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Synthesis, spectral properties and supramolecular dimerisation of heteroleptic triple-decker phthalocyaninato complexes with one outer crown-substituted ligand

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Abstract

Four complexes – [(15C5)₄Pc]M(Pc)M(Pc), (Pc²⁻ – phthalocyaninato-dianion, [(15C5)₄Pc]²⁻ – 2,3,9,10,16,17,24,25-tetrakis(15-crown-5) phthalocyaninato-dianion, M = Sm, Dy, Tm, Y) were obtained via the reaction of M(Pc)₂, H₂[(15C5)₄Pc] and M(acac)₃. The influence of the stability of starting M(Pc)₂ on the yields of target compounds was investigated. Increasing the stability of M(Pc)₂ leads to higher yields of [(15C5)₄Pc]M(Pc)M(Pc) and lower yields of scrambling products. All complexes were characterized by ¹H NMR, UV–Vis and FT-IR spectroscopy as well as MALDI TOF mass-spectrometry. The analysis of ¹H NMR spectra was performed in terms of lanthanide-induced shifts. Cation-induced dimerisation was studied by means of spectrophotometric titration. Supramolecular dimers {2[(15C5)₄Pc]M(Pc)M(Pc) · 4K⁺} are the largest discrete cofacial supramolecular assemblies built of phthalocyanine building blocks reported up-to-date. The observed increase of the intermolecular excitonic interaction between building blocks with the increase of REE(III) size is tentatively explained in terms of metal-size dependent deformation of phthalocyanine ligands in sandwich complexes.

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Keywords: Rare earths; Macrocyclic ligands; Phthalocyanines; Heteroleptic complexes; Supramolecular dimerisation

1. Introduction

Due to large aromatic π -system, phthalocyanines (Pc) and their complexes exhibit numerous unique physical-chemical properties, which are responsible for their wide applications [1]. To expand the conjugated Pc's π -system and to widen their fields of application, different approaches can be used. One of them is annelation of peripheral benzene rings with naphthalene [2a], helicene [2b], etc. Another approach is the synthesis of sandwich

double- and triple-decker complexes – M(Pc)₂ and M₂(Pc)₃ with the overlap of π -orbitals and consequent strong intramolecular π – π -interaction, which depends on the size of M [3a]. Comparison of the electrochemical properties of Zn[(C₈H₁₇O)₈Pc], M[(C₈H₁₇O)₈Pc]₂ and [(C₈H₁₇O)₈Pc]M[(C₈H₁₇O)₈Pc]M(Pc), where [(C₈H₁₇O)₈Pc] – octakis(4,5-octyloxy)phthalocyanine, M = Eu–Lu and Y, indicates that the HOMO–LUMO gap contracts almost linearly with the number of stacked Pc ligands [3b]. The third general approach to obtain compounds with the extended π -system is the synthesis of supramolecular assemblies [4]. Self-assembly of complementary molecular units leads to complexes with novel properties, which are not typical for starting building blocks [4b,4c]. The synthesis of heteroleptic double-decker complexes

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$[(15C5)_4Pc]M(Pc)$, $[(15C5)_4Pc]$ – tetra-15-crown-5-phthalocyanine, $M = La$ [5a], Sm [5a], Eu [5b], Dy [5a], Tm [5a], Lu [5c,5d,5e,5f] gave the possibility to investigate the formation of dimeric supramolecular assemblies – $\{2[(15C5)_4Pc]M(Pc)_2 \cdot 4K^+\}$ in the presence of potassium ions. It was demonstrated that in the case of early lanthanides, the excitonic interaction between the components of the supramolecular dimer is stronger than in the case of middle and late lanthanides [5a].

Herein, we describe the synthesis, spectral properties and the investigation of supramolecular dimerisation of new heteroleptic triple-decker phthalocyaninates, which contain one outer crown-substituted ligand – $[(15C5)_4Pc]M(Pc)M(Pc)$, $M = Sm, Dy, Tm, Y$. These complexes can form cation-induced supramolecular dimers in the same manner, as mono- and heteroleptic double-decker crown-phthalocyaninates [5,6].

The procedure of the synthesis of heteroleptic triple-decker complexes with one outer substituted ligand was firstly reported by Ishikawa et al. [7] They described the series of homo- and heteronuclear complexes $[(C_4H_9O)_4Pc]Ln(Pc)Ln(Pc)$, $[(C_4H_9O)_4Pc]Y(Pc)Ln(Pc)$ and $[(C_4H_9O)_4Pc]Ln(Pc)Y(Pc)$, where $[(C_4H_9O)_4Pc]$ – octakis(butoxy)phthalocyanine, $Ln = Tb–Yb$. The complexes were obtained via addition to the corresponding metal diphthalocyaninate of $[(C_4H_9O)_4Pc]Ln(acac)$, which was generated in situ from $H_2[(C_4H_9O)_4Pc]$ and $Ln(acac)_3$. The magnetic susceptibility measurements allow to firstly detect the effect of f–f interaction between lanthanide ions in triple-decker complexes [7b], and 1H NMR investigations demonstrated that lanthanide-induced shift in such complexes has predominantly magnetic-dipolar (pseudo-contact) origin [8].

A similar procedure was used by Jiang et al., who synthesized heteroleptic triple-decker complexes $[(\alpha-Et_2CHO)_4Pc](Pc)M(Pc)$, where $[(\alpha-Et_2CHO)_4Pc]$ – 1,8,15,22-tetrakis(3-pentyloxy)phthalocyaninate, $M = Sm, Gd, Lu$ [9]. The introduction of four 3-pentyloxy groups at non-peripheral positions of the outer ligand makes the complex chiral, which was demonstrated by X-ray structural analysis.

Previously, we reported the investigation of the reaction between $La(Pc)_2$, $H_2[(15C5)_4Pc]$ and $M(acac)_3 \cdot nH_2O$, $M = Sm, Tb, Dy, Tm$ and Y [10]. We expected the formation of heteronuclear heteroleptic complexes $[(15C5)_4Pc]M(Pc)La(Pc)$, which would decompose with the formation of heteroleptic double-decker complexes $[(15C5)_4Pc]M(Pc)$ due to low stability of lanthanum trisphthalocyaninates [11]. Unexpectedly, the major reaction products were heteroleptic triple-decker complexes $(Pc)M[(15C5)_4Pc]M(Pc)$ and $[(15C5)_4Pc]M[(15C5)_4Pc]M(Pc)$. It was supposed that their formation occurs due to the thermal decomposition of $La(Pc)_2$ with the formation of Pc^{2-} , which further reacts with $M(acac)_3 \cdot nH_2O$ yielding the mentioned complexes. To investigate the influence of the stability of starting $M(Pc)_2$ on the pathway of its reaction with $H_2[(15C5)_4Pc]$ and $M(acac)_3 \cdot nH_2O$, we performed the reactions between more stable $M(Pc)_2$, $M = Sm, Dy, Tm$ and Y .

