163. Stereospecific Formation of Pentaamine Complexes of Co(III) with Terdentate 2,6-Bis(aminomethyl)pyridine

by **Ursula Tinner and Werner Marty**

Laboratorium für Anorganische Chemie, ETH Zentrum, 8092 Zürich, Switzerland

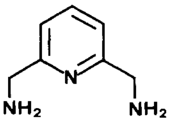
(15.III.77)

Summary

Some pentaamine complexes of Co(III) with 2,6-bis(aminomethyl)pyridine (bamp), a diamine ligand (or two ammonia ligands) and one unidentate ligand have been prepared *(Table 1)*. In all these species, bamp remains coordinated meridionally under a variety of conditions as shown by ^{1}H- and ^{13}C-NMR. spectroscopy and correlations by stereoretentive reaction cycles. The rates of amine proton exchange and of spontaneous aquation, Hg^{2+}-induced aquation and base hydrolysis of some chloropentaamine complexes have been determined. They essentially follow the patterns observed for complexes with purely aliphatic amine ligands; the presence of a pyridine donor in these complexes does not suggest deviations from the mechanistic schemes usually proposed for the solvolytic reactions investigated.

Introduction. For stereochemical work in progress we require a terdentate nitrogen donor which exclusively coordinates in a meridional arrangement at an octahedral Co(III) centre. Such a ligand must have a rigid backbone to prevent it from occupying facial positions. We further require that the chain of atoms containing the nitrogen donor atoms be as closely as possible in one plane and that further atoms of this ligand be at least arranged pairwise in symmetrical positions relative to that plane. For our purpose, the donor atom set should be as closely related as possible to that of a purely aliphatic linear-chain triamine, viz. diethylenetriamine. We therefore did not consider ligands like 2,2′,6′,2″-terpyridine [1] or any of the numerous terdentate *Schiff*'s base-type ligands known.

However, our structural requirements appear not to be met in any of the reasonably accessible purely aliphatic triamines. As a compromise, we have chosen to use 2,6-bis(aminomethyl)pyridine (I,≡bamp) in a study of Co(III) pentaamine complexes.


I

Bamp has been used recently for the similar purpose of selectively producing meridional $Co(bamp)(H_2O)_3^{3+}$ [2] and the data available are consistent with a meridional configuration; there is no indication that bamp behaves grossly differently from an aliphatic triamine.

In this paper, we assign configurations to several species $[Co(bamp)(AA)X]^{n+}$, with (AA) = diamine[1]) or $(NH_3)_2$ and X = unidentate ligand. We also report on the reactivity of some of these complexes in solvolytic reactions.

1. Preparations. The complexes prepared are listed in *Table 1* which also contains spectral data for the range 650–300 nm. The species with chelating diamine ligands were obtained by the well-known route *via* the μ-peroxo-decaamine dicobalt (III) species [3], which were then cleaved with concentrated aqueous HCl- or HBr-solutions to give the chloro-or bromo-pentaamines. From these, complexes with $X = N_3^-$, NO_2^- and NCS^- were prepared *via* the aqua complex. The complexes with NH_3 were not obtained from the peroxo complex. Dioxygen oxidation of a mixture of $Co(NO_3)_2 \cdot 6H_2O$, bamp · 3HCl and ammonium carbonate in aqueous ammonia gave a red species, presumably $[(bamp)(NH_3)_2CoOCO_2]^+$. From this, halogenopentaamines formed on treatment with hydrochloric or hydrobromic acid. Treatment of $[Co(bamp)(NH_3)_2X]^{2+}$ ($X = Cl^-$, Br^-) with HNO_2-solution gave $[Co(bamp)(NH_3)_2NO_2]^{2+}$. $[Co(bamp)_2]^{3+}$ was a major product in most of the preparations.

Table 1. *Pentaamine Complexes with meridional bamp and their UV./VIS. Light Absorption Spectra* (VIS.)

No.	Compound[a])	VIS. spectral parameters ε_λ $[M^{-1}cm^{-1}]$ at 25°, in 0,1M $HClO_4$			
		$\lambda_{max}(\varepsilon)$	$\lambda_{min}(\varepsilon)$	$\lambda_{max}(\varepsilon)$	$\lambda_{min}(\varepsilon)$
1	*cis*-$[Co(bamp)(NH_3)_2Cl]ZnCl_4$	470(112)	405(36.6)	358(108)	332(81.8)
2	*cis*-$[Co(bamp)(NH_3)_2Br]Br_2$	470(97.8)[c])	418(51.7)	–	–
3	*cis*-$[Co(bamp)(NH_3)_2OH_2]^{3+}$[b])	458(113)	394(27.6)	345(97)	320(73.6)
4	*cis*-$[Co(bamp)(NH_3)_2NO_2]ZnCl_4$	450(168)	392(49.0)	–	–
5	$[Co(bamp)(en)Cl]ZnCl_4$	479(116)	407(37.3)	358(114)	333(90)
6	$[Co(bamp)(en)Br](NO_3)_2$	518(144)[d])	416(57.6)	–	–
7	$[Co(bamp)(en)OH_2]^{3+}$[b])	460(131)	393(29.6)	344(100)	324(83.6)
8	$[Co(bamp)(en)NO_2]ZnCl_4$	447(195)	391(68.2)	–	–
9	$[Co(bamp)(en)N_3]ZnCl_4$	482(277)	422(112)	–	–
10	$[Co(bamp)(en)NCS](NCS)_2$	472(242)	417(109)	-	–
11	$[Co(bamp)(tmd)Cl]ZnCl_4$	477(105)	410(29)	362(103)	337(75)
12	$[Co(bamp)(danp)Cl]ZnCl_4$	478(111)	411(29.5)	361(108)	338(85)
13	$[Co(bamp)(ddb)Cl]ZnCl_4$	495(161)	420(53)	362(232)	340(189)
14	$[Co(bamp)_2]Br_3 \cdot 0.5\ H_2O$	452(261)	386(47.5)	342(155)	322(147)

[a]) Ligand abbreviations: bamp: 2,6-bis(aminomethyl)pyridine; en: 1,2-diaminoethane; tmd: 1,3-diaminopropane; danp: 1,3-diamino-2,2-dimethylpropane; ddb: 2,3-diamino-2,3-dimethyl-butane.

[b]) In aqueous solution only, prepared by Hg^{2+}-induced aquation.

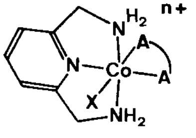
[c]) Shoulder at 525 nm.

[d]) Shoulder at 470 nm.

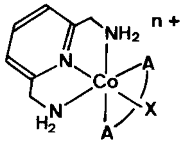
---

[1]) For simplicity, we call 'diamine' any chelating diamine.

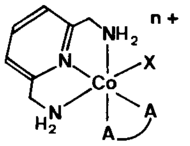
2. Assignment of configuration. For complexes $[Co(bamp)(AA)X]^{n+}$, three diastereoisomeric configurations can be drawn:



II
meridional

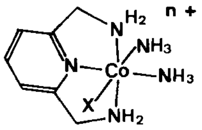


III
meso-facial

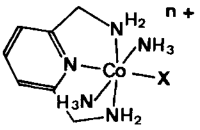


IV
(±)-facial

For AA = $(NH_3)_2$, two diastereoisomers with meridional bamp must be considered:



V
cis-meridional



VI
trans-meridional

Neglecting chelate ring conformations, II, III and V each contains a single plane of symmetry and VI contains two such planes. In II and V, the $-CH_2NH_2$ groups, the a,a' resp. β,β' pyridine carbon atoms of bamp are chemically equivalent but the $-CR_2NH_2$ groups of the diamine ligand (R = H, CH_3) or the NH_3 are not. In III and VI, bamp shows the same equivalences as above but also the $-CR_2NH_2$ of the diamines or the NH_3 are equivalent. In IV, no such equivalence exists. ^1H- and ^{13}C-NMR. data were collected to detect actual chemical equivalence as outlined above.

