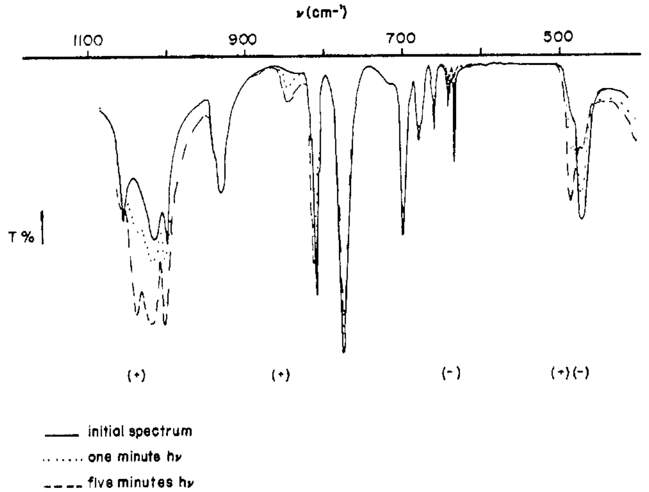

Figure 1.—Infrared spectra of $Co(acac)_2pyNO_2$ before and after irradiation. The regions of maximal change are indicated by (+) or (−) for enhanced and diminished absorption after photoisomerization. The total output of the PEK 200-W lamp was utilized.

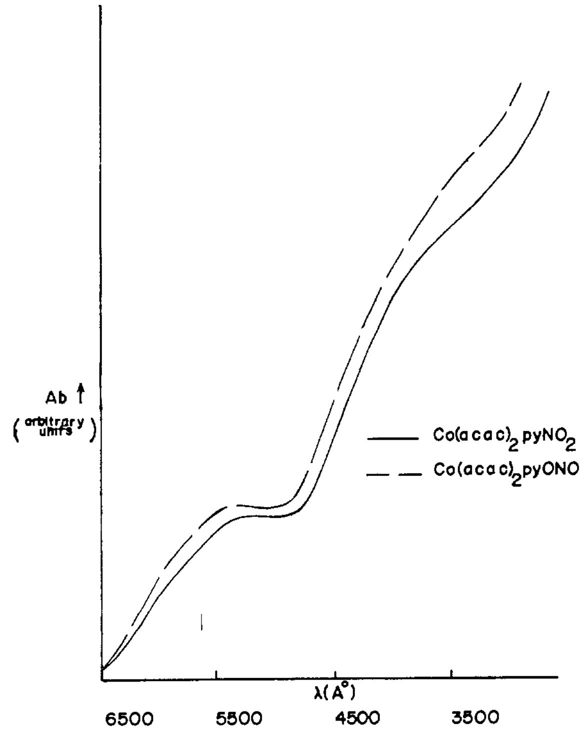

Figure 2.—Electronic spectrum of $Co(acac)_2pyNO_2$ prior to and following irradiation with total output of the PEK lamp. Samples were mulls in Nujol; the absorbance values are only relative.

large cage effect expected in these solid-phase reactions is considered.[3d] The observations in these complexes and other systems under investigation suggest that photolinkage isomerization of nitro groups will be fairly common for cobalt(III). Further work is in progress to ascertain the nature of the influence of the remainder of the coordination sphere upon this photochemical reaction. In general, lower conversion to the nitrito complex occurs for systems showing high rates of the thermal reverse reaction;[3b,12] however, it is not known, at present, whether the low conversion is due entirely to the enhanced rate of the reverse thermal reaction or if some lowering in the quantum yield for the forward reaction also occurs.

[12] D. A. Johnson, and L. E. Poplin, to be submitted for publication.

