a free energy difference of only -0.5 kcal mol^{-1} (assuming this represents the equilibrium distribution). With such a small difference it is difficult to pinpoint any particular steric factor as being dominant. Denning and Piper carried out a very exacting analysis of the $Co(aa)_3$ (aa = L-alanine, L-leucine, L-proline) isomer system.[17] They found that among the important steric factors was the relative pseudoaxial and pseudoequatorial positioning of the R group in the Δ and Λ isomers, respectively, the axial position being less favored. Such an argument might be invoked to rationalize the difference in stability between the Δ and Λ isomers of $Co(en)_2(\text{L-aa})^{n+}$. However, consideration of molecular models suggests that the steric interactions in these isomers are small relative to those found in the $Co(aa)_3$ isomers and that hydrogen bonding might even be favored when R is in an axial position. Furthermore molecular models suggest that the conformation of the ethylenediamine ring involved in hydrogen bonding makes little difference in the stability of the molecule. It should be noted, however, that the CD spectra obtained for the protonated and nonprotonated species of the Δ isomer exhibit a relatively smaller change. This observation supports the hydrogen-bond postulate, since this isomer was predicted not to be hydrogen bonded.

The aspartate isomers exhibit a *reversal* in CD behavior in going from the protonated to the nonprotonated form for both the Λ and Δ isomers as compared to the glutamate analogs. Molecular models suggest that hydrogen bonding is possible for both isomers. In fact the removal of one methylene group in changing from glutamate to aspartate would appear to eliminate some steric crowding arising from the puckered nature of the $-CH_2CH_2CO_2-$ group in glutamate. For the aspartate isomers even less stereospecificity was observed (a 60:40 distribution between the Λ and Δ isomers, respectively).

The foregoing observations lead to several important conclusions. First, in accounting for the distribution of isomers it is essential, if at all possible, to perform a careful chromatographic analysis of the contents of the total reaction solution. Such an analysis has cast a different light on the $Co(en)_2aa^{n+}$ system reported in this paper as it did for $Co(EDDA)(L)^-$ (L = ox and mal) where the presence and predominance of a hitherto undetected isomer were established.[12c] Second, when differences in stability involve less than 1 kcal/mol, any number of subtle variations in structure may be invoked to account for the difference. Third, although crystallographic analysis can be very helpful in suggesting structural behavior in solution, conclusions about stereochemical *details* in solution are tenuous at best.

Finally, we have previously demonstrated that when *three sites* are available for coordination as when a diethylenetriamine–cobalt(III) system is employed, aspartic acid functioning as tridentate shows absolute stereospecificity on coordination. This observation has been misinterpreted in a recent study where a comparison of stereospecificity in *bidentate* amino acid chelates was made[18] (see, for example, Table IV and associated discussion in the paper). The complexes that should be included in that report are those discussed in this paper and not $Co(dien)asp^+$.

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[17] R. G. Denning and T. S. Piper, *Inorg. Chem.*, **5**, 1056 (1966).

[18] F. F.-L. Ho, L. E. Erickson, S. R. Watkins, and C. N. Reilley, *ibid.*, **9**, 1139 (1970).

CONTRIBUTION FROM THE CÁTEDRA DE QUÍMICA INORGÁNICA,
FACULTAD DE QUÍMICA, MONTEVIDEO, URUGUAY

μ-Carbonato-bis(pentaamminecobalt(III)) Salts

BY EDUARDO KREMER AND CARLOS R. PÍRIZ MAC-COLL*

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Potentiometric titration, conductometric charge determination, visible, ultraviolet, and infrared spectra, behavior of resin ion exchange, counterion substitution, tga, and dta have been considered as evidence for binuclear carbonate-bridged structure, composition, and purity of $[(NH_3)_5CoCO_3Co(NH_3)_5](SO_4)_2\cdot 4H_2O$. The nitrate, perchlorate, and chloride of the binuclear cation are presented and characterized, using the same properties.

Several carbonato-bridged complexes of cobalt(III) have been described,[1,2] but so far they have not been studied in as much detail as mononuclear carbonato-cobalt(III) complexes.

