Copper Complexes. Copper derivatives were prepared by the metal acetate method.[28] A chloroform solution of the chelate was passed through a short column of activity III alumina to remove traces of copper salts.

Cobalt Complexes.[10] In the inert atmosphere box the free-base porphyrin was dissolved in warm toluene, adding THF, if necessary, for dissolution. A small excess of 2,6-lutidine was added, followed by a tenfold excess of a saturated solution of $CoCl_2$ (anhydrous) in THF. The solution was heated gently (about 60 °C) during 1 h. The visible spectrum should show no free-base bands at ca. 620 nm. The solvent was removed in vacuo and the residue dissolved in a minimum of toluene. (Adding THF and no more than 10% MeOH may help.) The resulting solution was chromatographed on neutral alumina (activity III), eluting with toluene–THF (5:1). The eluate (cobalt salts remain on the top of the column) was evaporated in vacuo to give the four-coordinate cobalt complex. For Co_2FTF-4,2,1-NH (**4b**), *m/e* 1096, 1097 (calcd, 1096).

Polyarsenide Anions.   Synthesis and Structure of a Salt Containing the Undecaarsenide(3−) Ion

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Abstract: Reaction of solid KAs_2 with 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazobicyclo[8.8.8]hexacosane) in ethylenediamine yields deep-red rods which have been shown to be $(crypt-K^+)_3As_{11}{}^{3-}$ by X-ray crystallography. The compound crystallizes in the $P\bar{1}$ space group with $Z = 2$ and $a = 14.248$ (4) Å, $b = 23.480$ (3) Å, $c = 14.015$ (4) Å, $\alpha = 99.17$ (2)°, $\beta = 101.60$ (2)°, and $\gamma = 98.24$ (2)° at 25 °C. Diffraction data were measured over four octants using an automatic Nonius CAD4 diffractometer and monochromated Mo $K\alpha$ radiation. The structure was solved by direct methods. The full-matrix, least-squares method refined the structure to $R = 0.112$ and $R_w = 0.142$ from 4521 independent reflections with anisotropic temperature factors for arsenic and potassium atoms and isotropic temperature factors for light atoms. The main feature of the structure is the existence of the $As_{11}{}^{3-}$ anion displaying an unusual geometry; its configuration is very close to the ideal D_3. Eight arsenic atoms are tricoordinated and arranged on a bicapped twisted triangular antiprism; the structure is achieved by three bridging waist arsenic atoms which are bicoordinated. According to Wade's theory, the geometry of the anion clearly derives from a 17-vertices polyhedron basis.

Introduction

Electrochemical studies of Zintl and co-workers[1] on sodium–arsenic alloys in liquid ammonia served to identify homopolyatomic anions $As_3{}^{3-}$, $As_5{}^{3-}$, and $As_7{}^{3-}$. Although $As_7{}^{3-}$ is reported in crystalline Ba_3As_{14},[2] any attempt to isolate other solid derivatives of Zintl anions has been generally fruitless since the only new solid products obtained by evaporation of NH_3 from the solutions were amorphous and reverted to the known alloy phases.

The other works reported on potassium or sodium polyarsenides are from Hugot,[3,4] Lebeau,[5] and Dorn and co-workers.[6] Hugot prepared the red compound $K_2As_4\cdot NH_3$ by directly reacting potassium with an excess of arsenic in liquid NH_3. More recently, Dorn investigated the system K–As using thermal analysis up to 60 atom % As and X-ray methods for As-richer regions. He found the compounds K_3As, K_5As_4, KAs, and KAs_2, the latter being described as a red compound that sublimes without decomposition and is similar to Hugot's compound.

Recently, a general way to stabilize homopolyatomic anions was found by Corbett and co-workers.[7] They used the bicyclic 2,2,2-crypt[8] to complex the sodium or potassium counterion and prevent electron transfer back to the cation and reversion to the known alloy phase. This procedure has now allowed the isolation and characterization of the stable homopolyatomic anions such as $Sn_9{}^{4-}$,[9,10] $Pb_5{}^{2-}$ and $Sn_5{}^{2-}$,[11] $Sb_7{}^{3-}$,[12] $Te_3{}^{2-}$,[13] $Ge_9{}^{4-}$ and $Ge_9{}^{2-}$,[14] and $Bi_4{}^{2-}$.[15]

In the present work, we have studied reactions in liquid ammonia and ethylenediamine (en) of 2,2,2-crypt with either KAs_2 or $K_2As_4\cdot NH_3$ compounds; the reaction schemes are different

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depending on the nature of the starting material. Two compounds could be isolated; the first of them crystallizes in the trigonal system, and the second is triclinic and formulated (crypt-K^+)$_3$As$_{11}^{3-}$, where the anion displays a very unusual configuration.

