typically underestimated by a factor of 2, to cast doubt on the significance of this feature (Tables I and II).

In the structure determination at 110 K reported here, the esd's are lower by a factor of 3, and the corresponding Pt–C bond distances (2.172 (6), 2.154 (5), 2.176 (6), 2.178 (6) Å) are much closer to being equivalent. Again assuming that X-ray standard deviations given by the refinement are underestimated by a factor of 2, the possibility that the bond distances are equivalent cannot be rejected on the basis of a χ^2 test at the 0.10 significance level.[7]

An ORTEP drawing[8] of the molecule is shown in Figure 1. The important features to note in the structure of (COD)PtCl$_2$ are as follows: (i) The COD molecule is symmetrically coordinated to the Pt atom. (ii) The ethylene portions of the COD molecule are twisted to avoid eclipsing, which lowers the point group symmetry of the molecule to C_s. (iii) The coordinated C=C double bonds are lengthened (1.375 (8) and 1.387 (8) Å) by an amount comparable to that found in the isomorphous palladium complex[9] and other similar systems.[10] This is contrasted with a double-bond distance of 1.334 Å in the cyclooctatetraene molecule[11] and 1.316 and 1.320 Å bond distances for the uncoordinated double bonds in dichloro(cyclooctatetraene)palladium(II).[10c] The Pt–Cl bond distances are in the range of those observed in similar structures.[12]

Acknowledgment. This contribution is based upon work supported by the National Science Foundation (Grant CHE8311704). Funds for the purchase of an automated diffractometer were also provided in part by the National Science Foundation (Grant CHE 8208754).

Registry No. (COD)PtCl$_2$, 12080-32-9.

Supplementary Material Available: Tables of positional and thermal parameters for H atoms, bond angles involving H atoms, and anisotropic thermal parameters for non-hydrogen atoms and a listing of observed and calculated structure factors (24 pages). Ordering information is given on any current masthead page.

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(4) The title compound crystallizes in the space group $P2_12_12_1$ with a = 6.818 (1) Å, b = 10.664 (2) Å, c = 12.423 (4) Å, Z = 4, D_{calcd} = 2.751 g cm^{-3}, and μ = 81.1 cm^{-1}. The intensities of 2265 unique reflections ($2\theta_{max}$ = 60°), were collected from a crystal of approximate dimensions 0.39 × 0.40 × 0.33 mm, on a CAD4 diffractometer in ω–2θ scan mode by using graphite-monochromated Mo Kα (λ = 0.71069 Å) radiation. Temperature was maintained at 110 (2) K with a cold stream of N$_2$ gas. A numerical absorption correction based on the measured shape of the crystal was applied (transmission factors: max = 0.172 min = 0.089). A total of 2032 reflections with $I > 3\sigma(I)$ was included in the least-squares refinement. The structure was solved by MULTAN 11/82: Main, P.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. "MULTAN 80", A System of Computer Programs for Automatic Solution of Crystal Structures from X-ray Diffraction Data"; Universities of York and Louvain: York, England and Louvain, Belgium, 1980. In the refinement process by full-matrix least-squares techniques, anisotropic temperature factors were applied for all non-hydrogen atoms in the symmetric unit. Hydrogen atoms were input at their calculated positions (d_{C-H} = 0.95 Å) and used in the structure factor calculations but not refined. Final refinement included an isotropic extinction parameter, giving a total of 101 parameters. At convergence, $R = \sum(||F_o| - |F_c||)/\sum|F_o| = 0.028$ and $R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.035$ where $w = 1/\sigma^2(F_o)$. The goodness of fit indicator $[\sum w(|F_o| - |F_c|)^2/(N_{observns} - N_{parameters})]^{1/2}$ was 1.437. A difference Fourier done at this stage did not show any significant peaks. Least-squares refinement of the structure with atomic positions inverted through a center of symmetry gave R = 0.048 and R_w = 0.062, indicating that the absolute configuration originally chosen for the structure was correct. Atomic scattering factors and anomalous dispersion corrections were taken from: "International Tables for X-Ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV. All the computations were performed on a PDP11/34 computer using the SDP system: Frenz, B. A. "Enraf-Nonius Structure Determination Package"; Enraf-Nonius: Delft, 1982.

