ATRANES

XXXII.* FERRATRANE-3,7,10-TRIONE AND ITS COMPLEXES

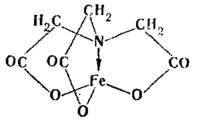
M. G. Voronkov and S. V. Mikhailova

UDC 547.898'257.7:541.49

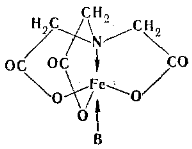
Complexes of ferratrane-3,7,10-trione $\overset{\downarrow}{\text{Fe}}(\text{OCOCH}_2)_3\text{N}$ (I) of the composition I · H_2O, I · H_2O_2, I · $OS(CH_3)_2$, and I · $2OS(CH_3)_2$ were synthesized. The IR spectra and derivatograms of these compounds were studied.

We have previously described [1-4] general methods for the synthesis of metalloatrane-3,7,10-triones $\overset{\downarrow}{\text{M}}(\text{OCOCH}_2)_3\text{N}$ and their hydrates, which are used to obtain a number of previously unknown heterocyclic chelated inorganic salts and mixed anhydrides of aminotriacetic acid.

In the present communication, we examine chelate compounds of the indicated type that contain Fe(III) as the heteroatom – complex ferratrane-3,7,10-trione (I) derivatives:



I



II

$B = H_2O,\ H_2O_2,\ (CH_3)_2SO,\ 2(CH_3)_2SO$

Of these, only monohydrate I · H_2O, which was first obtained in the last century [5], was known up until now. Methods for its preparation, several of its properties, and the possibility of using it in analytical chemistry [11] were subsequently described [6-10].

We have developed a simple and convenient method for obtaining ferratrane-3,7,10-trione monohydrate (I · H_2O) from free aminotriacetic acid (III) and ferric hydroxide or the ferric salts of volatile acids:

$$N(CH_2COOH)_3 + Fe(OH)_3 \rightarrow I \cdot H_2O + 2H_2O \quad (1)$$

$$N(CH_2COOH)_3 + FeX_3 + H_2O \rightarrow I \cdot H_2O + 3HX \quad (2)$$
$$X = Cl,\ CH_3COO \text{ etc.}$$

The I · H_2O complex can also be obtained in 72% yield by the reaction of Fe(III) salts with the trisodium salt of acid III:

$$FeX_3 + (NaOCOCH_2)_3N + H_2O \rightarrow I \cdot H_2O + 3NaX \quad (3)$$

Complex I · H_2O decomposes in aqueous ammonia solutions (with a yellow-brown coloration) and amines (in this case, ferric hydroxide does not precipitate, even on heating). The product of the decomposition of I · H_2O in ammonium hydroxide is the diammonium salt of acid III. Aqueous NaOH and Na_2CO_3 solutions convert I · H_2O to $Fe(OH)_3$. Complex I · H_2O reacts with a solution of ammonium thiocyanate in dilute acid to give an intense red coloration.

---

*See [1] for communication XXXI.

Institute of Organic Synthesis, Academy of Sciences of the Latvian SSR, Riga. Translated from Khimiya Geterotsiklicheskikh Soedinenii, No. 2, pp. 164-170, February, 1973. Original article submitted September 17, 1971.

TABLE 1. Isomeric Chemical Shifts (mm/sec) in the Nuclear Gamma-Resonance Spectra of Ferratrane-3,7,10-trione and Its Complexes

Formula	$T=100°$ K		$T=300°$ K	
$\overline{\text{N}(\text{CH}_2\text{COO})_3}\overset{\downarrow}{\text{Fe}}\cdot\text{H}_2\text{O}$	0,72	0,54	0,48	0,56
$\overline{\text{N}(\text{CH}_2\text{COO})_3}\overset{\downarrow}{\text{Fe}}\cdot\text{H}_2\text{O}_2$	0,53	0,66	0,49	0,60
$\overline{\text{N}(\text{CH}_2\text{COO})_3}\overset{\downarrow}{\text{Fe}}\cdot[\text{OS}(\text{CH}_3)_2]_2$	0,59	0,59	0,49	0,53
$\overline{\text{N}(\text{CH}_2\text{COO})_3}\overset{\downarrow}{\text{Fe}}\cdot\text{OS}(\text{CH}_3)_2$	0,88	1,92	0,53	1,76