Experimental Section

Synthesis. The 2,2,2-crypt ligand was obtained from Merck Laboratories (Kryptofix) and used without further purification. Liquid ammonia (Matheson) was distilled from a commercial tank into a Pyrex vessel where it was dried with sodium and then distilled into reactors through a high-vacuum apparatus. The ethylenediamine (en) was first dried with CaH$_2$, then distilled onto and stored over molecular sieve and again distilled from there for utilization. The reaction vessel was equipped with Teflon Rotaflo valves (Corning). Arsenic was used as received from Merck Laboratories while potassium (Merck) was purified through several fractional crystallizations.

K$_2$As$_4$·NH$_3$ was prepared as described by Hugot.[4] The phase KAs$_2$ was prepared by heating the stoichiometric amounts of the elements to 700 °C in a tantalum tube previously weld-sealed in an argon atmosphere. K$_2$As$_4$·NH$_3$ dissolves in en and NH$_3$ but reacts so rapidly when crypt is added that from deep red the solution turns instantaneously colorless and amorphous products deposit on the bottom of the reactor. Large, hexagonal single crystals can only be obtained by allowing two solutions of the compound and the crypt in NH$_3$ to diffuse slowly through a sintered glass. The reaction is quite different when carried out from the KAs$_2$ phase; the alloy dissolves readily in en in the presence of crypt and a brown-yellow solution forms immediately, then darkens to deep red-brown. A slight excess of crypt with respect to potassium is used. On long standing, deep-red, hexagonal crystals deposited irreversibly and X-ray studies showed that they were identical with those previously mentioned; after much longer standing, a few crystals deposited, which were different in shape, and their preliminary oscillation and Weissenberg photographs displayed a different symmetry. These last crystals were selected under microscope in the drybox under argon atmosphere. Instead of using some variety of grease to hold their positions, they were merely wedged in glass capillaries so as to avoid any chemical contact and further decay. A plate-shaped crystal of dimensions 0.10 × 0.40 × 0.67 mm which gave the best diffraction spots was investigated on a Nonius CAD4 automatic diffractometer.

Data Collection and Reduction. The preliminary orientation search confirmed that the crystal was triclinic. Integrated diffraction intensities were collected at ambient temperature (25 °C). The profile analysis of a few low-angle reflections indicated that an $\omega - ^5/_3\,\theta$ scan method was the most appropriate for data collection. Scan ranges were calculated from the formula Sr = $A + B$ tan θ where A depends on the mosaic spread of the crystal and B allows for increasing peak width due to Kα_1 and Kα_2 splitting; A and B were chosen as 1.2 and 0.35°, respectively. For each reflection, the calculated scan angle was extended by 25% on either side to estimate the background count. Cell parameters were obtained by least-squares refinement of the angular positions of 14 reflections automatically centered on the diffractometer: a = 14.248 (4) Å, b = 23.480 (3) Å, c = 14.015 (4) Å, α = 99.17 (2)°, β = 101.60 (2)°, γ = 98.24 (2)°, V = 4459.0 Å^3.

The data were collected in the four octants hkl, $h\bar{k}l$, $h k\bar{l}$, and $h\bar{k}\bar{l}$ using graphite-monochromated MoKα radiation (λ = 0.710 69 Å). The reflection data were collected in three stages, first for 3808 reflections within the four octants in the range 0 < 2θ < 30° and later, when the structure appeared red solvable, for 2304 reflections within the hkl octant in the range 30 < 2θ < 50° and, because just a few reflections were observed for 2θ > 40°, for 4410 reflections within the remaining three octants in the range 30 < 2θ < 40°. During data collection, the intensities of three standard reflections were checked after every 75 reflections. The loss in intensities was less than 7%; nevertheless, it was taken into account in data reduction. The data were corrected for background and Lorentz–polarization effects. Once the composition of the compound was known, the data were corrected for the effects of absorption by Gaussian integration[16] with μ = 44.7 cm^{-1}. The three data sets were then merged and duplicate reflections averaged, with each set being assigned a separate flag so that these could be scaled one to another with three refined scale factors. The final data set consisted in 4573 independent reflections with $I > 3\sigma(I)$. The initial structure solution and preliminary refinements were carried out with the data in the range 0 < 2θ < 30°, while all the data were used in final refinement cycles.

Structure Solution and Refinement. The structure was solved by direct methods. The Wilson test gave a strong indication of centricity so the structure solution was attempted in the space group $P\bar{1}$, which proved later on to be the correct choice.

