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Contribution from the Departments of Chemistry, University of Idaho,
Moscow, Idaho 83843, and Washington State University, Pullman, Washington 99164

# 5-(Perfluoroalkyl)tetrazoles: $\eta^5$ Ligands in Solution and $\mu$-2,3-$\eta^2$ Ligands in Solid Complexes

Earnest Obed John, Roger D. Willett,* Brian Scott, Robert L. Kirchmeier, and Jean'ne M. Shreeve*

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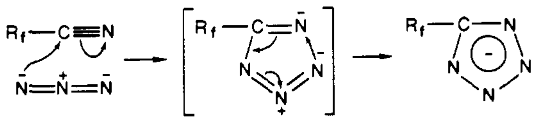
Sodium azide was reacted with (difluoroamino)difluoroacetonitrile, $NF_2CF_2CN$ (**1**), to give sodium 5-((difluoroamino)difluoromethyl)tetrazolate (**2**) in a reaction analogous to that with $CF_3CN$ where the previously known sodium 5-(trifluoromethyl)tetrazolate (**3**) was formed. Reactions of **2** and **3** with pentacarbonylmanganese bromide give the compounds $R_f\overline{CNNNNMn}(CO)_3$ ($R_f = NF_2CF_2$, $CF_3$). In solution, the local symmetry of the carbonyl groups is very similar to that of $(\pi\text{-}C_5H_5)Mn(CO)_3$, which is an $\eta^5$-$\pi$ complex. However, upon evaporation of the solvent, a reversible reorganization of the ligands gives rise to the compounds $[(R_f\overline{CNNNN})_3Mn_2(CO)_6]Mn(CO)_3$ ($R_f = NF_2CF_2$ (**6**), $CF_3$ (**7**)). The latter anion has been characterized by X-ray structural analysis of the compound $[(CF_3\overline{CNNNN})_3Mn_2(CO)_6]^-[Na(diglyme)_2]^+$ (**8**). In the solid, the tetrazole ligands are of the $\eta^2$ type with N-2 and N-3 of each tetrazole bridging between the two manganese atoms. The N-2---N-3 distance (1.34 Å) is much longer than that observed previously in copper and silver salts (1.12 Å).

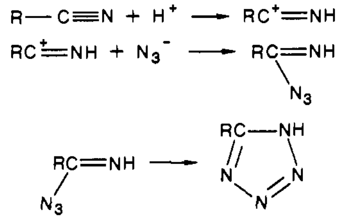
## Introduction

Tetrazoles and their salts containing the $-NF_2$ moiety may be useful as oxidizers when combined chemically with fuels such as anhydrous hydrazine.[1] Highly fluorinated nitrogen compounds that contain the $-NF_2$, $-NCl_2$, $-NFCl$, and $-N{=}N-$ functionalities are very reactive synthetic reagents and are potentially explosive materials.[2,3] Trifluoroacetonitrile[4] and pentafluoropropionitrile react exothermally with sodium azide to give the respective (perfluoroalkyl)tetrazolates. The high reactivity of trifluoroacetonitrile is in keeping with the observation that electronegative groups bonded to the nitrile functionality facilitate tetrazole formation; e.g., *p*-nitrobenzonitrile, terephthalonitrile, and perfluorocaprylonitrile react readily with sodium azide in dimethylformamide to form 5-substituted tetrazolates.[5,6] The reaction very likely proceeds by attack of the azide ion on the carbon of the nitrile group followed by ring closure to give the tetrazolate:



$R_f = F_2NCF_2$ (**2**), $CF_3$ (**3**)

Benzonitriles with more electropositive substituents and aliphatic nitriles require higher temperatures and acid catalysis to give good yields of tetrazolates; e.g., acetonitrile does not react with sodium azide even at 200 °C after 18 h. By the addition of 1:1 ammonium chloride and sodium azide, the reaction proceeds readily at 150 °C to give the 5-methyltetrazole probably by the general mechanism as stated by Lofquist:[5]



In principle, each of the four nitrogen atoms of the tetrazole ring is capable of acting as a coordination site. Variable modes of coordination for tetrazoles have been reported.[7-10] Monodentate coordination is observed in $Cu_2(CF_3CN_4)_2[(CH_2P(C_6H_5)_2)_2]_3$ at N-2 or N-4.[7] 2,3- and 3,4-bidentate tetrazolates are also known in $Ag_2(PPh_3)_4(CF_3CN_4)_2$[8] and in $[Ag(PMT)_2NO_3]_2$[9,10] (PMT ≡ pentamethylenetetrazole). The difference in architecture, i.e., bond angles and bond distances in the tetrazole ring, depends mainly upon the difference in their coordination behavior. There is no evidence to date that suggests any other type of bonding than by donation from the individual nitrogen atoms in the tetrazole ring to the acceptor moiety.

Tetrazoles are isoelectronic with cyclopentadienes and similar with respect to acidity and symmetry of the ring. To determine whether the tetrazolate ion participates in $\eta^5$-$\pi$ complexes as is well-known for cyclopentadienyl (Cp) anions, we carried out the reaction of $R_f\overline{CNNNN}^-Na^+$ with $BrMn(CO)_5$ and compared the product with that obtained by using $C_5H_5^-Na^+$.

