Table II. ^{13}C NMR Assignments

carbon	**1**[a]	**3**[a]	**4**[b]
1	52.9	53.0	
3	54.9	55.5	
4	27.2	30.0	
5	110.0	106.0	
6	159.7	157.0	
7	104.0	100.9	
8	155.8	154.7	
9	112.7	110.8	
10	137.7	136.0	
11	169.7	169.2	
12	37.3	37.8	
13	126.5	126.9	
14	130.5	130.2	
15	115.3	115.0	
16	156.4	156.0	
2′	137.8		141.1
4′	126.8		130.0
5′	131.1		134.8
6′	25.1		25.5
7′	52.3		54.5
8′	170.5		173.3
9′	32.3		34.0

[a] Spectra run in Me_2SO-d_6. [b] Spectra run in D_2O.

different from 1-methylhistidine by TLC comparison. The CI mass spectrum of **3** showed a parent ion at m/z 316 daltons (M^+ + H) and fragment ions at 270 ($M^+ - CO_2H$), 242 (M^+ − NH═CHCO$_2$H via retro Dields–Alder), 208 (M^+ − OHbenzyl), and 164 (M^+ − (OHbenzyl + CO_2)) daltons typical of benzyltetrahydroisoquinolines.[6] ^1H NMR resonances at 6.70 (d, J = 8 Hz, 2 H) and 7.01 (d, J = 8 Hz, 2 H) required that the benzyl residue in **3** contain a para hydroxyl substituent. Additional ^1H NMR resonances at 6.08 (d, J = 2 Hz) and 6.22 (d, J = 2 Hz) in the spectrum of **3** were assigned to meta protons on the aromatic ring of the isoquinoline moiety, requiring that the two hydroxyl substituents on this ring also be meta disposed. Imbricatine (**1**) has only a single proton on the isoquinoline aromatic ring (6.42 ppm, s), the other nonphenolic position being occupied by the thioether linkage.

Model compound 6 and its trans isomer were prepared according to literature procedures.[7] Comparison of the ^1H NMR spectra of the model compounds (6: ($CDCl_3$) 1.87 (s, CH_3CON); 2.88 (dd, J = 14, 8 Hz, H12); 3.21 (m, H4a and H4e); 3.28 (dd, J = 14, 6 *Hz*, H12′); 4.49 (t, J = 10 Hz, H3a); 4.73 (dd, J = 8, 6 Hz, H1a)) to that of derivative **5** (($CDCl_3$) 1.80 (s, CH_3CON); 2.88 (dd, J = 14, 8 Hz, H12); 3.24 (m, H4a and H4e); 3.30 (dd, J = 14, 6 Hz, H12′); 4.48 (t, J = 10 Hz, H3a); 5.04 (dd, J = 8, 6 Hz, H1a)) confirmed the benzyltetrahydroisoquinoline nature of **3** and indicated that the C1 and C3 substituents were cis as shown.

The H4e and H3a resonances are both strongly deshielded in imbricatine (**1**) relative to the resonances for the corresponding protons in the Ra-Ni reduction product **3** (Table I). The difference in chemical shifts observed for these two protons in **1** and **3** can best be explained if the thioether linkage in imbricatine is attached to C5 of the isoquinoline nucleus, which in turn requires that there be a proton meta to it at C7 and hydroxyl substituents at C6 and C8. A pair of INAPT experiments,[8] one of which showed three bond couplings between H1 and carbons 8 and 10, and another which showed two and three bond couplings between H7 and carbons 5, 6, 8, and 9 of imbricatine (**1**), confirmed this assignment.

Imbricatine (**1**) represents the first example of a benzyltetrahydroisoquinoline alkaloid from a marine organism, and it is apparently the first example from a nonplant source. The C3 carboxyl substituent, the C6/C8 hydroxylation pattern, and the thioether linkage to a histidine substituent represent structural features not previously encountered in this family of alkaloids.

