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# STRUCTURE OF THE TRIPHENYLCYANOBORONATE OF A BIS-DIMETHYLAMINOMETHYL[1,1-DIMERCURIO]FERROCENOPHANE DICATION

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## Summary

The X-ray structure of the salt $[(CH_3)_2NCH_2FcHg]_2^{2+}$ $(Ph_3BCN^-)_2$ was determined. The structures of both its cation and the corresponding neutral molecule are compared and discussed.

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## Introduction

Earlier we prepared a bis-dimethylaminomethyl derivative of [1,1-dimercurio]ferrocenophane (I) and determined its X-ray crystal structure [1]. Careful oxidation of this compound led to thermally unstable mono- and dicationic species. It was shown that a "phane" structure of the neutral compound, including C–Hg bonds, was retained on oxidation and that the dimethylaminomethyl groups were also intact. The electron absorption and Mössbauer spectra showed that there was no abnormality in the oxidation state of the iron atoms.

The spectral characteristics of the compounds studied are quite typical of ferrocene/ferrocenium species, no "mixed valence phenomena" being observed [2].

In our X-ray study of the structure of the more stable dicationic derivative (II), we were particularly concerned with elucidating the secondary non-valent interactions in the dication and its specific conformational effects.

## Experimental

Crystals of II $(C_{32}H_{30}BN_2HgFe)_2$ are monoclinic, at $-120\,^\circ C$ $a$ 9.788(3), $b$ 10.316(3), $c$ 27.040(2) Å, $\beta$ 98.29(3)°, $V$ 2702(2) Å$^3$, $d_{calc}$ 1.75 g cm$^{-3}$, $Z = 2$, space group $P2_1/c$.

The unit cell parameters and intensities of 3262 independent reflections with $I > 2\sigma(I)$ were measured with an automatic Syntex P2$_1$ four-circle diffractometer at $-120\,^\circ C$ ($\lambda$Mo-$K_\alpha$, graphite monochromator, $\theta/2\theta$ scan, $2\theta_{max}$ 52°). Absorption

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corrections were applied taking into account the real form of the crystal ($\mu$(Mo-$K_\alpha$) 63.68 cm$^{-1}$) according to [3].

The structure was solved by the heavy-atom method and refined by the least-squares technique first in full-matrix isotropic and then in anisotropic approximation, resulting in $R = 0.057$ ($R_w = 0.069$) based on 3107 reflections with $F > 3\sigma$. Localization of the hydrogen atoms was not attempted. All calculations were carried out with an Eclipse S/200 computer using INEXTL programs [4]. The atomic coordinates and isotropic equivalent thermal parameters are listed in Table 1.

TABLE 1

ATOMIC COORDINATES ($\times 10^4$; for Hg and Fe $\times 10^5$) AND THEIR THERMAL PARAMETERS $B_{iso}^{eq} = 1/3 \sum_i \sum_j B_{ij} a_i^{\star} a_j^{\star} (\vec{a}_i \vec{a}_j)$ (Å$^2$) FOR DICATION II

