

A new dinuclear amine–cobalt(III) complex containing two bridging amide ions

Patricia M. Angus, David P. Fairlie, Ranji Gunasingam, Tao Zhu
and W. Gregory Jackson*

Department of Chemistry, University College (NSW), Australian Defence Force Academy, Northcott Drive, Canberra, ACT 2600 (Australia)

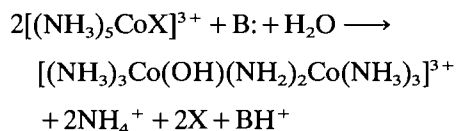
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Abstract

The classic tribridged dimer, $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)_2(\text{OH})\text{Co}(\text{NH}_3)_3]^{3+}$, the first tribridged species to contain two bridging NH_2^- groups, has been characterized. Some derivatives in which the OH^- bridge has been replaced by another are also described. ^1H NMR studies in dimethyl sulfoxide reveal bridging NH_2^- and OH^- proton signals at characteristically high chemical shifts, especially bridging OH^- which is above SiMe_4 , but the shifts are quite sensitive to structure.

Introduction

Werner [1, 2] succeeded in the synthesis of two of the four classical tribridged ions $[(\text{NH}_3)_3\text{Co}(\mu\text{-NH}_2)_n(\mu\text{-OH})_{3-n}\text{Co}(\text{NH}_3)_3]^{3+}$ ($n=0-3$). A third, the tris(amido) dinuclear ion has only recently been described [3], while the fourth, the bis(amido)hydroxo complex, was synthesized some ten years ago [4, 5] when we described the synthesis of a crimson-red 3+ ion as a by-product in the synthesis of pentaamminecobalt(III) complexes of N-bonded ureas and related ligands:



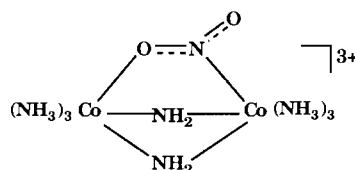
It was only later that we identified this crimson-red complex as the tribridged dinuclear ion. It has been independently synthesized by Heck [6] via a different route, and herein we establish its structure.

Results and discussion

The reaction between $[(\text{NH}_3)_5\text{CoOSMe}_2](\text{ClO}_4)_3$ and ambidentate ligands such as urea in the presence of

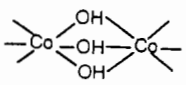
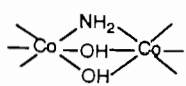
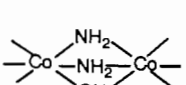
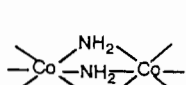
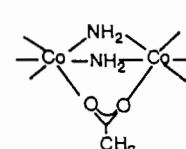
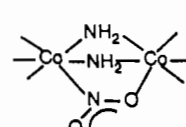
*Author to whom correspondence should be addressed.

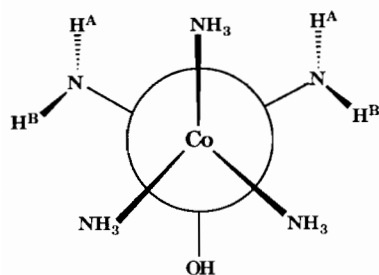
a sterically hindered and non-coordinating base, e.g., 2,2,6,6-tetramethylpiperidine, leads to a variety of products [4, 5, 7], but the major species (>60%) is the deprotonated N-bonded urea complex which was characterized previously. This elutes from a Sephadex (SP C25) ion-exchange column as a 2+ ion but always with (and separated from) a crimson-red 3+ ion which contains coordinated ammonia but no carbon [5, 7] (^1H and ^{13}C NMR; elemental microanalyses). The ^1H NMR spectrum in $\text{Me}_2\text{SO}-d_6$ (Table 1) of the ClO_4^- salt of this C-free compound reveals a 12:6 Co– NH_3 pattern (18H) as well as two unusually high-field signals (δ 0.43, 0.31) close to SiMe_4 , assigned as NH protons (4H) because of a $w_{1/2}$ indicative of ^{14}N quadrupolar broadening; we assign these NH protons as bridging NH_2^- . A very high field and sharper signal (δ –4.95) integrating for just one proton was also observed, and this is characteristic of bridging OH^- (*vide infra*). A structure consistent with these data is:



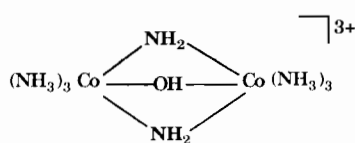
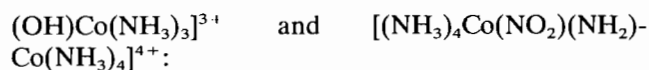
The bridging NH_2^- groups are equivalent but the individual protons on each NH_2^- are not; they are exo and endo to the bridging OH^- :

TABLE 1. Proton NMR spectra for some bridging hydroxo and amido dinuclear hexaamminedicobalt(III) complexes in Me₂SO-d₆ at 20 °C

	δ (ppm)		<i>trans</i> -OH -NH ₃	<i>trans</i> -NH ₂ -NH ₃
	Bridging -OH-	-NH ₂ -		
	-0.15 (3H)		3.04 (18H)	
	-2.56 (2H)	2.36 (2H)	2.46 (12H)	3.59 (6H)
	-4.95 (1H)	0.31 (2H) 0.43 (2H)	1.92 (6H)	2.98 (12H)
		-1.51 (6H)		2.47 (18H)
	Bridging -NH ₂ -	<i>trans</i> -X -NH ₃	<i>trans</i> -NH ₂ -NH ₃	Other -CH ₃
	0.15 (d, 2H) 0.42 (d, 2H) <i>J</i> = 3 Hz	2.59 (6H)	3.01 (12H)	2.00 (3H)
	0.65 (d, 2H) 1.16 (d, 2H) <i>J</i> = 3 Hz	2.73 (3H) 3.25 (3H)	2.82 (6H) 3.20 (6H)	



Nitrosation of the bridging OH⁻ leads readily to a yellow-orange nitrite-containing crystalline material in high yield. An N,O bridging derivative is implicated; the NO₂⁻ is presumably bonded unsymmetrically through N and one O as revealed in the single crystal X-ray structures [8, 9] of [(NH₃)₃Co(NO₂)₂-



The ¹H NMR spectrum (Me₂SO-d₆) confirms the persistence of the two bridging NH₂⁻ ligands and the loss of the OH⁻ bridge. The now inequivalent two halves of the dimer, each having two NH₃ of one kind (δ 3.20, 2.82) and one NH₃ of another (δ 3.25, 2.73), confirm the unsymmetrical bridge (Table 1). Treatment even with a large excess of nitrite, under forcing con-

ditions, does not lead to the incorporation of more than one nitrite ion.

The bis(amido)hydroxo tribridged species reacts with acetic acid to generate a symmetrically bridging acetate derivative, $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)_2(\text{OC}(\text{Me})\text{O})\text{Co}(\text{NH}_3)_3]^{3+}$, not unlike the known [10] $[(\text{NH}_3)_3\text{Co}(\text{OH})_2(\text{OC}(\text{R})\text{O})\text{Co}(\text{NH}_3)_3]^{3+}$ complexes. Again reaction under forcing conditions with excess acetic acid did not lead to the incorporation of more than one acetate ligand.

The derivatization experiments are consistent with a single OH^- bridge which can be opened with acid assistance, although they do not prove it. The experiments under forcing conditions were made because OH^- bridged dimeric ions having two or three such bridges are not necessarily easily substituted. The dimer $[(\text{NH}_3)_3\text{Co}(\text{OH})_3\text{Co}(\text{NH}_3)_3]^{3+}$, for example, takes on a first bridge readily (MeCO_2^-) but a second (MeCO_2^- or NO_2^-) with much greater difficulty [11]. Similarly $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)(\text{OH})_2\text{Co}(\text{NH}_3)_3]^{3+}$ will readily take on only one bridge (other than OH^-) such as NO_2^- or MeCO_2^- [11], although it (and the triol) can be forced to take on two NO_2^- ligands.

In summary, the structure of the new tribridged species follows from the ^1H NMR data and derivatization experiments which confirm two $\text{Co}(\text{NH}_3)_3$ units joined by three symmetrical bridges, one OH^- and two NH_2^- . Furthermore this structure confirms that deduced [6] from an alternative method of synthesis via bridge splitting of $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)_3\text{Co}(\text{NH}_3)_3]^{3+}$ since the ^1H NMR and electronic absorption spectra show the two materials to be identical.

Treatment of the $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)_2(\text{OH})\text{Co}(\text{NH}_3)_3]^{3+}$ complex with strong HCl cleaves the OH^- bridge, giving a grey-brown crystalline complex which is probably the $[(\text{NH}_3)_3\text{ClCo}(\text{NH}_2)_2\text{CoOH}_2(\text{NH}_3)_3]^{3+}$ or $[(\text{NH}_3)_3\text{ClCo}(\text{NH}_2)_2\text{CoCl}(\text{NH}_3)_3]^{2+}$ complex, analogous to Werner's [12] 'melano chloride'. Chromatography reveals a single olive-grey band eluting as a 3+ ion; this charge is consistent with the first but not the second formulation. The ^1H NMR spectrum in $\text{Me}_2\text{SO}-d_6$ is complex, possibly because coordinated water is being replaced by Me_2SO coupled with a rearrangement from *fac* to *mer* about either or both cobalt centers.

