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New alkoxycarbonyl derivatives of dibenzotetraaza[14]annulene. Crystal and molecular structure of [5,14-dihydro-7,16-diisopropoxycarbonyl-8,15-dimethyl-6,17-diphenyldibenzo[b,i][1,4,8,11]tetraazacyclotetra decinato(2-)-κ^4N]nickel(II)

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Abstract

The reaction of Ni(II) complex of 5,14-dihydro-6,17-dimethyl-8,15-diphenyldibenzo[b,i][1,4,8,11]tetraazacyclotetradecine with oxalyl chloride and appropriate alcohols and phenols afforded new *meso* alkoxy- and aryloxycarbonyl derivatives. The demetallation of Ni(II) complexes equipped with isopropoxycarbonyl-benzyloxycarbonyl-, 4-acetylphenoxycarbonyl- and biphenyloxycarbonyl- *meso* substituents by means of gaseous HCl gave corresponding free bases. Single crystal X-ray analysis of acetone solvate of isopropoxycarbonyl derivative disclosed the structure with saddle-shaped molecules arranged in stacking columns with molecules of acetone locked in the cavities and interacting with the host's molecules via CH·····O hydrogen bonds. The new products have been characterised by elemental analysis, ^{1}H, ^{13}C NMR, IR, ESI and MALDI MS spectra.

Keywords: Dibenzotetraaza[14]annulenes; Alkoxycarbonylation; Macrocyclic Schiff bases; Stacking; CH····O hydrogen bonds

1. Introduction

It is known from many reports that Ni(II) complex of dibenzotetraaza[14]annulene (**1**) (Scheme 1) can act as versatile supramolecular receptor for globular guests like carborane, C_{60}, C_{70}, S_8, and P_4Se_3 [1–3]. This was considered to be due to curved surfaces of the saddle-like molecules of **1**, exposed to interactions with complementary guests. The two concave surfaces, which provide the basis of a molecular cavity in the crystal lattice, are defined by the phenylene rings and diiminate fragments of **1**, tilted to opposite directions from the central N4 plane.

We have recently elaborated an efficient synthetic method allowing to easily introduce various substituents at the *meso* positions of dibenzotetraaza[14]annulene (**1**) via ester linkages [4]. In fact, the method enables to influence both the cavity dimensions and chemical character of the curvatures responsible for non-covalent interactions. The procedure has been already successfully applied for incorporation of **1** into crown ethers [5,6] and for preparation of new receptors equipped with chiral superstructure [7]. Herein we present a range of new ester-type derivatives of the complex **2**, synthesized by means of similar procedure (products **3**–**12**, Scheme 1). The demetallation of the complexes **4**, **7**, **8**, and **10** have also been accomplished with use of gaseous hydrogen chloride leading to corresponding macrocyclic Schiff bases **13**–**16** (Scheme 2).

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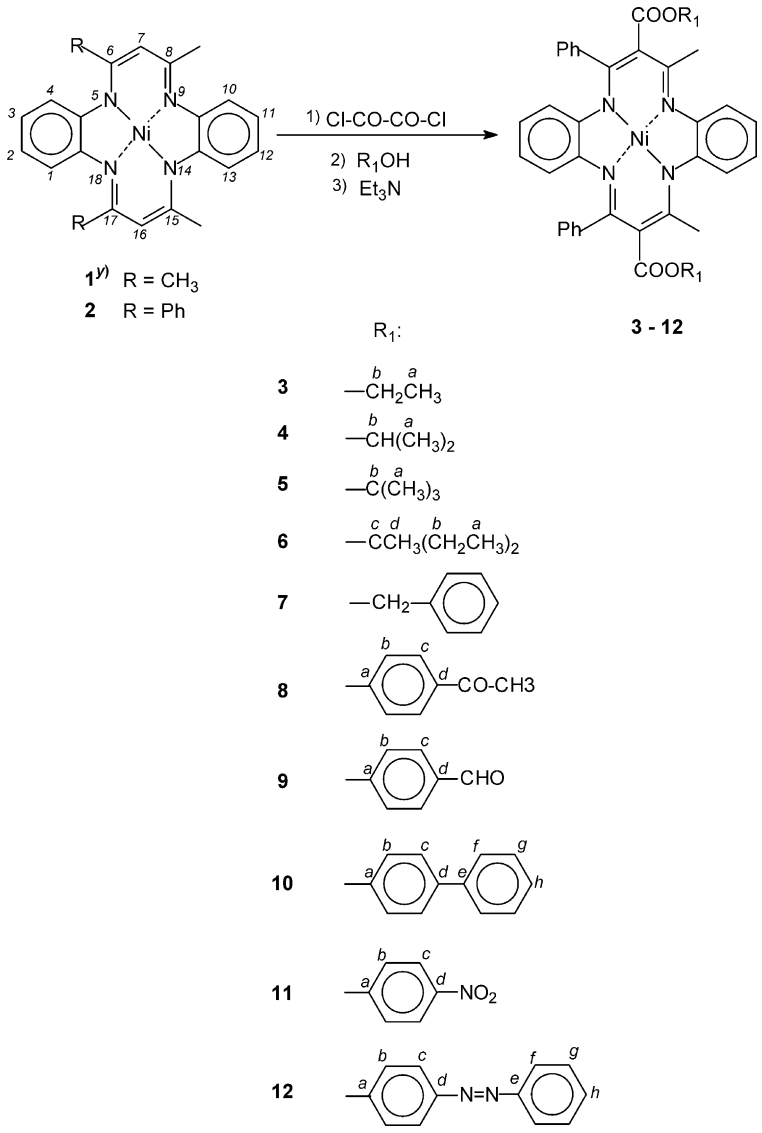


Scheme 1. (y) The results corresponding to $R = CH_3$ are reported in [4].

