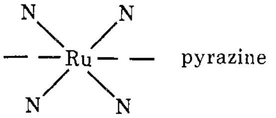
orbital with appropriate symmetry to overlap the d_{xy} basis set orbitals has nodes at the nitrogens. Very poor overlap is expected between the pyrazine π^* molecular orbitals and the ruthenium d_{xy} orbitals. Thus, a significant amount of unpaired spin would not be directly delocalized (*i.e.*, very little up spin in the π^* system), so an upfield Fermi contact shift would not arise at the protons. Instead, spin polarization of the paired electrons in B_{2u} and B_{3g} by the unpaired electron would increase positive spin density on the ruthenium in B_{2u} and B_{3g} and increase negative spin density in the pyrazine π system. The mechanism is similar to the spin polarization of the paired electrons in a C–H bond by an unpaired electron in an orthogonal carbon p orbital. This spin polarization would place up spin on the proton and be expected to give rise to a small downfield Fermi contact contribution. This would have to be about 1000 Hz larger than and in the opposite direction to the pseudo contact shift (Table I) to account for the magnitude of the shift expected from pyrazine coordinated to a diamagnetic ligand. In this model the low-energy electronic transition reported[1] at 1570 mμ for the 5+ ion would be attributed to a d–d transition involving the B_{3g} or B_{2u} and A_{2u} or B_{1g} orbitals. The similarity of the remaining bands of the 5+ species with those of the 4+ is not surprising in view of the reported[10] similarity of the hexaammines of Ru(II) and Ru(III).

We have also considered the possibility that steric repulsions between the pyrazine and ammine protons force the molecule into a skewed configuration with the plane of the pyrazine molecule bisecting the H_3N–Ru–NH_3 planes



Such a configuration leads to mo schemes which are analogous to those in Figure 1 and 2 and do not affect our conclusions. It is likely, however, that rotations about the metal–nitrogen bond axes in this complex are rapid on the nmr time scale.

These models for the bonding would approach the Creutz–Taube description (b) if, in the course of undergoing molecular vibrations, the potential energy curve for the appropriate normal mode had a minimum when the ammonia nitrogens around one ruthenium were stretched and those around the other ruthenium compressed. This would result in an unequal contribution from each ruthenium to the A_{2u} and B_{1g} mo's. The larger contribution by one of the rutheniums to the mo containing the unpaired electron would make that ruthenium more like Ru(III) and the dynamic nature of the vibration would very rapidly change a given ruthenium from one extreme to the other. With this model, the whole range of fractional oxidation states is covered depending only on where the minimum in the potential energy curve for the vibration occurs. We have no information available to support or reject this possibility.

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[10] T. Meyer and H. Taube, *Inorg. Chem.*, **7**, 2369 (1968).

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Chemistry of Fluorinated Derivatives of Azodiformamidine[1]

By J. B. Hynes,*[2] T. E. Austin, and L. A. Bigelow

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Earlier we reported that the solid fluorination of azodiformamidine dinitrate yielded the new highly fluorinated azo compounds difluorotetrakis(difluoroamino)azomethane, $(NF_2)_2CFN{=}NCF(NF_2)_2$, I, [bis(difluoramino)fluoromethylazo]trifluoroformamidine, $(NF_2)_2CFN{=}NC({=}NF)NF_2$ (two isomers), IIa and b, and hexafluoroazodiformamidine, $NF_2C({=}NF)$-$N{=}NC({=}NF)NF_2$ (three isomers), IIIa–c.[3] This report is concerned with the chemistry of these compounds and describes the preparation of several unique azo derivatives.

The thermal reaction of I with carbon monoxide yielded tetrafluoroazodimethylenimine, IV, as the principal product

$$(NF_2)_2CFN{=}NCF(NF_2)_2 \xrightarrow[180°]{CO} FN{=}CFN{=}NCF{=}NF \text{ (IV)}$$

The photolysis of IV with a sunlamp produced perfluoromethylenimine and cyanogen fluoride providing further confirmation of the structure. The reaction of either IIa or IIb with carbon monoxide at lower temperature gave two isomers of (trifluoroguanylazo)difluoromethylenimine, Va and b.

$$(NF_2)_2CFN{=}NC({=}NF)NF_2 \xrightarrow[120°]{CO} FN{=}CFN{=}NC({=}NF)NF_2 \text{ (Va, b)}$$

The probable stereochemical configurations for these compounds together with pertinent nmr and ultraviolet spectral data are presented in Table I. The assignments are based upon considerations discussed earlier in connection with the structures of the isomers of II and III.[3] At higher temperature, the reaction of IIa or IIb with carbon monoxide also produced IV. It should be noted that in each of the above-mentioned cases, the reaction involves the effective elimination of one or two molecules of nitrogen trifluoride and the formation of a more highly conjugated system.

