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Hydrazine Complexes of Iron(II) Halides

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As part of our study of hydrazine complexes of the first row transition elements we report here the reactions of iron halides with hydrazine, methylhydrazine and 1,1-dimethylhydrazine. The only reaction studied previously is that between iron(III) chloride and hydrazine hydrate in ethanol to give $FeCl_2(N_2H_4)_2$ [1].

The reaction between anhydrous iron(III) chloride and anhydrous hydrazine at room temperature results in the formation of a mixture of $FeCl_2(N_2H_4)_2$ and $N_2H_4 \cdot HCl$. The compounds $FeX_2(N_2H_4)_2$ (X = Cl, Br, or I) are most easily prepared by treating alcoholic solutions of the iron(II) halide hydrates with 100% hydrazine hydrate in the absence of air. They are white solids which turn brown upon exposure to air; in water they yield a green precipitate of iron(II) hydroxide. These compounds often undergo violent spontaneous decomposition (with evolution of smoke) during drying or upon standing as well as upon exposure to air. This thermodynamic instability is somewhat surprising since hydrazine has the tendency to stabilise lower oxidation states of some transition elements as in for example $CrCl_2(N_2H_4)_2$ [2]. It may however be associated with the fact that these compounds contain iron(II) ions which can catalyse the decomposition of hydrazine; anhydrous hydrazine has been known to detonate in the presence of iron compounds [3]. The infrared spectra of these compounds are as reported by Sacconi and Sabatini [4] for $FeCl_2(N_2H_4)_2$; in the light of recent work however the 1156 cm^{-1} band is re-assigned to ν(N–N) and is indicative of the presence of bridging hydrazine [5]. The magnetic moments and electronic spectra (by reflectance) of these compounds (Table) are in accord with a polymeric structure as in $ZnCl_2(N_2H_4)_2$ [6], the high spin iron(II) ion being surrounded tetragonally by two halide ions and four nitrogen atoms from the bridging hydrazines. The $^5T_{2g} \rightarrow {}^5E_g$ transition (O_h symmetry) is seen to be split into the $^5E_g \rightarrow {}^5A_{1g}$ and $^5E_g \rightarrow {}^5B_{1g}$ components typical of iron(II) complexes in D_{4h} symmetry.

Similarly the reactions of iron(III) chloride and iron(III) bromide with methylhydrazine and N,N-dimethylhydrazine result in reduction of the iron to the +2 oxidation state with the formation of the hydrazine hydrohalides and gaseous oxidation products of the hydrazines. The methylhydrazine complexes $FeX_2(MeNHNH_2)_2$ (X = Cl, Br or I) are most readily prepared in ethanolic solution but the dimethylhydrazine complexes could not be obtained this way. The ease of oxidation of these complexes FeX_2L_2 (L = N_2H_4, $MeNHNH_2$ or Me_2NNH_2) increases from hydrazine to dimethylhydrazine; the complexes of the latter ligand are so unstable (turning brown) in the presence of traces of oxygen that we have been unable to record reflectance spectra for them. The i.r. spectra of the $FeX_2(Me_2NNH_2)_2$ complexes are very similar to that of $NiCl_2(Me_2NNH_2)_2$ [7]; we believe them to contain six coordinated high spin iron(II) ions in a structure with either halide or hydrazine bridges. The methylhydrazine complexes again have electronic spectra and magnetic moments as expected for tetragonal high spin iron(II) complexes and their i.r. spectra are very similar to that of $CoCl_2(MeNHNH_2)_2$ [8] and quite unlike that of $CoCl_2(MeNHNH_2)_6$ which contains unidentate methylhydrazine. The most likely structure for these complexes is thus one with methylhydrazine bridges. In accord with the polymeric structures proposed, all of the complexes listed in the Table are insoluble in solvents with which they do not react.

Experimental

All reactions were carried out under an atmosphere of dry nitrogen or *in vacuo*.

