centration that were varied as described earlier. Because the emphasis in this study was on the change in the spectrum due to the presence of Fe atoms (indicating a chemical reaction between cyclopentadiene and iron), a spectrum showing the difference between the iron/cyclopentadiene spectrum and the cyclopentadiene "blank" spectrum was calculated; the relevant portions of the difference spectra are shown in Figure 1. It is noted that all of the cyclopentadiene absorptions showed a decrease in intensity, as indicated by the negative peaks in the difference spectrum, while simultaneously a new set of peaks appeared, as indicated by the positive peaks in the difference spectrum. The frequencies of the "product" peaks are given in Table III. The formation of the product was spontaneous and did not require photolysis; subsequent photolysis of the matrices showed no change in the spectrum. No annealing studies were done. Full absorption and difference spectra (Figures 2-S and 3-S) are available as supplementary material.

It is noteworthy that, at constant cyclopentadiene concentration, all of the cyclopentadiene peaks showed a decrease in intensity as the iron concentration was increased. This indicates that cyclopentadiene was consumed by reaction with Fe atoms. Since no new bands appeared in the conjugated C=C region, **2** can be discounted as a product.

One of the stronger product peaks occurs at 1748.4 cm^{-1} (see Figures 1 and 2-S and Table III). A similar absorption is shifted down to 1259.5 cm^{-1} for the deuterated product (see Figures 1 and 3-S and Table III). On the basis of its large deuterium shift as well as studies of Fe atom reactions with H_2O, CH_4, and other molecules,[5,7,8] this absorption is assigned to an iron–hydrogen stretch, indicating that the product has an Fe–H bond. This discounts structures **1**, **4a**, and **4b**.

It is seen that several of the product absorptions in Figure 2-S—especially those at 785.1, 1002.1, and 3106.5 cm^{-1}—correspond very well to certain absorptions of ferrocene, in particular the carbon-hydrogen modes; these peaks are assigned accordingly. This would indicate that the matrix product contains a hydrocarbon moiety similar to that in ferrocene, *i.e.*, a cyclopentadienyl ring. This argument, coupled with the fact that the product has an iron-hydrogen bond, indicates that the product is **3**, or cyclopentadienyliron hydride.

This identification is supported by an infrared spectrum of $Ni(\eta^5\text{-}C_5H_5)NO$. A vibrational assignment of this compound by Feltham and Fateley[22] lists vibrations of the C_5H_5 moiety that include absorptions at 3106, 1004, 895, and 807 cm^{-1} that correspond very well with vibrations of the matrix product; absorptions that appear at 1425 and 1050 cm^{-1} also seem to correspond with those of the matrix product.

There was no indication of ferrocene itself in any of the spectra, presumably because the matrices were too dilute in cyclopentadiene for ferrocene formation. Also, there was no indication of diiron products, again because the concentration of iron atoms in the matrices was too low for significant diiron formation. It was initially intended to keep the matrix concentrations too low for any dimer formation to occur.

Two other cyclopentadienyl metal hydrides are known: cyclopentadienylberyllium hydride[23-27] and cyclopentadienylmagnesium hydride.[28,29] Cyclopentadienylberyllium hydride has been reported by Dewar and Rzepa to be one of the most stable cyclopentadienylberyllium compounds.[24] Cyclopentadienylmagnesium hydride was reported by Goel and Ashby[28] and was synthesized by reacting cyclopentadiene with MgH_2 in THF. A comparison of the infrared spectra of CpBeH and CpMgH would
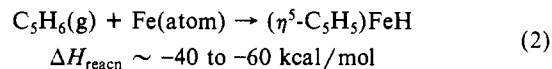
be useful, but the infrared spectrum of CpBeH has not yet been reported, while spectra of CpMgH show[30] that the molecule exists as a solvated dimer in THF solution, thereby negating the value of a direct comparison of IR spectra.

A molecule of this type has C_{5v} symmetry. It has 30 normal vibrational modes that can be classified as follows:

$$\Gamma_{vib} = 5\,A_1 + A_2 + 6\,E_1 + 6\,E_2 \qquad (1)$$

The A_1 and E_1 vibrations are infrared-active, giving 11 IR-active modes, 9 of which have been detected.

