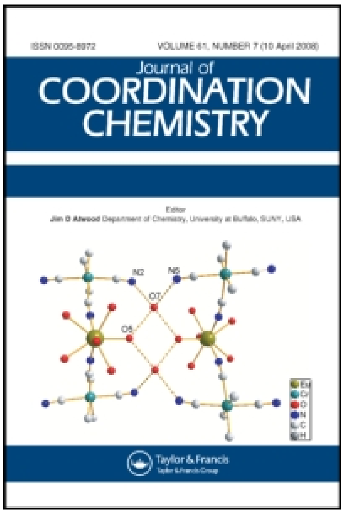

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

PREPARATION AND CRYSTAL STRUCTURE OF THE HOST-GUEST TYPE COMPLEX OF TRIS(BIPYRIDINE)NICKEL(II)-TETRAKIS(CYANO) NICKELLATE (II))-HEXAHYDRATE-HEMI (BIPYRIDINE)

Juraj Černák[a]; Erika Lengyelová[a]; Kamran Ahmadi[b]; Anne-Marie Hardy[b]
[a] Department of Inorganic Chemistry, P.J. Šafárik University, Košice, Slovakia [b] Laboratoire de Cristallochimie Minérale, Université de Poitiers, Poitiers, Cedex

To cite this Article Černák, Juraj , Lengyelová, Erika , Ahmadi, Kamran and Hardy, Anne-Marie(1996) 'PREPARATION AND CRYSTAL STRUCTURE OF THE HOST-GUEST TYPE COMPLEX OF TRIS(BIPYRIDINE)NICKEL(II)-TETRAKIS(CYANO) NICKELLATE (II))-HEXAHYDRATE-HEMI (BIPYRIDINE)', Journal of Coordination Chemistry, 37: 1, 55 — 62

To link to this Article: DOI: 10.1080/00958979608023540
URL: http://dx.doi.org/10.1080/00958979608023540

J. Coord. Chem., 1996, Vol 37, pp. 55–62
Reprints available directly from the publisher
Photocopying permitted by license only

Amsterdam B.V. Published in The Netherlands under
license by Gordon and Breach Science Publishers SA
Printed in Malaysia

PREPARATION AND CRYSTAL STRUCTURE OF THE HOST-GUEST TYPE COMPLEX OF TRIS(BIPYRIDINE)NICKEL(II)-TETRAKIS(CYANO) NICKELLATE (II))-HEXAHYDRATE-HEMI (BIPYRIDINE)

JURAJ ČERNÁK,* ERIKA LENGYELOVÁ

Department of Inorganic Chemistry, P.J. Šafárik University, Moyzesova 11, 041 54 Košice, Slovakia

KAMRAN AHMADI and ANNE-MARIE HARDY

Laboratoire de Cristallochimie Minérale, Université de Poitiers, 40, Avenue du Recteur Pineau, F-86022 Poitiers Cedex

(Received November 1, 1994; in final form April 10, 1995)

The title complex is built up of $[Ni(bpy)_3]^{2+}$ cations, $[Ni(CN)_4]^{2-}$ anions and non-coordinated bpy and water molecules. The water molecules along with one of the two crystallographically independent tetracyanonickellate anions form layers, in which H-bonds (HB's) of the types O-H . . O and O-H . . N are important. The remaining tetracyanonickellate anions bound by H-bonds to water molecules in the layers are placed approximately perpendicular to the layers making interconnection between them. So by HBs a 3D network is formed (hydrophilic host part of the structure). The cations and non-coordinated bpy molecules (hydrophobic guest part of the structure) are placed in cavities formed by HBs. The Ni-N distances in the cation are within the range 2.078(3)–2.100(3) Å and the Ni-C distances in the anion are within the range 1.854(5)–1.873(4) Å.

