and *trans* frequencies by interaction constants,[27] and because Van Hecke and Horrocks[22] found that the calculated CO stretching force constants parallel the raw frequency data for isosymmetric series.

It should be pointed out that there has been a recent attempt[32] to explain the variation of CO stretching frequencies of nickel carbonyl substituted with various trivalent phosphorus ligands as due entirely to σ inductive effects, with the admitted exceptions of organic phosphites, $(RO)_3P$. Although the σ bond is certainly important, there is considerably more support[22,29,31] for π bonding also being an important factor. We feel our data support the π-bonding arguments.

The novel mixed ligand compound, $(Bu_3P)(Ph_3P)Mo(CO)_4$, has one strong CO band in its infrared spectrum and is therefore assigned as the *trans* isomer. The compound contains two nonequivalent phosphorus atoms and has the expected ^{31}P nmr spectrum consisting of a pair of doublets with $J_{P-P} = 50 \pm 10$ cps, which is in good agreement with the coupling constant (*ca.* 60 cps) calculated by Verkade,[33] *et al.*, from proton nmr spectra of *trans*-$L_2Mo(CO)_4$ where L is a constrained phosphite. We believe this is the first directly measured phosphorus–phosphorus coupling in a coordination compound containing mixed ligands.[14]

Table IV. Proton Nmr Data

Compound	τ_α	τ_β	$J_{P-H\alpha}$, cps	$J_{P-H\beta}$, cps
Ph_2MeP	8.49	...	5.0	...
$Ph_2MePCr(CO)_5$	7.94	...	6.8	...
$Ph_2MePMo(CO)_5$	7.91	...	6.2	...
$Ph_2MePW(CO)_5$	7.72	...	6.8	...
Ph_2EtP	8.07	9.02	1.5	16.5
$Ph_2EtPCr(CO)_5$	7.50	8.98	7.5	17.5
$Ph_2EtPMo(CO)_5$	7.52	8.98	7.5	17.5
$Ph_2EtPW(CO)_5$	7.50	9.00	7.5	18.0
$Ph_2(t\text{-}Bu)P$	...	8.84	...	12.3
$Ph_2(t\text{-}Bu)PCr(CO)_5$	...	8.67	...	14.5
$Ph_2(t\text{-}Bu)PMo(CO)_5$	...	8.68	...	14.0
$Ph_2(t\text{-}Bu)PW(CO)_5$	...	8.67	...	14.5

Proton nmr results are listed in Table IV. The resonance positions of the α and β protons move downfield upon coordination as is expected from the greater electronegativity of phosphorus in the coordination compound than in the free phosphine. The chemical shift on coordination is not as great as on quaternization,[34] which is reasonable since phosphorus in a phosphonium salt should be more electronegative than in a coordination compound. Likewise, J_{P-C-H} and $J_{P-C-C-H}$ in the coordination compounds are intermediate between those in the free phosphine and those in phosphonium salts.[34]

Acknowledgments. We are grateful to Drs. Ivan Hyams and Gerald R. Miller for helpful discussions and aid in obtaining the infrared and nmr spectra, respectively. The National Science Foundation purchased the proton nmr instrument, and the Advanced Research Projects Agency, Department of Defense, purchased the phosphorus nmr equipment.

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The Solid-Phase *trans*-to-*cis* Isomerization of $[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$[1]

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Abstract: Studies were conducted which offer evidence that *cis*-$[Co(NH_3)_4Cl_2]IO_3$ is the product formed when solid *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ is heated. A kinetic study of this reaction gave $\Delta H^{\ddagger} = 52 \pm 6$ kcal mole^{-1} and $\Delta S^{\ddagger} = 61 \pm 18$ cal mole^{-1} deg^{-1} for the dehydration process and $\Delta H^{\ddagger} = 46 \pm 6$ kcal mole^{-1} and $\Delta S^{\ddagger} = 41 \pm 18$ cal mole^{-1} deg^{-1} for the isomerization. The isomerization is interpreted in terms of an aquation–anation reaction sequence.

The compound *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ has been found to readily undergo a distinct color change from green to dark violet during dehydration at temperatures near 110°.[3] On the basis of color and elemental analyses, Lobanov suggested that the product is *cis*-$[Co(NH_3)_4Cl_2]IO_3$. However, he did not eliminate the possibility that the violet substance is an iodato complex.

The present investigation was undertaken (1) to obtain further information which would allow a more definite structural assignment of this product, and (2) to determine the mechanism of the isomerization process. In seeking to accomplish the first goal, the spectral properties of the dark violet reaction product and a number of related substances were investigated. The visible spectra of *cis*-$[Co(NH_3)_4Cl_2]IO_3$ and other salts of *cis*-$[Co(NH_3)_4Cl_2]^+$ with colorless anions should be identical. However, few reliable spectra are available on compounds of this cation. It was therefore neces-

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(1) Abstracted in part from the Ph.D. Thesis of H. E. LeMay, Jr., University of Illinois, Oct 1966.

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(3) N. I. Lobanov, *Russ. J. Inorg. Chem.*, **4**, 151 (1959).

Table I. Analytical Data

Compound	Calcd, %					Found, %				
	C	H	N	Co	I	C	H	N	Co	I
trans-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$[a]	...	3.92	13.69	14.52	31.05	...	3.86	13.76	14.21	30.80
cis-$[Co(NH_3)_4Cl_2]IO_3$	...	3.22	15.01	15.80	34.02	...	3.40	14.83	15.45	33.72
cis-$[Co(NH_3)_4Cl_2]IO_3 \cdot H_2O$	...	3.58	14.33	...	32.46	...	3.48	14.50	...	32.73
trans-$[Co(NH_3)_4Cl_2]BrO_3$	...	3.96	17.19	...	...	...	3.73	17.04	...	...
trans-$[Co(en)_2Cl_2]IO_3$	11.28	3.76	13.19	...	29.87	11.31	3.88	13.01	...	29.53
cis-$[Co(en)_2Cl_2]IO_3 \cdot H_2O$	10.82	4.07	12.63	...	28.63	10.72	4.03	12.70	...	28.65
$[Co(NH_3)_6](IO_3)_3 \cdot 3H_2O$	...	3.24	11.33	...	51.47	...	3.31	11.27	...	51.24
$[Co(NH_3)_5Cl](IO_3)_2$	...	2.84	13.18	...	47.96	...	2.96	12.95	...	47.90
$[Co(NH_3)_4(H_2O)(IO_3)](IO_3)_2$	...	2.09	8.26	...	56.85	...	2.06	7.97	...	57.09
$[Co(NH_3)_3(H_2O)(IO_3)_2]IO_3$	...	...	6.43	9.02	58.34	...	...	6.19	9.11	58.66
$[Co(en)_2(H_2O)(IO_3)](IO_3)_2 \cdot 3HIO_3$	...	...	...	...	60.95	...	...	...	...	60.95
$[Co(NH_3)_5(H_2O)][Co(NH_3)_5(IO_3)](IO_3)_5$	...	2.36	10.34	...	56.18	...	2.37	10.41	...	56.27

[a] Calcd for H_2O: 8.80. Found: 8.70.