The hydroxo group in the well known dibridged complex $[(\text{NH}_3)_4\text{Co}(\text{NH}_2)(\text{OH})\text{Co}(\text{NH}_3)_4]^{4+}$ can be cleaved in acid and the resultant acido groups aminated to provide $[(\text{NH}_3)_5\text{Co}(\text{NH}_2)\text{Co}(\text{NH}_3)_5]^{5+}$ [13]. Heck [6] has succeeded in a related reaction in the synthesis of $[(\text{NH}_3)_4\text{Co}(\text{NH}_2)_2\text{Co}(\text{NH}_3)_4]^{4+}$ commencing with the tribridged species $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)_3\text{Co}(\text{NH}_3)_3]^{3+}$. Werner [14] claimed the existence of this $[(\text{NH}_3)_4\text{Co}(\text{NH}_2)_2\text{Co}(\text{NH}_3)_4]^{4+}$ ion, and Heck [6], in a modification of Werner's original method, has been successful. We however have been unable to aminate

$[(\text{NH}_3)_3\text{Co}(\text{NH}_2)_2(\text{OH})\text{Co}(\text{NH}_3)_3]^{3+}$, or any of its derivatives reported here, to generate this ion.

The reason for the appearance of the new bis(amido) bridging dimer $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)_2(\text{OH})\text{Co}(\text{NH}_3)_3]^{3+}$ as a by-product of the synthesis of $[(\text{NH}_3)_5\text{Co}(\text{urea-N})]^{2+}$ and related molecules is not clear. We attempted a more logical synthesis by simply reacting $[(\text{NH}_3)_5\text{CoOH}_2]^{3+}$ or $[(\text{NH}_3)_5\text{CoOSMe}_2]^{3+}$ in Me_2SO containing a strong non-coordinating base such as tetramethylpiperidine. Indeed such reactions did produce the dimer but admixed with $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)(\text{OH})_2\text{Co}(\text{NH}_3)_3]^{3+}$ confirmed by comparison with an authentic specimen [2]. These dimers were not readily separated without irreversible destruction of one or both, and so the preferred method of synthesis for the bis(amido) derivative remains the urea preparation. Why the urea prevents the formation of the dihydroxo dimer but not the monohydroxo dimer remains a mystery, and with a yield of 5% it is not reasonable to speculate on mechanism. (The very well-known and studied $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)(\text{OH})_2\text{Co}(\text{NH}_3)_3]^{3+}$ is obtained in a similarly abysmal yield, 5% or less [2, 15].)

^1H NMR spectra

The ^1H NMR spectra for the complete series of dinuclear ions all show the expected multiplicity for CoNH_3 signals. For the new dinuclear ion $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)_2(\text{OH})\text{Co}(\text{NH}_3)_3]^{3+}$ the chemical shifts for the NH_3 groups *trans* to the $-\text{NH}_2-$ bridges as well as for the NH_2 protons themselves occur almost precisely midway between the corresponding signals for $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)_3\text{Co}(\text{NH}_3)_3]^{3+}$ and $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)(\text{OH})_2\text{Co}(\text{NH}_3)_3]^{3+}$ (Table 1). Furthermore, from the spectra (Table 1) of $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)(\text{OH})_2\text{Co}(\text{NH}_3)_3]^{3+}$ and the structurally characterized [17] $[(\text{NH}_3)_3\text{Co}(\text{OH})_3\text{Co}(\text{NH}_3)_3]^{3+}$ ions, one could predict the shift for the NH_3 *trans* to OH^- in the new complex $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)_2(\text{OH})\text{Co}(\text{NH}_3)_3]^{3+}$ as δ 1.88 ($= 2.46 - (3.04 - 2.46)$) and the shift for the bridging OH^- as $\delta -4.97$ ($= -2.56 - (2.56 - 0.15)$); the observed values are δ 1.92 and $\delta -4.95$, respectively, in very close agreement. In general, replacement of $-\text{NH}_2-$ by an $-\text{OH}-$ bridge results in a downfield shift for a *cis*- NH_3 of *c.* 0.55 ppm, while an NH_3 *trans* to $-\text{OH}-$ is *c.* 0.6 ppm downfield compared to one *trans* to $-\text{NH}_2-$. A rationale for the NH_3 shifts has been given [18] for mononuclear $[(\text{NH}_3)_5\text{CoX}]^{n+}$, and in the context of bridging dinuclear species we note that the ^1H NMR spectrum [19] for the ion $[(\text{NH}_3)_5\text{Co-CN-Co}(\text{NH}_3)_5]^{5+}$

