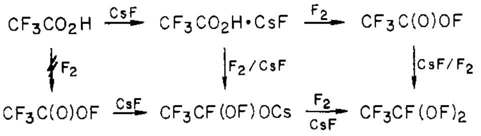
Warming to 22 °C while pumping on the reactor resulted in a 5% yield of unknown volatile compounds but no CF_3CO_2H. Addition of an additional molar equivalent of F_2 to the residue and treating in the same way resulted in another 45% of $CF_3CF(OF)_2$. The total gases formed corresponded to the original amount of CF_3CO_2H. If CF_3CO_2H is condensed onto CsF at −195 °C and then warmed to 22 °C, it cannot be removed under vacuum. If CF_3CO_2Cs is allowed to react with F_2 under these conditions, $CF_3CF(OF)_2$ is formed in good but not as high a yield as when the acid is used. Fluorine and CF_3CO_2H at −111 °C without CsF show little or no reaction. These observations taken together suggest the following possibilities, with the HF product omitted:



The second reaction with fluorine is probably very fast compared to the first, otherwise one would expect to see some CF_3CO_2F or other intermediate products. Whether or not free $CF_3C(O)OF$ is actually an intermediate is uncertain. The reaction of a known sample $CF_3C(O)OF$ with CsF/F_2 has not been carried out, but it should react readily at low temperature. A related compound has been shown to react in this way,[17] and the facile nature of this reaction with a variety of carbonyl compounds is well established (eq 5-7).[3]

$$FC(O)OF + F_2 \xrightarrow{CsF} CF_2(OF)_2 \qquad (5)$$

$$RC(O)F + F_2 \xrightarrow{CsF} RCF_2OF \qquad (6)$$

$$RC(O)R' + F_2 \xrightarrow{CsF} RR'CFOF \qquad (7)$$

R and R′ = fluoroalkyl

The characterization of the isolated 1,1-bis(fluorooxy)fluoroalkanes by IR and ^{19}F NMR spectroscopy was very straightforward. The low-field chemical shifts of the OF groups combined with the expected multiplicity and relative areas of the observed resonances provide unambiguous proof of structure.[3,18] The IR spectra contain absorptions in the 850–900 cm^{-1} region which can be assigned to $\nu(OF)$ and 900–1000 cm^{-1} due to $\nu(CO)$. In each case, minor impurities due to decomposition products were observed in the IR spectra.

The thermal stabilities of the $R_fCF(OF)_2$ compounds were compared at 53 °C as summarized in Table II. Their controlled thermolysis is nearly quantitative according to eq 8.

$$RCF(OF)_2 \rightarrow RF + COF_2 + {}^1/_2O_2 \qquad (8)$$

This is in agreement with the rapid decomposition of $CF_3CF(OF)_2$ determined in metal. In glass, however, earlier work suggested much greater glass attack than we have observed.[8]

Under our conditions, the stability decreases with increasing number of carbons with the greatest change from 2 to 3 carbons. $ClCF_2CF(OF)_2$ was too explosive to check in this way. In one instance with this compound, a 1-mmol sample detonated in the vacuum line while being transferred to an NMR tube. The damage was rather impressive considering the small sample size. For the four compounds R = $ClCF_2$, CF_3, C_2F_5, and n-C_3F_7, the greatest tendency toward explosive decomposition was at higher pressures in the gas phase. Workers at 3M Company found no evidence for decomposition of pure $CF_3CF(OF)_2$ up to 200 °C in metal.[8] This is surprising as the compound exploded on several occasions during handling in glass at 22 °C. A 2-mmol sample in an ~20 mL glass tube at 22 °C explodes when the tube is suddenly broken. In another instance, a 2-mmol sample exploded near 22 °C while it was being allowed to vaporize in the hood after removing the tube from liquid nitrogen and opening the glass–Teflon valve. Quite clearly, these energetic compounds are unpredictable. Their apparent stability depends on a variety of factors, and all geminal bis(fluorooxy) compounds should be considered explosive under all conditions.

