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# Preparation of *trans*-Dichlorocobalt(III) Complexes of *N*-Alkylethylenediamines

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**Synopsis.** *N*-Alkylethylenediamine ($RNHCH_2CH_2NH_2$; R=butyl, hexyl, isobutyl, and isopropyl) complexes of the type $[CoCl_2(diamine)_2]X$ prepared by usual air-oxidation method except the case of R=isopropyl. The *N*-ipren (R=isopropyl) complex was obtained by employing methanol as the solvent. A brief consideration of the steric effect of *N*-isopropyl group was given.

In the past ten years cobalt(III) complexes of *N*-methylethylenediamine(*N*-meen) and other *N*-methyl-1,2-diamines were studied extensively. The presence of secondary N atom, which provides a new asymmetric center upon coordination, opened a variety of problems in the stereochemistry of metal complexes.1—4) However, the cobalt(III) complexes of other *N*-alkyl-1,2-diamines such as *N*-eten,* *N*-npren,* *N*-nbuen,* *etc.* were attracted little attention.5—7)

Basolo obtained the *trans*-dichlorobis(diamine)-cobalt(III) complexes (diamine=*N*-eten, and *N*-npren) as the crystalline products.5) However, the *N*-nbuen complex of the same type was not isolated in the pure crystalline form, though its formation could be acknowledged from the green color of a reaction mixture.5) In this note we report the preraration of *trans*-dichlorocobalt(III) complexes of various *N*-alkylethylenediamines including *N*-nbuen by an air-oxidation method.

## Experimental

*Ligands.* To a solution of 2-bromoethylamine hydrobromide (52g; 0.25 mol) in ethanol (150 cm$^3$) was added *N*-monoalkylamine (1.3—1.5 mol) and the solution was heated under reflux for 7 h. Ethanol and excess amine were distilled off under reduced pressure and the oily residue was dissolved in a small volume of water (*ca.* 50—100 cm$^3$). An excess amount of sodium hydroxide (*ca.* 40 g) was added to the solution in small portions, with occasional removing of white precipitate (NaBr) by filtration through a glass filter. When the diamine separated from aqueous alkali, it was extracted with ether (total 300 cm$^3$). The ether extracts were combined and dried over potassium hydroxide pellets overnight. Ether was removed by distillation, and the diamine which remained was distilled at atmospheric or under reduced pressure. Yield; 45—60%. Bp: *N*-nbuen, 160 °C (atmospheric); *N*-ipren, 140 °C (atmospheric); *N*-ibuen, 160 °C (atmospheric); *N*-nhxen, 105—108 °C/17 mmHg; *N*-chxen, 115—116 °C/29 mmHg.

trans-$[CoCl_2(\text{N-}nbuen)_2]ClO_4$. To a solution of $CoCl_2 \cdot 6H_2O$ (2.38 g; 0.01 mol) in water (30 cm$^3$) was added *N*-nbuen (2.4 g; 0.02 mol), and the solution was aerated for 6 h at room temperature. After 15 cm$^3$ of concd hydrochloric acid had been added, the solution was evaporated on a water bath at 75—80 °C. When the volume was reduced to ca. 20 cm$^3$, 60% perchloric acid (3 cm$^3$) was added and the mixture was cooled in a refrigerator. Dull yellow-green crystals which deposited were collected, washed successively with cold water, ethanol, and ether, and air-dried. Yield, 1.50 g. The product was recrystallized from methanol. Found: C, 31.39; H, 7.15; N, 12.00%. Calcd for $C_{12}H_{32}N_4O_4Cl_3Co$: C, 31.22; H, 6.99; N, 12.14%.

trans-$[CoCl_2(\text{N-}ibuen)_2]ClO_4$ was obtained by the same procedure as that for the above *N*-nbuen complex, using *N*-ibuen in place of *N*-nbuen. Found: C, 30.19; H, 6.93; N, 11.96%. Calcd for $C_{12}H_{32}N_4O_4Cl_3Co$; C, 31.22; H, 6.99; N, 12.14%.

trans-$[CoCl_2(\text{N-}nhxen)_2]ClO_4$. To a solution of $CoCl_2 \cdot 6H_2O$ (1.19 g; 0.005 mol) in water (15 cm$^3$) was added a solution of *N*-nhxen (1.97 g; 0.012 mol) in ehtanol (15 cm$^3$), and the solution was aerated for 5 h, adding occationaly a few cm$^3$ of ethanol to dissolve deep brown oily materials. After 15 cm$^3$ of concd hydrochloric acid was added, the resultant solution was evaporated on a water bath at 75—80 °C. When a small amount of green crystals appeared, the mixture was cooled to room temperature, and then 60% perchloric acid (5 cm$^3$) was added. The oily product which deposited was separated by decantation, and crystallized from ethanol solution. Found: C, 37.11; H, 7.89; N, 10.69%. Calcd for $C_{16}H_{40}N_4O_4Cl_3Co$; C, 37.11; H, 7.79; N, 10.82%.

trans-$[CoCl_2(\text{N-}ipren)_2]_2(ZnCl_4)$. Cobalt(II) chloride hexahydrate (1.19 g; 5 mmol) dissolved in methanol (20 cm$^3$) was added dropwise to a solution of *N*-ipren (1.02 g; 10 mmol) in methanol (30 cm$^3$) with continuous bubbling of air. After the addition had been completed, air was passed through the solution for further 3 h, adding occasionally a few cm$^3$ of methanol to maintain the volume of reaction mixture at 40—50 cm$^3$. Then, methanol was rotary-evaporated and the residue was dissolved in concd hydrochloric acid (15 cm$^3$). The solution was heated on a boiling water bath for 30 min, and then evaporated on a rotary evaporator to a volume of 20 cm$^3$. After solid $ZnCl_2$ (5 g) had been added, the blue-green solution was cooled in a refrigerator overnight. Green crystals which appeared were filtered off, washed with cold hydrochloric acid, ethanol, and then ether, and dried under reduced pressure. Found: C, 27.49; H, 6.73; N, 13.08. Calcd for $C_{20}H_{56}N_8Cl_8Co_2Zn$: C, 27.44; H, 6.45; N, 12.80%.

