Preliminary communication

Crown compounds for anions. A polymeric complex of cyclic trimeric perfluoro-*o*-phenylenemercury with thiocyanate anion containing an infinite helical chain of alternating molecules of mercury-containing macrocycle and SCN⁻ ions

I.A. Tikhonova, F.M. Dolgushin, A.I. Yanovsky, Yu.T. Struchkov, A.N. Gavrilova,
L.N. Saitkulova, E.S. Shubina, L.M. Epstein, G.G. Furin, V.B. Shur *

A.N. Nesmeyanov Institute of Organoelement Compounds of the Russian Academy of Sciences, Vavilov St. 28, Moscow 117813, Russia

Abstract

It has been shown by IR spectroscopy that cyclic trimeric perfluoro-*o*-phenylenemercury $(o\text{-}C_6F_4Hg)_3$ is capable of binding thiocyanate anions in acetone solution, forming complexes whose composition is dependent on the ratio of reagents. In the interaction of $(o\text{-}C_6F_4Hg)_3$ with an equimolar amount of $[^nBu_4N]^+SCN^-$ in ethanol the complex formulated as $[(o\text{-}C_6F_4Hg)_3(SCN)]^-[^nBu_4N]^+$ has been isolated. An X-ray diffraction study of the complex has revealed that in the solid state it is polymeric and contains an infinite helical chain of alternating $(o\text{-}C_6F_4Hg)_3$ molecules and thiocyanate anions. Every SCN^- ion in the complex is bonded to the mercury atoms of two neighbouring molecules of the macrocycle through the sulphur atom and forms with each of these molecules two relatively short $Hg \cdots S$ bonds and one considerably longer $Hg \cdots S$ bond.

Keywords: Mercury; Crown compounds; Macrocycle

As part of our continuing studies [1] of anion binding and catalytic properties of cyclic multidentate Lewis acids we have recently described [1b] the unusual complexes of bromide and iodide anions with cyclic trimeric perfluoro-*o*-phenylenemercury $(o\text{-}C_6F_4Hg)_3$ (I)

(I)
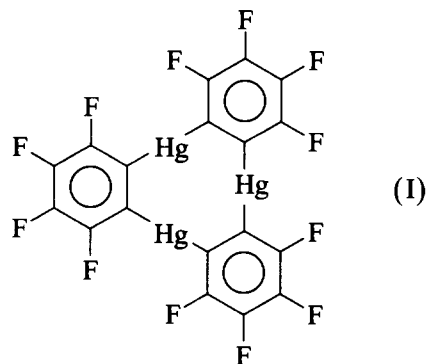
which contains three Hg atoms in a planar 9-membered

cycle [2][1]. The complexes are formulated as $[(o\text{-}C_6F_4Hg)_3X]^-$ (X = Br, I) and have (in the solid state) an unprecedented structure of polydecker bent sandwiches $[(\cdots I \cdots X \cdots)_n]^{n-}$ wherein each halide anion is coordinated with six mercury atoms of two neighbouring molecules of I.

Here we report the ability of macrocycle I to bind thiocyanate anions effectively with formation of complexes whose composition is strongly dependent on the reagent ratio.

On addition of I to the excess of $[^nBu_4N]^+SCN^-$ in acetone at room temperature $(I : SCN^- = 1 : 20\text{–}2,$ $[SCN^-]_0 = 0.02$ M) the intensity of the ν_{CN} band of free thiocyanate anions (at 2056 cm⁻¹) in the IR spectrum decreases and two new ν_{CN} bands (at 2022 and 2075 cm⁻¹) appear indicating a complexation of SCN⁻ with the mercury atoms of I. On raising the I : SCN⁻

---

* Corresponding author.

[1] For other works on binding of anions by cyclic multidentate Lewis acids see, e.g. Refs. [3–6].

molar ratio to 1:1, a band of free SCN^- ions disappears whereas the intensities of ν_{CN} bands of complexed SCN^- species increase. This is accompanied by a shift of a band at 2022 cm^{-1} to 2014 cm^{-1}. The position of the other ν_{CN} band (at 2075 cm^{-1}) is virtually unaffected by raising the $I : SCN^-$ ratio. Use of excess I with respect to SCN^- ($I : SCN^- = 20–2:1$, $[SCN^-]_0 = 0.002$ M) leads to a decrease in the intensities of the 2014 and 2075 cm^{-1} bands and to the appearance of one more ν_{CN} band at 2044 cm^{-1}. These spectral changes are apparently due to the formation of complexes with different compositions in the solution.

