A general synthetic route to pentaamminecobalt(III) complexes of N-bonded amides, ureas, carbamates, sulfinamides, sulfonamides and sulfamate

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Abstract

A general synthetic procedure for preparing stable cobalt(III) complexes containing selectively nitrogen-bonded ambidentate molecules e.g. amides, ureas, carbamates, sulfinamides, sulfonamides and sulfamate, is described. The method relies on the superior acidity of the nitrogen-bonded, relative to the oxygen-bonded, isomer and this is attributed to much better resonance stabilization of the anionic ligand while N-bonded. Thus the method should be applicable to complexes of other metal ions.

Introduction

In recent years the availability of the labile complex, $[(NH_3)_5CoO_3SCF_3](CF_3SO_3)_2$, has permitted the synthesis of a wide range of $[(NH_3)_5CoX]^{n+}$ ions [1]. The triflato complex reacts with amides, ureas, carbamates, sulfinamides and sulfonamides in weakly coordinating solvents (acetone, sulfolane) to give exclusively complexes in which these molecules are bonded to cobalt through oxygen [2]. In all these cases there is an alternative coordinating atom, the nitrogen, and for sulfinamides a sulfur atom as well. Nitrogen-bonded complexes of certain amides (e.g. acetamide [3], benzamide [4], *N,N*-dimethylurea [5]) can be obtained through base-catalyzed hydration of the corresponding nitrile complexes, $[(NH_3)_5CoNCR]^{3+}$, and this is a valuable high yield preparation which works well for other metal ions too (e.g. Ru(III), Rh(III) [6]. However this synthesis is restricted by the need for a precursor nitrile complex, often unavailable or non-existent, and it fails when R has an acidic α-proton (e.g. $R = NH_2$, NHR') [5, 7] due to deprotonation in basic solution and reduced electrophilicity of the formerly sp-carbon. We therefore developed a new high yield route to these and other complexes containing nitrogen-bonded ligands ($X = NHCONH_2$, $NHCOOC_2H_5$, $NHCOCH_2F$, $NHSOCH_3$, $NHSO_2NH_2$, $NHSO_2CH_3$, $NHSO_2C_6H_5$, etc.) which is now described.

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Results and discussion

When $[(NH_3)_5CoX]^{3+}$ complexes containing oxygen-bound amides ureas, carbamates (or sulfinamides) are dissolved in aqueous acid, there is slow solvolysis leading exclusively to $[(NH_3)_5CoOH_2]^{3+}$ plus free ligand ($t_{1/2} \sim$ h, 25 °C) [2]. In aqueous base rapid solvolysis ($t_{1/2} < 1$ s, 25 °C) yields primarily $[(NH_3)_5CoOH]^{2+}$ (>95%) but now traces of $[(NH_3)_5CoNHCOR]^{2+}$, absent in the reacting O-bonded isomers, are also produced [2, 8]. At pH ~ 7, these protonated N-bonded isomers are formed in ever higher yield (5–25%) and these observations [2] constitute the strategic basis for the current synthetic design.

The isomer equilibrium **1** ⇄ **2** favours formation of some N-bonded isomer at a pH above the pK'_a of the much more acidic form **2** which is selectively deprotonated to the inert **3**, a thermodynamic sink.

Note that **2** is more than eight orders of magnitude more acidic than **1** and so, while **2** is very unstable with respect to **1** for all ligands described here ($K'_{NO} = [1]/[2] \geq 100$) [2], it readily yields **3** at pH values above about 3.

The failure to obtain substantial amounts of the N-bonded isomers in the aqueous chemistry is due to irreversible solvolysis of **1** to **5** via **4**. The source of the problem is the existence of this second, thermodynamically stable sink – the substitution inert $[(NH_3)_5CoOH]^{2+}$ (**5**) formed through deprotonation of $[(NH_3)_5CoOH_2]^{3+}$ in basic solution. However by

