Crystalline and Liquid Phases in the Systems MeX_2/Aniline/Water (Me = Ni, Co; X = NO_3, ClO_4)

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Nickel nitrate, nickel perchlorate and cobalt nitrate can form homogeneous liquid phases with aniline and water. The shapes of the single phase regions in the ternary phase diagrams were determined. Five types of crystals were obtained in the system nickel nitrate/aniline/water. The structures of $Ni(NO_3)_2 \cdot 6C_6H_7N \cdot 2H_2O$, $Ni(NO_3)_2 \cdot 4C_6H_7N \cdot 2H_2O$, and $Ni(NO_3)_2 \cdot 2C_6H_7N \cdot 4H_2O$ have been determined by single crystal X-ray diffraction. All structures show chains of nickel ions and nitrate ions connected by water or aniline molecules. They can be interpreted as one dimensional ion pairs.

1. Introduction

Heteroselective solvation of a salt in a binary mixture of solvents can lead to interesting properties of the ternary systems. Two phenomena are especially remarkable: Liquids with unusual high salt concentrations can be prepared and the upper consolution temperature of normally immiscible solvents can be drastically decreased. Strehlow and coworkers [1, 2] determined some properties of a heteroselectively solvated salt quantitatively for silver nitrate in acetonitrile/water mixtures. Later, Das et al. [3] demonstrated some effects of heteroselective solvation of silver nitrate in mixtures of water with other organic nitriles. In order to increase our knowledge about the properties of highly concentrated salt solutions we tried to find new examples for heteroselectively solvated salts. In this paper we report on experiments with nickel nitrate in mixtures of aniline with water. Additionally some results with cobalt nitrate and with nickel perchlorate are also mentioned. In contrast to the system silver nitrate in organic nitrile/water mixtures, nickel nitrate forms ternary crystals with aniline and water. It seems promising to determine the crystal structure of these ternary solids, because they may reflect the structure of the concentrated solutions. In this paper we will report on the structures of the three compounds $Ni(NO_3)_2 \cdot 6C_6H_7N \cdot 2H_2O$, $Ni(NO_3)_2 \cdot 4C_6H_7N \cdot 2H_2O$ and $Ni(NO_3)_2 \cdot 2C_6H_7N \cdot 4H_2O$. All these compounds crystallize in the monoclinic system.

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2. Experimental

2.1. Materials

Nickel nitrate and cobalt nitrate were used as hexahydrates. They were of p.a. grade from Merck, Darmstadt. Nickel perchlorate hexahydrate puriss. was from Aldrich-Chemie. Aniline puriss. from Merck, Darmstadt was distilled prior to its use. Water was triply distilled in a fused silica apparatus.

In order to extent the range of aniline concentrations to higher values, we had to prepare nickel salt with less than 6 water molecules. Several efforts to dehydrate the hexahydrate failed. Eventually we prepared the compound $Ni(NO_3)_2 \cdot 2C_6H_7N \cdot 4H_2O$. This complex can be dehydrated completely by heating to 160 °C [4]. $Ni(NO_3)_2 \cdot 2C_6H_7N$ is stable and can be used to prepare aniline rich nickel nitrate/aniline/water mixtures.

2.2. Determination of the Ternary Phase Diagrams

The equilibrium curves in the phase diagrams were determined as follows: We used weighing bottles with ground caps. About 1 g of freshly distilled aniline is weighed in the bottle and the desired quantity of water is added. The mixture is stirred and the salt is added in small amounts until the phase boundary disappears. The mass of dissolved salt is now determined by weighing. Then small amounts of water or of aniline are added in order to return into the two phase region. Now more salt is added, until the mixture becomes homogeneous again. Discarding of the mixtures after four cycles helped to avoid the increase of error limits by addition of uncertainties. In order to determine the

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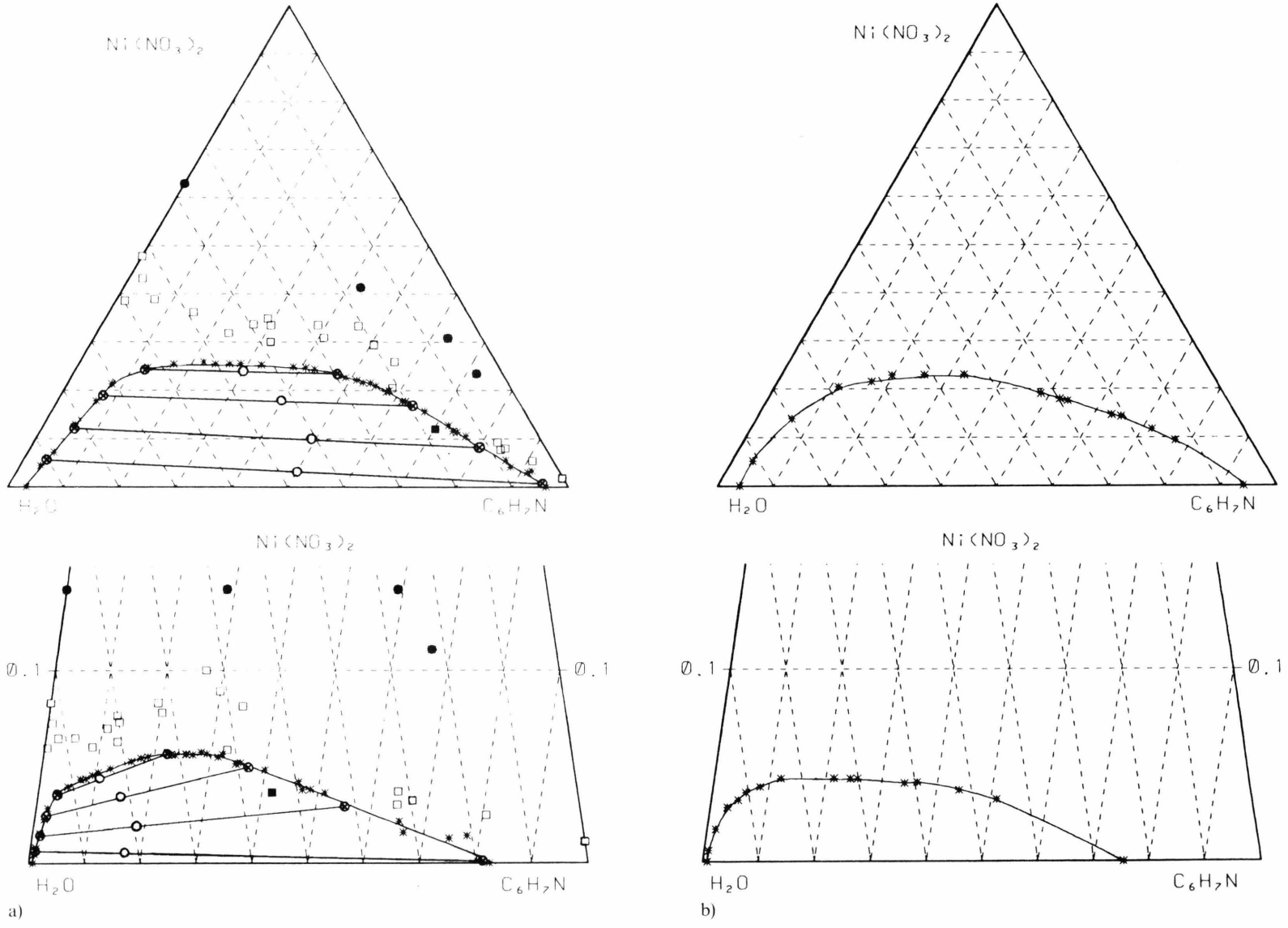


Fig. 1. Phase triangles of $Ni(NO_3)_2/H_2O$/aniline at 20 °C (a) and at 40 °C (b). Upper triangles: Weight fraction representation; lower (cut) triangles: Mole fraction representation. ∗: Composition of liquids defining the miscibility gap. ○: Overall composition of two coexisting liquids. ⊗: Individual composition of such liquids. The straight lines are the respective conodes. □: Composition of liquids in equilibrium with a solid. ■: Overall composition of two liquids in equilibrium with a solid. ●: Composition of solids studied by X-ray diffraction.