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Micelle-Trapped Tris(benzhydroxamato)iron(III) as a Siderophore Model Compound

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The central coordination units of microbial siderophore iron transport compounds are chelate iron(III) complexes of hydroxamate or catecholate ligands.[1-8] In important respects the properties of "simple" (hydroxamato)- or (catecholato)iron(III) complexes can therefore be expected to represent those of the biological iron compounds. In hydroxamato siderophore complexes the iron coordination center is, however, shielded from the external aqueous medium by a "shell" constructed from the organic backbone of a multibasic aliphatic hydroxamato ligand system, the carboxylic acid constituent of which is commonly the acetyl group and which possesses on the outside a dipolar structure due to attachment of strongly polar groups at the surface. These surface properties also lead to formation of a diffuse double layer around the siderophore and in this way provide control for the access of potential reactant molecules to the iron core.

The dipolar and double-layer effects are not reproduced by simple hydroxamato complexes. On the other hand, we show in the present work that iron(III) complexes of apolar hydroxamate ligands, represented here by tris(benzhydroxamato)iron(III) (TBH), can be trapped in anionic micelles. This compound has previously been forwarded as a siderophore model compound.[4-6] It is a shortcoming of this particular compound that the acid group is aromatic, whereas those of real siderophores are acyclic and very commonly the

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acetyl group. In contrast to simpler acylic hydroxamates it is, however, quite insoluble in water but solubilizes smoothly when the anionic micelle is present. In aqueous solution the complex is thus present solely on micellized form that strongly facilitates investigations of the complex in this form. Also, it appears that negatively charged groups on the micelle surface lead to significant double-layer effect, as reflected in the ionic charge distribution at the micelle surface. These effects represent a simulation of the dipolar double layer in siderophores that is absent in simple, soluble hydroxamato complexes.

Experimental Section

TBH and the analogous complex of salicylhydroxamic acid were prepared from AnalaR $Fe(NO_3)_3 \cdot 9H_2O$ and the hydroxamic acids as previously reported[9] and were recrystallized from aqueous ethanol. Other reagents were commercial AnalaR grade products. Solutions were prepared from weighed amounts of solute and Millipore water or AnalaR grade organic solvent.

Stability constants were measured and kinetic runs followed spectrophotometrically by means of a Beckman DBG spectrophotometer fitted with a Radiometer REC 61 Servograph x-t recorder and thermostated quartz cells. A Radiometer PHM 28 pH meter fitted with glass 202C and calomel K 401 electrodes was used for pH measurements and a Radiometer PO4 polarograph for recording of polarographic waves. Reported stability constants refer to 0.05 mol dm^{-3} Tris buffer solutions at 25 ± 0.2 °C. This buffer can maintain pH at 7.00 and ensures both thermodynamic stability and electroneutrality of the iron(III) complexes, which are deprotonated at higher pH.[5] Phosphate buffers of the same pH appeared to destroy the complexes completely. Solutions of variable pH were prepared by adding the appropriate amount of perchloric acid to the solutions.