2. Experimental

2.1. Reagents and apparatus

The compounds $H_2[(15C5)_4Pc]$ [6a], $M(Pc)_2$ [5a], and $M(acac)_3 \cdot nH_2O$ [12] were prepared according to the published procedures. 1,2,4-Trichlorobenzene (TCB, Acros Organics) was used as received. Chloroform was dried over anhydrous $CaCl_2$ followed by distillation over CaH_2 , and methanol was dried over molecular sieves, 4 Å. Column chromatography was carried out on neutral alumina (Merck, 0.063–0.200 mm, II–III activ. to Brockmann).

Sonication was performed in ElmasonicS70H ultrasonic bath (Elma), 37 kHz. The electronic (UV–Vis) spectra were recorded on a Cary-100 spectrophotometer (Varian) in $CHCl_3$ in quartz cells (1–10 mm). MALDI-TOF mass spectra were recorded on Ultraflex mass spectrometer (Bruker Daltonics), nicotinic acid was used as a matrix. IR spectra were registered on FT-IR spectrometer Nexus (Nicolet). Samples were prepared as films obtained by evaporation of chloroform solution of the complex on KRS-5 plates. 1H NMR spectra were recorded on Bruker Avance-400 (400 MHz) in $CDCl_3$ solution in the presence of 10 μl of 1% solution of $N_2H_4 \cdot H_2O$ in $DMSO-d_6$. Chemical shifts were reported as the δ [ppm] relative to internal standard (residual $CHCl_3$, $\delta = 7.25$ ppm) at $T = 298$ K. Cation-induced dimerisation was studied as described elsewhere [5a].

2.2. Preparation of $[(15C5)_4Pc]M(Pc)M(Pc)$

A mixture of $M(Pc)_2^{0*}$ (15.0 mg, 12 μmol), $H_2[(15C5)_4Pc]$ (16.4 mg, 12 μmol) and $M(acac)_3 \cdot H_2O$ ($M = Sm, Dy, Tm, Y$) (36 μmol) was dissolved in TCB under sonication and refluxed until no further changes in the UV–Vis spectrum of the reaction mixture were observed (typically, 1 h). The resulting blue solution was cooled. The reaction mixture was treated with hexane to bring about precipitation and was then filtered. The precipitate was dissolved in $CHCl_3$ and chromatographed on neutral alumina. $CHCl_3$ was used to remove $M(Pc)_2^{0*}$ and $M_2(Pc)_3$. Target complex was eluted with $CHCl_3 + 1$ vol.% MeOH. The physical and chemical data and yields for all the complexes are summarized in Tables 1–4.

Table 1

Yields and MALDI TOF mass spectroscopic data for the heteroleptic triple-deckers $[(15C5)_4Pc]M(Pc)M(Pc)$ together with ionic radii of M^{3+} [13]

M	R (Å) [13]	Yield (%)	MALDI TOF MS, m/z ^a	
			Observed	Calculated
Sm	1.078	39	2599.21	2599.11
Dy	1.027	52	2623.18	2623.38
Tm	0.994	70	2636.14	2636.26
Y	1.019	57	2476.39	2476.20

^a Average m/z are given, $[M]^{+}$ calculated for $C_{128}H_{104}N_{24}O_{20}M_2$.

3. Results and discussion

3.1. Synthesis of $[(15C5)_4Pc]M(Pc)M(Pc)$

Unsubstituted double-decker complexes $M(Pc)_2$, $M = Sm, Dy, Tm$ and Y were prepared via the direct interaction of $M(OAc)_3 \cdot nH_2O$ with $H_2(Pc)$ suspension in refluxing 1-chloronaphthalene in the presence of DBU [5a] and isolated via column chromatography.

$M(Pc)_2$ were treated with the mixture of $H_2[(15C5)_4Pc]$ and corresponding $M(acac)_3 \cdot nH_2O$ in refluxing 1,2,4-trichlorobenzene (Scheme 1). The reactions were monitored by UV–Vis spectroscopy. The target complexes $[(15C5)_4Pc]M(Pc)M(Pc)$ were isolated after column chromatography on neutral alumina with gradient chloroform/methanol elution.

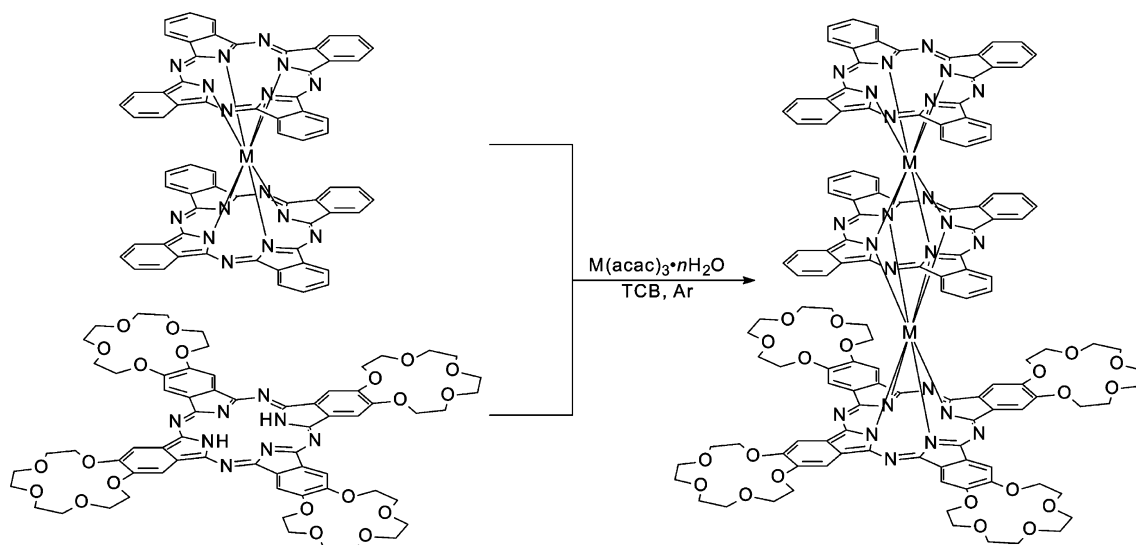
The stability of starting REE(III) diphthalocyaninate $M(Pc)_2$ determines the pathway of its reaction with $M(acac)_3 \cdot nH_2O$ and $H_2[(15C5)_4Pc]$. While lanthanum has the biggest size among REE(III), its diphthalocyaninate is too unstable to form heteronuclear complexes $[(15C5)_4Pc]M(Pc)La(Pc)$ in the reaction between $La(Pc)_2$, $H_2[(15C5)_4Pc]$ and $M(acac)_3 \cdot nH_2O$ under the synthetic conditions. Unexpectedly, only $(Pc)M[(15C5)_4Pc]M(Pc)$ and $[(15C5)_4Pc]M[(15C5)_4Pc]M(Pc)$ are obtained [10]. The formation of scrambling complexes $(Pc)M[(15C5)_4Pc]M(Pc)$ and $[(15C5)_4Pc]M[(15C5)_4Pc]M(Pc)$ was also observed in the case of more stable diphthalocyaninates. Their yields decrease upon the contraction of M^{3+} due to the growth of $M(Pc)_2$ stability and consequent increase of the yields of $[(15C5)_4Pc]M(Pc)M(Pc)$.