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The Reaction of Tricarbonatocobaltate(III) with Aqueous Ammonia[1a]

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Received February 14, 1969

Two isomers of the diamminedicarbonatocobaltate(III) anion were reported[2] as products from the reaction between ammonium carbonate and the green solutions from which potassium tricarbonatocobaltate(III) can be precipitated.[2] From the reaction sequence

$$\mathrm{Co(CO_3)_3^{3-}} \xrightarrow[\text{aq soln, warm}]{\text{ammonium carbonate}} \text{blue } \mathrm{Co(NH_3)_2(CO_3)_2^{-}} \xrightarrow[\text{heating}]{\text{further}} \text{“violet isomer”} \qquad (1)$$

the authors suggested[2,3] that the kinetically obtained blue isomer has a *cis* configuration (which requires no change in the positions of the two nonreplaced carbonato ligands) and that the subsequent change to violet is the formation of the *trans* ion of greater thermodynamic stability. The observation of only the *cis* isomer of the $Co(acac)_2(NH_3)_2^+$ cation from reactions of either the blue $Co(NH_3)_2(CO_3)_2^-$ isomer or the "violet isomer" with 2,4-pentanedione[4,5] and a similar result with ethylenediamine[6] have led to further investigation. The visible spectra for violet materials isolated only qualitatively agreed with that given earlier,[2] and the infrared spectrum[5] of one violet sample was not that expected for a $K[Co(CO_3)_2(NH_3)_2]$ salt. In an effort to find a reproducible method for preparing a product consistent with the *trans*-$Co(NH_3)_2(CO_3)_2^-$ structure, we have come to the conclusion that the violet product reported by the original authors is not

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[1] (a) Presented in part at the Northeast Regional Meeting of the American Chemical Society, Boston, Mass., 1968. (b) Texaco Fellow, University of Massachusetts, 1968–1969. (c) Author to whom correspondence should be sent.

[2] M. Mori, M. Shibata, E. Kyuno, and T. Adachi, *Bull. Chem. Soc. Japan*, **29**, 883 (1956).

[3] M. Mori, M. Shibata, E. Kyuno, and K. Hoshiyama, *ibid.*, **31**, 291 (1958).

[4] R. D. Archer and B. D. Catsikis, *J. Am. Chem. Soc.*, **88**, 4520 (1966).

[5] B. D. Catsikis, M.S. Thesis, Tulane University, New Orleans, La., 1966.

[6] R. D. Archer, B. D. Catsikis, and N. Cooke, presented at the 153rd National Meeting of the American Chemical Society, Miami Beach, Fla., 1967.

trans-$Co(NH_3)_2(CO_3)_2^-$ but is actually a mixture of several cobalt(III) complexes.

Experimental Section

All solution chemistry was conducted in the darkness, in the cold (near the ice point), and as rapidly as possible, except where noted otherwise.

Preparation of Blue $K[Co(NH_3)_2(CO_3)_2]$.—The blue solution was prepared as previously described.[2] After removing the less soluble green impurities by filtration, the product was precipitated from water by the addition of methanol. The precipitate was dissolved in water and reprecipitated with methanol two times. The resulting blue powder was dissolved in a minimum amount of aqueous 0.1 *M* $KHCO_3$ at 30° and filtered. Blue crystals were obtained by cooling the filtrate in an ice bath. The solubility of the final product in water is 0.08 g/ml at 3°. *Anal.* Calcd for $K[Co(NH_3)_2(CO_3)_2]$: C, 9.53; H, 2.40; N, 11.11. Found: C, 9.77;[7] H, 2.46;[7] N, 11.20.[7] Alternate methods of crystallization gave similar results.

Preparation and Violet Product Fractionation.—The violet solutions were prepared as previously described.[2] A tarry violet material (a) was obtained upon the addition of a large excess of ethanol to the violet solution which remained after the blue product and other solid impurities had been separated by filtration. The violet product (a) was solidified by washing with ether and drying *in vacuo*.

