =$ 2.247:1:1.563	$a:b:c =$ 2.2472:1:1.5625
Axial angles	α 62° 10'	α 62° 11'
	β 121° 35'	β 121° 34'
	γ 115° 20'	γ 115° 19'
Habit	Triclinic pinacoidal	Triclinic pinacoidal
Interfacial angles		
(100)(110)	77° 19'	77° 18'
(100)(1$\bar{1}$0)	53° 57'	53° 59'
(100)(101)	40° 8'	40° 6.5'
(100)(101)	73° 15'	73° 15'
(110)(10$\bar{1}$)	77° 25'	77° 24'
(110)(10$\bar{1}$)	60° 2'	59° 54'
($\bar{1}$01)(1$\bar{1}$0)	68° 10'	68° 7'
(100)(3$\bar{1}$0)	40° 12'	40° 16'
(310)(1$\bar{1}$0)	36° 57'	37° 2'
($\bar{1}\bar{1}$0)(1$\bar{1}$0)	48° 43'	48° 43'
(101)($\bar{1}$01)	66° 38'	66° 38.5'
Formula	L-$Co_2(d\text{-}cptdin)_7\text{-}$ $Cl_6 \cdot 4H_2O$	"D-$Co(l\text{-}cptdin)_3\text{-}$ $Cl_3 \cdot 3H_2O$"
Habit	Hexagonal-bipyramidal	Hexagonal-bipyramidal
Axial ratio	$a:c = 1:2.533$	$a:c = 1:2.5328$
Interfacial angles		
(10$\bar{1}$2)(10$\bar{1}$2)	68° 44'	68° 44'
(10$\bar{1}$2)(01$\bar{1}$2)	48° 44'	48° 50'
(10$\bar{1}$2)(10$\bar{1}$0)	34° 20'	34° 22'
(10$\bar{1}$2)(20$\bar{2}$3)	7° 47'	7° 51'
(20$\bar{2}$3)(02$\bar{2}$3)	53° 10'	53° 3'
(10$\bar{1}$2)(10$\bar{1}$3)	11° 15'	11° 5'

resolved forms are given in Table I and compared with the previous workers' results.

These results would seem to indicate that the two materials are the same, despite the fact that they have been assigned different formulas and were prepared by different means. The ORD curves given in Figure 2 also tend to support this conclusion.

Separation of the Isomers of $[Co_2(cptdin)_7(H_2O)_2]^{6+}$.—Repeated fractional crystallization of the chloride salt of the complex from 70% methanol separated the material into a less soluble fraction containing approximately 10% of the total material and the slightly more soluble remainder. When optically resolved the less soluble fraction was found to have a rotation of $[\alpha]D$ $-957°$. The resolution of the more soluble fraction gave somewhat variable results in the general region $[\alpha]D$ -350 to $-450°$.

A better separation of the material was obtained by the ion-exchange chromatographic procedure outlined in the Experimental section. A typical plot of the absorbance *vs.* effluent, Figure 1, clearly shows three components, one almost completely separated and the other two partially separated.

All three bands gave elementary analyses corresponding to the formula $Co_2(cptdin)_7Cl_6 \cdot 4H_2O$. All three were found to have a cationic charge to cobalt ratio of 3.00 ± 0.01, and their visible, ultraviolet, and infrared spectra were indistinguishable.
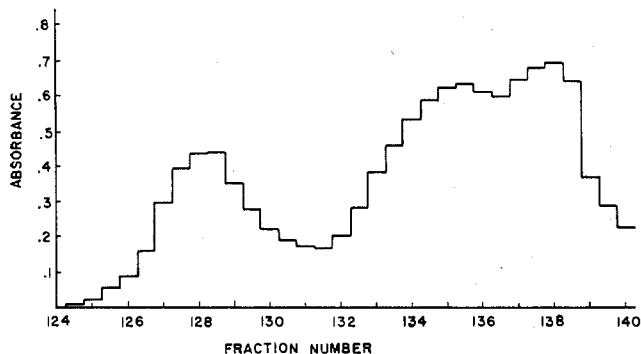
Figure 1.—Chromatographic elution of $[Co_2(cptdin)_7(H_2O)_2]^{6+}$; ion-exchange resin Amberlite CG-50, eluting agent HCl, solution of pH 2.1.