Table II. Visible Spectra of Iodate Salts and Iodato Complexes

Compound	Found λ_{max}, mμ[a]	Lit. λ_{max}, mμ[a,b]	Ref
$[Co(NH_3)_6][IO_3]_3$	470, 335	473, 338	*c*
$[Co(NH_3)_5(H_2O)](IO_3)_3$	490 (1.67), 347 (1.64)	490 (1.68), 345 (1.65)	*d*
$[Co(NH_3)_5Cl](IO_3)_2$	527, 352	535, 364	*e*
trans-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$	645, 475, 425	629 (1.63), 476 (1.38), 401 (1.54)	*f*
	635 (1.61), 476 (1.34), 400 (sh)	642 (1.62), 471 (1.36), 395 (1.54)	*g*
trans-$[Co(en)_2Cl_2]IO_3$	617, 412	617 (1.56), 455 (1.43), 387 (1.56)	*h*
	617 (1.57), 450 (1.45), 385 (1.58)	625 (1.54), 450 (1.40), 385 (1.64)	*i*
cis-$[Co(en)_2Cl_2]IO_3$	535, 395	536 (1.95), 392 (1.84)	*f*
	532 (1.93), 395 (1.95)	530 (1.88), 391 (1.89)	*i*
$[Co(NH_3)_4(H_2O)(IO_3)](IO_3)_2$	520, 360	...	...
$[Co(en)_2(H_2O)(IO_3)](IO_3)_2 \cdot 3HIO_3$	513, 372	...	...
$[Co(NH_3)_3(H_2O)(IO_3)_2]IO_3$	550, 382	...	...
$[Co(NH_3)_5(H_2O)][Co(NH_3)_5(IO_3)](IO_3)_5$	510–520, 355 (sh)	...	...

[a] The numbers in parentheses are log ϵ values. Those maxima given without log ϵ in the column labeled Found were taken from mull spectra. The solution spectrum of *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ was obtained in DMSO solution using 5-cm cells. The solution spectrum of *cis*-$[Co(en)_2Cl_2]IO_3$ was obtained in water using 10-cm cells. sh = shoulder. [b] Literature values are for other salts containing the same complex cation. [c] Y. Shimura and R. Tsuchida, *Bull. Chem. Soc. Japan*, **29,** 311 (1956). [d] P. Job in "Nouveau Traite de Chimie Minerale," Vol. XVIII, P. Pascual, Ed., Masson et Cie, Paris, 1959, p 462. [e] M. Linhard and W. Weigel, *Z. Anorg. Allgem. Chem.*, **266,** 49 (1951). [f] M. Linhard and W. Weigel, *ibid.*, **271,** 101 (1952). [g] N. Nakamoto, J. Fujita, M. Kobayashi, and R. Tsuchida, *J. Chem. Phys.*, **27,** 439 (1957). [h] J. Bjerrum, A. W. Adamson, and O. Bostrup, *Acta Chem. Scand.*, **10,** 329 (1956). F. Basolo, *J. Am. Chem. Soc.*, **72,** 4393 (1950).

sary to prepare a number of iodate salts and iodato complexes to aid in the structural assignment.

trans-to-*cis* isomerizations are well known in solution and have been studied in a number of solvents. However, no well-established solid phase *trans*-to-*cis* isomerization has been studied in any detail.

It has been suggested that *trans*-$[Co(NH_3)_4Cl_2]Cl$ undergoes such an isomerization at temperatures near 200°. Wendlandt, Robinson, and Yang[4] have observed that at a heating rate of 10° min^{-1} $[Co(NH_3)_4(H_2O)Cl]Cl_2$ undergoes deaquation and anation at 180°. However, an exothermic differential thermal analysis (DTA) peak was observed at 200°. It was suggested that *trans*-$[Co(NH_3)_4Cl_2]Cl$ might form as a result of the deaquation–anation of $[Co(NH_3)_4(H_2O)Cl]Cl_2$ and subsequently isomerize to the *cis* form at 200°. Watt and Butler[5] have also proposed such an isomerization in the course of a study of the thermal decomposition of *cis*- and *trans*-$[Co(NH_3)_4Cl_2]Cl$.

Throughout this paper, the dark violet reaction product will be represented by the formula *cis*-$[Co(NH_3)_4Cl_2]IO_3$. Evidence to substantiate that structural assignment will be presented and discussed later in this paper.

Experimental Section

Preparation of Compounds. The compounds *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$,[3] *cis*-$[Co(NH_3)_4Cl_2]IO_3$,[3] and *trans*-$[Co(NH_3)_4Cl_2]BrO_3$[6] were prepared as described in the literature. Analyses are shown in Table I. The visible absorption maxima of the *trans*-dichloro iodate and some related complexes are reported in Table II together with literature values for other salts containing the same complex cations. The agreement between the experimental values and those reported in the literature supports the structural assignments.

***cis*-$[Co(NH_3)_4Cl_3]IO_3 \cdot H_2O$.** A dark violet complex of this empirical formula was prepared from aqueous solution. A mixture of 0.2 g of *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ and 3 ml of water was heated on a steam bath until all the *trans* isomer had dissolved and a violet solution was obtained. This solution was evaporated to dryness *in vacuo* over phosphorus(V) oxide.

This evaporation first yielded a red-violet residue, the visible mull spectrum of which exhibited a maximum at 525 mμ and a shoulder at 370 mμ. This spectrum is similar to that of the *cis*-$[Co(NH_3)_4(H_2O)Cl]^+$ cation and suggests that the residue may have been partly *cis*-$[Co(NH_3)_4(H_2O)Cl]Cl \cdot IO_3 \cdot nH_2O$. We have found the compound *cis*-$[Co(NH_3)_4(H_2O)Cl]SO_4$ to exhibit a mull spectrum with distinct maxima at 525 and 370 mμ. The red-violet residue always contained some amount of a darker violet substance and could not be obtained in a pure state. The darker violet substance could be obtained easily from the red-violet one by further evacuation at room temperature or by heating to 100–110°.

The absorption spectrum of the dark violet substance was virtually identical with that of *cis*-$[Co(NH_3)_4Cl_2]IO_3$ in the infrared (both the

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sodium chloride and cesium bromide regions), and in the visible region as well. However, the complex prepared from solution contained a molecule of water per cobalt atom.

Efforts to completely dehydrate the substance prepared from solution were unsuccessful. When heated at 110° for 50 hr, a weight loss of 3.67% was observed (loss of one molecule of water per cobalt would correspond to 4.60%), but some decomposition was visually evident. Further heating was accompanied by increasing amounts of brown decomposition products.

