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SYNTHESIS OF A NEW HEXADENTATE LIGAND AND MEASUREMENT OF STABILITY CONSTANTS OF ITS METAL CHELATES

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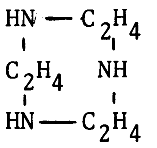
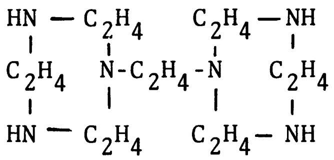
A new macrocyclic hexamine ligand, 1,2-di(1,4,7-triaza-1-cyclononyl)ethane, was synthesized and its protonation and chelate formation constants with manganese(II), cadmium(II), cobalt(II), zinc(II), and nickel(II) were measured at 25°C in 1 M KNO_3.

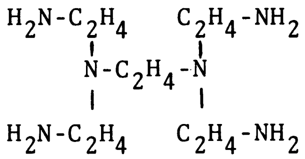
In a previous paper[1], the authors indicated that the metal chelates of triazacyclononane(tacn) are extremely stable. In this paper, are presented synthesis and complexity of a new hexadentate ligand, 1,2-di(1,4,7-triaza-1-cyclononyl)ethane (dtne), which is composed of two tacn rings combined with an ethylene bridge.



tacn



dtne



penten

N,N,N',N'-Tetrakis-(benzenesulfonyl-2-aminoethyl)ethylenediamine was prepared by employing W. Gauss et al.'s procedure[2], and recrystallized from dioxane, mp 150°C. Into its diluted solution in dimethylformamide twice molar of ethylene bromide and excess solid sodium hydroxide were added, then refluxing the mixed solution for 48 hours tetrabenzenesulfonate of dtne was obtained in about 1 % yield, which was recrystallized from benzene, mp 82°C. Hydrolizing this compound with 70 % sulfuric acid, sulfuric acid salt of dtne was yielded at 83 %, which was purified by repeating recrystallization from aqueous ethanol. Each product was characterized by means of its elementary analysis, infrared spectrum, and mass spectrum.

All the potentiometric measurements were performed at 25°C in 1 M KNO_3 in the usual way. The protonation constants of dtne were calculated by a method extended from that in the previous paper$^{1)}$, and further refined by the method of least squares using a digital computer. Because the formation rates of the metal chelates of dtne were too slow to apply the usual titration method, each stability constant was measured by a batch method as follows: an equimolar solution of metal ion and ligand containing a known quantity of alkali was sealded into a Pyrex glass tube, heated in a boiling water-bath for 5 hours, then cooled to 25°C and its potential was measured. From these data the stability constants of mono dtne complexes were calculated by the method described previously$^{1)}$.

The second, third, and fourth protonation constants of dtne were similar to those of penten, but the other three constants were considerably different. Stability of each dtne complex was expectedly much larger than that of the corresponding penten complex and also comparable to that of the stable chelates with the complexane type ligands such as trans-cyclohexanediaminetetraacetate and diethylenetriaminepentaacetate. These results are listed in the tables.

Protonation Constants

	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_4$	$\log K_5$	$\log K_6$
dtne	12.28	9.77	9.21	8.61	4.99	2.12
penten$^{3)}$	10.08	9.58	8.99	8.42	1.33	–

Stability Constants ($\log K_{ML}$)

	Mn(II)	Cd(II)	Co(II)	Zn(II)	Ni(II)
dtne	15.	18.5	18.5	20.	21.5
penten$^{3)}$	9.3	16.1	15.6	16.1	19.1
tacn(β_2)$^{1)}$	–	17.9	19.0	21.7	25.4
dtpa$^{4)}$	15.1	18.9	18.4	18.3	20.1

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