A thermodynamic cycle can be constructed, and literature values[31-34] can be used to give the overall ΔH_{reacn}:

$$C_5H_6(g) + Fe(atom) \rightarrow (\eta^5\text{-}C_5H_5)FeH$$
$$\Delta H_{reacn} \sim -40\ \text{to}\ -60\ \text{kcal/mol} \qquad (2)$$

The reaction, hence, has a substantial driving force, assuming $\Delta H \simeq \Delta G$ at very low temperatures. In the absence of any restrictive kinetic barriers, it would therefore be expected that this reaction be a spontaneous one.

Cyclopentadienyliron hydride is the first cyclopentadienyl transition-metal hydride detected. As is the case with metallocenes, it can be expected that other transition metals will form similar compounds under similar conditions; such syntheses are planned.

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EXAFS Studies of Zintl-Phase Solutions. Evidence for As_4^{2-} and As_6^{4-} Polyanions

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Solutions of Zintl phases, formed by fusion of an alkali metal with a main-group element, in basic solvents (ethylenediamine (en), ammonia) yield homo- or heteroatomic polyanions. In the 1930s Zintl established the stoichiometry of some of these ions in solution by potentiometric titration and analysis of solvent-extracted alloy phases.[2] Generally, solvent evaporation from the

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alloy solutions yields unstable amorphous material containing solvent molecules; complete loss of solvent causes a reversion to the known intermetallic phase.

However, using ethylenediamine, Kummer and collaborators succeeded in isolating, and identifying with single-crystal diffraction, $Na_4Sn_9 \cdot 7en$.[3] Considerable advances for solid-state work were achieved by the systematic use by Corbett and co-workers of 2,2,2-crypt (I) to complex the alkali-metal ion, which has

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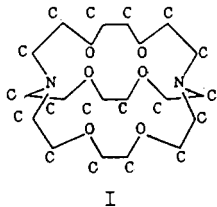
allowed single-crystal characterization of a large variety of anions.[4] Relative to this solid-state work, a paucity of recent information exists on solutions of Zintl ions although their existence and fluxionality have been identified by Rudolph using NMR methods.[5]

Extended X-ray absorption fine structure (EXAFS) spectroscopy has gained wide recognition in providing local structural information at metal centers, but attempts to establish metal skeletons in discrete cluster compounds have been limited. Skeletal identification relies on the observation of nonbonding metal–metal distances: successful use of EXAFS for osmium metal clusters has recently been achieved.[6]

The application of EXAFS to Zintl ion solutions can be impeded by the presence of equilibria between polyanions of different size and charge. This is exemplified by the simultaneous occurrence in the solid state of Ge_9^{2-} and Ge_9^{4-}.[7] We report here the characterization by the EXAFS method of two cyclic polyanions As_6^{4-} and As_4^{2-} present in K–As alloys in en solutions. This constitutes the first evidence for the existence of As_4^{2-} and the first research providing bond distances for cluster polyanions in solution.

Arsenic species As_3^{3-}, As_5^{3-}, and As_7^{3-} were electrochemically characterized by Zintl for sodium–arsenic alloys in liquid ammonia.[2] In the solid state, different anion species have been isolated, depending on the nature of the countercation: As_7^{3-} in Ba_3As_{14}[8b] and $Rb_3As_7 \cdot 3en$[8a] and As_6^{4-} in Rb_4As_6[8c] were identified by Von Schnering. More recently in this group, Belin reported the synthesis and single-crystal data for the undecaarsenide ion As_{11}^{3-} present in $[(2,2,2-crypt)K]_3As_{11}$.[9] Four-atom clusters of the heavier group 15^{20} elements Bi_4^{2-}[10] and Sb_4^{2-}[11] have been isolated by use of the crypt (I) in the solid state; however, to date As_4^{2-} has not been reported.

Potassium–arsenic alloys in an approximate 1:2 stoichiometric ratio were prepared by heating the appropriate amounts of the elements to 700 °C in a tantalum tube previously welded in an argon atmosphere. These alloys partly dissolve in ethylenediamine in the presence of excess crypt (I) to yield yellow to brown solutions, the analysis of which indicate a variable K/As composition (atomic ratio 1:1–2). In a typical experiment 0.2 g of alloy was
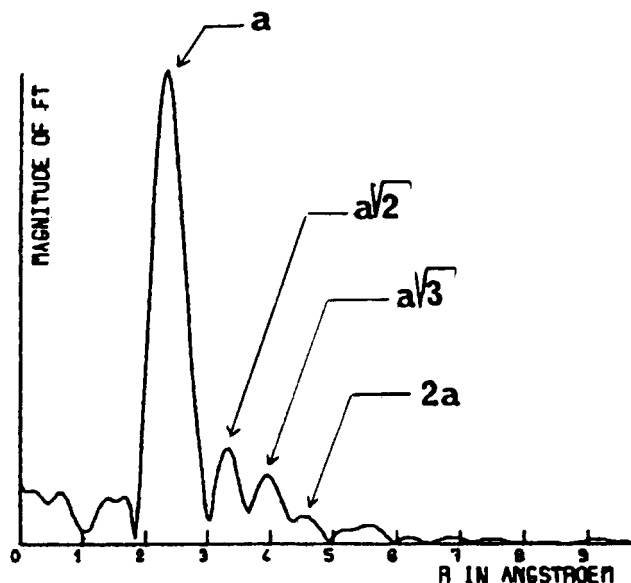

