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Dioxygen-Bridged and Monomeric Cobalt(III) Complexes with 1,3-Diamino-2-(aminomethyl)propane and Ethylenediamine

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Use of ethylenediamine (en) and the tripod ligand 1,3-diamino-2-(aminomethyl)propane (daap) results in cobalt(III)–pentamine complexes with obligate configuration. Optimization of the synthesis of $[(en)(daap)Co]_2O_2^{4+}$ *suggests that daap must undergo conformational change for complete coordination. Ultraviolet and visible spectra of* $[(en)(daap)Co]_2O_2^{4+}$, $[(en)(daap)Co]_2O_2^{5+}$, $[Co(daap)(enOH]^{2+}$, *and* $[Co(daap)(en)H_2O]^{3+}$ *are consistent with those of similar complexes. NMR spectra for* $[(en)(daap)Co]_2O_2^{4+}$ *and for paramagnetic* $[(en)(daap)Co]_2O_2^{5+}$ *were observed and assigned. The aqueous acidity of the cation* $[Co(daap)(en)H_2O]^{3+}$ *was obtained at various ionic strengths.*

Introduction

Studies of various properties of acidopentaminecobalt(III) complexes have been constrained by the availability of combinations of amine ligands which will provide a uniform chemical environment and ligand field about the central atom. Ammonia has been generally satisfactory but in a number of cases there has been insufficient stability for reliable physical and chemical measurements. Chelating amine ligands provide for more inertness but combinations of them employed so far have not provided five equivalent coordinating atoms.

An additional natural result of mixed ligand combinations has been that isomers occur in many of the systems and that isomerization can and does occur with the exchange of X in the acidopentamine complex (X = non-amine ligand). Gainsford and House have demonstrated this by identification of the four isomers of $[Co(dien)(en)Cl]^{2+}$ and $[Co(dien)(en)(H_2O)]^{3+}$ (dien = diethylenetriamine, en= ethylenediamine) [1]. Furthermore, during the exchange of X they observed pH-dependent isomer interconversion.

There are alternative amine combinations which can provide chelation for inertness, five coordinating nitrogens of the same kind (*i.e.* all primary amine nitrogens), and which are not subject to isomer formation. In the case of five primary amine nitrogens, two basic possibilities come to mind: ethylenediamine (en) with either of the tripod ligands *cis*-1,3,5-triaminocyclohexane or with 1,3-diamino-2-(aminomethyl)propane (daap). Derivatives of these tripod ligands have been prepared and complexes containing them have been studied. Most common among them is $CH_3C(CH_2NH_2)_3$ [2, 3]. This paper will consider the synthesis and some of the properties of cobalt(III) complexes with both en and daap.

Among the complexes studied are the dioxygen-bridged cobalt(III) pentamine complexes. This class of compounds has recently been reviewed extensively by Martell [4] and by Lever and Gray [5].

Experimental

Syntheses

A. 1,3-Diamino-2-(aminomethyl)propane Trihydrochloride, daap·3HCl (f. wt. = 212.6)

The triamine was prepared by means of the Curtius degradation of methanetriacetic acid as described by Geissman *et al.* [6]. Methanetriacetic acid was prepared according to the method of Kohler and Reid [7].

Calculated element analysis for $C_4H_{16}N_3Cl_3$: C, 22.60; H, 7.59; N, 19.77%, Found: C, 22.46; H, 7.69; N 19.73%.

B. μ-Peroxobis{[1,3-diamino-2-(aminomethyl)propane][ethylenediamine]cobalt(III)} Chloride Tetrahydrate, $[(en)(daap)Co]_2O_2Cl_4\cdot 4H_2O$ *(f. wt. = 690.3)*

A 0.210 g portion of daap 3 HCl (1.0 mmol) was dissolved in a minimum amount of water and was brought to a pH near ten by dropwise addition of 20% (wt/wt) NaOH. To this solution was added 0.060 g ethylenediamine (1.0 mmol). The solution was cooled in ice while nitrogen was bubbled through it *via* a small glass frit to remove oxygen.