Optical Resolutions.—The resolution of the third band from the column (isomer III) gave a rotation of $[\alpha]D$ $-418 \pm 2°$, and the resolution of the second band (isomer II) a rotation of $[\alpha]D$ $-478 \pm 2°$. When these resolved isomers were individually rechromatographed, they eluted as single relatively sharp bands and showed no apparent tendency to separate further. The optical rotations of the leading edge, the center, and the trailing edge of the bands were found to be identical. Therefore, it is felt that the separation of these two isomers was completed in the fractional crystallizations involved in the optical resolution, and that the above values represent the rotations of the pure isomers.

Only a very small amount of the first band from the column (isomer I) was available and a complete optical resolution could not be effected. However, a partial resolution of this material gave a specific rotation of $[\alpha]D$ $-600°$. Because the specific rotations of both isomers II and III were considerably lower than this, we believe that isomer I corresponds to the salt whose specific rotation was $[\alpha]D$ $-958°$ which was obtained by the fractional crystallization of the chloride salts from methanol. The material of lower rotation which was obtained from this fractionation would then consist of a mixture of isomers II and III.

The optical rotatory dispersion curves of the three isomers are shown in Figure 2. The marked similarity of these curves would seem to indicate that these three materials may have very similar structures. One unusual feature of these curves is perhaps worthy of comment. In these curves the center of the long wave length Cotton effect curve falls at a shorter wave length than the long wave length maximum in the absorption spectrum. This would seem to indicate that the E component of this transition is of higher frequency than the A component.[18] Tris-bidentate cobalt(III) complexes normally display the reverse order with the A component at higher frequency than the E. This could perhaps be taken as rather weak evidence that there is something unusual about the structure of these compounds.

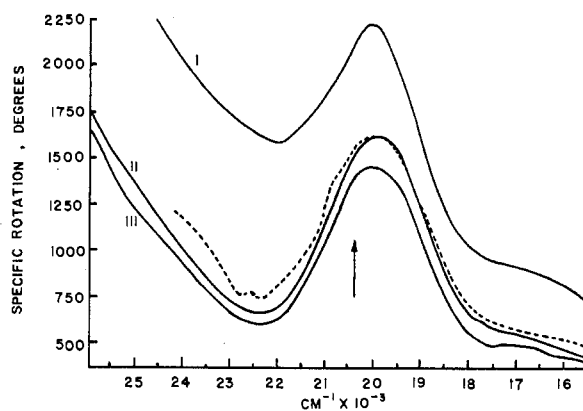Samples of the resolved isomers were destroyed, and the rotation of the recovered free amine was de-

(13) S. F. Mason and A. J. McCaffery, *J. Mol. Phys.*, **6**, 359 (1963).

Figure 2.—Optical rotatory curves. The broken line is the curve reported by Jaeger for $Co(cptdin)_3Cl_3$. The arrow marks the position of the long wave length maximum in the absorption spectrum.

termined. The amine recovered from isomers II and III was found to have specific rotations of $[\alpha]D$ $+42.3 \pm 1.0$ and $+41.5 \pm 1.08°$, respectively, and the amine recovered from a mixture of isomers I and II with a rotation of $[\alpha]D$ $-625°$ was found to have a rotation of $[\alpha]D$ $+42.3 \pm 1.5°$. These values are to be compared with the value of $[\alpha]D$ $-42 \pm 1°$ obtained by the resolution of the free amine. This would indicate that all seven amines in a given empirical formula unit $Co_2(cptdin)_7Cl_6·4H_2O$ are of the same optical configuration in each of the three geometrical isomers of this formula.

