

Monomeric and polymeric dinuclear complexes of Co(II) or Ni(II) with calix[4]arene-tetraphosphineoxide

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Abstract Monomeric and polymeric 1:2 complexes of a novel calix[4]arene-tetraphosphineoxide with Co(II) or Ni(II) nitrates were synthesized and analyzed by the X-ray method. In the monomeric complexes each metal cation is coordinated by two bidentate NO₃-ligands as well as by two proximal P=O groups at the calixarene skeleton. In the nickel metallopolymer one sort of the cations is bound by the two proximal P=O-groups but other cations link neighboring calixarene molecules through P=O...Ni...O=P chains. The complexes possess molecular cavities or channels filled by solvent molecules.

Keywords Calixarenes · Phosphine oxides · Cobalt and nickel complexes · Organometallic polymers

Introduction

Calix[4]arenes bearing donor ligand groups are suitable platforms for the design of transition metal complexes [1, 2]. Due to proximity of metalcentre to the molecular cavity these complexes can be applied as functional materials combining catalytic and supramolecular properties [3–5]. Recently the methods of anchoring of calix-

arenes onto silicagel surface have been developed, thus making calixarene metallocomplexes perspective for application in heterogeneous catalysis [6].

The structure of calixarenes metallocomplexes is determined by the nature and spatial organization of the ligand groups on the macrocyclic scaffold as well as by the coordination properties of the metal cation. Dimeric complexes where calixarenes fragments are bound by metal ions through oxygen atoms of the lower rim were synthesized by the reactions of tert-butylcalix[4]arene **1** with amide complexes of cobalt, iron and titanium [7]. In these complexes Ti⁴⁺ ions are coordinated only by de-protonated OH-groups of **1**, while the coordination sphere of Co and Fe is completed by THF or NH₃ molecules. The reaction of the calix[4]arene **1** with NbCl₅ also leads to dimeric product, bonding being performed by Nb₂OCl₄ cluster fragment [8].

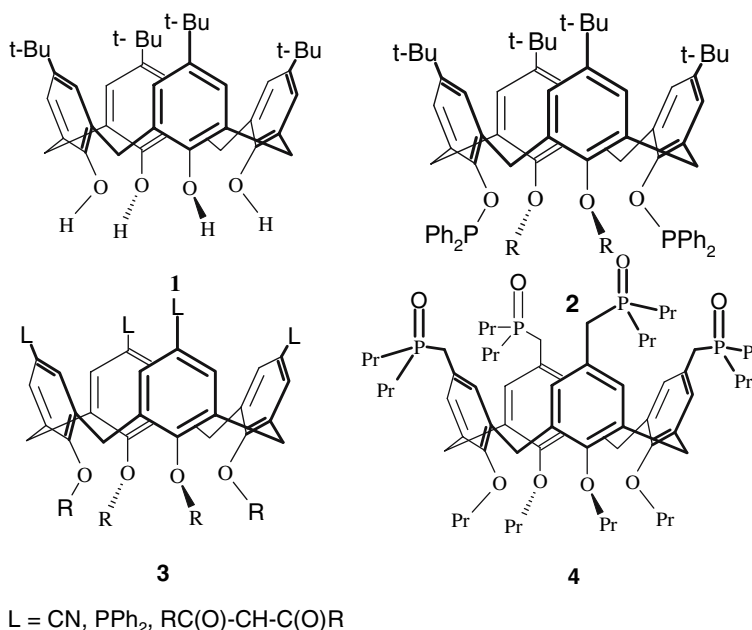
Calix[4]arene **2** modified at the lower rim of macrocycle with Ph₂P binding groups forms both monomeric and dimeric complexes with PtCl₂, PdCl₂, (CuCl)₂ [9, 10]. Dimeric capsular complexes were obtained by the reaction of palladium, cobalt, nickel and copper salts with calixarenes **3** upper-rim functionalized with phosphine, acetylacetonate, nitril, and sulfonate groups [11–13]. Few number of structurally characterized oligomeric and polymeric cyanocalixarene complexes with transition metals are reviewed in the survey [14]. Both porous organometallic polymers and calixarenes are considered as prospective materials for hydrogen storage [15, 16].

In the present paper we report the synthesis and the structural investigation of nickel and cobalt complexes with new tetradentate ligand—calix[4]arene **4** containing phosphineoxide donor groups at the upper rim of macrocycle. At the best of our knowledge this is first example of calixarene phosphineoxides complexes with transition metals characterized by X-ray method.

