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Stability of Xenon(II) Compounds. The Pentafluorooxyselenium and Pentafluorooxytellurium Radicals. Bis(pentafluorotellurium) Peroxide and Chlorine Pentafluoroorthotellurate

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Received December 28, 1972

The noble gas compounds xenon bis(pentafluoroorthoselenate) and xenon bis(pentafluoroorthotellurate) are the most thermally stable of the $Xe(OR)_2$ compounds known so far. Their first decomposition products, on the other hand, are the free radicals $OSeF_5$ and $OTeF_5$ and were detected by esr spectroscopy at low temperatures. Uv irradiation of the xenon bis(pentafluoroorthochalcogenates) at room temperature results in the quantitative formation of the peroxides $F_5SeOOSeF_5$ and $F_5TeOOTeF_5$. $F_5SeOXeOTeF_5$ exists only in equilibrium with $Xe(OSeF_5)_2$ and $Xe(OTeF_5)_2$. Attempts to prepare $FOTeF_5$ were unsuccessful, whereas $ClOTeF_5$ was obtained.

Introduction

The recently prepared compounds $Xe(OSeF_5)_2$[1] (A) and $F_5SeOXeF$[1] and the well-known pentafluoroorthotellurates $Xe(OTeF_5)_2$ (B) and $F_5TeOXeF$[2] have an unexpected thermal stability. Other xenon(II) compounds like $Xe(OSO_2F)_2$,[3] $Xe(OPOF_2)_2$,[4] $Xe(OOCCF_3)_2$,[2,5,6] and $Xe(ClO_4)_2$[3] decompose at room temperature. The decomposition products of the unstable fluorosulfates, fluorophosphates, etc., mainly are the peroxides (FSO_2OOSO_2F[3]) or their decomposition products ($F_2OPOPOF_2$,[4] $CF_3CF_3 + 2CO_2$[6]). Since one paramagnetic intermediate could be detected by esr[4] a radical mechanism for the decay reaction is probable[3]: $Xe(OSO_2F)_2 \rightarrow Xe + 2FSO_3 \rightarrow Xe + FSO_2OOSO_2F$.

Experimental Section

General. An all-Teflon distillation column, filled with Kel-F pieces, was used to purify $Xe(OSeF_5)_2$ (A) and $Xe(OTeF_5)_2$ (B). Fluorine nmr spectra were taken on a JEOL 60 HL instrument using $CFCl_3$ as internal or external reference. Samples were contained in 5-mm o.d. quartz or, if possible, glass tubes. Infrared spectra were recorded on a Perkin-Elmer 457 spectrometer. The window material was CsBr, this sometimes protected by an 0.025-mm FEP foil. Raman spectra were taken on a Coderc PH 1 instrument, using a He-Ne laser for excitation, 190 mW. Samples were contained in quartz or glass tubes as described above for the nmr spectra. Visible and uv spectra were taken on a Leitz Unicam SP 800 instrument. Samples were run in 10-mm quartz cuvettes with $CF_2ClCFCl_2$ as solvent.

Esr spectra were taken on a Varian E-3 X band spectrometer; samples were taken as crystals or dissolved in CF_3CF_3. Mass spectra were taken on a Varian MAT 7 instrument, 70 eV.

Reagents. Xenon difluoride was prepared in 10-g scale by the method of Falconer and Sunder.[7] Fluorosulfuric acid was redistilled *in vacuo*. SeO_2F_2 was prepared from H_2SeO_4 and HSO_3F.[8,9]

Preparation of $HOSeF_5$.[10] SeO_2F_2 (1 mol) and HF (3 mol) were condensed into a 2-l. quartz vessel, containing 10 mol of HSO_3F. The solution was stirred for several hours at room temperature. The progress of the reaction was controlled by measuring the ^{19}F nmr; the single line of SeO_2F_2 (−54.5 ppm) slowly disappeared while the AB_4 spectrum of $HOSeF_5$ increased. If the reaction remained incomplete, more HF must be added. After disappearance of the SeO_2F_2 signal the volatile material was pumped through a Teflon tube into a −196° cooled quartz vessel. The nonvolatile residue consisted mainly of H_2SO_4. The volatile material was stirred again at room temperature for several hours. By a further vacuum distillation HF, $HOSeF_5$, and some amounts of HSO_3F were separated from the main quantity of HSO_3F. The distillate was roughly fractionated in the described Teflon column in order to separate HSO_3F. A second slow fractionation gave first a solution of HF and $HOSeF_5$ and then pure $HOSeF_5$ (0.6 mol): mp 37°; bp 44°.