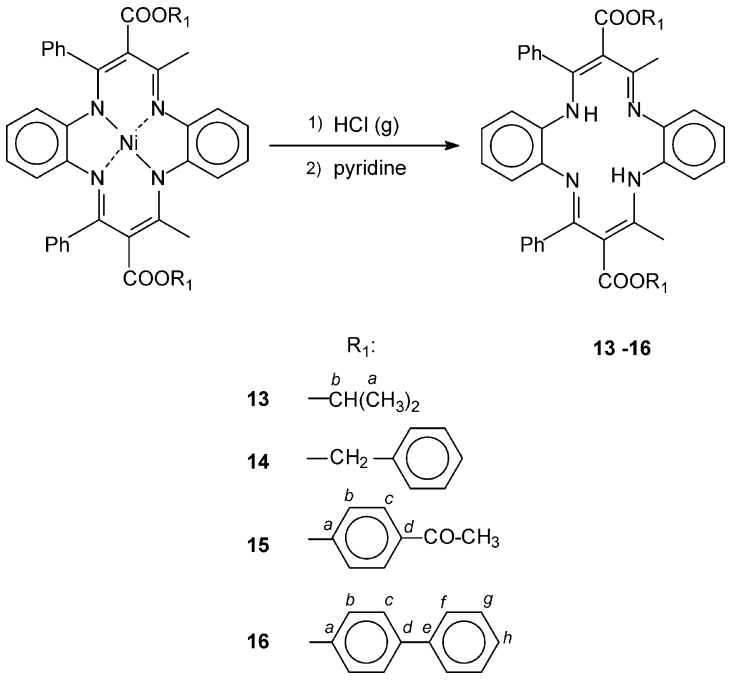
2. Experimental

2.1. Materials and equipment

Elemental analyses were performed with use of an Euro-EA (EuroVector) microanalyser. The IR spectra were recorded in KBr and hexachlorobutadiene with a BRUKER IFS 48 spectrometer. ^{1}H and ^{13}C NMR spectra were run on a BRUKER AMX instrument operating at 500 MHz, with TMS as internal standard ESI and MALDI-TOF MS spectra were taken on Finnigan MAT 95 and Voyager-Elite (PerSeptive Biosystem Inc.) mass spectrometers, respectively. The parent complex **2** was prepared by a procedure described earlier [8]. All solvents were dried using standard methods and freshly distilled before use. Alcohols and phenols as well as triethylamine were purchased from commercial sources (Fluka, Aldrich) and used as received. Oxalyl dichloride (Fluka) was distilled before use. Silica gel 60 (Fluka) (0.063–0.2 mm) and aluminum oxide 507 C (Fluka) were used for the column chromatography.

2.2. Synthesis of the complexes **3**–**12** *(general procedure)*

Oxalyl dichloride (0.35 g, 2.75 mmol) was added to a solution of the complex **2** (0.5 g, 0.95 mmol) in anhydrous toluene (50 ml). The reaction mixture protected from moisture was gently heated with stirring until initially green solution turned deep red (15 min). An alcohol (6 mmol) dissolved in small quantity of toluene was then added and the mixture was allowed to reflux for 30 min. During this time the colour of the solution changed slowly to deep green. An excess of triethylamine (3 ml) was then added and refluxing was



Scheme 2.

continued for further 30 min. A colourless precipitate of triethylamine hydrochloride was filtered off, the reaction mixture was evaporated to dryness under reduced pressure. The green solid residue was washed carefully with water and dried. Complexes **3**–**7** were isolated from the crude product with use of column chromatography (aluminum oxide, toluene–acetone (50:1)). Silica gel and methylene chloride as eluent were used for isolation of the complexes **8**–**12.** The main green fractions were collected, concentrated to small quantity and left for crystallisation. Crystals suitable for X-ray measurements were obtained by slow evaporation of acetone solution of the complex **4**.

2.3. Demetallation of the complexes **4**, **7**, **8**, and **10** (general procedure)

A stream of anhydrous hydrogen chloride was bubbled through a suspension of the appropriate complex (2 g) in acetonitrile (30 ml). The color of the reaction mixture changed slowly from green to orange. After about 20 min the passage of hydrogen chloride was stopped, the reaction flask was tightly closed and left overnight in a refrigerator. The solvent was evaporated under reduced pressure and solid residue was dissolved in pyridine (20 ml). An excess of cold water was then added with stirring to precipitate the free base. A yellow solid was filtered off, washed thoroughly with water and dried. The crude product was chromatographed on a column of silica gel with use of toluene–acetone (50:1) as eluent.