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Experimental

All reagents used were of standard pure grade. Co(NO₃)₂ · 6H₂O and Ni(NO₃)₂ · 6H₂O were additionally recrystallized from 0.1 M HNO₃. Routine NMR-spectra were recorded on the Varian spectrometer (VXR-300). Chemical shifts are in relation to TMS (inner standard) for (¹H) and to 5% H₃PO₄ (outer standard) for (³¹P). IR-spectra of the complexes were recorded in KBr pellets on the Specord M-80 instrument. To assign absorption bands respondent for coordinated NO₃-groups the IR-spectrum of pure ligand **4** was subtracted from spectra of complexes.

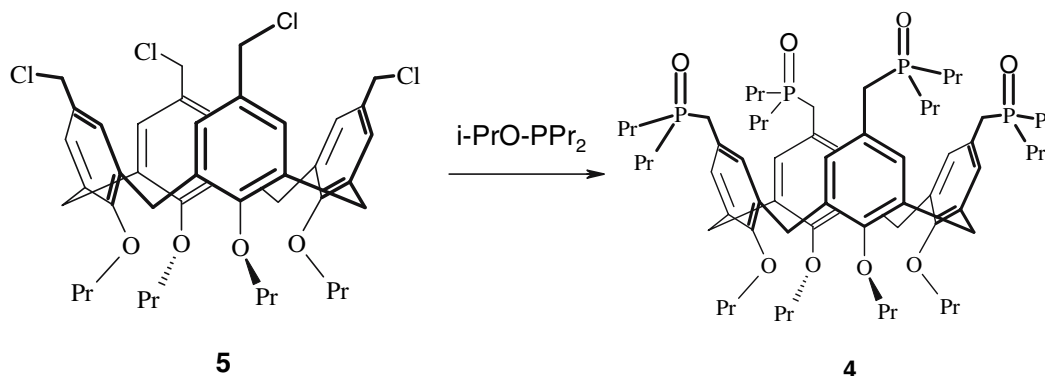
Synthesis of calixarene tetraphosphineoxide **4**

Calixarene **4** was synthesized by the Arbuzov reaction of tetrakis-(chloromethyl)calixarene **5** with isopropyl ester of dipropylphosphinic acid similar to method [17].

The AB spin system for axial and equatorial protons of the ArCH₂Ar methylene links in the ¹H NMR spectra ($\Delta\delta = 0.98$ ppm and $^2J_{\text{HH}} = 13.35$ Hz) confirms the *cone* conformation of the macrocyclic skeleton suitable for complexation of metal cation in solution.

5,11,17,23-tetrakis-(dipropylphosphinylmethyl)-25,26,27,28-tetrapropoxycalix[4]arene **4**

Mixture of tetrachloromethylcalix[4]arene **5** (5.0 g, 0.006 mol) and isopropyl dipropylphosphinite (22.5 g, 0.127 mol) was stirred under heating at 140 °C during 2 h. The excess of the phosphorylating agent was removed in vacuum. Solid residual was washed with dry hexane (3 × 25 ml) and dried in vacuum. Calixarene phosphineoxide **4** was obtained as white hygroscopic powder (6.78 g, 96%). Melting point 74–76 °C. ¹H NMR (δ ppm, CDCl₃, TMS): 0.97 (m, 36H, CH₃), 1.46 (m, 32H, -(CH₂)₂-CH₃),

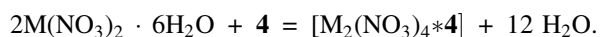


1.84 (m, 8H, O—CH₂—CH₂—CH₃), 2.72 (d, 8H, ³J_{PH} = 13.2 Hz, Ar—CH₂—P), 3.05 and 4.03 (two d, 8H, ²J_{HH} = 13.35 Hz, Ar—CH₂—Ar), 3.78 (t, 8H, O—CH₂), 6.44 (s, 8H, ArH). ³¹P NMR (δ, ppm, CDCl₃): 42.40.

For **5**: found, % C—68.55, H—8.71, P—10.53;
calculated, % C—69.38, H—9.18, P—10.53.

