The Absorption Spectra of Cobalt(III) Complexes. IV.[1] *The Preparation and the Absorption Spectra of Monohalogenomonoamine-bis(ethylenediamine)-cobalt(III) Complexes*

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It is well known that $[Co\,Cl(amine)en_2]^{2+}$ and $[Co\,Br(amine)en_2]^{2+}$ ions are formed in the reactions of chloro- and bromo-praseo salts, respectively, with aliphatic or aromatic primary amines,[2-4] but not with secondary and tertiary amines. In the cases of $[Co\,Cl(NH_3)en_2]^{2+}$ and $[Co\,Br(NH_3)en_2]^{2+}$ ions, both the cis and the trans isomers have been prepared by Werner,[5] and the cis salts have been resolved into the optically active isomers. The geometrical structures of the complexes containing organic amines, however, have not been precisely determined. A few studies[2,4] have been made trying to resolve the complexes by the use of α-bromo-*d*-camphorsulfonate, but none of these efforts have succeeded. Bailar and Clapp[4] investigated the reactions of an optically-active violeo salt with the organic amines, but they could not isolate the reaction products with optical activities, except for an optically-active complex of *p*-toluidine, *cis*-$[Co\,Cl(p\text{-toluidine})en_2]Cl_2$.

In the present paper, a few complexes which belong to the corresponding iodo series, i. e., *trans*- and *cis*-$[Co\,I(NH_3)en_2]I_2$ and *cis*-$[Co\,I(amine)en_2]I_2$ (amine=methylamine and pyridine), have been newly synthesized. Furthermore, some missing members of the chloro and the bromo series have also been prepared. The absorption spectra of the complexes have been measured in the region of 210∼1200 mμ, with especially great care in the near-infrared region, and the results will be discussed mainly in relation to the geometrical structures of the complex ions.

Experimental

Measurements.—A Beckman DU quartz spectrophotometer was used for the measurements of the absorption spectra in the 210∼1200 mμ region. All the aqueous solutions of the complexes obeyed Beer's law at concentrations of $1\sim10^{-5}$ mol./l. The measurements for the dilute solutions were made rapidly in the cold to avoid the aquotization of the complex ions.

The absorption spectrum of *cis*-$[Co\,I(NH_3)en_2]I_2$ coincided well with that of the corresponding chloride, *cis*-$[Co\,I(NH_3)en_2]Cl_2$. Therefore, the effects of the outer-sphere anions have not been considered as long as no extra hydrogen halide or halide salt was added to the sample solutions.

Materials.—*trans*-$[Co\,Cl(NH_3)en_2]Cl_2\cdot H_2O$.—This compound was prepared from *trans*-$[Co\,Cl(NCS)en_2]NCS$ by the procedure of Werner.[6] The color of the crystals isolated was ruby red.

cis-$[Co\,Cl(amine)en_2]Cl_2$.—The complex containing NH_3 instead of amine was prepared by the method of Werner[7] and was recrystallized from concentrated hydrochloric acid. The crystals were reddish in color and needle-shaped. The compounds containing methyl-, ethyl- or *n*-propyl-amine, or pyridine, instead of ammonia, were prepared by similar procedures. The *n*-propylamine complex is a new compound.

Found: C, 23.18; H, 7.50; N, 19.31; H_2O, 4.82. Calcd. for $C_7H_{25}N_5Cl_3Co\cdot H_2O = [Co\,Cl(C_3H_9N)(C_2H_8N_2)_2]Cl_2\cdot H_2O$: C, 23.43; H, 7.50; N, 19.16; H_2O, 4.96%.

cis-$[Co\,Cl(aniline)en_2]Cl_2$.—This complex was prepared by the method of Bailar and Clapp.[4] The toluidine complex, *cis*-$[Co\,Cl(p\text{-toluidine})en_2]Cl_2\cdot H_2O$, was obtained by a similar method. These complexes of aromatic amines are less soluble in water than those of aliphatic amines.

trans-$[Co\,Br(NH_3)en_2]Br_2\cdot H_2O$.—The compound was obtained by the method of Werner,[8] but this was somewhat modified as follows. A pure complex, *trans*-$[Co(OH_2)(NH_3)en_2]Br_3$, was suspended in an appropriate amount of concentrated hydrobromic acid and was gently heated to 70°C. After being kept for a few minutes at this temperature, the color of the solution changed from orange to violet. This solution was then cooled to room temperature and alcohol was added. By letting the solution stand in an ice-bath, the compound was obtained as reddish violet crystals.

cis-$[Co\,Br(NH_3)en_2]Br_2\cdot H_2O$.—This salt was obtained by the reactions of the bromo-praseo salt, *trans*-$[Co\,Br_2en_2]Br$, with aqueous ammonia upon

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[1] Part III of this series: J. Fujita and Y. Shimura, This Bulletin, **36**, 1281 (1963).

