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Trimethylenediamine Complexes. V.[1] Preparative and Kinetic Studies on the Reactions of (Ethylenediamine)tetranitro- and Tetranitro(trimethylenediamine)-cobaltates(III) with Several Nucleophiles

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Substitution reactions of a nitrite ligand in $Co(NO_2)_4(en\ or\ tn)^-$ with NH_3, py, N_3^-, and NCS^- have been investigated. The product trinitro complexes were isolated and their geometrical structures were assigned on the basis of NMR data. The preparation method for the two conformational isomers of *mer*-$Co(NO_2)_3NH_3(en)$ was established. The kinetic data of substitution with azide were analyzed according to the **D** mechanism. The relative nucleophilicity of ligands towards $Co(NO_2)_3(AA)$ is in the order: $OH^- \gg N_3^- > NO_2^-$, CH_3COO^-, $NCS^- \gg H_2O > Cl^-$, I^-. Dinitro complexes, $[Co(NO_2)_2(phen)(en\ or\ tn)]NO_2 \cdot H_2O$ and $K[Co(NO_2)_2(ox)(tn)]$ were also prepared.

In a previous paper[1] the acid and base hydrolysis reactions of (diamine)tetranitrocobaltates(III), $Co(NO_2)_4(AA)^-$, where AA is ethylenediamine (en) or trimethylenediamine (tn), were reported to proceed *via* the **D** mechanism with $Co(NO_2)_3(AA)$ as a common intermediate, and the relative reactivity towards the five-coordinate intermediate was found to be in the order: $OH^- \gg NO_2^- \gg H_2O$. The present paper is concerned with preparation and characterization of $Co(NO_2)_3X(AA)$ ($X=NH_3$, py, N_3^-, or NCS^-) and other related complexes, and also with competitive reactions of some nucleophiles with $Co(NO_2)_3(AA)$.

Experimental

Preparation of Complexes. Potassium Tetranitro(ethylenediamine or trimethylenediamine)cobaltate(III), $K[Co(NO_2)_4(AA)]$: These complexes were prepared by the literature method[2] and recrystallized twice from water–methanol. The trimethylenediamine complex was obtained as a hemihydrate in a 46% yield.[1]

Trinitro(pyridine)(ethylenediamine or trimethylenediamine)cabalt(III), $Co(NO_2)_3(py)(AA)$: In an aqueous solution (20 ml) $K[Co(NO_2)_4(en)]$ (1.0 g) was allowed to react with pyridine (0.25 ml) at 60 °C for 1 h. The mixture was then cooled with ice-water and a precipitate (monohydrate) was filtered and washed with methanol. The yield was 19% (0.2 g). The tn complex (anhydrous) was also obtained by a similar reaction at 60 °C for 30 min in a 42% (0.4 g) yield.

The Yellow Form and Brown Form of Ammine(ethylenediamine)-trinitrocobalt(III), $Co(NO_2)_3NH_3(en)$: To a solution (20 ml) of $K[Co(NO_2)_4(en)]$ (1 g) was added 28% aqueous ammonia (0.41 ml) and the mixture was stirred at 60 °C. After *ca.* 45 min white amorphous powder began to deposit on the wall around the liquid surface. On further heating yellow crystallites gradually increased. After reaction for about 2 h the mixture was cooled with ice. The precipitate was filtered and washed with methanol. The yield was 25% (0.2 g).

When the above reaction mixture was cooled with ice before the white powder appeared, a brown precipitate was produced, which was filtered and washed with methanol. The yield was also 25% (0.2 g).

Amminetrinitro(trimethylenediamine)cobalt(III), $Co(NO_2)_3NH_3(tn)$: The reaction of $K[Co(NO_2)_4(tn)] \cdot 1/2H_2O$ with ammonia in the same composition as above at 60 °C for about 20 min afforded a yellow precipitate. Only one kind of product was obtained in a 38% (0.3 g) yield in this case.

Potassium Azido(ethylenediamine)trinitrocobaltate(III), $K[Co(NO_2)_3(N_3)(en)]$: $K[Co(NO_2)_4en]$ (1 g) was allowed to react with sodium azide (0.19 g) in aqueous solution (55 ml) at 60 °C for 75 min. After cooling in ice–water, potassium iodide (*ca.* 5 g) was added to the solution, and a small amount of precipitate was filtered. Ethanol (*ca.* 10 ml) was added to the filtrate, and the solution was kept in a refrigerator for several days. Crude crystals of Isomer A (0.3 g) was separated and recrystallized from methanol–water (5:1) in a refrigerator (below 0 °C). The final yield was 8% (0.08 g).

