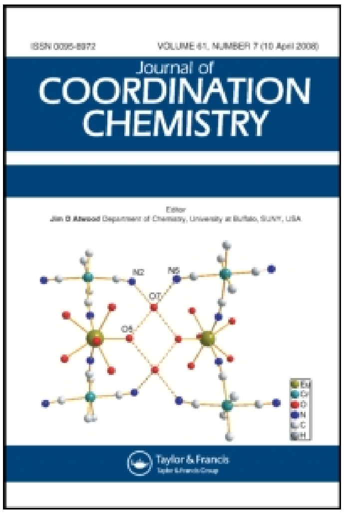

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Large 1,3,5-triazine-based ligands coordinating transition metal ions: syntheses and structures of the ligands and the ball shaped nanometer-scaled Co complex $[Co(2,4\text{-}R\text{-}6\text{-}R'\text{-}1,3,5\text{-triazine})_2](Br_{1.7}(OH)_{0.3}) \cdot 4.8H_2O$ {*R* = *bis*(2-diphenylmethylene) hydrazinyl; *R'* = piperidin-1-yl}

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Large 1,3,5-triazine-based ligands coordinating transition metal ions: syntheses and structures of the ligands and the ball shaped nanometer-scaled Co complex $[\mathrm{Co}(2,4\text{-}R\text{-}6\text{-}R'\text{-}1,3,5\text{-triazine})_2](\mathrm{Br}_{1.7}(\mathrm{OH})_{0.3})\cdot 4.8\mathrm{H_2O}$ {R = *bis*(2-diphenylmethylene) hydrazinyl; R' = piperidin-1-yl}

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Two new, large 1,3,5-triazine-based ligands with only N-donor functions were synthesized as well as the Co(II) salt $[\mathrm{Co(DHPTBenz)_2}](\mathrm{Br}_{1.7}(\mathrm{OH})_{0.3})\cdot 4.8\mathrm{H_2O}$ (DHPTBenz = 2,4-*bis*-(2-diphenylmethylene)-hydrazinyl-6-piperidin-1-yl-1,3,5-triazine). Single crystal X-ray structures of the Co(II) complex, DHPTBenz, and 2,4-dichloro-6-(piperidin-1-yl)-1,3,5-triazine (DCPT) have been determined. The last compound was used as starting material for the tridentate DHPTBenz ligand. Spectroscopic data of the ligand and the starting materials are reported. The Co(II) ion in the complex is distorted octahedrally coordinated by six N atoms of two DHPTBenz ligands. One N atom of the triazine ring of each ligand bonds axially with short distances of 1.953(3) Å and 1.954(3) Å, respectively, whereas two of the hydrazine-N atoms of two ligands form the equatorial plane with an average Co–N bond distance of 2.313 Å. The complex cation has a slightly elongated, nanometer-scaled ball shape with the longest diameter of 1.82 nm.

Keywords: Cobalt complex; Triazine ligand; Crystal structure; Nanostructure

1. Introduction

Triazine chemistry has attracted attention due to the utility of melamine derivatives as starting materials for a variety of polymers [1], as scavenging resins in organic manipulations [2], and in medicinal chemistry [3]. Heterocyclic derivatives of 1,3,5-triazine are useful as polydentate ligands [4] and for molecular encapsulation [5]. The appeal of the 1,3,5-triazine core is largely due to the ease of systematic substitution of the chlorine atoms in cyanuric chloride (2,4,6-trichloro-1,3,5-triazine) with amine nucleophiles to generate new compounds. In the last decade, interest has been focused on self-assembly of supramolecular architectures prepared from multifunctional ligands and transition metals [6, 7]. There has been a steady rise in attempts to design organic molecules as bi- or poly-dentate ligands that can form supramolecular systems. Of these

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ligands 1,3,5-triazine derivatives have been demonstrated to be versatile for the synthesis of metal complexes with a variety of structural architectures [8, 9]. Successive substitution reactions with good nucleophiles, such as secondary amines like piperidine, or with hydrazine hydrate [10], lead to precursors for new chelating agents for transition metals. The electrochemical, spectroscopic, and magnetic properties of known cobalt complexes have shown that they are significantly affected by the electron-deficient triazine ring and its weak ligand field strength [11]. The electrochemical properties of such complexes may be applied to the development of new redox mediators [12].