Thus, application of different starting donors of Pc units affords the possibility of selective synthesis of heteroleptic triple-decker phthalocyaninates with different numbers and arrangement of crown-substituted ligands.

3.2. Spectral properties

The isolated complexes $[(15C5)_4Pc]M(Pc)M(Pc)$ were characterized by different physical–chemical methods. MALDI-TOF mass-spectrometry afforded unambiguous support for the purity of the isolated complexes from higher- and lower-mass complexes (Table 1). The observed average m/z values together with the isotopic patterns are in good agreement with the calculated ones. However, mass-spectral analysis does not afford distinguishing between isomeric complexes $[(15C5)_4Pc]M(Pc)M(Pc)$ and $(Pc)M[(15C5)_4Pc]M(Pc)$.

The method, which proved the position of the crown-substituted ligand, is 1H NMR-spectroscopy (Table 2). The proton resonance signals, which are observed in the 1H NMR spectra of heteroleptic triple-decker crown-phthalocyaninates, are inner and outer aromatic α - and β -protons of the unsubstituted phthalocyanine ring (α -, β - H_{Ar}^i), aromatic protons of crown-substituted ligand (H_{Ar}^*) and CH_2 protons of the crown-ether fragments. In the case of the outer position of the crown-substituted ligand, five resonance signals of aromatic protons – α - H_{Ar}^i , α - H_{Ar}^o , β - H_{Ar}^i , β - H_{Ar}^o and H_{Ar}^{*o} – are observed with the equivalent integral intensities. In isomeric complex $(Pc)M[(15C5)_4Pc]M(Pc)$, there are only three resonance signals – α - H_{Ar}^o , β - H_{Ar}^o and H_{Ar}^{*i} with the 2:2:1 integral intensities ratio [10]. In the case of $[(15C5)_4Pc]M(Pc)M(Pc)$ two protons at one methylene-group in crown-ether substituents are nonequivalent with respect to the neighboring ligands (*exo*- and *endo*-), resulting in eight resonance signals, while in $(Pc)M[(15C5)_4Pc]M(Pc)$ each methylene-group contains two equivalent protons and only four signals are observed. The 1H NMR spectra of isomeric complexes $(Pc)Tm[(15C5)_4Pc]Tm(Pc)$ and $[(15C5)_4Pc]Tm(Pc)Tm(Pc)$ in $CDCl_3$ are given in Fig. 1 as an example.



Scheme 1.

Table 2

¹H NMR data for [(15C5)₄Pc]M(Pc)M(Pc) in CDCl₃

M	H _{Ar} ; δ (ppm)	–OCH ₂ –; δ (ppm)
Sm	7.87 (dd, ³ J = 5.1 Hz, ⁴ J = 2.7 Hz, 8H, α-H _{Ar} ^o) 7.85 (dd, ³ J = 5.5 Hz, ⁴ J = 2.9 Hz, 8H, β-H _{Ar} ⁱ) 7.72 (dd, ³ J = 5.1 Hz, ⁴ J = 2.7 Hz, 8H, β-H _{Ar} ^o) 7.39 (dd, ³ J = 5.5 Hz, ⁴ J = 2.9 Hz, 8H, α-H _{Ar} ⁱ) 7.30 (s, 8H, H _{Ar} ^{so})	4.36 (m, 8H, 1-CH ₂ ^o), 4.31 (m, 8H, 1'-CH ₂ ^o) ^a , 4.11 (br m, 16H, 2, 2'-CH ₂ ^o), 3.99 (m, 8H, 3-CH ₂ ^o), 3.87 (m, 24H, 3', 4, 4' – CH ₂ ^o)
Dy	–72.05 (s, 8H, α-H _{Ar} ⁱ) –34.37 (s, 8H, β-H _{Ar} ⁱ) –24.00 (s, 16H, α-H _{Ar} ^o + H _{Ar} ^{so}) –12.78 (s, 8H, β-H _{Ar} ^o)	–19.25 (s, 8H, 1-CH ₂ ^o), –8.38 (s, 8H, 1'-CH ₂ ^o), –7.22 (s, 8H, 2-CH ₂ ^o); –5.35 (s, 8H, 2'-CH ₂ ^o); –4.84 (s, 8H, 3-CH ₂ ^o); –4.29 (s, 8H, 3'-CH ₂ ^o); –3.41 (s, 8H, 4-CH ₂ ^o); –2.74 (s, 8H, 4'-CH ₂ ^o)
Tm	54.40 (s, 8H, α-H _{Ar} ⁱ) 33.56 (s, 8H, β-H _{Ar} ⁱ) 26.14 (s, 16H, α-H _{Ar} ^o + H _{Ar} ^{so}) 18.70 (s, 8H, β-H _{Ar} ^o)	18.24 (s, 8H, 1-CH ₂ ^o); 11.24 (s, 16H, 1'-CH ₂ ^o + 2-CH ₂ ^o); 9.39 (s, 8H, 2'-CH ₂ ^o); 8.93 (s, 8H, 3-CH ₂ ^o); 8.60 (s, 8H, 3'-CH ₂ ^o); 8.08 (s, 8H, 4-CH ₂ ^o); 7.67 (s, 8H, 4'-CH ₂ ^o)
Y	8.97 (dd, ³ J = 5.5 Hz, ⁴ J = 2.9 Hz, 8H, α-H _{Ar} ⁱ) 8.71 (dd, ³ J = 5.5 Hz, ⁴ J = 2.9 Hz, 8H, β-H _{Ar} ⁱ) 8.44 (dd, ³ J = 5.4 Hz, ⁴ J = 2.8 Hz, 8H, α-H _{Ar} ^o) 8.09 (dd, ³ J = 5.4 Hz, ⁴ J = 2.8 Hz, 8H, β-H _{Ar} ^o) 7.86 (s, 8H, H _{Ar} ^{so})	4.81 and 4.50 (2m, 2 × 8H, 1,1'-CH ₂ ^o); 4.33 and 4.22 (2m, 2 × 8H, 2,2'-CH ₂ ^o); 4.14 (m, 8H, 3 or 3'-CH ₂ ^o); 4.02 (m, 24H, 3' or 3, 4, 4'-CH ₂ ^o)