2.4. Crystallography

Single crystal X-ray diffraction data were collected on a KUMA4CCD κ-axis diffractometer with the use of graphite monochromated Mo Kα radiation applying ω-2θ and ω scan techniques. The crystal was positioned at 65 mm from the KM4CCD camera. Frames (1550) were measured at 0.7° intervals with a counting time of 35 s. The data were corrected for Lorentz, polarization effects and variation of a reference frames. No absorption correction was applied. Data reduction and analysis were carried out with the Kuma Diffraction (Wrocław, Poland) programs. The structure was solved by direct methods [9] and refined using SHELXTL [10]. The refinement was based on F^2 for all reflections except those with very negative F^2. Weighted R factors wR and all goodness-of-fit S values are based on F^2. Conventional R factors are based on F with F set to zero for negative F^2. The $F_o^2 > 2s(F_o^2)$ criterion was used only for calculating R factors and is not relevant to the choice of reflections for the refinement. The R factors based on F^2 are about twice as large as those based on F. Anisotropic temperature factors were used to describe the thermal motions of non-hydrogen atoms. Hydrogen atoms were located in an idealised averaged geometrical positions, allowed to ride at the heavy atoms and rotate around C–C bonds. The acetone is disordered over two sites with 50% probabilities. No hydrogen atoms for the acetone carbons were located. Atomic scattering factors for C, H, and O were derived from wave functions tabulated in Tables 6.1.1.4 and 4.2.4.2 from [11].

$2(C_{40}H_{38}N_4O_4Ni)\cdot CH_3COCH_3$ (**4**) formula weight = 1453; temp. = 293 K; wavelength = 0.71073 Å; triclinic; space group $P\bar{1}$; unit cell dimensions: $a = 11.376(2)$ Å, $b = 12.090(2)$ Å, $c = 14.155(3)$ Å, $\alpha = 91.53(3)°$, $\beta = 104.32(3)°$, $\gamma = 105.60(3)°$, vol. = 1807.8(6) Å^3; $Z = 1$; density(cal.) = 1.335 Mg/m^3; absorption coefficient = 0.586 mm^{-1}; $F(000) = 764$; crystal size = 0.40 × 0.30 × 0.20 mm; theta range for data collection = 3.65–22.5°; index ranges: $-12 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 13$, $-15 \leqslant l \leqslant 15$; reflections collected = 21,876; independent reflections = 9196[R(int) = 0.036]; refinement method: full-matrix least-squares on F^2; data/restraints/parameters = 9196/3/920; goodness-of-fit on $F^2 = 1.084$; final R indices [$I > 2\sigma(I)$]: $R1 = 0.0467$, $wR2 = 0.1102$; R indices (all data): $R1 = 0.0622$, $wR2 = 0.1228$, largest differential peak and hole = 0.51 and −0.34 e A^{-3};

3. Results and discussion

3.1. Synthesis and characterisation

The reactions of the complex **2** with oxalyl chloride and alcohols were carried out according to procedure similar to that described earlier [4]. The products were identified with use of the ^{1}H and ^{13}C NMR, IR, MS spectroscopy, and elemental analysis. Analytical and spectroscopic data and their assignments are compiled in Tables 1–3.

Worth of mention is that unlike to analogous derivatives of the complex **1** [4], pairs of geminal hydrogens and methyl groups placed at the α carbon of ester moieties in **3**, **4**, **7**, **13**, and **14** are considered to be diastereotopic. This is due to non-planar conformation of the macrocycle and to its non-symmetrical substitution by phenyl groups at the positions 6 and 17 of the ring. In consequence, non-equivalence of corresponding protons and methyl groups is observed in the ^{1}H and ^{13}C NMR spectra, respectively. Thus, protons of CH_2 groups of the complex **3** appear as two broad signals at δ 3.39 and 3.78 ppm (Table 2). Diastereotopic protons of methylene groups of the compound **7** and **14** show two doublets at δ 4.15 and 4.88 ppm, and at δ 4.42 and 4.91 ppm, respectively. Similarly, diastereotopic methyl groups of isopropoxycarbonyl substituents of **4** and **13** display two doublets in the ^{1}H NMR spectra – at δ 0.51 and 1.12 ppm, and at δ 0.61 and 1.07 ppm, respectively. Different resonances corresponding to these groups were also found in the ^{13}C NMR (δ 20.55 and 21.49 ppm, and δ 20.71 and 21.72 ppm, respectively) (Table 3).