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Cobalt(II) chloride hexahydrate (0.24 g, 0.10 mmol) was also dissolved in a minimal quantity of water and the solution was flushed with nitrogen gas while cooling to ice temperature. The amine and cobalt(II) solutions were then combined while the nitrogen flushing was continued. Still protected by the nitrogen stream, the pinkish-yellow solution was slowly warmed to 60 °C and kept there for forty-five minutes. At the end of the heating period, the solution was cooled in an ice bath and the gas stream was changed from nitrogen to air. During the forty-five minute aeration period, the solution turned dark brown. Isolation of the brown chloride salt was accomplished by slow addition of ethanol to the solution while stirring. Too rapid addition yielded a brown oil. The yield was 0.36 g (53%).

Calculated element analysis for $Co_2C_{12}H_{50}N_{10}O_6Cl_4$: C, 22.03; H, 7.09; N, 21.41%. Found: C, 21.97; H, 7.11; N, 21.25%.

C. $[(en)(daap)Co]_2O_2(ClO_4)_4 \cdot nH_2O$

A 2.5 mmol scale synthesis of this perchlorate salt was accomplished by the method above but without the initial cooling period and the later addition of ethanol. One gram of brown product was obtained (32% yield). Element analysis of this compound was not performed although that of a subsequent reaction product was (see below). The compound also may be obtained in yields as high as 80% by addition of sodium perchlorate (0.245 g) to a solution of the chloride salt prepared as in B but prior to the addition of ethanol.

D. μ-Superoxobis{[1,3-diamino-2-(aminomethyl)propane][ethylenediamine]cobalt(III)} Chloride Pentahydrate, $[(en)(daap)Co]_2O_2Cl_5 \cdot 5H_2O$ (f. wt. = 743.8)

The superoxide was prepared from a cold solution of the peroxo salt as prepared in B after it had been chilled and acidified to a pH of about 2 with conc. HCl. Oxidation was accomplished by bubbling through the solution a stream of air from an entrained chlorine generator ($HCl + NaClO_3$). Following conversion, the green compound was crystallized by slow addition of cold ethanol to the ice-chilled solution. The yield based on cobalt(II) chloride was 28%.

Calculated element analysis for $Co_2C_{12}H_{52}N_{10}O_7Cl_5$: C, 19.38; H, 7.05; N, 18.28%. Found: C, 19.42; H, 7.17; N, 18.66%.

E. $[(en)(daap)Co]_2O_2(ClO_4)_5 \cdot nH_2O$

Solutions of the corresponding peroxide were oxidized with chlorine gas as in D. Alternatively, sodium perchlorate was added to solutions of the previously oxidized chloride salt. In either case, we could obtain only small amounts of unstable light green solid which readily turned orange. No analyses were attempted although an NMR spectrum was obtained.

F. Chloro[1,3-diamino-2-(aminomethyl)propane][ethylenediamine]cobalt(III) Perchlorate Monohydrate, $[Co(daap)(en)Cl](ClO_4)_2 \cdot H_2O$ (f. wt. = 474.6)

The resulting solution from a 1.0 mmol-scale synthesis of the peroxo perchlorate salt (B and C, above) was diluted to 20 ml and then heated on a steam bath until the volume was reduced to 10 ml. After cooling, 10 ml conc. HCl was added and the solution was reheated to near boiling on the steam bath and then allowed to cool. When the red solution reached ambient temperature, 10 ml acetone was added and the solution was placed in a refrigerator overnight. The brick red solid was obtained in nearly 40% yield.

Calculated element analysis for $CoC_6H_{23}N_5O_9Cl_3$: Co, 10.99; C, 13.45; H, 4.33; N, 13.10%. Found: Co, 10.99; C, 13.50; H, 4.31; N, 13.07%.

G. $[Co(daap)(en)H_2O]^{3+}$ and $[Co(daap)(en)OH]^{2+}$

Aqueous solutions of the chloropentaminecobalt(III) ion from F are readily converted to the hydroxopentamine complex by addition of an equivalent amount of NaOH solution. Subsequent acidification yields the aquopentamine complex. Neither of these was isolated from solution but their spectra and acid-base properties (discussed below) were consistent with the assumed formulas.

