in a −20 °C freezer overnight afforded the product as very pale amber crystals; yield 1.1 g, 63%, mp = 158–160 °C (dec). In the case of cobalt, $CoCl_2$ was used to give a 65% yield of turquoise-dark green dichroic crystals; mp = 147–150 °C (with softening ca. 100 °C).

The structures of **1** and **2** were determined by X-ray crystallography[18] and are illustrated in Figures 1 and 2. Both compounds are monomeric with iron and cobalt bonded to two $-N(SiMePh_2)_2$ groups which are planar at nitrogen. Considerable deviation from the expected N–M–N linearity is apparent in the cobalt complex **2** and to a lesser degree in the iron complex **1**. Outside of d^{10} complexes and two[19] d^5, Mn(II) complexes[20,21] both **1** and **2** constitute rare instances of crystalline, two-coordinate transition-metal compounds, and they are the first such examples for the d^6 or d^7 configurations. In the iron compound the N(1)FeN(2) angle is 169.0 (1)° with an average Fe–N distance of 1.917 (2) Å, which is significantly longer than the 1.84 (2) Å seen in Fe$\{N(SiMe_3)_2\}_2$ vapor.[13] There is a rather long interaction between Fe and C(14) of about 2.7 Å and this is reflected in the assymetry of the FeN(1)Si(1) and Si(2) angles 121.9 (1)° vs 106.1 (1)°. The closest approach of any other phenyl carbons varies from about 2.96 to 3.2 Å, and any such interactions are consequently very weak. This fact is in agreement with the essentially symmetric nature of the FeN(2)Si(3) and Si(4) angles.

In contrast to **1** the central angle, 147.0 (1)°, in the cobalt complex **2** displays much more deviation from linearity. This appears to be a result of the interaction between the metal center and a phenyl ring from each $-N(SiMePh_2)_2$ group as shown by the distances CoC(7) = 2.588 (7) Å and Co–C(27) = 2.584 (7) Å. These interactions are supported by the large asymmetries (≈27°) in the CoNSi angles which are 103.4 (2)° (av) for CoNSi (1 and 3) and 130.5 (2)° (av) for CoNSi (2 and 4); however, detailed examination of the Si–N and C–C distances within the $-N(SiMePh_2)_2$ groups reveal little or no differences which would support the observed distortions. Although the metal centers are electron deficient, a fact which encourages the aromatic ring–metal interaction, there is no ready qualitative explanation for the structural differences between **1** and **2**. Quite possibly, the NMN angle is a "soft" one and even relatively weak interactions elsewhere in the molecule or, perhaps, crystal packing forces can effect large changes in this parameter.

The absorption spectra of both **1** and **2** were recorded in toluene at ambient temperature. The spectrum of **1** is almost featureless in the 400 → 800-nm region with slow rise in absorption toward the UV. A very weak shoulder at 560 nm (17 900 cm^{-1}) is apparent. The spectrum of the cobalt compound **2** displays three absorptions at 526 nm (19 010 cm^{-1}, $\epsilon = 70$), 634 nm (15 770 cm^{-1}, $\epsilon = 125$), and 802 nm (12 470, $\epsilon = 50$). If a linear, two-coordinate geometry is assumed for **2**, then these bands can be assigned[22] to the $^4\Sigma_g \rightarrow {}^4\Pi_g(P)$, $^4\Sigma_g \rightarrow {}^4\Sigma_g(P)$, and $^4\Sigma_g \rightarrow {}^4\Delta_g(F)$ transitions. However, a structural assignment on this basis is not possible, because the three observed bands are also consistent[23] with an approximate trigonal planar (as in a dimer) or a C_{2v} geometry as seen in the X-ray structure. The spectrum of **2** is, in fact, similar to that of solid Co$\{N(SiMe_3)_2\}_2$, which is a dimer, and $CoCl_2$ vapor, which is a linear monomer. Little can be said about the spectrum of **1**, except that within the scan range 300–850 nm it is similar to that of $FeCl_2$ vapor.[24]

It is planned to synthesize other metal (Cr, Mn, Ni) derivatives so that further conclusions may more readily be drawn. In addition, detailed ^1H NMR and magnetic studies on these interesting, two-coordinated species are currently underway.

