were determined by direct methods. All non-hydrogen atoms were located by subsequent different Fourier syntheses. Metal, S, and P atoms were refined anisotropically. Phenyl rings were refined as rigid bodies with the fixed C–C distance 1.395 Å and C–C–C angle 120°. The positions of hydrogen atoms on phenyl rings were calculated by using the fixed C–H bond length 0.96 Å. Their contributions were included in the structure factor calculations. The largest peak in the final difference Fourier map of **2**, 3.44 e/$\AA^3$, is 1.82 Å from the Tl atom. The largest peak in the final difference Fourier map of **3**, 0.78 e/$\AA^3$, is 1.39 Å from the Pb atom.

A disordered THF molecule located in the asymmetric unit of **3** was refined successfully. The occupancy factors were refined to 52% for C(4) and C(5) and 48% for C(4)′ and C(5)′, respectively. The packing of **3** with the THF solvate in the lattice is shown in Figure 11. The data used for crystallographic analyses of **2** and **3** are given in Table I.

Acknowledgment. We thank the Welch Foundation, the National Science Foundation (Grant CHE 8708625), and the available fund of Texas A&M University for financial support. We also thank Andy Sargent and Dr. Xue-Jun Feng for their kind help in performing the molecular orbital calculations.

Registry No. **1**, 109638-64-4; **2**, 114057-25-9; **3**·2THF, 123700-53-8; Tl_2SO_4, 7446-18-6; $Pb(NO_3)_2$, 10099-74-8; Au, 7440-57-5; Tl, 7440-28-0; Pb, 7439-92-1.

Supplementary Material Available: Tables of anisotropic thermal parameters and hydrogen atom parameters for **2** and **3** (2 pages); a table of observed and calculated structure factors for **3** (18 pages).

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Reactions of 5-(Perfluoroalkyl)tetrazolates with Cyanogen, Nitrosyl, and Cyanuric Chlorides

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Received May 26, 1989

Sodium tetrazolates, $Na^+\overline{NNNNC}R_f^-$ ($R_f = F_2NCF_2$ (**4**), C_2F_5 (**5**), CF_3 (**6**)), were formed when sodium azide was added across the triple bond of R_fCN ($R_f = F_2NCF_2$ (**1**), C_2F_5 (**2**), CF_3 (**3**)). Isomeric mixtures of nitroso, cyano, and cyanuric tetrazolates, $R_f\overline{CNNNN}X$ ($R_f = F_2NCF_2, C_2F_5, CF_3$; X = NO (**8–10**), CN (**11–13**), $(CN)_3$ (**14–16**)), were obtained by reacting **4**, **5**, and **6** with NOCl, CNCl, and $(CNCl)_3$, respectively. With hydrogen chloride or hydrazoic acid, **4** or **1** gave the stable hygroscopic solid 5-((difluoroamino)difluoromethyl)tetrazoic acid, $NF_2CF_2\overline{CNNNN}H$ (**7**). Stable complexes of tetrazolates **12** and **13**, $[Cu(CF_3\overline{CNNNN}CN)_6][Cu(CF_3\overline{CNNNN})_4]\cdot 2THF$ (**17**) and $[Cu(C_2F_5\overline{CNNNN}CN)_6](C_2F_5\overline{CNNNN})_2\cdot 2THF$ (**18**), were synthesized and characterized by infrared, NMR, and UV spectra, conductivity measurements, and elemental analysis. The ESR study of **17** is also reported.

Introduction

Compounds with high nitrogen content, especially tetrazoles and their salts, are high-energy materials and may explode when exposed to mechanical, thermal, or electrical stimulation.[1–6] Tetrazoles as well as their salts that contain the NF_2 moiety are useful oxidizers when chemically combined with fuels such as anhydrous hydrazine.[7] Sodium azide and hydrazoic acid may undergo 1,3-dipolar[8–16] or HI type addition reactions.[17–27] However, 1,3-dipolar addition is the most commonly observed mechanism in reactions with acetylene and nitriles. An exothermic reaction occurs between sodium azide and (difluoroamino)difluoroacetonitrile,[28] NF_2CF_2CN (**1**), to give sodium 5-((difluoroamino)difluoromethyl)tetrazolate[29] (**4**) in a reaction analogous to that found with R_fCN in which the previously known sodium (perfluoroalkyl)tetrazolates[30] $R_f\overline{CNNNN}^-Na^+$ ($R_f = CF_3$, C_2F_5) were formed. The enhanced reactivity of perfluoroalkyl nitriles toward tetrazole formation compared to that of nonfluorinated nitriles has been recorded and is not surprising on the basis of the increased electropositive character of the cyano carbon in fluorine-containing nitriles.[31]

