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# Triammine(1,4,7-triazacycloalkane)cobalt(III) and [(R)-2-Methyl-1,4,7-triazacyclononane] (1,4,7-triazacyclononane)cobalt(III)

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*The mixed ligand complexes* $[Co(NH_3)_3L]^{3+}$ *(L = 1,4,7-triazacyclononane, 1,4,7-triazacyclodecane, and (R)-2-methyl-1,4,7-triazacyclononane) and [Co(R)-2-methyl-1,4,7-triazacyclononane)(1,4,7-triazacyclononane)]*$^{3+}$ *were prepared and the (R)-2-methyl-1,4,7-triazacyclononane complexes separated into two isomers arising from two different coordination modes of the chiral ligand. The features of the electronic spectra of* $[Co(NH_3)_3L]^{3+}$ *were, as expected, intermediates between those of* $[CoL_2]^{3+}$ *and* $[Co(NH_3)_6]^{3+}$.

*The strengths of the circular dichroism spectra of* $[Co(NH_3)_3((R)\text{-2-methyl-1,4,7-triazacyclononane})]^{3+}$ *are unusually small and those of [Co(R)-2-methyl-1,4,7-triazacyclononane)(1,4,7-triazacyclononane)]*$^{3+}$ *are surprisingly large compared with those expected, based on the additivity rule of circular dichroism spectra, from the spectra of [Co(R)-2-methyl-1,4,7-triazacyclononane)*$_2$*]*$^{3+}$*. The results clearly show the presence of significant interligand interactions which restrain conformations of chelate rings in the bis(cyclic triamine) complexes.*

## Introduction

An exact nature of a ligand is required for a better understanding of its complexes and it is desirable to characterize complexes where there are as few interligand interactions as possible. Cobalt(III) complexes, $[Co(NH_3)_pL]^{3+}$ (L = an n-dentate ligand in question and n + p = 6) are expected to agree well with the above and several complexes of this type have been reported [1, 2]. Macrocyclic polydentate ligands are attractive because of the unique nature and at present their complexes are actively studied [3]. Cyclic triamine(L) complexes of the above type $[Co(NH_3)_3L]^{3+}$ have, however, not been studied so far. To characterize the nature of cyclic triamines we have studied the above type complexes of 1,4,7-triazacyclononane(abbreviated as tacn), 1,4,7-triazacyclodecane(tacd), and (R)-2-methyl-1,4,7-triazacyclononane(mtcn), and the mixed ligand complex $[Co(tacn)(mtcn)]^{3+}$ to reveal interligand interactions between the two cyclic triamines.

## Results and Discussion

The triammine complexes $[Co(NH_3)_3L]^{3+}$ (L = tacn, tacd, and mtcn) (Table I) are obtained by the reaction of L with $[CoCl(NH_3)_5]Cl_2$ in the presence of active charcoal in an aqueous ammonia–ammonium chloride buffer solution, while the mixed ligand complex $[Co(mtcn)(tacn)]^{3+}$ is prepared from mtcn and $[CoCl_3(tacn)]$ [4] in dmso. In the complexes of mtcn two isomers are possible since there are two different modes (*a* and *b*) of coordination of mtcn as shown in Fig. 1. The two isomers of $[Co(NH_3)_3(mtcn)]^{3+}$ and $[Co(mtcn)(tacn)]^{3+}$ are separated by SP Sephadex C-25 column chromatography with an aqueous disodium hydrogenphosphate solution as eluent [5]. In the $^1H$ NMR spectra measured for $D_2O$ solutions(sodium 2,2,-dimethyl-2-silapentanesulfonate as an internal standard) the faster eluted isomers, 1-$[Co(NH_3)_3(mtcn)]^{3+}$ and 1-$[Co(mtcn)(tacn)]^{3+}$, show the doublets of the methyl signals at $\delta = 1.35$ and at 1.36 ppm, respectively, and the slower eluted isomers, 2-$[Co(NH_3)_3(mtcn)]^{3+}$ and 2-$[Co(mtcn)(tacn)]^{3+}$, at 1.50 and at 1.52 ppm, respectively. The chemical shifts of the methyl groups of $[Co(mtcn)_2]^{3+}$ have been reported [6]: in one isomer 1-$[Co(mtcn)_2]^{3+}$ where the two mtcn ligands are coordinated in the mode *b* the value is 1.37 ppm, and in the other isomer 3-$[Co(mtcn)_2]^{3+}$. For both mtcn's in the *a* mode it is 1.52 ppm. Based on these values, 1-$[Co(NH_3)_3(mtcn)]^{3+}$ and 1-$[Co(mtcn)(tacn)]^{3+}$ are found to have the mode *b*, while 2-$[Co(NH_3)_3(mtcn)]^{3+}$ and 2-$[Co(mtcn)(tacn)]^{3+}$ the mode *a*.