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Supplementary Material Available: Summary data collection and refinement, tables of atom coordinates, thermal parameters, bond distances and angles, and hydrogen coordinates (15 pages). Ordering information is given on any current masthead page.

(18) Crystal data with Mo Kα (λ = 0.71069 Å) radiation at 130 K: **1**, $C_{52}H_{52}FeN_2Si_4$, $a = 10.928$ (3) Å, $b = 15.337$ (5) Å, $c = 26.855$ (7) Å, $\beta = 91.75$ (2)°, $Z = 4$, monoclinic, space group, $P2_1/c$, $R = 0.039$; **2**, $C_{52}H_{52}CoN_2Si_4$, $a = 13.436$ (3) Å, $b = 10.570$ (2) Å, $c = 32.807$ (16) Å, $\beta = 99.06$ (2)°, $Z = 4$, monoclinic $P2_1/c$, $R = 0.049$.

(19) There are now four mononuclear Mn(II) species which are known to be two-coordinate at or near ambient temperature. Two of these involve X-ray structures of solids[20,21] and two are diffraction studies of the vapors of Mn$\{N(SiMe_3)_2\}_2$[13] and $Mn(CH_2\text{-}t\text{-}Bu)_2$. Andersen, R. A.; Haaland, A.; Rypdal, K.; Volden, H. V. *J. Chem. Soc., Chem. Commun.* **1985**, 1807.

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A Synthetic Peptide Binds 16 Base Pairs of A,T Double Helical DNA

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One approach to the design of synthetic sequence specific DNA binding molecules that bind large sequences of double helical DNA is to couple together DNA binding domains of similar or diverse base pairs specificities.[1] The DNA binding domains should be linked together in a way that allows simultaneous binding of the units to contiguous DNA sequences.

Netropsin and distamycin are crescent-shaped di- and tripeptides containing two and three *N*-methylpyrrolecarboxamides, respectively. These natural products bind in the minor groove of B-DNA with a strong preference for A,T sequences.[2-6] X-ray analysis of the complex formed between netropsin and the duplex, 5′-CGCGAATTCGCG-3′, revealed that netropsin sits in the center of the minor groove of the DNA. Each of the three amide groups of netropsin forms bifurcated hydrogen bonds between adjacent adenine N3 or thymine O2 atoms on opposite strands of the helix.[4] We have previously shown that analogues of distamycin with four to six *N*-methylpyrrolecarboxamides (P4, P5, P6) bind six to eight base pairs of A,T DNA, respectively.[7,8] Recognition of larger sequences of A,T DNA sites by synthetic