The output from the Fourier step of MULTAN[17] contained 11 peaks of high weight and 3 peaks of lower weight in the asymmetric unit. The first 11 peaks had distances on the order of 2.4 Å and they were attributed to arsenic atoms while the three remaining peaks were attributed to potassium atoms. After a few cycles of positional and isotropic thermal parameters refinement, $R = \sum ||F_o| - |F_c||/\sum |F_o| = 0.29$. At this stage, a subsequent Fourier map contained, in addition to the heavy-atom peaks, many smaller peaks around potassium atoms indicative of oxygen, carbon, and nitrogen atoms in the crypt ligands. After a few successive refinements of these positions followed by Fourier synthesis, all of the light-atom positions had been defined. Final refinement of the complete structure was conducted in parts using all the 4573 reflections and full-matrix least squares. To reduce the computing time and cost, the 92 atoms were refined to convergence by cycling several times first for one pair of the three crypt-K$^+$ cations, then for the 11 arsenic atoms and the third crypt, the cycling ending on the second group. In these cycles, arsenic and potassium atoms were refined with anisotropic thermal parameters while light atoms in the cations were restricted to isotropic thermal parameters. Convergence was obtained by minimizing the function $w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma^2$ count $(F^2)/4(F)^2 + (0.02F)^2$ and using the final data sets corrected for absorption. The final agreement factors were $R(F)$ = 0.112 and R_w = 0.142 for 441 variables and 4521 reflections, 52 of the weakest and evidently mismeasured reflections being eliminated at this point by the criterion $||F_c| - |F_o||/F_o > 1.1$. A total of 108 hydrogen atoms in the asymmetric unit, representing 10% of the total electron density, were not located or their estimated positions included in the structure-factor calculation. The final Fourier difference map was flat except for a residual peak inside the cluster of less than 2.2 e/Å^3. This is not unreasonable since scattering factors for As^0 were used. Corrections for the anomalous dispersion effects were included in the neutral atom scattering factors of heavy atoms.[18] In the final cycle refinement the shift in heavy-atom parameters was <0.13σ (esd) in positions and 0.3σ in temperature factors while the changes in light-atom parameters were <0.4σ. The crystallographic programs[19] used were MULTAN, FORDAP for Fourier summations, ORXLFS3 for least-squares refinement, ORFFE3 for molecular and error functions, and ORTEP II, the thermal ellipsoid program for molecular plots.

Results and Discussion

The final positional and thermal parameters for the 92 non-hydrogen atoms in (crypt-K$^+$)$_3$As$_{11}^{3-}$ are listed in Table I. Bond distances, bond angles, and dihedral angles in the arsenic cluster are given in Table II. Bond distances and some angle data for the cations as well as some interionic distances (Table A) and the listing of observed and calculated structure factors are given in the supplementary material. The configuration of the As$_{11}^{3-}$ cluster is illustrated in Figure 1.

The asymmetric unit cell contains three crypt-K$^+$ cations implying a 3- charge for the corresponding anion. The structures of the cations are similar to those determined for similar symmetry-unconstrained units in (crypt-K$^+$)$_2$Te$_3^{2-}$[13] and (crypt-K$^+$)$_6$Ge$_9^{2-}$Ge$_9^{4-}$·2.5en[14] and the details will not be discussed here; some structural data are given in the supplementary material (Table A). The most interesting feature of this structure is, of course, the hitherto unknown As$_{11}^{3-}$ polyanionic arsenide; its structure is approximately the same as the one of P$_{11}^{3-}$[20] in Na$_3$P$_{11}$. Figures 1a and 1b present two different perspectives of the cluster, which clearly displays a symmetry close to D_3 with a threefold axis passing through atoms 1 and 5 and three twofold axes through waist atoms 9, 10, and 11 and respectively the middle of the opposite edges 4–7, 3–6, and 2–8. In other terms, the structure of the anion could be described as a trigonal antiprism composed of the atoms 2, 3, 4, 6, 7, and 8 capped by atoms 1 and 5 on triangular faces. The observed structure is then achieved by a

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Table I. Final Positional and Temperature Factor Parameters for Atoms in $(2,2,2\text{-crypt-}K^+)_3 As_{11}^{3-}$

