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Bis[(R)-2-methyl-1,4,7-triazacyclononane] Cobalt(III), Nickel(II), and Copper(II) Complexes

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Bis[(R)-2-methyl-1,4,7-triazacyclononane] cobalt(III), nickel(II), and copper(II) complexes have been prepared and characterized. The cobalt complex is separated into five components although there are nine possible isomers. The nickel and copper complexes were not separated into isomers. Since these optical active complexes contain, to a first approximation, no chiral chelate ring configuration, the optical activity results only from λ conformations of the six chelate rings. It is noteworthy that all the complexes show very strong positive CD extremes in the region of the first spin allowed d–d transitions in O_h *symmetry.*

Introduction

Two modes of coordination of (R)-2-methyl-1,4,7-triazacyclononane (L) (in the literature [1, 2] it is abbreviated as R-MeTACN) are possible as shown in Fig. 1 and hereafter they are represented as "a" and "b", respectively. In both the modes the C(2)–CH_3 bond is placed equatorial with respect to the mean plane of the chelate rings, but the configurations of coordinated secondary nitrogen atoms are reversed each other in the two modes: in mode "a", S(N_1), R(N_4), and S(N_7), while in mode "b", R(N_1), S(N_4), and R(N_7). A bis complex [ML_2] can be described as Ma_2, Mb_2 or Mab (charge of a complex is not shown for clarity). For Ma_2 there are further three possible geometrical isomers in respect to the two methyl groups and likely there are three for each of the remaining Mb_2 and Mab (Fig. 2). Nine geometrical isomers are thus possible for the bis complex [ML_2], although in the literature [1, 2] it has been reported that there are three for $[Co(R\text{-}MeTACN)_2]I_3\cdot5H_2O$. The crystal structure of a mixture of the three isomers has been determined [2] and the two R-MeTACN ligands found to be coordinated in mode "a", the complex being a mixture of Ma_2(aa-1, aa-2, and aa-3). It is intriguing that only the three isomers are formed. We have studied isomerism of [CoL_2] in detail and found that MaB and Mb_2 are indeed formed together with the reported Ma_2. However, we were not successful in identifying all the nine possible isomers so far.

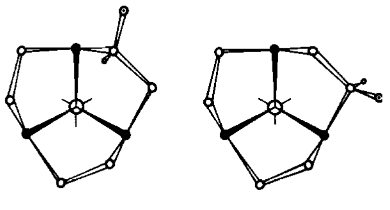

Figure 1. Two modes of coordination of (R)-2-methyl-1,4,7-triazacyclononane.

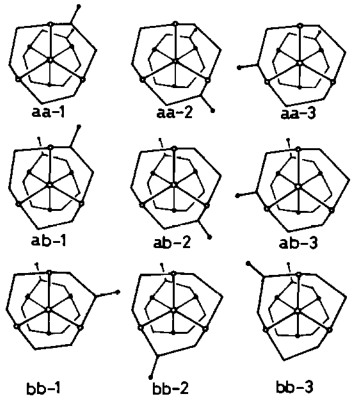

Figure 2. Nine possible isomers for a bis[(R)-2-methyl-1,4,7-triazacyclononane] metal complex.

It is very interesting that optical activity of the complexes of this ligand is due to chelate ring conformation alone, to a first approximation, and no configurational effect about the central metal ions is expected. Nickel(II) and copper(II) complexes were also prepared to see this effect.

Experimental

The ligand (L) was prepared by the method reported [1]. The cobalt(III) complex was prepared

TABLE I. Analytical Results for the Complexes.