Element Analyses were performed by Galbraith Laboratories of Knoxville, Tennessee, U.S.A. and by the Alfred Bernhardt Microanalytical Laboratory of Elbach, West Germany. All the analyses were single determinations; waters of hydration were estimated by variation in whole number multiples to give best agreement with analytical data.

Visible and Ultraviolet Spectra were obtained for aqueous $[(en)(daap)Co]_2O_2(ClO_4)_4$ using solutions 8.61×10^{-4}, $\times 10^{-5}$, and $\times 10^{-6}$ *M* in the wavelength regions 1100–625, 625–360, and 360–200 nm, respectively. The first region was observed manually with a Beckman DU (glass 1 cm cells) and the latter were recorded with a GCA/McPherson 721 spectrophotometer (fused silica 1 cm cells).

After cooling in ice, acidification of the above stock solution with two drops conc. $HClO_4$ and oxidation with a minimal excess of solid $K_2S_2O_8$ yielded the stock solution for the superoxide, $[(en)(daap)Co]_2O_2^{5+}$. The green cation was 4.30×10^{-4} *M*, $HClO_4$ was 5.0×10^{-2} *M*, and the reference solution was 5.0×10^{-2} *M* $HClO_4$.

A spectrum of 2.00×10^{-3} *M* $[Co(daap)(en)OH]^{2+}$ was obtained from a solution of $[Co(daap)(en)Cl](ClO_4)_2 \cdot H_2O$ to which 1 drop 6 *M* NaOH had been added and the solution allowed to stand overnight. Dilution to 4.00×10^{-4} *M* was necessary for the 200–270 nm region. Acidification of these solutions with 2 drops 3 *M* H_2SO_4 yielded $[Co(daap)(en)H_2O]^{3+}$ whose spectrum was also recorded.

Nuclear Magnetic Resonance Measurements were made of both the peroxide and superoxide complexes with variation in anions, solvents, and internal standards. The magnetic susceptibility of the superoxo complex was obtained from a solution of the chloride salt in dilute deuterium chloride in deuterium oxide (2.3% w/w conc. DCl). The NMR method of Evans [8] was employed, observing the HDO resonance signal. The instruments used were a Perkin-Elmer R-12B equipped with a variable temperature probe and a JEOL FX-60.

Acidity of $[Co(daap)(en)H_2O]^{3+}$

Apparatus, reagents and procedure, were similar to those employed by Beaumont in determining the acidity of κ-$[Co(dien)(en)H_2P]^{3+}$ [1, 9]. The main difference in procedure was that the pH meter was calibrated at 5.40 with sodium hydroxide-potassium hydrogenpthalate buffer rather than at 3.56 with saturated potassium hydrogentartrate [10]. Variation in ionic strength from 0.0025 to 0.055 *M* was provided by addition of KCl dried at 120 °C.

Results and Discussion

Syntheses

In establishing the best method for preparation of the peroxide-bridged complex containing both daap and en, we have obtained circumstantial confirmation of the mechanism of formation of these complexes [11, 12]. The fact that little or no yield is obtained without a prior period of warming the cobalt(II) amine mixture suggests that aquopentaminecobalt(II) must be formed before the initial complexation of dioxygen.

In this case the 1,3-diamino-2-(aminomethyl)-propane must not only displace coordinated water molecules from cobalt(II) but must undergo an inversion process. While there is no steric requirement upon coordination of the first amine nitrogen, coordination of the second will yield an intermediate which contains a 6-member ring in its more stable 'chair' conformation. In order for the third nitrogen to coordinate, conformation must change from chair to 'boat'. Coordination of four or five amine nitrogens to cobalt(II) sufficiently changes the redox potential of the latter so that coordination by dioxygen results in oxidation to cobalt(III) and transforms the complex from labile to inert character. Thus yield of the desired product is maximized when conditions have been optimal for complete coordination of both en and daap before oxygen is introduced to the system.

