

cis-Octahedral Nickel(II) Complexes with Symmetric and Unsymmetric Tripodal Tetraamine Ligands

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Nickel(II) complexes with the aliphatic tripodal tetraamine ligands $\text{N}(\text{CH}_2\text{CH}_2\text{NH}_2)_3$ (tren, **1**), $\text{N}[(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)(\text{CH}_2\text{CH}_2\text{NH}_2)_2]$ (baep, **2**), $\text{N}[(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_2(\text{CH}_2\text{CH}_2\text{NH}_2)]$ (abap, **3**), and $\text{N}(\text{CH}_2\text{CH}_2\text{CH}_2\text{NH}_2)_3$ (trpn, **4**) are reported. The tripodal tetradentate N_4 ligands **1–4** react with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ in acetonitrile or methanol to give the blue nickel(II) complexes $[\text{Ni}(\textbf{1})(\eta^1\text{-NO}_3)_2]$ (**5a**), $[\text{Ni}(\textbf{2})(\eta^1\text{-NO}_3)_2]$ (**5b**), $[\text{Ni}(\textbf{3})(\eta^2\text{-NO}_3)]\text{NO}_3 \cdot \text{CH}_3\text{CN}$ (**5c**· CH_3CN), and $[\text{Ni}(\textbf{4})(\eta^2\text{-NO}_3)]\text{NO}_3 \cdot \text{CH}_3\text{OH}$ (**5d**· CH_3OH). With $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$, the complexes $[\text{Ni}(\textbf{1})\text{Cl}(\text{H}_2\text{O})]\text{Cl} \cdot \text{H}_2\text{O}$ (**6a**), $[\text{Ni}(\textbf{2})(\mu\text{-Cl})_2\text{Ni}(\textbf{2})]\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}$ (**6b**· $2\text{CH}_3\text{OH}$), $[\text{Ni}(\textbf{3})\text{Cl}(\text{H}_2\text{O})]\text{Cl}$ (**6c**), and $[\text{Ni}(\textbf{4})(\text{H}_2\text{O})_2]\text{Cl}_2 \cdot \text{H}_2\text{O}$ (**6d**· H_2O) are obtained. The mo-

lecular structures of complexes **5a–d** and **6b–d** have been determined by X-ray diffraction analysis and they are compared with the molecular structure of the previously characterized complex **6a**. Complexes **5a–d** and **6b–d** exhibit octahedrally coordinated nickel atoms. The tripodal ligands occupy four of the six coordination sites in a *pseudo-facial* manner. Complexes of the unsymmetrical ligands **2** and **3** possess both five- and six-membered chelate rings. The extension of the ligand arms in **1–4** leads to a systematic variation in the geometric and UV/Vis spectroscopic properties of the complexes depending on the size of the chelate rings formed by the ligands.

Introduction

The sterically unhindered tripodal tetraamine ligand tren (**1**) is known to form a large number of coordination compounds with different metal ions. Comparatively little is known about the coordination chemistry of the unsymmetrical higher tren homologues, e.g. bis(2-aminoethyl)(3-aminopropyl)amine (baep, **2**), (2-aminoethyl)bis(3-aminopropyl)amine (abap, **3**), and the symmetric tris(3-aminopropyl)amine (trpn, **4**) (Figure 1).

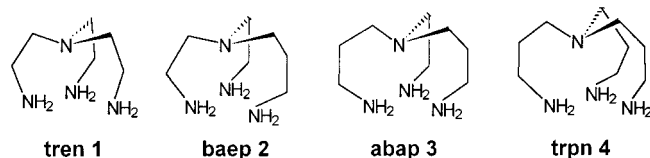


Figure 1. Topology of the tripodal tetraamine ligands studied

Complexes of Ni^{II} with **1** were first described in 1926.^[1] Since then, various monomeric octahedral,^[2–5] trigonal-bipyramidal,^[6–9] and dinuclear coligand-bridged octahedral^[10–12] Ni^{II} complexes of **1** or its hexamethylated analogue Me_6tren have been reported. Thermochemical and spectroscopic studies of aqueous solutions of Ni^{II} complexes of **4** have indicated that these complexes are octahedral.^[13,14] However, the precise molecular structures of the (trpn) Ni^{II} complexes remain unknown. Nickel complexes of

the unsymmetric ligands **2** and **3** have not hitherto been described.

