216 *Chem. Mater.* **1999,** *11,* 216−217

Superconducting Metallocene Intercalation Compounds of β-ZrNCl

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Received November 5, 1998
Revised Manuscript Received December 18, 1998

The metal nitride halides, MNX (M = Ti, Zr; X = Cl, Br, I), were first reported by Juza and Heners in 1964 along with a high temperature β-polymorph for ZrNCl and ZrNBr.[1] Subsequently, Ohashi et al. have shown that an alternative chemical vapor transport synthesis of β-ZrNCl and β-ZrNBr yields more highly crystalline samples of these compounds.[2,3] We have recently reported that these host lattices are in fact isostructural with rhombohedral SmSI.[4,5] In this structure each Zr atom is seven-coordinate and is best described as being in a distorted monocapped octahedral arrangement with three halide atoms and three N atoms adopting a *fac*-arrangement with a fourth capping nitrogen above the N_3 face. The octahedra are distorted by the displacement of the Zr atom from the center toward the capped N_3 face to such an extent that the Zr and N atoms become essentially coplanar. These monocapped octahedral units are arranged in an edge-sharing manner, forming the XZrNNZrX layer structure (Figure 1).

The intercalation of lithium into β-ZrNCl was first reported in 1984 and subsequent studies showed that other alkali metals could also be intercalated into this lattice.[6,7] Interest in these compounds was recently increased following reports that they become superconducting at temperatures below 15K.[8,9] In a more recent study, intercalation of lithium ions in the isostructural host lattice β-HfNCl was shown to yield $Li_{0.48}(THF)_y$-HfNCl, which exhibits a superconducting transition temperature of 25.5K.[10] Metallocenes and in particular cobaltocenes have previously been intercalated into a range of host lattices including MX_2 (M = Ti, Zr, Nb, Ta, Sn; X = S, Se),[11] MOCl (M = Fe, V, Ti),[12] MPS_3 (M = Mn, Cd, Fe),[13] and $Zr(HPO_4)_2{\cdot}H_2O$.[14] These intercalates have been widely studied with respect to their structural, electronic, and magnetic properties. In this study we report the metallocene intercalation chemistry of β-ZrNCl.

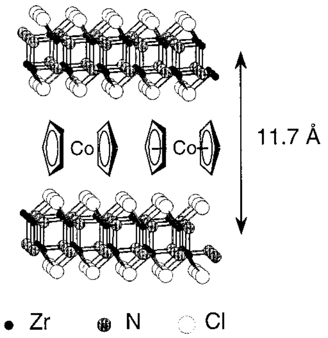

Figure 1. Schematic representation of the structure of ZrNCl-$\{Co(Cp)_2\}_{0.10}$. The change in the interlayer separation between the $Co(Cp)_2$ and $Co(Cp^*)_2$ intercalates suggests that the metallocenes are ordered with their principal axes parallel to the ZrNCl layers.

β-ZrNCl was prepared under conditions reported previously and intercalation was achieved by using excess guest solutions in THF of cobaltocene $\{Co(Cp)_2$; Cp = η-$C_5H_5\}$, 1,1′-dimethylcobaltocene $\{Co(Cp')_2$; Cp′ = η-$C_5H_4Me\}$, and decamethylcobaltocene $\{Co(Cp^*)_2$; Cp* = η-$C_5Me_5\}$ at 60 °C.[2,3] In each case, complete intercalation was confirmed by the absence of Bragg reflections characteristic of β-ZrNCl in the XRD pattern with the stoichiometry of the guest determined by elemental analysis. The characterizing data are summarized in Table 1. As the interlayer separations of the cobaltocene and 1,1′-dimethylcobaltocene are the same and less than that observed for the decamethylcobaltocene intercalate, it can be deduced that the guest molecules are orientated with their principal axes parallel to the host layers. This orientation is the same as has been observed for cobaltocene intercalates of other layered systems and is shown schematically in Figure 1.[15−19] We have also attempted intercalation reactions with other organometallic guests with similar redox potentials, including chromocene, bis(benzene)-chromium, and bis(indenyl)cobalt, but they all proved to be unsuccessful.

The temperature and field dependence of the magnetic susceptibility of $ZrNCl\{Co(Cp)_2\}_{0.10}$ is shown in Figure 2 from which it can be seen that there is a superconducting transition at 14 K. This is the highest T_c known for a metallocene intercalation compound. The field dependence measurements indicate that ZrNCl-$\{Co(Cp)_2\}_{0.10}$ is a type II superconductor. Both ZrNCl-$\{Co(Cp')_2\}_{0.09}$ and $ZrNCl\{Co(Cp^*)_2\}_{0.15}$ also show superconducting transitions at 14 K and type II behavior. In

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Table 1. Structural Data for the Intercalation Compounds of β-ZrNCl with Cobaltocenes

metallocene	stoichiometry[a]	interlayer separation[b] (Å)
$CoCp_2$	$ZrNCl\{Co(Cp)_2\}_{0.10}$	14.7
$Co(Cp')_2$	$ZrNCl\{Co(Cp')_2\}_{0.09}l$	14.7
$Co(Cp^*)_2$	$ZrNCl\{Co(Cp^*)_2\}_{0.15}$	16.5

[a] Stoichiometry was determined by elemental microanalysis. [b] Indexed on a hexagonal unit cell using *a* and *b* cell constants from pristine β-ZrNCl.

