action of potassium glycinate on *d,l*-potassium dinitrobis(glycinato)cobaltate(III) the β (red) isomer of tris(glycinato)cobalt(III) is obtained, which is possible only if the nitro groups are in the *cis* positions.

Besides, this reaction affords the possibility of determining the orientation of the glycine ligands in dinitrobis(glycinato)cobaltates(III) because only one of the three possible *cis* isomers of these salts could yield β (red) tris(glycinato)cobalt(III), *i.e.*, the 1,2,3-isomer of this compound,[4] which means that dinitrobis(glycinato)cobaltates(III) have the *cis,cis,cis* configuration.[5]

This conclusion was confirmed by opening of one of three rings of the 1,2,3- isomer of tris(glycinato)cobalt(III) by the action of potassium nitrite. This reaction gave a substance which was identical with potassium dinitrobis(glycinato)cobaltate(III) obtained through our reaction. The fact that the substitution of one of the glycine ligands with two nitro groups in the *cis* positions can yield only the above-mentioned isomer of dinitrobis(glycinato)cobaltate(III) can be taken as an additional proof that the configuration of our salts is *cis,cis,cis*.

[4] The 1,2,3- configuration of the β (red) isomer of tris(glycinato)cobalt(III) was established by the following authors: F. Basolo, C. J. Ballhausen, and J. Bjerrum, *Acta Chem. Scand.*, **9**, 810 (1955); K. Nakamoto, J. Fujita, M. Kobayashi, and R. Tsuchida, *J. Chem. Phys.*, **27**, 439 (1957); A. J. Saraceno, I. Nakagawa, S. Mizushima, C. Curran, and J. V. Quagliano, *J. Am. Chem. Soc.*, **80**, 5018 (1958).

[5] It was established the α (violet) 1,2,6- isomer of tris(glycinato)cobalt(III) cannot be transformed into the β (red) 1,2,3- isomer under the same experimental conditions, which proves that the β isomer is the primary product of the reaction described.

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A Study of β-Ferric Oxide Monohydrate Containing Excess Water

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Several workers[1-4] have shown that β-ferric oxide monohydrate requires an impurity in some of the interstitial positions. When the compound is prepared from ferric chloride or ferric fluoride, the impurity is chloride or fluoride ion. Bernal, *et al.*,[2] were unable to prepare the compound from solutions containing ferric ions and bromide ions because the bromide ion is too large for the interstitial positions.[4]

The Fe:Cl atomic ratios have often been reported in the range of about 5–45, while scant attention has been given to the water in excess of the structural water.[2,3] We have achieved a range of excess water from 0.8 to 0.01 mole of excess water per mole of $Fe_2O_3 \cdot H_2O$, along with Fe:Cl atomic ratios of about 7500. This has been done by varying the concentration of dilute aqueous ammonia used to wash the monohydrate from the ferric chloride hydrolysis. The influence of the amount of excess water on X-ray powder patterns, thermogravimetric curves, and magnetic susceptibility has been studied.

Experimental

The procedure of Weiser, *et al.*,[5] was used in the preparations of β-$Fe_2O_3 \cdot H_2O$. A constant rate of temperature rise was maintained for 8 hr. while the temperature rose to 80°. This temperature was maintained for 2 hr. The mixture was cooled rapidly to room temperature and allowed to stand 24 hr. Each product was washed in three stages, as shown in Table I. Throughout all stages, a centrifuge was necessary for separation. The products were dried at 110° in an electric oven for 24 hr. The dried products were stored in sealed vials placed inside a desiccator. Each was analyzed for iron and chlorine by standard procedures.

TABLE I

PREPARATION DATA AND RESULTS ON SEVERAL SYNTHESES OF β-FERRIC OXIDE MONOHYDRATE

Sample no.	Washing H_2O wash	 Aq. NH_3[a] wash	 Final H_2O wash	% Fe	Excess H_2O per mole of $Fe_2O_3 \cdot H_2O$
1	3 × 144 ml.	None	None	58.44	0.8
2	2 × 144 ml.	1 × 572 ml. (0.01 *M*)	1 × 572 ml.	60.36	0.4
3	3 × 430 ml.	11 × 1720 ml. (0.01 *M*)	1 × 1720 ml.	61.19	0.27
4	2 × 144 ml.	11 × 572 ml. (0.01 *M*)	1 × 572 ml.	61.48	0.21
5	3 × 144 ml.	11 × 572 ml. (0.1 *M*)	2 × 572 ml.	62.53	0.05
6	3 × 144 ml.	11 × 572 ml. (0.2 *M*)	2 × 572 ml.	62.67	0.03
7	3 × 144 ml.	11 × 572 ml. (0.1 *M*)	2 × 572 ml.	62.77	0.01

[a] Molarity of aqueous ammonia in parentheses.