| Atom | $x$ | $y$ | $z$ | $B_{iso}^{eq}$ |
|---|---|---|---|---|
| Hg | 14611(5) | 9728(6) | 2224(2) | 1.67(1) |
| Fe | 21513(19) | −2185(21) | −2949(8) | 1.40(5) |
| N(1) | 958(12) | 510(12) | 1213(5) | 1.9(3) |
| N(2) | 2372(11) | 2250(13) | 4403(5) | 2.1(4) |
| B | 3502(16) | 1551(17) | 3546(6) | 1.4(4) |
| C(1) | 65(13) | 2361(14) | 386(6) | 1.8(4) |
| C(2) | −411(14) | 2431(15) | 860(6) | 2.0(4) |
| C(3) | −1354(15) | 3516(16) | 848(6) | 2.1(4) |
| C(4) | −1498(14) | 4086(16) | 352(6) | 2.2(4) |
| C(5) | −611(13) | 3349(13) | 62(6) | 1.8(4) |
| C(6) | 2838(13) | −407(13) | 54(6) | 1.3(4) |
| C(7) | 3307(13) | −473(15) | −424(6) | 1.9(4) |
| C(8) | 4132(14) | −1672(15) | −430(7) | 2.3(5) |
| C(9) | 4162(14) | −2302(15) | 56(6) | 2.2(4) |
| C(10) | 3394(14) | −1538(16) | 361(7) | 2.5(4) |
| C(11) | 154(17) | 1705(17) | 1317(7) | 2.8(5) |
| C(12) | 2143(17) | 402(21) | 1605(7) | 4.0(6) |
| C(13) | 101(17) | −664(18) | 1165(7) | 3.2(5) |
| C(14) | 5036(13) | 940(16) | 3751(5) | 1.6(4) |
| C(15) | 6228(13) | 1432(16) | 3563(6) | 1.9(4) |
| C(16) | 7527(15) | 839(17) | 3729(6) | 2.5(4) |
| C(17) | 7672(15) | −153(17) | 4069(7) | 2.7(5) |
| C(18) | 6500(16) | −619(15) | 4258(7) | 2 5(5) |
| C(19) | 5195(15) | −59(16) | 4097(6) | 2.2(4) |
| C(20) | 2470(14) | 490(15) | 3250(6) | 1.6(4) |
| C(21) | 2907(15) | −682(14) | 3055(6) | 1.7(4) |
| C(22) | 2003(15) | −1562(16) | 2790(6) | 2.2(4) |
| C(23) | 592(16) | −1283(16) | 2701(6) | 2.5(5) |
| C(24) | 115(15) | −125(17) | 2870(7) | 2.5(5) |
| C(25) | 1037(14) | 731(15) | 314(6) | 1.8(4) |
| C(26) | 3627(11) | 2877(14) | 3217(5) | 1.3(4) |
| C(27) | 3367(13) | 2850(15) | 2697(6) | 1.7(4) |
| C(28) | 3588(14) | 3948(17) | 2411(6) | 2.2(4) |
| C(29) | 3996(14) | 5103(16) | 2643(6) | 2.2(4) |
| C(30) | 4246(14) | 5164(16) | 3162(7) | 2.4(5) |
| C(31) | 4073(14) | 4037(17) | 3448(6) | 2.1(4) |
| C(32) | 2834(13) | 1951(15) | 4051(6) | 1.5(4) |

## Results and discussion

Crystals of II are built up of $(Me_2NCH_2FcHg)_2^{2+}$ dications in the inversion centres and of $Ph_3BCN^-$ anions in the general positions. The structures of the dication and anion with bond distances (and bond angles in the anion) are shown in Figs. 1 and 2, respectively. The values of the bond angles in the dication are listed in Table 2.

The dication is a centrosymmetric 4-nuclear complex, the dimethylaminomethylferrocene residues being linked by two mercury bridges. The distances Hg–C(1), 2.06(1), and Hg–C(6), 2.07(1) Å, coincide with the corresponding values in the neutral molecule I, 2.041(7)–2.065(7) Å, and are typical of organic derivatives of mercury [5]. The bond angle C(1)HgC(6) is equal to 179.5(6)° and is, in fact, almost identical to the ideal value of 180° in organic derivatives of mercury.

The distance between the nitrogen atom of the dimethylaminomethyl group and the mercury atom bonded to the same cyclopentadienyl ring corresponds to the secondary Hg ··· N bonding, and is equal to 2.83(1) Å. It is significantly shorter than the corresponding distance in I, viz. 2.922(6) and 3.049(6) Å in two crystallographically independent molecules of I. The Hg ··· N distance in II (2.83(1) Å) is also less than the sum of the Van der Waals radii of Hg, 1.5–1.6 Å [5–8], and N, 1.55 Å [9], which is equal to 3.05–3.15 Å. The chelate cycle HgC(1)C(2)C(11)N, although not ideally planar, is, however, significantly more planar than that in I. The torsion angle C(1)C(2)C(11)N(1) is equal to −20.7° and in two independent

