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### Peierls Distortion in Polymeric Metal Complexes With Metal-Metal Chains

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## PEIERLS DISTORTION IN POLYMERIC METAL COMPLEXES WITH METAL-METAL CHAINS

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**Abstract** The polymeric complexes  $[M(\text{SPh})_3]_\infty$  ( $M = \text{Mo}, \text{W}, \text{Fe}, \text{Ru}; \text{Ph} = \text{C}_6\text{H}_5$ ) form columnar structures of face-sharing  $M(\text{SPh})_6$  octahedra resulting in a linear chain of metal atoms.  $[\text{Fe}(\text{SPh})_3]_\infty$  is paramagnetic with  $\mu = 5.2 \text{ B.M.}$ , indicating the absence of metal-metal interactions. The complexes of Mo, W and Ru exhibit a strong antiferromagnetic coupling, which is interpreted by the formation of  $M_2$  pairs.

### INTRODUCTION

Polymeric metal complexes  $[MX_3]_\infty$  with bridging ligands X and linear metal chains can occur in three forms:

- A) chains without metal-metal bonding and equal metal-metal distances
- B) chains with continuous metal-metal bonding and equal metal-metal distances
- C) chains with metal-metal bonding within pairs and alternating shortened and extended distances (see FIG. 1).

In case B) one-dimensional electrical conductivity can be expected.

### POLYMERIC COMPLEXES $[M(\text{SC}_6\text{H}_5)_3]_\infty$ , $M = \text{Mo}, \text{W}, \text{Fe}, \text{Ru}$

#### Synthesis

The metal carbonyls  $\text{Mo}(\text{CO})_6$ ,  $\text{W}(\text{CO})_6$  and  $\text{Fe}(\text{CO})_5$  react at elevated temperature with  $\text{PhSSPh}$  to yield the polymeric complexes  $[M(\text{SC}_6\text{H}_5)_3]_\infty$ .

$[\text{Ru}(\text{SPh})_3]_\infty$  is obtained from  $\text{Ru(III)acetylacetonate}$  and  $\text{HSPH}$ .

### Magnetic properties

$[\text{Fe}(\text{SPh})_3]_\infty$  is paramagnetic with  $\mu_{\text{eff}} = 5.2$  B.M., corresponding to  $\text{Fe}^{3+}$  in high spin configuration.

$[\text{Ru}(\text{SPh})_3]_\infty$ ,  $[\text{Mo}(\text{SPh})_3]_\infty$  and  $[\text{W}(\text{SPh})_3]_\infty$  show antiferromagnetic behaviour, indicating a strong electronic coupling (TAB. 1). The magnetic properties and the metal-metal interactions are comparable to those in the dinuclear ions  $\text{M}_2\text{X}_9^{3-}$  ( $\text{M} = \text{Mo}, \text{W}$ ;  $\text{X} = \text{Cl}, \text{Br}, \text{I}$ ).

TABLE 1    Magnetic properties, electrical conductivity and estimated metal-metal distances for complexes  $\text{M}(\text{SC}_6\text{H}_5)_3$ .

compound	$\mu_{\text{eff}}$ (B.M.)	conductivity (S/cm)	M-M distance (pm)
$\text{MoBr}_3$	1.20	$1.5 \cdot 10^{-6}$	291 <sup>1)</sup>
$\text{Mo}(\text{SPh})_3$	1.02	$1.5 \cdot 10^{-9}$	282
$\text{Cs}_3\text{Mo}_2\text{Cl}_9$	0.42		268 <sup>2)</sup>
$\text{RuBr}_3$	0.50		273 <sup>3)</sup>
$\text{Ru}(\text{SPh})_3$	0.58	$2.0 \cdot 10^{-6}$	287
$\text{Cs}_3\text{W}_2\text{Cl}_9$	0.43		241 <sup>2)</sup>
$\text{W}(\text{SPh})_3$	0.63		280
$\text{Fe}(\text{SPh})_3$	5.20	$1.0 \cdot 10^{-6}$	

### Electrical conductivity

The polymeric complexes  $[\text{M}(\text{SC}_6\text{H}_5)_3]_\infty$  exhibit only weak electrical conductivity (see TAB. 1) according to the absence of metal-metal interaction in  $[\text{Fe}(\text{SPh})_3]_\infty$  and to the Peierls distortion with the formation of  $\text{M}_2$  pairs in the case of  $[\text{M}(\text{SPh})_3]_\infty$  with  $\text{M} = \text{Mo}, \text{W}$  and  $\text{Ru}$ .

