centrations of anions known to form ion pairs are present suggests an SN1 mechanism. (2) The relatively small negative entropy of activation found for the aquation of the *cis*-dichloro(triaminotriethylamine)-cobalt (III) ion suggests an SN1 mechanism, since an SN2 mechanism usually produces a rather large negative entropy.

Assuming that the cobalt complexes with controlled configuration and with uncontrolled configuration follow the same reaction path during aquation reactions, it would be gratifying to be able to explain why the one with controlled configuration shows a greater reaction rate than do *cis*-$[Co(en)_2Cl_2]^+$, *cis*-$[Co(trien)Cl_2]^+$, and other dichlorocobalt ions.

Pearson and co-workers[6] have shown that the largest differences in rate are found between the completely ammoniated complexes and those which contain other bases in addition to or instead of coordinated ammonia. This suggests that the more rapid reactions of the ammonia complexes are due to the larger numbers of acidic hydrogen atoms and the absence of chelate effect in *cis*-$[Co(NH_3)_4Cl_2]^+$, as compared with *cis*-$[Co(en)(NH_3)_2Cl_2]^+$, *cis*-$[Co(en)_2Cl_2]^+$, and *cis*-$[Co(trien)Cl_2]^+$, and in *trans*-$[Co(NH_3)_4Cl_2]^+$, as compared with *trans*-$[Co(en)(NH_3)_2Cl_2]^+$ and *trans*-$[Co(en)_2Cl_2]^+$. In general, the rate of aquation decreases as the amount of chelation increases. The greater rate at which *cis*-$[Co(tren)Cl_2]^+$ aquates as compared with the other complexes containing organic amines is probably due simply to steric strains produced by the peculiar geometry of the complex. Rasmussen[7] has shown that in the complex $[Ni(tren)(NCS)_2]$, the bonds between the metal and the primary amine nitrogens are drawn back toward the tertiary nitrogen atom. This distortion would certainly put a strain on the complex, with resultant increase in reactivity. The reasonable assumption that the stereochemistry of $[Co(tren)Cl_2]^+$ is similar may afford a satisfactory explanation for the increased activity of the coordinated chlorine. It does not seem to be necessary to call upon inductive or other electrical effects.[6]

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Magnetic Properties of Copper Benzoate[1]

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The magnetic properties of copper acetate and other copper alkylcarboxylates have been the subject of many investigations. However, little attention has been paid to the copper arylcarboxylates. Ploquin[2] reported the results of his magnetic investigations of the copper salts of several organic acids. An abnormally low moment of 1.50 B.M. was obtained for copper benzoate. Recently, the presence of a low moment for copper benzoate has been verified by two groups.[3,4] The Japanese workers[3] obtained three values for the moment depending on the method of preparation of the sample. They attributed these values to different structure types. Lewis and co-workers[5,6] have measured the magnetic susceptibilities of a number of copper salts of substituted benzoic acids. In this note we wish to report the results of our studies of the temperature dependence of the magnetic susceptibilities of samples of copper benzoate and of copper *p*-methylbenzoate. The data show that the magnetic properties are a function not only of the method of preparation but also of the history of the sample.

Experimental

Preparation of the Compounds.—The compounds, prepared by standard techniques, were characterized thoroughly; we report in Table I complete analytical data for our samples.

Table I

Analytical Data

		Analyses		
	Sample	% carbon	% hydrogen	% copper
Copper benzoate	I[a]	54.28	3.44	
	II[b]	54.00	3.50	...
	III[c]	54.55	3.53	20.58
	Calcd.	54.99	3.27	20.78
Copper *p*-methylbenzoate	A[d]	56.83	4.19	19.20
	B[e]	56.28	4.49	...
	Calcd.	57.57	4.20	19.05

[a] Prepared by heating copper benzoate trihydrate at 90° under vacuum over P_2O_5. [b] Prepared by heating the trihydrate at 100° in air. [c] Prepared by heating $Cu(C_6H_5CO_2)_2 \cdot C_2H_5OH$ at 90° in air. [d] Prepared by heating $Cu(CH_3C_6H_4CO_2)_2 \cdot C_2H_5OH$ in air at 70° for 2 hr. [e] Prepared by heating sample A in air for 40 hr. at 90°.

X-Ray Powder Patterns.—X-Ray diffraction patterns of powdered samples were obtained using a 114.6-mm. Debye–Scherrer camera. Samples were mounted in glass capillary tubes with a diameter of 0.5 mm. and a wall thickness of 0.01 mm.

The powder pattern of anhydrous copper benzoate (sample III) consisted of lines corresponding to *d* spacings of 11.2 (9), 9.50 (10), 7.56 (2), 6.05 (7), 5.52 (4), 5.12 (5), 4.73 (8), 4.29 (1), 4.06 (6), 3.30 (4), 2.77 (3), and 2.62 (1) Å. The relative intensities which are given in parentheses were estimated visually.