Preparation of $HOTeF_5$.[11] H_6TeO_6 (1 mol) was dissolved in HSO_3F (12 mol). Fractional distillation of the solution immediately yielded pure (0.85 mol) $HOTeF_5$: mp 40°; bp 60°. Sometimes redistillation was necessary.

Preparation of $Xe(OSeF_5)_2$[1] (A) and $Xe(OTeF_5)_2$[2] (B). XeF_2 (0.1 mol) was loaded into a 50-ml Teflon vessel and $HOSeF_5$ (0.3 mol; $HOTeF_5$, 0.3 mol) was condensed on it. The Teflon vessel was connected to the Teflon distillation column. HF was distilled off by slowly heating on a water bath with magnetic stirring, until $HOSeF_5$ ($HOTeF_5$) was detected in the distillate. Excess of the acids was pumped off at −30°. The solid residue was sublimed in a glass apparatus at 0.1 Torr and room temperature, giving 70–80 mmol of A (B). A had mp 69°. *Anal.* Calcd for $F_{10}Se_2O_2Xe$: F, 37.4; Se, 29.7; Xe, 25.6. Found: F, 37.1; Se, 31.0; Xe, 25.6. B had mp 40.5°. *Anal.* Calcd for $F_{10}Te_2O_2Xe$: F, 31.3; Te, 41.0; Xe, 21.6. Found: F, 30.8; Te, 41.8; Xe, 21.6.

Preparation of $F_5TeOXeF$. See reference 2.

Preparation of $F_5SeOOSeF_5$ and $F_5TeOOTeF_5$. The xenon compounds (50 mmol) were each placed in a quartz tube and melted by cautious heating. A high-pressure mercury lamp (125 W, unfiltered) was brought as near as possible and gas evolution began immediately. It was necessary to protect the gas volume from uv light, as the peroxides were destroyed by irradiation in the gas phase. After several hours the yellow color of each melt had disappeared and the gas evolution ceased. Quick distillation of the clear liquids yielded $F_5SeOOSeF_5$ (mp −61.5°; bp 74°), or $F_5TeOOTeF_5$ (mp −39°; bp 81.5°). The yield is almost quantitative.

Extended fractional distillation at normal pressure caused slow decomposition. The products SeF_4, SeF_6, and $F_5SeOSeF_5$ were detected by ir and ^{19}F nmr spectroscopy, and the products TeF_6 and $F_5TeOTeF_5$ likewise. TeF_4 appeared as a white, crystalline and nonvolatile solid, mp >100°, with marked attack of the glass.[12] *Anal.* Calcd for $F_{10}Se_2O_2$: F, 50.0; Se, 41.5. Found: F, 50.0; Se, 41.3. The ir shows absorptions at 765 (s), 740 (s), 662 (w), 582 (m), 477 (m), 447 (m), 419 (vs), 390 (w), and 368 cm^{-1} (m). Raman bands occur at 903 (s, p), 765 (w, dp), 747 (m, p), 742 (w, dp), 660 (vs, p), 632 (m, dp), 578 (m, dp), 474 (vw, dp), 442 (m, p), 418 (m, p), 387 (m, p), 366 (w, dp), 329 (m, p), 301 (vw, dp), 275 (m, p), 259 (m, p), 183 (m, p), and 141 cm^{-1} (s, p). The mass spectrum gave evidence for the ions $F_{10}Se_2O_2^+$, $F_9Se_2O^+$, F_5SeO^+, F_5Se^+, F_3SeO^+, F_3Se^+, F_2Se^+, $FSeO^+$, FSe^+, SeO^+, and Se^+. *Anal.* Calcd for $F_{10}Te_2O_2$: F, 39.8; Te, 53.3. Found: F, 39.8; Te 53.0. The ir of $F_5TeOOTeF_5$ showed absorptions at 740 (vs), 721 (s), 665 (vw), 637 (w), 600 (m), 363 (w), 309 (s), 321 (m), and