The electronic spectra of the complexes prepared are given in Table II. The spectra are typical of a $[Co(III)N_6]$ chromophore. The absorption maxima of the d–d transitions of $[Co(NH_3)_3L]^{3+}$ are between those of $[Co(NH_3)_6]^{3+}$ and $[CoL_2]^{3+}$. There is nothing unusual about the electronic spectra on the basis of mean ligand fields.

The circular dichroism(CD) spectral data are given in Table III and Figs. 2 and 3. As has been reported [6, 7], the ligand mtcn when coordinated has no configurational chirality due to the arrangements of the chelate rings and has only conformational chirality of the chelate rings (the coordinated secondary nitrogen atoms are also chiral). The mtcn ligand is pre-

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TABLE I. Analytical Results of the Complexes.

| Complex | Found (calcd.), % | | |
|---|---|---|---|
| | C | H | N |
| $[Co(NH_3)_3(tacn)]Cl_3 \cdot 3/2H_2O$ | 19.12(19.34) | 7.31(7.30) | 22.86(22.55) |
| $[Co(NH_3)_3(tacd)]Cl_3 \cdot H_2O$ | 22.10(22.26) | 7.43(7.47) | 22.60(22.25) |
| 1-$[Co(NH_3)_3(mtcn)]Cl_3 \cdot 3/2H_2O$ | 21.65(21.75) | 7.53(7.56) | 21.88(21.74) |
| 2-$[Co(NH_3)_3(mtcn)]Cl_3 \cdot H_2O$ | 22.18(22.26) | 7.62(7.47) | 22.22(22.25) |
| $[Co(tacn)_2]Cl_3 \cdot 5H_2O$ | 28.07(28.05) | 7.73(7.85) | 16.45(16.36) |
| $[Co(tacd)_2]Cl_3 \cdot 2H_2O$ | 34.46(34.47) | 8.08(7.85) | 17.51(17.23) |
| 1-$[Co(mtcn)(tacn)]Cl_3 \cdot 5H_2O$ | 29.72(29.58) | 8.12(8.02) | 15.95(15.92) |
| 2-$[Co(mtcn)(tacn)]Cl_3 \cdot 5H_2O$ | 29.39(29.58) | 8.40(8.02) | 15.71(15.92) |

TABLE II. Electronic Spectra of the Complexes in Water.

| Complex | $\nu$max/$10^3$ cm$^{-1}$ (log $\epsilon$) | | |
|---|---|---|---|
| $[Co(NH_3)_3(tacn)]Cl_3 \cdot 3/2H_2O$ | 21.34(1.91) | 29.39(1.84) | 47.8(4.33) |
| $[Co(NH_3)_3(tacd)]Cl_3 \cdot H_2O$ | 21.04(1.91) | 29.07(1.86) | 46.5(4.29) |
| 1-$[Co(NH_3)_3(mtcn)]Cl_3 \cdot 3/2H_2O$ | 21.32(1.93) | 29.35(1.87) | 47.5(4.33) |
| 2-$[Co(NH_3)_3(mtcn)]Cl_3 \cdot H_2O$ | 21.33(1.93) | 29.42(1.86) | 47.6(4.33) |
| $[Co(tacn)_2]Cl_3 \cdot 5H_2O$ | 21.78(1.98) | 29.94(1.93) | 44.4(4.37) |
| $[Co(tacd)_2]Cl_3 \cdot 2H_2O$ | 21.29(1.89) | 29.24(1.95) | 43.2(4.30) |
| 1-$[Co(mtcn)(tacn)]Cl_3 \cdot 5H_2O$ | 21.65(2.03) | 29.90(1.97) | 44.2(4.38) |
| 2-$[Co(mtcn)(tacn)]Cl_3 \cdot 5H_2O$ | 21.67(1.98) | 29.91(1.94) | 44.4(4.36) |

