Table I. Results of the Fitting Procedure

R, Å	N_{exptl}	$N_{\text{theor}}{}^{a}$	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: $r_{\text{As}\cdots\text{As}}/r_{\text{As-As}}$ 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 (σ = 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.

Acknowledgment. Use of the synchrotron radiation source and technical assistance at LURE are acknowledged. The contribution of Rhône Poulenc at Salindres in the analyses of these materials is gratefully noted. We thank Dr. D. J. Jones for help with the EXAFS experiments and data processing.

Registry No. As_6^{4-}, 98064-38-1; As_4^{2-}, 98064-39-2; en, 107-15-3; K-As alloy, 98064-40-5.

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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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Received February 27, 1985

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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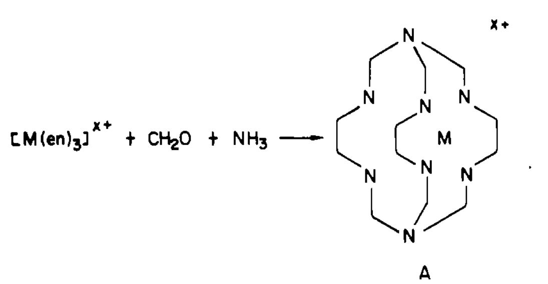
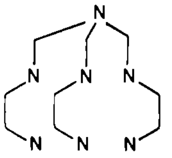
densation reaction of $[M(en)_3]^{x+}$, formaldehyde, and ammonia.[8-10]



A

In the formation of the Co(III) complex of sepulchrate, the complex of a polyamine B, tris(((aminoethyl)amino)methyl)amine (trivial name semisepulchrate (semisep)), has been proposed to be the intermediate.[8] However, details on the synthesis and properties of the complexes containing semisepulchrate have not been reported yet. In this paper, preparation and characterization of the Ni(II) complex of semisepulchrate are reported.



B

Experimental Section

Materials. All solvents and chemicals used in synthesis were of reagent grade and were used without further purification. For electrochemical experiments, high-purity acetonitrile was obtained from Aldrich Chemical Co. and dried over 5-Å molecular sieves.

Physical Measurements. Conductance measurements were performed by using an Industrial Instruments Model RC 216 B2 conductivity bridge in conjunction with a Beckman Model Cl-BB1 conductivity cell with the cell constant 0.10/cm. Infrared spectra were measured with a Perkin-Elmer Model 283 spectrophotometer. Electronic absorption spectra were recorded with a Varian Tectron 635D or a Cary 17 spectrophotometer. Magnetic susceptibilities were measured by the NMR method[9] on a Varian EM 360 60-MHz NMR spectrometer using a Wilmad 5-mm coaxial sample unit. Cyclic voltammetry was carried out with a Beckman Electroscan 30 electroanalytical system. The electrochemical data were obtained in acetonitrile with 0.1 M $(n\text{-Bu})_4NClO_4$ as supporting electrolyte. The working electrode was a platinum disk, the auxiliary electrode a coiled platinum wire, and the reference electrode a chloride-coated silver wire. Elemental analyses were performed by Galbraith Laboratories, Inc., Knoxville, TN.

Synthesis. To a stirred methanol solution (50 mL) of $NiCl_2 \cdot 6H_2O$ (9.8 g) were added 98% ethylenediamine (7.5 g), 28% ammonia (5.3 g), and 36% aqueous formaldehyde (14 g), and the mixture was refluxed for 5 h. The red solution was filtered hot, and then $LiClO_4$ (13 g) dissolved in methanol (25 mL) was added to the filtrate. The solution was left at room temperature for 4 h. The pink crystals formed were filtered, washed with 1:1 methanol–water, and recrystallized from hot water. Yield ≈ 70%. *Caution*! This perchlorate salt may be explosive and should be handled with caution. Anal. Calcd for $NiC_9H_{27}N_7Cl_2O_8$: C, 22.02; H, 5.54; N, 19.97; Ni, 11.96. Found: C, 22.21; H, 5.52; N, 19.98; Ni, 11.70.

Results and Discussion

The isolated complex (ClO_4^- salt) is soluble in hot water, Me_2SO, or CH_3CN, producing pink solutions. The molar conductance of the complex measured in DMF solutions was Λ_M = 143 Ω^{-1} M^{-1} cm at 20 °C, corresponding to a 2:1 electrolyte.[11] The complex did not react with thiocyanate ion, indicating that the complex is stable against ligand substitution. The complex, however, was unstable under acidic conditions. The absorption maximum at 527 nm of an aqueous solution of the complex (2×10^{-2} M) disappeared completely within 20 min upon addition of perchloric acid (6×10^{-2} M).