After the prolonged reaction in aqueous solution (25 ml) at 60 °C for 2 h and addition of potassium iodide at 0 °C as described above, an equal volume (*ca.* 25 ml) of methanol was added to the solution and the mixture was kept in a refrigerator overnight. A red powder (0.1 g), which gave Isomer A on recrystallization, was filtered and the filtrate was kept in a refrigerator for 2—3 months to deposit dark red crystals of Isomer B, which were separated and washed with methanol. The yield was 35% (0.35 g).

Potassium Azidotrinitro(trimethylenediamine)cobaltate(III) $K[Co(NO_2)_3N_3(tn)]$: In aqueous solution (15 ml) at 60 °C $K[Co(NO_2)_4(tn)] \cdot 1/2H_2O$ (1.0 g) was allowed to react with sodium azide (0.18 g) for 20 min. After filtration, potassium iodide (*ca.* 0.5 g) was added to the filtrate followed by 15 ml of methanol and the mixture was kept in a refrigerator for a week. A dark red precipitate was recrystallized from methanol–water (5:1 by volume). The final yield was 19% (0.2 g) and the compound was analyzed to contain two molecules of lattice water and proved to be a mixture of fac and mer isomers (Table 2). When the filtrate, which had been separated from the crude reaction product, was kept in a refrigerator for a few weeks, dark red crystals deposited on the glass wall in a 10% yield (0.1 g). This specimen was a monohydrate of the mer isomer as will be described in Results. Then the separation of a mixture of the geometrical isomers was tried. A solution of $K[Co(NO_2)_3N_3(tn)] \cdot 2H_2O$ was passed through a column ($\phi 1 \times 10$ cm) containing an anion exchanger QAE-Sephadex A-25 which was cooled by ice–water circulating in a jacket. Two adsorbed bands were observed and eluted with an aqueous solution ($0.4\ mol \cdot l^{-1}$) of sodium chloride. The early portion of eluates containing the lower band showed an absorption spectrum which is identical with that of $K[Co(NO_2)_3N_3(tn)] \cdot H_2O$, and is concluded to be the mer isomer. The upper adsorbed band may be attributed to the fac isomer and showed an absorption maximum at 470 nm with $\varepsilon = 380\ l \cdot mol^{-1} \cdot cm^{-1}$. The cobalt content in the eluate was determined by the photochemical reduction to cobalt(II) followed by the spectrophotometric analysis of the latter as the tetrakis (isothiocyanato)cobaltate(II) complex.[3]

Potassium Isothiocyanatotrinitro(trimethylenediamine)cobaltate(III) Monohydrate, $K[Co(NO_2)_3NCS(tn)]\cdot H_2O$: The reaction of $K[Co(NO_2)_4(tn)]\cdot 1/2H_2O$ (0.5 g) with potassium thiocyanate (0.133 g) in aqueous solution (20 ml) at 60 °C was conducted for 15—20 min. To the solution cooled in ice–water was added potassium iodide (*ca.* 5 g) followed by an equivolume of methanol and the mixture was kept in a refrigerator for 2—3 days to precipitate small reddish plates in a 15% (0.08 g) yield.

Dinitro(1,10-phenanthroline)(ethylenediamine or trimethylenediamine)cobalt(III) Nitrite Monohydrate, $[Co(NO_2)_2(phen)(AA)]NO_2\cdot H_2O$: To an aqueous solution (20 ml) of $K[Co(NO_2)_4(AA)]$ (1 g) at 60 °C was added a small quantity of methanol solution containing 1,10-phenanthroline (0.579 g) and the mixture was stirred for about 5 min to deposit red-brown (AA=en) or brown (AA=tn) crystals in a 60% (0.8 g) or a 70% (0.9 g) yield, respectively.

Potassium Dinitro(oxalato)(trimethylenediamine)cobaltate(III), $K[Co(NO_2)_2(ox)(tn)]$: A solution (20 ml) of oxalic acid (2 g) was added to a suspension of $K[Co(NO_2)_4(tn)]\cdot 1/2H_2O$ (5 g) in water (30 ml), and the mixture was kept at 60 °C under reduced pressure to vaporize the solvent. The concentrate was filtered during hot and the filtrate was kept standing at room temperature. The product was filtered and recrystallized from water containing potassium nitrite. The method is an extension of that used for preparation of the corresponding en complex,[4] and the yield was 4% (0.2 g) in the present tn case.