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285 cm^{-1} (w). The Raman spectrum showed bands at 907 (m, p), 740 (w, dp), 725 (m, p), 674 (vs, p), 658 (sh, dp), 637 (m, p), 599 (m, dp), 363 (m, dp), 335 (m, p), 315 (s, p), 284 (w, dp), 258 (m, dp), 218 (m, p), 169 (w, dp), 142 (m, p), and 116 cm^{-1} (s, p). The mass spectrum showed ions $F_{10}Te_2O_2^+$, $F_9Te_2O^+$, $F_5TeO_2^+$, F_5TeO^+, F_5Te^+, F_4Te^+, F_3TeO^+, F_3Te^+, F_2Te^+, $FTeO^+$, FTe^+, and Te^+.

Irradiation in the Presence of Selenium Tetrafluoride. A or B was dissolved in a large excess of SeF_4 (1:20 molar proportion), and the solution was irradiated as described above. ^{19}F nmr showed no other reaction products than the two peroxides.

$F_5SeOXeOTeF_5$. An equimolar mixture of A and B was fused. ^{19}F nmr spectra in solution of $CFCl_3$ showed a new compound, $F_5SeOXeOTeF_5$, in a proportion of 1.85:1:1 to the starting compounds. Further purification seemed at this time to be hopeless.

Preparation of $Hg(OTeF_5)_2$. Mercuric fluoride (0.25 mol) and $HOTeF_5$ (0.6 mol) were placed in a 250-ml Teflon vessel. The reaction mixture was shaken at room temperature for 24 hr. The volatile material was pumped off, and the remaining white residue was sublimed in a glass apparatus at 180° and 0.01 Torr: yield, 0.18 mol of $Hg(OTeF_5)_2$ as white crystals, slowly turning yellow by hydrolysis; dec pt *ca.* 200°. *Anal.* Calcd for $F_{10}Te_2O_2Hg$: F, 28.1; Te, 37.8; Hg, 29.7. Found: F, 27.3; Te, 38.2; Hg, 29.5. The ir spectrum showed absorptions at 810 (s), 718 (s), 680 (s), 624 (m), 345 (m), and 320 cm^{-1} (s). The Raman spectrum showed bands at 830 (m, p), 814 (m, dp), 636 (s, p), 486 (s, p), 466 (s, p), 385 (m, p), 370 (w, dp), 330 (m, dp), 233 (s, p), 177 (m, p), 148 (w, dp), and 131 cm^{-1} (s, p) in solution of methylene chloride. The mass spectrum showed ions $F_{10}Te_2O_2Hg^+$, $F_9Te_2O_2Hg^+$, F_5TeOHg^+, F_5Te^+, Hg^+, F_3Te^+, F_2Te^+, FTe^+, and Te^+.

