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Syntheses and Characterizations of μ-Dicarboxylato-bis[pentaamminecobalt(III)] Complexes

Hiroshi Ogino,* Keiichi Tsukahara,† Yoshiyuki Morioka, and Nobuyuki Tanaka
Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Aramaki, Sendai 980

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Five new complexes, $[(NH_3)_5Co(dicarboxylate)Co(NH_3)_5]X_4$ (dicarboxylate=oxalate, succinate, pimelate, fumarate, and maleate; $X=ClO_4^-$ or Cl^-), were synthesized by the reactions of $[Co(hydrogen\ dicarboxylate)(NH_3)_5](ClO_4)_2$ with $[Co(NH_3)_5(H_2O)](ClO_4)_3$ and characterized by chromatographic behavior and electronic and NMR techniques. When maleate was used as the dicarboxylate, the formation of $[(NH_3)_5Co(fumarate)Co(NH_3)_5]^{4+}$ as well as $[(NH_3)_5Co(maleate)Co(NH_3)_5]^{4+}$ was observed. The IR and Raman spectra of $[(NH_3)_5Co(oxalate)Co(NH_3)_5]^{4+}$ indicate that the symmetry of the oxalate ion in the complex may be approximated by D_{2h}.

The syntheses of a series of μ-dicarboxylato-bis[pentaamminecobalt(III)] complexes were reported by Duff,[1] where malonic, glutaric, adipic, malic, phthalic, citraconic, and itaconic acids were used as the μ-bridging ligands. However, the synthetic procedure of Duff is time consuming, that is, it takes a week or more. Our attempt to prepare μ-malonato-bis[pentaamminecobalt(III)] complex using Duff's procedure failed. Furthermore, synthesis of the simplest complex of this series, $[(NH_3)_5Co(O_2CCO_2)Co(NH_3)_5]X_4$, has not been reported.

This paper reports the syntheses and characterizations of the bis[pentaamminecobalt(III)] complexes containing μ-oxalate, malonate, succinate, pimelate, fumarate, and maleate ligands.[2] Some observations on the products of the reaction of $[Co(Hdic)(NH_3)_5]^{2+}$ with $[Co(NH_3)_5(H_2O)]^{3+}$ are also described.

Experimental

Materials. The complexes $[Co(NH_3)_5(H_2O)](ClO_4)_3$ and $[Co(Hox)(NH_3)_5](ClO_4)_2$ were prepared by the published methods.[3,4] The other complexes containing Hdic, $[Co(Hdic)(NH_3)_5](ClO_4)_2$, were prepared by the published method with slight modifications:[5,6] The H_2dic (0.2 mol) was dissolved into 200 cm³ of water containing NaOH (0.2 mol). After the addition of $[Co(NH_3)_5(H_2O)](ClO_4)_3$ (0.02 mol), the temperature of the solution was kept at 70—75 °C for 3 h, and then the solution was cooled, and diluted to 3 dm³ with water. The solution was poured into an SP-Sephadex C-25 column (4.5 cm × 35 cm). The desired species was eluted out with a 0.1 M $NaClO_4$ solution of pH 2—3 adjusted with $HClO_4$ (1 M=1 mol dm^{-3}).[7] Small amounts of $[Co(NH_3)_5(H_2O)]^{3+}$ and $[(NH_3)_5Co(dic)Co(NH_3)_5]^{4+}$ (yield=2—3%) remained in the column. The eluate was evaporated to a small volume with a rotary evaporator whereupon red crystals of $[Co(Hdic)(NH_3)_5](ClO_4)_2$ were obtained; yield 80—90%.