Reactions of Iron(III) Halides

With hydrazine

An excess of anhydrous hydrazine was condensed onto anhydrous iron(III) chloride (0.1438 g) at −196 °C and the mixture warmed to room temperature. Reaction occurred as soon as the hydrazine melted and nitrogen and ammonia were evolved. Removal of all volatiles from the mixture *in vacuo* left a white residue (0.2289 g); the i.r. spectrum of this material indicates it to be a mixture of $FeCl_2(N_2H_4)_2$ and $N_2H_4 \cdot HCl$ (weight increase during reaction corresponds to the formation of "$FeCl_3 \cdot 3.00N_2H_4$").

With methylhydrazine

Iron(III) chloride (2.055 g) in anhydrous ether (100 cm^3) was treated with a 2% solution of methylhydrazine in ether added dropwise with stirring.

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TABLE. Hydrazine Complexes of Iron(II) Halides.

Complex	μ_{eff} BM (20 °C)	Electronic Spectra (cm^{-1})		Analytical Data			
		$^5E_g \rightarrow {}^5B_{1g}$	$^5E_g \rightarrow {}^5A_{1g}$	%Fe Found	Theory	%X^a Found	Theory
$FeCl_2(N_2H_4)_2$	5.15	11,700	8,900	29.4	29.27	37.1	37.18
$FeBr_2(N_2H_4)_2$	5.08	11,800	9,400	20.1	19.97	57.0	57.15
$FeI_2(N_2H_4)_2$	5.04	12,200	9,100	15.1	14.95	67.6	67.92
$FeCl_2(MeNHNH_2)_2$	5.20	10,200	8,700	25.2	25.53	31.9	32.41
$FeBr_2(MeNHNH_2)_2$	5.01	10,500	7,500	18.4	18.15	51.8	51.94
$FeI_2(MeNHNH_2)_2$	4.95	10,600	7,400	14.1	13.91	63.1	63.19
$FeCl_2(Me_2NNH_2)_2$	5.05			22.7	22.63	30.1	28.73
$FeBr_2(Me_2NNH_2)_2$	5.10			16.7	16.63	46.9	47.61

^{a}X = Cl, Br or I.

Vigorous effervescence occurred, the initially brown precipitate becoming white as an excess of the hydrazine was added. The precipitate was filtered off *in vacuo*, washed with anhydrous ether and dried *in vacuo*. The i.r. spectrum indicated it to be a mixture of $FeCl_2(MeNHNH_2)_2$ and $MeNHNH_2 \cdot HCl$. Found: Fe, 18.6; Cl, 33.7%; $FeCl_2(MeNHNH_2)_2 + MeNHNH_2 \cdot HCl$ requires Fe 18.54; Cl, 35.30%. Similarly iron(III) bromide gave a white mixture of $FeBr_2(MeNHNH_2)_2$ and $MeNHNH_2 \cdot HBr$. Found: Fe, 12.7; Br, 54.7%; $FeBr_2(MeNHNH_2)_2 + MeNHNH_2 \cdot HBr$ requires Fe, 12.85; Br, 55.16%.

With N,N-dimethylhydrazine

The direct reactions between iron(III) chloride and dimethylhydrazine gave effervescence with the formation of a dark red solution from which white crystals slowly precipitated. Filtration of the mixtures and washing of the white crystals with dimethylhydrazine gave the bis-hydrazinates (Table).

Reactions of iron(II) Halides

With hydrazine

Treatment of solutions of the freshly prepared hydrated halides (1 g) in absolute ethanol (200 cm^3) with hydrazine hydrate (10 cm^3) gave white precipitates of the bis-hydrazinates (Table). These were washed with ethanol and ether and dried *in vacuo*.

With methylhydrazine

There was no reaction between anhydrous $FeCl_2$ and methylhydrazine. The hydrates $FeX_2 \cdot 4H_2O$ (X = Cl, Br or I), however, (~ 5 g) in absolute ethanol (200 cm^3) gave white precipitates of the bis-hydrazinates (Table) when treated with a 5% solution of methylhydrazine in absolute ethanol.

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