TABLE 2. Ferratrane-3,7,10-trione (I) and Its Derivatives $\overline{\text{N}(\text{CH}_2\text{COO})_3}\overset{\downarrow}{\text{Fe}}\cdot n\text{B}$

B	n	Color	Solubility in water at 20°C, g/100 ml	Decomposition temp. °C	Empirical formula	Found, %				Calc., %				Yield, % (preparat. method)
						C	H	Fe	N	C	H	Fe	N	
	0	Brown	0,0	240—245	$C_6H_6FeNO_6$	29,3	2,5	21,9	6,0	29,5	2,5	22,9	5,7	89 (*4*); 76 (*5*)
H_2O	1	Yellow-green	0,0	190—195	$C_6H_8FeNO_7$	27,1	3,3	20,5	5,6	27,5	3,1	21,3	5,4	72 (*1*); 77 (*2*); 72 (*3*)
H_2O_2	1	Brown	0,0	170—175	$C_6H_8FeNO_8$	25,3	3,1	20,1	5,4	25,9	2,9	20,1	5,0	79
$(CH_3)_2SO$	1	Orange-red	2,0	160—165	$C_8H_{12}FeNO_7$*	29,2	3,6	16,9	4,2	29,8	3,8	17,3	4,4	54
$(CH_3)_2SO$	2	Yellow	2,85	180—185	$C_{10}H_{18}FeNO_8S_2$†	30.4	4,1	14,6	3,5	30,0	4,5	14,05	3,5	23
$HCON(CH_3)_2$	3	Orange-brown	0,0		$C_{15}H_{27}FeN_4O_9$	38,2	5,1	11,8	12,3	38,9	5,9	12,1	12,1	25

---

* Found,%: S 10.4. Calculated,%: S 9.9.

† Found,%: S 16.4. Calculated,%: S 16.0.

TABLE 3. Absorption Frequencies (cm^{-1}) in the IR Spectra of Ferratrane-3,7,10-trione and Its Complexes

$N(CH_2COO)_3Fe$ (I)	I · H_2O	I · H_2O_2	I · $OS(CH_3)_2$	I · $2OS(CH_3)_2$	Assignment
1	2	3	4	5	6
		405 m			
	420 w	425 w		446 m	Fe—O
	476 w			475 m	
	485 m				
	503 s	509 m		504 m	
	524 s	529 m	517 w	525 m	
572s		569 vw		569 s	
	616 s	620 m	619 w	618 s	
			622 w		
	719 w		724 m		
				730 s	
		755 m			
815w					
850w	865 w		857 s	858 s	
	900 s		910 s	904 vs	H—O—H
				919 s	
	927 m	925 s	935 m		
	962 m	m	955 m	957 m	S=O
	979 s	975 m		980 w	
			995 s	993 m	
995 m	1006 m				
		1012 w			
				1036 m	
1166 w					
	1203 m				
		1225 s	1222w	1228 m	
	1241 m				
	1267 m	1278 m	1276 m	1258s	
			1295 w		
	1314 m	1325 s	1313 m	1313s	ν_s CH_3
1325 m	1330 m	1340 s	1356 m	1337m	
	1377 s	1370 m	1378 s	1375s	
		1380 w			
		1385 w	1400 w		
1400 s	1411 m			1410m	
			1426 w		
1435 m		1444 s	1449 w	1440m	ν_{as} CH_3
	1460 s			1461 m	
		1480 vs			$\nu_s(COO^-)$
	1510 w				
	1525 w	1520 vs			
	1550 m	1540 vs		1549 s	
	1562 w	1560 w			
	1580 w	1590 w		1595w	
1615 vs	1625 w			1604 vs	$\nu_{as}(COO^-)$
			1624 vs		
1660 vs	1682 w	1658 vs		1661 s	
	1695 w				
	1720 m				$\nu(COOH)$
				2311 w	
	2330 vw			2334 w	
				2489 vw	
				2602 vw	
				2608 w	
	2662 vw				
				2720 w	
	2824 m				
	2869 m			2881 w	
				2918	
	2950 m				
				2967	
	2977 s			2970 s	
	2987			2997	
	3026			3015	
	3030				
	3035				
				3258 w	
				3416 w	

