Stabilization of an Unusual Conformation of an Encapsulated Metal Ion Cobalt(methylarsasarcophagine): Synthesis and Structure

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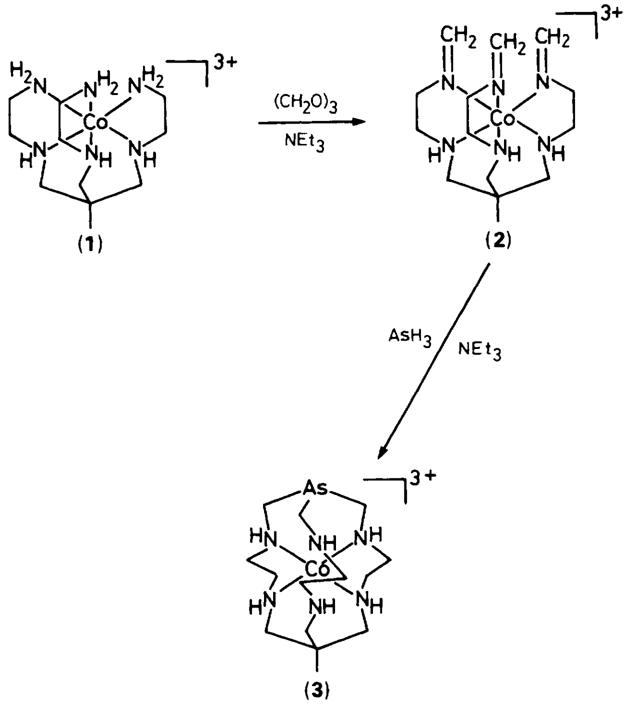
Base-catalysed condensation of $[Co(sen)]^{3+}$ (**1**) [sen = 4,4′,4″-ethylidyne-tris(3-azabutan-1-amine)] with formaldehyde yields the stable tri-imine $[Co(sim)]^{3+}$ (**2**) [sim = 6,6′,6″-ethylidyne-tris(2,5-diazahex-1-ene)] that is converted into the arsenic capped cage molecule $[Co(Mearsasar)]^{3+}$ (**3**) (Mearsasar = 8-methyl-1,3,6,10,13,16,19-arsahexa-azabicyclo[6.6.6]icosane) by reaction with AsH_3; an *X*-ray crystallographic analysis of (**3**) reveals an unusual oblique conformation of the encapsulating ligand, which affects the properties of the complex in a marked manner.

Encapsulated metal ions having sar (sar = 3,6,10,13,16,19-hexa-azabicyclo[6.6.6]icosane) or one of its derivatives as a ligand are numerous.[1—3] Most examples show a parallel (*lel*$_3$) orientation of the C–C axis of the ethane-1,2-diamine moieties of the hexa-aza-bicycle to the pseudo C_3-axis of the molecule. Considerable effort has been made to stabilize a conformer with an oblique (*ob*$_3$) arrangement, but few examples have been reported.[3—5]

It was expected that changes in the basic framework of the encapsulating ligand might lead to different physical properties of the encapsulated metal ion. Changing the cavity size by introducing a heavy element into the apical position of the cage molecule should, to some extent, expand the cap thus forcing the molecule to adopt the less common *ob*$_3$-conformation. In this paper we report the unusual addition of AsH_3 to a trialdimine precursor yielding a symmetric tertiary bicyclic arsine.

Early attempts to add the AsH-moiety of arsines to double bonds were unsuccessful.[6] However, more recently this method of preparing organoarsenic compounds has been of synthetic utility. The observation that only activated C=C bonds (*i.e.*, having electron-withdrawing substituents) allow facile addition of the As–H group implies a nucleophilic attack of the arsenic atom on the unsaturated system.[7,8] Consequently only activated C=N bonds are prone to nucleophilic attack by arsines.[7,9] Such an activation is expected with the co-ordinated Co^{III} exo-imines ($Co–N=CH_2$) formed in the base-catalysed reaction of $[Co(sen)]^{3+}$ [sen = 4,4′,4″-ethylidyne-tris(3-azabutan-1-amine)] (**1**) with formaldehyde.