The previous workers[2] reported a specific rotation of $[\alpha]D$ $\pm 36°$ for cptdin in water. We find $[\alpha]D$ $\pm 39 \pm 1°$ in water ($\pm 42°$ in dry benzene).

Determination of Noncoordinated Amine Groups.—A consideration of the empirical formula of the isomers indicates that there are seven amine groups per cobalt, which makes it highly unlikely that they are all coordinated.

The number of noncoordinated amine groups per cobalt was determined by the modification of the Van Slyke nitrogen procedure described in the Experimental section. A mixture of isomers I and II was found to have 2.00 ± 0.07 noncoordinated amine groups per cobalt, and a mixture of isomers II and III gave 1.93 ± 0.09 noncoordinated amines per cobalt. These results thus indicate five coordinated amine groups per cobalt in all three complexes.

This use of the Van Slyke method for the determination of primary amines to distinguish between noncoordinated primary amine groups and coordinated primary amine groups (which are effectively secondary amines) gave excellent results and should be applicable to any reasonably substitution-inert complex.

Attempts to titrate the noncoordinated amine groups directly with acid in several acidic or aprotic solvents failed because the solubility of the complex was too low to give meaningful results.

The Degree of Polymerization of $[Co_2(cptdin)_7$-$(H_2O)_2]^{6+}$.—If we make the reasonable assumption that the cobalt is six-coordinate in these compounds,

the only formula which is consistent with the analytical data, the cationic charge to cobalt ratio, and the number of noncoordinated amine groups per cobalt is $[Co_{2n}(cptdin)_{7n}(H_2O)_{2n}]Cl_{6n}\cdot 2nH_2O$ where n is a whole number. Thus n must be determined in order to specify the formula completely.

The conventional methods for the determination of the molecular weight (colligative properties or electrical conductance of solutions) are of little use in this case because of the high charge, $+6n$, on the cation.

Another method of obtaining the desired information would be to measure the charge on the cation instead of the molecular weight. Note that since the charge on the cation must be $+6n$, the actual charge on the ion must be $+6$, $+12$, $+18$, ..., and so the charge on the cation needs to be determined only with sufficient accuracy to distinguish among these possibilities. Thus these measurements need to be made only to a very low degree of accuracy.

One method of obtaining the charge on the cation is the very old technique[14] of measuring the solubility of a sparingly soluble salt in the presence of a salt containing a common ion (the common ion effect). The high charge on the cation, however, assures that activity effects in solution will be large. Two methods suggest themselves as possible ways to deal with this difficulty: (1) use solutions of constant ionic strength, and (2) attempt to calculate activity coefficients. The first of these alternatives was not feasible in this case because moderate concentrations of any of the common anions precipitate the complex and thus constant ionic solutions could not be made up.

The second approach of allowing the ionic strength to vary and calculating the appropriate activity coefficients met with greater success. Such a calculation may be carried out in the following way. The Debye–Hückel formula for the rational activity coefficient, f_j, of the j ion in solution may be written as[15]

$$\log f_j = -\frac{Z_j^2 A \sqrt{I}}{1 + B a \sqrt{I}} \quad (1)$$

where all symbols have their usual meaning. The thermodynamic solubility product of the salt MX_{Z_+}, where X is a uninegative anion and Z_+ is the charge on the cation, may be written

$$K_{sp} = Y_+ C_+ (Y_- C_-)^{Z_+} \quad (2)$$

where C represents the molar concentration and Y the molar activity coefficient of the ions in question.

For our purposes the differences between the rational activity coefficient and the molar activity coefficient in dilute aqueous solutions will be sufficiently small that they can safely be neglected. Then combining eq. 2 and eq. 1, one obtains

$$\log K_{sp} = \log C_+ (C_-)^{Z_+} - \frac{(Z_+ + 1)Z_+ A \sqrt{I}}{1 + B a \sqrt{I}} \quad (3)$$

In our case

$$C_+ = 3[Co]/Z_+$$

where [Co] is the formal concentration of cobalt.