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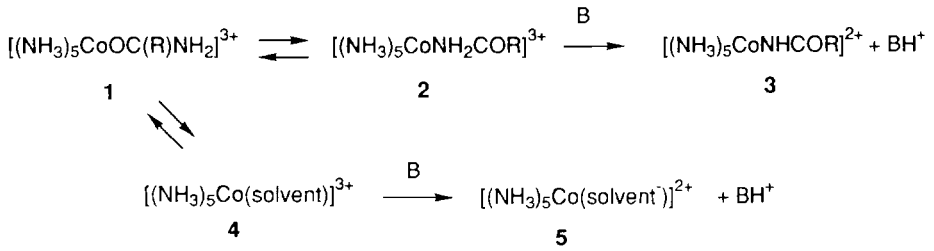
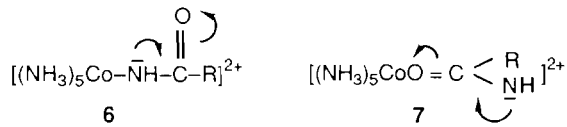


working with dry dipolar aprotic solvents (DMSO, DMF, DMA, $OP(OMe)_3$) and sterically hindered, non-coordinating bases (2,2,6,6-tetramethylpiperidine, 2,6-lutidine, NEt_3), the desired O- to N- rearrangement **1**→**3** proceeds because the irreversible solvolysis path **1**→**5** is eliminated.

The use of non-aqueous solution and non-coordinating base might not appear to be a new synthetic strategy. For example, Jordan *et al.* [9, 10] have prepared N-bonded sulfamide and sulfonamides by reaction of the triflato complex in dry acetone or sulfolane containing 2,6-lutidine to effect the deprotonation. However these methods fail for less acidic ligands such as urea or urethane because basic acetone and sulfolane solutions are extremely moisture sensitive and decomposition sets in before any significant amounts of the desired N-bonded species are obtained (even when molecular sieves [9, 10] are used). Thus the virtue of using an aprotic yet coordinating solvent such as Me_2SO is that the resultant basic solution containing $[(NH_3)_5CoOSMe_2]^{3+}$ is substantially less prone to the irreversible generation of $[(NH_3)_5CoOH]^{2+}$ (with subsequent decomposition) than basic solutions of $[(NH_3)_5Co(acetone)]^{3+}$, $[(NH_3)_5Co(sulfolane)]^{3+}$ or $[(NH_3)_5Co(triflate)]^{2+}$, each of which is an extremely labile complex.

Our strategy works equally well when commencing with solutions of **1** or **4** with a five- to ten-fold excess of ambidentate ligand, and a one- to three-fold excess of base under forcing conditions ($\geq$1 h, 60°C, NEt_3 or tetramethylpiperidine; $\geq$5 h, 60 °C, lutidine). (The starting Me_2SO complex could presumably be generated *in situ* in Me_2SO from the readily available $[(NH_3)_5CoOH_2](ClO_4)_3$ (by heating in the presence of a dehydrating agent such as molecular sieves), but we did not attempt this.) Yields of isolated **3** approach 80% under anhydrous conditions; the major side-product is $[Co(NH_3)_6]^{3+}$ which probably arises following hydrolysis of the ambidentate molecule by adventitious moisture (whence the poisoning OH^- is generated). Small amounts (<5%) of lilac $[(NH_3)_4Co(NHCOR)_2]^+$ were also identified in product mixtures and it is speculated that these arise via Co(II)-catalyzed amide substitution of an ammonia ligand (it has been verified that traces of Co(II) are produced under the conditions). The synthesis is more rapid and requires less basic and lower temperature conditions for the more acidic ambidentate molecules (e.g. sulfinamide, sulfonamides, sulfamate > carbamates > ureas > amides, imides).

Table 1 summarizes the visible absorption and ^1H NMR spectral data for some representative complexes synthesized by this new method. In many cases the *cis*- (12H) and *trans*- (3H) NH_3 proton resonances are coincident or only slightly separated. The more striking feature of the ^1H NMR spectra is the high field position of the CoNH proton of the ambidentate ligand and this appears to be diagnostic of these 2+ ions. On protonation, irrespective of the site of ligand protonation, this signal shifts downfield to 5–7 ppm consistent with loss of some electron density from the bound nitrogen. Also on protonation, the orange–red 2+ ions turn to their yellow 3+ conjugate acids, and concomitantly the lower energy visible absorption maximum shifts 10–20 nm to shorter energy indicative of an increased ligand field [8]. All of these complexes protonate below pH 4, and their conjugate acids are much more acidic than the respective O-bonded linkage isomer, presumably due to much greater resonance stabilization in **6** than in **7** in comparison with their respective protonated forms.