Acknowledgment. The support of this research by the Army Research Office—Durham, Grant No. DAAG 29-77-G-0071, is gratefully acknowledged.

Registry No. $CF_3CF_2CF(OF)_2$, 72985-54-7; $CF_3CF_2CF_2CF(OF)_2$, 72985-55-8; $ClCF_2CF(OF)_2$, 72985-56-9; F_2, 7782-41-4; CF_3CO_2H, 76-05-1; $CF_3CF_2CO_2H$, 422-64-0; $CF_3CF_2CF_2CO_2H$, 375-22-4; $ClCF_2CO_2H$, 76-04-0; $CF_3CF(OF)_2$, 16329-92-3.

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Synthesis and Properties of 2-(Pentafluorothio)-3,3-difluorooxaziridine

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The synthesis and properties of the novel perfluorooxaziridine $F_5S\overline{NCF_2O}$, is achieved by dehydrofluorination of $F_5SN(H)CF_2OOCF_3$ with NaF. The peroxide is prepared by the addition of CF_3OOH to the azaalkene $SF_5N{=}CF_2$. The new oxaziridine is only the second example of a perfluorinated compound of this type, and its reaction chemistry is suprisingly different from that of $CF_3\overline{NCF_2O}$. The latter is reactive to fluoride only at nitrogen, whereas $SF_5\overline{NCF_2O}$ undergoes attack at both nitrogen and carbon.

Introduction

We recently reported the synthesis of the first perfluorooxaziridine, $CF_3\overline{NCF_2O}$.[1] This novel compound is the only perfluorinated, two-heteroatom, three-membered heterocycle known. It exhibits an interesting reaction chemistry which is quite analogous to $CF_2\overline{CFCF_2O}$.[2-4] Nucleophiles attack the nitrogen exclusively forming a variety of compounds of the type $CF_3N(Nu)C(O)F$. As an indication of its utility in

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(2) Sekiya, A.; DesMarteau, D. D. *Inorg. Chem.* **1979**, *18*, 919.

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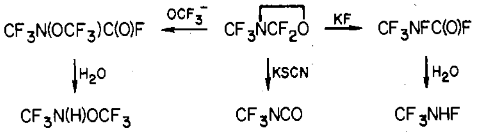
synthesis, the following reactions occur in high yield:



To further understand and extend the chemistry of fluorinated oxaziridines, it was of interest to synthesize additional members of this class of compounds. In this paper, the synthesis of the second member SF_5NCF_2O is reported. Its chemistry is surprisingly different from that of CF_3NCF_2O.

Experimental Section

General Data. Compounds were handled in glass and stainless-steel vacuum systems employing Teflon-packed valves and glass–Teflon valves. Connections to the system were by means of compression fittings or glass joints lubricated with Halocarbon 25-S grease. Pressures were measured with a precision Heise Bourdon tube gauge or a Wallace and Tiernan differential pressure gauge (series 1500). Boiling points were determined by the method of Kellogg and Cady with least-squares analysis of the data.[5] Melting points were determined by a modified Stock method.

Infrared spectra were recorded on PE 337 and 180 spectrometers by using 10-cm glass cells fitted with AgCl windows. NMR spectra were taken on a Varian XL-100-15 spectrometer by using ~15 mol % solutions in $CFCl_3$ (ϕ^* values).[6] Spectra were taken at 34 °C.

Previously reported compounds were identified by IR, NMR, and molecular weight by comparison to literature values and by comparison to known samples that were determined under identical conditions.

Reagents. The compounds CF_3OOH,[7] $SF_5N{=}CCl_2$,[8] and $SF_5N{=}CF_2$[8] were prepared by literature methods. ClF was obtained by reaction of equimolar amounts of F_2 and Cl_2 in Monel at 250 °C for 18 h. ClF was removed from the reactor at −111 °C to avoid contamination by ClF_3. All other chemicals were from commercial sources and were appropriately purified, if needed, before use.

