

Cyano-bridged Organotin Compounds. Crystal Structure of a Trinuclear Dianion containing a Nearly Linear Array of Nine Atoms

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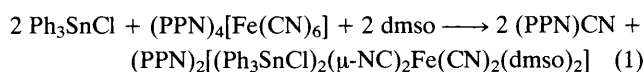
The use of PPN⁺ [PPN⁺ = (Ph₃P)₂N⁺] instead of K⁺ as counter-cation for cyanometallate anions, permits variation of the reactivity of the latter species towards electrophilic compounds such as organotin halides: an unusual trinuclear dianion [(Ph₃SnCl)₂(μ-NC)₂Fe(CN)₂(dmsO)₂]²⁻ (dmsO = dimethyl sulphoxide) has been obtained in this way, instead of the polymeric material produced by the corresponding potassium cyanoferrate.

Cyanometallate compounds of the type M_x[M'(CN)₆]_y represent an interesting class of chemical species, displaying molecular sieve properties, which can be predicted on the basis of their specific structure.¹ Furthermore Uson *et al.*,² and more recently Fischer *et al.*,³ found that organotin compounds of the type R₃SnX (X = halide, R = alkyl or aryl) react with K₃[M(CN)₆] (M = Fe or Co), giving polymeric substances of formula [(R₃Sn)₃M(CN)₆]_∞. The crystal structure of the trimethyl/cobalt derivative, solved by single-crystal X-ray methods,³ consists of distorted octahedral Co(CNSn)₆ fragments and trigonal-bipyramidal (tbp) N₂SnMe₃ units, within a strictly three-dimensional network. Only one third of all (Co-CN-Sn-NC)_∞ chains are linear, the remaining Co-CN-Sn sections being bent at the N atoms (157.7 or 146.2°). The lattice displays strictly parallel channels, with nearly square cross-sections, in such a way that the isostructural iron derivative was found to be able to give an unusual intercalation compound by a solid-state reaction with ferrocene.⁴

Our current interest in the field of tin chemistry⁵ has led us to investigate new *sub*-families of cyano-bridged tin-iron compounds of general formulae [(R₂Sn)_n{Fe(CN)₆}]_{n-1} (*n* = 2, 3) and [K₂Sn(L⁵){Fe(CN)₆}] (L⁵ = dianionic planar quinquedentate ligand).⁶ These species, which are produced by reaction of the suitable tin chlorides with potassium hexacyanometallates in water/ethanol mixtures, are polymeric substances practically insoluble in all common solvents.

With the aim of possibly producing soluble, polynuclear species, we have substituted the potassium cation with PPN⁺ in the starting material.[†] In this way, it has been possible to

use less polar aprotic media, resulting in an expected modification of the reaction pathways. Thus in dimethyl sulphoxide (dmsO), at room temperature, reaction (1) takes place.



Compound (1),‡ a pale yellow, crystalline solid, crystallizes slowly from the reaction mixture and can be redissolved in hot dimethyl sulphoxide. Its IR spectrum exhibits two partially overlapped CN stretching bands at 2081 and 2074 cm⁻¹. The identity of (1) has been determined by single-crystal X-ray diffraction analysis.§ The whole crystal structure consists of PPN cations and trinuclear dianions held together by van der Waals interactions, the shortest anion-cation contact being O(dmsO)-C(Ph), 3.11(1) Å. This represents, to our knowledge, the first structural example of a nonpolymeric substance

‡ Complex (1) can also be obtained by reaction of Ph₃SnCl and (PPN)₃[Fe(CN)₆]; in this case reduction of the iron centre occurs, probably at the expense of the leaving CN ions. Yellow thick platelets, suitable for X-ray analysis, were obtained after several days.