It is appropriate to note that $[(NH_3)_5CoNH_2COR]^{3+}$ is substantially more acidic than $[(NH_3)_5CoOC(NH_2)R]^{3+}$ not *simply* because the acidic centre is closer to the polarizing metal ion. We have argued [8], for example, that $[(NH_3)_5CoNHC(OH)NH_2]^{3+}$ is more acidic than $[(NH_3)_5CoNH_2CONH_2]^{3+}$ and here the proximity of the acidic centres to the metal ion is reversed.

Several mechanisms could account for the synthesis, for example: (i) direct displacement of the neutral solvent molecule from **4** by the anionic ambidentate molecule; (ii) direct intramolecular O- to N-rearrangement **1**→**3** without intervention of **2**, and proceeding via $[(NH_3)_5Co–OC(R)NH^-]^{2+}$ or its

TABLE 1. Spectral properties of $[(NH_3)_5CoNHR](ClO_4)_2$ complexes

R	Electronic spectrum	^{1}H NMR spectrum, δ (ppm)[b]			
	λ_{max} (nm) ($\epsilon(M^{-1}\ cm^{-1})$)[a]	*cis*-NH_3	*trans*-NH_3	CoNH	Other
$-C(=O)H$	484(68.0), 349(81.7)	3.20	3.20	3.83	8.05(CH)[c]
$-C(=O)CH_3$	484(73.9), 344(87.3)	3.22	3.22	3.73	1.97(CH_3)
$-C(=O)CH_2F$	486(69.9), 348(79.2)	3.35	3.22	3.78	4.66(CH_2)[d]
$-C(=O)CF_3$	480(68.4), 345(73.4)	3.30	3.22	5.22	
$-C(=O)C_6H_5$	486(88.9), 347(118.2)	3.35	3.20	4.60	7.37 7.65(C_6H_5)[e]
$-C(=O)NH_2$	498(90.4), 350(125)	3.22	3.07	1.62	5.00(NH_2)
$-C(=O)NHC_6H_5$	500(121.0)	3.38	3.20	2.02	8.25(CNHC) 7.28 7.15(C_6H_5)[e]
$-C(=O)OC_2H_5$	495(80.8), 353(105.1)	3.27	3.27	2.37	3.93(CH_2)[f] 1.13(CH_3)[g]
$-S(=O)CH_3$	508(103.3), 285(2193)	3.17	3.73	1.67	2.57(CH_3)
$-S(=O)_2NH_2$		3.30	3.03	1.73	5.77(NH_2)
$-S(=O)_2CH_3$		3.33	3.07	1.53	2.83(CH_3)
$-S(=O)_2C_6H_5$		3.43	3.10	2.15	7.60 7.75(C_6H_5)[e]
$-SO_3^-$		3.23	3.23	1.42[h]	

[a]0.1 M Tris. [b]Downfield of TMS in d_6-Me_2SO. [c]$J_{HH}=4$ Hz, doublet. [d]$J_{HF}=48$ Hz, doublet. [e]Locations of two most intense peaks of multiplet. [f]$J_{HH}=7$ Hz, quartet. [g]$J_{HH}=7$ Hz, triplet. [h]For the complex crystallized from Me_2SO using tetramethylpiperidine and ethanol (and P_2O_5/vacuum dried). In aqueous base, the complex crystallizes preferentially as a 1:1 'double-salt' containing equal numbers of $[(NH_3)_5Co\text{–}NH_2SO_3]^{2+}$ and $[(NH_3)_5Co\text{–}NHSO_3]^+$; in the ^{1}H NMR spectrum, the NH and NH_2 protons are exchange averaged (and with any H_2O present), as are the corresponding *cis*- and *trans*-NH_3 signals for the protonated and deprotonated forms.

tautomer $[(NH_3)_4(NH_2^-)Co\text{–}OC(R)NH_2]^{2+}$; or (iii) O- to N-isomerization (**1** → **2**) driven by the selective deprotonation step **2** → **3**. We are inclined to dismiss (i) due to the low acidity (in H_2O) of many of the ambidentate molecules, even though the relevance of these acidities in dipolar aprotic solvents is uncertain. The weak base lutidine can effect the synthesis, yet the concentration of the anionic ambidentate molecule would be extremely low. Consistent with our observations on the reactivity of the O-isomers in water leading to deprotonated N-bonded isomers [8] (and here there is *no* possibility that the ambidentate molecule leaves the metal and reattaches as an anionic N-bonding ligand), we support the notion that direct linkage isomerization (O → N) via paths (ii) or (iii) is responsible for the formation of **3**.