Complex	C%	H%	N%
$[CoL_2]Cl_3 \cdot 5H_2O^a$			
Calcd.	31.03	8.19	15.51
Found *I*	30.97	7.84	15.57
II-1	31.11	8.23	15.30
II-2	30.57	8.20	15.23
II-3	31.17	8.00	15.21
III	30.93	7.85	15.45
$[NiL_2](ClO_4)_2$			
Calcd.	30.91	6.30	15.45
Found	31.11	6.53	15.50
$[CuL_2](ClO_4)_2$			
Calcd.	30.63	6.24	15.31
Found	30.19	6.41	15.16

^{a}Calcd. for $[CoL_2]Cl_3 \cdot 5H_2O$: Cl 19.63; H_2O 16.62%. Found for *II*: Cl 19.73; H_2O 16.79%.

either by the method reported [1] or by the method described below.

A mixture of 4 mmol of L·3HCl and 12 mmol of sodium hydroxide in 20 cm^3 of water was added to a suspension of 2 mmol of $[CoCl(NH_3)_5]Cl_2$ in 20 cm^3 of water. The suspension was heated for 4 hours on a steam bath. After cooling to room temperature, the reaction mixture was charged on the top of a column (2.7ϕ × 120 cm) packed with SP-Sephadex and elution with a 0.2 *M* aqueous solution of sodium sulfate gave three yellow bands (Fig. 3A). In the order of elution they were labelled as *I*, *II*, and *III*. The three bands were subjected to recromatography on the same column with a 0.2 *M* aqueous solution of sodium monohydrogen phosphate as an eluent. The bands *I* and *III* were not further separated, while the band *II* gave the elution curve as shown in Fig. 3B. The first effluent (*II-1*) was separated completely from the following effluents. The second and the third components overlapped each other. The first half of the second (*II-2*) and the second half of the third (*II-3*) effluents were collected and the complexes were crystallized from water and ethanol.

The five fractions were formulated as $[CoL_2]Cl_3 \cdot 5H_2O$ (Table I). The complexes were not isomerized in acidic, neutral, or weak basic aqueous solutions.

The copper(II) and nickel(II) complexes were synthesized by mixing required amounts of L·3HCl, metal chloride, sodium hydroxide, and sodium perchlorate in water and then concentrating the mixture on a steam bath to crystallize the product (*ca.* 70% yield) [3].

Measurements

Electronic absorption spectra were recorded on a Hitachi 323 spectrophotometer and CD spectra on JASCO J-20 and J-40C spectropolarimeters. PMR spectra (at 60 MHz) were obtained with JEOL C-60H and PMX-60 spectrometers and DSS was used as an internal standard. Infrared spectra of KBr disks were measured with a JASCO IR-A3 spectrometer.

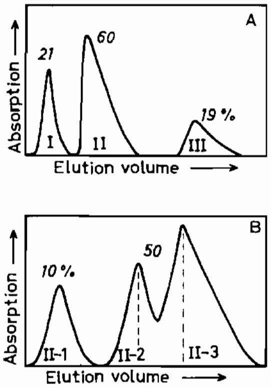

Figure 3; A: Elution curve of chromatography on an SP-Sephadex column of the reaction product eluted with 0.2 *M* aqueous sodium sulfate. B: Elution of the second component (*II*) of the preceding chromatography (A) eluted with 0.2 *M* aqueous sodium monohydrogen phosphate. Italic numbers show formation ratios.

Results and Discussion

Reaction of $[CoCl(NH_3)_5]Cl_2$ with (R)-2-methyl-1,4,7-triazacyclononane in an 1:2 molar ratio in water gave a yellow solution and upon chromatography on an SP-Sephadex column with sodium sulfate and sodium monohydrogen phosphate as eluents, from the solution were separated five components: *I*, *II-1*, *II-2*, *II-3*, and *III* (Fig. 3). No further separation was observed with other eluents such as sodium tartrate, sodium tartratoantimoniate, and sodium tripolyphosphate.

The method of preparation reported by Mason *et al.* [1] gave only the components corresponding to the bands *II-1* and *III*. The mother liquor of the preparation was shown to contain the remaining three *I*, *II-2*, and *II-3* upon chromatography. The five components were characterized by proton magnetic resonance, ultraviolet, visible, circular dichroism, and infrared spectra as discussed below.