***cis*-$[Co(en)_2Cl_2]IO_3\cdot H_2O$.** One gram of finely pulverized *cis*-$[Co(en)_2Cl_2]Cl\cdot H_2O$ was added to 3 ml of ice-cold water. This was stirred for several minutes to obtain a nearly saturated solution, and 10 ml of saturated (at room temperature) potassium iodate solution was added. The resulting mixture was stirred briefly and then quickly filtered through a coarse sintered-glass filter to remove any undissolved *cis*-$[Co(en)_2Cl_2]Cl$. The filtrate was cooled in ice with constant stirring, whereupon the violet iodate salt slowly crystallized from solution. The product was removed from the solution by filtration and washed once with a 50% ethanol–water mixture, then with ethanol, and finally with ether. It was dried in air.

This product was then recrystallized from cold water. For this, the crude *cis*-$[Co(en)_2Cl_2]IO_3\cdot H_2O$ (0.90 g) was added to 6 ml of ice-cold water. A saturated potassium iodate solution (5 ml) was added and the resulting solution stirred for several minutes in an ice bath. The product was collected and washed as before and dried overnight *in vacuo* over phosphorus(V) oxide, yield 0.76 g (52% based on the starting chloride complex).

When *cis*-$[Co(en)_2Cl_2]IO_3\cdot H_2O$ was heated at 70–110° under vacuum for 12–24 hr, it slowly lost its lattice water. During this time, the visible absorption spectrum of the complex remained unchanged.

$[Co(NH_3)_6](IO_3)_3\cdot 3H_2O$. A saturated solution of potassium iodate (50 ml) was added to a hot solution of 1.5 g of $[Co(NH_3)_6]Cl_3$ in 20 ml of water. Precipitation of the pale yellow iodate salt of the complex began immediately and continued while the solution cooled. The product was collected by filtration, washed with cold water, ethanol, and ether, and dried *in vacuo* over phosphorus(V) oxide, yield 3.8 g (93%). The lattice water was easily lost on heating at 100–110°.

$[Co(NH_3)_5Cl](IO_3)_2$. When 1.5 g of $[Co(NH_3)_5Cl]Cl_2$ was added to 50 ml of a saturated potassium iodate solution, the red-violet iodate formed immediately. This was collected by filtration, washed with cold water, ethanol, and ether, and air-dried, yield 1.37 g (91%). Purification was achieved by recrystallization from water. Water (60 ml) at room temperature was added to 1.37 g of the complex, and the resulting solution was filtered. Saturated potassium iodate solution (30 ml) was added to the filtrate. The resulting precipitate was collected, washed as before, and dried *in vacuo* over phosphorus(V) oxide.

$[Co(NH_3)_4(H_2O)(IO_3)](IO_3)_2$. A solution containing 1 g of $[Co(NH_3)_4(H_2O)_2]_2(SO_4)_3$ in 25 ml of water was added dropwise to 50 ml of saturated potassium iodate solution. A pale pink-violet precipitate formed immediately. This was removed by filtration, washed with cold water, ethanol, and ether, and air-dried, yield 20.5 (92%).

The very insoluble crude product was added to 40 ml of water and the resulting mixture was stirred mechanically for 24 hr. After this time, 10 ml of saturated potassium iodate solution was added, and the solution was stirred for an additional hour. The compound was removed by filtration, washed with cold water, ethanol, and ether, and dried *in vacuo* over phosphorus(V) oxide, yield 1.9 g (87%).

The water in this complex could not be removed by heating at 135°. After 20 hr, a weight loss of 1.31% was observed (the calculated amount of water in this compound is 2.69%), but decomposition was evident.

$[Co(NH_3)_5(H_2O)][Co(NH_3)_5(IO_3)](IO_3)_5$. When $[Co(NH_3)_5(H_2O)](IO_3)_3\cdot 2H_2O$ is heated in the solid phase to 110°, it reportedly loses three molecules of water with the formation of $[Co(NH_3)_5(IO_3)](IO_3)_2$.[3] However, efforts to obtain this product were unsuccessful. When $[Co(NH_3)_5(H_2O)](IO_3)_3\cdot 2H_2O$ was heated, a change of color from red-orange to rose-red occurred. Measurements of the loss of weight accompanying this reaction consistently showed that only 2.5 molecules of water had been removed per molecule of $[Co(NH_3)_5(H_2O)](IO_3)_3\cdot 2H_2O$. The observed losses of weight were 6.10, 6.28, 6.15, and 6.50% for four experiments, each carried out on a different preparation. The calculated weight loss corresponding to loss of 2.5 molecules of water per cobalt atom from this complex is 6.23%. Furthermore, the visible mull spectrum of the thermal decomposition product exhibited a broad absorption maximum centered at approximately 510 mμ which seemed to be comprised, in part, of a maximum at 490 mμ due to the $[Co(NH_3)_5(H_2O)]^{+3}$ cation. Finally, the elemental analyses showed that a residual half-molecule of water per cobalt atom was present even after heating to 160°. It is proposed that this residual water is in the coordination sphere and that the product of the deaquation is $[Co(NH_3)_5(H_2O)][Co(NH_3)_5(IO_3)](IO_3)_5$.

$[Co(NH_3)_3(H_2O)(IO_3)_2]IO_3$. A solution of 2 g of recrystallized *trans*-$[Co(NH_3)_3(H_2O)Cl_2]Cl$ in 250 ml of water was added to a solution containing 15 g of iodic acid in 50 ml of water. A gray precipitate formed immediately. When this reaction mixture was heated on a steam bath for 2–4 hr, a violet product was obtained. This was removed by filtration and washed with cold water, ethanol, and ether. It was dried to constant weight at 100°. Analysis of this product indicated the presence of one molecule of water per cobalt atom. Since this water was not lost even after extended periods at 100°, it is probably (though not necessarily) in the coordination sphere.

$[Co(en)_2(H_2O)(IO_3)](IO_3)_2\cdot 3HIO_3$. This pale violet compound was prepared by the reaction of $[Co(en)_2CO_3]Cl$ with iodic acid as described in the literature for the preparation of $[Co(en)_2(IO_3)_2]IO_3\cdot 3HIO_3$.[7] Analysis of the product obtained in this study suggests the presence of one molecule of water per cobalt atom not noted in the original work.

Upon heating above 100° in the solid phase, there was a gradual loss in weight accompanied by decomposition. Thus, the water appears to be in the coordination sphere.

Physical Measurements. Electronic spectra were obtained on a Cary Model 14M recording spectrophotometer. Transmittance mull spectra were obtained using Nujol mulls applied to Whatman No. 1 filter paper and run against filter paper soaked in Nujol as a reference. Each mull spectrum was obtained at three mull concentrations to aid in assigning the wavelengths of absorption maxima.

Infrared spectra were obtained on Nujol mulls using a Beckman IR5A recording spectrophotometer with sodium chloride optics. To aid in assigning vibrational frequencies which were masked by Nujol, and also to verify peak locations, spectra were also obtained on disks of the compounds pelleted with KBr using a Perkin-Elmer Model 21 recording spectrophotometer with sodium chloride optics.

X-Ray diffraction data were obtained using a Norelco recording diffractometer and also by means of a 14.32-cm diameter camera. Nickel-filtered Cu Kα radiation was used in both methods. The samples used to obtain the powder photographs were contained in 0.5-mm Lindemann glass capillaries, and exposure times ranged from 12 to 24 hr.