Thus, if the solubility of a sparingly soluble salt of the complex cation is measured in a solution containing a known concentration of a salt containing the same anion, all of the quantities in eq. 3 are known except $\log K_{sp}$, Z_+, and a. A series of such measurements in solutions of different salt concentration would make it possible to determine Z_+ which in turn would indicate the number of cobalts per cation.

The solubilities of the nitrate salts of isomer I and of an approximately equimolar mixture of isomers II and III were determined in a series of potassium nitrate solutions with the results shown in Table II.

TABLE II

SOLUBILITY OF $[Co_2(cptdin)_7(H_2O)_2](NO_3)_6$ IN KNO_3 SOLUTIONS

KNO_3 concn., M	[Co] (isomer I), $M \times 10^4$	[Co] (isomers II and III), $M \times 10^4$
0.0759	5.54	10.83
0.1012	4.34	7.21
0.1129		6.95
0.1264	3.34	6.92
0.1401		6.34
0.1520	3.00	5.38
0.1570		5.28
0.1771	3.27	5.25
0.202	2.58	4.15
0.226	2.57	3.31
0.253	2.47	3.23
0.278	2.17	
0.304	2.03	

Since eq. 3 is a rather complicated function of Z_+, the general calculation of the best least-squares values for the three unknowns Z_+, $\log K_{sp}$, and a presents computational difficulties. Therefore, the computation was simplified in the following way. An approximate value was chosen for a and the best values of Z_+ and $\log K_{sp}$ were calculated for that value of a. This procedure is justified by the fact that eq. 3 is not critically dependent on a. (A 10% change in a changes Z_+ by less than 2%, and a 50% change in a changes Z_+ by approximately 30%.)

Since a is an average property of all of the electrolyte in the solution, *not* of the complex alone,[16] a reliable estimate of this parameter can be made. The concentration of the complex in these solutions was at most only 5% as great as the concentration of potassium nitrate, and in most cases it was considerably less than this. Therefore, the value of a in these solutions should be very close to the value of a appropriate for a pure potassium nitrate solution of this concentration. The parameter a is approximately equal to 2.8 for KNO_3 solutions of the concentrations used here,[17] and so this was the value used in the calculation.

The best least-squares value of Z_+ found in this way was 5.9 ± 0.4 in both cases. This indicates that the

(14) A. A. Noyes, *Z. physik. Chem.*, **6**, 241 (1890).

(15) R. A. Robinson and R. H. Stokes, "Electrolyte Solutions," 2nd Ed., Academic Press, New York, N. Y., 1959, p. 229.

(16) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," 3rd Ed., Reinhold Publishing Corp., New York, N. Y., 1958, pp. 586–591, especially eq. 14-1-3, 14-1-4, and 14-1-5.

(17) T. Cromwall, V. LaMer, and K. Sandved, *Physik. Z.*, **29**, 358 (1928).

correct formula for the cation in all three isomers is $[Co_2(cptdin)_7(H_2O)_2]^{6+}$. The best values of K_{sp} were calculated to be $1.5 \pm 0.2 \times 10^{-15}$ for isomer I and $2.2 \pm 0.1 \times 10^{-15}$ for the mixture of isomers II and III.

The method was checked by determining the charge on two cations of known charge, $[Pt(en)_3]^{4+}$ and $[Co_2(trien)_3]^{6+}$. The solubility of $[Pt(en)_3](NO_3)_4$ in KNO_3 solutions (ionic strength 0.1–0.6 M) gave an indicated Z_+ of 3.8 ± 0.2, and the solubility of $[Co_2(trien)_3][B(C_6H_5)_4]_6$ in $Na[B(C_6H_5)_4]$ (the nitrate salt was too soluble) gave an indicated Z_+ of 6.0 ± 0.3 ($a = 3.5$) (ionic strength 0.01–0.15 M).