KEYWORDS: host-guest complex, tetracyanonickellate(2 –), bipyridine, nickel, Hydrogen bond system

INTRODUCTION

Magnetic properties of infinite 1, 2 and 3-dimensional (D) solids are intensively studied at present.[1,2] Recently the low-temperature magnetic properties of 1D compound $Ni(en)_2Ni(CN)_4$ (en = ethylenediamine)[3] were reported and the magnetic studies of some other tetracyanonickellates are in progress.[4] To enlarge the number of studied complexes we replace ethylenediamine by other ligands. The first report about such a complex containing bpy ($Ni(bpy)_2Ni(CN)_4$; bpy = 2,2′-bipyridine) was published by Feigl, Demant and de Oliveira in 1945.[5] The possibility of preparing other tetracyanonickellate complexes containing bpy was

---

* Author for correspondence.

demonstrated by Rostášová[6] and recently the 2-dimensional structure of the Cd(bpy)Ni(CN)$_4$ complex was reported.[7] During our study we have unexpectedly obtained reddish-violet single crystals of the new title complex. The elemental analysis indicated the peculiar 1:3.5 ratio of Ni(cationic):bpy. It is well known that tetracyanonickellates form different types of inclusion compounds,[8,9] so we decided to undertake an X-ray analysis of the title complex in order to elucidate its structure. The results are reported here.

EXPERIMENTAL

Preparation

To a solution of NiCl$_2$·6H$_2$O (1 mmol, 238 mg) in 200 mL water was added a solution of bpy (4 mmol, 625 mg) in 20 mL of ethanol. To the resulting pink solution was added a solution of K$_2$[Ni(CN)$_4$]·H$_2$O (1 mmol, 260 mg) in 200 mL of water with stirring. Immediately a pink-red crystalline powder of the product [Ni(bpy)$_3$][Ni(CN)$_4$]·6H$_2$O·0.5bpy (Nibp3) separated out and was filtered. Single crystals suitable for X-ray analysis were prepared by recrystallization from a mixture of water-methanol (1:3). The stoichiometric composition of the product was determined analytically. Anal calcd. for [Ni(bpy)$_3$][Ni(CN)$_4$]·6H$_2$O·0.5bpy (Nibp3) (%): C, 53.46; H, 4.60; N, 17.58; Ni, 13.40. Found: C, 53.58; H, 4.23; N, 17.61; Ni, 13.34.

Crystal Structure Analysis

Preliminary unit cell dimensions and space group symmetry were obtained by the photographical method. Accurate cell dimensions were measured on a CAD4L diffractometer which was also used for data collection. The data were Lp corrected using the program LOPOTRI.[10] The structure was solved by the heavy atom method using the program SHELXS86.[11] For the refinement the program SHELXL93[12] was used. The hydrogen atoms from bpy rings were placed in the calculated positions assuming the riding model with freely refined U's. It was possible to elucidate the positions of the hydrogen atoms of water molecules from the difference map. The refinement of their positional parameters (U's were fixed to 0.1 Å^2) with a fixed O-H distance (0.96 Å) converged. This could not be done for the hydrogen atoms bound to the O(6) water molecule, maybe due to the presence of another small local maximum of 0.57 eÅ^{-3} near (1.64 Å) the O(6) atom; so these hydrogen atoms were not included in the refinement and were only placed in the found positions. The relevant crystallographic data are given in Table 1. The geometrical analysis was made using the program SHELXL93.[12] The figures were obtained with ORTEP[13] and MOLDRAW[14] programs. The final atomic parameters along with equivalent thermal parameters are listed in Table 2. Selected geometric parameters are listed in Table 3.

RESULTS AND DISCUSSION

The structure of Nibp3 contains nickel atoms in two different coordination polyhedra: the coordination is octahedral in the [Ni(bpy)$_3$]$^{2+}$ cation and square-

Table 1 Crystal data and structure refinement for Nibp3.

Empirical formula	$C_{39}H_{40}N_{11}Ni_2O_6$
Formula weight	876.24
Temperature	293(2) *K*
Wavelength	0.70930 Å
Crystal system	monoclinic
Space group	$P2_1/n$
Unit cell dimensions	*a* = 20.061(4)Å
	b = 13.114(1) Å
	c = 16.553(3) Å
	β = 105.49(1)°
Volume	4196.6(12) $Å^3$
Z	4
Density (calculated)	1.387 Mg/m^3
Density (measured)	1.38(2) Mg/m^3
Absorption coefficient	0.955 mm^{-1}
F(000)	1820
Crystal size	0.35 × 0.27 × 0.17 mm
Theta range for data collection	2.01 to 24.92°.
Index ranges	$-23< h <22$, $0< k <15$, $0 < l <19$
Reflections collected	7632
Independent reflections	7360 [R(int) = 0.0214]
Absorption correction	No
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	7359/10/585
Goodness-of-fit on F^2	0.904
Final *R* indices [I>2sigma(I)]	R1 = 0.0422, wR2 = 0.0848
R indices (all data)	R1 = 0.0971, wR2 = 0.1174
Largest diff. peak and hole	0.573 and -0.232 e.$Å^{-3}$