To this end $[Co(sen)]Cl_3$ (**1**) was dissolved in acetonitrile by stirring it with an excess of $NaClO_4 \cdot H_2O$. After the addition of paraformaldehyde (10 equiv.) and triethylamine, an instantaneous colour change (orange to purple) indicated a rapid reaction, which was quenched with hydrochloric acid after 20 minutes. Only one product was isolated in almost quantitative yield (95%) by ion exchange chromatography (Dowex 50W-



Scheme 1

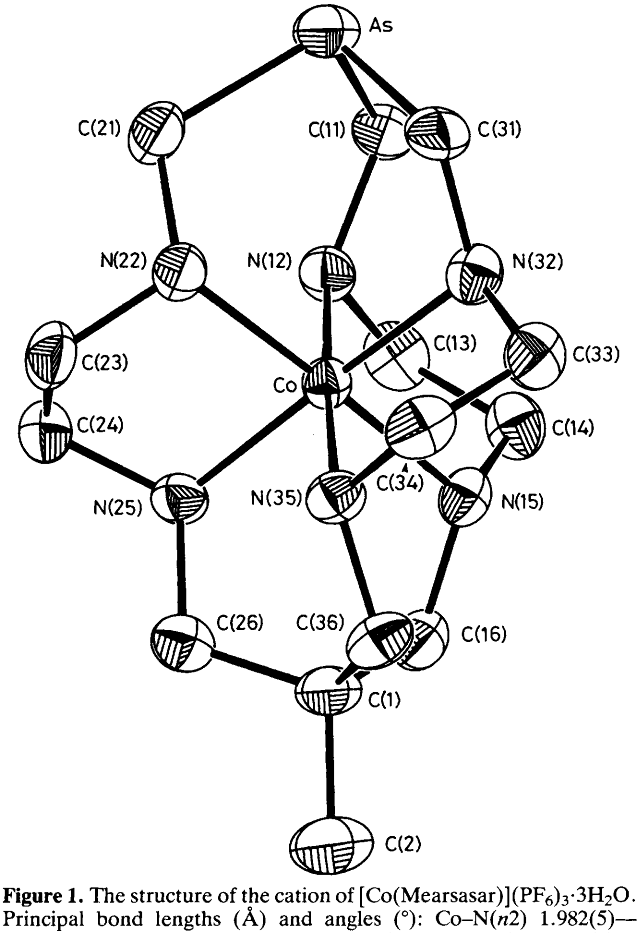


Figure 1. The structure of the cation of $[Co(Mearsasar)](PF_6)_3 \cdot 3H_2O$. Principal bond lengths (Å) and angles (°): Co–N(*n*2) 1.982(5)—1.993(5), Co–N(*n*5) 1.969(4)—1.976(5), As–C(*n*1) 1.965(6)—1.973(7). C–As–C 95.8(2)—96.7(3), C(*n*1)–N(*n*2)–C(*n*3)–C(*n*4) 89.4(6)—91.3(6), C(*n*3)–C(*n*4)–N(*n*5)–C(*n*6) 90.6(6)—93.7(5).

X2, 200—400 mesh, 3 M HCl) as its trichloride salt. The compound was assigned as the Co^{III} complex (**2**) of sim [sim = 6,6′6″-ethylidyne-tris(2,5-diazahex-1-ene)] by its elemental microanalysis (C, H, N), and ^1H and ^{13}C n.m.r. spectra.† In particular, the singlet for the imine carbon at δ 177.2 in the ^{13}C n.m.r. spectrum and the relatively small number of signals is in accordance with the proposed structure of (**2**) where three molecules of formaldehyde have condensed with $[Co(sen)]^{3+}$ (**1**), to form the tri-imine derivative (**2**), with average C_3-symmetry in solution. The orange complex was stable in neutral and acidic aqueous solutions but decomposed rapidly in the presence of OH^-. Therefore (**2**) was converted into its $CF_3SO_3^-$ salt by treatment with trifluoromethanesulphonic acid followed by recrystallisation from MeCN, MeOH, and Et_2O (5 : 5 : 1). In this form, the complex of (**2**) was soluble in acetonitrile and stable in the presence of a sterically hindered tertiary amine base. Such a solution was exposed to AsH_3[10] carried by a stream of argon for 10 min at 10 °C. One yellow complex was isolated (50—60% yield) after quenching with HCl and ion exchange chromatography (SP-Sephadex C-25, 0.1 M Na_2SO_4). The product appeared to be the arsenic capped cage $[Co(Mearsasar)]^{3+}$ (**3**) by consideration of the elemental microanalysis (C, H, N, As) of its trichloride salt and its ^1H and ^{13}C n.m.r. spectra.†