In this article we report new, large 1,3,5-triazine-based ligands coordinating a transition metal. We synthesized 2,4-dihydrazinyl-6-(piperidin-1-yl)-1,3,5-triazine (DHPT) and 2,4-*bis*(2-diphenylmethylene)hydrazinyl-6-(piperidin-1-yl)-1,3,5-triazine (DHPTBenz) in high yields starting from 2,4-dichloro-6-(piperidin-1-yl)-1,3,5-triazine (DCPT). We also report spectral properties of these compounds and the new ball-shaped nanometer-scaled Co complex [Co(2,4-R-6-R'-1,3,5-triazine)$_2$] $(Br_{1.7}(OH)_{0.3})\cdot 4.8H_2O$ $\{R = bis$-(2-diphenylmethylene)hydrazinyl; $R' =$ piperidin-1-yl$\}$. The molecular structures of the compounds DCPT, DHPTBenz, and Co-DHPTBenz were determined by single crystal X-ray diffraction.

2. Experimental

2.1. *Physical measurements*

^{1}H NMR (300 MHz) and ^{13}C NMR spectra (75.5 MHz) were recorded on a Bruker ARX 300 spectrometer. Spectra were calibrated with respect to the solvent signal ($CDCl_3$: $\delta_H = 7.26$, $\delta_C = 77.1$ ppm: DMSO-d$_6$: $\delta_H = 2.50$, $\delta_C = 39.5$ ppm) [13]. IR spectra were recorded as KBr pellets on a Nicolet Protégé 460 spectrometer or by using ATR technique on a Thermo Nicolet 380 FT-IR spectrometer (diamond: 30,000–200 cm^{-1}). Mass spectra were measured with an AMD 402/3 spectrometer (EI, 70 eV). Elemental analyses for C, H, and N were obtained with a Flash EA 1112 NC Analyzer from CE Instruments. UV–Vis spectra were recorded using a Perkin Elmer Lambda 2 spectrometer with quartz cuvettes (Suprasil®, $d = 10$ mm). All melting points are not corrected. Bromide analysis was performed by using ion chromatography of single crystal material.

2.2. *Materials*

All starting materials and solvents were purchased from Merck KGaA, Germany and were used without purification or drying, except piperidine, which was distilled prior to use.

2.3. *Syntheses*

2.3.1. 2,4-Dichloro-6-(piperidin-1-yl)-1,3,5-triazine: DCPT. To a stirred solution of 3.7 g (20 mmol) cyanuric chloride in 30 mL acetone, a mixture of 1.7 g (20 mmol) freshly distilled piperidine and 2.9 g (21 mmol) potassium carbonate in 70 mL water is slowly added at −10°C using a dropping funnel. The stirred reaction mixture is allowed to warm to room temperature over a period of 1 h. The resulting precipitate is filtered off by suction and washed with water until pH = 7. The white solid is dried in a desiccator using P_4O_{10} as drying agent. Yield: 4.0 g (86%). m.p. 90°C (lit. 90–91°C [14]). Anal. Calcd for $C_8H_{10}Cl_2N_4$: C, 41.22; H, 4.32; N, 24.04. Found: C, 41.30; H, 4.33; N, 23.71. ^{1}H NMR ($CDCl_3$): $\delta = 1.66$ (6H, m, –CH_2–); 3.81 (4H, m, –CH_2–N); ^{1}H NMR (DMSO-d_6): $\delta = 1.61$ (6H, m, –CH_2–); 3.73 (4H, m, –CH_2–N); ^{13}C NMR (DMSO-d_6): $\delta = 23.5$ (C-3′); 25.0 (C-2′); 44.7 (C-1′); 162.8 (C-6); 169.0 (C-2). IR (KBr, cm^{-1}, ν_{max}): 2943, 1594, 1467, 1348, 1230, 1155, 988, 845. MS (EI): *m*/*z* 232.0 (M^+). UV–Vis (acetonitrile, λ_{max}/nm): 244, 279 (shoulder).

2.3.2. 2,4-Dihydrazinyl-6-(piperidin-1-yl)-1,3,5-triazine: DHPT. To a stirred solution of 20 mL hydrazine hydrate (80%) in 50 mL acetonitrile, 5.25 g (22.5 mmol) of DCPT dissolved in 50 mL acetonitrile are added. The resulting suspension is stirred under reflux for 3 h to complete the reaction. After the reaction mixture is cooled in a refrigerator at 0°C overnight, the resulting precipitate is filtered off by suction and washed several times with acetonitrile. The white solid is washed with a small amount of diethyl ether and finally dried overnight in a drying oven at 60°C. Yield: 4.8 g (95%). m.p. 162°C. Anal. Calcd for $C_8H_{16}N_8$: C, 42.84; H, 7.19; N, 49.96. Found: C, 43.07; H, 7.19; N, 50.54. ^{1}H NMR (DMSO-d_6): $\delta = 1.44$–1.59 (6H, m, –CH_2–); 3.67 (4H, m, –CH_2–N); 4.64 (4H, very broad, –NH_2); 7.72 (2H, very broad, –NH–); ^{13}C NMR (DMSO-d_6): $\delta = 24.3$ (C-3′); 25.4 (C-2′); 43.3 (C-1′); 163.9 (C-6); 167.5 (C-2). IR (KBr, cm^{-1}, ν_{max}): 3352, 3314, 2928, 1569, 1541, 1506, 1286, 1080, 805. MS (EI): *m*/*z* 224.2 (M^+). UV–Vis (acetonitrile, λ_{max}/nm): 221.