Synthesis of complexes

Complexes M₂(NO₃)₄***4** (M = Co, Ni) were prepared with almost quantitative yields (90–95%) by the reaction of solid salts M(NO₃)₂ · 6H₂O with solution of **4** in CH₂Cl₂ or acetone at stoichiometric reagent ratio:



M = Co. Co(NO₃)₂ · 6H₂O (59 mg, 0.2 mmol) was stirred at the room temperature in solution of **4** (120 mg, 0.1 mmol) in CH₂Cl₂ (3–5 ml) until complete dissolving of cobalt nitrate. After evaporation of the mixture to 1–1.5 ml the violet [Co₂(NO₃)₄***4**] (complex **6**) was precipitated by addition of (C₂H₅)₂O (10–15 ml). The complex is well soluble in CH₂Cl₂, CHCl₃ and acetone and almost insoluble in ether and heptane. Single crystal **6** suitable for X-ray analysis was prepared by slow diffusion of (C₂H₅)₂O to the solution of complex in CH₂Cl₂ during 1–2 days. The complex crystallizes as solvate Co₂(NO₃)₄***4** · 2CH₂Cl₂ (C₂H₅)₂O losing solvent molecules on air. IR (cm⁻¹): 810—δ(NO₃); 1288—ν_s(ONO₂); 1487—ν_{as}(ONO₂); 1022—ν(N = O); 1149—ν(P = O).

For C₆₈H₁₀₈P₄O₂₀Co₂N₄

Calcd.

(without solvent) %: C—52.9 H—7.0 N—3.63 Cl—0.

Found, %: C—50.8 H—6.9 N—3.56, Cl—1.35.

M = Ni. The mixture of Ni(NO₃)₂ · 6H₂O (59 mg, 0.2 mmol) and **4** (120 mg, 0.1 mmol) was boiled 2–3 h in CH₂Cl₂ (3–5 ml). The gold-yellow precipitate of Ni₂(NO₃)₄***4** (complex **7**) was formed after addition of (C₂H₅)₂O (10–15 ml) to the cooled reaction mixture. Single crystals suitable for X-ray analysis was prepared by slow diffusion of (C₂H₅)₂O to diluted (≈10⁻⁴–10⁻³ M) solution of the complex in CH₂Cl₂ during 10–15 days. IR (cm⁻¹): 808—δ(NO₃); 1282—ν_s(ONO₂); 1500—ν_{as}(ONO₂); 1020—ν(N = O); 1141—ν(P = O).

For C₆₈H₁₀₈P₄O₂₀Ni₂N₄

Calcd.

(without solvent) %: C—52.9 H—7.0 N—3.63, Cl—0.

Found, %: C—53.8 H—7.1 N—3.30, Cl—0.

The measurement of diffraction was performed on automatic diffractometer Bruker Nonius X8Apex CCD at 100 K (MoK_α-radiation, graphite monochromator, φ, ω-scanning). The absorption was corrected by SADABS program [18]. All structures were solved by means of the direct methods and refined by full-matrix least-square techniques with the use of the program SHELXTL [18]. Hydrogen atoms were calculated to their idealized positions and were refined as riding atoms. Crystal data and structural refinements details are shown in Table 1. Powder diffraction pattern of **6** shows that the lattice is partially disordered on the air though the long-distance order retains (Fig. 1). The crystals of the complex **7** are quickly destroyed at air resulting to X-ray amorphous product. Cell parameters were defined for three single crystals of **7** separated from different syntheses (Table 2). The quality and the size of the crystals did not allow solving the structure in all cases but similar values of cell parameters indirectly testify the crystals are representative of the solid as the whole.

Table 1 Crystal data and structural refinement for M₂(NO₃)₄***4**

M=	Co	Ni
Gross formula	C ₆₈ H ₁₀₈ N ₄ O ₂₀ P ₄ Co ₂ * (C ₂ H ₅) ₂ O*2CH ₂ Cl ₂	C ₆₈ H ₁₀₈ N ₄ O ₂₀ P ₄ Ni ₂
Molecular weight	1787.37	1225.87
Space group	P2 ₁ 2 ₁ 2 ₁	Pbca
a, Å	17.1761(14)	39.0511(13) 39.65 ^a ; 39.18 ^a
b, Å	17.4337(15)	57.409(2) 57.31 ^a ; 57.66 ^a
c, Å	29.691(2)	17.4346(5) 17.42 ^a ; 17.43 ^a
Cell volume, Å ³	8890.6(13)	39086.5(12)
Z	4	16
Data collected	33932	135858
Unique data	16074	34275
R (I < 2δ)	R = 0.0736 wR = 0.175	R = 0.152 (0.203 ^b) wR = 0.367
R _{all}	R = 0.108 wR = 0.187	R = 0.226 wR = 0.403
T, K	100	100
Crystal size, mm	0.32 * 0.3 * 0.24	0.9 * 0.35 * 0.32