Magnetic Susceptibility Determinations.—Magnetic susceptibilities were determined by the Faraday method using equipment and procedures which have been described previously.[7]

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A cryostat based on the design described by Richardson and Beauxis[8] was used to achieve temperature control.

Results

Powder Patterns of Anhydrous Copper Benzoate.—The powder patterns of samples I and II (obtained by dehydrating the trihydrate at high temperatures) consisted of only two broad bands at $d = 11.80$ and 4.65 Å., respectively. The powder pattern of sample III (obtained by decomposition of the monoethanol adduct) consisted of many sharp and well-defined lines. The powder patterns of samples I and II were similar to that of the α modification reported by Inoue, *et al.*[3] Our sample III corresponds to their β modification.

The Magnetic Data.—The temperature dependence of the magnetic susceptibilities of two samples of copper *p*-methylbenzoate and three samples of anhydrous copper benzoate has been determined and the data are given in Table II. The magnetic moments were calculated from the expression $\mu_{eff} = 2.84[\chi_M^{cor} - N\alpha]T^{1/2}$, where a value of 60×10^{-6} c.g.s. unit was assumed for the temperature-independent paramagnetism of the copper ion. Diamagnetic corrections were estimated from Pascal's constants. When $1/\chi_M^{cor}$ for sample I is plotted *vs.* temperature the data define a straight line which intercepts the temperature axis at $-120°$. The magnetic data for sample II yield an even greater Weiss constant than those for sample I.

TABLE II

MAGNETIC DATA, $\chi_M(T)$ AND $\mu(T)$, FOR COPPER(II) BENZOATES

T, °K.	$10^6\chi_g$, c.g.s. units	$10^6\chi_M^{cor}$, c.g.s. units	μ_{eff}
	$Cu(C_6H_5CO_2)_2$ (sample I)		
299	3.62	1243	1.69
273	3.85	1324	1.67
196	5.05	1678	1.60
77	7.74	2501	1.23
	$Cu(C_6H_5CO_2)_2$ (sample II)		
300	2.91	1024	1.53
196	3.17	1104	1.15
77	3.64	1247	0.82
	$Cu(C_6H_5CO_2)_2$ (from ethanol adduct)		
300	2.73	969	1.49
276	2.86	1010	1.45
260	2.83	1000	1.40
250	2.87	1014	1.40
240	2.88	1017	1.36
230	2.89	1020	1.33
220	2.86	1010	1.30
210	2.87	1014	1.27
200	2.85	1005	1.24
190	2.82	999	1.20
180	2.77	982	1.16
170	2.69	959	1.11
155	2.60	930	1.04
140	2.43	878	0.96
125	2.20	808	0.87
112	2.02	752	0.78
	$Cu(p\text{-}CH_3C_6H_4CO_2)_2$ (sample A)		
300	2.09	857	1.38
196	1.92	800	1.08
77	2.02	833	0.69
	$Cu(p\text{-}CH_3C_6H_4CO_2)_2$ (sample B)		
300	2.54	1009	1.51
196	2.75	1074	1.27
77	5.25	1912	1.07

Discussion

The temperature dependence of the magnetic susceptibility of the sample of copper benzoate prepared by the decomposition of the ethanol adduct is approximated by the theoretical expression

$$\chi_M = \frac{g^2N\beta^2}{3kT}\,\frac{1}{1 + \frac{1}{3}e^{J/kT}} + N\alpha$$

for an electronic system of a singlet state and a triplet state separated by an energy difference J. In the expression g is the Landé splitting factor, β the Bohr magneton, k the Boltzmann constant, and $N\alpha$ the temperature-independent paramagnetism. The data are best fitted with $J = 250$ cm.$^{-1}$ and $g = 2.14$. The maximum in the temperature dependence curve, the Néel temperature, was estimated to be 225°K. The sample of anhydrous copper benzoate prepared from the decomposition of $Cu(C_6H_5CO_2)_2 \cdot C_2H_5OH$ probably has a structure similar to that of anhydrous copper acetate. However, the structures of the samples prepared by the dehydration of the trihydrate are probably not as simple. This can be understood in terms of the structures of the precursors. Inoue, *et al.*,[3] have shown that copper benzoate forms 1:1 adducts with a variety of Lewis bases. In view of the magnetic[3] and spectral[9] properties they probably have the copper acetate type structure. When the adduct is heated to form anhydrous copper benzoate, extensive rearrangement of the ligands is not necessary since the copper acetate structure is already present. The structure of copper benzoate trihydrate has been shown by an X-ray diffraction study of single crystals[10] to consist of linear chains of copper ions bridged by two water oxygens and one carboxylate group. The second benzoate ion and the third molecule link the chains laterally into sheets by means of hydrogen bonds. Upon dehydration extensive rearrangement of the ligands is necessary. On the basis of the magnetic data it appears that the rearrangement occurs in a more or less random manner, probably to give extensively cross-linked polymeric structures. The amount of polymerization may depend on the method of dehydration.

