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Polynuclear complexes of vanadium(IV) and lithium with branched triazine-based Schiff base ligands

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ABSTRACT

Four dendrimeric hexa- or nona-dentate Schiff base ligands based on triazine structure and several lithium and vanadium(IV) complexes with these ligands were synthesized and characterized by elemental analysis, ¹H NMR and IR spectra. The synthetic methods are described, and we paid special attention to the need to use a co-ligand (in case of vanadium complexes) to prevent the creation of polynuclear systems. All complexes belong to a small group of compounds with dendrimeric Schiff base ligands.

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Triazine; Schiff base; vanadium; lithium; spectroscopy



1. Introduction

Control of structures using supramolecular interactions is an area of great interest in chemistry and biochemistry as well as in crystal engineering [1, 2]. Crystal engineering

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and supramolecular synthetic methodology require knowledge of the strength and directional characteristics of the intermolecular forces. Part of supramolecular chemistry concentrates on dendrimers which are monodispersed, highly branched molecules terminated with multiple functional groups. Their structures lead to several interesting properties, including good solubility and low viscosity [3, 4]. Many dendritic architectures have been described, including polyamines [5], polyphenylene [6], triazine-containing dendrimers [7, 8], polyamidoamines [9], carbosilanes [10] and polynuclear metal complexes [11].

1,3,5-Triazine-containing compounds are powerful chelating agents and have been used for preparation of metal complexes [12] and liquid crystals [13]. S-triazine derivatives have proven their great potential in supramolecular chemistry [14]. Recently triazines have found extensive use as reagents in the conversion of functional groups [15]. Stepwise selective substitution of cyanuric chloride is utilized in the preparation of triazine-based dendrimers [16]. The systematic replacement of chlorine atoms under appropriate temperature improves the utility of this inexpensive and readily available compound for the preparation of mono-, di- and tri-substituted S-triazines [17, 18] and offers access to a number of useful molecules, from medicinal chemistry to advanced materials [19, 20]. Despite the possibility to obtain mono- and di-substituted triazines we concentrated only on tri-substituted products due to the problems with substitution of the remaining chlorine atoms by NH₂ group of hydrazides in the next step of the synthesis. Most literature data relate to the properties and applications of triazine is very limited.

In the present paper we describe the synthesis of four dendrimeric Schiff base ligands based on triazine which were used in synthesis of lithium and vanadium complexes. The composition of ligands and complexes was determined based on elemental analysis, IR and ¹H NMR spectra.

2. Experimental

2.1. Materials and methods

In syntheses the 2,4,6-trichloro-1,3,5-triazine, 4-hydroxybenzaldehyde, 4-hydroxyacetophenone, sodium hydroxide, 4-pyridinecarboxylic acid hydrazide, 3-pyridinecarboxylic acid hydrazide, 2-pyridinecarboxylic acid hydrazide, 3-hydroxy-2-naphthoic acid hydrazide, acetone, THF, [VO(acac)₃], metallic lithium and NaOH were used. All chemicals were of analytical grade (Aldrich) and were used as supplied. Microanalysis of carbon, hydrogen and nitrogen were performed using an Elementar Vario MICRO Cube elemental analyzer. Magnetic susceptibility measurements were performed on a SHERWOOD SCIENTIFIC magnetic susceptibility balance. Solid samples for IR spectroscopy were recorded on a Nicolet iS5 FT-IR spectrophotometer. ¹H NMR spectra were measured on a Bruker AVANCE III 600 MHz Instrument in DMSO-d₆. Thermogravimetric measurements were performed TGA/SDTA 851e Mettler Toledo on а Microthermogavimeter at scan speed 10 °/min from 25 to 600 °C under argon. The vanadium content in complexes was determined using spectrometric determination of vanadium peroxides, the calibration curve was made using NH_4VO_3 . The electronic

absorption spectra in UV-Vis range were recorded on a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer equipped with a CPS-240 temperature controller.

