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The Reaction of a Nitro-Capped Cobalt(III) Cage Complex with Base: the Crystal Structure of a Contracted Cage Complex, and the Mechanism of its Formation*

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Abstract

The synthesis, properties and crystal structure of the cage complex (1-hydroxy-8-methyl-3,6,10,13,15,18-hexaazabicyclo[6.6.5]nonadecane)cobalt(III) chloride hydrate ([Co(Me,OH-absar)] $Cl_3.H_2O$) are reported. The mechanism of the formation of this contracted cavity cage from a nitro-capped hexaazabicycloicosane type cage has been investigated. Treatment of (1-methyl-8-nitro-3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane)cobalt(III) chloride ([Co(Me,NO_2-sar)]$^{3+}$) with excess base in aqueous solution leads initially to rapid ($t_{1/2} < 1$ ms) and reversible deprotonation of one coordinated secondary amine. This species undergoes a retro-Mannich type reaction and imine hydrolysis ($t_{1/2} \approx 90$ s). Quenching the reaction with acid gives rise to a pair of isomeric intermediate species which have been isolated and characterized. They have a pendant arm macrocyclic structure, resulting from the loss of a methylene unit from one of the arms of the cap. Heating either isomer in aqueous solution gives the new cage compound with the contracted cap. It is postulated that this occurs through a Nef reaction, resulting in the formation of a ketone which then condenses with the coordinated primary amine. A comparison with the corresponding bicycloicosane analogue indicates a reduced chromophoric cavity size for the contracted cage. The reduction potential of the cobalt(III)/cobalt(II) couple is 170 mV more negative for the smaller cage, and, in the electronic spectrum of the cobalt(III) complex, the d–d transitions are both shifted to higher energy, corresponding to a stronger ligand field.

Introduction

The syntheses and properties of a large range of cobalt complexes encapsulated by a cage ligand of the 'sar' type (1) have been reported, and their unusual properties have been documented.[1] Various modifications to this basic cage have since been investigated, to determine their effect on the encapsulated metal.

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* Dedicated to the memory of Graeme Searle, a good friend and colleague, and devoted chemist and teacher, with many sterling contributions to the chemical literature.

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The apical substituents have been varied,[2] as have the donor groups[3–5] and the bridgehead atoms,[6,7] Also, the effect of fixing conformational configurations through *C*-substituted peripheral alkyl groups has been explored in detail.[8–10] Differences in the apical substituent change the electronic properties (reduction potential, electron self exchange rate) to a modest extent, whereas changing the conformational geometry has a profound effect on the electronic and spectroscopic properties. As expected, replacing the amine donor groups by thioethers has a marked effect on the electronic properties, electron transfer rates and stability. More recently, symmetrical larger cages based on trimethylene bridging units have been prepared both with N_6 [11–14] and with S_6 [15] donor sets, and these variations have brought about some exceptional new properties for the resulting complexes.

During earlier studies in which cages with different apical substituents were prepared, it was found that diazotization of an apical primary amine led to the formation of an adamantyl type carbocation which captured a variety of nucleophiles.[2] A number of minor products were also isolated, in which it was apparent that this adamantyl-like carbocation had rearranged in an unexpected manner to give a primary carbocation (presumably to relieve strain in the carbocation and to reduce the electrostatic repulsion between the Co^{3+} centre and the C^+) prior to attack by the nucleophile. This resulted in the formation of a contracted ('absar') cage (2) in which one 'arm' of the cap has lost a methylene unit.[1,2,16] Similar behaviour has also been noted for the related complexes with an N_3S_3 donor set.[4]

For $[Co((NO_2)_2\text{-sar})]^{3+}$ ($[Co(1)]^{3+}$, $X = Y = NO_2$),* the enhanced acidity of the coordinated secondary amine hydrogen had previously been noted;[2] above

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* For clarity, throughout this paper the apically substituted derivatives of the two cage types, sar (1) and absar (2), will be abbreviated as X,Y-sar, X_2-sar (where X = Y) and X,Y-absar.

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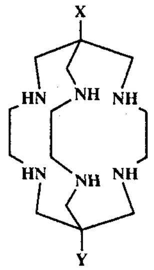

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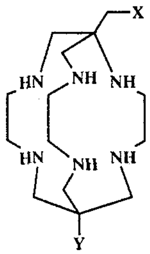

(2)

pH 10, for example, a solution of $[Co((NO_2)_2\text{-sar})]^{3+}$ has a characteristic intense purple colour resulting from the presence of a deprotonated coordinated amine. The crystal structure of the complex was determined, and indeed showed the expected shortening of one Co–N bond, as well as a slight flattening of the structure around this nitrogen compared with the tetrahedral values of the other coordinated amines.[2] In more concentrated base, the complex undergoes a complicated set of ring opening reactions, but the $[Co(Me,NO_2\text{-sar})]^{3+}$ ion reacts by a somewhat simpler path. The kinetics of its reaction with base and the mechanism of the rearrangement, together with an examination of the properties of the product, are the subject of this article.

Experimental

General Methods

All evaporations were carried out at <20 Torr with a Büchi rotatory evaporator so that the temperature of the sample did not exceed 25°C. ^1H and proton-decoupled ^{13}C n.m.r. spectra were recorded with a Varian Gemini 300 MHz Fourier-transform n.m.r. spectrometer, by using 1,4-dioxan as internal reference (the signals for dioxan in D_2O are taken as 3·74 ppm for ^1H n.m.r. and 67·39 ppm for ^{13}C n.m.r. relative to tetramethylsilane). ^{13}C peak multiplicities were assigned by using the APT or DEPT techniques as appropriate. Electronic absorption spectra and kinetic traces were obtained with a Hewlett–Packard 8450A u.v./visible spectrophotometer. Electronic spectra of the cobalt(II) complexes (300–1100 nm) were obtained with a Cary 5 spectrophotometer. Electrochemistry was carried out with a BAS 100 electrochemical analyser, by using 0·2 M aqueous KCl solution saturated with high-purity argon, a glassy carbon working electrode, a platinum wire auxiliary electrode, and a saturated calomel reference electrode; measurements were made at 22°C and the scan rate was varied from 10 to 100 mV s^{-1} with no effect on the reduction potential. The spectral parameters and reduction potentials are listed in Table 1.

Kinetic Measurements

Kinetic measurements were performed by using a Hewlett–Packard 8450A u.v./visible spectrophotometer in repeat scan mode, or an Applied Photophysics SF 17MV stopped flow spectrophotometer. For the stopped flow experiments, the ionic strength was held constant ($I = 1\cdot 0$ M) with NaCl. The temperature was 25°C in all cases.

$[Co(Me,NO_2\text{-sar})]Cl_3$

The synthesis was carried out as previously reported,[2] and the *product* was recrystallized from aqueous HCl (Found: C, 34·5; H, 6·5; Cl, 20·2; N, 18·5. $C_{15}H_{33}Cl_3CoN_7O_2.H_2O$ requires C, 34·2; H, 6·7; Cl, 20·2; N, 18·6%). ^1H n.m.r. δ (D_2O): 3·9–2·4, complex pattern,

CH_2N, 24H; 0·93, s, CH_3, 3H (Fig. 1*a*). ^{13}C n.m.r. δ (D_2O): 88·60, C_qNO_2; 55·81, approx. double intensity, NCH_2CH_2N; 55·15, $\mathbf{C}H_2C_qCH_3$; 51·82, $\mathbf{C}H_2C_qNO_2$; 43·53, $\mathbf{C}_qCH_3$; 20·06, CH_3.