It was called to our attention that comparisons including the behavior of carbonato-bridged complexes are missing in the whole subject of physical chemistry researches on carbonatoammines of cobalt(III) such as aquation, base hydrolysis, exchange kinetics, and corresponding mechanisms. The only comparative study including carbonato-bridged compound we have noted refers to infrared spectra.[3]

Considering particularly the μ-carbonato-bis(pentaamminecobalt(III)) sulfate tetrahydrate, the older and better known bridged complex,[4,5] we believe that the reason

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[1] C. R. Píriz Mac-Coll, *Coord. Chem. Rev.*, **4**, 147 (1969).

[2] B. K. W. Baylis and J. C. Bailar, Jr., *Inorg. Chem.*, **9**, 641 (1970).

[3] V. E. Sahini and M. Damaschin, *Rev. Chim., Acad. Repub. Pop. Roum.*, **8**, 193 (1963).

[4] G. Vortman and O. Blasberg, *Ber.*, **22**, 2648 (1889).

[5] J. Kranig, *Ann. Chim. (Paris)*, [11] **41**, 87 (1929).

TABLE I

ANALYTICAL RESULTS[a]

	%							
	Co		NH_3		CO_3^{2-}		Anion	
	Calcd	Found	Calcd	Found	Calcd	Found	Calcd	Found
$[(NH_3)_5CoCO_3Co(NH_3)_5](NO_3)_4\cdot 3H_2O$	18.2	18.5	26.2	27.2	9.3	9.2	...	...
$[(NH_3)_5CoCO_3Co(NH_3)_5]Cl_4\cdot 3H_2O$	21.7	21.2	31.2	31.0	11.0	10.7	26.2	26.1
$[(NH_3)_5CoCO_3Co(NH_3)_5](ClO_4)_4\cdot 2H_2O$	15.1	15.1	21.7	21.7	7.7	7.8	50.9	50.5

[a] Molar absorptivity, pH titration inflection point, and tga also support the number of crystallization water molecules assigned.

for such a situation is that the compound has not been sufficiently well characterized for use in quantitative measurements. Its very existence is disregarded in a recent review[6] on the chemistry of metal–carbonato complexes.

Available information supporting the binuclear formulation of "decaammine" sulfate consists of (1) analytical results fairly consistent with the formula $[(NH_3)_5CoCO_3Co(NH_3)_5](SO_4)_2\cdot 4H_2O$ and (2) $BaSO_4$ precipitation from the neutral solution without coprecipitation of $BaCO_3$ if filtration is rapid. The $BaSO_4$ filtrate solution, having Ba^{2+} in excess, slowly yields $BaCO_3$.[5]

In an effort to obtain further evidence for the binuclear formula as well as to check the purity of the compounds we carried out the following work.

Experimental Section

Preparation of $[(NH_3)_5CoCO_3Co(NH_3)_5](SO_4)_2\cdot 4H_2O$.—The procedure used as described by Kranig[5] involved separation as an oil, which could be transformed into a solid by gradually increasing the ethanol concentration.

The crude product was not homogeneous and had the appearance of a powdered aggregate. To accomplish recrystallization the compound was dissolved in the minimum amount of water and the alcohol precipitation was repeated. After one precipitation the spectral absorption showed no changes as compared with the products of the second and third recrystallizations. The sulfate content of the solids became constant also. *Anal.* Calcd for $[(NH_3)_5CoCO_3Co(NH_3)_5](SO_4)_2\cdot 4H_2O$: Co, 19.3; NH_3, 27.8; SO_4^{2-}, 31.4; CO_3^{2-}, 9.8; H_2O, 11.8. Found: Co, 19.9; NH_3, 27.9; SO_4^{2-}, 30.1; CO_3^{2-}, 9.7; H_2O, 10.9.

Kranig[5] reported high cobalt and sulfate results and low ammonia, which he ascribed to some ammonia loss due to slow solid decomposition, corresponding to the poor thermal stability of this compound. We found that the recrystallized product showed constant analytical and spectra results after a period of several months; the weight of a sample also became constant after reducing 1.6% over $CaCl_2$ at 20° for 48 hr.