Assignment on the basis of the ^1H-NMR. spectra (Table 2) *and proton exchange phenomena.* The three pyridine protons of bamp appear at constant chemical shifts between $\delta = 7.5$–8.4 ppm (rel. to TSP, in DMSO-d_6) for all species investigated. At $\delta = 5$–6 ppm, **1**, **4** and **5** show two broad signals in DMSO-d_6 but only one at

Table 2. *^1H-NMR. data for $[Co(bamp)(AA)X]^{n+}$; δ [ppm], relative to TSP*

No	Co bamp $(AA)X^{2+}$	bamp-NH_2		AA–CH_2	AA–NH_2	
		DMSO-d_6	D_2O/D_2SO_4		DMSO-d_6	D_2O/D_2SO_4
1	*cis*-Co bamp $(NH_3)_2Cl^{2+}$	5.4/5.8	5.5	-	4.6	3.2/4.1
4	*cis*-Co bamp $(NH_3)_2NO_2^{2+}$	5.0/5.8	-	-	3.6/4.0	-
5	$[Co\ bamp\ en\ Cl]^{2+}$	5.6/6.1	5.1	2.9	~5	4.6[d])/5.9
11	$[Co\ bamp\ tmd\ Cl]^{2+}$	~5.5	5.4[c])	1.9/2.3/2.7	~5.4	4.2/5.1
12	$[Co\ bamp\ danp\ Cl]^{2+}$	5.6	5.5	2.0/2.4[a])	4.8/5.1	4.3/~5[c])
13	$[Co\ bamp\ ddb\ Cl]^{2+}$	5.5/6.25	-	-[b])	5.7/4.5	-
14	$[Co\ bamp_2]^{3+}$	6.0	5.3	-	-	-

[a]) CH_3-danp 1.0; [b]) CH_3-ddb 1.2/1.3.[c]) Coincidence with HOD. [d]) Coincidence with bamp-CH_2.

intermediate position in D_2O/D_2SO_4. The separation between the two signals in DMSO-d_6 is largest in **4**, but **11** and **12** show only one signal. Exchange of these protons is rapid in neutral or alkaline D_2O. They can be assigned to the $-NH_2$ groups of bamp. In all species, the methylene protons of bamp appear as one broad signal at $\delta = 4.2$-4.7 ppm in DMSO-d_6. This signal shows incipient splitting under certain conditions of recording. The amine protons of the ligands (AA) mostly appear in two distinctly separated signals over a wider range of δ. Their assignment as amine protons is again supported by rapid exchange in neutral D_2O. Protons bound to carbon atoms in these ligands appear separately at high field. The methyl groups in **12** give a single, sharp line in D_2SO_4/D_2O. In **13**, two methyl resonances are observed which are each assigned to two methyl groups attached to different carbon atoms of the chelate ring.

The non-equivalence of the amine protons of bamp in DMSO-d_6 was examined further in **1** by double resonance experiments. Irradiating at the bamp methylene resonance frequency produces the same change in both of the bamp amine proton signals *(Fig. 1)*. Conversely, irradiating either of the bamp amine proton signals sharpens the methylene signal. The amine functions are therefore chemically equivalent but they each contain two non-equivalent protons which may be termed

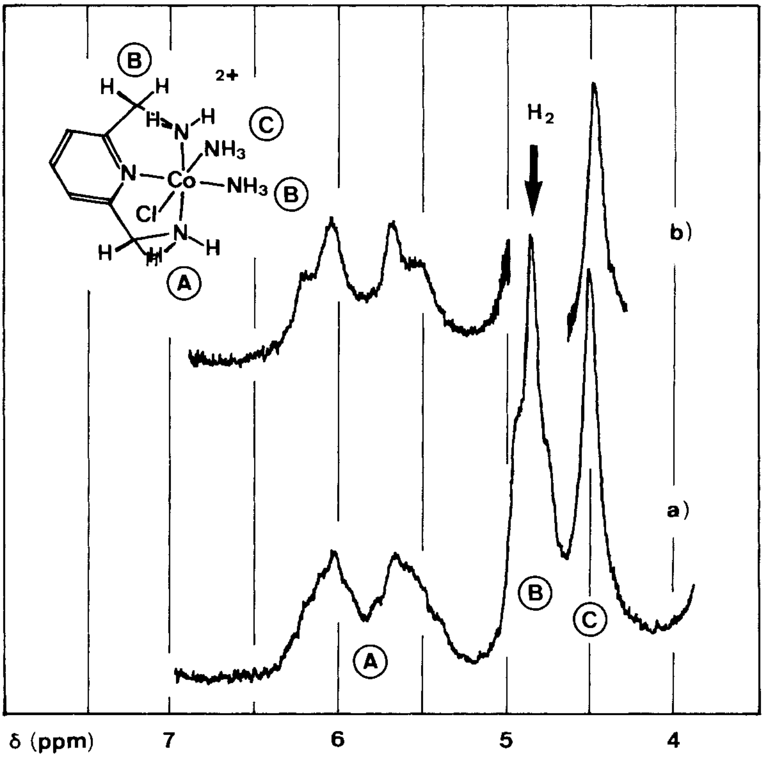


Fig. 1. *Portion of the ^1H-NMR. spectrum of* **1**, relative to internal TSP standard. a) Undecoupled spectrum; b) after irradiating frequency H_2 (arrow).

exo and *endo* with respect to the Cl-atom *(Fig. 1)*. Such non-equivalence has been observed, for example, in DMSO-d_6 but not in acidic D_2O solutions of $Co(en)_3{}^{3+}$ This effect has been attributed to differences in solvation [4].

Assignments for the amine proton signals of the diamine ligands in some of the chloro complexes were made on the basis of double resonance experiments and of H/D-exchange rates for these protons. As the signals of the two diamine $-NH_2$ *cis* or *trans* to the Cl-atom are equal in number, our assignments are based on known regularities in the chemical shifts and relative H/D-exchange rates. In **5**, **11** and **12**, decoupling experiments show that the diamine-NH_2 resonance at lower field is coupled to the methylene resonance at lower field and *vice versa*.

Proton exchange rates in the chloro complexes **1**, **5**, **11** and **12** were examined cursorily. They were measured by ^{1}H-NMR. in acetate, formate and $H_2PO_4{}^-$/$HPO_4{}^{2-}$ buffers in D_2O at 38 °C in the pD range 4.06-6.22. At these acidities one diamine-NH_2 signal was close to the HOD peak in all cases, and in some instances no exchange rate for this is obtained. The numerical results are listed in *Table 3*. In all cases, the diamine-NH_2 protons at highest field were found to exchange fastest. The bamp-NH_2 protons exchange faster or slower relative to the slower of the two diamine-NH_2 groups. There is now much evidence that primary amine protons *trans* to the Cl-atom exchange fastest in Co(III) pentaamines [5]. These *trans*-protons are generally found at higher field than the *cis* protons [6] and this is also found here. Therefore, the ^{1}H-NMR. spectra are consistent with the assumption that in all these complexes, bamp is in a meridional arrangement. The most obvious cases are **1** and **4**, where two, well separated NH_3 signals appear. In other cases, decoupling experiments or integrating the peak areas assisted the assignment of the signals.