planar in two crystallochemically different $[Ni(CN)_4]^{2-}$ anions (Fig. 1). The peculiar ratio of 1:3.5 (Ni(cat):bpy) arises from the fact that besides bpy molecules acting as chelate ligands non-coordinated bpy molecules (half per formula unit of the complex) lying on the symmetry center are present. This requires the nitrogen atoms to be in opposite positions and the planarity of the molecule. Searching the Cambridge Structural Database[15] showed that the title compound represents the first example of a complex containing free bpy. On the other hand, this type compound is described for the similar ligand 1,10-phenantroline (phen), *e.g.*, $Cu(phen)(tu)_2I\cdot phen$ (tu = thiourea).[16]

One may compare the mean C-N, C-C(in the rings) and C-C(between the rings) bond distances in free and coordinated bpy molecules. The corresponding values are: 1.344(3); 1.370(7); 1.502(7) Å (for the free bpy molecule) and 1.347(12); 1.375(8); 1.477(10) Å (for the coordinated bpy). The values found in both types of bpy molecules are as expected and almost the same within experimental error.

The content of the unit cell is completed by non-coordinated water molecules. They form infinite layers along with one of the two tetracyanonickellate anions, in which they are interconnected by O-H..O and O-H..N hydrogen bonds (HBs) (Fig. 2, Table 4). The second tetracyanonickellate anion is placed approximatively perpendicularly to these layers and connects these layers by HBs. Thus by HBs a 3D network is formed with large cavities (hydrophilic part of the structure) in which cations and non-coordinated bpy molecules are placed (hydrophobic part of the structure). A similar structure was found for the analogous dicyanoargentate

Table 2 Atomic coordinates (× 10^4) and equivalent isotropic displacement parameters ($Å^2 \times 10^3$) for Nibp3. U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Atom	*x*	*y*	*z*	U_{eq}
Ni(1)	0	5000	5000	50(1)
Ni(2)	5000	5000	5000	43(1)
Ni(3)	1935(1)	757(1)	3347(1)	37(1)
O(1)	2996(2)	2391(2)	6638(2)	84(1)
O(2)	2627(2)	1551(3)	8025(2)	90(1)
O(3)	3895(2)	1308(2)	5902(2)	73(1)
O(4)	1653(2)	2450(3)	8690(2)	90(1)
O(5)	908(2)	4266(3)	8556(2)	100(1)
O(6)	3021(2)	4564(3)	6810(2)	109(1)
C(11)	112(2)	4611(3)	6105(3)	63(1)
N(11)	165(2)	4401(3)	6793(3)	85(1)
C(12)	844(2)	5673(3)	5281(3)	65(1)
N(12)	1361(2)	6084(4)	5437(3)	102(2)
C(21)	4921(2)	3620(3)	5251(2)	49(1)
N(21)	4848(2)	2779(3)	5399(2)	69(1)
C(22)	4415(2)	5331(3)	5663(2)	50(1)
N(22)	4052(2)	5523(3)	6065(2)	75(1)
N(31)	2947(1)	219(2)	3497(2)	41(1)
C(31)	3203(2)	380(3)	2823(2)	41(1)
C(32)	3861(2)	51(3)	2843(3)	62(1)
C(33)	4261(2)	-444(3)	3533(3)	72(1)
C(34)	4003(2)	-601(3)	4216(3)	63(1)
C(35)	3346(2)	-257(3)	4163(3)	54(1)
N(41)	2107(1)	1164(2)	2206(2)	41(1)
C(41)	2740(2)	914(2)	2114(2)	39(1)
C(42)	2922(2)	1164(3)	1387(2)	49(1)
C(43)	2456(2)	1665(3)	745(2)	57(1)
C(44)	1818(2)	1905(3)	837(2)	55(1)
C(45)	1664(2)	1648(3)	1569(2)	50(1)
N(51)	1857(1)	163(2)	4489(2)	38(1)
C(51)	1566(2)	-778(3)	4435(2)	40(1)
C(52)	1547(2)	-1316(3)	5148(2)	54(1)
C(53)	1815(2)	-886(3)	5923(3)	62(1)
C(54)	2101(2)	70(3)	5979(2)	56(1)
C(55)	2108(2)	570(3)	5251(2)	49(1)
N(61)	1483(1)	-662(2)	2964(2)	41(1)
C(61)	1294(2)	-1181(3)	3572(2)	40(1)
C(62)	863(2)	-2019(3)	3387(3)	51(1)
C(63)	633(2)	-2333(3)	2563(3)	62(1)
C(64)	846(2)	-1836(3)	1952(3)	58(1)
C(65)	1269(2)	-1001(3)	2182(2)	50(1)
N(71)	2224(1)	2194(2)	3853(2)	39(1)
C(71)	1691(2)	2811(3)	3884(2)	41(1)
C(72)	1795(2)	3706(3)	4333(2)	55(1)
C(73)	2456(2)	3995(3)	4752(3)	65(1)
C(74)	2998(2)	3396(3)	4701(3)	61(1)
C(75)	2869(2)	2504(3)	4251(2)	49(1)
N(81)	970(1)	1488(2)	3100(2)	37(1)
C(81)	997(2)	2444(3)	3413(2)	40(1)
C(82)	410(2)	3038(3)	3287(2)	55(1)
C(83)	-222(2)	2643(3)	2835(3)	61(1)
C(84)	-246(2)	1686(3)	2521(2)	56(1)
C(85)	354(2)	1132(3)	2667(2)	45(1)
N(91)	363(2)	208(3)	6108(2)	66(1)
C(91)	174(2)	422(3)	5286(2)	50(1)