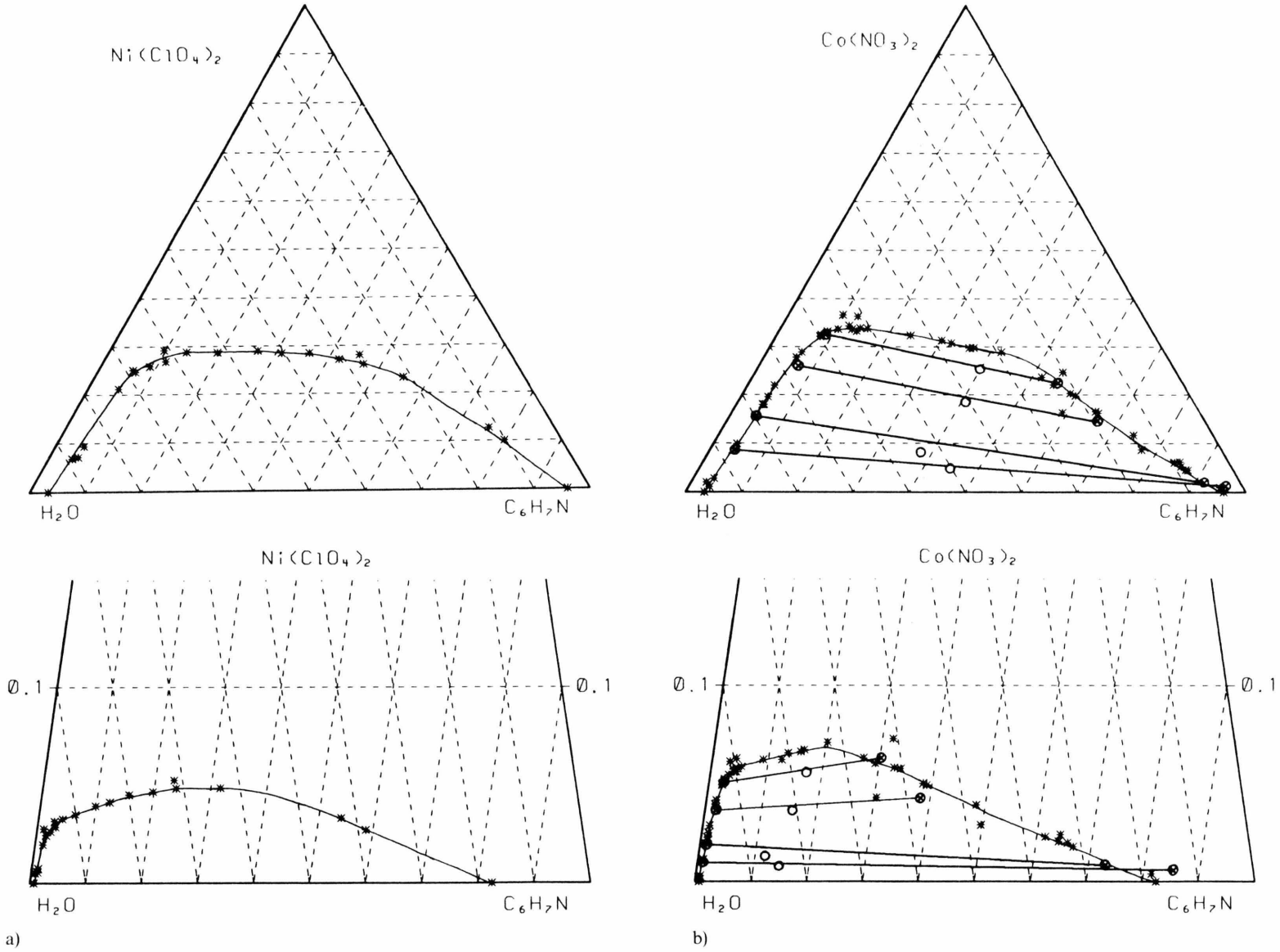
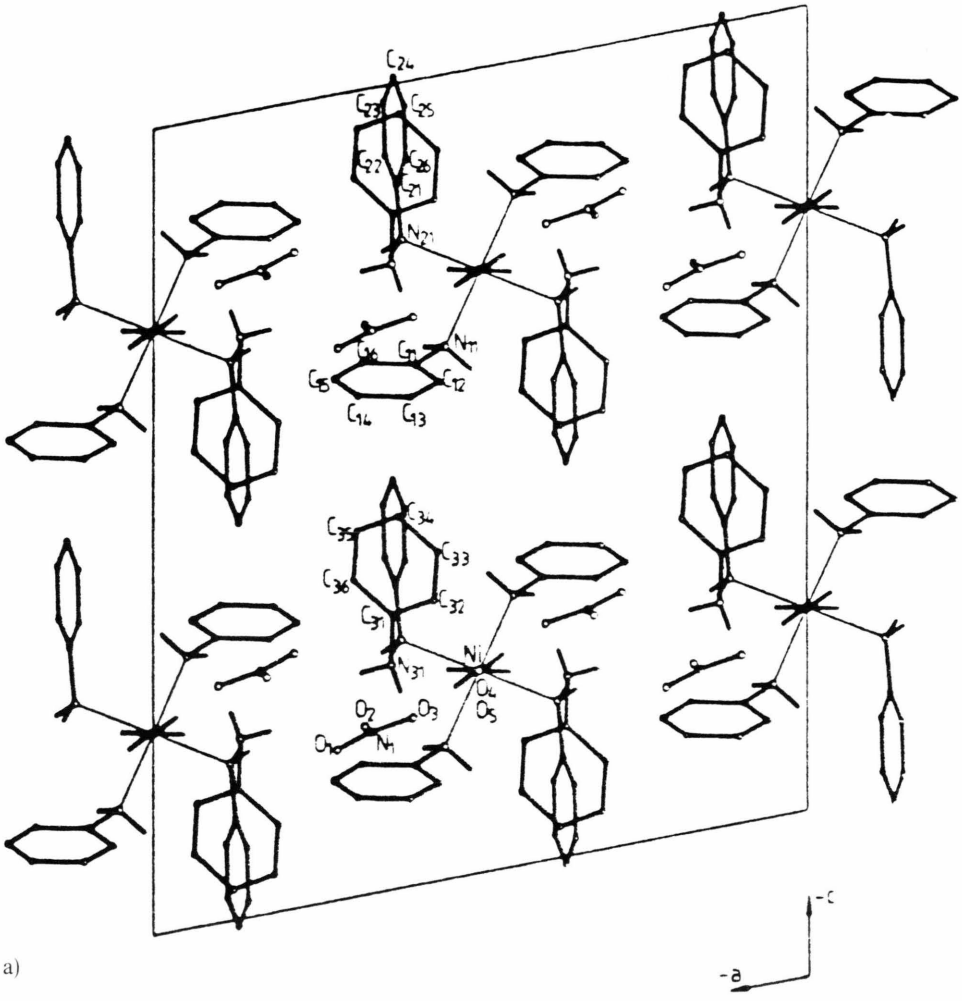


Fig. 2. Representation in the phase triangle of the systems a: nickel perchlorate/aniline/water; b: cobalt nitrate/aniline/water. Symbols: see legend to Figure 1.