X-Ray powder diffractometer traces were run on several of the preparations. Zirconium-filtered Mo radiation of 0.70926 Å. wave length was used. Mackay[3] has reported 21 lines of the powder pattern for β-ferric oxide monohydrate, the strongest of which have the following *d* values in Å. and relative intensities in parentheses: 7.40 (10), 5.25 (4), 3.311 (10), 2.616 (4), 2.543 (8), 2.285 (4), 1.944 (6), 1.746 (4), 1.635 (10), 1.515 (4), 1.438 (8), 1.374 (4).

Thermogravimetric curves for samples 1, 3, and 7 were obtained with an apparatus similar to that of Loriers.[6] A 2 ml./sec. stream of dry helium was used in the apparatus. The rate of temperature rise was 1.4°/min. The quartz helix balance had a force constant of 1 mg./mm., and the extension of the helix was read to 0.005 mm. Sample weights of about 30 mg. were used.

Magnetic susceptibilities were measured by the Faraday method using a quartz helix from which the sample was suspended.[7] The apparatus was calibrated with a gaussmeter and with massive Pt and Re standards. Helium, at 1 atm., was used in the apparatus.

The gram susceptibility at zero reciprocal field (χ_∞) was obtained from a plot of apparent susceptibility *vs.* reciprocal field

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[7] P. W. Selwood, "Magnetochemistry," 2nd Ed., Interscience Publishers, Inc., New York, N. Y., 1956, p. 14.

for each sample used and at each temperature employed. In all cases the slope of apparent susceptibility *vs.* reciprocal field was small. The gram-ionic paramagnetic susceptibilities of the Fe^{3+} ion (χ_P) were calculated from the χ_∞ values by using the appropriate diamagnetic corrections.

Results and Discussion

In all preparations, the Fe:Cl atomic ratio was about 7500 and the yields were about 20% of theoretical. Table I includes the concentrations of the aqueous ammonia solutions used, the volumes of these solutions, and the number of times each volume was used. The amounts of excess water are those calculated assuming only water as the impurity. The negligible chloride contents justify the assumption. In general, the amount of excess water decreases with increasing ammonia contact. The last three entries of Table I show about the same amount of excess water even though the ammonia concentration in the case of sample 6 was twice that for samples 5 and 7. This may indicate that one can reach a point of diminishing returns once the ammonia concentration has reached the level of 0.1 *M*. The same kind of thing is indicated between samples 3 and 4. Here the volume of aqueous ammonia was changed instead of the concentration.

TABLE II

CORRECTED GRAM MAGNETIC SUSCEPTIBILITIES AND GRAM-IONIC MAGNETIC SUSCEPTIBILITIES OF Fe^{3+} IONS OF SOME β-FERRIC OXIDE MONOHYDRATE PREPARATIONS[a]

Temp., °K.	Sample 1		Sample 2		Sample 3		Sample 7	
	$\chi_\infty \times 10^6$	$\chi_P \times 10^6$	$\chi_\infty \times 10^6$	$\chi_P \times 10^6$	$\chi_\infty \times 10^6$	$\chi_P \times 10^6$	$\chi_\infty \times 10^6$	$\chi_P \times 10^6$
372	21.5	2100	22.7	2130			17.5	1590
b	22.2	2170	23.7	2230	22.7	2110	19.0	1720
226	23.1	2260					21.3	1930
88	27.7	2700	37.7	3520			30.7	2760

[a] Units of χ_∞ are cm.^{3} g.$^{-1}$; units of χ_P are cm.^{3} (g.-ion)$^{-1}$. [b] Room temperature (296°K. for samples 1 and 2, 297°K. for samples 3 and 4).