Thermogravimetric analyses (TGA) were obtained using an automatic recording thermobalance built according to the specifications of Groot and Troutner.[8] Samples weighing 0.2 to 0.5 g and heated in a static air atmosphere at a rate of 1° min^{-1} were employed.

Differential thermal analyses (DTA) were obtained in a static air atmosphere using an automatic recording instrument which has been described in part by Grim and Rowland.[9] The instrument which they describe was modified by employing a Beckman photocell recorder to measure the differential thermocouple signals. The applied temperature was followed by means of a thermocouple–potentiometer arrangement. A scan rate of 2° min^{-1} was employed.

Elemental analyses were carried out in the University of Illinois laboratories by Mr. Josef Nemeth and his staff.

The Rate of Dehydration of *trans*-$[Co(NH_3)_4Cl_2]IO_3\cdot 2H_2O$. The dehydration of *trans*-$[Co(NH_3)_4Cl_2]IO_3\cdot 2H_2O$ was followed isothermally on a thermobalance. All weighings were made on the balance before heating was started, and a minor correction factor was applied for sample buoyancy.

After the initial weighing, the sample and sample holder were removed from the balance, and the oven was allowed to equilibrate at slightly above the temperature desired for the kinetic run. The sample and sample holder were then placed in the oven, and weight loss was followed as a function of time. Generally, the weight loss was automatically recorded throughout the entire determination. At 70°, however, only initial measurements were taken automatically; further readings were made manually after the reaction had slowed.

The Rate of Isomerization of *trans*-$[Co(NH_3)_4Cl_2]IO_3$. The *trans* compound $[Co(NH_3)_4Cl_2]IO_3$ is soluble in DMSO and only slowly

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[7] N. I. Lobanov, *Russ. J. Inorg. Chem.*, 2, 81 (1957).

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Table III. The Vibrational Frequencies of a Number of Iodate Salts in the 600–900-Cm^{-1} Region[a]

Compound	ν_1 (sym str) and $2\nu_2$ (sym bend), cm^{-1}	ν_3 (asym str), cm^{-1}	$-NH_2$ rock, cm^{-1}
NH_4IO_3	730 (s)	790 (sh, m)	. . .
$[Co(NH_3)_6](IO_3)_3 \cdot 3H_2O$	755 (s, b)	790 (s)	873 (m, b)
$[Co(NH_3)_6](IO_3)_3$	774 (s, b)	815 (m)	870 (m, b)
$[Co(NH_3)_5(H_2O)](IO_3)_3 \cdot 2H_2O$	728 (sh, s), 740 (s, b)	783 (sh, s)	865 (m, b)
$[Co(NH_3)_5(H_2O)](IO_3)_3 \cdot HIO_3$	720 (s), 770 (s)	788 (sh, s)	810 (sh, s), 870 (w)
$[Co(NH_3)_5Cl](IO_3)_2$	763 (s)	790 (s)	850 (sh, w), 890 (m)
trans-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$	761 (s), 782 (s)	806 (s)	855 (w)
trans-$[Co(en)_2Cl_2]IO_3$	748 (s), 776 (s)	794 (s)	825 (w)
cis-$[Co(NH_3)_4Cl_2]IO_3$	718 (s)	780 (s, b)	850 (sh, ml)
cis-$[Co(en)_2Cl_2]IO_3 \cdot H_2O$	718 (s), 756 (s)	769 (s)	785 (s), 795 (sh, s)
cis-$[Co(en)_2Cl_2]IO_3$	717 (s)	774 (s)	814 (s), 886 (w)
cis-$[Co(en)_2Cl_2]IO_3 \cdot 3HIO_3$	720 (s), 758 (s)	778 (sh, s, b)	805 (s), 840 (s)

[a] s = strong, m = medium, w = weak, sh = shoulder, b = broad.

solvolyzed in that solvent. In contrast, the *cis* isomer exhibits negligible solubility in DMSO except upon long standing in contact with this solvent. This difference in solubility allowed the *trans* isomer to be leached from solid reaction mixtures. Since the concentration of the *trans* isomer in the DMSO solution could be determined spectrophotometrically, it was possible to determine the extent of isomerization in a reaction mixture as a function of time. The procedure is outlined below.

Kinetic runs were conducted by heating 0.04- to 0.08-g samples of *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ in uncapped 5-ml vials. Four to six of these vials were heated simultaneously during a single experiment. These were removed from the heating apparatus at various time intervals and quickly cooled to room temperature where the isomerization proceeded at a negligible rate. Each sample was then pulverized and weighed into a 25-ml volumetric flask. DMSO was added, and the resulting mixture was shaken for approximately 5 min before being filtered into a 5-cm quartz sample cell. The visible spectrum of the filtered solution was scanned as soon as possible after dissolution. The concentration of *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ (and hence its mass in the original solid sample) was calculated from the observed absorbance of the DMSO solution at the 635-mμ absorption maximum. Solutions of *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ in DMSO were found to follow Beer's law with ϵ 41.2 at 635 mμ. Furthermore, little change in absorbance occurs at this wavelength within 30 min at room temperature (although larger increases were observed in the vicinity of 550 mμ). In calculating the concentration of the *trans* isomer in solutions obtained from the reaction mixture, it was assumed that the contribution of dissolved *cis*-$[Co(NH_3)_4Cl_2]IO_3$ to the total absorbance would be negligible owing to the very slight solubility of the *cis* isomer. The quantity of *cis*-$[Co(NH_3)_4Cl_2]IO_3$ in the solid sample was obtained by difference. Knowledge of the relative amounts of *cis* and *trans* isomers present in the reaction mixture as a function of time allows the determination of a rate law for the isomerization process in terms of the fraction of the *trans* isomer which has reacted. Although this actually gives only the rate at which the *trans* isomer disappears, no intermediates were detected in the isomerization process, and it is assumed that any steps between the disappearance of the *trans* isomer and the appearance of the *cis* isomer must be relatively rapid. Hence the rate at which the *trans* isomer disappears is referred to as the rate of isomerization.

Temperature control during the course of the kinetic runs was maintained by placing the sample in the drying chamber of an Abderhalden drying apparatus and a liquid of appropriate boiling point in the boiler. Methanol (bp 64.6°), benzene-water azeotrope (bp 69.9°), isopropyl alcohol (bp 82.4°), carbon tetrachloride (bp 76.8°), and isopropyl acetate (bp 88.0°) were employed. In this way the temperature could be controlled within about ±0.5°.

Each kinetic run was made on a separate preparation of *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$. These samples were not pulverized except where noted. They were stored in tightly capped vials prior to reaction and were not desiccated.

The effect of reduced pressure on the rate of isomerization was investigated by reducing the pressure within the Abderhalden apparatus to 50–100 torr. The effect of water vapor was studied by sealing a small vial containing water in such a way that only the water vapor came in contact with the complex. The reaction did not appear to be photosensitive.