Figure 1. Fourier transform of the weighted EXAFS spectra in direct space corrected for the As–As phase shift. The first peak corresponds to As–As, $a = 2.35$ Å.
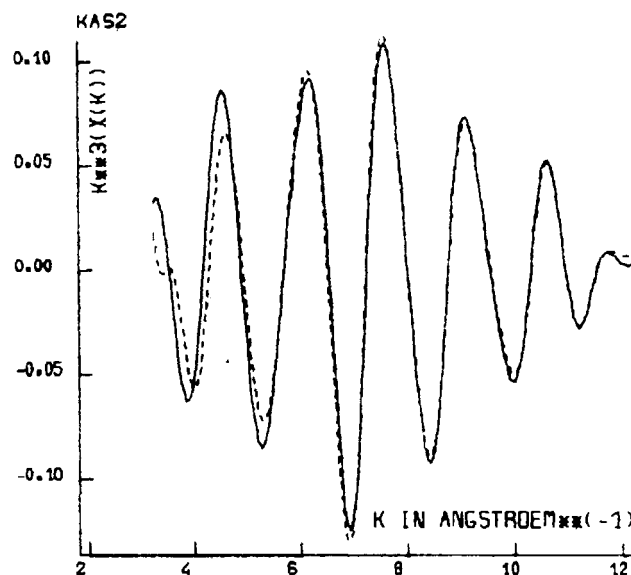

Figure 2. k-Space spectra filtered over the range 1–4 Å to include the first peaks in the Fourier transform: (—) calculated curve for the As_4^{2-}/As_6^{4-} model; (···) experimental curve. Residual = $\sum_k(\chi_{exptl} - \chi_{calcd})/\sum_k\chi_{exptl}^2 = 1.08\%$.

dissolved in ethylenediamine and the solution evaporated to 5 cm³. EXAFS spectra were taken of a solution containing K/As corresponding to a K_3As_5 stoichiometry, which was found in Zintl's original work.[2]

Arsenic K-edge absorption spectra were recorded for elemental arsenic and for the above en solution by using the synchrotron radiation source DCI at Orsay on the EXAFS I setup.[12] Data processing using the EXAFS suite of programs at the Centre National Universitaire Sud de Calcul followed the standard procedures of background removal and Fourier transform described elsewhere.[13] The Fourier-transformed spectrum of the experimental EXAFS data, corrected for the arsenic phase shift, is shown in Figure 1.

For the fitting procedure the tabulated ab initio phase and amplitude functions of Teo and Lee[14] were employed. Tested

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Table I. Results of the Fitting Procedure

R, Å	N_{exptl}	N_{theor}[a]	σ,[c] Å
2.35 (1)[b]	3.2 (5)	2	0.08 (1)
3.29 (2)	0.5 (2)	0.4	0.05 (4)
4.06 (2)	0.8 (4)	1.2	0.02 (4)
4.65 (12)	0.6 (11)	0.6	0.07 (2)

[a] Calculated coordination number for a 50% As_4^{2-}/As_6^{4-} mixture. [b] In each case, the standard deviation in parentheses refers to the least significant figure. [c] EXAFS Debye–Waller-like factor, which includes thermal and static disorder contributions.

against the EXAFS data for elemental arsenic these functions gave identical bond distances and satisfactory coordination numbers (3 ± 1) compared with those of the reported structure.[15] The k^3-weighted EXAFS oscillations $\chi(k)$, corresponding to the filtered four peaks in the Fourier transform, vs. the photoelectron wave vector k are represented in Figure 2.

