

Five Coordinate Nickel(II) Isothiocyanato and Chloro Complexes of Triazacycloalkanes

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Received March 3, 1976

The new nickel(II) complexes $[Ni(pqr-cy)(NCS)_2]$, $[Ni(pqr-cy)Cl]ClO_4$, and $Ni_2(pqr-cy)_3(ClO_4)_4 \cdot nH_2O$ ($n = 4$ or 5) have been prepared, where $pqr-cy$ is a triazacycloalkane, $\overline{NH(CH_2)_pNH(CH_2)_qNH(CH_2)_r}$, ($p, q = 2, 3$; $r = 2-6$). The isothiocyanato complexes are six-coordinate, NCS-bridged octahedral when t ($= p + q + r$) is small ($t \leq 9$), but they are five-coordinate when t is large ($t \geq 9$). The five-coordination is peculiar and its origin is attributable to blocking of a coordination site by the backbone polymethylene groups of the $pqr-cy$ ligands. Only the ligands with $t=9$ and 10 form the chloro complexes, which are Cl-bridged dimers and are also five-coordinate because of the same steric hindrance. It is worth noting that these five-coordinate nickel(II) complexes are isolated from aqueous solutions. The 2:3 perchlorate complexes are octahedral and available only for the ligands with $t=9$.

Introduction

A number of complexes with reduced coordination numbers (*i.e.* four- or five-coordination) are prepared by using ligands containing bulky substituents on the donor atoms. It is also possible to reduce coordination numbers by blocking of coordination sites with backbone polymethylene groups of ligands, as was found in the nickel(II) and copper(II) complexes of 1,4-diazacycloheptane and 1,5-diazacyclooctane¹⁻³, and 1,5-diazacyclooctane-*N,N'*-diacetic acid⁴. Examples of this type of steric blocking are found only rarely and therefore of very interest. It is expected that similar blocking is of importance in determining the stereochemistry of the complexes of triazacycloalkanes, $\overline{HN(CH_2)_pNH(CH_2)_qNH(CH_2)_r}$, ($p, q = 2, 3$; $r = 2-6$) (abbreviated as $pqr-cy$) as ligands⁵. With these ligands, another type of blocking may also be important; increased ring size may increase the angle at the metal and thereby reduce the coordination number. To verify these assumptions we have prepared a series of nickel(II) isothiocyanato complexes, $[Ni(pqr-cy)(NCS)_2]$ and several chloro complexes, $[Ni(pqr-cy)$

$Cl]ClO_4$, as a part of our continuing study on triazacycloalkane ($pqr-cy$) complexes of transition metals⁵.

Results and Discussion

When an aqueous solution of nickel(II) chloride and $pqr-cy \cdot 3HCl$ was neutralized with sodium hydroxide and then concentrated in the presence of excess sodium perchlorate, the complex formed depends upon the total number t ($= p + q + r$) of backbone methylene groups of the $pqr-cy$ ligand. The bis-type complexes $[Ni(pqr-cy)_2](ClO_4)_2$ are obtained for the ligands with small t (≤ 8) and for 225-cy, as has been reported previously⁵. As the ring sizes of the $pqr-cy$ ligands increase, accommodation of six donor atoms proximate to the central metal ion, however, becomes difficult and bis-type complexes are no longer available. This is attributed to mutual interactions of backbone methylene groups between the two $pqr-cy$ ligands.

The ligands with $t=9$ gave both $[Ni(pqr-cy)Cl]ClO_4$ and $Ni_2(pqr-cy)_3(ClO_4)_4 \cdot nH_2O$ ($n=4$ or 5), and the ligands with $t = 10$ except 226-cy formed only the chloro complexes. The ligands with large t (≥ 11) and 226-cy, however, formed no nickel complex under the above conditions and nickel hydroxide precipitated. These facts suggest that the backbone polymethylene groups produce significant steric hindrance which make coordination of the ligands difficult as t increases.

It is remarkable that, in the presence of excess thiocyanate ion, all the $pqr-cy$ ligands studied here formed the same type of complexes $[Ni(pqr-cy)(NCS)_2]$ without precipitation of nickel hydroxide. It seems that the nature of the anion may be the important factor. The complexes prepared are given in Table I together with their colours and analytical data.

