BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN, VOL. 45, 481—484 (1972)

Syntheses of Some Medium Sized Cyclic Triamines and Their Cobalt(III) Complexes[1]

Hiroyuki KOYAMA* and Tamotsu YOSHINO

Department of Chemisty, Faculty of Science, Kyushu University, Hakozaki, Fukuoka

(Received July 30, 1971)

Four cyclic triamines of a medium ring size (9—12-membered ring) which form three mutually-adjacent five- and/or six-membered chelate rings on complexation, such as 1,4,7-triazacyclononane (abbreviated TACN), 1,4,7-triazacyclodecane (TACD), 1,4,8-triazacycloundecane (TACUD), and 1,5,9-triazacyclododecane (TACDD) were synthesized and isolated as their trihydrobromides. The complexation of TACN and TACD with a cobalt(III) salt yielded metal complexes of a sandwich-type structure, such as $[Co(TACN)_2]Br_3$ and $[Co(TACD)_2]Br_3 \cdot H_2O$, which were then isolated. In the case of TACUD, a complex $[Co(TACUD)BrCl_2]$ containing only one molecule of the triamine was isolated. However, although the formation of a cobalt(III) complex with TACDD in solution was inferred spectroscopically, no expected complex was isolable. On the basis of the spectrophotometric data, the ligand-field strength was found to increase in the following order:

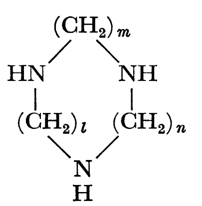
$$[Co(NH_3)_6]^{3+} < [Co(TACD)_2]^{3+} < [Co\ en_3]^{3+} < [Co(TACN)_2]^{3+}.$$

In this decade a large number of metal chelates with a quadridentate macrocyclic compound have been synthesized, and most of them have been investigated in considerable detail.[2] In contrast with this, only a few metal complexes with cyclic tridentate ligands of a medium ring size have been studied.[3,4] It is well known that an appreciable strain exists in a cyclic hydrocarbon of a medium ring size.

A similar strain appears to exist also in a comparable cyclic triamine,[5] whose coordination to a metal ion may result in the formation of three mutually-adjacent five- and/or six-membered chelate rings.

The stability of the complex formed by the coordination of such a cyclic triamine to metal ions is expected to depend on the sizes of the three chelate rings in addition to the above-mentioned strain. It seems to be of interest to synthesize such cyclic triamines and to examine the relative stability of their metal complexes.

With this in mind, we synthesized four cyclic triamines of a medium ring size (9—12-membered ring), such as 1,4,7-triazacyclononane (abbreviated TACN, formula I, expected to form three 5-membered chelate rings), 1,4,7-triazacyclodecane (TACD, II, one 6-membered and two 5-membered rings), 1,4,8-triazacycloundecane (TACUD, III, two 6-membered and



I	$l=2,\ m=2,\ n=2$	TACN
II	$l=3,\ m=2,\ n=2$	TACD
III	$l=3,\ m=3,\ n=2$	TACUD
IV	$l=3,\ m=3,\ n=3$	TACDD

Fig. 1. Structures of the ligands.

---

[1] Presented at the 20th Symposium on Coordination Chemistry, Tokyo, November, 1970.

* Present address: Laboratory of Chemistry, College of General Education, Kyushu University, Ropponmatsu, Fukuoka.

[2] B. Bosnich, C. K. Poon, and M. L. Tobe, *Inorg. Chem.*, **4**, 1102 (1965); J. P. Collman and P. W. Schneider, *ibid.*, **5**, 1380 (1966); N. F. Curtis, *J. Chem. Soc.*, **1964**, 2644; E. Ochiai and D. H. Busch, *Inorg. Chem.*, **8**, 1474 (1969).

[3] L. T. Taylor and D. H. Busch, *ibid.*, **8**, 1366 (1969).

[4] W. Rosen and D. H. Busch, *ibid.*, **9**, 262 (1970).

[5] J. Dale, *J. Chem. Soc.*, **1963**, 93.