2.2. Synthetic procedures

2.2.1. Synthesis of 2,4,6-tris(4-formylphenoxy)-1,3,5-triazine (1) $[N_3C_3(-OC_6H_4-p-CHO)_3]$ 2,4,6-tris(4-formylphenoxy)-1,3,5-triazine (1) was synthesized according to general literature method [21]. To 2,4,6-trichloro-1,3,5-triazine (0.012 mol, 2.30 g) in 20 mL of acetone, 4-hydroxybenzaldehyde (0.036 mol, 4.43 g), dissolved in 20 mL of acetone was added. The reaction mixture was stirred and held in an ice bath (0–5 °C) as long as the NaOH (0.037 mol, 1.51 g), dissolved in 15 mL of water, was added. The mixture was stirred at room temperature for 120 minutes and then heated at 70 °C in an oil bath for 180 minutes. The white precipitate was filtered off, washed with water and air dried. Yield: 85%. Anal. Calc. for $C_{24}H_{15}N_3O_6$: C, 65.31; H, 3.43; N, 9.52%. Found: C, 64.37; H, 3.38; N, 9.57%. IR (ATR, cm⁻¹): 1698 (C = O), 1567 (C = N_{triazine}), 1162 (C–O), 842 (C–N_{triazine}).

2.2.2. Synthesis of 2,4,6-tris(4-acetylphenoxy)-1,3,5-triazine (2) $[N_3C_3(-OC_6H_4-p-CH_3O)_3]$

2,4,6-tris(4-acetylphenoxy)-1,3,5-triazine (**2**) was synthesized similarly to **1**. To 2,4,6-trichloro-1,3,5-triazine (0.012 mol, 2.30 g) in 20 mL of acetone, 4-hydroxyacetophenone (0.036 mol, 5.03 g), dissolved in 20 mL of acetone, was added. The reaction mixture was stirred and held in an ice bath (0–5 °C) as long as the NaOH (0.037 mol, 1.53 g), dissolved in 15 mL of water, was added. The mixture was stirred at room temperature for 120 minutes and then heated at 70 °C in an oil bath for 180 minutes. The white precipitate was filtered off, washed with water and air dried. Yield: 90%. Anal. Calc. for $C_{27}H_{21}N_3O_6$: C, 67.07; H, 4.39; N, 8.69%. Found: C, 66.90; H, 4.68; N, 8.63%. IR (ATR, cm⁻¹): 1688 (C = O), 1566 (C = N_{triazine}), 1169 (C–O), 848 (C–N_{triazine}).

2.2.3. Synthesis of triazine-based Schiff base ligands (3a-d)

2,4,6-tris(4-formylphenoxy)-1,3,5-triazine (1) (0.221 g, 0.5 mmol) was added to a solution of 4-pyridinecarboxylic acid hydrazide (0.208 g, 1.5 mmol) in THF (70 mL). The colorless solution was heated under reflux for 19 h. The solvent was then removed by evaporation under reduced pressure. The residue (**3a**) was filtered off, washed with the hot THF and dried in air at room temperature. The same procedure was performed for **3bd**. As hydrazide components the 3-pyridinecarboxylic acid hydrazide (**3b**), 2-pyridinecarboxylic acid hydrazide (**3c**) or 3-hydroxy-2-naphthoic acid hydrazide (**3d**) were used. The scheme of the syntheses is presented in Figure 1.

For **3a** - yield: 78%. Anal. Calc. for $C_{42}H_{38}N_{12}O_{10}$: C, 57.93; H, 4.40; N, 19.30%. Found: C, 57.26; H, 4.025; N, 18.73%. IR (ATR, cm⁻¹): 3219 (N–H), 1660 (C = O), 1608 (C = N_{imine}), 1572 (C = N_{triazine}), 1361 (C–O–Ar). ¹H NMR (DMSO-d₆, 25 °C) (δ : ppm): 7.36 (d, 2H, Ar–H), 7.81 (d, 2H, Ar–H), 7.81 (d, 4H, Ar–H), 8.49 (s, 1H, N = CH), 8.76 (d, 2H, Ar–H), 12.08 (s, 1H, N–H).

For **3b** – yield: 74%. Anal. Calc. for $C_{42}H_{34}N_{12}O_8$: C, 60.43; H, 4.11; N, 20.13%. Found: C, 60.19; H, 4.165; N, 19.69%. IR (ATR, cm⁻¹): 3223 (N–H), 1659 (C = O), 1607



Figure 1. Scheme of the dendrimer Schiff base ligands (3a-3d) syntheses.