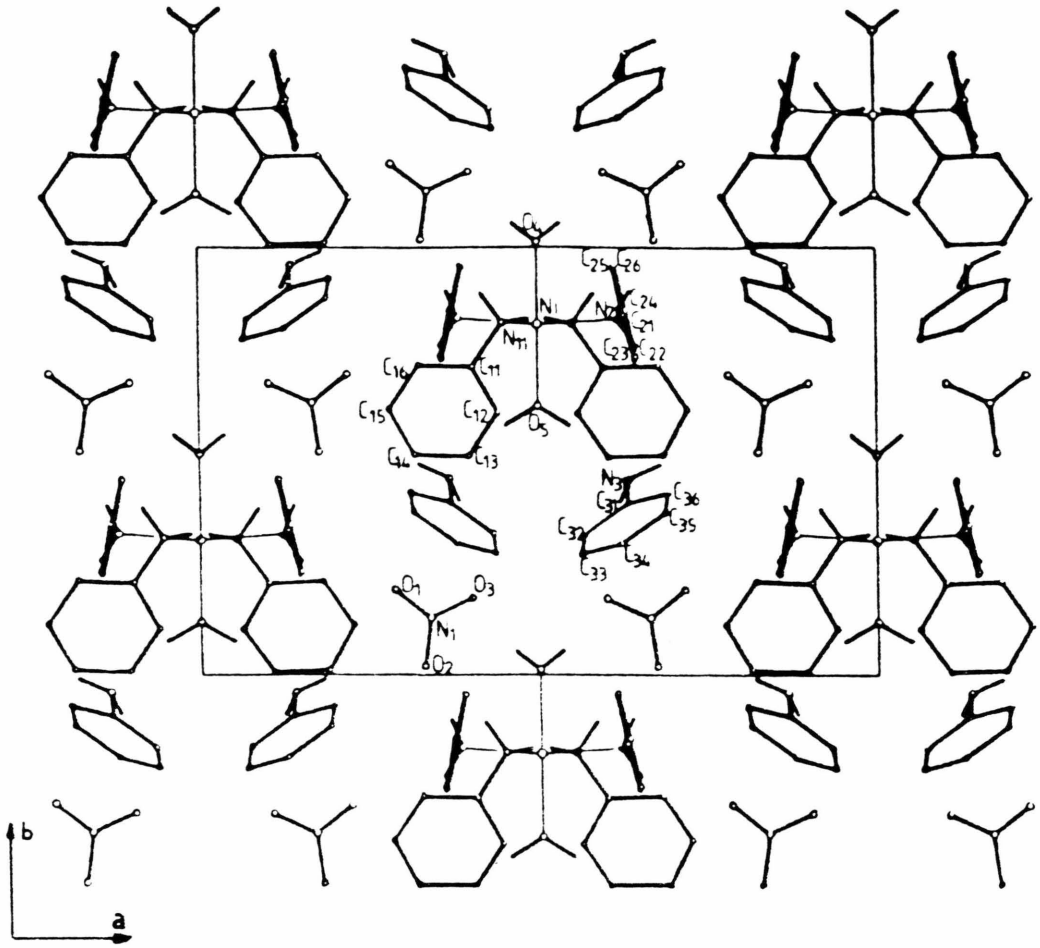
a)

Fig. 3. Structure of the compound $Ni(NO_3)_2 \cdot 6C_6H_7N \cdot 2H_2O$. a) Projection along the *b*-axis. b) Projection along the *c*-axis. Only a half unit cell is plotted.

coexistence curve liquid/solid phases, we prepared supersaturated liquids. These mixtures are very concentrated solutions and after some hours crystals will precipitate. Within one night, the solid/liquid equilibrium is attained. The remaining mother liquid is analyzed: The metal ions are titrated with EDTA. In the case of nickel, Murexide metal indicator was employed, in the case of cobalt we used Xylenol orange. Aniline is titrated with nitrite solutions. The equivalence point is determined by the dead-stop method described by Ferrero [5]. The amount of water is calculated as the difference to 100%. The conodes were determined in the following way: We prepared ternary mixtures, the compositions of which were located in the two phase region. After stirring for 15 minutes, the phases were allowed to separate. Both phases were analyzed as described above.

2.3. Preparation of Crystals

In the system nickel nitrate/aniline/water we obtained crystals by the following method: First we prepared a supersaturated ternary solution. After several hours at constant temperature, crystals precipitated. A few of them were transferred into another concentrated solution were they were allowed to grow, until



b)

their sizes were suitable for X-ray structure determination. By this technique, five one phase solids could be obtained in form of single crystals. They all are of a dark green colour.

2.4. Structure Determination

The crystal structures of $Ni(NO_3)_2 \cdot 6C_6H_7N \cdot 2H_2O$, $Ni(NO_3)_2 \cdot 4C_6H_7N \cdot 2H_2O$, and $Ni(NO_3)_2 \cdot 2C_6H_7N \cdot 4H_2O$ were investigated with the help of an automatic diffractometer from Stoe. About 4000 signals per crystal were recorded. The structures were determined by use of the program Shelx [6]. Only three of the five different crystals were of sufficient stability, two of them decomposed during the time of sampling of the signals.

3. Results

3.1. Ternary Phase Diagrams

Figure 1 shows the equilibrium points in the Gibbs phase triangle for the system nickel nitrate/aniline/water at 20 °C and at 40 °C. The curves, which are constructed from the experimental points, given as

Table 1. Experimental conditions for the structure determination and crystal data of the studied compounds. 1: $Ni(NO_3)_2 \cdot 6C_6H_7N \cdot 2H_2O$; 2: $Ni(NO_3)_2 \cdot 4C_6H_7N \cdot 2H_2O$; 3: $Ni(NO_3)_2 \cdot 2C_6H_7N \cdot 4H_2O$.