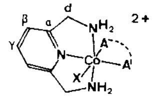
Table 3. *Proton exchange rates for* $[Co(bamp)(AA)Cl]^{2+}$

AA		*trans*-NH_2R[a])		*cis*-NH_2R[a])			bamp-NH_2	
		k_{obs} $[s^{-1}]$	k_{HD} $[M^{-1}s^{-1}]$[b])	k_{obs} $[s^{-1}]$	k_{HD} $[M^{-1}s^{-1}]$[b])		k_{obs} $[s^{-1}]$	k_{HD} $[M^{-1}s^{-1}]$[b])
$(NH_3)_2$	**(1)**	2.1×10^{-3}	1.8×10^{8}[c])	1.5×10^{-4}[d])	9.3×10^{4}		4.2×10^{-4}[e]) 1.6×10^{-4}[f])	1×10^{6}
en	**(5)**	$(\geqslant 3 \times 10^{7})$[g])		1.7×10^{-4}[d])	1.0×10^{5}		4.7×10^{-4}[f])	2.7×10^{6}
tmd	**(11)**	1.6×10^{-3}[f])	9.2×10^{6}		3×10^{-4}[f]) 3×10^{-5}[f])	1.7×10^{6} 1.7×10^{5}		
damp	**(12)**			4.4×10^{-5}[f])	2.5×10^{5}		2.8×10^{-4}[f])	1.6×10^{6}

[a]) R = $-H$, $-CH_2-$, *cis* and *trans* relative to Cl^-. [b]) Assuming the general validity of rate law: rate = $k_{HD}[OD^-] \cdot$ [complex] generally found in pentaamines of Co(III) [10] [15]. [c]) Formate buffer, pD = 4.06, $\mu = 1.0$. [d]) $H_2PO_4^-$ buffer, pD = 6.22, $\mu = 1.0$. [e]) Acetate buffer, pD = 5.46, $\mu = 4.0$. [f]) Acetate buffer, pD = 5.24, $\mu = 4.0$. [g]) Verified from change in coupling pattern in the signal of adjacent CH_2.

Assignment on the basis of the ^{13}*C-NMR. Spectra.* The above structural assignments are also unambiguously supported by the ^{13}C-NMR. data *(Table 4)*. The examples are chosen such that appreciable bond anisotropy differences are expected

Table 4. *^{13}C-NMR. Chemical Shifts for [Co(bamp)(AA)X]$^{n+}$ Complexes*[a])

Complex		Chemical shifts (ppm, rel to TMS, ±0.1 ppm)[b])				
		Carbon atoms of ligand (AA)	Carbon atoms of bamp[c]) γ	β	α	d
1	AA=$(NH_3)_2$, X=Cl^-	-	139.8	120.3	162.9	51.8
5	AA=(en), X=Cl^-	44.5, 45.1	140.0	120.3	162.9	51.9
8	AA=(en), X=NO_2^-	43.8, 44.4	140.2	120.3	162.8	52.0
9	AA=(en), X=N_3^-	43.7, 44.9	140.0	120.5	162.7	51.9
11	AA=(tmd), X=Cl^-	24.8, 37.9, 39.1	139.9	120.4	162.9	51.8
13	AA=(ddb), X=Cl^-	24.5[d]), 63.1, 64.6	140.4	120.3	163.0	52.6
	AA=$(NH_3)_2$, X=OH^-[e])	-	139.7	120.2	163.1	51.8

[a]) As $ZnCl_4^{2-}$ salts, saturated solutions in $(CD_3)_2SO$. [b]) Measured on a *Bruker* HX90 instrument, FT mode, 10 mm tubes. [c]) Resonances of γ, β and d but not of α split under off-resonance conditions. [d]) Methyl carbon resonance. [e]) Mixture of products obtained from base hydrolysis of **1** for $10 \times t_{1/2}$ in water; chloride counterion.

from the variation of the diamine and X ligands. Accidental coincidence of signals in all of these compounds is therefore unlikely. In all complexes investigated, the pyridine α, β and γ and the methylene carbon atoms each give rise to only one signal occurring at very similar frequencies. Two clearly separated signals are found for the carbon nuclei adjacent to the diamine-NH_2 groups. We therefore assign the meridional configuration II to **5**, **8**, **9**, **11** and **13**. The *cis*-meridional configuration V is assigned to **1** based on the ^{13}C- and ^{1}H-NMR. spectra. The mixture of base hydrolysis products of **1** gave nearly the same ^{13}C-NMR. spectrum as the other compounds, suggesting the presence of meridionally coordinated bamp in the bulk of the species present.

Assignment by chemical correlations. From the NMR. spectra, $\lesssim 5\%$ of other diastereoisomers may go undetected. Numerous ion-exchange procedures on Dowex 50 WX-2 and Sephadex SP-C25 ion exchangers, using different electrolyte solutions as the eluents gave no separation of isomeric pentaamines both in crude and analytically pure samples of **1**, **2**, **4–6**, **8**, **9**, and **11**. In another experiment, the entire reaction mixture containing **5** was separated by ion exchange chromatography. The sole pentaamine species present was (mer-)[Co(bamp)(en)Cl]$^{2+}$ from its VIS. spectrum and the spectral change on Hg^{2+}-induced aquation. The further products were hexaamine complexes.

In order to correlate the configurations of some of the species not investigated by NMR. with those of known configuration, and also to check further the isomeric purity of the compounds, some stereochemical reaction cycles were established *(Fig. 2)*. The reactions carried out, viz. Hg^{2+}-induced aquation of halogenopentaamines [7] [8], the nitrosation of an azidopentaamine [7] [8] and the chlorination of a bromopentaamine [9] are known to proceed with full retention of configuration at Co(III). In these reactions, the spectra of the product agreed, within the experimental error (±1%), for the different sources. This result is compatible with the occurrence of one diastereoisomer of each species in the preparative routes used.

On the other hand, base hydrolysis of pentaamines frequently occurs with rearrangement of configuration [10]. The chloro complexes **1** and **5** were base hydrolysed to 30% and 50% of reaction, respectively. The mixtures were acidified with $HClO_4$ and separated by ion exchange chromatography. In the ethylenediamine complex, the resulting aqua ion was spectrally identical with that produced by the other induced aquations. The spectra of **1** were different; some *cis→trans* rearrangement of NH_3 or loss of NH_3 as a consequence of base hydrolysis may

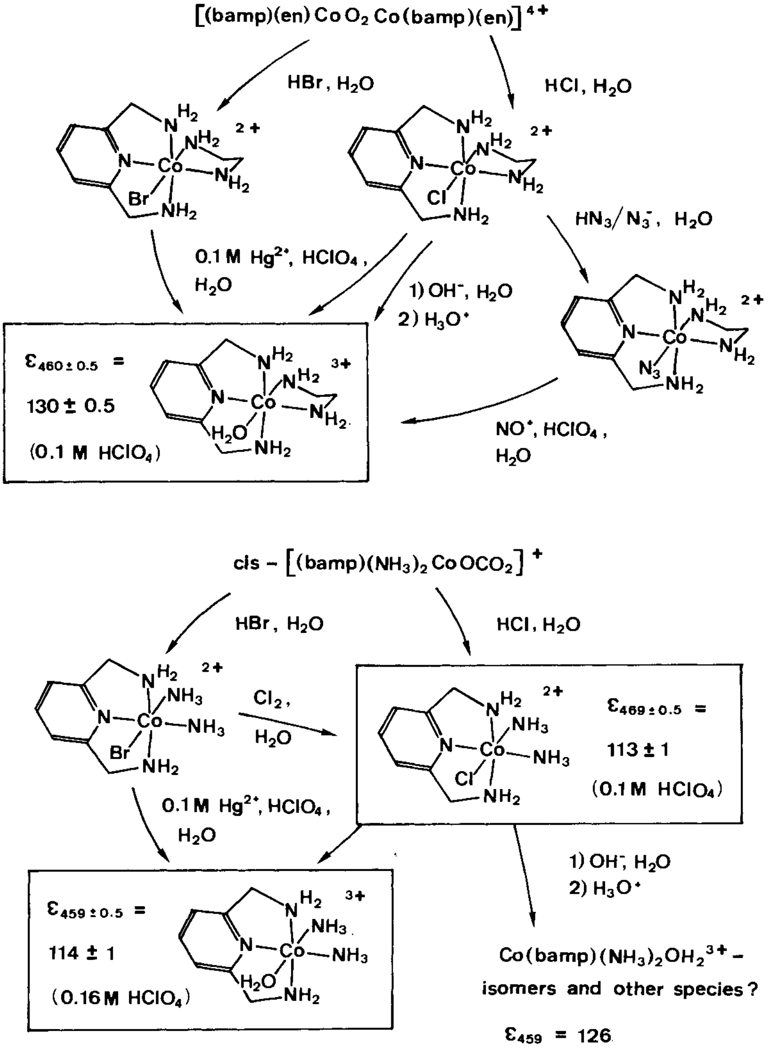


Fig. 2. *Reaction cycles on [Co(bamp)(en)X]$^{2+}$ and on* cis*[Co(bamp)(NH$_3$)$_2$X]$^{2+}$.* The molar extinction coefficients ε are indicated for the long-wavelength absorption maximum. Minima and maxima at higher energy agree qualitatively but in some cases, the ε values are affected by the spectral effect of the reagents.