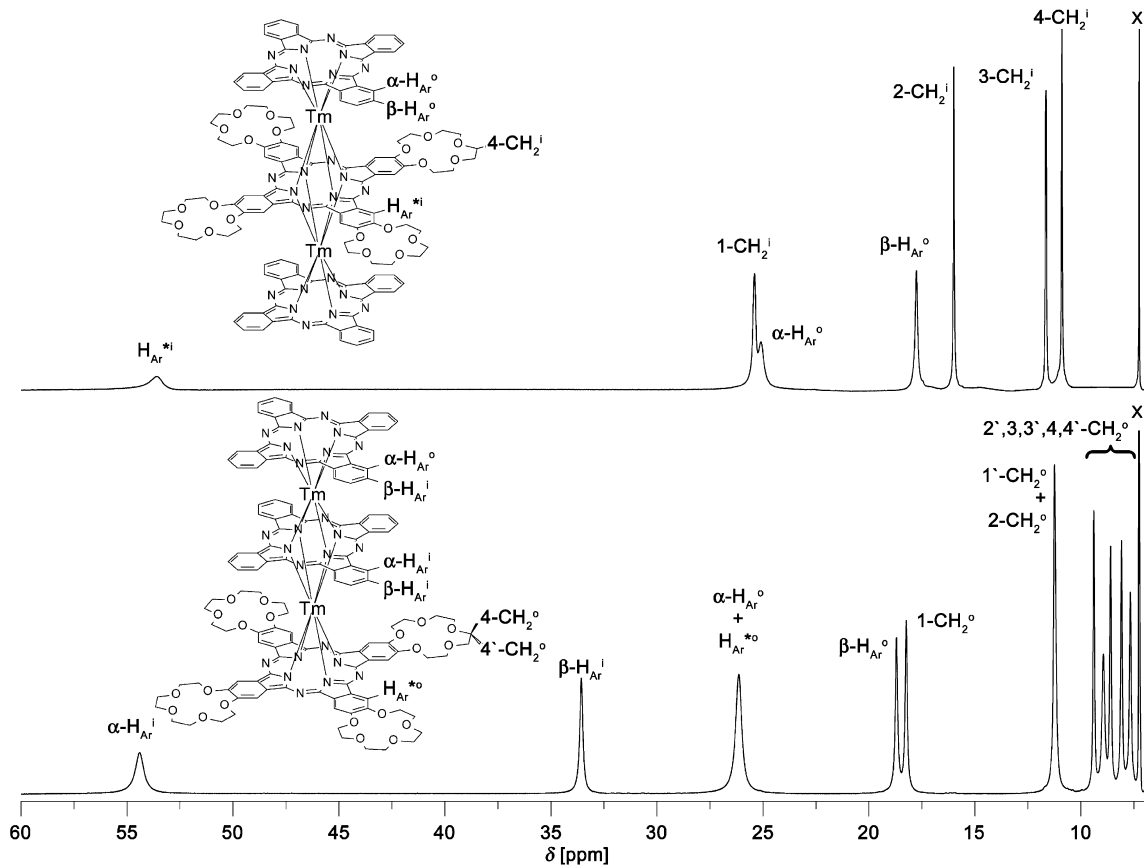
^a Primes '′' indicate *exo*-protons.Fig. 1. ¹H NMR spectra of isomeric complexes (Pc)Tm[(15C5)₄Pc]Tm(Pc) [10] and [(15C5)₄Pc]Tm(Pc)Tm(Pc) in CDCl₃. «x» indicates the signal of residual CHCl₃.

Table 3
LIS and relative LIS in the ^1H NMR spectra of $[(15\text{C}5)_4\text{Pc}]\text{M}(\text{Pc})\text{M}(\text{Pc})$ in CDCl_3

M	$\alpha\text{-H}_{\text{Ar}}^{\text{i}}$	$\beta\text{-H}_{\text{Ar}}^{\text{i}}$	$\text{H}_{\text{Ar}}^{\text{o}}$	$\alpha\text{-H}_{\text{Ar}}^{\text{o}}$	$\beta\text{-H}_{\text{Ar}}^{\text{o}}$
$\Delta\delta(\text{H}_{\text{Ar}})$; (ppm)					
Sm	−1.60	−0.89	−0.63	−0.57	−0.37
Dy	−81.02	−43.08	−31.86	−32.44	−20.87
Tm	45.43	24.85	18.28	17.70	10.61
$\Delta\delta(\text{H}_{\text{Ar}})/\Delta\delta(\text{H}_{\text{Ar}}^{\text{o}})$					
Sm	2.54	1.41	1.00	0.90	0.59
Dy	2.54	1.35	1.00	1.02	0.66
Tm	2.49	1.36	1.00	0.97	0.58

In the case of diamagnetic yttrium complex $[(15\text{C}5)_4\text{Pc}]\text{Y}(\text{Pc})\text{Y}(\text{Pc})$, the most downfield-shifted signal ($\delta = 8.97$ ppm) is attributed to $\alpha\text{-H}_{\text{Ar}}^{\text{i}}$ due to electron-withdrawing nature of two yttrium ions. On the analogy of data for $[(\text{C}_4\text{H}_9\text{O})_8\text{Pc}]\text{Y}(\text{Pc})\text{Y}(\text{Pc})$, reported previously [8], the signals at 8.71, 8.44 and 8.09 ppm are attributed to $\beta\text{-H}_{\text{Ar}}^{\text{i}}$, $\alpha\text{-H}_{\text{Ar}}^{\text{o}}$ and $\beta\text{-H}_{\text{Ar}}^{\text{o}}$, respectively. Interestingly, the separation between the resonance signals of $\alpha\text{-H}_{\text{Ar}}$ and $\beta\text{-H}_{\text{Ar}}$ ($\Delta\delta = 0.26$ ppm for inner protons and 0.35 ppm for outer protons) is smaller than the one for the previously reported complexes $(\text{Pc})\text{Y}[(15\text{C}5)_4\text{Pc}]\text{Y}(\text{Pc})$ and $[(15\text{C}5)_4\text{Pc}]\text{Y}[(15\text{C}5)_4\text{Pc}]\text{Y}(\text{Pc})$ ($\Delta\delta = 0.66$ and 0.56 ppm, respectively) [10].