The structure of (**3**) was established by a single crystal *X*-ray study of the PF_6 salt‡ which confirmed the arsenic-capped cage assignment. The unusual feature of the ion is the oblique orientation of the C–C bonds of the ethane-1,2-diamine moiety to the C_3-axis of the ion. The enantiomeric conformational stereoisomers of (**3**) may therefore be designated Δ-*ob*$_3$(*R,R*) and Λ-*ob*$_3$ (*S,S*) where (*R,R*) and (*S,S*) describe the right- and left-handed helical relationship between the N–C bonds of the caps and the C_3-axis of the ion.[11] The conformation has rarely been seen in related Co^{III}–N_6-cage complexes; only one example has been reported for the carbon-capped cage with hydroxyamino substituents.[4]

The ^1H n.m.r. spectrum of (**3**) shows AB patterns for both the $As(CH_2)_3$ and $C(CH_2)_3$ cap methylene resonances and an ABXY system for the CH_2–CH_2 moiety. The signals associated with one of the unique protons of all the methylene carbons show considerable line-broadening. Conformational changes in solution are unlikely to be the reason, since the effect persists in a series of spectra taken between 20 and 95 °C. Decoupling experiments exclude broadening due to coupling to the ^{59}Co nucleus; therefore we suggest that it is caused by quadrupolar coupling to the ^{14}N nucleus. This effect is strongly dependent on the orientation of the lone pair of electrons on the N atom.[12] In contrast to a *lel*$_3$-conformation, dihedral angles (H–C–N–Co) in (**3**) are almost ideal for observing the effect, indicating that little or no conformational change occurs on dissolving the title compound in water. Visible absorption bands at λ_{max} ($\varepsilon/dm^3\,mol^{-1}\,cm^{-1}$) 466 (91) and 338 nm (240), and also the electrochemical Co^{III}/Co^{II} reduction potentials (measured by cyclic voltametry: E' −0.34 V in aqueous 0.1 M $NaClO_4$ *vs.* normal hydrogen electrode) are typical and indicative of an *ob*$_3$-conformation for Co-cage complexes of similar cavity size.[13]

Exploiting the synthetic utility of $[Co(sim)]^{3+}$ (**2**) should give access to related systems which will determine the generality of the observed phenomenon.

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† $[Co(sim)]^{3+}$ (**2**): ^1H n.m.r. (499.84 MHz, D_2O, δ in p.p.m. *vs.* sodium 3-trimethylsilylpropane sulphonate, *J* in Hz) 0.91 (s, CH_3), 2.37, 2.95 (2d, *J* 13.7, quat.-C–CH_2), 2.77, 3.03, 3.75, 4.06 (ABXY, CH_2CH_2), 7.34 (d, *J* 7.4, N=CH_2) 7.87 (br. s, N=CH_2); $^{13}C\{^1H\}$ n.m.r. (75.43 MHz, D_2O, δ in p.p.m. *vs.* $SiMe_4$ 20.5 (CH_3), 42.6 (quat.-*C*), 54.6 (CH_2–C-quat.), 55.2, 62.1 (CH_2CH_2), 177.2 (CH_2=N). $[Co(Mearsasar)]^{3+}$ (**3**): ^1H n.m.r. (499.84 MHz, D_2O) 0.93 (s, CH_3), 2.62, 2.69 (AB, *J* 13.7, CH_2–C-quat.), 2.72, 2.77, 3.55, 3.68 (ABXY, CH_2CH_2), 3.05, 3.07 (AB, *J* 14.0, CH_2–As); $^{13}C\{^1H\}$ n.m.r. (75.43 MHz, D_2O) 21.3 (CH_3) 40.1 (*C*-quat.), 40.5 (CH_2–As), 50.6, 54.4 (CH_2CH_2), 55.0 (CH_2–C-quat.). All ^1H and ^{13}C n.m.r. assignments were made and confirmed using reported shift data and 2D homonuclear (COSY) and heteronuclear (C-H-HETCOR) experiments.

‡ *Crystal data* for (**3**): $C_{14}H_{39}AsCoF_{18}N_6O_3P_3$, M = 908.24, monoclinic, space group *C*2/*c*, a = 19.045(1), b = 17.615(3), c = 19.252(2) Å, β = 101.06(1)°, U = 6338.6 Å^3, Z = 8, D_c = 1.903 g cm^{-3}, $\mu(Mo\text{-}K_\alpha)$ = 18.56 cm^{-1}. Data were collected on a Philips PW-1100 diffractometer using graphite-monochromated Mo-K_α radiation yielding 3198 reflections with $I > 3\sigma(I)$ to $2\theta = 47°$. An absorption correction was applied. The structure was solved by direct methods and difference Fourier techniques and refined by full-matrix least-squares using weights derived from counter statistics. Hydrogen atoms were included at calculated positions and not refined; a small degree of disorder of one of the PF_6-groups was observed. Final *R* factor 0.043. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

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