The stepwise insertion of a CH_2 group into each of the ligand arms in **1** leads to the ligands **2–4**.^[15–17] Compared to **1**, these ligands possess an unchanged set of donor groups with expanded linkers between them. This slight topological variation has profound consequences. Ligands **2–4** are more basic than **1**,^[17] since the ammonium groups formed upon protonation are further apart in these ligands than they would be in tren. The geometric parameters of the five- and six-membered chelate rings that could be formed by **2–4** have been analyzed and it was concluded that for complexes with both macrocyclic and non-macrocyclic ligands, an increase of the chelate ring size from five-membered to six-membered will increase the stability of complexes of smaller relative to larger metal ions.^[18]

A systematic study of these contradicting effects was carried out with a complete series of Cu^{II} complexes with the ligands **1–4**.^[16a,17,19] Depending on the ligand topology, these complexes adopt either a trigonal-bipyramidal or a distorted square-pyramidal geometry.^[16,17]

The stability constants of the copper complexes were found to decrease systematically over five orders of magnitude depending on the number of six-membered chelate rings present.^[17] Studies on the octahedral Co^{III} complexes with **1**,^[20] **2**,^[16b] **3**,^[15] and **4**^[20] revealed differences in the catalytic activities of these complexes in the hydrolysis of phosphate esters. It would appear that the stability and reactivity of complexes with tripodal tetraamine ligands may be controlled and significantly manipulated by the ligand topology if the governing principles are fully understood. This might ultimately prove useful for the modelling of nitrogen-rich active sites in metalloproteins. To study the con-

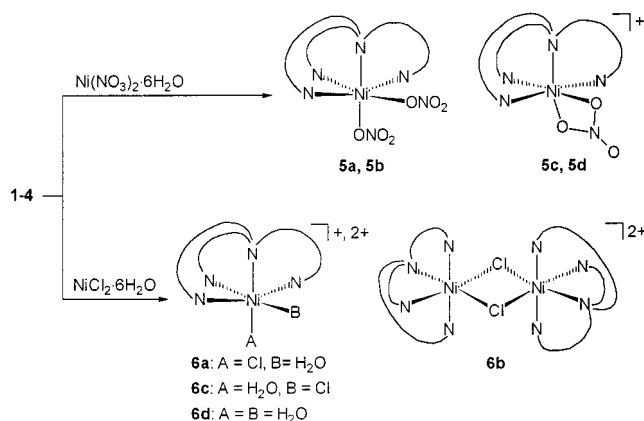
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sequences of a variation of the ligand topology of tripodal tetraamines with respect to the properties of octahedral metal complexes, we have prepared the Ni^{II} complexes of **1–4**. It was assumed that octahedral complexes with two monodentate coligands in *cis* positions would be formed. Furthermore, we have studied the effects of the counterions by preparing two series of complexes starting from NiCl₂·6H₂O and Ni(NO₃)₂·6H₂O. The molecular structures and spectroscopic properties of the nickel complexes obtained are compared with the data for the previously characterized nickel complex with the ligand tren [Ni(**1**)Cl(H₂O)]Cl·H₂O (**6a**).^[2]

Results and Discussion

Seven new octahedral Ni^{II} complexes with the symmetric and unsymmetric tripodal tetraamine ligands **1–4** have been synthesized and structurally characterized. Depending on the ligand topology, complexes of type **5** (Scheme 1) contain either two η¹-coordinated nitrate ions or an η²-coordinated nitrate ion and a nitrate counterion. A second series of complexes **6** has been synthesized from ligands **1–4** and nickel dichloride in water. In this series, the complex **6a** with the ligand **1** has been described previously.^[2] In both series, the ligand topology is systematically varied by the stepwise insertion of methylene groups into the ligand arms. The structural and spectroscopic trends observed in the two series are discussed below.