Preparation of $[(NH_3)_5CoCO_3Co(NH_3)_5](NO_3)_4\cdot 3H_2O$, $[(NH_3)_5CoCO_3Co(NH_3)_5](ClO_4)_4\cdot 2H_2O$, and $[(NH_3)_5CoCO_3Co(NH_3)_5]Cl_4\cdot 3H_2O$.—The solid salts can be obtained from the sulfate by ion exchange or by quantitative double decomposition with the corresponding barium salt, followed by freeze-drying. This method was convenient since the complexes decompose in solution at mild temperatures and as a result conventional evaporation cannot be employed for solid recovery.

A 20-ml solution containing 0.5 g of the $[(NH_3)_5CoCO_3Co(NH_3)_5](SO_4)_2\cdot 4H_2O$ was poured through a 50 cm high, 1-cm diameter column of Dowex 2X8 resin previously transformed to the NO_3^- or Cl^- form and properly washed.

The perchlorate ion was not suitable for interchange at high concentrations because of the high selectivity coefficient of the resin.

With regard to the perchlorate, as well as with regard to the other salts, double decomposition can be applied. In a typical preparation, 10 ml of a solution containing 1 g of the complex as sulfate was treated at room temperature with an equivalent amount of $BaX_2\cdot nH_2O$ in saturated solution. The precipitate of $BaSO_4$ was removed by centrifugation and filtration. The resulting solution or the one from the resin interchange was submitted to freeze-drying.

See Table I for analyses of these compounds.

Analytical Methods.—Cobalt was determined electrogravimetrically.[7] Ammonia was determined by treating the complexes with arsenic(III) oxide and sodium hydroxide and then by titrating the distilled ammonia retained over boric acid.[8] Sulfate was determined gravimetrically as $BaSO_4$. Chloride was determined gravimetrically as AgCl. Perchlorate was determined hydrovolumetrically (Mohr's method), after NaOH decomposition of the complex cation, filtration, total evaporation, and reduction of $NaClO_4$ to NaCl by heating in solid with NH_4Cl. Carbonate content was obtained from potentiometric titration; see text. Water content was obtained from tga; see text.

Apparatus.—For the physical chemistry studies we used the following instruments: Pye Model 79 pH meter, Philips Gm 4249/01 conductance bridge,[9a] a Beckman DB for visible spectra, a Bausch & Lomb Spectronic 505 for ultraviolet spectra,[9b] a Beckman IR5A for infrared spectra,[9c] and Netzch equipment 409 and 404 for tga and dta,[9d] respectively.

Results and Discussion

The $[(NH_3)_5CoCO_3Co(NH_3)_5](SO_4)_2\cdot 4H_2O$ dissolves easily in water producing a deep red solution. The light absorption of such a solution is quite similar to that of the related carbonatopentaammine ion.

The spectrum shows two absorption bands: ν_1, 505 mμ, log $\epsilon = 2.18$, $w_{1/2} = 135$ mμ; ν_2, 350 mμ, log $\epsilon = 2.23$, ... The ν_2 band is a shoulder on a band in the ultraviolet spectrum, with a much higher molar absorptivity.

The data for $[Co(NH_3)_5CO_3]NO_3\cdot H_2O$[10] are as follows: ν_1, 510 mμ, log $\epsilon = 1.97$, $w_{1/2} = 110$ mμ; ν_2, 335-mμ shoulder in growing uv absorption.

Such absorptions are assigned in both cases to d–d transitions: $^1T_{1g} \leftarrow {}^1A_{1g}$ for ν_1; $^1T_{2g} \leftarrow {}^1A_{1g}$ for ν_2. The observed similarity is consistent with CO_3^{2-}-bridged binuclear formulation since both complexes have the same chromophore N_5Co–O–CO–O– per cobalt atom.

For the binuclear complex, which can be considered as a carboxylic monosubstituted cobalt(III) ammine, some kind of extra distortion from O_h symmetry can be expected, due to the size of the O–CO–O–$Co(NH_3)_5$ substituting group in an octahedral arrangement. The small change observed in the band frequencies shows the resultant variation in the average ligand field. Such variation also corresponds with the observed band width change considering the strong slope of the energy diagram for the excited states $^1T_{1g}$ and $^1T_{2g}$.[11]

The molar absorptivity for the binuclear compound at ν_1 is 151 M^{-1} cm^{-1} which is significantly different from the value of 142 M^{-1} cm^{-1} which corresponds to

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(6) K. Krishnamurty, G. Harris, and V. Sastri, *Chem. Rev.*, **70**, 171 (1970).