The data on sample 1 indicate that water washing alone was sufficient to remove the chloride, but with retention of a large excess of water. The necessity of using a centrifuge throughout washing indicates that the preparations were of very small particle size and the broad lines of the X-ray patterns appear to confirm this.

The observations connected with the aqueous ammonia washing indicate a tendency for the excess water to "migrate" out of the interstitial positions as ammonia contact increases. This may be due to a lowering of the chemical potential of the water in the external solution relative to that of the water in interstices, as the ammonia concentration increases. The interstitial positions form straight lattice channels parallel to the *c* dimension of the unit cell.

Weiser and Milligan[1] reported only nine Bragg spacings for each of four of their preparations. They did not observe the 7.40 Å. spacing, which causes one of the strongest lines. X-Ray patterns for samples 1 and 2 showed nineteen of the Bragg spacings. The spacing corresponding to 7.40 Å. was observed in the patterns of samples 1, 2, 3, and 7. The pattern of sample 3 showed only eleven spacings. The pattern of sample 7 showed ten spacings, but those corresponding to 7.40 and 5.25 Å. were so weak as to be barely discernible. Line broadening was more pronounced in patterns of samples 3 and 7 than those of samples 1 and 2.

From these patterns, and the preceding results, it is apparent that the excess water can function to stabilize the β-ferric oxide monohydrate lattice, even in the absence of chloride. When the amount of excess water falls below about 0.4 mole per mole of $Fe_2O_3 \cdot H_2O$, the crystallographic order begins to disappear. Severe lattice disintegration accompanies small amounts of excess water.

Mackay has pointed out that the β-ferric oxide monohydrate lattice has two interstitial cavities and eight FeOOH units per unit cell. When all interstitial cavities are occupied by water, the amount of excess water is 0.5 mole per $Fe_2O_3 \cdot H_2O$ unit. Sample 1 seemingly represents a case in which about every third unit cell contains three molecules of water in addition to eight FeOOH units. A preferable alternative is adsorption of the excess water, above 0.5 mole, on the surface of the particles. Viewed in this manner, the presence of 0.4 mole of excess water in sample 2, after only one washing with 0.01 *M* aqueous ammonia, appears consistent with the requirement of much more ammonia contact to achieve the lower excess water content.

Thermogravimetric curves were obtained for samples 1, 3, and 7. They show that decomposition started at about 112° in all cases. The preparations of Weiser and Milligan[1] which contained the lowest amounts of chloride started to decompose at about the same temperature. Their preparations containing the highest amounts of chloride did not start to decompose until about 150°. Others[2] have reported 250–260°, and Mackay[3] has reported 230° as the temperature at which rapid loss of water occurred in preparations containing some excess water and chloride in relatively large amounts. Apparently, water can serve as the impurity upon which the β-ferric oxide monohydrate lattice depends. It is not as good a stabilizer to thermal decomposition as is chloride ion.

The fraction of the total water remaining at 510° was 0.09, 0.12, and less than 0.01 for samples 1, 3, and 7, respectively. This fraction is more a property of the product of decomposition than of the monohydrate, but it serves to set sample 7 apart from samples 1 and 3.

Plots of $\chi_P T$ *vs.* T are presented in Figure 1 and the

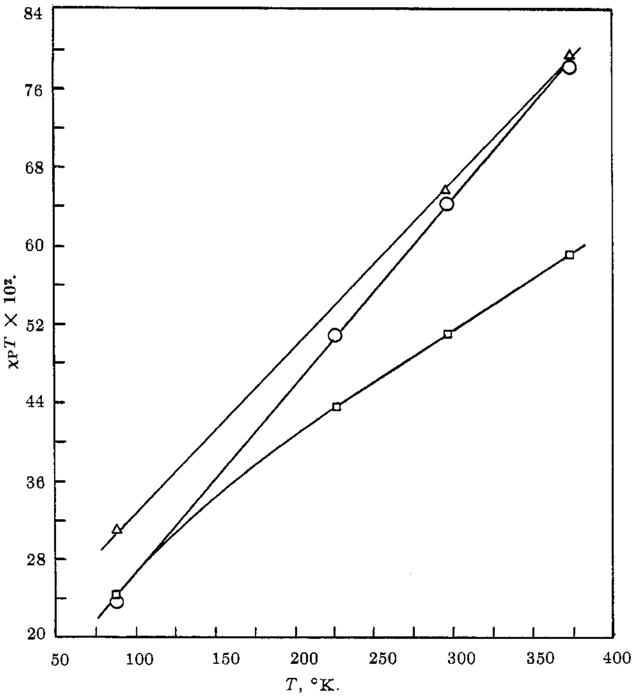

Figure 1.—Magnetic susceptibilities per gram-ion of Fe^{3+} ions times absolute temperature *vs.* absolute temperature for sample 1 (○), sample 2 (△), and sample 7 (□).