Diffractometer:	STOE-Stadi-4		
Wavelength/pm:	71.073 ($Mo K_\alpha$)		
Scan:	$\omega/2\Theta = 1/1$		
Crystal:	1	2	3
Habitus:	short pyramids	rhomboid plate	prisms
Size/mm^{-3}	(0.22 × 0.32 × 0.5)	(0.45 × 0.5 × 0.67)	(0.26 × 0.28 × 0.62)
Temperature/K:	297	299	299
Linear absorption coefficient, μ/m^{-1}	582	734	1066
$(\sin\vartheta/\lambda)_{max}/pm^{-1}$:	0.0054	0.0054	0.0059
Measured reflections:	4286	4995	3349
Symmetry independent reflections:	2489	3724	1677
R_{int}	0.012	0.015	0.012
Reflections considered:	2358	3487	1597
$R(F)$:	0.031	0.036	0.030
$R_w(F)$:	0.029	0.034	0.028
Lattice constants: a/pm:	1730.2 (5)	1301.1 (5)	2205.6 (6)
b/pm:	1075.4 (3)	1002.8 (4)	671.7 (2)
c/pm:	2078.2 (5)	2472.8 (9)	1338.8 (4)
$\beta/^\circ$:	100.46(1)	118.26(1)	105.34(1)
Space group:	C 2/c	$P 2_1/C$	C 2/c
Formula units per cell:	4	4	4
$\varrho_{calc}/Mg\,m^{-3}$:	1.36	1.38	1.53
Melting point/°C	57	54	70

Table 2. Positional and thermal parameters (with standard deviations) for $Ni(NO_3)_2 \cdot 2C_6H_7N \cdot 4H_2O$. The temperature factor has the form $T = \exp\{-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\}$. The U_{ij} are in $(pm)^2$. U is the isotropic mean-squares thermal amplitude.

Atom	x/a	y/b	z/c	U_{11} or U	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni	0	0	0	359 (2)	244 (2)	225 (2)	5 (1)	90 (2)	−25 (2)
Nitrate:									
N_1	0.4232 (1)	−0.0057 (3)	0.1793 (1)	412 (11)	362(12)	381(12)	−21 (9)	186 (9)	−30 (9)
O_1	0.4291 (1)	0.1532 (2)	0.2276 (1)	826 (13)	414(10)	538(11)	−193 (9)	297(10)	−127(10)
O_2	0.4261 (1)	−0.1689 (2)	0.2255 (1)	839 (13)	384(10)	560(11)	105 (9)	283(10)	−7(10)
O_3	0.4140 (1)	−0.0044 (2)	0.0845 (1)	1138 (16)	497(12)	368(10)	−33 (8)	312(10)	−136(11)
Water:									
O_4	−0.0302 (1)	−0.0146 (3)	0.1331 (1)	624 (11)	350(10)	312 (9)	25 (8)	229 (8)	11 (9)
H_{11}	−0.0427(12)	0.0860(38)	0.1558(19)	679 (97)					
H_{12}	−0.0433(11)	−0.1145(35)	0.1556(17)	523 (82)					
O_5	0.0421 (1)	0.2694 (2)	0.0527 (1)	535 (11)	315 (9)	358(10)	−17 (8)	117 (8)	−102 (8)
H_{21}	0.0535(11)	0.2985(37)	0.1151(19)	668 (94)					
H_{22}	0.0604(12)	0.3225(41)	0.0178(20)	725(104)					
Aniline:									
C_1	0.6417 (1)	0.4199 (3)	0.0956 (2)	371 (12)	275(12)	346(12)	32 (9)	71(10)	35(10)
C_2	0.6629 (1)	0.5157 (3)	0.1896 (2)	465 (14)	411(15)	393(13)	−43(11)	68(11)	61(12)
H_2	0.6345 (1)	0.5191 (3)	0.2443 (2)	515 (69)					
C_3	0.7207 (1)	0.6131 (4)	0.2131 (2)	522 (16)	456(16)	619(17)	−113(13)	−25(14)	−16(14)
H_3	0.7374 (1)	0.6891 (4)	0.2863 (2)	810 (86)					
C_4	0.7567 (1)	0.6116 (4)	0.1439 (2)	424 (15)	506(18)	925(23)	−12(16)	88(15)	−77(14)
H_4	0.8015 (1)	0.6874 (4)	0.1625 (2)	812 (87)					
C_5	0.7359 (1)	0.5137 (4)	0.0508 (2)	495 (16)	547(17)	808(21)	79(15)	302(15)	9(14)
H_5	0.7646 (1)	0.5121 (4)	−0.0032 (2)	724 (85)					
C_6	0.6782 (1)	0.4168 (3)	0.0259 (2)	487 (14)	438(15)	440(14)	−4(12)	177(12)	22(12)
H_6	0.6619 (1)	0.3398 (3)	−0.0472 (2)	603 (72)					
N	0.5806 (1)	0.3275 (3)	0.0694 (1)	406 (11)	289(10)	282(10)	2 (9)	97 (8)	−7 (9)
H_7	0.5807(19)	0.2320(34)	0.0239(16)	465 (70)					
H_8	0.5716 (9)	0.2651(31)	0.1266(16)	431 (64)					

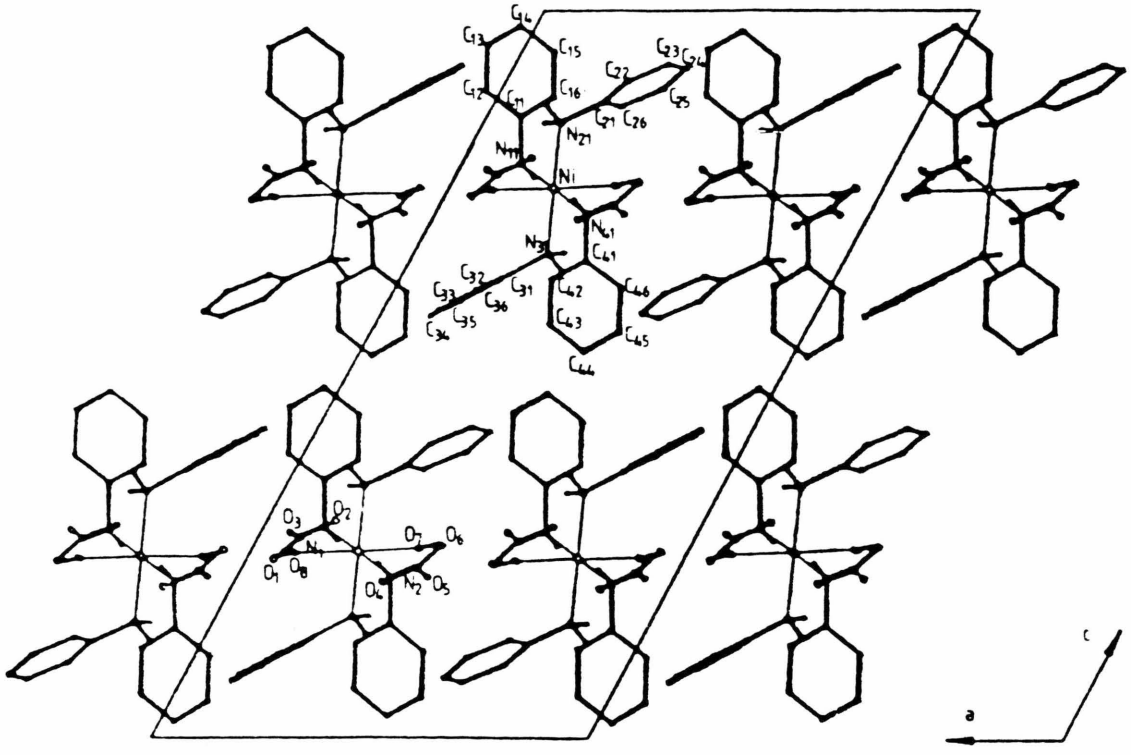


Fig. 4. Structure of the compound $Ni(NO_3)_2 \cdot 4C_6H_7N \cdot 2H_2O$. Projection along the *b*-axis.

stars in Fig. 1, represent the liquid/liquid equilibrium. Consistency of the results is demonstrated by the fact, that the points, which represent the overall concentrations of the mixtures coincide with the conodes (open circles in Figure 1). Open squares show the compositions of liquids, which are in equilibrium with a solid phase. The full square gives the overall composition of liquids in equilibrium with a solid. When a conode is drawn in the correct direction through this point, the equilibrium composition of the liquids can be obtained. Full circles represent the composition of those solids which could be characterized by X-ray diffraction.

