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# First cation radical salt of a tetrathiafulvalene–based phosphine metal complex

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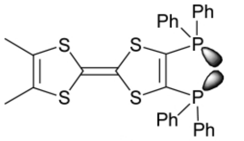
*Received (in Cambridge, UK) 1st March 2004, Accepted 8th April 2004*
*First published as an Advance Article on the web 5th May 2004*

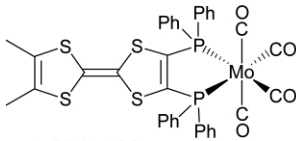
**Electrocrystallization of (*o*-P2)Mo(CO)$_4$, where *o*-P2 is the tetrathiafulvalene-based chelating diphosphine *o*-Me$_2$TTF-(PPh$_2$)$_2$, in the presence of the Linquist anion Mo$_6$O$_{19}$$^{2-}$ affords a 2:1 salt, formulated as [(*o*-P2)Mo(CO)$_4$]$_2$[Mo$_6$O$_{19}$], with a Heisenberg spin chain magnetic behaviour.**

Attempts to interplay the magnetic properties of high-spin metal complexes with the conducting properties of tetrathiafulvalene-based mixed-valence salts were recently fulfilled in several BEDT-TTF[1] and BEDT-TSF (BETS)[2] salts of paramagnetic counter ions such as Cr(oxalate)$_3$$^{3-}$ or FeCl$_4$$^-$. In those materials, the electronic coupling between the conducting and magnetic moieties is very weak but is able to strongly influence the electronic properties.[1,2] It was therefore expected that a stronger link between the metal complex and the π-redox core of the TTF would eventually increase these interactions and numerous tetrathiafulvalenes functionalized with coordinating ligands, essentially pyridines[3] and phosphines,[4,5] have been prepared for that purpose. However, among TTF-pyridines, only one acetylacetonate metal complex has been successfully oxidized to afford cation radical salts,[6] while none of the TTF-phosphine metal complexes described so far[4b,5,7,8] has been electro-crystallized to the corresponding radical cation salts.

Metal carbonyl complexes of the chelating *o*-Me$_2$-TTF(PPh$_2$)$_2$ (*o*-**P2**) (see below) were recently isolated and electrochemical investigations have shown that [*o*-**P2**][Mo(CO)$_4$], [*o*-**P2**][W(CO)$_4$] and [*o*-**P2**][Re(CO)$_3$Cl] are reversibly oxidised to the cation radical state, at least at the cyclic voltammetry time scale.[9]



*o*-**P2**



(*o*-**P2**)Mo(CO)$_4$

We show here for the first time that such low-valent metal complexes are able to sustain oxidation of the tetrathiafulvalene core to the cation radical state and describe the solid state and electronic structures of a salt of [*o*-**P2**][Mo(CO)$_4$] with the dianionic Mo$_6$O$_{19}$$^{2-}$ polyoxometallate.

[*o*-**P2**][Mo(CO)$_4$] was prepared as previously described.[9] Its crystal structure is reported here for comparison purposes ( Fig. 1).† In the two crystallographically independent complexes, the metallacycles are slightly folded along the P–P hinge, by 25° in the C$_2$P$_2$Mo(1) cycle, by 22° in the C$_2$P$_2$Mo(2) cycle. Similarly, the dithiole rings bearing the two phosphorus atoms are also folded (by 20 and 23° respectively), a recurrent feature of such neutral TTF derivatives. Electrocrystallisation of [*o*-**P2**][Mo(CO)$_4$] in the presence of ($n$-Bu$_4$N)$_2$(Mo$_6$O$_{19}$)[10] in CH$_3$CN at a constant current density of 1 μA cm$^{-2}$ afforded black parallelepipeds on the electrode which analyse as the 2:1 salt, *i.e.* ([*o*-**P2**][Mo(CO)$_4$])$_2$-(Mo$_6$O$_{19}$). It represents the first example of an organometallic complex of a TTF derivative, isolated in the solid state as its cation radical, and demonstrates that the TTF moiety in these metal carbonyl complexes can be oxidized, without decomplexation and/or oxidation to the phosphine oxide.

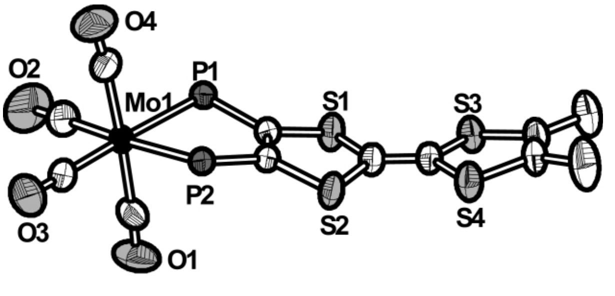


**Fig. 1** ORTEP view of one of the two independent molecules of [*o*-**P2**][Mo(CO)$_4$] (H atoms and Ph rings omitted for clarity).

