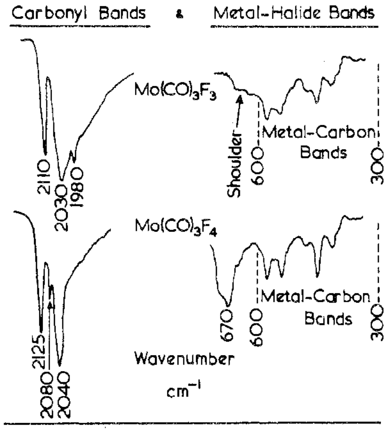

Figure 1. Absorptions in the ir spectra of Nujol mulls of (top) trifluorotricarbonylmolybdenum(III) and (bottom) tetrafluorotricarbonylmolybdenum(IV).

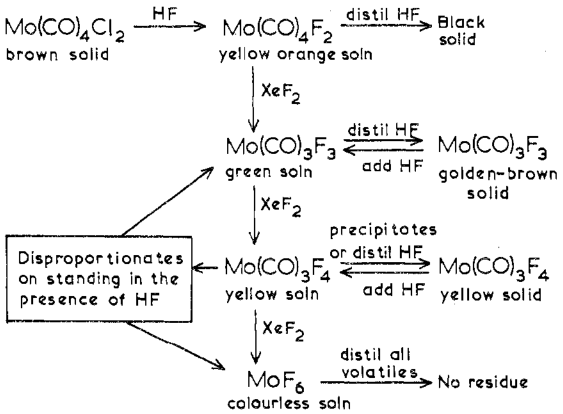

Figure 2. Related series of reactions of molybdenum carbonyl fluorides obtained using xenon difluoride as oxidant.

so the spectrum is not consistent with two carbonyl ligands.

Both ir spectra (Figure 1) have similar bands in the metal-carbon region. In the case of the molybdenum(IV) compound, the band at 670 cm^{-1} is in the region for terminal fluorides.[5] In the case of the molybdenum(III) compound, the metal-fluoride absorption would be expected at a slightly lower wave number, where the weak absorption shoulder just above 600 cm^{-1} appears. In our previous work,[1] we found that the metal-halide absorptions may have intensities similar to those of the metal-carbon absorptions.

Hence, from their predetermined compositions, the gases evolved during their preparations, and their ir spectra, the products of the oxidations appear to be trifluorotricarbonylmolybdenum(III) which is green in hydrogen fluoride and golden brown as a solid and tetrafluorotricarbonylmolybdenum(IV) which is unstable in hydrogen fluoride and is yellow both in solution and as a solid. See Figure 2.

Yellow tetrafluorotricarbonylmolybdenum(IV) is unstable in hydrogen fluoride, but it does not decompose by eliminating one carbonyl ligand to form orange tetrafluorodicarbonylmolybdenum(IV).[5] Instead, it decomposes to form the green soluble products as described above. One factor favoring this is the higher entropy change associated with formation of soluble rather than insoluble products. This instability can be applied to isolation of pure samples of carbonyl fluorides in the following way. To prepare the molybdenum(III) compound, use slightly *more* than the stoichiometric amount of oxidant; on standing, the small amount of molybdenum(IV) compound decomposes and evaporation leaves the pure golden brown product. To prepare the molybdenum(IV) compound, first prepare the molybdenum(III) compound, and then add slightly *less* than the stoichiometric amount of oxidant; filter immediately and dry the yellow solid by evaporation of volatile compounds.

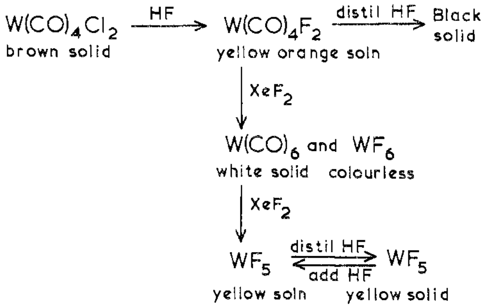

Figure 3. Related series of reactions of tungsten carbonyl fluoride obtained using xenon difluoride as oxidant.