	x	y	z	$\beta_{11}{}^a$	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
As1	0.7216 (3)	0.7425 (2)	0.2988 (3)	43 (4)	26 (2)	41 (4)	5 (2)	10 (3)	14 (2)
As2	0.7303 (4)	0.6502 (3)	0.1964 (4)	64 (4)	30 (2)	46 (4)	5 (2)	8 (3)	10 (2)
As3	0.5984 (3)	0.7805 (3)	0.1919 (3)	24 (3)	34 (2)	42 (4)	10 (2)	5 (3)	7 (2)
As4	0.8750 (3)	0.8080 (3)	0.3014 (4)	32 (4)	32 (2)	45 (4)	2 (2)	-5 (3)	9 (2)
As5	0.7743 (3)	0.7560 (2)	0.0290 (3)	46 (4)	28 (2)	36 (4)	7 (2)	15 (3)	11 (2)
As6	0.6028 (4)	0.7259 (3)	0.0298 (4)	38 (4)	46 (2)	34 (4)	9 (2)	-7 (3)	-6 (2)
As7	0.8255 (3)	0.8466 (3)	0.1527 (4)	37 (4)	33 (2)	59 (4)	5 (2)	5 (3)	20 (2)
As8	0.8536 (4)	0.6837 (3)	0.1104 (4)	57 (4)	30 (2)	50 (4)	21 (2)	24 (3)	6 (2)
As9	0.5901 (4)	0.6300 (3)	0.0644 (4)	69 (5)	39 (2)	57 (5)	-7 (2)	-4 (4)	-7 (2)
As10	0.9759 (4)	0.7452 (3)	0.2453 (4)	39 (4)	40 (2)	61 (4)	19 (2)	5 (3)	6 (2)
As11	0.6762 (4)	0.8741 (3)	0.1773 (4)	44 (4)	37 (2)	58 (4)	22 (2)	11 (3)	15 (2)
K2	0.2706 (7)	0.5380 (5)	0.3031 (7)	46 (8)	21 (4)	54 (8)	7 (4)	-3 (6)	8 (4)
K3	0.8261 (6)	0.1866 (4)	0.2041 (6)	30 (7)	21 (3)	28 (7)	2 (4)	1 (5)	3 (4)
K1	0.6810 (7)	0.9628 (5)	0.6975 (7)	25 (7)	31 (4)	33 (7)	3 (4)	4 (6)	-3 (4)