Note. s is strong, w is weak, m is medium, vs is very strong, and vw is very weak.

The paramagnetic character of I is confirmed by an investigation of its magnetic susceptibility (at 399°K, $\chi_g = 62.17$, $\chi_m = 0.016375$, $\mu_{exp} = 6.28$, and $\mu_{calc} = 5.92$). The magnitude of μ_{exp} indicates that the iron atom in I · H_2O contains five unpaired electrons. The somewhat greater magnitude of the effective magnetic moment of I · H_2O as compared with the calculated value is due to the contribution of the spin-orbital interaction characteristic for complexes [12].

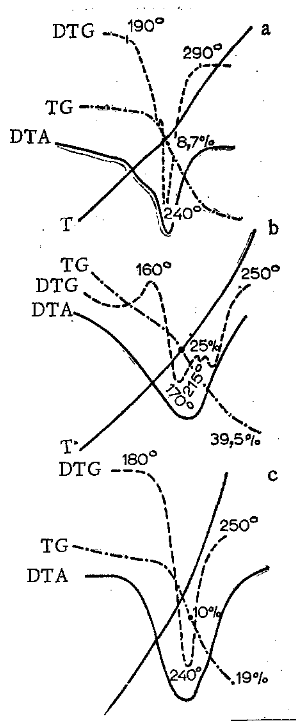


Fig. 1. Derivatograms of $N(CH_2COO)_3Fe \cdot H_2O$ (a), $N(CH_2COO)_3Fe \cdot OS(CH_3)_2$ (b), and $N(CH_2COO)_3Fe \cdot [OS(CH_3)_2]_2$ (c) at a heating rate of 12 deg/min (T is the heating curve, TG is the thermogravimetric curve, DTA is the differential heating curve, and DTG is the weight-loss rate curve).

The nuclear γ-resonance spectra of all of the compounds are represented by two lines characteristic for iron compounds with quadrupole splitting (Table 1). The isomeric chemical shifts relative to stainless steel (0.48-0.53 mm/sec at 300°K and 0.53-0.88 mm/sec at 100°K) are characteristic for trivalent iron compounds. The small quadrupole splittings of $I \cdot H_2O$ and its complexes are also characteristic for trivalent iron compounds.

The quadrupole splitting of $I \cdot OS(CH_3)_2$ (Table 1), the magnitude of which is close to the quadrupole splitting of divalent iron compounds, differs considerably from that of $I \cdot H_2O$. Two additional lines, the isomeric shift and quadrupole splitting of which coincide with the corresponding values of $I \cdot 2OS(CH_3)_2$, are observed in the NGR spectrum of this compound. Complex $I \cdot OS(CH_3)_2$ apparently contains about 10% $I \cdot 2OS(CH_3)_2$.

The derivatogram of $I \cdot H_2O$ (see Fig. 1, curve a) demonstrates that the compound does not change and that the associated water is not split out when it is heated to 190°C. A water molecule is lost on subsequent heating to 240° and is accompanied by an endothermic minimum. The bond of I with an H_2O molecule of such strength indicates that water enters into the inner sphere and is coordinately bonded to the iron atom (structure II).