^a Cell parameters defined for crystals of **7** separated from different syntheses. The cell is orthorhombic in all cases

^b Before SQUEEZE

Fig. 1 Experimental (a) and calculated (b) powder diffraction patterns of complex **6**

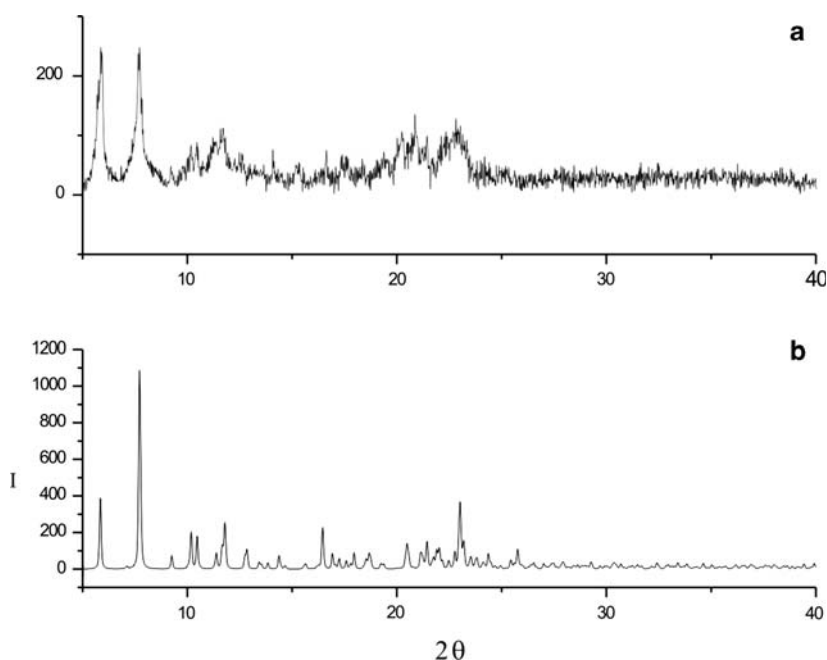


Table 2 Average distances and bond lengths in $M_2(NO_3)_4 \cdot 4$

	$Co_2(NO_3)_4 \cdot L$	$Ni_2(NO_3)_4 \cdot L$ monomer	$Ni_2(NO_3)_4 \cdot L$ polymer
$d(M-OP)$, Å	1.968–1.988	1.962–1.983	1.891–1.995
$d(M-ON)$, Å	2.108–2.215	2.039–2.159	2.082–2.259
$d(N-O_{coord})$, Å	1.259–1.286	1.255–1.329	1.277–1.369
$d(N-O_{free})$, Å	1.211–1.229	1.191–1.240	1.205–1.263
$d(P1-P2)$	5.457(2)	5.321(4)	5.192(4)
$d(P3-P4)$	5.371(2)	5.415(4)	7.736(6)
$d(P2-P3)$	7.932(2)	7.600(3)	7.153(7)
$d(P1-P4)$	7.771(3)	7.824(4)	7.467(5)
$\angle [C4]-A^a$	81.6	79.3	95.4
$\angle [C4]-B^a$	81.4	79.5	95.5
$\angle [C4]-C^a$	140.5	141.9	130.9
$\angle [C4]-D^a$	136.6	136.0	137.2

^a Angles between planes through the inner calixarene cavity

Both crystal packages contain large cavities, in the lattice of **6** the cavities are filled with disordered solvent molecules that were identified and refined by routine structural analysis. The refinement of the structure **7** shown large channels filled with strongly disordered solvent molecules that could not be refined properly by means of SHELX. The additional analysis by means of SQUEEZE procedure of the PLATON [19] was carried out to calculate the electron density in the channels and to estimate the number of solvent molecules. SQUEEZE analysis found the large cavity with 2193 \AA^3 volume at (0.206, 0.260, 0.601) and three symmetric cavities ($1/2 - x, -y, 1/2 + z$; $1/2 + x, 1/2 - y, -z$; $-x, 1/2 + y, 1/2 - z$) corresponding to centers of the channels. Also four voids of lower volume (192 \AA^3) were found at (0,0,0; $1/2, 0, 1/2$; $1/2, 1/2, 0$; $0, 1/2, 1/2$). The residual electron number in each of the large cavities is

equal $119 \pm 2 e^-$ and in each small one is $33.3 \pm 0.1 e^-$. Since molecules of used solvents (CH_2Cl_2 or $(C_2H_5)_2O$) have 42 electrons, the total electron number per unit cell ($609 e^-$) corresponds to 14.5 solvent molecules. From these molecules 3 or 4 one are located in small cavities and others are in the channels of lattice.

