

Sterically induced transmutations in cobalt amine chemistry†

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Received (in Cambridge, UK) 7th September 1999, Accepted 6th October 1999

Steric forces within a hexaaza bicyclic cobalt cage system cause chromophore expansions which bring about extraordinary transformations in the CoN₆ chemistry, leading to Co^{III/II}N₆ redox potentials close to +0.8 V (vs. SHE) and Co^{III} hexamine complexes that are air and substitution stable.

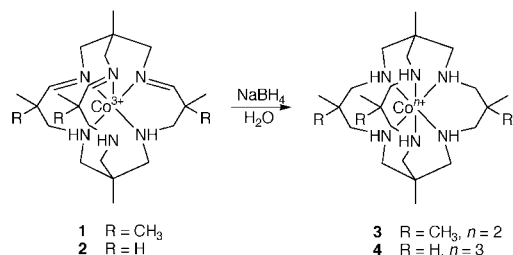
Steric factors pervade chemistry and their capacity to affect isomerism, structure and reactivity in transition metal coordination chemistry is well known.¹ They have also dramatically influenced metal complex stabilities and electron transfer rates, especially for macrocyclic² and polycyclic cage³ ligand systems. When the steric forces cooperate to change the intrinsic geometry or rigidity of a metal complex chromophore, its spectroscopic, redox and photophysical characteristics change in response to the new ligand field and potential energy (PE) surfaces. Recently, the incorporation of relatively high stability and stereorigidity factors with modified chromophore PE surfaces in sterically crowded, expanded cavity cage complexes has led to unusual ground and excited state properties for MN₆(M = Co^{III}, Rh^{III}, Pt^{IV}, Cr^{III}) amine type chromophores.⁴

In the pursuit of kinetically stable metal amine systems that radically transform MN₆ chemistry, a Co^{II} cage complex [Co(Me₈tricosatrieneN₆)]³⁺ **1** (Me₈tricosatrieneN₆ = 1,5,5,9,13,13,20,20-octamethyl-3,7,11,15,18,22-hexaazabicyclo[7.7.7]tricoso-3,14,18-triene) was synthesized by an approach based on the [Co(tame)₂]³⁺ {tame = ethyldiynetrakis(methanamine)} template.^{5a,c} A vigorously agitated mixture of [Co(tame)₂]Cl₃ (2 g) and NaClO₄ (9.4 g) in acetonitrile (50 ml) was treated with paraformaldehyde (5 equiv.), 2-methylpropanal (50 equiv.) and triethylamine (8 ml), quenched with HCl after stirring for 30 min at 20 °C, and chromatographed by cation exchange methods to give a bright crimson major product (15–20% yield), which was identified as the C₃ symmetric Co^{III} triimine ion **1** by its ¹H and ¹³C NMR spectra,[†] and a single crystal X-ray analysis of its tetrachlorozincate salt.^{†‡} The cation structure has virtual C₃ symmetry in the crystal with equivalent imines as well as equivalent chiral nitrogen centres. Although the CoN₆ geometry in the structure is close to octahedral, the Co–N distances are remarkably long compared to those found in complexes with near optimal Co^{III}N₆ (amine, imine) dimensions.^{3c,5} In particular, the average

Co–N (endoimine) distance of 2.011 Å is 0.11 Å longer than the value of 1.90 Å for analogous bonds in relatively unstrained systems.⁵ In spite of this exceptional expansion of the Co^{III}N₆ module, triimine **1** is stable to metal ion substitution and imine hydrolysis in aqueous solution from 6 M HCl to pH ca. 8 at 20 °C. This result contrasts with the relatively high lability found for most Co^{III} amines having mean Co–N distances ≥2.00 Å,^{3c} but is consistent with that observed for another expanded cavity cage complex^{4a} with a mean§ Co^{III}–N (amine) distance of 2.023(±0.01) Å.