Measurements. The hydrogen ion activity in solution was determined by means of a Beckman "Century" SS-1 pH meter with a Beckman 39301 glass electrode and a Beckman 39400 calomel electrode, and converted to the hydrogen ion concentration by virtue of the activity coefficient $f_H=0.83$ at 25 °C and $\mu=0.1$.[5] Absorption spectra were recorded on a Hitachi EPS-3T spectrophotometer and NMR spectra on a JEOL C-60HL with tetramethylsilane as an internal reference. IR spectra were measured in Nujol with JASCO IR-E (4000—600 cm^{-1}) and Hitachi EPI-L (700—200 cm^{-1}) Infrared Spectrophotometers.

The kinetic measurement was performed by the spectrophotometric method. In a dark measuring flask were placed desired amounts of a sodium nitrite solution and a NaX solution ($X^-=Cl^-$, I^-, N_3^-, NCS^-, or CH_3COO^-). Solutions of perchloric acid and sodium perchlorate were added to the mixture to adjust pH and maintain the ionic strength at 0.1. Into the flask kept in a thermostat at 25 °C was poured a solid specimen of $K[Co(NO_2)_4(AA)]$ by the help of thermostated pure water, and a 100 ml reaction mixture was made up. The complex was rapidly dissolved on agitation and the reaction started. Aliquots were pipetted at appropriate time intervals and spectra were recorded over the 400—550 nm region.

Results and Discussion

In order to examine the possibility of studying the competitive reactions of some nucleophiles with the five-coordinate species $Co(NO_2)_3(AA)$ postulated as an intermediate in the hydrolysis reactions of $Co(NO_2)_4(AA)^-$, the reaction products $Co(NO_2)_3X(AA)$ ($X=NH_3$, py, N_3^-, or NCS^-) and the related complexes $Co(NO_2)_2(BB)(AA)$ (BB=phen or an oxalate anion) were prepared (Table 1).

Characterization of Newly Prepared Complexes. $K[Co(NO_2)_3N_3(en)]$, *A-form and B-form*: As was described in Experimental section, two forms of the azido(ethylenediamine)trinitrocobaltate(III) were obtained. Each of them shows a single absorption maximum in the visible region in aqueous solution at 2 °C, but the exact position is a little different: A, $\lambda_{max}=466$ nm ($\varepsilon=508$); *B*, $\lambda_{max}=480$ nm ($\varepsilon=480$). The spectra in the ultraviolet region are also different: A, $\lambda_{max}=346$ ($\varepsilon=8.10\times10^3$) and 258 nm ($\varepsilon=1.59\times10^4$); B, $\lambda_{max}=316$ ($\varepsilon=1.09\times10^4$) and 259 nm ($\varepsilon=1.94\times10^4$). The most remarkable difference in the IR spectra is noticed on the $\delta(NH_2)$ band. A-form shows a broad band at 1574 cm^{-1}, while B-form two distinct bands at 1593 and 1571 cm^{-1}. Thus the two forms seem to constitute a couple of geometrical isomers, *viz.* facial and meridional, such as depicted in Fig. 1.

The chelate rings in both ethylenediamine and trimethylenediamine complexes are known to undergo a rapid interconversion among possible conformations

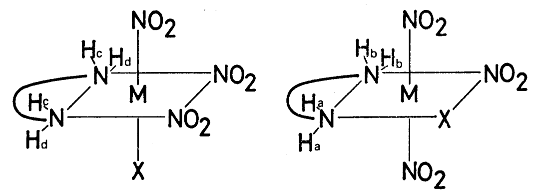
Table 1. Newly prepared complexes

Compound	Found (%) C	Found (%) H	Found (%) N	Calcd (%) C	Calcd (%) H	Calcd (%) N
$K[Co(NO_2)_3N_3(en)]$				7.10	2.38	33.14
A-form	7.18	2.64	32.58			
B-form	7.11	2.56	33.52			
$Co(NO_2)_3NH_3(en)$				8.77	4.05	30.66
Yellow form	8.79	4.06	30.39			
Brown form	8.59	4.08	30.59			
$Co(NO_2)_3(py)(en)\cdot H_2O$	22.99	3.84	24.07	23.74	4.27	23.73
$[Co(NO_2)_2(phen)(en)]NO_2\cdot H_2O$	36.91	3.95	21.95	36.94	3.98	21.55
$K[Co(NO_2)_3N_3(tn)]\cdot 2H_2O$	9.72	2.97	28.70	9.28	3.64	28.86
$K[Co(NO_2)_3N_3(tn)]\cdot H_2O$	9.19	3.27	30.18	9.73	3.27	30.27
$K[Co(NO_2)_3NCS(tn)]\cdot H_2O$	11.92	3.07	21.56	12.44	3.13	21.76
$Co(NO_2)_3NH_3(tn)$	12.64	4.53	29.63	12.51	4.55	29.17
$Co(NO_2)_3(py)(tn)$	26.75	4.28	23.81	27.44	4.32	23.99
$[Co(NO_2)_2(phen)(tn)]NO_2\cdot H_2O$	38.17	4.22	21.40	38.39	4.30	20.89
$K[Co(NO_2)_2(ox)(tn)]$	16.73	2.98	15.69	17.05	2.86	15.91