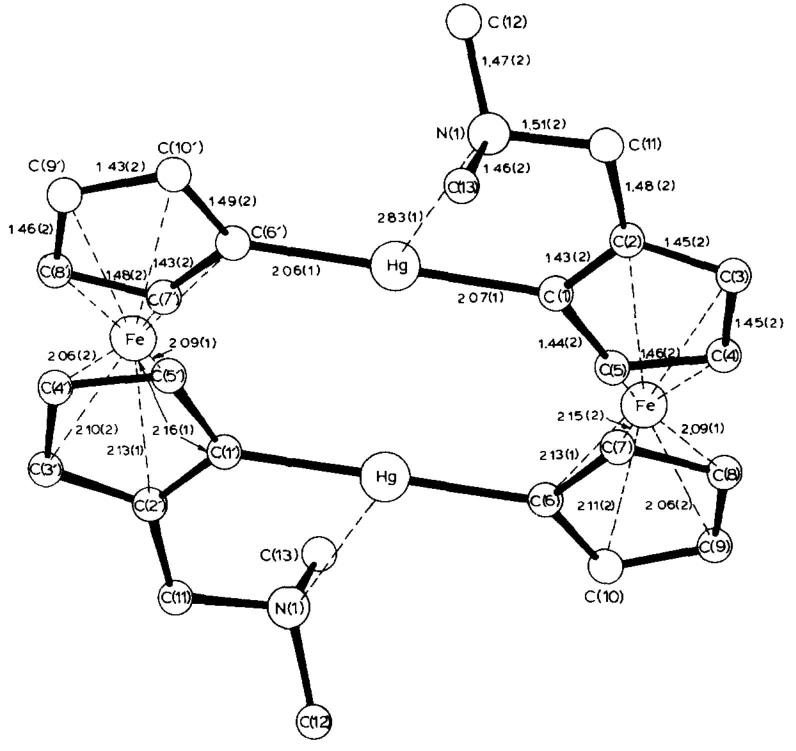

Fig. 1. Structure of the dication $(Me_2NCH_2FcHg)_2^{2+}$ showing the bond distances.

molecules of I it is twice this value, being 45.2(5) and 55.4(5)°. The bond angles HgN(1)C(11,12,13) are equal to 102, 118 and 103°, respectively, and thus the lone electron pair of the N atom is directed towards the Hg atom.

In crystals of 1-chloromercurio-2-dimethylaminomethylferrocene (III), shortening of the Hg ··· N distance, which in this case is intermolecular, is even more pronounced, being 2.772(5) Å, and the molecules form dimers due to the Hg ··· N interaction.

On the basis of the structural data of complexes of phenanthroline with organomercury compounds, it was shown previously that electron accepting groups linked with mercury by covalent bonds significantly affect the energy of secondary Hg ··· N bonding [1]. The same trend is evident in the I–II–III series. The replacement of the electron-donating ferrocenyl in I by electron-accepting Cl in III results in shortening of the Hg ··· N distance, corresponding to a secondary interaction from 2.922 and 3.049 Å in I to 2.772 Å in III. The Hg ··· N distance in II (2.83 Å) is shorter than the corresponding distance in I, but longer than that found in III. Thus, ferrocenium ion is not as strong an electron acceptor as Cl, and delocalization of a positive charge of the ferrocenium moiety does not involve the mercury atom to a considerable degree.

The average C–C distances in the ferrocenyl moieties are 1.45(2) and 1.46(2) Å for di- and monosubstituted Cp rings, respectively. The average Fe–C distance, 2.11(1) Å, and the distance Fe–centroid of the Cp ring is 1.71(1) Å. In molecules I and III, the corresponding values are 2.053 and 1.66 Å and 2.049 and 1.65 Å, i.e. slightly less than those found in II. According to structural studies [10–14], this feature is typical of ferrocenium salts.