χ_P values are given in Table II. The plots for samples 1 and 2 closely approximate a straight line over the whole temperature range. The temperature dependence of χ_P is of the form

$$\chi_P - a = c/T \qquad (1)$$

where a and c are constants. The plot for sample 7 closely approximates a straight line only between 372 and 226°K. The slope is appreciably smaller than the slope of the other plots. Creer[8] has indicated that his preparations of β-ferric oxide monohydrate, of less than 50 Å. particles, almost obeyed a Curie law.

Takada, *et al.*,[9] have reported the Mössbauer spectrum for β-ferric oxide monohydrate. At 110°K. it shows magnetic splitting of the energy levels of the iron nucleus, while at 300°K. this splitting is not observed. Takada, *et al.*, have interpreted this as indicating an antiferromagnetic Curie point between 300 and 110°K. The details of preparation of their sample were not given but they state that their sample was of high purity. We assume that their sample and sample 7 were largely the same. The deviation of $\chi_P T$ *vs.* T from a straight line at 88°K. can be accounted for by the onset of antiferromagnetic behavior by sample 7 between 226 and 88°K. If sample 7 obeyed eq. 1 at 88°K., χ_P would be about 3180×10^{-6}.

The low magnetic dilution indicated by antiferromagnetic behavior can account for the low slope of the straight line portion of the plot for sample 7 and the corresponding low values of χ_P. An appreciable difference in magnetic dilution between sample 7 and other samples may be due to a need of the β-ferric oxide monohydrate lattice to find another source of stability as the amount of stabilizing impurity approaches zero. The onset of low magnetic dilution might provide this stability.

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Difluoraminocarbonyl Fluoride

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Trifluoronitrosomethane (CF_3NO) has been reported as a product derived from the fluorination of silver cyanide.[1] When the former contacted 8% aqueous sodium hydroxide, nearly quantitative conversion to its isomer, difluoraminocarbonyl fluoride (NF_2CFO), occurred.[2] This isomer was said to be a colorless, stable compound with a boiling point of −83.4°. However, although Haszeldine and Jander[3] have demonstrated that trifluoronitrosomethane may be slowly decolorized when heated with activated charcoal or when agitated with aqueous base to give several compounds, including hexafluoroazoxymethane ($CF_3{}^+N(O^-)NCF_3$) and trifluoronitromethane (CF_3NO_2), no evidence was found to confirm the formation of difluoraminocarbonyl fluoride. It was concluded that the compound reported as the latter was either perfluoroethane (C_2F_6) or perfluoromethylamine (CF_3NF_2) and, therefore, that difluoraminocarbonyl fluoride was yet to be prepared.[3]

Bumgardner and Lustig[4] have reported the synthesis of difluoraminosulfuryl fluoride by the ultraviolet radiation of a mixture of tetrafluorohydrazine (N_2F_4) and sulfur dioxide. By a similar reaction involving tetrafluorohydrazine and carbon monoxide, it now has been possible to synthesize difluoraminocarbonyl fluoride with properties quite different from those reported heretofore.

Experimental

Reagents.—Tetrafluorohydrazine, obtained from Air Products, Inc., was used without further purification. Carbon monoxide, obtained from the Matheson Company, Inc., was passed through a tube at −183° to remove carbon dioxide and water. Reagents used for analyses were of analytical reagent grade.

Analytical Methods.—After sodium fusion, fluorine was determined through the use of a null-point method,[5,6] carbon was obtained as the carbonate formed by basic hydrolysis, and nitrogen was determined iodometrically. Vapor pressure measurements were made in a vacuum system of small volume by maintaining the compound in a liquid state at various low temperatures in appropriate slush baths and by reading the pressure on a mercury manometer. Vapor density was determined through the use of Regnault's method with a 244.4-ml. Pyrex flask

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