Scheme 1. Preparation of Ni^{II} complexes of ligands **1–4**

Improved Synthesis of Bis(2-aminoethyl)(3-aminopropyl)-amine (**2**)

The previously described preparation of **2**,^[16a] by addition of 1 equiv. of acrylonitrile to ammonia followed by Strecker synthesis, reaction of the resulting dinitrile with glyconitrile (HOCH₂CN),^[21] and finally reduction of the trinitrile with AlH₃, has not always given satisfactory results. The critical step has proved to be the condensation reaction of the dinitrile with HOCH₂CN for the introduction of the third ligand arm at the central nitrogen atom. Under the conditions described, the reaction often yields polymeric products with the desired trinitrile present only

in trace amounts. We assume that this is due to the low basicity of the central nitrogen atom of the dinitrile precursor. It is known that α-cyanomethyl and β-cyanoethyl groups at a nitrogen atom markedly lower its basicity.^[22] Under such conditions, decomposition and self-condensation reactions of the glyconitrile are favored over the condensation reaction with the amine. Consequently, the only possible means of enhancing the condensation reaction is through activation of the glyconitrile. This is best achieved by tosylation and tosylated glyconitrile can easily be prepared from glyconitrile and *p*-toluenesulfonyl chloride.^[23] The condensation reaction of TsOCH₂CN with HN(CH₂CN)(CH₂CH₂CN) proceeds at 50 °C in DMF within 5 d. The resulting ammonium salt was converted into the free amine with aqueous sodium carbonate. The crude product could be recrystallized from hot chloroform. As reported previously,^[16] ligand **2** is obtained from the trinitrile by hydrogenation with AlH₃.

Preparation of Nickel Complexes

Addition of stoichiometric amounts of the tripodal ligands **1–4** to solutions of Ni(NO₃)₂·6H₂O in methanol or acetonitrile gives deep-blue solutions, from which the complexes [Ni(N₄)(η¹-NO₃)₂] (**5a**: N₄ = **1**; **5b**: N₄ = **2**) and [Ni(N₄)(η²-NO₃)₂]NO₃·X (**5c**: N₄ = **3**, X = CH₃CN; **5d**: N₄ = **4**, X = CH₃OH) can be crystallized by slow diffusion of gaseous diethyl ether into them. Reactions of **1–4** with

