# Crystal Structure of the Cyclopentadienyl Sodium Tetramethylethylenediamine Adduct $Na(C_5H_5)(Me_2NCH_2CH_2NMe_2)$

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*Summary* The adduct $Na(C_5H_5)(Me_2NCH_2CH_2NMe_2)$, prepared from $Na(C_5H_5)$ and an equimolar proportion (or excess) of $Me_2NCH_2CH_2NMe_2$ in THF, adopts a puckered chain structure in the crystal in which $Na(Me_2NCH_2CH_2NMe_2)$ units are linked by bridging $h^5$-$C_5H_5$ rings.

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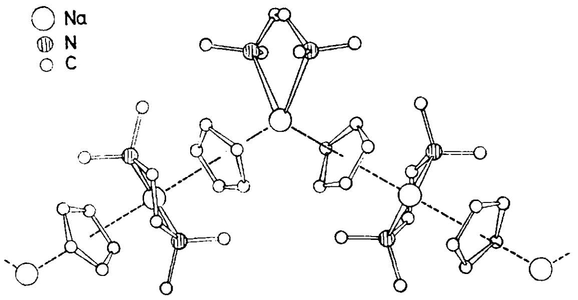
WHEREAS some areas of alkali metal chemistry, *e.g.* organolithium compounds,[1,2] and alkali metal complexes of cyclic polyethers,[3] have been the subject of much recent structural work, organosodium compounds have been comparatively neglected. We here report what is believed to be the first single crystal *X*-ray study of an organosodium compound, the cyclopentadienylsodiumtetramethylethylenediamine complex, $NaC_5H_5(Me_2NCH_2CH_2NMe_2)$ (NaCpTMED; I). Previous *X*-ray studies on organosodium compounds have been confined to powder work on NaMe,[4] $NaC{\vdots}CH$,[5] $NaC{\vdots}CMe$,[5] and NaEt,[6] though various 'ate' complexes such as $NaInMe_4$,[7] $NaCrPh_54Et_2O$,[8] and $NaInPh_4$,[9] in which the main metal–carbon interactions do not involve sodium, have been the subjects of single crystal work.

Compound (I) was prepared from equimolar proportions of NaCp and TMED in tetrahydrofuran, and recrystallised from hot benzene as chunky colourless platelets which decompose immediately, turning brown and then black, on exposure to air. It is of too low solubility in cold benzene to allow cryoscopic determination of M, and decomposes slowly in boiling benzene, depositing NaCp. Compound (I), and not the expected NaCp,2TMED, was also obtained from NaCp–TMED systems containing an excess of TMED. Characteristic absorptions in its i.r. spectrum (Nujol mull, $\nu_{C-H}$, 3060 m; $\delta_{C-H}$, 1005 s; $\gamma_{C-H}$, 720 vs $cm^{-1}$) and the singlet absorption due to its cyclopentadienyl protons at 4·27 $\tau$ in the $^1H$ n.m.r. spectrum (THF solution, 60 MHz) indicate[10] the pentahapto, predominantly ionic, interaction between the Cp groups and metal atoms established by the *X*-ray crystallographic study.

The crystals of (I) are orthorhombic, with $a = 15{\cdot}961$, $b = 8{\cdot}949$, $c = 18{\cdot}408$ Å, space group *Pcca*, with 8 formula units in the unit cell. The intensity data were collected on a Hilger and Watts four-circle diffractometer, using Zrfiltered Mo radiation, to a limit of $\theta = 20^\circ$. The structure was solved by the symbolic addition method, and refined by least squares methods. At the present stage of refinement, $R = 0{\cdot}102$ for the 771 reflections with net counts $\geqslant \sigma$.



The structure (Figure) consists of puckered chains of sodium atoms, each with a chelating TMED molecule attached, linked by pentahapto cyclopentadienyl rings. The sodium atoms occupy two crystallographically independent sets of sites on 2-fold axes which are alternately in the plane and perpendicular to the plane of the Figure. Each metal atom is surrounded by a distorted tetrahedral arrangement of two $Me_2N$ groups and two $h^5$-Cp rings, the latter inclined at 88° to, and bisecting, the Na–Na axes, which are displaced 0·11 Å from the ring centres. This slippage from the ideal $h^5$ geometry may be attributed to nonbonded repulsions between adjacent Cp rings.

The –MCpMCpMCp– chain structure resembles those of $PbCp_2$,[11] InCp,[12] and TlCp.[12] The degree to which the chain is puckered (the Na–Na–Na angles are 128 and 119°) reflects the distorted tetrahedral co-ordination of the metal atoms (in $PbCp_2$, the Pb–Pb–Pb angles are 118 and 121°,[11] while in InCp, the In–In–In angle is 137°[12]). The chelating TMED groups have N–N distances of 3·08 Å and 3·05 Å, and both subtend an N–Na–N angle at the metal of only 72°, underlining the importance of the size of the metal atom in determining whether TMED chelates (as in this case) or bridges (as in the potassium fluorenyl complex $KC_{13}H_9$-[TMED][2]).

This structure is consistent with an ionic model of the bonding in terms of $Na(TMED)^+$ cations and $C_5H_5^-$ anions, although the metal–carbon distances [average 2·92(1) Å] are short enough to allow a degree of covalency similar to that in the cyclopentadienyl–Grignard complex $Mg(C_5H_5)Br$-$(Et_2NCH_2CH_2NEt_2)$,[13] for which Mg–C is 2·55 Å and Mg–N 2·26 Å, difference 0·29 Å [*cf.* Na–C, 2·92(1) Å, Na–N, 2·62(1) Å, difference 0·30 Å, for (I)]. The failure of (I) to take up a second TMED molecule, forming $Na(TMED)_2^+$ $C_5H_5^-$, indicates the strength of the metal–ring bonding.

A further pointer to the anionic character of the cyclopentadienyl rings of (I) is the ring C–C distance of 1·38(1) Å (average), shorter than is usual for metal cyclopentadienides, *cf.* 1·425 Å for various beryllium compounds BeCpX,[14] 1·43 Å for $FeCp_2$[15] and $NiCp_2$,[16] and 1·42 Å for $MgCp_2$[17] (all by electron diffraction studies on gas-phase molecules).

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