2.3.3. 2,4-*Bis*(2-diphenylmethylene)hydrazinyl-6-(piperidin-1-yl)-1,3,5-triazine: DHPT Benz. About 4.62 g benzophenone and 2.84 g of DHPT are placed in a 500 mL round-bottom flask and 350 mL 1-propanol are added. The suspension is stirred under reflux for 20 h. After cooling, the solvent is removed from the clear, light yellow solution. The residue is slurried with 50 mL methanol and filtered off by suction to yield a colorless precipitate. The solid is dried overnight in a drying oven at 60°C. Yield: 5.25 g (75%). m.p. 138°C. Anal. Calcd for $C_{34}H_{32}N_8$: C, 73.89; H, 5.84; N, 20.27. Found: C, 73.42; H, 5.92; N, 19.83. ^{1}H NMR ($CDCl_3$): $\delta = 1.64$ (6H, broad, –CH_2–); 3.85 (4H, broad, –CH_2–N); 7.60–7.29 (20H, m, phenyl); 8.10 (2H, broad, –NH–). IR (ATR, cm^{-1}, ν_{max}): 3347, 3053, 3025, 2932, 2920, 2851, 1590, 1531, 1478, 1442, 1409, 1279, 1189, 1140, 765, 702, 690. UV–Vis (acetonitrile, λ_{max}/nm): 225, 311.

2.3.4. [Co(2,4-*R*-6-*R*′-1,3,5-triazine)$_2$](Br$_{1.7}$(OH)$_{0.3}$) · 4.8H$_2$O {*R* = *bis*(2-diphenylmethylene)hydrazinyl; *R*′ = piperidin-1-yl}: Co-DHPTBenz. About 1.66 g (3 mmol) of DHPTBenz are suspended in a mixture of 100 mL methanol and 5 mL water and heated under reflux. After addition of 35 mL chloroform to the refluxing mixture a clear solution is obtained. A solution of 325 mg (1.5 mmol) anhydrous $CoBr_2$ in 20 mL methanol is added to the warm, not refluxing, solution of the ligand. The color of the reaction mixture spontaneously changes to green. To complete the formation of the complex, the solution is stirred under reflux for 1 h and the solid is obtained as green-yellow needles by slow evaporation of the solvents. The complex is insoluble in water and chloroform, but soluble in acetone or acetonitrile. Anal. Calcd for $C_{68}H_{73.88}Br_{1.74}CoN_{16}O_{5.08}$: C, 58.57; H, 5.34; N, 16.07; Br, 9.97. Found: C, 58.39; H, 5.00; N, 15.89; Br, 10.6. IR (ATR, cm^{-1}, ν_{max}): 3355, 3047, 2933, 2919, 2849, 1634, 1574, 1482, 1441, 1097, 756, 696, 668. UV–Vis (acetonitrile, λ_{max}/nm): 234, 303, 618, 675.

2.4. *Crystal structure studies*

Single crystals of DCPT were obtained by cooling a saturated acetone solution in a refrigerator for one week at 0°C. Single crystals of DHPTBenz were obtained by heating the microcrystalline powder in a sealed glass ampoule in a tube furnace for 2 weeks at 125–130°C, which is about 10°C below the melting point. Suitable single crystals of Co-DHPTBenz were obtained directly from the reaction flask. X-ray intensity data of DCPT, DHPTBenz, and Co-DHPTBenz were collected at room temperature with a Bruker-Nonius Apex-X8-diffractometer equipped with a CCD detector. Graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) was used. Crystal data, data collection and refinement parameters for the three compounds are given in table 1. Unit cell dimensions of all three structures were determined from the reflections of 60 frames measured in three different crystal directions. Data collection and data reduction including corrections for Lorentz and polarization effects were done using the Bruker-Nonius software [15]. Absorption corrections were performed using SADABS [16]. All structures were solved via direct methods, the structures completed using difference-Fourier maps and refined by full-matrix least-squares methods on F^2 using

Table 1. Crystal, X-ray diffraction and refinement data for DCPT, DHPTBenzo and Co-DHPTBenz.