explain this latter result. However, in both cases the recovered chloro complex was spectrally identical with the starting material *(Fig. 2)*.

3. Solvolytic reactivity. For all the chloro complexes except for **12**, spontaneous aquation, Hg^{2+}-induced aquation and base hydrolysis were studied in water by spectrophotometry *(Table 5)*. Spontaneous aquation was followed for 0.5 to 2 half-lives and a first-order dependence on $[Co(bamp)(AA)Cl^{2+}]$ was observed. The rate constants, k_{H_2O}, were determined by the *Guggenheim* method [31]. Possible influence of Cl^- anation on the rate was neglected as $[Cl^-]$ was very low. The Hg^{2+}-induced aquation was followed in solutions of mercuric perchlorate containing excess perchloric acid to keep $[HgOH^+]+[Hg(OH)_2]$ small [11]. $[Hg^{2+}]$ was in at least 40-fold excess over $[Co]_t$ and first-order kinetics were observed for $\geqslant 4$ half-lives. Isosbestic points in the region 650 ÷ 300 nm were observed for at least 90% of the reaction, for **1** at 484, 403, 355 and 330 nm, for **5** at 475, 400, 354 and 324 nm, for **11** at 482, 405, 360 and 330 nm and for **13** at 482, 412 and 367 nm. For every complex, the

Table 5. *Kinetic data for spontaneous aquation, Hg^{2+}-induced aquation and base hydrolysis of $[Co(bamp)(AA)Cl]^{2+}$ ions at 25.0 ± 0.1 °C*

Reactant	Spontaneous aquation[a])		Hg^{2+}-Induced hydrolysis[b])				Base hydrolysis[c])			
(AA)=	λ[b]) [nm]	$10^7 k_{H_2O}$[d]) [s^{-1}]	λ [nm]	[Hg^{2+}][e]) [M]	$10^2 k_{obs}$[d]) [s^{-1}]	$10^2 k_{Hg^{2+}}$ [$M^{-1}s^{-1}$]	λ [nm]	pH[f])	$10^2 k_{obs}$[d]) [s^{-1}]	$10^{-3} k_{OH}$ [$M^{-1}s^{-1}$]
tmd	305	170(2)	295	0.0625	8.57(4)	140	310	8.54[g])	2.37(6)	6.8
				0.125	17.9 (5)	140		8.74[g])	4.05(2)	7.3
								8.72[h])	4.78(5)	9.1
	mean values $1.7 \times 10^{-5} s^{-1}$					$1.40 M^{-1}s^{-1}$				$(7.7 \pm 1.2) \times 10^3 M^{-1}s^{-1}$
en	305	16(2)	295	0.125	1.04(4)	8.3	530	8.98[g])	0.469(6)	0.47
				0.25	1.97(4)	7.9		9.16[g])	0.582(6)	0.41
								9.00[i])	0.515(2)	0.52
								9.16[i])	0.683(2)	0.48
								10.02[h])	5.24 (4)	0.52
	mean values $1.6 \times 10^{-6} s^{-1}$					$(0.081 \pm 0.003) M^{-1}s^{-1}$				$(480 \pm 45) M^{-1}s^{-1}$
cis-$(NH_3)_2$	305	15(1)	295	0.125	1.46(3)	12	310	10.02[h])	10.7(4)	1.0
				0.25	2.60(3)	10		10.16[h])	17.4(3)	1.2
	mean values $1.5 \times 10^{-6} s^{-1}$					$(0.11 \pm 0.010) M^{-1}s^{-1}$				$(1100 \pm 100) M^{-1}s^{-1}$
ddb	260	4.6(1)	260	0.125	0.563(4)	4.5	260	8.47[h])	3.43(3)	12
				0.25	1.10(4)	4.2		8.58[h])	4.42(3)	12
								8.79[h])	6.54(3)	11
	mean values $4.6 \times 10^{-7} s^{-1}$					$(0.0435 \pm 0.002) M^{-1}s^{-1}$				$(11600 \pm 500) M^{-1}s^{-1}$

[a]) $\mu = 1.0$ ($HClO_4$), $[Co]_t = 3 \div 6 \times 10^{-3}$M; (ddb complex $= 2 \times 10^{-5}$M). [b]) $\mu = 1.0$ (ClO_4^-); $[Co]_t = 1.2 \div 1.5 \times 10^{-3}$M. [c]) $\mu = 1.0$ (ClO_4^-); $[Co]_t = 2 \div 5 \times 10^{-3}$M. [d]) Number of runs in parentheses. [e]) $[HClO_4] = 0.05 \div 0.1$M. [f]) $pK_w \equiv 14.00$. [g]) Triethanolamine/$HClO_4$ buffer; [triethanolamine] = 1.00. [h]) Diethanolamine/$HClO_4$ buffer; [diethanolamine] = 1.00. [i]) Triethanolamine/$HClO_4$ buffer; [triethanolamine] = 0.10.

dependence of the rate on $[Hg^{2+}]$ was checked and the usual rate law [12] $-d[complex]/dt = k_{Hg^{2+}}[complex][Hg^{2+}]$ was found to hold under the conditions of the experiments *(Table 5)*. Base hydrolysis was studied in triethanolamine and diethanolamine buffers at various pH values *(Table 5)*. Precipitation of $Zn(OH)_2$ from the $ZnCl_4^{2-}$ anion was never observed in these buffers. Repetitive spectral scans (650÷300 nm) showed isosbestic points for ≥9 half-lives in **5** (492, 394 nm), in **11** (502, 404, 352, 328 nm) and in **13** (488, 403, 353, 330 nm) and first-order kinetics were observed for ≥5 half-lives. For **1**, however, isosbestic points at 490, 375 and 343 nm were observed only for *ca.* 30% of the base hydrolysis reaction. At later stages of the reaction small deviations from these were noted. Plots of $\ln(A_t\text{-}A_\infty)$ at 310 nm against time were linear if a correction (≤5% of optical density change) was made to allow for a secondary reaction with increasing absorbance. This slower reaction was not studied further. In all runs, the concentration of the buffer base was in at least 20-fold excess over $[Co]_t$. The rate data indicate first-order dependence on $[OH^-]$, in accord with the commonly found rate law $-d[complex]/dt = k_{OH}[complex][OH^-]$ [10]. In one case, a 10-fold variation of the buffer base concentration showed the usual absence of general base catalysis [10]. A sample of **11** was hydrolysed for 40% reaction in $D_2O/NaDCO_3/Na_2CO_3$ and quenched in acid. No amine protons were then detected by NMR. Thus, in this complex, all amine protons exchange $\gtrsim 10\times$ faster than base hydrolysis which is consistent with the single proton exchange rate measurements and with the usual behaviour of Co(III) pentaamine complexes.