TABLE III. C.D. Spectra of the Complexes in Water.

| Complex | $\nu$ext/$10^3$ cm$^{-1}$ ($\Delta\epsilon$) | | | |
|---|---|---|---|---|
| 1-$[Co(NH_3)_3(mtcn)]Cl_3 \cdot 3/2H_2O$ | 21.2(0.78) | 28.4(0.10) | 47.5(14.4) | |
| 2-$[Co(NH_3)_3(mtcn)]Cl_3 \cdot H_2O$ | 21.5(0.87) | 29.0(0.13) | 47.7(19.5) | |
| 1-$[Co(mtcn)(tacn)]Cl_3 \cdot 5H_2O$ | 21.1(3.98) | 29.5(−0.29) | 42.6sh | 46.8(13.3) |
| 2-$[Co(mtcn)(tacn)]Cl_3 \cdot 5H_2O$ | 21.2(4.06) | 29.5(−0.25) | 42.2sh | 46.4(16.2) |
| 1-$[Co(mtcn)_2]Cl_3 \cdot 5H_2O$[a] | 20.8(4.35) | 29.2(−0.31) | 41.7(10.3) | 46.3(10.8) |
| 3-$[Co(mtcn)_2]Cl_3 \cdot 5H_2O$[a] | 21.0(4.72) | 29.3(−0.24) | 42.8sh | 45.9(15.7) |

[a] From ref. 6. The coordination mode of mtcn in the isomer 1 is the same as that in 1-$[Co(mtcn)L]^{3+}$ (L = tacn and $(NH_3)_3$) and that of the isomer 3 is the same as that in 2-$[Co(mtcn)L]^{3+}$ (L = tacn and $(NH_3)_3$).

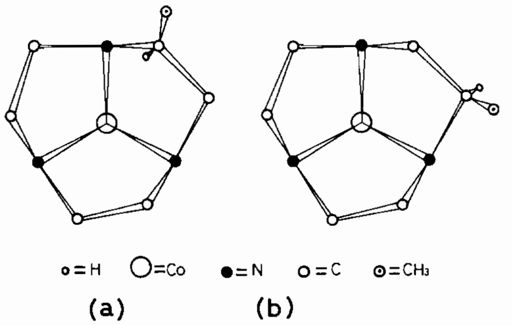

Fig. 1. Two modes of coordination of (R)-1,4,7-triazacyclononane. In the two modes the methyl group occupies an equational direction.

pared from (R)-1,2-diaminopropane((R)-pn) [7] and the methyl substituted chelate ring should be fixed to a λ conformation when the methyl group adopts an equatorial orientation [7, 8].

The CD spectra of the two isomers of $[Co(NH_3)_3(mtcn)]^{3+}$ are similar in patterns (Fig. 2) but their intensities are slightly different (Table III). Similar features were also noted for $[Co(mtcn)(tacn)]^{3+}$, suggesting that within each pair the mtcn ligand has similar conformations. The effect of addition of sodium sulfate is also similar within each pair. To reveal the conformation of mtcn in these complexes the CD spectra in the region of the ligand field transitions, especially in the region of the band I ($^1A_{1g} \rightarrow {}^1T_{1g}$ in Oh symmetry), of $[Co(NH_3)_3(mtcn)]^{3+}$ are

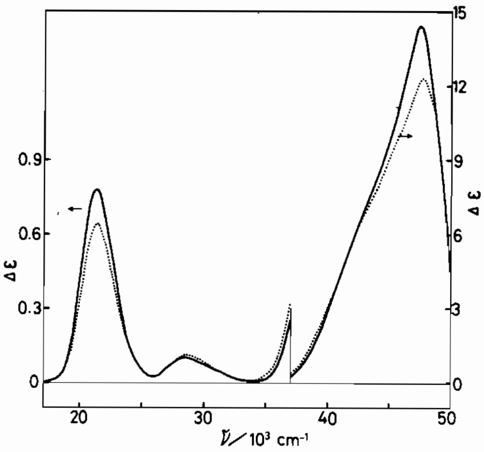

Fig. 2. Circular dichroism spectra of 1-$[Co(NH_3)_3(mtcn)]^{3+}$ in water (——) and in a 0.1 *M* aqueous sodium sulfate solution (· · ·).