Tungsten System. Oxidation of the tungsten(II) compound did not form higher oxidation state carbonyl fluorides. This different behavior, as compared with the molybdenum system, is consistent with the greater stability of tungsten hexafluoride as compared with molybdenum hexafluoride.[6] Thus, attempted oxidation to tungsten(III) or -(IV) results in disproportionation so as to form the stable hexafluoride. See Figure 3.[7]

Registry No. HF, 7664-39-3; XeF_2, 13709-36-9; $Mo(CO)_4Cl_2$, 15712-13-7; $Mo(CO)_4F_2$, 38703-63-8; $Mo(CO)_3F_3$, 38708-79-1; $Mo(CO)_3F_4$, 38703-64-9; MoF_6, 7783-77-9; $W(CO)_4Cl_2$, 22172-29-8; $W(CO)_4F_2$, 38703-66-1; $W(CO)_6$, 1440-11-0; WF_6, 7783-82-6; WF_5, 19357-83-6.

Acknowledgment. Financial support from the Australian Atomic Energy Commission is gratefully acknowledged.

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(5) T. A. O'Donnell and K. A. Phillips, *Inorg. Chem.*, 9, 2611 (1970).

(6) T. A. O'Donnell and D. F. Stewart, *Inorg. Chem.*, 5, 1434 (1966).

(7) Our attention has been drawn by a reviewer to a conference report that xenon difluoride has been used in reactions with metal carbonyls: C. J. Marshall and R. D. Peacock, Abstracts of Papers, 6th International Symposium on Fluorine Chemistry, 1971, No. C-33.

Contribution from the Department of Chemistry, University of Alberta, Edmonton, Alberta, Canada T6G 2G2

Nuclear Overhauser Studies on Formato and Formamido Complexes of Pentaamminecobalt(III)

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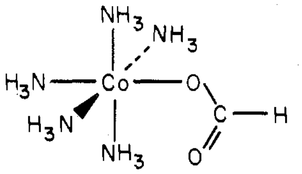
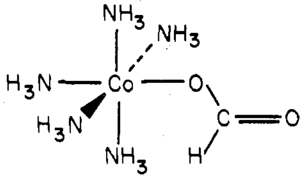
Received October 6, 1972

We wish to report the results of nuclear Overhauser effect (NOE) studies on some complexes of pentaamminecobalt(III). The NOE has been used to determine the conformation of the coordinated formate ion and to help in the assignment of the pmr spectrum of a new dinuclear formamide complex.

In the first application it was of interest to determine if an NOE could be observed and then to use it to study the conformation of the coordinated formate ion in $(NH_3)_5CoO_2CH^{2+}$. Two reasonable conformational possibilities are shown in I and II. The dominant steric interaction in these conformations is between the cis NH_3 hydrogen atoms and the carbonyl oxygen in I and the formate hydrogen atom in II. Steric considerations favor II over I but models indicate that I is certainly not excluded. However in other cases, such as with the acetate complex, the form analogous to I (with CH_3 replacing H) would be greatly favored. This has been confirmed in the solid state by an X-ray diffraction study[1] of the acetato complex.



I



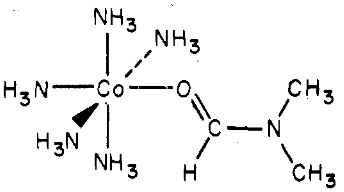
II

Therefore it seems possible at least that a conformational difference might exist between the formato and other simple carboxylato complexes. This difference might be responsible, at least in part, for the much larger rate of reduction by chromium(II) of $(NH_3)_5Co(formate)^{2+}$ compared to $(NH_3)_5Co(acetate)^{2+}$.[2] The conformation of the formate ligand might provide a more favorable geometry for the bridged activated complex formed in the reaction.

The I and II forms may be differentiated by an NOE study because in II the formate hydrogen is close to the cis NH_3 hydrogens, while it is much further removed from these atoms in I. Thus in II the predominant relaxation mechanism is likely to be *via* the intramolecular dipole–dipole interaction with the cis NH_3 hydrogen atoms. Irradiation of the latter in the NOE experiment should produce a marked effect on the intensity of the formate hydrogen nmr resonance if II is the favored form but little effect if I predominates.