Table 1. Spectral and electrochemical properties

Complex	λ_{max} (ϵ_{max})^A				$E^{o\prime}$(mV)^B
Cobalt(III)					
$[Co(Me,NO_2\text{-sar})]^{3+}$	345 (117)	472 (135)			−264
$[Co(Me,NO_2\text{-sar} - H^+)]^{2+}$	330 (790)	476 (275)			—
$[CoL]^{3+\,C}$					
Isomer *A*	348 (146)	478 (143)			−196
Isomer *B*	346 (132)	478 (137)			−196
$[Co(Me,OH\text{-absar})]^{3+}$	336 (172)	458 (175)			−551
$[Co(Me,OH\text{-sar})]^{3+}$	344 (124)	472 (143)			−385
Cobalt(II)^D	$^4T_{1g}(P)$	$^2T_{1g}(P)$	$^2T_{1g}(G)$ $^2T_{2g}(G)$	$^4T_{2g}(F)$	
$[Co(Me,OH\text{-sar})]^{2+}$	458 (12)	583 (6)	638 (sh, 5)	952 (7)	
$[Co(Me,OH\text{-absar})]^{2+}$	467 (13)	550 (5·3)	658 (3·4)	870 (6)	
$[Co(Me\text{-azasar})]^{2+\,E}$	463 (8·6)	551 (3·5)	644 (0·9)	921 (5·5)	
$[Co(sep)]^{2+\,E}$	467 (8·2)	545 (2·0)	664 (0·8)	910 (4·9)	

[A] λ_{max} in nm (ϵ_{max} in dm^3 mol^{-1} cm^{-1}).

[B] *v.* s.h.e., 22°C.

[C] L = 6-(4-amino-2-azabutyl)-6-methyl-13-nitro-1,4,8,11-tetraazacyclotetradecane.

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[Co(Me, OH-sar)] Cl₃

$NaNO_2$ (350 mg) was added over 30 min to a stirred solution of $[Co(Me,NH_3\text{-sar})]$ $(CF_3SO_3)_4$ [2] (4·85 g) in water (50 ml) at 0°C. Two aliquots of triflic acid (2 M, 5 ml) were added at 30-min intervals. The solution was diluted to 5 litres and loaded onto a column of SP-Sephadex C-25. Elution with 0·1 M K_2HPO_4 gave four fractions; the third fraction was loaded onto Dowex 50W-X2 (200–400 mesh) cation exchange resin, washed with water, 1 M HCl, eluted with 4 M HCl, evaporated to dryness, and recrystallized from water/acetone. Yield 60%. ^1H n.m.r. δ (D_2O): 3·4–2·4, complex pattern, CH_2N, 24H; 0·91, s, CH_3, 3H. ^{13}C n.m.r. δ (D_2O): 73·76, C_qOH; 55·84, approx. double intensity, 55·13, 54·91, CH_2N; 43·14, $\mathbf{C}_qCH_3$; 20·12, CH_3. Electronic spectrum in aqueous HCl (0·1 M) [λ_{max} in nm (ϵ_{max} in dm^3 mol^{-1} cm^{-1})]: 472 (143), 344 (124).

[Co(Me, OH-sar)]²⁺

$[Co(Me,OH\text{-sar})]^{2+}$ was prepared by reduction of an argon-saturated aqueous solution of $[Co(Me,OH\text{-sar})]^{3+}$ with zinc dust directly in the spectrophotometer cell. Electronic spectrum in H_2O [λ_{max} in nm (ϵ_{max} in dm^3 mol^{-1} cm^{-1})]: 952 (7), 638 (sh, 5), 583 (6), 458 (12).

(3) [Co(Me,NO₂-sar – H⁺)]²⁺

A sample of $[Co(Me,NO_2\text{-sar})]$ Cl_3 was dissolved in D_2O and 1 equiv. of NaOD was added. The solution darkened immediately, and the ^1H and ^{13}C n.m.r. spectra were recorded; the spectra that were recorded after 90 min were identical to those of the initial product. ^1H n.m.r. δ (D_2O+1 equiv. NaOD): 3·62, d, *J* 14 Hz,, 3H; 3·3–2·5, complex pattern, CH_2N, 18H; 2·38, d, *J* 14 Hz, 3H; 0·87, s, CH_3. ^{13}C n.m.r. δ (D_2O+1 equiv. NaOD): 90·25, C_qNO_2; 56·51, 55·75, 55·66, 53·01, CH_2N; 42·90, $\mathbf{C}_qCH_3$; 20·33, CH_3. N.m.r. spectra were acquired for solutions of [Co(Me,NO_2-sar)]$^{3+}$ (*c.* 0·3 M) containing 1 equiv. of NaOD, excess Na_2CO_3, and NaOD (*c.* 1 M) respectively. The peak positions (but not the splitting patterns) were strongly dependent on pH. (See Results and Discussion.) Electronic spectrum in aqueous NaOH (0·1 M) [λ_{max} in nm (ϵ_{max} in dm^3 mol^{-1} cm^{-1})]: 476 (275), 330 (790).

(5) [Co(6-Me,13-NO_2,6-$CH_2NHCH_2CH_2NH_2$-[14]aneN$_4$)] Cl_3.3H_2O (Isomer A*), (6-(4-Amino-2-azabutyl)-6-methyl-13-nitro-1,4,8,11-tetraazacyclotetradecane)cobalt*(III) *Chloride Trihydrate*

A solution of NaOH (6·1 g) in 30 ml of water was added to a solution of [Co(Me,NO_2-sar)] Cl_3 (3·14 g) in 50 ml of water. The mixture immediately darkened. After stirring for 15 min at 20°C, the mixture was quenched with 11·7 M HCl (15 ml; final pH < 1), and then diluted to *c.* 500 ml with dilute HCl (0·2 M). It was sorbed onto a column of Dowex 50W-X2 cation exchange resin. The column was washed with 1 M HCl, and then eluted with 4 M HCl. The eluate containing the cationic complexes was evaporated to dryness, and the residue was dissolved in water, loaded onto a column of SP-Sephadex, and eluted with 0·05 M K_2SO_4. A band corresponding to starting material was eluted first, and the diffuse band that followed was collected, made basic with Na_2CO_3, reacidified, and loaded onto Dowex 50W-X2 cation exchange resin. The column was washed with 1 M HCl, and then eluted with 4 M HCl. The eluate was evaporated to dryness, to give the product.

A *sample* was recrystallized from methanol/absolute ethanol (Found: C. 31·0; H, 7·1; N, 17·4. $C_{14}H_{33}Cl_3CoN_7O_2.3H_2O$ requires C, 30·5; H, 7·1; N, 17·8%). Electronic spectrum in aqueous HCl (0·1 M) [λ_{max} in nm (ϵ_{max} in dm^3 mol^{-1} cm^{-1})]: 478 (143), 348 (146). ^{13}C n.m.r. δ (0·1 M DCl): 80·51, $CHNO_2$; 57·98, 55·87, 55·77, 54·35, 54·16, 54·05, 53·95, 50·73, 49·15, 46·41, 43·25, CH_2N; 43·14, $\mathbf{C}_qCH_3$; 20·13, CH_3. The peak at 80·51 diminished with time as the attached proton exchanged with deuterium.

A sample was also converted into the diethyldithiocarbamate (Et_2dtc^-) *salt* by treating an aqueous solution of the chloride salt with Na(Et_2dtc), filtering the precipitate, and washing with water (Found: C, 40·5; H, 7·9; N, 16·1; S, 21·9. $C_{29}H_{63}CoN_{10}O_2S_6.2H_2O$ requires C, 40·0; H, 7·8; N, 16·1; S, 22·1%).

(5) [Co(6-Me,13-NO_2,6-$CH_2NHCH_2CH_2NH_2$-[14]aneN$_4$)] Cl_3.3H_2O (Isomer B*), (6-(4-Amino-2-azabutyl)-6-methyl-13-nitro-1,4,8,11-tetraazacyclotetradecane)cobalt*(III) *Chloride Trihydrate*

The product from the previous preparation (isomer *A*) was maintained at 20°C in aqueous solution for 24 h. The solution was loaded onto a column of SP-Sephadex C-25, and eluted with 0·1 M K_2SO_4. The single band which was obtained was loaded onto Dowex 50W-X2, washed with 1 M HCl, eluted with 4 M HCl, and evaporated to dryness. A *sample* was recrystallized from HCl/acetone (Found: C, 30·7; H, 6·8; Cl, 19·9; N, 17·6. $C_{14}H_{33}Cl_3CoN_7O_2.3H_2O$ requires C, 30·5; H, 7·1; Cl, 19·3; N, 17·8%). Electronic spectrum in aqueous HCl (0·1 M) [λ_{max} in nm (ϵ_{max} in dm^3 mol^{-1} cm^{-1}]: 478 (137), 346 (132). ^{13}C n.m.r. δ (0·1 M DCl): 76·77, $CHNO_2$; 57·96, 56·16, 55·95, 54·43, 54·30, 54·16, 53·74, 50·77, 50·29, 47·39, 43·08, CH_2N; 43·06, $\mathbf{C}_qCH_3$, overlapping; 20·16, CH_3.