This procedure is of course subject to rather large errors. Probably the greatest difficulty is ion-pair formation in solution which would tend to reduce the apparent Z_+, but this does not seem to be serious, in NO_3^- solutions, as long as the ionic strength of the solution is below about 0.5. This can probably be attributed to the fact that these ions are so large that their charge per unit of surface area is quite small despite their high charge. Despite these difficulties, we feel that our results are certainly reliable enough to distinguish between a cation of +6 charge and a cation of +12 charge which is all that we are calling on them to do.

Discussion

The cptdin was prepared in much the same manner as described by the previous workers, but, contrary to their report, the amine was not pure. There seems to be no reason to doubt that the amine used by Jaeger and Blumendal contained a significant amount of *cis*-1,2-cyclopentanediamine. Because the *cis* isomer of the amine has a configuration more suitable for chelate formation than the desired *trans* isomer and because the amine is present in considerable excess over the cobalt during the preparation, the complexes which they obtained may have contained considerable amounts of *cis*-1,2-cyclopentanediamine in addition to the expected *trans* isomer. The slightly higher values which we find for the specific rotation of the free amine would tend to support this conclusion.

We have prepared three compounds which, judging by their colors, crystal habits, and general reactions and behavior, seem to be three of the compounds reported by Jaeger and Blumendal. However, our analytical results are such that we are forced to assign different formulas to these materials.

We have concentrated our attention on one of these materials: a pink material to which we assign the empirical formula $Co_2(cptdin)_7Cl_6 \cdot 4H_2O$. Despite the difference in empirical formula we believe that this is the material reported by Jaeger to be $[Co(cptdin)_3]Cl_3 \cdot 3H_2O$ for the following reasons: the crystal behavior of our material is identical with that reported by Jaeger and the optical rotatory dispersion curve given by Jaeger very closely resembles a weighted average of our three curves (Figure 2). The crystal evidence in particular seems to be quite conclusive.
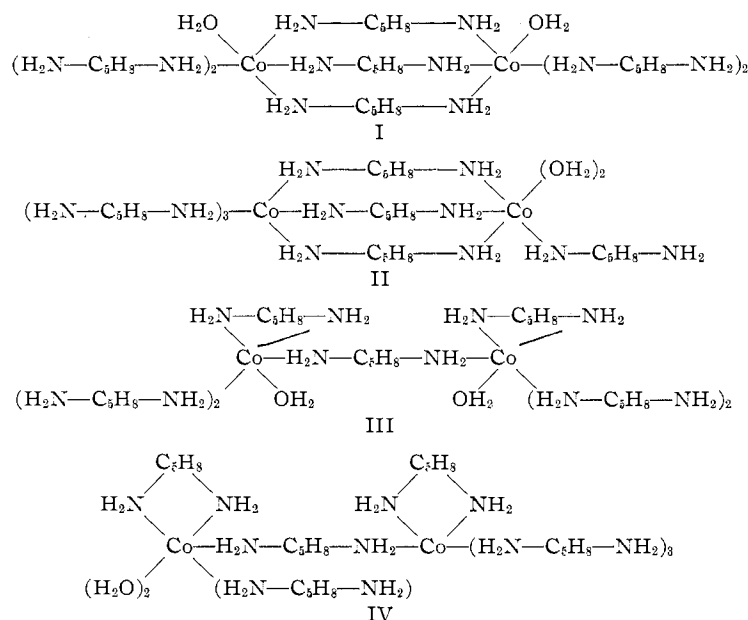
There are several properties of this material which would seem to be more in accord with our formula than the previously proposed formula. The pink color of the material, which Jaeger also commented on, is not what would be expected for a Co(III) coordinated to six amine groups. The visible spectrum tends to confirm this in that the spectrum of this material is essentially identical with that of the $[Co(NH_3)_5-H_2O]^{3+}$ ion. The material is also somewhat more reactive than most tris-bidentate hexaammine cobalt(III) compounds. It reacts rapidly (5 min.) with strongly basic solutions at room temperature, and it is converted to $[Co(NH_3)_6]^{3+}$ by prolonged heating in aqueous ammonia.