	Co-DHPTBenz	DHPTBenz	DCPT
Empirical formula	$C_{68}H_{73.87}Br_{1.73(1)}CoN_{16}O_{5.07}$	$C_8H_{10}Cl_2N_4$	$C_{34}H_{32}N_8$
M (g mol^{-1})	1394.08	466.20	552.68
Temperature (K)	293(2)	293(2)	293(2)
λ (Å)	0.71073	0.71073	0.71073
Crystal system	Triclinic	Monoclinic	Monoclinic
Space group (Z)	$P\bar{1}$, 2	$C2/c$, 4	$C2/c$, 8
Unit cell dimensions (Å, °)			
a	12.1891(3)	16.6635(6)	19.0485(3)
b	13.2768(3)	7.6208(3)	11.5341(3)
c	21.3010(5)	17.5038(6)	27.2316(5)
α	96.341(1)		
β	99.383(1)	107.966(1)	90.416(1)
γ	98.607(1)		
V (Å^3)	3330.5(1)	2114.4(1)	5982.8(2)
$2\theta_{max}$	54.0	55.5	56.6
Independent reflections	13,929	2469	7420
Parameters	842	128	380
ρ_{Calcd} (g cm^{-1})	1.390	1.465	1.227
μ (mm^{-1})	1.361	0.580	0.076
$R_1(F)^a$	0.0622	0.0380	0.0513
$wR_2(F^2)^b$	0.1866	0.1188	0.1489
Weighting, A, B	0.1034, 0.0	0.0565, 0.6469	0.0555, 2.6332
GoF	1.015	1.036	0.990

[a] $R_1 = \Sigma_{hkl}||F_o| - |F_c||/\Sigma_{hkl}|F_o|$; [b] $wR_2 = \sqrt{\Sigma_{hkl}w(F_o^2 - F_c^2)^2/\Sigma_{hkl}w(F_o^2)^2}$; $w = 1/[\sigma^2(F_o^2) + A^2 + B \cdot P]$; $P = (F_o^2 + 2F_c^2)/3$; GoF $= \Sigma_{hkl}w(||F_o^2| - |F_c^2||)^2/(m - n)$; m = number of observed reflections, n = number of parameters.

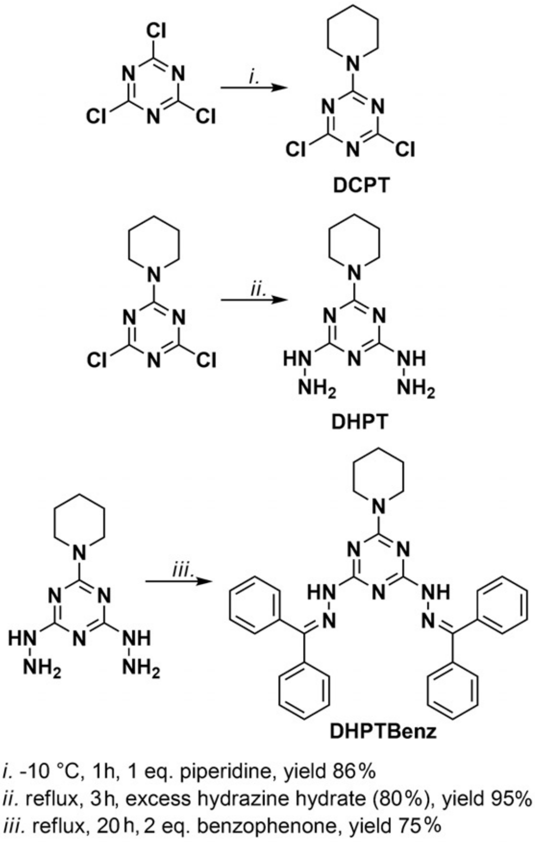
the SHELXL-97 program package [17]. All atoms (except for hydrogen) were treated anisotropically. Hydrogen atoms were fixed on idealized positions and refined with isotropic thermal parameters based on the bonded carbon atom. In the structure of Co-DHPTBenz the Br atoms are located on two symmetry independent sites. Br2 is disordered on two positions and mixed with hydroxide. This situation was treated with a SUMP restrain (SHELXL-97) [17].

The crystallographic information of the structures has been deposited in 'cif' format with the Cambridge Crystallograhic Data Centre, reference numbers are: CCDC-665515 (DCPT), CCDC-665516 (DHPTBenz), and CCDC-665514 (Co-DHPTBenz).