Table 1. Properties of the products

Compound[a]	Formula	Analysis % Found (Calcd) C	H	N	Mp °C	Yield %	Molecular weight Found(Calcd)
I	$C_6H_{18}Br_3N_3$	19.39 (19.38	4.85 4.88	11.25 11.30)	274—275	88	—
II	$C_7H_{20}Br_3N_3$	21.61 (21.78	5.27 5.22	10.65 10.88)	242—243	82	—
III	$C_8H_{22}Br_3N_3$	23.83 (24.02	5.53 5.54	10.51 10.51)	239.5—240	79	—
IV	$C_9H_{24}Br_3N_3$	25.89 (26.11	5.87 5.84	10.08 10.15)	267.5—268.5	62	—
V	$C_{25}H_{31}N_3O_6S_3$	53.28 (53.07	5.35 5.52	7.04 7.43)	173[b]	97	—
VI	$C_{26}H_{33}N_3O_6S_3$	54.02 (53.86	5.82 5.74	7.12 7.25)	119.5—121.5	66	—
VII	$C_{27}H_{35}N_3O_6S_3$	—	—	—	—	57	—
VIII	$C_{28}H_{35}N_3O_6S_3$	55.48 (55.51	5.89 5.82	6.90 6.94)	230—232	24	610 (605.8)
IX	$C_{29}H_{37}N_3O_6S_3$	56.08 (56.17	6.11 6.01	6.80 6.82)	213	25	618 (620.1)
X	$C_{30}H_{39}N_3O_6S_3$	56.67 (56.85	6.32 6.20	6.58 6.63)	172	8	638 (633.9)

a) I, II, III, and IV: As trihydrobromides.

b) Lit, mp 173°C: D. H. Peacock and U. C. Dutta, *J. Chem. Soc.*, **1934**, 1303.

one 5-membered rings), and 1,5,9-triazacyclododecane (TACDD, IV, three 6-membered rings), and isolated them as their trihydrobromides; we also characterized the intermediates obtained in the course of the syntheses as well as the products.

As the central metal ion to which the ligand coordinates, we chose the cobalt(III) ion, which is noted for its typical octahedral coordination, and studied the electronic spectra of the metal complexes formed. We wish now to report the results.

Experimental

All the melting and decemposition points are uncorrected. The infrared spectra were determined in potassium bromide disks on a Hitachi EPI-S2 spectrophotometer. The NMR spectra were recorded at 60 MHz with a Hitachi R-20 spectrometer with $CDCl_3$ as the solvent, and the chemical shifts were reported in τ values relative to tetramethylsilane as the internal standard except for those attributable to *p*-toluenesulfonyl groups in VIII, IX, and X. The NMR data are given in the order of increasing multiplicity (*s*=singlet, *t*=triplet, *q*=quintet, and *m*= unresolved multiplet), integration, and coupling constant. The molecular weights were determined on a Hitachi Osmometer, type 115, using benzene as the solvent in the case of the tritosyl derivative of cyclic triamines and methanol in the case of the TACUD complex.

*N,N′,N″-Tri(*p*-toluenesulfonyl)derivative of Open-chain Triamines V, VI, and VII.* To a solution of a triamine $H_2N(CH_2)_{2-3}NH(CH_2)_{2-3}NH_2$ (0.1 mol) and sodium hydroxide (0.3 mol) in water (80 m*l*), there was added, drop by drop, a solution of *p*-toluenesulfonyl chloride (0.3 mol) in ether (150 m*l*); the mixture was then stirred for 1 hr at room temperature. A white precipitate thus formed was collected by filtration, washed with water, and recrystallized from a large amount of methanol to give colorless needles. VII was left as a pale yellow oil and used in the next step without further purification. The data are summarized in Table 1.

*N,N′,N″-Tri(*p*-toluenesulfonyl)derivative of Cyclic Triamines VIII, IX, and X.* To a vigorously-stirred mixture of anhydrous potassium carbonate (40 g) in dimethylformamide (2 *l*) maintained at 120°C, there was added, drop by drop, a solution of tritosyl triamine (V,VI of VII) (0.03 mol) and 1,3-dibromopropane (0.03 mol) in dimethylformamide (350 m*l*) through a Hershberg's dropping funnel for 30—40 hr at the rate of one drop per 10 sec; the mixture was further stirred for 7 hr at 115—120°C, and then it was cooled to room temperature and filtered to remove any inorganic substances. The filtrate was concentrated to one tenth of the original volume and water (3 *l*) was added to deposit a precipitate, which was then extracted with hot benzene (2 *l*).

The benzene extract was dried over anhydrous sodium sulfate. The solvent benzene was removed to leave a viscous brown-yellow oil of crude tritosyl derivative of the cyclic amine, which was dissolved in ethanol (200 m*l*) and then left to stand to separate colorless needles, which were subsequently recrystallized from ethanolic benzene. The data are summarized in Table 1.