Results

Spectra. The visible absorption maxima of the complexes reported above are given in Table II. The compound formulated as *cis*-$[Co(NH_3)_4Cl_2]IO_3$ and whose identity we wish to establish exhibited a visible transmittance mull spectrum with a maximum at 535 mμ. It slowly dissolved in water to give a pink solution which possessed absorption maxima at 510 mμ (log ϵ 1.72) and 353 mμ (log ϵ 1.67), in agreement with literature values for *cis*-$[Co(NH_3)_4(H_2O)_2]^{+3}$.[10] The *cis*-$[Co(NH_3)_4Cl_2]IO_3$ also dissolved slowly in DMSO when allowed to stand in contact with this solvent for several hours. The resulting solution exhibited an absorption maximum at 545 mμ and a shoulder at 375 mμ.

The infrared spectra of the iodate salts in the 600–900-cm^{-1} region are shown in Table III. The iodate ion has C_{3v} symmetry and hence four infrared-active modes. Two of these, the symmetric stretch, ν_1, and the asymmetric stretch, ν_3, occur in the 600–900-cm^{-1} region. The first overtone of the symmetric bend, $2\nu_2$, occurs at approximately the same frequency as ν_1.[11] Since both modes of vibration have A_1 symmetry, Fermi resonance can take place. It is not possible to distinguish between ν_1 and $2\nu_2$, and hence these have been included in a single column in Table III. The band assignments were made by analogy to the spectra of simple salt iodates which have been reported and interpreted elsewhere.[11,12] The amine modes which occur in the 700–900-cm^{-1} region were assigned by comparison with the spectra of the corresponding chloride salts. These vibrations were usually less intense and at higher frequencies than the iodate modes so that the assignments seemed to be without ambiguity.

The complex *cis*-$[Co(NH_3)_4Cl_2]IO_3$ possesses two strong but relatively broad iodate modes in the 600–900-cm^{-1} region, one centered at 718 cm^{-1} and the other at 780 cm^{-1}. The infrared spectrum of *cis*-$[Co(NH_3)_4Cl_2]IO_3 \cdot H_2O$ is the same as that of the anhydrous material except for the occurrence of an oxygen–hydrogen stretching vibration at 3400 cm^{-1} in the spectrum of the hydrate. The visible spectra of these two salts are identical. It is noteworthy that the pres-

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[10] M. Mori, R. Tsuchiya, R. Takemura, and E. Matsuda, *Bull. Chem. Soc. Japan*, **34**, 1757 (1961).

[11] S. T. Shen, Y. T. Yao, and T. Wu, *Phys. Rev.*, **51**, 235 (1937).

[12] W. E. Dasent and T. C. Waddington, *J. Chem. Soc.*, 2429 (1960).

Table IV. The Vibrational Frequencies of a Number of Iodato Complexes in the 600–900-Cm^{-1} Region[a]

Compound	ν_1 (O–I str), cm^{-1}	ν_{3a} (IO_2 asym str), cm^{-1}	ν_{3b} (IO_2 sym str), cm^{-1}	–NH_2 rock, cm^{-1}
$[Co(NH_3)_5(IO_3)]^{+2}$ [b]	690 (sh, m)	782 (sh, m)	747 (s, b)	870 (m)
$[Co(NH_3)_4(H_2O)(IO_3)](IO_3)_2$	702 (s)	788 (s)	755(s)	851 (w), 882 (m)
$[Co(en)_2(H_2O)(IO_3)](IO_3)_2 \cdot 3HIO_3$	707 (s)	793 (s)	745 (sh, s)	?
$[Co(NH_3)_3(H_2O)(IO_3)_2]IO_3$	680 (s)	793 (s)	750 (sh, s)	880 (w)
$K_2Mn(IO_3)_6$	630 (s)	786 (s)	755 (s)	. . .
$(NH_4)_2Mn(IO_3)_6$	640 (s)	789 (s)	758 (s)	. . .
$K_2Pb(IO_3)_6$	695 (s)	783 (sh, m)	757 (s)	. . .
$K_2Ti(IO_3)_6$	656 (s)	787 (s)	757 (s)	. . .
$Fe(IO_3)_3$	695 (s)	808 (m)	757 (s)	. . .
$Pb(IO_3)_2$	690 (s)	770 (m)	720 (s)	. . .

[a] s = strong, m = medium, w = weak, sh = shoulder. [b] $[Co(NH_3)_5(H_2O)][(Co(NH_3)_5(IO_3)](IO_3)_5$.

Table V. The Prominent Lines of the X-Ray Powder Patterns of *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ and *trans*-$[Co(NH_3)_4Cl_2]BrO_3$[a]

trans-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ *d*, A	*trans*-$[Co(NH_3)_4Cl_2]BrO_3$ *d*, A
8.42 (vw)	. . .
5.74 (m)	. . .
5.48 (vw)	5.48 (m)
4.95 (w)	. . .
4.76 (s)	4.77 (m)
4.39 (s)	4.41 (m)
4.22 (s)	4.25 (s)
4.07 (m-s)	4.03 (w-m)
3.80 (vw)	3.85 (s)
3.67 (vw)	3.72 (w)
3.19 (m)	3.10 (w)
2.93 (m)	2.91 (m)
2.74 (m)	2.70 (w)
2.64 (m)	2.63 (m)
2.58 (w)	. . .
2.54 (w)	2.55 (w)
2.47 (w)	. . .
. . .	2.19 (w)
2.08 (vw)	. . .
2.05 (vw)	. . .

[a] s = strong, m = medium, w = weak, vw = very weak.

ence of lattice water in several of the iodate complexes affects the position of the iodate modes, presumably through hydrogen bonding to the iodate.

The infrared spectra of the iodato complexes are shown in Table IV. The iodate can coordinate through the iodine atom (giving C_{3v} symmetry to the iodate) or through the oxygen atom (giving C_s symmetry). The band assignments have been made assuming the latter type of coordination in analogy to iodato complexes previously studied.[10] The assignments, however, are necessarily tentative since the compounds used in this study contain ionic as well as covalently bonded iodate ions. Further discussion of the mode of coordination will be presented later.

TGA, DTA, and X-Ray Studies. When *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ was heated at a rate of 1° min^{-1}, loss of water began at approximately 70°. Only a single inflection at 110° was observed in the TGA curve. The dehydration was complete at approximately 160°, and the weight remained constant until 170–180° was reached, whereupon loss of ammonia began to occur.

The DTA curve exhibited two relatively broad endothermic peaks and one which was sharp and exothermic. The main endothermic peak was centered at 110–115°. This coincides with the inflection point of the TGA curve and therefore appears to be due to the loss of water from the solid. This endothermic peak had a less intense endothermic shoulder at 90–95°, but no corresponding changes were found in the TGA. However, it is possible that a corresponding inflection in the TGA was not observed because of instrumental limitations. The strong exothermic peak occurred at 175° and was probably due to a redox reaction between IO_3^- and the coordinated NH_3. The DTA and TGA curves of *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ are shown in Figure 1.

