Crystal Structure of $3\,Ni(NO_3)_2 \cdot 16\,C_6H_5NH_2$

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The compound $3\,Ni(NO_3)_2 \cdot 16\,C_6H_5NH_2$ was obtained by crystallization from solutions of $Ni(NO_3)_2 \cdot 6\,C_6H_5NH_2 \cdot 2\,H_2O$ in aniline. Its crystal structure was determined by single crystal X-ray diffraction. The crystals are triclinic, space group $P\bar{1}$ with lattice constants $a = 985.2$ pm, $b = 1004.5$ pm and $c = 2514.3$ pm, $\alpha = 96.34°$, $\beta = 92.63°$ and $\gamma = 89.82°$. The structure shows units of four aniline molecules and two slightly distorted nitrate ions in the coordination sphere of each nickel ion. These units are similar to contact ion pairs in concentrated ionic solutions.

1. Introduction

Recently we investigated the heteroselectively solvated systems MeX_2/aniline/water (Me = Ni, Co; $X = NO_3$, ClO_4) [1]. We found homogeneous liquid phases and determined the single phase regions in the ternary phase diagrams. In the system $Ni(NO_3)_2$/aniline/water, we obtained ternary crystals and determined the structure of three of them. They exhibit structure elements known for concentrated ionic solutions, namely solvated ion-pairs. Water molecules of the coordination sphere of nickel ions form hydrogen bonds to nitrate ions. We now prepared a new crystalline compound, $3\,Ni(NO_3)_2 \cdot 16\,C_6H_5NH_2$. In this paper we report on the crystal structure of this compound.

2. Experimental

Starting materials were nickel nitrate hexahydrate (p.a. grade, Merck, Darmstadt) and aniline (puriss., Merck, Darmstadt, distilled prior to its use).

Nickel nitrate hexahydrate was dissolved in aniline. After several hours crystals with the stoichiometry $Ni(NO_3)_2 \cdot 6\,C_6H_5NH_2 \cdot 2\,H_2O$ precipitated. These crystals were isolated and dissolved in aniline at 40 °C. Cooling of the solution led to the formation of a supersaturated solution. After some hours at room temperature the desired crystals precipitated.

The X-ray intensities were measured with an automatic Enraf-Nonius CAD4 diffractometer. About 5900 signals were recorded. Because of the instability of the crystal at room temperature the measurement was carried out at 10 °C. The structure was determined by use of the program Shel x-76 [2].

3. Results

The crystals are triclinic, space group $P\bar{1}$. The lattice constants are $a = 985.2$ pm, $b = 1004.5$ pm and $c = 2514.3$ pm, $\alpha = 96.34°$, $\beta = 92.63°$ and $\gamma = 89.82°$. Figure 1 displays a projection of the structure along the a-axis. In Fig. 2, the different atoms in the lattice are identified. In Table 1 the positional and thermal parameters are listed. The nitrogen atoms of four aniline molecules form a plane. Using the coordinates given in Table 1, we can show that a nickel ion is located in this plane. Perpendicular to this plane, two oxygen atoms from NO_3^--groups are situated. The coordination sphere of nickel ions therefore is a slightly distorted octahedron. Table 2 contains characteristic distances. The distances between nickel ions and nitrogen atoms of the aniline molecules vary between 213.2(6) and 218.6(6) pm. The distances between nickel ions and oxygen atoms of the nitrate ions range from 206.2(6) pm to 209.0(6) pm. All these distances are in the ranges known for bonds in strong complexes, thus the bond lengths from the nitrogen atom to the oxygen atom coordinated to the nickel ion are 127.6(10) pm, 127.8(9) pm and 129.1(11) pm while the bond lengths of the other N–O bonds vary between 120.1(10) pm and 124.8(11) pm. Hence a considerable distortion of the NO_3^--ion results.

* Part of the dissertation of M. Mahr.

