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The Preparation of Trivalent Metal Chelates with Some N_3O_3-Type Ligands

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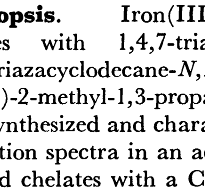
Synopsis. Iron(III), chromium(III), and cobalt(III) chelates with 1,4,7-triazacyclononane-*N,N′,N″*-triacetate, 1,4,7-triazacyclodecane-*N,N′,N″*-triacetate, and 2-(aminomethyl)-2-methyl-1,3-propanediamine-*N,N′,N″*-triacetate were synthesized and characterized by means of the electronic absorption spectra in an aqueous solution. As they are non-charged chelates with a C_3 symmetry, their spectra resemble those of facial tris(glycinato) complexes.

One of the present authors reported earlier that 1,4,7-triazacyclononane formed extremely stable complexes with some hexa-coordinating metal ions,[1] and that the stability constants of divalent metal chelates with its triacetate derivative could be measured polarographically.[2] This complexane-type ligand includes three nitrogen and three oxygen atoms as donors; therefore, a trivalent metal ion can form a non-charged chelate which has a C_3 symmetry. This paper is concerned with the preparation of iron(III), chromium(III), and cobalt(III) chelates with similar tripodal ligands, 1,4,7-triazacyclononane-*N,N′,N″*-triacetate (tnta), 1,4,7-triazacyclodecane-*N,N′,N″*-triacetate (tdta), and 2-(aminomethyl)-2-methyl-1,3-propanediamine-*N,N′,N″*-triacetate (apta).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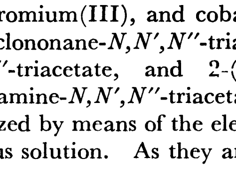
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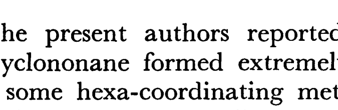
apta

Experimental

Preparation of Ligands. Each ligand was synthesized by the carboxymethylation of the corresponding triamine, 1,4,7-triazacyclononane,[1,3,4] 1,4,7-triazacyclodecane,[3,4] or 2-(aminomethyl)-2-methyl-1,3-propanediamine,[5,6] which had all been prepared according to the methods in the literature. The procedures of all these carboxymethylations were like those to be described below. Triamine trihydrochloride (40 mmol) and excess chloroacetic acid (140 mmol) were dissolved in water (100 cm^3). The mixture was heated to 45 °C, while the pH of the solution was maintained at 10 by adding lithium hydroxide intermittently. After consuming 400 mmol of alkali, the alkaline solution was refluxed for several hours. Then the pH of the solution was adjusted to about 2 with hydrochloric acid, and the mixture was evaporated almost to dryness. After having been washed throughly with methanol, the residue was twice recrystallized from aqueous ethanol. Yields: H_3tnta, 55%; H_3tdta, 35%; H_3apta·HCl, 30%.

Preparation of Chelates. *Iron(III) Chelates*: A solution of $Fe(NO_3)_3 \cdot 9H_2O$ (3.0 mmol in 5 cm^3 of water) was added to a warm solution of the ligand (3.3 mmol in 5 cm^3 of water). In the case of [Fe^{III}(tnta)], bright yellow needles were deposited almost quantitatively in a few minutes. The crystals were washed with water and ethanol. They were pure enough without further purification. Yield, 85%. [Fe^{III}(tdta)] and [Fe^{III}(apta)] were also obtained in a similar way, but the gentle evaporation of the mixture was needed to form the crystals. These were purified by recrystallization from aqueous ethanol. Yields, 30—50%.