(7) H. Siebert, *Z. Anal. Chem.*, **206**, 20 (1964).

(8) H. A. Horan and H. J. Eppig, *J. Amer. Chem. Soc.*, **71**, 582 (1949).

(9) The authors are grateful to: (a) Cátedra de Electroquímica, Professor G. Spangenberg for the use of this instrument; (b) Cátedra de Q. Orgánica, Dr. O. González Correa for running the KBr samples; (c) Cátedra de Q. Orgánica, Dr. M. Falco for the use of this instrument; (d) Lab. Investigaciones Científicas de Ancap, Professor R. Martres for the running and interpretation of the tga and dta curves.

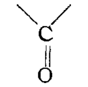
(10) T. P. Dasgupta and G. M. Harris, *J. Amer. Chem. Soc.*, **90**, 6360 (1968).

(11) D. Sutton, "Electronic Spectra of Transition Metal Complexes," McGraw-Hill, New York, N. Y., 1968, p 165.

an equimolecular mixture of $Co(NH_3)_5CO_3^+$ and $Co(NH_3)_5H_2O^{3+}$. Experimentally we found that the spectrum of such a mixture has the following absorption bands: ν_1, 508 mμ, log $\epsilon = 2.15$, $w_{1/2} = 140$ mμ; ν_2, 360 mμ, log $\epsilon = 2.16$, $w_{1/2} = 90$ mμ. The ν_2 maximum also is different enough to eliminate the possibility of such a mixture.

Furthermore, if the complex cation is binuclear with a carbonato bridge as proposed, it can be predicted to have an angular shape, on the basis of CO_3^{2-} stereochemistry. The spectrum is in accordance with such a prediction since it has been observed that when the oxygen atoms form angular bridges, the spectra of the derivative proves to be a superposition of the absorption of the parts thus linked. Quite a different behavior is expected for a linear O–C–O bridge.[12]

Hence, the visible d–d spectral interpretation can be considered in good agreement with the two quasioctahedral Co(III) ions, linked by a bent



bridge structure.

The near-ultraviolet spectrum shows a strong absorption assigned to charge transfer.

The water solution shows no spectral changes for 24 hr at 20°. After 30 hr, decomposition is spectrophotometrically detectable and after 2 days formation of insoluble cobalt compounds is visible at initial concentration of 10^{-3} *M*. Dilution or concentration from such a value does not affect the spectral features but if acid (H_2SO_4) is added, the bands quickly shift to 490 and 340 mμ, respectively, these values corresponding to $Co(NH_3)_5H_2O^{3+}$. If the added acid exceeds the 2:1 ratio on a molar basis with the complex, the absorption of the resulting solution at 490 and 340 mμ corresponds quantitatively to all the cobalt passing to form $Co(NH_3)_5H_2O^{3+}$. In fact, the solution reproduces the figure of log $\epsilon = 1.68$ at 490 mμ[13] for this cation after transformation. This result rules out the possible existence, in the complex, of some other type of bridge, such as NH_2^-, which would produce different hydrolysis products.

The addition of stoichiometrically insufficient acid with respect to

$$(NH_3)_5CoCO_3Co(NH_3)_5^{4+} + 2H^+ \longrightarrow 2Co(NH_3)_5H_2O^{3+} + CO_2$$

causes spectral shifts which correspond to the same partial transformation with resultant mixtures of aquopentaammine and the original complex (or some carbonatopentaammine derivative). The transformation indicates a rapid aquation process which is presently under investigation. The preliminary aquation kinetic experiments[14] show a rate law of the type

$$k_{obsd} = k_0 + k_1(H^+)$$

similar to the one for the carbonatotetraammine ion, although with different *k* values.