NMR for VIII: τ 7.80 (*m*, 2H), 6.79 (*t*, 4H, J=6 Hz), 6.62 (*s*, 8H).

NMR for IX: τ 8.10 (*m*, 4H), 6.98 (*t*, 4H, J=6 Hz), 6.71 (*s*, 4H), 6.56 (*t*, 4H, J=7 Hz).

NMR for X: τ 8.80 (*q*, 6H, J=6.5 Hz), 6.76 (*t*, 12H, J=6.5 Hz).

Trihydrobromide of 1,4,7-Triazacyclononane (I). This compound (TACN·3HBr) was obtained by hydrolyzing *N,N′*-ditosyl TACN[6] with 30% hydrobromic acid and acetic acid.[7]

Trihydrobromides of Cyclic Triamines II, III, and IV. A tosyl derivative of the cyclic triamine (VIII, IX, or X)

---

[6] D. H. Peacock and Y. S. Gwan, *J. Chem. Soc.*, **1937**, 1468.

[7] A mixture prepared by adding glacial acetic acid (9 volume) to 47% hydrobromic acid (16 volume).

(0.004 mol) was dissolved by heating it in 30% hydrobromic acid and acetic acid⁷⁾ (300 m*l*) and then refluxed with stirring for 2 days. The solution was concentrated to one tenth of the original volume; after cooling, ether (200 m*l*) was added to separate crystals, which were collected, washed repeatedly with ether and then with ethanol, and recyrstallized from 95% acetic acid. The data are summarized in Table 1.

Syntheses of Co(III) Complexes. The amounts of cobalt(II) salt, the cyclic triamine trihydrobromide, and alkali were chosen so as have a molar ratio of 1 : 2 : 5.

Bis(1,4,7-triazacyclononane)cobalt(III) Tribromide (TACN Complex). A solution of $CoCl_2 \cdot 6H_2O$ (94 mg) in water (2 m*l*) was mixed with a solution of TACN·3HBr(I) (294 mg) and sodium hydroxide (79 mg) in water (3 m*l*). Air bubbles were passed through the mixture until yellow plates separated fully on the wall of the vessel. After the orange-yellow color of the solution had turned deep red, the precipitate was collected by filtration and washed with ethanol. The concentration of the filtrate gave an additional product (127 mg, 58%); dp>280°C, Λ_M 376 ohm^{-1} cm^{2}mol^{-1}.

Found: C, 25.95; H, 5.63; N, 14.98%. Calcd for $CoC_{12}H_{30}Br_3N_6$: C, 25.87; H, 5.43; N, 15.08%.

IR: 3080, 3020 (νNH), 990, 905 cm^{-1} (δ_{rock} CH$_2$).

Bis(1,4,7-triazacyclodecane)cobalt(III) Tribromide Monohydrate (TACD Complex). Air was bubbled for 7 hr into a solution of $CoCl_2 \cdot 6H_2O$ (94 mg), TACD·3HBr(II) (334 mg), and sodium hydroxide (87 mg) in water (10 m*l*). After the reddish-orange color of the solution had turned dark purple, the solution was concentrated to a half of its original volume; ethanol of twice the volume of the concentrated solution was then added to separate orange needles (135 mg, 56.9%); dp 230—270°C, Λ_M 350 ohm^{-1} cm^2 mol^{-1}.

Found: C, 28.34; H, 6.20; N, 13.50%. Calcd for $CoC_{14}H_{34}Br_3N_6 \cdot H_2O$: C, 27.88; H, 6.02; N, 13.93%.

IR: 3095, 3030 (νNH), 980, 910 cm^{-1} (δ_{rock} CH$_2$).

Bromodichloro(1,4,8-triazacycloundecane)cobalt(III) (TACUD Complex). Air was bubbled for 6 hr into a solution of $CoCl_2 \cdot 6H_2O$ (85 mg), TACUD·3HBr(III) (286 mg), and potassium hydroxide (100 mg) in 60% aqueous ethanol (10 m*l*). The mixture was evaporated to dryness. The residue was dissolved in a small amount of hot ethanol. Undissolved inorganic materials were removed by filtration. The filtrate was concentrated on a steam-bath, and the wall of the vessel was rubbed with a glass rod to separate dull red prisms. After the repetition of the treatment to remove the undissolved materials, the crystals were collected, washed with a small amount of ethanol, and dried at 65°C *in vacuo* (51 mg, 38.9%); dp 195—210°C, Λ_M 176 ohm^{-1} cm^2 mol^{-1}.

