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 | $\bar{\nu}_1$, cm$^{-1}$ ($\lambda_1$, nm) | $\bar{\nu}_2$, cm$^{-1}$ ($\lambda_2$, nm) | $\epsilon_1/\epsilon_2$ |
|---|---|---|---|
| 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$_3$)$_4$CO$_3$]NO$_3$ | 18,200 (525) | 27,600 (362) | 0.93 |

$^a$ The $\bar{\nu}_2$ 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$_4$O$_2$ type and the anionic is of

(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.

the CoN$_2$O$_4$ 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$_4$O$_2$][CoN$_2$O$_4$] 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.

(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

BY W. ROBERT SCHEIDT AND PAUL G. RASMUSSEN

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

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

work has been reported on tetrahydrofuran and 1,4-dioxane complexes with divalent metal ions.[2,3] Although most of these complexes were not characterized beyond the establishment of stoichiometries, the importance of the carbon ring in sterically freeing the oxygen was demonstrated. In order to prepare more stable complexes which will allow thorough investigation, we have used ligands in which the sterically free ether function is incorporated into a potentially bidentate chelate. In particular, complexes of 2-tetrahydrofuroic acid (TFA) and 2-tetrahydrofuranacetic acid (TFAA) have been investigated. As the anions, these



TFA                                        TFAA
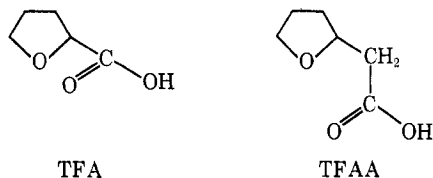
ligands offer the possibility of five- and six-member chelate ring formation.

## Experimental Section

**Preparation of Reagents.**—2-Tetrahydrofuroic acid was prepared by the literature method[4] (catalytic hydrogenation of 2-furoic acid) except that higher yields (46–50%) were obtained using *t*-butyl alcohol instead of ethanol as the solvent. 2-Tetrahydrofuranacetic acid was purchased from the Aldrich Chemical Co. The sodium salts of both acids were prepared by neutralization with sodium hydroxide in water solution. The water was removed first with a rotary evaporator and then by vacuum over phosphorus pentoxide.

**Preparation of the Complexes. Cobalt(II) and Copper(II) Complexes of Tetrahydrofuroic and Tetrahydrofuranacetic Acid.** —These complexes were prepared by stirring a slurry of the sodium salts (13 mmol) with the appropriate anhydrous metal chloride (5 mmol) in 150 ml of chloroform in a glass-stoppered erlenmeyer flask. After 4–6 hr, the slurry was filtered on a fritted-glass filter to remove starting materials and sodium chloride. After evaporation of the chloroform, the solid complex was mixed with sand and extracted with benzene in a Soxhlet extractor fitted with a calcium chloride drying tube. Removal of benzene gave the desired complex.

*Anal.* Calcd for $CoC_{10}H_{14}O_6$: C, 41.54; H, 4.88. Found: C, 41.96; H, 5.4. Calcd for $CoC_{12}H_{18}O_6$: C, 45.44; H, 5.72. Found: C, 45.28; H, 5.84. Calcd for $CuC_{12}H_{18}O_6$: C, 44.79; H, 5.64. Found: C, 44.37; H, 5.51. Calcd for $CuC_{10}H_{14}O_6$: C, 40.89; H, 4.80. Found: C, 40.91; H, 5.10. Qualitative analyses for halide were uniformly negative.

Magnetic susceptibilities were measured by the Gouy method. The apparatus used is described elsewhere.[5] Molecular weights were measured using a Hitachi Perkin-Elmer Model 115 osmometer.

Attempts to prepare analogous Ni(II) and Cr(III) complexes gave products which could not be freed of halide. The attempt to prepare a Ni(II) compound followed the same procedure described above, while the Cr(III) attempt utilized $CrCl_3$·(THF)$_3$ as a starting material.

## Results and Discussion

The ligands tetrahydrofuroic acid and tetrahydrofuranacetic acid can potentially coordinate through

(2) P. Hamilton, R. McBeth, W. Bekebrede, and H. H. Sisler, *J. Am. Chem. Soc.*, **75**, 2881 (1953).

(3) R. J. Kern, *J. Inorg. Nucl. Chem.*, **24**, 1105 (1962).

(4) W. E. Kaufmann and R. Adams, *J. Am. Chem. Soc.*, **45**, 3029 (1923).