The ability of IIa or IIb to undergo addition reactions was found to depend upon the basicity of the attacking reagent. For example, no reaction occurred with hydrogen chloride, hexafluoroisopropyl alcohol, isocyanic acid, or water at ambient or lower temperature. A partial reaction occurred with methanol but the resulting adduct was very unstable. The low-temperature reaction of IIa or IIb with ammonia produced an orange solid which decomposed upon warming. However, fluorination of this material at −110° produced

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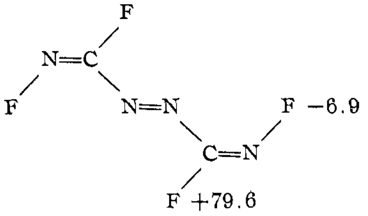
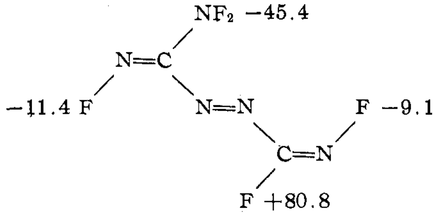
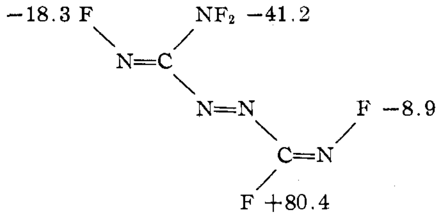
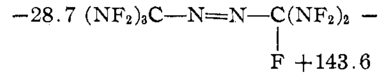
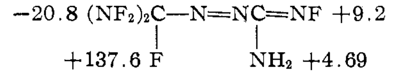
[1] The experimental work described herein was conducted prior to May 30, 1967 and was supported by the Advanced Research Projects Agency through the Army Research Office (Durham) under Contract DA-31-124-ARO(D)-179.

[2] To whom all correspondence may be directed at the Department of Pharmaceutical Chemistry, College of Pharmacy, Medical University of South Carolina, Charleston, S. C. 29401.

[3] J. B. Hynes, T. E. Austin, and L. A. Bigelow, *Inorg. Chem.*, **7**, 1647 (1968).

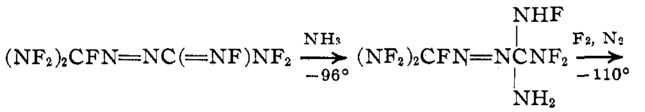
TABLE I

SPECTROSCOPIC PROPERTIES AND PROBABLE STRUCTURAL ASSIGNMENTS OF NEW COMPOUNDS

Compd no.	—^{19}F (ϕ)[a] and ^{1}H (τ)[b] nmr chem shifts, ppm[c]—	Uv absorption max (vapor phase), mμ
IV		433
Va		462
Vb		444
VI	 $-28.7\ (NF_2)_3C{-}N{=}N{-}\underset{\displaystyle F\ +143.6}{C}(NF_2)_2\ -22.6$	418
VII	 $-20.8\ (NF_2)_2\underset{\displaystyle +137.6\ F}{C}{-}N{=}N\underset{\displaystyle NH_2\ +4.69}{C}{=}NF\ +9.2$	336[d]

[a] Relative to $CFCl_3$ in $CFCl_3$ solution. [b] Relative to $Si(CH_3)_4$ in CCl_4 solution. [c] In each case, the relative peak areas were in accord with the assignments presented. [d] CCl_4 solution.

the following azo compounds listed in order of decreasing abundance. The new compound, fluoropentakis(difluoramino)azomethane, VI, was isolated



$$(NF_2)_2CFN{=}NC({=}NF)NF_2 \xrightarrow[-96^\circ]{NH_3} (NF_2)_2CFN{=}N\overset{\displaystyle NHF}{\underset{\displaystyle NH_2}{C}}NF_2 \xrightarrow[-110^\circ]{F_2,\ N_2}$$

IIa, $(NF_2)_3CN{=}NCF(NF_2)_2$ (VI), IIb, and I

chromatographically in a very small amount; however, the structure was confirmed by its spectroscopic properties which are presented in Table I. As expected its infrared spectrum was very similar to that of I.