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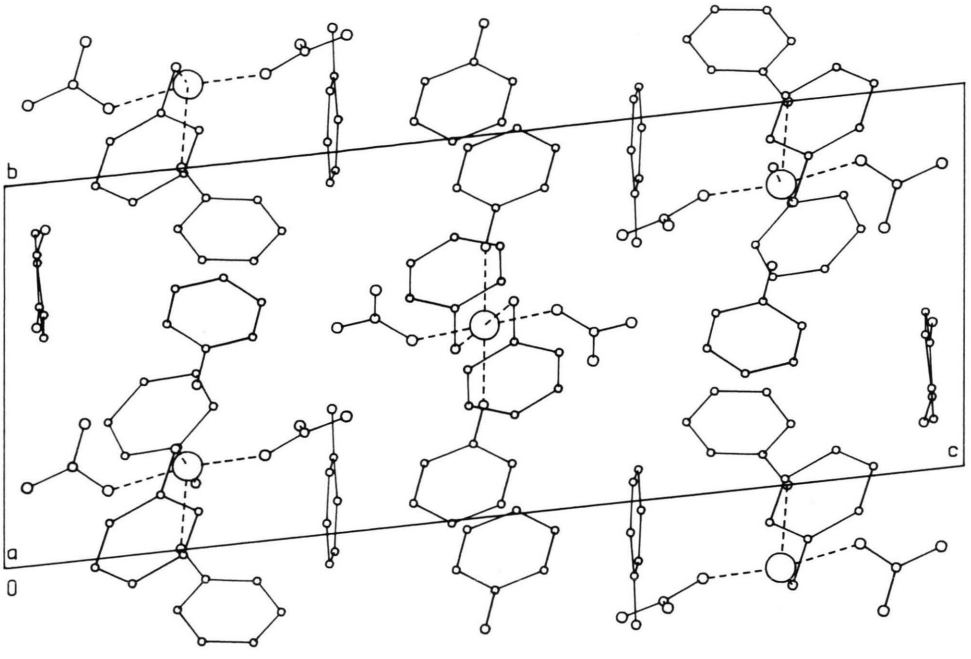

Fig. 1. Projection of the structure along the *a*-axis.

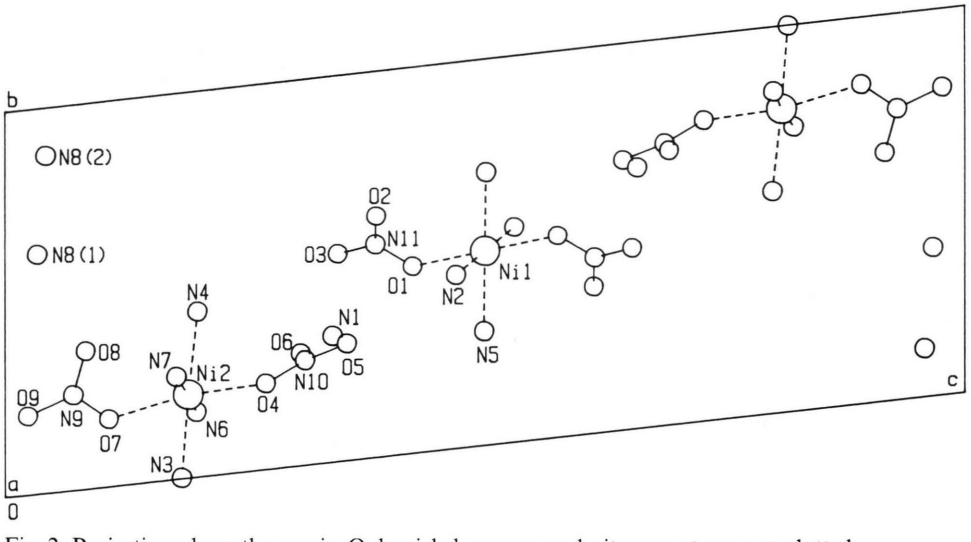

Fig. 2. Projection along the *a*-axis. Only nickel, oxygen and nitrogen atoms are plotted.

The unit cell contains three of these units and four aniline molecules which are not coordinated to nickel ions. Two of them are disordered: The difference Fourier map shows two maxima at two possible positions of nitrogen atoms N 8, see Table 1, with intensities of a half nitrogen atom. It seems that there are two possible arrangements which are both half occupied. In the second position, the aniline molecule is rotated about 60° around the 6-fold axis of its benzene constituent and tilted about 5° with respect to the first one. This disorder is the reason, that even after the usual refinement the R-index is not smaller than 0.095.