Table 2. Absorption maxima (the first band) and NMR data[a)]

Compound	λ_{max} nm	ε $l \cdot mol^{-1} \cdot cm^{-1}$	Chemical shift/ppm NH_2[b)]	$CH_2(\alpha)$[b)]	$CH_2(\beta)$[b)]	Others	Proposed structure
$K[Co(NO_2)_4(en)]$	430	494	4.27	c)			
$K[Co(NO_2)_3N_3(en)]$							
A-form	466	508	4.06	2.40			fac
B-form	480	480	4.19, 4.25	2.43			mer
$Co(NO_2)_3NH_3(en)$	430	282	4.43(1),[d)] 4.73(1)[e)]	c)		3.58(NH_3)	mer
$Co(NO_2)_3(py)(en) \cdot H_2O$	439	437	4.73	2.63		7.5—8.7(py)	fac
$[Co(NO_2)_2(phen)(en)]NO_2 \cdot H_2O$	425	345(sh)	4.28, 4.55, 4.83	c)		7.6—9.3(phen)	cis
$K[Co(NO_2)_4(tn)] \cdot 1/2H_2O$	435	438	4.20(2)	2.31(2)	1.43(1)		
$K[Co(NO_2)_3N_3(tn)] \cdot 2H_2O$	481	432	3.93(2/3), 4.23(4/3)	2.26+2.32(2)	1.40+1.46(1)		fac+mer
$K[Co(NO_2)_3N_3(tn)] \cdot H_2O$	481	487	3.93(1), 4.23(1)	2.26(2)	1.40(1)		mer
$K[Co(NO_2)_3NCS(tn)] \cdot H_2O$	454	379	4.24(2)	2.34(2)	1.45(1)		fac
$Co(NO_2)_3NH_3(tn)$	437	256	4.30(1),[d)] 4.58(1)[e)]	2.18(2)	1.51(1)	3.60(NH_3)	mer
$Co(NO_2)_3(py)(tn)$	450	302	f)				
$[Co(NO_2)_2(phen)(tn)]NO_2 \cdot H_2O$	450	278(sh)	4.12, 4.40	2.03(1), 2.33(1)	1.44(1)	7.5—9.3(phen)	cis
$K[Co(NO_2)_2(ox)(tn)]$	483	202					

a) The electronic spectra were measured in aqueous solutions at 2 °C, and NMR spectra in DMSO-d_6 at room temperature with TMS as an internal reference. b) Figures in parentheses show the relative area. c) Masked by the impurity band. d) NH_2 trans to the NO_2 ligand. e) NH_2 trans to the NH_3 ligand. f) Not stable in DMSO at room temperature.



facial meridional

Fig. 1. Geometrical isomers of the $Co(NO_2)_3X(AA)$ complex.

in solution.[6)] Then both of the (diamine)tetranitrocobaltates(III) have a pseudo C_2 axis and the amine protons are all equivalent. However, the trinitro complex has a lower symmetry and the amine protons are no longer equivalent. In *mer*-$Co(NO_2)_3X(AA)$ one amine group occupies a site trans to a nitro ligand and the other to X. Different chemical shifts will be observed for NH_2^a and NH_2^b protons and the separation between them will depend on the nature of X.

In the case of *fac*-$Co(NO_2)_3X(AA)$ both amine groups are trans to the nitro ligands, but the magnetic environments of H^c and H^d are not strictly equal due to nonequivalence of the nitro and X ligands, although the difference in chemical shifts of the two type of protons will be smaller than in the mer form. Thus when a couple of the geometrical isomers are available, the proton NMR spectra will be helpful in identifying them.

As is listed in Table 2, the spectrum of A-form in DMSO-d_6 exhibits a broad band of amine protons at 4.06 ppm from TMS, whereas the amine signal of B-form shows two maxima at 4.19 and 4.25 ppm, suggesting that A-form is facial and B-form is meridional. Interconversion between the two forms cannot be studied since the complex is liable to hydrolysis and other ligand substitution reactions.