Metathetical reactions of sodium 5-(trifluoromethyl)tetrazolate with HCl, Cl_2, and CH_3I gave 5-(trifluoromethyl)tetrazole, 2-chloro-5-(trifluoromethyl)tetrazolate, and an isomeric mixture of 1-methyl-5-(trifluoromethyl)tetrazole and 2-methyl-5-(trifluoromethyl)tetrazole, respectively. Norris[30] isolated individual isomers successfully by fractional distillation. The vibrational

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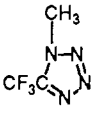
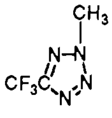
Table I. C=N and N=N Stretching Frequencies (cm^{-1}) for 5-(Perfluoroalkyl)tetrazolate Derivatives

A[a] (14%)	B[a] (86%)	**8**	**9** (60:40)[b]	**10** (88:12)[b]	**11** (90:10)[b]	**12** (50:50)[b]	**13** (60:40)[b]	**14**	**15**	**16**
1533		1560	1562	1532	1580	1586	1667	1604	br	br
	1514	1516	1523	1500	1525	1530	1638	1581	br	br
1472	1480	1489	1490	1450	1435	1460	1573	1537	1579	1608
	1404	1462	1469	1440	...	1437	1553	...	1476	1461
1400		1447	...	...	...	...	1421	1428	...	...
	1360	1417	1420	1410	1400	1395	1403	1387	1401	1418
1302		1336	1343	1330	1380	1337	1383	1365	1384	1399
		1316	...	1310	1345			1305	1340	

[a] Reference 30,



A



B

[b] Ratio of A form to B form.

spectrum and structural assignments for (trifluoromethyl)tetrazoic acid and 1-methyl-5-nitrotetrazole indicate that the proton is attached to N-1 of the tetrazole ring.[32,33] This agrees with electronic structural calculations (CNDO), which indicate a maximum electron density on N-1 and N-4 in the tetrazole ring.[34] Successful regiospecific alkylation at N-1 has also been reported.[35,36]

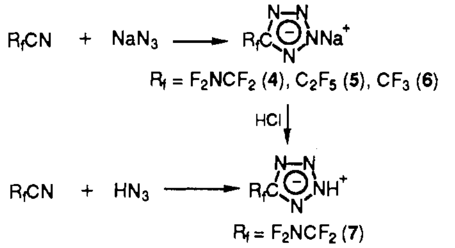
In this paper we report metathetical reactions of sodium 5-((difluoroamino)difluoromethyl)tetrazolate (**4**) and 5-(perfluoroalkyl)tetrazolates (**5** and **6**) with NOCl, CNCl and $(CNCl)_3$. In addition we have synthesized Cu^{2+} complexes of *N*-cyano-5-(perfluoroalkyl)tetrazoles, $R_f\overline{CNNNN}CN$ ($R_f = CF_3$, C_2F_5), with formulas $[Cu(CF_3\overline{CNNNN}CN)_6][Cu(CF_3\overline{CNNNN})_4]\cdot 2THF$ and $[Cu(C_2F_5\overline{CNNNN}CN)_6](C_2F_5\overline{CNNNN})_2\cdot 2THF$.

Results and Discussion

Compounds that contain the NF_2 moiety are potentially unstable, yet very interesting, materials. Recently we have reported a high-yield synthesis of (difluoroamino)difluoroacetonitrile (**1**)[28] from the reaction of tetrafluorohydrazine with 1,1-difluoroethylene in the presence of KF as in eq 1. Sodium azide

$$CH_2{=}CF_2 + N_2F_4 \xrightarrow[160\ ^\circ C]{KF} \underset{\mathbf{1}}{F_2NCF_2CN} \qquad (1)$$

when reacted with **1** as well as with **2** (C_2F_5CN) or **3** (CF_3CN) formed crystalline tetrazolates[28,29] according to eq 2.



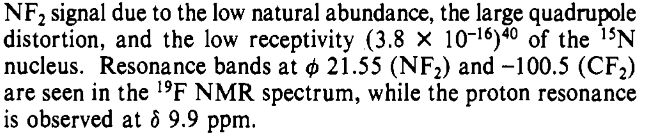
(2)

$R_f = F_2NCF_2$ (**4**), C_2F_5 (**5**), CF_3 (**6**)

(3)

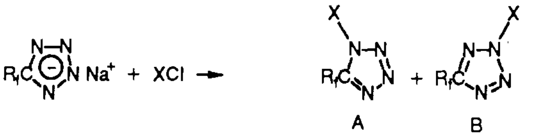
$R_f = F_2NCF_2$ (**7**)