Synthesis of $SF_5N(H)CF_2OOCF_3$. Reaction of CF_3OOH (4.0 mmol) and $SF_5N{=}CF_2$ (4.0 mmol) was carried out in a 100-mL glass bulb fitted with a glass–Telfon valve. The reactants were added by vacuum transfer to the vessel held at −195 °C. The vessel was then warmed to 0 °C and held there for 6 h. The products were then pumped thorugh traps at −63 and −195 °C. The −195 °C trap contained small amounts of unreacted starting materials along with COF_2 and SiF_4. Some noncondensable gas passed through this trap and was probably oxygen from some decomposition of CF_3OOH. The −63 °C trap contained a colorless liquid identified as $SF_5N(H)CF_2OOCF_3$ (79%).

$SF_5N(H)CF_2OOCF_3$: bp 77.3 °C; mp, glass <−140 °C; mol wt 296.0, calcd 293.08; $\log [P\ (\mathrm{mm})] = 6.2585 - 614.153/T - 199603/T^2$; $\Delta H_{vap} = 8.02$ kcal/mol; $\Delta S_{vap} = 22.9$ eu; IR 3460 (m), 1461 (s), 1280 (vs), 1241 (vs), 1165 (vs), 1126 (vs), 1115 (vs), 974 (vs), 930 (vw), 910 (vs), 867 (vs), 795 (m), 757 (w), 692 (m), 610 (s), 460 (w) cm^{-1}; NMR $F^ASF_4{}^BN(H^C)CF_2{}^DOOCF_3{}^E$ ϕ_A^* ~−75 (m), ϕ_B^* ~−74 (m), δ_C 6.3 (m), ϕ_D^* 69.1 (m), ϕ_E^* 68.6 (t) [$J_{DE} = 4.0$ Hz; other couplings J_{AB}, J_{CD}, and J_{BD} not determined (relative areas of A + B, D, and E were 5.0:2.0:3.0)].

Synthesis of SF_5NCF_2O. Reaction of $SF_5N(H)CF_2OOCF_3$ (3.0 mmol) with NaF (100 mmol) was carried out in a 100-mL glass bulb fitted with a glass–Telfon valve. The dried NaF was placed in the reactor and cooled to −195 °C. The amine was then added by vacuum transfer and the mixture allowed to warm from −195 to 22 °C over 3 h. The reaction products were passed through traps cooled to −111 and −195 °C. The −195 °C trap contained COF_2 (2.9 mmol). The contents of the −111 °C trap were separated by GLC with a 10 ft × $^3/_8$ in. column packed with 40% Halocarbon 11-21 polymer oil on Chromosorb P. This separation produced two major components in yields of 83 and 8%. The major component was identified as SF_5NCF_2O and the minor one as $SF_5N(CF_3)C(O)F$.

SF_5NCF_2O: bp 14.9 °C; mp, formed a glass at −195 °C; mol wt 208.2, calcd 207.07; $\log [P\ (\mathrm{mm})] = 6.4230 - 645.66/T - 107890/T^2$; $\Delta H_{vap} = 6.38$ kcal/mol; $\Delta S_{vap} = 22.16$ eu; IR 1477 (w), 1435 (vs), 1392 (w), 1325 (vw), 1270 (vs), 1236 (vw), 1057 (s), 944 (m), 915 (vs), 865 (vs), 700 (m), 606 (s), 550 (w), 515 (w), 464 (m) cm^{-1}. NMR $F^ASF_4{}^BNCF^CF^DO$ ϕ_A^* −59.4 (m), ϕ_B^* −56.7 (m), ϕ_C^* 105.1 (basic quintet-d-d, ϕ_D^* 85.7 (br s) [$J_{AB} \approx 150$, $J_{BC} \approx 18$–21, $J_{AC} \approx 3$–10, $J_{CD} \approx 3$ Hz (relative areas of A + B, C, and D were 5.0:1.0:1.0)].