In this paper, we report the synthesis of sodium 5-((difluoroamino)difluoromethyl)tetrazolate, $F_2NCF_2\overline{CNNNN}^-Na^+$ (**2**), sodium 5-(trifluoromethyl)tetrazolate,[4] $CF_3\overline{CNNNN}^-Na^+$ (**3**), and their $\eta^5$ complexes $F_2NCF_2\overline{CNNNNMn}(CO)_3$ (**4**) and $CF_3\overline{CNNNNMn}(CO)_3$ (**5**) in solution. However, in the solid state, rearrangement occurs to give $[(F_2NCF_2\overline{CNNNN})_3Mn_2(CO)_6]^-[Mn(CO)_3]^+$ (**6**) and $[(CF_3\overline{CNNNN}Mn_2(CO)_6]^-[Mn(CO)_3]^+$ (**7**). A similar rearrangement is observed for the complex $Ag_2(PPh_3)_4(CF_3CN_4)_2$.[8] Cationic exchange between $[(CF_3\overline{CNNNN})_3Mn_2(CO)_6]^-[Mn(CO)_3]^+$ and $[Na(digly)_2]^+Br^-$ (digly = diglyme) gives rise to the yellow crystalline compound $[(CF_3\overline{CNNNN})_3Mn_2(CO)_6]^-[Na(digly)_2]^+$ (**8**), the structure of which has been confirmed by single-crystal X-ray analysis.

## Results and Discussion

The earlier method for synthesis of (perfluoroalkyl)tetrazoles required large amounts of starting materials, and a rather complicated system was needed to diffuse the gaseous perfluoroalkanenitriles into the reaction mixture.[4] In our work a comparatively simple, one-pot synthesis was used in which a slight

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* To whom correspondence should be addressed: R.D.W., Washington State University; J.M.S., University of Idaho.

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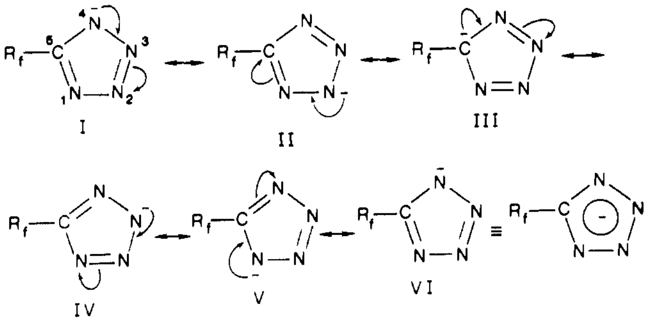
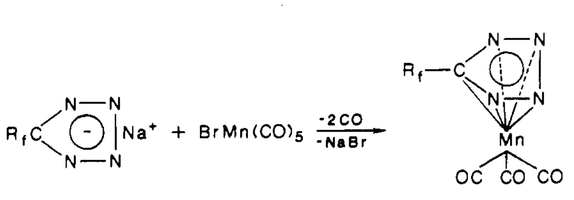
excess of the perfluoroalkanenitrile was condensed into a suspension of sodium azide in acetonitrile at −196 °C. When the mixture was heated at 65 °C and stirred constantly, a clear solution of the tetrazole was obtained. On the basis of $NaN_3$ consumed, the yield was essentially quantitative. The extent of the reaction was monitored by observing the decrease in intensity of the azide stretch in the range of 2000–2100 cm$^{-1}$ in the infrared spectrum. As is the case for $CF_3\overline{CNNNN}^-Na^+$ (**3**), $NF_2CF_2\overline{CNNNN}^-Na^+$ (**2**) is highly soluble in THF, acetonitrile, ethanol, DMF, and water.

Compound **2** is a highly hygroscopic crystalline substance that showed a characteristic IR spectrum with the feature at 1603–1633 cm$^{-1}$ assigned to $C\doteq N$. A band in this region was considered initially to be due to a shifted water molecule deformation band in other tetrazoles since it was absent from complexes bearing electron-withdrawing groups in the 5-position when obtained from nonaqueous solution.[11] However, later workers observed the band even when an iron tetrazolate material was obtained from ethyl acetate and preserved under anhydrous conditions.[12] The $C\doteq N$ bonds of the tetrazole ring, which become stronger and shift to a higher frequency in the tetrazole salt (1520 and 1635 cm$^{-1}$, respectively),[4,12] are also observed in compound **2** (1603–1633 cm$^{-1}$) and the analogous acid (1520 cm$^{-1}$). A band at 1420 cm$^{-1}$ is assigned to the N-2$\doteq$N-3 stretch on the basis of an earlier study of 80 azo compounds where bands in the 1400–1450-cm$^{-1}$ region were assigned to $\nu_{N=N}$.[13] Harris ascribed the $\nu_{N=N}$ vibration to a band in the region of 1408–1410 cm$^{-1}$ that was shifted to 1449 and 1420 cm$^{-1}$, respectively, when 5-nitro- and 5-(trifluoromethyl)tetrazole was associated with iron.[14] A strong band at 1492 cm$^{-1}$ is assigned to the mixed mode $\nu_{C-CF_2}$. A similar band observed from 1500 to 1505 cm$^{-1}$ in several 5-(trifluoromethyl)tetrazole salts was assigned as $\nu_{C-CF_3}$.[11] Bands centered from 1250 to 1150 cm$^{-1}$ are attributable to $\nu_{C-F}$.[15] Principal absorption bands for $\nu_{N-F}$ are found between 1000 and 900 cm$^{-1}$.[16] The bands at 1050 cm$^{-1}$ may arise from skeletal motions of the tetrazole ring.[17]