A number of attempts were made to effect the addition of 2 mol of ammonia to the isomers of III. A brown solid was produced at low temperature, but fluorination of this material yielded primarily I and no products containing the $(NF_2)_3C$ moiety were detected.

After prolonged contact times at ambient temperature, the reaction of IIa or IIb with lithium amide yielded the interesting compound [bis(difluoramino)-fluoromethylazo]fluoroformamidine, VII. This substance

$$(NF_2)_2CFN{=}NC({=}NF)NF_2 \xrightarrow{LiNH_2} (NF_2)_2CFN{=}NC({=}NF)NH_2 \quad (VII)$$

stance was a greenish yellow liquid possessing remarkable thermal stability. Its infrared spectrum clearly showed the presence of a primary amino group by the sharp doublet located in the N–H region. The ^{1}H and ^{19}F nmr data are summarized in Table I. The compound was found to possess sufficient basicity to produce a stable but very hygroscopic salt with anhydrous perchloric acid. The infrared spectrum of this material, which displayed bands characteristic of the $(NF_2)_2CF$ group, also had broad peaks at 3279 cm^{-1} (NH_3^+) and 1075 cm^{-1} (ClO_4^-). Complete characterization of this compound was not achieved.

It should be noted that most of the compounds mentioned above are *highly explosive* and should be handled only with adequate shielding.

Experimental Section

The infrared spectra were measured using a Beckman IR-8 spectrophotometer, while the ultraviolet data were obtained with a Beckman DB spectrophotometer. Unless noted otherwise, the infrared spectra were determined in the vapor phase. The chromatographic separations were performed with a Micro-tek 1500 gas chromatograph. The columns and trapping procedures employed have been described previously.[3]

Reaction of I with Carbon Monoxide.—The conditions which produced the best yield of IV of the eight experiments performed are as follows. One millimole of I was condensed into a 100-ml Pyrex bulb equipped with a Teflon stopcock. The vessel was then pressurized to 735 mm with CO (3.95 mmol). After 6 hr at 180 ± 5°, the contents of the bulb were separated into two portions by vacuum trap to trap distillation. The material volatile at −96° consisted of COF_2, SiF_4, N_2O, CF_4, and NF_3, as identified by ir analysis, and at least one unidentified compound. The material not volatile at −96° consisted of three compounds the most abundant of which was IV. The latter had a molecular weight of 140 as determined by molecular effusion using *m/e* 64 and 148 using *m/e* 92; molecular weight calculated for $C_2F_4N_4$, 156. The mass spectrum (ionization voltage, 100 V) gave the following ions in order of decreasing relative intensity: 64 (CF_2N^+), 31 (CF^+), 92 ($CF_2N_3^+$), 45 (CFN^+), 109 ($C_2F_3N_2^+$), 83 (CF_3N^+), 54 (CN_3^+), 33 (NF^+), 50 (CF_2^+), 156 ($C_2F_4N_4^+$) (parent ion), and 73 (CFN_3^+). Its ir spectrum consisted of bands at 1789 (s), 1312 (s), 1010 (s), 918 (s), 718 (m), and 701 (m) cm^{-1}.

A small sample of IV was irradiated in a 55-cm^3 cylindrical tube with a GE sunlamp for 1 hr. The principal products were identified by infrared analysis as $CF_2{=}NF$,[4] FCN,[5] COF_2, and SiF_4.

Reaction of IIb with Carbon Monoxide.—A 2-mmol sample of IIb was condensed into a 285-ml cylindrical vessel equipped with a Teflon stopcock. Next, the reactor was pressurized with 8 mmol of CO at −80° and warmed to 120 ± 5° for 14 hr. The portion of the product which was not volatile at −80° was diluted with $CF_2ClCFCl_2$ and resolved chromatographically. The two principal products were identified as Va and Vb by nmr and ultraviolet spectroscopy; *cf* Table I. Va had a molecular weight of 179 ± 10 (vapor density); molecular weight calculated for $C_2F_5N_5$, 189. It exhibited major ir bands at 1637 (m), 1500 (w), 1280 (m), 1208 (m), 1022 (m), 1000 (s), 926 (s), and 880 (s) cm^{-1}. Vb showed ir bands at 1637 (m), 1287 (m), 1218 (w), 1020 (m), 997 (s), 985 (s), 888 (m), and 862 (w) cm^{-1}.