Compound **4** reacted quantitatively with HCl to give 5-((difluoroamino)difluoromethyl)tetrazole (**7**), which can be synthesized by reacting compound **1** with hydrazoic acid. Various mechanisms for 1,3-dipolar addition reactions of sodium azide and hydrazoic acid across alkyne and cyano functionalities have been proposed.[30,31,37,38] However, the mechanism suggested by Norris[30] where the reaction proceeds by attack of the azide ion on the carbon of the nitrile group followed by ring closure is most probable for the above sodium azide addition reactions. 5-((Difluoroamino)difluoromethyl)tetrazole (**7**) is a low-melting, hygroscopic, crystalline solid. In the infrared spectrum, a broad absorption band between 3500 and 2500 cm^{-1} centered at 3091, 2924, and 2818 cm^{-1} is the result of hydrogen-bonded NH. Bands at 1520, 1496, 1490, 1473, and 1380 cm^{-1} are assigned to ring vibrations and indicate that hydrogen is attached to N-1 of the tetrazole ring.[32,33] The presence of two resonance signals at δ −39.73 (γ) and −65.21 ppm (β) in the ^{15}N NMR spectrum for the tetrazole ring indicates the ionization reaction.[39]



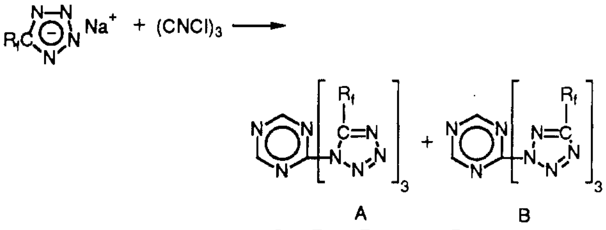
In the ^{15}N NMR spectrum it was not possible to observe the NF_2 signal due to the low natural abundance, the large quadrupole distortion, and the low receptivity (3.8×10^{-16})[40] of the ^{15}N nucleus. Resonance bands at ϕ 21.55 (NF_2) and −100.5 (CF_2) are seen in the ^{19}F NMR spectrum, while the proton resonance is observed at δ 9.9 ppm.

Metathetical reactions of compounds **4–6** with NOCl, CNCl, and $(CNCl)_3$ give N-1- and N-2-substituted isomeric mixtures (A–B) of nitroso, cyano, and cyanuric tetrazolates as is expected from the electronic structure of the tetrazolate anion, in which N-1 and N-2 can act as nucleophilic centers. These reactions are shown in eq 4 and 5.



(4)

X = NO, $R_f = F_2NCF_2$ (**8**), C_2F_5 (**9**), CF_3 (**10**)
X = CN, $R_f = F_2NCF_2$ (**11**), C_2F_5 (**12**), CF_3 (**13**)



(5)

$R_f = F_2NCF_2$ (**14**), C_2F_5 (**15**), CF_3 (**16**)

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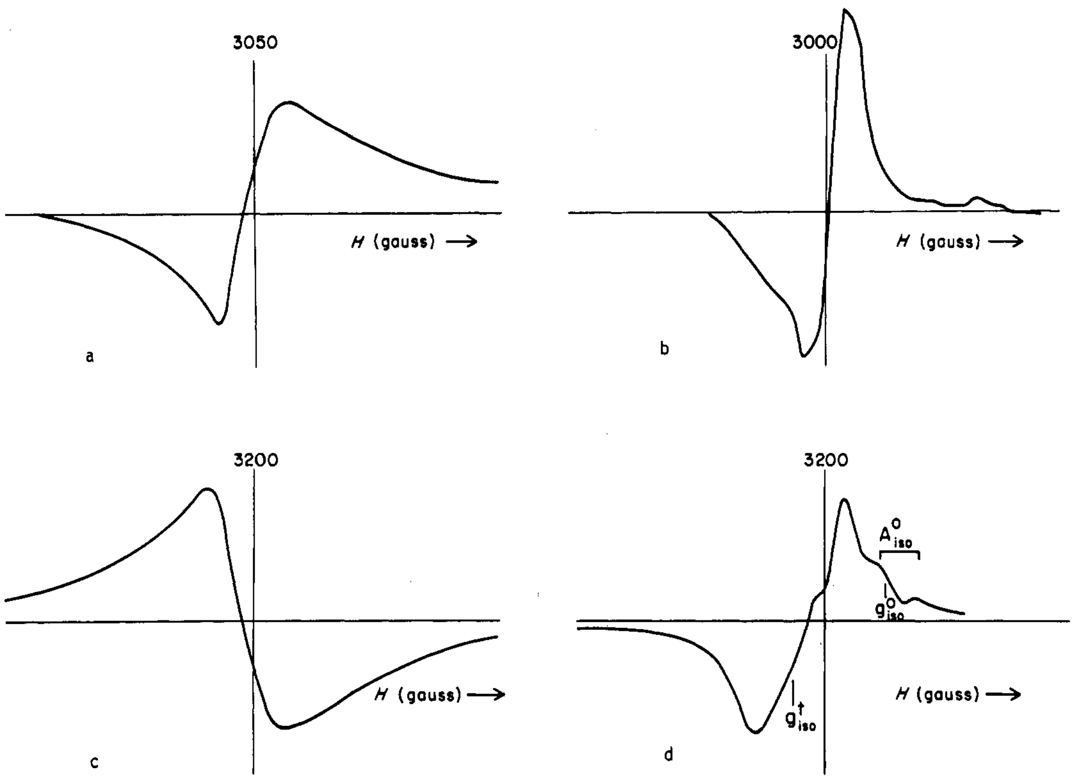

Figure 1. ESR spectra: (a) spectrum for compound **17** (solid, −196 °C); (b) computer-generated spectrum for Cu(II)–Cu(II) dimer ($I = {}^{1}/_{2}$);[56] (c) spectrum for compound **17** (solid, room temperature); (d) spectrum for compound **17** in THF (0.75 g/cm^3, room temperature).