3.2. Structure

The Ni(II) complex of isopropoxycarbonyl derivative **4** cocrystallises with one molecule of acetone in a general position of the triclinic $P\bar{1}$ space group with two moieties of **4** and one acetone molecule in the independent part of the unit cell. The structure consists of columns of stacked molecules of **4** mixed with acetone locked in cavities formed by the host moieties (see Fig. 1). The acetone molecules are disordered. The asymmetric location of the solvent molecule makes possibly centrosymmetric crystal of **4** acentric. All Ni–N bonds lengths are quite typical ranging from 1.81 to 1.87 Å. Also the values of the valence angles around the central Ni ion

Table 1

Compounds	Yield (%)	m.p. (°C)	Molecular formula	Molecular mass	MS (*m*/*z*)	Elemental analysis (%)					
						Found			Calculated		
						C	H	N	C	H	N
3	82	290	$C_{38}H_{34}N_4O_4Ni$	669.40	670.1[b]	67.9	4.90	8.45	68.18	5.12	8.37
4	74	>300	$C_{40}H_{38}N_4O_4Ni$	696.22	697.4[a]	69.03	5.46	7.56	68.88	5.49	8.03
5	81	205	$C_{42}H_{42}N_4O_4Ni$	724.26	725.4[a]	70.71	6.04	7.24	70.77[c]	5.96[c]	7.26[c]
6	85	236–239	$C_{46}H_{50}N_4O_4Ni$	780.32	780.8[a]	70.99	6.51	6.90	70.69	6.45	7.17
7	79	195–200	$C_{48}H_{38}N_4O_4Ni$	792.22	792.6[a]	72.27	6.64	6.84	72.21[d]	6.98[d]	6.81[d]
8	28	273–275	$C_{50}H_{38}N_4O_6Ni$	848.21	849[b]	70.92	4.39	6.43	70.69	4.51	6.59
9	63	280–285	$C_{48}H_{34}N_4O_6Ni$	820.18	821[b]	69.98	4.28	6.60	70.18	4.17	6.82
10	96	284	$C_{58}H_{42}N_4O_4Ni$	916.26	917[b]	75.92	4.52	6.10	75.91	4.61	6.11
11	25	258 dec.	$C_{46}H_{32}N_6O_8Ni$	854.16	855.10[b]	64.50	3.73	9.52	64.58	3.77	9.82
12	46	>300	$C_{58}H_{42}N_8O_4Ni$	972.27	973[b]	71.26	4.41	11.73	71.54	4.35	11.51
13	43	173–175	$C_{40}H_{40}N_4O_4$	640.30	641[b]	75.21	6.28	8.78	74.98	6.29	8.74
14	72	188	$C_{48}H_{40}N_4O_4$	736.30	737[b]	78.17	5.42	7.60	78.24	5.47	7.60
15	28	155	$C_{50}H_{40}N_4O_6$	792.29	815[a] [M + Na$^+$]	75.60	5.08	6.90	75.74	5.08	7.07
16	43	212–213	$C_{58}H_{44}N_4O_4$	860.34	861.3[a]	81.39	5.28	6.35	80.91	5.15	6.51

[a] ESI-MS.
[b] MALDI-TOF.
[c] Calc. for $M\cdot 1/2C_6H_5CH_3$.
[d] Calc. for $M\cdot 1/2CH_3COCH_3$.