Table 1. Positional and thermal parameters (with standard deviations). The temperature factor has the form

$$T = \exp\{-2\pi(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)\}.$$

The U_{ij} are in $(\mathrm{pm})^2$. 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}
Ni1	0.5000(0)	0.5000(0)	0.5000(0)	0.018(1)	0.038(1)	0.041(1)	0.005(1)	-0.001(1)	0.005(1)
Ni2	0.1929(1)	0.2141(1)	0.1901(0)	0.020(1)	0.043(1)	0.051(1)	0.002(2)	-0.004(1)	0.002(1)
Aniline 1									
N1	0.1478(7)	0.6758(7)	0.6598(3)	0.055(6)	0.043(6)	0.093(7)	0.014(5)	0.016(5)	-0.005(5)
C11	0.1904(10)	0.8041(11)	0.6579(4)	0.037(6)	0.097(9)	0.035(7)	0.006(7)	0.007(5)	0.026(7)
C21	0.3299(10)	0.8419(10)	0.6623(4)	0.044(7)	0.071(9)	0.073(9)	0.010(7)	0.011(6)	0.014(6)
H21	0.4058(10)	0.7642(10)	0.6635(4)	0.05					
C31	0.3724(11)	0.9734(11)	0.6650(4)	0.053(8)	0.097(11)	0.088(10)	-0.008(9)	0.016(7)	-0.022(8)
H31	0.4801(11)	0.9938(11)	0.6697(4)	0.05					
C41	0.2853(13)	1.0796(12)	0.6622(5)	0.110(12)	0.064(10)	0.099(11)	-0.008(8)	0.029(10)	-0.022(9)
H41	0.3215(13)	1.1815(12)	0.6643(5)	0.05					
C51	0.1490(12)	1.0484(10)	0.6566(4)	0.103(11)	0.047(8)	0.074(9)	0.004(7)	0.012(8)	0.023(8)
H51	0.0755(12)	1.1277(10)	0.6541(4)	0.05					
C61	0.1051(9)	0.9181(10)	0.6539(4)	0.038(6)	0.083(9)	0.058(8)	0.007(7)	0.005(5)	0.013(7)
H61	-0.0030(9)	0.9004(10)	0.6484(4)	0.05					
Aniline 2									
N2	0.2938(6)	0.4456(6)	0.4694(3)	0.010(4)	0.047(5)	0.067(6)	-0.003(4)	-0.009(4)	0.007(3)
C12	0.1895(8)	0.5521(8)	0.4688(4)	0.020(5)	0.046(7)	0.054(7)	-0.003(6)	-0.003(5)	-0.010(5)
C22	0.1372(8)	0.6108(8)	0.5175(4)	0.024(5)	0.054(7)	0.066(8)	0.001(6)	-0.002(5)	-0.010(5)
H22	0.1775(8)	0.5827(8)	0.5554(4)	0.05					
C32	0.0332(9)	0.7053(9)	0.5162(4)	0.026(6)	0.050(8)	0.114(11)	-0.019(7)	0.023(6)	0.003(5)
H32	-0.0080(9)	0.7498(9)	0.5531(4)	0.05					
C42	-0.0163(10)	0.7414(11)	0.4682(5)	0.034(7)	0.052(9)	0.159(15)	-0.010(9)	-0.031(8)	0.012(6)
H42	-0.0977(10)	0.8134(11)	0.4669(5)	0.05					
C52	0.0374(11)	0.6862(10)	0.4221(5)	0.077(9)	0.059(9)	0.108(11)	0.003(8)	-0.058(8)	0.019(7)
H52	-0.0018(11)	0.7171(10)	0.3845(5)	0.05					
C62	0.1398(9)	0.5923(9)	0.4212(4)	0.048(7)	0.063(8)	0.062(8)	0.004(6)	-0.019(6)	0.014(6)
H62	0.1803(9)	0.5510(9)	0.3837(4)	0.05					
Aniline 3									
N3	0.1500(6)	0.0016(6)	0.1833(3)	0.024(4)	0.021(4)	0.083(6)	0.018(4)	-0.017(4)	0.010(3)
C13	0.2386(8)	-0.0844(8)	0.2087(4)	0.034(6)	0.039(7)	0.039(7)	-0.009(5)	0.005(5)	-0.019(5)
C23	0.3350(9)	-0.1573(8)	0.1798(4)	0.043(6)	0.042(7)	0.049(7)	0.008(6)	-0.000(6)	-0.006(5)
H23	0.3441(9)	-0.1463(8)	0.1379(4)	0.05					
C33	0.4215(9)	-0.2457(9)	0.2048(4)	0.027(6)	0.042(7)	0.099(10)	0.003(7)	0.013(6)	-0.002(5)
H33	0.4966(9)	-0.3016(9)	0.1816(4)	0.05					
C43	0.4126(10)	-0.2629(9)	0.2586(4)	0.047(7)	0.045(8)	0.088(10)	0.020(7)	-0.022(7)	-0.006(6)
H43	0.4798(10)	-0.3312(9)	0.2772(4)	0.05					
C53	0.3169(11)	-0.1915(9)	0.2877(4)	0.079(9)	0.053(8)	0.057(8)	-0.004(7)	0.001(7)	-0.010(7)
H53	0.3066(11)	-0.2033(9)	0.3295(4)	0.05					
C63	0.2335(9)	-0.1036(8)	0.2623(4)	0.039(6)	0.034(7)	0.070(9)	-0.005(6)	0.007(6)	0.006(5)
H63	0.1598(9)	-0.0467(8)	0.2858(4)	0.05					
Aniline 4									
N4	0.2384(6)	0.4253(6)	0.1995(3)	0.023(4)	0.020(4)	0.096(7)	-0.004(4)	0.007(4)	0.017(3)
C14	0.1323(9)	0.5175(9)	0.2087(4)	0.049(7)	0.045(7)	0.043(7)	0.005(6)	-0.008(6)	-0.026(6)
C24	0.0712(9)	0.5343(8)	0.2574(4)	0.056(7)	0.038(7)	0.073(9)	0.005(6)	-0.017(6)	0.012(6)
H24	0.1073(9)	0.4769(8)	0.2891(4)	0.05					
C34	-0.0367(10)	0.6241(9)	0.2665(4)	0.067(8)	0.049(8)	0.066(9)	-0.002(6)	0.004(7)	-0.001(6)
H34	-0.0846(10)	0.6336(9)	0.3045(4)	0.05					
C44	-0.0813(9)	0.7001(9)	0.2269(4)	0.036(6)	0.039(7)	0.106(10)	-0.003(7)	-0.007(7)	0.004(5)
H44	-0.1624(9)	0.7715(9)	0.2340(4)	0.05					
C54	-0.0207(10)	0.6841(9)	0.1771(4)	0.059(8)	0.050(8)	0.073(9)	0.017(7)	-0.020(7)	-0.017(6)
H54	-0.0557(10)	0.7424(9)	0.1455(4)	0.05					
C64	0.0856(9)	0.5921(8)	0.1685(4)	0.039(6)	0.039(7)	0.079(9)	0.001(6)	0.012(6)	-0.005(5)
H64	0.1315(9)	0.5793(8)	0.1301(4)	0.05					