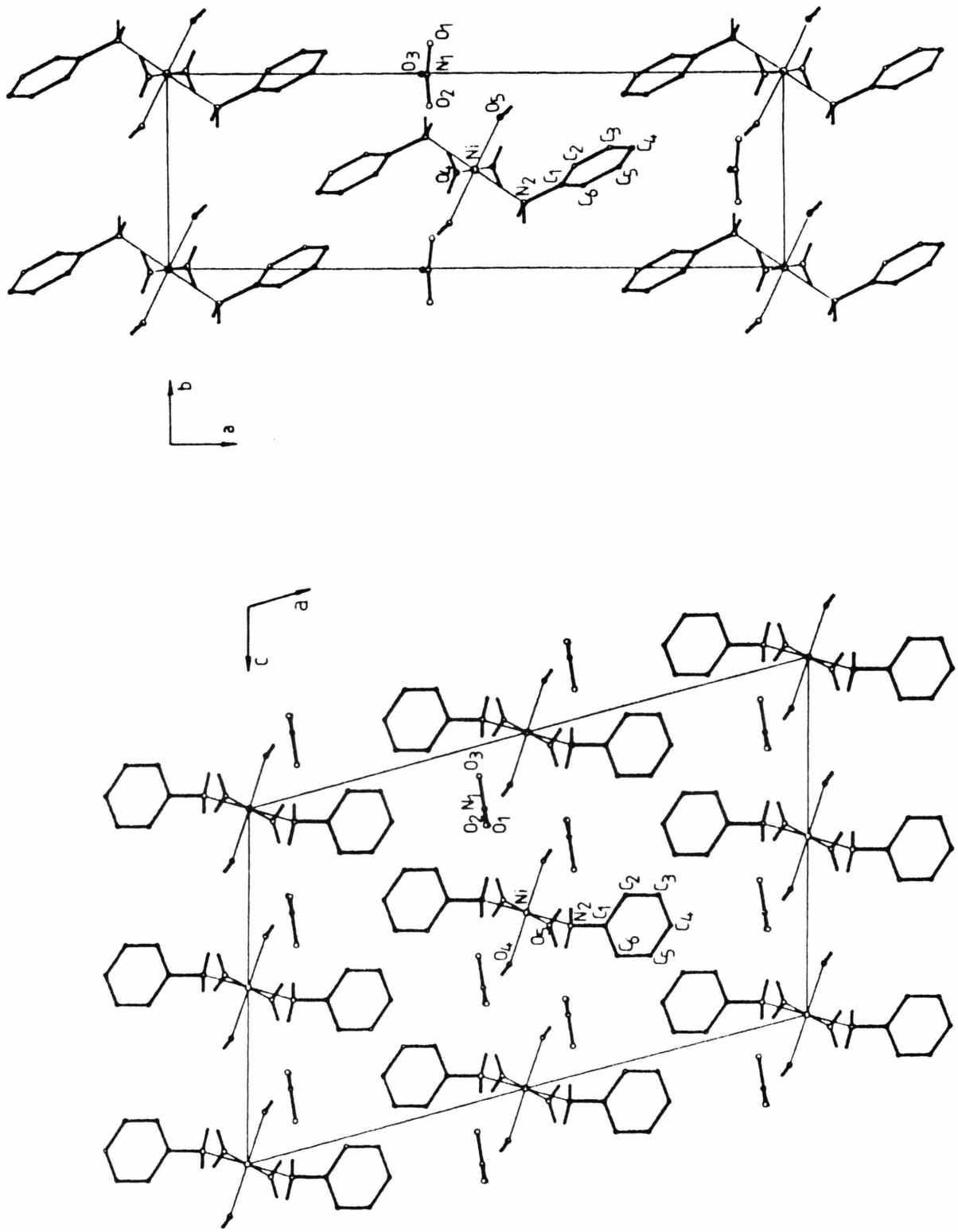
In Fig. 2 we present the results for the systems nickel perchlorate/aniline/water and cobalt nitrate/aniline/water. These data were obtained at a temperature of 20 °C. Only the liquid/liquid coexistence curves were measured in these cases.

3.2. Structures

In Table 1 the experimental conditions of the structure determinations are collected, together with the results concerning the space groups and the unit cell constants. Tables 2, 3, and 4 contain the positional and the thermal parameters for the three studied compounds. Characteristic distances are collected in the Tables 5, 6, and 7.

Figure 3 shows the structure of the compound $Ni(NO_3)_2 \cdot 6C_6H_7N \cdot 2H_2O$. The projections along the *b*-axis and along the *c*-axis are plotted. The nickel ion shows octahedral coordination: four aniline molecules form a plane and two water molecules are located above and below it. Two aniline molecules do not belong to the first coordination sphere of Ni^{2+}. The distances between the nickel ions and the water molecules are 207 pm and between the nickel ions and the aniline molecules 216 pm. The nitrate ions are reflected at the position of the nickel ions. The shortest distance from the oxygen of the nitrate ions to the oxygen of the water molecules is 276 pm, the distance to the nitrogen atoms of aniline molecules is 292 pm.

The crystals of $Ni(NO_3)_2 \cdot 4C_6H_7N \cdot 2H_2O$ are also monoclinic. The projection of the structure along the *b*-axis is drawn in Figure 4. The symmetry of the cation is nearly octahedral. Four aniline molecules form



b)

a)

Fig. 5. Structure of the compound $Ni(NO_3)_2 \cdot 2C_6H_7N \cdot 4H_2O$. a) Projection along the *b*-axis. b) Projection along the *c*-axis. Only a half unit cell is shown.

Table 3. Same as Table 2 for $Ni(NO_3)_2 \cdot 6C_6H_7N \cdot 2H_2O$.