Discussion. - In all complexes described in this work, the configuration of bamp is meridional regardless of the nature of the ligands (AA) or X. The search for minor amounts of other isomeric species by chromatography, NMR. spectroscopy and by establishing stereoretentive reaction cycles was negative in all cases involving chelating diamines in addition to bamp. Base hydrolysis of *cis*-$[Co(bamp)(NH_3)_2Cl]^{2+}$ gives a mixture of hydroxo complexes but these are not likely to contain species with facially coordinated bamp.

This observed stereospecificity of bamp agrees with the expectation created from the inspection of molecular models. A facial coordination of bamp at Co(III) would cause severe distortions within the pyridine ring of bamp or, alternatively would distort the angle C_γ(pyridine)-N(pyridine)-Co from close to 180° to smaller values. However, even the meridional arrangement of bamp is not free of strain. There are so far no structural data on bamp complexes, but some data are available on somewhat similar chelates, e.g. of 2,6-pyridinedicarboxylate (= dipic) with some transition metals. The N—M—O angles within the chelate rings are 75.7° in $[Fe(dipic)(OH)(OH_2)]_2$ [13] and 76.6° in $[Ag(II)(dipic)(H_2dipic)] \cdot H_2O$ [14].

A meridional arrangement of bamp appears to be favoured, but experimental check for the expected stereospecificity for meridional coordination is required in view of the known examples of the trapping of thermodynamically unstable configurational isomers [15]. In dibenzoylmethanato-*O,O'*-[*N,N'*-*o*-phenylene bis(salicylideneiminato)] cobalt (III), prepared by air oxidation of Co(II) in methanol in the presence of the ligands, the quadridentate *Schiff*'s base ligand adopts the strained *cis*-configuration [16] but here, two six-membered chelate rings are fused to one five-membered chelate ring. With the purely aliphatic ligand 2,2′-bis(aminoethyl)amine(=dien), pentaamines $[Co(dien)(en)Cl]^{2+}$ are obtained with dien facially or meridionally coordinated [17].

As stated in the introduction, we require that, neglecting all other atoms of the complex, the coordinated bamp molecule must contain a plane of symmetry on which all the *C* and *N* atoms of bamp are positioned. Possible puckering of the chelate rings may violate this requirement but its influence may be neglected if interconversion of these conformers is fast relative to the time scale of reactions studied. While the experiments presented give no information on the conformation and their dynamics, molecular models suggest that little puckering of the chelate rings may be expected.

We assume that, in the solvolytic reactions studied, the usual mechanistic proposals are sufficient to rationalize the kinetics and the basis for this hypothesis will be discussed in the following.

The complexes **1**, **5**, **11** and **13** have meridionally coordinated bamp and a Cl-atom as common structural elements. Thus, the differences in reactivity within this series should largely depend on the (*cis*)-diamine moiety. On the whole, the rates of spontaneous aquation, Hg^{2+}-induced aquation and base hydrolysis vary only $\sim 10^2$-fold within the series for all three reactions. The rates of spontaneous aquation vary in the order expected from earlier studies on species containing these diamines: $tmd > en \sim (NH_3)_2 > ddb$. The high rate for the tmd complex has been associated with the strain and non-bonded interactions inherent in a six-membered diaminoalkane chelate ring [18]. Reduced solvent assistance in attaining the transition state has been proposed for a ddb complex which bears hydrophobic substituents on the chelate ring [19]. The Hg^{2+}-induced aquations follow roughly the same order except for the similar values for en and $(NH_3)_2$: $tmd > (NH_3)_2 \sim en > ddb$. A linear correlation log k_{H_2O} *vs.* log $k_{Hg^{2+}}$ has been found for the series *cis*/*trans*-$[Co(en)_2XY]^{n+}$ (X, Y: anions or H_2O or uncharged *N* donors) [12], but the small number of data presented here does not pass the test for linear correlation. The rates of base hydrolysis vary in the order: $ddb > tmd > (NH_3)_2 \sim en$. This is in keeping with the known acceleration of the base hydrolysis reaction caused by bulky ligands [20]. For all four species, the magnitudes of k_{H_2O} [19] lie roughly within the range of comparable compounds. This and the effects of diamine variation are thus compatible with the mechanisms proposed in earlier studies.

For the base hydrolysis reactions some discussion is required in view of a recent mechanistic proposal. A dissociative, conjugate-base mechanism for base hydrolysis is now commonly accepted for most Co(III) pentaamines [10] [15]. However, a different mechanism has been discussed for **15** *(Fig. 3)* [10a] to explain its faster base hydrolysis relative to **16** *(Table 6)*. In this alternative proposal, a hydroxo adduct of the pyridine ligand has been suggested to labilize the leaving group. So far, no specific evidence for this mechanism has been advanced for this particular compound. However, a recent X-ray crystal structure investigation of *cis*-$[Co(en)_2(pyridine)Br](NO_3)_2$ shows some nonbonded interaction between Br^- and pyridine [21]. While this interaction should be smaller in the chloro complex, the faster base hydrolysis of **15** relative to **16** may still be attributed to steric acceleration.

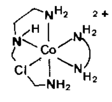
Table 6. *Rates of Base Hydrolysis of some Co(III)-Pentaamines at 25°C*

	complex	k_{OH}[M^{-1}sec^{-1}]	medium	ref.
15	*cis*[Co(en)$_2$(pyridine)Cl]$^{2+}$ [a]	199	$\mu = 1.0$ (NaClO$_4$)	[22]
		1600	μ unspecified, low	[23]
16	*cis*[Co(en)$_2$NH$_3$Cl]$^{2+}$ [b]	8.1	$\mu = 0.1$ (KCl)	[23]
		1–4	$\mu = 1.0$, estimated value	
5	[Co(bamp)(en)Cl]$^{2+}$	480	$\mu = 1.0$ (NaClO$_4$)	this work
17	κ-[Co(dien)(en)Cl]$^{2+}$ [c]	3.0×10^4	$\mu = 0.1$ (NaClO$_4$)	[24]
		1.6×10^4	$\mu = 1.0$ (NaClO$_4$)	[22]
18	π-[Co(dien)(en)Cl]$^{2+}$ [d]	26.6	$\mu = 0.1$ (NaClO$_4$)	[24]
19	ω-[Co(dien)(en)Cl]$^{2+}$ [e]	7.26	$\mu = 0.1$ (NaClO$_4$)	[24]
11	[Co(bamp)(tmd)Cl]$^{2+}$	7700	$\mu = 1.0$ (NaClO$_4$)	this work
20	a-[Co(dien)(tmd)Cl]$^{2+}$ [c]	5.02×10^5	$\mu = 0.1$ (NaClO$_4$)	[18]
21	d-[Co(dien)(tmd)Cl]$^{2+}$ [d]	138	$\mu = 0.1$ (NaClO$_4$)	[18]
22	h-[Co(dien)(tmd)Cl]$^{2+}$ [e]	10.6	$\mu = 0.1$ (NaClO$_4$)	[18]

[a] Rate of spontaneous aquation, $k_{H_2O} = 2.6\text{–}6.2 \times 10^{-7}$s^{-1}, 25°, $\mu = 0.1$ [23].