The formal similarities between [Co(Me₈tricosatrieneN₆)]³⁺ **1** and its homologue^{4a} [Co(Me₅tricosatrieneN₆)]³⁺ **2** are obvious, especially the identical bonding frameworks linking the nitrogen atoms of the chromophore. However, the apparent likeness between the two species is largely limited to their C₃ symmetry and solution stability (at pH ≤ 8), and they exhibit important fundamental differences in their chromophore electron chemistry. The electronic spectrum of the octamethyl complex **1** (Cl₃ salt in H₂O) shows the first spin-allowed ligand field absorptions at λ_{max} (ε_{max}) 518 (150) and 367 (150), compared with 468 (107) and 343 nm (135 dm³ mol⁻¹ cm⁻¹) for the corresponding bands of the pentamethyl homologue **2**,^{4a} which by spectral comparison with analogous Co^{III} (amine, imine) systems⁵ is thought to have a fairly optimal Co^{III}N₆ geometry. These results imply that the Co–N distances in **1** are much longer than those of **2**. The striking differences in the chromophore sizes and ligand field spectra of the two homologues are attributed to steric factors arising from the three additional methyl groups of [Co(Me₈tricosatrieneN₆)]³⁺, which block the ligand conformation that is needed to form an optimal cavity size for Co^{III}. Reduction potentials (vs. SHE) of E +0.40 and –0.16 V for the Co^{III/II} couples of **1** and **2** were determined using cyclic voltammetry in aqueous 0.1 M NaCl. It is likely that the expanded cavity of the conformation adopted by **1** to accommodate its extra methyl groups, is a good fit for Co^{II} and is probably also preferred by **2** in the Co^{II} state. This would imply that the 560 mV positive shift in the Co^{III/II} potential for the larger cavity species **1** arises mainly from a destabilization of its Co^{III} state rather than a stabilization of Co^{II}. Furthermore, the difference in the Co^{III}N₆ sizes of **1** and **2** means that a substantial part of the destabilization energy is associated with the expansion of the chromophore.

More profound CoN₆ redox and spectral behaviour results when [Co^{III}(Me₈tricosatrieneN₆)]³⁺ is reduced to the more sterically crowded saturated amine form [Co^{II}(Me₈tricosatrieneN₆)]²⁺ **3**. These phenomena involve fundamental changes in the nature of CoN₆ (amine) chemistry and are not entirely understood at present. The Co^{II} complex **3** was first formed by stirring the trichloride salt of **1** with NaBH₄ (6 equiv.) in basic aqueous solution (pH 10) for 20 min at 20 °C and quenching with saturated NaHCO₃ solution (1 h), and then isolated as a pink dinitrate salt (95% yield), following cation-exchange chromatography using aqueous LiNO₃ as eluent and evaporation of the eluted complex solution. A violet tetrachlorozincate salt of **3** was also obtained by anion-exchange chromatography (Cl⁻ form) of the aqueous nitrate solution, addition of excess ZnCl₂ solution (pH 5) and concentration at 20 °C. All operations



Scheme 1

† Electronic supplementary data (ESI) available: Cyclic voltammetry, NMR and crystallographic data. See <http://www.rsc.org/suppdata/cc/1999/2351/>

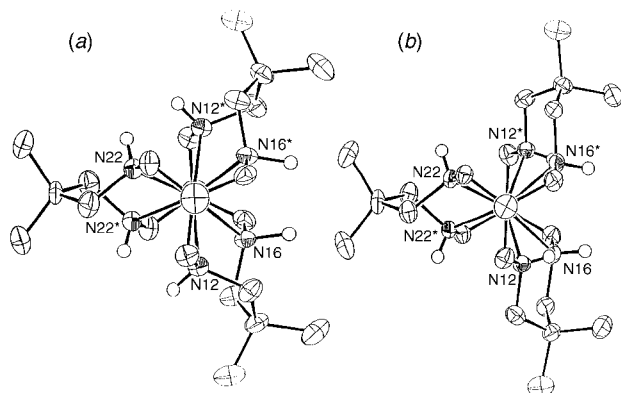


Fig. 1 The (a) $\Lambda(S_6)$ and (b) $\Lambda(S_4R_2)$ cations of **3** in its $(\text{NO}_3)_2\text{H}_2\text{O}$ and ZnCl_4 salts. Selected bond lengths (\AA) and angles ($^\circ$) for (a) (D_3 averaged \S): Co–N 2.223 (± 0.020); N(12)–Co–N(16) 86.3(± 0.4), Co–N–C (cap) 114.1(± 0.4). For (b) (C_2 independent): Co–N(12) 2.135(4), Co–N(16) 2.355(4), Co–N(22) 2.206(4); N(12)–Co–N(16) 82.2(2), N(22)–Co–N(22*) 88.8(2), Co–N(22)–C(21) 116.2(3), Co–N(12)–C(11) 117.0(3), Co–N(16)–C(15) 116.7(3).