Preparation of $ClOTeF_5$. $Hg(OTeF_5)_2$ (0.05 mol) was transferred to a 250-ml stainless steel autoclave, and chlorine monofluoride (0.12 mol) was condensed on it. The mixture was warmed to room temperature and shaken for 1 day. The volatile compounds were trapped at −196°; excess ClF was removed at −100°. The remaining liquid could be distilled in a glass system: mp −121°; bp 38.1°; quantitative yield. Hydrolysis of the yellow liquid afforded Cl_2O and $HOTeF_5$, as can be detected by ir and uv spectroscopy. *Anal.* Calcd for F_5TeOCl: F, 34.6; Te, 46.5; Cl, 12.93. Found: F, 35.0; Te, 46.8; Cl, 12.85. The ir spectrum showed absorptions at 811 (vs), 735 (vs), 708 (vs), 551 (m), 327 (vs), 315 (m, sh), and 288 cm^{-1} (m). The Raman spectrum showed bands at 811 (m, dp), 736 (w, dp), 711 (s, p), 661 (vs, p), 656 (m, dp, sh), 552 (s, p), 329 (w, dp), 316 (m, dp), 307 (m, dp), 278 (s, dp), 216 (m, p), and 140 cm^{-1} (m, p). The mass spectrum showed ions F_5TeOCl^+, F_5Te^+, F_4TeO^+, F_3Te^+, F_2Te^+, FTe^+, and Te^+.

Attempted Preparation of $FOTeF_5$. $Hg(OTeF_5)_2$ (0.05 mol) and fluorine (0.1 mol) were handled as described above. The volatile reactants consisted of oxygen and tellurium hexafluoride, which was detected by its characteristic ir spectrum.

Results

The thermal decomposition of A begins slowly at 100° and becomes fast at 130°;[13] at the same temperature B begins to decompose.[2] The main products of that thermal reaction are the oxides $F_5SeOSeF_5$ and $F_5TeOTeF_5$ besides some hexafluorides, tetrafluorides, and oxygen. No peroxide could be detected so far.

The yellow color and the uv spectra suggest possible sensitivity (Figure 1) of compounds A and B toward light. The irradiation of A and B yields the two peroxides $F_5SeOOSeF_5$ and $F_5TeOOTeF_5$ quantitatively. The formation of the two peroxides is accompanied by the appearance of paramagnetic intermediates. On irradiating pure solid A or B at −150° a single broad epr line of half-width 10.2 G (peak to peak) is observed. The values for the *g* factors are 2.00 in both cases. The signal becomes smaller on heating and disappears at about −30°.

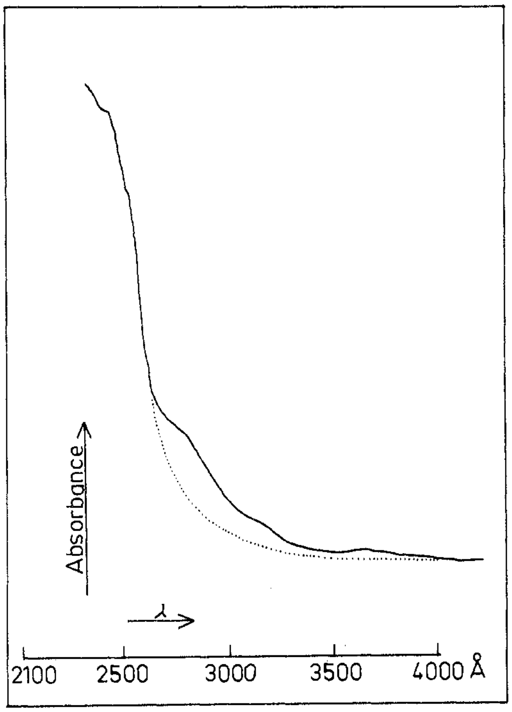

Figure 1. Uv spectra of xenon bis(pentafluoroorthoselenate) (———) and xenon bis(pentafluoroorthotellurate) (·······).