Chromium Chelates: (A) Metallic chromium powder (10 mmol), water (10 cm^3), and ligroin (40 cm^3) were placed in a conical flask (100 cm^3), into which concentrated HCl (3 cm^3) was then slowly poured without stirring. After the bubbling reaction had then settled, the flask was put into a warm water bath (50 °C) for 15 min. A ligand solution (5 mmol in 25 cm^3 of water) was degassed by boiling and added to the earlier bluish mixture. The excess acid was neutralized with solid $NaHCO_3$, and the ligroin was pipetted out. Then 30% H_2O_2 (2 cm^3) was added to the bluish solution, which was heated several minutes. After the chromium hydroxide thus formed was filtered off, the filtrate was ice-cooled for several hours. Deep red crystals were slowly isolated in the case of [Cr^{III}(tnta)], but the tdta or apta chelate was obtained by evaporating the filtrate. The solid product was washed and recrystallized with aqueous ethanol. Yields, 30—50%.

(B) $[Cr^{III}(NH_3)_6]Cl_3$ (3.0 mmol) and the ligand (3.3 mmol) were dissolved in water (30 cm^3), after which solution was refluxed for 8 h with stirring (if it did not turn wine red, a few drops of 5% NaOH were added and refluxing was continued). The little chromium hydroxide thus formed was filtered off while hot; then the filtrate was ice-cooled. Deep red crystals of [Cr^{III}(tnta)] were gradually formed, but the concentration of the solution was needed in the case of the tdta or the apta chelates. They were purified in a manner similar to the above. Yields, 30—50%.

Cobalt(III) Chelates: (A) $CoCl_2 \cdot 6H_2O$ (3.0 mmol) and H_3tnta (3.3 mmol) were dissolved in hot water (15 cm^3), and 30% H_2O_2 (2 cm^3) was added to the solution, which was then warmed for several minutes before being ice-cooled. Wine-red crystals of [Co^{III}(tnta)] were slowly deposited. By the evaporation of the filtrate, more chelate could be recovered. The crude complexes were recrystallized from hot water by adding ethanol and concentrating the solution. The product was washed thoroughly with aqueous ethanol. Yield, 70%. [Co^{III}(tdta)] and [Co^{III}(apta)] could also be prepared by the above procedure except for the addition of a little active charcoal, which had to be removed after the reaction. As these chelates were much more soluble in water than the tnta chelate, the filtrate was evaporated to solidify the complexes. They were recrystallized from aqueous ethanol. Yields, 30—50%.

(B) Cobalt chelates were prepared from the hexaamminecobalt(III) complex in the way that described in (B) for