Table 3 Selected bond lengths [Å] and angles [deg] for Nibp3.

C(92)	293(2)	1351(3)	4973(3)	64(1)
C(93)	626(2)	2101(4)	5517(3)	75(1)
C(94)	831(2)	1900(4)	6354(3)	76(1)
C(95)	689(2)	956(4)	6619(3)	73(1)
Ni(1)-C(12)	1.854(5)	C(12)-Ni(1)-C(11)	91.2(2)	
Ni(1)-C(11)	1.854(5)			
Ni(2)-C(21)	1.873(4)	C(22)-Ni(2)-C(21)	89.4(2)	
Ni(2)-C(22)	1.860(4)			
Ni(3)-N(31)	2.100(3)			
Ni(3)-N(41)	2.078(3)	N(41)-Ni(3)-N(31)	78.72(11)	
Ni(3)-N(51)	2.088(3)	N(51)-Ni(3)-N(61)	79.14(11)	
Ni(3)-N(61)	2.093(3)			
Ni(3)-N(71)	2.080(3)	N(71)-Ni(3)-N(81)	78.90(11)	
Ni(3)-N(81)	2.100(3)			
C(11)-N(11)	1.149(5)	N(11)-C(11)-Ni(1)	177.4(4)	
C(12)-N(12)	1.137(5)	N(12)-C(12)-Ni(1)	178.6(4)	
C(21)-N(21)	1.147(5)	N(21)-C(21)-Ni(2)$^{\#2}$	177.7(4)	
C(22)-N(22)	1.137(4)	N(22)-C(22)-Ni(2)$^{\#2}$	179.2(4)	
N(31)-C(35)	1.332(4)	C(35)-N(31)-C(31)	118.3(3)	
N(31)-C(31)	1.364(4)			
C(31)-C(41)	1.465(5)			
N(41)-C(45)	1.343(4)	C(45)-N(41)-C(41)	118.0(3)	
N(41)-C(41)	1.359(4)			
N(51)-C(55)	1.339(4)	C(55)-N(51)-C(51)	118.1(3)	
N(51)-C(51)	1.358(4)			
C(51)-C(61)	1.484(5)			
N(61)-C(65)	1.326(4)			
N(61)-C(61)	1.351(4)	C(65)-N(61)-C(61)	118.4(3)	
N(71)-C(75)	1.349(4)			
N(71)-C(71)	1.353(4)	C(75)-N(71)-C(71)	117.7(3)	
C(71)-C(81)	1.482(5)			
N(81)-C(85)	1.337(4)	C(85)-N(81)-C(81)	117.8(3)	
N(81)-C(81)	1.351(4)			
N(91)-C(91)	1.341(5)	C(91)-N(91)-C(95)	116.3(4)	
N(91)-C(95)	1.346(5)			
C(91)-C(91)$^{\#1}$	1.502(7)			

Symmetry transformations used to generate equivalent atoms: $^{\#1}$ $-x, -y, -z+1$; $^{\#2}$ $-x+1/2, y+1/2, -z+1/2$

Table 4 Hydrogen bond data for Nibp3.