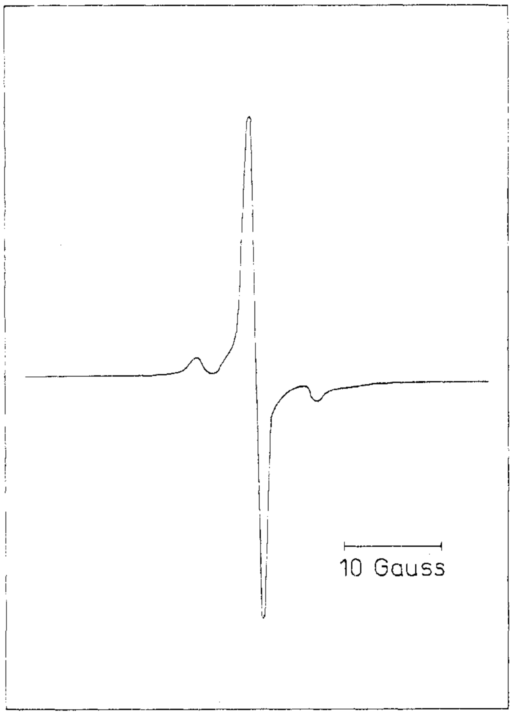

Figure 2. Epr spectrum of a solution of xenon bis(pentafluoroorthoselenate) in F_3CCF_3 at −150° during uv irradiation.

A solution of A and B in hexafluoroethane shows epr signals during uv irradiation (Figures 2 and 3). Raising the temperature or interruption of the irradiation immediately causes a decrease in signal intensity. Two satellite peaks (a_{Se} = 11.1 G, a_{Te} = 28.8 G) in the epr spectra are due to the isotopes ^{77}Se (natural abundance 7.58%, $I = 1/2$) and ^{125}Te (6.99%, $I = 1/2$). The ratio of the hyperfine coupling constants in A and B (=0.38) is about the same as the ratio of the nmr coupling constants ^{77}Se-^{19}F and ^{125}Te-^{19}F, *e.g.*, in the bis(pentafluorochalcogen) peroxides (=0.37). The

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(13) The similarity of the physical properties of $F_5TeOOTEF_5$ and $F_5TeOTeF_5$ might be the reason that the peroxide was not detected earlier. The fluorination of a Te–TeO_2 mixture with oxygen-diluted fluorine leads to small amounts of $F_5TeOTeF_5$ and F_5TeO-$OTeF_5$. This fraction was described as F_5TeTeF_5;[14] later this was identified as $F_5TeOTeF_5$.[11,15]

(14) P. Campbell and P. L. Robinson, *J. Chem. Soc.*, 3454 (1956).

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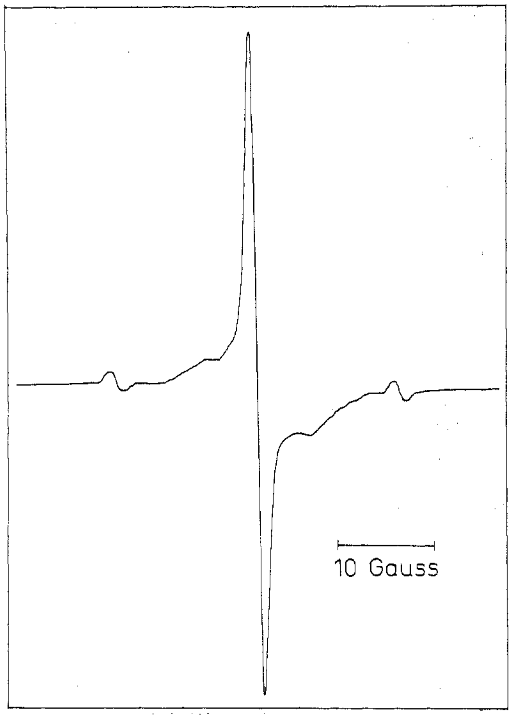

Figure 3. Epr spectrum of a solution of xenon bis(pentafluoroorthotellurate) in F_3CCF_3 at −150° during uv irradiation.

existence of the satellite lines shows that the electron spin density is distributed over the oxygen and the chalcogen atoms.