Similar boiling points and thermal instabilities exhibited by each of the above isomeric mixtures made separation and elemental analysis difficult. At room temperature in the absence of solvent these compounds slowly release N_2. On the basis of the amount of NaCl formed, these reactions are approximately quantitative. The formation of isomeric mixtures is supported by two sets of ^{19}F NMR signals for each type of fluorine in the products obtained. Moreover, the IR spectra in the C═N and N═N regions of the tetrazole ring (Table I) in these products is similar to the spectral sum of N-1 and N-2 methyl-substituted 5-(trifluoromethyl)tetrazoles.[30] Characteristic nitroso, cyano, and triazine stretching vibrations for the respective compounds were also observed by IR spectroscopy.

Cyanogen chloride with compounds **5** and **6** in the presence of a solution of $CuCl_2 \cdot 2H_2O$ in THF gave hexakis(N-cyano-5-(trifluoromethyl)tetrazole)copper(II) tetrakis(5-(trifluoromethyl)tetrazolato)cuprate(II)–bis(tetrahydrofuran) (**17**; eq 6) and hexakis(1-cyano-5-(pentafluoroethyl)tetrazole)copper(II) bis(5-pentafluoroethyltetrazolate)–bis(tetrahydrofuran) (**18**; eq 7). Alkylation studies of coordinated tetrazole rings suggest that

$$CF_3\overline{CNNNN}Na + CuCl_2 + CNCl \xrightarrow{THF} \underset{\mathbf{17}}{[Cu(CF_3\overline{CNNNN}CN)_6][Cu(CF_3\overline{CNNNN})_4]} \cdot 2THF \quad (6)$$

$$C_2F_5\overline{CNNNN}Na + CuCl_2 + CNCl \xrightarrow{THF} \underset{\mathbf{18}}{[Cu(C_2F_5\overline{CNNNN}CN)_6][C_2F_5\overline{CNNNN}]_2} \cdot 2THF \quad (7)$$

^{+}CN must be attacked regiospecifically by N-1 because N-2 is blocked by a prior coordination with Cu^{2+}.[35,36] Molar conductance values of 632 and 281 mho cm^2/mol in acetone correspond to six and three ions per molecule in complexes **17** and **18**.[41] Since it has been conclusively found that acetone coordinates with transition metals, especially with Cu^{2+} and Co^{2+},[42–46] the change from two to six ions per molecule for complex **17** is rationalized by eq 8. In compound **18** no change in the number of ions per molecule

$$[Cu(CF_3\overline{CNNNN}CN)_6][Cu(CF_3\overline{CNNNN})_4] \xrightarrow{acetone} 2[Cu(acetone)_x]^{2+} + 4CF_3\overline{CNNNN}^{-} + 6CF_3\overline{CNNNN}CN \quad (8)$$

would occur with a similar solvent exchange. One possible conclusion is that complex **17** has the structure $[Cu(CF_3\overline{CNNNN}CN)_6][(CF_3\overline{CNNNN})_2\text{–}Cu(CF_3\overline{CNNNN})_2] \cdot 2THF$. The presence of three resonance signals with an area ratio of 3:1:1 in the ^{19}F NMR spectrum of compound **17** supports such a structure with considerable distortion from tetrahedral geometry in the anion. The higher ϵ (170) value in the visible spectrum supports the presence of a tetrahedral environment around the Cu(II) ion.[47] Moreover, two separate bands at λ 605 and 703 nm in the solid-state UV–visible spectrum indicates the presence of both four- and six-coordinated Cu(II) species. These values are comparable to the value found for four- and six-coordinated Cu(II) complexes of pentamethylenetetrazole as shown in Table II.[48–50] Therefore, it is likely that in **17** copper exists in both hexacoordinated cationic and tetracoordinated anionic forms. The distorted-tetrahedral geometry of the anion appears to be due to steric and interligand repulsions.[51,52] When R_f is C_2F_5, the magnitude of these repulsions