Ten grams of violet material (a) was dissolved in 10 ml of water and filtered (residue = b). Five grams of another violet material (c), which was obtained from the above filtrate by precipitation with ethanol, was dissolved in 2.5 ml of 1 *M* $KHCO_3$ and the solution was filtered (residue = d). The most soluble fraction (e) of the violet material was recovered from this filtrate by precipitation with ethanol. The infrared spectra of the various fractions were recorded.

In another instance, the violet product prepared by the method originally described[2] was dissolved in 200 ml of water and poured into 2 l. of cold methanol with vigorous stirring. The precipitate was filtered and dried at room temperature over P_4O_{10} *in vacuo*. This procedure was repeated three times, but no changes in the infrared spectra were observed. Infrared and visible spectra were recorded and the complex was analyzed. *Anal.* Calcd for $K[Co(NH_3)_2(CO_3)_2]\cdot H_2O$ (original[2] formulation): C, 8.89; H, 2.96; N, 10.4; Co, 21.8. Calcd for $[Co(NH_3)_4(CO_3)][Co(NH_3)_2(CO_3)_2]\cdot 2H_2O$: C, 8.26; H, 5.08; N, 19.3; Co, 27.0. Found: C, 8.16;[8] H, 4.74;[8] N, 18.2;[8] Co, 28.0.[9]

Ion-Exchange Separations.—Aqueous ethanol solutions (1:1 v/v) of the violet product (original method[2]) were rapidly passed through columns of Amberlite IR-120 CP (Na^+ form converted to K^+ form with 2 *M* KCl) and Amberlite IRA-401 S (Cl^- form conditioned with 2 *M* HCl) and visible spectra were recorded. Even though the experiments were conducted at 0° in jacketed burets, some decomposition invariably took place.

Visible Spectra.—All spectra were taken in 1 *M* $KHCO_3$ aqueous solutions at room temperature on a Model EPS-3T Hitachi ratio recording spectrophotometer between 340 and 700 nm.

Infrared Spectra.—The spectra between 4000 and 300 cm^{-1} were measured with a Beckman IR-10 infrared spectrometer. KBr disks were employed throughout.

Magnetic Properties.—A qualitative Faraday method, which entailed the visual observation of repulsion or attraction of a sample in a strong magnetic field gradient, was used to distinguish diamagnetic cobalt(III) species from paramagnetic contaminants.

Results and Discussion

Repeated preparations of the violet product by the original method[2] gave qualitatively reproducible infrared spectra; however, peaks unlikely for potassium *trans*-diamminedicarbonatocobaltate(III) were observed. In addition, the corresponding visible spectra had appreciable variation in extinction coefficients and energy maxima. In order to identify the properties of the impurities, fractionation of the violet product was carried out at cold temperatures, in darkness, and as rapidly as possible in order to minimize the decomposition of the easily hydrolyzable species. The infrared spectra of the fractions (Figure 1) and the observed diamagnetism of the original violet product indicate that the product is a mixture of cobalt(III) complexes. Although complete assignments have not been made, the spectrum of the original violet product (Figure 1a) shows the absorptions noted for the blue $Co(NH_3)_2(CO_3)_2^-$ ion[6,10] and is a simple addition of the spectra of the isolated fractions (Figure 1b–e). The absorption peaks at 2935, 1850, and 1400 cm^{-1} indicate the presence of ammonium ion, and those at 1480, 1370, 970, 740, and 690 cm^{-1} can be assigned to unidentate carbonato or aquo complexation and/or free carbonate. The infrared spectrum of the most soluble fraction is identical with the spectrum of $[Co(NH_3)_4(CO_3)]Cl$[11] except for a medium shoulder at 1480 cm^{-1}, which may be due to either free carbonate or unidentate carbonato ligand.[11a]