Atom	x/a	y/b	z/c	U_{11} or U	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni	0	0.3171 (0)	0.25	308 (3)	303 (3)	377 (3)	0	130 (2)	0
Nitrate:									
N_1	0.3359 (1)	0.1349 (1)	0.3003 (2)	419 (16)	457(14)	470(13)	−1(11)	123(12)	38(13)
O_1	0.2836 (1)	0.2003 (2)	0.3146 (1)	559 (15)	694(14)	866(15)	−129(12)	247(12)	235(12)
O_2	0.3260 (1)	0.0204 (2)	0.2919 (1)	645 (15)	379(12)	943(16)	29(11)	298(12)	16(10)
O_3	0.3991 (1)	0.1800 (2)	0.2928 (1)	530 (16)	638(14)	1598(23)	−186(15)	525(16)	−148(12)
Water:									
O_4	0	0.5134 (2)	0.25	419 (19)	327(15)	707(19)	0	274(15)	0
H_1	−0.0364(16)	0.5593(25)	0.2639(15)	936(115)					
O_5	0	0.1263 (2)	0.25	461 (20)	334(14)	580(17)	0	224(15)	0
H_2	0.0480(15)	0.0813(26)	0.2585(15)	1020(120)					
Aniline 1:									
C_{11}	−0.0980 (1)	0.2160 (2)	0.3521 (1)	334 (17)	386(15)	341(13)	−29(11)	160(12)	−36(13)
C_{12}	−0.0603 (2)	0.1095 (2)	0.3798 (1)	354 (18)	563(18)	485(16)	94(14)	161(13)	59(14)
H_{12}	0.0030 (2)	0.1058 (2)	0.3914 (1)	540 (75)					
C_{13}	−0.1046 (2)	0.0083 (2)	0.3924 (1)	607 (22)	459(17)	562(17)	152(14)	253(16)	71(16)
H_{13}	−0.0755 (2)	−0.0748 (2)	0.4136 (1)	758 (87)					
C_{14}	−0.1855 (2)	0.0125 (2)	0.3782 (1)	548 (21)	477(17)	551(17)	26(14)	205(16)	−132(16)
H_{14}	−0.2197 (2)	−0.0672 (2)	0.3879 (1)	666 (88)					
C_{15}	−0.2226 (2)	0.1189 (2)	0.3517 (1)	361 (19)	602(19)	529(16)	30(14)	114(14)	−90(15)
H_{15}	−0.2860 (2)	0.1233 (2)	0.3415 (1)	663 (85)					
C_{16}	−0.1789 (1)	0.2207 (2)	0.3379 (1)	331 (17)	444(16)	434(15)	40(12)	119(13)	−10(13)
H_{16}	−0.2082 (1)	0.3031 (2)	0.3160 (1)	660 (81)					
N_{11}	−0.0527 (1)	0.3210 (2)	0.3363 (1)	332 (15)	402(13)	434(13)	−29(11)	147(11)	−28(12)
H_{17}	0.0134(13)	0.3308(21)	0.1299(11)	442 (76)					
H_{18}	0.0839(14)	0.3908(22)	0.1671(11)	510 (82)					
Aniline 2:									
C_{21}	0.1273 (1)	0.3409 (2)	0.3756 (1)	247 (16)	469(16)	455(15)	15(13)	59(12)	−52(13)
C_{22}	0.1443 (2)	0.2356 (3)	0.4135 (1)	481 (20)	534(18)	616(19)	125(15)	40(16)	38(15)
H_{21}	0.1559 (2)	0.1485 (3)	0.3912 (1)	858 (98)					
C_{23}	0.1463 (2)	0.2426 (4)	0.4801 (2)	703 (27)	951(28)	636(23)	305(21)	−3(19)	−37(22)
H_{23}	0.1598 (2)	0.1604 (4)	0.5099 (2)	1126(120)					
C_{24}	0.1315 (2)	0.3526 (4)	0.5089 (2)	774 (28)	1300(35)	452(20)	−27(22)	68(18)	−255(26)
H_{24}	0.1328 (2)	0.3568 (4)	0.5610 (2)	1392(137)					
C_{25}	0.1149 (2)	0.4578 (3)	0.4709 (2)	734 (26)	830(15)	620(21)	−246(19)	160(18)	−207(20)
H_{25}	0.1033 (2)	0.5446 (3)	0.4935 (2)	917(103)					
C_{26}	0.1130 (2)	0.4532 (2)	0.4041 (1)	477 (19)	467(17)	556(17)	−52(15)	100(14)	−90(14)
H_{26}	0.1007 (2)	0.5359 (2)	0.3745 (1)	661 (82)					
N_{21}	0.1191 (1)	0.3311 (2)	0.3058 (1)	368 (15)	407(14)	481(14)	8(12)	139(11)	42(12)
H_{27}	0.1475(14)	0.2676(23)	0.2953(12)	554 (89)					
H_{28}	0.1360(14)	0.3975(23)	0.2875(12)	567 (91)					
Aniline 3:									
C_{31}	0.3675 (2)	0.4035 (2)	0.1607 (1)	449 (19)	358(15)	499(16)	−18(13)	152(15)	−106(14)
C_{32}	0.4313 (2)	0.3307 (2)	0.1523 (1)	480 (20)	473(17)	599(18)	−29(14)	97(15)	−21(15)
H_{32}	0.4773 (2)	0.3108 (2)	0.1935 (1)	670 (83)					
C_{33}	0.3459 (2)	0.2836 (3)	0.0910 (2)	651 (24)	511(19)	809(24)	−87(17)	352(20)	−28(17)
H_{33}	0.4855 (2)	0.2273 (3)	0.0844 (2)	763 (93)					
C_{34}	0.3763 (2)	0.3092 (3)	0.0379 (2)	977 (30)	623(21)	531(20)	−53(17)	255(20)	−161(21)
H_{34}	0.3798 (2)	0.2732 (3)	−0.0100 (2)	1014(108)					
C_{35}	0.3134 (2)	0.3805 (3)	0.0469 (1)	774 (26)	644(22)	557(20)	93(16)	42(19)	−100(19)
H_{35}	0.2672 (2)	0.4001 (3)	0.0057 (1)	1153(120)					
C_{36}	0.3082 (2)	0.4272 (2)	0.1074 (1)	460 (19)	464(17)	604(19)	72(14)	100(15)	−46(15)
H_{36}	0.2579 (2)	0.4824 (2)	0.1137 (1)	734 (90)					
H_{31}	0.3659 (2)	0.4582 (2)	0.2224 (1)	525 (19)	525(16)	563(16)	−74(13)	159(14)	−18(14)
H_{37}	0.1795(16)	−0.0089(25)	0.2755(13)	685(108)					
H_{38}	0.1202(16)	−0.0926(27)	0.2432(14)	882(117)					

Table 4. Same as Table 2 for $Ni(NO_3)_2 \cdot 4C_6H_7N \cdot 2H_2O$.