3. Results and discussion

3.1. *Syntheses*

Synthesis of the tridentate ligand, 2,4-*bis*-(2-diphenylmethylene)-hydrazinyl-6-(piperidin-1-yl)-1,3,5-triazine, DHPTBenz, which carries only nitrogen donor functions, is done in a three-step procedure, as sketched in scheme 1. In a typical experiment, the first



i. -10 °C, 1h, 1 eq. piperidine, yield 86%
ii. reflux, 3h, excess hydrazine hydrate (80%), yield 95%
iii. reflux, 20h, 2 eq. benzophenone, yield 75%

Scheme 1. The three-step procedure of the preparation of the tridentate ligand DHPTBenz, starting from cyanuric chloride.

step is to substitute one chloride in cyanuric chloride with one equivalent of piperidine at low temperature. The second step is to substitute the two other chlorine atoms with hydrazine moieties. In the following step, the hydrazine groups react with a suitable ketone such as benzophenone to form a hydrazone structure. The reaction conditions are summarized in scheme 1. Finally, the chelating ligand is reacted with a transition metal halide to form a 1 : 2 complex with two molecules of the chelating ligand.

3.2. *Description of structures*

In order to have accurate data for structural comparison, the X-ray single crystal structure of DCPT was re-determinated [18]. A view of the molecular structure of DCPT with the atom labeling scheme is given in figure 1. Figure 2 shows the arrangement of molecules within the unit cell in a view down the crystallographic *b*-axis.

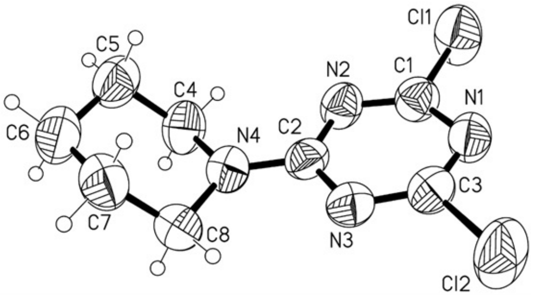


Figure 1. Molecular structure of DCPT in the solid state (displacement ellipsoids at the 50% probability level).

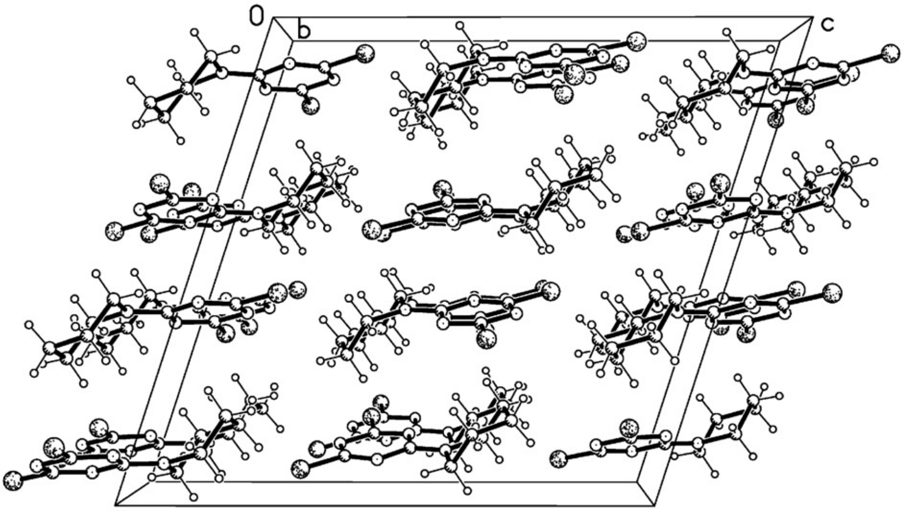


Figure 2. Perspective view of the crystal structure of 2,4-dichloro-6-(piperidin-1-yl)-1,3,5-triazine, DCPT, along the crystallographic *b*-axis (Cl: irregularly dotted, N: regularly dotted, C: shaded circles, H: empty circles).

Piperidine adopts a chair configuration. The planar 2,4-dichlorotriazine residues are parallel to each other and stacked along *a*. Selected bond lengths and angles are given in table 2. The determined bond lengths and angles are in accordance with the previously reported bond lengths and angles [18].

The single crystal structure determination of DHPTBenz again shows that the piperidine ring is in the most favorable chair configuration. A view of the molecular structure of DHPTBenz with the atom labeling scheme is given in figure 3. Figure 4 shows the arrangement of molecules within the unit cell in a view down the crystallographic *b*-axis. Selected bond lengths and angles are given in table 3. Due to the C=N double bond, the C9–N6 and C22–N8 bond lengths are the shortest of the C–N bonds in the molecule with an average length of 1.289 Å. The N–NH and NH–$C_{(triazine)}$ bonds are significantly longer, with average bond lengths of 1.364 Å and 1.370 Å, respectively. These values are in good accordance with bond lengths determined in ref. [19]. The substitution of the two chlorine atoms of DCPT

Table 2. Selected bonds lengths and angles of the triazine core of DCPT.