When $I \cdot H_2O$ is heated for a long time at 200° in vacuo, it is dehydrated to give free I (dark-brown crystals), which is apparently somewhat contaminated by decomposition products. Purer anhydrous I was obtained in 76% yield by reaction of $FeCl_3$ with III in dimethylformamide. In addition to free I, its complex with DMF $[I \cdot 3HCON(CH_3)_2]$ can be isolated.

Starting from $I \cdot H_2O$, we obtained the previously unknown complexes of ferratrane-3,7,10-trione with dimethyl sulfoxide (DMSO) – $I \cdot OS(CH_3)_2$ and $I \cdot 2OS(CH_3)_2$. The reaction of $I \cdot H_2O$ with 30% H_2O_2 gives a complex with the $I \cdot H_2O_2$ composition (see Table 2).

The derivatograms of these compounds (Fig. 1, curves b and c) show that the complexes are stable up to 160°. Above this temperature, $I \cdot 2OS(CH_3)_2$ dissociates (two endothermic minima at 170-215-250°). The first $OS(CH_3)_2$ molecule is lost even before 170° (25% weight loss), after which the second $OS(CH_3)_2$ molecule is lost (39.5% weight loss).

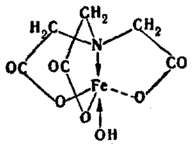
Complex $I \cdot H_2O_2$ does not decompose up to 180°. An endothermic minimum corresponding to the loss of from 10 to 20% of the initial weight, i.e., 1 mole of H_2O_2, is observed at 240-280°.

The aminotriacetic acid entering into the composition of I and its derivatives functions as a tetradentate ligand. This is confirmed by the IR spectroscopic data (Table 3). The absence of absorption at 1700-1750 cm^{-1} in the spectra of all of the compounds (except for $I \cdot H_2O$) indicates that there are no unionized COOH groups in the molecules of I and its derivatives. All of the CH_2COO groups in $I \cdot OS(CH_3)_2$ and $I \cdot H_2O_2$ are equivalent and bonded to the iron atom; this is confirmed by the presence of only one strong $\nu_{as}(COO^-)$ absorption band at 1624-1658 cm^{-1}, respectively. The $\nu_{as}(COO^-)$ band in the spectra of the rest of the compounds is split into two bands; this may attest to their polymeric structure.

The bands at 420, 425, and 446 cm^{-1} (see [13]) correspond to the stretching vibrations of the Fe–O bond in the spectra of $I \cdot H_2O$, $I \cdot H_2O_2$, and $I \cdot 2OS(CH_3)_4$.

The absence of absorption at 3200-3350 cm^{-1} in the spectrum of $I \cdot H_2O$ shows that the water molecule in it is not crystallization water but coordinated water; this is also confirmed by the presence of a strong band at 900 cm^{-1} (this frequency is evidence for the presence of vibrations of the H–O–H group of coordinated water) [13]. This compels us to assign a structure of possibly polymeric character to $I \cdot H_2O$

(the free COOH group participates in intermolecular coordination). The IV structure is confirmed by the presence of the absorption of a free carboxyl group in the spectrum of I · H_2O.



IV

The spectra of I · $OS(CH_3)_2$ and I · $2OS(CH_3)_2$ are evidence that coordination of DMSO with the iron atom is accomplished through oxygen, since the frequency of the SO stretching vibrations (950 and 955 cm^{-1}) lies lower than in free DMSO (1050-1100 cm^{-1}) [14].

The bands at 724 and 730 cm^{-1} in the spectra of I · $OS(CH_3)_2$ and I · $2OS(CH_3)_2$ are related to the stretching vibrations of the C−S bond [15].

The presence of a coordinated Fe ← N bond in all of the investigated compounds is confirmed by the maximum at 250 nm in their UV spectra.

EXPERIMENTAL

Aminotriacetic acid (III) was obtained via the method in [16] and purified by recrystallization from hot water. The ferric chloride (hexahydrate) was a chemically pure preparation. Ferric hydroxide was prepared immediately prior to introduction into the reaction by precipitation with ammonia from a ferric chloride solution. The dimethyl sulfoxide was a chemically pure preparation and was dried and vacuum distilled prior to use.