Found: C, 26.01; H, 5.60; N, 11.21%; mol wt 371. Calcd for $CoC_8H_{19}BrCl_2N_3$: C, 26.18; H, 5.22; N, 11.45%; mol wt 367.0.

IR: 3255, 3095 (νNH), 985, 900 cm^{-1} (δ_{rock} CH$_2$).

An Attempt to Isolate the TACDD Complex. Although the initial yellow-orange color of a solution of cobalt(II) salt, the ligand (TACDD·3HBr), and alkali in 60% ethanol turned dull red upon an air oxidation similar to that described above, an attempt to isolate the complex was unsuccessful.

Results and Discussion

The trihydrobromide of TACN (I) was obtained by hydrolyzing *N,N'*-ditosyl TACN,⁶⁾ whose IR spectrum showed, as expected, a band of medium intensity at 3360 cm^{-1} due to the NH stretching vibration, indicating the existence of a hydrogen atom attached to a nitrogen atom.

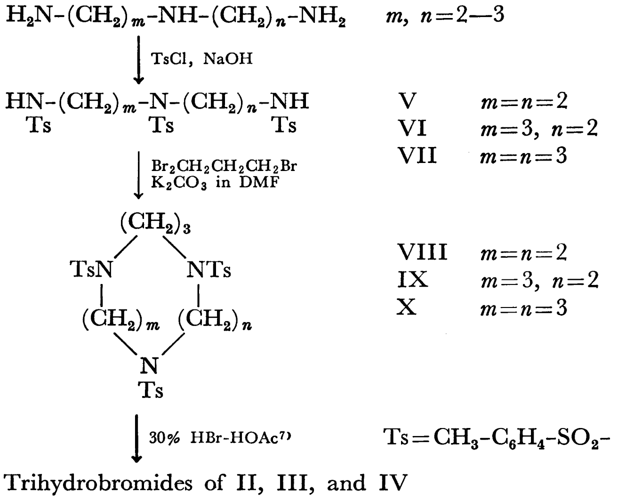


Fig. 2. The synthetic schemes of cyclic triamines (10—12-membered ring).

The synthetic schemes of cyclic triamines (10—12-membered ring) are shown in Fig. 2. The tritosylates of TACD (VIII), TACUD (IX), and TACDD (X) were each synthesized by the cyclization of an appropriate tritosylated open-chain triamine with 1,3-dibromopropane in the presence of anhydrous potassium carbonate in dimethylformamide under the conditions of a high dilution. These tritosylated triamines showed no NH stretching band. This means that the tritosylates have no end $-NH-SO_2C_6H_4CH_3$ group. The NMR spectra also supported the lack of the end group. The absence of the end group, coupled with the results of the elementary analyses and of the molecular-weight determination, indicates that these tritosylated triamines are monomers with a cyclic structure.

These tritosylated triamines were hydrolyzed with 30% hydrobromic acid and acetic acid⁷⁾ to yield the corresponding trihydrobromides of the triamines.

The IR spectra of the trihydrobromides exhibited complicated absorption bands with a strong intensity between 2900 and 2200 cm^{-1} characteristic of secondary amine salt, and also exhibited two resolved peaks or a peak with a shoulder between 1595 and 1545 cm^{-1} due to the bending vibration of NH_2^+. These facts are also consistent with the cyclic structure of the triamines. In order to study the metal complex, a mixture containing cobalt(II) salt, the cyclic triamine trihydrobromide, and alkali in a molar ratio of 1 : 2 : 5 was oxidized by passing air bubbles through; the separated metal complex was thus isolated. The composition of cobalt(III) complexes of TACN, TACD, and TACUD was confirmed by elementary analyses. The cobalt(III) complexes of TACN and TACD were formulated as, respectively, $[Co(TACN)_2]Br_3$ and $[Co(TACD)_2]Br_3 \cdot H_2O$. Their molar conductance data showed that the complexes of TACN and TACD were 3 : 1 electrolytes.