Table 1 (continued)

Atom	x/a	y/b	z/c	U_{11} or U	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Aniline 5									
N5	0.4513(6)	0.7071(5)	0.5010(3)	0.018(4)	0.013(4)	0.072(6)	-0.002(4)	-0.001(4)	-0.012(3)
C15	0.5514(8)	0.8068(8)	0.5115(4)	0.036(6)	0.045(7)	0.030(6)	0.003(6)	0.010(5)	0.029(5)
C25	0.6019(9)	0.8442(8)	0.5630(4)	0.043(6)	0.038(7)	0.065(9)	0.008(6)	0.025(6)	0.007(5)
H25	0.5654(9)	0.7936(8)	0.5953(4)	0.05					
C35	0.6984(10)	0.9455(10)	0.5746(4)	0.051(7)	0.064(9)	0.058(8)	-0.010(7)	-0.010(6)	0.014(6)
H35	0.7353(10)	0.9739(10)	0.6154(4)	0.05					
C45	0.7454(9)	1.0079(10)	0.5339(5)	0.026(6)	0.042(8)	0.135(12)	-0.004(8)	0.008(8)	-0.001(5)
H45	0.8195(9)	1.0873(10)	0.5426(5)	0.05					
C55	0.7003(10)	0.9718(9)	0.4821(4)	0.042(7)	0.049(8)	0.084(10)	0.018(7)	0.030(7)	0.020(6)
H55	0.7395(10)	1.0216(9)	0.4501(4)	0.05					
C65	0.6025(9)	0.8693(8)	0.4707(4)	0.036(6)	0.036(6)	0.057(8)	0.003(6)	0.011(5)	0.017(5)
H65	0.5675(9)	0.8399(8)	0.4297(4)	0.05					
Aniline 6									
N6	0.4072(6)	0.1670(7)	0.1985(3)	0.012(4)	0.057(6)	0.078(6)	0.022(5)	0.001(4)	0.002(4)
C16	0.5003(8)	0.2664(9)	0.1798(4)	0.017(5)	0.055(7)	0.058(8)	0.000(6)	-0.009(5)	0.019(5)
C26	0.5621(8)	0.3647(9)	0.2165(4)	0.025(5)	0.052(7)	0.059(8)	0.000(6)	-0.004(5)	0.003(5)
H26	0.5414(8)	0.3699(9)	0.2585(4)	0.05					
C36	0.6497(9)	0.4551(10)	0.1987(4)	0.030(6)	0.054(8)	0.105(10)	0.006(7)	-0.008(7)	-0.004(6)
H36	0.6970(9)	0.5319(10)	0.2269(4)	0.05					
C46	0.6778(10)	0.4486(10)	0.1448(5)	0.029(6)	0.072(9)	0.119(12)	0.022(9)	0.006(7)	-0.005(6)
H46	0.7478(10)	0.5198(10)	0.1319(5)	0.05					
C56	0.6181(10)	0.3529(11)	0.1074(4)	0.037(7)	0.112(11)	0.081(10)	0.026(8)	0.009(7)	-0.001(7)
H56	0.6397(10)	0.3494(11)	0.0655(4)	0.05					
C66	0.5283(9)	0.2597(9)	0.1252(4)	0.028(6)	0.076(9)	0.058(8)	0.002(7)	-0.008(5)	0.004(6)
H66	0.4810(9)	0.1832(9)	0.0969(4)	0.05					
Aniline 7									
N7	-0.0208(6)	0.2632(7)	0.1777(3)	0.011(4)	0.053(5)	0.086(7)	-0.009(5)	-0.015(4)	0.007(4)
C17	-0.1131(8)	0.1470(8)	0.1621(4)	0.016(5)	0.048(7)	0.063(8)	0.010(6)	-0.003(5)	0.015(5)
C27	-0.1874(9)	0.0936(10)	0.2015(4)	0.036(6)	0.079(9)	0.036(7)	0.011(6)	0.002(6)	0.031(6)
C37	-0.2751(10)	0.9851(11)	0.1856(5)	0.020(6)	0.056(8)	0.132(13)	0.057(8)	0.009(7)	0.001(5)