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Alloy Clusters: The Encapsulation of Transition Metals (Mn, Fe, Co, Ni) within Cluster Halides of Zirconium and the Rare-Earth Metals

Timothy Hughbanks, Guy Rosenthal, and John D. Corbett*

Department of Chemistry, Iowa State University
Ames, Iowa 50011

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We have recently reported that numerous zirconium analogues of the long-known $(Nb,Ta)_6X_{12}^{n+}$ clusters (X = Cl, Br, and some I, n = 2, 3, 4)[1,2] may be stabilized by the inclusion of an interstitial atom Be, B, C, N, Al, Si, or P, the last three only in iodides so far.[3–6] The interstitial atom Z contributes both additional electrons and strong Zr–Z bonds. Similar strategies have allowed the synthesis of different scandium and lanthanide cluster phases[7,8] and condensed cluster compounds[8–10] but only with Z = B, C, C_2, or N.[11] To this profusion there is now even more; we here report the synthesis and structural classification of a wide variety of remarkable rare-earth-metal and zirconium cluster compounds (Table I) in which a 3d transition metal (Mn, Fe, Co, or Ni so far) is ensconced. The zirconium phases were made by allowing stoichiometric proportions of MI_2, ZrI_4, Zr powder (or excess Zr strips), and CsI where appropriate to react in sealed Ta tubing between 700 and 925 °C for 2–4 weeks. The rare-earth-metal compounds were similarly obtained using MI_3, M = Sc, Y, Pr, Gd, and a 20% excess of the appropriate metal (as strips). The black microcrystalline powders or blue-black gemlike crystals are usually obtained as single-phase products (>95% yield) as judged by Guinier powder diffraction. This technique also shows that the phases occur in the same structure types as reported earlier for analogous phases stabilized by interstitial carbon, etc.[3,4,8,9] Single-crystal X-ray structure determinations have also been performed on $Cs_{0.63}Zr_6I_{14}Fe$, $CsZr_6I_{14}Mn$, and $Sc_7I_{12}Co$.

The principal structural points of interest involve the bonding within the clusters. The Zr_6 cluster in $Cs_{0.63}Zr_6I_{14}Fe$ is expanded to give a mean Zr–Zr distance of 3.51 Å while the average Sc–Sc distance in $Sc_7I_{12}Co$ is 3.44 Å. These distances are to be compared with 3.28 and 3.26 Å in the corresponding iodide carbides. Relatively short Zr–Fe and Sc–Co distances of 2.48 and 2.43 Å, respectively, are also found. In the series of $M_6X_{12}Z$-type cluster compounds, these new examples are near the terminus where

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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.

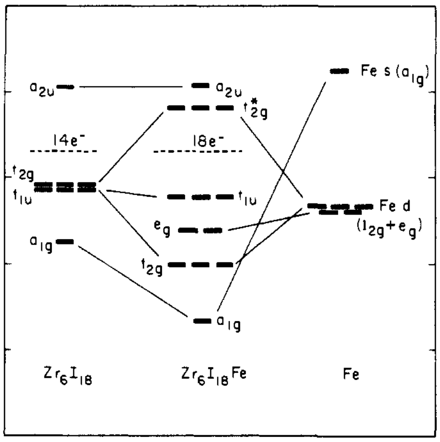

Figure 1. Molecular orbital interaction diagram for $(Zr_6I_{12}Fe)I_6^{4-}$. Iron contributions to the MO's shown are the following: a_{1g}, 25% s; t_{2g}, 41% d; e_g, 89% d; t_{1u}, 7.4% p; t^*_{2g}, 54% d; a_{2u}, 0%. Note how the inclusion of the pair of nonbonding Fe e_g levels changes the cluster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

Carla E. A. M. Degenhardt, George R. Van Den Berg,
Leo P. A. De Jong, and Hendrik P. Benschop*

Prins Maurits Laboratory TNO
2280 AA Rijswijk, The Netherlands

John Van Genderen and Dory Van De Meent

Medical Biological Laboratory TNO
2280 AA Rijswijk, The Netherlands

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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-

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(1) **WARNING**: nerve agents are extremely toxic and should be handled only in laboratories where specifically trained medical personnel is available.

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