Table 2

Compounds	IR ν (cm^{-1})	^1H NMR δ (ppm), $CDCl_3$	
		Macrocycle	7, 16-Substituents
3	1705 (C=O)	2.23 (s, 6H, CH_3), 5.45 (dd, 2H, *o*-C_6H_4, $H^{1,4}$), 5.94 (dd, 2H, *o*-C_6H_4, $H^{2,3}$), 6,73 (m, 2H, *o*-C_6H_4, $H^{10,13}$), 6.81 (m, 2H, *o*-C_6H_4, $H^{11,12}$), 7.32 (m, 10H, C_6H_5).	0.77 (b.t, 6H, CH_3), 3.39 (b.s, 2H, CH_2), 3.78 (b.s, 2H, CH_2)
4	1705 (C=O)	2.21 (s, 6H, CH_3), 5.39 (dd, 2H, *o*-C_6H_4, $H^{1,4}$), 5.91 (dd, 2H, *o*-C_6H_4, $H^{2,3}$), 6.71 (m, 2H, *o*-C_6H_4, $H^{10,13}$), 6.80 (m, 2H, *o*-C_6H_4, $H^{11,12}$), 7.24–7.32 (m, 10H, C_6H_5).	0.51 (d, $J = 5.0$ Hz, 6H, CH_3), 1.12 (d, $J = 4.7$ Hz, 6H, CH_3), 4.54 (m, 2H, CH)
5	1704 (C=O)	2.23 (s, 6H, CH_3), 5.41 (dd, 2H, *o*-C_6H_4 $H^{1,4}$), 5.91 (dd, 2H, *o*-C_6H_4, $H^{2,3}$), 6.72 (dd, 2H, *o*-C_6H_4, $H^{10,13}$), 6.80 (dd, 2H, *o*-C_6H_4, $H^{11,12}$), 7.35 (m, 10H, C_6H_5)	1.09 (s, 18H, H^a)
6	1705 (C=O)	2.22 (s, 6H, CH_3), 5.33 (dd, 2H, *o*-C_6H_4, $H^{1,4}$), 5.87 (dd, 2H, *o*-C_6H_4, $H^{2,3}$), 6.69 (dd, 2H, *o*-C_6H_4, $H^{10,13}$), 6.78 (dd, 2H, *o*-C_6H_4, $H^{11,12}$), 7.23–7.25 (m, 4H, C_6H_5), 7.32 (m, 6H, C_6H_5).	0.67 (t, 6H, CH_3^a), 0.76 (t, 6H, CH_3^a), 0.90 (s, 6H, CH_3^d), 1.16 (m, 2H, CH_2), 1.50 (m, 4H, CH_2), 1.84 (m, 2H, CH_2)
7	1718 (C=O)	2.22 (s, 6H CH_3), 5.43 (dd, 2H, *o*-C_6H_4, $H^{1,4}$), 5.93 (dd, 2H, *o*-C_6H_4, $H^{2,3}$), 6.73 (dd, 2H, *o*-C_6H_4, $H^{10,13}$), 6.81 (dd, 2H, *o*-C_6H_4, $H^{11,12}$), 7.04–7.06 (m, 4H, C_6H_5), 7.16–7.18 (m, 4H, C_6H_5), 7.26–7.28 (m, 12H, C_6H_5).	4.15 (d, $J = 11.5$ Hz, 2H, CH_2), 4.88 (d, $J = 11.3$ Hz, 2H, CH_2)[a]
8	1686 ($COCH_3$), 1732 (COO)	2.31 (s, 6H, CH_3), 5.48 (dd, 2H, *o*-C_6H_4, $H^{1,4}$), 6.02 (dd, 2H, *o*-C_6H_4, $H^{2,3}$), 6.82 (dd, 2H, *o*-C_6H_4, $H^{10,13}$), 6.90 (dd, 2H, *o*-C_6H_4, $H^{11,12}$), 7.27–7.47 (m, 10H, C_6H_5)	2.54 (s, 6H, $COCH_3$), 6.45 (d, $J = 8.7$ Hz, H^b), 7.80 (d, $J = 8.7$ Hz, H^c)
9	1704 (CHO), 1734 (COO)	2.39 (s, 6H, CH_3), 5.48 (dd, 2H, *o*-C_6H_4, $H^{1,4}$), 6.02 (dd, 2H, *o*-C_6H_4, $H^{2,3}$), 6.81 (dd, 2H, *o*-C_6H_4, $H^{10,13}$), 6.90 (dd, 2H, *o*-C_6H_4, $H^{11,12}$), 7.28 (m, 2H, C_6H_5), 7.35–7.42 (m, 8H, C_6H_5),	6.56 (d, $J = 8.3$ Hz, 2H, H^b), 7.71 (d, $J = 8.4$ Hz, 2H, H^c), 9.90 (s, 2H, CHO)