Atom	x/a	y/b	z/c	U_{11} or U	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ni	0.7567 (0)	0.0591 (0)	0.7547 (0)	310 (2)	246 (2)	365 (2)	12 (2)	186 (2)	−8 (2)
Nitrate 1:									
N_1	0.9032 (2)	0.6325 (3)	0.7738 (1)	348(15)	341(17)	613(17)	8(14)	215(13)	10(13)
O_1	0.9352 (2)	0.7065 (2)	0.7432 (1)	719(16)	431(15)	894(17)	150(13)	572(14)	61(13)
O_2	0.8440 (2)	0.6806 (2)	0.7962 (1)	577(14)	525(15)	794(15)	29(13)	473(13)	144(13)
O_3	0.9309 (2)	0.5139 (2)	0.7800 (1)	615(15)	282(14)	1095(19)	81(13)	505(15)	87(12)
Nitrate 2:									
N_2	0.5991 (2)	0.0165 (3)	0.2310 (1)	363(15)	337(16)	596(17)	−1(14)	25(13)	−8(13)
O_4	0.6634 (2)	0.0656 (2)	0.2122 (1)	527(14)	621(17)	771(15)	5(13)	425(13)	−178(13)
O_5	0.5650 (2)	−0.0992 (2)	0.2196 (1)	744(17)	351(15)	1255(22)	−197(15)	623(17)	−188(14)
O_6	0.5683 (2)	0.0865 (2)	0.2628 (1)	786(17)	509(16)	991(18)	−185(15)	651(16)	−82(14)
Water 1:									
O_7	0.6203 (2)	0.1512 (2)	0.7586 (1)	521(14)	292(13)	923(17)	89(14)	529(13)	34(12)
H_{71}	0.5697(23)	0.1157(29)	0.7656(12)	500					
H_{72}	0.6113(26)	0.2266(29)	0.7566(14)	500					
Water 2:									
O_8	0.8952 (2)	−0.0326 (2)	0.7530 (1)	477(13)	292(13)	833(16)	81(13)	461(12)	45(12)
H_{81}	0.9425(24)	−0.0043(31)	0.7455(13)	500					
H_{82}	0.9037(25)	−0.1138(29)	0.7557(13)	500					
Aniline 1:									
C_{11}	0.9222 (2)	0.2636 (3)	0.8527 (1)	431(17)	262(17)	408(16)	−14(14)	208(15)	−86(15)
C_{12}	1.0325 (3)	0.2112 (3)	0.8885 (1)	481(20)	494(22)	551(20)	−31(18)	199(17)	23(18)
H_{12}	1.0756 (3)	0.1555 (3)	0.8676 (1)	500					
C_{13}	1.0868 (3)	0.2312 (4)	0.9516 (2)	550(22)	781(30)	560(22)	74(22)	48(19)	30(22)
H_{13}	1.1721 (3)	0.1889 (4)	0.9799 (2)	500					
C_{14}	1.0341 (3)	0.3035 (4)	0.9784 (2)	831(28)	758(30)	445(20)	−81(21)	219(21)	−192(25)
H_{14}	1.0776 (3)	0.3191 (4)	1.0275 (2)	500					
C_{15}	0.9254 (3)	0.3564 (4)	0.9423 (2)	850(28)	625(27)	612(23)	−164(20)	439(22)	−118(23)
H_{15}	0.8830 (3)	0.4135 (4)	0.9632 (2)	500					
C_{16}	0.8694 (3)	0.3374 (3)	0.8794 (1)	535(20)	432(21)	500(19)	−58(16)	262(17)	−49(17)
H_{16}	0.7843 (3)	0.3804 (3)	0.8513 (1)	500					
N_{11}	0.8623 (2)	0.2360 (3)	0.7882 (1)	381(15)	294(15)	428(15)	0(12)	212(12)	−24(12)
H_{17}	0.8159(23)	0.3020(29)	0.7690(12)	500					
H_{18}	0.9126(23)	0.2322(29)	0.7742(12)	500					
Aniline 2:									
C_{21}	0.7496 (2)	−0.0633 (3)	0.8724 (1)	403(17)	420(20)	309(15)	59(15)	166(14)	−13(16)
C_{22}	0.7208 (3)	0.0351 (4)	0.9015 (1)	975(29)	457(23)	699(23)	23(19)	552(23)	−3(21)
H_{22}	0.7573 (3)	0.1338 (4)	0.9061 (1)	500					
C_{23}	0.6455 (4)	0.0083 (4)	0.9249 (2)	1106(35)	903(35)	797(28)	138(26)	713(28)	313(30)
H_{23}	0.6232 (4)	0.0860 (4)	0.9478 (2)	500					
C_{24}	0.5996 (3)	−0.1153 (5)	0.9193 (2)	553(24)	1266(43)	611(24)	272(28)	343(21)	11(27)
H_{24}	0.5399 (3)	−0.1357 (5)	0.9372 (2)	500					
C_{25}	0.6284 (3)	−0.2136 (4)	0.8912 (2)	739(26)	777(31)	674(24)	40(23)	342(22)	−339(24)
H_{25}	0.5920 (3)	−0.3121 (4)	0.8874 (2)	500					
C_{26}	0.7039 (3)	−0.1894 (3)	0.8672 (1)	639(22)	484(23)	509(19)	−24(17)	300(18)	−152(19)
H_{26}	0.7265 (3)	−0.2681 (3)	0.8449 (1)	500					
N_{21}	0.8231 (2)	−0.0328 (3)	0.8450 (1)	402(16)	366(17)	443(15)	27(13)	198(13)	−40(13)
H_{27}	0.8588(24)	−0.1052(27)	0.8443(13)	500					
H_{28}	0.8761(24)	0.0163(28)	0.8683(13)	500					

Table 4. (continued)

Atom	x/a	y/b	z/c	U_{11} or U	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Aniline 3:									
C_{31}	0.7547 (2)	0.1912 (3)	0.6344 (1)	378(17)	470(21)	308(15)	13(15)	151(14)	−26(16)
C_{32}	0.7669 (3)	0.3244 (3)	0.6261 (1)	887(27)	485(24)	615(22)	−87(19)	496(21)	−197(21)
H_{32}	0.7272 (3)	0.3986 (3)	0.6420 (1)	500					
C_{33}	0.8313 (4)	0.3621 (4)	0.5970 (2)	1343(40)	718(31)	878(29)	−154(25)	740(30)	−570(29)
H_{33}	0.8413 (4)	0.4666 (4)	0.5900 (2)	500					
C_{34}	0.8821 (3)	0.2685 (5)	0.5773 (2)	813(29)	1273(44)	632(25)	−138(29)	502(23)	−393(32)
H_{34}	0.9317 (3)	0.2990 (5)	0.5546 (2)	500					
C_{35}	0.8702 (3)	0.1381 (5)	0.5861 (1)	653(25)	1145(39)	508(21)	−20(25)	357(20)	147(27)
H_{35}	0.9112 (3)	0.0643 (5)	0.5708 (1)	500					
C_{36}	0.8064 (3)	0.0978 (4)	0.6144 (1)	627(22)	571(24)	439(18)	64(18)	259(17)	126(20)
H_{36}	0.7969 (3)	−0.0071 (4)	0.6209 (1)	500					
N_{31}	0.6881 (2)	0.1487 (3)	0.6642 (1)	399(16)	389(18)	449(15)	41(14)	210(13)	−40(13)
H_{37}	0.6513(25)	0.2084(29)	0.6656(13)	500					
H_{38}	0.6379(24)	0.0868(27)	0.6411(12)	500					
Aniline 4:									
C_{41}	0.5921 (2)	−0.1429 (3)	0.6542 (1)	423(18)	314(18)	387(17)	3(14)	168(15)	−111(15)
C_{42}	0.6488 (3)	−0.2114 (3)	0.6281 (1)	595(21)	634(25)	459(18)	−103(18)	208(17)	32(20)
H_{42}	0.7350 (3)	−0.2514 (3)	0.6567 (1)	500					
C_{43}	0.5953 (4)	−0.2289 (4)	0.5653 (2)	934(32)	1014(37)	582(24)	−294(25)	378(24)	−77(29)
H_{43}	0.6400 (4)	−0.2829 (4)	0.5448 (2)	500					
C_{44}	0.4865 (4)	−0.1788 (4)	0.5288 (2)	1022(36)	1000(38)	412(22)	−111(24)	160(24)	−252(31)
H_{44}	0.4457 (4)	−0.1917 (4)	0.4797 (2)	500					
C_{45}	0.4295 (3)	−0.1122 (4)	0.5549 (2)	586(24)	854(33)	557(24)	82(23)	4(20)	−61(24)
H_{45}	0.3430 (3)	−0.0732 (4)	0.5262 (2)	500					
C_{46}	0.4816 (3)	−0.0944 (3)	0.6176 (1)	485(21)	556(23)	560(21)	3(18)	181(18)	−43(18)
H_{46}	0.4357 (3)	−0.0424 (3)	0.6380 (1)	500					
N_{41}	0.6496 (2)	−0.1174 (3)	0.7189 (1)	387(15)	307(15)	403(15)	−1(12)	192(12)	−36(13)
H_{47}	0.6969(23)	−0.1879(28)	0.7391(12)	500					
H_{48}	0.6024(23)	−0.1151(30)	0.7340(12)	500					