Results and discussion

The structure of $Co_2(NO_3)_4 \cdot 4$

The main asymmetric unit of the crystal cell is the molecular fragment $Co_2(NO_3)_4 \cdot 4$ (Fig. 2), both cobalt atoms being coordinated by two adjacent PO-groups of the calixarene upper rim and by two bidentate NO_3^- -ligands.

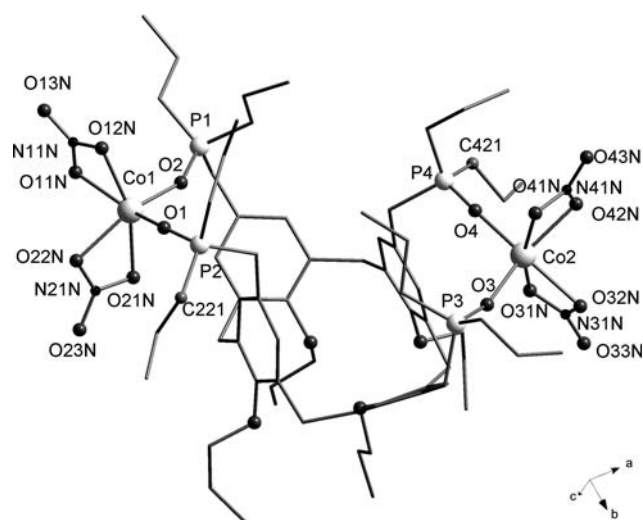


Fig. 2 The structure of $\text{Co}_2(\text{NO}_3)_4 \cdot 4$ unit

Shortest intermolecular contacts between uncoordinated oxygen of the nitrate-groups and hydrogen atoms of methylene groups $\text{P}-\text{CH}_2$ $\text{O13N}-\text{C221}$ ($x, y - 1/2, 3/2 - z$, $3.246(8) \text{ \AA}$) и $\text{O33N}-\text{C421}$ ($1 - x, 1/2 + y, 3/2 - z$, $3.171(9) \text{ \AA}$) leads to the formation of planes composed from the complex molecules parallel to $[001]$ plane. In each plane $\text{Co}_2(\text{NO}_3)_4 \cdot 4$ fragments are packed with alternation of “upper-lower rim” orientation that leads to channel-like voids along a axis with total volume equal 1476 \AA^3 per unit cell (17% of cell volume) containing four complex molecules (Fig. 3). The voids are completely filled by partially disordered molecules of CH_2Cl_2 and $(\text{C}_2\text{H}_5)_2\text{O}$. On the air the crystals slowly lose the solvent molecules that should be the reason for deviation between calculated and experimental data of the elemental analysis. According to the chlorine content after 3 months the substance retains $\approx 10\%$ of CH_2Cl_2 molecules if compared with structural data for the fresh crystal. Small angle peaks in experimental and calculated powder X-ray pattern of **6** are the same (Fig. 1). So we suppose that the sample keeps the long-distance order and main structural features after solvent removal. At the same time disorder in positions of alkyl radicals leads to partially amorphous structure.

Each of cobalt atoms in **6** is coordinated by six oxygen atoms. Two adjacent PO-groups of calixarene **4** are *cis*-coordinated to cobalt and two nitrate ligands have a bidentate coordination filling the coordination sphere of the metal to distorted octahedron (Fig. 2; Table 2). Distances $\text{Co}-\text{O}(\text{P})$ for both metal atoms are shorter ($1.968\text{--}1.988 \text{ \AA}$) than bond lengths $\text{Co}-\text{O}(\text{N})$ ($2.111\text{--}2.215 \text{ \AA}$), the former distances being close to ones for $\text{CoX}_2(\text{R}_3\text{PO})_2$ complexes ($1.976\text{--}1.990 \text{ \AA}$ depending on X [20]). All four $\text{Co}-\text{O}(\text{N})$ distances for Co1 atom are in the range $2.139\text{--}2.167 \text{ \AA}$ and the coordination of NO_3 -groups to this metal atom is