These facts, as well as their electronic spectra, indicated that all six nitrogen atoms of the cyclic ligands were coordinated to a central metal atom. This means that the complexes of TACN and TACD probably

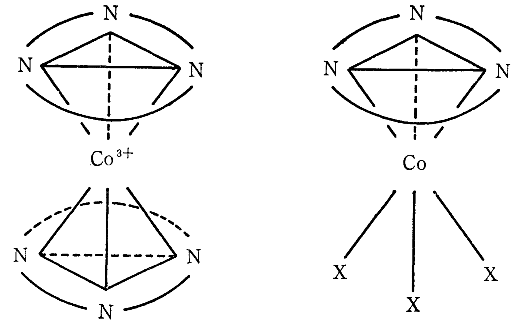


Fig. 3. A sandwich-type complex and a complex molecule (X=halogen).

have the sandwich-type structure shown in Fig. 3. The cobalt(III) complex of TACUD was formulated as [Co(TACUD)BrCl$_2$]. Its electronic spectrum is distinctly different from that of the complex of TACN and TACD described above. These facts suggest that three nitrogen atoms of the cyclic ligand occupy the corners of one octahedral face of the central metal atom, as is shown in Fig. 3. The TACUD complex showed molar conductance data nearly corresponding to those of a 2 : 1 electrolyte.

This suggests that the TACUD complex may be subject to hydrolysis in an aqueous solution much like a diethylenetriamine complex [Co(dien)Cl$_3$].[8)]

The formation of a complex with TACDD in an aqueous solution was inferred from its visible spectral similarity with the TACUD complex. The complexes of TACN, TACD, and TACUD exhibited two NH stretching bands of a strong intensity in the range of 3095 to 3020 cm^{-1}, and also exhibited two bands of medium intensity between 990 and 900 cm^{-1}; they were assigned to the CH$_2$ rocking vibration. On the basis of X-ray analysis[9)] and infrared studies[10)] of ethylenediamine complexes, it was confirmed that the conformation of the ethylene portions in the chelate ring of cyclic triamine complexes was nearly *gauche*. The electronic absorption maxima of the complexes in aqueous solutions are summarized in Table 2, along with those of the other Co–N$_6$ complexes. The ligand-field strength increased in the following order:

$$[Co(NH_3)_6]^{3+} < [Co(TACD)_2]^{3+} < [Co\,en_3]^{3+} < [Co(TACN)_2]^{3+}$$

TABLE 2. ELECTRONIC ABSORPTION MAXIMA OF THE COBALT(III) COMPLEXES IN AQUEOUS SOLUTIONS

$\tilde{\nu}_{max}$[a)] (log ε_{max})

Complex	First band	Second band
[Co(NH$_3$)$_6$]$^{3+}$	20.92 (1.75)	29.15 (1.66)
[Co(en)$_3$]$^{3+}$	21.47 (1.94)	29.60 (1.90)
[Co(TACN)$_2$]$^{3+}$	21.64 (2.00)	30.03 (1.95)
[Co(TACD)$_2$]$^{3+}$	21.19 (1.87)	29.24 (1.95)
Co(TACUD)BrCl$_2$[b)]	18.69	*ca.* 26.38
TACUD complex[c)]	18.94	*ca.* 26.45
TACDD complex[c)]	18.52	*ca.* 26.32

a) In the unit of kK.
b) Reflectance data.
c) Aquated complex.

From an examination of the Dreiding model, in the cases of TACN and TACD complexes the interatomic distances for the three inner-oriented hydrogens in a cyclic ligand were estimated to be 2.0—2.2 Å and 1.7—1.9 Å; the distances between hydrogens projecting from the two separate cyclic ligands were measured as 1.9—2.1 Å and 1.8—2.0 Å respectively. From the above investigation, the TACN complex can be said to be almost strain-free with respect to bond lengths and bond angles; therefore, the non-bonded H–H interaction must be negligible. It is interesting to note that TACN has stronger ligand-field strength than ethylenediamine. On the contrary, it appears that the TACD complex is more unstable than the TACN complex because of the increasing repulsion between non-bonded atoms and the expansion of the bond angles of nitrogen-metal-nitrogen.

On the other hand, the sandwich-type complexes of TACUD and TACDD were no longer formed because of cumulative ring strain and repulsion; in return, only one cyclic tridentate ligand and three halogens were coordinated to a metal ion.

---

8) P. H. Crayton and J. A. Mattern, *J. Inorg. Nucl. Chem.*, **13**, 248 (1960).

9) A. Nakahara, Y. Saito, and H. Kuroya, This Bulletin, **25**, 331 (1952); K. Nakatsu, Y. Saito, and H. Kuroya, *ibid.*, **29**, 428 (1956).

10) S. Mizushima, I. Ichijima, I. Nakagawa, and J. V. Quagliano, *J. Phys. Chem.*, **59**, 293 (1955).