In conversion of brown peroxide $[(en)(daap)Co]_2O_2^{4+}$ to green superoxide $[(en)(daap)Co]_2O_2^{5+}$, it is necessary that the solution be cold and acidic before addition of the oxidizing agent. Under these

TABLE I. Ultraviolet and Visible Spectra of Complexes.

	$[(en)(daap)Co]_2O_2^{4+}$	$[(en)(daap)Co]_2O_2^{5+}$	$[Co(daap)(en)H_2O]^{3+}$	$[Co(daap)(en)OH]^{2+}$
λ_{max}[a]	216	225	223	217
ϵ	7.9×10^4	1.0×10^5	2.2×10^4	2.3×10^4
λ_{min}	250	275	308	320
ϵ	2.5×10^4	2.0×10^4	15	19
λ_{max}	296	306	351	339
ϵ	5.0×10^4	7.5×10^4	35	27
λ_{min}	384		400	417
ϵ	2.0×10^4		10	2
λ_{max}	404 (sh)	354 (sh)	482	495
ϵ	1.58×10^3	1.06×10^4	25	22
λ_{min}		411		
ϵ		1.12×10^4		
λ_{max}	533 (sh)?	471		
ϵ	5.0×10^2	2.5×10^3		
λ_{min}		563		
ϵ		6.0×10^2		
λ_{max}	653 (sh)	702		
ϵ	2.2×10^2	4.47×10^3		
λ_{max}		855 (sh)		
ϵ		6.3×10^2		

[a] λ is in nanometer units while ϵ is in $l \cdot mol^{-1}\ cm^{-1}$.

conditions quantitative conversion has been demonstrated for $[(en)(dien)Co]_2O_2^{4+}$ [13]. Acid catalyzes the decomposition of the peroxo complex but lower temperatures retard that mechanism. However, acid also stabilizes the superoxide, presumably by preventing dissociation of N–H bonds which would occur more readily in the +5 complex. While protonated dibridged complexes containing dioxygen have been observed, those containing only a dioxygen bridge generally have not yielded isolatable protonated species [4].

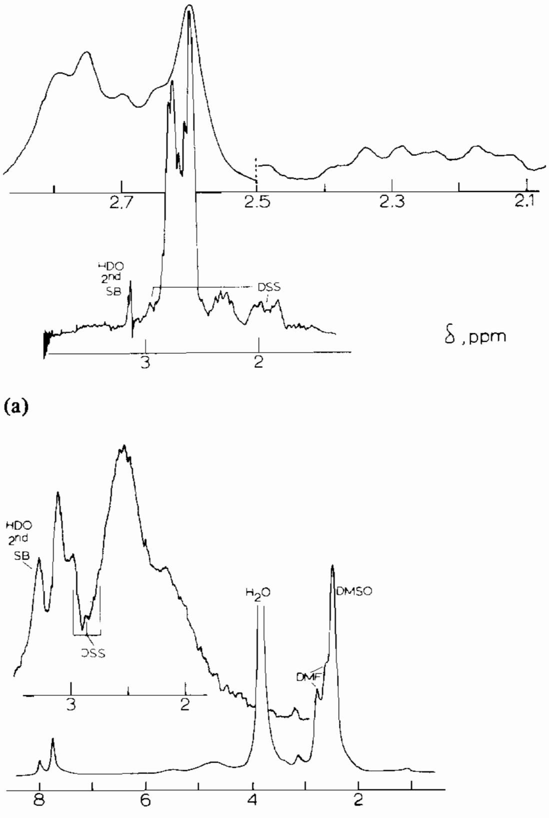
Ultraviolet and Visible Spectra

Summarized in Table I, the spectra of the en/daap peroxide- and superoxide-bridged cations are nearly identical with those of the analagous en/dien cations and of other similar compounds [1, 14]. The spectra of $[Co(daap)(en)H_2O]^{3+}$ and $[Co(daap)(en)OH]^{2+}$ are also very much like those of the en/dien complexes. The replacement of dien by daap in the coordination sphere of cobalt(III) was expected to produce narrowing of the ligand field bands but this effect was not significant. Ligand field splitting by O_2^{2-}, O_2^{-}, OH^-, and H_2O *versus* primary amine is probably at least as important as that caused by secondary amine *versus* primary amine. Additionally, there are steric constraints on the daap amine groups which distort the symmetry of these complexes from a purely octahedral arrangement of coordinating atoms [3].