A sample was also converted into the diethyldithiocarbamate (Et_2dtc^-) *salt* as described for isomer *A* (Found: C, 40·6; H, 7·9; N, 16·1; S, 21·3. $C_{29}H_{63}CoN_{10}O_2S_6.H_2O$ requires C, 40·8; H, 7·7; N, 16·4; S, 22·6%).

Interconversion of Isomers A *and* B*, and Proton Exchange*

In neutral aqueous solution, isomer *A* was converted into isomer *B* at 20°C over 24 h, as shown by the n.m.r. experiments. In 0·1 M DCl after 24 h at 20°C, although there was very little isomerization from *A* to *B*, the ^{13}C resonance $CHNO_2$ of isomer *A* (at 80·5 ppm) had been replaced by a triplet at almost the same chemical shift (80·2 ppm). There was no apparent change in the corresponding resonance of isomer *B* (76·7 ppm) at the same pD over the same time scale. When isomer *B* was dissolved in base and quenched with acid after a few seconds, the n.m.r. showed that it had been converted quantitatively into isomer *A*.

Both isomers *A* and *B* contain a number of distinct broad bands between 4·5 and 7·5 ppm, corresponding to NH resonances. These disappear on exchange with solvent deuterium. In neutral solution this exchange is complete in <1 h at 20°C, and the rate decreases with decreasing pH. In 1 M DCl at 95°C, complete exchange occurs in *c.* 45 min, whereas in 7 M DCl it is complete after 16 h.

(4) [Co(6-Me,13-NO$_2$,6-CH$_2$NHCH$_2$CH$_2$NH$_2$-[14]aneN$_4$ – H$^+$)]$^{2+}$ (Deprotonated Species from Isomer A *or* B*)*

A sample of either isomer *A* or *B* was dissolved in D_2O, and K_2CO_3 was added. The ^1H and ^{13}C n.m.r. spectra of the initial product showed no change over 12 h at 22°C. ^1H n.m.r. δ (D_2O): 4·35, d, J 13 Hz, 1H; 4·01, d, J 13 Hz, 1H; 3·48, d, J 13 Hz, 1H; 3·2–2·2, complex pattern, 19H; 0·93, s, 3H, CH_3. ^{13}C n.m.r. δ (D_2O): 95·29, C^-NO_2; 57·84, 56·39, 55·90, 54·31, 54·12, 54·04, 52·98, 50·63, 49·96, 46·64, 43·09, CH_2N; 43·09, $\mathbf{C}_qCH_3$, overlapping; 20·40, CH_3.

*(6) [Co(Me,OH-absar)]Cl$_3$.3H$_2$O (1-Hydroxy-8-methyl-3,6,10,13,15,18-hexaazabicyclo-[6.6.5]nonadecane)cobalt(*III*) Chloride Trihydrate)*

A sample of either isomer *A* or *B* was heated at 80°C in water (or aqueous 0·2 M K_2SO_4) for 7 h. It was diluted and loaded onto a column of SP-Sephadex, and eluted with 0·08 M K_2SO_4. Two bands were collected. The first band corresponded to a small amount of unreacted starting material, and the second band was freed of eluent by treatment with Dowex/HCl as described above, to yield the desired product. Yield >90%.

A *sample* was recrystallized from water/acetone (Found: C, 32·3; H, 7·8; Cl, 20·6; N, 16·1. $C_{14}H_{32}Cl_3CoN_6O.3H_2O$ requires C, 32·4; H, 7·4; Cl, 20·5; N, 16·2%). Electronic spectrum in aqueous HCl (0·1. M) [λ_{max} in nm (ϵ_{max} in $dm^3\ mol^{-1}\ cm^{-1}$)]: 458 (175), 336 (172). ^1H n.m.r. (D_2O): the proton spectrum was complex, but was readily differentiated from the precursors and from $[Co(Me,NO_2\text{-}sar)]^{3+}$ by doublets at δ 2·38 (J 14 Hz), 2·58 and 2·64 (J 6 Hz) and the cap methyl singlet at 0·92. ^{13}C n.m.r. δ (D_2O): 91·73, C_qOH; 60·35, 59·93, 59·20, 58·73, 57·28, 55·23, 53·49, 52·38, 51·83, 50·59, 43·82, CH_2N; 43·51, $\mathbf{C}_qCH_3$; 20·62, CH_3.

[Co(Me,OH-absar)](ClO$_4$)$_2$

Caution! Transition metal perchlorates are potentially hazardous, and the appropriate precautions should be taken.

A solution of [Co(Me,OH-absar)] $Cl_3.3H_2O$ (93 mg) in 5 ml water was degassed with argon. Zinc powder (*c.* 100 mesh) was added; this led to a rapid loss of the yellow colour. After 1 min, the solution was filtered into an argon-saturated aqueous solution of $NaClO_4$ (15 ml) containing sufficient additional solid $NaClO_4$ to ensure that the final solution was almost saturated. The excess salt dissolved, and a fine solid precipitated. The mixture was left for 3 h to ensure complete precipitation. The product was collected by filtration, washed with argon-saturated methanol, and dried under a stream of argon. Yield 102 mg (*c.* 100%) of pale greyish powder. This was used to record the spectrum of the cobalt(II) complex. Electronic spectrum in H_2O [λ_{max} in nm (ϵ_{max} in $dm^3\ mol^{-1}\ cm^{-1}$)]: 870 (6), 658 (3·4), 550 (5·3), 467 (13). The concentration of complex (and hence ϵ) was determined by recording the spectrum of the solution after reoxidation to the cobalt(III) state.

X-Ray Crystal Structure Determination

Crystal data.—Orange crystals of [Co(Me,OH-absar)] $Cl_3.H_2O$ (*c.* 0·2 by 0·2 by 0·2 mm) suitable for crystallography were grown from aqueous acetone solution kept at –5°C. $C_{14}H_{34}Cl_3CoN_6O_2$, monoclinic, $P2_1/_n$ (No. 14), point group $2/m$, a 9·862(2), b 17·841(1), c 11·910(1) Å, β 93·47(2)°, V 2091·7 Å^3, Z 4, D_c 1·529, D_m 1·524 g cm^{-3}, λ(Mo Kα) 0·7107 Å, μ 12·26 cm^{-1}, $F(000)$ 1008·0, T 293 K.

Structure solution and refinement.—Three-dimensional intensity data were collected on an Enraf–Nonius CAD4 diffractometer by using graphite monochromatized Mo Kα radiation to a θ limit of 23·5° in the $\omega/2\theta$ mode. The data were corrected for Lorentz and polarization effects but not for absorption. The structure was solved by using MULTAN-80,[17] and refined by the full-matrix least-squares program LALS.[18] The refinement of the scale factor, positional and anisotropic thermal parameters of non-hydrogen atoms, as well as positional and isotropic thermal parameters of hydrogen atoms, converged at R 0·042 and R_w 0·052, where $R = \sum||F_o| - |F_c||/\sum|F_o|$ and $R_w = \sum(w||F_o| - |F_c||)^{1/2}/\sum(w|F_o|)^{1/2}$.[18] The weighting function used was $w = 1$. The shifts in the parameters in the last cycle were less than 0·0001σ.

A perspective view of the molecule drawn with PLUTO,[19] with the numbering scheme, is shown in Fig. 2. Fractional coordinates are listed in Table 2. Tables 3–5 list the bond lengths, bond angles and torsional angles respectively. Deposited material includes hydrogen atom parameters, selected least-squares planes, and a figure showing the stereo packing of the complex (these can be obtained on application to the Australian Journal of Chemistry, P.O. Box 89, East Melbourne, Vic. 3002).

Results and Discussion

Reactions

Although the cobalt complexes of 'sar' and its derivatives are noted for their generally remarkable stability even in the cobalt(II) state,[1,2] the nitro-capped species are susceptible to a retro-Mannich reaction in base. The reactions of $[Co(Me,NO_2\text{-sar})]^{3+}$ in base have been followed both spectrophotometrically and by ^1H and ^{13}C n.m.r.