The corresponding tn complex, $K[Co(NO_2)_3N_3(tn)] \cdot 2H_2O$ seems to be a mixture of mer and fac isomers, since the amine protons show two resonances at 3.93 and 4.23 ppm with the area ratio of 1: 2. The signals assignable to the $CH_2(\alpha)$ and $CH_2(\beta)$ protons in NH_2-$CH_2(\alpha)CH_2(\beta)CH_2(\alpha)NH_2$ also have two double maxima at 2.26, 2.32 ppm and 1.40, 1.46 ppm, respectively, maintaining the area ratio of 2: 1. On the other hand the monohydrate species which separated from the mother liquor exhibits a simpler spectrum, the amine protons resonating at 3.93 and 4.23 ppm in the area ratio of 1: 1 and the methylene protons at 2.26 and 1.40 ppm in the area ratio of 2: 1. Then the monohydrate is considered to be meridional, and the fac isomer, which has not been isolated, may be responsible for the signals at 4.23 (NH_2), 2.32 (α-CH_2) and 1.46 (β-CH_2) ppm. These chemical shifts nearly coincide with those for $K[Co(NO_2)_3NCS(tn)] \cdot H_2O$.

$Co(NO_2)_3NH_3(en)$: The compound exists in two forms which have different crystal habits, colors and IR spectra in Nujol, but give identical absorption spectra in solution. Both of the brown and yellow forms were concluded by MacDermott and Barfoed[7a)] to be meridional on the basis of NMR spectra. This conclusion was ascertained by X-ray analysis.[8)] The essential difference is the conformations of the nitro groups, and the two forms were termed rotational or conformational isomers.

This interesting compound was prepared by other methods and a mixture of two forms in an unfixed ratio was obtained in each case.[7a)] The reproducible synthetic method to prepare each isomer exclusively has not been established.[7b)] Now it is possible to obtain either form selectively by controlling the temperature of crystallization. As was described in Experimental section, if a solution containing $K[Co(NO_2)_4(en)]$ and ammonia is kept at 60 °C to allow deposition of the product, the yellow form is obtained solely. On the other hand, when he reaction mixture is rapidly cooled with ice prior to deposition of crystallites, the brown form is produced exclusively. The yellow form looks more stable than the brown form, and it is easier to convert the brown form into the yellow isomer than the opposite transformation in the recrystallization processes.

The corresponding tn complex, $Co(NO_2)_3NH_3(tn)$ was prepared under various conditions, but only one form has been isolated so far. The NMR spectra were assigned by reference to those of $Co(NO_2)_3NH_3(en)$,7a) and the meridional structure is inferred.

$K[Co(NO_2)_3NCS(tn)]\cdot H_2O$: The linkage isomerism displayed by the thiocyanate ion in metal complexes has been amply documented,9) and IR spectra are utilized as the convenient and useful technique for structural assignments.10) In the case of cobalt(III) complexes, $[CoNCS(NH_3)_5](ClO_4)_2$11) and $K_3[CoNCS(CN)_5]$12) exhibit broad $\nu(CN)$ bands at 2125 and 2065 cm^{-1}, and the $\nu(CS)$ bands at 806 and 810 cm^{-1}, respectively, whereas $[CoSCN(NH_3)_5](ClO_4)_2$11) and $K_3[CoSCN(CN)_5]$13) show sharp $\nu(CN)$ bands at 2100 and 2110 cm^{-1}, and weak $\nu(CS)$ bands at 710 and 719 cm^{-1}, respectively. In the IR spectrum of $K[Co(NO_2)_3NCS(tn)]\cdot H_2O$, a strong band at 2120 cm^{-1} assignable to the $\nu(CN)$ band is broad in the lower frequency side and a small peak at 825 cm^{-1} accompanying a sharp strong $\delta(NO_2)$ band at 835 cm^{-1} may be attributed to the $\nu(CS)$ vibration. Thus the thiocyanate ligand in $K[Co(NO_2)_3NCS(tn)]\cdot H_2O$ is considered to be N-bonded rather than S-bonded.

The NMR spectrum of this complex in DMSO-d_6 shows a single broad peak at 4.24 ppm which is ascribed to the amine protons, suggesting that the complex has a facial structure. The reaction of $K[Co(NO_2)_4(en)]$ with an equimolar amount of potassium thiocyanate in water has been carried out to prepare $K[Co(NO_2)_3NCS(en)]$, but a product of satisfactory purity has not yet been obtained.

Other Complexes: $[Co(NO_2)_3py(en)]\cdot H_2O$ shows a single peak of amine protons at 4.73 ppm and seems to have a facial structure. The corresponding tn complex is not stable enough in DMSO to allow the NMR measurement at room temperature. For the $CoX_2(AA)_2$ complexes too, the NMR spectra are usually most helpful in assigning the geometrical structure. The amine protons of a trans isomer will resonate as a single peak, whereas those of a cis isomer will exhibit two or more peaks.14–16) Both of $[Co(NO_2)_2(phen)(en)]NO_2\cdot H_2O$ and $[Co(NO_2)_2(phen)(tn)]NO_2\cdot H_2O$, which were produced by the reactions of the tetranitro(diamine) complexes with 1,10-phenanthroline, show two broad bands attributable to the amine protons, and seem to have the cis structure. Recently properties of *cis*-$K[Co(NO_2)_2(ox)(en)]$ were reported by Ito and Shibata.17) The structural assignment of $K[Co(NO_2)_2(ox)(tn)]$ now prepared is not unambiguous as yet.