The position of the resonance signals in the complexes of the paramagnetic lanthanides is strongly affected by the lanthanide-induced shift effect [7a,8,14]. Dysprosium and thulium are strongly paramagnetic, leading to significant lanthanide-induced shifts (LIS) of resonance signals in comparison with diamagnetic yttrium complexes. All signals are broadened and only singlets are observed in the spectra; however, all signals and even those of crown-ethers are well resolved. Previously, it was demonstrated that pseudo-contact (magnetic-dipolar) effect predominantly contributes to LIS in various series of trisphthalocyaninates [8]. Thus, in a first approximation, the closer the proton is to the paramagnetic centers, the higher the LIS value. This allowed us to assign all resonance signals in Dy and Tm complexes. The performed attribution is in good agreement with the previously reported data for $[(\text{C}_4\text{H}_9\text{O})_8\text{Pc}]\text{M}(\text{Pc})\text{M}(\text{Pc})$ [8]. We calculated LIS for each aromatic proton in the spectra of Dy and Tm as $\Delta\delta(\text{H}_{\text{Ar}}) = \delta(\text{H}_{\text{Ar}}^{\text{M}}) - \delta(\text{H}_{\text{Ar}}^{\text{Y}})$ and evaluated the relative terms $\Delta\delta(\text{H}_{\text{Ar}})/\Delta\delta(\text{H}_{\text{Ar}}^{\text{o}})$ (Table 3). The latter has close values for both Dy and Tm complexes, indicating that LIS has predominantly magnetic-dipolar nature.

The assignment of signals in samarium complex is more complicated. Due to the weak paramagnetic nature of Sm ion, the resonance signals of aromatic protons are only slightly shifted and some of them overlap. To make the complete assignment, the chemical shifts of aromatic protons were sorted out to get the best fit with $\Delta\delta(\text{H}_{\text{Ar}})/\Delta\delta(\text{H}_{\text{Ar}}^{\text{o}})$, found for Dy and Tm complexes (Table 3). For Sm complex, LIS decrease in the sequence $\alpha\text{-H}_{\text{Ar}}^{\text{i}}$, $\beta\text{-H}_{\text{Ar}}^{\text{i}}$, $\text{H}_{\text{Ar}}^{\text{o}}$, $\alpha\text{-H}_{\text{Ar}}^{\text{o}}$ and $\beta\text{-H}_{\text{Ar}}^{\text{o}}$ in accordance with the increase of

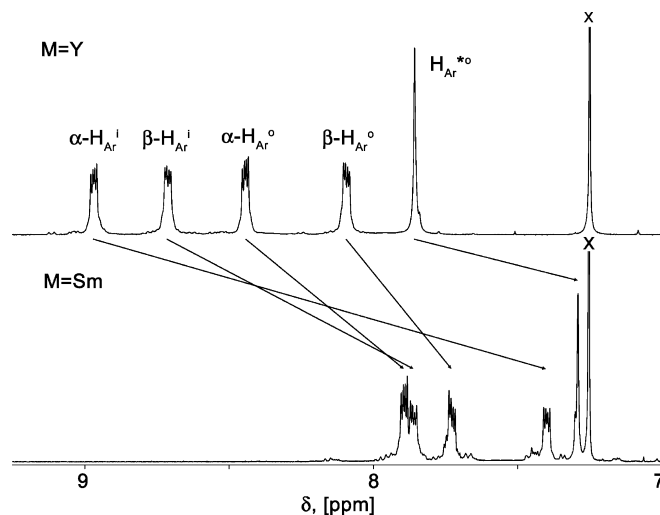


Fig. 2. Aromatic region of ^1H NMR spectra of complexes $(\text{Pc})\text{M}[(15\text{C}5)_4\text{Pc}]\text{M}(\text{Pc})$, $\text{M} = \text{Sm}, \text{Y}$ in CDCl_3 . «X» indicates the signal of residual CHCl_3 .

the distance between certain protons and paramagnetic nuclei. Fig. 2 represents the aromatic region of ^1H NMR spectra of $(\text{Pc})\text{M}[(15\text{C}5)_4\text{Pc}]\text{M}(\text{Pc})$, $\text{M} = \text{Sm}, \text{Y}$.

The UV–Vis spectra of the synthesized complexes are typical for triple-decker complexes (Table 2). They exhibit the split Q-band; splitting increases with the decrease of the ionic radius of M. The position of the Soret band is almost insensitive to the metal ion, but its position and the shape depend on the position and the number of electron-donating crown-ether substituents [10,15]. While the complex $(\text{Pc})\text{Sm}[(15\text{C}5)_4\text{Pc}]\text{Sm}(\text{Pc})$ was previously structurally characterized [10], the unambiguous correspondence between the structure of such type of complexes and their UV–Vis spectra was made. In the case of $(\text{Pc})\text{M}[(15\text{C}5)_4\text{Pc}]\text{M}(\text{Pc})$, the Soret band is relatively broad and it has the maximum around 333–334 nm and the shoulder in the 360 nm region. In the case of $[(15\text{C}5)_4\text{Pc}]\text{M}(\text{Pc})\text{M}(\text{Pc})$ the shoulder vanishes, the band has a triangular-like shape and the maximum shifts to 338 nm (Fig. 3, Table 2). Thus, the Soret band region can be used as a marker band, which allows us to establish the structure of isomeric complexes with inner and outer crown-substituted ligands.

IR-spectroscopy is a powerful method to investigate the state of tetrapyrrolic ligands within sandwich complexes [16]. To the best of our knowledge, we have firstly examined FT-IR spectra of pairs of isomeric complexes with inner and outer crown-substituted ligands to determine if IR-spectroscopy can allow us to distinguish between these isomers. While these complexes have different static symmetries, approximately D_{4h} [10] and C_{4v} , respectively, it was expected that the former complex would have more vibration modes due to lower symmetry.