Syntheses of μ-Dicarboxylato-bis[pentaamminecobalt(III)] Perchlorates. The complex $[Co(Hdic)(NH_3)_5](ClO_4)_2$ (0.01 mol) was dissolved into 150 cm³ of water. The pH of the solution was adjusted to 4 with $NaHCO_3$. To this solution was added 0.01 mol of $[Co(NH_3)_5(H_2O)](ClO_4)_3$. The solution was kept at 70—75 °C for 2—3 h and then cooled to room temperature. After diluting the solution to 1.5 dm³ with water, the pH was adjusted to 3 with $HClO_4$. This was poured into the SP-Sephadex C-25 column. The adsorbed species were eluted with $NaClO_4$ solutions of pH 2—3 adjusted with $HClO_4$. Major species on the column were identified as $[Co(Hdic)(NH_3)_5]^{2+}$,[7] $[Co(NH_3)_5(H_2O)]^{3+}$, and $[(NH_3)_5Co(dic)Co(NH_3)_5]^{4+}$. Detailed product distribution will be given in Results and Discussion. The $[(NH_3)_5Co(dic)Co(NH_3)_5]^{4+}$ was eluted with a 0.4 M $NaClO_4$ solution,[9] after the species less charged than 4+ had been eluted out. The eluate was evaporated to a small volume with a rotary evaporator whereupon red crystals of the perchlorate salt were obtained. The recrystallizations were made from water. The chloride salt of $[(NH_3)_5Co(ox)Co(NH_3)_5]^{4+}$ was obtained when 0.4 M KCl solution was used in place of the 0.4 M $NaClO_4$ eluant.

The analytical data for the complexes are given in Table 1.

Apparatus. Electronic spectra of the complexes in aqueous solutions were recorded on a Union-Giken SM-401 spectrophotometer. ¹H-NMR spectra (in D_2O containing 0.1 M D_2SO_4, with sodium 2,2-dimethyl-2-silapentane-5-sulfonate as the internal standard) were obtained by the use of a Varian A 60 spectrometer and a JEOL MH-100 spectrometer. ¹³C-NMR spectra were recorded on a Varian XL-200 at a frequency of 50 MHz (D_2O lock) in the proton noise decoupled mode. The solubility of the perchlorate salts of

Table 1. Analytical data of the complexes

Compound	Found(Calcd)(%)		
	C	H	N
$[Co(Hpim)(NH_3)_5](ClO_4)_2$	16.58(16.74)	5.43(5.23)	14.05(13.95)
$[(NH_3)_5Co(ox)Co(NH_3)_5](ClO_4)_4$	3.01(3.10)	4.01(3.91)	17.93(18.10)
$[(NH_3)_5Co(ox)Co(NH_3)_5]Cl_4$	4.51(4.63)	6.11(5.84)	26.87(27.04)
$[(NH_3)_5Co(malo)Co(NH_3)_5](ClO_4)_4\cdot 2H_2O$	4.50(4.37)	4.23(4.41)	17.06(17.00)
$[(NH_3)_5Co(suc)Co(NH_3)_5](ClO_4)_4$	6.26(5.99)	4.46(4.28)	17.62(17.47)
$[(NH_3)_5Co\ (fum)\ Co(NH_3)_5]\ (ClO_4)_4\cdot 0.5H_2O$	6.11(5.94)	4.20(4.12)	17.23(17.31)
$[(NH_3)_5Co(male)Co(NH_3)_5](ClO_4)_4\cdot 2H_2O$	5.89(5.75)	4.25(4.35)	16.78(16.76)
$[(NH_3)_5Co(pim)Co(NH_3)_5](ClO_4)_4\cdot 3H_2O$	9.71(9.36)	4.82(5.17)	15.19(15.60)

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† Present address: Department of Chemistry, Faculty of Science, Shimane University, Nishikawatsucho, Matsue 690.