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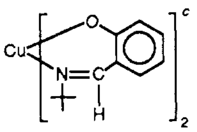
Table II. Electronic Absorption Spectra of Copper(II) Complexes of Pentamethylenetetrazole (PMT) and 5-(Trifluoromethyl)tetrazole (Tz)

complex	state	λ_{max}, nm (ϵ_{molar})
$[Cu(PMT)_4](ClO_4)_2$[a]	soln[d]	670 (81)
$[Cu(PMT)_4](ClO_4)_2$[a]	solid	625
$[Cu(PMT)_6](ClO_4)_2$[a]	soln[d]	680 (103)
$[Cu(PMT)_6](ClO_4)_2$[a]	solid	740
$[Cu(TzCN)_6][Cu(Tz)_4]$[b]	soln[e]	710 (170)
$[Cu(TzCN)_6][Cu(Tz)_4]\cdot 2THF$ (**17**)[b]	solid	560 605 703
	soln[f]	746 (180)

[a] References 48–50. [b] This work; Tz = $CF_3\overline{CNNNN}$. [c] Reference 47, flattened tetrahedral. [d] Nitromethane. [e] Tetrahydrofuran. [f] Chloroform.

Table III. ESR Data for Cu(II) Complexes

	point grp	$g_{\parallel}$[i]	$g_{\perp}$[i]	g_{iso}[j]	A_{iso}, 10^4 cm^{-1} [k]
$[Cu(py)_4]$[a]					
in $[Pt(py)_4](NO_3)_2$	D_{4d}	2.236	2.050	2.112	81
$Cu(8\text{-}Hq)_2$[b]					
frozen soln	D_{4d}	2.172	2.042	2.085	67
solid		2.287	2.066	2.139	77
$[Cu(PMT)_6](ClO_4)_2$[c]					
solid at room temp	D_{4d}	2.331			12 ($A_{\parallel}$)
CH_2Cl_2 soln		2.299	2.08	2.16	164 ($A_{\parallel}$)
$[Cu(PMT)_4](ClO_4)_2$[c]					
in $PhNO_2$	D_{4d}	2.285	2.08	2.197	177 ($A_{\parallel}$)
$[CuCl_4]^{2-}$ [d]	D_{4d}	2.221[f]	2.040[f]	2.100	
		2.221[g]	2.048[g]	2.105	
$[CuCl_4]^{2-}$ [d]	D_{2d}	2.435[f]	2.078[f]	2.197	
		2.435[g]	2.112[g]	2.220	
$[Cu(TzCN)_6]^{2+}$ [e]	D_{4d}			2.014[h]	75
$[Cu(Tz)_4]^{2-}$ [e]	D_{2d}			2.167[h]	126

[a] Reference 61. [b] Reference 62. [c] Reference 49. [d] Reference 60. [e] This work; Tz = $CF_3\overline{CNNNN}$. [f] Experimental. [g] Calculated. [h] ±0.004. [i] ±0.005. [j] Calculated $g_{iso} = {}^1/_3 g_{\parallel} + {}^2/_3 g_{\perp}$. [k] ±5.

apparently increases to the point that formation of such an ion is not observed. For compounds **17** and **18**, nitrile stretching vibrations were assigned at 2232, 2169, and 2161 cm^{-1} in the infrared spectra. Absorption bands at 1656, 1570, 1513, and 1445 cm^{-1} were found for C=N and N=N of cyanotetrazole and tetrazolate rings in compound **17**. In the IR spectrum of compound **18**, however, only a broad absorption band between 1500 and 1600 cm^{-1} was observed. Carbon–fluorine stretching vibrations were also observed. Two pairs of ^{19}F NMR resonance signals in a 3:1 ratio were observed for compound **18**. Compounds **17** and **18** were also characterized by elemental analysis.

ESR Spectra. Compound **17** is ESR active. In the solid state, a highly unsymmetrical broad signal is observed, apparently arising from the overlap of signals (Figure 1a) that indicates the existence of independent six- and four-coordinated Cu(II) species, in which each Cu(II) atom has a spin of $^1/_2$. The computed spectrum (Figure 1b)[56] for spin $^1/_2$ (Cu–Cu distance 5 Å) of a dipolar coupled Cu(II)–Cu(II) pair agrees very well with the observed spectrum (Figure 1a). The broadening of ESR signals can arise from strong dipolar interactions without pairing of spins between the Cu(II) cation and the Cu(II) anion (Figure 1a,c).[53-58] Interestingly, when compound **17** was dissolved in THF, which reduces the extent of interactions, the resulting spectrum became more complex (Figure 1d). Here g^{hex} is overshadowed by contributions from the tetrahedral species. In such cases, normally only $g_{\parallel}$ and $g_{\perp}$ can be obtained. In $[Cu(PMT)_6](ClO_4)_2$[49] and Cu porphyrin[59] complexes, nuclear hyperfine splitting was observed in undiluted samples because the interactions between nieghboring ions are significantly reduced by bulky ligands around the Cu^{2+} ion. However, in the case of **17**, cationic–anionic interactions are significant, and it is necessary to dissolve the solid in a solvent (THF) to reduce these forces and to ensure minimum ligand exchange. Results of NMR spectral studies of **17** suggest the equilibrium