([*o*-**P2**][Mo(CO)$_4$])$_2$(Mo$_6$O$_{19}$) crystallizes in the monoclinic space group $P2_1/c$ and the X-ray crystal structure determination† (Fig. 2) shows a Linquist anion on an inversion centre while the oxidized cationic complex is located in general position in the unit cell. From a structural point of view, only the TTF moiety of the complex is affected by the oxidation, with a lengthening of the central C=C bond (1.388(5) Å *vs.* 1.345(5) Å in the neutral complex) and shortening of the central C–S bonds, particularly within the dithiole ring bearing the two methyl groups (1.705 *vs.* 1.744 Å in the neutral complex) while the shortening is much less pronounced in the dithiole ring bearing the organometallic complex (1.726 *vs.* 1.758 Å in the neutral complex). In contrast, the Mo(CO)$_4$ fragment seems little affected, since, for example, the average length of the CO triple bonds amounts to 1.148 Å in the case of the neutral complex and 1.140 Å for the cation radical salt. All the other structural parameters are in the usual range.

In the solid state, the molecules do not dimerise as is often the case within the full charge transfer TTF-based salts, but organize into isolated uniform chains along the *b*-axis ( Fig. 3) with only a very long intermolecular S3···S4 distance (4.48 Å).

The temperature dependence of the molar magnetic susceptibility exhibits a maximum value at around 11 K (Fig. 4). According to the structural analysis, the susceptibility variation can be properly

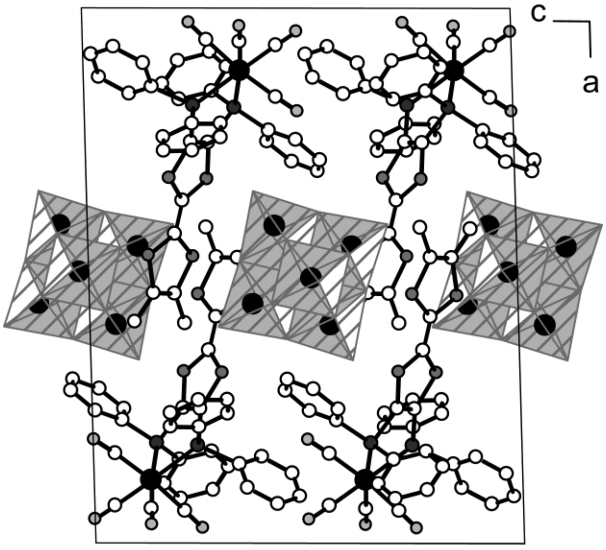


**Fig. 2** Unit cell of ([*o*-**P2**][Mo(CO)$_4$])$_2$(Mo$_6$O$_{19}$) (H atoms omitted).

DOI: 10.1039/b403168g

fitted as a Heisenberg spin chain, following the Bonner-Fisher model,[11] with $J/k = -17$ K, demonstrating the presence of a weak but sizeable intermolecular interaction even if the S3···S4 distance is very long. It is also confirmed by the extended Hückel calculation of the HOMO···HOMO overlap interaction energy $\beta = 8$ meV. The observation of the spin chain behaviour[12] despite this very weak interaction demonstrates the strongly one-dimensional nature of the system, a consequence of the steric bulk provided by the $(PPh_2)_2Mo(CO)_4$ and $Mo_6O_{19}$ moieties.

A very interesting feature of the (*o*-**P2**)Mo(CO)$_4$ complex and its $Mo_6O_{19}{}^{2-}$ salt is also the variation of the IR absorption frequencies of the carbonyl ligands, a powerful tool to detect tiny changes in electronic effects on the coordinated metallic centre. Shifts towards larger wavenumbers are observed upon oxidation for the four carbonyl absorption bands, as follows: $\nu$ (cm$^{-1}$) (*o*-**P2**)Mo(CO)$_4$: 1891, 1908, 1934, 2024 and ([*o*-**P2**][Mo(CO)$_4$])$_2$(Mo$_6$O$_{19}$): 1906, 1925, 1952, 2029. Such an increase of the IR absorption frequencies of the CO ligands has already been observed within a series of metallocene-based diphosphine transition metal carbonyl complexes, upon one-electron oxidation to the corresponding metallocenium.[14] This trend can be rationalized in terms of a lower degree of π-back retrodonation from metal-d to CO-π* orbitals, as a consequence of a weaker electron density on the metal in the oxidized complex, according to the Dewar–Chatt–Duncanson model.[15]