Another rate law of the form

$$k_{obsd} = \frac{k_1(H^+)}{K + (H^+)}$$

is found for the carbonatopentaammine cobalt(III) ion.[6]

Such results again rule out the possibility of the complex aqueous solution being an equimolecular mixture of aquo- and carbonatopentaammine derivatives.

To add to such a conclusion we checked the differential behavior of the complex- and aquopentaammine-containing solutions with respect to iodide precipitation. This ion produces a scarcely soluble salt with $Co(NH_3)_5H_2O^{3+}$ (solubility 0.155 mol $l.^{-1}$, at 17.5°).[13] An equimolar mixture of aquo- and carbonatopentaammine shows a strong positive reaction and a solution of the binuclear complex containing an equal amount of cobalt(III) gives no precipitation.

pH titrations have been used to study the stoichiometry of the reaction of the binuclear species with acid in comparison with its counterpart $Co(NH_3)_5CO_3^+$.

Such titrations show some delay in attaining pH stability after each acid addition because of the required time for aquation and CO_2 liberation. Measurements show that once a fraction of acid is added, the pH decreases immediately and then increases slowly taking more than 1 hr in attaining stability.

Plotting the pH measured immediately after addition of the acid or the pH corresponding to any definite Δ_t after addition *vs.* the number of moles of added H^+ per mole of cobalt, we found the curves as on Figure 1.

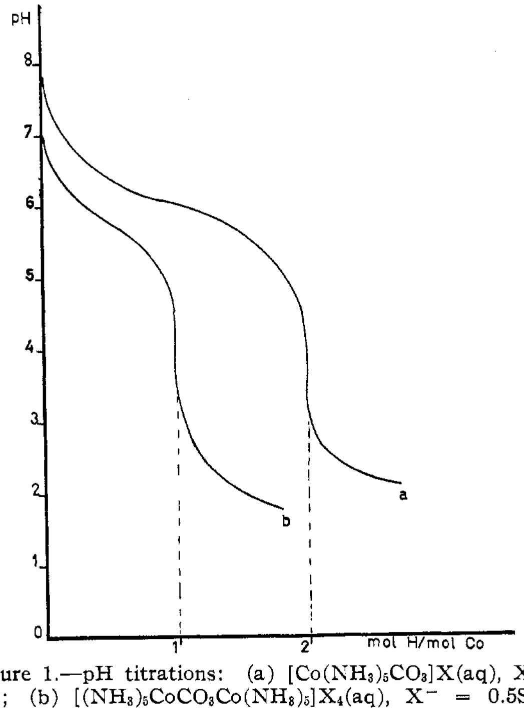


Figure 1.—pH titrations: (a) $[Co(NH_3)_5CO_3]X(aq)$, $X^- = NO_3^-$; (b) $[(NH_3)_5CoCO_3Co(NH_3)_5]X_4(aq)$, $X^- = 0.5SO_4^{2-}$, Cl^-, NO_3^-, or ClO_4^-.

The ratio of moles of H^+ to moles of Co at the inflection point is 0.99 for the binuclear complex as sulfate, nitrate, perchlorate, or chloride and 1.99 for the carbonatopentaammine derivative. Thus the binuclear salts need 1 mol of H^+ per mole of Co(III) for decomposition, while the mononuclear pentaammine complex needs 2 mol of H^+ per mole of Co(III).

We also know that once the reaction is completed

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[12] C. E. Schäffer and C. K. Jørgensen, *J. Inorg. Nucl. Chem.*, **8**, 143 (1958).

[13] P. Pascal, Ed., "Nouveau Traité de Chimie Minerale," Vol. XVIII, Masson et Cie, Paris, 1959, p 462.

[14] These experiments were run initially at Dr. A. Haim's laboratory, State University of New York, Stony Brook, N. Y., and are presently pursued in ours.

regardless of the detailed path, all of the cobalt transforms into aquopentaammine, liberating CO_2.

These experimental results enable us to state the stoichiometric equation

$$(NH_3)_5CoCO_3Co(NH_3)_5{}^{4+} + 2H^+ \xrightarrow{+H_2O} 2Co(NH_3)_5H_2O^{3+} + CO_2$$

corresponding to the experimental ratio (mol of H^+)/(mol of Co) = 1 and the known[1] total aquation of the pentaammine complex

$$Co(NH_3)_5CO_3{}^+ + 2H^+ \longrightarrow Co(NH_3)_5H_2O^{3+} + CO_2$$

producing the experimental ratio of 2.