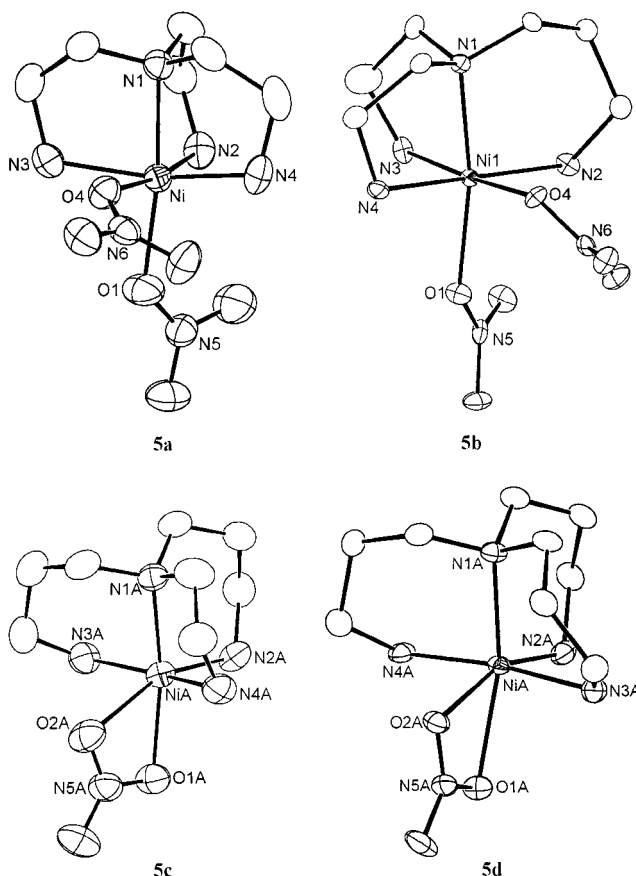


Figure 2. ORTEP plots of complexes **5a** and **5b** and of the cations in complexes **5c** and **5d**; solvent molecules and counterions in **5c** and **5d** have been omitted for clarity

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in acetonitrile or methanol yield complexes $[\text{Ni}(\text{N}_4)\text{Cl}(\text{H}_2\text{O})]\text{Cl}$ (**6a**: $\text{N}_4 = \mathbf{1}$,^[2] **6c**: $\text{N}_4 = \mathbf{3}$), $[\text{Ni}(\text{N}_4)(\mu\text{-Cl})_2(\text{N}_4)\text{Ni}]\text{Cl}_2 \cdot 2\text{CH}_3\text{OH}$ (**6b**: $\text{N}_4 = \mathbf{2}$), and $[\text{Ni}(\text{N}_4)(\text{-H}_2\text{O})_2]\text{Cl}_2$ (**6d**: $\text{N}_4 = \mathbf{4}$). Crystallization of the complexes was achieved in the same manner as described for **5a–d**, or by slowly concentrating a methanolic solution. With acetonitrile as the solvent, all the complexes were found to be air-stable and soluble in water. A schematic representation of complexes of types **5** and **6** is presented in Scheme 1.

Molecular Structures of the Nitrate Salts

The molecular structures of complexes **5a–d** have been determined by X-ray diffraction methods. In all cases, *cis*-octahedral complexes were formed. As can be seen from Figure 2, the main difference between the complexes lies in the coordination mode of the nitrate anions. In **5a** and **5b**, the *cis*-octahedral coordination is completed by two η^1 -coordinated nitrate anions, while in both **5c** and **5d** only one η^2 -coordinated nitrate anion is found.

This difference arises from differences in the steric bulk and demand of the coordinated tripodal tetraamines. The relationship between steric demand of the coordinated tetraamine and the coordination mode of the nitrate anions is best reflected in the $\text{N}_{\text{tert}}\text{--Ni--NH}_2$ angles. Complex **5a** contains only five-membered chelate rings and all the $\text{N}_{\text{tert}}\text{--Ni--NH}_2$ angles are smaller than 90° (Table 1). The larger six-membered chelate rings in **5d** lead to $\text{N}_{\text{tert}}\text{--Ni--NH}_2$ angles that are all larger than 90° . Complexes **5b** and **5c**, containing both five- and six-membered chelate rings, are intermediate between these limiting cases with $\text{N}_{\text{tert}}\text{--Ni--NH}_2$ angles larger than 90° for the six-membered rings and smaller than 90° for the five-membered ones. A similar relationship between the $\text{N}_{\text{tert}}\text{--Cu--NH}_2$ angles and the different chelate ring sizes has been described for trigonal-bipyramidal^[16a] and tetragonal-pyramidal^[17] copper complexes. As a consequence of this geometrical situation, the size of the cavity left for coligands decreases on going from **5a** to **5d**. In **5a** and **5b**, it is still large enough to accommodate two monodentate nitrate anions, while in **5c** and **5d** only one bidentate nitrate anion can fit into the cavity and the second nitrate anion is left uncoordinated as a counterion. Not only the number of coordinated nitrate anions, but also the Ni--O distances are at least partially determined by the topology of the tripodal tetraamine. The shortest Ni--O distance [2.075(3) Å] is observed for **5a** and, as expected, the largest values [2.224(4) Å and 2.195(4) Å] are found in **5d**. It would appear that this is not exclusively due to steric effects. In complexes **5a**, **5b**, and **5c**, the shorter of the two Ni--O distances is found *trans* to the tertiary nitrogen atom of the tripod, while the longer one is found *trans* to a primary amine group [2.075(3) Å vs. 2.280(2) Å for **5a**, 2.087(3) Å vs. 2.171(3) Å for **5b**, 2.139(4) Å vs. 2.280(4) Å and 2.147(4) Å vs. 2.216(4) Å for **5c**; Table 1]. This trend is reversed in **5d**, where the shorter Ni--O distance in each of the two independent molecules in the asymmetric unit lies *trans* to a primary amine group [2.174(4) Å vs. 2.224(4) Å and 2.168(4) Å vs. 2.195(4) Å]. Moreover, the differences in the Ni--O distances (Ni--O