The ^1H n.m.r. spectrum of the C_3 ion $[Co(Me,NO_2\text{-sar})]^{3+}$ is complex (Fig. 1*a*), but it has been possible to assign the resonances by comparison with the related complexes which have D_3 symmetry,[2] i.e. $[Co((NO_2)_2\text{-sar})]^{3+}$ and $[Co(Me_2\text{-sar})]^{3+}$. Addition of NaOH to a solution of $[Co(Me,NO_2\text{-sar})]^{3+}$ leads to rapid darkening of the yellow solution (<1 ms) resulting from deprotonation of a coordinated secondary amine. The positions of the visible bands are not altered to any great extent, although their intensities increase significantly, and an intense tail from the u.v. extends to *c.* 400 nm. The proton spectrum of the deprotonated species $[Co(Me,NO_2\text{-sar} - H^+)]^{2+}$ (Fig. 1*b*) has a pattern similar to that of the precursor $[Co(Me,NO_2\text{-sar})]^{3+}$ (i.e. the average solution symmetry is retained) although the peak positions are shifted; this implies that there is a rapid exchange of the remaining amine protons with the deprotonated nitrogen. The signals least affected are those in the cap bearing the methyl substituent; this implies that the deprotonation involves principally the amines nearer the NO_2-capped end. The ^{13}C n.m.r. spectrum also shows that the C_3 symmetry has been retained on the n.m.r. time scale, and that the amine protons are switching rapidly among the three sites. When a sample of $[Co(Me,NO_2\text{-sar})]^{3+}$ containing only 1 equiv. of base was reacidified after 90 min, the starting material was recovered almost quantitatively. Similar behaviour has been observed previously with $[Co((NO_2)_2\text{-sar})]^{3+}$, and the crystal structure of $[Co((NO_2)_2\text{-sar} - H^+)](ClO_4)_2$ has been reported,[2] but the reaction sequence following deprotonation is more complex.

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[17] Main, P., Hull, S. E., Lessinger, L., Germain, G., Decelerq, J. P., and Woolfson, M. M., 'MULTAN-80', A System of Computer Programs for Automatic Structure Solution, University of York, England, 1980.

[18] Gantzel, P. K., Sparks, R. A., and Trueblood, K. N., 'Programs-UCLALS-1', University of California, 1961.

[19] Motherwell, W. D., and Clegg, W., 'PLUTO', Program for Plotting Molecular and Crystal Structures, University of Cambridge, England, 1978.

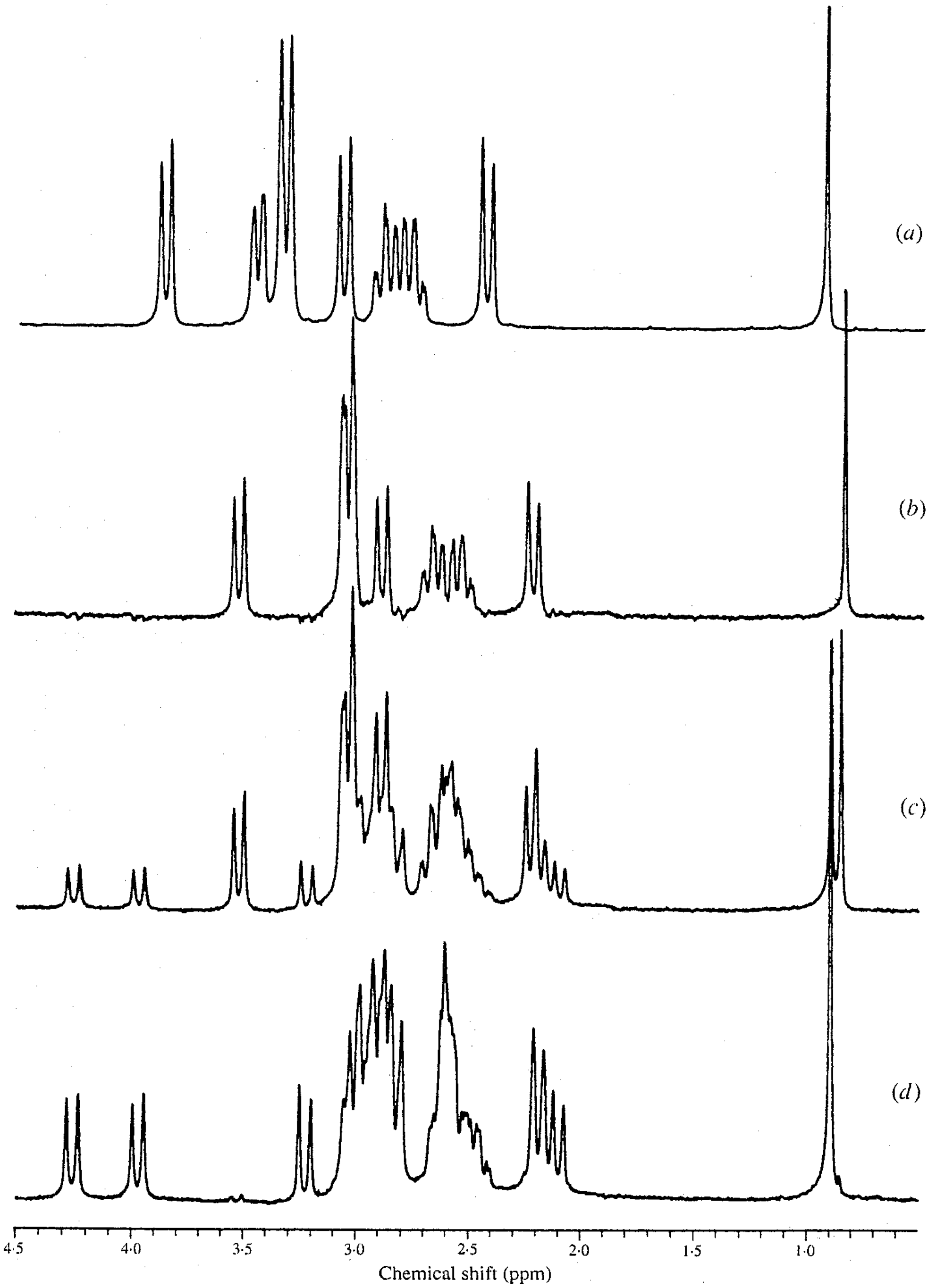


Fig. 1. ^{1}H n.m.r. spectra of solutions of $[Co(Me,NO_2\text{-}sar)]^{3+}$ (*c.* 0·3 M) in: (*a*) D_2O; (*b*) 1 M NaOD at $t = 0$ [obtained by subtraction of (*d*) from (*c*) after normalization]; (*c*) 1 M NaOD after 1 min; (*d*) 1 M NaOD after 10 min.

Addition of more than 1 equiv. of base to a solution of $[Co(Me,NO_2\text{-sar})]Cl_3$ leads to the formation of a deprotonated species [(4) in Scheme 1] with one fewer carbon atoms, as shown by microanalysis and ^{13}C n.m.r., and loss of the C_3 symmetry. The reaction follows clean first-order kinetics in excess base, and the $[OH^-]$ dependence gives rise to the rate law