Results and Discussion

TBH is insoluble in water but dissolves readily in mixed aqueous solvents containing a comparable volume of methanol, ethanol, dioxane, acetonitrile, or dimethyl sulfoxide. It also dissolves in water and 0.05 mol dm^{-3} aqueous Tris buffer to which sodium dodecyl sulfate (SDS) has been added in sufficient amount both to exceed the critical micelle concentration (CMC) and to ensure that the concentration of micelles, each containing about 60 SDS molecules,[10] exceeds the total iron(III) concentration, [Fe(III)]. The CMC is 8×10^{-3} mol dm^{-3} for pure water,[10,11] but lower for finite ion concentrations,[10,12] being 2.3×10^{-3} mol dm^{-3} for 0.05 mol dm^{-3} sodium chloride.[11] In most cases, the SDS concentration was 3.4×10^{-2} mol dm^{-3} and $[Fe(III)] = 1.8 \times 10^{-4}$ mol dm^{-3} corresponding to a micelle:Fe(III) ratio of about 3:1. This value ensures that all iron is micellized, but from a purely statistical view trapping of more than a single iron(III) complex molecule in a particular micelle cannot be excluded. However, multiple trapping appears unlikely for steric reasons as two iron complex molecules would reach almost across the hydrophobic interior of the micelle. Also, our subsequent conclusions concerning double-layer effects remain valid in qualitative terms if multiple trapping should occur, and different figures for stability constants and double-layer potentials only emerge if the stability constants of individual, multiply trapped complexes are different.

In the pure organic solvents the complex possesses broad, rather solvent-insensitive, absorption bands with a maximum at 435 nm. Beer's law is well obeyed in the range (5–25) × 10^{-5} mol dm^{-3} and gives molar extinction coefficients at the maximum, ϵ_{max}, ranging from 3.92×10^4 dm^2 mol^{-1} in methanol to 3.45×10^4 dm^2 mol^{-1} in dioxane. Addition of water leads to pronounced absorption decrease and a slight shift toward longer wavelengths. ϵ_{max} is thus 1.93×10^4 dm^2 mol^{-1} for 1:1 (v/v) dioxane/water. For pure acetonitrile, ϵ_{max} is 3.50×10^4 and 2.55×10^4 dm^2 mol^{-1} for 2:3 (v/v) acetonitrile/water. These effects appear to be caused partly by dissociation of the complex, and the absorption band in the mixed solvents thus represents absorption of two species, as addition of excess benzhydroxamic acid leads to an increase of ϵ_{max}. The value for the pure organic solvent is, however, not recovered. ϵ_{max} thus reaches a limiting value of 2.75 × 10^4 dm^2 mol^{-1} in 2:3 (v/v) acetonitrile/water as free ligand is added, indicative of specific solvent effects on the absorption spectrum, perhaps from hydrogen bonding.

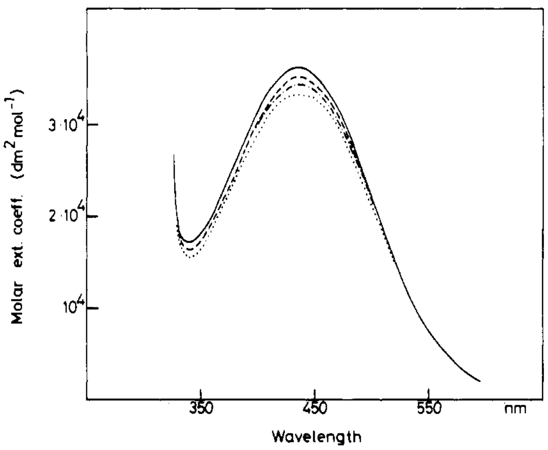

Figure 1. Molar extinction coefficients for different $[HL]_{ad}$ ($[Fe(III)] = 2.013 \times 10^{-4}$ mol dm^{-3}; $[Tris] = 5.00 \times 10^{-2}$ mol dm^{-3}; pH 7.00; $[SDS] = 3.36 \times 10^{-2}$ mol dm^{-3}): (···) $[HL]_{ad} = 0$; (–·–) $[HL]_{ad} = 0.490 \times 10^{-4}$ mol dm^{-3}; (- - -) $[HL]_{ad} = 1.962 \times 10^{-4}$ mol dm^{-3}; (—) $[HL]_{ad} = 49.04 \times 10^{-4}$ mol dm^{-3}.

