Table I. Cluster Compounds Containing Interstitial Transition Metals

host metal	interstitial compds[a]	electron count[b]	lattice parameters, Å		
			a	*b*	*c*
Zr	$Cs_{0.63}Zr_6I_{14}Fe$	18.63	16.021 (1)	14.380 (1)	13.075 (1)
	$CsZr_6I_{14}Mn$	18	16.088 (1)	14.409 (1)	13.140 (1)
	$Cs_xZr_6I_{14}Co$	19+x	16.065 (2)	14.360 (3)	13.096 (3)
	$CsZr_6Br_{15}Fe$[c,d]	18	19.721 (3)	14.863 (3)	10.265 (2)
	$Zr_6Br_{14}Fe$[d]	18	14.988 (3)	13.408 (2)	12.232 (2)
	$Zr_6I_{14}Fe$	18	15.976 (2)	14.355 (4)	13.019 (2)
	$Zr_6I_{12}Mn$	19	14.747 (1)		10.094 (1)
Sc	$Sc_7I_{12}Co$	18	14.800 (1)		10.202 (1)
	$Sc_7I_{12}Ni$	19	14.814 (1)		10.115 (1)
Y	$Y_7I_{12}Fe$	17	15.351 (1)		10.661 (1)
	$Y_7I_{12}Co$	18	15.332 (1)		10.683 (1)
Pr	$Pr_7I_{12}Mn$	16	15.788 (2)		10.955 (3)
	$Pr_7I_{12}Fe$	17	15.821 (1)		10.787 (1)
	$Pr_7I_{12}Co$	18	15.815 (1)		10.805 (1)
	$Pr_7I_{12}Ni$	19	15.833 (1)		10.734 (1)
Gd	$Gd_7I_{12}Fe$	17	15.492 (1)		10.624 (2)
	$Gd_7I_{12}Co$	18	15.458 (1)		10.737 (1)

[a] Compounds with a Zr:I ratio of 6:14 adopt the $CsZr_6I_{14}C$ (Nb_6Cl_{14}) structure (*Cmca*) while $Zr_6I_{12}Mn$ has the $Zr_6I_{12}C$ ($R\bar{3}$) structure type.[4] $R_7I_{12}Z$ phases have the closely related $Sc_7Cl_{12}(B,N)$ structure ($R\bar{3}$)[8] achieved by addition of an isolated R^{+3} ion to the $Zr_6I_{12}C$ type. [b] Cluster based electrons. [c] $CsZr_6Cl_{15}C$ ($CsNb_6Cl_{15}$) type. [d] Ziebarth, R. P.; Corbett, J. D., unpublished results.

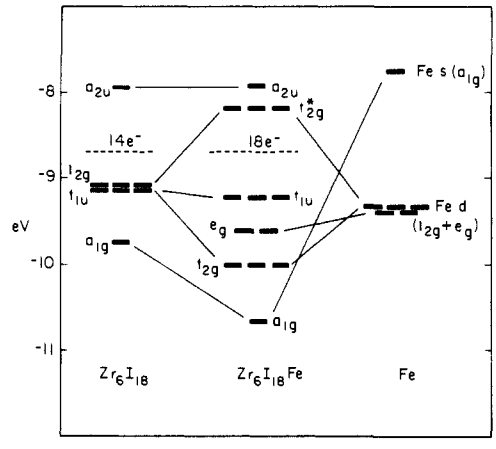

Figure 1. Molecular orbital interaction diagram for $(Zr_6I_{12}Fe)I_6^{4-}$. Iron contributions to the MO's shown are the following: a_{1g}, 25% s; t_{2g}, 41% d; e_g, 89% d; t_{1u}, 7.4% p; t^*_{2g}, 54% d; a_{2u}, 0%. Note how the inclusion of the pair of nonbonding Fe e_g levels changes the cluster "magic number" from 14 to 18.

bonding to the "interstitial" is primary while bonding among the peripheral cluster metal atoms is secondary.

The electronic structure of the new clusters is in sharp contrast to that in other interstitially stabilized clusters as well as in the empty $(Nb,Ta)_6X_{12}^{n+}$ congeners. As indicated in Table I, all of these examples seem to possess a surplus of electrons according to the 14-e⁻ "requirement" derived from previous experience.[3,4,8] The MO diagram in Figure 1 is useful in understanding the altered state of affairs that obtains when the "interstitial" atom is a transition metal. The diagram is the result of an extended Hückel (EH) calculation on an octahedral $(Zr_6I_{12}Fe)I_6$ cluster using parameters obtained from a self-consistent-charge EH calculation of $Zr_6I_{14}Fe$ using a realistic structural model with one cluster per unit cell. The diagram shows the lower lying metal-based levels only and the percentage of iron character in each. At the 18-e⁻ count a gap of 1.04 eV is found which is related to a comparable value for 14-e⁻ clusters[4] through the addition of the iron e_g set to the occupied valence orbitals. Fourteen-electron clusters characteristically possess filled metal–metal bonding levels of a_{1g}, t_{1u} (both interstitial bonding), and t_{2g} (metal bonding) symmetry, with none of e_g symmetry. The t_{1u} levels now include only a small amount of Fe p character and are weakly Zr–Zr bonding while the bulk of the Zr–Fe bonding is carried by the t_{2g} and a_{1g} orbitals in consonance with their more even orbital populations.