Both bis(pentafluoroselenium) peroxide and bis(pentafluorotellurium) peroxide are unstable above 80°.[13] Distillation under atmospheric pressure yields $F_5SeOSeF_5$ or $F_5TeOTeF_5$ and the tetra- and hexafluorides of the chalcogens, *i.e.*, the same reaction mixture as from the thermal decomposition of the xenon compounds A and B.[2,16]

No homolytic decomposition is observed under normal conditions. This is in agreement with the fact that the oxygen-oxygen bonds are unusually strong as is evidenced by the high O–O valence frequencies in the Raman spectra. The increased frequency of 907 cm^{-1} in $F_5TeOOTeF_5$ compared with that of 903 cm^{-1} in the lighter $F_5SeOOSeF_5$ suggests that the tellurium compound possesses the stronger O–O bond. For comparison, FO_2SOOSO_2F which is known to dissociate easily into radicals has a ν_{O-O} value of 798 cm^{-1}.[17] The mass spectra of $F_5SeOOSeF_5$ and $F_5TeOOTeF_5$ show the parent peaks, but surprisingly the fragments produced by loss of one fluorine could not be detected.

The similar properties of the $OSeF_5$ and $OTeF_5$ groups lead us to the assumption that $F_5SeOXeOTeF_5$ could exist. Indeed, an equimolar mixture of A and B gives rise to a ^{19}F nmr spectrum that displays a new group of lines in addition to the well-known resonance absorptions of the pure compounds. The ratio of the line intensities in A, B, and the new species corresponds to the statistical expectation of 1:1:2. In the new compound the ^{19}F resonances of both AB_4 groups are shifted compared with those of A and B; especially the A resonances are affected (see Table I).

Table I. ^{19}F Nmr Data of the Pentafluoroorthochalcogenates,[a] AB_4 spectra, 56.4 MHz

	A	B	J_{AB}	J_i[b]
$Xe(OSeF_5)_2$ (A)	−81.1	−70.0	229	1338
$Xe(OTeF_5)_2$ (B)	41.8	43.3	183	3600
$F_5SeOXeOTeF_5$	−80.8 41.6	−70.0 43.3	229 181	
$F_5SeOOSeF_5$	−55.2	−54.4	230[c]	1431
$F_5TeOOTeF_5$	54.6	54.9	180[c]	3830
$Hg(OTeF_5)_2$ (CH_2Cl_2)	38.2	40.1	186	3560
(CH_3CN)	27.8	40.4	180	3580
$ClOTeF_5$	51.7	55.1	183	3755

[a] Chemical shifts in ppm; $CFCl_3$ as internal standard; coupling constants in c sec^{-1}. [b] J_i = coupling constant between ^{77}Se (^{125}Te) and ^{19}F. [c] Estimated value.

In an attempt to prepare the still unknown fluorooxytellurium pentafluoride, $FOTeF_5$, xenon fluoride pentafluoroorthotellurate, $F_5TeOXeF$, was irradiated with uv light, but instead of the expected product the already described peroxide $F_5TeOOTeF_5$ was formed.

The most suitable route to $FOSeF_5$ involves fluorination of $Hg(OSeF_5)_2$;[13] hence, an analogous synthesis of $FOTeF_5$ was attempted. Treatment of HgF_2 with $HOTeF_5$ resulted in the new mercury compound $Hg(OTeF_5)_2$. Its ^{19}F resonance spectrum depends very strongly on the polarity of the solvent.

While the reaction of mercury bis(pentafluoroorthotellurate) with fluorine gives no $FOTeF_5$, treatment with chlorine monofluoride affords the chlorine compound $ClOTeF_5$. The chlorine in that molecule is positively charged as proved by the hydrolysis reaction. The other pentafluoroorthochalcogenates are known.[13,18]

Discussion

The irradiation-induced conversion of xenon bis(pentafluoroorthochalcogenates) to the corresponding peroxides appears to proceed *via* homolytic bond dissociation. This is especially supported by the appearance of radical intermediates at low temperatures. The decay of the peroxides above 80° leads to products that are identical with the thermal decomposition products of the xenon bis(pentafluoroorthochalcogenates). We therefore assume that the reaction pathways for both the thermal and the optical-induced reactions of the xenon bis(pentafluoroorthochalcogenates) are essentially the same.

$$F_5SeOXeOSeF_5 \rightarrow 2OSeF_5 + Xe \rightarrow F_5SeOOSeF_5 \rightarrow$$
$$F_5SeOSeF_5 + SeF_4 + SeF_6 + O_2$$