 $(C = N_{imine})$, 1570 ($C = N_{triazine}$), 1369 (C-O-Ar). ¹H NMR (DMSO-d₆, 25 °C) (δ : ppm): 7.36 (d, 2H, Ar-H), 7.56 (t, 1H, Ar-H), 7.80 (d, 2H, Ar-H), 8.25 (d, 1H, Ar-H), 8.48 (s, 1H, N = CH), 8.75 (d, 1H, Ar-H), 9.06 (s, 1H, Ar-H), 12.03 (s, 1H, N-H).

For **3c** - yield: 76%. Anal. Calc. for $C_{42}H_{34}N_{12}O_8$: C, 60.43; H, 4.11; N, 20.13%. Found: C, 60.87; H, 4.01; N, 19.90%. IR (ATR, cm⁻¹): 3289 (N–H), 1682 (C = O), 1610 (C = N_{imine}), 1572 (C = N_{triazine}), 1360 (C–O–Ar).

For **3d** - yield: 82%. Anal. Calc. for $C_{57}H_{41}N_9O_{10}$: C, 67.66; H, 4.08; N, 12.46%. Found: C, 67.72; H, 4.04; N, 12.22%. IR (ATR, cm⁻¹): 3057 (O–H), 1668 (C=O), 1611 (C=N_{imine}), 1582 (C=N_{triazine}), 1371 (C–O–Ar). ¹H NMR (DMSO-d₆, 25 °C) (δ : ppm): 7.30–7.85 (d, Ar–H), 8.50 (s, 1H, N=CH), 11.28 (s, 1H, O–H), 11.99 (s, 1H, N–H).

2.2.4. Synthesis of $[Li_3(3d)(H_2O)_6] \cdot 4H_2O$ (4)

0.40 M MeOLi solution was prepared by dissolving 70 mg of lithium in 25 mL of methanol. To 10 mg (10 μ mol) of **3d**, a MeOLi solution was added until a clear solution was formed (*ca.* 0.158 mL, 63.2 μ mol). After a few hours, the resulting precipitate was filtered off, rinsed with a small amount of methanol and then air dried. Anal. Calc. for C₅₇H₅₆Li₃N₉O₁₉: C, 57.44; H, 4.74; N, 10.58%. Found: C, 57.34; H, 4.19; N, 10.02%.

2.2.5. Synthesis of $[VO(OMe)(3d)_{2/3}]_n$ (5) and $[{VO(EtO)(phen)}]$ (3d) (6)

 $[VO(acac)_2]$ was used in a molar ratio to the ligand of 3:1. All reactions were performed under argon to prevent oxidation of vanadium(IV) to vanadium(V). The synthesis of the vanadium(IV) complex with **3d** was carried out in two different ways. In method

A, **3d** ligand was used and the reaction was performed in methanol. The second method (B) was carried out by *in situ* ligand formation, the individual components (**1** and 3-hydroxy-2-naphthoic acid hydrazide) in a molar ratio of 1:3 were dissolved in ethanol. In method B additionally 1,10-phenanthroline was added at the end of the reaction to precipitate the product by saturation of coordination sphere of vanadium.

A. To 0.0987 g (0.1 mmol) of the **3d** ligand, dissolved in 30 mL of methanol, 0.0795 g (0.3 mmol) of $[VO(acac)_2]$ was added. The mixture was refluxed under argon for 90 minutes. The resulting gray-green amorphous precipitate was filtered and rinsed with a small amount of methanol. The solid was then air dried and 0.0723 g of **5** was obtained.

B. To 0.256 g (0.5 mmol) of **1**, 30 mL of ethanol and 0.303 g (1.5 mmol) of 3-hydroxy-2-naphthoic hydrazide were added. The mixture was refluxed under argon for 30 minutes. 0.398 g (1.5 mmol) of $[VO(acac)_2]$ was then added to the yellow solution and heated for 10 minutes. Then 0.270 g (1.5 mmol) of 1,10-phenanthroline was added to the brown solution, followed by filtration of the brown fine-crystalline precipitate, rinsing with a small amount of ethanol and air dried giving 0.496 g of **6**. Anal. Calc. for C₉₉H₇₅N₁₅O₁₅V₃: C, 63.67; H, 4.05; N, 11.25; V, 8.20%. Found: C, 63.53; H, 3.97; N, 10.95; V, 8.50%.