The negative charge of the tetrazolate can be delocalized in the ring by the strongly electron-withdrawing nature of $R_f$ groups in the following manner:[5]

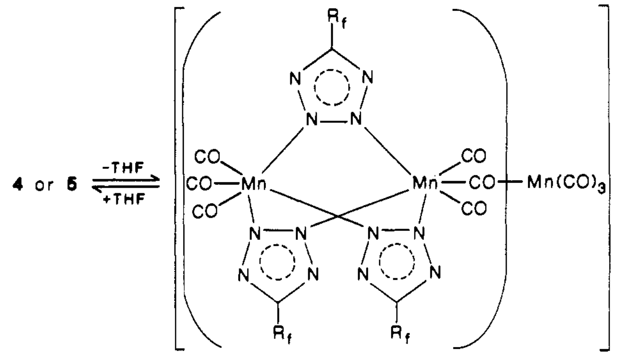


If the lone pair of electrons on each nitrogen atom in the above structures is neglected, there is a close similarity to the cyclopentadienyl anion. Since delocalization of the negative charge into the ring of the tetrazolate anion gives the ring an aromatic sextet, utilization of the $R_f$ group as a substituent in the 5-position increases the coordinating ability of the ring. Also, since the (trifluoromethyl)tetrazolate anion has a $\pi$ cloud, either $\pi$ complexes or normal addition complexes may be formed. To investigate this possibility, target compounds of the general formula $R_f\overline{CNNNN}Mn(CO)_3$ were synthesized in THF according to



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

When the solvent is removed from **4** or **5**, **6** or **7** is formed as indicated:



$R_f = F_2NCF_2$ (**6**), $CF_3$ (**7**)

+

$[Na(diglyme)_2]^+Br^-$

On the basis of the literature,[18,19] the structures of **4** and **5** can be determined by infrared spectra and consideration of the local symmetry of the carbon monoxide groups only. Cotton assumed that long-range interactions between the sandwich ring and the carbon monoxide group are small in $(\pi\text{-}C_5H_5)Mn(CO)_3$ and many other ($\pi$-cyclopentadienyl)metal carbonyl complexes. He proposed that $\nu_{C\equiv O}$ can be obtained by considering only the local symmetry of the carbon monoxide groups.[18] The influence of the sandwich ring can be neglected. Assuming that $R_f\overline{CNNNN}^-$ behaves as an $\eta^5$-$\pi$-bonding ligand, the local symmetry of the CO ligands should be $C_{3v}$. The predicted stretching vibrations for this model are

| no. | sym type | activity |
|---|---|---|
| I | $A_1$ | R–IR |
| II | E | R–IR |

The observed infrared spectrum in solution satisfies the requirements of the proposed structures for **4** and **5** with two bands observed for $\nu_{C\equiv O}$ at 2056 and 1967 cm$^{-1}$ ($CH_2Cl_2$) and 2043 and 1977 cm$^{-1}$ ($CH_2Cl_2$). In the solid state, however, the number of carbonyl stretching frequencies suggests a more complicated structure. Comparison of the shifts of the carbonyl stretching frequencies for **4** and **5** with those reported for $(\pi\text{-}C_5H_5)Mn(CO)_3$ in solution and the solid state indicates a structural change in **4** and **5** in which the $\pi$ structure of the tetrazole is lost in the solid state. The loss of $\pi$ structure is indicated by the increase in the number of carbonyl frequencies observed for **4** and **5** in the solid state, i.e., solid compounds **6** and **7** compared to compounds **4** and **5** in solution. The pertinent vibrational data are given in Table I. In addition, the skeletal region stretches at 1072 and 1038 cm$^{-1}$ for the tetrazole ring of $CF_3\overline{CNNNN}^-Na^+$ (**3**) and at 1050 cm$^{-1}$ for $NF_2CF_2\overline{CNNNN}^-Na^+$ (**2**) are shifted to lower frequencies, to 1065 and 1030 cm$^{-1}$ for **5** and to 1037 cm$^{-1}$ for **4**. These decreases in stretching energy may result from minor $\pi$ interactions.[11] These shifts are analogous to those previously reported for cyclopentadienyl salts and complexes.[20] The ring deformations in $Mg(Cp)_2$, where there are no $\pi$ interactions, are found at 1428 and 1108 cm$^{-1}$, while the ring deformation modes

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(11) Jonassen, H. B.; Terry, O.; Harris, A. D. *J. Inorg. Nucl. Chem.* **1963**, *25*, 1239.
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(20) Martell, A. E. In *Coordination Chemistry*; Beringer, F. M., Ed.; Van Nostrand-Reinhold: New York, 1971; Vol. 1, Chapter 3, p 174.