Both series of complexes exhibit typical spectra of substituted sandwich phthalocyaninates. For example, in

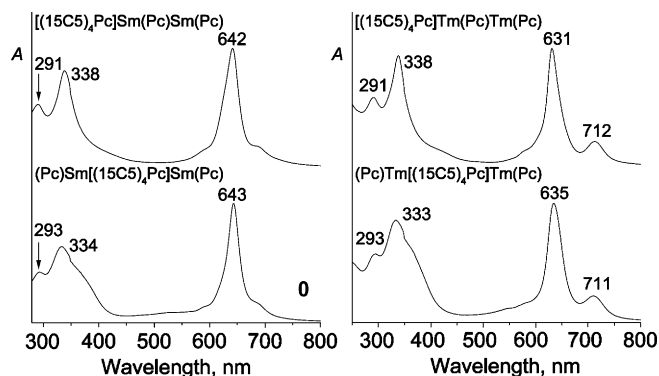


Fig. 3. UV-Vis spectra of isomeric complexes $[(15C5)_4Pc]M(Pc)M(Pc)$ and $(Pc)M[(15C5)_4Pc]M(Pc)$, $M = Sm, Tm$ in $CHCl_3$.

Table 4
UV-Vis spectral data for the heteroleptic triple-deckers $[(15C5)_4Pc]M(Pc)M(Pc)$ in $CHCl_3$

M	UV-Vis, $CHCl_3$, λ_{max} (nm)			
	Q ₂ -band	Q ₁ -band	Soret band	N-band
Sm	682 (sh.)	642	338	291
Dy	700	640	338	293
Tm	712	631	338	291
Y	702	639	338	294

the case of Sm complexes the most intensive bands lay around 730 cm^{-1} (aromatic C–H wagging of Pc rings) and 1078 cm^{-1} (coupling of isoindole deformation and aza stretching) [16c]. Both complexes exhibit two pyrrole stretching bands of medium and low intensity – 1329 and 1309 cm^{-1} ; their position does not depend on the position of crown-substituted ligand. The former band shifts to higher energy upon REE(III) contraction [16c]. The frequencies of benzene stretching are almost invariant in both series of isomers. These bands are marker bands of Pc^{2-} fragment within sandwich complexes, indicating that no unpaired electrons are delocalized over phthalocyanine ligands. The frequency of unsymmetrical C–O–C stretching band shifts slightly from 1273 cm^{-1} in $[(15C5)_4Pc]Sm(Pc)Sm(Pc)$ to 1278 cm^{-1} in the case of isomeric complex. However, this slight difference cannot be used as a structure marker band, which allows us to distinguish between isomers with outer and inner crown-substituted ligands. As a result, the lowering of molecular symmetry does not lead to the appearance of new bands and moreover to any significant changes in the position of relative intensities of vibration bands in the IR spectra.

3.3. Cation-induced formation of supramolecular dimers

The combination of Pc macrocycle and peripheral crown-ether substituents gives the possibility to obtain supramolecular assemblies of different architecture, depending on the structure of the receptor molecule. Previously, various crown-substituted phthalocyaninates were synthesized and it was demonstrated that potassium, rubid-

ium and cesium ions cause their aggregation [5,6] which is followed by significant changes of their UV-Vis spectra, indicating the existence of strong intermolecular excitonic interaction between building blocks.

Cation-induced dimerisation of heteroleptic complexes $[(15C5)_4Pc]M(Pc)M(Pc)$ was studied by spectrophotometric titration of the solutions of complexes in chloroform with the solution of KOAc in methanol (Fig. 4). The observed hypsochromic shift of the Q-band indicates the formation of the cofacial aggregates in accordance with Kasha's model of chromophore interaction [17]. Also, the slight hypsochromic shift of the Soret band is observed. The presence of isosbestic points clearly indicates that only one type of supramolecular aggregate is formed. The stoichiometry of the reaction was determined from the titration curves (Fig. 5). It was demonstrated that 1 mol of the complex reacts with 2 mol of potassium salt. These data indicate the formation of supramolecular dimers $\{2[(15C5)_4Pc]M(Pc)M(Pc) \cdot 4K^+\}$.

Supramolecular dimerisation of $[(15C5)_4Pc]M(Pc)M(Pc)$ was also investigated by means of West-Pearce plots [18]. The value of $\lg[\text{monomer}]$ was plotted versus $\lg[\text{dimer}]$ and the curves with three different regions were obtained (Fig. 6). This is in agreement with the nonlinear cooperative two-step three-stage process, which was proposed previously for supramolecular dimerisation of square-planar d-elements crown-phthalocyaninates $M[(15C5)_4Pc]$, $M = Zn, Co, Ni, Cu$ [6d]. At the first step, one potassium ion binds together two molecules with the formation of non-cofacial dimer. It occurs at $[K^+]/[\text{complex}]$ ratio, equal to 0.5. This step is characterized by the slope of West-Pearce plot, equal to 2. At the next step, the formation of cofacial dimer occurs due to the binding of the second cation. Subsequent interaction with potassium salt leads to saturation of the vacant crown-ether moieties and does not affect the geometry of the dimer, and the slope of the

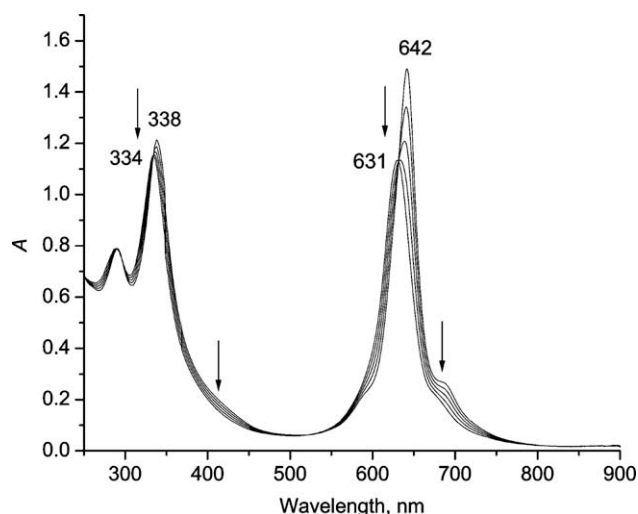


Fig. 4. Changes in the absorption spectra of $[(15C5)_4Pc]Sm(Pc)Sm(Pc)$ in $CHCl_3$ upon titration with KOAc in CH_3OH . The final spectrum corresponds to the ratio $[K^+]/[\text{complex}] = 3.0$.