This scheme agrees with the proposed decomposition steps of other mainly covalent xenon(II) compounds.[2,4,17]

A correlation is observable between the stability of these xenon(II) compounds and the oxygen-oxygen bond strength in the corresponding peroxides, probably because the first decomposition products of the xenon compounds and of the peroxides are the same, more or less reactive free radicals. Even the small difference in the stability of A and B is reflected in the different oxygen-oxygen bond strength in the peroxides as well as in the higher reactivity of the $OTeF_5$ radical compared with $OSeF_5$.

Recently it was shown that the ^{19}F nmr spectra of compounds containing a more ionic bonded $OSeF_5$ ($OTeF_5$) group differ characteristically from those containing a more covalently bonded group.[19] For instance, a solution of $Hg(OTeF_5)_2$ in methylene chloride shows the absorption of covalently bonded groups, whereas a solution in acetonitrile shows the typical spectrum of the ion $(OTeF_5)^-$.

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The ^{19}F magnetic resonance spectrum of the mixed compound $F_5TeOXeOSeF_5$ provides for the comparison of the ionicity of the two different Xe–O ligand bonds. It is seen that the $OSeF_5$ group has slightly more covalent character and the $OTeF_5$ group slightly more ionic character compared with the related compounds A and B. This means that the first of the two canonical forms in the resonance hybrid[20] $(F_5SeOXe)^+(OTeF_5)^- \leftrightarrow (F_5SeO)^-(XeOTeF_5)^+$ is of greater importance.

Acknowledgment. We are indebted to Professor W. Sundermeyer and Professor H. J. Keller for the support of this work.

Registry No. $Xe(OSeF_5)_2$, 38344-58-0; $Xe(OTeF_5)_2$, 25005-56-5; $F_5SeOOSeF_5$, 37988-78-6; $F_5TeOOTeF_5$, 41524-11-2; $F_5SeOXeOTeF_5$, 41524-12-3; $Hg(OTeF_5)_2$, 41517-06-0; $HOTeF_5$, 19583-94-9; $ClOTeF_5$, 41524-13-4; ClF, 7790-89-8; mercuric fluoride, 7783-39-3.

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Iron(II) Complexes with Two and Three Dialkyldithiocarbamate Ligands. Mossbauer and Electronic Spectra

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Received February 5, 1973

A series of tris(*N*,*N*-dialkyldithiocarbamato)iron(II) complexes has been synthesized for the first time. The Mossbauer and electronic spectra of these complexes together with those of bis(*N*,*N*-dialkyldithiocarbamato)iron(II) have been measured. Small isomer shift values confirm the covalent character of the iron–sulfur bonds. The quadrupole splitting differs for six- and five-coordination; both coordination numbers occur in the bis(dimethyldithiocarbamato)iron(II) complex.

I. Introduction

Tris(*N*,*N*-dialkyldithiocarbamato)iron(III) complexes ($Fe(R_2dtc)_3$) have been investigated thoroughly with the help of Mossbauer spectroscopy and other techniques.[1-5] Recently the iron(IV) analog $(BF_4)Fe(R_2dtc)_3$ was prepared by Pasek and Straub.[6] Pignolet, Lewis, and Holm have reported the synthesis of $Fe(R_2dtc)_2tdf$[7] and $Fe(R_2dtc)_2mnt$[8] where tdf = perfluoromethyldithiolene and mnt = maleonitriledithiolene. These complexes contain similarly a FeS_6 core. A review on this type of compound was given by Coucouvanis.[9] In this work the preparation and properties of the corresponding iron(II) complexes $(R'_4N)Fe(Et_2dtc)_3$ (R'_4N^+ is a tetraalkylammonium ion) are discussed in connection with measurements on $Fe(R_2dtc)_2$ complexes.[7,10,11] These iron(II) complexes were investigated mainly by means of Mossbauer spectroscopy and electronic spectroscopy. Because of the air sensitivity of the compounds these techniques offer advantages over other experimental procedures.