$$[Cu(TzCN)_6][Cu(Tz)_4]\cdot 2THF \rightleftharpoons [Cu(TzCN)_6]^{2+}\cdot x(\text{solvent}) + [Cu(Tz)_4]^{2-}\cdot x(\text{solvent})$$

$$Tz = R_f\overline{CNNNN}$$

Similarly the solution ESR spectrum (Figure 1c) of **17** contains two slightly overlapped signals for the $[Cu(TzCN)_6]^{2+}$ and the $[Cu(Tz)_4]^{2-}$ moieties. The copper nuclear hyperfine splitting makes the octahedral portion of the spectrum more complex. By comparison with data in Table III, the average values of $A_{iso}{}^{hex} = 75 \times 10^{-4}$ cm^{-1} and $g_{iso}{}^{hex} = 2.014$ leads to the conclusion that the cationic Cu(II) complex has distorted-octahedral geometry and that the distortion is tetragonal, similar to that of $Cu(PMT)_6(ClO_4)_2$.[49] The g values for D_{2d} salts are substantially larger than those for D_{4d} salts.[60] Since $g_{iso} = 2.167$ is larger than $g_{iso} = 2.014$, the latter is assigned to the cationic copper complex (D_{4d}; Figure 1d). The ESR data are included in Table III. Due to the line width dependence on an isotropic and spin-rotational relaxation mechanism,[61] electric field fluctuation, and electron exchange,[62-64] it was not possible to observe the ligand hyperfine splitting at 25 °C in solution. Some factors such as electron exchange[58,65-70] and dipolar interactions[55,56] were minimized by adjusting the concentration of the solution while the ligand-exchange process[57,71-73] was minimized by selecting a mild coordinating solvent (THF). Through the use of ESR spectroscopy, it is possible to demonstrate that **17** has the formula $[Cu(CF_3\overline{CNNNN}CN)_6][Cu(CF_3\overline{CNNNN})_4]\cdot 2THF$ in which the copper cation is hexacoordinated while the copper anion has a flattened-tetragonal geometry arising from the presence of a bulky cation.[60]

Experimental Section

Materials. Reagents were purchased as indicated: trifluoroacetonitrile, pentafluoropropionitrile (PCR); cyanogen chloride (Solkatronic Chemical). (Difluoroamino)difluoroacetonitrile, sodium 5-((difluoroamino)difluoromethyl)tetrazolate, sodium 5-(trifluoromethyl)tetrazolate, and sodium 5-(pentafluoroethyl)tetrazolate were synthesized by literature methods.[28,29]

General Procedures. Perkin-Elmer 1710 and Digilab Qualimatic 010-0100 FT infrared spectrometers, a JEOL FX90Q FT nuclear magnetic resonance spectrometer, a Perkin-Elmer Lambda 4C UV–visible spectrometer, and a Sybron/Barnstead conductivity bridge (Model PM70CB) were used for obtaining spectral and conductivity data. In

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obtaining the conductance of **17** and **18**, we used $NaClO_4$ (3.4×10^{-3} M) with a molar conductance of 194 mho cm^2/mol in acetone for conductivity calculations. ^{15}N NMR data were recorded on an IBM (Bruker) NR/300 FT NMR spectrometer. Electron spin resonance measurements were carried out with a Varian E3 spectrometer equipped with 100-kHz modulation frequency in the X-band region. Microwave power, field, and receiver gain were set at 16, 20 mw 3050, 3200 G, and 3.2×10^2, 6.2×10^3, respectively, for powder spectra of compound **17** at −106 and +20 °C, while in solution (0.075 g/cm^3) at 20 °C these values were set at 50 mw, 3200 G, and 6.2×10^4. The values of time scan, time constant, and modulation amplitude were fixed at 4 m, 1 s, and 10 G, respectively. Gases and volatile liquids were handled in a Pyrex vacuum apparatus equipped with a Heise-Bourdon tube gauge. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, FRG.

Synthesis of 5-((Difluoroamino)difluoromethyl)tetrazole (7). Diethyl ether (5 mL) and HCl (2.0 mmol) were condensed into a 50-mL Pyrex bulb that contained sodium 5-((difluoroamino)difluoromethyl)tetrazolate (1.5 mmol) at −196 °C. The reactants were warmed slowly to 25 °C, and the mixture was agitated for 2 h. Sodium chloride was removed by filtration. Ether was evaporated, and a quantitative yield of **7** was obtained. Spectral data obtained for **7**: IR (KBr thin film) 3090 b, 2924 b, 2872 w, 2818 b, 1520 m, 1396 s, 1380 m, 1236 vs, 1210 vs, 1191 vs, 1115 s, 1054 s, 1021 s, 990 s, 950 vs, 927 vs, 794 m, 664 m, 633 s, 570 vw, 550 vw, 540 vw, 500 vw cm^{-1}; ^{19}F NMR ϕ 21.55 (NF_2), −100.5 (CF_2); ^1H NMR δ 9.9; ^{15}N NMR ($CDCl_3$/THF) δ −39.73, −65.21. Anal. Calcd for $C_2HF_4N_5$: C, 14.03; H, 0.59; N, 40.93. Found: C, 13.87; H, 0.62; N, 40.93.