PMR spectra measured in 2% DCl–D_2O can be divided into three distinct types: the spectra of *I*, of *II-1* and *III*, and of *II-2* and *II-3*. Signals of the methyl groups of *II-1* and *III* are observed as a doublet at the same field 1.52 ppm (downfield from DSS) (J = 6 Hz, the intensity corresponds to 6 H). The signals of the amino protons are split into two absorptions at *ca.* 6.8 (4 H) and at *ca.* 5.8 (2 H) ppm in both cases. A mixture of *II-1* and *III* have already

TABLE II. Absorption and CD Spectra of the Complexes in H_2O.

Complex	Absorption spectra $\tilde{\nu}$max/10^3 cm^{-1} (log ϵ)	CD spectra $\tilde{\nu}$ext/10^3 cm^{-1} ($\Delta\epsilon$)
$[CoL_2]Cl_3 \cdot 5H_2O$		
I	21.53(2.08)	20.8(4.35)
	29.72(2.01)	29.2(−0.31)
	44.0(4.41)	41.7(10.3)
		46.3(10.8)
II-1	21.67(2.00)	21.1(4.77)
	29.82(1.97)	29.4(−0.25)
	44.3(4.42)	42.6sh
		45.7(16.7)
II-2	21.57(2.03)	20.9(4.58)
	29.74(1.98)	29.3(−0.28)
	44.1(4.41)	41.9(12.4)
		45.9(13.3)
II-3	21.58(2.05)	21.0(4.68)
	29.78(1.99)	29.4(−0.29)
	44.1(4.42)	42.0(12.6)
		46.1(13.7)
III	21.61(2.02)	21.0(4.72)
	29.83(1.98)	29.3(−0.24)
	44.2(4.41)	42.8sh
		45.9(15.7)
$[CuL_2](ClO_4)_2$	16.0(1.60)	16.1(1.04)
		31.5(−0.117)
	38.5(3.75)	40.3(4.28)
		>47(−)
$[NiL_2](ClO_4)_2$	11.2sh	11.5sh
	12.3(0.91)	12.5(1.21)
	18.0sh	17.4(0.0461)
		20.3sh
	19.7(0.77)	21.1(0.0342)
	30.6(0.82)	29.0(−0.0219)
		42.3(−1.06)
	>48	>47(+)

been isolated and the structure determined [1, 2]. In the mixture both the ligands are coordinated as "a" (Fig. 1) and aa-1, aa-2, and aa-3 (Fig. 2) are incorporated in crystals with equal probability. Taking into account the formation ratio, *II-1* is assumed to be one of the three isomers and *III* a mixture of the remaining two isomers.

The PMR spectrum of *I* shows a doublet at 1.37 ppm (J = 6 Hz, 6H) due to methyl groups and a broad absorption of amino protons at *ca.* 6.8 ppm (6 H). The two ligands in *I* are, therefore, equivalent and *I* is a mixture of bb-1, bb-2, and bb-3. The remaining *II-2* and *II-3* show an intermediate spectral pattern between the above two categories. Resonances of the methyl groups are observed as two doublets at 1.41 (3 H) and 1.56(3 H) for *II-2*, and at 1.37(3 H) and 1.55(3 H) ppm for *II-3*. The amino proton resonances are also split at 6.8(5 H) and 5.8(1 H) for the both. These facts suggest that the two ligands are coordinated in different modes and that *II-2* is one of the three isomers ab-1, ab-2, and ab-3 and *II-3* a mixture of the other two isomers.