Variation of the apparent molar extinction coefficient at the wavelength 435 nm, ϵ_{435}, with the concentration of benzhydroxamic acid, [HL], in the range (1–6) × 10^{-3} mol dm^{-3} is compatible with a value of (2 ± 0.3) × 10^4 dm^3 mol^{-1} for the equilibrium constant $[FeL_3]/[FeL_2^+][HL]$ in 2:3 (v/v) acetonitrile/water, 0.05 mol dm^{-3} in Tris buffer. pK_A for HL in this solvent is not known. The value of 8.79 reported for water[13] can be taken as a lower limit since less dissociation occurs in the less polar solvent. Drastic differences are, however, not necessarily expected since the proton is strongly preferentially solvated by water in mixed aqueous solvents. pK_A for water then gives a lower limit of (1.2 ± 0.2) × 10^6 dm^3 mol^{-1} for the third consecutive equilibrium constant of the iron complex, K_3, i.e. for the process

$$FeL_2^+ + L^- \rightleftarrows FeL_3 \qquad (1)$$

in 2:3 (v/v) acetonitrile/water. In comparison, the value 2.5 × 10^7 dm^3 mol^{-1} has been reported for 0.1 mol dm^{-3} aqueous perchlorate.[13,14]

Polarographic reduction of TBH at a dropping-mercury electrode in 3:1 (v/v) dioxane/water containing 0.05 mol dm^{-3} Tris buffer gives a single diffusion-controlled wave with a half-wave potential of −0.59 V against a saturated calomel electrode. In comparison, a single reduction wave, with a half-wave potential of −0.48 V, is also obtained for the salicyhydroxamato complex, but the limiting current is here independent of the mercury drop rate, indicative of kinetically controlled predissociation of the complex. In the presence of excess benzhydroxamic acid the current–voltage plots display a nonmonotonous dependence of the current on the overpo-

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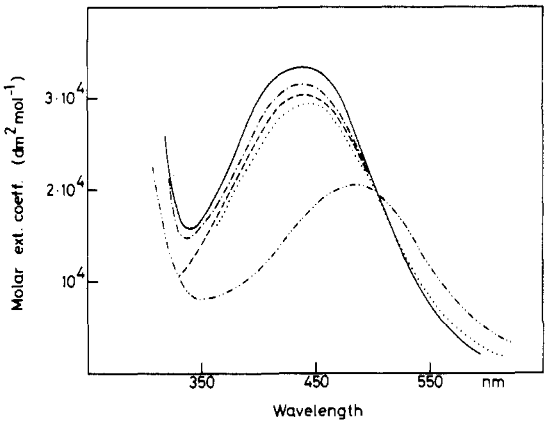

Figure 2. Molar extinction coefficients for different values of pH ($[HL]_{ad} = 48.75 \times 10^{-4}$ mol dm^{-3}; $[Fe(III)] = 1.84 \times 10^{-4}$ mol dm^{-3}; $[SDS] = 3.36 \times 10^{-2}$ mol dm^{-3}): (—) pH 7.00; (-·-) pH 6.22 (no buffer added); (---) pH 5.74; (···) pH 5.16; (-··-) pH 3.55.

tential for large cathodic overvoltages, presumably due to adsorption of the free ligand at the mercury surface.

TBH trapped in SDS micelles in aqueous 0.05 mol dm^{-3} Tris buffer of pH 7.00 exhibits rather similar features as in the organic solvents. Without excess HL, ϵ_{max} is thus 3.33×10^4 dm^2 mol^{-1} at the maximum wavelength of 435 nm. Figure 1 shows the spectral changes when increasing amounts of HL are added. These changes are compatible with eq 1, according to the equation

$$\frac{1 + [HL]_{ad}/[Fe(III)]}{\epsilon_{435} - \epsilon_2} = \frac{1}{\epsilon_3 - \epsilon_2} + \frac{[H^+]}{[Fe(III)]}\frac{1}{K_AK_3}\frac{1}{\epsilon_3 - \epsilon_{435}} \qquad (2)$$