In Table 2 are collected the absorption maxima (the first band) together with the NMR data. As was noted in previous papers,18) the first band of each trimethylenediamine complex lies at a little longer wavelength side than that of the corresponding ethylenediamine complex, indicating that the ligand field of trimethylenediamine is weaker than that of ethylenediamine.

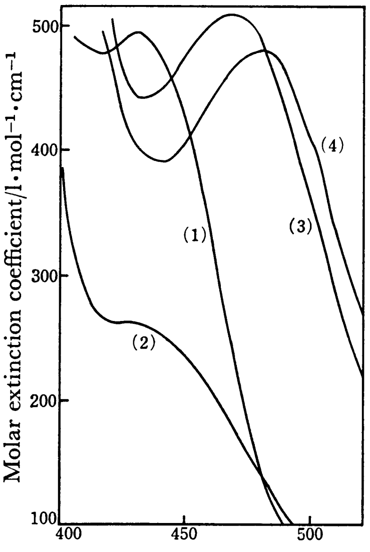


Fig. 2. The absorption spectra in the 400—550 nm region of $K[Co(NO_2)_4(en)]$ (1), $Co(NO_2)_3(H_2O)(en)$ (2), *fac*-$K[Co(NO_2)_3N_3(en)]$ (3), and *mer*-$K[Co(NO_2)_3N_3(en)]$ (4) in aqueous solutions at 2 °C.

Kinetic Studies. *The Reactions of (Diamine)tetranitrocobaltates(III) with Azide Ions*: The absorption spectra in the 400—550 nm region of $K[Co(NO_2)_4(en)]$, $Co(NO_2)_3(H_2O)(en)$, *fac*- and *mer*-$K[Co(NO_2)_3N_3(en)]$ in aqueous solutions at 2 °C are displayed in Fig. 2. The spectral change accompanying the reaction of $Co(NO_2)_4(en)^-$ with excess azide ions exhibits two isosbestic points at 424 and 443 nm up to about 70% conversion. These two wavelengths correspond to the isosbestic points of $Co(NO_2)_4(en)^-$ and *fac*-$Co(NO_2)_3N_3(en)^-$, indicating that the facial isomer is primarily produced in this substitution reaction. The reaction was followed spectrophotometrically by measuring the

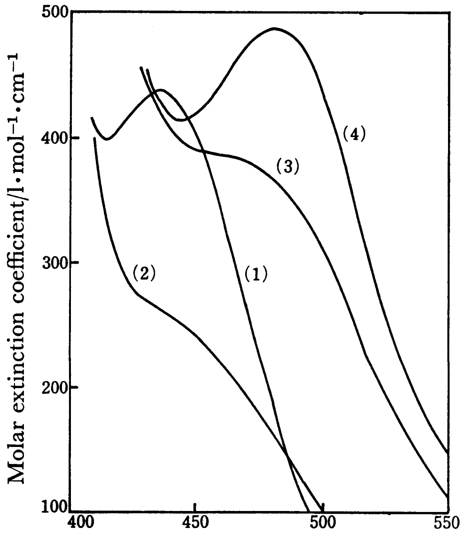


Fig. 3. The absorption spectra in the 400—550 nm region of $K[Co(NO_2)_4(tn)]\cdot 1/2H_2O$ (1), $Co(NO_2)_3(H_2O)(tn)$ (2), *fac*-$Co(NO_2)_3N_3(tn)^-$ (3), and *mer*-$K[Co(NO_2)_3N_3(tn)]\cdot H_2O$ (4) in aqueous solutions at 2 °C.

absorbance at 476 nm. The first order rate law was obeyed up to *ca.* 70% conversion in the presence of excess nitrite and azide ions.