	x	y	z	B		x	y	z	B
N(101)^b	0.073 (3)	0.452 (2)	0.219 (3)	6.2 (11)	C(114)	0.209 (4)	0.695 (2)	0.235 (4)	7.4 (15)
C(102)	0.093 (4)	0.413 (3)	0.145 (4)	7.9 (16)	C(115)	0.132 (3)	0.626 (2)	0.169 (4)	5.6 (13)
C(103)	0.179 (4)	0.383 (2)	0.173 (4)	6.0 (14)	O(116)	0.102 (2)	0.577 (2)	0.199 (2)	6.4 (9)
O(104)	0.264 (2)	0.430 (2)	0.194 (2)	6.5 (8)	C(117)	0.029 (4)	0.533 (2)	0.129 (4)	5.8 (13)
C(105)	0.352 (4)	0.400 (2)	0.212 (3)	5.7 (13)	C(118)	0.004 (4)	0.501 (2)	0.191 (4)	6.5 (14)
C(106)	0.437 (4)	0.443 (3)	0.217 (4)	7.1 (15)	C(119)	0.049 (3)	0.423 (2)	0.304 (3)	4.5 (11)
O(107)	0.450 (2)	0.499 (1)	0.291 (2)	4.4 (7)	C(120)	0.060 (3)	0.468 (2)	0.405 (3)	4.6 (11)
C(108)	0.523 (3)	0.546 (2)	0.294 (3)	4.7 (11)	O(121)	0.167 (2)	0.489 (1)	0.433 (2)	4.8 (8)
C(109)	0.545 (3)	0.591 (2)	0.380 (3)	3.1 (9)	C(122)	0.187 (4)	0.521 (2)	0.524 (4)	6.7 (14)
N(110)	0.461 (2)	0.618 (2)	0.391 (3)	4.4 (9)	C(123)	0.301 (4)	0.536 (2)	0.557 (4)	6.8 (14)
C(111)	0.467 (4)	0.673 (3)	0.322 (4)	10.2 (19)	O(124)	0.333 (2)	0.580 (1)	0.513 (2)	5.2 (8)
C(112)	0.374 (3)	0.710 (2)	0.313 (3)	6.1 (13)	C(125)	0.439 (3)	0.601 (2)	0.550 (3)	4.1 (11)
O(113)	0.289 (3)	0.654 (2)	0.255 (3)	8.7 (10)	C(126)	0.468 (3)	0.652 (2)	0.502 (3)	4.6 (11)
N(201)	0.935 (2)	0.110 (2)	0.328 (2)	3.0 (8)	C(214)	0.616 (4)	0.079 (2)	0.065 (3)	5.8 (13)
C(202)	0.026 (3)	0.101 (2)	0.289 (3)	4.0 (11)	C(215)	0.685 (4)	0.027 (3)	0.074 (4)	6.8 (15)
C(203)	0.080 (3)	0.160 (2)	0.270 (3)	4.4 (12)	O(216)	0.749 (2)	0.069 (1)	0.178 (2)	5.6 (8)
O(204)	0.018 (2)	0.172 (1)	0.183 (2)	4.1 (7)	C(217)	0.813 (4)	0.019 (2)	0.207 (4)	7.0 (15)
C(205)	0.069 (3)	0.220 (2)	0.162 (3)	3.3 (10)	C(218)	0.872 (4)	0.057 (3)	0.328 (4)	7.6 (15)
C(206)	0.009 (3)	0.233 (2)	0.071 (3)	4.1 (11)	C(219)	0.962 (3)	0.141 (2)	0.436 (3)	5.0 (12)
O(207)	0.919 (2)	0.254 (1)	0.098 (2)	5.1 (8)	C(220)	0.880 (3)	0.166 (2)	0.467 (3)	4.8 (12)
C(208)	0.859 (4)	0.268 (2)	0.010 (4)	6.3 (14)	O(221)	0.867 (2)	0.215 (1)	0.413 (2)	3.2 (7)
C(209)	0.782 (4)	0.295 (3)	0.061 (4)	7.1 (16)	C(222)	0.818 (3)	0.251 (2)	0.462 (3)	4.6 (12)
N(210)	0.714 (3)	0.255 (2)	0.090 (3)	5.2 (10)	C(223)	0.811 (4)	0.296 (3)	0.407 (4)	7.8 (16)
C(211)	0.648 (3)	0.224 (2)	0.003 (3)	3.6 (10)	O(224)	0.741 (2)	0.276 (1)	0.297 (2)	4.7 (8)
C(212)	0.599 (4)	0.171 (2)	0.028 (4)	5.9 (13)	C(225)	0.720 (4)	0.323 (2)	0.243 (4)	5.9 (14)
O(213)	0.658 (2)	0.128 (2)	0.050 (2)	5.4 (9)	C(226)	0.656 (4)	0.281 (2)	0.154 (4)	5.8 (13)
N(301)	0.532 (3)	0.852 (2)	0.645 (4)	8.9 (13)	C(314)	0.819 (4)	0.927 (3)	0.925 (4)	8.2 (16)
C(302)	0.506 (4)	0.840 (3)	0.518 (5)	9.6 (18)	C(315)	0.738 (4)	0.891 (2)	0.916 (4)	6.5 (14)
C(303)	0.595 (4)	0.834 (3)	0.479 (4)	7.3 (16)	O(316)	0.696 (2)	0.880 (2)	0.813 (3)	6.2 (9)
O(304)	0.656 (2)	0.889 (1)	0.511 (2)	4.0 (7)	C(317)	0.619 (4)	0.832 (3)	0.798 (4)	7.6 (17)
C(305)	0.747 (3)	0.890 (2)	0.475 (3)	4.5 (12)	C(318)	0.575 (4)	0.804 (2)	0.692 (4)	6.4 (14)
C(306)	0.794 (3)	0.948 (2)	0.480 (3)	3.3 (10)	C(319)	0.443 (5)	0.877 (3)	0.672 (5)	9.7 (19)
O(307)	0.823 (2)	0.982 (1)	0.582 (2)	4.3 (8)	C(320)	0.412 (4)	0.927 (3)	0.622 (4)	8.9 (17)
C(308)	0.874 (4)	0.040 (3)	0.592 (4)	7.4 (15)	O(321)	0.484 (2)	0.969 (2)	0.692 (2)	5.9 (9)
C(309)	0.915 (3)	0.059 (2)	0.704 (4)	5.7 (13)	C(322)	0.460 (4)	0.019 (3)	0.649 (5)	8.7 (18)
N(310)	0.826 (3)	0.070 (2)	0.750 (3)	6.9 (12)	C(323)	0.517 (4)	0.074 (2)	0.720 (4)	7.4 (15)
C(311)	0.857 (4)	0.089 (3)	0.865 (4)	7.8 (16)	O(324)	0.619 (2)	0.073 (1)	0.700 (2)	5.9 (8)
C(312)	0.894 (4)	0.041 (3)	0.900 (4)	7.2 (15)	C(325)	0.691 (5)	0.137 (3)	0.753 (5)	11.4 (22)
O(313)	0.810 (2)	0.985 (2)	0.888 (2)	6.3 (9)	C(326)	0.790 (5)	0.134 (3)	0.718 (5)	10.9 (20)

^{a} $\beta_{ij} \times 10^4$ is listed. The thermal parameter expression is $\exp\{-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})\}$. ^{b} The first digit keys on the crypt cation, the second and third on the atoms therein in the order previously given in ref 14.

(23.1°) slight twist around the threefold axis of the antiprism to form three bonds instead of six between top and bottom triangles on the short edges, while the long edges so created are bridged by added-waist arsenic 9, 10, and 11. Comparison of bond distances provides a good quantification of the degree of distorsion from the ideal D_3 symmetry. Obviously, atom 10 is closer to atom 4 than to atom 8 by 0.049 Å (>6σ). In fact, a glance at the shortest distances between arsenic atoms and light atoms in crypt-K$^+$ cations indicates a distance of 3.71 Å between arsenic 10 and carbon C(114). Steric strain might account for the nonequality of the two As–As distances around arsenic 10; however, two shortest distances between arsenic 11 and carbon atoms C(217) and C(323) (3.59 and 3.64 Å, respectively) are also indicative of strain, but these carbon atoms are adequately located around the bridging arsenic atom such as to balance this effect and the bonds lengths remain equal. Arsenic atoms 1–8 are

