The Ternary Systems Cobalt Chloride–Dioxane–Water and Nickel Chloride–Dioxane–Water at 25° C.

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On the two phase diagrams, solutions rich in water were in equilibrium with the solid hexahydrates of the two chlorides; solutions containing little water and, hence, very little dissolved salt were in equilibrium with the two solid monodioxanates. Over a wide range of liquid compositions including the miscibility gap, the two diaquomonodioxanates were the equilibrium solids. Dioxane was a rather strong ligand, because it reacted exothermally with the anhydrous chlorides, and the resulting monodioxanates had low vapor pressures. Moreover, during progressive desolvation, the diaquomonodioxanates released water before dioxane. According to all indications, dioxane acted as bidentate in both ternary systems.

TERNARY SYSTEMS comprising a metal halide, 1,4-dioxane, and water have been described for the chlorides of lithium (*15*), calcium and barium (*5*), mercury (II) (*14*), magnesium, cadmium, and copper (II) (*24*), and iron (III) (*19*). These phase studies were extended to the chlorides of the transition metals, cobalt (II) and nickel (II). In addition to hydrates, these two salts form adducts with dioxane (dioxanates) (*9, 21*) and mixed solvates (diaquomonodioxanates) (*20*).

The purpose of this work was to ascertain which of the solvates were present in the two ternary systems at 25° C., to look for new solvates and miscibility gaps, and to determine, from the composition of the solvates found in the condensed system and the known relationship between color and coordination of cobalt (II) and nickel (II), whether dioxane acts as uni- or bidentate.

Ternary systems involving cobalt chloride, water, and another liquid have been described for acetone (*10, 16*) and *tert*-butanol (*12*).

EXPERIMENTAL

Purification and characteristics of the 1,4-dioxane used have been described (*23*). Reagent-grade cobalt and nickel chloride hexahydrates were used without purification. The molar ratio, Co/2Cl, was 1.0028 and Ni/2Cl, 1.0018. The salts were weighed out as concentrated aqueous solutions, as hexahydrates, or as finely ground anhydrous powders. Before equilibrating the mixtures in a water bath at 25.00 ± 0.05° C., they were shaken and then stored at 30° C. Saturated solutions were separated from the solid phase by filtering under nitrogen pressure at 25° C. Isolation and identification of the solid phases was carried out in several ways. Large crystals, such as the two hexahydrates and a few samples of cobalt chloride diaquomonodioxanate, were blotted free of adhering solution with filter paper.

The two monodioxanates were fine powders which could not be blotted dry. Since the equilibrium solutions contained only traces of salt, evaporation of the retained solution would not deposit measurable amounts of additional solid. Therefore, these wet pastes were dried externally at room temperature under reduced pressure or in a nitrogen current. To ensure that no solvent of constitution was being removed together with the adhering mother liquor, the residues were weighed at short intervals. When the weight loss–time curves turned parallel to the time axis, the samples had lost the smell of dioxane. The two diaquomonodioxanates were in equilibrium with solutions containing from more than 30% to less than 0.1% solids. To extend this external drying procedure to a few diaquomonodioxanate samples wetted by concentrated solutions, the latter were first replaced with very dilute saturated solutions.

Whenever one of the three components became concentrated almost completely either in the liquid or in the solid phase, the composition of the latter was calculated by a material balance. This was feasible for those solutions which were in equilibrium with the solid hexahydrates and, thus, contained all of the dioxane, and for solutions near the salt-dioxane side of the triangle, where the solubility of salt was nearly zero.

Schreinemakers' method of wet residues was modified by tracing each tie line through three points representing the compositions of liquid phase, initial mixture, and wet solid. Their alignment provided a check of the accuracy of the analyses. The convergence of these tie lines at the composition of the solid phase was sharper than that of the tie lines based on two points.

X-ray powder diffraction diagrams of the wet solids provided a final confirmation of the range of composition over which each solid phase prevailed. It was particularly useful in identifying two solid phases appearing together, or a single solid phase in equilibrium with two immiscible liquid phases, where it was difficult to isolate a wet residue suitable for analysis.

The diagrams were taken with a Norelco Geiger counter diffractometer Type No. 12045, using a cobalt target to avoid fluorescence and an iron filter to eliminate the K_β radiation. The effective wavelength, corresponding to the average of the cobalt K_{α_1} and K_{α_2} radiation, was 1.791 A. Evaporation of solvents and uptake of atmospheric moisture was avoided by covering the sample surfaces with undrawn Mylar film, 0.00025 inch thick. Constancy of the Bragg spacings in all diffraction patterns of a given solid phase ruled out the existence of solid solutions.