2.2.6. Synthesis of [{VO(acac)}₃(tkh)] (7)

The Schiff base ligand (tkh) derived from **2** and 3-hydroxy-2-naphthoic acid hydrazide was prepared *in situ*. To 0.251g (0.5 mmol) of **2**, 30 mL of methanol and 0.307g (1.5 mmol) of 3-hydroxy-2-naphthoic acid hydrazide were added. The mixture was refluxed under argon for 30 minutes. 0.387g (1.5 mmol) [VO(acac)₂] was added to the clear yellow solution and the resulting fine crystalline brown precipitate was filtered off and rinsed with a small amount of methanol. 0.473g of **7** was obtained. Anal. Calc. for $C_{75}H_{63}N_9O_{18}V_3$: C, 58.83; H, 4.15; N, 8.23; V, 10.00%. Found: C, 58.61; H, 4.32; N, 8.37; V, 9.64%.

2.2.7. Synthesis of $[{VO(EtO)(phen)}_{3}(tkh)] \cdot 4H_{2}O$ (8)

To 0.256 g (0.5 mmol) of **2**, 30 mL of ethanol and 0.303 g (1.5 mmol) of 3-hydroxy-2-naphthoic hydrazide were added. The mixture was refluxed under argon for 30 minutes. 0.398 g (1.5 mmol) of [VO(acac)₂] was then added to the clear yellow solution and the resulting brown solution was heated for a further 30 minutes. Then 0.270 g (1.5 mmol) of 1,10-phenanthroline was added, and the resulting red fine crystalline precipitate was filtered off and rinsed with a small amount of ethanol. 0.549 g of product was obtained. Anal. Calc. for $C_{102}H_{89}N_{15}O_{19}V_3$: C, 61.82; H, 4.53; N, 10.60; V, 7.73%. Found: C, 61.56; H, 4.37; N, 10.17; V, 7.42%.

2.2.8. Synthesis of [VO(acanh₂)(OEt)] (9)

Complex **7** (0.2 g) was dissolved in ethanol and refluxed 15 minutes. After 2 days the formed crystals were filtered off, washed with a small amount of ethanol and air dried. Anal. Found: C, 54.83; H, 4.86; N, 7.10%. Calculated for $C_{18}H_{19}N_2O_5V$: C, 54.81, H, 4.92, N, 7.13%.

3. Results and discussion

3.1. General remarks to the syntheses

As **1** and **2** were obtained according to methods described in the literature, only purity of the products was checked by elemental analyses and infrared spectra, which were found to be consistent with the literature data [21, 22]. In our research we planned to receive the asymmetrical systems in which only one or two chlorine atoms in cyanuric chloride were substituted. However, the resulting products were unstable, and we observed a change in their color, even if the products were stored at -20 °C.

All three chlorine atoms in 2,4,6-trichloro-1,3,5-triazine have been substituted on 4-hydroxybenzaldehyde or 4-hydroxyacetophenone for **1** and **2**, respectively, and the obtained ligands were used in the synthesis of complexes and more extensive polynuclear systems.