Figure 3 shows the visible absorption spectra of *mer*-$K[Co(NO_2)_3N_3(tn)]\cdot H_2O$ and *fac*-$Co(NO_2)_3N_3(tn)^-$ which was isolated in solution, together with those of $K[Co(NO_2)_4(tn)]\cdot 1/2H_2O$ and $Co(NO_2)_3(H_2O)(tn)$. The change of spectrum accompanying the reaction of $Co(NO_2)_4(tn)^-$ with excess azide ions shows two isosbestic points at 432 and 452 nm up to *ca.* 80% conversion which coincide exactly with the isosbestic points of $Co(NO_2)_4(tn)^-$ and *fac*-$Co(NO_2)_3N_3(tn)^-$, revealing that the facial isomer of the trinitroazido complex is produced specifically in the case of the trimethylenediamine complex, too. The pseudo first order plot based on the absorbance at 484 nm also gives a good straight line through the duration of 80% reaction.

$$Co(NO_2)_4(AA)^- + N_3^- \xrightarrow{k_{obsd}} Co(NO_2)_3N_3(AA)^- + NO_2^- \qquad (1)$$

The pseudo first order rate constants (k_{obsd}) of Reaction 1 decrease with increase in the nitrite ion concentration. According to the mechanism proposed in a previous paper,[1)] the ligand substitution reactions of $Co(NO_2)_4(AA)^-$ should proceed *via* a five-coordinate intermediate.

$$Co(NO_2)_4(AA)^- \underset{k_{NO_2}}{\overset{k_{-NO_2}}{\rightleftarrows}} Co(NO_2)_3(AA) + NO_2^- \qquad (2)$$

$$Co(NO_2)_3(AA) + H_2O \underset{k_{-H_2O}}{\overset{k_{H_2O}}{\rightleftarrows}} Co(NO_2)_3(H_2O)(AA) \qquad (3)$$

$$Co(NO_2)_3(AA) + OH^- \xrightarrow{k_{OH}} Co(NO_2)_3(OH)(AA)^- \qquad (4)$$

$$Co(NO_2)_3(AA) + N_3^- \xrightarrow{k_{N_3}} Co(NO_2)_3(N_3)(AA)^- \qquad (5)$$

Since the isosbestic points of the tetranitro, and trinitroazido complexes are maintained in the present experimental conditions, the concentration of trinitroaqua complexes, of which spectra are included in Figs. 2 and 3, is negligible and the reverse step of Eq. 3 may be ignored. Assuming a steady state for $Co(NO_2)_3(AA)$, the pseudo first order rate constant of the azide complex formation may be expressed by

$$k_{obsd} = \frac{k_{-NO_2}k_{N_3}[N_3^-]}{k_{H_2O} + k_{OH}[OH^-] + k_{NO_2}[NO_2^-] + k_{N_3}[N_3^-]}, \qquad (6)$$

which is transformed into Eq. 7.

$$\frac{k_{-NO_2}}{k_{obsd}} = 1 + \frac{k_{H_2O} + k_{OH}[OH^-]}{k_{N_3}[N_3^-]} + \frac{k_{NO_2}[NO_2^-]}{k_{N_3}[N_3^-]}. \qquad (7)$$

In a previous paper,[1)] the value of k_{-NO_2} was obtained as $(2.08\pm0.01)\times10^{-4}$ and $(9.27\pm0.03)\times10^{-4}\ s^{-1}$ for AA=en and tn, respectively, at 25 °C and $\mu=0.1$. Thus, if k_{obsd} is determined at various nitrite concentrations with constant azide and hydrogen ion concentrations, the plot of k_{-NO_2}/k_{obsd} against the nitrite concentration will give a straight line with

$$\text{slope} = k_{NO_2}/k_{N_3}[N_3^-], \qquad (8)$$

$$\text{intercept} = 1 + (k_{H_2O} + k_{OH}[OH^-])/k_{N_3}[N_3^-]. \qquad (9)$$

In fact the observed rate data give rise to straight lines which are shown in Fig. 4. Since nitrite and azide ions were used in large excess as compared with the complex anions, the concentrations of added nitrite and azide, c_{NO_2} and c_{N_3}, were used for the calculation instead of $[NO_2^-]$ and $[N_3^-]$. From the slopes of the straight lines, the values of k_{NO_2}/k_{N_3} were calculated to be 0.65 ± 0.02 and 0.25 ± 0.04 for AA=en and tn, respectively, at 25 °C and $\mu=0.1$.