*Measurements.* Absorption spectra were obtained on a Shimadzu UV-210 spectrometer.

## Results and Discussion

Basolo observed that addition of *N*-ipren to an aqueous solution of coblat(II) chloride resulted in the

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* Abbreviations of *N*-alkylethylenediamine ($RNHCH_2CH_2NH_2$) are as follows: *N*-eten (R=ethyl)=*N*-ethylethylenediamine, *N*-npren (R=propyl)=*N*-propylethylenediamine, *N*-nbuen (R=butyl)=*N*-butylethylenediamine, *N*-nhxen (R=hexyl)=*N*-hexylethylenediamine, *N*-ipren (R=cyclohexyl)=*N*-isopropylethylenediamine, *N*-ibuen (R=isobutyl)=*N*-isobutylethylenediamine, *N*-chxen (R=cyclohexyl)=*N*-cyclohexylethylenediamine.

separation of cobalt(II) hydroxide.[5] This implies that the introduction of the bulky isopropyl group disturbs the coordination of *N*-ipren to the $Co^{2+}$ ion due to steric hindrances and that the $Co^{2+}$ ion interacts with hydroxide ions to deposite as cobalt(II) hydroxide. We supposed that the coordination of *N*-ipren to the $Co^{2+}$ ion might be permitted to give rise to *trans*-$[CoCl_2(N\text{-ipren})_2]^+$, if the coexistence of hydroxide could be prevented by using an organic solvent. It was actually observed that the air-oxidation of a mixture of $Co^{2+}$ and *N*-ipren in methanol resulted in the formation of *trans*-$[CoCl_2(N\text{-ipren})_2]^+$ after the treatment with HCl. The addition of $ZnCl_2$ to the reaction mixture gave crystals of the *N*-ipren complex of tetrachlorozincate(II) ($ZnCl_4^{2-}$) salt, though the yield was relatively low (*ca.* 20%). A similar effect of organic solvent which improves the formation of complex ions has been noted for the *trans*-dichlorocobalt(III) complex of 1,3-diaminopropane.[8]

On the other hand, *trans*-dichlorocobalt(III) complexes of *N*-nbuen, *N*-nhxen, and *N*-ibuen were readily obtained as perchlorate salts with considerable yields according to the usual air-oxidation method in aqueous media. It was noted that *N*-ibuen behaved in the same manner as *N*-nbuen, though the isobutyl group, as well as the isopropyl group, had a branch at the alkyl substituent. This indicates that primary *N*-alkyl groups permit the coordination of *N*-substituted en to the $Co^{2+}$ ion even in aqueous solution.

The difference between isopropyl and other primary alkyl groups was also observed in the absorption spectra of *trans*-$[CoCl_2(\text{diamine})_2]^+$ complexes. As Fig. 1 shows, the absorption maxima(15600, 20100, and 25000(sh) $cm^{-1}$) of the *N*-ipren compex shift to the lower energy side by 300—600 $cm^{-1}$ than those of the other complexes (*N*-nbuen; 15900, 20800, and 25300 $cm^{-1}$. *N*-nhxen; 15900, 20700, and 25000 $cm^{-1}$. *N*-ibuen; 15900, 20700, and 25100 $cm^{-1}$). The red shift should be ascribed to the steric effects caused by the bulkiness of isopropyl group.

It is very suggestive that *N*-chxen no longer forms the *trans*-dichlorocobalt(III) complex according to the same method as for the *N*-ipren complex. The cyclohexyl group is also a secondary alkyl group but its bulkiness should have more significant effects than that of isopropyl. Thus, it seems likely that the isopropyl group has the critical size not to prevent the formation of Co(III) species by air-oxidation.

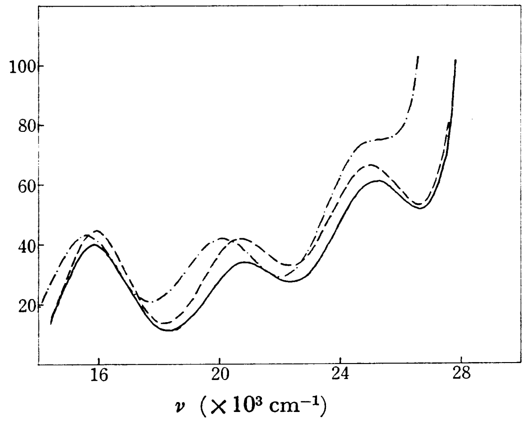

Fig. 1. Absorption spectra of *trans*-$[CoCl_2(\text{diamine}_2)]^+$: *N*-nbuen (——), *N*-nhxen (– – –), and *N*-ipren (—·—·—).

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