We expect the above picture of the electronic structure to be qualitatively useful for all of these cluster compounds, at least insofar as electron counting is concerned. The closed-shell "magic number" of 14 found for previous $M_6X_{12}Z$-type clusters is transformed to 18 by the inclusion of the interstitially localized e_g set of orbitals. In accord with this, $CsZr_6I_{14}Mn$ is found to be a diamagnet while $Zr_6I_{12}Mn$ is paramagnetic with one unpaired spin per cluster. Full details regarding the syntheses, structures, calculations, and magnetic susceptibilities will be published later.

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Supplementary Material Available: Tables of structural parameters and refinement data for $Cs_{0.63}Zr_6I_{14}Fe$ and $Sc_7I_{12}Co$ (2 pages). Ordering information is given on any current masthead page.

Enantiospecific Complexation Gas Chromatography of Nerve Agents. Isolation and Properties of the Enantiomers of Ethyl *N,N*-Dimethylphosphoramidocyanidate (tabun)

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Previously we described the gas chromatographic resolution of the four stereoisomers of the nerve agent[1] 1,2,2-trimethylpropyl methylphosphonofluoridate, $Me_3CC(H)MeO(Me)P(O)F$, C(±)P(±)-soman,[2] on capillary Chirasil-Val columns.[3,4] This procedure enabled us to study the toxicology of each soman stereoisomer.[5,6] The enantiomers of two other nerve agents, i.e., ethyl *N,N*-dimethylphosphoramidocyanidate, $EtO(Me_2N)P(O)CN$ (tabun), and isopropyl methylphosphonofluoridate, *i*-PrO(Me)P(O)F (sarin), are not or are incompletely resolved on Chirasil-Val, respectively. ^1H NMR spectroscopy with tris[(1*R*)-3-(heptafluorobutyryl)camphorate]europium(III) allows the analysis of all stereoisomers of soman, sarin, and tabun,[7] but a 10^8 times larger sample is required than for chiral gas chromatography.[4] We report the gas chromatographic resolution of all stereoisomers of soman, sarin, and tabun and the use of this procedure to monitor the isolation of the tabun enantiomers.

The strong association of lanthanide shift reagents with phosphoryl compounds[8,7] suggests that enantiospecific complex-

(1) **WARNING**: nerve agents are extremely toxic and should be handled only in laboratories where specifically trained medical personnel is available.
(2) The stereoisomers of soman are assigned C(−)P(−), C(−)P(+), C(+)P(−), and C(+)P(+), in which C stands for the 1,2,2-trimethylpropyl moiety.
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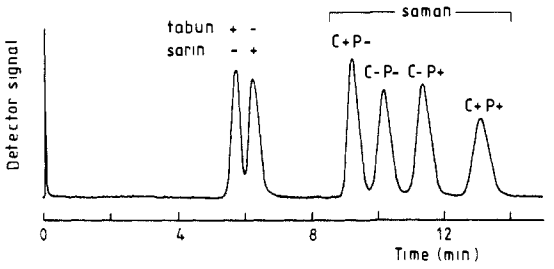

Figure 1. Gas chromatogram (NP detection) after direct injection of a 0.5-μL sample in *i*-PrOH, containing 0.1 mM each of C(±)P(±)-soman, (±)-sarin, or (±)-tabun on a glass column (l = 2 m, i.d. = 0.44 mm) coated with bis[(1*R*)-3-(heptafluorobutyryl)camphorate]nickel(II) in OV 101, operated at 120 °C. Helium (5×10^{-1} m/s) was used as carrier gas. Static coating of the Duran 50 glass column was performed with a solution of the nickel(II) derivative (0.024%, w/v) and OV 101 (0.4%, w/v) in *n*-pentane.[10,11] The enantiomeric peaks of sarin and tabun coincide.

ation gas chromatography[9-12] might be suitable for resolution of nerve agent stereoisomers. We found (Figure 1) that a 2-m capillary column, coated with bis[(1*R*)-3-(heptafluorobutyryl)-camphorate]nickel(II) in OV-101, separates the four stereoisomers of soman and the enantiomers of sarin and tabun almost completely. The stereoisomers of soman were identified by addition of single isomers to C(±)P(±)-soman,[5] whereas (+)- and (−)-sarin were identified in samples enriched with these isomers by synthesis.[7] Since the gas chromatographic resolution of enantiomers increased sharply with a decrease in the amount of analyte, an NP detector was used, which allows detection in the pg range.[4] GC/MS detection confirmed that the peaks, which are within experimental error of equal size for enantiomeric pairs, correspond with unchanged nerve agent. As expected, the elution order of the enantiomers inverted when the complexation phase was synthesized from (1*S*)-3-(heptafluorobutyryl)camphor instead of the 1*R* isomer.[9]