The first peak in Figure 1 corresponds to the bonded metal-metal distance. More importantly, the peaks at increasing distance from the absorber correspond to nonbonded interactions. Incorporation of the phase parameters for As absorber and backscatterers leads to distances of 2.35, 3.30, and 4.05 Å for the three major peaks and 4.70 Å for a weaker feature in the Fourier transform. The peak distribution and bond distances immediately permit the rejection of an As_7^{3-} or an As_{11}^{3-} cluster.[8] Taking the ratio of these distances allows further deductions to be made concerning angular information: $r_{As \cdots As}/r_{As-As}$ values are 1.40 and 1.72, indicating that the bond angles are almost exactly 90 and 120°.

The most naive approach assumes that the three features in the Fourier transform arise from a single "type" of cluster in solution. Refinements of the coordination number are consistent with a five-atom cluster, which appears to be in agreement with Zintl's original conclusions. However the As–As distance ($a = 2.35$ Å) is shorter than a "normal" As–As single bond (~ 2.45 Å) and conforms to a bond order >1 and a nonsaturated cluster. Moreover, neither the isoelectronic Se_5^{2+} cluster nor the related anionic clusters Sb_5^{3-} and Bi_5^{3-} have been isolated. Finally it is difficult to reconcile the geometry of the hypothetical As_5^{3-} predicted by using classical electron-counting procedures[16] with that derived by EXAFS. In the case of bismuth, doubt has been expressed[10,17] on the original stoichiometries for Bi_7^{3-} and Bi_5^{3-} suggested by Zintl, who interpreted these polyanion geometries in terms of a central metal anion symmetrically bonded to neutral metal atoms and who, moreover, was unable to find Sb_4^{2-}, later isolated by Corbett.[11]

Our EXAFS results can be satisfactorily explained in terms of an equilibrium between square-planar As_4^{2-} and hexagonal As_6^{4-} species. For As_4^{2-}, the second-shell arsenic atom is expected at $2^{1/2}a$ likewise second- and third-shell atoms in As_6^{4-} should occur at $3^{1/2}a$ and $2a$ given that the two species have nearly the same As–As bond length.

For the case of 50% mixture of the two species, the calculated coordination numbers are 2 (first peak) 0.4 (second), 1.2 (third), and 0.6 (fourth), which are in qualitative agreement with values obtained by the fitting to EXAFS data (Table I).

The first peak in the Fourier transform probably represents the superposition of two shells of arsenic atoms belonging to different cluster species (which is not the case for the remaining peaks). Hence the assumption of a purely symmetric Gaussian distribution function might no longer be valid. Neglecting this effect may lead to errors in determining the coordination number in the composite shell and probably accounts for the relatively poor agreement between the expected and calculated values for N in the first shell.

The absence of clusters containing three-coordinate As, such as As_7^{3-} and As_{11}^{3-}, already surmised from the Fourier transform, was confirmed by a poor agreement on fitting. Although these cluster species have been characterized in the solid state, prepared from en solutions, their isolation depends on the type of countercation. Evaporation of our crypt/alloy en solutions does not necessarily yield the same cluster species.

As_6^{4-} is the most highly charged Zintl type ion that has been identified in solution. Its geometry is known to be planar (D_{6h}) in Rb_4As_6,[8a] $r(As-As) = 2.37$ Å, which is consistent with a bond order of 1.16 and a nonsaturated structure. As_4^{2-} remains to be identified in the solid state: Te_4^{2+}, Se_4^{2+} [18] and Bi_4^{2-}, Sb_4^{2-} have, however, been identified crystallographically.[10,11] As expected, the As_4^{2-} ion is square planar (D_{4h}). The observed bond distance of 2.35 Å is in agreement with a bond order close to 1.25.[19] This distance must nevertheless correspond to a weighted average of slightly different bond lengths (the bond distances in As_6^{4-} and As_4^{2-} are not necessary identical) as indicated by the elevated Debye–Waller factor derived ($\sigma = 0.08$ Å). It is intended to undertake a study of solutions of different compositions to determine the relative abundance of coexisting polyanions. Further work is in progress on the application of EXAFS to the structural characterization of the species present in solution of Zintl phases.

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(20) In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

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Template Synthesis and Characterization of a Nickel(II) Complex with Tris(((aminoethyl)amino)methyl)amine: (Semisepulchrate)nickel(2+)

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Various complexes have been synthesized by the template condensation of amines with aldehydes or ketones in the presence of metal ions.[1-7] In particular, formaldehyde has been utilized for cyclization to link two amine moieties.[5-7] Recently Co(III), Pt(IV), and Ni(II) complexes of the macrobicyclic ligand A, 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane (trivial name sepulchrate (sep)), have been prepared from the template con-

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