Solutions and solids were analyzed for metal halide, and the ratio of water to dioxane was determined refractometrically (*23*). Nickel and cobalt were determined gravimetrically as chelates of anthranilic acid (*8*), and chloride as silver chloride. The following direct gravimetric determination of cobalt chloride was also used: Prior to drying at 105° C. and subsequent heating at 180° C., an excess of dioxane was added to the solutions or wet residues to remove the free water as the minimum boiling azeotrope

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and to form the diaquomonodioxanate initially. This compound decomposed to $CoCl_2$ without hydrolysis (see below). The procedure was not applicable to solutions of nickel chloride because of hydrolysis.

For solutions containing less than 0.7% salt, the ratio of water to dioxane was obtained from the refractive index after applying an empirical correction for the salt. For solid residues and for most liquid phases, the solvents were separated by distillation; the residues were heated to incipient sublimation to ensure complete solvent removal. Hydrolysis of the metal chlorides was unavoidable. To remove the hydrogen chloride formed and to regenerate the lost water, the distillate was redistilled quantitatively over anhydrous sodium carbonate before its refractive index was taken. This method was accurate to ±0.1% dioxane in the final analysis. The limiting factor was the accuracy of the refractive index measurements.

RESULTS

Phase Diagrams. The 25° C. isotherms of the two systems, represented in Figures 1 and 2, were qualitatively and quantitatively similar. The Roman numerals designate phase fields and the letters, except *P*, designate isothermally invariant points. Table I compares the solubility of the salts in pure water at 25° C. (point *A*) with previously published values. Tables II and III contain the remaining data for the two ternary systems.

The solubility of the chlorides remained constant along *AB* on a mole basis, but decreased along *BC* by 25 to 27% as the dioxane content of the mixtures increased. At still higher levels of dioxane, the chlorides salted out the solvent, producing a miscibility gap. Compositions inside the triangular region II consisted of the coarse hexahydrate crystals and of powders identified by x-ray diffraction as diaquomonodioxanates, plus a liquid phase of constant composition given by *B*. The position of the binodal curve, *CPD*, which represents the compositions of the two liquid phases in region V, was checked by the single-phase compositions designated as unsaturated solutions in Tables II and III. The region of immiscibility expanded with increasing temperature. The triangular region IV consisted of a solid identified by x-ray diffraction as the diaquomonodioxanate, plus two liquid phases of constant compositions represented by points *C* and *D*. Curve *DE* gives the compositions of solutions in equilibrium with the two solid diaquomonodioxanates. It nearly coincided with the water-dioxane side of the composition triangle (see Figure 2). Since identical results were obtained when the invariant liquid *E* was prepared by treating the pure solid diaquomonodioxanates with dry dioxane, by adding small amounts of water to dioxane slurries of solid monodioxanates, and by equilibrating the anhydrous chlorides with slightly aqueous dioxane, its composition is an equilibrium value. The two solid phases present in the triangular region VII were identified as the diaquomonodioxanates and the monodioxanates by their colors and diffraction patterns.

The very narrow region VIII corresponds to solutions of compositions given by the curve *E*-Dioxane in equilibrium with solid monodioxanate. Anhydrous dioxane did not dissolve any chloride, but all other liquid phases contained traces of dissolved salt.

The colors of the liquid phases of the cobalt chloride system were: deep wine red, *A* and Nos. 1 and 2; dark purple, *B* and Nos. 6–8; dark purple violet, No. 9; dark violet, Nos. 10–14; dark violet, but steel blue when seen by transmitted light in thin layers, Nos. 15–20. Of the conjugate liquids, the heavy layers (*C*, Nos. 21–24) were dark violet in reflected light but dark blue by transmitted light, the light layers (*D*, Nos. 21–24) were weak blue. The unsaturated solutions (Nos. 25–27) were rather weak purple. The remaining saturated solutions, Nos. 31, 32 and *E*, were very faint blue. Most saturated solutions of the nickel chloride system were of the same grass to emerald green hue, varying only in saturation as a function of salt content. Only at high dioxane concentrations did the green color turn into a greenish yellow (*D*, the light layers of Nos. 16–20). The yellowish tint of *E* was barely discernible.

Phase-rule considerations applied to point *B* preclude the existence of a hydrate lower than the hexahydrate in contact with liquid at 25° C. The diaquomonodioxanates did not lose solvent when stored for a month at 25° C. over an excess of the corresponding anhydrous chloride. This and the coexistence at *E* of the diaquomonodioxanates and the monodioxantes rule out the existence of a monoaquomonodioxanate at 25° C. There was no transfer of solvent between finely ground hexahydrate and the corresponding diaquomonodioxanate within six weeks at 25° C.