Atoms	Bond length (Å)	Atoms	Bond angle (°)
C1–Cl1	1.728(2)	N1–C1–Cl1	114.3(2)
C3–Cl2	1.720(2)	N1–C3–Cl2	114.6(2)
C1–N1	1.323(2)	N2–C1–Cl1	115.8(2)
C3–N1	1.327(2)	N3–C3–Cl2	116.0(2)
C1–N2	1.302(2)	C1–N1–C3	110.1(2)
C3–N3	1.305(2)	N1–C3–N3	129.4(2)
C2–N2	1.357(2)	N1–C1–N2	129.8(2)
C2–N3	1.356(2)	N2–C2–N3	123.2(2)
C2–N4	1.330(2)		
Average C–N(triazine)		1.328	
Average C–N(piperidine)		1.465	
Average C–C(piperidine)		1.510	

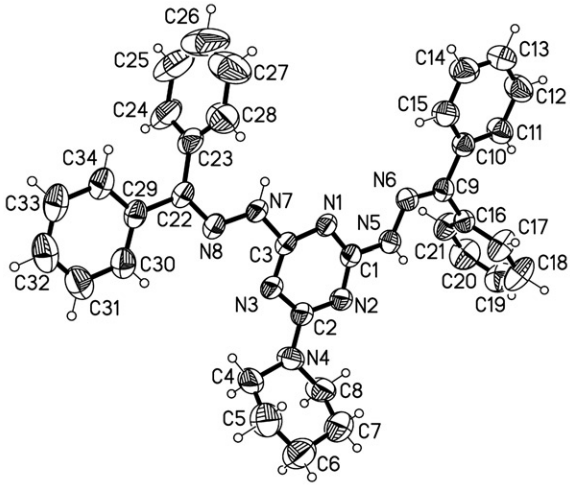


Figure 3. View of the molecular structure of DHPTBenz with atom labeling scheme (thermal ellipsoids at the 50% probability level).

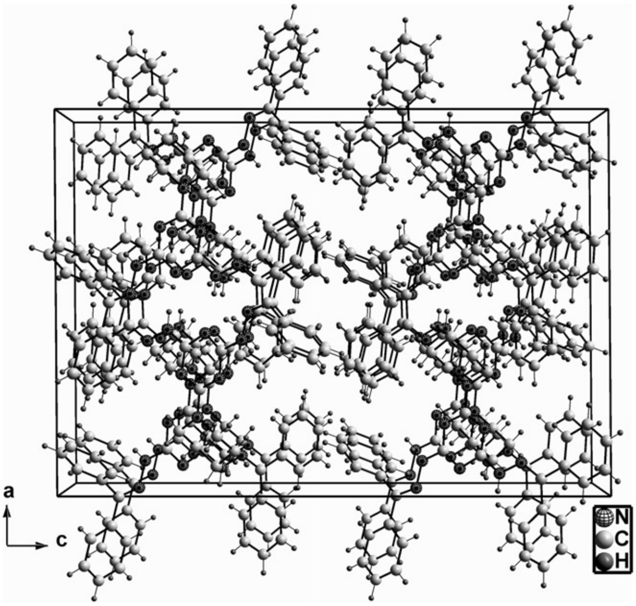


Figure 4. View of the arrangement of the DHPTBenz molecules in the unit cell in a view along the crystallographic *b*-axis.

Table 3. Selected bond lengths and angles around the triazine core of the tridentate ligand DHPTBenz.

Atoms	Bond length (Å)	Atoms	Bond angle (°)
C1–N5	1.370(2)	N1–C1–N5	118.8(2)
C3–N7	1.370(2)	N1–C3–N7	113.4(2)
N5–N6	1.361(2)	C1–N5–N6	121.5(2)
N7–N8	1.367(2)	C3–N7–N8	118.6(2)
C9–N6	1.291(2)	C9–N6–N5	117.2(2)
C22–N8	1.287(2)	C22–N8–N7	119.3(2)
Average C–N(triazine)		1.337	
Average C–N(piperidine)		1.458	
Average C–C(piperidine)		1.502	

by *bis*-(2-diphenylmethylene)-hydrazinyl residues does not change the distances within the piperidine or the triazine ring to a significant extent.