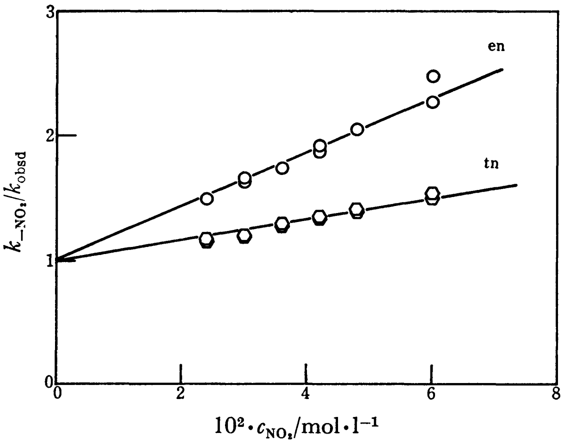


Fig. 4. The linear plots of rate data for the reaction (1) referring to Eq. 7: $c_M=1.169\times10^{-3}\ mol\cdot l^{-1}$ (in the case of AA=en) or $1.369\times10^{-3}\ mol\cdot l^{-1}$ (AA=tn), $c_{N_3}=3.000\times10^{-2}\ mol\cdot l^{-1}$, pH=6.5—6.7, $\mu=0.1$, 25 °C.

In Fig. 4 both of the two straight lines intercept the ordinate at 1.0, indicating that for both systems

$$(k_{H_2O} + k_{OH}[OH^-])/k_{N_3}[N_3^-] \ll 1. \qquad (10)$$

In the studies on the hydrolysis reactions of $Co(NO_2)_4(AA)^-$, k_{H_2O}/k_{NO_2} was reported to be $(2.15\pm0.14)\times10^{-3}$ and $(1.79\pm0.13)\times10^{-2}\ mol\cdot l^{-1}$ for AA=en and tn, respectively, at 25 °C and $\mu=0.1$.[1)] Thus $k_{H_2O}/k_{N_3}=(1.39\pm0.13)\times10^{-3}$ and $(4.4\pm1.0)\times10^{-3}\ mol\cdot l^{-1}$ for AA=en and tn, respectively. The concentration of azide added, c_{N_3}, is $3\times10^{-2}\ mol\cdot l^{-1}$ and hence $k_{H_2O}/k_{N_3}[N_3^-]=0.046$ (AA=en) and 0.14 (AA=tn), nearly satisfying a part of Eq. 10.

Since pK_a of hydrazoic acid is 4.44 at 25 °C and $\mu=1\ mol\cdot l^{-1}(NaClO_4)$,[19)] pH of the reaction system was kept in the 6.5—6.7 region in order to prevent participation of HN_3, and thus contribution of the base hydrolysis (Eq. 4) must be taken into account. In the previous studies of hydrolysis,[1)] k_{OH}/k_{NO_2} was estimated to be $\gg5\times10^3$ for both the en and tn systems. Now Eq. 10 gives the upper limit of k_{OH}. In order to satisfy Eq. 10, the condition $k_{OH}\leq0.1\ k_{N_3}[N_3^-]/[OH^-]$ must be met. Since $[N_3^-]/[OH^-]\fallingdotseq6\times10^5$ in the present experiments, $k_{OH}/k_{N_3}\leq6\times10^4$, leading to the estimation: $9.3\times10^4\geq k_{OH}/k_{NO_2}\gg5\times10^3$ for AA=en and $2.4\times10^5\geq k_{OH}/k_{NO_2}\gg5\times10^3$ for AA=tn. In this way the relative nucleophilicity of OH^-, NO_2^-, and N_3^- toward $Co(NO_2)_3(AA)$ is estimated as listed in Table 3 with reference to H_2O.

The Reactions of (Diamine)tetranitrocobaltates(III) with Other Nucleophiles: In the presence of excess nitrite and azide ions, substitution of a nitrite ligand in $Co(NO_2)_4(AA)^-$ with an azide ion seems to proceed to completion, although displacement of the second nitrite ligand

Table 3. Relative nucleophilicity of some ligands toward $Co(NO_2)_3(AA)$ at 25 °C and $\mu=0.1$

AA	H_2O	NO_2^-	N_3^-	OH^-
en	1	$(2.59\pm0.17)\times10^4$	$(4.02\pm0.37)\times10^4$	$\gg1.3\times10^8$ and $\leq2.4\times10^9$
tn	1	$(3.11\pm0.23)\times10^4$	$(1.25\pm0.29)\times10^4$	$\gg1.6\times10^7$ and $\leq7.8\times10^8$

contributes in a later stage of the reaction. On the contrary halide ions such as chloride and iodide cannot replace the nitrite ligand, but give rise to the aqua complex alone. The thiocyanate and acetate ions can compete with water and yields the trinitro(aniono) complex besides the trinitro(aqua) complex, but the quantitative competition ratios are not obtained. The relative nucleophilicity of ligands examined towards $Co(NO_2)_3(AA)$ is in the order: $OH^-\gg N_3^->NO_2^-$, CH_3COO^-, $NCS^-\gg H_2O>Cl^-$, I^-. The order coincides with that of the proton affinity of these ions (except the thiocyanate ion), suggesting that $Co(NO_2)_3(AA)$ is a hard acid.

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