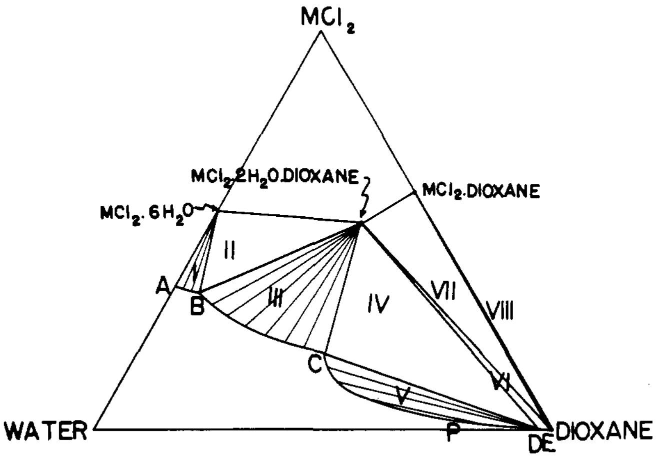

Figure 1. 25° C. isotherm for the systems MCl_2–dioxane–water

M represents cobalt or nickel

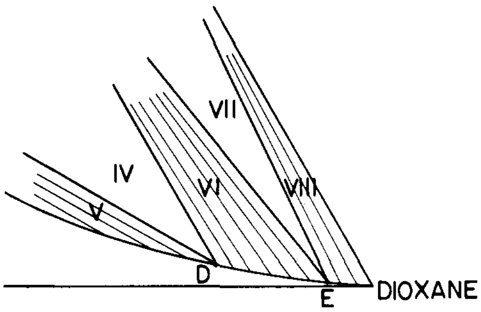

Figure 2. Schematic enlargement of the dioxane corner of the two phase diagrams

Table I. Solubilities of the Chlorides of Cobalt (II) and Nickel (II) in Water at 25.0° C.[a]

As Anthranilate[b]	As Silver Chloride[c]	Published Values	Ref.
	$CoCl_2$, %		
36.08 ± 0.04	35.98 ± 0.04	35.67	(*6*)
		35.72	(*10*)
		35.87	(*1*)
		36.08	(*18*)
		36.28	(*3*)
	$NiCl_2$, %		
39.70 ± 0.05	39.63 ± 0.07	37.53	(*7*)
		38.88	(*18*)
		39.58	(*4*)

[a] In equilibrium with solid hexahydrates. [b] Average of three determinations; ± signs precede range. [c] Average of four determinations.

Table II. Compositions in the System Cobalt Chloride–Dioxane–Water, Expressed as Weight %

Designation	Liquid Phase		Initial Mixture		Wet Residue or Solid Phase	
	$CoCl_2$	H_2O	$CoCl_2$	H_2O	$CoCl_2$	H_2O
			Region I			
A	36.03	63.97	no dioxane		54.56	45.44[a]
1	35.3	62.6	39.9	58.5	54.51	...[a]
2	34.6	60.9	39.1	57.4	54.36	45.64[a]
			theory for $CoCl_2 \cdot 6H_2O$		54.57	45.43
			Region II			
3	34.5	59.8	38.2	57.0		
4	34.4	59.7	39.8	52.9		
5	34.4	59.7	38.3	50.5		
B	Av. 34.43	59.75				
			Region III			
6	32.4	59.4	36.9	49.1	50.1	18.9[b]
7			31.9	57.1	51.15 ± 0.05	14.40[a]
8	29.3	57.0	33.2	49.6	47.6	22.3[b]
9	27.7	55.3	31.9	48.6	46.5	22.6[b]
10	25.9	52.5	30.1	46.7	47.3	21.6[b]
11	25.8	51.9	31.6	43.9	36.8	36.4[b]
12	24.5	49.6	29.3	44.5	47.1	20.8[b]
13	24.2	48.8	34.1	35.9		
14	23.1	47.8	24.2	47.3	51.15 ± 0.00	14.2[a]
15	21.9	45.7	27.7	40.0	45.9	21.9[b]
16	21.3	44.5	25.3	41.0	43.0	23.8[b]
17	20.6	43.0	26.9	37.9		
18			23.0	39.9	51.21 ± 0.07	14.6[a]
19	19.6	41.0	23.0	38.6	47.4	19.0[b]
19					51.02 ± 0.02	...[a]
20	19.2	40.5	24.0	36.9	44.0	20.2[b]
			theory for $CoCl_2 \cdot 2H_2O \cdot C_4H_8O_2$		51.13	14.19
	Heavy Layer		Initial Mixture		Light Layer	
	$CoCl_2$	H_2O	$CoCl_2$	H_2O	$CoCl_2$	H_2O
			Region IV			
21	19.2	39.4	18.9	30.0	0.10	4.7[c]
22	19.3	39.8	22.3	27.2	0.14	4.5
23	19.2	39.4	30.4	22.8	0.11	4.1[c]
24	19.2	39.5	20.1	20.0	0.14	4.5
C	Av. 19.24	39.50		*D*	Av. 0.13	4.44
			Region V			
25	15.0	41.3	9.4	28.5	0.12	6.0
26	12.4	40.7	9.4	33.9	0.20	8.0
27	7.4	35.2	1.9	17.6	0.61	13.0
P			3.0	24.3[d]		
			Unsaturated Solutions			
28			6.2	37.5		
29			2.3	23.4		
30			1.9	20.7		
	Liquid Phase		Initial Mixture		Wet Residue or Solid Phase	
	$CoCl_2$ p.p.m.	H_2O	$CoCl_2$	H_2O	$CoCl_2$	H_2O
			Region VI			
31	60	1.2	7.5	3.1[e]	51.36 ± 0.04	14.0[f]
31					51.2	14.2[g]
32	30	0.7	4.4	1.9[h]	51.12	...[f,c]
32					51.2	14.2[g]
			Region VII			
33	20	0.15	9.7	2.8[h]	54.9	...[j]
34	25	0.2	9.9	1.7[e]	[j]	
35	20	0.2	9.6	2.7[i]	[j]	
E	Av. 22	0.18				