The same principles have been used to assign the cis NH_3 resonances in the pmr spectrum of a new dinuclear formamide complex, μ-formamido-decaamminedicobalt(III).

***N,N*-Dimethylformamidopentaamminecobalt(III).** This compound was studied as a model in which the equivalent of II would be strongly favored for steric reasons. The carbonyl oxygen in formate is replaced by the bulky $-N(CH_3)_2$ group, and the only form likely to be present is



III

It was decided that the study of the formate complex would be worthwhile only if the DMF complex showed an NOE. The pmr spectrum of the DMF complex has been published[3] and shows resonances at τ 2.6 (CH), 6.14 (cis NH_3), 7.28 (trans NH_3), and 6.92 and 7.10 ($N(CH_3)_2$). Irradiation of the cis NH_3 resonance was found to produce a 14% enhancement in the integrated intensity of the CH resonance. It seemed reasonable therefore to expect an NOE if II is the preferred form of the formate complex.

In a different connection the CH resonance was integrated while separately irradiating the high- and low-field *N*-CH_3 resonances. Irradiation of the high-field methyl produced no effect, but irradiation of the low-field methyl produced a 12% NOE. This experiment is analogous to that of Anet and Bourn[4] on free DMF and shows that the low-field methyl is cis to the formyl hydrogen in the coordinated DMF, just as it is in the free molecule.

Formatopentaamminecobalt(III). The pmr spectrum of this compound shows resonances at τ 2.54 (CH), 6.32 (cis NH_3), and 7.34 (trans NH_3). Irradiation of the cis NH_3 peak produces an NOE of 17% on the CH peak. The fact that the NOE is larger in this case than with coordinated DMF is consistent with the fact that additional modes of relaxation (*i.e.*, *via* interaction with CH_3 and ^{14}N) are available in DMF, as well as the dipolar interaction with the cis NH_3 protons.

The observed NOE for the formate complex indicates that at least a significant proportion of the compound must exist in conformation II. For steric reasons this conformation is likely to be unique for formate among the simple carboxylate ligands. This may be a factor in explaining the larger rate of bridged electron transfer between $(NH_3)_5CoO_2CH^{2+}$ and chromium(II).[2]

μ-Formamido-decaamminedicobalt(III). This complex was prepared as a by-product during our earlier work on formamide complexes.[3] The preparation and physical properties are given in the Experimental Section. The characterization was puzzling for some time, but the ion-exchange properties, which indicated a charge of $\geqslant 4+$, and the fact that the compound can be prepared by heating $(NH_3)_5CoOH_2{}^{3+}$ and $(NH_3)_5CoNHCHO^{2+}$ in an inert solvent provided strong evidence for a dimeric formamide complex.

The pmr spectrum shown in Figure 1 is consistent with a dimer but could also indicate a mixture of two similar species. However, the latter possibility did not seem reasonable when it was found that the peaks which appear in pairs in the pmr spectrum were always of equal intensity,[5] independent of various purification procedures. Spin-decoupling experiments also showed that the peaks labeled (a) and (b) in Figure 1 were coupled with $J = 5$ Hz.

The pmr spectrum can be assigned as shown in Figure 1, except that peaks (c) and (f) could be interchanged. We have used the NOE to determine the assignment of (c) and (f) by observing the CH resonance while irradiating (c) and (f) separately. When the lower field peak (c) was irradiated, an NOE of 15% was observed, while no effect (±2%) was detected when the higher field peak (f) was irradiated. This result shows that the CH proton is near the cis NH_3 protons giving resonance (c) and that these must be on the cobalt bonded to the oxygen atom of the formamide ligand, as assigned in Figure 1.

The assignment of the trans NH_3 protons, (d) and (e) in Figure 1, remains somewhat uncertain. However, for a wide range of oxygen-coordinating ligands we have observed that the trans NH_3 resonance is always at τ 7.2 or greater, while with nitrogen-coordinating ligands it occurs in the range τ 6.5–7.0. On this basis (d) and (e) have been assigned as shown in Figure 1.

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(1) E. B. Fleischer and R. Frost, *J. Amer. Chem. Soc.*, **87**, 3998 (1965).