When the reaction of I with an equimolar amount of $[^nBu_4N]^+ SCN^-$ is carried out in ethanol ($[SCN^-]_0 = 0.02$ M) at 20°C, rapid precipitation of a fine crystalline colourless complex of the composition $[(o-C_6F_4Hg)_3-(SCN)]^- [^nBu_4N]^+$ (II) occurs. The IR spectrum of acetone solution of the complex ($[II]_0 = 0.02$ M) contains the above-mentioned ν_{CN} bands at 2014 and 2075 cm^{-1} with the same intensity ratio ($\sim 1:4$). The IR spectrum of II in Nujol mull differs markedly from that in acetone and shows two ν_{CN} bands of equal intensity at 2056 and 2096 cm^{-1}. A study of the Raman spectra of the single crystal of II (2057 and 2098 cm^{-1}) in polarized light has shown that the appearance of two ν_{CN} bands in the spectra of solid complex is caused by the Davydov splitting [7], hence, the value of ~ 2077 cm^{-1} can be ascribed to the stretching vibrations of the CN bond of the thiocyanate ligand in II. The IR spectrum of $[^nBu_4N]^+ SCN^-$ in Nujol mull displays the sole ν_{CN} band at 2056 cm^{-1}, i.e. coordination of the SCN^- ion to I with formation of II increases the ν_{CN} frequency by 21 cm^{-1}. A band of ν_{SC} in the IR spectrum of II (Nujol mull) is observed at 668 cm^{-1}, which is 64 cm^{-1} lower than the corresponding ν_{SC} frequency (732 cm^{-1}) in the spectrum of solid $[^nBu_4N]^+ SCN^-$. Thus, the coordination of the SCN^- ion to I probably leads to some strengthening of the CN bond of the thiocyanate ligand and to weakening of its SC bond.

An X-ray diffraction study of II [8] has shown that in the solid state the complex is polymeric $\{[(o-C_6F_4Hg)_3(SCN)]_n\}^{n-}$ and contains an infinite helical chain which is made up of alternating molecules of I and thiocyanate anions (Fig. 1). Every SCN^- ion in the complex is bonded to the mercury atoms of two neighbouring molecules of the macrocycle through the sulphur atom and forms with each of these molecules two relatively short $Hg \cdots S$ bonds (3.06(1), 3.36(1) Å and 3.19(1), 3.36(1) Å) and one considerably longer $Hg \cdots S$ bond (3.74(1) and 3.87(1) Å; the sum of the Van der Waals radii of the Hg and S atoms is 2.1 + 1.85 = 3.95 Å [10]). A pronounced asymmetry of the sulphur atom coordination with the mercury atoms in II is apparently due to the steric repulsions between the CN fragment of the coordinated SCN^- ion and the carbon and fluorine atoms of I which results in pushing
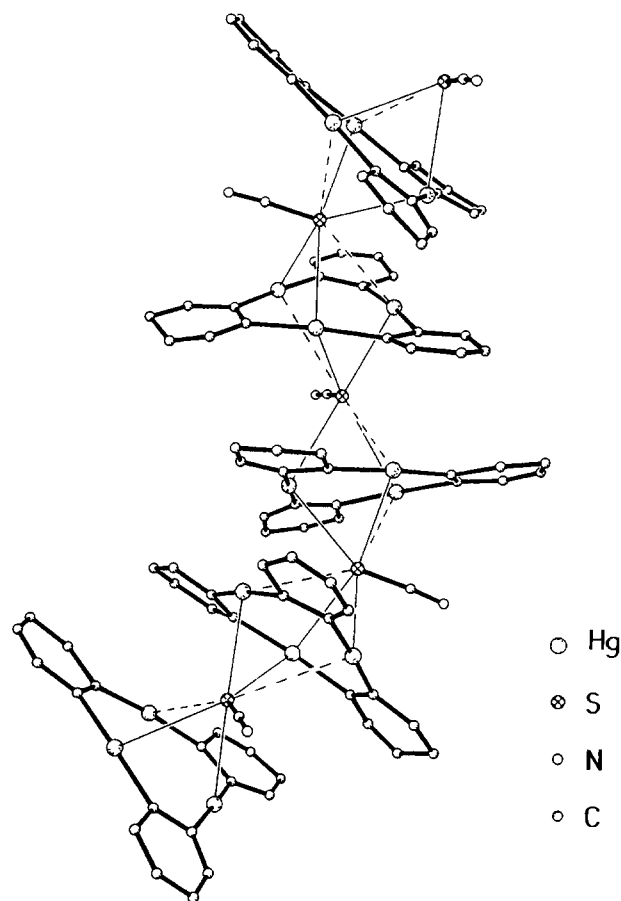