Reaction of IIa and IIb with Ammonia and Subsequent Fluorination.—In a special 5-ml glass reactor equipped with gas inlet and exit tubes, designed to permit the addition reaction and fluorination to be conducted in the complete absence of O_2 and moisture, were placed 1.5 mmol of KCN and 3.0 mmol of NaF. Then 6.77 mmol of CCl_2F_2 and 0.55 mmol of IIa and IIb were condensed in successively. Next, 1.5 mmol of NH_3 was added and the resulting mixture allowed to stand at −96° for 2.5 hr. The materials volatile at −96° under full vacuum were removed leaving a brown solid. After the addition of 28 mmol of CCl_2F_2, F_2 diluted with N_2 (30 cm^3/min:70 cm^3/min) was passed through the solution maintained at −111° for 6 hr. The following azo products were isolated chromatographically and identified:

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(4) D. H. Dybvig, *Inorg. Chem.*, **5**, 1795 (1966).

(5) F. S. Fawcett and R. D. Lipscomb, *J. Amer. Chem. Soc.*, **82**, 1509 (1960).

I (6%), IIa (13.5%), IIb (4.5%), and VI (10.5%). (Percentages are based on chromatographic peak areas assuming equal thermal conductivities for all components.) The component with the longest retention time, VI, showed ir bands at 1282 (m), 1144 (w), 1019 (m), 994 (m), 974 (s), 950 (s), and 9.08 (s) cm^{-1}. The nmr and ultraviolet data for this compound are presented in Table I.

Reaction of IIa with Lithium Amide.—Into a 10-ml glass reactor equipped with a gas inlet tube and a Teflon stopcock and containing 1 mmol of $LiNH_2$ were condensed 2.5 ml of $CF_2ClCFCl_2$ and 1 mmol of IIa. The mixture was warmed to ambient temperature and stirred for 3 days. All volatile material was removed from the reactor by continuous pumping and condensed at −196°. The condensate was warmed to room temperature and distilled without pumping into another trap at −196°. The volatile products were identified by ir as *cis*-N_2F_2, N_2F_4, and unreacted IIa. The remaining material was a greenish yellow liquid which strongly oxidized KI solution and had an apparent atmospheric boiling point of 124° with slight decomposition. The ir spectrum in CCl_4 showed bands located at 3546 (s), 3425 (s), 1667 (s), 1512 (w), 1353 (m), 1267 (s), 1143 (m), 1086 (m), 1015 (m), 943 (s), 922 (s), and 897 (s) cm^{-1}. The nmr and ultraviolet data for compound VII are presented in Table I. Mol wt of $C_2H_2F_6N_6$: calcd, 224; found, 226 (cryoscopic in benzene).

A sample of VII was fluorinated in the presence of NaF in CCl_2F_2 at −96° using a F_2:N_2 ratio of 5 cm^3/min:80 cm^3/min for 5 hr. The major product was IIb together with traces of I and IIa.

Acknowledgment.—The authors are indebted to Dr. Frederic A. Johnson, Mrs. Carolyn Haney, and Dr. Charles B. Colburn of the Rohm and Haas Co., Redstone Arsenal Research Division, for the nmr and mass spectral data reported herein. The technical assistance of Mr. Charles Walker was invaluable.

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Kinetics of Formation of Mixed Ligand Complexes. III. The Cobalt(II)-2,2′-Bipyridyl-Glycine System[1]

BY ROBERT F. PASTERNACK,* PETER R. HUBER,
U. M. HUBER, AND HELMUT SIGEL

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Potentiometric titration studies involving ternary complexes of Cu(II)-bipy, Co(II)-bipy and Ni(II)-bipy have demonstrated the enhanced thermodynamic stabilities of many of these species.[2,3] We are reporting on the kinetics of formation of a ternary complex of Co(II)-bipy which is thermodynamically quite stable relative to the appropriate binary system (*cf.* Table I). The stability data for the binary systems are typical in that $\log K^{CoL}_{CoL_2} - \log K^{Co}_{CoL} \leq -0.7$.[4] However, for the ternary system, $\log K^{Co(bipy)}_{Co(bipy)(gly)} - \log K^{Co}_{Co(gly)} = -0.17$.[3]

TABLE I

STABILITY CONSTANTS AT μ = 0.1 AND 25°

L	$pK^H_{H_2L}$	pK^H_{HL}	Log K^{Co}_{CoL}	Log $K^{CoL}_{CoL_2}$	Log $K^{Co(bipy)}_{Co(bipy)L}$
2,2′-Bipyridyl[a]	. . .	4.49	6.06	5.36	. . .
Glycine[2,3,b]	2.33	9.68	4.63	3.87	4.46
Bromothymol blue[c]	. . .	7.10	. . .	. . .	. . .