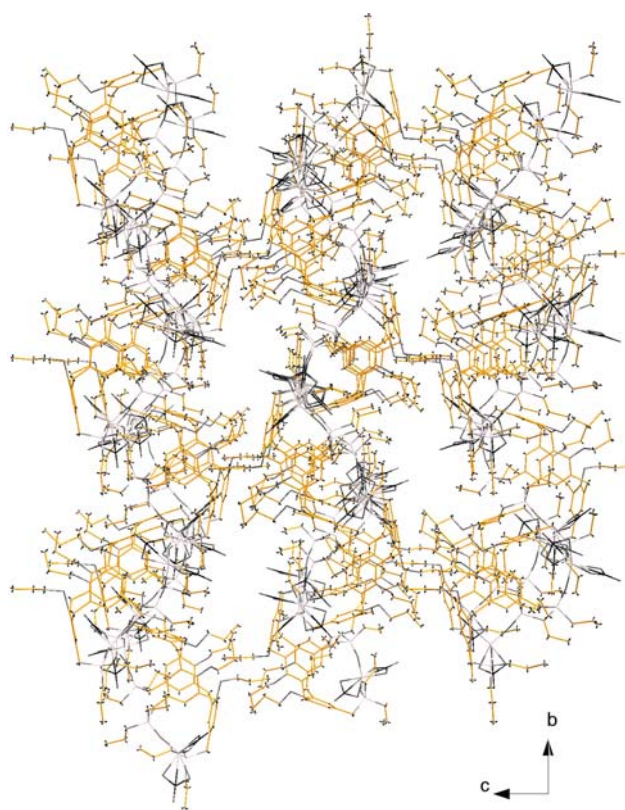


Fig. 3 View down $[100]$ of the crystal packing of $\text{Co}_2(\text{NO}_3)_4 \cdot 4$. Solvent molecules are omitted

almost symmetric. The coordination of nitrate anions to the Co2 is less symmetric and the difference between “short” and “long” $\text{Co}-\text{O}(\text{N})$ distances is near 0.1 \AA . In each of the four nitrate ligands bond lengths $\text{N}-\text{O}_{\text{coord}}$ ($1.259\text{--}1.286 \text{ \AA}$) are systematically higher than $\text{N}-\text{O}_{\text{free}}$ ($1.211\text{--}1.229 \text{ \AA}$). Since O13N and O33N take part in the intermolecular contacts, the bond lengths N11N–O13N ($1.229(9) \text{ \AA}$) and N31N–O33N ($1.224(8) \text{ \AA}$) are the longest ones among all $\text{N}-\text{O}_{\text{free}}$ distances.

Coordination of two $\text{Co}(\text{NO}_3)_2$ fragments by the $\text{P}=\text{O}$ groups leads to the “flattened cone” conformation of the calix[4]arene skeleton slightly deviating from C_{2v} -symmetry. Benzene rings A and B (Fig. 4; Table 2) are almost normal to the $[\text{C}4]$ plane including carbon atoms of methylene bridges $\text{Ar}-\text{CH}_2-\text{Ar}$ (angles between A, B planes and $[\text{C}4]$ are equal to 81.6° and 81.4°) while planes of C and D rings in respect to $[\text{C}4]$ are at angles 140.5° and 136.6° correspondingly. It is interesting to note that plane $[\text{P}4]$ including phosphorus atoms at the upper rim, plane $[\text{C}4]$ and plane $[\text{O}4]$ passing through oxygen atoms of the lower rim are almost parallel and angles between these planes do not exceed 3° . Bidentate coordination of each cobalt atom by two closest phosphoryl groups results in its spatial organisation. $\text{P}-\text{P}$ distances between PO-groups coordinated to the same cobalt atom are $5.457(2)$ and

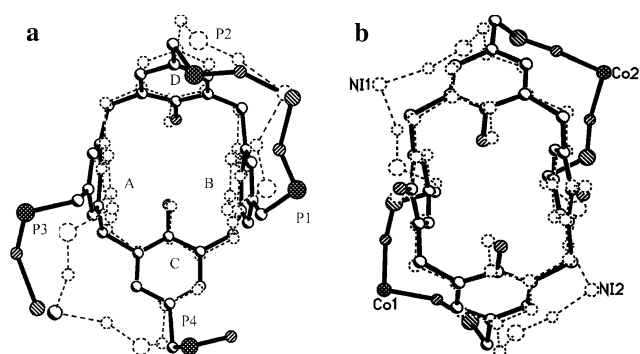


Fig. 4 Calixarene conformation in: (a) polymeric chain $\text{Ni}_2(\text{NO}_3)_4 \cdot 4$ and monomeric fragment $\text{Ni}_2(\text{NO}_3)_4 \cdot 4$ (dotted lines); (b) monomers $\text{Co}_2(\text{NO}_3)_4 \cdot 4$ and $\text{Ni}_2(\text{NO}_3)_4 \cdot 4$ (dotted lines)