10	1732 (C=O)	2.40 (s, 6H, CH_3), 5.50 (dd, 2H, *o*-C_6H_4, $H^{1,4}$), 6.01 (dd, 2H, *o*-C_6H_4, $H^{2,3}$), 6.80 (m, 2H, *o*-C_6H_4, $H^{10,13}$), 6.90 (m, 2H, *o*-C_6H_4, $H^{11,12}$), 7.25–7.48 (m, 20H, C_6H_5)	6.41 (d, $J = 8.5$ Hz, 4H, H^b), 7.39 (d, $J = 8.6$ Hz, 4H, H^c)[a]
11	1737 (C=O)	2.40 (s, 6H, CH_3), 5.50 (dd, 2H, *o*-C_6H_4, $H^{1,4}$), 6.01 (dd, 2H, *o*-C_6H_4, $H^{2,3}$), 6.80 (m, 2H, *o*-C_6H_4, $H^{10,13}$), 6.90 (m, 2H, *o*-C_6H_4, $H^{11,12}$), 7.25–7.48 (m, 20H, C_6H_5)	6.41 (d, $J = 8.5$ Hz, 4H, H^b), 7.39 (d, $J = 8.6$ Hz, 4H, H^c)
12	1732 (C=O)	2.42 (s, 6H, CH_3), 5.50 (m, 2H, *o*-C_6H_4, $H^{1,4}$), 6.02 (m, 2H, *o*-C_6H_4, $H^{2,3}$), 6.81 (dd, 2H, *o*-C_6H_4, $H^{10,13}$), 6.92 (dd, 2H, *o*-C_6H_4, $H^{11,12}$), 7.38–7.52 (m, 10H, C_6H_5)	6.53 (d, $J = 8.7$ Hz, 4H, H^b), 7.48 (d, $J = 7.8$ Hz, 4H, C_6H_5), 7.87 (d, $J = 7.1$ Hz, 4H, H^f), 7.31 (m, 2H, C_6H_5), 7.77 (d, $J = 8.7$ Hz, 4H, H^c)
13	1701 (C=O), 3390 (N–H)	2.35 (s, 6H, CH_3), 6.09 (dd, 2H, *o*-C_6H_4, $H^{1,4}$), 6.43 (dd, 2H, *o*-C_6H_4, $H^{2,3}$), 7.13 (m, AA′BB′, 4H, *o*-C_6H_4), 7.20 (m, 2H, C_6H_5), 7.31 (m, 6H, C_6H_5), 14.31 (s, 2H, NH)	0.61 (d, $J = 6.3$ Hz, 6H, CH_3), 1.07 (d, $J = 6.2$ Hz, 6H, CH_3), 4.66 (h, $J = 6.3$ Hz, 2H, CH)
14	1707 (C=O), 3350 (N–H)	2.35 (s, 6H, CH_3), 6.11 (dd, 2H, *o*-C_6H_4, $H^{1,4}$), 6.44 (dd, 2H, *o*-C_6H_4, $H^{2,3}$), 6.97 (m, AA′BB′, 4H, *o*-C_6H_4), 7.11–7.21 (m, 7H, C_6H_5), 7.21–7.26 (m, 13H, C_6H_5), 14.37 (s, 2H, NH)	4.42 (d, $J = 12.2$ Hz, 2H, CH_2), 4.91 (d, $J = 12.1$ Hz, 2H, CH_2)
15	1686 (C=O), 1727 (COO), 3350 (N–H)	2.51 (s, 6H,CH_3), 6.30 (dd, 2H, *o*-C_6H_4, $H^{1,4}$), 6.58 (dd, 2H, *o*-C_6H_4, $H^{2,3}$), 7.20 (m, AA′BB′ 4H, *o*-C_6H_4), 7.24–7.33 (m, 10H, C_6H_5), 14.58 (s, 2H, NH)	2.53 (s, 6H, $COCH_3$), 6.53 (d, $J = 8.5$ Hz, 4H, H^b), 7.81 (d, $J = 8.6$ Hz, 4H, H^c)
16	1727 (C=O), 3455 (N–H)	2.53 (s, 6H, CH_3), 6.30 (dd, 2H, *o*-C_6H_4, $H^{1,4}$), 6.56 (dd, 2H, *o*-C_6H_4, $H^{2,3}$), 7.22 (b.s, 4H, *o*-C_6H_4), 7.28–7.50 (20H, C_6H_5), 14.52 (s, 2H, NH)	6.52 (d, $J = 8.6$ Hz, 4H, H^b), 7.41 (d, $J = 8.6$ Hz, 4H, H^c)[a]