(5) W. R. Scheidt, Ph.D. Thesis, The University of Michigan, Ann Arbor, Mich., 1968.

both the carboxyl and ether functions, thus acting as bidentate chelates. The ligands could also coordinate solely through the acid function with the carboxyl group acting as a monodentate, a bidentate, or a bridging ligand. If the complexes formed involve coordination of the carboxyl group alone, they should be analogous to other complexes formed from simple, *i.e.*, no other donor sites available, carboxylic acids. On the other hand, if the ether function is also involved, analogies with dioxygen univalent chelates are appropriate.

The complexes were characterized by their electronic absorption and infrared spectra, elemental analysis, magnetic properties, and molecular weights.

The magnetic properties of the four complexes obtained in the pure state as a function of temperature are given in Table I. All of the complexes except bis-(tetrahydrofuranacetato)copper(II) deviate but slightly from the Curie law.

TABLE I

MAGNETIC PROPERTIES OF
BIS(TETRAHYDROFURANACETATO)COBALT(II),
BIS(TETRAHYDROFUROATO)COBALT(II),
BIS(TETRAHYDROFURANACETATO)COPPER(II), AND
BIS(TETRAHYDROFUROATO)COPPER(II)

| Compound | Temp, °K | $10^6\chi_m'$, cgsu | $\mu_{eff}$, BM |
|---|---|---|---|
| Bis(tetrahydrofuranacetato)cobalt(II) | 79 | 38,940 | 4.92 |
| | 95 | 31,512 | 4.93 |
| | 126 | 26,150 | 5.00 |
| | 167 | 18,100 | 4.98 |
| | 201 | 15,676 | 5.07 |
| | 293 | 11,260 | 5.10 |
| Bis(tetrahydrofuroato)cobalt(II) | 79 | 31,630 | 4.44 |
| | 95 | 27,108 | 4.55 |
| | 126 | 20,578 | 4.55 |
| | 167 | 15,078 | 4.50 |
| | 201 | 12,156 | 4.50 |
| | 293 | 9,115 | 4.64 |
| Bis(tetrahydrofuranacetato)copper(II) | 79 | 779 | 0.7 |
| | 95 | 647 | 0.7 |
| | 126 | 637 | 0.8 |
| | 167 | 609 | 0.9 |
| | 201 | 756 | 1.1 |
| | 293 | 724 | 1.3 |
| Bis(tetrahydrofuroato)copper(II) | 79 | 4,245 | 1.63 |
| | 95 | 3,931 | 1.73 |
| | 126 | 2,913 | 1.72 |
| | 167 | 2,234 | 1.94 |
| | 201 | 1,790 | 1.73 |
| | 293 | 1,401 | 1.80 |

The electronic absorption spectra of the two cobalt complexes are very similar. They show a peak at 8000 cm$^{-1}$ and a band envelope around 20,000 cm$^{-1}$ with low molar extinction coefficients. The spectra, measured in chloroform, showed little concentration dependence. The spectra are similar to those recorded for hexaaquocobalt(II)[6] and are consistent with those expected for complexes with distorted octahedral coordination. The low-energy band can be identified as the $^4T_{1g} \rightarrow {}^4T_{2g}$ transition while the higher energy transition is $^4T_{1g} \rightarrow {}^4T_{1g}(P)$. The magnetic moment of bis-

(6) F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry," Interscience Publishers, New York, N. Y., 1962, p 725.

(tetrahydrofuranacetato)cobalt(II), 4.9–5.1 BM, confirms the assignment of an octahedral geometry to this complex.[7] The moment of bis(tetrahydrofuroato)cobalt(II) is lower, however; moments of this magnitude have been observed for the octahedral complex hexakis-(pyridine N-oxide)cobalt(II) perchlorate, 4.69 BM,[8] potassium tris(acetylacetonato)cobalt(II), 4.79 BM,[9] and dinitratobis(triphenylphosphine oxide)cobalt(II), 4.69 BM.[10] The electronic absorption spectra of the two copper complexes are typical of copper(II) complexes and do not appear to have the "dimer" band at 375 nm identified by Yamada, *et al.*,[11] although a strong charge-transfer band centered at approximately 300 nm may be obscuring the relatively weak 375-nm band.

Bis(tetrahydrofuranacetato)copper(II) does not follow the Curie–Weiss law but rather shows a temperature-dependent magnetic moment. The temperature dependence is similar to the temperature dependence shown by the copper acetate dimer[12] and other copper–carboxylic acid complexes.[13] Thus a copper acetate dimer structure is suggested. Molecular weight measurements in chloroform confirm the dimeric nature of this compound (see Table II).