[a] Analysis of coarse crystals blotted dry. [b] Analysis of wet residue. [c] Solid phase is $CoCl_2 \cdot 2H_2O \cdot C_4H_8O_2$, since it has the same x-ray diffraction pattern as samples 7, 14 and 18. [d] Composition of plait point *P* was estimated graphically with a conjugation curve. [e] Anhydrous cobalt chloride was added to aqueous dioxane. [f] Analysis of solvate externally dried at room temperature. [g] From material balance. [h] Water was added to $CoCl_2 \cdot C_4H_8O_2$ suspended in dioxane. [i] $CoCl_2 \cdot 2H_2O \cdot C_4H_8O_2$ was added to dioxane. [j] In equilibrium with two distinct solid phases, one pink, the other lavender-blue.

Table III. Compositions in the System Nickel Chloride–Dioxane–Water, Expressed as Weight %

Desig-nation	Liquid Phase		Initial Mixture		Wet Residue or Solid Phase	
	$NiCl_2$	H_2O	$NiCl_2$	H_2O	$NiCl_2$	H_2O
			Region I			
A	39.67	60.33	no dioxane		54.55	45.45[a]
1	38.1	57.4	45.7	52.0	54.49	45.51[a]
			theory for $NiCl_2 \cdot 6H_2O$		54.52	45.48
			Region II			
2	38.1	56.5	44.8	50.0		
3	38.0	56.8	42.7	49.1		
B	Av. 38.05	56.65				
			Region III			
4	37.1	56.8	39.3	49.4		
5	34.7	55.7	36.8	49.9	44.3	32.5[b]
6	32.9	54.3	34.7	50.4	47.3	24.3[b]
7	32.5	53.8	34.4	50.0		
8	30.6	51.4	33.8	45.9	41.8	31.2[b]
9			31.1	49.9	51.11 ± 0.04	14.2[a]
9					51.1	14.3[c]
10	28.5	48.7	30.9	45.0	42.4	28.9[b]
11	25.4	45.2	28.6	41.6	44.9	22.1[b]
12	23.5	42.2	26.5	38.6	40.1	25.7[b]
12					51.15	14.2[a]
			theory for $NiCl_2 \cdot 2H_2O \cdot C_4H_8O_2$		51.08	14.20

	Heavy Layer		Initial Mixture		Light Layer	
	$NiCl_2$	H_2O	$NiCl_2$	H_2O	$NiCl_2$	H_2O
			Region IV			
13	23.6	42.5	19.0	27.7	0.04	3.4
14	23.5	42.2	9.0	13.1	0.05	3.3
15	23.4	42.2	16.8	24.4	0.04	3.3
C	Av. 23.49	42.26		*D*	Av. 0.04	3.33
			Region V			
16	[b]		0.07	3.8	0.05	3.8
17	[d]		0.23	4.7	0.06	4.6
18	19.5	43.4	10.3	25.2	0.07	4.6
19	15.2	43.1	8.4	27.4	0.11	6.7
20	9.8	39.7	6.3	29.7	0.29	9.7
21	7.3	36.4	3.0	21.9	0.59	13.3
22	4.4	29.6	2.2	21.5	1.6	19.1
P			3.0	24.5[e]		
			Unsaturated Solutions			
23			4.0	31.4		
24			2.9	25.3		
25			2.6	23.5		