[2] J. Meisenheimer and E. Kiderlen, *Ann.*, **438**, 238 (1924).

[3] A. Ablov, *Bull. soc. chim. France*, **3**, 2270 (1936); **4**, 1783 (1937).

[4] J. C. Bailar, Jr., and L. B. Clapp, *J. Am. Chem. Soc.*, **67**, 171 (1945).

[5] A. Werner, *Ann.*, **386**, 55 (1912); *Ber.*, **44**, 1887 (1911).

[6] A. Werner, *Ann.*, **386**, 176 (1912).

[7] A. Werner, ibid., **386**, 55 (1912).

[8] A. Werner, ibid., **386**, 182 (1912).

cooling in a freezing mixture.[9] The same compound was also obtained by dehydrating *cis*-[Co-$(OH_2)(NH_3)en_2]Br_3$ in a drying apparatus.

cis-[Co Br(methylamine)en$_2$*]Br*$_2$. — This compound was prepared by the same procedure as was the ammine complex, *cis*-$[Co Br(NH_3)en_2]Br_2$.

cis-[Co Br(amine)en$_2$*]Br*$_2$.—The ethylamine, *n*-propylamine and pyridine complexes were easily synthesized from bromo-praseo salt and the respective amines. The latter two complexes are new.

Found: C, 17.86; H, 5.23; N, 14.70. Calcd. for $C_7H_{25}N_5Br_3Co = [Co Br(C_3H_9N)(C_2H_8N_2)_2]Br_2$: C, 17.59; H, 5.27; N, 14.65%.

Found: C, 21.70; H, 4.28; N, 14.25. Calcd. for $C_9H_{21}N_5Br_3Co = [Co Br(C_5H_5N)(C_2H_8N_2)_2]Br_2$: C, 21.71; H, 4.25; N, 14.06%.

trans-[Co I(NH$_3$*)en*$_2$*]I*$_2$. — A finely powdered, pure complex, *trans*-$[Co(OH_2)(NH_3)en_2]I_3$,[10] was spread on a watch-glass and was dehydrated in vacuo at room temperature for two or three days. The color of the powder changed from brown to brownish-black. The crude product obtained was purified as follows. A more soluble by-product was extracted by a small amount of water; the greenish residue remaining was then dissolved in a large quantity of water, and the solution was filtered. In an ice-bath, the greenish crystals were deposited from the filtrate. The crystals collected by filtration were recrystallized repeatedly from water by the addition of potassium iodide. The greenish-brown crystals obtained were washed with cold water, with alcohol, and then with acetone. The trans-salt was less soluble in water than the corresponding cis salt.

Found: C, 8.31; H, 3.57; N, 12.00. Calcd. for $C_4H_{19}N_5I_3Co = [Co I(NH_3)(C_2H_8N_2)_2]I_2$: C, 8.33; H, 3.32; N, 12.14%.

cis-[Co I(NH$_3$*)en*$_2$*]I*$_2$.—Purified *cis*-$[Co(OH_2)(NH_3)en_2]I_3$ was spread on a watch-glass and dehydrated in a drying apparatus at 70~75°C for about three hours. The color of the compound gradually changed from brown to brownish-black. The crude product was dissolved in a little amount of water, and then the solution was filtered. To the filtrate, powdered potassium iodide was added. After this solution had cooled in an ice-bath, a large number of dark brown, hexagonal crystals were deposited. The product separated by filtration was recrystallized from water by the addition of potassium iodide, and it was washed with cold water, with alcohol and then with acetone.