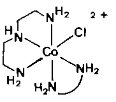
[b] Rate of spontaneous aquation, $k_{H_2O} = 3.3\text{–}5.7 \times 10^{-7}$s^{-1}, 25°, μ low [23].

c)



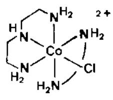
κ, a [17]

d)



π, d [17]

e)



ω, h [17]

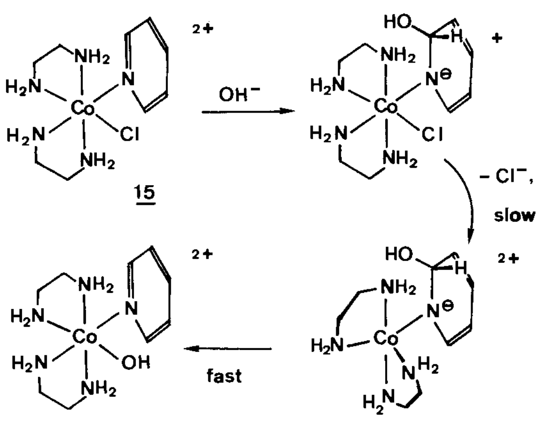


Fig. 3. *Mechanism for base hydrolysis of* **15** after a proposal by *Tobe* [10a].

Our base hydrolysis rate data may be compared to those available for [Co(dien)-(diamine)Cl]$^{2+}$ *(Table 6)* where there are large differences in reactivity for the different isomers with en and tmd, respectively. In our case, **5** and **11** react slower than the mer-dien analogues but faster than any of the fac-dien species. This observation is difficult to rationalize as in terms of the SN$_1$CB mechanism $k_{OH} = K_a k_{CB}/K_{H_2O}$ under most experimental conditions [10]. However, the site of deprotonation and the reactivity of the most reactive conjugate base are not known for the dien complexes and may be different from those of the bamp analogues. In spite of these unresolved problems, the reactivity of the $[Co(bamp)(AA)Cl]^{2+}$ species appears neither unusually high nor low. Finally, the proton exchange data of *Table 3* are also consistent with the usual patterns. From all these observations we do not consider it necessary to invoke a mechanism other than the usual SN_1CB scheme to rationalize the present results.

In conclusion, the complexes of bamp reported here appear to meet our structural requirements in that bamp is coordinated in a meridional arrangement in all species investigated. No isomer with facially coordinated bamp was detected in the experiments described. The solvolytic reactivity of several of the species is not unusual in comparison with analogues containing purely aliphatic amine ligands and can be rationalized in terms of the commonly proposed mechanisms. These two results are important for our further work in this area.

We wish to thank Mr. *G. Balimann* for a great portion of the NMR. spectra and Mr. *W. Manser* and his staff of the Microanalytical Laboratory, ETH for the elemental analyses. This work was supported by the *Swiss National Science Foundation* (project 2.225-0.74).

Experimental Part

Physical measurements. UV./VIS. spectra and kinetic runs were measured on a *Cary* 14 spectrophotometer with the cell compartments thermostated to 25±0.1° by means of a *Lauda* thermostat. Except in the aquation kinetics, the mixing of the thermostated reactant solutions was performed by a stopped-flow reactor [25]²) adapted to the spectrophotometer. For the spontaneous aquation kinetics, solutions were mixed manually and measurements were taken for 60 sec at intervals of 15 to 30 min preset by a timing device. ^{1}H-NMR. spectra were recorded at 38° on a *Perkin-Elmer* R12B 60 MHz instrument or on a *Bruker* HX90-E instrument at 90 MHz in the FT mode. pH-values of the buffer solutions were measured at 25° with a combined glass electrode connected to a *Metrohm* potentiometer. The glass electrode was calibrated in standard solutions of known pH [26].

Materials. Except for some of the ligands, all chemicals were of commercial *purissimum* or analytical reagent grade. Deionized water was used in all experiments. Mercuric perchlorate stock solutions were prepared by dissolving red mercuric oxide *(pro analysi, Merck)* in a known stoichiometric excess of $HClO_4$. The solution was filtered to remove unweighable amounts of a faint turbidity. In these solutions, no Hg(I) was detected by Cl^-. Stock solutions of reagents and electrolyte $NaClO_4$ were filtered before use in kinetic runs. 2,3-Diamino-2,3-dimethylbutane dihydrochloride (ddb · 2HCl) [27] and 1,3-diamino-2,2-dimethylpropane [28] were prepared by published procedures. 2,6-Bis-(aminomethyl)pyridine trihydrochloride (bamp · 3HCl) [29] was prepared according to *Schwarzenbach et al.* [2] by catalytic hydrogenation of 2,6-dicyanopyridine [30] (CH_3OH/37% HCl, Pd/C (5 or 10%), 5-10 atm H_2, room temperature). It was recrystallized from H_2O/HCl and isolated as trihydrochloride.

$C_7H_{14}N_3Cl_3$ (246.5) Calc. C 34.10 H 5.72 N 17.04% Found C 34.20 H 5.81 N 17.04%

Preparations. All compounds were dried i.V. (12-18 h, 5-20× 10^{-3} Torr, 20°) before characterization. cis-*Chloro-[2,6-bis(aminomethyl)pyridine] (diammine) cobalt(III) tetrachlorozincate* (**1**). Ammonium carbonate (22.5 g, 200 mmol), 25% aqueous NH_3 (22.5 ml, 330 mmol) and bamp · 3HCl (10 g, 41 mmol) in H_2O (10 ml) were added to $Co(NO_3)_2 \cdot 6H_2O$ (14.55 g, 50 mmol) in H_2O (7.5 ml). A stream of dioxygen was passed through the solution for 24 h. Half of the resulting red solution presumably containing *cis*-$[Co(bamp)(NH_3)_2CO_3]^+$ was treated with aqueous HCl (37%, 12.1 ml) at 0°. When the evolution of CO_2 was complete, $ZnCl_2$ (20 g) was added. On standing, red crystals of **1** (4 g, 46%) separated. They were

---

²) We are indebted to Dr. *A. M. Sargeson*, Australian National University, Canberra, for making the design of this instrument available to us and to Mr. *W. Lussy* for the construction.

washed with 2-propanol and ether. Recrystallization from hot 1M $HCl/ZnCl_2$ first gave some $[Co(NH_3)_5Cl]Cl_2$ which was removed.

$C_7H_{17}N_5Cl_5CoZn$ (427.8) Calc. C 17.78 H 3.62 N 14.81% Found C 17.52 H 3.58 N 14.90%

cis-*Bromo-[2,6-bis(aminomethyl)pyridine](diammine)cobalt(III)dibromide* (**2**). To the other half of the solution containing the presumed carbonato complex from the first preparation, aqueous HBr-solution (48%, 15 ml) was added slowly at 0°. If cooling is insufficient, Br_2 and Co(II) are formed. At the end of the CO_2 evolution, NaBr (20 g) was added. The resulting dark red crystals of **2** (4.98 g, 52%) were collected. The product (1.77 g) was dissolved in dilute aqueous acetic acid at 80°. Some $[(H_3N)_5CoBr]Br_2$ was filtered off and 1.3 g (38%, based on bamp · 3HCl) of **2** were recovered on cooling.

$C_7H_{17}N_5Br_3Co$ (469.9) Calc. C 17.89 H 3.65 N 14.90% Found C 17.86 H 3.68 N 14.73%

cis-*Nitro-[2,6-bis(aminomethyl)pyridine](diammine)cobalt(III)tetrachlorozincate* (**4**). Chloro complex **1** (500 mg, 1.17 mmol) was dissolved in 10 ml 0.2M aqueous HCl and treated with $NaNO_2$ (1.5 g) at 60° for *ca.* 30 min until the colour appeared orange. The warm solution was then poured onto 50 ml warm acetone/2-propanol 1:1 containing 1.2 g $ZnCl_2$. Yellow crystals of **4** separated slowly (500 mg, 88%). They were recrystallized twice by dissolving in the minimum amount of 0.2M HCl and pouring the solution onto acetone/2-propanol 1:1.