**Table I.** Tabulation of Carbonyl Stretching Frequencies

| compd | state | obsd bands, $cm^{-1}$ | | | |
|---|---|---|---|---|---|
| $(\pi\text{-}C_5H_5)Mn(CO)_3$[a,b] | solid | 2023 | 1935 | | |
| | soln | 2023 | 1935 | | |
| $NF_2CF_2\overline{CNNNN}Mn(CO)_3$ (**4**) | soln ($CH_2Cl_2$) | 2056 | 1967 | | |
| $CF_3\overline{CNNNN}Mn(CO)_3$ (**5**) | soln (diglyme) | 2044 | 1958 | | |
| $[(NF_2CF_2\overline{CNNNN})_3Mn_2(CO)_6]Mn(CO)_3$ (**6**) | soln ($CH_2Cl_2$) | 2043 | 1977 | | |
| | solid | 2055 | 1954 | 1949 | |
| $[(CF_3\overline{CNNNN})_3Mn_2(CO)_6]Mn(CO)_3$ (**7**) | solid | 2042 | 1969 | 1958 | 1950 |
| $[(CF_3\overline{CNNNN})_3Mn_2(CO)_6][Na(digly)_2]^+$ (**8**) | solid | 2042 | 1973 | 1954 | 1908 |
| | | | | 1897 | 1893 |

[a] Reference 18. [b] Reference 19.

**Table II.** Crystal and Data Collection Parameters for **8**

| | |
|---|---|
| formula | $[(CF_3\overline{CNNNN})_3Mn_2(CO)_6]^-[Na(digly)_2]^+$ |
| $M_r$ | 980 |
| space group | $C2/m$ |
| $a$, Å[a] | 24.772 (4) |
| $b$, Å | 19.908 (3) |
| $c$, Å | 17.051 (3) |
| $\beta$, deg | 93.77 |
| $V$, Å$^3$ | 8391 (2) |
| $d_c$, g $cm^{-3}$ | 1.55 |
| $Z$ | 8 |
| $F(000)$ | 3936 |
| cryst size, mm | 0.42 × 0.31 × 0.23 |
| radiation | Mo K$\alpha$ ($\lambda$ = 0.71069 Å) |
| temp, K | 298 |
| $hkl$ values scanned | $\pm h,+k,+l$ |
| scan type | $\omega$ |
| scan speed, deg $min^{-1}$ | 4.0–29.3 |
| $2\theta_{max}$, deg | 45 |
| no. of reflns collcd | 6871 |
| no. of unique reflns | 5933 |
| no. of obsd reflns with $I > 3\sigma(I)$ | 3736 |
| abs cor | none |
| no. of variables refined | 572 |
| $R$ | 0.0824 |
| $R_w$ | 0.0927 |

[a] Estimated standard deviations in the least significant figure(s) are given in parentheses.

for $Fe(Cp)_2$, which exhibits $\pi$ interactions, appear at 1408 and 1101 $cm^{-1}$. Lastly, the Mn–N bond distance as determined by the crystal structure of **8** is 2.05 Å, which is identical with the Mn–N single-bond distance previously reported for $Mn_2(CO)_{10}CH_2N_2$ (2.05 Å)[21] and $[Mn(CO)_4]_3N_2CH_3$ (2.06 Å).[22]

The fact that the structural changes observed for **4** and **5** were reversible was demonstrated when the solvent (THF) was removed slowly under a constant flow of dry nitrogen from a solution of either compound. The shapes and positions of the carbonyl stretching vibrations were noted as a function of time. As the solution became more concentrated, the infrared spectra became more complex until three peaks were resolved as shown in Figure 1 (A → D). When the solid **8** was redissolved in THF, the infrared spectrum reverted to A (**5** in THF solution):

$$\mathbf{8}(s) \underset{-THF}{\overset{+THF}{\rightleftharpoons}} \mathbf{25}(soln) + \mathbf{3}$$

$$\mathbf{6}(s) \text{ or } \mathbf{7}(s) \underset{-THF}{\overset{+THF}{\rightleftharpoons}} \mathbf{34}(soln) \text{ or } \mathbf{35}$$