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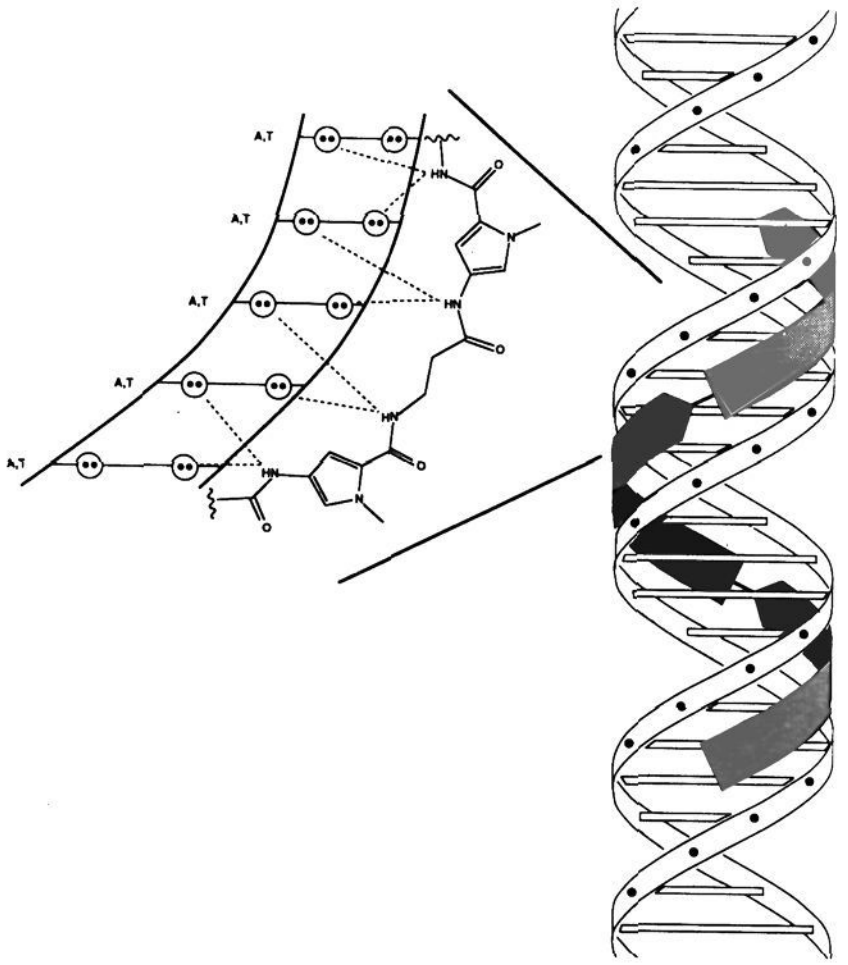

Figure 1. Model for trimer of tetra-*N*-methylpyrrolecarboxamide connected by β-alanine binding to the minor groove of DNA.

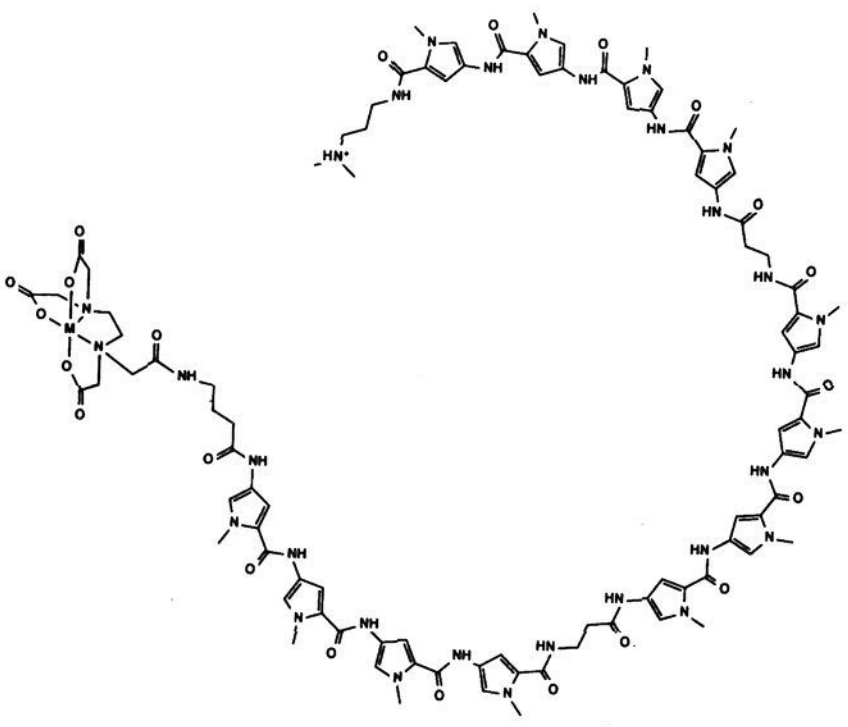

Figure 2. Structure of peptide $(P4)_3E$. M = In(III) which complexes the EDTA and allows the peptide to bind but not cleave the DNA. This is used in the MPE·Fe(II) footprinting (cleavage protection) studies. M = Fe(II) for the affinity cleaving reaction.