$[Ni(pqr-cy)(NCS)_2]$

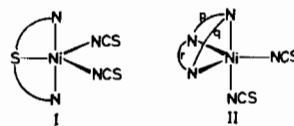
On the basis of the following spectral data, the complexes $[Ni(pqr-cy)(NCS)_2]$ are classified into two distinct groups. The complexes Nos. 1–6 of Table I fall in group *S* and those Nos. 7–13 in group *F*.

TABLE I. Colours and Analytical Data for the Complexes.

Complex	Colour	Analysis, Found (Calcd.) %			
		C	H	N	Other
1 [Ni(222-cy)(NCS) ₂]	Violet	31.83 (31.60)	5.00 (4.97)	23.31 (23.03)	
2 [Ni(223-cy)(NCS) ₂]	Violet	33.80 (33.98)	5.41 (5.39)	22.18 (22.01)	
3 [Ni(224-cy)(NCS) ₂]	Bluish violet	36.09 (36.16)	5.76 (5.77)	21.04 (21.09)	
4 [Ni(233-cy)(NCS) ₂]	Violet	35.99 (36.16)	5.81 (5.77)	21.09 (21.09)	
5 [Ni(234-cy)(NCS) ₂]	Violet- blue	37.98 (38.17)	6.13 (6.11)	20.16 (20.23)	Ni: 16.67 (16.96)
6 [Ni(333-cy)(NCS) ₂]	Blue	38.19 (38.17)	5.94 (6.11)	20.24 (20.23)	
7 [Ni(225-cy)(NCS) ₂]	Violet	37.71 (38.17)	6.14 (6.11)	19.98 (20.23)	
8 [Ni(226-cy)(NCS) ₂]	Violet- blue	39.69 (40.02)	6.35 (6.44)	19.47 (19.44)	
9 [Ni(235-cy)(NCS) ₂]	Bluish violet	39.77 (40.02)	6.32 (6.44)	19.33 (19.44)	
10 [Ni(236-cy)(NCS) ₂]	Bluish violet	41.44 (41.73)	6.65 (6.73)	18.42 (18.71)	
11 [Ni(334-cy)(NCS) ₂]	Greenish blue	39.86 (40.02)	6.54 (6.44)	19.56 (19.44)	Ni: 16.10 (16.30)
12 [Ni(335-cy)(NCS) ₂]	Blue	41.29 (41.73)	6.59 (6.73)	18.53 (18.71)	
13 [Ni(336-cy)(NCS) ₂]	Blue	43.65 (43.31)	7.01 (7.01)	18.01 (18.04)	Ni: 14.87 (15.12)
14 [Ni(225-cy)Cl]ClO ₄	Greenish blue	28.91 (29.62)	5.70 (5.80)	11.45 (11.51)	Cl: 9.84 (9.72)
15 [Ni(234-cy)Cl]ClO ₄	Green	29.27 (29.62)	5.82 (5.80)	11.33 (11.51)	
16 [Ni(235-cy)Cl]ClO ₄	Bluish green	31.69 (31.70)	6.42 (6.12)	10.82 (11.09)	
17 [Ni(333-cy)Cl]ClO ₄	Green	29.99 (29.62)	5.78 (5.80)	11.62 (11.51)	
18 [Ni(334-cy)Cl]ClO ₄	Green	31.77 (31.70)	6.17 (6.12)	11.24 (11.09)	Cl: 9.42 (9.30)
19 Ni ₂ (225-cy) ₃ (ClO ₄) ₄ · 4H ₂ O	Blue	29.39 (29.45)	6.34 (6.50)	12.01 (11.45)	H ₂ O: 6.25 (6.54)
20 Ni ₂ (234-cy) ₃ (ClO ₄) ₄ · 5H ₂ O	Blue	29.07 (28.98)	6.28 (6.57)	10.73 (11.26)	H ₂ O: 7.80 (8.05)
21 Ni ₂ (333-cy) ₃ (ClO ₄) ₄ · 5H ₂ O	Blue	29.21 (28.98)	6.23 (6.57)	10.84 (11.26)	H ₂ O: 7.97 (8.05)