Found: C, 8.15; H, 3.50; N, 12.15. Calcd. for $C_4H_{19}N_5I_3Co = [Co I(NH_3)(C_2H_8N_2)_2]I_2$: C, 8.33; H, 3.32; N, 12.14%.

cis-[Co I(methylamine)en$_2$*]I*$_2$. — Twenty grams of *cis*-$[Co Cl(methylamine)en_2]Cl_2 \cdot H_2O$ was dissolved in 30 ml. of an aqueous solution of potassium hydroxide (1 : 5). After it had stood for a while, the solution was filtered with a glass filter. When an excess of concentrated hydrobromic acid was added to the filtrate drop by drop and cooled in an ice-bath, crystals began to deposit. After the solution had cooled in an ice-bath for a few hours, a large amount of the mono-aquo bromide, $[Co(OH_2)(methylamine)en_2]Br_3$ was obtained. This complex was transformed to the iodide by double decomposition with potassium iodide.

By the dehydration of the mono-aquo iodide, $[Co(OH_2)(methylamine)en_2]I_3$, at 80~85°C for two to three hours, a crude, brownish-black product was obtained. The recrystallization was made by a procedure to that used with *trans*-$[Co I(NH_3)en_2]I_2$. After repeated recrystallizations, the crystal was a dark greenish-brown, hexagonal plate. This is sparingly soluble in water.

Found: C, 10.40; H, 3.69; N, 11.68. Calcd. for $C_5H_{21}N_5I_3Co = [Co I(CH_5N)(C_2H_8N_2)_2]I_2$: C, 10.16; H, 3.58; N, 11.85%.

cis-[Co I(pyridine)en$_2$*]I*$_2$. — The aquo complex, $[Co(OH_2)(pyridine)en_2]I_3$, was obtained by a method similar to that used for the methylamine complex, and this was dehydrated at 70~80°C for a day. From the crude product, a more soluble substance was extracted with a little water. A large amount of water was saturated with the greenish residue, and the solution was filtered. A few drops of saturated potassium iodide solution were then added to the filtrate. The solution was cooled in an ice-bath until dark green, octahedral crystals were deposited. A pure sample was sparingly soluble in water.

Found: C, 17.22; H, 3.35; N, 10.54. Calcd. for $C_9H_{21}N_5I_3Co = [Co I(C_5H_5N)(C_2H_8N_2)_2]I_2$: C, 16.92: H, 3.31; N, 10.96%.

The aquo complexes, $[Co(OH_2)(aniline)en_2]I_3$ and $[Co(OH_2)(p\text{-toluidine})en_2]I_3$, which were obtained by procedures similar to those used for the pyridine complex, were unstable. Therefore, the corresponding iodo-amine complexes could not be isolated.

Results and Discussion

The Near-infrared Absorption Spectra. — It has been known that the cobalt(III) complexes generally have two weak absorption bands in the near-infrared region,[1,11-13] of which the band appearing at the longer wavelength is named the A band and the band at the shorter wavelength, the B band. In most cases the B band is overlapped by the so-called first band, which is located just adjacent to the B band in a shorter wavelength and which has a moderate intensity.

The absorption maxima of the complexes of the $[Co X(NH_2\text{-}R)en_2]X_2$ type, which were measured in aqueous solutions, are summarized in Table I. In Figs. 1 and 3—5, the representative absorption curves are shown. As may be understood from the table and the figures, the molar extinction coefficients of the A bands increase by a factor of about ten in each substitution of the ligand X in the

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[9] A. Werner, ibid., **386**, 111 (1912).

[10] A. Werner, ibid., **386**, 185 (1912).

[11] C. K. Jørgensen, *Acta Chem. Scand.*, **8**, 1502 (1954).

[12] M. Linhard and M. Weigel, *Z. physik. Chem. N. F.*, **11**, 308 (1957).

[13] Y. Tanabe and S. Sugano, *J. Phys. Soc. Japan*, **9**, 766 (1954).