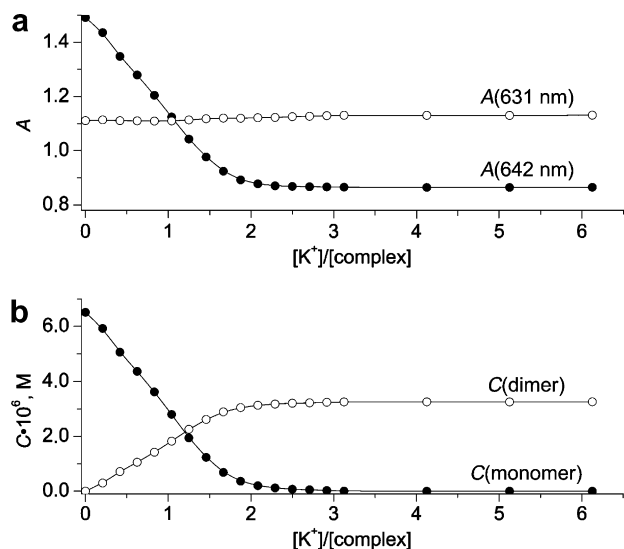


Fig. 5. (a) Plots of A_{max} for the monomer and dimer Q-bands upon titration of $[(15C5)_4Pc]Sm(Pc)Sm(Pc)$ in $CHCl_3$ upon titration with KOAc in CH_3OH . (b) Dependence of monomer and dimer concentrations vs. $[K^+]/[complex]$.

curve approaches zero. Thus, cation-induced supramolecular aggregation of $[(15C5)_4Pc]M(Pc)M(Pc)$ occurs in the same manner, as in the case of crown-substituted monophthalocyanines. Altogether, the obtained data allow us to propose the architecture of the supramolecular dimer, demonstrated in Fig. 7.

Interestingly, Q-band's hypsochromic shift increases from Tm complex ($\Delta\lambda^Q = 6\text{ nm}$) to Sm complex ($\Delta\lambda^Q = 11\text{ nm}$). A similar increase of Q-bands blue shift with the increase of REE(III) size was previously reported in the case of the potassium-induced dimerisation of $[(15C5)_4Pc]M(Pc)$, $M = La, Sm, Dy, Tm$ [5a]. Such trend indicates that in the case of complexes of early and middle lanthanides, there exists stronger intermolecular excitonic interaction between building blocks in comparison with complexes of late lanthanides.

The X-ray data for REE(III) sandwich phthalocyanines indicate that phthalocyanine ligands adopt domed conformation because of intermolecular repulsion [19].

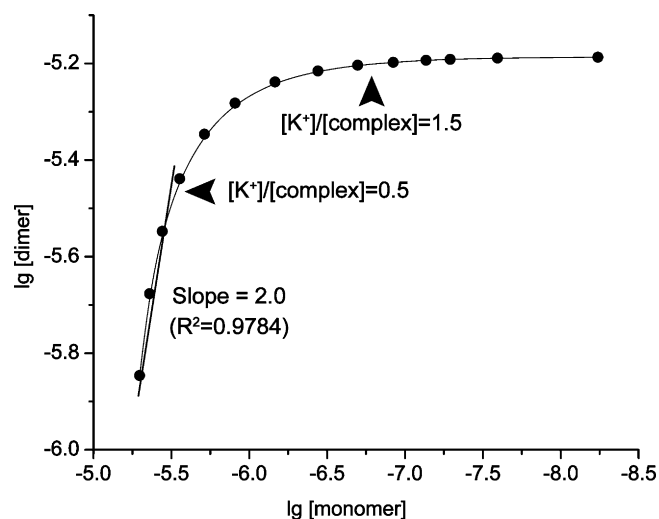


Fig. 6. West-Pearce plots of $\lg [dimer]$ vs. $\lg [monomer]$ of $[(15C5)_4Pc]Sm(Pc)Sm(Pc)$ in $CHCl_3$ upon titration with KOAc in CH_3OH .

The smaller REE(III) ion is, the higher the deformation of the macrocycle is. More significant deviation of outer crown-substituted ligand from planarity is expected in the case of Tm complex in comparison with Sm complex. Thus, in the former case the distance between interacting crown-substituted ligands within supramolecular dimer is likely to be higher. While the excitonic interaction is dependent on the distance between building blocks [6d], it is likely that less domed compounds should exhibit stronger intermolecular interaction.

Heteroleptic sandwich complexes $[(15C5)_4Pc]M(Pc)$, where $M = La$ [5a], Sm [5a], Eu [5b], Dy [5a], Tm [5a], Lu [5c,5d,5e,5f] form supramolecular dimers $\{2[(15C5)_4Pc]M(Pc) \cdot 4K^+\}$, which are believed to be the simple models of infinite supramolecular assemblies [5f], which are responsible for unique semiconductive properties of sandwich phthalocyanines in solid state. Also, the unusual supramolecular quasi-quadruple-decker complex $\{2[(\alpha-OBu)_8Pc^{2-}]Sm^{3+}(Pc^{2-})_2Na^+\}$, in which two anionic double-decker units are linked together by two sodium

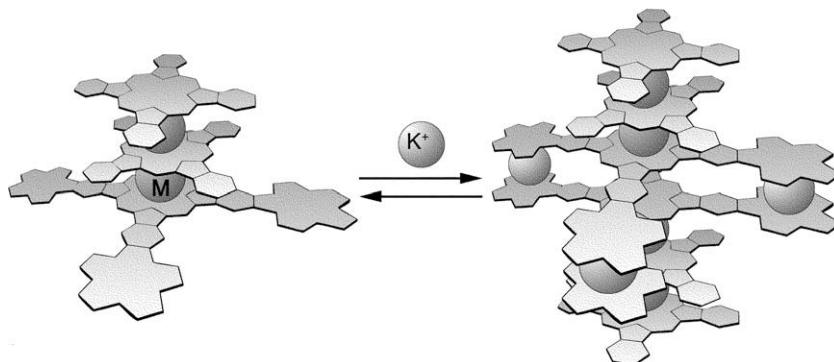


Fig. 7. Scheme of cation-induced dimerisation of $[(15C5)_4Pc]M(Pc)M(Pc)$.

ions, was reported [20]. Described herein are supramolecular dimers that contain six phthalocyanine subunits per assembly, so their investigation affords new possibilities to fill in the gap between monomeric Pc compounds and their infinite supramolecular assemblies.