As pointed out above, in mode "a" the configuration of N(1) is S while it is R in mode "b". The configuration at C(2) is R in both cases and the relation between N(1)-H and C(2)-CH_3 is, therefore, different in the two models; SR or RR. This may cause magne-

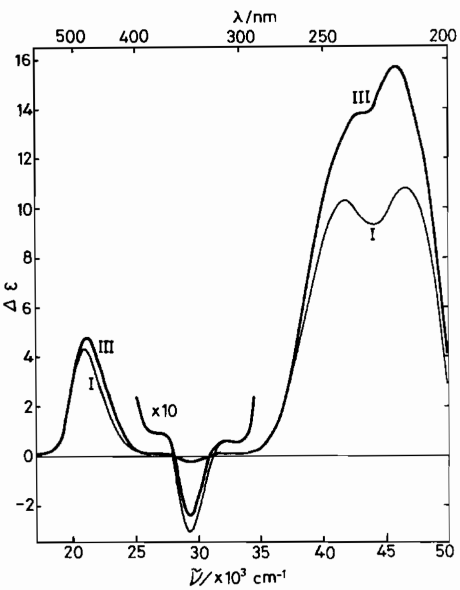

Figure 4. CD spectra of the cobalt(III) complexes *I* and *III*.

tically different environments about N(1)-H and C(2)-CH_3 between the two modes*.

Absorption spectra of the complexes (Table II) are typical of an octahedral CoN_6 chromophore and appear at higher frequencies than that of $[Co(en)_3]^{3+}$, implying a stronger ligand field of the cyclic ligand [3, 4]. Among the isomers there are small but significant differences in spectroscopic properties. The aa isomers (*II-1* and *III*) have the strongest ligand field with smallest molar extinction coefficients. On the other hand, the bb isomers (*I*) have the weakest ligand field with the highest molar extinction coefficient. The remaining ab isomers (*II-2* and *II-3*) show middle properties. Coordination in mode "b" may produce more distortion and/or strain, so that this results in a weaker ligand field with higher molar extinction coefficient [3].

The CD spectra of the aa isomers (*II-1* and *III*) are more intense than that of the bb isomer (*I*) in the region of both the first d–d and CT bands**. The X-ray structural analysis of the former shows that all the six chelate rings are in λ conformation with mode "a", which is reported to result in very intense CD spectra in the d–d region [1]. The lower intensity of the CD spectrum of the bb isomer may result from distortion of chelate rings from an ideal λ conformation. The remaining ab isomers (*II-2* and *II-3*) again have intermediate properties. These results are consistent with the assumption obtained from the absorption spectra.

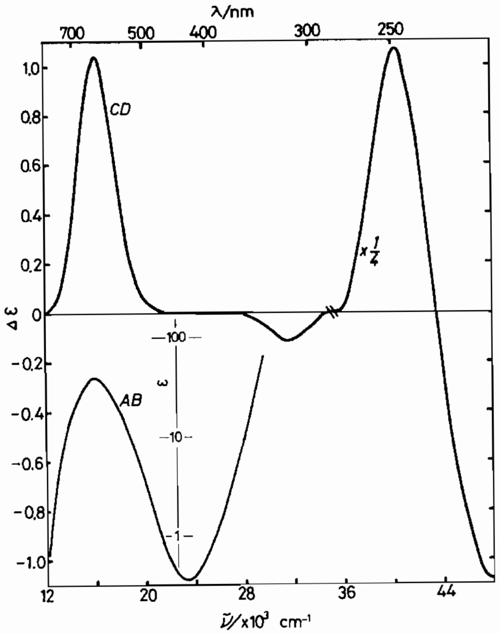

Fig. 5. CD and absorption spectra of the copper(II) complex.