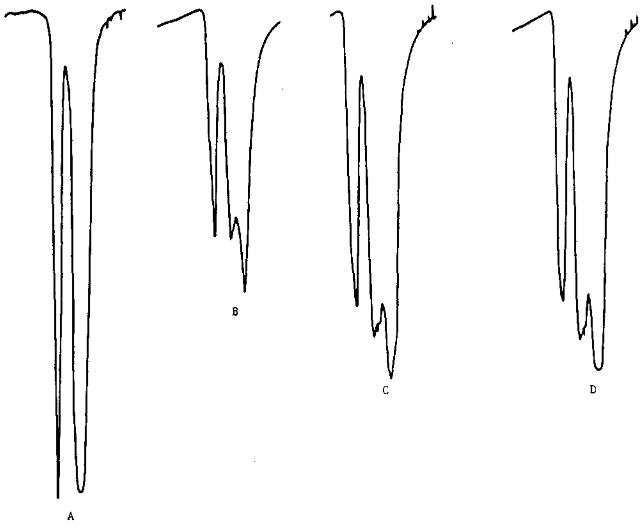
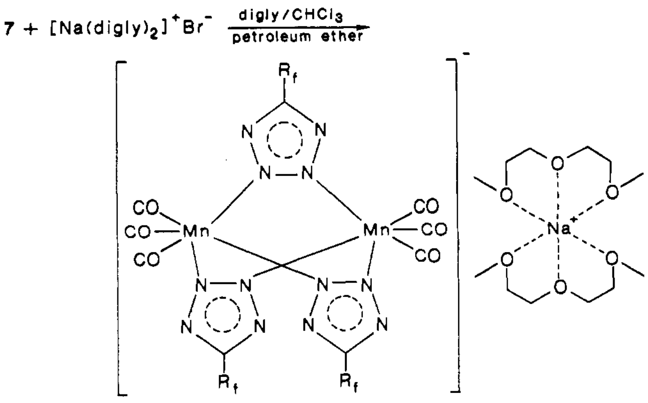


**Figure 1.** Change in $\nu_{CO}$ pattern of **5** upon increasing concentration of solution by evaporation of solvent (THF) (A (dilute solution) → D (solid)).

**Table III.** Selected Structural Parameters for **8**

| Bond Distances (Å) | | | |
|---|---|---|---|
| Mn(1)–N(1) | 2.054 (6) | C(4)–C(5) | 1.460 (17) |
| Mn(1)–N(3) | 2.054 (6) | C(4)–N(2A) | 1.328 (9) |
| Mn(1)–N(5) | 2.040 (6) | C(4)–N(2) | 1.328 (9) |
| N(1)–N(1A) | 1.345 (11) | N(1)–N(2) | 1.339 (9) |
| Mn(1)–C(1) | 1.829 (9) | | |
| **Bond Angles (deg)** | | | |
| Mn(1)–Mn(1)–N–(3) | 87.4 (2) | N(1)–Mn(1)–N(5) | 87.3 (2) |
| Mn(1)–N(1)–N(2) | 124.5 (5) | N(3)–Mn(1)–N(5) | 88.4 (3) |
| Mn(1)–N(1)–N(1A) | 126.5 (2) | | |

Compound **7**, i.e. compound **5** in the solid state, did not give rise to crystals suitable for single-crystal X-ray analysis. However, compound **8**, $[(CF_3\overline{CNNNN})_3Mn_2(CO)_6]^-[Na(digly)_3]^+$, was obtained as a yellow crystalline solid by an ion-exchange reaction between **7** and $[Na(digly)_2]^+Br^-$, and the structure of the anion in the solid state was confirmed to be $[(CF_3\overline{CNNNN})_3Mn_2(CO)_6]^-$:



$R_f = CF_3$ (**8**)

With the exception of the carbonyl regions, the infrared spectra

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(21) Herrman, W. A.; Ziegler, M. L.; Weidenhammer, K.; Biersack, H.; Mayer, K. K.; Minard, R. D. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 165.

(22) Herrman, W. A.; Ziegler, M. L.; Weidenhammer, K. *Angew. Chem., Int. Ed. Engl.* **1976**, *15*, 369.

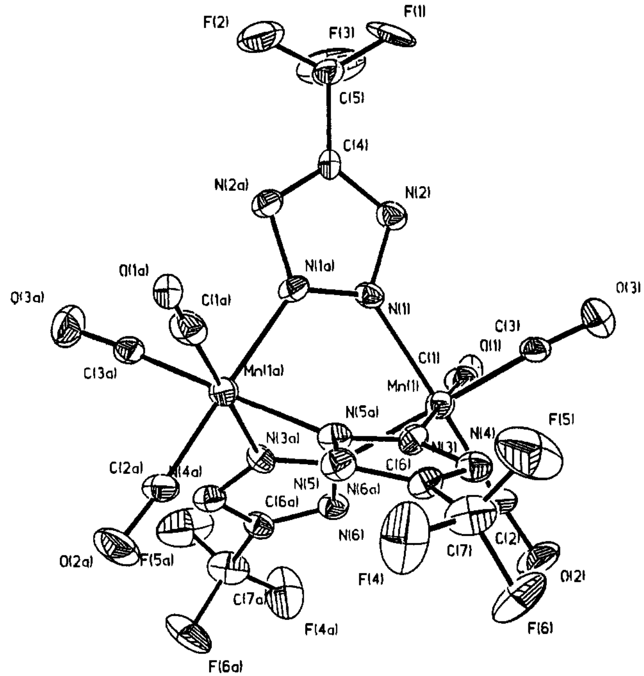

**Figure 2.** Structure of the $[(CF_3\overline{CNNNN})_3Mn_2(CO)_6]^-$ anion of **8**. ORTEP thermal ellipsoids represent 50% probability surfaces.

of compounds **7** and **8** are nearly identical, indicating that the anions are the same in both compounds.