Synthesis of 8–13. A small excess of NOCl or CNCl (2.2 mmol) was added to compound **4**, **5**, or **6** (1.5 mmol) in THF (5 mL) in a 50-mL Pyrex bulb at −196 °C. The reactants were warmed slowly to 25 °C, and the mixture was agitated for 24–36 h. The mixture was filtered to remove NaCl. Solvent and excess NOCl and CNCl were evaporated to give ~90% yields of compound **8–13**. Spectral data obtained for **8** (A–B): IR (KBr pellet) 1703 s (NO), 1672 s (NO), 1560 s, 1516 s, 1498 m, 1462 m, 1447 m, 1417 m, 1336 m, 1316 s, 1236 vs, br, 1202 vs, br, 1113 s, 1140 vs, 1023 vs, 979 vs, 951 vs, 925 vs, 885 vw, 796 m, 762 w, 670 m, 635 m cm^{-1}; ^{19}F NMR ϕ 20.58, 20.07 (NF_2), −100.3, −100.6 (CF_2). Spectral data obtained for **9** (A–B): IR (KBr pellet) 1687 m (NO), 1655 m, 1562 vw, 1523 vw, 1490 m, 1469 vw, 1420 m, 1342 vs, 1213 vs, 1160 vs, 1087 s, 1041 m, 976 vs, 826 vw, 751 vs, 735 w, 638 m, 545 w cm^{-1}; ^{19}F NMR ϕ −84.56 (A–B two triplets, $J = 2.56$ Hz), −115.02 (multiplet, two overlapping quartets). Spectral data obtained for **10** (A–B): IR (KBr pellet) 2900 vw (THF), 1720 s (NO), 1520 s, 1500 w, 1450 m, 1440 m, 1410 w, 1310 m, 1270 vs, 1220 vs, 1050 vs, 1010 vs, 940 m, 770 m, 755 s, 730 m, 680 s, 520 w cm^{-1}; ^{19}F NMR ϕ −63.48, −63.71 (CF_3). Spectral data obtained for **11** (A–B): IR (KBr pellet) 2185 s (CN), 1580 s, 1525 s, 1435 s, 1400 w, 1380 w, 1345 w, 1210 vs, br, 1050 s, 980 s, 965 w, 930 s, 845 w, 820 w, 770 w, 675 vw, 640 w, 550 w cm^{-1}; ^{19}F NMR ϕ 20.0 (NF_2), −100.0 (CF_2). Spectral data obtained for **12** (A–B): IR (KBr pellet) 2263 vw, 2245 vw, 2236 vw, 2180 s (CN), 2156 s (CN), 1586 vs, 1530 vs, 1460 s, 1395 s, 1337 s, 1221 vs, 1195 vs, 1183 vs, 1160 vs, 1075 m, 1031 m, 986 s, 970 s, 925 w, 831 m, 817 m, 751 w, 740 w, 710 w cm^{-1}; ^{19}F NMR ϕ −84.10, −84.98 (CF_3), −114.68, −115.3 (CF_2). Spectral data obtained for **13** (A–B): IR (KBr pellet) 2207 m, 2146 s (CN), 1667 vs, 1638 vs, 1573 s, 1553 vs, 1421 m, 1403 m, 1383 vs, 1209 vs, 1085 vw, 1041 s, 988 m, 830 m, 750 m, 730 w, 710 w cm^{-1}; ^{19}F NMR ϕ −64.38, −64.61 (CF_3).

Synthesis of 14–16. A solution of $(CNCl)_3$ (1.6 mmol) in THF (5 mL) was added slowly under anhydrous conditions to a solution of **4**, **5**, or **6** (1.5 mmol) in THF (5 mL). The mixture was agitated for 36 h in the dark. NaCl was removed by filtration. Partial removal of THF and recrystallization from a 50:50 chloroform–petroleum ether mixture at 0 °C gave ~60% yields of pure **14–16**. Spectral data obtained for **14** (A–B): IR (KBr disk) 1604 vs, 1581 vs, 1537 m, 1428 vs, 1387 vs, 1364 w, 1305 vw, 1187 vs, 1114 w, 1046 vs, 980 vs, 950 s, 925 vs, 839 s, 817 m, 795 w, 670 w, 632 w, 604 w, 540 m, 483 w cm^{-1}; ^{19}F NMR ϕ 22.53, 22.07 (NF_2), −100.25, −100.54 (CF_2). Spectral data obtained for **15** (A–B): IR (KBr disk) 1579 vs, 1476 vw, 1428 vs, 1401 w, 1384 m, 1340 s, 1219 vs, 1181 s, 1156 vs, 1071 m, 1033 vw, 973 vs, 839 m, 828 m, 809 m, 769 w, 751 s, 635 m cm^{-1}; ^{19}F NMR ϕ −83.69, −84.32 (CF_3), −113.92, −113.59 (CF_2). Spectral data obtained for **16** (A–B): IR (KBr disk) 1705 vs, 1509 m, 1461 s, 1419 s, 1399 s, 1208 m, 1170 vs, 1045 m, 985 vw, 850 m, 765 m, 530 s cm^{-1}; ^{19}F NMR ϕ −64.62, −64.33.