Such results support the $CO_3{}^{2-}$ content and can be used as an analytical determination. In addition, the overall course of the aquation becomes experimentally established for the binuclear complex.

If the sulfate of the binuclear complex ion is transformed into other salts through the use of ion-exchange resins or by double-decomposition reactions, the pH titrations run before and after the transformation are identical, giving evidence of the unchanged character of the binuclear ion, containing the $CO_3{}^{2-}$ radical.

It is interesting to note that a binuclear complex–water solution has a pH of 7.0 at 25° while the equimolecular mixture of carbonato- and aquopentaammine produces a pH of 5.8 and a highly alkaline value should be expected for a mixture of $Co(NH_3)_5OH^{2+}$ and $Co(NH_3)_5CO_3H^{2+}$ which can account for the stoichiometry also.

For charge determination of the complex cation we have used the Onsager equation $\lambda_c = \lambda_0 - B\sqrt{c}$, as applied by Feltham and Hayter[15] for complex ions. λ_c and λ_0 are the equivalent conductances at concentrations c and 0, respectively, and B is a constant. Both λ_0 and B are characteristic for each electrolyte and can be experimentally found as well as estimated on the basis of the assumed type of electrolyte.

Plotting λ_c or $\lambda_0 - \lambda_c$ *vs.* $\sqrt{c}$, the λ_0 and B values are obtained by intercept and slope.

Figure 2 shows the plots obtained for the complex in the form of sulfate, perchlorate, nitrate, and chloride. Different salt solutions have been obtained by passing the sulfate through the anion-exchange resin Dowex 2X8 in the appropriate form.

The λ_0 value obtained for the salt is the sum of the limiting ion conductances (lic) of the ions. The lic of the complex ion can be deduced from the experimental λ_0(25°) and the known anion contributions, which are as follows for 25° (in $ohm^{-1}\ cm^{-2}\ equiv^{-1}\ l.$): Cl^-, 76.34; $NO_3{}^-$, 71.44; $ClO_4{}^-$, 68.0; $0.5SO_4{}^{2-}$, 79.8. Table II shows the data obtained.

TABLE II

ONSAGER PARAMETERS

	λ_0[a]	Lic[a] (cation)	*B*
$[(NH_3)_5CoCO_3Co(NH_3)_5](SO_4)_2$	127.0	47.2	568
$[(NH_3)_5CoCO_3Co(NH_3)_5](ClO_4)_4$	140.0	72.0	525
$[(NH_3)_5CoCO_3Co(NH_3)_5](NO_3)_4$	155.0	84.0	534
$[(NH_3)_5CoCO_3Co(NH_3)_5)]Cl_4$	161.5	85.2	522

[a] Units: $ohm^{-1}\,cm^{-2}\,equiv^{-1}\,l.$

These experimental data show consistent results for the 4+ charge of the cation in the perchlorate, nitrate, and chloride derivatives. The Onsager B constant is in fairly good agreement with the 525 value for a 4:1 type of electrolyte.[15]