**Structural Analysis.** Crystal and data collection parameters are given in Table II. Selected structural parameters are found in Table III. The coordinates of the manganese atoms were found from direct methods. The positions of the carbon, hydrogen, nitrogen, oxygen, fluorine, and sodium atoms were found from subsequent difference Fourier maps. Several cycles of least-squares refinement of positional and isotropic thermal parameters were performed. Final refinement included the variation of all positional parameters and anisotropic thermal parameters on all atoms except O1, C4, C14, C15, F4′, F5′, F6′, and the protons. The hydrogen atoms were refined with rigid-body constraints and isotropic thermal parameters fixed at approximately 1.2 times the corresponding heavy-atom thermal parameters. In the final refinement 52 reflections were omitted due to a small twin in the crystal. These reflections had double peaks, and their observed structure factors were significantly greater than the calculated structure factors. The criteria used for eliminating reflections is as follows: (1) reflections for which the observed structure factor was significantly greater than the calculated structure factor were chosen; (2) these reflections were checked for double peaks by looking at the peak scans from the data collection; (3) deflections exhibiting double peaks were reported. This procedure was repeated after several least-squares refinements until no more reflections meeting step 1 could be found. This method is not complete, but it is hoped that in eliminating the reflections with the largest violations between observed and calculated structure factors a better model of the true structure may be obtained. Final values of $R = 0.084$ and $R_w = 0.0927$ were obtained for all reflections with $F \geq 3\sigma$ and $2\theta \leq 45°$.

The crystal structure revealed eight anions per unit cell, each of which consists of two manganese atoms bridged by three tetrazole ligands. These tetrazole ligands are of the $\eta^2$ type, with the two nitrogens opposite the carbon atom taking part in bonding (Figure 2). The octahedral geometry about each manganese atom is completed by three carbonyl ligands, resulting in trans angles of 178.7 (3), 178.3 (3), and 178.4 (3)°. The Mn–N bond lengths average 2.05 Å while the Mn–C distances average 1.81 Å. The bridging tetrazoles each contain a trifluoromethyl group bonded to the carbon atom of the tetrazole. The trifluoromethyl groups are all disordered; one $CF_3$ group in each anion sits on a 2-fold axis and must be disordered to accommodate this symmetry, while the other two $CF_3$ groups are disordered due to thermal motion.

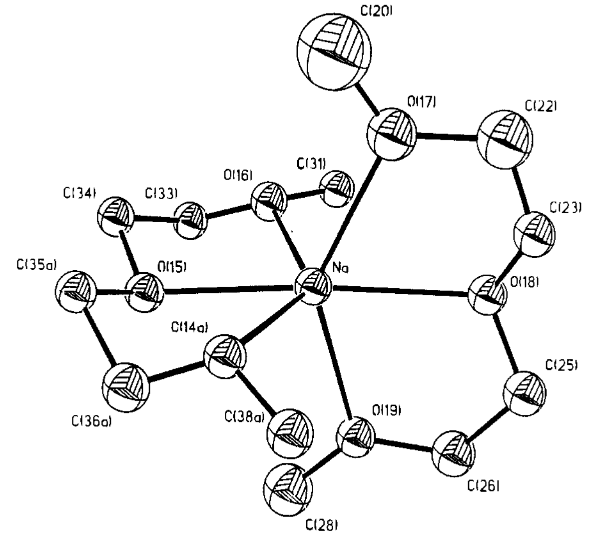

**Figure 3.** Structure of the $[Na(digly)_2]^+$ cation. ORTEP thermal ellipsoids represent 50% probability surfaces. Hydrogen atoms are omitted for clarity.

The $CF_3$ setting on the 2-fold axis has each set of disordered fluorine atoms assigned to a site occupany factor of $^1/_2$. The disorder in the other two $CF_3$ groups, which are related by a 2-fold operation, is taken into account by assigning the site occupancy to a free variable. This leads to a site occupany factor of 0.85 for F4, F5, and F6 and a site occupancy factor of 0.15 for F4′, F5′, and F6′. Since the primed and unprimed fluorines are crystalographically inequivalent, they were assigned independent thermal parameters. All $CF_3$ groups were loosely constrained to tetrahedral geometry. Each anion is charge balanced by a sodium atom coordinated to two diglyme molecules with a Na–O bond distance averaging 2.35 Å (Figure 3).

In conclusion, we have demonstrated that, with the (trifluoromethyl)tetrazolate anion, both $\pi$ complexes and normal addition complexes are found with Mn and that these two forms are readily interconverted. Furthermore, the $\pi$ electrons in the tetrazole rings of $[(CF_3\overline{CNNNN})_3Mn_2(CO)_6]MnCO_3$ are delocalized over the ring, as evidenced by the approximately equal bond lengths observed for C$\overset{\cdots}{-}$N (1.33 Å) and N$\overset{\cdots}{-}$N (1.34 Å). This is in contrast to the previously reported results for Cu[7] and Ag[8] complexes, where the $\pi$ electron density is localized in the N-2$\overset{\cdots}{-}$N-3 (1.12 Å) bond of the tetrazole ring.