with no detectable contribution from the mono complex FeL^{2+}. $[HL]_{ad}$ is the concentration of added HL. The following values of the molar extinction coefficients for FeL_2^+ (ϵ_2) and FeL_3 (ϵ_3) and of K_3 constitute the best fit to the data: $\epsilon_2 = (2.7 \pm 0.2) \times 10^4$ dm^2 mol^{-1} $\epsilon_3 = (3.6 \pm 0.1) \times 10^4$ dm^2 mol^{-1}; $K_3 = (1.8 \pm 0.2) \times 10^6$ dm^3 mol^{-1}. The value of K_3 is based on $pK_A = 8.79$ for HL. While pK_A may in fact differ from this value, it is not expected to do so by a large amount since it still represents an equilibrium constant in the aqueous phase, but close to the micelle surface where ligand exchange is likely to occur.

With this reservation, K_3 is then smaller by an order of magnitude than values previously obtained for aqueous perchlorate solution from glass electrode measurements.[13] It is, however, rather close to the value obtained above as a lower limit for an acetonitrile/water solution. Field effects from the anionic micellar surface groups on the negatively charged external ligand group L^- therefore appear to be of minor importance.

Significant effects are, however, observed if the free ligand concentration is controlled by pH variation. Figure 2 shows the spectral changes by pH variation in the range from 7.0 to 5.0. These data were reproduced by eq 1 and 3, a plot of

$$\log\left[\frac{\epsilon_3 - \epsilon_2}{\epsilon_3 - \epsilon_{435}} - 1\right] = \log(K_3K_A[HL]) + pH \qquad (3)$$

which is shown in Figure 3. The best fit was here obtained for molar extinction coefficients that coincide, within experimental accuracy, with the ones obtained by varying [HL] at constant pH, while K_3 is now $(7 \pm 1) \times 10^4$ dm^3 mol^{-1}, i.e. smaller by a factor of 23. This result is unaffected if the value of pK_A is different from 8.79, as long as this value is the same when $[H^+]$ and [HL] are varied. The difference is understandable if protons are attracted by the anionic micellar groups. Close to the iron(III) complex location the local value of $[H^+]$ is then larger than in the bulk. This leads to increased complex dissociation, or an apparently smaller stability constant. Since the surface groups (sulfate) also form strong hydrogen bonds, it is expected that such field effects are particularly pronounced for proton attachment, and much less important for large, non-hydrogen bonded ligand groups.

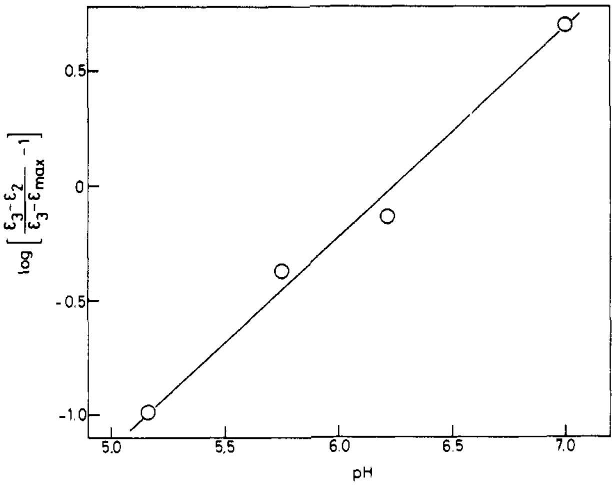

Figure 3. Plot of eq 3 for $\epsilon_2 = 2.8 \times 10^4$ dm^2 mol^{-1} and $\epsilon_3 = 3.60 \times 10^4$ dm^2 mol^{-1} ($[Fe(III)] = 1.84 \times 10^{-4}$ mol dm^{-3}; $[HL]_{ad} = 5.22 \times 10^{-3}$ mol dm^{-3}; $[SDS] = 3.36 \times 10^{-2}$ mol dm^{-3}; $[Tris] = 5.00 \times 10^{-2}$ mol dm^{-3}).

