Phospha-capped Cobalt(III) Cage Molecules: Synthesis, Properties, and Structure

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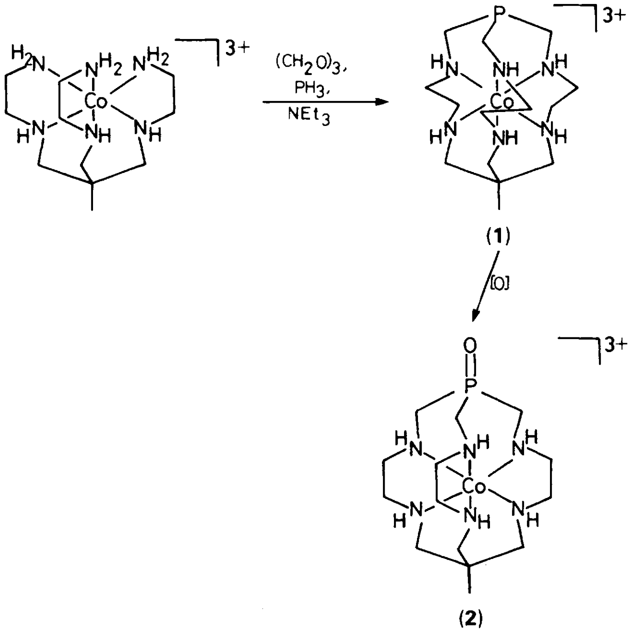
Base-induced condensation of $[Co(sen)]^{3+}$ [sen = 4,4′,4″-ethylidynetris(3-azabutan-1-amine)] with paraformaldehyde and phosphine leads to the phospha-capped bicyclic cage complexes $[Co(Mephosphasar)]^{3+}$ (Mephosphasar = 8-methyl-3,6,10,13,16,19,1-hexa-azaphosphabicyclo[6.6.6]icosane) and its phosphine oxide derivative $[Co(Me,Ophosphasar)]^{3+}$; the complexes have surprisingly different spectral and electrochemical properties which are attributed to their different conformations and the *X*-ray crystal structure of $[Co(Me,Ophosphasar)][ZnCl_4]Cl$ has been determined.

The $[Co(en)_3]^{3+}$ (en = ethane-1,2-diamine) and $[Co(sen)]^{3+}$ [sen = 4,4′,4″-ethylidynetris(3-azabutan-1-amine)] complexes have been condensed with aqueous formaldehyde and ammonia in a highly organized template procedure to give bicyclic icosane cage molecules with apical nitrogen atoms.[1,2] This paper addresses analogous chemistry with the much less basic phosphine nucleophile in order to introduce new influences into the cage framework.

Rapid reactions of PH_3 with $R_2N^+{=}CH_2$ ions have been implicated in the condensation of formaldehyde, secondary amines, and phosphine to form tris-α-aminophosphines.[3,4] The same type of condensation could be expected with the co-ordinated Co^{III} exo-imines ($Co{-}N{=}CH_2$) in the base-catalysed reaction of $[Co(sen)]^{3+}$ with formaldehyde, but here the imines are less susceptible to nucleophilic attack than the iminium ions,[1] and only low concentrations of such imines were obtained when the reactions were executed in aqueous media.[5] By using a hindered tertiary amine base in a suitable non-aqueous medium[6] it was thought that the $Co^{III}{-}N{=}CH_2$ imines might be formed more rapidly and prolifically, have greater stability, and show enhanced reactivity towards the phosphine nucleophile.

In the course of exploring such an encapsulation approach $[Co(sen)](CF_3SO_3)_3$ was treated with excess of paraformaldehyde, phosphine, and triethylamine in acetonitrile for 30 min at ~20 °C. Two main products were isolated in modest yield (total 40—50%) after quenching with acetic acid and ion-exchange chromatography (SP-Sephadex C-25, 0.1 M Na_2SO_4).

A fast moving orange compound was assigned as the phosphine oxide capped cage $[Co(Me,Ophosphasar)]^{3+}$ [Me,Ophosphasar = 8-methyl-1-oxo-3,6,10,13,16,19,1-hexa-azaphosphabicyclo[6.6.6]icosane, (**2**)] by elemental microanalysis (C, H, N, and P) of its trichloride salt and by its ^1H, ^{13}C, and ^{31}P n.m.r. spectra.† These results indicated that three formaldehyde and one phosphine molecules had condensed with $[Co(sen)]^{3+}$, that the complex had an average C_3 symmetry in solution, and that the phosphine moiety had been oxidised to the phosphine oxide. The structure of (**2**) (Figure 1) was established by a single crystal *X*-ray study of the $Cl[ZnCl_4]$ salt‡ confirming the phosphine oxide capped cage assignment. The enantiomeric conformational stereoisomers of (**2**) found in the crystal may be designated Δ-*lel*$_3$ (*R,R*) and Λ-*lel*$_3$ (*S,S*), where *lel*$_3$[7] indicates that the en C–C bonds are parallel to the pseudo C_3 axis, and (*R,R*) and (*S,S*) describe the right- or left-handed helical relationship between the N–C bonds of the caps and the C_3 axis of the ion. The conformation is very similar to that of the Λ-D_3*lel*$_3$ (*S,S*) form found in