[a] G. Anderegg, *Helv. Chim. Acta*, **46,** 2397 (1963). [b] G. Anderegg, *ibid.*, **44,** 1673 (1961). [c] I. M. Kolthoff, *J. Phys. Chem.*, **34,** 1466 (1930).

Experimental Section

The solutions[5] for the kinetic runs were always freshly prepared using aliquots of a cobalt stock and a carefully weighed amount of 2,2′-bipyridyl such that, in all experiments, $[Co^{2+}]_{total} = [2,2'\text{-bipy}]_{total}$. Previous thermodynamic work[2,3] has shown that under the conditions of these experiments at equilibrium there is negligible concentration of free cobalt ion and free bipyridyl. A weighed sample of glycine was added to the reaction mixture, the ionic strength was adjusted to 0.1 *M* with KNO_3, and the solution was made 2.5×10^{-5} *M* in bromothymol blue. The solutions were degassed and maintained under a nitrogen atmosphere. The pH was adjusted with small amounts of HNO_3 and/or NaOH to ±0.01 pH unit (*cf.* Table II).

TABLE II

RESULTS OF THE RELAXATION EXPERIMENTS

$[Co^{2+}]_{tot}$ = $[bipy]_{tot}$, *M*	$[Gly]_{tot}$, *M*	pH	τ_{obsd}, msec
2.49×10^{-3}	2.49×10^{-3}	6.60	0.71
2.49×10^{-3}	3.74×10^{-3}	6.68	0.67
2.49×10^{-3}	3.74×10^{-3}	6.35	0.82
2.49×10^{-3}	1.25×10^{-3}	6.54	1.50
2.49×10^{-3}	1.25×10^{-3}	7.00	1.09
1.25×10^{-3}	2.49×10^{-3}	6.75	1.50
1.25×10^{-3}	6.24×10^{-4}	6.82	2.88
1.25×10^{-3}	6.24×10^{-4}	7.15	2.39
1.25×10^{-3}	1.25×10^{-3}	6.84	1.78
1.25×10^{-3}	1.25×10^{-3}	7.08	1.67
4.99×10^{-4}	4.99×10^{-4}	7.10	5.87
4.99×10^{-4}	4.99×10^{-4}	6.85	6.31
4.99×10^{-4}	7.48×10^{-4}	6.89	4.93

The study of the ternary complex formation was carried out by application of the temperature-jump technique;[6] the final temperature after the "jump" was 25°. In all cases, solutions containing cobalt(II), bipyridyl, glycine, potassium nitrate, and bromothymol blue showed a single relaxation effect. Blank tests in the absence of either cobalt(II) or glycine showed no relaxation effect in the time range of the instrument. Each relaxation time represents an average of at least three photographic determinations, with the relative error of these measurements at ±10%.[7]

Results and Discussion

The equilibria which must be considered under the experimental conditions described in Table II are

$$Co(bipy)^{2+} + gly^- \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} Co(bipy)(gly)^+ \qquad (1)$$

$$Co(bipy)^{2+} + Hgly \underset{k_{21}'}{\overset{k_{12}'}{\rightleftharpoons}} Co(bipy)(gly)^+ + H^+ \qquad (2)$$

$$H_2gly^+ \rightleftharpoons H^+ + Hgly \qquad (3)$$

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* To whom correspondence should be addressed at Ithaca College.

[1] (a) Part I: R. F. Pasternack and H. Sigel, *J. Amer. Chem. Soc.*, **92,** 6146 (1970); (b) part II: R. F. Pasternack, P. R. Huber, U. M. Huber, and H. Sigel, *Inorg. Chem.*, **11,** 276 (1972).

[2] R. Griesser and H. Sigel, *ibid.*, **9,** 1238 (1970).

[3] R. Griesser and H. Sigel, *ibid.*, **10,** 2229 (1971).

[4] L. G. Sillén and A. E. Martell, *Chem. Soc., Spec. Publ.*, **No. 17** (1964).

[5] The reagents employed were Baker reagent grade nitrate salts of potassium and cobalt(II) used without further purification. Glycine and 2,2,-bipyridyl were purchased from Eastman Organic Chemicals. The course of the reaction was followed by use of Eastman Organic Chemicals bromothymol blue as an indicator.

[6] R. F. Pasternack, K. Kustin, L. A. Hughes, and E. Gibbs, *J. Amer. Chem. Soc.*, **91,** 4401 (1969).

[7] Calculations were carried out on the Ithaca College RCA 70/35 computer. The equilibrium concentrations of the species in solution were calculated using a Newton–Raphson routine.