C47	-0.2872(10)	0.9243(10)	0.1328(4)	0.052(7)	0.079(9)	0.053(8)	-0.013(7)	-0.017(7)	0.014(6)
C57	-0.2131(10)	0.9771(10)	0.0939(4)	0.041(7)	0.072(8)	0.080(9)	0.007(7)	0.003(6)	-0.016(6)
C67	-0.1269(9)	0.0886(10)	0.1090(4)	0.036(6)	0.083(9)	0.032(7)	-0.008(6)	-0.002(5)	0.002(6)
Aniline 8									
N8(1)	0.0594(15)	0.6184(14)	0.0332(6)	0.087(11)	0.123(11)	0.085(11)	0.040(9)	-0.002(9)	-0.011(9)
N8(2)	0.1067(15)	0.8762(15)	0.0419(6)	0.057(11)	0.106(12)	0.073(12)	0.004(9)	0.011(9)	0.020(9)
C18	0.2032(19)	0.6721(18)	0.0358(5)	0.172(20)	0.105(14)	0.052(10)	0.018(10)	0.018(12)	-0.050(14)
C28	0.2097(15)	0.8123(18)	0.0333(5)	0.090(12)	0.125(16)	0.046(9)	0.011(10)	0.009(8)	-0.003(11)
C38	0.3435(20)	0.8701(13)	0.0317(5)	0.140(14)	0.092(13)	0.041(8)	-0.001(8)	0.001(10)	-0.021(12)
C48	0.4561(14)	0.7906(23)	0.0338(5)	0.054(10)	0.285(24)	0.032(8)	-0.011(13)	-0.021(7)	0.002(14)
C58	0.4413(21)	0.6497(20)	0.0405(6)	0.194(22)	0.123(17)	0.076(11)	0.023(12)	-0.027(14)	0.014(16)
C68	0.3157(20)	0.5898(20)	0.0404(7)	0.140(21)	0.182(23)	0.084(12)	0.040(13)	-0.003(14)	-0.011(17)
Nitrate 1									
N9	0.1722(8)	0.2455(9)	0.0703(4)	0.042(6)	0.081(8)	0.059(8)	0.016(7)	-0.002(6)	-0.012(5)
O7	0.2120(6)	0.1735(6)	0.1075(2)	0.027(4)	0.086(6)	0.051(5)	0.004(4)	-0.005(3)	0.006(4)
O8	0.1175(8)	0.3559(7)	0.0832(3)	0.122(8)	0.075(6)	0.112(8)	0.011(6)	0.014(6)	0.033(6)
O9	0.1852(8)	0.2031(8)	0.0236(3)	0.125(8)	0.158(9)	0.047(6)	-0.004(6)	0.007(6)	0.029(7)
Nitrate 2									
N10	0.2281(8)	0.2697(8)	0.3116(3)	0.032(5)	0.070(7)	0.054(7)	0.011(6)	0.001(5)	0.007(5)
O4	0.1563(5)	0.2211(6)	0.2705(2)	0.024(4)	0.076(5)	0.047(5)	-0.010(4)	-0.007(3)	-0.009(3)
O5	0.1797(6)	0.3008(7)	0.3551(2)	0.043(4)	0.100(6)	0.057(5)	-0.012(5)	0.003(4)	0.002(4)
O6	0.3471(6)	0.2890(9)	0.3069(3)	0.023(4)	0.288(12)	0.068(6)	-0.011(7)	-0.002(4)	-0.032(6)
Nitrate 3									
N11	0.4545(8)	0.4516(8)	0.6153(3)	0.046(6)	0.074(7)	0.031(6)	0.000(5)	0.007(5)	-0.004(5)
O1	0.4242(5)	0.5194(6)	0.5763(2)	0.034(4)	0.080(5)	0.033(4)	0.020(4)	-0.002(3)	0.017(4)
O2	0.5535(6)	0.3764(7)	0.6144(3)	0.059(5)	0.104(6)	0.076(6)	0.029(5)	0.008(4)	0.049(5)
O3	0.3831(7)	0.4652(7)	0.6545(2)	0.077(6)	0.096(6)	0.056(5)	0.022(5)	0.020(5)	0.024(5)