were conducted in air and the $[\text{Co}^{\text{II}}(\text{Me}_8\text{tricosaneN}_6)]^{2+}$ ion was identified by elemental microanalysis (C, H, N, Cl, Co), $^1\text{H NMR}^\ddagger$ and VIS-near IR electronic spectra, and the single crystal X-ray analyses of its $(\text{NO}_3)_2$ and ZnCl_4 salts. $\ddagger\ddagger$ The synthesis and isolation of an *air* and relatively substitution stable Co^{II} hexamine species is an unusual development that involves new CoN_6 redox chemistry.

The $^1\text{H NMR}$ spectrum \ddagger of $[\text{Co}^{\text{II}}(\text{Me}_8\text{tricosaneN}_6)]^{2+}$ in D_2O solution at 25°C is consistent with the presence of two main species that do not interconvert on the 300 MHz $^1\text{H NMR}$ timescale. The CH_2 and CH_3 proton resonances display paramagnetic broadening and upfield δ shifts within the range -10 to -50 ppm, and are clearly in accord with two dominant species averaging D_3 (6 signals) and C_2 (15 discrete signals) symmetry in D_2O . These two forms of **3** most likely correspond to diastereoisomers of the type $\Lambda(S_6)$ and $\Lambda(S_4R_2)$, and their enantiomers $\Delta(R_6)$ and $\Delta(R_4S_2)$, where R or S defines the configuration of each of the six chiral nitrogen centres and Λ or Δ the configuration about the metal ion. The Co^{II} system appears to be stable to net ligand dissociation in the presence of anions such as Cl^- , ClO_4^- , NO_3^- , SO_4^{2-} , CH_3CO_2^- and CO_3^{2-} in a variety of solvents. However, the lability of individual $\text{Co}^{\text{II}}\text{--N}$ bonds should facilitate interconversion between the diastereoisomers within minutes. Diagrams of the two distinct Co^{II} cations found in single crystals of the *pink* $(\text{NO}_3)_2$ and *violet* ZnCl_4 salts of **3** are shown in Fig. 1(a) and (b), viewed down their bridgehead axes. The crystal structures clearly reveal the virtual D_3 symmetry of the $\Lambda(S_6)$ cation (a) and the C_2 symmetry of the $\Lambda(S_4R_2)$ cation (b), consistent with their being the major components in solution. Mean $\text{Co}^{\text{II}}\text{--N}$ distances are very similar for the $\Lambda(S_6)$ (2.223 \AA) and $\Lambda(S_4R_2)$ (2.232 \AA) structures, but the latter has two short (2.135(4) \AA) and two very long (2.355(4) \AA) bonds. Notably, the mean distances are 0.05–0.07 \AA longer than those of 2.16–2.18 \AA observed for other $\text{Co}^{\text{II}}\text{N}_6$ (amine) structures 6 having nearly optimal $\text{Co}^{\text{II}}\text{N}_6$ sizes. It follows from the data that these two conformations of the free ligand would prefer a larger ion than Co^{II} . Overall, the implication is that strong steric influences in the $[\text{Co}(\text{Me}_8\text{tricosaneN}_6)]^{n+}$ system stabilize larger cavity conformations, which markedly expand both $\text{Co}^{\text{II}}\text{N}_6$ and $\text{Co}^{\text{III}}\text{N}_6$ centres relative to those of the formally analogous $[\text{Co}(\text{fac-Me}_5\text{tricosaneN}_6)]^{n+}$ system, 4a which has a C_3 tris-(chair) conformation in the Co^{III} complex (**4**) and probably also in the Co^{II} state. 4a The structures also show sizeable $\text{Co}^{\text{II}}\text{N}_6$ twist distortions away from O_h geometry about the molecular bicyclic axes, with the average \S twist angles (ϕ) \P being $46.0(\pm 0.8)^\circ$ for the $\Lambda(S_6)$ isomer (assuming D_3 symmetry), and 46.2 and 31.5° for the two independent angles of the C_2 symmetric $\Lambda(S_4R_2)$ form. However the distortions are decidedly less than that of $[\text{Co}^{\text{II}}(\text{NH}_3)_2\text{sar}]^{4+}$ (sar =