The electronic spectra of the solid group *S* complexes (Figure 1 and Table II) can be assigned based on six-coordinate octahedral nickel(II). The lowest frequency peak (ν_1) is assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g}$, the second main peak (ν_2) to ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (F), and the highest energy peak (ν_3) to ${}^3A_{2g} \rightarrow {}^3T_{1g}$ (P). The ratios ν_2/ν_1 for the group *S* complexes are in the range 1.64–1.80, typical values of six-coordinate octahedral nickel(II) complexes^{6,7}. The three main peaks of the group *F* complexes are labeled by ν_1 , ν_2 , and ν_3 as shown in Table II and the typical spectral pattern is

represented in Figure 1. The ratios ν_2/ν_1 for the group *F* complexes are in the range 2.07–2.25, which differ significantly from the normal ratio for octahedral nickel(II) complexes. The ratio has been reported to be close to two in the five-coordinate nickel(II) complex [Ni(Me₄daes)(NCS)₂] (Me₄daes = bis(2-dimethyl-



aminoethyl)sulfide), which has the following five-coordinate structure [I] with approximately D_{3h} symmetry⁸. The spectra of the group *F* complexes are very similar to that of the Me₄daes complex and the group *F* complexes are, therefore, presumed to have a similar five-coordinate structure [II].

Only the two complexes [Ni(335-cy)(NCS)₂] and [Ni(336-cy)(NCS)₂] are soluble in acetone without colour change, and the spectra of the solutions (Table

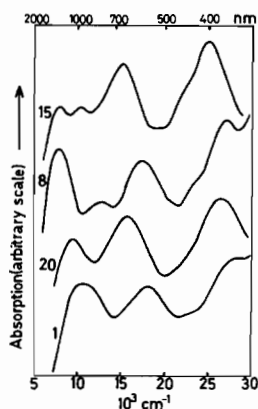
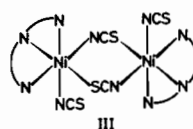


Figure 1. Electronic spectra of the solid complexes: (1) [Ni(222-cy)(NCS)₂], (20) Ni₂(234-cy)₃(ClO₄)₄·5H₂O, (8) [Ni(226-cy)(NCS)₂], and (15) [Ni(234-cy)Cl]ClO₄.

III and Figure 2) show two additional bands between ν_1 and ν_2 . The large molar extinction coefficients (ϵ) of the spectra are too large for usual octahedral nickel(II), but typical for five-coordinate nickel(II) complexes⁹. The essential features of the spectra do not significantly differ from those of the solid complexes. Thus these complexes in acetone are also five-coordinate having the same structure [II]. However, it is inadequate to preclude the possibility of a square pyramidal geometry only from the above spectral data.

The infrared spectra of the group *S* complexes show, at least, one component of $\nu(C\equiv N)$ of NCS above 2100 cm^{-1} (Table IV) and are similar to those of the complex [Ni(dien)(NCS)₂] (dien = diethylenetriamine) which contains one terminal and one bridged NCS groups as shown in the following dimeric structure [III]¹⁰.



Structure [III] is also reported for [Ni(Et₄dien)(NCS)₂] (Et₄dien = bis(2-diethylaminoethyl)amine)¹¹. The group *S* complexes may have a related structure

TABLE II. Magnetic Moments and Solid Electronic Spectra.

Complex	μ_{eff}^a (B.M.)	Absorption Maxima, $\times 10^3 cm^{-1}$					
		ν_1		ν_2		ν_3	
1	3.13	10.7br ^b	15.6sh, w	18.1	22.7sh, w	28.4	
2	3.12	10.4	11.6sh	18.1		28.6sh	
			15.6sh, w				
3	3.20	9.62	11.1sh	17.3		27.4	
4	3.12	8.3sh, w	10.05	11.1sh, 15.4sh, w	17.6	22.7sh, w	27.6
5	3.17	8.2sh, w	9.90	15.2sh, w	17.1		27.1
6	3.19	8.1sh, w, 9.3sh	10.4		17.1		27.0
7	3.18		8.00	12.9w	17.9		27.5
8	3.14		7.87	12.9w	17.4		27.0
9	3.19		8.00	13.2sh, w	17.2		26.7
10	3.14		8.37	11.4sh, w	17.3		26.9
11	3.18		7.63	12.7sh, w	16.4		26.1
12	3.10		7.84	12.6sh, w	16.4		26.0
13	3.19		7.72	12.3sh, w	16.3	19.6sh, w	25.7
14	3.18		8.38	10.3sh	15.9		25.7
15	3.22		7.87	10.2	15.1		25.0
16	2.93		8.20	10.3sh	15.7		25.4
17	3.22		8.33	9.3sh	15.2		25.0
18	3.18		7.75	10.0sh, w	15.2		24.9
19	3.37		9.48		15.3		26.4
20	3.20		9.48		15.6		26.5
21	3.29		9.67		16.1	22.2sh	26.4

^a At room temperature. ^b br = broad, w = weak, and sh = shoulder.