D	H	A	D-A	D-H	H..A	D-H..A	Symmetry of A
O(1)	H(O11)	O(2)	2.817(5)	0.96	1.87(1)	169(4)	x,y,z
O(1)	H(O12)	O(6)	2.863(5)	0.96	2.06(3)	141(4)	x,y,z
O(2)	H(O21)	O(4)	2.751(5)	0.96	1.83(2)	161(4)	x,y,z
O(2)	H(O22)	N(12)	2.868(6)	0.96	1.94(2)	161(4)	$0.5 - x,y - 0.5,1.5 - z$
O(3)	H(O31)	O(1)	2.816(5)	0.96	1.859(7)	174(4)	x,y,z
O(3)	H(O32)	N(21)	2.988(5)	0.96	2.04(1)	171(4)	x,y,z
O(4)	H(O41)	N(22)	2.976(5)	0.96	2.12(3)	148(4)	$0.5 - x,y - 0.5,1.5 - z$
O(4)	H(O42)	O(95)	2.788(5)	0.96	1.83(1)	172(4)	x,y,z
O(5)	H(O51)	N(11)	2.906(6)	0.96	2.21(4)	129(4)	x,y,z
O(5)	H(O52)	O(3)	2.818(5)	0.96	1.92(2)	154(5)	$0.5 - x,y + 0.5,1.5 - z$
O(6)	H(O61)	N(22)	2.957(5)	1.17	1.88	151(4)	x,y,z
O(6)	H(O62)	O(2)	2.957(5)	1.10	1.89	162(4)	$0.5 - x,y + 0.5,1.5 - z$