Table 5. Selected interparticle distances in $Ni(NO_3)_2 \cdot 2C_6H_7N \cdot 4H_2O$ in pm.

$Ni-N_2$	212.0
$Ni-O_5$	207.1(2)
$Ni-O_4$	206.4(2)
N_2-O_1	301.7
N_2-O_3	301.7
O_4-O_1	282.6
O_4-O_2	291.1
O_5-O_2	289.5
O_5-O_3	278.3

Table 6. Selected interparticle distances in $Ni(NO_3)_2 \cdot 6C_6H_7N \cdot 2H_2O$ in pm.

$Ni-O_4$	211.0(3)
$Ni-O_5$	205.2(2)
$Ni-N_{11}$	215.6(2)
$Ni-N_{21}$	217.9(2)
$N_{11}-O_2$	302.5
$N_{21}-O_1$	315.0
$N_{21}-O_2$	314.1
O_4-O_2	328.3
O_4-O_3	275.9
$N_{11}-O_4$	298.7
$N_{11}-O_5$	300.5
$N_{21}-O_4$	292.7
$N_{21}-O_5$	309.4
$N_{31}-O_5$	291.5

Table 7. Selected interparticle distances in $Ni(NO_3)_2 \cdot 4C_6H_7N \cdot 2H_2O$ in pm.

$Ni-O_7$	204.2(2)
$Ni-O_8$	204.2(2)
$Ni-N_{11}$	215.5(2)
$Ni-N_{21}$	218.1(3)
$Ni-N_{31}$	217.3(3)
$Ni-N_{41}$	216.6(2)
$N_{11}-O_1$	309.4
$N_{11}-O_3$	296.2
$N_{11}-O_4$	309.5
$N_{12}-O_2$	317.8
$N_{13}-O_4$	317.5
$N_{14}-O_2$	309.4
$N_{14}-O_5$	305.1
$N_{14}-O_6$	309.0
O_7-O_5	275.9
O_7-O_6	273.1
O_8-O_1	270.0
O_8-O_3	278.4

a plane and the two water molecules are opposite above and below it. There are oxygen-oxygen distances between water molecules and nitrate ions of 270 pm and oxygen nitrogen distances between nitrate ions and aniline molecules of 309 pm.

For $Ni(NO_3)_2 \cdot 2C_6H_7N \cdot 4H_2O$ plots of the projections along the *b*- and the *c*-directions are shown in Figure 5. The nickel ion occupies a special position on a two-fold axis: it is the centre of inversion of the cation $[Ni \cdot 2C_6H_7N \cdot 4H_2O]^{++}$. The aniline molecules occupy trans positions, with parallel phenyl groups. The nitrate ions are between the cations with distances O(nitrate)-O(water) of 278 pm and 291 pm.

As mentioned, two more solids crystallized, but these were unstable. So it was not yet possible to determine their structures and compositions. One of them is triclinic, $P\bar{1}$. The unit cell constants are $a = 2520.6$ pm, $b = 1007.1$ pm, and $c = 991.6$ pm, $Z = 2$. The angles are $\alpha = 89.76°$, $\beta = 87.14°$ and $\gamma = 83.60°$. The dark green crystal has a melting point of 91 °C.

4. Discussion

Aniline and water show an upper critical solution temperature of 168 °C. With added nickel nitrate, for a broad range of aniline:water ratios homogeneous solutions can be formed. This decrease of the upper critical solution temperature indicates heteroselective solvation. All phase diagrams are of the same shape. The curve enclosing the two phase region can be approximated by three straight lines. The first in the water rich region is nearly parallel to the side of the triangle. Therefore, aniline is only sparely soluble in aqueous nickel nitrate solutions. The curve in the aniline rich region has a smaller slope which is equal in all investigated systems. With each dissolved nickel nitrate unit, 7.5 molecules of water are transferred into the aniline rich phase. A third line closes the gap between the first two lines. In this region, the concentration of nickel nitrate is nearly constant. From the conodes we see, that nickel nitrate has a higher solubility in the solutions, which contain both solvents in nearly equal amounts, than in the co-existing water rich mixtures which contain only little aniline. This phenomenon is expected for heteroselective solvation, because anions and cations can be surrounded by different components of the solvent.

The features described above for the system nickel nitrate/aniline/water are virtually independent from the temperature, as can be seen from a comparison of part *a* and *b* in Figure 1. We also find them for the other investigated systems (see Figure 2).

By comparison of the crystal structures the following common features are to be mentioned: All nickel ions are octahedrally coordinated. The numbers of aniline ligands are either two or four, they are always arranged in trans positions. The nitrate ions are placed between the complex ions. The distances to the water and to the aniline molecules are short: the $O_{(H_2O)} - O_{(NO_3)}$ distances are between 270 and 280 pm, the $N_{(aniline)} - O_{(NO_3)}$ distances are about 300 pm. These distances are typical for hydrogen bridged oxygen or nitrogen atoms. These hydrogen bonds connect water and aniline from the solvation shell of the nickel ions with the nitrate ions. They form infinitely extended chains. The chains are arranged along the *a*-axis in the crystals containing 2 or 4 four aniline molecules and in *a*-*b*-direction in the crystal with 6 aniline molecules. In these chains, nickel and nitrate ions share the same solvent molecules. This behaviour is known from concentrated ionic solutions and is called ion pair formation.

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[1] H. Schneider and H. Strehlow, Z. Physik. Chem. NF **49**, 44 (1966).
[2] H. Strehlow and H.-M. Koepp, Z. Elektrochem. 63, 373 (1958).
[3] S. P. Das, B. Wittekopf, and K. G. Weil, Z. Naturforsch. **43a**, 977 (1988).
[4] P. Lumme and J Peltonen, Suomen kemist. Pt.B **37** (11), 189 (1964).
[5] P. Ferrero and J. Brehain, L'ind. Chem. Belge **1951**, 103.
[6] Program Shelx, G. M. Sheldrick, Cambridge, England, 1976.