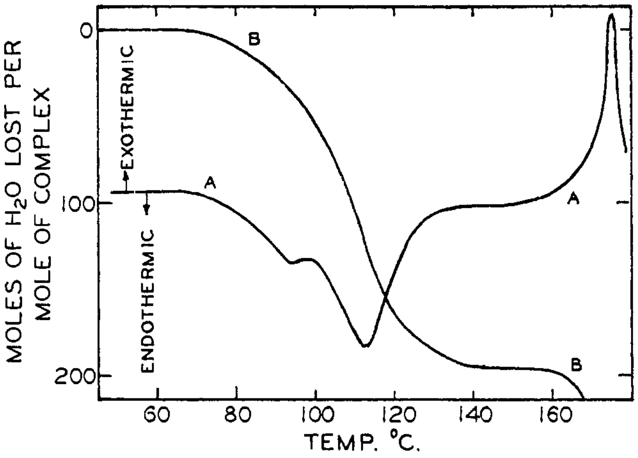

Figure 1. The DTA curve (A) and TGA curve (B) of *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$. The vertical scale for the DTA curve is arbitrary.

The prominent lines of the X-ray powder patterns of *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ and *trans*-$[Co(NH_3)_4Cl_2]BrO_3$ are given in Table V. As can be seen, the two substances have very similar lattices. However, only the iodate was found to undergo isomerization in the solid state.

As *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ was heated in the solid phase, the X-ray reflections of this substance broadened and decreased in over-all intensity until the formation of *cis*-$[Co(NH_3)_4Cl_2]IO_3$ was complete. This latter compound was microcrystalline, exhibiting no diffraction pattern. Furthermore, no intermediate crystal phases could be detected during the course of the isomerization. Attempts to obtain a crystalline product by slowly heating *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ in the presence of water vapor were unsuccessful.

Rate Studies. The dehydration of *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ followed a rate law of the type

$$\ln(1 - \alpha) = c - kt$$

where α is the fraction of dehydration which has occurred at any time t. The weight of lattice water evolved was assumed to equal the measured loss of weight of the complex. The initial weight of lattice water in the complex was determined in two ways. On most occasions it was calculated assuming the presence of 2.00 moles of lattice water per mole of complex. On certain other occasions it was measured at the end of the kinetic run by increasing the temperature of the sample to 120–130° and holding it there until constant weight was achieved. These measured values usually agreed with the calculated values within 5%.

At 80, 85, 90, and 95°, the constant c was always less than 0.125, but its value was dependent upon the thermal lag between the sample and the oven. Dehydration at these temperatures was frequently characterized by a very brief rapid weight loss due, perhaps, to loss of occluded water or to slight overheating of the furnace. At 70°, however, induction periods of up to 50 hr were observed. The rate constants for the dehydration studies are shown in Table VI. Because the dehydration proceeded very slowly at 70°, the reaction was never studied for a complete half-life at this temperature. However, the reaction was followed for two to three half-lives at the other temperatures.

Table VI. The Rate of Dehydration of *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$

Temp, °C	k, sec^{-1}	Av k, sec^{-1} [a]
70	3.5×10^{-6}	$(2.0 \pm 1.0) \times 10^{-6}$
	1.2×10^{-6}	
	1.4×10^{-6}	
80	3.5×10^{-5}	$(3.5 \pm 0.6) \times 10^{-5}$
	2.6×10^{-5}	
	4.3×10^{-5}	
85	5.7×10^{-5}	$(7.1 \pm 0.9) \times 10^{-5}$
	7.8×10^{-5}	
	7.8×10^{-5}	
90	1.4×10^{-4}	$(1.4 \pm 0.2) \times 10^{-4}$
	1.7×10^{-4}	
	1.0×10^{-4}	
	1.6×10^{-4}	
95	2.4×10^{-4}	$(4.2 \pm 1.2) \times 10^{-4}$
	4.5×10^{-4}	
	5.8×10^{-4}	

[a] Uncertainties are deviations from the mean.

The isomerization of *trans*-$[Co(NH_3)_4Cl_2]IO_3$ followed the same rate law as that found for dehydration, except that α represents extent of isomerization. The rate constants are given in Table VII. The constant c was zero except at temperatures of 76.8° and lower at which temperatures induction periods were observed. Induction periods of up to 20 hr were observed at 69.9°. At 64.6° very little reaction took place during the first 500 hr, after which the reaction proceeded at the expected rate.

Using absolute rate theory and the method of least squares, these kinetic data yield $\Delta H^{\ddagger} = 52 \pm 6$ kcal mole^{-1} and $\Delta S^{\ddagger} = 61 \pm 18$ cal mole^{-1} deg^{-1} for the dehydration process and $\Delta H^{\ddagger} = 46 \pm 6$ kcal mole^{-1} and $\Delta S^{\ddagger} = 41 \pm 18$ cal mole^{-1} deg^{-1} for the isomerization.

The error limits given are twice the standard deviations (95% confidence level) and seem to indicate that the two processes studied have the same or nearly the same activation parameters.

Table VII. The Rate of Isomerization of *trans*-$[Co(NH_3)_4Cl_2]IO_3$

Temp, °C	k, sec^{-1}	Av k, sec^{-1} [a]
69.9	2.3×10^{-6}	$(3.2 \pm 0.6) \times 10^{-5}$
	3.8×10^{-6}	
	3.4×10^{-6}	
76.8	1.1×10^{-5}	$(1.3 \pm 0.2) \times 10^{-5}$
	1.3×10^{-5}	
	1.6×10^{-5}	
82.4	2.8×10^{-5}	$(3.5 \pm 0.5) \times 10^{-5}$
	4.0×10^{-5}	
	4.0×10^{-5}	
	3.1×10^{-5}	
88.0	11.5×10^{-5}	$(9.0 \pm 1.7) \times 10^{-5}$
	7.6×10^{-5}	
	7.9×10^{-5}	

[a] Uncertainties are deviations from the mean.

Reducing the total pressure from 1 atm to *ca.* 40–80 torr produced a fivefold increase in the rate of isomerization at 82.4°. Isomerization was also observed when samples were kept under vacuum over phosphorus(V) oxide at room temperature. In fact, all attempts to dehydrate *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ led to isomerization.

When *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ was heated in closed vials so that water vapor remained in contact with the sample, the rate of isomerization was increased. Approximate rate constants obtained at 82.4° indicated a four- to fivefold increase in rate when heating was conducted in this manner. However, it was observed on some occasions that condensation occurred on the sample. This appeared to take place only during the later stages of reaction and rapid reaction was evident prior to any evidence of condensation.

Because *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ was prepared by relatively rapid precipitation from solution, it was never obtained as very large crystals. Pulverization of these samples had little or no effect on the rate of isomerization.

In contrast to the iodate salt, *trans*-$[Co(NH_3)_4Cl_2]BrO_3$ did not undergo a solid-phase isomerization. When heated at a rate of 1° min^{-1}, a freshly prepared sample lost moisture beginning at temperatures as low as 40° and attained a constant weight by the time the temperature reached 70°. At 105°, the compound decomposed violently.