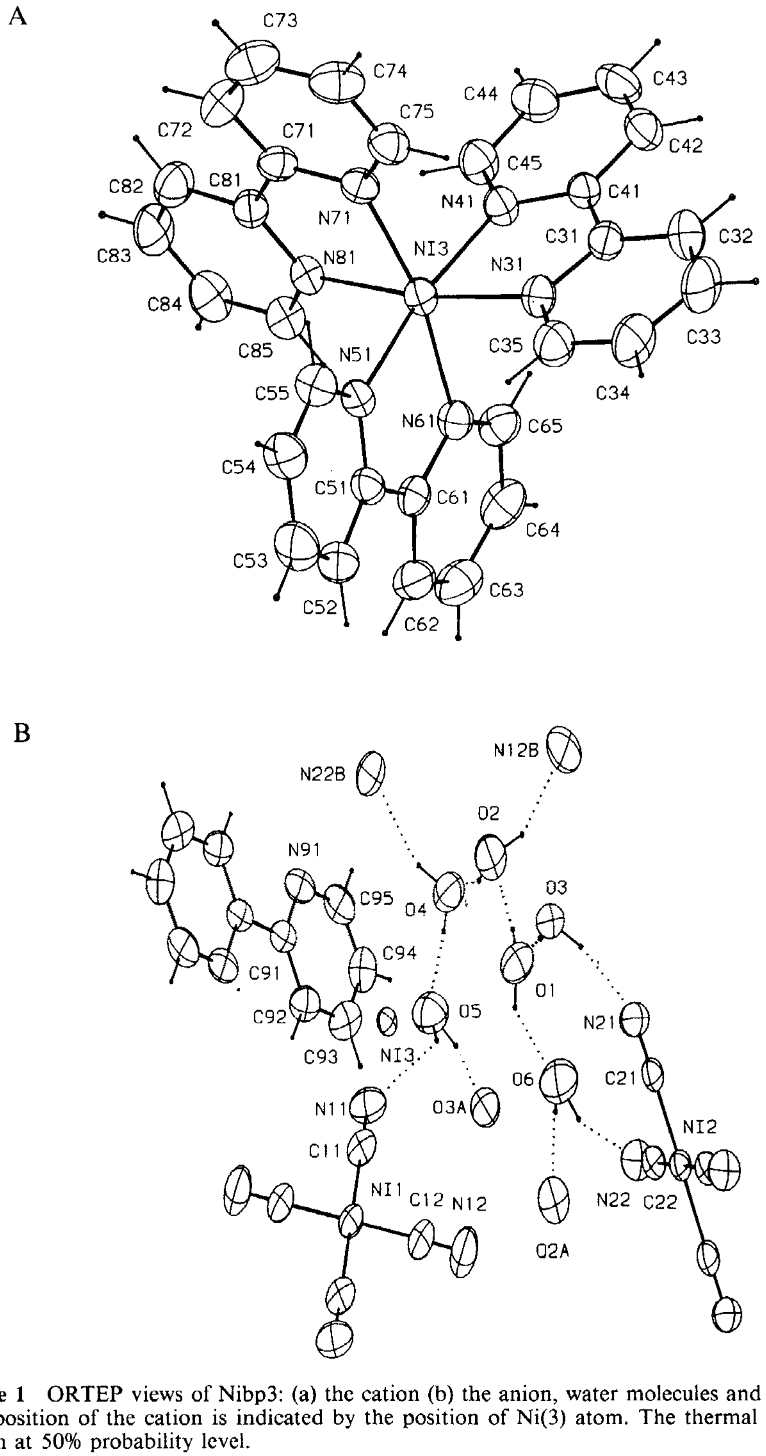

Figure 1 ORTEP views of Nibp3: (a) the cation (b) the anion, water molecules and bpy molecule. The position of the cation is indicated by the position of Ni(3) atom. The thermal ellipsoides are drawn at 50% probability level.

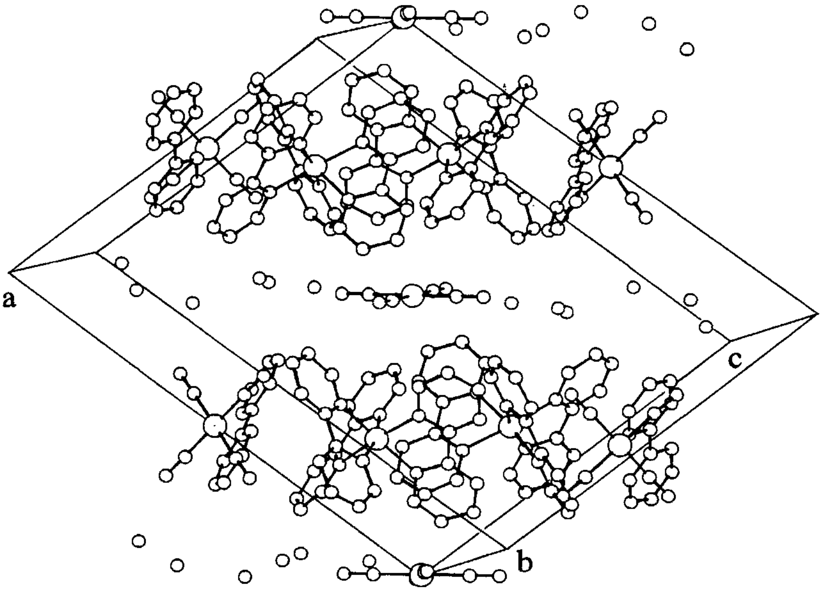

Figure 2 View on the layered structure of Nibp3.

complex $[Ni(bpy)_3]_2[Ag(CN)_2]_3 \cdot Cl \cdot nH_2O$.[17] The presence of additional bpy could be explained as filling the free space in the cavities formed by HBs to obtain better packing of the structure. If one regards the hydrophilic part as a host and the hydrophobic part as a guest, this complex could be included in the group of host-guest complexes. Similarity with regard to the host-guest type structure shows the compound $K_2[H_3NCH_2COCH_2NH_3]$ $[PtCl_4]_2 \cdot 3H_2O$.[18]