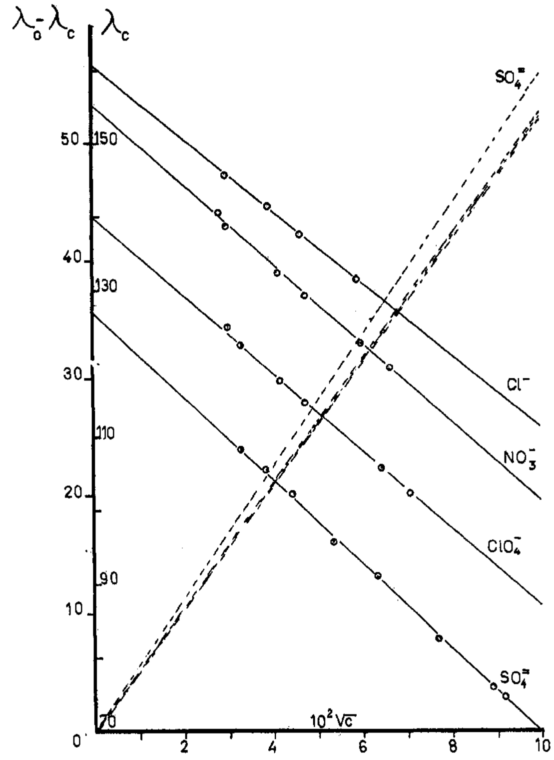

Figure 2.—Onsager equation plots: ——, $\lambda_c = f(\sqrt{c})$; – – –, $\lambda_0 - \lambda_c = f(\sqrt{c})$. Units: λ, $ohm^{-1}\,cm^{-2}\,equiv^{-1}\,l.$; c, $equiv\ l.^{-1}$.

The original sulfate derivative does not behave in a similar way; the conductance contribution corresponding to the cation is smaller than those of the other salts studied.

This fact, considered independently, should build up the concept that the sulfate of the complex ion may contain impurities affecting the conductivity, *e.g.*, polynuclear compounds, but the results cannot be considered independently because the perchlorate, nitrate, and chloride derivatives, which yield results consistent with the 4:1 type of electrolyte, are directly obtained from the sulfate of the complex cation which is dissolved in water and percolated through anion resin in the form of Cl^-, $NO_3{}^-$, or $ClO_4{}^-$. Such anion exchange proceeds with total maintenance of the cation concentration tested by measuring the absorption at 505 mμ.

According to such results the possibility of impurities is ruled out and therefore we consider the sulfate ion association as responsible for the difference of conductometric behavior of the sulfate derivative of the complex.

The value B = 568 obtained for the sulfate cannot be compared with 525 because of a different type of electrolyte, 4:2. Although an experimental reference value is not available in obtainable literature, the increase of B is in accordance with the predictions of Onsager's equations. Furthermore, it must be taken into account that the Onsager method presents stronger limitations as the electrolytes depart from the simpler monovalent counterion types.[16]

The measurement of a 4+ charge of the complex ion eliminates the possibility of considering the substance as being a mixture of lower charged ions. The B value

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(15) R. D. Feltham and R. G. Hayter, *J. Chem. Soc.*, 4587 (1964).

(16) D. MacInnes, "The Principles of Electrochemistry," Dover Publications, New York, N. Y., 1961, p 327.

resulting from an equimolecular mixture of $[Co(NH_3)_5CO_3](NO_3)$ and $[Co(NH_3)_5H_2O](ClO_4)_3$ was experimentally found to be 375 and the mixture of $[Co(NH_3)_5OH]X_2$ and $[Co(NH_3)_5CO_3H]X_2$ thus behaves as a 2:1 electrolyte ($B = 185$).

The metathetical reactions have been tried by Kranig[5] using $BaCl_2$, KI, and $(NH_4)_2C_2O_4$, in attempts to prepare the chloride, iodide, or oxalate of the decaammine series, but in every case he obtained salts of different series, not containing the CO_3^{2-} ligand, *e.g.*, $[Co(NH_3)_5H_2O]ISO_4$.

We found that the anion exchange, using Dowex 2X8 in Cl^-, NO_3^-, or ClO_4^- form, provides a convenient way of substitution of the counterion and gives the classical type of evidence of the unchanged nature of the complex cation in the reaction. The quantitative transformation has been tested by negative SO_4^{2-} assay, use of spectral measurement, and pH titration. The counterion character of SO_4^{2-} and coordinated nature of CO_3^{2-} becomes established.

The ν_1 maximum at 505 mμ for a solution passing through the resin bed for interchange reproduces in all cases (Cl^-, NO_3^-, ClO_4^-) that of the original sulfate solution before the interchange. The ν_2 shoulder does not change at all in the case of perchlorate transformation, and the complete spectrum reproduces perfectly before and after quantitative percolation. For nitrate and chloride a small change appears in the region 345–320 mμ, consisting of a better definition of the ν_2 band from the strong charge-transfer absorption. If decomposition had occurred, the position and absorptivity of the first band would not be so perfectly maintained, and roseo cobaltic or carbonate pentaammine ions would influence the spectrum, producing different absorptions in both zones, as is not the case.