The original authors[2] reported that a hygroscopic violet isomer was precipitated by ethanol. However, the repeated preparation in our laboratory by the original method never gave a neat precipitate but always gave tarry materials which could be solidified by drying *in vacuo* or washing with ether. This sticky material can be understood as a phase separation characteristic of the alcohol–carbonate system, which should occur in the presence of free carbonate or some labile unidentate carbonato species. This complication was avoided by pouring the dilute violet solution into cold methanol, which gave a dry violet powder. The repetition of the same process did not cause any changes in the infrared spectrum of the product (Figure 1f), which is consistent with the formulation given in the Experimental Section, except for the 1480-cm^{-1} peak. Whether this peak is due to free or unidentate carbonate is difficult to ascertain. Unidentate carbonato ligands usually show a weak peak at about 1070 cm^{-1},[11] which may be obscured in the violet species.

The possibility of the cobalt existing in both the anionic and the cationic parts of the complex, as in the formulation $[Co(NH_3)_4(CO_3)][Co(NH_3)_2(CO_3)_2]\cdot 2H_2O$, was examined with ion-exchange experiments which

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(7) Microanalyses by Mr. Charles Meade, University of Massachusetts Microanalytical Laboratory, Amherst, Mass.

(8) Microanalyses by Huffman Laboratories, Wheatridge, Colo.

(9) Analyzed colorimetrically with nitroso-R salt; cobalt metal as standard.

(10) The infrared spectra of our blue products are equivalent with that reported by J. Fujita, A. E. Martell, and K. Nakamoto, *J. Chem. Phys.*, **36**, 339 (1962).

(11) (a) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley & Sons, Inc., New York, N. Y., 1963, pp 159–163; (b) K. Nakamoto, J. Fujita, S. Tanaka, and M. Kobayashi, *J. Am. Chem. Soc.*, **79**, 4904 (1957).

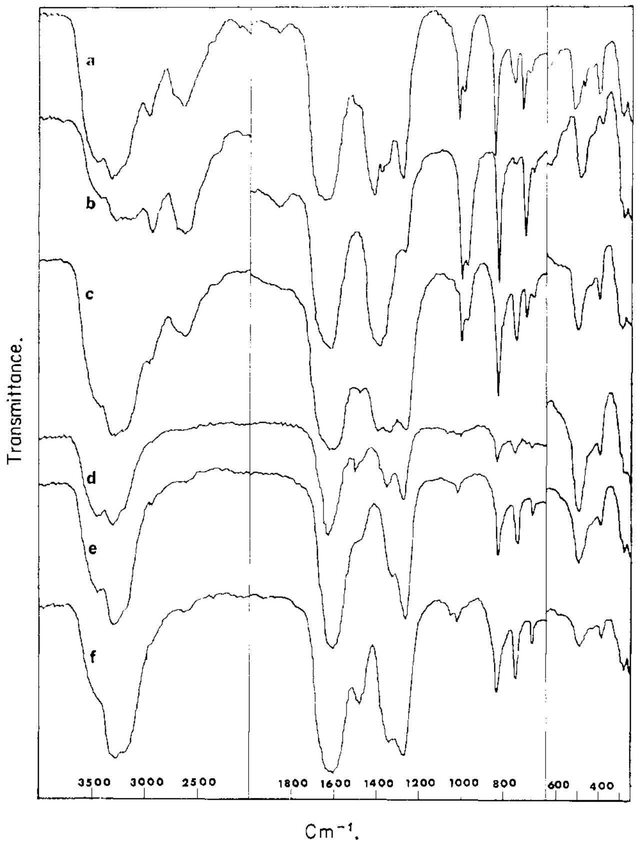

Figure 1.—Infrared spectra of violet species: (a) violet complex by regular[2] method; (b) least soluble violet fraction; (c) and (d) intermediate fractions; (e) most soluble violet fraction; (f) violet powder prepared by alternate precipitation procedure.