Discussion

Identification of *cis*-$[Co(NH_3)_4Cl_2]IO_3$. The green-to-violet color change which occurs when *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ is heated in the solid phase is reminiscent of the *cis–trans* isomerizations which are familiar in the solution chemistry of *trans*-$[Co(en)_2Cl_2]^+$.[13] Since the product of this solid-phase reaction is violet, and because its elemental analysis indicates only the loss of water during this reaction, it has been suggested that the product is *cis*-$[Co(NH_3)_4Cl_2]IO_3$.[1]

Unfortunately, there are few reliable data involving *cis*-$[Co(NH_3)_4Cl_2]^+$ and its salts which would allow ready comparison with the substance formulated as *cis*-[Co-

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(13) See, for example, F. Basolo and R. G. Pearson, "Mechanisms of Inorganic Reactions," John Wiley and Sons, Inc., New York, N. Y., 1958, p 241; M. L. Tobe and D. W. Watts, *J. Chem. Soc.*, 4614 (1962); 2991 (1964).

$(NH_3)_4Cl_2]IO_3$. Although several reports of the visible spectrum of *cis*-$[Co(NH_3)_4Cl_2]Cl$ appear in the literature, there is much disagreement between them. The disagreements probably result from the rapid hydrolysis of this complex in water, its isomerization in methanol, its confusion with *cis*-$[Co(NH_3)_4(H_2O)Cl]Cl_2$, or a combination of these factors.

Absorption maxima have been reported to occur at 390 and 590 mμ in methanol solution,[14] but it has been reported elsewhere that isomerization to the *trans* isomer occurs readily in this solvent.[15] A maximum at 540 mμ in aqueous solutions has been reported by three research groups.[15–17] However, it has been noted by yet another group that the aquation of *cis*-$[Co(NH_3)_4Cl_2]Cl$ was too rapid for them to study by conventional spectrophotometric techniques.[18] The spectrum of a single crystal of *cis*-$[Co(NH_3)_4Cl_2]Cl$ has been reported.[19] However, the rapid aquation of this compound would seem to preclude the possibility of obtaining crystals for such a study. It is possible that *cis*-$[Co(NH_3)_4(H_2O)Cl]Cl_2$ was mistaken for *cis*-$[Co(NH_3)_4Cl_2]Cl$. This suggestion is supported by the close agreement between the spectrum of the chloro–aquo complex and the spectrum reported for the single crystal. The chloro–aquo cation exhibits a maximum at 525 mμ. The single crystal was reported to have a maximum at 522–525 mμ. Finally, a reflectance spectrum is reported in which the main visible absorption maximum is almost as low in wavelength as that of $[Co(NH_3)_4(H_2O)_2]^{+3}$.[20]

The absorption maximum at 535 mμ exhibited by *cis*-$[Co(NH_3)_4Cl_2]IO_3$ is in the region expected for the *cis*-$[Co(NH_3)_4Cl_2]^+$ cation. The analogous *cis*-$[Co(en)_2Cl_2]^+$ cation also exhibits a maximum at about 535 mμ.[21,22] This is as expected, for the absorption maxima of ethylenediamine complexes generally occur at approximately the same wavelengths or at slightly shorter wavelengths than those of their ammine analogs. Furthermore, we have observed that the visible mull spectrum of the substance formed by deaquation of $[Co(NH_3)_4(H_2O)_2]Cl_3$ has a maximum at approximately 535 mμ. Reportedly, this deaquation product is *cis*-$[Co(NH_3)_4Cl_2]Cl$.[10] However, we have observed that loss of ammonia begins before complete deaquation has occurred. The reaction product also shows some absorption in the 600–700-mμ region due possibly to $[CoCl_4]^{-2}$. Similar spectra have been reported previously as a result of a study of this deaquation reaction using dynamic reflectance spectroscopy.[23] It was found that as $[Co(NH_3)_4(H_2O)_2]Cl_3$ was heated, the absorption maximum at 510 mμ shifted to longer wavelengths. However, it is not possible to unambiguously assign an absorption maximum to the product (supposedly *cis*-$[Co(NH_3)_4Cl_2]Cl$) because the two deaquation steps overlap and deammination begins before deaquation is complete. The spectrum assigned to *cis*-$[Co(NH_3)_4Cl_2]Cl$ in ref 23 showed considerable absorption in the 600–700-mμ region, due, we believe, to deamminated and/or reduction products, including $[CoCl_4]^{-2}$.

The infrared spectrum of *cis*-$[Co(NH_3)_4Cl_2]IO_3$ appears to offer a stronger substantiation of Lobanov's structural assignment than can be obtained at this time from visible spectroscopy. A comparison of the iodate stretching frequencies reported in Tables III and IV suggests that coordination of the iodate ion to cobalt(III) lowers the frequency of one of these modes or produces a mode of lower frequency than that exhibited by the iodate ion. The compounds possessing coordinated iodate each exhibit a band in the 680–707-cm^{-1} region. The low-frequency iodate vibration of salts containing only ionic iodate is in the 717–780-cm^{-1} area. The iodate modes of *cis*-$[Co(NH_3)_4Cl_2]IO_3$ are at 718 and 780 cm^{-1}. Not only does the spectrum of this compound in the iodate region appear more like that of compounds containing only ionic iodate, but it is especially like that of *cis*-$[C(en)_2Cl_2]IO_3$. This latter compound, identified by its elemental analysis and visible spectrum, exhibits absorption at 717 and 774 cm^{-1}. In the same manner, the iodate modes of *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ and *trans*-$[Co(en)_2Cl_2]IO_3$ are similar. In each of these two sets of compounds, the ammine complexes possess broader iodate bands than the ethylenediamine compounds.

The shift in iodine–oxygen stretching frequencies upon coordination of IO_3^- to cobalt(III) is indicative of the mode of coordination to the iodate. The iodine–oxygen bond has been shown to possess some double-bond character.[24] This may be considered to result from the superposition of $p\pi \rightarrow d\pi$ bonding from oxygen to iodine upon the $I \rightarrow O$ σ bonding. Attachment of oxygen to a positive atom should lessen the $p\pi \rightarrow d\pi$ back-bonding and hence lower the iodine–oxygen bond order and the iodine–oxygen stretching frequency.

The sulfite ion has the same symmetry as the iodate ion and is thought to coordinate to cobalt(III) through the sulfur atom when functioning as a monodentate ligand. Such coordination leads to an increase in stretching frequencies[25,26] in agreement with the discussion in the previous paragraph.