Fig. 1. The fragment of infinite polyanionic chain $\{[(o-C_6F_4Hg)_3(SCN)]_n\}^{n-}$ in the structure of II. The F atoms of phenylene rings are omitted for clarity.

the thiocyanate anion out of the space between the macrocycles. The above-mentioned complexes of I with iodide and bromide anions, which also have a polymeric structure $\{[(o-C_6F_4Hg)_3X]_n\}^{n-}$ in the solid state, are characterized by considerably more symmetrical coordination of the anionic centre with the Hg atoms.

The geometry of the thiocyanate ligand in II just as that of free SCN^- ion is close to linear (the SCN bond angle in II is 173(4)°). Unfortunately, the limited accuracy of the X-ray experiment would not allow judgement on the influence of the complexation of SCN^- with I on the CN bond length (1.10(5) Å in II). Nevertheless, some elongation of the SC bond in II (1.74(4) Å) as compared with the corresponding value for the free SCN^- ion (e.g. 1.613 and 1.643 Å in the structures of trimethylsulfoxonium [11] and sodium [12] thiocyanates respectively) is obvious. It is consistent with the above-mentioned decrease in the ν_{SC} frequency in the IR spectra on transition from $[^nBu_4N]^+ SCN^-$ to complex II.

Molecules of I in II exhibit, as a whole, considerable deviations from planarity (up to 0.4 Å), their mercury–carbon frameworks being non-planar as well (maximum

displacements from the mean planes are as large as 0.3 Å). Only the central 9-membered rings may be considered planar, although even these rings show noticeable deviations (up to 0.1 Å) from planarity. The mean planes of the neighbouring rings in the chain are non-parallel, forming the dihedral angle of 36.9°.

The S $\cdots$ N vector in **II** is inclined by 14.6 and 22.3° to the mean planes of the central 9-membered rings of two neighbouring molecules of **I**. Two adjacent SCN$^-$ groups in the polymeric chain of **II** are related by the 4_1 symmetry operation and the S $\cdots$ N vector is almost normal to the z-axis of the unit cell. Therefore, the angle formed by the S $\cdots$ N vectors of the adjacent SCN$^-$ groups (89.7°) is close to 90°.

Acknowledgements

References and notes

[1] (a) V.B. Shur, I.A. Tikhonova, P.V. Petrovskii and M.E. Vol'pin, *Metalloorg. Khim*, 2 (1989) 1431 (*Organomet. Chem. USSR, 2* (1989) 759);

(b) V.B. Shur, I.A. Tikhonova, A.I. Yanovsky, Yu.T. Struchkov, P.V. Petrovskii, S.Yu. Panov, G.G. Furin and M.E. Vol'pin, *J. Organomet. Chem., 418* (1991) C29; *Dokl. Akad. Nauk SSSR, 321* (1991) 1002;

(c) V.B. Shur, I.A. Tikhonova, F.M. Dolgushin, A.I. Yanovsky, Yu.T. Struchkov, A.Yu. Volkonsky, E.V. Solodova, S.Yu. Panov, P.V. Petrovskii and M.E. Vol'pin, *J. Organomet. Chem., 443* (1993) C19; *Dokl. Akad. Nauk, 328* (1993) 339;

(d) A.P. Zaraisky, O.I. Kachurin, L.I. Velichko, I.A. Tikhonova, G.G. Furin, V.B. Shur and M.E. Vol'pin, *Izvest. Akad. Nauk, Ser. Khim.*, (1994) 547;

(e) A.P. Zaraisky, O.I. Kachurin, L.I. Velichko, I.A. Tikhonova, A.Yu. Volkonsky and V.B. Shur, *Izvest. Akad. Nauk, Ser. Khim.*, (1994) 2047.