TABLE 2. NUMERICAL DATA FOR THE ELECTRONIC SPECTRA OF THE COMPLEXES PREPARED IN THIS WORK AND RELATED COMPLEXES

Compound	Medium	λ_{max}/nm(ε/M^{-1} cm^{-1})$^{a)}$	Ref.
$[(NH_3)_5Co(ox)Co(NH_3)_5](ClO_4)_4$	H_2O	505(156), 344sh(240), 274sh(4690), 220sh(23700)	This work
$[Co(Hox)(NH_3)_5](ClO_4)_2$	pH<2.5	505(73.0)	10
	pH 7.5	505(76.0)	
$[(NH_3)_5Co(malo)Co(NH_3)_5](ClO_4)_4\cdot 2H_2O$	H_2O	505(174), 352(135), 228(24900)	This work
$[Co(Hmalo)(NH_3)_5](ClO_4)_2$	0.05 M $HClO_4$	505(74.9), 350(58.2)	11
$[(NH_3)_5Co(suc)Co(NH_3)_5](ClO_4)_4$	H_2O	505(158), 353(120), 227(24400)	This work
$[Co(Hsuc)(NH_3)_5](ClO_4)_2$	0.05 M $HClO_4$	505(68.2), 355(54.8)	11
$[(NH_3)_5Co(fum)Co(NH_3)_5](ClO_4)_4\cdot 0.5H_2O$	H_2O	504(170), 351(142), 232(36700)	This work
$[Co(Hfum)(NH_3)_5](ClO_4)_2$	pH 1—10	502(75.3), 351(61.8)	12
$[(NH_3)_5Co(male)Co(NH_3)_5](ClO_4)_4\cdot 2H_2O$	H_2O	505(160), 353(131), 229(25800)	This work
$[Co(Hmale)(NH_3)_5](ClO_4)_2$	H_2O	502.5(76.8), 351(66.5)	13
$[(NH_3)_5Co(pim)Co(NH_3)_5](ClO_4)_4\cdot 3H_2O$	H_2O	504(152), 353(122), 229(23600)	This work
$[Co(Hpim)(NH_3)_5](ClO_4)_2$	0.1 M $HClO_4$	505(76.3), 355(60.9)	

a) sh=Shoulder.

the μ-dicarboxylato complexes into D_2O was found to be too low for the measurement of the NMR spectra. These complexes converted to the chloride salts with the aid of Dowex 1 X-4 resin in the chloride form, because the chlorides were found to be much more soluble than the perchlorates. The IR spectra (KBr disks) were recorded on a Hitachi EPI-S2 spectrometer. Raman spectra of $[(NH_3)_5Co(ox)Co(NH_3)_5](ClO_4)_4$ were recorded on a JEOL JRS-400T spectrometer. The 488 nm line of an Ar-ion laser (150 and 250 mW of power) was used as a light source. The spectra were measured in the solid state with KBr as a support. The rotating sample technique was employed to avoid decomposition.

Results and Discussion

Formulation of the Complexes. The analytical results of the $[(NH_3)_5Co(dic)Co(NH_3)_5]X_4$ shown in Table 1 are compatible with the assigned formulation. The positions of the absorption maxima due to the d-d transitions are characteristic for the $[CoN_5O]$ chromophores (Table 2) and the molar absorption coefficients (ε/M^{-1} cm^{-1}) are approximately 2 times larger than those of the corresponding $[Co(Hdic)(NH_3)_5]^{2+}$ complexes. The dimeric complex ions showed flow rates on a Sephadex column such that the ions must be the 4+ charged species.[14]

The ^{1}H-NMR spectra of $[(NH_3)_5Co(dic)Co(NH_3)_5]^{4+}$ showed only two NH_3 peaks at 2.90—2.94 ppm (6H) and 3.86—3.93 ppm (24H) (Table 3). This result also supports the μ-dicarboxylato-bis[pentaamminecobalt(III)] formulation, because the two peaks can be assigned to *trans*-NH_3 and *cis*-NH_3 to the μ-dicarboxylate ion, respectively, on the basis of the assignment reported for the spectra of $[CoX(NH_3)_5]^{n+}$ complexes.[15,16] The ^{1}H-NMR spectra of $[Co(Hmale)(NH_3)_5]^{2+}$ and $[Co(Hfum)(NH_3)_5]^{2+}$ showed AB splitting patterns due to the presence of CH=CH protons. Chemical shifts (coupling constants) were 6.10 and 6.43 ppm (J_{H-H}= 12.0 Hz) for the Hmale complex and 6.53 and 6.75 ppm (J_{H-H}=16.0 Hz) for the Hfum complex. In the spectra of $[(NH_3)_5Co(male)Co(NH_3)_5]^{4+}$ and $[(NH_3)_5Co(fum)Co(NH_3)_5]^{4+}$, each complex showed a singlet signal for the CH=CH protons which is compatible with the assigned formulation.