$SF_5N(CF_3)C(O)F$: bp ~41 °C; mol wt 261.1, calcd 257.08; IR 1885 (s), 1440 (w), 1300 (vs), 1262 (m), 1212 (w), 1194 (vs), 1089 (m), 1000 (w), 930 (vs), 896 (w), 860 (vs), 802 (vw), 693 (m), 667 (m), 608 (s), 463 (m) cm^{-1}; NMR $F^ASF_4{}^BN(CF_3{}^C)C(O)F^D$ ϕ_A^* −60 (m), ϕ_B^* −63 (m), ϕ_C^* 66.0 (m), ϕ_D^* 3.0 (quintet-m) [$J_{AB} \approx 150$, $J_{BD} = 8.5$ Hz; J_{BC}, J_{CD}, J_{AC}, and J_{AD} not readily determined (relative areas of A + B, C, and D were 5.0:3.0;1.0)].

Reaction of SF_5NCF_2O with KF and CsF. Reaction of the oxaziridine was carried out in a 100-mL glass bulb fitted with a glass–Telfon valve. A 3.0-mmol sample of SF_5NCF_2O was condensed onto 30 mmol of KF at −195 °C. The mixture was then warmed to 22 °C and allowed to stand for 1 day. After the volatiles were pumped into a −195 °C trap, analysis showed essentially pure oxaziridine with 90% recovery. The oxaziridine was then recondensed into the reactor, and the mixture was held at 50 °C for 1 day. Collection through traps at −111, −135 and −195 °C resulted in a small amount of an unknown compound in the −111 °C trap. The −135 °C trap contained pure OSF_2 (1.43 mmol), and the contents of the −195 °C trap were SiF_4 (0.31 mmol), CF_3NO (1.24 mmol), COF_2 (0.96 mmol), and SF_6 (0.69 mmol) as determined by ^{19}F NMR integration.

Reaction with CsF was carried out as above in a 30-mL stainless-steel reactor for 1 day at 22 °C. The volatile products were SF_6 (0.09 mmol) and CF_3NO (0.9 mmol). Fluorine (10 mmol) was then added to the reactor at −195 °C and the mixture warmed to 20 °C for 1 h. Excess fluorine was removed at −195 °C and the volatile products were separated by GLC. They were SF_6 (0.5 mmol), CF_3OF (1.26 mmol), and SF_5NFCF_3 (0.9 mmol). The IR of the latter agreed well with the previously reported values.[9] The ^{19}F NMR values of the CF_3 and NF groups were also identical with the reported values. The SF_5 NMR signals were not directly comparable because the earlier spectra were recorded at 40 mHz causing increased second-order effects.

Results and Discussion

The addition of CF_3OOH to $SF_5N{=}CF_2$ occurs readily at 0 and 25 °C to form the new amine $CF_3OOCF_2N(H)SF_5$. This reaction is completely analogous to the addition with $CF_3N{=}CF_2$ (eq 1 and 2).[1] Higher yields are obtained at 0 °C, and some minor decomposition of CF_3OOH was observed at 25 °C. In either case, unreacted starting materials are observed after a few hours, and the actual yield of product is probably dependent on pressure as found previously with $CF_3N{=}CF_2$. The amine showed no tendency to decompose at 25 °C in glass when kept at its equilibrium vapor pressure for 1 day. Stability at higher temperatures was not determined, but it is probably similar to $CF_3OOCF_2N(H)CF_3$ and $SF_5OOCF_2N(H)CF_3$ which decompose suddenly at ~75 °C.