[2] (a) P. Sartori and A. Golloch, *Chem. Ber., 101* (1968) 2004;

(b) M.C. Ball, D.S. Brown, A.G. Massey and D.A. Wickens, *J. Organomet. Chem., 206* (1981) 265.

[3] (a) M. Newcomb, J.H. Horner and M.T. Blanda, *J. Am. Chem. Soc., 109* (1987) 7878;

(b) M. Newcomb, A.M. Madonic, M.T. Blanda and J.K. Judice, *Organometallics, 6* (1987) 145;

(c) M. Newcomb and M.T. Blanda, *Tetrahedron Lett., 29* (1988) 4261;

(d) M. Newcomb, J.H. Horner, M.T. Blanda and P.J. Squatritt, *J. Am. Chem. Soc., 111* (1989) 6294.

[4] M.E. Jung and H. Xia, *Tetrahedron Lett., 29* (1988) 297.

[5] (a) K. Jurkschat, H.G. Kuivila, S. Lui and J.A. Zubieta, *Organometallics, 8* (1989) 2755;

(b) K. Jurkschat, A. Rühlemann and A. Tzschach, *J. Organomet. Chem., 381* (1990) C53.

[6] (a) X. Yang, C.B. Knobler and M.F. Hawthorne, *Angew. Chem., Int. Ed. Engl., 30* (1991) 1507; *J. Am. Chem. Soc., 114* (1992) 380; *J. Am. Chem. Soc., 115* (1993) 4904;

(b) X. Yang, S.E. Johnson, S.I. Khan and M.F. Hawthorne, *Angew. Chem., Int. Ed. Engl., 31* (1992) 893;

(c) X. Yang, Z. Zheng, C.B. Knobler and M.F. Hawthorne, *J. Am. Chem. Soc., 115* (1993) 193.

[7] A.S. Davydov, *Uspekhi Fiz. Nauk, 3* (1964) 393

[8] Crystal data for **II**: $C_{35}H_{36}N_2F_{12}SHg_3$, $M = 1346.5$, tetragonal, space group $p4_12_12$, at $-85°C$, $a = 20.724(4)$, $c = 18.099(4)$ Å, $V = 7773(4)$ Å^3, $Z = 8$, $d_{calc.} = 2.301$ g cm^{-3}, $F(000) = 4992$. Intensity data were collected with a Syntex P2$_1$ diffractometer ($-85°C$, Mo Kα radiation, $\theta/2\theta$ scan mode, $2\theta \leq 48°$, 3450 independent reflections, the empirical absorption correction (μ(Mo Kα) $= 119.6$ cm^{-1}) based on the azimuthal scans of 18 reflections was applied). The structure was solved by direct method and refined by full-matrix least-squares in anisotropic (Hg, S, F and N), isotropic (C) approximation; no attempts for location of H atoms were undertaken. The absolute structure was determined by the Hamilton test at 99.5% probability ($R_{inv} = 0.0518$). The final refinement converged to $R = 0.0450$, $R_W = 0.0442$ and $S = 1.15$ for 1658 observed ($I > 3\sigma(I)$) independent reflections. All calculations were carried out on IBM PC using the SHELXTL PLUS programs [9]. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

[9] W. Robinson and G.M. Sheldrick, SHELX, in N.W. Isaacs and M.R. Taylor (eds.), *Crystallographic Computing — Techniques and New Technologies*, Oxford University Press, Oxford, UK, 1988, p. 366.

[10] S.S. Batsanov, *Zh. Neorg. Khim., 36* (1991) 3015.

[11] R. Puget, M. Jannin, R. Perret and C. DeBrauer, *Acta Cryst., C47* (1991) 2232.

[12] J.W. Bats, P. Coppens and A. Kvick, *Acta Cryst., B33* (1977) 1534.