As the structure is centrosymmetric, both enantiomers of the cation are present in the unit cell. The observed bond distances and angles in the cation are similar to the corresponding values found in $[Ni(bpy)_3]SO_4 \cdot 7.5H_2O$.[19] In both crystallographically independent $[Ni(CN)_4]^{2-}$ anions the nitrogen atoms are displaced from the planes formed by nickel and carbon atoms, the maximal deviation being 0.052(4) Å for the N(11) atom. Such deformation may be due to the formed HBs with water molecules. The bond distances and angles are normal.[9]

Acknowledgement

The authors thank Prof. E. Davies (Univ. of Lancaster, GB) for valuable discussions and Prof. A. Hardy (Univ. of Poitiers, France) for the permission to use the diffractometer. (JČ) thanks the University of Poitiers (France) for financial support.

Supplementary Data

Anisotropic displacement parameters, hydrogen coordinates, full bond lengths and angles and F_o/F_c tables are available from JČ.

References

1. A. Caneschi, D. Gatteschi, L. Pardi, and R. Sessoli, in Perspectives in Coordination Chemistry, (Eds., A.F. Williams, C. Floriani, A.E. Merbach, Verlag Helvetica Chimica Acta, Basel & Verlag Chemie, Weinheim, 1992), pp. 109–128.
2. H.O. Stumpf, Y. Pei, O. Kahn, J. Sletten and J.P. Renard, *J. Am.Chem. Soc.*, **115**, 6738 (1993).
3. M. Orendáč, A. Orendáčová, J. Černák, A. Feher, P.J.C. Signore, M.W. Meisel, S. Merah and M. Verdaguer, *Journal of Magnetism and Magnetic Materials*, **140-4**, 1643 (1995).
4. M. Orendáč, A. Orendáčová, A. Fehér, J. Chomič, J. Černák, V.V. Szvyagin, V.V. Eremenko and V.V. Pishko, *Journal of Magnetism and Magnetic Materials*, **140-5**, 1645 (1995).
5. F. Feigl, V. Demant, and O.E. de Oliveira, *Anais Assoc. Quím. Brasil*, **3**, 72 (1945).
6. L. Rostášová, (1989). Diploma work, Dept. Inorg. Chem., P. J. Šafárik University, Košice, Slovakia.
7. M. Hashimoto and T. Iwamoto, *Acta, Cryst.* **C50**, 496 (1994).
8. T. Iwamoto, In *Inclusion Compounds*, **Vol. 5** (Eds., J.L. Atwood, J.E.D. Davies, D.D. MacNicol, Oxford University Press, Oxford, 1991), p. 177.
9. J. Černák, M. Dunaj-Jurčo, M. Melník, J. Chomič and J. Skoršepa, *Rev. Inorg. Chem.*, **9**(2–3), 259 (1989).
10. P. Gravereau, (1982). LOPOTRI. Program for data reduction. Univ. of Bordeaux, France. Unpublished.
11. G.M. Sheldrick, *Acta Cryst.*, **A46**, 467 (1990).
12. G.M. Sheldrick, *J. Appl. Cryst.* In preparation.
13. C.K. Johnson, (1965). ORTEP. Report ORNL-3794. Oak Ridge National Laboratory, Tennessee, USA.
14. P. Ugliendo, G. Borzani, D. and Viterbo, *J. Appl. Cryst.* **21**, 75 (1988).
15. F.H. Allen, S.A. Bellard, M.D. Brice, B.A. Cartwright, A. Doubleday, H. Higgs, T. Hummelink, B.G. Hummelink-Peters, O. Kennard, W.D.S. Motherwell, J.R. Rodgers and D.G. Watson, Cambridge Structural Database System (CSDS). Univ. of Cambridge, England (1993).
16. S.R. Hall, D.L. Kepert, C.L. Raston, and A.H. White, *Aust II J. Chem.*, **30**, 1955 (1977).
17. J. Černák, M. Kaňuchová, I. Potočňák, J. Chomič, J. Kameníček and Z. Žák, *Acta Cryst.*, **C50**. 1563 (1994).
18. M. Kapon, D. Cwikel, I. Agmon and M. Cais, *J. Incl. Phenom. Mol. Recogn. Chem.*, **10**, 225 (1991).
19. A. Wada, N. Sakabe and J. Tanaka, *Acta Cryst.*, **B32**, 1121 (1976).