By a combination of fractional crystallization and ion-exchange chromatography, it was possible to separate this material into three geometrical isomers. The three isomers have indistinguishable visible, ultraviolet, and infrared spectra and their elementary composition is identical. Isomer I can be distinguished from the other two by a slightly lower solubility and has a specific rotation of $[\alpha]_D$ $-958°$ when optically resolved. Isomers II and III, which were separated only with considerable difficulty, have very similar solubilities and have specific rotations of $[\alpha]_D$ -478 and $-418°$, respectively.

Because the three geometrical isomers can be separated only with great difficulty (the preparation of 20-mg. samples of the completely separated and resolved isomers required approximately 3 months), several of the experiments which were carried out to characterize these materials further were performed with a mixture of two of the three isomers. However, the properties measured are of such a nature that the results obtained are still definitive and unambiguous. For example, the number of cobalts per cation in a mixture of approximately equal amounts of isomer II and isomer III was found to be two. Since the formula precludes a value smaller than this for either isomer, both isomers must be dimers. All three isomers were found to be dimeric with respect to cobalt, have cation charge to cobalt ratios of three, and contain four non-coordinated NH_2 groups per dimeric cation. Also in each of the three isomers all seven cptdin molecules in a given cation were found to be of the same optical configuration, *i.e.*, they are all of the type L-$[Co_2(l\text{-cptdin})_7(H_2O)_2]^{6+}$.

At this point it is possible to consider possible structures for these materials. The only structures which seem to be consistent with all of the data are the following.

Amido and hydroxo bridges are ruled out by the formula, while bridging water molecules would be distinctly acid, and no such acidity was observed. Structures III and IV can probably be ruled out by the argument that if part of the cptdin molecules chelate, there is no apparent reason why all of them should not, which would lead to a stable tris-bidentate structure. Structure II can exist as one geometrical isomer, and thus not more than one of our three isomers

$$H_2O \qquad H_2N\text{---}C_5H_8\text{---}NH_2 \quad OH_2$$
$$(H_2N\text{---}C_5H_8\text{---}NH_2)_2\text{---}Co\text{---}H_2N\text{---}C_5H_8\text{---}NH_2\text{---}Co\text{---}(H_2N\text{---}C_5H_8\text{---}NH_2)_2$$
$$H_2N\text{---}C_5H_8\text{---}NH_2$$

<center>I</center>

$$H_2N\text{---}C_5H_8\text{---}NH_2 \quad (OH_2)_2$$
$$(H_2N\text{---}C_5H_8\text{---}NH_2)_3\text{---}Co\text{---}H_2N\text{---}C_5H_8\text{---}NH_2\text{---}Co$$
$$H_2N\text{---}C_5H_8\text{---}NH_2 \quad H_2N\text{---}C_5H_8\text{---}NH_2$$

<center>II</center>

$$H_2N\text{---}C_5H_8\text{---}NH_2 \qquad H_2N\text{---}C_5H_8\text{---}NH_2$$
$$Co\text{---}H_2N\text{---}C_5H_8\text{---}NH_2\text{---}Co$$
$$(H_2N\text{---}C_5H_8\text{---}NH_2)_2 \quad OH_2 \qquad OH_2 \quad (H_2N\text{---}C_5H_8\text{---}NH_2)_2$$

<center>III</center>

$$C_5H_8 \qquad\qquad C_5H_8$$
$$H_2N \qquad NH_2 \qquad H_2N \qquad NH_2$$
$$Co\text{---}H_2N\text{---}C_5H_8\text{---}NH_2\text{---}Co\text{---}(H_2N\text{---}C_5H_8\text{---}NH_2)_3$$
$$(H_2O)_2 \qquad (H_2N\text{---}C_5H_8\text{---}NH_2)$$

<center>IV</center>

could be of this structure with the other two being of structure I. If this were the case, it would be difficult to explain why the spectra and solubilities of the three materials are all so similar. Thus structure II seems unlikely.