If the difference between the two stability constant values in fact reflects proton concentration differences at the micelle surface and in the bulk, the average proton location has an electrochemical potential, ΔV, of about −80 mV relative to the bulk, when this potential is estimated as a concentration potential, i.e. from the relation $\Delta V = -(RT/eF)\ln([H^+]_s/[H^+]_b)$, where R is the gas constant, T is the absolute temperature, e is the proton charge, F is Faraday's number, and the indices s and b refer to $[H^+]$ at the micelle surface and in the bulk, respectively. This is surprisingly close to the −75 mV calculated for the ζ potential of SDS in 0.05 mol dm^{-3} aqueous sodium chloride on the basis of electrophoretic mobility data and the assumption that the solvent can be regarded as a structureless dielectric.[11,15] The ζ potential is here the potential at the surface of the first micelle hydration layer, and real coincidence between the two potentials would then suggest that this is a likely average location for those protons that interact with micelle-trapped iron(III).

TBH in mixed aqueous and organic solvents has rather low standard redox potentials (cf., ref 5 and 6 and the half-wave potential reported above). The complex is, however, reduced smoothly by sodium dithionate and ascorbic acid, also in the micelle-trapped state. Preliminary kinetic investigations of the reduction of TBH by ascorbic acid have provided the following information concerning the mechanism of this reaction:

(1) Addition of a 10-fold or larger excess of ascorbic acid rapidly induces a small but detectable spectral shift that is followed by slower irreversible iron(III) decay. The half-life in 3:1 (v/v) dioxane/water containing 0.05 mol dm^{-3} Tris buffer of pH 7.00 (where monoprotonated ascorbate is the dominating form[16]), 4×10^{-3} mol dm^{-3} ascorbic acid (40-fold excess), and 2×10^{-4} mol dm^{-3} excess HL is about 100 s, but somewhat larger for micelle-trapped iron(III).

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(2) The rate is approximately inversely proportional to $[HL]_{ad}$ and practically vanishes for large $[HL]_{ad}$.

These features strongly suggest that the process proceeds by ligand dissociation, followed by complex formation between FeL_2^+ and ascorbic acid and electron transfer inside this complex.

(3) Such a pathway is supported by the reaction orders. The initial rate in both organic solvents and micelles is first order with respect to iron(III) for $[Fe(III)] \lesssim 10^{-4}$ mol dm^{-3} and a large excess of ascorbic acid. At higher [Fe(III)] "saturation" with slower rate variation with [Fe(III)] appears. The rate dependence on the ascorbic acid concentration is "S-shaped", approaching a limiting value for large concentrations, but tends toward first-order dependence for small concentrations.

Ligand substitution is thus apparently of rather crucial importance in the release of iron from the micelle-trapped complex by reduction with ascorbic acid. The double-layer effects from the polar micelle surface groups will therefore exert a pronounced influence not only on the thermodynamic stability of the iron complex but also on the kinetics of the release by ascorbic acid reduction.

Registry No. TBH, 67009-50-1; ascorbic acid, 50-81-7.

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Synthesis and Characterization of an Oxygen-Bridged Vanadium(III) Dimer

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Dinuclear and polynuclear oxygen-bridged compounds of vanadium occur mainly in the higher valence states of the transition metal, primarily as oxides[1,2] and vanadates in aqueous solution,[3,4] while they are virtually unknown in nonaqueous media.[5,6] For V(III) and lower oxidation states of V, a hydrolytic dimer, $V^{III}–O–V^{III}$, has been known to exist fleetingly in aqueous perchlorate solutions;[7–9] it is believed to be an intermediate in the oxidation of V(II) to V(III) (vide infra). Such a dimeric species, if definitively characterized, would give some insight into the bonding characteristics of V in its lower oxidation states. This is at present limited primarily due to the experimental difficulties encountered in working with the lower oxidation states of vanadium.[10,11] This paper reports the first isolation in crystalline form, to our knowledge, of the V(III) dimeric species $[(THF)_3Cl_2VOVCl_2(THF)_3]$. This was obtained as an isolable intermediate during the reduction of VCl_3 by triethylaluminum in tetrahydrofuran (THF).