TABLE 3. NUMERICAL DATA FOR THE ^{1}H-NMR SPECTRA OF $[(NH_3)_5Co(dic)Co(NH_3)_5]^{4+}$ COMPLEXES

dic	Chemical shift δ/ppm		
	trans-NH_3	*cis*-NH_3	C–H_n
ox	2.93	3.93	—
malo	2.90	3.90	3.33(CH_2)
suc	2.90	3.86	2.46(CH_2CH_2)
pim	2.92	3.89	2.19, 2.26, 2.34 triplet (CH_2COO) 1.12—1.64 multiplet ($CH_2CH_2CH_2$)
fum	2.94	3.92	6.45 (CH=CH)
male	2.94	3.92	6.11 (CH=CH)

TABLE 4. NUMERICAL DATA FOR THE ^{13}C-NMR SPECTRA OF $[(NH_3)_5Co(dic)Co(NH_3)_5]^{4+}$ COMPLEXES$^{a)}$

dic	ox	malo	suc	pim	fum	male
$O_2\underline{C}$–	165.8	181.3	186.8	188.5	178.3	179.3
$O_2C\underline{C}$–	—	49.1	34.5	38.7	135.2	130.4
$O_2CC\underline{C}$–	—	—	—	25.8	—	—
$O_2CCC\underline{C}$–	—	—	—	29.0	—	—

a) Dioxane (δ=67.4 ppm *vs.* tetramethylsilane) was used as the internal standard. Chemical shifts were referenced to tetramethyl silane, downfield shifts having positive values.

As expected from the symmetric nature of the complexes, the ^{13}C-NMR spectra showed only one signal for the μ-ox complex, two signals for the μ-malo, μ-suc, μ-fum, and μ-male complexes, and four signals for the μ-pim complex (Table 4).

Product Distribution of the Reaction of $[Co(Hdic)(NH_3)_5](ClO_4)_2$ with $[Co(NH_3)_5(H_2O)](ClO_4)_3$. Figure 1 shows a chromatogram for the solution produced in the reaction between $[Co(Hox)(NH_3)_5]^{2+}$ and $[Co(NH_3)_5(H_2O)]^{3+}$. The distribution of the species formed in the reaction of $[Co(Hdic)(NH_3)_5](ClO_4)_2$ with $[Co(NH_3)_5$-

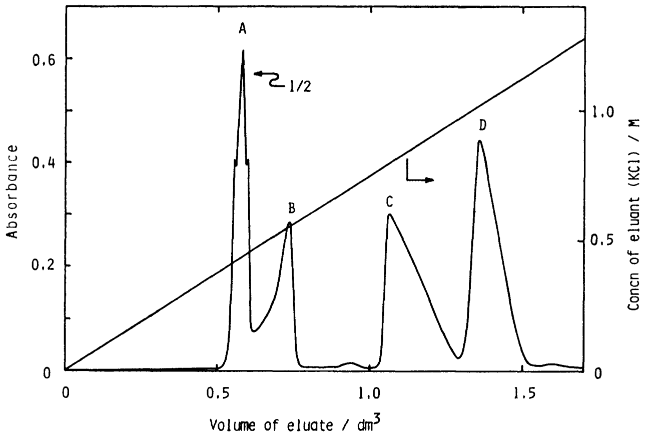

Fig. 1. Chromatogram for the solution produced in the reaction between $[Co(Hox)(NH_3)_5](ClO_4)_2$ and $[Co(NH_3)_5(H_2O)](ClO_4)_3$. The bands A, B, C, and D correspond to $[Co(ox)(NH_3)_5]^+$, $[Co(Hox)(NH_3)_5]^{2+}$, $[Co(NH_3)_5(H_2O)]^{3+}$, and $[(NH_3)_5Co(ox)Co(NH_3)_5]^{4+}$, respectively. The preparative scale was one-fourth of that given in Experimental. Heating time of the mixture was 4 h. The chromatography was made with an SP-Sephadex C-25 column (ϕ2.6×40 cm). The pH of the eluant was asjusted to 3 with HCl. Absorbance was measured at 505 nm with a flow-cell of 0.5 cm optical length.