*The structure of the acetate derivative $(\text{NH}_4)[(\text{NH}_3)_3\text{Co}(\text{NH}_2)(\text{OH})(\text{OC}(\text{CH}_3)\text{O})\text{Co}(\text{NH}_3)_3](\text{HSO}_4)_4$ has been determined, but not that of the amidodihydroxo ion itself.

is almost the same as a 1:1 mixture of $[(\text{NH}_3)_5\text{Co-CN}]^{2+}$ plus $[(\text{NH}_3)_5\text{Co-NC}]^{2+}$.

There are no mononuclear complexes containing a Co-NH₂ unit for comparison, but in the dinuclear ions the NH₂⁻ protons are to high field compared to Co-NH₃ signals. Although the signals are somewhat ¹⁴N quadrupole broadened, the gem proton coupling to nitrogen can just be observed (*J c.* 3 Hz). Also, the observation of coupling establishes that the protons on each NH₂⁻, rather than the two NH₂⁻ groups, are inequivalent.

Perhaps the most interesting feature of the spectra (Table 1) is the consistently high field OH⁻ proton signal, even higher than SiMe₄, and possibly it has not been observed previously for this reason. The mononuclear species $[(\text{NH}_3)_5\text{CoOH}]^{2+}$ also shows a high field OH⁻ signal, at $\delta -3.15$ [20] (cf. $[(\text{NH}_3)_5\text{CoOH}_2]^{3+}$, at $\delta +5.7$ (2H) [21]) but it is very difficult to observe if the solvent is not completely anhydrous, since it is exchange averaged with the signal for free H₂O (normally at $\delta +3.3$ in Me₂SO-d₆). The bridging OH⁻ is much less basic and does not show this exchange averaging; indeed, it is quite sharp, and thus characteristic of Co-OH-Co since the Co-NH₂-Co signals, also at higher fields, are broadened by the ¹⁴N quadrupole.

The shifts for the bridging OH⁻ and NH₂⁻ protons show a marked sensitivity to the nature of the other bridge. Thus, each substitution of an OH⁻ by an NH₂⁻ leads to an upfield shift, *c.* 2 ppm in the case of Co-NH₂-Co protons and *c.* 2.4 ppm for the Co-OH-Co proton.

Potential uses

The amide ion NH₂⁻ is well known to labilize Co(III) complexes towards ligand substitution, especially as a monodentate group [22-24]. Secondly while bridging two metal ions it is saturated, and thus the bridge is not subject to acid-assisted cleavage* like its isoelectronic counterpart OH⁻. This property permits the construction of dinuclear species held together by an NH₂⁻ bridge with one metal containing a nucleophile and the other a coordinated electrophile, and enormous enhancements in reactivity are achieved in this manner [24, 26, 27]. Entrance to this class of compounds is achieved through the dibridged Co(μ -NH₂)(μ -OH)Co species, with either labilized loss of NH₃ [23, 24] or acid cleavage of the OH⁻ bridge [26, 27] as options to introduce coordinated reagents. It was anticipated that dinuclear species having Co(μ -NH₂)₂Co or Co(μ -NH₂)₂(μ -OH)Co fragments would be even more useful than Co(μ -NH₂)(μ -OH)Co in this respect because two NH₂⁻ bridges remove the rotational flexibility and can

provide an ideal juxtaposition of electrophile and nucleophile. However, until now, there had been no synthetic routes to such species.

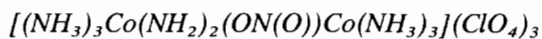
Experimental

¹H and ¹³C NMR spectra were recorded for Me₂SO-d₆ solutions on a Varian XL300 spectrometer at 25 °C; all shifts are reported as ppm downfield from SiMe₄. Known dinuclear complexes were synthesized as described in the literature. Where not given, the analytical data for new compounds were satisfactory for C, H, N and halide as appropriate.