5.371(2) Å. While the shortest P–P distances between PO-groups coordinated to different cobalt atoms in $\text{Co}_2(\text{NO}_3)_4 \cdot 4$ fragment are 7.932(2) and 7.773(3) Å.

The structure of $\text{Ni}_2(\text{NO}_3)_4 \cdot 4$

The crystallographic R-factor for the structure **7** is rather high as a consequence of significant disorder of the lattice solvent molecules and the extreme propensity to desolvate. Nevertheless gross structural features can be defined properly. In the crystal structure of **7** two types of main structural units are present both having the gross formula $\text{Ni}_2(\text{NO}_3)_4 \cdot 4$. The first one is the monomeric fragment $\text{Ni}_2(\text{NO}_3)_4 \cdot 4$ that is mirror-like to the structure of $\text{Co}_2(\text{NO}_3)_4 \cdot 4$ (Fig. 4b) with average bond lengths close to the lengths observed in $\text{Co}_2(\text{NO}_3)_4 \cdot 4$. Another unit is polymeric tape directed along axis *c*. The fragment of the tape is $\text{Ni}_2(\text{NO}_3)_4 \cdot 4$ complex where one nickel atom is coordinated by two adjacent PO-groups of one calixarene molecule while another Ni atom is bridging between two calixarene fragments and coordinated by two PO-groups from different calixarene molecules (Fig. 5). Due to the weak intermolecular interactions $\text{N}=\text{O} \cdots \text{H}-\text{CP}$ similar to the cobalt complex the package of monomeric fragments and polymeric tapes in the lattice of $\text{Ni}_2(\text{NO}_3)_4 \cdot 4$ results in the formation of channels along axis *c* (Fig. 6). The total volume of the channel voids is 8772 Å³ per one unit cell (22% of total cell volume). It is apparent that in the fresh-prepared crystals the cavities are filled by solvent molecules but because of strong solvent disorder these molecules cannot be defined by usual structural techniques. The residual electron number in the cavities is consistent with the presence of 14–15 molecules of CH_2Cl_2 or $(\text{C}_2\text{H}_5)_2\text{O}$ per unit cell. As long as both solvents have the same number of electrons per molecule we can estimate only total number of the solvent molecules. According to elemental analysis (no chlorine was found for the **7**) there are no CH_2Cl_2 molecules in dried compound. The small

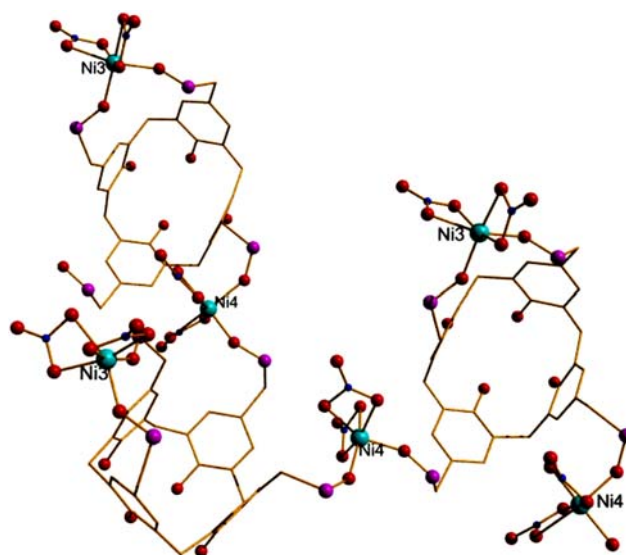


Fig. 5 Part of the polymeric chain $\text{Ni}_2(\text{NO}_3)_4 \cdot 4$. Propyl groups at the upper rim phosphorus atoms and the lower rim oxygen atoms are omitted for clarity

solvent weight in respect to the complex does not allow to make such unambiguous conclusion about the absence of $(\text{C}_2\text{H}_5)_2\text{O}$. Wide uncertain bands in powder diffraction pattern of aged samples of **7** indicate the formation of