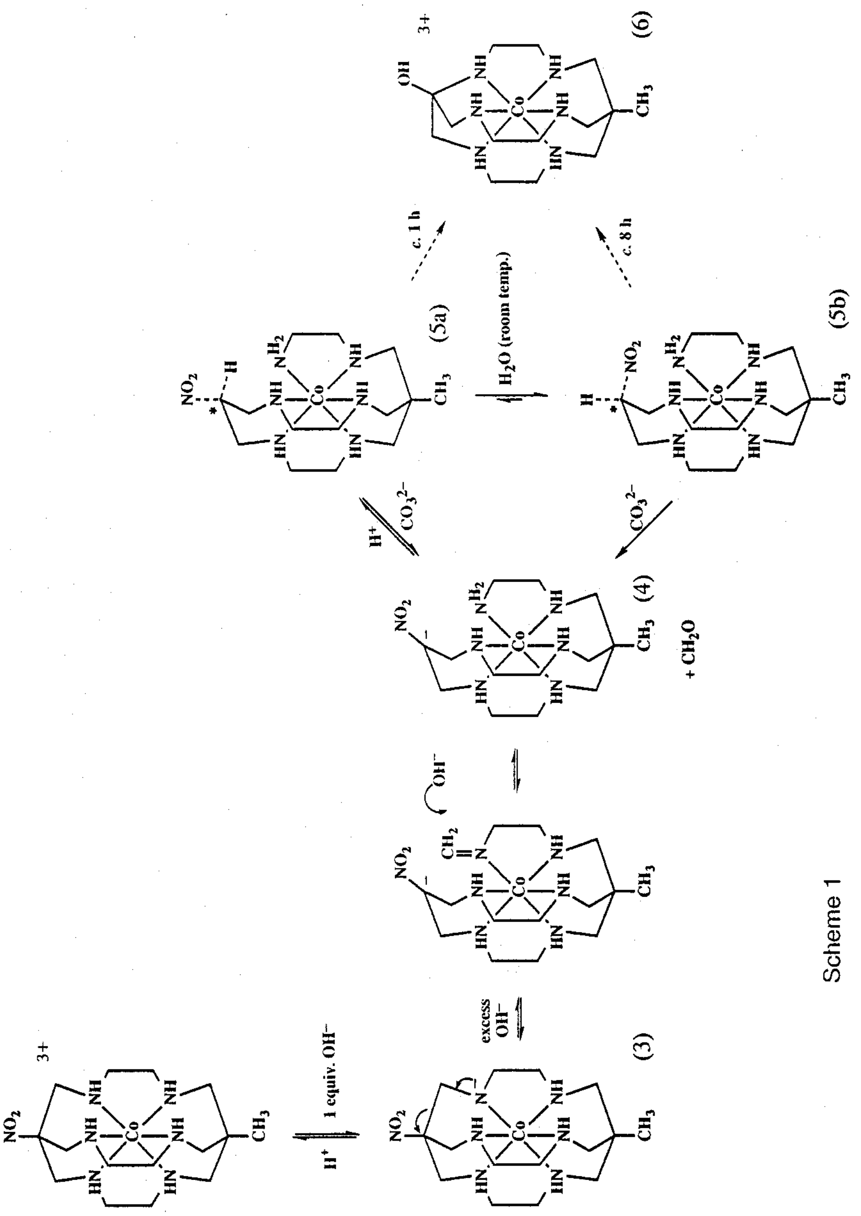
$$k_{obs} = \frac{0\cdot15[OH^-]}{1+14[OH^-]}$$

with a limiting rate in the high base concentration region (1 M OH^-). In 1 M NaOH, the reaction has a half-life of *c*. 1 min. The visible spectrum of this deprotonated product was very similar to that of the $[Co(Me,NO_2\text{-sar}-H^+)]^{2+}$ precursor, but with the intensity reduced uniformly by about half. Quenching the product with acid gave (after workup) the reprotonated products (5a) and (5b), in which the d–d bands of $^1T_{1g}$ and $^1T_{2g}$ origin had moved *c*. 7 nm to lower energy with respect to $[Co(Me,NO_2\text{-sar})]^{3+}$.

The formation of the deprotonated intermediate (4) from $[Co(Me,NO_2\text{-sar}-H^+)]^{2+}$ was readily followed in the ^1H n.m.r. spectrum (Figs 1*c* and 1*d*) by the appearance of a new methyl singlet 0·04 ppm downfield from that of the precursor, the disappearance of the doublet at 3·52 ppm and the appearance of three doublets at 4·25, 3·97 and 3·22 ppm (*J* 13 Hz), which were assigned to three of the four CH_2 protons remaining on the NO_2 cap. The ^1H n.m.r. spectrum of the intermediate (4) formed in the reaction was identical with that obtained when either (5a) or (5b) was dissolved in 1 M NaOD. It was not possible to obtain the ^1H n.m.r. spectrum of the deprotonated complex $[Co(Me,NO_2\text{-sar}-H^+)]^{2+}$ in 1 M NaOD due to the rapid subsequent reaction of this species. However, by using spectral editing techniques, it was possible to derive the spectrum of this species from the spectra recorded, 1 and 10 min after mixing (Figs 1*c* and 1*d* respectively). This spectrum is shown in Fig. 1*b*. It shows the same splitting pattern as the ^1H n.m.r. spectra of $[Co(Me,NO_2\text{-sar})]^{3+}$ in neutral solution, in aqueous Na_2CO_3 and in a solution with 1 equiv. of added NaOD. The peak positions depend on the pH, but the identical splitting patterns show that the deprotonated product initially formed in 1 M NaOH still preserves the symmetry of the parent $[Co(Me,NO_2\text{-sar})]^{3+}$ complex.

The ^{13}C n.m.r. spectrum of the reaction mixture after 10 min clearly showed the loss of one carbon atom and the attendant loss of symmetry, as well as the presence of a single product (4). This product reacted further with base only slowly, with a half-life of *c*. 4 h. The products of the reaction included (amongst others) significant amounts of $[Co(sen)]^{3+}$ [sen = 4,4′,4″-ethylidynetris(3-azabutan-1-amine)], the precursor of the capping reaction used to form $[Co(Me,NO_2\text{-sar})]^{3+}$.

The loss of the first methylene unit occurs through a retro-Mannich type reaction, involving deprotonation at a secondary nitrogen, followed by imine formation through carbanion dissociation from the negatively charged fragment. The imine is then hydrolysed under the basic conditions of the reaction (Scheme 1). Subsequent loss of a second methylene unit by a similar mechanism is significantly slower, presumably because in species (4) deprotonation occurs preferentially at the carbon atom bearing the NO_2 group. [The pK_a of $(CH_3)_2C(H)NO_2$ is *c*.


NO2
3+
CH3
Co
H+
1 equiv. OH−
(3)
excess OH−
CH2
OH−
(4)
+ CH2O
H+
CO3 2−
(5a)
H2O (room temp.)
(5b)
c. 1 h
c. 8 h
OH
(6)

Scheme 1

7·7,[20] and the presence of the Co^{3+} centre will lower the pK_a even further.] This leads to a species where the carbanion is held close to the reaction centre by chelation, thus hindering deprotonation of another secondary amine. The presence of $[Co(sen)]^{3+}$ as the principal decomposition product (together with the absence of the nitro product which had lost two methylene units) implies that rupture of the final methylene unit in the cap may be more rapid.

The difference in the rates of loss of the first and subsequent methylene units enabled the isolation of the intermediate species, by quenching the reaction mixture with acid after *c.* 15 min. This gives a mixture of starting material and one product (designated isomer *A* in the Experimental section). The product isomerizes under the conditions of the chromatography on the Sephadex column to another species (designated isomer *B*). These two isomers have been separated by chromatography and characterized by microanalysis and n.m.r. as tetraaza macrocyclic units with a pendant bidentate arm ($CH_2NHCH_2CH_2NH_2$). They appear to differ only in the configuration about the $\rangle C(H)NO_2$ carbon atom. The proton on this carbon atom is quite acidic in both isomers, but it is significantly more acidic in isomer *A* than in isomer *B*. Proton exchange occurs more rapidly in isomer *A*, where it is readily exchanged at 22°C even in 0·1 M DCl, as shown by the appearance of a triplet at 80·2 ppm in the ^{13}C n.m.r. spectrum, corresponding to the formation of $\rangle C(D)NO_2$, and the concomitant loss of the $\rangle C(H)NO_2$ resonance at 80·5 ppm.

If a solution of $[Co(Me,NO_2\text{-sar})]Cl_3$ that had been treated with excess base for 15 min then quenched with acid was kept acidified during chromatography and subsequent workup, only isomer *A* was obtained. However, heating this isomer even in the solid state led to partial conversion into isomer *B*. In non-acidic solution, the conversion occurred readily at 20°C. Treatment of either isomer with base (K_2CO_3) gave a common deprotonated product, with ^1H and ^{13}C n.m.r. spectra corresponding to those observed for a solution of $[Co(Me,NO_2\text{-sar})]^{3+}$ in D_2O with excess NaOD after 10 min. Isomer *B* was quantitatively reconverted into isomer *A* by treatment with K_2CO_3 (or NaOH) for a few seconds followed by quenching with acid. This experiment confirms that the two isomers are related by a simple deprotonation/inversion reaction.