TABLE III. Molar Conductances and Electronic Spectra of $5 \times 10^{-3} M$ Solutions at $25^\circ C$.

Complex ^a	Solvent	Λ_M^b	Absorption Maxima, $\times 10^3 \text{ cm}^{-1} (\epsilon)^c$			
			ν_1		ν_2	ν_3
12	(CH ₃) ₂ CO	0.8	7.55(41.3)	11.4(7.92) 12.4(7.20)	16.3(52.0)	25.9(164)
13	(CH ₃) ₂ CO	0.5	7.58(55.3)	11.1(10.1) 12.5(11.4)	16.2(54.8)	25.7(162)
14	CH ₃ CN	141	8.10(21.0)		16.6(20.5)	26.2(40.2)
15	CH ₃ CN	140	9.44(7.92)	11.6sh ^d	15.6(14.8)	17.5sh 25.5(20.7)
16	CH ₃ CN	158	8.20(19.4)	12.8sh	16.5(30.6)	26.2(58.0)
17	CH ₃ CN	142	9.44(6.09)	11.6sh	15.6(16.3)	17.5sh 25.5(20.0)
18	CH ₃ CN	132	7.78(19.9)	12.8sh	16.0(46.6)	22.5sh 25.8(88.4)

^aNos. 12 and 13: [Ni(pqr-cy)(NCS)₂] and 14–18: [Ni(pqr-cy)Cl]ClO₄ (see Table I). ^bMho cm²/mol. ^c ϵ = molar extinction coefficient. ^dsh = shoulder.

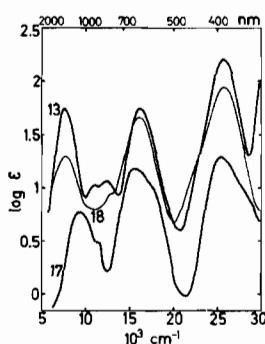
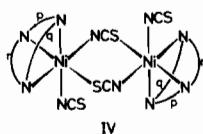


Figure 2. Electronic spectra of the complexes in solutions: (13) [Ni(336-cy)(NCS)₂] in acetone, (17) [Ni(333-cy)Cl]ClO₄ in acetonitrile, and (18) [Ni(334-cy)Cl]ClO₄ in acetonitrile.

[IV] (assignments of p, q, and r to arms are arbitrary), which is consistent with the result of the electronic spectral study.



The infrared spectra of the group *F* complexes have bands due to $\nu(\text{C}\equiv\text{N})$ of NCS below 2100 cm^{-1} and the spectra resemble that of the five-coordinate [Ni(Me₄daes)(NCS)₂] with two terminal NCS groups (Structure [I]). In the region $200\text{--}300 \text{ cm}^{-1}$ the spectra of the group *S* complexes are more complicated than those of the group *F* complexes (Table IV). The more complicated pattern may result from the presence of both $\nu(\text{Ni-N})$ and $\nu(\text{Ni-S})$ bands in the former complexes, while the rather simple pattern of the group *F* complexes may be related to the presence of

only $\nu(\text{Ni-N})$ bands¹². This interpretation is in agreement with the proposed structures [II] and [IV].

[Ni(pqr-cy)Cl]ClO₄

The complexes [Ni(pqr-cy)Cl]ClO₄ are obtained only for the ligands having appreciable steric hindrance of backbone methylene groups ($t = 9, 10$). The infrared spectra show non-coordination of ClO₄. Coordination of Cl was suggested by the presence of $\nu(\text{Ni-Cl})$ bands which appear as two peaks or as one broad absorption (Table IV). The positions of the bands are in the frequency region slightly higher than those of $\nu(\text{Ni-Cl})$ expected for octahedral, six-coordinate nickel(II) complexes^{13,14} but lower than those of $\nu(\text{Ni-Cl})$ of five-coordinate nickel(II) complexes¹⁵.