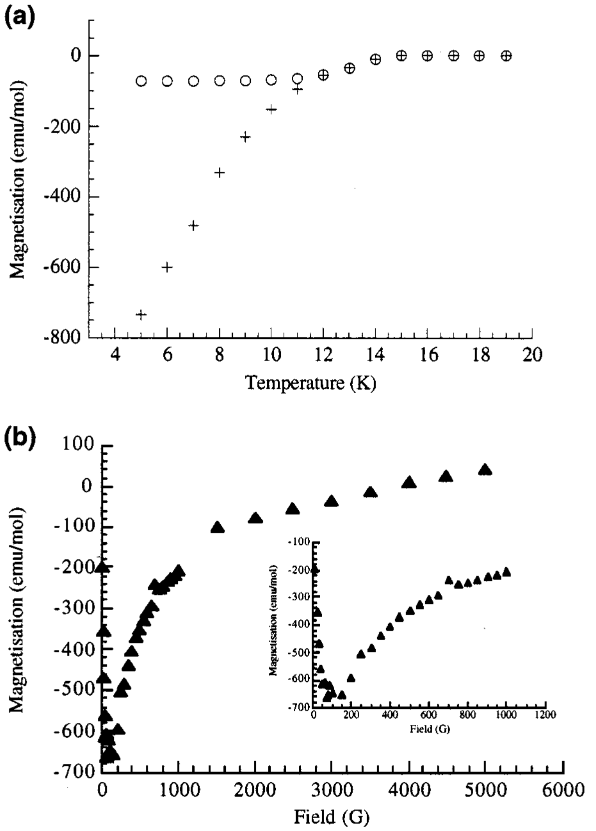

Figure 2. Dependence of the magnetization of $ZrNCl\{Co(Cp)_2\}_{0.10}$ on (a) temperature at a field of 40 G [+ = zero field cooled (ZFC), ○ = field cooled (FC)] and (b) field at a temperature of 3 K.

Table 2. Summary of the Magnetic Data for the Intercalation Compounds of β-ZrNCl with Cobaltocenes

compound	T_c (K)	H_{c1} (G)	H_{c2} (G)	shielding fraction (%)
$ZrNCl\{Co(Cp)_2\}_{0.10}$	14	100	4500	50
$ZrNCl\{Co(Cp')_2\}_{0.09}$	14	80	5000	55
$ZrNCl\{Co(Cp^*)_2\}_{0.15}$	14	100	7000	50

all three cases the shielding fractions can be estimated as being approximately 50%, indicating that the intercalation compounds are bulk superconductors. The magnetic data are summarized in Table 2.

The electrical conductivity of pressed pellets of all three intercalates was measured using the four wire dc technique over the temperature range 4−300 K. The temperature dependence of the resistivity for all three intercalation compounds showed the same behavior and is shown in Figure 3 for $ZrNCl\{Co(Cp)_2\}_{0.10}$. Above approximately 70 K the intercalate displays metallic behavior, and below this temperature there is an increase in the resistivity, indicative of a degree of electron localization. This is followed by a sharp drop in the resistivity at 16 K, with it becoming zero at 12 K. The 10−90% width of this transition is approximately 1.5 K. The dramatic change in the electronic properties can be further confirmed by comparison of the room-temperature conductivities which are 5.6 Ω^{-1} cm^{-1} for $ZrNCl\{Co(Cp)_2\}_{0.10}$ and 4 × 10^{-7} Ω^{-1} cm^{-1} for pristine β-ZrNCl.[6] The conductivity data for all three intercalates are summarized in Table 3, from which the similarity in their behavior is apparent.

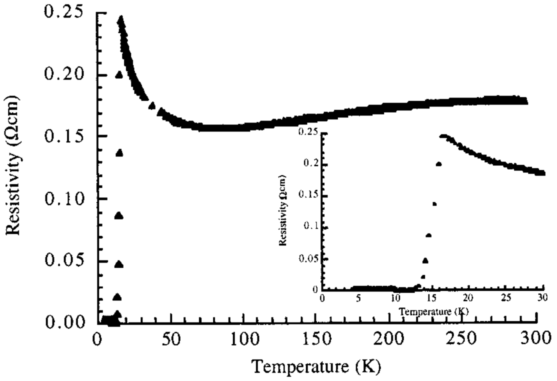

Figure 3. Temperature dependence of the resistivity of $ZrNCl\{Co(Cp)_2\}_{0.10}$.

Table 3. Summary of the Conductivity Data for the Intercalation Compounds of β-ZrNCl with Cobaltocenes

compound	transition temperature (K) onset	zero	10−90% width	room temp conductivity $(\Omega\ cm)^{-1}$
$ZrNCl\{Co(Cp)_2\}_{0.10}$	16	12	1.5	5.6
$ZrNCl\{Co(Cp')_2\}_{0.09}$	17	11	3.0	0.42
$ZrNCl\{Co(Cp^*)_2\}_{0.15}$	16	11	2.0	1.5

The superconducting transition temperatures for these metallocene intercalation compounds are the same as those in the alkali metal intercalates, with the same doping level reported by Yamanaka et al.[8,9] The transition temperature appears to be independent of the interlayer separation and of the doping level, which suggests that the superconductivity is largely confined to the thin two-dimensional ZrN layers of the host lattice. The existence of superconductivity in these compounds is perhaps not surprising given the structural similarities between these ZrN layers and the rock salt structure of zirconium nitride, which is itself a superconductor below 9.05 K.[20] It is hoped that future band structure calculations on β-ZrNCl will provide further insights into the origins of the superconductivity in these materials. Finally, the use of substituted metallocene derivatives appears to be another efficient method of chemically controlling the interlayer separation and the electron doping in these materials.

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