II. Experimental Section

Preparation of the Complexes. The complexes discussed in this paper are very air sensitive, even when dry; hence all preparations were carried out under exclusion of air using vacuum techniques.

The bis(*N*,*N*-dialkyldithiocarbamato)iron(II) complexes ($Fe(R_2dtc)_2$ with R = methyl, ethyl, *n*-propyl, *n*-butyl, or phenyl) were prepared by mixing aqueous solutions of stoichiometric amounts of ferrous sulfate and the sodium salt of the dithiocarbamate required.[7,10] The ligand solution may also be prepared by adding CS_2 to an aqueous stirred solution of NaOH and the appropriate dialkylamine or diphenylamine. The sulfate and ligand solutions were thoroughly degassed by a repeated freezing, pumping, and thawing procedure. After mixing both solutions the suspension of the complex was deposited on a filter and flushed with previously degassed water. The washing water was collected for later analysis and the complex was dried by immersing part of the apparatus in liquid nitrogen.

The iron(II) tris(dithiocarbamate) complexes ($Fe(Et_2dtc)_3^-$) were prepared in the same way, but now an excess of tetraalkylammonium chloride (R'_4NCl, R' = butyl or ethyl) or tetraphenylphosphonium chloride (Ph_4PCl) was added to the ferrous sulfate solution. The purification of the tris complexes has to take place within a short time, otherwise $Fe(Et_2dtc)_2$ is formed. This can be observed by a change of color from brightly yellow to brown. In the final product the presence of $Fe(Et_2dtc)_2$ is easily revealed by its Mossbauer spectrum. On adding dithiocarbamate ligand to the reaction mixture, the tris complex can be formed again from the bis complex. The stability of the tris complexes decreases with decreasing size of the cation: $(Et_4N)Fe(Et_2dtc)_3$ transforms easily into the bis complex and attempts to prepare $NaFe(Et_2dtc)_3$ were unsuccessful. No evidence was found for the formation of $Fe(Et_2dtc)_2Cl^-$: (a) the Mossbauer spectra of complexes prepared with an excess of Bu_4NCl, Bu_4NBr, and Bu_4NI are identical, (b) the complex could also be prepared with the use of $(Bu_4N)_2SO_4$, (c) no Et_2dtc^- has been found in the washing water if stoichiometric amounts of starting materials were used, and (d) no halogen was found in the complex and no iron-chlorine band was observed in the infrared spectrum. The products have been characterized by ir, Mossbauer, and electronic spectra and by elemental analyses. Since elemental analyses could only be carried out in the presence of air, oxidation could not be excluded.

Anal. Calcd for $Fe(Me_2dtc)_2$: C, 24.32; H, 4.09; N, 9.46. Found: C, 23.93; H, 3.96; N, 9.29. Calcd for $Fe(Et_2dtc)_2$: C, 34.06; H, 5.71; N, 7.94. Found: C, 33.67; H, 5.81; N, 7.85. Calcd for $Fe(Ph_2dtc)_2$: C, 57.33; H, 3.69; N, 5.13. Found: C, 55.45; H, 3.85; N, 4.81. (The agreement is further improved by comparing the experimental values with the percentages calculated for oxidation products $[Fe(R_2dtc)_2]_2O$. Calcd for R = Me: C, 23.68; H, 3.98; N, 9.21. Calcd for R = Et: C, 33.33; H, 5.59; N, 7.77. Calcd for R = Ph: C, 56.50; H, 3.64; N, 5.06.) Calcd for $(Et_4N)Fe(Et_2dtc)_3$: C, 43.79; H, 7.99; N, 8.88. Found (after oxidation): C, 41.50; H, 7.35; N, 8.66. Calcd for $(Bu_4N)Fe(Et_2dtc)_3$: C, 50.10; H, 8.95; N, 7.54. Found: C, 48.01; H, 8.62; N, 7.27. Calcd for $(Ph_4P)Fe$-

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