The Fe atom is situated almost precisely on the line connecting the centroids of the Cp rings, the angle Cp-centroid–Fe–Cp-centroid being 177.7°. The cyclopentadienyl rings in the ferrocenyl moiety are in an eclipsed conformation, but they are slightly non-parallel, the angle between their planes being 7.38°. This may be due to

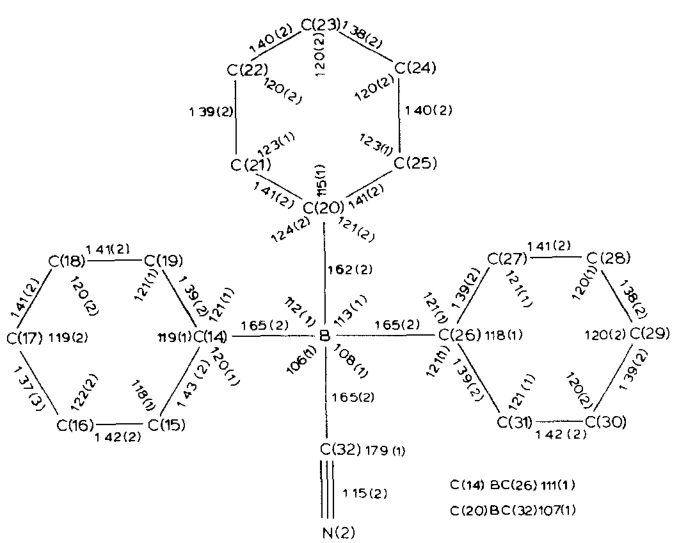

Fig. 2. Structure of the anion $Ph_3BCN^-$ showing the the bond distances and bond angles.

TABLE 2

BOND ANGLES ω (deg.) IN DICATION II

| Angle | ω | Angle | ω |
|---|---|---|---|
| C(1)HgC(6) | 179.5(6) | HgC(6)C(10) | 128(1) |
| N(1)HgC(1) | 72.9(9) | C(10)C(6)C(7) | 109(1) |
| N(1)HgC(6) | 107.6(9) | C(6)C(7)C(8) | 107(1) |
| HgC(1)C(2) | 123(1) | C(7)C(8)C(9) | 108(1) |
| HgC(1)C(5) | 128(1) | C(8)C(9)C(10) | 109(1) |
| C(5)C(1)C(2) | 109(1) | C(9)C(10)C(6) | 107(1) |
| C(1)C(2)C(3) | 108(1) | C(2)C(11)N(1) | 114(1) |
| C(1)C(2)C(11) | 126(1) | C(11)N(1)C(12) | 108(1) |
| C(3)C(2)C(11) | 125(1) | C(11)N(1)C(13) | 112(1) |
| C(2)C(3)C(4) | 108(1) | C(12)N(1)C(13) | 113(1) |
| C(3)C(4)C(5) | 107(1) | HgN(1)C(11) | 102(1) |
| C(4)C(5)C(1) | 107(1) | HgN(1)C(12) | 118(1) |
| HgC(6)C(7) | 123(1) | HgN(1)C(13) | 103(1) |

the general rigidity of the structure of cyclic "phane" cation, which also results in distortion of the exocyclic bond angles at C(1) (123(1) and 128(1)°) and C(6) (128(2) and 123(1)°). A similar angular deformation is also found in the "phane" molecule I but is absent in molecule III.

The boron atom of the anion has a distorted tetrahedral coordination, the range of C–B–C angles being 106(1)–113(1)°. The angles involving the carbon atom of the CN group are regularly smaller (106(1), 107(1), 108(1)) than the angles C(Ph)–B–C(Ph) (112(1), 111(1), 113(1)°), which is mostly due to steric interactions. Within the experimental accuracy, the B–C(Ph) and B–C(CN) bond lengths are equal (1.62(2)–1.65(5) Å) and identical to those found in $Ph_4B^-$ anion (1.630–1.656 Å [15]).

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