4. Conclusions

Four new complexes $[(15C5)_4Pc]M(Pc)M(Pc)$ were prepared with the application of general methodology, which implies the reaction between $M(Pc)_2$, $H_2[(15C5)_4Pc]$ and the corresponding $M(acac)_3 \cdot nH_2O$. The influence of stability of the starting $M(Pc)_2$ on the pathway of the reaction was investigated. It was demonstrated, that lower stability of $M(Pc)_2$ leads to the increase of scrambling products, affording the possibility to synthesize heteroleptic complexes of different compositions and structures, applying different $M(Pc)_2$ as a source of Pc unit. The solid spectral criteria, which allows us to distinguish between structures of isomeric complexes $[(15C5)_4Pc]M(Pc)M(Pc)$ and $(Pc)-M[(15C5)_4Pc]M(Pc)$, were established. Investigation of potassium-induced dimerisation of synthesized receptors allowed us to firstly obtain extended discrete models of infinite supramolecular phthalocyanine aggregates, which contain six phthalocyanine units.

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References

- [1] (a) C.G. Claessens, W.J. Blau, M. Cook, M. Hanack, R.J.M. Nolte, T. Torres, D. Wöhrle, *Monatsh. Chem.* 132 (2001) 3;
(b) G. de la Torre, P. Vazquez, F. Agullo-Lopez, T. Torres, *J. Mater. Chem.* 8 (1998) 1671.
- [2] (a) J. Andzelm, A.M. Rawlett, J.A. Orlicki, J.F. Snyder, K.K. Baldrige, *J. Chem. Theory Comput.* 3 (2007) 870;
(b) T. Sooksimuang, B.K. Mandal, *J. Org. Chem.* 68 (2003) 652.
- [3] (a) R. Rosseau, R. Aroca, M.L. Rodriguez-Mendez, *J. Mol. Struct.* 356 (1995) 49;
(b) P. Zhu, N. Pan, C. Ma, X. Sun, D.P. Arnold, J. Jiang, *Eur. J. Inorg. Chem.* (2004) 518.
- [4] (a) F.J.M. Hoeben, P. Jonkheijm, E.W. Meijer, A.P.H.J. Schenning, *Chem. Rev.* 105 (2005) 1491;
(b) J. Wojaczynski, L. Latos-Grazynski, *Coord. Chem. Rev.* 204 (2000) 113;
(c) T. Imamura, K. Fukushima, *Coord. Chem. Rev.* 198 (2000) 133.
- [5] (a) A.G. Martynov, Yu.G. Gorbunova, *Inorg. Chim. Acta* 360 (2007) 122;
(b) N. Sheng, R. Li, C.-F. Choi, W. Su, D.K.P. Ng, X. Cui, K. Yoshida, N. Kobayashi, J. Jiang, *Inorg. Chem.* 45 (2006) 3794;
(c) Yu.G. Gorbunova, E.O. Tolkacheva, A.Yu. Tsivadze, *Russ. J. Coord. Chem.* 22 (1996) 884;
(d) N. Ishikawa, Y. Kaisu, *Chem. Phys. Lett.* 203 (1993) 472;
(e) N. Ishikawa, Y. Kaisu, *Chem. Lett.* 27 (1998) 183;
(f) N. Ishikawa, Y. Kaisu, *Coord. Chem. Rev.* 226 (2002) 93.
- [6] (a) A.R. Koray, V. Ahsen, O. Bekaroglu, *J. Chem. Soc., Chem. Commun.* (1986) 932;
(b) R. Hendriks, O.E. Sielecken, W. Drenth, R.J.M. Nolte, *J. Chem. Soc., Chem. Commun.* (1986) 1464;
(c) N. Kobayashi, Y. Nishiyama, *J. Chem. Soc., Chem. Commun.* (1986) 1462;
(d) N. Kobayashi, A.B.P. Lever, *J. Am. Chem. Soc.* 109 (1987) 7433;
(e) Yu.G. Gorbunova, L.A. Lapkina, A.Yu. Tsivadze, *J. Coord. Chem.* 56 (2003) 1223;
(f) A.Yu. Tsivadze, *Russ. Chem. Rev.* 73 (2004) 5.
- [7] (a) N. Ishikawa, T. Iino, Y. Kaizu, *J. Phys. Chem. A* 106 (2002) 9543;
(b) N. Ishikawa, T. Iino, Y. Kaizu, *J. Am. Chem. Soc.* 124 (2002) 11440.
- [8] N. Ishikawa, T. Iino, Y. Kaizu, *J. Phys. Chem. A* 107 (2003) 7879.
- [9] Y. Bian, L. Li, L.; D. Wang, C.-F. Choi, D.Y.Y. Cheng, P. Zhu, R. Li, J. Dou, R. Wang, N. Pan, D.K.P. Ng, N. Kobayashi, J. Jiang, *Eur. J. Inorg. Chem.* (2005) 2612.
- [10] A.G. Martynov, O.V. Zubareva, Yu.G. Gorbunova, S.G. Sakharov, S.E. Nefedov, F.M. Dolgushin, A.Yu. Tsivadze, *Eur. J. Inorg. Chem.* (2007) 4800.
- [11] A.G. Martynov, I.V. Nefedova, Yu.G. Gorbunova, A.Yu. Tsivadze, *Mendeleev Commun.* 17 (2007) 66.
- [12] J.G. Stites, C.N. McCarty, L.L. Quill, *J. Am. Chem. Soc.* 70 (1948) 3142.
- [13] R.D. Shannon, *Acta Crystallogr., Sect. A* 32 (1976) 751.
- [14] D.P. Arnold, J. Jiang, *J. Phys. Chem. A* 105 (2001) 7525.
- [15] W. Lui, J. Jiang, N. Pan, D.P. Arnold, *Inorg. Chim. Acta* 310 (2000) 140.
- [16] (a) J. Jiang, D.P. Arnold, H. Yu, *Polyhedron* 18 (1999) 2129;
(b) J. Jiang, M. Bao, L. Rintoul, D.P. Arnold, *Coord. Chem. Rev.* 205 (2006) 424;
(c) M. Bao, N. Pan, C. Ma, D.P. Arnold, J. Jiang, *Vib. Spectrosc.* 32 (2003) 175.
- [17] M. Kasha, H.R. Rawls, M.A. El-Bayomi, *Pure. Appl. Chem.* 11 (1965) 371.
- [18] W. West, S. Pearce, *J. Phys. Chem.* 69 (1965) 1894.
- [19] H. Hückstädt, A. Tutaß, M. Göldner, U. Cornelissen, H. Homborg, *Z. Anorg. Allg. Chem.* 627 (2001) 485.
- [20] H. Zhang, R. Wang, P. Zhu, Z. Lai, J. Han, C.-F. Choi, D.K.P. Ng, X. Cui, C. Ma, J. Jiang, *Inorg. Chem.* 43 (2004) 4740.