TABLE I. ABSORPTION MAXIMA OF THE $[Co\,X(NH_2\text{-}R)en_2]X_2$-TYPE COMPLEXES
ν_{max} 10^{13} sec^{-1} (log ε)

Structure	R-NH$_2$*	X	A Band	I Band		II Band	Charge transfer band	
				Ia	Ib**			
trans	NH$_3$	Cl	34.1($\bar{1}$.52)	56.7(1.62)	66.2(1.28)	83.3(1.66)	109.7(2.98)	133 (4.28)
		Br	33.3(0.67)	55.1(1.71)	66.4(1.30)		93.8(2.81)	120 (4.24)
		I	32.7(1.47)	52.2(1.85)			78.5(3.41)	105.5(4.23)
cis	NH$_3$	Cl	35.8($\bar{1}$.64)	56.9(1.86)	65.6(1.36)	82.2(1.87)	110.3(2.98)	131 (4.28)
		Br	33.9(0.69)	55.6(1.92)	65.0(1.43)		94.7(2.85)	117 (4.24)
		I	33.3(1.50)	52.5(2.06)			80.0(3.48)	105 (4.25)
cis	Me-NH$_2$	Cl	35.3($\bar{1}$.69)	56.9(1.89)	65.0(1.40)	81.8(1.92)	108.8(3.02)	131 (4.29)
		Br	33.3(0.64)	55.1(1.90)			94.7(2.88)	119 (4.27)
		I	33.0(1.47)	52.2(2.04)			79.0(3.45)	105 (4.22)
cis	Et-NH$_2$	Cl	35.1($\bar{1}$.66)	56.9(1.87)	64.8(1.41)	81.8(1.92)	108.7(3.00)	131.5(4.30)
		Br	33.0(0.66)	55.1(1.91)			94.5(2.89)	119 (4.27)
cis	Pr-NH$_2$	Cl	35.0($\bar{1}$.69)	56.9(1.89)	64.6(1.43)	81.7(1.94)	109.0(3.00)	131 (4.35)
		Br	33.3(0.64)	55.0(1.92)			94.5(2.90)	119 (4.30)
cis	Py	Cl	35.6($\bar{1}$.73)	57.1(1.88)	64.6(1.49)	81.5(1.91)	106.6(2.94)	129 (4.38)
		Br	33.3(0.71)	55.1(1.93)			91.1(2.88)	116 (4.24)
		I	33.2(1.57)	51.7(2.05)			75.0(3.41)	100.5(4.18)
cis	Anil	Cl	ca. 34.5($\bar{1}$.96)	56.5(2.01)				
		Br	32.7(0.63)	55.0(1.93)				
cis	Tol	Cl	ca. 34.3($\bar{1}$.94)	56.4(1.98)				

* Me-NH$_2$=Methylamine; Et-NH$_2$=Ethylamine; Pr-NH$_2$=*n*-Propylamine; Py=Pyridine; Anil=Aniline; Tol=*p*-Toluidine

** Values calculated from the observed curves by the separation of the Ia component.

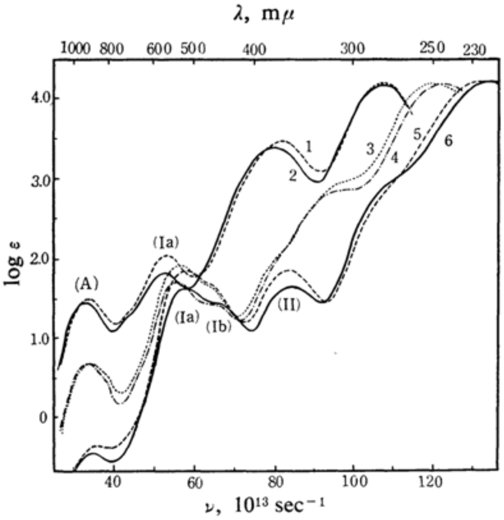

Fig. 1. Absorption curves of:

1. *cis*-$[Co\,I(NH_3)en_2]I_2$
2. *trans*-$[Co\,I(NH_3)en_2]I_2$
3. *cis*-$[Co\,Br(NH_3)en_2]Br_2\cdot 2H_2O$
4. *trans*-$[Co\,Br(NH_3)en_2]Br_2\cdot H_2O$
5. *cis*-$[Co\,Cl(NH_3)en_2]Cl_2$
6. *trans*-$[Co\,Cl(NH_3)en_2]Cl_2\cdot H_2O$

order of $Cl^- \rightarrow Br^- \rightarrow I^-$. This factor is larger than that of the first band. This finding agrees well with Linhard's finding for the halogenopentammine cobalt(III) complexes.[12] The first and the second bands of the cobalt(III) complexes arise from the forbidden transitions between the splitted d-energy levels which have the same spin-multiplicity, while the A and B bands arise from those between the levels of the different spin-multiplicity values (from singlet to triplet). More particulary, the A and B bands are spin-forbidden and their intensities are very weak, in accordance with the theoretical considerations.[13]