	Liquid Phase		Initial Mixture		Wet Residue or Solid Phase	
	$NiCl_2$ p.p.m.	H_2O	$NiCl_2$	H_2O	$NiCl_2$	H_2O
			Region VI			
26	220	2.6	2.0	2.9[f]	51.07	14.6[g]
27	61	1.2	16.3	5.3[h]	51.23	14.1[g]
27					51.2	14.0[i]
			Region VII			
28	60	0.15	17.0	3.0[h]	[k]	
29	55	0.15	9.7	2.8[f]	[k]	
30	50	0.15	9.6	2.7[j]	[k]	
E	Av. 55	0.15				

[a] Analysis of coarse crystals blotted dry. [b] Analysis of wet residue. [c] Solution replaced by solution No. 27 before external drying of solid in nitrogen current. [d] Very small volume. [e] Is center of tie line of No. 22, which nearly coincides with binodal curve; same plait point composition was obtained by graphical extrapolation using a conjugation curve. [f] Anhydrous nickel chloride was added to aqueous dioxane. [g] Analysis of solvate externally dried at room temperature. [h] Water was added to $NiCl_2 \cdot C_4H_8O_2$ suspended in dioxane. [i] From material balance. [j] $NiCl_2 \cdot 2H_2O \cdot C_4H_8O_2$ was added to dioxane. [k] In equilibrium with two distinct solid phases, one brownish, $NiCl_2 \cdot C_4H_8O_2$, the other pastel chartreuse, $NiCl_2 \cdot 2H_2O \cdot C_4H_8O_2$, identified by x-ray diffraction.

Monodioxanates. The reaction between the anhydrous chlorides and dioxane was exothermic. Cobalt chloride monodioxanate, a lavender powder, was prepared by treating the anhydrous chloride with dioxane at 25° C., or at the boiling point, followed by storage at 25° C. (*9*, *21*). It contained 27.09 ± 0.08% cobalt (theory, 27.04%) and lost 40.30 ± 0.19% weight at 160° C. (theory, 40.42%). The reaction between anhydrous nickel chloride and dioxane at 25° C. produced adducts containing at most 0.87 moles dioxane per mole $NiCl_2$. The monodioxanate was obtained as a brownish yellow powder by refluxing dioxane over the anhydrous salt, followed by storage at 25° C. The nickel content was 26.81 ± 0.12% (theory, 26.96%); the weight loss at 180° C. was 40.30% (theory, 40.47%). Juhasz prepared a similar adduct (*9*), whereas Rheinboldt obtained an unstable bidioxanate (*21*).

Both monodioxanates were quite hygroscopic; in contact with aqueous dioxane, they removed all but 0.2% water, transforming themselves into the diaquomonodioxanates (point E). Therefore, they coexisted with liquid phases only in a very narrow slice of the phase diagram. In the absence of water, they were rather stable. Nickel chloride monodioxanate lost only 0.08% dioxane when stored one or two hours at 0.3 mm. of mercury and 25° C. The cobalt adduct lost only 2.1% dioxane during five hours at 15 mm. and 70° C. At 0.20 mm., cobalt chloride monodioxanate had a dissociation temperature between 120° and 130° C.; at 0.03 mm., it decomposed between 95° and 110° C. (see below). The monodioxante of cobalt chloride dissolved readily in water, absolute methanol, and acetone; that of nickel chloride was soluble in the two former but not in the latter solvent.

Diaquomonodioxanates. The cobalt solvate crystallized as magenta needles with a density of 1.835 grams per cm.^{3}, or as a pink-lavender powder. It was soluble in water, ethanol, and acetone but practically insoluble in ethyl ether. The nickel solvate was a pastel chartreuse powder, soluble in water, ethanol, and ethylene glycol but insoluble in acetone and ethyl ether. Had it been obtained as larger crystals, the color would have been a deeper green.

The diaquomonodioxanates are remarkably stable since they prevailed over most of the phase diagrams where solid and liquid phases coexisted—namely, in the range of solvent composition from 99.8% dioxane/0.2% water to 8.7% dioxane/91.3% water. The color changes observed when the diaquomonodioxanates were heated in capillaries indicate that they lost the water of crystallization first and the dioxane second (see Table IV).

Quantitative desolvation experiments were made by sealing 2 to 4 grams of ground solvate, weighed to the milligram, into the stem of a filter with a fritted glass disk having an average pore size of 40 to 60 μ. The fritted glass served to prevent loss of solid particles through entrainment by the released vapor. The top of the filter was closed off with a perforated rubber stopper bearing a glass stopcock, which was connected to a vacuum system. Pressures were measured with a McLeod gage. A trap cooled with a dry ice and acetone mixture froze out the vapors coming off. The filter was immersed just below the stopper in a constant temperature bath. Each desolvation run was carried out at a constant reduced pressure, while the temperature was increased stepwise until a significant amount of solvent was released. The assembly was maintained for 30-minute periods at each temperature, at the end of which the filter plus stopcock was weighed to determine the amount of solvent lost. This was small (less than 10 mg. per 30 minutes) until the temperature was reached at which the dissociation pressure of the solid solvate exceeded the pressure of the system. The rate of solvent evolution was then over 100 mg. per 30 minutes, and the temperature was not raised until it fell again below 10 mg. per 30 minutes. The composition of the released vapors was determined by measuring the refractive index of the liquids frozen in the trap, and testing for hydrochloric acid by pH or silver nitrate.

