ATRANES

XXX.* FERRATRANE, COBATRANE, AND THEIR C-METHYL-SUBSTITUTED DERIVATIVES

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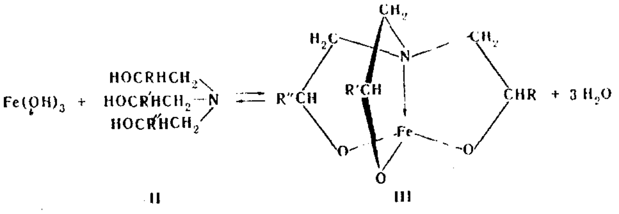
Methods were developed for the synthesis of ferratrane, the previously unknown cobatrane, and their derivatives. The methods are based on the reactions of $Fe(OH)_3 \cdot Fe(OC_2H_5)_3$ and $CoO(OH)$ with tris(2-hydroxyalkyl)amines.

Of the metalloatranes [2,3] that contain a group VIII metal atom, only ferratrane (I) $Fe(OCH_2CH_2)_3N$. has been known until now [4,5].

It was obtained by the reaction of $FeCl_3$ with triethylamine, with ammonia or triethylamine as the HCl acceptor.

We have developed methods for the synthesis of ferratrane and its derivatives (III) that are based on the reaction of ferric hydroxide or ethoxide with the appropriate tris(2-hydroxyalkyl)amines (II). The reaction (1) is accomplished by means of continuous azeotropic distillation of the water from the mixture of reagents with an inert solvent. Reaction (2) proceeds by direct mixing of II with a suspension of $Fe(OC_2H_5)_3$ in methanol.



(1)

$$Fe(OC_2H_5)_3 + II \rightleftharpoons III + 3\ C_2H_5OH \quad (2)$$

R, R', R'' = H, Alk

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*See [1] for communication XXIX.

TABLE 1. Ferratranes (III) and Cobatranes (IV)

Comp.	*M*	R	R′	R″	Empirical formula	Found, %				Calc., %				Yield, % (preparative method)
						C	H	N	*M*	C	H	N	*M*	
I	Fe	H	H	H	$C_6H_{12}FeNO_3$	34,6	5,7	7,0	28,1	35,6	5,9	6,9	27,6	64 (1); 68 (2)
V	Fe	CH_3	H	H	$C_7H_{14}FeNO_3$	39,0	6,6	6,6	25,4	38,9	6,5	6,5	25,9	52 (1); 41 (2)
VI	Fe	CH_3	CH_3	H	$C_8H_{16}FeNO_3$	40,3	7,1	6,2	25,0	41,7	6,9	6,1	24,3	38 (1); 44 (2)
VII	Co	H	H	H	$C_6H_{12}CoNO_3$	32,6	5,6	6,0	25,9	32,1	5,3	6,2	26,3	49
VIII	Co	CH_3	H	H	$C_7H_{14}CoNO_3$	35,4	6,1	5,9	24,2	35,3	5,9	5,9	24,8	51
IX	Co	CH_3	CH_3	H	$C_8H_{16}CoNO_3$	39,2	6,9	5,8		38,1	6,3	5,5		45
X	Co	CH_3	CH_3	CH_3	$C_9H_{18}CoNO_3$	40,2	6,9	5,2	21,9	40,6	6,8	5,3	22,2	55

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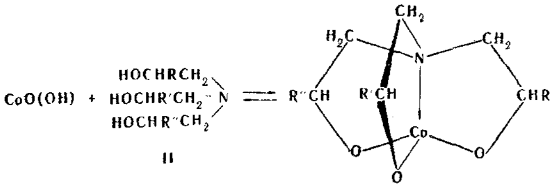
The ferratranes (see Table 1) are greenish-brown crystalline substances that decompose without melting. They are soluble in alcohols and chloroform and are rapidly hydrolyzed by water.

We obtained the previously unknown cobatranes (IV) in yields of 44-55% by means of reaction of the appropriate tris(2-hydroxyalkyl)amines with CoO(OH) via the scheme



R, R', R'' = H, Alk

The process is accomplished in the same way as reaction (1).

The cobatranes (see Table 1) are infusible, violet-brown, crystalline substances that are soluble in methanol and chloroform. They are rapidly hydrolyzed by water.

EXPERIMENTAL

3-Methylferratrane (V). A mixture of 1.07 g (0.01 mole) of freshly prepared $Fe(OH)_3$ [6], 1.69 g (0.01 mole) of bis(2-hydroxyethyl)-2-hydroxypropylamine (II, R = R' = H, R'' = CH_3), and 50 ml of xylene was refluxed with removal of the water by continuous azeotropic distillation. The precipitate (2.1 g) was removed by filtration and dissolved in 50 ml of methanol. The solution was filtered away from the unchanged ferric hydroxide, and 30 ml of triethylamine was added to the filtrate. The resulting precipitate of V was separated and vacuum dried to give 1.3 g (64%) of product.

3,7-Dimethylferratrane (VI). A 1.76-g (0.01 mole) sample of 2-hydroxyethylbis(2-hydroxypropyl)-amine (II, R = R' = CH_3, R'' = H) was added to a suspension of 1.91 g (0.01 mole) of $Fe(OC_2H_5)_3$ [7] in 50 ml of dry benzene. All of the ferric ethoxide dissolved in the process. The solution was filtered, and 30 ml of dry triethylamine was added to the filtrate. The resulting precipitate of VI was separated and vacuum-dried to give 0.95 g (41%) of product.

Cobatrane (VII). A mixture of 1.49 g (0.01 mole) of tris(2-hydroxyethyl)amine, 0.92 g (0.01 mole) of CoO(OH) [8], and 50 ml of xylene was heated to the boiling point. After water evolution had ceased, the solid precipitate was dissolved in 50 ml of absolute methanol, and the solution was filtered. The filtrate was evaporated to 25 ml, and VII [1.1 g (49%)] was precipitated from it by the addition of dry ether. All of the remaining cobatranes were similarly obtained.

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