tricoordinated while waist bridging atoms 9, 10, and 11 are bicoordinated; therefore, the mean distance between tricoordinate–tricoordinate atoms is 0.07 Å longer than between tricoordinate–bicoordinate atoms. Before the geometrical features of previously discovered homopolyatomic anionic species[9-15] were definitively determined by X-ray investigation, some attempts to describe their possible geometry had been made referring to analogies with isoelectronic species. Wade's theory[21] is widely used to predict possible borane or carborane geometries and it also applies reliably to the prediction of the majority of post-transition elements polyatomic anions structures. For instance, this theory could be utilized to rationalize the geometry differentiation between Ge$_9^{2-}$ and Ge$_9^{4-}$ in (crypt-K$^+$)$_6$Ge$_9^{2-}$Ge$_9^{4-}$.

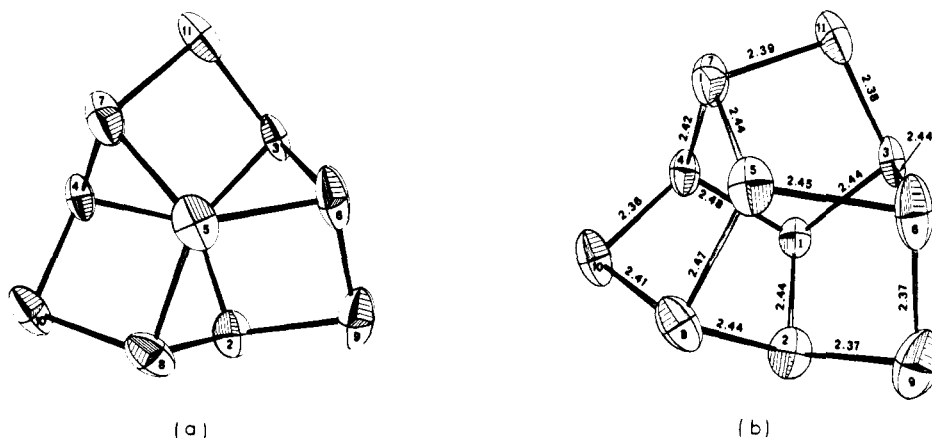(21) K. Wade, *Adv. Inorg. Chem. Radiochem.*, **18**, 1 (1976).

(a)　　　　　　　　　　　　　　　　(b)

Figure 1. Two views of cluster As_{11}^{3-} in the compound $(2,2,2\text{-crypt-}K^+)_3As_{11}^{3-}$. Thermal ellipsoids are shown at the 50% probability level. (a) Viewed down the threefold axis; arsenic 1 is eclipsed by arsenic 5. (b) Slightly tilted.

Table II. Bond Distances, Angles, and Dihedral Angles in Cluster As_{11}^{3-}

arsenic atoms	d, Å	arsenic atoms	d, Å
1-2	2.435 (8)	4-10	2.357 (7)
1-3	2.440 (7)	4-7	2.424 (7)
1-4	2.481 (7)	4-8	3.563 (7)
1-8	3.741 (7)	4-11	3.692 (7)
1-6	3.743 (7)	4-5	3.733 (7)
1-7	3.767 (7)	5-7	2.437 (8)
1-9	3.823 (7)	5-6	2.452 (7)
1-11	3.835 (8)	5-8	2.474 (7)
1-10	3.845 (7)	5-11	3.795 (7)
1-5	4.054 (6)	5-10	3.805 (7)
2-9	2.369 (7)	5-9	3.834 (8)
2-8	2.436 (7)	6-9	2.369 (9)
2-6	3.534 (8)	6-11	3.643 (8)
2-10	3.750 (8)	6-7	3.844 (7)
2-5	3.757 (7)	6-8	3.849 (7)
2-3	3.819 (8)	7-11	2.385 (7)
2-4	3.877 (8)	7-10	3.647 (7)
3-11	2.377 (8)	7-8	3.870 (8)
3-6	2.440 (7)	8-10	2.406 (7)
3-7	3.575 (7)	8-9	3.683 (7)
3-9	3.670 (8)	3-5	3.760 (6)
		3-4	3.857 (6)

atoms	angle, deg	atoms	angle, deg
2-1-3	103.1 (2)	7-5-8	104.0 (2)
3-1-4	103.2 (2)	8-5-6	102.8 (3)
4-1-2	104.1 (2)	6-5-7	103.7 (2)
5-1-3	65.4 (2)	1-5-6	64.9 (2)
5-1-2	65.3 (2)	1-5-7	65.5 (2)
5-1-4	64.5 (2)	1-5-8	64.7 (2)
1-2-8	100.4 (3)	5-7-4	100.4 (3)
1-2-9	105.4 (3)	5-7-11	103.8 (2)
8-2-9	100.0 (3)	4-7-11	100.3 (3)
1-3-6	100.2 (3)	5-8-10	102.5 (3)
1-3-11	105.5 (2)	5-8-2	99.8 (2)
6-3-11	98.2 (3)	10-8-2	101.5 (3)
1-4-7	100.4 (2)	5-6-9	105.3 (3)
1-4-10	105.3 (3)	5-6-3	100.5 (2)
7-4-10	99.4 (3)	9-6-3	99.5 (3)
2-9-6	96.4 (3)	4-10-8	96.8 (2)
3-11-7	97.3 (3)		