If the A band arises from the splitted d-levels, it is expected that the bands will split because of the lower symmetries of the halogeno-amine complexes, just as the first bands split to Ia and Ib. As may be seen in Fig. 4, a weak splitting of the A bands was observed in some of the bromo complexes. In Fig. 1, the absorption spectra of the trans- and the cis-forms of $[Co\,X(NH_3)en_2]X_2$ are shown. The A band of the trans-form is at a longer wavelength and has a weaker intensity than that of the corresponding cis-form.

For the measurements of the A bands, rather concentrated solutions were necessary in most cases because of the lower absorption intensities of the complexes in this region. For some cases, two or three irregular fine structures were observed on the longer wavelength side of the A bands. It could be ascertained that such a phenomenon arose from the difference in the concentrations of the solvent water between the sample and the reference cells. For example, the near-infrared absorption spectra of water and of *trans*-$[Co\,Cl(NH_3)en_2]Cl_2\cdot H_2O$ are shown in Fig. 2. The A

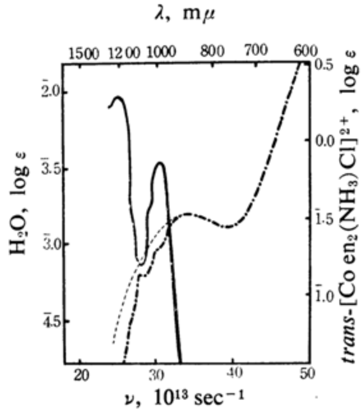

Fig. 2. Absorption curves of solvent water and the complex ion in the near-infrared region.

——: Water —·—·— Complex ion

----: Absorption curve corrected for the absorption by the solvent water which is present in excess in the reference cell.

band of the complex shows minima in a region corresponding to that of the absorption maxima of the solvent water (30.7 and 29.1 × 10^{13} sec^{-1}).

The Visible and Ultraviolet Spectra. — The so-called first and second absorption bands which appear in the visible and ultraviolet region also belong to the d-d transitions. The first bands of the complexes concerned split into two components, Ia and Ib, because of the lower symmetries of the complex ions (Figs. 1 and 3). In the iodo complexes, only the Ia components are observed, while the Ib components are hidden under the strong charge-transfer bands, as Fig. 5 shows. The molar extinction coefficient of the first band increases with an increase in the atomic weight of the coordinated halogen, but this is not so remarkable as that of the A band.

The absorption spectra of the trans- and the cis-forms of $[Co X(NH_3)en_2]X_2$, ($X = Cl^-$, Br^-) showed some differences in the Ia bands. The difference in the intensities was about 0.2 by log ε. The iodo-ammine complexes also showed the same trend. It was concluded, therefore, that the complex which showed a higher intensity in the Ia band was the cis-form, while that which showed a lower intensity was the trans-form (Fig. 1). If this conclusion is applicable to the complexes containing organic amines, it may be possible to determine the geometrical structures of theses complexes. As is shown in Table I and Figs. 3—5, the intensities of the Ia bands of the complexes which have aliphatic amines are almost identical with those of the cis-forms of $[Co X(NH_3)en_2]X_2$. Therefore, all these complexes, except for those containing aromatic amines, probably have the cis configuration. This conclusion agrees with the inference by Meisenheimer and Kiderlen²⁾ and that by Bailar et al.⁴⁾ The first absorption bands of the complexes of aromatic amines do not necessarily coincide with those of *cis*-$[Co X(NH_3)en_2]X_2$, because of the overlapped specific absorption bands of the aromatic amines (Fig. 3). The spectrum of the bromoaniline complex, however, coincides very well with that of *cis*-$[Co Br(NH_3)en_2]Br_2$, as Fig. 4 shows.

In their spectral features the pyridine complexes resemble the aliphatic amine complexes.