Ligand 1 contains three aldehyde groups. Due to large steric hindrances, triazine nitrogens and oxygens are hardly available as donors for *d*-electron metals. The oxygens of the aldehyde groups may be coordinated to the metallic center, however, in synthesis of the Schiff bases they are converted to nitrogens with the separation of water molecules. Thus, it can be considered that in **3a-3d**, the core originated from **1** does not have donor atoms available for coordination and all donor atoms must come from amine or hydrazide components of the Schiff base. In syntheses of **3a-3d**, selected aromatic hydrazides possessing two donor atoms in positions enabling formation of a five-membered ring after coordination of the metal ion have been used. Additionally, a third donor was introduced - nitrogen in the pyridine ring, by using such hydrazides as pyridine-4-carbohydrazide, pyridine-3-carbohydrazide and pyridine-2-carbohydrazide. The presence of a nitrogen in the aromatic ring increases the hydrophilic properties of the ligand, compared to those with benzene ring, this increase in solubility of ligands in polar solvents is crucial for complex formation. Another aspect is the position of the nitrogen in the pyridine ring of selected hydrazides. In the case of pyridine-2-carbohydrazide (a substituent in the ortho position), there is an additional possibility of coordinating the nitrogen of the pyridine ring with the oxygen of the carbonyl moiety (also a five-membered ring after coordination of the metal ion). It is therefore possible to obtain more complicated structures, on the other hand, these may cause problems with the formation of mixtures in which the metal will be coordinated once to the carbonyl oxygen and to the imine nitrogen, and once to the carbonyl oxygen and to the pyridine nitrogen. Therefore, it was decided to obtain ligands in which the pyridine nitrogen would be in the *meta* and *para* position (pyridine-3-carbohydrazide and pyridine-4-carbohydrazide were used). Then, the resulting complexes with such ligands could be compared with the complex with a ligand in which the amine component is pyridine-2-carbohydrazide. It should also be mentioned that in the case of meta and para positions, it is also possible to coordinate to the nitrogen of the pyridine ring due to the flexibility of the obtained ligands. The ligand with the pyridine nitrogen in the para position may coordinate as a single-binding ligand (with lower power), however, in this case no competition between the metal ions appears. Complexes with **3a** and **3b** can serve as metaloligands in formation of more complicated polymeric structures. Due to geometry of **3a-3d** only two donor atoms (from six available) can coordinate to one metal center, so ligands **3a-3d** can bind three metal centers in total.

Initially, syntheses of 1 and pyridine-carbohydrazide ligands were carried out as Schiff base syntheses - the components, in a suitable molar ratio, were dissolved in ethanol and refluxed for 60 minutes. Using this synthetic procedure, one of the substrates (usually 1) was obtained as a result of the reaction, which was confirmed by the infrared spectra and elemental analysis. It was decided to perform the synthesis using a literature method, in which the authors received similar type of ligands based on 1 and *para*-substituted aromatic hydrazides [23]. THF was used to dissolve the Schiff base components and the synthesis was carried out in an oil bath at 70 °C for 18 h. The resulting **3a-d** ligands are amorphous, yellow solids, stable in solid state and almost insoluble in water and most organic solvents except DMSO (excluding 3c). Only 3d dissolves relatively well in MeOH and EtOH. The characterization of ligands was made using methods such as elemental analysis, infrared spectroscopy and ^{1}H NMR. The results of ¹H NMR are summarized in section 2.2.3 and the spectra are presented in Supplementary Material. For 3c due to the problems with solubility the structure was proposed based on elemental analysis and comparison of IR spectra of all three pyridine-carbohydrazide Schiff base ligands. Due to the insignificant solubility of **3a-3c** only **3d** was used for the synthesis of complexes with metals such as lithium and vanadium(IV).

3.2. Characteristics of 4

Complex **4**, $[Li_3(3d)(H_2O)_6]\cdot 4H_2O$, is a light yellow amorphous solid. It is poorly soluble in water and in selected organic solvents such as ethanol, methanol, acetonitrile and acetone. In Figure 2 the proposed structure is presented, omitting four waters of hydration.

In **4**, the lithium coordination sphere is composed of a bidentate **3d** ligand with oxygen donor carbonyl and hydroxyl moieties, as well as two water ligands and thus the coordination number is four. The branched Schiff base ligand coordinates one lithium in each arm, resulting in a multi-core complex compound.

The infrared spectrum in the 550–4000 cm⁻¹ range for **4** (Figure 3) was compared to the spectrum of **3d**. Figure 3 presents the spectra with a cutoff between 1800 and 2500 cm^{-1} due to the lack of bands in this region.