The electronic spectra (Table II and Figure 1) of the solid complexes are significantly different from those of typical octahedral nickel(II) complexes^{8,9}. The ratios ν_2/ν_1 are 1.83–1.93 and the values are, however, intermediate between those for five-coordinate and for six-coordinate nickel(II) complexes discussed above.

The absorption spectra of acetonitrile solutions, in which [Ni(pqr-cy)Cl]ClO₄ show conductivities typical for 1:1 (for monomeric) or 1:2 (for dimeric formulation) electrolytes¹⁶, were measured (Table III). The spectra of [Ni(333-cy)Cl]ClO₄ and [Ni(234-cy)Cl]ClO₄, the colours of which turn light blue upon dissolution, are those of octahedral nickel(II)⁷ and the ratio ν_2/ν_1 is 1.65. However, the spectra of the other [Ni(pqr-cy)Cl]ClO₄ (Nos. 14, 16, and 18) are very intense with different features (Figure 2 and Table III) and the ratio ν_2/ν_1 exceeds two^{6,9}. Five-coordination (Structure [V]) is, therefore, suggested for the latter

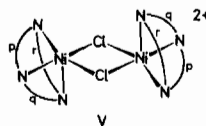


TABLE IV. Infrared Spectra Measured of Nujol Mulls.

Complex	Absorption, cm ⁻¹		
	$\nu(\text{N-H})$	$\nu(\text{C}\equiv\text{N})$	$\nu(\text{Ni-X})^a$
1 [Ni(222-cy)(NCS) ₂]	3340, 3275 3230	2128sh ^b , 2115 2093, 2050sh	268br, 255 213
2 [Ni(223-cy)(NCS) ₂]	3288, 3265 3229	2135sh, 2127sh 2107, 2099	278, 263 245, 229
3 [Ni(224-cy)(NCS) ₂]	3288, 3250 3220	2123sh, 2103 2094, 2058sh	273, 253 232, 221
4 [Ni(233-cy)(NCS) ₂]	3291, 3258, 3212	2125sh, 2113, 2096	256, 237, 225 213
5 [Ni(234-cy)(NCS) ₂]	3308w, 3286w, 3245, 3187	2140, 2119, 2097	234br, 210
6 [Ni(333-cy)(NCS) ₂]	3288, 3230, 3178	2127sh, 2118sh 2108, 2093	223br, 202
7 [Ni(225-cy)(NCS) ₂]	3252, 3230, 3185	2099, 2092sh	272, 218
8 [Ni(226-cy)(NCS) ₂]	3250, 3212, 3190	2098, 2090sh, 2047sh	271, 241
9 [Ni(235-cy)(NCS) ₂]	3315w, 3222	2097, 2076	261, 243
10 [Ni(236-cy)(NCS) ₂]	3258, 3202	2095, 2077	251, 241
11 [Ni(334-cy)(NCS) ₂]	3264, 3220	2092, 2072	245, 237
12 [Ni(335-cy)(NCS) ₂]	3280, 3194	2095, 2080sh	241, 225
13 [Ni(336-cy)(NCS) ₂]	3248	2088, 2063	234br
14 [Ni(225-cy)Cl]ClO ₄	3265, 3318		270, 232
15 [Ni(234-cy)Cl]ClO ₄	3300, 3263		258, 240
16 [Ni(235-cy)Cl]ClO ₄	3300, 3265		265, 238
17 [Ni(333-cy)Cl]ClO ₄	3277		239br
18 [Ni(334-cy)Cl]ClO ₄	3265		253br
19 Ni ₂ (225-cy) ₃ (ClO ₄) ₄ · 4H ₂ O	3290, 3245	3510br ^c	
20 Ni ₂ (234-cy) ₃ (ClO ₄) ₄ · 5H ₂ O	3280	3520br ^c	
21 Ni ₂ (333-cy) ₃ (ClO ₄) ₄ · 5H ₂ O	3277, 3200	3535br ^c	

^a X=N, S, or Cl. ^b sh = shoulder, br = broad, and w = weak. ^c $\nu(\text{O-H})$ of water.

complexes in the solutions. The spectra of the solid complexes are rather similar to those of the latter solutions and a similar five-coordinate structure is assumed for the solid complexes [Ni(pqr-cy)Cl]ClO₄. The bridging nature of the chloride ions may lead to the lower frequency $\nu(\text{Ni-Cl})$ bands than those of terminal Ni-Cl bonds of five-coordinate nickel(II) complexes¹³⁻¹⁵. The same Cl-bridged dimer has been previously adopted for the copper complexes of composition [Cu(pqr-cy)Cl]ClO₄⁵.