Our samples of anhydrous copper benzoate are probably contaminated with traces of CuO. O'Keefe and Stone[11] have shown that the magnetic properties

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of CuO are dependent upon particle size; the susceptibility increases with a decrease in particle size. The deviations of the measured magnetic susceptibilities for sample III from the theoretical predictions are very likely due to a contamination of the sample with finely divided copper oxide suspended on the copper benzoate. It is interesting to note that not one of the eight samples of anhydrous copper benzoate prepared during the course of this study was found to have a higher percentage of carbon than the calculated percentage. We interpret this to mean that the copper arylcarboxylates undergo some decarboxylation upon heating with the formation of CuO and the loss of volatile organic decomposition products.

The initial goal of this research was the determination of the magnetic properties of a series of copper salts with substituted benzoic acids. It soon became evident that the magnetic properties of samples were very sensitive to the method of preparation and the history of the sample.[12] We wish to report only one additional set of representative data which illustrates this effect.

The magnetic properties of copper *p*-methylbenzoate were determined on two samples from the same monoethanolate preparation. Sample A was taken after heating $Cu(CH_3C_6H_5CO_2)_2 \cdot C_2H_5OH$ in air for 2 hr. at 70°, and sample B after heating sample A for 40 hr. at 90° in air. The magnetic properties of the compound were greatly affected by the heating process. The large increase of susceptibility at low temperature after prolonged heating may arise from a finely divided CuO impurity.

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CONTRIBUTION FROM THE RESEARCH INSTITUTE OF
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Formation of Xenon Difluoride from Xenon and Oxygen Difluoride or Fluorine in Pyrex Glass at Room Temperature[1]

BY L. V. STRENG AND A. G. STRENG

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The synthesis of $XePtF_6$ by Bartlett[2] opened an entirely new chapter of chemistry, the chemistry of noble gases. Since then, a series of binary noble gas compounds has been obtained, first at the Argonne National Laboratory[3] and then by others. Thermal and electric-discharge methods,[3] photolysis,[4] and high-pressure technique[5] have been used to induce the reaction of xenon with fluorine. With oxygen difluoride, xenon reacted when a 1:1, by volume, mixture of OF_2 and Xe was heated in a nickel tube to 300–400° at 3.25–3.75 atm. pressure, or when the Xe–OF_2 mixture was fed into a reaction vessel in which a high-voltage electric discharge was established, at low temperature and pressure.[6]

Recently, in the course of the study of slow reactions of oxygen fluorides under gentle conditions,[7] we found that both oxygen difluoride and fluorine reacted with xenon at room temperature and ordinary pressure when exposed (in a Pyrex glass flask) to ordinary daylight without any artificial addition of energy.

Experimental Procedure and Results

A series of experiments was made. A typical one is described here in detail.

A 2-l. Pyrex glass flask was filled with the gaseous mixture of 350 mm. of Xe and 374 mm. of F_2. The total pressure in the flask was 724 mm. at 25°. The flask was kept for 3 weeks at room temperature exposed to ordinary daylight.

The formation of tiny crystals was noticed on the second day of standing. The crystals grew with time to a size of 3–5 mm. These large transparent glistening crystals are identical in appearance with xenon fluorides. The initial rate of formation of the reaction product was about 35 mg./day. The yield varied depending on the intensity of sunlight, temperature, etc. The total amount of product obtained during 3 weeks varied from 0.5 to 0.75 g.

The product was analyzed and found to be XeF_2. The analysis was made by hydrolysis, as described elsewhere.[6,8] A 40-mg. sample of product on hydrolysis with water gave 0.25 mmole of Xe, 0.12 mmole of O_2, and 0.55 mmole of HF; *i.e.*, the reaction proceeded in accordance with the equation

$$XeF_2 + H_2O \longrightarrow Xe + 0.5O_2 + 2HF \qquad (1)$$

Only HF was obtained in slight excess, $\simeq 0.55$ mmole instead of the theoretical amount of 0.48 mmole.

Infrared absorption spectra of the gaseous phase of the product taken on a Beckman IR-9 spectrophotometer confirmed the results of the chemical analysis. Two characteristic peaks, at 570 and 555 cm.$^{-1}$, were obtained identical with those described by Smith.[9]

Oxygen difluoride, as expected, also reacts with xenon at the conditions described above. A 1:1, by volume, mixture of xenon and OF_2 at 1 atm. pressure produced crystals with an initial rate of 35 mg./day. The formation of the crystals was noticed on the third day of standing. Chemical analysis and the infrared spectrum showed that the reaction product was also XeF_2. It is possible that at different Xe:OF_2 ratio, temperature, pressure, and light intensity, the composition of the reaction product may be different. The possibility of formation of XeF_4 and $XeOF_2$, for example, is not excluded.

Similar experiments with OF_2–Xe and F_2–Xe mixtures repeated in darkness for a period of 4 weeks gave no visible trace of xenon fluorides.

Discussion

The fact that there was no formation of XeF_2 in the dark proves that the reactions between F_2 or OF_2 and Xe described above are photochemical.

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