## Experimental Section

**Materials.** Reagents were purchased as indicated: $Mn(CO)_5Br$ (Strem) and $CF_3CN$ (PCR, Inc.). (Difluoroamino)difluoroacetonitrile was prepared by a literature method.[2a]

**General Procedures.** Perkin-Elmer 599 B, Perkin-Elmer 1710 FT, and Digilab Qualimatic FT infrared spectrometers and a JEOL FX90Q FT nuclear magnetic resonance spectrometer were used for IR and NMR studies. Gases and volatile liquids were handled in a Pyrex vacuum apparatus equipped with Heise Bourdon tube and Televac thermocouple pressure gauges. Elemental analyses were performed by Beller Mikroanalytisches Laboratorium, Göttingen, FRG. The X-ray diffraction data on a colorless thin plate of dimensions 0.42 × 0.31 × 0.23 mm mounted on a thin glass fiber were collected on a fully automated Nicolet R3m/e diffractometer,[23] with graphite monochromator and Mo K$\alpha$ radiation ($\lambda = 0.71069$ Å) source. The orientation matrix and lattice parameters of this monoclinic crystal were optimized from the least-squares refinement to the angular settings of 25 carefully centered reflections with high Bragg angles. The SHELXTL 5.1 software package was used for the data reduction and refinement.[24] Details of the data collection are given in Table II. Final positional parameters for **8** are given in Table III.

**Synthesis of Sodium 5-((Difluoroamino)difluoromethyl)tetrazolate and Sodium 5-(Trifluoromethyl)tetrazolate.** To a suspension of sodium azide

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[23] Campana, C. F.; Shepard, D. F.; Litchman, W. M. *Inorg. Chem.* **1981**, *20*, 4039.

[24] Sheldrick, G. "SHELXTL"; Nicolet Analytical Instruments: Madison, WI, 1984.

(~7 mmol) in dry acetonitrile (20 mL) at −196 °C in a thick-walled tube was added (difluoroamino)difluoroacetonitrile (12 mmol) or trifluoroacetonitrile (12 mmol) under vacuum. The reaction mixture was warmed slowly to 25 °C and then heated at 65 °C with constant stirring until the mixture became a clear solution. While still hot, the solution was filtered under a dry atmosphere. After evaporation of $CH_3CN$, the respective tetrazolate salt remained in essentially quantitative yield. Further purification was realized by recrystallization from $CH_3CN$. Spectral data for $Na^+NF_2CF_2CNNNN^-$ (**2**): IR (KBr disk) 3620 w, 1618 m, br, 1492 s, 1420 w, 1230 vs, 1192 vs, 1170 vs, 1115 s, 1050 s, 960 s, 948 s, 920 s, 800 m, 765 w, 672 w, 633 m $cm^{-1}$; $^{19}F$ NMR, $\phi$ 19.81 ($NF_2$), −100.3 ($CF_2$). Anal. Calcd for $C_2F_4N_5Na$: Na, 11.91; N, 36.27. Found: Na, 11.17; N, 36.36.

**Synthesis of 4 and 6.** Sodium 5-((difluoroamino)difluoromethyl)tetrazolate (2 mmol) and manganese pentacarbonyl bromide (2 mmol) were dissolved in THF (5 mL) to form a clear solution that was heated at 40 °C for 36 h. Sodium bromide was removed by filtration and the solvent by evaporation to give the desired compound. Further purification resulted from paper chromatography under dry $N_2$; yield 56%. Spectral data for **6**: IR (KBr disk, Digilab FT), 3400 ($H_2O$), 2055 s, 1954 vs, 1949 vs, 1690 br, 1500 m, 1460 w, 1400 br, 1250 m, 1200 s, 1180 vs, 1110 m, 1070 m, 1035 m, 1025 m, 990 w, 950 m, 930 m, 920 s, 870 w, 850 w, 705 w, 620 w, 590 m $cm^{-1}$. Spectral data for **4** ($CH_2Cl_2$, Perkin-Elmer FT), 3055 w, 2989 w, 2056 vs, 1967 vs, 1658 br, 1638 br, 1495 m, 1461 w, 1439 w, 1423 w, 1385 w, 1266 vs, 1245 m, 1202 s, 1181 s, 1108 w, 1066 w, 1037 w, 972 vw, 950 w, 919 w, 898 w, 848 w, 794 vw, 741 vs, 706 s, 681 vw, 632 vw $cm^{-1}$; $^{19}F$ NMR (THF), $\phi$ 109.6 ($CF_2$), 16.4 ($NF_2$). Anal. Calcd for $C_5F_4MnN_5O_3$: C, 19.42; Mn, 17.77; N, 22.66. Found: C, 19.63; Mn, 17.70; N, 22.75.