§ *Crystal data* for (1): 0.16 × 0.45 × 0.42 mm, *M* = 2164.27, triclinic, space group *P* $\bar{1}$, *a* = 17.239(3), *b* = 13.915(2), *c* = 11.140(2) Å, α = 106.65(1), β = 87.10(2), γ = 99.46(2)°, *U* = 2519.5(8) Å³, *Z* = 1, *D*_c = 1.426 g cm⁻³, *F*(000) = 1108, λ(Mo-K_α) = 0.71069 Å, μ = 8.45 cm⁻¹. Intensity data collected using a computer-controlled Siemens AED automated diffractometer, Nb-filtered Mo-K_α radiation, ω-2θ scan technique, 7935 reflections measured to 2θ(max.) 48°, 5004 observed with *I* > 2σ(*I*); no crystal decay. Data processed with the peak-profile analysis procedure and corrected for Lorentz, polarization, and absorption effects. Final *R* = 0.0579, *R*_w = 0.0768, 322 parameters, weighting scheme *w* = 0.4789/[σ²(*F*_o) + 0.005095*F*_o²], max. Δρ 0.7 e Å⁻³. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

† (PPN)_n[Fe(CN)₆] (*n* = 3 or 4) is prepared by stirring a dichloromethane solution of (PPN)Cl with an aqueous solution of K₃[Fe(CN)₆], in large molar excess; after 24 h the organic phase is dried and evaporated to dryness, yielding the expected PPN⁺ complex salt.

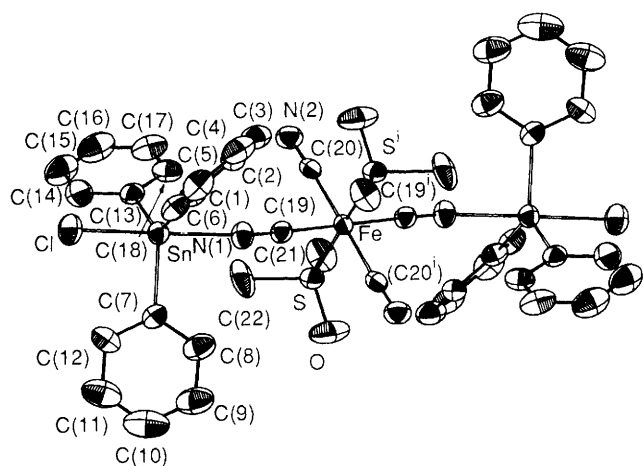


Figure 1. ORTEP view of the trinuclear dianion; important bond lengths (Å) and angles (°): Sn–Cl 2.535(3), Sn–N(1) 2.340(7), Sn–C(1) 2.140(4), Sn–C(7) 2.149(4), Sn–C(13) 2.144(6), Fe–S 2.201(2), Fe–C(19) 1.912(8), Fe–C(20) 1.941(9), N(1)–C(19) 1.16(1), N(2)–C(20) 1.14(1); Cl–Sn–N(1) 175.5(2), C(19)–N(1)–Sn 170.6(7), Fe–C(19)–N(1) 176.2(7).

containing an organotin fragment cyano-bridged to a transition metal.

The molecular structure of the trinuclear dianion (Figure 1) can be viewed as that of a donor–acceptor adduct, in which the electron-rich cyanometallate anion interacts with the electrophilic tin centres, without causing the loss of chlorine ions. As shown by the values of the angles at Sn, N(1), and C(19), this molecular ensemble contains a nearly linear array of nine atoms, whose total length is about 15 Å. The crystallographic inversion centre at the iron atom imposes its chain angle to be 180° and the configuration of the tin-bound phenyl groups to be staggered.

The environment of the tin atom is that of a slightly distorted trigonal bipyramid, with equatorial phenyl groups and the chlorine and nitrogen atoms occupying axial positions. The Sn–C(Ph) equatorial distances are slightly longer than those normally found in SnPh₃ tbp polyhedra,^{7–9} whereas the Sn–N distance is practically the same as that in the polymeric

material of ref. 3. The Sn–Cl bond is as long as that found in another tbp chlorotriphenyltin complex,⁹ at the top of the range (2.475–2.532 Å; eleven entries in the Cambridge Crystallographic Data Files) observed for this kind of fragment, if one excludes the values of 2.601 Å found in the Ph₃SnCl₂[–] anion.¹⁰

The iron atom adopts an essentially octahedral geometry, the co-ordination sites being occupied by four carbon atoms from the bridging and terminal CN ligands and two sulphur atoms from the dimethyl sulphoxide molecules. The two Fe–C bond distances are significantly different, that involving terminal cyanide being longer than those usually found in iron(II) cyano complexes.¹¹ The ligand dmsco co-ordinates to iron through sulphur, indicating a rather soft character for the metal centre, and the distance Fe–S suggests a little iron to sulphur π back-donation.¹²

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