TABLE II

MOLECULAR WEIGHTS OF BIS(TETRAHYDROFUROATO)COBALT(II),
BIS(TETRAHYDROFURANACETATO)COBALT(II),
BIS(TETRAHYDROFUROATO)COPPER(II), AND
BIS(TETRAHYDROFURANACETATO)COPPER(II) IN CHLOROFORM

| Compound | Concn, g/100 g of solvent | Mol wt | Polymerizn no.[a] |
|---|---|---|---|
| Bis(tetrahydrofuroato)cobalt(II) | 0.1548 | 1485 | 5.13 |
| | 0.2846 | 1443 | 4.95 |
| | 0.6433 | 1522 | 5.26 |
| | 1.6172 | 1773 | 6.12 |
| Bis(tetrahydrofuranacetato)cobalt-(II) | 0.1816 | 1401 | 4.42 |
| | 0.4293 | 1635 | 5.15 |
| | 0.3550 | 1464 | 4.63 |
| | 1.4764 | 1400 | 4.42 |
| Bis(tetrahydrofuroato)copper(II) | 0.2939 | 1107 | 3.82 |
| | 1.1795 | 1398 | 4.81 |
| Bis(tetrahydrofuranacetato)-copper(II) | 0.2178 | 486 | 1.54 |

[a] The polymerization number is the experimental molecular weight divided by the molecular weight of the hypothetical monomeric complex.

Bis(tetrahydrofuroato)copper(II) follows the Curie–Weiss law with a normal magnetic moment. It is more highly associated in solution, and we believe it is best considered as a chelate involving ethereal oxygens. This is in agreement with the solution studies of Sigel, *et al.*,[1] on the 1:1 complex of this ligand with copper(II).

The differences observed between the two copper complexes are consistent with the different stabilities

expected for five- and six-member chelate ring formation.

The possibility that the cobalt complexes were polymers coordinated only by the carboxyl oxygens and different from simple carboxylic acid salts because of the steric effects of the ring was considered. Therefore, the sterically similar bis(phenylacetate)cobalt(II) and other carboxylate complexes were synthesized. These compounds in the anhydrous state were purple solids, insoluble in organic solvents and not at all similar to the ether complexes, but similar to other simple carboxylic acid derivatives of cobalt.

The metal complexes of TFA and TFAA have many properties consistent with ether coordination. They are water-sensitive and decompose in coordinating solvents, even such weakly coordinating solvents as acetone and alcohol. The infrared spectra show small shifts of the C–O–C band to lower frequencies for the tetrahydrofuroate complexes but not for the tetrahydrofuranacetate complexes. This type of shift has been recognized before[3] although it is not a definite test for ether coordination. The complexes did not show indications of water or free carboxylic acid in their infrared spectra.

Neither ether oxygens nor individual carboxyl oxygens are likely to serve as bridging donors in the manner commonly found for chloride ions. Therefore, in order to satisfy the observed stoichiometry and preserve six-coordination of the metal ions (as the above data require), it is necessary to bridge metal ions with the carboxyl group. This feature is of course familiar in the $Cu(CH_3CO_2)_2 \cdot 2H_2O$ structure, but here it is combined with ether coordination. These complexes are quite different from those previously reported to be formed by the tetrahydrofurfurylamine ligand.[14] In view of these differences, it would appear risky to postulate ether coordination whenever halide is present for possible bridging. When the anion is perchlorate, or when the anion is part of the ligand itself, as in the present case, ether coordination can be firmly established.

(14) M. D. Joesten, K. G. Claus, and K. P. Lannert, *J. Inorg. Nucl. Chem.*, **29**, 1421 (1967).

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# Iron Carbonyl Complex of a Conjugated Azo Olefin

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AND AKIRA NAKAMURA

Previously we have shown[1] that enimine systems (–CH=CHCH=N–) can be coordinated to the Fe(CO)₃ moiety through the pπ-conjugated double bonds like

(7) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 287–291 (1964).
(8) J. A. Walmsley and S. Y. Tyree, *J. Am. Chem. Soc.*, **83**, 3770 (1961).
(9) B. N. Figgis and R. S. Nyholm, *J. Chem. Soc.*, 338 (1959).
(10) E. Bannister and F. A. Cotton, *ibid.*, 2276 (1960).
(11) S. Yamada, H. Nishikawa, and S. Miki, *Bull. Chem. Soc. Japan*, **37**, 576 (1964).
(12) B. N. Figgis and J. Lewis, *Progr. Inorg. Chem.*, **6**, 217–219 (1964).
(13) R. L. Martin and H. Waterman, *J. Chem. Soc.*, 2545 (1957).

(1) S. Otsuka, A. Nakamura, and T. Yoshida, *Inorg. Chem.*, **6**, 20 (1967).