$(H_2O)](ClO_4)_3$ was determined semi-quantitatively. The results are shown in Table 5. In the case of ox, malo, male, or pim system, a small amount of a violet species was detected at the lowest band. The species could be eluted out very easily with a 0.1 M $NaClO_4$ solution and hence the charge of the species was considered to be 1+. For the ox and malo systems, the species were characterized as chelated complexes $[Co(dic)(NH_3)_4]^+$ from a comparison of the electronic spectra with published data.17,18)

In most systems, the amounts of $[Co(Hdic)(NH_3)_5]^{2+}$ which remained unreacted were less than those of $[Co(NH_3)_5(H_2O)]^{3+}$ unreacted. This suggests the simultaneous occurrence of the dimerization reaction with $[Co(NH_3)_5(H_2O)]^{3+}$ and the aquation reaction of the $[Co(Hdic)(NH_3)_5]^{2+}$.

The ^{1}H-NMR spectra of the starting material pentaamminemaleatocobalt(III) complex did not show a detectable amount of pentaamminefumaratocobalt(III) complex (<2%). However, the formation of $[(NH_3)_5Co(fum)Co(NH_3)_5]^{4+}$ was observed in the male system. Therefore, the μ-fum complex is thought to be formed by the isomerization of $[(NH_3)_5Co(male)Co(NH_3)_5]^{4+}$.

IR and Raman Spectra. IR spectra of all the dimeric complexes show intense bands in the regions of 1300—1400 cm^{-1} and 1600—1650 cm^{-1}, which can be assigned to the CO stretching vibrations, though these bands are obscured by the overlap of the NH_3 deformation vibrations.19) The deuterated μ-ox complex exhibits three CO stretching absorptions, *i.e.*, at 1625 (strong), 1435 (weak), and 1302 cm^{-1} (strong). Table 6 shows the IR and Raman spectral data of $[(NH_3)_5Co(ox)Co(NH_3)_5](ClO_4)_4$ and related compounds. The IR spectral pattern of $[(NH_3)_5Co(ox)Co(NH_3)_5]^{4+}$ is quite similar to that of free $C_2O_4{}^{2-}$ whose symmetry is known to be D_{2h} and hence the symmetry of the oxalate ion in the complex may be approximated by D_{2h}. A strong Raman band at 1438 cm^{-1} can be assigned to vibration of a_g mode. A weak IR band at 1435 cm^{-1} may be also assigned to the vibration of a_g mode which appears by the lowering of symmetry in a crystal.

The complexes $[(NH_3)_5Cr(ox)Cr(NH_3)_5]^{4+}$ and $[(NH_3)_5Co(ox)Co(NH_3)_4(H_2O)]^{4+}$ have been prepared

TABLE 5. PRODUCT DISTRIBUTION OF THE REACTION OF $[Co(Hdic)(NH_3)_5]^{2+}$ WITH $[Co(NH_3)_5(H_2O)]^{3+}$ a)

Order of elution	Complex	Dicarboxylate b)							Concn of eluant
		ox	ox c)	malo	suc	fum d)	male	pim	
1	$[Co(dic)(NH_3)_4]^+$	3	— e)	1.5	0	0	tr f)	tr f,g)	0.1 M $NaClO_4$
2	$[Co(Hdic)(NH_3)_5]^{2+}$	87	72	32	80	73	87	— e)	0.1—0.2 M $NaClO_4$
3	$[Co(NH_3)_5(H_2O)]^{3+}$	90	70	120	90	76	96	— e)	0.3 M $NaClO_4$
4	$[(NH_3)_5Co(dic)Co(NH_3)_5]^{4+}$	10	24	12	15	20	2 h) 4 i)	8	0.4 M $NaClO_4$ q)
≥5	Complexes which were not characterized	tr j)	tr j)	0.44 k,l) 0.7 k,m) 0.4 k,p)	tr(pink) tr(pink)	tr(violet) tr n)	tr(pink)	— e)	0.5—1 M $NaClO_4$ r)