The final product $[Co(Me,OH\text{-absar})]^{3+}$ (6) was readily obtained by heating a neutral aqueous solution of isomer *A* at *c.* 90°C for 1 h. However, under these conditions, isomer *A* was also converted into isomer *B*, which in turn reacted considerably more slowly to give the product. Heating either isomer for 8 h at *c.* 90°C in neutral aqueous solution or in dilute acid (*c.* 0·1 M), followed by SP-Sephadex chromatography (with K_2SO_4 as eluent), gave good yields of the final product, although significantly more decomposition (to unidentified products) was observed when this reaction was carried out with isomer *B*. The structure of the product (6) has been established by an X-ray crystallographic analysis (Fig. 2), and the details of the structure are discussed below.

The formation of the condensed cap species is argued to proceed through a Nef reaction[21] followed by condensation of the carbonyl group with the deprotonated primary amine of the pendant arm (Scheme 2).

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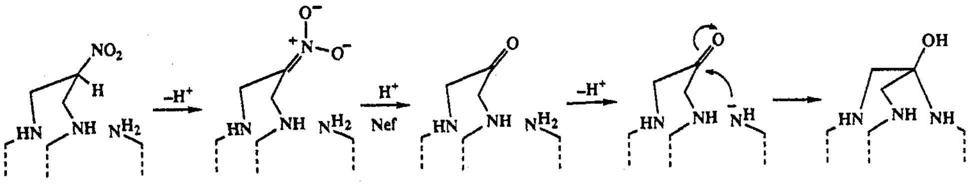
[20] Turnbull, D., and Maron, S. H., *J. Am. Chem. Soc.*, 1943, **65**, 212.

[21] For example, March, J., 'Advanced Organic Chemistry' p. 786 (John Wiley: New York 1985).



Scheme 2

The conversion of isomers *A* and *B* into the contracted cap product [Co(Me,OH-absar)]$^{3+}$ was readily followed by n.m.r. Although the ^{1}H n.m.r. spectra of all three compounds contain a complex overlapping pattern corresponding to the methylene units, the overlapping singlet resonances of the cap methyl groups of isomers *A* and *B* are clearly distinguishable from that of [Co(Me,OH-absar)]$^{3+}$ which is 0·035 ppm further upfield. Considering the close similarity of isomers *A* and *B*, it is not surprising that their ^{13}C n.m.r. spectra contain a number of overlapping resonances. Still, they do display a number of resonances that can be used to differentiate them. In particular, the resonances at 80·5, 49·2 and 46·4 ppm in isomer *A*, and at 76·8, 50·3 and 47·4 ppm in isomer *B* are characteristic. The ^{13}C n.m.r. spectrum of [Co(Me,OH-absar)]$^{3+}$ is quite different, and the cap methyl resonance is shifted 0·4 ppm downfield from that of the two precursors.

Proton exchange and formation of [Co(Me,OH-absar)]$^{3+}$ were observed even in concentrated acid (7 M DCl), although this required prolonged heating at 95°C and a significant amount of decomposition occurred. The ^{13}C and ^{1}H n.m.r. spectra of a solution of isomer *A* heated in 7 M DCl at *c.* 90°C for 9 h showed three distinct methyl resonances, despite the fact that after workup only the starting materials (isomers *A* and *B*) and product were observed. The methyl signals of isomers *A* and *B* overlap so only two resonances were expected from the three products. It is possible that the third methyl resonance corresponds to a complex containing the ketone intermediate which undergoes condensation with the primary coordinated amine only slowly at such low pH. However, due to the partial decomposition that occurred under the experimental conditions, it was not possible to detect a carbonyl resonance in the ^{13}C n.m.r. spectrum of the 7 M DCl reaction solution.

The contracted cage species [Co(Me,OH-absar)]$^{3+}$ eluted more slowly on SP-Sephadex (with 0·05 M K_2SO_4) than the two 'open cage' species (5a) and (5b), and it was readily purified this way. It was easily differentiated on the column by its more lemon-yellow appearance than the precursor species which both had the same orange colour that is characteristic of many of the cobalt(III) complexes based on the 'sar' and 'sen' frameworks.

Structural Results (Fig. 2 and Tables 2–5)

The structure of the complex cation [Co(Me,OH-absar)]$^{3+}$ is shown in Fig. 2. The general structural features are rather similar to those of the [Co(Cl,CH$_2$Cl-absar)] $(NO_3)_3$ complex.[16] The three five-membered chelate rings forming the 'Co(en)$_3$' core adopt a *lel*$_2$*ob* conformation about the pseudo-C_3 axis in both

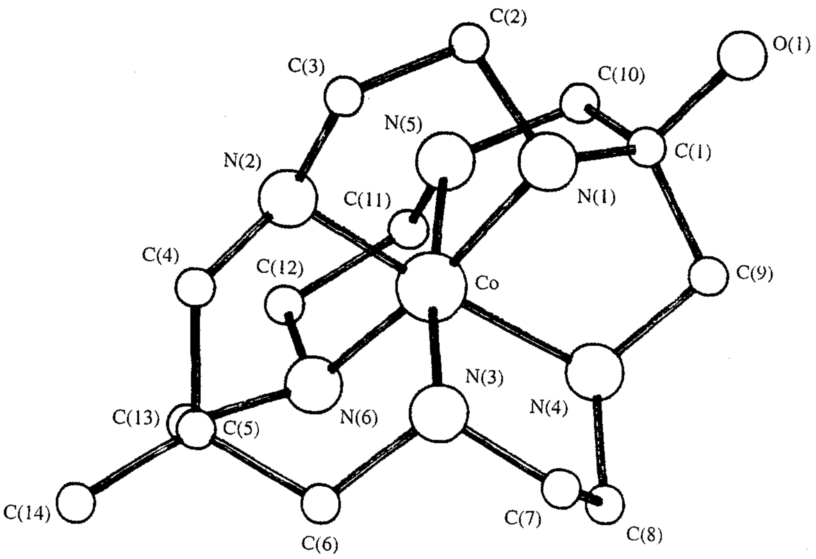


Fig. 2. Structure of the [Co^{III}(Me,OH-absar)]$^{3+}$ cation, showing the atomic numbering.

Table 2. Fractional atomic coordinates of the non-hydrogen atoms

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Co	0·3211(2)	0·1438(9)	0·7065(10)	C(2)	0·3351(13)	0·2893(7)	0·7972(10)
Cl(1)	0·1856(4)	0·4251(4)	0·9799(3)	C(3)	0·1971(13)	0·2599(6)	0·8251(10)
Cl(2)	0·7616(4)	0·3717(2)	0·5873(3)	C(4)	0·0492(13)	0·1474(8)	0·7900(10)
Cl(3)	0·2349(5)	0·3646(2)	0·5192(3)	C(5)	0·0622(12)	0·0625(6)	0·7521(10)
O_w	0·4985(13)	0·2358(7)	0·0487(9)	C(6)	0·1841(12)	0·0240(6)	0·8163(9)
O(1)	0·6360(9)	0·2813(5)	0·7670(7)	C(7)	0·4310(12)	0·0363(7)	0·8657(9)
N(1)	0·4238(10)	0·2217(5)	0·7946(7)	C(8)	0·5019(14)	0·0208(7)	0·7570(11)
N(2)	0·1573(9)	0·1962(5)	0·7411(8)	C(9)	0·6123(13)	0·1520(7)	0·7349(10)
N(3)	0·3044(10)	0·0777(5)	0·8349(7)	C(10)	0·4992(13)	0·2436(7)	0·5996(10)
N(4)	0·5022(10)	0·0935(5)	0·6892(8)	C(11)	0·3462(13)	0·1628(6)	0·4719(9)
N(5)	0·3601(10)	0·2088(5)	0·5789(8)	C(12)	0·2122(12)	0·1194(6)	0·4834(8)
N(6)	0·2207(10)	0·0798(6)	0·5964(9)	C(13)	0·0795(12)	0·0582(6)	0·6267(9)
C(1)	0·5452(11)	0·2263(8)	0·7246(9)	C(14)	−0·0712(13)	0·0214(8)	0·7785(12)