Table 1. Elemental analyses and absorption spectral data

Substance	Elemental analyses Found, % (Calcd, %)				Absorption bands $\tilde{\nu}/10^3$ cm^{-1} (log ε)		
	C	H	N	Cl or M			
H_3tnta	47.22	6.96	13.88				
($C_{12}H_{21}N_3O_6$)	(47.52)	(6.98)	(13.85)				
H_3tdta	48.79	7.23	13.05				
($C_{13}H_{23}N_3O_6$)	(49.20)	(7.31)	(13.24)				
H_3apta·HCl	40.16	6.83	12.94	10.71			
($C_{11}H_{22}N_3O_6Cl$)	(40.31)	(6.77)	(12.82)	(10.82)			
[Cr(tnta)]	40.30	5.10	11.77	14.62	19.5	25.7	
($CrC_{12}H_{18}N_3O_6$)	(40.91)	(5.15)	(11.93)	(14.76)	(2.39)	(2.18)	
[Cr(tdta)]	43.25	5.40	11.34	14.05	19.4	26.0	
($CrC_{13}H_{20}N_3O_6$)	(42.63)	(5.50)	(12.49)	(14.19)	(2.33)	(2.12)	
[Cr(apta)]	38.07	5.38	12.18	15.19	20.1	26.4	
($CrC_{11}H_{18}N_3O_6$)	(38.83)	(5.33)	(12.35)	(15.28)	(2.24)	(2.04)	
fac[Cr(gly)$_3$]	26.05	4.58	15.04	18.60	19.4	26.0	
($CrC_6H_{12}N_3O_6$)	(26.29)	(4.41)	(15.33)	(18.70)	(2.23)	(2.02)	
[Co(tnta)]	39.70	5.01	11.64	16.89	19.6	27.1	43.5
($CoC_{12}H_{18}N_3O_6$)	(40.12)	(5.05)	(11.70)	(16.40)	(2.54)	(2.34)	(4.26)
[Co(tdta)]	41.59	5.41	11.15	15.66	19.0	26.3	42.4
($CoC_{13}H_{20}N_3O_6$)	(41.83)	(5.40)	(11.26)	(15.79)	(2.46)	(2.31)	(4.35)
[Co(apta)]	37.79	5.20	11.84	17.10	19.6	27.0	46.0
($CoC_{11}H_{18}N_3O_6$)	(38.05)	(5.23)	(12.10)	(16.97)	(2.44)	(2.24)	(4.34)
fac[Co(gly)$_3$]	25.51	4.12	14.98	21.18	19.2	26.6	45.6
($CoC_6H_{12}N_3O_6$)	(25.64)	(4.30)	(14.95)	(21.20)	(2.24)	(2.17)	(4.30)
[Fe(tnta)]	40.36	5.08	11.84	15.73	20.0		38.8
($FeC_{12}H_{18}N_3O_6$)	(40.47)	(5.09)	(11.80)	(15.68)	(0.5)		(4.0)
[Fe(tdta)]	41.76	5.08	11.72	15.01	20.2		38.6
($FeC_{13}H_{20}N_3O_6$)	(42.18)	(5.45)	(11.35)	(15.09)	(0.5)		(4.2)
[Fe(apta)]	38.32	5.25	12.32	16.34	21.0		38.5
($FeC_{11}H_{18}N_3O_6$)	(38.39)	(5.27)	(12.21)	(16.23)	(shoulder)		(3.9)

chromium chelates, however, these reactions were relatively slow compared with that of the corresponding chromium complexes. Yields, 30—50%.

Facial Glycinato (gly) Complexes: [Cr^{III}(gly)$_3$]·3H_2O and [Co^{III}(gly)$_3$]·H_2O were prepared and purified according to the methods of Ley and Winkler⁷⁾ and Israily.⁸⁾ They were converted into anhydrous complexes by heating *in vacuo* at 130 °C.

Measurements. The electronic absorption spectra of metal chelates were measured on a Hitachi Model 124 recording spectrophotometer using a 10-mm cell. Sample cell of 50 mm or 100 mm was also used to measure the visible spectra of [Cr^{III}(gly)$_3$], [Co^{III}(gly)$_3$], and the iron(III) chelates, which were sparingly soluble in water. The absorption spectra of two glycinato complexes were measured anew under the same conditions, although they had already been reported.⁸⁾

Results and Discussion

All these N_3O_3-type ligands could expel ammonia molecules from hexaamminechromium(III) or -cobalt(III) complexes. The replacement of ammonia with glycine also occurred in the chromium complex, but it was very difficult in the cobalt complex. Although the apta forms six-membered chelate rings upon coordination, it has great chelate effects. This ligand presumably has a very suitable structure for the octahedral coordination. Metal chelates of tnta seem to be the most stable and to have the smallest solubility in water. All these solid chelates were decomposed above 300 °C, leaving metal oxide. A tripodal ligand, apta, which contains three -NH-groups, did not react further with chloroacetate, and only this ligand was obtained as a monohydrochloride. Syntheses of similar triacetate derivatives of 1,4,8-triazacycloundecane and 1,5,9-triazacyclododecane were also attempted, but they failed to isolate any pure solids.

As expected, all the absorption spectra of the chromium(III) and cobalt(III) chelates with these tripodal ligands resemble those of the facial tris(glycinato) complexes. It is of interest that each apta chelate has the first absorption band of the highest energy.

The data of the elemental analysis and the absorption spectra are summarized in Table 1.

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