This material was synthesized as described previously [5], commencing with $[(\text{NH}_3)_5\text{CoO}_3\text{SCF}_3](\text{CF}_3\text{SO}_3)_2$ (40 g). After ion-exchange separation of the crimson-red 3+ band (in 0.5 M NaClO₄), it was freeze-dried; crystals were obtained from the chilled concentrate, and recrystallized from water/NaClO₄. The product was washed with ethanol and ether, and dried *in vacuo* over P₂O₅ (yield 0.95 g; 5%). *Anal.* Calc. for $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)_2(\text{OH})\text{Co}(\text{NH}_3)_3](\text{ClO}_4)_3$: H, 4.09; N, 19.75; Cl, 18.74. Found: C, 0.00; H, 3.98; N, 19.56; Cl, 18.65%.

Alternative syntheses using either the aqua or Me₂SO complex instead of the triflate species, and omitting the phenylurea, resulted in variable yields of a crimson-red complex. This proved to be a mixture of $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)_2(\text{OH})\text{Co}(\text{NH}_3)_3](\text{ClO}_4)_3$ and $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)(\text{OH})_2\text{Co}(\text{NH}_3)_3](\text{ClO}_4)_3$ (¹H NMR; comparison with authentic specimens). In a separate experiment, the chromatography employed a NaCH₃CO₂/CH₃COOH buffer instead of NaClO₄ and a mixture of the corresponding acetate derivatives, $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)_2(\text{OC}(\text{CH}_3)\text{O})\text{Co}(\text{NH}_3)_3](\text{ClO}_4)_3$ and $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)(\text{OH})(\text{OC}(\text{CH}_3)\text{O})\text{Co}(\text{NH}_3)_3](\text{ClO}_4)_3$, was isolated, again identified by comparison (¹H, ¹³C NMR) with authentic specimens (see below for an independent synthesis of the former); the latter derivative was known previously (¹³C NMR (Me₂SO-d₆): δ 185.3 (-CO₂-), 24.1 ppm (CH₃)) [16].



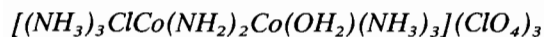
To $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)_2(\text{OH})\text{Co}(\text{NH}_3)_3](\text{ClO}_4)_3$ (0.30 g) in water (8 ml) containing NaNO₂ (0.10 g; 3 equiv.) was added HClO₄ (1 M, 2.6 ml; 5 equiv.) and the mixture was warmed (40 °C) while stirred continuously. After 30 min, saturated NaClO₄ (2 ml) was added, the mixture cooled and the orange fibrous needles collected, washed with ethanol and ether and air-dried (0.28 g, 90%). The experiment was repeated using the bare minimum of NaNO₂ (0.036 g; 1 equiv.) with the same

*The reaction can be acid-assisted, as distinct from catalyzed, under special conditions.

amount of HClO_4 , and then excesses of NaNO_2 (1 g) and HClO_4 (12 M, 1 ml) coupled with stronger heating (70 °C, 1 h); after recrystallization, an identical product was obtained in each case.



A sample of $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)_2(\text{OH})\text{Co}(\text{NH}_3)_3](\text{ClO}_4)_3$ (0.30 g) was dissolved in a minimum volume of water and treated with an equal volume of glacial acetic acid. After standing overnight the mixture had darkened slightly; the addition of NaClO_4 (7.5 g per 10 ml) yielded yellow–brown crystals which were recrystallized from minimum water using a fifth volume of saturated NaClO_4 . An independent synthesis using 10 min heating at 80 °C resulted in a similar yield (85%) of this acetate derivative. ^{13}C NMR ($\text{Me}_2\text{SO}-d_6$): δ 184.1 ($-\text{CO}_2-$), 23.6 ppm (CH_3).



A sample of $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)_2(\text{OH})\text{Co}(\text{NH}_3)_3](\text{ClO}_4)_3$ was dissolved directly in a minimum of HCl (11 M); the solution quickly became brown–green. The addition of a fifth volume of HClO_4 (12 M) resulted in grey–brown crystals which were collected, washed with ethanol and ether and air-dried.

Acknowledgements

We are grateful to Professor Heck (Saarbruecken) for providing samples of $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)_3\text{Co}(\text{NH}_3)_3](\text{ClO}_4)_3$ and $[(\text{NH}_3)_4\text{Co}(\text{NH}_2)_2\text{Co}(\text{NH}_3)_4](\text{ClO}_4)_4$, and his synthesis for $[(\text{NH}_3)_3\text{Co}(\text{NH}_2)_2(\text{OH})\text{Co}(\text{NH}_3)_3]^{3+}$. We also thank the Australian Research Council for financial support, and the University of Guizhou, People's Republic of China, for leave and financial assistance (T.Z.).

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