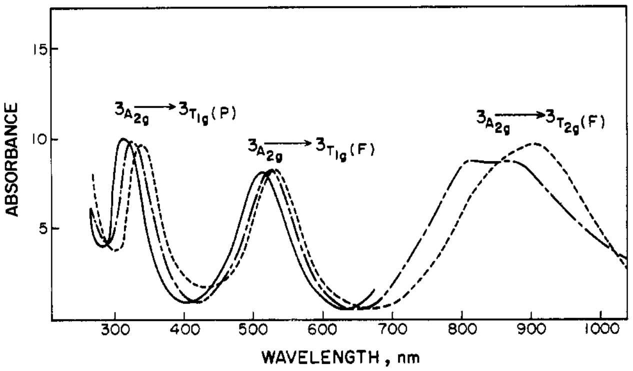


Figure 1. Absorption spectra of nickel(II) complexes in CH_3CN: $[Ni(semisep)](PF_6)_2$, – – –; $[Ni(en)_3](PF_6)_2$, - - -; $[Ni(sep)](PF_6)_2$, —.

The infrared spectrum showed bands at 3292 and 3345 cm^{-1} for N–H stretchings and a band at 1610 cm^{-1} for N–H deformation, indicating the presence of primary amines.

The electronic absorption spectrum of the acetonitrile solution of the complex (PF_6^- salt) revealed absorption maxima at 337 nm (ϵ = 10), 527 nm (ϵ = 8.3), and 810 and 870 nm (ϵ = 9.2). The spectrum is compared with those of $[Ni(en)_3]^{2+}$ and $[Ni(sep)]^{2+}$ in Figure 1. The spectra indicate that the arrangement of the donor atoms in the new complex is intermediate between those of $[Ni(en)_3]^{2+}$ and $[Ni(sep)]^{2+}$. The order of ligand field strength is $[Ni(en)_3]^{2+}$ < isolated Ni complex < $[Ni(sep)]^{2+}$, as indicated by the shifts of absorption maxima.

On the basis of these data as well as the result of elemental analysis, the isolated complex is assigned as $[Ni(semisep)](ClO_4)_2$. The spectra of Figure 1 indicate that the ligand field strength increases slightly as capping of the $[Ni(en)_3]^{2+}$ moiety with the tris(methylene)amino group progresses.

According to the molecular structure of $[Ni(sep)](ClO_4)_2$ determined by X-ray diffractometric analysis,[10] the six nitrogen atoms are coordinated to the Ni(II) ion in a pseudooctahedral geometry. In addition, the bond distances and angles around the Ni(II) ion in the sepulchrate complex are very similar to those of $[Ni(en)_3]^{2+}$.[10,12] Analogous structural features would be present in $[Ni(semisep)](ClO_4)_2$.

The magnetic susceptibility of the isolated complex, measured by the NMR method in Me_2SO solution,[13,14] gave a magnetic moment of 2.87 μ_B at 25 °C. This also supports the existence of d^8 electronic systems in an octahedral geometry.

Cyclic voltammetry for $[Ni(semisep)](ClO_4)_2$ in CH_3CN solutions indicated a quasi-reversible one-electron-oxidation potential at +0.99 V and no reduction up to −1.8 V vs. Ag/AgCl reference electrode, while that for $[Ni(en)_3](ClO_4)_2$ gives a one-electron-oxidation potential at +1.02 V. Thus, the electron density on the nickel atom is only slightly increased by capping with a tris(methylene)amino group.

Attempts to obtain the Ni(II) complex of sepulchrate by refluxing Me_2SO solutions of $[Ni(semisep)](ClO_4)_2$ with formaldehyde and ammonia were unsuccessful. Instead, the reaction produced the Ni(II) square-planar complex of 3,7-bis(2-aminoethyl)-1,3,5,7-tetraazabicyclo[3.3.1]nonane, C.[15]

In general, methylenediamine groups ($R_2N–CH_2–NR_2$) are unstable when they contain primary or secondary amines.[16] The

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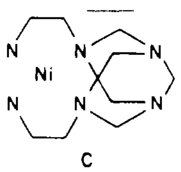

C

Ni(II) complex of semisepulchrate ligand prepared in this study, as well as the Co(III), Pt(IV), and Ni(II) complexes of sepulchrate,[8-10] contains methylenediamine linkages with secondary nitrogens. Therefore, methylenediamine groups containing secondary amines can be stabilized by coordination of the secondary nitrogens to a metal ion. However, the formation of C from $[Ni(semisep)]^{2+}$ indicates that the secondary nitrogens of methylenediamine groups are still reactive enough to produce tertiary nitrogens upon reaction with formaldehyde in the presence of free amines.

Acknowledgment. This work was supported by the Basic Research Institute Program (1984), Ministry of Education, Korea.

Registry No. $[Ni(semisep)](ClO_4)_2$, 98087-70-8; NH_3, 7664-41-7; CH_2O, 50-00-0; en, 107-15-3.

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Time of Flight Neutron Powder Rietveld Refinement of the $ZrKH(PO_4)_2$ Structure

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In a recent publication[1] we described the structure of $ZrKH(PO_4)_2$ as determined from Rietveld refinement of X-ray powder data. This compound is prepared by ion exchange of the parent α-zirconium phosphate, $Zr(HPO_4)_2{\cdot}H_2O$, followed by dehydration at 200 °C.[2] The structures of both the acid phosphate[3,4] and the half-exchanged potassium ion salt are layered. In the salt, the potassium ions are located exactly midway between the layers and are bonded to four $P-O^-$ type oxygens designated as O7 and O10. However, each of these oxygens bonds to two K^+ ions, the charge deficiency being compensated by protons. The location of the protons could not be determined from the X-ray data, but their positions were inferred from the structure.[1,5] This study was carried out in an effort to locate the protons precisely.