$C_7H_{17}Cl_4N_6O_2CoZn$ (483.4) Calc. C 17.39 H 3.55 N 17.39% Found C 17.54 H 3.59 N 17.25%

Chloro-[2,6-bis(aminomethyl)pyridine](ethylenediamine)cobalt(III) tetrachlorozincate (**5**). To a solution of $Co(NO_3)_2 \cdot 6H_2O$ (7.25 g, 25 mmol) and $NaClO_4 \cdot H_2O$ (7.5 g) in water (125 ml), a solution containing ethylenediamine (98%, 1.5 g, 25 mmol), bamp · 3HCl (5.8 g, 24 mmol) and NaOH (1 g, 25 mmol) in water (50 ml) was added dropwise. A stream of dioxygen was passed through the mixture for *ca.* 2 h. Black crystals of presumed $[Co_2(bamp)_2(en)_2O_2](ClO_4)_4$ separated from the resulting dark-brown solution. They were washed with 2-propanol and ether and air-dried (6.9 g, 30% based on bamp · 3HCl). Adding one equivalent of NaOH gave the best yield under otherwise identical conditions. The peroxo complex (4.5 g, 5 mmol) was treated with hydrochloric acid (37%, 12 ml) and $ZnCl_2$ (8 g) in water (25 ml) at 80° until the evolution of gas was complete. On cooling, red crystals of **5** (3.9 g, 78%) separated. They were recrystallized from 0.2M HCl by adding $ZnCl_2$ in 6M HCl and washed with 2-propanol and ether.

$C_9H_{19}Cl_5N_5CoZn$ (498.8) Calc. C 21.67 H 3.84 N 14.04% Found C 21.58 H 3.77 N 13.94%

Bromo-[2,6-bis(aminomethyl)pyridine](ethylenediamine)cobalt(III)dinitrate (**6**) *and -tetrabromozincate* (**6a**). A sample of the presumed μ-peroxo complex described in the preceding preparation (1.2 g, 1.2 mmol) was dissolved in a mixture containing aqueous HBr-solution (48%, 3.3 ml), ZnO (2 g) and water (6.6 ml). The mixture was then heated (80°, 30 min) and cooled to RT. Purple crystals of **6a** (1.5 g, 98%) were filtered off and purified by conversion to the dinitrate salt **6** by dissolving it in the minimal amount of H_2O at 60° and by adding solid $NaNO_3$.

$C_9H_{19}BrN_7O_6Co$ (460.1) Calc. C 23.49 H 4.16 N 21.31% Found C 23.59 H 4.12 N 21.39%

Nitro-[2,6-bis(aminomethyl)pyridine](ethylenediamine)cobalt(III) tetrachlorozincate (**8**). A sample of **6a** (1.7 g, 3.4 mmol) was dissolved in 40 ml 0.2M HCl and treated with $NaNO_2$ (5 g) at 80° for 30 min. The hot yellow solution was added dropwise to a hot mixture of $ZnCl_2$ (4.25g), acetone/2-propanol 1:1 (170 ml). Yellow crystals of **8** (1.4g, 81%) resulted on cooling which were washed with acetone and ether. They were recrystallized from 0.2M HCl/acetone.

$C_9H_{19}Cl_4N_6O_2CoZn$ (509.4) Calc. C 21.22 H 3.76 N 16.50% Found C 21.30 H 3.79 N 16.30%

Azido-[2,6-bis(aminomethyl)pyridine](ethylenediamine)cobalt(III) tetrachlorozincate (**9**). **5** (0.3g, 0.6 mmol) was dissolved in 6 ml 0.2M aqueous CH_3COOH containing NaN_3 (1g) and heated (80°, *ca.* 15 min). The colour of the solution turned deep red. 30 ml 2-propanol/methanol 1:1 and $ZnCl_2$ (1.6g) was added to the solution at RT. After one day, a first crop of purple crystals of **9** was collected, and more was obtained by adding $ZnCl_2$ (1g) in 2-propanol (10 ml). Yield: 160 mg (53%).

$C_9H_{19}Cl_4N_8CoZn$ (505.5) Calc. C 21.39 H 3.79 N 22.16% Found C 21.43 H 3.85 N 22.16%

Isothiocyanato-[2,6-bis(aminomethyl)pyridine](ethylenediamine) cobalt(III)dithiocyanate (**10**). **6** (150 mg, 0.33 mmol) was added to a solution of $Hg(ClO_4)_2$ (1.65 ml, 0.1M, acidified with $HClO_4$, 0.16 mmol). After *ca.* 1 h at RT., $HgBr_2$ was filtered off and the filtrate was neutralized (NaOH, pH 6) and saturated with KNCS. After *ca.* 4 days, orange crystals of **10** (100 mg, 71%) were filtered off.

$C_{12}H_{19}N_8S_3Co$ (430.5) Calc. C 33.48 H 4.45 N 26.03% Found C 33.43 H 4.37 N 26.10%

Chloro-[2,6-bis(aminomethyl)pyridine](1,3-diaminopropane) cobalt(III) tetrachlorozincate (**11**). To a solution of $Co(NO_3)_2 \cdot 6H_2O$ (7.25g, 25 mmol) and $NaClO_4 \cdot H_2O$ (7.5g) in water (100 ml) was added dropwise a solution of bamp · 3HCl (5.8g, 24 mmol), 1,3-diaminopropane (1.85g, 25 mmol) and NaOH (1.1g, 27.5 mmol) in water (30 ml). Dioxygen was passed through the mixture for 12 h. A pink precipitate formed immediately but gradually dissolved to give ochre platelets (2.45g, 22%) of the presumed $[Co_2(bamp)_2(tmd)_2O_2](ClO_4)_4$. This material was treated with aqueous HCl-solution (37%, 20 ml) and $ZnCl_2$ (5 g) for 1 h at 80°. A clear red solution formed with evolution of gas. From this, red crystals of **11** (2.03 g, 17%) separated on cooling. They were recrystallized from hot 5M $HCl/ZnCl_2$ (5 g).

$C_{10}H_{21}Cl_5N_5CoZn$ (512.9) Calc. C 23.42 H 4.13 N 13.66% Found C 23.45 H 4.12 N 13.80%

Chloro-[2,6-bis(aminomethyl)pyridine](1,3-diamino-2,2-dimethylpropane)cobalt(III)tetrachlorozincate (**12**). This compound was made on a similar scale in analogy to **11** *via* the presumed μ-peroxo perchlorate (ochre crystals, 25% yield) which gave **12** as described (69%) as red crystals which were recrystallized twice from 5M $HCl/ZnCl_2$ and dried i.V. at 120° for 24 h.

$C_{12}H_{25}Cl_5N_5CoZn$ (541.0) Calc. C 26.64 H 4.66 N 12.95% Found C 26.71 H 4.62 N 13.01%

Chloro-[2,6-bis(aminomethyl)pyridine](2,3-diamino-2,3-dimethylbutane)cobalt(III)tetrachlorozincate (**13**). Bamp · 3HCl (5.8 g, 24 mmol), ddb · 2HCl (4.8 g, 25 mmol) and NaOH (2.5 g, 63 mmol) in water (50 ml) were added dropwise to a solution of $Co(NO_3)_2$. $6H_2O$ (7.25 g, 25 mmol) and $NaClO_4 \cdot H_2O$ (7.5 g) in water (95 ml). Dioxygen was passed through the mixture for 24 h. Olive/brown crystals of presumed $[Co_2(bamp)_2(ddb)_2O_2](ClO_4)_4$ (2.55 g, 19%) separated. This material (2 g) was treated with aqueous HCl-solution (37%, 6 ml) and water (10 ml) containing $ZnCl_2$ (4 g). On heating (80°, 10 days), the peroxo complex gradually dissolved to give first a green and finally a red solution. From this, red crystals of **13** (*ca.* 80%) separated at 0° which were washed with 2-propanol and ether.