Reaction of vanadium halides with metal alkyls is a frequently used and not always successful route to lower valence vanadium compounds,[12] the other methods commonly employed being electrochemical reduction[13,14] and the use of reducing agents such as zinc dust.[15] Reactions of this sort, which have been the subject of intense mechanistic study,[16] are frequently employed to obtain low-valence-state organometallic compounds of vanadium,[17,18] as well as to produce highly specific catalytic systems,[19] one of the most important of which are of course the Ziegler–Natta catalysts.[20,21] The precise nature of the stereospecific action of these catalysts is unfortunately still not too well understood today.[22] In addition, it is recognized that one of the most common poisons for these catalysts is molecular oxygen,[23,24] which sometimes turns up even in the most thoroughly purified organic solvents. The precise nature of the poisoning effect of molecular oxygen also remains poorly understood.[23] Since the reaction system described in this work (i.e. $VCl_3 + AlEt_3$ in THF) is capable of acting as a highly stereospecific homogeneous Ziegler–Natta catalyst in hydrocarbon solvents,[25] it is believed that the results of the present paper may give some insight into this subject.

Experimental Section

All experiments were carried out under a dry N_2 or argon atmosphere by using standard Schlenkware, drybox, and vacuum-line techniques. Tetrahydrofuran (Fisher) was triply distilled over Na (under N_2) until a blue coloration was obtained with benzophenone and then redistilled under high vacuum. Dimethylformamide, diethyl ether, and other solvents (Fisher) were dried and deoxygenated in the customary manner.[26] $ZnEt_2$ was prepared from EtI–EtBr and a Zn–Cu couple as described elsewhere.[27] Elemental analyses were performed by Galbraith Laboratories (Knoxville, TN). IR measurements of solid samples, prepared as Nujol mulls between AgCl windows, were carried out on a Perkin-Elmer IR 599 (double-beam) spectrometer. UV–vis measurements of solutions under argon atmosphere were carried out on a Pye-Unicam SP8-100 (double-beam) spectrometer. High-purity VCl_3 and $AlEt_3$ (Alfa, Division of Ventron) were used as supplied by the manufacturer. EtI and EtBr (Fisher) were distilled under high vacuum prior to use.

$[(THF)_3Cl_2VOVCl_2(THF)_3]$ (A). Five milliliters of 0.1 M $AlEt_3$ in THF and 5 mL of 0.1 M VCl_3 in THF were cooled to ca. −50 °C (ether–liquid N_2 slush), and the VCl_3 solution was added slowly to the $AlEt_3$ with stirring (via syringe and septa). The initial brown coloration quickly turned to an intense violet on warming to ca. −35 °C. The reaction mixture was reduced to one-third of its original volume by high-vacuum distillation, and the contents were left at ca. −20 °C for 48 h, yielding crystals of A, which were washed with ether, recrystallized from THF, and dried in vacuo. Variation of the $AlEt_3/VCl_3$ ratio did not yield a different product. Compound A was obtained as brilliant violet crystals. UV–vis (nm): in THF, 487 (ϵ 631, CT), 600 (ϵ 149, ${}^4A_{2g} \rightarrow {}^4T_{1g}$, V(II)), 766 ($\epsilon$ 30); in CH_3CN, 487 (ϵ 600, CT), 680 (ϵ 70, ${}^4A_{2g} \rightarrow {}^4T_{1g}$, V(II)); in DMF, 482 ($\epsilon$ 4000

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