trans to N_{tert} vs. Ni--O *trans* to NH_2) diminish in the series of complexes on going from **5a** (0.205 Å) to **5c** (0.141 Å and 0.069 Å) and are finally reversed in **5d** (0.05 Å and 0.027 Å). We explain this observation in terms of an increase in the basicity of the central nitrogen atom of the tripodal ligands. The basicity of N_{tert} increases from $\text{p}K_{\text{a}} < 2$ for **1** to $\text{p}K_{\text{a}} = 5.8$ for **4**, while the basicity of the primary amine groups remains essentially unchanged.^[17] The diminishing difference in the basicities of the primary and tertiary amine functions in **1** to **4** leads to a less pronounced difference in the Ni--O distances *trans* to N_{tert} and *trans* to the NH_2 groups. While the Ni--O bond *trans* to the tertiary amine becomes longer on going from **5a** to **5d**, the Ni--O bond length *trans* to a primary amine group changes less and ultimately becomes shorter than the Ni--O bond *trans* to N_{tert} in the case of **5d**. From this, it can be concluded that the ligand topology in complexes **5a–d** determines both the steric and, to a lesser extent, the electronic situation at the metal center.

Molecular Structures of the Chloride Salts

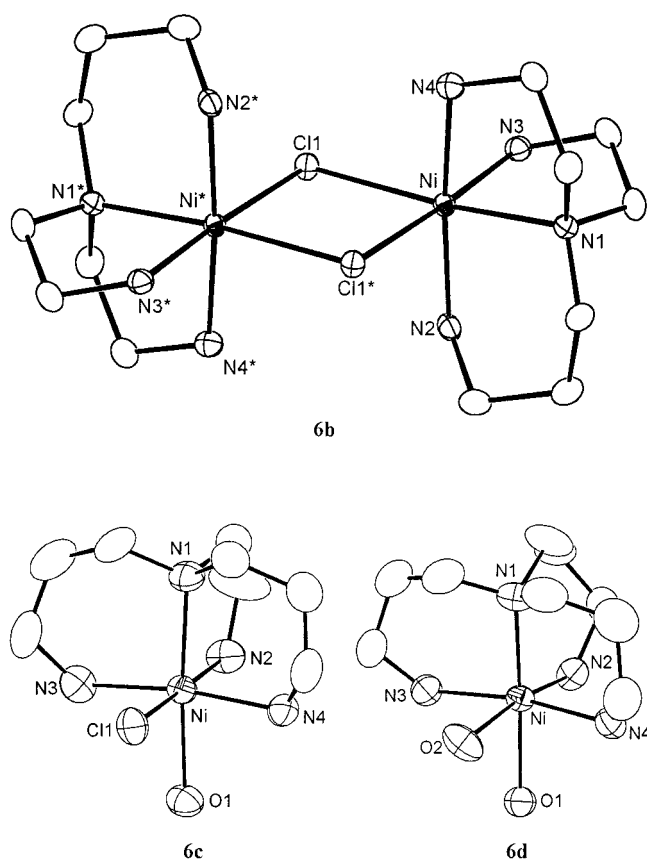
The molecular structures of complexes **6b–d** are depicted in Figure 3. Again, *cis*-octahedral complexes with chloride or water coligands were formed. It would appear that the distribution of the coligands among the two free coordination sites at the nickel atom is random and seemingly depends on the conditions used for crystallization of the complexes. Complex **6b**, which was obtained by slow concentration of a methanolic solution, crystallizes as a dinuclear species where two bridging chloride atoms complete the octahedral coordination environments at the nickel atoms. On the other hand, **6c** and **6d** were crystallized by diffusion of diethyl ether into acetonitrile solutions and are mononuclear complexes. In complex **6c**, a water molecule occupies the *trans* position and a chloride ion the *cis* position relative to N_{tert} , while in **6d** two coordination sites at nickel are occupied by water molecules. The series is completed by compound $[\text{Ni}(\mathbf{1})\text{Cl}(\text{H}_2\text{O})]\text{Cl} \cdot \text{H}_2\text{O}$ (**6a**).^[2] Its molecular structure was first investigated by Jørgensen in 1956.^[24] On the basis of its electronic spectra in aqueous solution, it was suggested that **6a** should be formulated as $[\text{Ni}(\mathbf{1})(\text{H}_2\text{O})_2]\text{Cl}_2$. Some years later, it was shown that it is $[\text{Ni}(\mathbf{1})\text{Cl}(\text{H}_2\text{O})]\text{Cl} \cdot \text{H}_2\text{O}$ in the solid state,^[2] while $[\text{Ni}(\mathbf{1})(\text{H}_2\text{O})_2]^{2+}$ cations exist in water. Interestingly, in the solid state, the coordination of the monodentate ligands in **6a** (Cl *trans* to N_{tert}) is exactly opposite to that found in **6c** (Cl *cis* to N_{tert}).