$$CF_3OOH + SF_5N{=}CF_2 \rightarrow CF_3OOCF_2N(H)SF_5 \quad (1)$$

$$CF_3OOH + CF_3N{=}CF_2 \rightarrow CF_3OOCF_2N(H)CF_3 \quad (2)$$

An adequate proof of structure for $CF_3OOCF_2N(H)SF_5$ is given in the Experimental Section. The IR shows the expected $\nu(SF)$ and $\nu(CF)$. The strong absorption at 610 cm^{-1} is a $\delta(SF_5)$ mode. The ^{19}F NMR is conclusive but complicated. The observed AB_4 pattern for the SF_5 group was not analyzed in detail. The remaining resonances for the CF_2 and CF_3OO groups are readily assigned by the observed multiplicities, with a simple triplet for CF_3OO and complex multiplet for the CF_2

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(6) Filipovich, G.; Tiers, G. V. D. *J. Phys. Chem.* **1959**, *63*, 761.
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(8) Tullock, C. W.; Coffman, D. D.; Muetterties, E. L. *J. Am. Chem. Soc.* **1964**, *86*, 357.
(9) Lustig, M.; Ruff, J. K. *Inorg. Chem.* **1965**, *4*, 1444.

group. The CF_2 group is strongly coupled to the nitrogen proton and to the equatorial fluorines of the SF_5 group and to a small degree to the axial SF_5 fluorine.

The dehydrofluorination of $SF_5N(H)CF_2OOCF_3$ proceeds in high yield forming the oxaziridine (eq 3). This reaction

$$SF_5N(H)CF_2OOCF_3 + NaF \rightarrow SF_5\overline{NCF_2O} + COF_2 + NaF{\cdot}HF \quad (3)$$

is identical with that for the formation of $CF_3\overline{NCF_2O}$ and serves to indicate the generality of the reaction for compounds of the type $R_fN(H)CF_2OOCF_3$.[1,2] A mechanism for this reaction involving initial hydrogen bond interaction of the amine with NaF has been proposed.[2] In the formation of $CF_3\overline{NCF_2O}$, a minor side reaction results in the formation of $CF_3NFC(O)F$.[2] In the pentafluorosulfur case, a related byproduct is observed, $SF_5N(CF_3)C(O)F$. Whereas the $CF_3NFC(O)F$ is formed via the isomerization of $CF_3\overline{NCF_2O}$, the origin of the above (fluoroacyl)amine is unclear. One possible route involving the reaction of SF_5NHCF_3[8] with COF_2 was eliminated by carrying out this reaction under the same conditions. Both COF_2 and SF_5NHCF_3 were recovered unchanged after standing together at 22 °C over NaF.

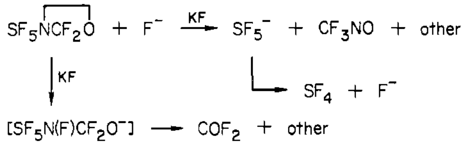
The characterization of the new oxaziridine by IR, NMR, and molecular weight data, given in the Experimental Section, offers convincing proof of structure. The three absorptions at 1435 (vs), 1057 (s), and 944 (m) cm^{-1} are due to the C–N–O ring. In $CF_3\overline{NCF_2O}$, these are found at 1458 (vs), 1071 (m), and 956 (s) cm^{-1}. The strong absorption at 1270 cm^{-1} is due to $\nu(CF)$. The remaining three strong absorption bands are due to $\nu(SF_5)$ 915 and 865 cm^{-1} and $\delta(SF_5)$ 606 cm^{-1}. The ^{19}F NMR, although complicated, is unequivocal for the cyclic compound, especially when compared to $CF_3\overline{NCF_2O}$.[1] A similar nonequivalence of the methylene fluorines is observed in both compounds with one of the fluorine atoms coupled strongly to other fluorine atoms in the molecule and one coupled very weakly. The observation of the two different signals indicates that inversion at nitrogen must be slow on the NMR time scale. The higher field signal of the CF_2 group, which is coupled strongly to the SF_5 group, is assumed to be the fluorine cis to the SF_5 group. Accurate values of the various coupling constants were not determined due to the complexity of the spectra, which can be assigned to an AB_4MX spin system. In $CF_3\overline{NCF_2O}$, the spectrum was essentially first order. In $SF_5\overline{NCF_2O}$, the trans methylene fluorine is an unresolved singlet, the same as in $CF_3\overline{NCF_2O}$. The cis fluorine in $SF_5\overline{NCF_2O}$, however, is not first order, although it is basically a quintet of doublets indicating spin–spin coupling to all other fluorines in the molecule.