Nuclear Magnetic Resonance

The proton NMR studies of the perioxide- and superoxide-bridged complexes were hampered by low solubilities due to high cation charge and by oxidation–reduction instability of the +5 cation in organic solvents. Additional difficulty was caused by methyl proton signals from the deuterated solvents which overlapped with the C–H region of the complexes and which were of the same magnitude because of the dilute nature of the samples. The C–H portion of the spectrum was best observed in D_2O while the N–H signals were observed in nonaqueous solvents due to rapid exchange of N–H protons in D_2O. Example spectra of $[(en)(daap)Co]_2O_2^{4+}$ and $[(en)(daap)Co]_2O_2^{5+}$ are shown in Figs. 1 and 2 while assignments are in Table II.

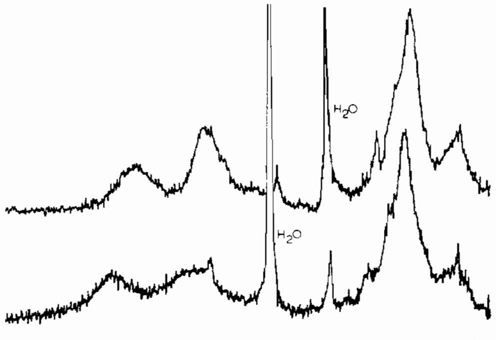
In the peroxo complex, the two broad but well-resolved NH_2 peaks at –4.04 and –5.07 ppm are in area ratios 3:2, respectively. The best interpretation seems to be that here chemical shift is dependent primarily upon the organic molecule to which the NH_2 belongs; unexpectedly, distance and angle from dioxygen has no more than a broadening effect and the potentially five chemically different pairs of amine hydrogens appear as only two signals. In κ,κ-$[(en)(dien)Co]_2O_2^{4+}$ this is also observed in that the en-amines occupy sites both *cis* and *trans* to dioxygen but their NMR signals are unresolved at 100 MHz (4.8 ppm *vs.* TMS). The dien-NH_2 signals are resolved at –3.74 and –4.04 ppm with the latter split, presumably by hydrogen bonding to dioxygen [1,



(a)

(b), (c)

Fig. 1. NMR spectra. (a) $[(en)(daap)Co]_2O_2^{4+}$ in D_2O. (b) $[(en)(daap)Co]_2O_2^{5+}$ in D_2O. (c) $[(en)(daap)Co]_2O_2^{5+}$ in Polysol-d + DMF-d_7.



(a), (b)

Fig. 2. Temperature dependence of NMR spectrum. (a) $[(en)(daap)Co]_2O_2^{4+}$ in Polysol-d + DMF-d_7 at 45 °C. (b) $[(en)(daap)Co]_2O_2^{4+}$ in Polysol-d + DMF-d_7 at –25 °C.

TABLE II. NMR Assignments.

Cation	$[(en)(daap)Co]_2O_2^{4+}$	$[(en)(daap)Co]_2O_2^{4+}$	$[(en)(daap)Co]_2O_2^{5+}$	$[(en)(daap)Co]_2O_2^{5+}$
Anion	Cl^-	Cl^- or ClO_4^-	Cl^-	ClO_4^-
Solvent	D_2O	Polysol-d + DMF-d_7	D_2O + DCl	Polysol-d + DMF-d_7 + DCl
Internal Standard	DSS[a]	TMS	DSS	CH_2Cl_2
Assignments (No. of Protons)	δ, ppm	δ, ppm	δ, ppm	δ, ppm
Tertiary CH (2)	−2.26 wk multiplet, J = 3 Hz	−2.20 wk, no fine struct	not distinguishable	not distinguishable
en CH *cis*[b] (4) *trans* (4)	−2.59 str, unsplit	−2.44 to −2.83 overlapped by solvent CH	−2.18 broadest	overlapped by solvent CH
daap CH *cis–cis*[b] (4) *cis–trans* (4)	−2.75 str, apparent doublet, J = 2.5 Hz		−2.53 broader	
trans (4)	−2.66 med doublet J = 3 Hz		−3.10 broadened	−3.10 wk
daap NH (12)		−4.04, broad		−4.6 wk, broad
en NH (8)		−5.07, broader		−5.5 wk, broad

[a] DSS = Sodium 2,2-dimethyl-2-silapentane-5-sulfonate. [b] *Cis* and *trans* refer to location relative to dioxygen. See Fig. 3.

