Peierls Distortion in Polymeric Metal Complexes With Metal-Metal Chains

Ulrich Berger [a] & Joachim Strähle [a]

[a] Inst. Inorg. Chem., University, D-7400, Tübingen, Germany
Version of record first published: 17 Oct 2011.

PLEASE SCROLL DOWN FOR ARTICLE

whatsoever or howsoever caused arising directly or indirectly in connection with or arising out of the use of this material.

PEIERLS DISTORTION IN POLYMERIC METAL COMPLEXES WITH METAL-METAL CHAINS

ULRICH BERGER, JOACHIM STRÄHLE
Inst. Inorg. Chem., University, D-7400 Tübingen (Germany)

Abstract   The polymeric complexes $[M(SPh)_3]_\infty$ (M = Mo, W, Fe, Ru; Ph = C_6H_5) form columnar structures of face-sharing $M(SPh)_6$ octahedra resulting in a linear chain of metal atoms. $[Fe(SPh)_3]_\infty$ is paramagnetic with μ = 5.2 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 $[M(SC_6H_5)_3]_\infty$, M = Mo, W, Fe, Ru

Synthesis

The metal carbonyls $Mo(CO)_6$, $W(CO)_6$ and $Fe(CO)_5$ react at elevated temperature with PhSSPh to yield the polymeric complexes $[M(SC_6H_5)_3]_\infty$.

$[Ru(SPh)_3]_\infty$ is obtained from Ru(III)acetylacetonate and HSPh.

Magnetic properties

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

$[Ru(SPh)_3]_\infty$, $[Mo(SPh)_3]_\infty$ and $[W(SPh)_3]_\infty$ 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 $M_2X_9^{3-}$ (M = Mo, W; X = Cl, Br, I).

TABLE 1   Magnetic properties, electrical conductivity and estimated metal-metal distances for complexes $M(SC_6H_5)_3$.

compound	μ_{eff} (B.M.)	conductivity (S/cm)	M-M distance (pm)
$MoBr_3$	1.20	$1.5 \ 10^{-6}$	291[1]
$Mo(SPh)_3$	1.02	$1.5 \ 10^{-9}$	282
$Cs_3Mo_2Cl_9$	0.42		268[2]
$RuBr_3$	0.50		273[3]
$Ru(SPh)_3$	0.58	$2.0 \ 10^{-6}$	287
$Cs_3W_2Cl_9$	0.43		241[2]
$W(SPh)_3$	0.63		280
$Fe(SPh)_3$	5.20	$1.0 \ 10^{-6}$	

Electrical conductivity

The polymeric complexes $[M(SC_6H_5)_3]_\infty$ exhibit only weak electrical conductivity (see TAB. 1) according to the absence of metal-metal interaction in $[Fe(SPh)_3]_\infty$ and to the Peierls distortion with the formation of M_2 pairs in the case of $[M(SPh)_3]_\infty$ with M = Mo, W and Ru.
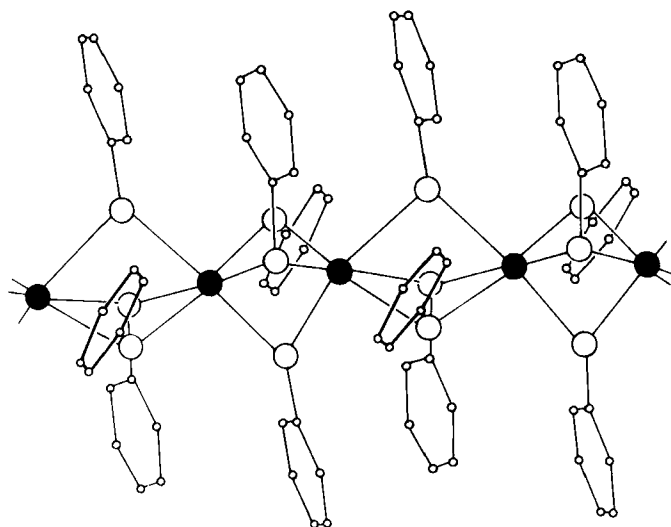
FIGURE 1   Proposed structure for the complexes
$[M(SPh)_3]_\infty$, M = Mo, W, Ru

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 experimen-
tal 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 inter-
mediates $Fe_3(CO)_6(SPh)_6$ and $Ru_3(CO)_6(SPh)_6$ can be obtained.
The structure is shown in Fig. 2. The trinuclear complexes of Fe
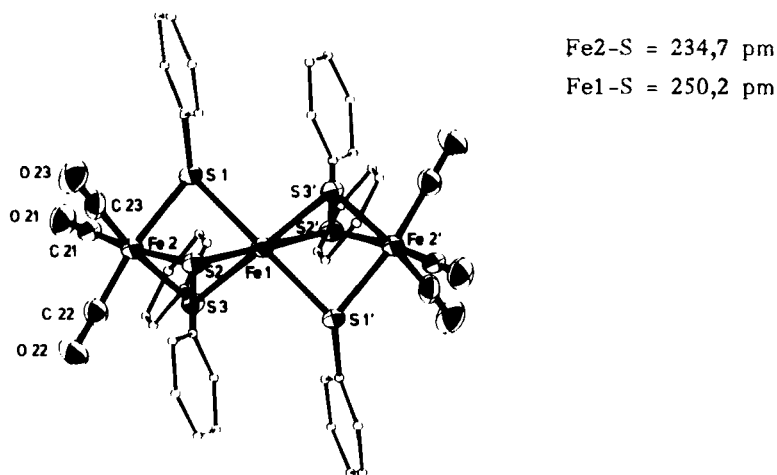and Ru are isotypic.

Fe2-S = 234,7 pm

Fe1-S = 250,2 pm

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, = 89.5°, ß = 98.36°,
 = 99.12°. 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 μ = 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 con-
figuration.

REFERENCES

1) D. Babel, J.Solid State Chem., 4, 410 (1972)

2) I.E. Grey, P.W. Smith, Aust.J.Chem., 22, 121 (1969)

3) H.K. Breitbach, Dissertation, Erlangen 1967.