Scheme 1

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† $[Co(Mephosphasar)]^{3+}$: ^{31}P n.m.r. (D_2O, δ *vs.* external phosphoric acid) −15.95; ^1H n.m.r. [D_2O, centred proton δ shifts *vs.* sodium 3-(trimethylsilyl)propane sulphonate] 2.73, 2.77, 3.42, 3.51 (ABCD pattern, J_{AB} unresolved, J_{AC}, J_{AD}, J_{BC}, J_{BD}, J_{CD} = 13.5, 4.4, 4.4, 13.5, 13.5 Hz, en CH_2), 3.17, 2.91 (ABX, X = ^{31}P; J_{AB}, J_{AX}, J_{BX} = 15.5, 0, 19.8 Hz, Pcap CH_2), 2.56, 2.71 (AB quartet, J = 12.8 Hz, Ccap CH_2), 0.91 (s, CH_3); $^{13}C\{^1H\}$ n.m.r. (D_2O, δ *vs.* $SiMe_4$) 54.04, 51.63 (en CH_2), 55.08 (Ccap CH_2), 41.62 (d, J_P 26.1 Hz, Pcap CH_2), 41.03 (quat. C), 21.22 (CH_3).

$[Co(Me,Ophosphasar)]^{3+}$: ^{31}P n.m.r. (D_2O) δ 46.81; ^1H n.m.r. (D_2O) 2.67, 2.83, 3.30, 3.42 (ABCD, J_{AB}, J_{AC}, J_{AD}, J_{BC}, J_{BD}, J_{CD} = 4.8, 13.8, 9.2, 6.3, 13.8, 6.0 Hz, en CH_2), 3.39, 3.69 (ABX, X = ^{31}P; J_{AB}, J_{AX}, J_{BX} = 14.6, 13.5, 11.3 Hz, POcap CH_2), 2.42, 2.81 (AB, J, 13.4 Hz, Ccap CH_2), 0.87 (s, CH_3); $^{13}C\{^1H\}$ n.m.r. (D_2O) 55.27, 53.86 (en CH_2), 55.04 (Ccap CH_2), 42.88 (d, J_P = 73.9 Hz, POcap CH_2), 42.73 (quat. C), 20.64 (CH_3). 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 on Varian VXR 500 and XL 200E instruments.

‡ *Crystal data*: $CoC_{14}H_{33}N_6OPClZnCl_4$; monoclinic, a = 9.644(2), b = 24.394(4), c = 10.419(2) Å, β = 91.89(1)°, space group $P2_1/n$; D_c = 1.718 g cm^{-3} for Z = 4. Intensity data were collected on a Picker FACS-I diffractometer in θ/2θ scan mode to 2θ = 55° using graphite-monochromated Mo-K_α radiation. The structure was solved by direct methods and difference Fourier techniques, and refined by full-matrix least-squares on 4855 reflections with $I > 3\sigma(I)$ (corrected for absorption, μ = 23.13 cm^{-1}) to a final R factor of 0.032. Hydrogen atoms were included in calculated positions but their parameters were not refined. 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.

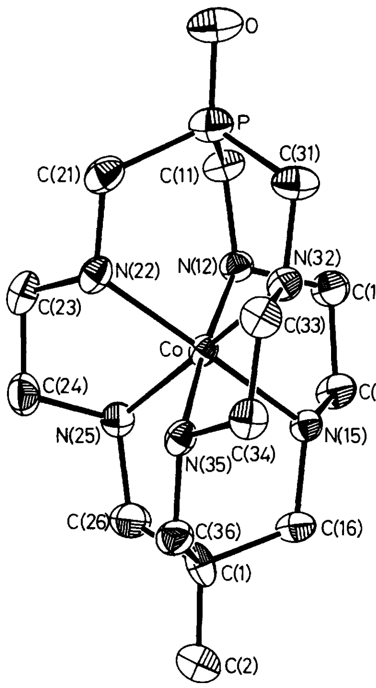

Figure 1. The molecular structure of $[Co(Me,Ophosphasar)]^{3+}$ in the $Cl[ZnCl_4]$ salt. Bond lengths (Å): Co–N(*n*2) 1.998(2)—2.008(2); Co–N(*n*5) 1.977(2)—1.994(2); P–C 1.790(3)—1.815(3); P–O 1.476(3); N–C 1.482(4)—1.504(4); C(*n*3)–C(*n*4) 1.495(4)—1.500(5). Relevant bond angles (°): N(*n*2)–Co–N(*n*5) 85.0(1)—85.7(1); C–P–C 103.2(2)—105.9(2); O–P–C 113.8(2)—114.8(2).

crystals of the diaza-capped cage molecules[1,2,8] obtained from $[Co(en)_3]^{3+}$.