As for the nitrate salts **5**, certain bonding parameters of the tripodal tetraamine in complexes **6** (Table 2) are strongly dependent on the topology of the ligand. The $\text{N}_{\text{tert}}\text{--Ni--L}_{\text{trans}}$ axis is essentially linear for all complexes of type **6**. As for the nitrate complexes, the $\text{N}_{\text{tert}}\text{--Ni--N}_{\text{cis}}$ angles are smaller than 90° for five-membered chelate rings and larger than 90° for six-membered rings.

In contrast to the nitrate complexes of type **5**, the monodentate ligands in complexes **6** are sterically non-demanding. The distances between the nickel atoms and these ligands allow an evaluation of the dependence of the *trans*

Table 1. Selected bond lengths [Å] and angles [°] for complexes of type **5**

	5a	5b	5c ·CH ₃ CN		5d ·CH ₃ OH	
			molecule A	molecule B	molecule A	molecule B
Ni–N1	2.089(3)	2.109(4)	2.086(4)	2.099(4)	2.109(5)	2.111(5)
Ni–N2	2.055(3)	2.061(4)	2.035(5)	2.054(5)	2.054(5)	2.061(5)
Ni–N3	2.095(3)	2.067(4)	2.061(5)	2.062(4)	2.098(5)	2.068(5)
Ni–N4	2.072(3)	2.095(4)	2.062(5)	2.068(4)	2.065(5)	2.079(5)
Ni–O1	2.075(3)	2.087(3)	2.139(4)	2.147(4)	2.224(4)	2.195(4)
Ni–O2 (O4)	2.280(2)	2.171(3)	2.280(4)	2.216(4)	2.174(4)	2.168(4)
N1–Ni–N2	83.6(1)	94.6(1)	96.6(2)	98.3(2)	100.4(2)	100.9(2)
N1–Ni–N3	83.5(1)	84.4(2)	90.7(2)	91.4(2)	94.6(2)	91.5(2)
N1–Ni–N4	84.4(1)	83.7(2)	84.5(2)	84.0(2)	90.9(2)	92.8(2)
N2–Ni–N3	96.0(1)	94.1(2)	96.3(2)	94.6(2)	90.3(2)	91.8(2)
N2–Ni–N4	94.0(1)	173.0(2)	97.2(2)	96.5(2)	92.6(2)	89.9(2)
N3–Ni–N4	163.4(1)	92.6(2)	166.1(2)	168.5(2)	173.3(2)	175.0(2)
O1–Ni–N1	172.1(1)	166.8(1)	164.1(2)	162.3(2)	159.9(2)	158.8(2)
O2(O4)–Ni–N1	89.3(1)	90.4(2)	106.4(2)	103.8(2)	101.6(2)	99.6(2)
O2(O4)–Ni–O1	84.5(1)	88.1(1)	58.1(1)	58.7(2)	58.5(2)	59.3(2)