(2) M. B. Barrett, J. H. Swinehart, and H. Taube, *Inorg. Chem.*, **10**, 1983 (1971).

(3) R. J. Balahura and R. B. Jordan, *J. Amer. Chem. Soc.*, **92**, 1533 (1970).

(4) F. A. L. Anet and A. J. R. Bourn, *J. Amer. Chem. Soc.*, **87**, 5250 (1965).

(5) The integrated relative intensities of the peaks, in order of increasing field, are 1:1:12:3:12:3 within experimental error.

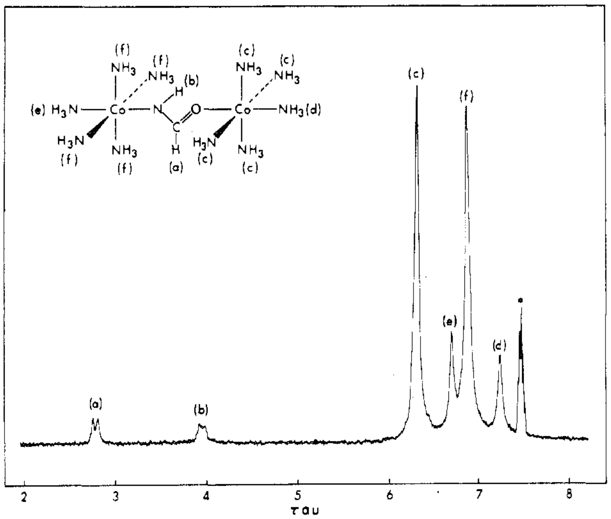

Figure 1. Pmr spectrum of μ-formamido-decaamminecobalt(III) perchlorate in dimethyl sulfoxide-d_6. The asterisk denotes the solvent peak.

It should be noted that this assignment of peak (e) requires a modification of our empirical rule[6] that the cis and trans NH_3 resonance should be separated by 0-0.6 τ unit for a nitrogen-coordinating ligand on $(NH_3)_5Co^{3+}$. The range must be extended now to cover from -0.2 to $+0.6$ τ unit.

Experimental Section

The preparation and characterization of *N,N*-dimethylformamidopentaamminecobalt(III) perchlorate has been described elsewhere.[3] The formatopentaamminecobalt(III) was prepared in the standard way[2] and purified by ion-exchange chromatography on Rexyn 102 (Fisher Scientific Co.) in the sodium ion form.

The μ-formamido-decaamminedicobalt(III) perchlorate was isolated as a pink crystalline by-product during the preparation of the nitrogen-bonded isomer of formamidopentaamminecobalt(III).[3] The same compound has also been prepared by heating 2.5 g of $(NH_3)_5CoOH_2(ClO_4)_3$ and 2.1 g of $(NH_3)_5CoNHCO(ClO_4)_2$ in 50 ml of trimethyl phosphate, over 5 g of Linde 3A molecular sieve, for 3 hr on a steam bath. The product was isolated by addition of *sec*-butyl alcohol as described previously.[3] The crude product may be purified by chromatography on the weak-acid cation-exchange resin Rexyn 102, in the sodium ion form. Elution was carried out with sodium acetate in increasing concentrations up to 2.0 *M*. This served to elute all impurities from the column and left the desired product, which is clearly highly charged since it cannot be eluted with a 2 *M* solution. The product was removed from the resin with dilute perchloric acid and was essentially quantitatively precipitated by adding concentrated perchloric acid to a final concentration of 1 *M*. *Anal.* Calcd for $(NH_3)_{10}Co_2NHCHO(ClO_4)_5$: C, 1.45; H, 3.86; N, 18.6. Found: C, 1.75; H, 3.86; N, 18.3.

The visible spectrum of the dimer in water shows maxima at 341 nm (ϵ 164 M^{-1} cm^{-1}) and 492 nm (ϵ 141 M^{-1} cm^{-1}). The infrared spectrum is complex but deuteration leaves a strong absorption at 1601 cm^{-1} (KBr disk) which may be assigned to the C=O stretching frequency. The pmr spectrum is shown in Figure 1 and discussed elsewhere in this paper.