This new route to the inert complexes of the type $[(NH_3)_5CoNHCOR]^{2+}$ avails us the opportunity to examine a wide range of linkage isomeric complexes, compare modes of ligand reactivity, measure isomer equilibria and study the factors controlling the position of equilibrium. These studies are continuing. In other work [2] we show that the O- ⇄ N-bonded isomer equilibrium in these complexes is not only sensitive to pH, because of the very different pK'_as for the two isomers, but also to the substituent R. The tautomeric equilibrium position for the site of protonation in these molecules (e.g. at N or O in **3**) is also sensitive to the substituent R and affects the **1** ⇄ **2** equilibrium position [11]. Finally, there is a real prospect that less acidic, biologically relevant metal ions may be able to switch coordination sites in ambidentate molecules *in vivo*, thus activating or deactivating bound ligand to further reaction (e.g. hydrolysis, oxidation), and this possibility should be considered in future studies.

Experimental

^{1}H NMR spectra were recorded for Me_2SO-d_6 solutions containing TMS using a Varian T60 continuous wave spectrometer. UV and visible spectra were measured with the use of Cary 118 and 210 spectrophotometers. All reagents were analytical grade.

Method 1

The synthetic procedure given below for urea is representative.

$[Co(NH_3)_5(O_3SCF_3)](CF_3SO_3)_2$ (8.9 g, 0.017 mol) [1] mixed with urea (3.5 g, 0.06 mol), 2,2,6,6-tetra-

methylpiperidine (5.5 g, 0.039 mol) and dimethyl sulfoxide (30 ml) was heated at 70 °C for 2 h. The mixture was cooled to 20 °C before adding an equal volume of butan-2-ol and diethylether (1 l). A pink residue precipitated and was crystallized by first dissolving it in a minimum volume of cold water (pH 9.5, Tris), addition of a one-fifth volume of saturated aqueous $NaClO_4$ and removal (filtration) of some precipitated yellow $[Co(NH_3)_6](ClO_4)_3$ just after crystallization began. The bulk of the product then precipitated as large crimson–pink plates of pure $[(NH_3)_5CoNHCONH_2]ClO_4 \cdot CF_3SO_3 \cdot H_2O$. Yield 70%.

In general, to ensure purity, reaction mixtures were routinely sorbed on SP-Sephadex C-25 cation exchange resin and eluted with 0.3 M $NaClO_4$ (pH 9.5, Tris). Under these conditions the elution order was $[(NH_3)_4Co(NHCONH_2)_2]^+ > [(NH_3)_5CoNHCONH_2]^{2+} > [(NH_3)_5CoOH]^{2+} >$ unknown crimson–brown 3+ ion $> [Co(NH_3)_6]^{3+}$. The salt $[(NH_3)_5CoNHCONH_2](ClO_4)_2 \cdot H_2O$ was isolated following removal of solvent by vacuum evaporation, and recrystallized from warm aqueous Tris by addition of a saturated aqueous solution of $NaClO_4$. The crimson–pink crystals were washed with absolute ethanol, ether, and air-dried. Yield 61%. ^1H NMR spectra indicated 1.0 mol of lattice water which could be removed by storage over P_2O_5 *in vacuo*. *Anal.* Calc. for $[(NH_3)_5CoNHCONH_2](ClO_4)_2$: C, 8.37; H, 5.12; N, 22.79. Found: C, 8.20; H, 5.37; N, 22.42%.