molecules has been achieved by using dimers of distamycin.[9-13] Bis(EDTA-distamycin)fumaramide, an octamide containing two tripeptides coupled tail-to-tail via amino termini to fumaric acid,

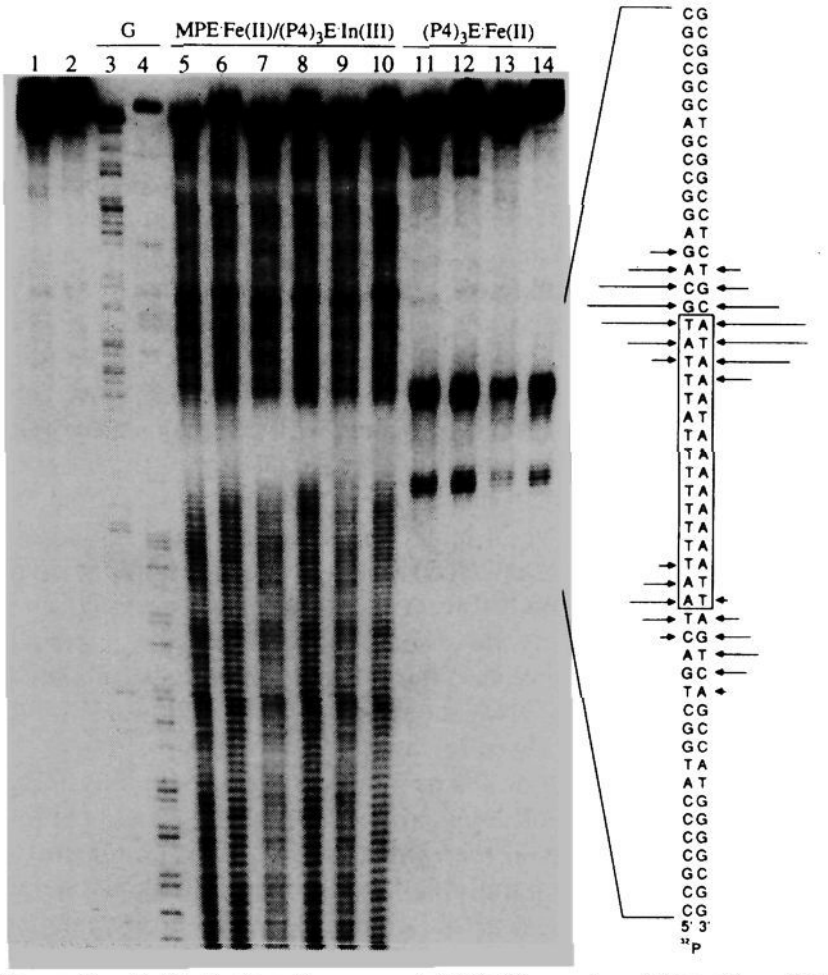

Figure 3. (left) Autoradiogram of 5′ (odd-numbered lanes) and 3′ (even-numbered lanes) ^{32}P end-labeled 205 bp fragment from SV 40 run on a high resolution denaturing gel. Lanes 1 and 2 are intact DNA control lanes incubated under reaction conditions; lanes 3 and 4 are chemical sequencing lanes containing the products of Maxam–Gilbert G reactions; lanes 5 and 6 are DNA cleavage reactions containing 3 μM MPE·Fe(II); lanes 7 and 8 are DNA cleavage reactions containing 3 μM MPE·Fe(II) and 1 μM $(P4)_3E$·In(III); lanes 9 and 10 are DNA cleavage reactions containing 3 μM MPE·Fe(II) and 0.3 μM $(P4)_3E$·In(III); lanes 11 and 12 are DNA cleavage reactions containing 1 μM $(P4)_3E$·Fe(II); lanes 13 and 14 are DNA cleavage reactions containing 0.3 μM $(P4)_3E$·Fe(II). (right) Histograms derived from densitometry of autoradiogram. Arrows represent amount of cleavage resulting in removal of indicated base. Boxes define binding site location and size based on model described in ref 1.