[a] Signals of phenyl protons obscured by that of 6, 17-Ph (column 3).

are close to 90° (from 85° up to 95°). Numerical values of the most important structural parameters are given in Table 4.

The geometry of the saddle is defined by a number of angles between the best planes calculated for particular molecular fragments. It appears that the angles between the aromatic rings and the central planar N(1)N(2)N(3)N(4)Ni(1) fragment are equal ca. 33.2° and 34.1° whereas the C(1)C(2)C(3) and C(6)C(7)C(8) – the other walls of cavities – have angles equal to 33.6° and 35.2° with the central NNNNNi(1) atomic plane. Similar angles for the second moiety are equal to 32.2° and 33.6° for the angles between the fused aromatic rings and N(5)N(6)N(7)N(8)Ni(2), and 32.5° and 35.0° for the angles between N(5)N(6)N(7)N(8)Ni(2) and C(47)C(48)C(49) and C(42)C(43)C(44) molecular fragments, respectively. The phenylene rings of the saddle molecules in the stacks are arranged in such a manner as

Table 3

Compounds	^{13}C NMR, δ (ppm), $CDCl_3$	
	Macrocycle	7, 16-Substituents
3	118.36 ($C^{7,16}$), 121.91, 122.16, 122.29, 123.10 (*o*-C_6H_4), 127.52, 128.4, 128.79, 130.07, 137.09 (C_6H_5), 147.29, 147.12 (*o*-C_6H_4), 157.35, 156.57 (C=N)	13.51 (CH_3), 21.61 (CH_3), 60.46 (CH_2), 170.65 (C=O)
4	21.83 (CH_3), 118.82 ($C^{7,16}$) 121.78, 122.07, 122.20, 123.01 (*o*-C_6H_4), 127.96, 128.40, 128.86, 130.18, 136.81, (C_6H_5), 147.13, 147.34 (*o*-C_6H_4), 156.04, 156.80 (C=N)	20.55 (CH_3), 21.49 (CH_3), 67.84 (CH), 169.99 (C=O)
5	21.21 (CH_3), 120.22 ($C^{7,16}$), 121.69, 121.86, 122.10, 122.81 (*o*-C_6H_4), 128.16, 128.36, 128.96, 136.99 (C_6H_5), 147.16, 147.35 (*o*-C_6H_4), 155.85, 156.48 (C=N)	27.36 (C^a), 80.07 (C^b), 169.40 (C=O)
6	21.56 (CH_3), 120.52 ($C^{7,16}$), 121.60, 121.90, 122.16, 122.79 (*o*-C_6H_4), 128.20, 128.43, 128.80, 129.00, 130.24, 136.66 (C_6H_5), 147.22, 147.47 (*o*-C_6H_4), 155.46, 156.25 (C=N)	8.23 (C^a) 21.29 (C^d), 29.53 (C^b) 86.22 (C^c) 169.70 (C=O)
7	21.65 (CH_3), 118.04 ($C^{7,16}$), 121.94, 122.14, 122.29, 123.15 (*o*-C_6H_4), 127.37, 127.85, 128.20, 128.39, 128.86, 130.04, 135.85, 136.84 (C_6H_5), 147.04, 147.22 (*o*-C_6H_4), 156.62, 157.34 (C=N)	66.64 (CH_2), 170.51 (C=O)[a]
8	21.76 (CH_3), 116.74 ($C^{7,16}$), 121.31, 122.13, 122.60, 123.63 (*o*-C_6H_4), 127.95, 129.55, 129.08, 129.43, 130.16, 134.22 (C_6H_5), 147.89, 147.12 (*o*-C_6H_4), 157.30, 158.45 (C=N)	26.52 (CH_3), 122.50 (C^b), 128.9 (C^c), 136.90 (C^d), 154.48 (C^a), 168.34 (COO), 196.88 ($COCH_3$)
9	21.72 (CH_3), 116.74 ($C^{7,16}$), 122.18 (*o*-C_6H_4), 122.56, 122.70, 123.70 (*o*-C_6H_4), 128.01, 128.94, 129.11, 129.46, 130.19, 136.98 (C_6H_5), 146.96, 147.17 (*o*-C_6H_4) 157.46 (C=N), 158.62 (C=N)	121.86 (C^b), 130.81 (C^c), 133.62 (C^d), 155.61 (C^a), 168.14 (COO), 190.84 (CHO)
10	23.20 (CH_3), 118.72 ($C^{7,16}$), 123.55, 123.82, 123.87,124.88 (*o*-C_6H_4), 128.46, 129.23, 130.11, 129.51, 130.25, 130.50, 130.75, 131.67, 138.41, 141.93 (C_6H_5), 148.42, 148.66 (*o*-C_6H_4), 158.44, 159.48 (C=N)	122.94 (C^b), 128.57 (C^c), 139.94 (C^d), 151.52 (C^a), 170.53 (C=O)[a]
11	21.75 (CH_3), 116.23 ($C^{7,16}$), 122.17, 122.59, 122.84, 123.84 (*o*-C_6H_4), 127.88, 129.02, 129.14, 129.55, 130.14, 136.94 (C_6H_5), 146.85, 147.06 (*o*-C_6H_4), 155.60, 157.60 (C=N)	121.82 (C^b), 124.75 (C^c), 144.89 (C^d), 158.92 (C^a), 167.80 (C=O)
12	21.79 (CH_3), 117.06 ($C^{7,16}$), 121.78, 122.52, 122.77, 123.68 (*o*-C_6H_4), 128.02, 128.89, 129.04, 129.41, 130.22, 130.90, 136.96 (C_6H_5), 146.98, 147.21 (*o*-C_6H_4), 157.27, 158.36 (C=N),	122.16 (C^c), 123.56 (C^b), 152.58 (C^e), 149.91 (C^a), 152.82 (C^d), 168.60 (C=O)[a]
13	20.01 (CH_3), 105.04 ($C^{7,16}$), 122.84, 123.15, 124.18, 124.59 (*o*-C_6H_4), 128.24, 128.28, 128.44 (C_6H_5), 136.82, 136.99 (*o*-C_6H_4), 137.70 (C_6H_5), 161.21, 161.60 (C=N),	20.71 (CH_3), 21.72 (CH_3), 67.76 (CH), 169.99 (C=O)
14	20.13 (CH_3), 104.17 ($C^{6,17}$), 122.96, 123.24, 124.34, 124.77 (*o*-C_6H_4), 127.82, 128.02, 128.24, 128.46, 135.52 (C_6H_5), 136.77, 136.92 (*o*-C_6H_4), 137.49 (C_6H_5), 161.95, 162.22 (C=N),	66.58 (CH_2), 170.37 (C=O)[a]
15	19.88 (CH_3), 102.42 ($C^{7,16}$), 121.33, 125.12, 125.59 (*o*-C_6H_4), 128.39, 128.56, 129.52, 134.16 (C_6H_5), 136.95, 137.30 (*o*-C_6H_4), 163.62, 164.23 (C=N)	26.46 (CH_3), 123.50 (C^b), 137.00 (C^d), 154.64 (C^b), 167.82 (COO), 196.85 ($COCH_3$)
16	20.01 (CH_3), 103.08 ($C^{7,16}$) 123.34, 123.41, 124.95, 125.35 (*o*-C_6H_4), 127.02, 127.79, 128.68, 127.14, 128.46, 128.59 (C_6H_5), 137.05, 137.16 (*o*-C_6H_4), 137.27 (C_6H_5), 140.52 (C_6H_5), 163.13, 163.62 (C=N)	121.57 (C^b), 128.80 (C^c), 138.42 (C^d), 168.73 (C=O)[a]

[a] Signals of phenyl protons obscured by that of 6, 17-Ph (column 2).

to allow close contacts (ca. 3.1 Å) of terminal aromatic carbon atoms of a given ring of a saddle moiety with a hydrogen atom of a similar ring from the neighbouring

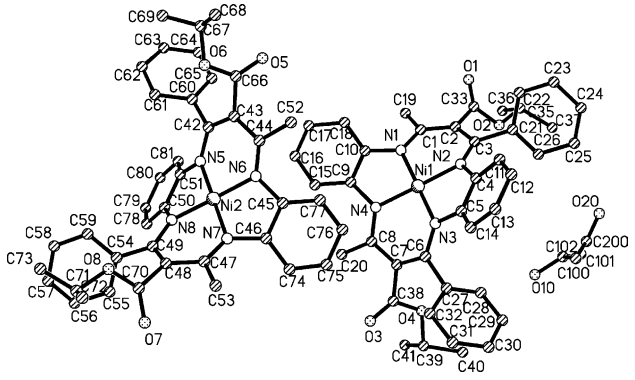


Fig. 1. Labelling of the non-hydrogen atoms. The hydrogen atom label numbers are the same as the ones carried by their parental carbons.

