The Crystal and Molecular Structure of Bis(perfluorophenyl)-tetramethyltetrazenezinc(II)

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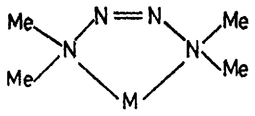
Summary A three-dimensional *X*-ray structural analysis for single crystals of bis(perfluorophenyl)tetramethyltetrazenezinc(II) reveals several features of the solid-state structure of this molecule; the zinc atom is tetrahedrally bonded to a single carbon atom of each perfluorophenyl ligand and to two nitrogen atoms of the tetramethyltetrazene ligand and the 4-atom tetrazene group exists in the *trans* isomeric form and is 1,3-bonded to the zinc atom.

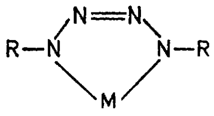
A NUMBER of complexes of tetramethyl-2-tetrazene (TMT) with various metals have been reported, particularly with cadmium and mercury(II) halides,[1] aluminium alkyls,[2] beryllium alkyls,[3] and ZnX_2[4] (X = Cl, Br, Bu^n, Ph, and C_6F_5). The structures of all these complexes were believed to contain tetrazenes in the *cis* isomeric form which were 1,4-bonded to the metal as in (**1**) (inconclusive i.r. and n.m.r. evidence and analogy with ethylenediamine complexes).

cis-Disubstituted tetrazenes which are 1,4-bonded to a metal, as in (**2**), have been crystallographically documented for *cis*-1,4-dimethyltetrazenetricarbonyliron(II)[5] (**3**) and the *cis*-1,4-di-*p*-fluorophenyltetrazenecarbonylbis-(triphenylphosphine)iridium(I) cation (**4**).[6]

Recently[7] we reported reactions of the TMT–$ZnCl_2$ complex and attempted to rationalize these in terms of structure (**1**), but the structural data on *NN'*-azomorpholine (**5**)[8] and the cyclic ditetrazene, 1,4,7,10-tetramethyl-1,2,3,4,-

7,8,9,10-octa-azacyclododeca-2,8-diene (**6**),[9] indicated that tetra-alkyl-2-tetrazenes prefer the *trans* configuration.


(1)


(2)

The tetra-alkyltetrazene configuration in metal complexes has now been investigated by determining the solid-state structure of the TMT-bis(perfluorophenyl)zinc complex by single crystal X-ray diffractometry. *Crystal data:* bis-(perfluorophenyl)tetramethyltetrazenezinc(II), $(C_6F_5)_2Zn(N_4Me_4)$, (**7**), orthorhombic, space group $P2_12_12_1$ (D_2^4, 19), a = 7·098(1) Å, b = 15·926(2) Å, c = 17·924(3) Å, Z = 4. Data collected using Nb-filtered Mo-K_α radiation and θ—2θ scans on a Syntex $P\bar{1}$ autodiffractometer gave 1239 independent reflections having 2θ(Mo-K_α) <43° and $I > \sigma(I)$. The structure was solved using standard heavy-atom and difference Fourier techniques. Unit-weighted full-matrix least-squares refinement of the positional and anisotropic thermal parameters for the 31 crystallographically independent non-hydrogen atoms has resulted in a conventional unweighted residual, R, of 0·070.

The analysis shows that the crystal contains discrete monomeric molecules in which the zinc atom, as anticipated, is tetrahedrally bonded to single carbon atoms of both perfluorophenyl groups and to two nitrogen atoms of the TMT ligand. As shown in the Figure, however, the 4-atom tetrazene group in $(C_6F_5)_2Zn$(TMT), unlike the N_4 systems in (**3**) and (**4**), exists in the *trans* isomeric form and bonds to the metal atom through the first and third nitrogen atoms of the group. The molecule possesses approximate $C_{s\text{-}m}$ symmetry, the Zn atom and the four nitrogen atoms being coplanar to within 0·03 Å and comprising the pseudo-mirror plane. The Zn atom is essentially coplanar with both 11-atom C_6F_5 rings inclined at 65° to the pseudo-mirror plane. Lengths of 2·13(2) Å, 2·25(2) Å, and 1·91-(2,0,0) Å† were determined for the Zn—N(1), Zn–N(3), and average Zn–C bonds, respectively. Values of 1·46(3) Å, 1·27(3) Å, and 1·35(3) Å were found for the N(1)–N(2), N(2)–N(3) and N(3)–N(4) bond lengths. Corresponding values of 1·251(2) Å and 1·253(2,1,1) Å for the middle [N(2)–N(3)] and 1·393(1) Å and 1·385(2,4,7) Å for the terminal [N(1)–N(2) and N(3)–N(4)] bonds were found in the uncomplexed tetrazenes of (**5**) and (**6**) respectively. Complexing of the tetrazene to the Zn atom is probably responsible for the closing of the N(1)–N(2)–N(3) angle of 105(1)° relative to the 115(1)° N(2)–N(3)–N(4) angle in (**7**) and the average 113·0(2,2,4)° N–N–N angles in (**5**) and (**6**). Refinement of (**7**) is continuing with a data set three times as large.

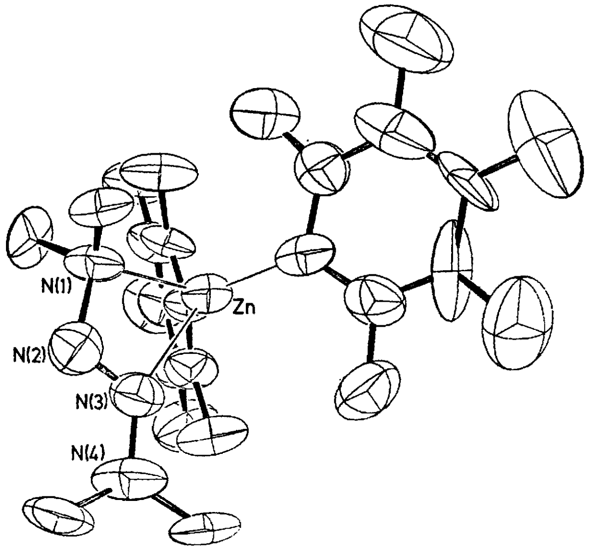


FIGURE. A perspective ORTEP drawing showing the solid-state molecular structure of bis(perfluorophenyl)tetramethyltetrazenezinc(II). All atoms are represented by thermal vibration ellipsoids which encompass 50% of their electron density.

The other complexes reported[1–4] between metal ions and TMT, probably have structures similar to (**7**) in the solid state. The structure of (**7**) in solution is however, much less clear. The n.m.r. spectrum of the substance in [$^2H_8$]-toluene shows only a sharp singlet for the tetrazene methyl protons when the temperature is varied from ambient to −95°. The methyl resonance of the complex dissolved in [$^2H_8$]-toluene is shifted upfield by 0·29 p.p.m. from that of 'free' TMT (2·72 p.p.m.). Addition of excess TMT, however, brings the methyl resonance down to the uncomplexed value. These data are consistent with the assumption of rapid ligand exchange in solution, according to equation (1).

$$\text{TMT} + \text{TMT–ZnAr}_2 \rightleftharpoons \text{TMT–ZnAr}_2 + \text{TMT} \qquad (1)$$

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† The first number in parentheses following a given bond length or angle is the r.m.s. estimated standard deviation of an individual datum. The second and third numbers, when included, are the average and maximum deviations from the average value, respectively.

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