The structure of the other new compound $SF_5N(CF_3)C(O)F$ is adequately supported by the data in the Experimental Section. A strong $\nu(C{=}O)$ is observed at 1885 cm^{-1} along with strong $\nu(CF)$ at 1300, 1262, and 1194 cm^{-1}. The strong bands at 930, 860, and 608 cm^{-1} are readily assigned to the SF_5 group. The ^{19}F NMR exhibits a characteristic AB_4 pattern for the SF_5 group and resonances assignable to the CF_3 and $C(O)F$ groups. There was initially some question as to whether the CF_3 group might be a CF_3O group. The large coupling to the B fluorines in the SF_5 group and the somewhat broad signals, however, clearly indicate that it is a CF_3 group. CF_3O groups attached to nitrogen in related compounds such as $CF_3N(H)OCF_3$[10] or $CF_3N(OCF_3)C(O)F$[2] exhibit sharp spectra. The molecular weight, while not as accurate due to the small size of the sample, also supports the presence of the CF_3–N group.

The reaction chemistry of $SF_5\overline{NCF_2O}$ was expected to be very similar to that of $CF_3\overline{NCF_2O}$. This is not the case. As mentioned in the Introduction, $CF_3\overline{NCF_2O}$ is attacked by a variety of nucleophiles, with attack occurring exclusively at nitrogen (eq 4). Both KF and CsF were reactive sources of

$$CF_3\overline{NCF_2O} + Nu^- \rightarrow CF_3N(Nu)C(O)F + F^- \quad (4)$$

F^-. The new oxaziridine is less reactive, and the isomerization to $SF_5NFC(O)F$, which occurs so readily with $CF_3\overline{NCF_2O}$, does not occur. Apparently attack by nucleophiles takes place less readily and occurs at both carbon and nitrogen. With KF, $SF_5\overline{NCF_2O}$ is quite unreactive at 25 °C and must be heated to achieve reaction. At 50 °C, in glass, one observed a variety of products which can be attributed to the following reactions in part. The SF_4 is not observed directly, but as OSF_2 and SiF_4, the products expected from reaction of SF_4 with the glass.



The SF_4 can arise from attack by F^- at carbon and the COF_2 by attack at nitrogen. With KF, the SF_5^- and the $SF_5N(F)CF_2O^-$ anions are not especially stable, although the material balance indicates that some of the oxaziridine remains chemisorbed on the KF in some form.

Cesium fluoride reacts readily with $SF_5\overline{NCF_2O}$ at 22 °C. In this case, one expects the $CsSF_5$[8,11] and $CsOCF_2N(F)SF_5$ to be more stable. In addition, any COF_2 should be readily absorbed to form $CsOCF_3$.[12] Initial reaction with CsF forms CF_3NO (~30%) and a small amount of SF_6 as the only fluorine-containing products. If the residue contains the above cesium salts, then reaction with F_2 should lead to the formation of SF_6,[13] CF_3OF,[14] and $SF_5N(F)CF_2OF$.[15] Three products are observed: see eq 5–7. The observation of these products

$$CsSF_5 + F_2 \rightarrow CsF + SF_6\ (\sim 20\%) \quad (5)$$

$$CsOCF_3 + F_2 \rightarrow CsF + CF_3OF\ (\sim 40\%) \quad (6)$$

$$CsOCF_2N(F)SF_5 + F_2 \rightarrow CsF + [SF_5N(F)CF_2OF] \rightarrow SF_5N(F)CF_3\ (\sim 30\%) + {}^1/_2O_2 \quad (7)$$

lends support to the proposed reaction scheme, but the overall reaction is clearly complex. The material balance for S and N is low, and the direct formation of SF_6 in the initial reaction is not readily explainable. The results, however, clearly show that the two oxaziridines $SF_5\overline{NCF_2O}$ and $CF_3\overline{NCF_2O}$ are quite different in their reactivity. We hope to prepare additional examples of fluorinated oxaziridines containing additional substituents at nitrogen and carbon. These compounds will provide access to many new materials and allow a better