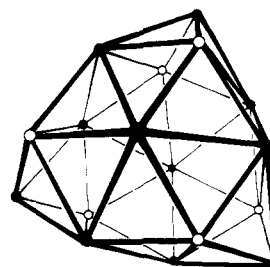| atoms		angle, deg	atoms		angle, deg
6-8-7	3-4-2	179.2 (2)	3-7-6	6-7-5	22.3 (4)
7-5-6	8-5-7	72.8 (3)	10-8-4	8-7-4	60.7 (3)
8-5-7	6-5-8	72.3 (3)	8-7-4	8-5-7	21.0 (3)
6-5-8	7-5-6	72.1 (3)	2-9-6	2-6-8	59.3 (3)
3-1-4	1-2-4	72.6 (3)	2-6-8	6-5-8	22.1 (3)
1-2-4	1-3-2	72.7 (3)	8-10-4	8-4-2	56.4 (4)
1-3-2	3-1-4	72.0 (3)	8-4-2	2-4-1	20.2 (4)
3-1-5	1-5-6	37.0 (2)	6-9-2	6-2-3	59.4 (3)
1-5-7	1-5-4	36.6 (2)	6-2-3	2-1-3	22.8 (3)
1-5-8	1-5-2	37.3 (2)	7-11-3	7-3-4	57.7 (3)
3-11-7	3-7-6	61.0 (3)	7-3-4	4-3-1	22.3 (3)

Figure 2. The fundamental 17-vertices polyhedron, basis for the structure of As_{11}^{3-}, approximately viewed down the threefold axis.

2.5en.[14] It clearly comes out that Ge_9^{2-} must have a "closo" configuration with D_{3h} symmetry (tricapped trigonal prism) and Ge_9^{4-} a "nido" configuration based on a bicapped Archimedean antiprism with C_{4v} symmetry in full agreement with diffraction results. For As_{11}^{3-} the problem appears more difficult because the cluster is of higher order than commonly found. Assuming that for each atom in the cluster an electron pair is nonbonding, the 36 remaining valence shell electrons must be regarded as skeletal bonding electrons, i.e., 18 bonding pairs, implying that the structure derives from a 17-vertices "closo" polyhedron. In a recent investigation on the hypothetical "closo" boron hydride structures in the range $B_{13}H_{13}^{2-}$ to $B_{24}H_{24}^{2-}$, Lipscomb and Brown[22] propose three structures for $B_{17}H_{17}^{2-}$, one with D_{5h}, the others with C_{2v} symmetries. None of these structures can be regarded as a good starting model to derive the As_{11}^{3-} geometry. Figure 2 presents a 17-vertices cage which displays the same D_3 symmetry as As_{11}^{3-}. Referring to Föppl's[23] notation it can be described as a 1:3:3:3:3:3:1 polyhedron with eight six-coordinate, six five-co-ordinate, and three four-coordinate vertices; its structure is oblate, flattening occurring along the threefold axis. Blank vertices are considered as caps to be removed to obtain the 11-vertices poly-hedron relative to As_{11}^{3-}. This structure is the one which best fits the geometry and particularly the twist of 23.1° observed in the trigonal-antiprismatic base previously described in As_{11}^{3-}.

Among elements of group 5, the P_7^{3-},[24] P_{11}^{3-},[20] As_7^{3-},[2] Sb_7^{3-},[12] and Bi_4^{2-}[15] anion derivatives have been isolated so far; As_{11}^{3-} is the second homopolyatomic anion discovered for arsenic. Despite the fact that the element is more characteristically nonmetallic, structural analogies between possible arsenic lower order po-lyanions with those of the group 5 heavier elements should be expected. The isolation for As of red crystals with trigonal symmetry is probably indicative of the existence of a lower order polyanion. Unfortunately, this structure has not yet been solved because of important disorder problems on anion sites, but the unit cell contains four crypt-K^+ cations implying a 2- charge for

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both corresponding anions which are suspected to be As_6^{2-}. This formulation is not surprising since this anion would be isoelectronic (valence electrons) with Te_6^{4+}, which was recently reported as a trigonal-prismatic species.[25]