Significant changes are observed in the spectrum of **4** relative to that of **3d** which can be attributed for the formation of a lithium salt of **3d**. These changes include intensity and band position changes. The bands located at 1298 and 1322 cm⁻¹, attributed to the oscillation of the OH group, disappeared on coordination to lithium. Similar changes are observed in the $2800-3500 \text{ cm}^{-1}$ region. In addition, the shift of the band from 1668 cm^{-1} to 1634 cm^{-1} associated with the oscillation of the carbonyl moiety is observed. These changes, as well as changes in all other band positions and intensities indicate bidentate coordination of **3d** to lithium. The estimated stoichiometry Li:**3d** (3:1), changes in the IR spectra in OH and C = O region and relatively small changes in the C = N and NH bands support the formula of **4** presented in Figure 2. The infrared spectrum confirms the presence of water molecules (bands at



Figure 2. The structure of 4; waters of hydration are omitted for clarity.



Figure 3. IR (with ATR correction) spectra for 3d (black, solid line) and 4 (red, dashed line).



Figure 4. Scheme of the monomer unit of 5.



Figure 5. The structure of 6.

700–890 cm⁻¹, 1260–1410 cm⁻¹, 1640 cm⁻¹ and the broad bands at 2750–3750 cm⁻¹); it is however difficult to attribute these bands directly to water of hydration or water as aqua ligands. This is probably caused by the fact that the interactions of aqua ligands with lithium are relatively weak and overlaps with those of water of hydration resulting in band broadening.



Figure 6. IR spectra of 3d (black, solid line), 5 (red, dotted line) and 6 (blue, dashed line).

3.3. Characteristics of 5 and 6

Reaction of [VO(acac)₂] with **3d** results in ligand coordination, but in methanol as solvent fast precipitation of gray-green, amorphous product is observed. Its composition indicates that vanadium is coordinated to two **3d** ligands, resulting in a polymeric structure presented in a simplified manner in Figure 4. The product is almost insoluble in water and in organic solvents.

To avoid formation of **5**, ethanol was used as a solvent and **3d** was synthesized *in situ*; phen (as a co-ligand) was used to precipitate **6** and to prevent further coordination of **3d**. Fine crystalline, brown precipitate of **6**, with formula presented in Figure 5, was isolated. The isolated salt, in contrast to **5**, shows good solubility in organic solvents; only in water poor solubility is observed. Despite many attempts to recrystallize isolated compounds, large enough single crystalls, suitable for X-ray structural analysis, were not obtained. Longer period of crystallization results in slow formation of **5** and release of phen.

Both complexes were stable as solids. The vanadium is six coordinate with oxido, methoxy (5) or ethoxy (6), bidentate **3d** (5 and 6) and phen (6) ligands. When phen was not used as a co-ligand, the coordination sphere of vanadium is filled with a second **3d** ligand. This results in formation of polymeric compound, thus **5** is almost insoluble. Presence of phen during synthesis results in its coordination and formation of monomeric **6**. The synthetic procedure may also indicate that polymeric **5** is less stable and its heating in the presence of phen should convert it into **6**.

The IR spectra of **5** and **6** were compared with the spectrum of **3d** (Figure 6). In the spectrum of **5**, an intense band at 990 cm⁻¹ is observed, which is related to the V = O moiety. For **3d**, the vibrations associated with the carbonyl group (1668 cm⁻¹), the imine bond (1611 cm⁻¹) and the hydroxyl group (3057 cm⁻¹) are observed. In the spectrum of **5**, the bands related to the carbonyl and imine moieties were changed (the carbonyl group shifted to 1659 cm⁻¹ and the imine band shifted to 1638 cm⁻¹),



Figure 7. The structure of 7.

which is connected with coordination of vanadium to the carbonyl oxygen. Based on the infrared spectrum, it can be concluded that the resulting compound is a polymer in which the vanadium coordination sphere can be saturated by another **3d** ligand. The structure of this compound is indicated by the presence of the one intense band at 990 cm⁻¹. In a similar system, $[VO(acac)_2]$ band at 995 cm⁻¹ was also attributed to V = O vibration [24]. This supports proposed structure of **5** in which only oxygen donors are present around vanadium. The polymeric structure of 5 was confirmed also by magnetic measurements based on which the molar weight can be estimated on 783 ± 80 per one vanadium d^1 center. A gram susceptibility value for **5** is 1.62×10^{-6} cm³·g⁻¹. Assuming the vanadium magnetic moment at 1.73 µB, the molar mass of the compound per vanadium of 778 g is obtained. This corresponds to the coordination of not one, but two ligand molecules to one vanadium ion, which gives a total 2/3 mole of ligand per one mole of vanadium, as schematically shown in Figure 4. With the compound structure assumed in the figure, vanadium is also coordinated with oxo ligand, and for filling the charge and coordination number with methoxy group, which gives a molar mass of $778 \text{ g} \cdot \text{mol}^{-1}$.