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(15) Fluorination of $CF_3NFC(O)F$ over CsF resulted in CF_3NF_2 and CF_3OF, indicating elimination of COF_2 from $CF_3N(F)CF_2OF$.[3]

understanding of the effects governing their reactivity.

Acknowledgment. Support of this research by the Army Research Office—Durham (Grant No. GAAG29-77-G-0071) is gratefully acknowledged.

Registry No. $SF_5\overline{NCF_2O}$, 73002-62-7; $SF_5N(CF_3)C(O)F$, 73002-63-8; $SF_5N(H)CF_2OOCF_3$, 73002-64-9; CF_3OOH, 16156-36-8; $SF_5N{=}CF_2$, 2375-32-8; COF_2, 353-50-4; SF_6, 2551-62-4; CF_3NO, 334-99-6; CF_3OF, 373-91-1; SF_5NFCF_3, 4101-60-4; KF, 7789-23-3; CsF, 13400-13-0; SF_4, 7783-60-0.

Contribution from the Istituto di Chimica Generale ed Inorganica, Facoltà di Farmacia, University of Florence,
the Laboratorio per lo Studio dei Composti di Coordinazione del CNR, Florence,
and the Istituto di Chimica Generale ed Inorganica, University of Florence, Florence, Italy

Adducts of Bis(N-substituted ethylenediamine)copper(II) Complexes with Hexacyanoferrate(III)

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The interactions between bis(*N*-R-ethylenediamine)copper(II), where R = H, C_2H_5, and C_3H_7, and hexacyanoferrate(III) have been studied by means of electronic spectra, magnetic resonance spectroscopies, and magnetic susceptibility measurements. Complexes with formulas $K[Cu(en)_2][Fe(CN)_6]$, $[Cu(N\text{-Et-en})_2]_3[Fe(CN)_6]_2{\cdot}4H_2O$, and $[Cu(N\text{-Pr-en})_2]_3[Fe(CN)_6]_2{\cdot}5H_2O$ have been obtained. Although the magnetic susceptibility data are essentially the sum of those of the parent complexes in the range 77–300 K, the electronic relaxation times of copper(II) in the mixed complexes are so much changed that the ESR signal disappears whereas the ^1H NMR signals of the R group sharpen, showing the existence of metal–metal interactions. The electronic spectroscopy data are consistent with such specific interactions. The analogous $K[Cu(en)_2][Co(CN)_6]$ compound has been prepared and characterized; ^{13}C NMR data show evidence of a cyanide bridge between the two metals in solution, suggesting similar behavior in the other systems.

Introduction

It is well-known that the cyanide ion may coordinate through the carbon atom acting as a monodentate ligand or through both carbon and nitrogen atoms acting as a bridging ligand.[2] With respect to the latter type of coordination, studies have been performed on the hexacyanoferrate(III) of various metal ions where moieties M—N≡C—Fe account for the physical properties of the compounds. In particular, magnetic exchange interactions between the two metal ions have been investigated as well as their role in heteronuclear intervalence transfer.[3-5]

The hexacyanoferrate(III) ion is commonly used in biochemistry as a mild oxidizing agent especially to oxidize copper(I) to copper(II).[6] The problem arises therefore to determine whether $[Fe(CN)_6]^{3-}$ is capable of interacting with coordinatively unsaturated copper(II) complexes and, if so, to understand the physicochemical consequences of such interactions. With this in mind several adducts between $[Fe(CN)_6]^{3-}$ and $[Cu(N\text{-R-en})_2]^{2+}$ ions, where *N*-R-en represents an N-substituted ethylenediamine, have been prepared and characterized.