Treatment of $CoBr_2$ with DHPTBenz in wet methanol under reflux results in formation of $[Co(DHPTBenz)_2]^{2+}$. It crystallizes with a mixture of bromide and hydroxide counter anions and water solvent molecules in the triclinic space group $P\bar{1}$. All the atoms are located on general positions. Br1 fully occupies one site, whereas Br2 is disordered on two sites with partial occupation. Charge balance is achieved by additional hydroxides, which originate from the water content of the methanol solvent. The final formula of this material from the X-ray structure determination is $[Co(C_6H_5)_4(CN_2)_2(C_3N_3)(NC_5H_{10})_2](Br_{1.73(1)}(OH)_{0.27})\cdot 4.8H_2O$. The number of bromide ions being lower than two per complex cation is affirmed by the ion chromatographic determination of the bromine content of selected crystals of Co-DHPTBenz. Bromine content in the title phase is found at 10.6%. The value for a

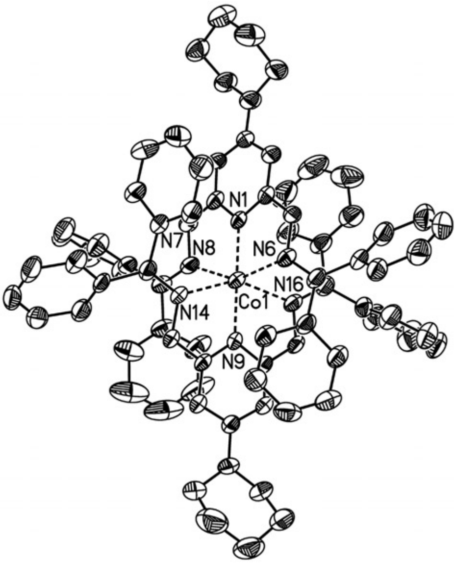


Figure 5. A view of the molecular structure of Co-DHPTBenz. Displacement ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted for clarity.

hypothetical material with the anion sites being fully occupied by bromine is 11.3%. The lower experimental value confirms the partial occupation of the Br2 site. The Br^-, the hydroxide anion, as well as the co-crystallized water molecules are located outside the complex cation with distances larger than 5.5 Å from Co. The mononuclear complex cation of Co-DHPTBenz contains two ligands bonded to Co(II). A thermal ellipsoid plot of the cation is shown in figure 5.

Each of the two DHPTBenz molecules are tridentate coordinating the Co through the triazene-N atom opposite to the piperidine moiety (N1) and both the N atoms of the hydrazinyl residue, which are bonded to the methylene group (N6 and N8). Thereby a distorted octahedral coordination environment is achieved around Co. Figure 6, which is divided into two drawings for better visibility, gives the atom numbering scheme. Selected bond distances and angles are listed in table 4.

As in the free DHPTBenz, the *bis*-hydrazine-triazine units in both ligands (L1: N1–N8, C1–C3; L2: N9–N16, C35–C37) of the complex cation are almost planar. The two planes are oriented orthogonally to each other.

Around Co the four coordinating N atoms of the hydrazinyl residues are not located exactly within a CoN_4 plane as could be expected for a regular octahedron. The two N atoms of one ligand are located above the Co and the two of the other ligand below the Co with N–Co–N angles of 149.7(1)° (N6–Co1–N8) and 149.5(1)° (N14–Co1–N16). The two Co1–N(triazine) distances [L1: N1–Co1: 1.954(3) Å and L2: N9–Co1: 1.953(3) Å, respectively] are much shorter than the average of the four Co–N(hydrazinyl) bond lengths (2.313 Å). This tetragonally compressed octahedron results from the rigid bite distance of the tridentate DHPTBenz. Homoleptic cobalt(II) complexes with comparable tridentate triazine-based ligand systems are 2,4-di-(2′-pyridyl)-6-*R*)-1,3,5-triazine units (*R* = organic residue), for example $[Co(L)_2][PF_6]$ with *L* = 2,4-di-(2′-pyridyl)-6-(p-bromophenyl)-1,3,5-triazine) [12]. The Co–N(triazine) bond