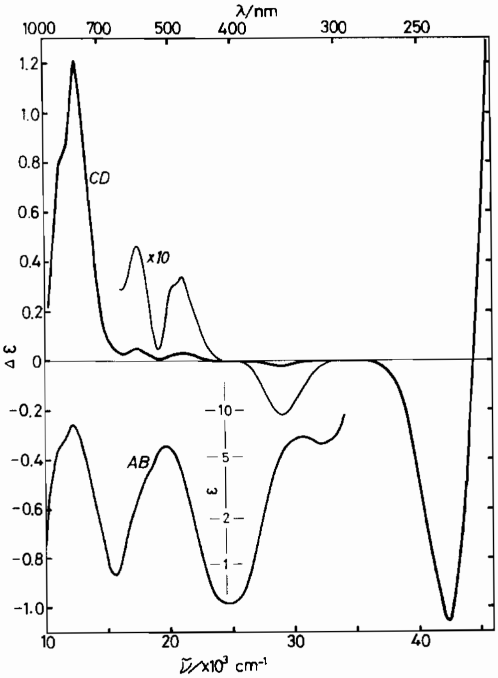

Fig. 6. CD and absorption spectra of the nickel(II) complex.

In addition to the λ conformation of the chelate rings, another origin in optical activity that must be considered is the configuration of coordinated secondary nitrogen atoms. The configurations in mode "a" are reversed in mode "b" (Fig. 1). However it is difficult to estimate the relative effects of the two origins. We feel, at present, that the effects of chelate ring conformations are predominant at least in the

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*$[Co(1,4,7\text{-triazacyclononane})_2]^{3+}$ shows a broad resonance of amino protons at *ca.* 6.8 ppm in 2% DCl–D_2O [4].

**In the literature [1] $[Co(R\text{-}MeTACN)_2]^{3+}$ is reported to show no observable CD spectrum in the ultraviolet region.

d–d transition region, since the CD intensity in this region differs only slightly among the isomers. In the UV region there are marked differences in CD strength (Fig. 4).

To obtain further information on CD spectra due to chelate ring conformations without contribution of chelate ring configurations, nickel(II) and copper(II) complexes were prepared and characterized. Both the complexes show also two CD components in the CT region (Table II) but the signs of the extremes of the nickel complex are reversed in the copper complex (Figs. 5 and 6). The copper complex shows a single positive extreme in the d–d transition region ($^2E_g \rightarrow {}^2T_{2g}$) and there is no indication of splitting to show effective O_h symmetry around copper ion.

The CD spectrum of the nickel complex is complicated. In O_h symmetry the first spin-allowed d–d transition $^3A_{2g} \rightarrow {}^3T_{2g}$ (ν_1) is magnetic dipole-allowed while the second $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ (ν_2) and the third transition $^3A_{2g} \rightarrow {}^3T_{1g}(P)$ (ν_3) are forbidden. The CD of ν_1 is expected to be more intense than those of ν_2 and ν_3. This is the case observed but in the regions ν_1 and ν_2 two and three extremes and/or shoulder are, respectively, observed. The absorption spectrum also shows shoulders in the regions (Table II and Fig. 6). Actual symmetry may be lower than O_h and approaching D_3. In this symmetry T_{1g} splits into A_2 and E, and T_{2g} into A_1 and E (an $A_2 \rightarrow A_2$ transition is forbidden). This cannot explain the situation in the ν_2 region. Appearance of spin-forbidden transitions should be taken into account [5]. Assignments of each component of the CD spectrum are, however, difficult and seem to require measurement of a single crystal spectrum.

The CD strength of ν_1 ($\Delta\epsilon = 1.21$) is surprisingly large [6], compared to the molar extinction coefficient of the band ($\log \epsilon = 0.91$). As pointed out above, the six chelate rings are all fixed to a λ conformation and this is the origin of the result. It is very interesting that the first spin-allowed d–d transitions of the cobalt(III), nickel(II), and copper(II) complexes have the same positive sign with high intensity in CD spectra and these transitions correspond, respectively, to $^1A_{1g} \rightarrow {}^1T_{1g}$, $^3A_{2g} \rightarrow {}^3T_{2g}$, and $^2E_g \rightarrow {}^2T_{2g}$ in an O_h approximation. The d-electron optical activity [1] produced only by a chiral conformation of chelate rings seems to be similar for these ions.

Acknowledgment

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