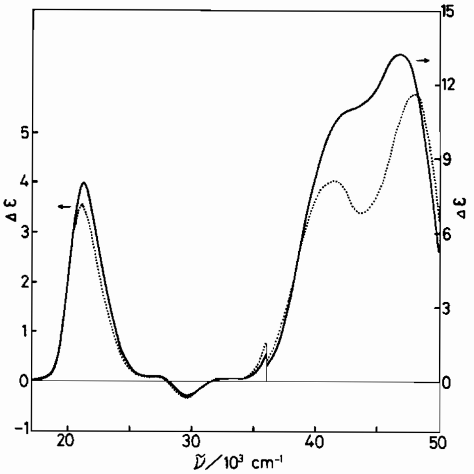

Fig. 3. Circular dichroism spectra of 1-$[Co(mtcn)(tacn)]^{3+}$ in water (——) and in a 0.1 *M* aqueous sodium sulfate solution (· · ·).

compaired with those of $[Co(mtcn)_2]^{3+}$ ($\Delta\epsilon = 4.35 - 4.77$) where all the six chelate rings are fixed to λ conformations [8]. If we admit that the CD spectra of these complexes originate mainly from chelate ring conformations and that all the three chelate rings of $[Co(NH_3)_3(mtcn)]^{3+}$ are fixed like those of $[Co(mtcn)_2]^{3+}$, the value $\Delta\epsilon = 2.18 - 2.39$ (half the above value) would be expected for $[Co(NH_3)(mtcn)]^{3+}$. If the methyl substituted chelate ring only is assumed to be fixed to a λ conformation and the other chelate rings are flexible, the value $\Delta\epsilon = 0.73 - 0.80$ (one-sixth the above value) may be expected.

The observed Δε values are near to the latter suggesting that only the methyl substituted chelate ring of $[Co(NH_3)_3(mtcn)]^{3+}$ is, in a first approximation, assumed to be fixed to a λ conformation and the other chelate rings to be flexible with little chirality. The CD spectra of the complexes $[CoX_3(mtcn)]$ (X = $NO_2$, NCS, Cl, and Br) [9] show similar features in the d-electron transition region and the Δε values of the first absorption bands are comparable to those of $[Co(NH_3)_3(mtcn)]^{3+}$. It is assumed that in these mono mtcn complexes the methyl substituted chelate ring alone is limited to a λ conformation while the remaining two are almost free from a chiral conformation.

The CD spectra of $[Co(NH_3)_4L']^{3+}$ (L′ = (R)-pn and (R)-chxn ((R)-1,2-diaminocyclohexane)) are reported: $\Delta\epsilon = +0.34$ for L′ = (R)-pn and $\Delta\epsilon = +0.50$ for (R)-chxn. Comparison of the value of $[Co(NH_3)_3(mtcn)]^{3+}$ with those of $[Co(NH_3)_4L']^{3+}$ suggests that in the former some other factors which intensify the CD spectra exist. Trigonal distortions and chiral coordinated secondary amino nitrogen atoms may have some contributions.

The extreme values Δε of the CD spectra of $[Co(mtcn)(tacn)]^{3+}$ are quite different from those of $[Co(NH_3)_3(mtcn)]^{3+}$ even though the same mtcn ligand is only the origin of chirality in both the complexes. The values of $[Co(mtcn)(tacn)]^{3+}$ are near to those of $[Co(mtcn)_2]^{3+}$, suggesting that in the mixed complex nearly all the six chelate rings have λ conformations. The addition of sodium sulfate causes similar CD spectral changes for $[Co(mtcn)(tacn)]^{3+}$ and the reported [7] $[Co(mtcn)_2]^{3+}$ indicating that these have similar conformations. Introduction of only one chiral center(methyl group) into the complex $[Co(tacn)_2]^{3+}$ results in very effective regulation of the conformations of all the six chelate rings. In other words, interligand interactions in the bis(1,4,7-triazacyclononane) and related complexes make chelate ring conformations uniform.