Hoskin and Trick[13] reported that phosphorylphosphatases in rat serum hydrolyze preferentially the enantiomer of tabun which is presumably more toxic in mice than (±)-tabun. Polarimetry in rat serum suggested that the remaining enantiomer was levorotatory. Augustinsson[14] confirmed the stereospecificity of tabun breakdown in rat plasma and suggested that phosphorylphosphatases in human and rabbit plasma are not stereospecific for hydrolysis of (±)-tabun. We identified, isolated, and studied the anticholinesterase properties of the two enantiomers of tabun.

Analogous to the procedure for isolation of P(+)-soman epimers,[5,6] we incubated a 2.3 mM solution of bovine pancreas chymotrypsin (Sigma, type II, dialyzed at pH 3.0) in phosphate buffer (pH 7.5, 25 °C) with a 15% molar excess of (±)-tabun for 5 min. Extraction on Extrelut (Merck) with CCl_4 gave a single tabun enantiomer in 25% yield, which corresponded with the second peak in the gas chromatogram (Figure 1). ^{1}H NMR analysis[7,15] of such a solution in CCl_4, α_{578}^{25} −0.0770° (l = 1; c = 3.35 mg/mL), i.e., $[\alpha]_{578}^{25}$ −23°, confirmed that the levorotatory isomer of tabun was obtained with ≥98% ee. Dilute (≤10 mM) solutions of (−)-tabun in CCl_4 and in *i*-PrOH are optically stable for several months at −25 °C.

To obtain the (+)-enantiomer of tabun by means of stereospecific hydrolysis by phosphorylphosphatases,[5] (±)-tabun (4 mM) was incubated at 25 °C for 30 min in plasma of various species. Plasma from horses and cows gave (+)-tabun with 20% and 28% ee, respectively, whereas incubation in plasma from mice, sheep, rabbits, pigs, guinea pigs, and men gave a slight (≤30% ee) enrichment of residual tabun with the (−)-enantiomer. Only by incubation in rat plasma for 45 min was (+)-tabun[16] obtained with 92–100% ee, albeit in low yields (5–10%). Our results confirm the stereospecific hydrolysis of (±)-tabun by phosphorylphosphatases from rat plasma.[13,14] However, the residual isomer is dextrorotatory instead of levorotatory, as suggested by Hoskin and Trick.[13]

The rates of inhibition of electric eel acetylcholinesterase (AChE) were measured (pH 7.5, 25 °C) at various concentrations of tabun stereoisomers. In contrast with the extreme P(−)-selectivity of AChE with (±)-sarin and C(±)P(±)-soman, the overall rate constant for inhibition of AChE with (−)-tabun is only 6.3 times larger than with (+)-tabun: 3.9×10^4 and 0.62×10^4 $M^{-1} \cdot s^{-1}$, respectively. The dissociation constants for the complexes of AChE with (+)- and (−)-tabun are 13.1 and 0.62 μM, respectively, with rates of phosphorylation of 8.1×10^{-2} and 2.4×10^{-2} s^{-1} for (+)- and (−)-tabun, respectively. Surprisingly, the overall stereoselectivities of AChE and chymotrypsin (vide supra) for (+)- and (−)-tabun are opposite, whereas both enzymes are preferentially inhibited by the P(−)-isomers of soman and sarin.[5,6]

The LD50's of (−)-, (+)-, and (±)-tabun in mice, after intravenous administration, are 119 (113–130), 837 (771–905),[17] and 208 (193–224) μg/kg, respectively. Hence, in spite of the modest selectivity of AChE for inhibition by (−)-tabun, this isomer is substantially more toxic in mice than (+)-tabun. The species dependence for the stereoselectivity of tabun enantiomer hydrolysis in plasma (vide supra) may influence the relative toxicities of these enantiomers in various species, e.g., in mice and rats.

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(16) Absolute values of the positive rotations of (+)-tabun in CCl_4 were inconsistent, probably due to coisolated optically active components from rat plasma.
(17) Contained 4% of the (−)-enantiomer.

tert-Butyl Peroxide Complexes of Permethylhafnocene, $(\eta^5\text{-}C_5Me_5)_2Hf(R)(OOCMe_3)$. Stoichiometric Transformation of Alkyl *tert*-Butyl Peroxide Derivatives to Alkoxy *tert*-Butoxides, $(\eta^5\text{-}C_5Me_5)_2Hf(OR)(OCMe_3)$

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Alkyl peroxide complexes of the group 4 transition metals have been invoked as intermediates in titanium-catalyzed epoxidation of allylic alcohols,[1] in the Shell propylene oxide synthesis[2,6] and

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