In the spectrum of **6**, a band located at 961 cm^{-1} characteristic for V = O is observed. In addition, there is a band related to the $v_{C=N}$ vibration at 1622 cm^{-1} , a band at $2600-3500 \text{ cm}^{-1}$ characteristic for the vibration of the hydroxyl group present in the hydrazide fragment, as well as the band originating from the vibration of the carbonyl group of hydrazide (1637 cm^{-1}). The intense band at 1365 cm^{-1} is derived



Figure 8. The structure of 8; waters of hydration are omitted for clarity.

from the vibration of the C–O–Ar moiety present in the resulting Schiff base ligand. There is also observed a band attributed to the $C = N_{triazine}$ (1582 cm⁻¹). In general, spectra of **5** and **6** are similar. The main differences relate to the presence of bands derived from the phen ligand at 744 cm⁻¹, 1438 cm⁻¹ and 1505 cm⁻¹, as observed in other complexes with phen ligand [25].

The TG analysis (Supplementary Material) indicates that above 300 °C decomposition of the Schiff base ligand is observed. The EtO ligands at 250 °C are released first ($\Delta m_{exp} = 7.62\%$, $\Delta m_{calc} = 7.40\%$).

3.4. Characteristics of 7 and 8

The *in situ* formed ligand based on **2** and 3-hydroxy-2-naphthoic acid hydrazide react with [VO(acac)₂] yielding **7** as a stable, fine-crystalline brown precipitate. When phen was added, before isolation of **7**, the acac⁻ ligand in **7** is substituted with phen, resulting in formation of **8** as a stable, red, finely crystalline precipitate. Structures of **7** and **8** are presented in Figures 7 and 8, respectively.

In each arm of **7** and **8** the Schiff base ligand coordinates by oxygen of the carbonyl group and oxygen of the deprotonated hydroxyl group, and the coordination sphere is filled additionally with oxido (**7** and **8**), $acac^{-}$ (**7**), ethoxy (**8**) and phen (**8**) ligands.



Figure 9. IR spectra of 2 (black, solid line), 3-hydroxy-2-naphthoic acid hydrazide (red, dashed line) and 7 (blue, dotted line).

The complexes form very fine crystals that we were unable to measure single crystal X-ray structures. **7** is unstable in ethanolic solution and decomposes to a new crystalline product (**9**), whose single crystal X-ray was identical with that described in literature as a product of reaction of $[VO(acac)_2]$ and 3-hydroxy-2-naphthoic acid hydrazide [26]. The decomposition of **7** after recrystallization indicates that the Schiff base imine bond is not very stable and acetylacetone ligand from $[VO(acac)_2]$ can exchange the triazine part. In this process we also observed a simple vanadium oxidation from V(IV) to V(V).

The IR spectra of **7** and **8** are presented in Figures 9 and 10, respectively. For comparison, the spectra of **2** and 3-hydroxy-2-naphthoic acid hydrazide are also included. Figure 11 summarizes the spectra of **7** and **8**.