Furthermore, in a recent study of the infrared spectra of a number of iodato complexes, several of which contained ions of the type $M(IO_3)_6^{-2}$, both the spectral shifts and splittings which were observed suggest coordination of the iodate through the oxygen atom.[10] Such coordination would be expected not only to produce a stretching mode of lower frequency, but also to split the doubly degenerate asymmetric stretch, ν_3, of the iodate. Coordination through the iodine atom, on the other hand, would not disturb the symmetry of the iodate group greatly and would not give rise to additional iodine–oxygen modes. As previously noted, *cis*-$[Co(NH_3)_4Cl_2]IO_3$ exhibits only two iodate vibrational frequencies in the 600–900-cm^{-1} region. This is

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(14) J. Rigg and E. Sherwin, *J. Inorg. Nucl. Chem.*, 27, 653 (1965).

(15) R. C. Brasted and C. Hirayama, *J. Phys. Chem.*, 63, 780 (1959).

(16) R. Luther and A. Nikolopulos, *Z. Physik. Chem.*, 82, 366 (1913).

(17) J. P. Mathieu, *Bull. Soc. Chim. France*, 3, 463 (1936), is frequently cited as a reference for the visible spectrum of *cis*-$[Co(NH_3)_4Cl_2]Cl$. However, this work simply cites ref 16.

(18) R. G. Pearson, C. R. Boston, and F. Basolo, *J. Phys. Chem.*, **59**, 304 (1955).

(19) M. Kobayasi and R. Tutida, *J. Chem. Soc. Japan*, **60**, 769 (1939).

(20) A. V. Babaeva and R. I. Rudyi, *Russ. J. Inorg. Chem.*, 1, 42 (1956).

(21) See footnote *f*, Table II.

(22) See footnote *i*, Table II.

(23) W. W. Wendlandt, W. R. Robinson, and W. Y. Yang, *J. Inorg. Nucl. Chem.*, **25**, 1495 (1963).

(24) E. R. Nightingale, *J. Phys. Chem.*, **64**, 162 (1960).

(25) M. E. Baldwin, *J. Chem. Soc.*, 3123 (1961).

(26) A. V. Babaeva, Y. Y. Kharitonov, and I. B. Baranovskii, *Russ. J. Inorg. Chem.*, 7, 643 (1962).

in keeping with the assignment of the iodate group to the crystal lattice rather than the coordination sphere.

Mechanism of Isomerization. It appears that the process of dehydration plays an important role in the isomerization of *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$. This compound could not be dehydrated without accompanying isomerization by any procedure that we tried. Furthermore, the rate of dehydration and the rate of isomerization were found to be the same within experimental error over the range of temperatures studied. The reduction of pressure increased the isomerization rate, and isomerization could be brought about at room temperature by vacuum desiccation. In addition, while *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$ and *trans*-$[Co(NH_3)_4Cl_2]BrO_3$ have very similar if not identical crystal structures, only the hydrated iodate undergoes isomerization. It might be possible to induce the bromate to isomerize in the presence of water vapor. However, preliminary investigations have been unsuccessful.

The apparent involvement of water in the isomerization process suggests a mechanism similar to that proposed for the *trans*-to-*cis* isomerization of $[Co(en)_2Cl_2]Cl$ in concentrated aqueous solutions. It has been found that if solutions of the green *trans*-$[Co(en)_2Cl_2]Cl$ are concentrated on a steam bath, the crystals which separate from solution are largely the violet *cis*-$[Co(en)_2Cl_2]Cl$.[18] This reaction apparently proceeds by aquation and subsequent anation of the aquated intermediate. The change in geometry can take place *via* a trigonal bipyramid intermediate or transition state, and the product is largely of the *cis* configuration because this isomer is less soluble than the *trans*.

During the course of the solid-phase isomerization of *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$, the color of the mass goes progressively from green to gray to violet. This appears to indicate that the isomerization proceeds slowly across the surface of each particle, and it is likely that the reaction is proceeding simultaneously toward the interior. However, this could not be observed because of the lack of suitably sized crystals. Hence this conclusion is necessarily tentative. It has been shown[27] that if nucleation (the initial stage of reaction) occurs randomly over a small spherical particle, and then each interface, as it forms, grows both along the surface and toward the center of the sphere, the following rate law results.

$$\ln(1 - \alpha) = c - 4\pi K_1 N_0 r^2 t$$

Here K_1 is the probability that the decomposition of a single molecule will lead to the formation of a nucleus, N_0 is the number of potential nucleus-forming sites, and r is the radius of the particle. This law corresponds to that found for the dehydration and isomerization of *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$.

It should be noted that, in this rate law, the constant $k = 4\pi K_1 N_0 r^2$ is a function of particle size. However, this is not a simple relation, because as r decreases, the total surface area per unit weight increases, increasing the number of potential nucleus-forming sites, N_0. Little or no particle size dependence was observed experimentally for the isomerization of *trans*-$[Co(NH_3)_4Cl_2]IO_3 \cdot 2H_2O$, perhaps for this reason.

Since lowering of the pressure increases the rate of isomerization, it appears likely that the initial and rate-determining step in the isomerization process is the dissociation of water from its lattice positions. This dissociation is followed by aquation and finally by anation. The dissociation of water from its lattice positions is probably an equilibrium process, and the vacuum simply serves to remove water from the dehydration interface and thus to shift the equilibrium. It is proposed that the water reacts rapidly with *trans*-$[Co(NH_3)_4Cl_2]IO_3$ at the dehydration interface and that the aquation is followed by rapid anation so that no $[Co(NH_3)_4(H_2O)Cl]Cl \cdot IO_3$ is observed under the conditions employed. As the dehydration interface proceeds through the solid, it is followed by isomerization *via* the aquation–anation pathway, the water escaping through the disrupted crystal lattice behind the interface. Hence, although aquation and anation occur readily, the water does not have the opportunity to pass through the entire crystal. Isomerization occurs only on and behind the dehydration interface, and the rate of disappearance of *trans*-$[Co(NH_3)_4Cl_2]IO_3$ and the rate of dehydration are nearly equal.

When heating is conducted in a closed container, the water vapor pressure builds up. While the dehydration interface is moving through a given particle only in certain spots, water from the atmosphere can enter the particle from all directions. In this way a much larger isomerization interface is formed. Furthermore, the water is forced to move more through the crystal. The previous rate-determining step is by-passed, and the reaction rate becomes dependent on the diffusion of the water vapor through the particle. This offers an explanation for the surprising observation that both vacuum and high water-vapor pressures increase the rate of isomerization.

The rapidity with which aquation and anation take place explains the existence of a single TGA inflection. If anation were slower, there should be some observable difference between the rate of evolution of that water which enters the coordination sphere of the complex and that which does not. Also, observable amounts of intermediate should accumulate.

The DTA curve is more of a puzzle. The main endothermic peak seems to correspond to loss of water from the system. It is possible that the weaker endothermic peak results from the removal of water from its lattice positions prior to removal from each particle. However, since we must postulate rapid aquation and anation following dehydration, only a single peak might be expected. No phase change was detected by X-ray techniques prior to the formation of the microcrystalline *cis*-$[Co(NH_3)_4Cl_2]IO_3$.

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(27) P. W. N. Jacobs and F. C. Tompkins in "Chemistry of the Solid State," W. E. Garner, Ed., Academic Press Inc., New York, N. Y., 1955, pp 206–210.