With the successful preparation and structural characterization of the cation radical salt of the (*o*-**P2**)Mo(CO)$_4$ complex, we demonstrate that the TTF-phosphines are promising electroactive ligands for allowing access to molecular materials in which a metallic centre lies in the close vicinity of a TTF radical. The nature and oxidation state of the coordinated metal, with the appealing eventuality of having a paramagnetic metallic centre, might vary with the electronic properties of the phosphine, which can be finely tuned by changing the substituents at phosphorus.

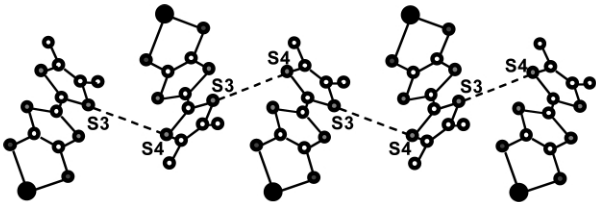


**Fig. 3** The uniform chain structure of ([*o*-**P2**][Mo(CO)$_4$])$^{+\cdot}$ radical species with S3···S4 interaction (dotted line). Hydrogen atoms, phenyl rings and CO groups omitted for clarity.

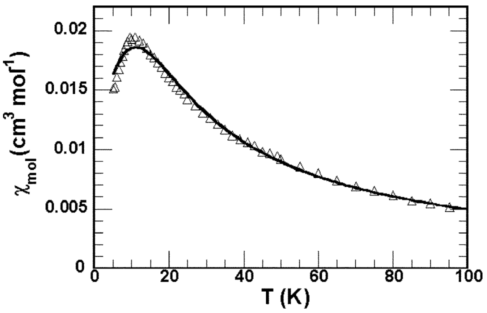


**Fig. 4** Temperature dependence of the magnetic susceptibility of ([*o*-**P2**][Mo(CO)$_4$])$_2$(Mo$_6$O$_{19}$). The solid line is a fit to the Heisenberg uniform chain model with the following spin Hamiltonian:[13] $H = -J\Sigma\, S_iS_{i+1}$

## Notes and references

† Crystal data for [*o*-**P2**][Mo(CO)$_4$]: $C_{36}H_{26}MoO_4P_2S_4$, $M = 808.69$, triclinic, space group $P\bar{1}$, $a = 12.821(1)$, $b = 18.266(2)$, $c = 18.629(2)$ Å, $\alpha = 114.96(1)$, $\beta = 105.50(1)$, $\gamma = 95.50(1)°$, $V = 3701.1(5)$ Å$^3$, $Z = 4$, $T = 293(2)$ K, $\mu$(Mo-K$\alpha$) = 0.703 mm$^{-1}$, $D_{calc} = 1.451$ g cm$^{-3}$, 38275 reflections measured of which 13477 independent ($R_{int} = 0.064$), $R(F) = 0.0371$ [7383 data with $I > 2\sigma(I)$], $wR(F^2) = 0.0623$.

Crystal data for ([*o*-**P2**][Mo(CO)$_4$])$_2$(Mo$_6$O$_{19}$): $C_{72}H_{52}Mo_8O_{27}P_4S_8$, $M = 2497.02$, monoclinic, space group $P2_1/c$, $a = 21.602(4)$, $b = 11.893(2)$, $c = 17.225(3)$ Å, $\beta = 91.68(3)°$, $V = 4423.4(15)$ Å$^3$, $Z = 2$, $T = 293(2)$ K, $\mu$(Mo-K$\alpha$) = 1.430 mm$^{-1}$, $D_{calc} = 1.875$ g cm$^{-3}$, 36239 reflections measured of which 8433 independent ($R_{int} = 0.076$), $R(F) = 0.0324$ [6088 data with $I > 2\sigma(I)$], $wR(F^2) = 0.0738$. The structures were solved by direct methods (SHELXS-97) and refined by full-matrix least-square on $F^2$ (SHELXL-97). CCDC 233488 for [*o*-**P2**][Mo(CO)$_4$], CCDC 233489 for ([*o*-**P2**][Mo(CO)$_4$])$_2$(Mo$_6$O$_{19}$). See http://www.rsc.org/suppdata/cc/b4/b403168g/ for crystallographic data in .cif or other electronic format.

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