The presented spectra indicate formation of a vanadium(IV) complex with a Schiff base ligand based on **2** and 3-hydroxy-2-naphthoic acid hydrazide. In the spectrum of the product (blue line) a band located at 958 cm⁻¹ (for **7**) and 959 cm⁻¹ (for **8**) characteristic for the V = O group appears. Bands associated with vibration of the C–O–Ar group (1362 cm⁻¹ for **7** and 1373 cm⁻¹ for **8**), the vibration of the C=O bond originating from the hydrazide ligand fragment (1681 cm⁻¹ for **7** and 1683 cm⁻¹ for **8**), as well as the vibration originating from the formed imine bond C = N (1638 cm⁻¹ for **7** and 1626 cm⁻¹ (for **7**) and 1584 cm⁻¹ for **8**, which can be assigned to the C = N_{triazine} linkage, confirming the presence of a triazine ring in the resulting compounds. In spectra of **7** and **8** there is no band at 1688 cm⁻¹ (C = O), which is observed in the spectrum of **2**, indicating condensation of all three carbonyl groups by 3-hydroxy-2-naphthoic acid hydrazide. The change in the spectra of the resulting complexes above 3000 cm⁻¹, relative to the spectrum of 3-hydroxy-2-naphthoic acid hydrazide, indicates



Figure 10. IR spectra of 2 (black, solid line), 3-hydroxy-2-naphthoic acid hydrazide (red, dashed line) and 8 (blue, dotted line).



Figure 11. Comparison of the IR spectra of 7 (black, solid line) and 8 (red, dashed line).

participation of the hydroxyl group in the formation of the vanadium coordination sphere - the disappearance of the band characteristic for the OH group. The spectra of **7** and **8** are similar, which is related to the coordination of the same Schiff base ligand (tkh), whose vibrations dominated the spectra of **7** and **8**. Only the changes connected with different ligands, bands at 1266 cm^{-1} , 1435 cm^{-1} and 1503 cm^{-1} (for acac⁻ ligand in **7**) and 724 cm^{-1} , 1426 cm^{-1} and 1506 cm^{-1} (for phen ligand in **8**), are observed.

The TG measurements for **7** and **8** indicate that complexes are moisture sensitive and similarly, to previous study, the Schiff base ligand decomposes [27]. For **8** water molecules are released at 200 °C (Table S1 in Supplementary Material), assigned to $2.5 H_2O$ ($\Delta m_{exp} = 2.11\%$, $\Delta m_{obl} = 2.27\%$). The elemental analysis results give the formula with $4 H_2O$, however it was measured directly after complex isolation, while the TG measurements are much later. As seen in TG for **6-8**, the constant mass loss is observed starting from room temperature, for **8**, it means that only the water, which remained after this time, could be determined by TG measurements. As the water is not strongly bonded, this is a common problem for such materials of porous structure.

4. Conclusion

Six symmetrical branched ligands based on triazine structure were synthesized and characterized. 2,4,6-Trichloro-1,3,5-triazine, used in syntheses, gives the opportunity to obtain asymmetrical systems in which only one or two chlorine atoms would be substituted. Despite the literature descriptions, we have found that with 4-hydroxybenzaldehyde the resulting unsymmetrical compounds were not stable. Decomposition processes were observed, along with a change in their color, even if the products were stored at -20 °C. It was necessary to substitute all chlorine atoms. We also proved that choosing the right solvent in synthesis is important, as well as selection of the Schiff base components that will increase the solubility of the resulting dendrimeric ligands based on triazine. Initially, ligand 1 was used as an aldehyde component and pyridine carbohydrazides as amine components due to the presence of at least two donors and a nitrogen in the pyridine ring, which increases the solubility of the entire ligand molecule. As a result, pyridine-based dendrimeric ligands (3a-3c) had poor solubility, therefore 3-hydroxy-2-naphthoic acid hydrazide was chosen, in which the presence of the hydroxyl group increased the solubility of the branched ligand and it was possible to use **3d** in the synthesis of complexes.

Five complexes were isolated and characterized both in one- and in multi-stage reactions. The type of solvent was very important for the synthesis of vanadium(IV) complexes with **3d** and **tkh** ligands. Syntheses carried out in methanol did not require the use of additional ligands as precipitation of the fine crystalline product occurred when [VO(acac)₂] was added. In ethanol, formation of polymeric compound was observed, the coordination sphere is occupied by another arm of **3d** ligand from another molecule forming a polymeric structure. To prevent polymer formation 1,10-phenanthroline was used to saturate the coordination sphere and precipitation of monomer was observed. In the case of the **tkh** ligand, the monomeric compounds were formed, whether phenanthroline was used or not.

Disclosure statement

No potential conflict of interest was reported by the author(s).

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