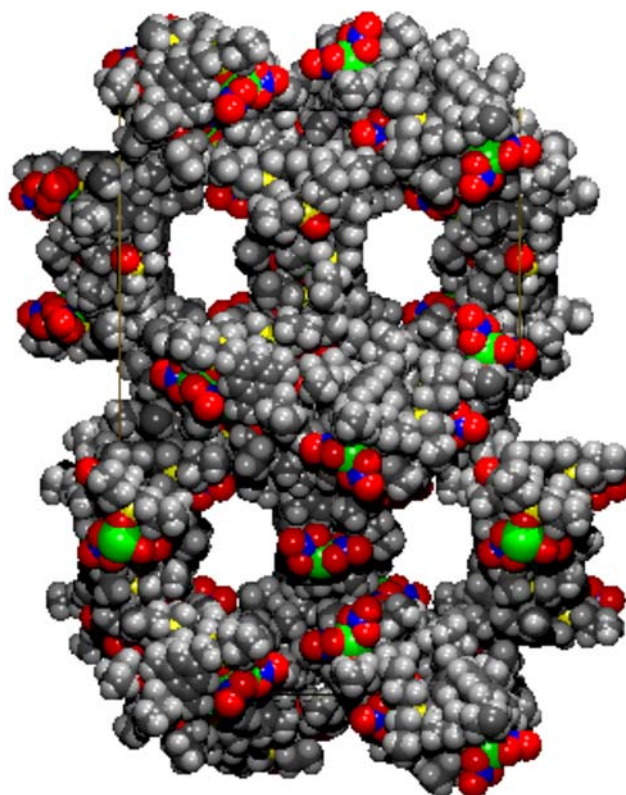


Fig. 6 Van-der-Vaals view down [001] of the crystal packing in $\text{Ni}_2(\text{NO}_3)_4 \cdot 4$

amorphous phases that can be related with the destruction of lattice after desolvation.

Coordination sphere of all four asymmetric nickel atoms is composed of six oxygens. Distances Ni–O(P) for three nickel atoms (two are from monomer and one is from polymeric chain that not bridging) are in the range 1.956–1.983 Å while Ni–O(P) bond lengths for bridging Ni atom is equal to 1.891(9) and 1.998(10) Å. Ni–O(N) distances varies from 2.039 to 2.259 Å and the average Ni–O(N) bond length for nickel atoms in monomer (2.089 Å) is slightly shorter than for bidentate coordinated (2.108 Å) and bridging (2.139 Å) nickel atoms of polymeric chains. In all NO₃-groups N–O_{coord} (1.255–1.369 Å) distances are longer than N–O_{free} (1.191–1.263 Å) as for the cobalt compound.

In the monomeric unit Ni₂(NO₃)₄*4 the calixarene adopts the “flattened cone” conformation with C_{2v}-symmetry. The angles between rings planes are practically the same as for Co₂(NO₃)₄*4 (Table 2; Fig. 4b). In the polymeric chain if compared with Co and Ni monomeric units arene rings A and B are turned out of the calixarene center while planes C and D are turned to the center. (Fig. 4a; Table 2). Angles between [C4] plane and A and B planes are 95.4° and 95.5° while angles between [C4] and C or D planes are corresponding to 130.9° and 137.2°. Polymeric coordination also leads to slight shrinking of P–P distance between PO-groups coordinated to the same nickel atom (Table 2) while d(P–P) between PO-groups coordinated to bridging nickel atoms in polymeric chain is equal to 7.736(6) Å.

Generally nickel and cobalt have the same (octahedron or distorted octahedron) coordination mode in the most part of the complexes. But the difference in distances and angles is always present. In M(Ph₃PO)₂(NO₃)₂ complexes distances M–OP for both metals are similar (1.972 Å for Ni and 1.977 Å for Co) while average M–ONO₂ distance for Co is 0.07 Å greater than for Ni [21]. The same picture was found for heterometallic complexes with Ph₃PO and [Ru–NO(NO₂)₄OH]²⁻ as ligands [22]. The tetrahedral distortion of CoO₆ polyhedron is larger than for NiO₆ both for heterometallic and for triphenylphosphine oxide complexes. It is possible that slight differences insignificant for monodentate ligands drastically change the coordination in case of preorganized calixarene-phosphineoxide.

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