A slow moving yellow complex was also isolated and identified as the phospha-capped cage $[Co(Mephosphasar)]^{3+}$ (**1**) by elemental microanalysis (C, H, N and P) and the ^1H, ^{13}C, and ^{31}P n.m.r. spectra† of $[Co(Mephosphasar)]Cl_3·4H_2O$. Although (**1**) appeared to be stable to air in the solid state, it slowly oxidised in aqueous solution in the presence of air to give the phosphine oxide derivative (**2**). It was also converted rapidly and quantitatively into (**2**) by treatment with aqueous hydrogen peroxide. These results confirm the identify of (**1**) and imply that the occurrence of (**2**) in the chromatography experiments arises from the prolonged aqueous treatment of the reaction mixtures in the presence of air.

The $[Co(Mephosphasar)]^{3+}$ (**1**) and $[Co(Me,Ophosphasar)]^{3+}$ (**2**) ions display some intriguing differences in their n.m.r. spectra, visible absorption spectra, and Co^{III}/Co^{II} electrochemical potentials, which are largely unrelated to any direct electronic interaction between the Co^{III} ion and the phosphine and phosphine oxide moieties. Both the $P(CH_2)_3$ and $C(CH_2)_3$ caps of (**1**) give methylene proton resonances (ABX, X = ^{31}P and AB patterns) in which the signals associated with one of the unique protons [centred at δ 3.17 for the $P(CH_2)_3$ cap and 2.71 for the $C(CH_2)_3$ cap†] are nearly twice as broad as those arising from the other. This effect persists in the ^{59}Co decoupled proton spectra of (**1**) whereas all the cap methylene proton signals in the ^1H n.m.r. spectrum of (**2**) have relatively narrow line widths (<10 Hz). The en methylene carbon signals of the ^{13}C n.m.r. spectra are shifted downfield on going from (**1**) (δ 54.04, 51.63) to (**2**) (55.27, 53.86), with the shift being almost twice as large for the carbon more remote from the phosphine and phosphine oxide caps. There is a modest difference in position and intensity of the visible absorption bands of d–d origin for (**1**) [λ_{max}/nm (ε dm^3 mol^{-1} cm^{-1}) in H_2O: 460 (86), 328 (131sh)] and (**2**) [474 (129), 348 (146)], which leads to a distinctive yellow (**1**) to orange (**2**) colour change for the complexes in aqueous solutions. The most striking difference between (**1**) and (**2**) was seen in the electrochemical Co^{III}/Co^{II} potentials. These gave *E* values of −0.32 V (**1**) and −0.02 V (**2**) in aqueous 0.1 mol dm^{-3} $NaClO_4$ (*vs.* standard hydrogen electrode),§ and the 300 mV variation in the potentials is much larger than that expected for a single substituent change in cobalt(3+) complexes.[9]

The contrasting spectral and electrochemical features of the aqueous $[Co(Mephosphasar)]^{3+}$ and $[Co(Me,Ophosphasar)]^{3+}$ complexes closely resemble those found for carbon-capped cage analogues which have constrained Δ-*ob*$_3$ (*S,S*) and Δ-*lel*$_3$(*R,R*) conformations.[10] This implies that the conformation of the $[Co(Mephosphasar)]^{3+}$ ion in aqueous solution is predominantly Δ-*ob*$_3$ (*S,S*) whereas that of the $[Co(Me,Ophosphasar)]^{3+}$ ion is Δ-*lel*$_3$ (*R,R*), the conformation found in the crystal structure (Figure 1). The Δ-*ob*$_3$ (*S,S*) form, where the en C–C bonds are oblique to the C_3 axis, has rarely been seen in analogous cage complexes with similar $Co^{III}N_6$ chromophores. However one solid-state example has been reported in the *X*-ray structure of a carbon-capped cage with hydroxyamino substituents.[11]

The structure of (**2**) also shows that the larger phosphorus cap causes an expansion of the adjacent Co–N bonds [Co–N_{av} (Pcap) = 2.003(1) Å] compared with those of the aza[8] and carbon-capped analogues.[5,10] This is reflected in the more positive electrochemical potentials, and signals an interesting approach to cavity size expansion and the stabilization of low oxidation states for metal ions. Experiments to stabilize both the Δ-*ob*$_3$ (*S,S*) conformations and the low oxidation states of the larger Rh^{III} and Ir^{III} cage analogues by the introduction of phosphine caps are being pursued.

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§ *E* values obtained from cyclic voltammetry at a glassy carbon electrode (*vs.* Ag/AgCl/sat. NaCl, 100 mVs^{-1}, 10^{-3} M complex, 22 °C) = −0.522 V for (**1**), −0.222 V for (**2**).