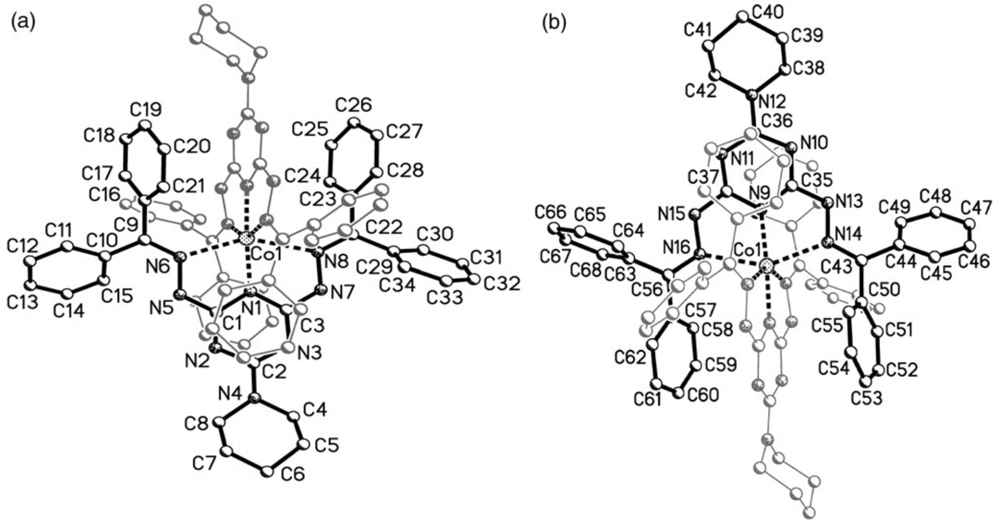


Figure 6. View of the structure of the complex cation in Co-DHPTBenz. Because of better visibility, the picture on the 1eft shows the numbering scheme of ligand 1 only, whereas the picture on the right side shows that of ligand 2.

Table 4. Selected bond lengths and angles in Co-DHPTBenz.

Atoms	Bond length (Å)	Atoms	Bond length (Å)
Ligand 1		**Ligand 2**	
Co1–N1	1.954(3)	Co1–N9	1.953(3)
Co1–N6	2.253(3)	Co1–N14	2.240(3)
Co1–N8	2.386(3)	Co1–N16	2.373(3)
C1–N5	1.344(4)	C35–N13	1.369(4)
N5–N6	1.378(4)	N13–N14	1.390(4)
C9–N6	1.307(4)	N14–C43	1.301(4)
C3–N7	1.350(5)	C37–N15	1.354(4)
N7–N8	1.387(4)	N15–N16	1.379(4)
C22–N8	1.289(5)	C56–N16	1.299(5)
Average C–N(triazine)			
1.341		1.337	
Atoms	Angle (°)	Atoms	Angle (°)
N1–Co1–N6	76.1(2)	N9–Co1–N14	75.7(2)
N1–Co1–N8	73.7(2)	N9–Co1–N16	73.8(2)
C1–N5–N6	119.4(3)	C35–N13–N14	116.2(3)
C3–N7–N8	119.5(3)	C37–N15–N16	118.8(3)
N6–Co1–N8	149.7(1)	N14–Co1–N16	149.5(1)

length is 1.986 Å, only slightly longer than that in our complex. Another comparable homoleptic Co complex contains the 2,4,6-*tris*-(2′-pyridyl)-1,3,5-triazine ligand where the Co–N(triazine) bond length is even longer (2.058 Å) [20, 11].

Bond distances within the ligands of the complex cation do not deviate much from those found in the free ligand. An interesting feature of this complex cation is its overall size, resulting from the large coordinated ligand molecules. Figure 7 gives a view of the molecular packing within the unit cell. One molecule is presented as a space filling

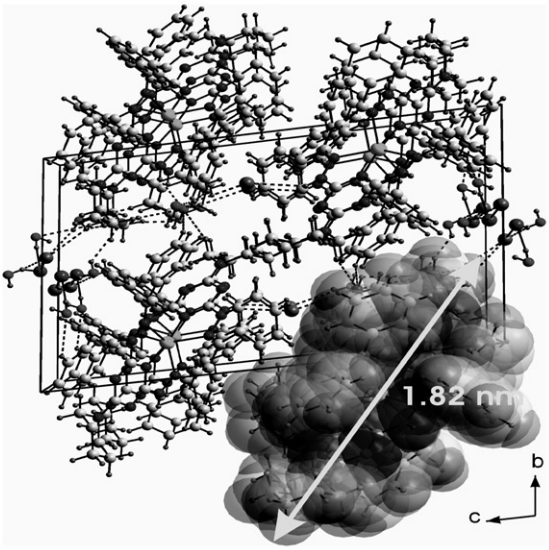


Figure 7. View of the unit cell of Co-DHPTBenz with one complex cation presented as space filling model and the nanometer-scaled diameter added.

model to show its size. The longest diameter through the cation measures 1.82 nm, therefore it may be called a nanometer-scaled complex cation.

4. Conclusion

A new large 1,3,5-triazine-based ligand, which carries only nitrogen donors, was prepared using a three-step reaction procedure. Treated with a Co(II) salt, this ligand forms a mononuclear complex, which has an overall nanometer-scaled ball shape. The coordination environment of Co(II) is distorted octahedrally. The X-ray structures of the complex salt, the free ligand and one of the precursors are reported. Besides the synthesis and the structures, elemental analysis, IR, UV, and NMR spectroscopic as well as mass spectroscopic data of the new compounds were measured.

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