made to reexchange the NO^+ ions in nitrosonium β-alumina with Ag^+ or Na^+ ions; however, a partially exchanged silver β-alumina crystal (1.5-mm diameter) containing 37 mol % NO was heated *in vacuo* at 490° for 1 hr in order to see whether Ag^{2+} ions could be produced by the reaction

$$Ag^+_{lattice} + NO^+_{lattice} \xrightarrow{\Delta} NO(g) + Ag^{2+}_{lattice}$$

The crystal was examined by electron spin resonance spectroscopy at room temperature but no absorption peaks were found which would indicate that a paramagnetic species such as the Ag^{2+} ion was present. The crystal remained colorless and transparent after the heat treatment, but absorption bands between 1700 and 4000 cm^{-1} were no longer present in the ir spectrum. This latter work was not pursued any further.

Conclusions

Silver ions in silver-substituted β-alumina are completely exchanged for NO^+ ions in a $NOCl \cdot AlCl_3$ melt without altering the β-alumina structure.

The proposed reaction in the thermal decomposition of nitrosonium β-alumina is

$$2NO^+_{lattice} + O^{2-}_{lattice} \xrightarrow{\Delta} NO\uparrow + NO_2\uparrow$$

This reaction is based on (1) the amount of weight loss from the sample, (2) the evolution of a yellow-brown gas believed to be NO_2, and (3) the alteration of the β-alumina crystal structure.

The ir spectrum of nitrosonium β-alumina contains a strong absorption band at 2245 cm^{-1}, a frequency indicative of the N–O stretching motion of the nitrosonium ion.

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The Preparation of Copper(I) Trifluoroacetate Carbonyl[1]

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In a variety of different environments,[2] Cu(I) ion binds carbon monoxide, the limiting ratio CO:Cu being 1:1. This note describes the preparation of the carbonyl derived from copper(I) trifluoroacetate, with and without a molecule of solvent trifluoroacetic acid (TFA). The novel observations encompass the usefulness of TFA as a solvent for the dissolution of Cu(I) in the presence of carbon monoxide, the usefulness of trifluoroacetic anhydride (TFAA) to simplify the handling of the Cu(I) salt, and the fact that pumping away the carbon monoxide from the complex leaves a stable[3] Cu(I) salt.

Experimental Section

The reaction system is sensitive to air oxidation. Cu(I) complexes were prepared and handled under dry, oxygen-free nitrogen or carbon monoxide.

Materials.—Carbon monoxide (The Matheson Co.) was deoxygenated by alkaline pyrogallol, dried over Drierite, and stored over 1-butyl phthalate. Cuprous oxide was prepared by reduction of cupric sulfate by sucrose in basic solution. *Anal.* Cu, 89.1. Trifluoroacetic acid (Matheson Coleman & Bell) was distilled through a bubble-plate column. Trifluoroacetic anhydride was prepared from the acid and phosphorus pentoxide under reflux. It was then distilled through the bubble-plate column.

Copper(I) Trifluoroacetate Carbonyl–Trifluoroacetic Acid. Method A.—Cuprous oxide (2.0318 g) under carbon monoxide was covered with 13.95 ml of trifluoroacetic acid, and the dark brown slurry was stirred magnetically. Over 2 hr it absorbed 775 ml (0.0346 mol) of carbon monoxide and colorless crystals had separated from the then blue-green solution. The crystals were filtered, dried, and transferred under nitrogen; yield, 3.20 g (35.3%). *Anal.* Calcd for $C_5HCuF_6O_5$: Cu, 19.94. Found: Cu, 18.75.

Method B.—Cuprous oxide (2.0476 g) under carbon monoxide was covered with 15.82 ml of freshly prepared trifluoroacetic anhydride and the slurry was stirred magnetically. It absorbed no carbon monoxide. Water (0.60 ml, 0.056 mol) was injected; the mixture became warm and rapidly absorbed carbon monoxide. After 0.5 hr the colorless crystals were filtered and dried; yield, 4.95 g (54.2%). *Anal.* Calcd for $C_5HCuF_6O_5$: Cu, 19.94; $C_2HF_3O_2$, 35.79. Found: Cu, 19.93; $C_2HF_3O_2$, 35.78,[4] 36.39;[5] weight loss *in vacuo*, 39.30%. ν_{max}^{nujol}: 2155, 1667, 1212, 1164, 854, 792, 735 cm^{-1}.

Copper(I) Trifluoroacetate Carbonyl.—The solvated complex (3.3725 g) was subjected to oil pump vacuum for 45 min at room temperature. In other experiments all condensable liquid was collected by pumping for 45 min or less. Essentially 1 equiv of TFA is lost (see analysis above) to give colorless crystals of the unsolvated complex. *Anal.* Calcd for $C_3CuF_3O_3$: Cu, 31.06. Found: Cu, 31.9. ν_{max}^{nujol}: 2155 cm^{-1}.

Prolonged pumping on the solvated complex left a colorless product with a composition approaching that of cuprous trifluoroacetate. The characteristic absorption of CO was absent. *Anal.* Calcd for $C_2CuF_3O_2$: Cu, 35.9. Found: Cu, 34.8. ν_{max}^{KBr}: 1670, 1438, 1220, 1201, 1150 cm^{-1}.

The X-ray crystal structure determination of copper(I) trifluoroacetate carbonyl is in progress.