binds nine base pairs of A,T DNA.[11] Recent studies in our group suggest that β-alanine may be an effective linking group for *N*-methylpyrrolecarboxamides connected in a *head-to-tail* sense.[14]

We report the synthesis of a peptide $(P4)_3E$ that is a trimer of tetra-*N*-methylpyrrolecarboxamide[7] coupled head-to-tail by β-alanine (Figures 1 and 2).[15] Attachment of EDTA to the amino terminus of the peptide allows the use of the affinity cleaving method[1,3] to determine the binding site size, sequence, orientation preference, and groove location through analysis of cleavage patterns on a ^{32}P end-labeled DNA restriction fragment. In addition, the binding site location and size were confirmed by MPE·Fe(II) footprinting (cleavage inhibition) with $(P4)_3E$·In(III), a molecule which is competent to bind but not cleave DNA. This synthetic peptide binds 16 base pairs of DNA in the minor groove.

The DNA used in these studies was a 205 base pair restriction fragment which includes the SV40 promoter region (5174–5129) cloned into a pUC18 plasmid.[16] The DNA was labeled separately at both the 3′ and 5′ ends of an Xba I derived restriction fragment with use of standard techniques. The end-labeled DNA (100 μM in bp) was allowed to equilibrate with $(P4)_3E$·Fe(II) or $(P4)_3E$·In(III) (1–0.3 μM) at peptide/DNA base pair ratios of 0.01–0.003 for 1 h at 67 °C. In the footprinting reactions with $(P4)_3E$·In(III), cleavage was initiated by the addition of MPE·Fe(II) and dithiothreitol (37 °C, pH 7.6). The cleaving reactions with $(P4)_3E$·Fe(II) were initiated by the addition of

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dithiothreitol (37 °C, pH 7.6). The DNA fragments were visualized by autoradiography of a high resolution denaturing gel, and the extent of DNA cleavage was quantitated by densitometry (Figure 3). Footprinting reactions revealed cleavage inhibition at the sequence 5′-AATTTTTTTTATTTAT-3′. The affinity cleaving reactions showed two cleavage patterns, asymmetric to the 3′ side, flanking this same 16 bp stretch of A,T DNA.

According to the $n + 1$ rule,[7a] peptide $(P4)_3E$ which contains 15 amide groups suitable for DNA recognition should bind 16 contiguous base pairs of A,T DNA (Figures 1 and 2). The correspondence of the cleavage loci for $(P4)_3E$·Fe(II) flanking the same 16 bp site as the cleavage inhibition patterns (footprinting) for $(P4)_3E$·In(III) is consistent with one major recognition mode for the peptide at that site. The asymmetry of the observed cleavage patterns to the 3′ side confirms that the peptide is binding in the minor groove of right-handed DNA. The cleavage intensity flanking the 16 bp site is 2:1 which suggests two binding orientations that are not too different in energy. The observation of 16 base pair binding in the absence of obvious dimeric binding (11 base pairs) or monomeric (six base pairs) demonstrates that, at least for this 16 bp DNA sequence, β-alanine allows simultaneous binding of the three tetrapeptide subunits.

In summary, a peptide, 14 amino acid residues in length, has been constructed which is capable of binding 16 base pairs of contiguous A,T DNA in the minor groove. This demonstrates the feasibility of linking multiple DNA-binding subunits together to produce a synthetic scaffold amenable to further refinement that can bind a turn and a half of the DNA helix[17] in a sequence-specific fashion.

Acknowledgment. We are grateful to the National Institutes of Health for research support (GM-27681).

(17) Netropsin binds DNA in the B-form.[4] If the $(P4)_3E$:DNA complex is in the B-form (average 10.4 bp/turn), then this synthetic peptide binds a turn and one-half of the DNA helix.