An examination of structure I shows that there are three geometrical isomers possible for this structure. The structures may be differentiated by the relative positions of the two water molecules with respect to one another. A scale model of this cation indicates that the structure may be visualized as three octahedra joined together at the faces, as shown in Figure 3a. The two outer octahedra are the coordination octahedra of the two cobalt ions, and the six amine groups of the three skewed bridging diamines describe a nearly regular empty octahedron between the two cobalts. This is illustrated in Figure 3b.

The three geometrical isomers can then be seen to be: one isomer in which the two water molecules are
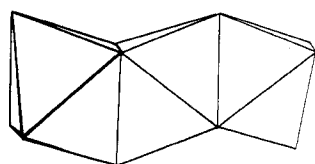
<center>A</center>
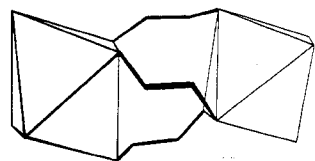
<center>B</center>

Figure 3.—Schematic representation of the structure proposed for $[Co_2(cptdin)_7(H_2O)_2]^{8+}$.

trans with respect to one another and the other two isomers are the two nonequivalent *gauche* configurations. We feel that isomer I which is slightly less soluble and which eluted from the ion-exchange column most rapidly, indicating a somewhat less polar structure, is probably the *trans* isomer. Isomers II and III would then be the two very similar *gauche* isomers.

An interesting feature of this structure is that, in contrast to the tris-bidentate structure,[6] this structure is completely stereospecific in the sense that the optical configuration about both of the metal ions is completely determined by the optical configuration of the three bridging ligands. This can be seen by considering the bridging amines and the empty octahedron that they enclose. The conformation of this octahedron shown in Figure 3b is the stable lel conformation of right chirality.[18] Thus it corresponds to the L-*ddd* as compared to the tris(ethylenediamine)-cobalt(III) ion. The ob conformation, which corresponds to the D-*ddd* isomer, can be obtained by rotating one extreme octahedron 120° with respect to the other extreme octahedron. This rotation can be accomplished without breaking any bonds, and, therefore, the ob conformation is only a sterically hindered conformer of the stable lel conformation and can have no independent existence. Since the optical configuration of the two extreme octahedra is determined by the optical configuration of the central octahedron, when all seven amine molecules in the cation are of the same configuration, only one optical structure is possible for each geometrical structure.

An examination of a model of the structure indicates that considerable steric hindrance is introduced when all of the amine molecules in a given cation are not of the same optical configuration. This is particularly true of the bridging amine molecules. Because of the fixed skewed configuration of the amine, severe

(18) This leads to the absolute configuration of the cptdin molecule given by Corey and Bailar.[6]

steric hindrance and bond strain are introduced when the three groups are not all the same. This strain is probably sufficient to preclude the stable existence of such isomers.

The requirement that the singly attached amine molecules have the same configuration as the bridging molecules should be less stringent. Models show that isomers of the L-(ddd)(llll) type complexes might possibly occur. We feel that if such isomers would have been present in our mixtures to the extent of several per cent they would have been detected, and so we can only say that our procedure must have formed them only in very small amounts, if at all.

Steric hindrance probably also accounts for the failure to replace the last water molecule on each cobalt despite the presence of large excesses of the amine used in the preparation. Rather severe steric crowding occurs when a third singly attached amine molecule is placed on a given cobalt.