Analysis. Carbon and hydrogen were determined by combustion in a stream of oxygen, while nitrogen was determined by a microanalytical Dumas method. Iron was determined as Fe_2O_3, which remained after calcination of the substance at 1000° in a stream of oxygen.

The derivatograms were obtained with the derivatograph of the system in [17]. The IR spectra of KBr pellets of the compounds were recorded with UR-10 and IKS-14 spectrographs. The UV spectra were recorded with a UV-2 automatic recording spectrophotometer prepared and designed in the Institute of Organic Synthesis of the Academy of Sciences of the Latvian SSR. The spectrograms were obtained from $2 \cdot 10^{-4}$ M aqueous solutions of the compounds. The cuvette thickness was 1 cm.

The nuclear gamma resonance (NGR) for Fe^{57} nuclei was measured with a device of the electrodynamic type with a constant accelerator. The NGR spectra were recorded with an A-100 analyzer. The source (Co^{57} in stainless steel) was at room temperature in all of the measurements. The NGR measurements of the investigated samples were made at 100 and 300°K.

Ferratrane-3,7,10-trione Hydrate (I · H_2O). Method 1. A 4.2-g (0.04 mole) sample of freshly prepared ferric hydroxide was added to a hot solution of 7.6 g (0.04 mole) of II in 500 ml of water. The mixture was refluxed for 3 h, as a result of which all of the ferric hydroxide went into solution, from which a greenish-yellow finely crystalline precipitate of I · H_2O formed. It was removed by filtration, washed with hot water, alcohol, and ether, and dried in vacuo to give 4.73 g (72%) of product.

Method 2. A solution of 6.76 g (0.025 mole) of $FeCl_3 \cdot 6H_2O$ in 100 ml of water was added to a filtered hot solution of 4.75 g (0.025 mole) of II in 400 ml of distilled water. The water and resulting hydrochloric acid were completely removed from the solution in a rotary vacuum evaporator at 50°, and the residual greenish-yellow fine crystals of I · H_2O were washed with hot distilled water, alcohol, and ether and dried in vacuo to give 5.04 g (77%) of product.

Method 3. A solution of 1.62 g (0.01 mole) of anhydrous $FeCl_3$ in 10 ml of water was added to 30 ml of an aqueous solution of 2.11 g (0.01 mole) of the trisodium salt of III, and the mixture was refluxed for 20 min. The solvent was removed by distillation in a rotary vacuum evaporator at 50°, the residue was treated with distilled water to dissolve the NaCl, and the insoluble portion (greenish-yellow crystals of I · H_2O) was removed by filtration, washed with water, alcohol, and ether, and dried in vacuo to give 1.95 g (72%) of product.

Ferratrane-3,7,10-trione (I). Method 4. A weighed sample of I · H_2O was heated on an oil bath at 200° and 1 mm to constant weight (4 h). The resulting dark-brown crystals were anhydrous I (apparently somewhat contaminated with decomposition products). The yield was 89%.

Method 5. A solution of 4.86 g (0.03 mole) of anhydrous $FeCl_3$ in 20 ml of dry dimethylformamide (DMF) was added to a solution of 5.73 g (0.03 mole) of III in 50 ml of DMF and the mixture was refluxed for 3 h, during which light-brown crystals began to precipitate from the solution. The crystals were removed by filtration, washed with DMF, alcohol, and ether, and dried in vacuo to give 5.57 g (76%) of product. Found,%: C 29.3; H 2.8; Fe 21.8; N 6.0. $C_6H_6FeNO_6$. Calculated,%: C 29.5; H 2.5; Fe 22.8; N 5.7.