Table 3. Bond lengths (Å) involving non-hydrogen atoms

Atoms	Distance	Atoms	Distance	Atoms	Distance
Co–N(1)	1·983(10)	N(2)–C(4)	1·519(16)	C(1)–C(9)	1·482(19)
Co–N(2)	1·933(10)	N(3)–C(6)	1·530(15)	C(1)–C(10)	1·561(16)
Co–N(3)	1·946(9)	N(3)–C(7)	1·477(16)	C(2)–C(3)	1·514(18)
Co–N(4)	2·020(10)	N(4)–C(8)	1·528(16)	C(4)–C(5)	1·588(18)
Co–N(5)	1·969(9)	N(4)–C(9)	1·579(16)	C(5)–C(6)	1·546(17)
Co–N(6)	1·961(10)	N(5)–C(10)	1·512(16)	C(5)–C(13)	1·516(16)
O(1)–C(1)	1·402(15)	N(5)–C(11)	1·515(14)	C(5)–C(14)	1·555(15)
N(1)–C(1)	1·502(15)	N(6)–C(12)	1·518(14)	C(7)–C(8)	1·534(17)
N(1)–C(2)	1·491(16)	N(6)–C(13)	1·509(15)	C(11)–C(12)	1·544(17)
N(2)–C(3)	1·549(15)				

Table 4. Bond angles (degrees) involving non-hydrogen atoms

Atoms	Angle	Atoms	Angle
N(1)–Co–N(2)	87·4(4)	Co–N(5)–C(11)	108·5(7)
N(1)–Co–N(3)	94·2(4)	C(10)–N(5)–C(11)	113·3(9)
N(1)–Co–N(4)	86·5(4)	Co–N(6)–C(12)	108·6(7)
N(1)–Co–N(5)	83·0(4)	Co–N(6)–C(13)	115·1(7)
N(1)–Co–N(6)	169·4(4)	C(12)–N(6)–C(13)	109·2(9)
N(2)–Co–N(3)	90·8(4)	O(1)–C(1)–N(1)	110·5(9)
N(2)–Co–N(4)	172·8(4)	O(1)–C(1)–C(9)	108·9(10)
N(2)–Co–N(5)	94·8(4)	O(1)–C(1)–C(10)	110·3(10)
N(2)–Co–N(6)	91·7(4)	N(1)–C(1)–C(9)	105·8(10)
N(3)–Co–N(4)	85·9(4)	N(1)–C(1)–C(10)	110·1(9)
N(3)–Co–N(5)	173·6(4)	C(9)–C(1)–C(10)	111·0(10)
N(3)–Co–N(6)	96·3(4)	N(1)–C(2)–C(3)	105·1(10)
N(4)–Co–N(5)	88·1(4)	N(2)–C(3)–C(2)	108·0(9)
N(4)–Co–N(6)	95·0(4)	N(2)–C(4)–C(5)	111·5(10)
N(5)–Co–N(6)	86·6(4)	C(4)–C(5)–C(6)	110·9(10)
Co–N(1)–C(1)	98·2(7)	C(4)–C(5)–C(13)	110·1(10)
Co–N(1)–C(2)	107·3(7)	C(4)–C(5)–C(14)	108·0(10)
C(1)–N(1)–C(2)	117·2(9)	C(6)–C(5)–C(13)	109·5(9)
Co–N(2)–C(3)	108·1(7)	C(6)–C(5)–C(14)	109·5(9)
Co–N(2)–C(4)	114·8(7)	C(13)–C(5)–C(14)	108·8(9)
C(3)–N(2)–C(4)	109·2(9)	N(3)–C(6)–C(5)	111·5(9)
Co–N(3)–C(6)	111·5(7)	N(3)–C(7)–C(8)	107·6(10)
Co–N(3)–C(7)	112·8(7)	N(4)–C(8)–C(7)	107·9(10)
C(6)–N(3)–C(7)	111·1(9)	N(4)–C(9)–C(1)	105·5(10)
Co–N(4)–C(8)	107·0(7)	N(5)–C(10)–C(1)	106·4(9)
Co–N(4)–C(9)	105·4(7)	N(5)–C(11)–C(12)	103·4(9)
C(8)–N(4)–C(9)	113·7(9)	N(6)–C(12)–C(11)	108·1(9)
Co–N(5)–C(10)	109·5(7)	N(6)–C(13)–C(5)	112·5(9)

Table 5. Torsion angles (degrees) for the rings involving the cobalt atom

Ring	Atoms	Angle	Ring	Atoms	Angle
1	Co–N(4)–C(9)–C(1)	−23·5(10)	2	Co–N(1)–C(1)–C(10)	55·6(9)
	N(4)–C(9)–C(1)–N(1)	59·4(11)		N(1)–C(1)–C(10)–N(5)	−30·6(12)
	C(9)–C(1)–N(1)–Co	−64·4(9)		C(1)–C(10)–N(5)–Co	−10·7(10)
	C(1)–N(1)–Co–N(4)	39·4(7)		C(10)–N(5)–Co–N(1)	35·4(7)
	N(1)–Co–N(4)–C(9)	−9·7(7)		N(5)–Co–N(1)–C(1)	−49·2(7)
3	Co–N(4)–C(8)–C(7)	−38·9(10)	4	Co–N(5)–C(11)–C(12)	45·6(9)
	N(4)–C(8)–C(7)–N(3)	46·9(12)		N(5)–C(11)–C(12)–N(6)	−52·6(10)
	C(8)–C(7)–N(3)–Co	−33·1(11)		C(11)–C(12)–N(6)–Co	35·6(10)
	C(7)–N(3)–Co–N(4)	9·1(7)		C(12)–N(6)–Co–N(5)	−7·6(7)
	N(3)–Co–N(4)–C(8)	17·1(7)		N(6)–Co–N(5)–C(11)	−22·3(7)
5	Co–N(1)–C(2)–C(3)	45·9(10)	6	Co–N(3)–C(6)–C(5)	−36·9(10)
	N(1)–C(2)–C(3)–N(2)	−52·3(11)		N(3)–C(6)–C(5)–C(13)	84·7(11)
	C(2)–C(3)–N(2)–Co	34·0(10)		C(6)–C(5)–C(13)–N(6)	−46·6(12)
	C(3)–N(2)–Co–N(1)	−6·4(7)		C(5)–C(13)–N(6)–Co	−23·2(11)
	N(2)–Co–N(1)–C(2)	−22·5(7)		C(13)–N(6)–Co–N(3)	55·3(8)
				N(6)–Co–N(3)–C(6)	22·0(7)

complexes, i.e. where the 'en' C–C axes are paral*lel* or *ob*lique to the pseudo-C_3 axis of the complex ion.

The coordination around the cobalt atom is a distorted octahedron composed of six nitrogen atoms. The principal distortion from octahedral symmetry is dictated by the form of the ligand framework. The least-squares plane involving atoms Co, N(2), N(3), N(4) and N(5) shows that they are not in the plane. The cobalt atom is shifted by 0·08 Å towards N(6) from the least-squares plane through the four nitrogen atoms (supplementary material). The four nitrogens deviate ±0·03 Å, alternately above and below the plane.

Two of the Co–N bond lengths are significantly different from the other four. Co–N(4) is elongated [2·020(10) Å] while the Co–N bond in the *trans* position is shortened [Co–N(2) 1·933(10) Å] as expected. However, the average Co–N length (1·969 Å) is typical for Co^{III}–N in saturated amine complexes. There are five five-membered chelate rings and four six-membered rings. The two five-membered rings in the cap possess an approximate envelope conformation, which is enforced by the stereochemistry of the cap. The distribution of the torsion angles within the six-membered chelate rings (Table 5) require twisted boat conformations, and again this is enforced by the cap geometries.