Once we obtained such evidence, we tried barium salt double decomposition using stoichiometric or excess (double) amounts and the solutions obtained showed maintenance of spectral characteristics as well as other checks as previously described.

According to these experiments we interpret Kranig's failure to accomplish double-decomposition syntheses as due to the solid recovery procedures or, in the case of $[Co(NH_3)_5H_2O]ISO_4 \cdot 0.5H_2O$, to the relatively low solubility of such salt produced from the hydrolysis of the binuclear ion.

When the $[(NH_3)_5CoCO_3Co(NH_3)_5](SO_4)_2(aq)$ is poured onto cationic resin (IRA 120), the effluent presents no absorption in the visible and near-ultraviolet spectra, an indication of the cationic nature of the cromophore. The cation is strongly retained by the resin.

The infrared spectrum of $[(NH_3)_5CoCO_3Co(NH_3)_5](SO_4)_2 \cdot 4H_2O$ has been compared with those of the chlorides of the mononuclear species.[3] We have measured the spectra of the new salts of the binuclear cation and found a complete correspondence among them. We focused our attention on the chloride, so as to eliminate anion absorptions thus permitting resolution of the 1030-cm^{-1} frequency. All other frequencies from the carbonato group (675, 760, 830, 1340, and 1480 cm^{-1}) are detected, with overlapping of strong NH_3 absorptions at 830 and 1310 cm^{-1}.

The empirical assignment and observations of the differences and similarities of the bands of the bridged carbonate sulfate derivative have also been considered in agreement with C_{2v} symmetry[3] and they apply to the other salts as well. Nevertheless some further progress can be expected since a more detailed understanding will result from the normal-coordinate analysis of bridge derivatives as compared with the mononuclear species.[1,17–19]

We also studied the thermal decomposition of the sulfate and chloride of the binuclear ion in air. The tga diagram for $[(NH_3)_5CoCO_3Co(NH_3)_5](SO_4)_4 \cdot 4H_2O$ shows a continuous weight loss from 55 to 430°. From 430 to 550° the weight remains constant. The total weight loss is 48.6% in agreement with the sum of one CO_3^{2-}, ten NH_3, and four H_2O per mole of the above formula, producing the figure of 48.4% for total volatiles. These experimental results are a check for the crystallization water since all other volatile radicals, NH_3, and CO_3^{2-} are known independently, and the $CoSO_4$ is surely the stable product at the temperatures used.[20]

The tga curve shows three consecutive overlapping and unresolved processes according to slope changes. Also three processes appear in the dta curve with peak temperatures of 170, 290, and 350°. We consider these processes to be, respectively, water, ammonia, and carbon dioxide losses.

The tga for the chloride is similar to that described for the sulfate, showing the gradual weight loss from 55 to 430° where the constant-weight zone is maintained only to 460°. The total weight loss amounts to 51.5% in good agreement with 52.2% calculated for the sum of one CO_3^{2-}, ten NH_3, and three H_2O corresponding to the transformation of $[(NH_3)_5CoCO_3Co(NH_3)_5]Cl_4 \cdot 3H_2O$ in $CoCl_2$. The stability zone for $CoCl_2$ in air is short; further heating over 500° produces oxide transformation, the final product being Co_3O_4.

It is noteworthy that this thermal decomposition is different from the known scheme for $[Co(NH_3)_4CO_3]Cl(aq)$ and that of the $[Co(NH_3)_5CO_3]Cl(aq)$ has not been reported.

The dta curve shows four processes at peak temperatures of 115, 225, 250, and 365°, indicating a more complicated decomposition scheme involving probably a double-step ammonia loss including chloride–ammonia substitution.[21]

The nitrate and perchlorate of the binuclear ion explode at temperatures of 150 and 215°, respectively.

As a conclusion, all the evidence submitted agrees with the statement of purity and the binuclear carbonate-bridge character of the complex ion $(NH_3)_5CoCO_3Co(NH_3)_5^{4+}$, in the four salts studied.

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