There was, however, another compelling reason for carrying out a neutron diffraction study. The structure of the subject compound was initially solved by Patterson and Fourier methods using 47 reflections that could be unambiguously indexed[5] in the X-ray powder pattern. This model was then refined by the X-ray Rietveld method. The procedures for solving structures from such minimal data sets have been described elsewhere.[6] There has been a certain amount of disagreement over the accuracy and validity of Rietveld refinement of X-ray data. This controversy centers around the falloff in intensities with increasing Bragg angle and the correspondence of experimental errors to refinement errors.[7-9] It was therefore of interest to compare the accuracy of the X-ray study with a detailed neutron diffraction study.

Table I. Neutron TOF Refinement Parameters for $ZrKH(PO_4)_2$

space group	*P*2/*c*
cell params	
a, Å	9.2208 (7)
b, Å	5.3280 (4)
c, Å	16.6336 (17)
β, deg	114.351 (11)
V, Å^3	744.47 (7)
Z	4
data range, μs	5275–20000
data range, Å	0.92–3.67
no. of contributing reflcns	971
no. of deg of freedom	2099
T, K	295

$R_{wp} = [\sum_i w_i[Y_i(\text{obsd}) - Y_i(\text{calcd})]^2/\sum_i w_i[Y_i(\text{obsd})]^2]^{1/2}$	0.0242
$R_P = \sum_i[Y_i(\text{obsd}) - Y_i(\text{calcd})]/\sum_i[Y_i(\text{obsd}) - \text{bkgd}_i]$	0.0702
$R_e = df^{1/2}/\sum_i w_i[Y_i(\text{obsd})]^2$	0.0146

Table II. Positional Parameters for $ZrHK(PO_4)_2$

atom	*x*	*y*	*z*
Zr	0.7504 (15)	0.7729 (15)	0.9945 (9)
K1	0.5	0.0559 (57)	0.25
K2	0.0	−0.0740 (63)	0.25
P1	0.1715 (17)	0.7063 (19)	0.1176 (10)
P2	0.6632 (15)	0.2742 (33)	0.1115 (9)
O1	−0.0015 (16)	0.7709 (30)	0.0959 (11)
O2	0.2158 (15)	0.4938 (26)	0.0728 (9)
O3	0.2438 (17)	0.9480 (31)	0.0952 (12)
O4	0.6754 (13)	0.5260 (27)	0.0667 (8)
O5	0.5171 (15)	0.7634 (29)	0.9139 (8)
O6	0.7293 (15)	0.0559 (33)	0.0807 (10)
O7	0.2602 (14)	0.6969 (27)	0.2221 (8)
O10	0.2730 (14)	0.2907 (29)	0.2952 (8)
H1	0.2485 (35)	0.5108 (50)	0.2285 (19)

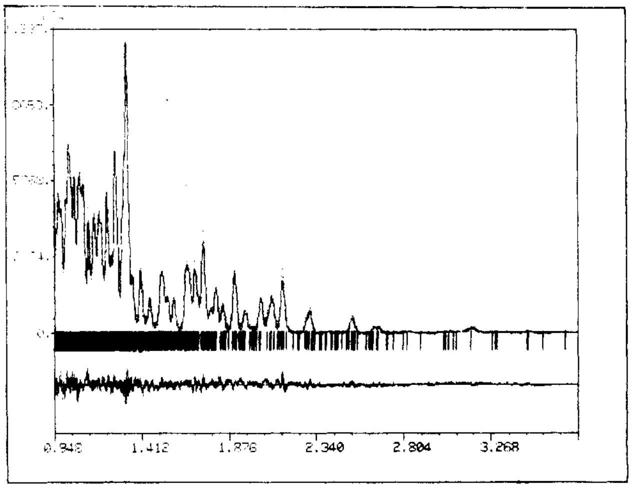

Figure 1. Plot of neutron intensity (counts) vs. *d* spacing (Å) for $ZrKH(PO_4)_2$. Observed data are represented by dots, calculated as the solid line. The lower plot is the difference. Vertical strikes indicate calculated Bragg peak positions.

Experimental Section

A neutron time of flight data set was collected on a sample of $ZrKH(PO_4)_2$ that had been loaded into a sealed vanadium can under an inert dry atmosphere. Data were taken on the special-environments powder diffractometer (SEPD) at the intense pulsed neutron source (IPNS), Argonne National Laboratory.[10] Data collection on the sample, about 5.2 cm^3, required 12 h. Data reduction was performed on data from the 90° data banks, and the X-ray Rietveld refined structural parameters[1] were used as the starting model. Refinement was carried out with a neutron Rietveld analysis program[11] in the *d*-spacing range of 3.67–0.92

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