The non-coordinating 2,2,6,6-tetramethylpiperidine was successfully replaced by NEt_3 (80 °C, 45 min) or 2,6-lutidine (60–80 °C, 6 h) without noticeable reduction in yield although more $[(NH_3)_4Co(NHCONH_2)_2]^+$ is formed in the latter case at the expense of the other side-products.

Method 2

The procedure given below for ethylcarbamate (urethane) is representative.

$[(NH_3)_5CoOS(CH_3)_2](ClO_4)_3 \cdot H_2O$ (10 g, 0.0185 mol) [12] and $NH_2CO_2C_2H_5$ (15.5 g, 0.174 mol) were reacted in Me_2SO (25 ml) with NEt_3 (0.08 mol) for 4 h at 70–80 °C. Butan-2-ol (30 ml) and diethylether (1 l) were successively added to the cooled reaction mixture causing quantitative precipitation of cobalt. The products were dissolved in water and chromatographed as above except that the initial eluant was phosphate buffered NaCl (pH 7). $[(NH_3)_4Co(NHCO_2C_2H_5)_2]^+$ eluted ahead of $[Co(NH_3)_5NHCO_2C_2H_5]^{2+}$, which was removed with 0.5 M $NaClO_4$ and isolated following vacuum evaporation, leaving $[Co(NH_3)_6]^{3+}$ on the column. ^1H NMR spectroscopy indicated that the complex was a monohydrate; the lattice water was removed by storage *in vacuo* over P_2O_5. Yield 5.6 g (70%). *Anal.* Calc: C, 8.35; H, 4.87; N, 19.49; Cl, 16.47. Found: C, 8.28; H, 4.92; N, 19.23; Cl, 16.31%.

$[(NH_3CoNHSOCH_3](ClO_4)_2$

This was prepared by method 2 (tetramethylpiperidine, 65 °C, 2 h) in 62% yield. *Anal.* Calc.: C, 2.85; H, 4.51; N, 19.95; Cl, 16.86. Found: C, 2.81; H, 4.62; N, 19.68; Cl, 16.71%. After chromatography on Sephadex, the product was freed of a $[Co(NH_3)_5OH]^{2+}$ contaminant by chromatography on Biorex (Na^+ form, 200–400 mesh) resin using 1 M $NaClO_4$ (pH 9.5, Tris) as eluent and isolation as the monohydrate. Reaction with NEt_3 at 65 °C for 30 min also produced $[(NH_3)_5CoNHSOCH_3](ClO_4)_2$ (yield 65%) together with 10% $[Co(NH_3)_6]^{3+}$, 10% $[(NH_3)_5CoOS(NH_2)CH_3]^{3+}$, some $[(NH_3)_5CoOSOCH_3]^{2+}$ and $[(NH_3)_5CoSO_2CH_3]^{2+}$, traces of 1+ ions and an unidentified yellow–brown 2+ ion suspected to be $[(NH_3)_5CoS(:O)(NH)CH_3]^{2+}$.

$[(NH_3)_5CoNHSO_2R](ClO_4)_2$ ($R = NH_2$, CH_3, C_6H_5)

By method 2 using a ten-fold excess of sulfonamide, three-fold excess of the base NEt_3 and heating at 65 °C for 2 h, the yield was 75%. *Anal.* ($R = C_6H_5$). *Calc.*: C, 14.43; H, 4.21; N, 16.84. Found: C, 14.61; H, 4.53; N, 16.68%. Elution order (Sephadex): $[(NH_3)_4Co(NHSO_2R)_2]^+$ (<5%), $[(NH_3)_5Co(NHSO_2R)]^{2+}$, $[(NH_3)_5CoOH]^{2+}$, $[(NH_3)_5CoOS(CH_3)_2]^{3+}$, $[Co(NH_3)_6]^{3+}$; using 0.25 M $NaClO_4$ (pH 9.5, Tris). Using 2,6-lutidine, and a 5 h reaction time at 75 °C, the yield of $[NH_3)_5Co(NHSO_2R)]^{2+}$ was *c.* 40%, with ~10% $[(NH_3)_4Co(NHSO_2R)_2]^+$.