On the whole, all the N–Co–N angles deviate significantly from 90°. The angle N(3)–Co–N(6) which is part of a six-membered ring is enlarged [96·3(4)°] whereas the angle opposite to it, N(1)–Co–N(5), is contracted [83·0(4)°]. The other angles around the cobalt core vary between these two values. The deviations from octahedral geometry about the cobalt centre are very similar to those found in [Co(Cl,CH$_2$Cl-absar)] (NO$_3$)$_3$.[16]

The crystal structure is stabilized by a network of hydrogen bonds N–H···Cl, N–H···O (water), O–H···Cl$^-$ and O–H (water)···Cl$^-$ with lengths: N(1)–H···O(H$_2$O) 3·081 Å; N(2)–H···O(H$_2$O) 2·957 Å; N(3)–H···Cl(2) 3·19 Å; N(4)–H···Cl(1) 3·18 Å; N(5)–H···Cl(3) 3·106 Å; N(6)–H···Cl(1) 3·066 Å; O(hydroxyl)···Cl(2) 3·006 Å; O–H(H$_2$O)···Cl(2) 3·079 Å; O–H(H$_2$O)···Cl(3) 2·978 Å. These interactions are normal for such amine complex cations and associated anions.

Spectral and Electrochemical Properties of the Complexes

Table 1 lists the relevant spectroscopic properties and reduction potentials. The electronic spectra of [Co(Me,OH-absar)]$^{3+}$ and [Co(Me,OH-sar)]$^{3+}$, which differ only in the absence or presence of an additional methylene unit in the cap (corresponding to the regular 'sar' cavity) are shown in Fig. 3. The hypsochromic shift of the band maxima from [λ_{max} in nm (ϵ_{max} in dm^3 mol^{-1} cm^{-1})] 472 (143) and 344 (124) in [Co(Me,OH-sar)]$^{3+}$ to 458 (175) and 336 (172) in [Co(Me,OH-absar)]$^{3+}$ is consistent with an increased ligand field strength in the contracted cage complex. A modest increase in the molar absorption coefficient (ϵ) is consistent with the loss of symmetry between the 'sar' and the 'absar' based cages and the increased probability of mixing with ungerade electronic states to make the transition more allowed.[22] The spectra of the corresponding cobalt(II) complexes are shown in Fig. 4, together with that of

[22] For example, Figgis, B. N., in 'Comprehensive Coordination Chemistry' (Ed. G. Wilkinson) Vol. 1 (Pergamon: Oxford 1987).

$[Co(sep)]^{2+}$ (sep = 1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]icosane) for comparison. The spectrum of the contracted cage species $[Co(Me,OH\text{-}absar)]^{2+}$ is reminiscent of that reported for $[Co(Me\text{-}azasar)]^{2+}$,[23] and $[Co(sep)]^{2+}$,[24] in contrast to that

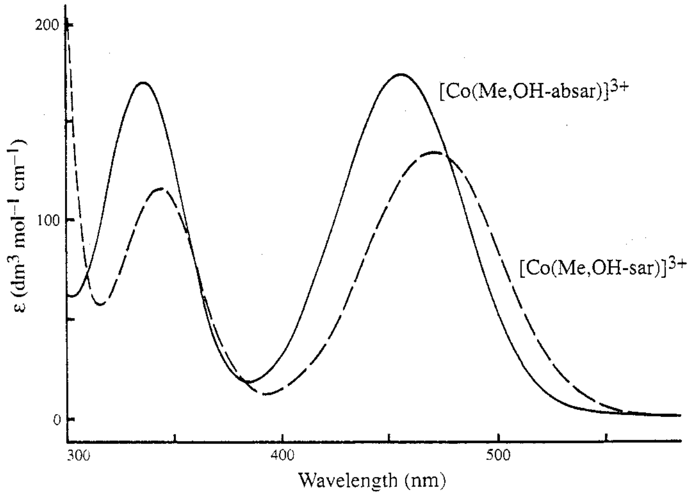


Fig. 3. Electronic spectra of $[Co(Me,OH\text{-}sar)]^{3+}$ and $[Co(Me,OH\text{-}absar)]^{3+}$ in H_2O.

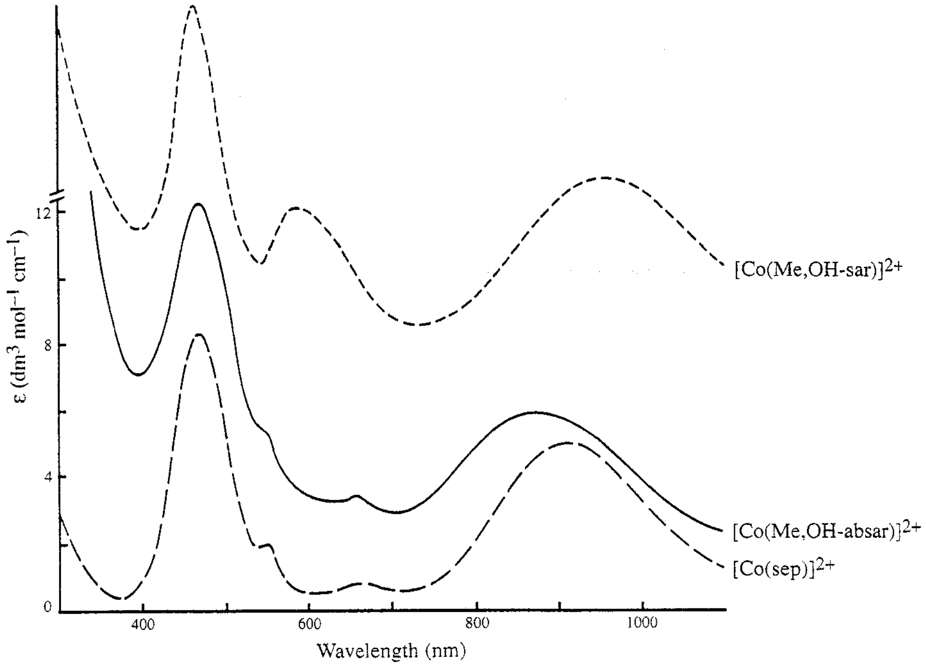


Fig. 4. Electronic spectra of $[Co(Me,OH\text{-}sar)]^{2+}$, $[Co(Me,OH\text{-}absar)]^{2+}$ and $[Co(sep)]^{2+}$ in H_2O. The spectrum of $[Co(Me,OH\text{-}sar)]^{2+}$ has been displaced (ϵ+6) for clarity.

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[23] Creaser, I. I., Geue, R. J., Harrowfield, J. M., Herlt, A. J., Sargeson, A. M., Snow, M. R., and Springborg, J., *J. Am. Chem. Soc.*, 1982, **104**, 6016.

[24] Creaser, I. I., Harrowfield, J. M., Herlt, A. J., Sargeson, A. M., Snow, M. R., Springborg, J., Geue, R. J., and Snow, M. R., *J. Am. Chem. Soc.*, 1977, **99**, 3181.

of $[Co(Me,OH\text{-}sar)]^{2+}$ which has a similar peak pattern but significantly shifted peak positions. It is evident, however, that the Co^{II}–absar complex is a high-spin molecule like the Co^{II}–sar type complexes despite the contracted cage engineered by the extrusion of a methylene group.

The fact that the contracted absar cage has a smaller preferred cavity for cobalt(II) than the sar cages is also apparent from the reduction potentials. The potential of the $[Co(Me,OH\text{-}sar)]^{3+/2+}$ couple is −385 mV (*v.* s.h.e. in 0·2 M KCl), whereas that of the $[Co(Me,OH\text{-}absar)]^{3+/2+}$ couple is −551 mV, reflecting the significantly increased strain accompanying the reduction of the cobalt(III) centre in the smaller 'absar' cage. The reduction potential of the ruptured cage (5) $[Co(6\text{-}Me,13\text{-}NO_2,6\text{-}CH_2NHCH_2CH_2NH_2\text{-}[14]aneN_4)]^{3+}$ is the same for both isomers (−196 mV), and only marginally more positive than that of the parent complex $[Co(Me,NO_2\text{-}sar)]^{3+}$ (−264 mV).

Summary

This paper essentially describes a new method of contracting the 'sar' type cage to give such products in relatively high yield. The new molecule has a stronger ligand field than the parent, and, as it accommodates the cobalt(III) ion better than the cobalt(II) ion, it destabilizes the latter oxidation state. The reaction process represents a ready route to modulating the electronic properties of the cage complexes by altering the cavity size.

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