$C_{13}H_{27}Cl_5N_5CoZn$ (555.0) Calc. C 28.14 H 4.90 N 12.62% Found C 28.23 H 4.84 N 12.60%

Bis-[2,6-(aminomethyl)pyridine]cobalt(III)tribromide hemihydrate (**14**) *and -tetrachlorocobaltate.* The cation $[Co(bamp)_2]^{3+}$ constituted a major by-product in most of the preparations, mainly in those of the presumed peroxo complexes. It was crystallized as a more soluble component from their mother liquors and recrystallized as the bromide hemihydrate from HBr/H_2O.

$C_{14}H_{22}Br_3N_6Co \cdot \frac{1}{2}H_2O$ (581.9) Calc. C 28.89 H 3.98 N 14.44% Found C 29.05 H 3.99 N 14.44%

In some cases, addition of aqueous HCl-solution (37%) to mother liquors of the chloro complexes precipitated green $[Co(bamp)_2]_2(CoCl_4)_3$. Its identity follows from ion exchange chromatography of the yellow solution of the complex in water. Co^{2+} was detected in the first eluate and $[Co(bamp)_2]^{3+}$ was eluted and identified by its VIS. spectrum.

Product analysis in the preparation of **5** *in homogeneous solution.* $Co(NO_3)_2 \cdot 6H_2O$ (725 mg, 2.5 mmol), bamp · 3HCl (580 mg, 2.4 mmol), 1,2-diaminoethane (150 mg, 2.5 mmol), NaOH (2.5 ml, 0.1M solution in water) and $NaClO_4 \cdot H_2O$ (750 mg) were dissolved in water (20 ml). A stream of dioxygen was passed through the solution for 2 h. The solution was then treated with HCl-solution (37%, 10 ml) and $ZnCl_2$ (1.6 g), kept at 70° for 4 h and allowed to stand overnight at RT. The resulting homogeneous red-orange solution was then made up to 50 ml in a volumetric flask. An aliquot of 10 ml was diluted to 250 ml and sorbed on Bio-Rad 50WX2 AG, 200-400 mesh, cation exchange resin in the H^+-form. A red species which from its spectrum ($\lambda_{max} = 479.5$ nm, $\lambda_{min} = 407$ nm, $\varepsilon_{min}/\varepsilon_{max} = 0.322$) was assumed to be $[Co(bamp)(en)Cl]^{2+}$ (5.431×10^{-4}M, 13% based on total cobalt) was eluted with 1M $HClO_4$. This solution was reacted with a slight excess of solid $Hg(NO_3)_2 \cdot 0.5\ H_2O$ to complete aquation ($\lambda_{max} = 459$ nm, $\lambda_{min} = 393.5$ nm, $\varepsilon_{max}/\varepsilon_{min} = 0.238$). Using the extinction coefficients of **7**, the concentration of this species is calculated as 5.435×10^{-4}M. The remaining yellow band on the column was treated with chlorhydric acid but no detectable amounts of a chloro complex were formed.

Chemical correlations between [Co(bamp)(AA)X]$^{n+}$ species (Fig. 2). The base hydrolysis reactions were performed in appropriate buffer solutions for $10 \times t_{1/2}$ and quenched with 60% $HClO_4$-solution. Spectra of the products were run against blanks of the quenched buffer solutions. The mercury induced aquations were performed as described above. Competition of nitrate from $Hg(NO_3)_2 \cdot 0.5\ H_2O$ may be neglected at the low concentrations used. Nitrosation of **9** was effected in 1M $HClO_4$ by adding a small excess of solid $NaNO_2$ and chlorination of **2** by passing a stream of Cl_2 through a 1M $HClO_4$-solution, followed by a stream of dinitrogen to remove excess Cl_2.

REFERENCES

[1] *W. W. Brandt, F. P. Dwyer & E. C. Gyarfas,* Chem. Rev. *54,* 959 (1954); *E. N. Maslen, C. L. Raston & A. H. White,* J. chem. Soc. Dalton *1974,* 1803.

[2] *G. Schwarzenbach, J. Bösch & H. Egli,* J. inorg. nucl. Chemistry *33,* 2141 (1971).

[3] *J. A. Connor & E. A. V. Ebsworth,* Adv. inorg. Radiochemistry *6,* 327 (1964).

[4] *B. M. Fung,* J. Amer. chem. Soc. *89,* 5788 (1967).

[5] *D. A. Buckingham, P. A. Marzilli & A. M. Sargeson,* Inorg. Chemistry *8,* 1595 (1969).

[6] *H. Yoneda & Y. Nakashima,* Bull. chem. Soc. Japan *47,* 669 (1974).

[7] *D. A. Buckingham, I. I. Olsen & A. M. Sargeson,* J. Amer. chem. Soc. *90,* 6654 (1968).

[8] *D. A. Buckingham, I. I.. Olsen & A. M. Sargeson,* Austral. J. Chemistry *29,* 597 (1967).

[9] *J. F. Remar, D. E. Pennington & A. Haim,* Inorg. Chemistry *4,* 1832 (1965).

[10] a) *M. L. Tobe,* Accounts chem. Res. *3,* 377 (1970); b) *C. K. Poon,* Inorg. chim. Acta Reviews *1970,* 123.

[11] *S. Hietanen & L. G. Sillén,* Acta chem. Scand. *6,* 747 (1952).

[12] *C. Bifano & R. G. Linck,* Inorg. Chemistry, *7,* 908 (1968).

[13] *J. A. Thich, Ch. Ch. Ou, D. Powers, B. Vasiliou, D. Mastropaolo, J. A. Potenza & H. J. Schugar,* J. Amer. chem. Soc. *98,* 1425 (1976).

[14] *M. G. B. Drew, R. W. Matthews & R. A. Walton,* J. chem. Soc. (A), *1970,* 1405.

[15] *A. M. Sargeson,* Pure appl. Chemistry *33,* 527 (1973).

[16] *D. Cummins, E. D. McKenzie & H. Milburn,* J. chem. Soc. Dalton *1976,* 130.

[17] a) *A. R. Gainsford & D. A. House,* Inorg. chim. Acta *3,* 367 (1969); b) *J. H. Johnston & A. G. Freeman,* J. chem. Soc. Dalton *1975,* 2153.

[18] *L. S. Dong & D. A. House,* Inorg. chim. Acta *19,* 23 (1976).

[19] *F. Basolo & R. G. Pearson,* Mechanisms of Inorganic Reactions, 2nd ed., New York, London, Sydney 1967, p. 158ff.

[20] *D. A. Buckingham, B. M. Foxman & A. M. Sargeson,* Inorg. Chemistry *9,* 1790 (1970).

[21] *O. Börtin,* Acta chem. Scand. A, *30,* 475 (1976).

[22] *U. Tinner & W. Marty,* unpublished work.

[23] *J. O. Edwards, F. Monacelli & G. Ortaggi,* Inorg. chim. Acta *11,* 47 (1974).

[24] *R. W. Hay & K. B. Nolan,* J. inorg. nucl. Chemistry *38,* 2118 (1976).

[25] *Y. Inoue & D. D. Perrin,* J. phys. Chemistry *66,* 1689 (1962).

[26] *D. D. Perrin & B. Dempsey,* Buffers for pH and Metal Ion Control, London 1974.

[27] *L. W. Seigle & H. B. Hass,* J. org. Chemistry *5,* 100 (1940); *J. Beward,* Ber. deutsch. Chem. Ges. *39,* 1231 (1906).

[28] *E. B. Fleischer, A. E. Gebala, A. Levey & P. A. Tasker,* J. org. Chemistry *36,* 3042 (1971).

[29] *F. Lions & K. V. Martin,* J. Amer. chem. Soc. *79,* 2733 (1957).

[30] *R. Lukeš & M. Pergál,* Coll. czechoslov. chem. Commun. *24,* 36 (1959).

[31] *E. S. Swinbourne,* Analysis of Kinetic Data, London 1971.