TABLE I
ABSORPTION SPECTRA OF COMPLEXES

Complex	$\tilde{\nu}_1$, cm^{-1} (λ_1, nm)	$\tilde{\nu}_2$, cm^{-1} (λ_2, nm)	ϵ_1/ϵ_2
Blue anion(s) of violet solution, K^+ salt	17,300 (577)	25,400 (393)	0.80[a]
$K[Co(NH_3)_2(CO_3)_2]$, blue species	17,300 (579)	25,400 (394)	0.77[a]
Red cation(s) of violet solution, Cl^- salt	18,200 (525)	27,800 (360)	0.83[a]
$[Co(NH_3)_4CO_3]NO_3$	18,200 (525)	27,600 (362)	0.93

[a] The $\tilde{\nu}_2$ peak is quite sensitive to the solution environment and time.

indicate red cationic and blue anionic components (Table I). The visible spectra of the blue solutions which result after the violet solutions are passed through cationic exchangers are very similar to the spectrum exhibited by the blue isomer of the diamminedicarbonatocobaltate(III) ion. The red solutions which pass directly through anionic exchangers are very similar to solutions of the tetraamminecarbonatocobalt(III) ion.[12] The oxygen donors aquo and unidentate and bidentate carbonato have similar ligand field strengths which are much lower than that of ammine; therefore, the visible spectrum shows that the cationic component is of the CoN_4O_2 type and the anionic is of the CoN_2O_4 type, where N and O are nitrogen and oxygen donors. A clearer definition of the violet product is not possible.

Professor Shibata,[13] who has had serious doubts about the isomer for some time, has suggested aquation as opposed to isomerization, and Dr. Kyuno[14] has been unable readily to prepare the pure violet isomer. Although some aquation does occur, evidence for a $[CoN_4O_2][CoN_2O_4]$ type of salt is compelling. Consequently, the earlier reports relating to this complex as a *trans*-diamminedicarbonatocobaltate(III) species should be disregarded.

Support of a *cis* configuration for the blue $Co(NH_3)_2(CO_3)_2^-$ anion is obtained from the absence of any *trans*-$Co(acac)_2(NH_3)_2^+$ from the reaction between the blue isomer and 2,4-pentanedione.[4] Similar retention reactions were observed by Kyuno[15] for the reaction of aqueous HCl and the blue isomer and by Cooke[5] for the reaction of ethylenediamine with this species. Similar results with the violet solutions are now quite logical, and the earlier hypothesized intermediate based on the strain in a four-membered ring[4] is unnecessary.

Acknowledgment.—Communications with Professor Shibata and Doctor Kyuno, written and oral, respectively, are deeply appreciated. Partial support of this research by the National Science Foundation is also gratefully acknowledged.

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[12] Sample courtesy of John Meyer. Absorption maxima consistent with previously published data; *cf.* "Gmelin's Handbuch der Anorganischen Chemie," 8th ed, System No. 58B, Verlag Chemie, Weinheim, 1964, p 494.

[13] M. Shibata, private communication. In a summary report by M. Shibata, *Nippon Kagaku Zasshi*, **87**, 771 (1966), no mention is made of the violet product.

[14] E. Kyuno, private communication.

[15] E. Kyuno, *Nippon Kagaku Zasshi*, **80**, 849 (1959).

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Coordination of Ethers. Tetrahydrofuroic Acid and Tetrahydrofuranacetic Acid

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Received March 4, 1969

The excellent solvent properties of ethers for many solutes are well known. Examples are the stabilization of Grignard reagents and the solubilities of magnesium iodide, ferric chloride, heteropolyacids, and $LiAlH_4$ in simple ethers. These phenomena have been rationalized in terms of the donor properties of ethereal oxygen and the consequent formation of addition compounds. Sigel, *et al.*,[1] have investigated a number of complexes of ethers, including one of the ligands used in this work. Their studies were limited to solutions, however, and no compounds were isolated for characterization. Some

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[1] H. Erlenmeyer, R. Griesser, B. Prijs, and H. Sigel, *Helv. Chim. Acta*, **51**, 339 (1968).