Table IV. Transitions of Diaquomonodioxanates Heated in Capillaries[a]

Open Capillary	Sealed Capillary[b]	Sealed Capillary[c]
COBALT CHLORIDE DIAQUOMONODIOXANATE		
126–132° C.	129–135° C.	140° C.
large, magenta crystals break up into small, lavender crystals of monodioxanate		
	and condensate appears	and blue liquid separates at bottom
207–212° C.		ca. 225° C.
lavender crystals turn to blue $CoCl_2$		some liquid solidifies to deep blue needles (monodioxanate)
no further change observed up to 230° C.		
NICKEL CHLORIDE DIAQUOMONODIOXANATE		
135° C.		
condensate appears		
146–148° C.	144–146° C.	145° C.
pastel chartreuse powder turns to yellow-grey monodioxanate		
172° C.	171–173° C.	179° C.
yellow-grey powder turns to brown $NiCl_2$		
		and little liquid accumulates at bottom

[a] Rate of heating 1–2° C./minute; temperatures are averaged from duplicate or triplicate determinations. [b] Immersed one-third in heating bath; solid completely immersed, distillate condenses in colder upper end. [c] Completely immersed in bath.

Only traces of hydrochloric acid were found in the distillates of cobalt chloride diaquomonodioxanate, indicating that practically no hydrolysis took place during desolvation. The separation of the two solvents of crystallization was fairly sharp. At the temperature where all of the water had been released, only between 10 and 16% of the dioxane had come off (see Figure 3). This small overlapping was probably due entirely to entrainment of dioxane vapor above the solid by the released water. The gaseous dioxane swept away by the water vapor being flashed off was continually replaced by the solid, in order to maintain a constant partial vapor pressure of dioxane above it. This is shown by the sharp kink and displacement in the dioxane release isobar at the temperature at which dehydration occurred (Figure 4). The rate of dioxane evolution at that temperature was much higher than at 5° or 10° C. above it.

Hydrolysis during the desolvation of nickel chloride diaquomonodioxanate was shown by an excessive weight loss (50.21% compared with a calculated value of 48.92%) and an 1.026-fold excess in the weight of recovered solvent. Analysis of the residue indicated that 9% of the chlorine atoms was lost through hydrolysis. The data of Figure 3 were corrected for this. This figure shows that there was considerable overlapping in the release of water and dioxane.

One of the reasons for the separate release of water and dioxane during desolvation of the diaquomonodioxanate of cobalt chloride and the considerable overlapping during desolvation of the nickel chloride solvate is that the latter lost its water of crystallization at higher temperatures and its dioxane of crystallization at lower temperatures than did the cobalt chloride solvate at comparable pressures.

The premature evolution of dioxane in the stepwise desolvation of nickel chloride diaquomonodioxanate could account for the occurrence of hydrolysis. The presence of

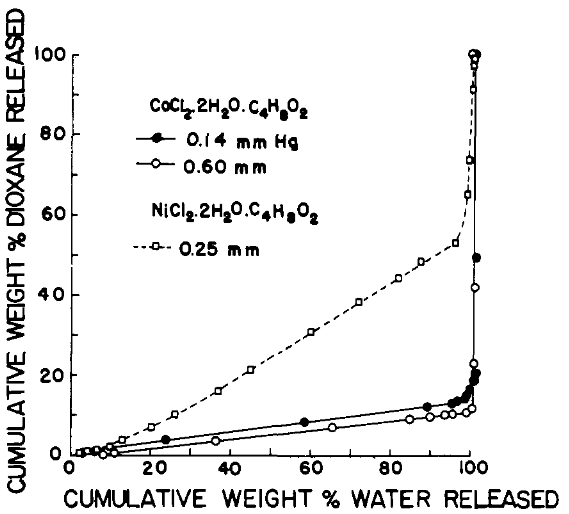

Figure 3. Sequence of evolution of water and dioxane during isobaric desolvation of cobalt and of nickel chloride diaquomonodioxanates