Figure 3. ORTEP plots of the cations in complexes **6b–d**; solvent molecules and chloride counterions have been omitted for clarity

effect of the different amine groups of the tripodal tetra-amine on the ligand topology. For two identical monodentate ligands, as found in **6b** (Cl[−]) and **6d** (H₂O), the following trends were found. In **6b**, containing the ligand **2**, the bond to the monodentate ligand *trans* to N_{tert} [Ni–Cl1 2.4449(6) Å] is shorter than that to the ligand *cis* to N_{tert} [Ni–Cl1* 2.4840(6) Å]. This situation is reversed in **6d**, containing ligand **4** with an increased basicity of the central nitrogen atom.^[17] In **6d**, the distance to the ligand *cis* to N_{tert} [Ni–O2 2.165(3) Å] is shorter than that to the ligand

Table 2. Selected bond lengths [Å] and angles [°] for complexes of type **6** (N_{tert}–N1 = ligand *trans* to N1, N_{c-N1} = ligand *cis* to N1; L_{tert-N1} = Cl (**6a,b**), H₂O (**6c,d**); L_{c-N1} = H₂O (**6a,d**), Cl (**6b,c**); see also Figure 2)

	6a ^[a]	6b	6c	6d
Ni–N1	2.105(3)	2.109(2)	2.144(4)	2.147(3)
N–N2	2.100(2)	2.095(2)	2.093(4)	2.096(3)
Ni–N3	2.095(2)	2.093(2)	2.084(4)	2.114(3)
Ni–N4	2.114(3)	2.106(2)	2.078(4)	2.084(3)
Ni–L _{tert-N1}	2.413(3)	2.4449(6)	2.162(3)	2.174(3)
Ni–L _{c-N1}	2.239(2)	2.4840(6)	2.432(1)	2.165(3)
N1–Ni–N2	82.67(8)	90.94(7)	83.1(1)	98.43(13)
N1–Ni–N3	84.0(2)	84.76(7)	94.0(2)	94.45(14)
N1–Ni–N4	82.2(1)	83.23(7)	93.8(1)	94.43(14)
N2–Ni–N3	97.5(2)	91.30(8)	91.7(2)	90.74(13)
N2–Ni–N4	93.7(1)	174.02(8)	91.3(2)	90.92(14)
N3–Ni–N4	161.0(1)	89.50(8)	171.9(1)	170.63(13)
L _{c-N1} –Ni–N1	93.57(9)	96.74(5)	96.22(11)	92.59(13)
L _{tert-N1} –Ni–N1	178.61(8)	175.25(5)	174.15(13)	177.09(14)
L _{tert-N1} –Ni–L _{c-N1}	87.16(6)	85.59(2)	89.29(9)	84.88(12)

[a] Data from ref.^[2]

trans to N_{tert} [Ni–O1 2.174(3) Å]. However, even the increase in the basicity of the tertiary nitrogen atom on going from **1** to **4** does not lead to a shortening of the N_{tert}–Ni distance in either series of complexes due to the concomitant increase in the number of sterically less favored six-membered chelate rings.