$\overline{N(CH_2COO)_3Fe}\cdot H_2O_2$. A 2.61-g (0.01 mole) sample of I · H_2O was added to 50 ml of 30% hydrogen peroxide, and the mixture was stirred and heated carefully to 60° on a water bath, during which there was a vigorous reaction and a light-brown finely crystalline precipitate of I · H_2O_2 formed. It was removed by filtration, washed several times with water, alcohol, and ether, and dried in vacuo to give 2.18 g (78%) of product.

$\overline{N(CH_2COO)_3Fe}\cdot OS(CH_3)_2$. A 6.02-g (0.023 mole) sample of I · H_2O was dissolved by heating in 50 ml of dimethyl sulfoxide (DMSO). After some time, an orange precipitate of I · $OS(CH_3)_2$ formed. It was removed by filtration, washed with alcohol and ether, and dried in vacuo to give 4.00 g (54%) of product.

$\overline{N(CH_2COO)_3Fe}\cdot 2OS(CH_3)_2$. A solution of 2.62 g (0.01 mole) of I · H_2O in 15 ml of DMSO was heated at 100° for 30 min and filtered hot. The resulting I · $2OS(CH_3)_2$ was precipitated from the cooled solution with anhydrous acetone–xylene (1:1). The precipitate was washed with dry acetone and vacuum dried to give 1.73 g (23%) of yellow crystals that decomposed on heating.

$\overline{N(CH_2COO)_3Fe}\cdot 3HCON(CH_3)_2$. A 4.86-g (0.03 mole) sample of anhydrous $FeCl_3$ was dissolved in 20 ml of dry DMF, and the solution was added to a solution of 5.73 g (0.03 mole) of II in 50 ml of DMF. The mixture was refluxed for 3 h, and the precipitated light-brown crystals of I were removed by filtration. The filtrate was allowed to stand at 0° for 7 days, and the precipitated orange-red crystals of I · $3HCON(CH_3)_2$ were washed with DMF and vacuum dried to give 3.45 g (25%) of product.

LITERATURE CITED

1. M. G. Voronkov and S. V. Mikhailova, Khim. Geterotsikl. Soedin., 1174 (1972).
2. M. G. Voronkov and S. V. Mikhailova, Khim. Geterotsikl. Soedin., 49 (1969).
3. M. G. Voronkov and S. V. Mikhailova, Khim. Geterotsikl. Soedin., 795 (1969).
4. M. G. Voronkov and S. V. Mikhailova, Khim. Geterotsikl. Soedin., No. 2, 334 (1970).
5. W. Lüddeke, Ann., 147, 272 (1868).
6. H. Brintzinger and G. Hesse, Z. Anorg. Chem., 249, 299 (1942).
7. R. Sallmann, Swiss Patent No. 317,355 (1957); Chem. Abstr., 51, 15,055 (1957).
8. C. E. Wymore, US Patent No. 3,172,898 (1965); Chem. Abstr., 63, 277 (1965).
9. J. J. Singer and M. Weisberg, US Patent No. 3,115,511 (1963); Chem. Abstr., 60, 10,262 (1964).
10. Y. Takashima and Y. Tateishi, Bull. Chem. Soc. Japan, 38, 1688 (1965).
11. F. C. Besworth and A. E. Frost, US Patent No. 2,847,308 (1958); Chem. Abstr., 52, 20,880 (1958).
12. V. A. Chetverikova, V. A. Kogan, S. V. Mikhailova, O. A. Osipov, and M. G. Voronkov, Khim. Geterotsikl. Soedin., 379 (1969).
13. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, Wiley (1970).
14. F. A. Cotton, R. Francis, and W. D. Horroks, J. Phys. Chem., 64, 1534 (1960).
15. J. Selbin, W. E. Bull, and L. H. Holmes, J. Inorg. Nucl. Chem., 16, 219 (1961).
16. Yu. A. Bankovskii and A. F. Ievin'sh, Izv. Akad. Nauk Latv. SSR, 107 (1957).
17. G. Paulik, J. Paulik, and L. Erdey, Z. Anal. Chem., 160, 241 (1958).