Experimental Section

Preparation of the Complexes. $K_3[Fe(CN)_6]$ was analytical grade and was used without any further purification. $K_3[Co(CN)_6]$ and $K_3[Co(^{13}CN)_6]$ were prepared by reacting $CoSO_4$ with KCN or $K^{13}CN$ in 1:2 ratio. The dicyanide cobalt salt was then dissolved in an excess of potassium cyanide solution. Solid potassium hexacyanocobaltates were obtained by concentration and twice recrystallized. The $[Cu(N\text{-R-en})_2](ClO_4)_2$ (R = H, C_2H_5) and $[Cu(N\text{-Pr-en})_2]Cl_2$ complexes were prepared as previously described.[7] The adducts were obtained by mixing water solutions of the complexes in a 1:1 ratio (10^{-1} M in the case of N-substituted ethylenediamine and ca. 1 M in the case of $[Cu(en)_2]^{2+}$) and allowing the solutions to evaporate in a desiccator.

Physical Measurements. The electronic spectra were recorded on a Cary 17 D, the ESR spectra on a Varian E 9, the ^1H NMR spectra on a Perkin-Elmer R 32, and the ^{13}C NMR spectra on a Varian CFT20. The Mössbauer spectra were obtained on a spectrometer which consisted of a linear velocity drive unit (MWE, Canberra), a

Table I. Analytical Data (%) of the Complexes

		C	H	N	O	Cu	Fe
$K[Cu(en)_2][Fe(CN)_6]$	calcd	27.6	3.70	32.2			
	found	27.4	3.66	32.2			
$K[Cu(en)_2][Co(CN)_6]$	calcd	27.4	3.68	32.0			
	found	27.0	3.73	31.8			
$[Cu(N\text{-Et-en})_2]_3$-$[Fe(CN)_6]_2{\cdot}4H_2O$	calcd	35.6	6.63	27.7	5.26	15.7	9.18
	found	35.5	6.49	28.4	5.40	15.6	8.90
$[Cu(N\text{-Pr-en})_2]_3$-$[Fe(CN)_6]_2{\cdot}5H_2O$	calcd	38.3	7.24	25.5	6.07	14.5	8.47
	found	37.8	7.04	25.9	6.40	14.4	8.73

Table II. Some Physical Data of the Complexes in Solution

	absorp max. 10^3 cm^{-1} [a] (molar absorb, M^{-1} cm^{-1})[b]	Λ_M, S cm^2 mol^{-1} [c,d]	mol wt-(found)/mol wt-(calcd)[d]
$[Cu(en)_2](ClO_4)_2$	18.4 (60)		
$K[Cu(en)_2][Fe(CN)_6]$	18.1 (65)[e]	260 (w)[f]	0.57 (w)
$K[Cu(en)_2][Co(CN)_6]$	18.2 (65)		
$[Cu(N\text{-Et-en})_2](ClO_4)_2$	18.0 (90)		
$[Cu(N\text{-Et-en})_2]_3$-$[Fe(CN)_6]_2{\cdot}4H_2O$	17.5 (105)[e]	18 (D)	
$[Cu(N\text{-Pr-en})_2](ClO_4)_2$	18.1 (95)		
$[Cu(N\text{-Pr-en})_2]_3$-$[Fe(CN)_6]_2{\cdot}5H_2O$	17.5 (110)[e]	23 (D)	

[a] In H_2O. [b] Calculated per mole of Cu(II) ions. [c] w = water; D = dimethyl sulfoxide. [d] 10^{-3} M solution at 25 °C. [e] The $Fe(CN)_6^{3-}$ moiety shows an intense charge-transfer band at 24.0 × 10^3 cm^{-1}, which does not change in the adducts. [f] $\Lambda_M = 137$ for a 10^{-2} M water solution.

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