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Transition-Metal Complexes of Vitamin B₆ Related Compounds. 3. X-ray, Mössbauer, and Magnetic Properties of a Binuclear Iron(III) Complex Containing an Unusual Pyridoxal Derivative[1]

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Abstract: The slow air evaporation of an aqueous solution containing pyridoxal, alanine, and iron(II) perchlorate in a 2:2:1 molar ratio resulted in the precipitation of a dimeric iron(III) complex containing the previously unreported ligand $N(PL)_2ala^{2-}$ (IV). We propose that this ligand has resulted from the formation of the Schiff base between pyridoxal and pyridoxamine and the subsequent nucleophilic attack of the Schiff-base imino group upon the α-keto carbon atom of pyruvic acid. The presence of pyruvic acid and pyridoxamine is expected because of the transamination equilibrium catalyzed by the presence of iron(III). The structure of this new ligand was determined through an X-ray structural study of the resulting crystals, which were orthorhombic, *Pccn*, with $a = 13.029$ (3), $b = 20.052$ (4), $c = 19.066$ (3) Å, and $Z = 8$. The molecular structure, $\{[Fe(N-(PL)_2ala)]ClO_4\}_2\cdot2.6H_2O$, was found to be disordered in several respects and refinement yielded a final R value of 0.087. The dimeric pseudooctahedral iron(III) structure derives from the bridging of two oxygen atoms from the α-keto groups of the two ligands present. Mössbauer and magnetic measurements indicate the presence of iron(III) ions which are antiferromagnetically coupled ($J = -5.2$ cm^{-1}) via superexchange through the two bridging oxygen atoms. The structure of this compound is similar to those of several other dimeric iron(III) compounds for which Mössbauer data are also reported. This is the first report of this ligand and the first iron(III) dimer to contain a ligand chelated to each iron ion.

Introduction

The importance of pyridoxal (I) in enzymatic transamination reactions has been known for about 50 years.[2-4] Metzler and Snell[5] and Longenecker and Snell[6] have studied the influence of various metal ions on the reversible transamination of various amino acids with pyridoxal and pyridoxamine. This work indicated that various metal ions were catalytically effective in promoting pyridoxal transamination and Metzler et al.[7] proposed a mechanism involving an amino acid–pyridoxal Schiff base intermediate which was chelated in a tridentate fashion to the metal ion.[4] The efficiency of the catalysis was found[5,6] to increase in the order $Cu^{2+} > Al^{3+} > Fe^{2+} > Fe^{3+} > Zn^{2+} > Ni^{2+} > Co^{2+}$. We have subsequently shown[2] that the studies involving divalent iron actually utilized iron(III). As a result, we have been interested in preparing and studying the iron(III) complexes containing these Shiff-base intermediates. We have recently reported[1] on several iron(III) complexes containing one tridentate Schiff-base ligand prepared from pyridoxal and glycine and are currently studying the bis complexes. Herein we report an unusual result from one of our attempted syntheses of a bis complex.

Pyridoxal can undergo a Schiff-base condensation with pyridoxamine to form the corresponding Schiff base, III.[8] Aluminum(III) and copper(II) chelates containing this ligand have been reported by Cennamo.[9] We believe, based upon the resulting solid-state structure, that, in the presence of iron(III), compound III undergoes further reaction with alanine to form the unusual dianion $N(PL)_2ala^{2-}$ (IV)[10] This is apparently the first report of this compound. Its structure was determined by single-crystal X-ray techniques in a dimeric iron(III) complex. The X-ray structure, Mössbauer, and magnetic properties of this complex are reported herein. Because of the wide interest in the bonding in oxygen-bridged systems such as $[(H_2O)_4FeOH]_2^{4+}$ we have also studied the Mössbauer-effect spectra of several related dimeric iron(III) complexes which contain the $[LFeO]_2$ bridging group.

Experimental Section

Pyridoxal hydrochloride and alanine were purchased from Sigma Chemical Co., St. Louis, Mo. Pyridoxal free base was prepared by titrating a saturated aqueous solution of the hydrochloride with 2 N KOH. Infrared spectra were recorded on a Perkin-Elmer 180 spectro-

* University of Missouri—Rolla.
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(8) The systematic *Chemical Abstracts* name for this compound is 5-hydroxy-4-[[[[3-hydroxy-5-(hydroxymethyl)-2-methyl-4-pyridyl]-methylene]amino]methyl]-6-methyl-3-pyridinemethanol.
(9) Cennamo, C. *Ric. Sci.* **1968**, *38*, 31.
(10) The systematic *Chemical Abstracts* name for the protonated form of this compound, $N(PL)_2alaH_2$, is α,3-dihydroxy-β-[[[3-hydroxy-5-(hydroxymethyl)-2-methyl-4-pyridyl]methylene]amino]-5-(hydroxymethyl)-α,2-dimethyl-4-pyridinepropanoic acid.