An examination of the possible conformations of other *trans*-1,2-cycloalkanediamines shows that rings containing more than five carbon atoms should be sufficiently flexible to permit unhindered chelation by the two amine groups, while rings containing five or fewer carbons would be expected to introduce considerable steric strain. This predicted difference between the compounds containing five- and six-membered rings is supported by the contrast between the results reported here and the normal behavior of the tris-(*trans*-1,2-cyclohexanediamine)cobalt(III) ion.[19] This difference is also illustrated by the observation[20,21] that *trans*-1,2-cyclopentanediaminetetraacetic acid is a much weaker coordinating agent than *trans*-1,2-cyclohexanediaminetetraacetic acid.

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CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY AND THE RADIATION LABORATORY,[1]
UNIVERSITY OF NOTRE DAME, NOTRE DAME, INDIANA

Electric Moments of Complexes of Pyridine and Hexamethylphosphoramide with Metal Halides, Isocyanates, and Isothiocyanates

BY SR. MICHAEL SCHAFER AND COLUMBA CURRAN

Electric moments of bispyridine complexes of CdI_2, NiI_2, $ZnBr_2$, ZnI_2, $Zn(NCO)_2$, and $Zn(NCS)_2$ and of bishexamethylphosphoramide complexes of $CdBr_2$, CdI_2, $CoCl_2$, $CoBr_2$, CoI_2, $Co(NCO)_2$, $Co(NCS)_2$, $ZnCl_2$, $ZnBr_2$, ZnI_2, $Zn(NCO)_2$, and $Zn(NCS)_2$ have been determined in benzene or dioxane solution. The increase in moments from chlorides to iodides corresponds to the order of increasing polarizability. The complexes of cobalt and of zinc containing the NCO group appear to be isocyanates. The P–O–M bond angle in hexamethylphosphoramide complexes is appreciably less than 108°. The order of dipole moments of corresponding complexes is Co > Zn > Cd.

The electric dipole moments of dichlorobis(pyridine)-zinc and dichlorobis(γ-picoline)zinc indicate[2] a regular tetrahedral configuration for these complexes in dioxane. As an extension of this study, the moments of other tetrahedral complexes of pyridine and of hexamethylphosphoramide have been determined. The bispyridine complexes of $ZnBr_2$, ZnI_2, $Zn(NCO)_2$, $Zn(NCS)_2$, CdI_2, and NiI_2 proved to be sufficiently soluble in benzene or dioxane for dielectric constant measurements. The nickel complex is the first of its type (containing two Ni–N bonds) for which evidence has been offered[3] for a tetrahedral configuration. Infrared spectra obtained in this laboratory indicate a tetrahedral configuration for the other above compounds also. This configuration for the cadmium iodide complex is in contrast to the bridged, tetragonal

structure revealed by infrared and/or X-ray diffraction measurements for the bispyridine complexes of cadmium chloride,[4] bromide, isocyanate,[5] and isothiocyanate. The very low solubility of these complexes in benzene indicates that this solvent does not break these bridges. The low solubility of the complexes of pyridine with cobalt(II) halides in benzene and their reaction with dioxane prevented the determination of their electric moments.

Complexes of hexamethylphosphoramide, $[(CH_3)_2N]_3$-PO (HMPA), with cobalt(II) halides and isothiocyanate have been reported by Donoghue and Drago.[6] Similar compounds of zinc were prepared, along with $Co(NCO)_2(HMPA)_2$ and $Zn(NCO)_2(HMPA)_2$. The preference of palladium(II) for Pd–N bonds and the similar frequencies observed[7] for the NCO symmetric stretching vibration in $M(NCO)_2(C_5H_5N)_2$ complexes (1340, 1348, and 1347 cm.[-1] for Pd, Co, and Zn,

(1) The Radiation Laboratory is operated by the University of Notre Dame under contract with the Atomic Energy Commission. This is A.E.C. document No. COO-38-381.
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