As for the ultraviolet spectra of the chloro- and bromo-amine complexes, some studies

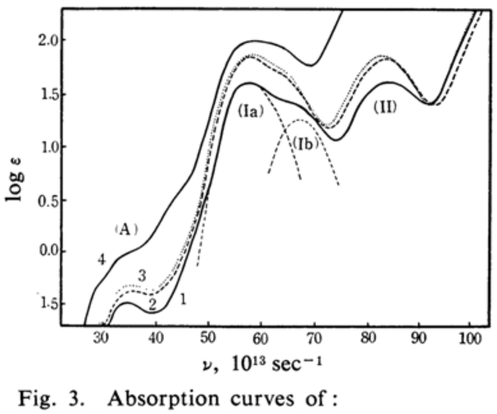

Fig. 3. Absorption curves of:

1. *trans*-$[Co Cl(NH_3)en_2]Cl_2 \cdot H_2O$
2. *cis*-$[Co Cl(NH_3)en_2]Cl_2$
3. *cis*-$[Co Cl(NH_2 \cdot Me)en_2]Cl_2 \cdot H_2O$
4. *cis*-$[Co Cl(Anil)en_2]Cl_2$

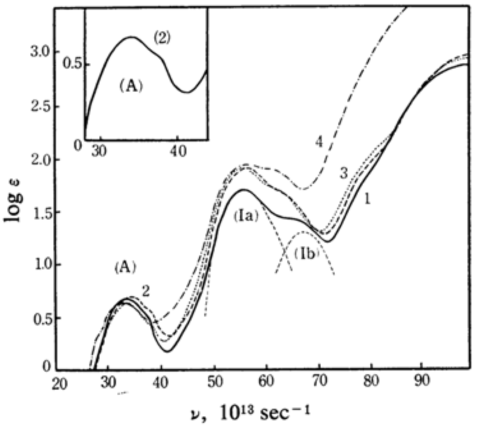

Fig. 4. Absorption curves of the bromo complexes:

1. *trans*-$[Co Br(NH_3)en_2]Br_2 \cdot H_2O$
2. *cis*-$[Co Br(NH_3)en_2]Br_2 \cdot 2H_2O$
3. *cis*-$[Co Br(NH_2\text{-}Me)en_2]Br_2$
4. *cis*-$[Co Br(Anil)en_2]Br_2 \cdot 1/2H_2O$

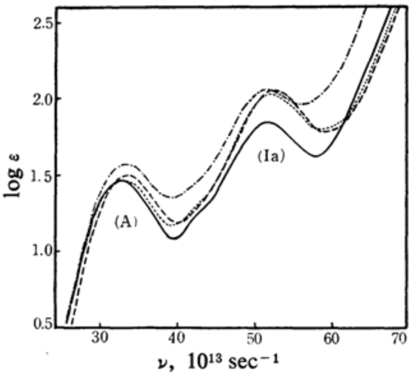

Fig. 5. Absorption curves of the iodo-complexes:
——— *trans*-[Co I$(NH_3)en_2$]I_2
------ *cis*-[Co I$(NH_3)en_2$]I_2
········ *cis*-[Co I$(NH_2\text{-}Me)en_2$]I_2
—·—· *cis*-[Co I(Py)en_2]I_2

have been reported by Ablov and Filippov.[14,15] We investigated all the chloro-, bromo-, and iodo-amine complexes in this region. As Table I and Fig. 1 show, the charge transfer bands shift to longer wavelength in the following order of ligand halogens: $Cl^- \rightarrow Br^- \rightarrow I^-$. Some differences between the spectra of the trans- and the cis-forms were also noted in this region.

Summary

The four iodo-amine complexes and some chloro- and bromo-amine complexes belonging to [Co X$(NH_2\text{-}R)en_2$]X_2 type have been newly synthesized to complete the series.

From the measurements of the near-infrared, visible and ultraviolet absorption spectra, the geometrical structures of the complexes have been determined. The ammine complexes, [Co X$(NH_3)en_2$]X_2, exist in both the cis- and the trans-forms, but the organic amine complexes, [Co X$(NH_2\text{-}R)en_2$]X_2, exist only in the cis-form.

The weak splitting of the A band has been observed for the first time in the bromo-amine complexes.

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[14] A. Ablov and M. P. Filippov, *Zhur. Neorg. Khim.*, **2**, 42 (1957); *Chem. Abstr.*, **51**, 17441i (1957).

[15] A. Ablov and M. P. Filippov, *Zhur. Neorg. Khim.*, **2**, 2390 (1957); *Chem. Abstr.*, **53**, 2774i (1959).