The elution order of the mtcn complexes, $[Co(mtcn)_2]^{3+}$, $[Co(NH_3)_3(mtcn)]^{3+}$, $[Co(mtcn)(tacn)]^{3+}$, and $[Co(mtcn)(tame)]^{3+}$ (tame = 1,1,1-tris(aminomethyl)ethane), upon chromatography on an SP Sephadex C-25 column was studied with disodium hydrogenphosphate solution as an eluent: the complexes coordinated with mtcn in the mode *b* elute faster and those coordinated with mtcn in the mode *a* elute slower. The different interactions of the complexes with an eluting reagent should be influenced by the dissimilar surroundings around the N–H groups. The differences are found in $^1H$ NMR spectra of $[Co(mtcn)_2]^{3+}$ and $[Co(mtcn)(tacn)]^{3+}$. The signals of the three N–H groups of mtcn coordinated in the mode *b* appear at the same field, *ca.* 6.8 ppm, while those of mtcn in the mode *a* split into two, one at *ca.* 6.8 ppm (2 H) and the other at *ca.* 5.8 ppm (1 H).

## Experimental

### *Measurements*

Measurements were carried out by the methods reported previously [6].

### *Preparations*

The ligands were prepared by the methods reported in the literature [4, 7]. The analytical results for the complexes are given in Table 1.

#### *$[Co(NH_3)_3L]Cl_3$ (L = tacn, tacd, and mtcn)*

A mixture of 1 mmol of pentaamminechlorocobalt (III) chloride, 1 mmol of L·3HCl, 10 mmol of ammonium chloride, 5 ml of concentrated aqueous ammonia, and a small amount of active charcoal in 15 ml of water was stirred at 45 – 50 °C for 5 h to give an orange solution. The active charcoal was filtered off and the filtrate was evaporated to dryness under reduced pressure. The residue was dissolved in a small amount of water and poured onto a column (50 cm X 2.8 cm ϕ) of SP Sephadex C-25. The column was eluted with a 0.2 *M* aqueous solution of sodium sulfate and the main yellow band was collected. The effluent was treated in the usual methods [5] and the product was isolated as the chloride.

#### *$[Co(NH_3)_3(mtcn)]Cl_3$ (Isomers 1 and 2)*

The mixture of isomers of $[Co(NH_3)_3(mtcn)]^{3+}$ prepared as above was absorbed on a top of an SP Sephadex C-25 column (120 X 2.8 cm ϕ) and the band was eluted with 0.2 *M* aqueous disodium hydrogenphosphate. Two incompletely separated yellow bands, 1-$[Co(NH_3)_3(mtcn)]^{3+}$ and 2-$[Co(NH_3)_3(mtcn)]^{3+}$ were eluted in this order. The first half of the band-1 and the last half of the band-2 were collected separately and the overlapping middle part was subjected to the repeated chromatography. The two isomers were isolated as the chlorides from the separately collected effluents of the band-1 and band-2. The formation ratio band-1/band-2 was *ca.* 45/55.

#### *$[Co(tacn)_2]Cl_3 \cdot 5H_2O$ and $[Co(tacd)_2]Cl_3 \cdot 2H_2O$*

The two complexes were prepared by the methods in the literature [10] but isolated as the chlorides.

#### *$[Co(mtcn)(tacn)]Cl_3 \cdot 5H_2O$ (Isomers 1 and 2)*

A mixture of 1 mmol of mtcn and 1 mmol of $[CoCl_3(tacn)]$ [4] in 25 ml of dimethylsulfoxide was warmed on a steam bath for *ca.* 8 h to give a yellow solution. The solution was diluted with 150 ml of water and poured onto a column (120 cm X 2.8 cm ϕ) filled with SP Sephadex C-25. The column was eluted with 0.2 *M* aqueous disodium hydrogenphosphate to give two well-separated yellow bands. The two bands 1-$[Co(mtcn)(tacn)]^{3+}$ and 2-$[Co(mtcn)(tacn)]^{3+}$ were eluted in this order and were isolated as the chlorides. The formation ratio band-1/band-2 was *ca.* 52/48.

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