14–16]. The near chemical equivalence of the en and daap methylene groups results in overlapped CH_2 multiplets with the two strongest peaks at −2.58 and −2.72 ppm (*vs.* DSS). Despite lack of resolution and multiplet detail, tentative assignments were made. In κ,κ-$[(en)(dien)Co]_2O_2^{4+}$, the methylene signals are similarly overlapped.

The signal from the tertiary carbon proton is assignable to the weak signal at −2.30 ppm. In D_2O, it takes the form of a multiplet with six of the seven peaks observable and with splitting uniformly near 3 Hz. In organic solvent the peak is not resolved, presumably due to additional, weaker coupling with amine protons which have not been replaced by deuterium. The area of this multiplet is approximately 1/10 that of the region assigned to methylene CH_2.

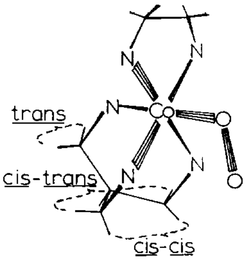


Fig. 3. Steric equivalences for hydrogens in the Co(daap)(en)O_2 fragment.

At the temperature of the above measurements (35 °C), there seemed to be no evidence for conformational preference by the en or daap rings or for a single rotational conformer about the dioxygen or cobalt–oxygen bonds. In exploring these possibilities, a solution of $[(en)(daap)Co]_2O_2(ClO_4)_4$ in Polysol D/DMF [17] showed little change as temperature was varied between 45 and −25 °C: the water signal moved from −3.30 to −3.79 ppm and the daap-NH_2 signal broadened more at the lower temperature than the en-NH_2 signal. This change of signal for daap-NH_2 was the only observable suggestion of conformational or rotational preference. At lower temperatures, slower Co–O_2–Co rotation would provide a longer half life for hydrogen bonds between dioxygen and the neighboring amine hydrogens. Also, hydrogen bonding between the amines and dissolved water would become more prevalent. That the broadening occurs more for the daap-NH_2 than en-NH_2 suggests either that hydrogen bonding occurs more for daap than for en or that daap begins to resolve into its stable 'twist' conformers [3, 18]. For the superoxo complex, the CH signals were again only partially resolved. Different degrees of broadening suggested a *prima facie* set of assignments based on proximity to the paramagnetic center and on bonding to nitrogen *cis* or *trans* to dioxygen. The amine hydrogen signals were shifted downfield from their positions in the peroxo complex. This shift may be due more to an increase in acidity than an isotropic shift due to paramagnetism. These assignments are in Table II.

Determination of magnetic susceptibility by the NMR bulk susceptibility shift method was limited in accuracy by the solubility of $[(en)(daap)Co]_2O_2Cl_5 \cdot 5H_2O$ in the DCl-acidified D_2O and by the employed field strength. Observing the HDO signal, we obtained 1.8 ± 0.1 Bohr Magneton for the complex, in agreement with the one unpaired electron observed in these compounds.

Acidity of $[Co(daap)(en)H_2O]^{3+}$

In the titrations of $[Co(daap)(en)H_2O]^{3+}$ with base and of the hydroxo complex with acid, the half-equivalence points extrapolated to 5.74 ± 0.05 pH units at zero ionic strength. A number of such acidities have been measured but with widely varying temperatures, ionic strengths, and methods [9, 19]. Only when the acidities of these complexes have been measured under a uniform set of conditions will it be possible to assess the influence of the ligands lying *cis* and *trans* to the coordinated water molecule. When these factors are established, it may be possible to use acidity, along with other data, as an aid in assignment of isomer configuration.

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