Catalytic Oxidative Cleavage of Vicinal Diols and Related Oxidations by Ruthenium Pyrochlore Oxides: New Catalysts for Low-Temperature Oxidations with Molecular Oxygen

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Oxidative cleavage of vicinal diols constitutes a key reaction encountered in the determination of carbohydrate structure[1] and in the metabolism of various polyhydroxylated substances.[2] Although stoichiometric high-valent oxidants are well-known reagents for glycol cleavage,[3] efficient nonenzymatic systems that function with molecular oxygen are relatively rare.[4,5] During evaluation of possible catalysts for the oxidative cleavage of various carbohydrates to yield ether polycarboxylates, reports appeared

Table I. Oxidation of 1,2-Cyclohexanediol, 1,6-Hexanediol, and Cyclohexanone by Ruthenium Pyrochlore Oxide Catalysts

A. Batch Autoclave Reactor Oxidations[a,b]

catalyst	substrate	T, °C	time, h	substrate conv,[c] %	sel,[d] %
$Pb_{2.62}Ru_{1.38}O_{6.5}$	TCD	25	7.00	100.0	71.7
$Pb_{2.62}Ru_{1.38}O_{6.5}$	CCD	25	4.00	98.5	74.6
$Pb_{2.15}Ru_{1.85}O_{6.5}$	TCD	25	7.17	45.4	57.7
$Pb_{2.00}Ru_{2.00}O_{6.5}$	TCD	35	1.00	11.0	0.0
$Bi_{2.46}Ru_{1.54}O_{7-y}$	TCD	40	6.33	70.0	99.6
$Pb_{2.63}Ru_{1.37}O_{6.5}$	HD	55	6.00	100.0	57.0
$Pb_{2.62}Ru_{1.38}O_{6.5}$	CHO	30[e]	1.42[f]	100.0	68.9

B. Continuous Trickle Bed Reactor Oxidations[g]

catalyst	substrate	T, °C	contact time,[h] h	substrate conv,[c,i] %	sel,[d,i] %
$Pb_{2.63}Ru_{1.37}O_{6.5}$	TCD	55	0.21	99.8	85.6
$Bi_{2.39}Ru_{1.61}O_{7-y}$	TCD	55	0.21	99.7	86.8
$Bi_{2.86}Ru_{1.14}O_{7-y}$	TCD	95	0.056	100.0	81.0
		95	0.021	65.2	74.2
$Bi_{2.39}Ru_{1.61}O_{7-y}$	HD	95	0.062	100.0	91.3

[a] Performed in a 300-mL 316-stainless steel Autoclave Engineers reactor with 4.00 g of below 325 mesh powder, 100 mL of 0.517 M substrate in 1.5 N NaOH, 100 psi O_2 pressure, and an agitation rate of 1500 rpm. [b] Abbreviations: conv = conversion; sel = selectivity; TCD = *trans*-1,2-cyclohexanediol; CCD = *cis*-1,2-cyclohexanediol; HD = 1,6-hexanediol; CHO = cyclohexanone. [c] Analyses were made on 100-μL aliquots acidified with 100 μL of 1.5 N HCl. Samples were evaporated, taken up in 100 μL of pyridine containing xylitol as an internal standard, and then converted to the trimethylsilyl derivatives with ca. 0.3 mL of Regis RC-3 reagent (100 °C, 30 m). Portions of 0.2 μL were injected onto a methyl silicone capillary column in a gas chromatograph with FID that was programmed as follows: 100–250 °C at 8 °C/m with an 8-m hold at 250 °C. [d] Calculated selectivity to adipic acid product. Minor amounts of glutaric and succinic acids were observed (trimethylsilyl derivatives); all compounds were confirmed by GC/MS analysis. [e] Average temperature recorded throughout the oxidation. [f] Used 9.00 g (0.092 mol) CHO in 150 mL of 1.5 N NaOH. [g] Performed in 3.2-mm glass-lined tubing as a reactor containing 40–60 mesh (0.373–0.250 mm) catalyst particles packed between 0.12–0.18-mm glass beads with ca. 0.5 M substrate in 1.5 N NaOH, 100 psi O_2 pressure, and a downflow feed of liquid substrate and 30–45 cc/m O_2. [h] Contact time = volume of catalyst/volumetric substrate flow rate. [i] Average values for multiple samples taken at the conditions given; see Table IVS.[17]

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