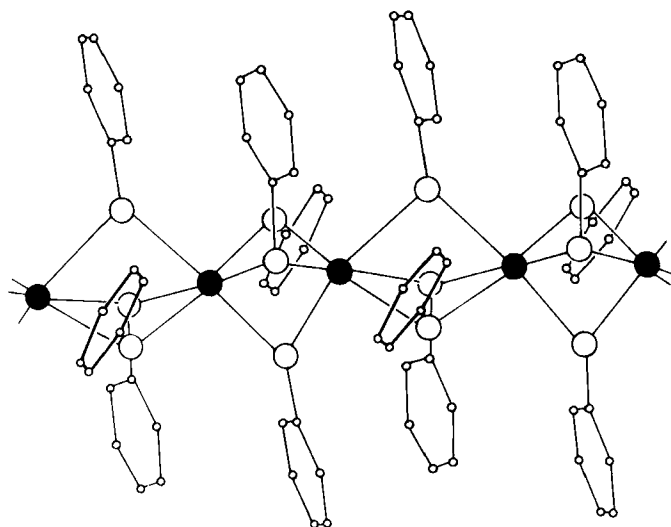


FIGURE 1 Proposed structure for the complexes  $[M(SPh)_3]_{\infty}$ ,  $M = Mo, W, Ru$

### Structure

Based on electrical and magnetic properties, IR- and UV-spectrum and the X-ray powder diagram as well, a structure of type C with alternating extended and shortened metal-metal distances along the chain can be proposed for the polymeric complexes (see FIG. 1). The calculation of the X-ray diffraction intensities for the proposed structure of  $[Mo(SPh)_3]_{\infty}$  shows good agreement with the experimental data.

For  $[Fe(SPh)_3]_{\infty}$  a similar structure but with equidistant metal atoms (type A) is likely.

### OLIGOMERIC COMPLEXES $(OC)_3M(SPh)_3M(SPh)_3M(CO)_3$ , $M = Fe, Ru$

On the route to the polymeric complexes the oligomeric intermediates  $Fe_3(CO)_6(SPh)_6$  and  $Ru_3(CO)_6(SPh)_6$  can be obtained. The structure is shown in Fig. 2. The trinuclear complexes of Fe and Ru are isotypic.

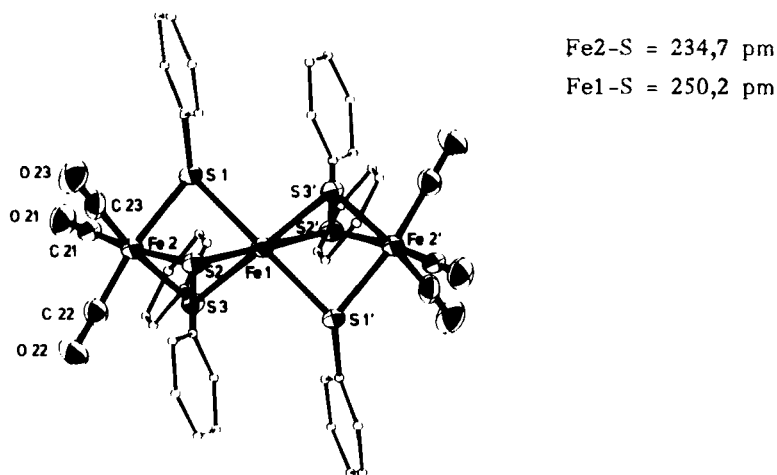


FIGURE 2 Structure of  $(OC)_3Fe(SPh)_3Fe(SPh)_3Fe(CO)_3$

$Fe_3(CO)_6(SPh)_6$  crystallizes triclinic with the lattice constants  $a = 1195.3$  pm,  $b = 1388.4$  pm,  $c = 1594.2$  pm,  $\alpha = 89.5^\circ$ ,  $\beta = 98.36^\circ$ ,  $\gamma = 99.12^\circ$ . The structure was solved and refined to  $R = 4.6\%$  by single crystal X-ray data.

$Fe_3(CO)_6(SPh)_6$  is paramagnetic with  $\mu = 6.1$  B.M. This can be explained by a low spin character of the two outer  $Fe^{2+}$  ions and high spin behaviour of the central  $Fe^{2+}$  ion. Spin-orbit coupling has to be taken into account. This assumption is in agreement with the results of the Mößbauer experiment and with the observed difference in the Fe-S distances.

$Ru_3(CO)_6(SPh)_6$  is diamagnetic, indicating  $Ru^{2+}$  in low spin configuration.

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