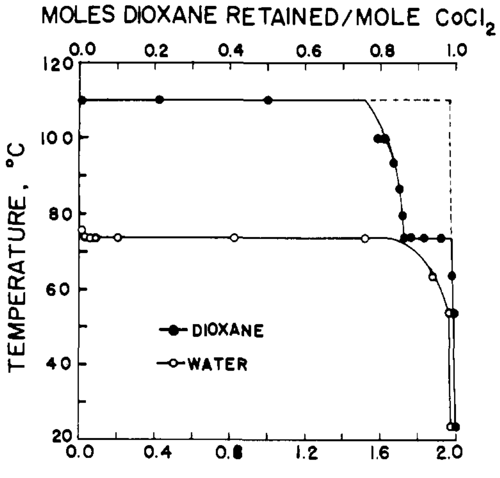

Figure 4. Desolvation isobar of cobalt chloride diaquomonodioxanate

Moles solvent remaining per mole $CoCl_2$ as a function of temperature

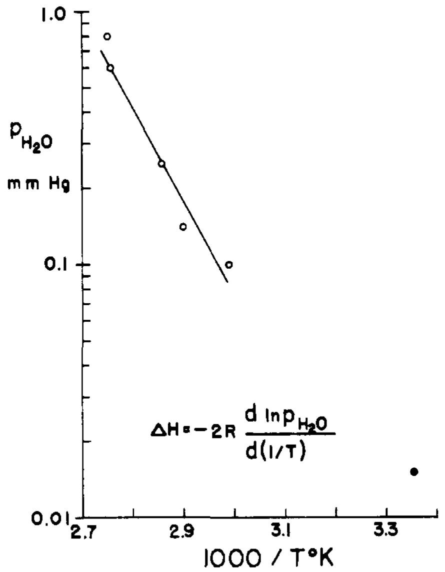

Figure 5. van't Hoff plot for dehydration of $CoCl_2 \cdot 2H_2O \cdot C_4H_8O_2$

dioxane probably stabilizes the chloride against hydrolysis, while nickel chloride dihydrate undergoes hydrolysis when heated, and some dihydrate may have been produced during desolvation of the mixed solvate. Since cobalt chloride diaquomonodioxanate lost little dioxane before all of its water was removed, no cobalt chloride dihydrate was formed and, hence, no hydrolysis occurred.

Since there was a fairly sharp separation between the release of water and of dioxane during the progressive desolvation of $CoCl_2 \cdot 2H_2O \cdot C_4H_8O_2$, it is possible to estimate its heat of dehydration from these experiments by means of the van't Hoff equation. Desolvations were carried out at five levels of reduced pressure. Each pressure was maintained constant within ±3%. The temperature at which the equilibrium vapor pressure of the solvate (which is very nearly equal to its partial vapor pressure of water) reached the pressure in the system was marked by rapid evolution of water vapor. These temperatures are thus known within ±1° C. For the reaction $CoCl_2 \cdot 2H_2O \cdot C_4H_8O_2\ (s) \rightleftarrows CoCl_2 \cdot C_4H_8O_2\ (s) + 2H_2O\ (g)$, $K_p = p^2_{H_2O}$. Figure 5 shows the van't Hoff plot. The heat of this reaction, 34,000 ± 3,000 cal., is somewhat larger than the heats of the reactions $CoCl_2 \cdot n{+}2H_2O\ (s) \rightleftarrows CoCl_2 \cdot nH_2O\ (s) + 2H_2O\ (g)$ at 25° C., which are 29,500 cal. for $n = 0$; 28,700 for $n = 2$; and 26,100 for $n = 4$ (*22*), or 30,130 cal. for $n = 0$; 27,570 for $n = 2$; and 27,050 for $n = 4$ (*11*). This difference may have arisen because some dioxane was released together with the water, or because the effective vapor pressure of the solid was probably somewhat greater than the pressure in the system as measured by the pressure gage, to cause the flow of released vapor. The lowest point in the $\log p_{H_2O}$ *vs.* $1/T$ plot of Figure 5 (solid circle) is the partial vapor pressure of water calculated by interpolation for the liquid of composition *E*, which should be the same as that of the solid diaquomonodioxanate at 25° C.

DISCUSSION

The well-known correlation between color and constitution (*13*) permits ready identification of the species present in solution and of their structure in the solid state. At high water content, the predominant form of cobalt is $[Co(H_2O)_6]^{+2}$. This is shown by the wine red color of the solutions and of the solid compound in equilibrium with them—namely, the hexahydrate. With increasing dioxane concentration, that solvent competes with water for the coordination sites of cobalt. At the same time, the dielectric constant of the medium is lowered, the cobalt-chlorine bond becomes more covalent and chlorine also enters the coordination sphere of cobalt. The magenta-colored solid diaquomonodioxanate is most likely an undissociated octahedral complex, with dioxane being bidentate. The purple to violet solutions with which it is in equilibrium probably contain the same undissociated species. The fact that water was released before dioxane during the desolvation of cobalt chloride diaquomonodioxanate is further evidence for dioxane being a bidentate ligand.