**Synthesis of 5, 7, and 8.** Sodium 5-(trifluoromethyl)tetrazolate (2.2 mmol) and manganese pentacarbonyl bromide (2.2 mmol) were dissolved in THF (5 mL) to give a clear solution, which was heated at 40 °C for 48 h under vacuum. A crude filtration was accomplished while the solution was hot. Crystals were grown in a diglyme, petroleum ether, and $CHCl_3$ mixture (1:1:1). Compound **5** (**7**) was purified by using paper chromatography. The same experiment was repeated without removing the NaBr, and crystals were grown in the same mixture of solvents. The compound obtained was $[Mn_2(CO)_6(CF_3\overline{CNNNN})_3]^-Na^+\cdot 1.5digly\cdot CHCl_3\cdot H_2O$. Anal. Calcd for $[Mn_2(CO)_6(CF_3\overline{CNNNN})_3]Na\cdot 1.5(CH_3OC_2H_4)_2O\cdot CHCl_3\cdot H_2O$: C, 25.14; H, 2.19; N, 16.00. Found: C, 25.19; H, 2.57; N, 16.05. When the latter was recrystallized from diglyme, $[(CF_3\overline{CNNNN})_3Mn_2(CO)_6]^-[Na(digly)_2]^+$ (**8**) was found. The change in solvent of crystallization depended on the concentration of NaBr and the presence of trace amounts of $H_2O$. Spectral data for **8**: IR (Nujol), 2952 vs, 2926 vs, 2854 vs, 2042 m, 1959 s, 1949 m, 1461 s, 1377 s, 1369 m, 1306 vw, 1262 m, 1245 w, 1169 m, 1150 m, 1114 m, 1061 w, 1036 w, 975 w, 973 w, 954 vw, 736 s, 480 s $cm^{-1}$; IR (diglyme) two bands for $\nu_{CO}$ at 2030 m and 1915 s $cm^{-1}$; $^{19}F$ NMR (diglyme), $\phi$ −65.21 ($CF_3$).

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**Supplementary Material Available:** Listings of atomic positional and isotropic thermal parameters for non-hydrogen atoms, all bond distances and angles, anisotropic thermal parameters for non-hydrogen atoms, and atomic positional and isotropic thermal parameters for hydrogen atoms (7 pages); a listing of observed and calculated structure factors (32 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry and Biochemistry,
Utah State University, Logan, Utah 84322-0300

# Synthesis and Characterization of Cyanoborane Adducts of Dialkyl ((Dialkylamino)methyl)phosphonates

M. P. Kaushik, M. R. M. D. Charandabi, M. L. Ettel, T. J. Lofthouse, and K. W. Morse*

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Cyanoborane adducts of dialkyl ((dialkylamino)methyl)phosphonates were prepared from dialkyl ((dialkylamino)methyl)phosphonates and macrocyclic cyanoborane oligomers,[6] by the reaction of the hydrochloride salts of dialkyl ((dialkylamino)methyl)phosphonates with sodium cyanotrihydroborate and by a base displacement reaction. The products have been characterized by spectroscopy and elemental analysis. Comparison of the methods shows that the reaction with the cyanoborane oligomer is the method of choice due to the absence of decomposition products and ease of purification.

The synthesis and biological importance of an extensive series of amine–$BH_2R$ (R = CN, COOH, COOR′, C(O)NHR′) adducts have recently been reported.[1-4] The isoelectronic and isostructural relationship of the amine–carboxyboranes with the dipolar form of the corresponding amino acid (e.g., $(CH_3)_3NBH_2CO_2H$ and betaine, $(CH_3)_3N^+CH_2COO^-$) was pointed out. The syntheses of cyanoborane adducts of dialkyl ((dialkylamino)methyl)phosphonates were pursued with the goal of comparing their chemical and biological activity with that of amine–cyanoboranes. The inclusion of the phosphorus moiety will allow examination for the first time of the effect on biological activity of the (aminoalkyl)phosphonate moiety in cyanoborane compounds. In this paper we report the synthesis and characterization of cyanoborane adducts of $(RO)_2P(O)CH_2NR'_2$ (R = Me, Et, 2-Pr, Ph; R′ = Me, Et, H).

## Experimental Section

**Materials.** All glass equipment was dried in an oven at 110 °C and assembled under a stream of dry nitrogen gas. All reactions were carried out under a $N_2$ atmosphere.

The $^1H$ NMR spectra were taken (TMS internal standard) on Varian XL-300 and JEOL FX-90Q spectrometers operating at 300 and 90 MHz, respectively. The $^{31}P$ NMR and $^{11}B$ NMR spectra were recorded on a JEOL FX-90Q instrument with the chemical shifts reported relative to 85% $H_3PO_4$ and $BF_3\cdot OEt_2$, respectively.

Infrared spectra were run as KBr disks or as neat liquids on a Perkin-Elmer 1750 FT spectrometer. Elemental analyses were preformed by M-H-W Laboratories, Phoenix, AZ 85018, and are reported in Table I. $NaBH_3CN$ (Sigma) and 1.0 M anhydrous HCl in diethyl ether (Aldrich) were used without further purification. Phosphonates were prepared by modification of the method reported by Fields.[5a] $(BH_2CN)_x$

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