Table 4
Selected bond lengths (Å) and valence angles (°) for **4**

Bond lengths (Å)	
N(1)–Ni(1)	1.809(9)
N(2)–Ni(1)	1.859(9)
N(3)–Ni(1)	1.845(9)
N(4)–Ni(1)	1.851(9)
N(5)–Ni(2)	1.824(9)
N(6)–Ni(2)	1.86(1)
N(7)–Ni(2)	1.870(8)
N(8)–Ni(2)	1.83(1)
Bond angles (°)	
N(1)–Ni(1)–N(3)	177.4(5)
N(1)–Ni(1)–N(4)	85.4(4)
N(3)–Ni(1)–N(4)	94.9(4)
N(1)–Ni(1)–N(2)	94.5(4)
N(3)–Ni(1)–N(2)	85.1(4)
N(4)–Ni(1)–N(2)	178.8(5)
N(8)–Ni(2)–N(5)	85.5(4)
N(8)–Ni(2)–N(7)	94.4(4)
N(5)–Ni(2)–N(7)	179.2(4)
N(8)–Ni(2)–N(6)	178.3(5)
N(5)–Ni(2)–N(6)	94.2(4)
N(7)–Ni(2)–N(6)	85.9(4)

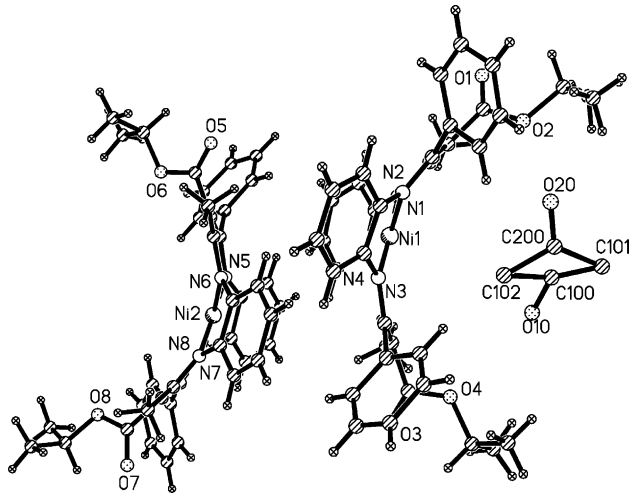


Fig. 2. The saddle shape of **4** and disordered positions of the solvent moiety.

molecule located above or below in the crystal lattice (Fig. 2).

The disordered acetone moiety forms weak hydrogen bonds involving oxygen of the keto group and a proton of the phenyl ring with O(20)·····H(25)–C(25) hydrogen bond distance equal to 2.11 Å. There is also a number of similar C–H·····O peak interactions with slightly longer H·····O distances (close to 2.4 Å) (see Fig. 3).

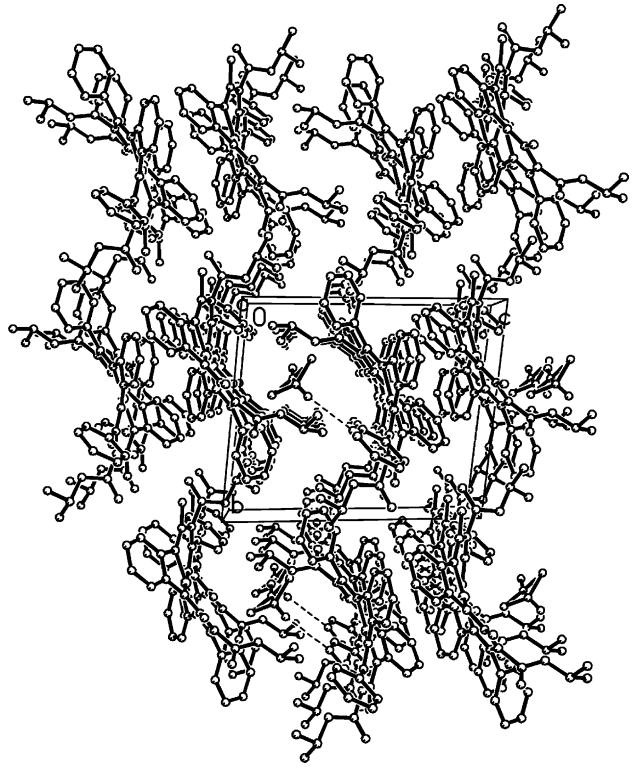


Fig. 3. 3D packing of molecules in the crystal lattice of **4** – view along *X*-axis. Stacking of saddle molecules, host–guest interactions with acetone.

4. Conclusions

New saddle-shaped supramolecular receptors with extended divergent curved surfaces have been synthesized. Single crystal X-ray diffraction studies of isopropoxycarbonyl derivative **4** revealed its potential to associate with the molecules of appropriate guests.

5. Supplementary material

Crystallographic data (excluding structural factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre and allocated the deposition number: CCDC 204872. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EW, UK (fax: Int code + (1223)336-033; e-mail: deposit@ccdc.cam.ac.uk).

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