3,6,10,13,16,19-hexaazabicyclo[6.6.6]icosane, apically substituted) in its $(\text{NO}_3)_4$ salt structure 6c [ϕ $29.0(\pm 0.9)^\circ$], which accommodates an optimal $\text{Co}^{\text{II}}\text{--N}$ mean distance of $2.170(\pm 0.021)$ \AA .

The expanded $\text{Co}^{\text{II}}\text{N}_6$ cores of the $[\text{Co}^{\text{II}}(\text{Me}_8\text{tricosaneN}_6)]^{2+}$ components exert substantial influences on the positions of the main ligand field bands, in the visible and near-IR absorption spectrum of **3** in aqueous solution at 25°C . These transitions, of origin $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{2g}$ and $^4\text{T}_{1g}(\text{F}) \rightarrow ^4\text{T}_{1g}(\text{P})$ at λ_{max} (ϵ) 1062 (4.8) and 498 nm ($11.1 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), are red shifted by 150 and 35 nm ($> 1500 \text{ cm}^{-1}$) from those of analogous cobalt(II) amine complexes 4a,6a with relatively optimal chromophore dimensions. Although the binary composition of **3** may cause broadening, asymmetry and lower resolution, particularly for the lower intensity bands, its overall spectral profile remains similar to that of the smaller cavity analogues. 4a,6a

Cyclic voltammetry of the $[\text{Co}^{\text{II}}(\text{Me}_8\text{tricosaneN}_6)]^{2+}$ system in aqueous 0.1 M KCl reveals unusual $\text{Co}^{\text{III/II}}$ redox behaviour. A complete interpretation requires more data for the isolated Co^{III} species, 7 but the general features account for the extraordinary air stability of the Co^{II} system, which is not oxidised by O_2 or H_2O_2 . The voltammogram \ddagger is distinctly asymmetric, with the oxidation and main reduction wave peaks occurring at *ca.* +0.84 and +0.29 V (*vs.* SHE at 100 mV s^{-1}), and was reproduced using multiple and reverse scans and several different salts of **3**. The system is electrochemically irreversible but chemically reversible, and the main wave features are consistent with configurations of $[\text{Co}(\text{Me}_8\text{tricosaneN}_6)]^{3+/2+}$ that reduce at *ca.* 0.3 V and oxidise at *ca.* 0.8 V (*vs.* SHE). The system has not been completely unravelled yet but there are clearly at least two diastereoisomers of the Co^{II} complex involved, and recently a blue and an orange form of the Co^{III} complex have been characterized after coulometric oxidation (800 mV *vs.* SCE) of the Co^{II} form. 7 The Co^{III} forms appear to be conformationally interconvertible, both with D_3 symmetry and clearly very different ligand fields (λ_{max} for $^1\text{A}_{1g} \rightarrow ^1\text{T}_{1g}$ *ca.* 600 and 480 nm).

The results in total show some astonishing changes in $\text{Co}^{\text{II/III}}$ amine spectroscopy and redox chemistry that are tied to dimensional changes in the $\text{Co}^{\text{II/III}}\text{N}_6$ chromophores, and clearly demonstrate the potential of sterically crowded expanded cavity cage systems in the development of new ML_6 chemistry.

Notes and references

\ddagger CCDC 182/1433. See <http://www.rsc.org.suppdata/cc/1999/2351/> for crystallographic files in .cif format.

\S The number in parentheses defines the range of observed values.

\P ϕ is defined by the torsion angles $\text{N}\cdots\text{C}_{\text{quat}}\cdots\text{C}'_{\text{quat}}\cdots\text{N}'$ for $\Lambda(S_6)$ and $\text{N}\cdots\text{C}_{\text{quat}}\cdots\text{Co}\cdots\text{N}'$ for $\Lambda(S_4R_2)$, with N,N' in the same bridge.

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