Ni₂(pqr-cy)₃(ClO₄)₄ · nH₂O (n = 4 or 5)

The complexes of this type are obtained only for the ligands with t = 9 containing appreciable steric hindrance. The infrared spectra show bands due to $\nu(\text{N-H})$ of the coordinated secondary amino groups and those due to $\nu(\text{O-H})$ of water in the expected regions¹⁷, and also show non-coordination of ClO₄. The electronic spectra of the solid state complexes are typical of octahedral, six-coordinate nickel(II) complexes⁷. The structures are, however, difficult to envisage.

Conclusions

The ligands with t = 9 are of very interest, since the properties of the complexes change discontinuously at this point. The complexes [Ni(pqr-cy)(NCS)₂] are six-coordinate for the ligands with t < 9, but five-coordinate for the ligands with t > 9. For the ligands with t = 9, the complex [Ni(225-cy)(NCS)₂] is five- and [Ni(234-cy)(NCS)₂] and [Ni(333-cy)(NCS)₂] are six-coordinate. The same is true for [Ni(pqr-cy)Cl]ClO₄ in acetonitrile: the species in the solutions is five- for 225-cy and six-coordinate for 234-cy and 333-cy. A coordination site of nickel(II) is, thus, more effectively blocked by the backbone polymethylene groups of 225-cy than by those of 234-cy and 333-cy. The fact that, under the conditions under which 235-cy and 334-cy form [Ni(pqr-cy)Cl]ClO₄, 226-cy forms no complex with precipitation of nickel hydroxide is closely related. These facts may indicate that when t is the same, the larger the size of a backbone methylene group is, the more effective the steric hindrance of the group becomes.

Experimental

Preparation of the Complexes

Colours and analytical data are given in Table I.

$[Ni(pqr-cy)(NCS)_2]$

A hot aqueous solution (50 ml) containing 2 mmol of pqr-cy·3HCl, 2 mmol of NiCl₂·6H₂O, and 10 mmol of KNCS was neutralized by addition of 6 mmol of NaOH dissolved in 10 ml of water and allowed to stand few hours. The solution was concentrated on a steam bath if required. A precipitate was washed with water and dried in air. The yield was ca. 60–80%.

$[Ni(pqr-cy)Cl]ClO_4$

To a hot aqueous solution (30 ml) of 2 mmol of pqr-cy·3HCl and 2 mmol of NiCl₂·6H₂O was added 6 mmol of NaOH in 5 ml of water and the mixture was stirred for about ten minutes on a hot plate to complete reaction. The mixture was filtered and to the filtrate was added 10 mmol of NaClO₄ in 10 ml of water. The resulting solution was concentrated to a small volume, and the crystals obtained were washed with water and dried in air. The yield was ca. 20–50%.

$Ni_2(pqr-cy)_3(ClO_4)_4 \cdot 5H_2O$ (pqr-cy = 234-cy and 333-cy)

In 30 ml of water were dissolved 2 mmol of NiCl₂·6H₂O and 3 mmol of pqr-cy·3HCl and the solution was mixed with 9 mmol of NaOH in 10 ml of water. The mixture was stirred on a hot plate for ca. ten minutes and filtered. To the filtrate were added 10 mmol of NaClO₄ in 10 ml of water. On concentration of the filtrate, blue crystals were obtained, which were washed with water and dried in air. The yield was ca. 50%.

Ni₂(225-cy)₃(ClO₄)₄·4H₂O was prepared by a similar method, utilizing 3.8 mmol of 225-cy·3HCl and 11.4 mmol of NaOH instead of 3 mmol of pqr-cy·3HCl and 9 mmol of NaOH.

Measurements

Conductivities of $5 \times 10^{-3} M$ solutions were measured at 25°C with a TOA CM-6A Conduct Meter and absorption spectra of $5 \times 10^{-3} M$ solutions were recorded at 25°C on a Hitachi 323 spectrophotometer. The methods for the other measurements were reported in a previous paper⁵.

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