Synthesis of 17 and 18. Into a 50-mL Pyrex bulb containing compound **5** or **6** in THF (5 mL) at −196 °C was condensed CNCl (2.2 mmol). A solution of $CuCl_2 \cdot 2H_2O$ (1 mmol) in THF (5 mL) was added to the frozen solution. The reaction mixture was warmed slowly to room temperature and was agitated for 48 h. Solid NaCl and some unidentified insoluble copper complex was removed by filtration. Crystallization and recrystallization from a 50:50 mixture of petroleum ether–THF gave pure compound **17** or **18** in 25–30% yield. The purity was determined by TLC. Spectroscopic data obtained for **17**: IR (KBr disk) 3300–2900 br (THF), 2232 s (CN), 2169 m (CN), 1656 s, 1570 m, 1513 m, 1446 m, 1367 vw, 1345 w, 1330 w, 1179 vs, 1072 m, 1037 s, 774 m, 756 s, 740 m cm^{-1}; ^{19}F NMR (in THF) ϕ −66.67 vbr (3), −77.49 br (1), −82.64 br (1). Anal. Calcd for $Cu_2C_{34}H_{16}F_{30}N_{46}O_2$: C, 22.70; H, 0.89; N, 35.84; Cu, 7.06. Found: C, 23.27; H, 1.11; N, 37.29; Cu, 6.97. Spectral data obtained for **18**: IR (KBr disk) 3300–2900 br (THF), 2161 s (CN), 1600–1500 vbr, 1376 m, 1337 s, 1220 vs, 1162 vs, 1073 w, 1038 w, 992 w, 972 s, 901 w, 882 w, 751 s, 637 w, 540 vw, 484 vw, 409 vw cm^{-1}; ^{19}F NMR (in THF) ϕ −82.01 br, −84.55 br, −115.03 br, −120.75 br. Anal. Calcd for $CuC_{38}H_{16}F_{40}N_{38}O_2$: C, 24.52; H, 0.86; F, 40.9; Cu, 3.42. Found: C, 24.84; H, 0.94; F, 41.5; Cu, 3.54.

Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, to the NSF (Grants CHE-8404974 and CHE-8703790), and to the AFOSR (Grant 87-0067).

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Dinuclear Complexes of a $[30]Py_2N_4O_4$ Macrocyclic Ligand Containing Two α,α'-Bis(aminomethyl)pyridine Moieties. Comparison with Analogous 22- and 24-Membered Macrocyclic Ligands

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Received May 1, 1989

The synthesis of the hexaaza macrocycle L = 3,12,20,29,35,36-hexaaza-6,9,23,26-tetraoxatricyclo[29.3.1.1^{14,18}]hexatriaconta-1(34),14,16,18(36),31(35),32-hexaene (O2-BISBAMP) is reported. Protonation as well as metal binding constants with Cu(II), Co(II), Ni(II), and Zn(II) have been determined at 25.0 °C and 0.100 M ionic strength. Mononuclear and dinuclear chelates of these metal ions are identified in all systems investigated. Mono- and diprotonated and monohydroxy mononuclear complexes of O2-BISBAMP are formed with all metal ions studied. Strong tendencies toward hydroxide ion bridging between the two metal centers in the dinuclear complexes were not found except for the dinuclear Cu(II) complex. The metal ion affinities as well as the binucleating and bridging tendencies of L are compared to those of analogous ligands containing macrocyclic rings.

Introduction

The protonation constants and metal ion stability constants in aqueous solution of the binucleating macrocyclic ligands C-BISBAMP (3,8,16,21,27,28-hexaazatricyclo[21.3.1.1^{10,14}]octacosa-1(26),10(28),11,13,23(27),24-hexaene, **2**) and O-BISBAMP (3,9,17,23,29,30-hexaaza-6,20-dioxatricyclo[23.3.1.1^{11,15}]triaconta-1(28),11,13,15(30),25(29),26-hexaene, **3**) have been measured by Arnaud-Neu et al.[1] and Basalotte et al.,[2] respectively.

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