$[(NH_3)_5CoNHSO_3]ClO_4$ and $[(NH_3)_5CoNH_2SO_3](ClO_4)_2$

By method 2 using lutidine (<5 equiv.), sulfamic acid (20 equiv.), 80 °C, and a 4 h reaction time, a yield of 53% was realized. The total product mixture from Sephadex showed 47% $[(NH_3)_5CoOSO_3]^+$ and 53% $[(NH_3)_5CoNH_2SO_3]^{2+}$ and eluted in that order with 0.5 M $NaClO_4$ (unbuffered). Crystals of $[(NH_3)_5CoNH_2SO_3](ClO_4)_2$ were obtained by adding $HClO_4$ (70%) to the eluate. ^1H NMR (Me_2SO-d_6): δ 6.87 ppm (br, 2H, NH_2); δ 3.80 ppm (br, 12H, *cis*-NH_3), δ 3.50 ppm (br. 2H, *trans*-NH_3). A deprotonated form was obtained quantitatively from its conjugate acid by adding aqueous Tris/$NaClO_4$, and this proved to be the interesting 'double salt' $[(NH_3)_5CoNHSO_3]ClO_4 \cdot [(NH_3)_5CoNH_2SO_3](ClO_4)_2 \cdot H_2O$. The genuine $[(NH_3)_5CoNHSO_3]ClO_4$ species was obtained by deprotonation of $[(NH_3)_5CoNH_2SO_3](ClO_4)_2$ using tetramethylpiperidine or NEt_3 in Me_2SO, and crystallized using ethanol. It was dried *in vacuo* over P_2O_5.

$[(NH_3)_5CoNHCOR](ClO_4)_2$ ($R = H$, CH_3, C_6H_5, CH_2F, CF_3)

Method 1 or 2, 2 h reaction time, yields 60–80%. *Anal.* Calc. (R = H): C, 3.10; H, 4.39; N, 21.71; Cl, 18.35. Found: C, 3.17; H, 4.37; N, 21.49; Cl, 18.15%. Calc. ($R = CH_3$): C, 5.98; H, 4.74; N, 20.94; Cl, 17.71. Found: C, 5.96; H, 4.75; N, 20.62; Cl, 17.68%. Calc. ($R = C_6H_5$): C, 18.14; H, 4.54; N, 18.14; Cl, 15.33. Found: C, 18.21; H, 4.63; N, 18.01; Cl, 15.42%. The product eluted just ahead of $[Co(NH_3)_5OH]^{2+}$, well ahead of $[Co(NH_3)_6]^{3+}$ but together with some $[(NH_3)_5CoOCOR]^{2+}$ using 0.5 M NaCl (pH 9.5, Tris) and Sephadex resin. Rechromatography on Sephadex using acidified (CH_3CO_2H) $NaClO_4$ separated $[(NH_3)_5CoOCOR]^{2+}$ from the partially protonated $[(NH_3)_5CoNHCOR]^{2+/3+}$; the pH was raised again with Tris before reduction in volume by rota-evaporation (< 40 °C) and crystallization. Recrystallization of the latter salt from aqueous $NaClO_4$/Tris gave pure product. The perchlorate complexes of fluoroacetamide and especially trifluoroacetamide were much less water-soluble than the other N-bonded amide complexes.

Note that up to 20% $[(NH_3)_5CoOCOR]^{2+}$ is observed as a side-product due in part to the sensitivity of the O-bonded amide complex (generated in situ) to base-catalyzed hydrolysis of the amide ligand itself.

$[(NH_3)_5CoNHCONHC_6H_5](ClO_4)_2 \cdot H_2O$

By method 2 and using 40 equiv. phenylurea, 20 equiv. tetramethylpiperidine, 80 °C, and a 1 h reaction time, a yield of 52% was obtained for the crystallized material. *Anal.* Cald.: C, 17.39; H, 4.97; N, 20.29; Cl, 14.70. Found: C, 17.28; H, 5.03; N, 20.01; Cl, 14.68%. For the total product, chromatography on Sephadex revealed $[(NH_3)_5CoNHCONHC_6H_5]^{2+}$ (76%), which eluted behind a trace of $[(NH_3)_4Co(NHCONHC_6H_5)_2]^{+}$ and ahead of an unknown crimson–brown 3+ ion, yellow $[(NH_3)_6Co]^{3+}$ and traces of two more highly charged ions.

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