The blue color in solutions of high dioxane content—namely, the light layers in the immiscible region and the saturated solutions beyond point *D*—indicates that tetrahedrally coordinated $[CoCl_2(C_4H_8O_2)]$ is the prevalent species. Color and composition of the solid monodioxanate are strong indication that dioxane acts as a bidentate. So is the thermal stability of cobalt chloride dioxanate, which in fact exceeds that of the dihydrate.

Five solid hydrates were found in the ternary system cobalt chloride–acetone–water, ranging from hexa- to monohydrate, but no mixed solvates (*10*). Acetone was capable of dehydrating $[Co(H_2O)_6]^{+2}$ but was too weak an electron donor to compete with water and chlorine for coordination positions of cobalt. This is in line with the low stability of the blue cobalt chloride acetonate, which decomposes above 19.5° C. even under acetone (*2*). In the system cobalt chloride-*tert*-butanol-water, $CoCl_2 \cdot 4H_2O \cdot 2BuOH$ was found in addition to the hexa-, di-, and monohydrate and an alcoholate (*12*). However, the mixed solvate was in equilibrium with only a narrow range of liquid compositions, showing the alcohol to be a comparatively weak ligand. The absence of lower hydrates in the present system and the wide range of compositions over which the mixed solvate prevailed was probably due to the strong electron donor properties of dioxane together with its bidentate nature.

The color of solutions in the nickel chloride system was emerald green, acquiring a yellowish tinge only at very high dioxane contents. The former color is indicative of paramagnetic nickel, either hexacovalent octahedral or tetracovalent tetrahedral (*17*). At high water contents, the prevalent form was $[Ni(H_2O)_6]^{+2}$. With increasing dioxane content, either some water was replaced by dioxane while maintaining the ionic nature of the complex, or chlorine became a covalent ligand owing to the lower dielectric constant of the medium. The solid diaquomonodioxanate could be the octahedral $[NiCl_2(H_2O)_2(C_4H_8O_2)]$, matching the probable structure of the corresponding cobalt complex. The less likely tetrahedral structure $[Ni(H_2O)_2(C_4H_8O_2)]Cl_2$ has the advantage that it might account for the hydrolysis during desolvation of the nickel solvate. The brownish yellow color of solid nickel chloride monodioxanate and the yellowish tint of solutions of very high dioxane content are indicative of a square planar and diamagnetic complex (*17*).

CONCLUSIONS

The two diagrams were qualitatively and quantitatively similar. The hexahydrates of the two chlorides were the solids in equilibrium with solutions rich in water. Because of their hygroscopicity, the two solid monodioxanates only coexisted with solutions of such high dioxane content that they contained little dissolved salt. The two diaquomonodioxanates were the solid phases prevailing over most of the diagram where solid and liquid phases coexisted, including the region where there were two immiscible liquids. This region expanded with increasing temperature. According to their color, the light, dioxane-rich phase contained tetracovalent complexes of both metals and the heavy layer hexacovalent cobalt and also probably hexacovalent nickel.

The exothermic reaction between the anhydrous chlorides and dioxane, the thermal stability and low vapor pressure of the diaquomonodioxanates and monodioxanates, and the release of water before that of dioxane during the progressive desolvation of the diaquomonodioxanates all indicate that dioxane is a rather strong ligand. The bidentate nature of dioxane is demonstrated by the foregoing as well as by the relation between the composition of its complexes, their color, and the coordination chemistry of bivalent cobalt and nickel.

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Fluoroalkyl Phosphonitrilates, a New Class of Potential Fire-Resistant Hydraulic Fluids and Lubricants

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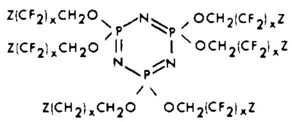
The synthesis of various trimeric and tetrameric aryl-1,1-di-*H*-polyfluoroalkyl phosphonitrilates (III), a new class of compounds, is reported. The effects of structural modifications on properties such as density, viscosity, ASTM slope, pour point, and spontaneous ignition temperature are discussed.

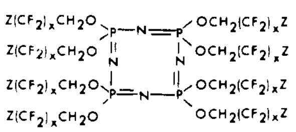
TRIMERIC and tetrameric polyfluoroalkyl phosphonitrilates (Ia,Ib) as well as aryl-1,1,ω-tri-*H*-polyfluoroalkyl phosphonitrilates (IIa, IIb) (*5, 6, 8, 9, 10*) have recently been evaluated for potential use as fire-resistant naval hydraulic fluids (*5, 6*).

Representatives of I and II meet many requirements specified for certain lubricants and hydraulic fluids (*3, 4, 7*),



Ia

Z=H or F



Ib

Z=H or F