a) The reaction conditions are the same as those given in Experimental, unless otherwise indicated. b) The numerical values given in this table denote the yields(%) which were calculated by means of the following relation: yield=(mol of the indicated species)×100/(mol of $[Co(Hdic)(NH_3)_5](ClO_4)_2$ (=mol of $[Co(NH_3)_5(H_2O)](ClO_4)_3$) used as the starting material). Symbol "tr" denotes a trace amount. c) The reaction conditions are given in Fig. 1. The gradient elution was made with KCl solution. d) Two species (trace amounts) were found between fractions $[Co(Hfum)(NH_3)_5]^{2+}$ and $[Co(NH_3)_5(H_2O)]^{3+}$ (λ_{max}=524 and 357 nm) and between fractions $[Co(NH_3)_5(H_2O)]^{3+}$ and $[(NH_3)_5Co(fum)Co(NH_3)_5]^{4+}$ (λ_{max}=506 and 532 nm). e) Not determined. f) The species is assigned tentatively to the chelated complex $[Co(dic)(NH_3)_4]^+$. g) λ_{max}=515 nm. h) The yield of $[(NH_3)_5Co(fum)Co(NH_3)_5]^{4+}$. i) The yield of $[(NH_3)_5Co(male)Co(NH_3)_5]^{4+}$. j) λ_{max}=505 and 345 nm. k) The yield was calculated on the assumption that the species is a monomer. l) λ_{max}=508 and 353 nm. m) λ_{max}=509 and 353 nm. n) λ_{max}=512 and 354 nm. p) λ_{max}=504 and 350 nm. q) For fum system, 1.0 M CH_3CO_2H-1.0M CH_3CO_2Na buffer solution was used. r) For fum system, 1 M HCl was used.

TABLE 6. NUMERICAL DATA FOR THE IR AND RAMAN BANDS OF OXALATE IONS IN VARIOUS COMPOUNDS[a]

Free $C_2O_4^{2-}$ [b]		$[(NH_3)_5Co(ox)-Co(NH_3)_5]^{4+}$		$[(NH_3)_5Cr(ox)-Cr(NH_3)_5]^{4+}$ [c]	$[(NH_3)_5Co(ox)Co(NH_3)_4-(H_2O)]^{4+}$ [d]
IR	Raman	IR[e]	Raman	IR	IR
	1664 s (b_{1g})			1705 s	1721 ms, 1701 s
1627 s (b_{2u})		1625 s		1620 m, 1680 s	1629 vs, 1670 ms
	1450 s, 1485 s (a_g)	1435 w	1438 s	1395 s,	1430 s, 1439 vs
1338 s (b_{3u})		1302 s		1240 s	1250 m, 1276 ms

a) vs=Very strong; s=strong; m=moderate; w=weak. Numerical values are wave numbers/cm^{-1}. b) From Ref. 20. c) From Ref. 21. d) From Ref. 22. e) Deuterated sample.

and characterized in two laboratories.[21,22] The IR spectral patterns of these complexes are quite different from that of $[(NH_3)_5Co(ox)Co(NH_3)_5]^{4+}$. The symmetry of the oxalate ion in $[(NH_3)_5Cr(ox)Cr(NH_3)_5]^{4+}$ has been assigned to C_{2v}[21] and that in $[(NH_3)_5Co(ox)-Co(NH_3)_4(H_2O)]^{4+}$, to C_{2v} or C_2.[23]

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2) Abbreviations used in this paper are as follows: dic= dicarboxylate; ox=$O_2CCO_2^{2-}$; malo=$O_2CCH_2CO_2^{2-}$; suc= $O_2CCH_2CH_2CO_2^{2-}$; pim=$O_2C(CH_2)_5CO_2^{2-}$; fum=*trans*-$O_2CCH{=}CHCO_2^{2-}$; male=*cis*-$O_2CCH{=}CHCO_2^{2-}$.

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7) Under the present experimental conditions, the pentaaminecobalt(III)–ox complex shows two bands on the Sephadex column (see Fig. 1). This may arise from the fact that $[Co(Hox)(NH_3)_5]^{2+}$ is rather strongly acidic ($pK_a=2.06$)[8] and the complex is present as the equilibrium mixture of $[Co(Hox)(NH_3)_5]^{2+}$ and its conjugate base form, $[Co(ox)(NH_3)_5]^+$. Restricted supply of acid during the elution prevents interconversion between these two forms.

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9) For the elution of $[(NH_3)_5Co(fum)Co(NH_3)_5]^{4+}$, 1 M CH_3CO_2H–1 M CH_3CO_2Na buffer solution was used to avoid crystallization of the perchlorate salt in the column. When a small amount of $HClO_4$ was added to the eluate which was then evaporated, the desired perchlorate salt was obtained.

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