Discussion

Earlier experiments in this laboratory[6] had indicated the suitability of TFA as a solvent in facilitating the reaction of Cu(I) with carbon monoxide. Owing to the extraordinary sensitivity of the complexes to oxygen and the difficulty of obtaining it free of the solvent TFA, since pumping rather readily removes the carbon monoxide as well, we had only rough indications[6] of the stoichiometry of the complex prior to preparing it in TFAA.

The preparation in the anhydride as a solvent, however, affords a number of cogent observations. There is no absorption of carbon monoxide by the stirred mixture

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[1] This work was supported by Grant G-18827 from the National Science Foundation.

[2] (a) R. Stewart and D. G. Evans, *Anal. Chem.*, **35**, 1315 (1963); (b) summarized in "Gmelins Handbuch der Anorganischen Chemie," Kupfer Teil B, Lieperung 1, 1958, pp 223–237; (c) C. W. Alegranti and E. L. Muetterties, private communication.

[3] Other simple salts such as Cu^INO_3 cannot ordinarily be obtained unsolvated; they disproportionate.

[4] By titration.

[5] Based on the weight of trapped liquid, assuming it to be pure TFA.

[6] A. F. Scott and J. Colony, results unpublished except as reported (1960) to the Atomic Energy Commission.

of cuprous oxide and TFAA until water is added. The addition of 4 equiv of water brings about immediate reaction, presumably through the formation of TFA and its dissolution of the Cu(I) ion. Uptake of 1 equiv of carbon monoxide per Cu(I) is rapid and stops sharply. Separation of the crystals of the carbonyl complex from the cooled solution by filtration in a glove bag is necessary, as the indicative blue-green color of Cu(II) is almost impossible to avoid.

Analysis of the crystals, their infrared spectrum, and the pumping experiment all support the postulated stoichiometry of Cu^{+}:CO:TFA^{-}:TFA as 1:1:1:1. That the carbon monoxide is still present in the solvent-free crystals prepared by brief pumping is shown by its appearance at 2155 cm^{-1}; the frequency is unshifted from that characteristic of the initially prepared complex.

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Correspondence

On the Existence of the *β-cis* Configuration of Chelated Ethylenediamine-N,N′-diacetate

Sir:

The use of ethylenediaminediacetate (edda) as a coordinating ligand has been the subject of several recent papers.[1–3] These papers concern the preparation, resolution, and characterization of complexes in which edda acts as a tetradentate ligand and the other two positions in the coordination sphere are occupied by various bidentate groups.

Legg and Cooke[1] distinguished the coordination of edda in the so-called *trans* configuration from the so-called *cis* configuration by means of nuclear magnetic resonance spectroscopy. We feel that complexes with edda in these configurations should be called *α-cis* and *β-cis,* respectively, in accord with the nomenclature used for triethylenetetramine complexes.[4] This enables complexes where edda assumes a planar disposition about the central metal atom (allowing two unidentate ligands to occupy positions *trans* to one another) to be described as *trans.* Such a compound has been prepared.[5]

Small amounts of the *β-cis* isomer of some edda complexes have been isolated by ion-exchange chromatography.[1,2] However, in the systems so far reported[1–3] the *α-cis* isomer appears to have been formed almost exclusively. This together with an analysis of nmr data and a consideration of molecular models led Legg and Cooke[1] to conclude that edda favored an *α-cis* configuration due to increased "steric interaction between the ligands" in the *β-cis* isomers. Specifically there appears to be a greater interaction between the amine protons of ethylenediamine and the protons of edda in the *β-cis* isomer. Our present work has shown that the *α-cis* configuration of edda is not preferred in all complexes and in particular in the case of the $Co(edda)CO_3^{-}$ isomers and their oxalate (ox) and malonate (mal) analogs. It is noteworthy that in the *β-cis* isomers of these complexes the steric interactions postulated for the corresponding diamine analogs are absent. Van Saun and Douglas only found the *α-cis* isomers for $Co(edda)CO_3^{-}$ and related complexes.[3] However, they isolated less than 30% of the total possible yield, and it is conceivable that the *β-cis* isomers still remained in solution.

We have prepared a series of edda complexes and are studying the kinetics of their aquation and isomerization. The *α-cis* and *β-cis* isomers of $Co(edda)CO_3^{-}$, $Co(edda)(ox)^{-}$, $Co(edda)(mal)^{-}$, $Co(edda)(OH_2)_2^{+}$, and $Co(edda)Cl_2^{-}$ have been prepared. A previous nmr study showed that in the *α-cis* isomers the acetate ring protons exhibited only one AB quartet but in the *β-cis* isomers the spectrum was much more complex.[1] Our complexes confirm this conclusion. Further support for our assignment of configuration has come from the retention of configuration when the carbonato isomers are aquated with dilute perchloric acid and regenerated with bicarbonate. These reactions occur with retention as had previously been found in the reactions of related complexes.[6]

The *α-cis* and *β-cis* isomers of $Co(edda)(OH_2)_2^{+}$ were separable by cation-exchange chromatography and in aqueous solution the *β-cis* form isomerizes to the more stable *α-cis.* However, in contrast to the findings of Van Saun and Douglas[3] and unlike any of the systems so far investigated[1–3], the *β-cis* isomer of $Co(edda)CO_3^{-}$ is more stable than the *α-cis* isomer in aqueous solution. The *β-cis* isomer is thermodynamically favored over the *α-cis* by about 600 cal/mol.

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