Table 2. Selected interparticle distances in pm.

Atom 1	Atom 2	*d*/pm	Atom 1	Atom 2	*d*/pm
Ni1	N2	218.6(6)	O1	N11	127.6(10)
Ni1	N5	213.2(6)	O2	N11	123.2(10)
Ni2	N3	216.3(6)	O3	N11	123.3(10)
Ni2	N4	215.5(6)	O4	N10	127.8(10)
Ni2	N6	216.8(6)	O5	N10	121.9(9)
Ni2	N7	217.6(6)	O6	N10	120.1(10)
Ni1	O3	208.0(5)	O7	N9	129.1(11)
Ni2	O4	206.2(6)	O8	N9	124.8(11)
Ni2	O7	209.0(6)	O9	N9	122.0(11)
			N1	O3	313.0
			N1	O5	324.1
			N8(1)	O8	308.3
			N8(2)	O9	330.7

4. Discussion

As in $Ni(NO_3)_2 \cdot 6\,C_6H_5NH_2 \cdot 2\,H_2O$, $Ni(NO_3)_2 \cdot 4\,C_6H_5NH_2 \cdot 2\,H_2O$, and $Ni(NO_3)_2 \cdot 2\,C_6H_5NH_2 \cdot 4\,H_2O$ [1], the nickel ions are octahedrally coordinated. In the compounds mentioned above, all six coordination sites are occupied by solvent molecules. Two of them form in addition hydrogen bridges to ions. Thus this configuration may represent an ion pair where the ions share the primary solvation shell. In the present case, two sites are occupied by the counterions, NO_3^-. In analogy to the terminology which is used in order to describe concentrated ionic solutions, these configurations represent direct contact ion pairs [3].

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