The pmr samples for the NOE studies were all prepared by mixing about 0.1 g of the cobalt(III) complex, about 0.01 g of 2,4-dinitrobenzene (used as an integration standard),[7] 0.05 ml of TMS, and 1 ml of DMSO-d_6 over some molecular sieve in a tube with ground-glass joints suitable for attachment to a standard vacuum line. The sample was taken through three freeze-pump-thaw cycles and stored under vacuum for 3-4 hr for residual water to be removed by the molecular sieve. Then the solution was poured, while still under vacuum, through a glass wool plug into a standard nmr tube and sealed off.

The pmr spectra were recorded on a Varian HA 100 and all integrations were performed with the standard electronic integrator. Both the sample and internal integration reference (2,4-dinitrobenzene) peaks were integrated in each sweep through the spectrum. At least six integrations were performed at a particular irradiating power and the results averaged. A maximum deviation of about 3% was observed in the ratio of standard to sample integral under a given set of conditions.

Registry No. $(NH_3)_5CoOH_2(ClO_4)_3$, 13820-81-0; $(NH_3)_5CoNHCHO(ClO_4)_2$, 26729-10-2; $(NH_3)_5CoOCHN(Me)_2(ClO_4)_3$, 18897-02-4; $(NH_3)_5CoO_2CH(ClO_4)_2$, 28660-81-3; $(NH_3)_{10}Co_2NHCHO(ClO_4)_5$, 38894-74-5.

Acknowledgment. The authors wish to acknowledge the financial support for this research and fellowship support to R. J. B. from the National Research Council of Canada and to thank Mr. G. Bigam and Mr. D. Brisbane for running the pmr spectra.

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(6) R. J. Balahura and R. B. Jordan, *Inorg. Chem.*, **9**, 1567 (1970).

(7) These quantities give about 0.2 *M* cobalt(III) and 0.06 *M* standard and make the single proton of the complex about equal in intensity to the four protons from the standard.

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Reaction of Thiols with the One-Equivalent Oxidants Neptunium(VI) and Cerium(IV) in Aqueous Acidic Media[1]

D. K. Lavallee,[2] J. C. Sullivan,*[3] and E. Deutsch[2]

Received October 11, 1972

A determination of the stoichiometry of the reaction between a series of thiols and the 1-equiv oxidant Np(VI) was undertaken prior to dynamic studies on such systems. During the course of this study our attention was brought to the recent reports by Danehy and coworkers,[4] who investigated stoichiometries of thiol oxidations with the 2-equiv reagent iodine. These investigators demonstrated (a) that the excessive consumption of iodine (to yield products of higher oxidation states than disulfides) is dependent upon the concentration of thiol and (b) that thiols containing a free β-carboxylate group have the greatest tendency to be oxidized beyond the disulfide.

The data presented in this note demonstrate that the 1-equiv oxidants Np(VI) and Ce(IV) yield results that are similar to those obtained with iodine. The results obtained with Ce(IV) are in good agreement with thermometric titration data[5] but are not consistent with a previous report that the oxidation of mercaptocarboxylic acids by Ce(IV) stoichiometrically yields disulfides.[6] We have also demonstrated that both the stoichiometry and dynamics of oxidation of thiols by Np(VI) are markedly affected by the presence of molecular oxygen in the solutions.

Experimental Section

Materials. Unless otherwise specified, all chemicals are reagent

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(1) A portion of this investigation was conducted under the auspices of the United States Atomic Energy Commission.

(2) University of Chicago.

(3) Argonne National Laboratory.

(4) (a) J. P. Danehy, *Int. J. Sulfur Chem. C*, 6, 159 (1971); (b) J. P. Danehy, B. T. Doherty, and C. P. Egan, *J. Org. Chem.*, 36, 2525 (1971); (c) J. P. Danehy, C. P. Egan, and J. Switalski, *ibid.*, 36, 2530; (d) J. P. Danehy and M. Y. Oester, *ibid.*, 32, 1491 (1967).

(5) W. A. Alexander, C. J. Mash, and A. McAuley, *Talanta*, 16, 535 (1969).

(6) J. Hill and A. McAuley, *J. Chem. Soc. A*, 156 (1968).