UV/Vis Spectra

A d⁸ ion like Ni^{II} in an octahedral ligand field gives rise to four absorption bands.^[25] The three strongest ones are caused by the spin-allowed transitions from the ground state ³A_{2g} to the excited triplet states ³T_{2g}, ³T_{1g(F)}, and ³T_{1g(P)}. A weaker band of low intensity can be attributed to the spin-forbidden transition to the singlet state ¹E_g. In practice, it is seldom observed as a discrete band, but more often as a shoulder of the ³A_{2g} → ³T_{2g} transition band at about 800 nm.^[26,27]

For complexes of types **5** and **6**, three distinct absorption bands are observed. The transitions from ³A_{2g} to the ³T_{1g(P)} and ³T_{1g(F)} excited states appear as sharp bands of high

intensity in the regions 350–380 nm and 560–620 nm, respectively, whereas the absorption band at about 950–1100 nm, due to the $^3A_{2g} \rightarrow ^3T_{2g}$ transition, is broad and of low intensity. A shoulder at about 800 nm is found for complexes **5a,b** and **6a,b**, while for the rest of the complexes this feature seems to be superimposed by the long-wavelength $^3A_{2g} \rightarrow ^3T_{2g}$ transition. The exact values for the absorption maxima and the molar extinction coefficients are listed in Table 3.

Table 3. UV/Vis spectroscopic data (λ [nm], ϵ [$10^3 \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$]) for complexes of types **5** and **6**

$^3A_{2g} \rightarrow$	$^3T_{1g(P)}$	$^3T_{1g(F)}$	$^3T_{2g}$
5a	358 (18.6)	565 (13.5)	952 (14.1)
5b	358 (10.7)	572 (8.9)	980 (10.1)
5c	360 (33.9)	570 (22.4)	980 (11.1)
5d	364 (51.0)	577 (28.0)	1070 (8.8)
6a ^[a]	361	565	952
6a ^[b]	349 (22.9)	570 (9.3)	962 (11.1)
6b	363 (20.9)	580 (15.6)	984 (20.5)
6c	370 (21.0)	592 (13.0)	1025 (8.5)
6d	380 (33.7)	613 (17.6)	1050 (4.4)

^[a] Data from ref.^[2] – ^[b] Complex **6a** synthesized for this study.

One of the most notable results is the observation of a bathochromic shift with increasing number of six-membered chelate rings. This can be ascribed to the weaker ligand field generated by the six-membered chelate rings, which are known to be less stable than five-membered chelate rings.^[17,28] Thus, the distance between the energy sublevels is decreased and the transitions are seen to be shifted to longer wavelengths.

Conclusion

With complexes **5a–d** and **6b–d** we present seven new complexes forming two series of octahedral Ni^{II} complexes with aliphatic tripodal tetraamine ligands. The series **6b–d** is completed by compound **6a**, which has previously been characterized by Marzotto et al.^[2] The variation of the lengths of the ligand arms leads to complexes with different size chelate rings. This causes a distortion of the octahedral coordination environment, a variation in the space available for binding and in the strengths of the bonds to monodentate coligands, and a slight shift of the absorption maxima in the UV/Vis spectra. These effects will allow, at least in part, control over the binding of monodentate ligands depending on the topology of the tripodal tetraamine without a change in the nature of the donor groups. Ligands **1–4** might therefore prove useful for the introduction of minute changes in the modelling of amine-rich reaction centers in metalloproteins.

Experimental Section

Materials and Methods: All manipulations were carried out under air. Solvents were purified by standard methods and freshly distilled prior to use. – Infrared spectra were recorded from samples

in KBr with a Perkin–Elmer IR 983 instrument. – Elemental analyses (C, H, N) were performed with a Vario EL Elemental Analyzer. – FAB mass spectra were recorded with Finnigan MAT 112 or Finnigan MAT 711 instruments. – UV/Vis spectra were recorded in methanol with a Perkin–Elmer Lambda 9 UV/Vis NIR spectrophotometer.

Ligand Syntheses: Tris(2-aminoethyl)amine (**1**) was purchased from Aldrich and was used without further purification. Ligands **2**, **3**, and **4** were synthesized according to the method of Dittler-Klingemann and Hahn.^[16a] Alternatively, ligand **3** can be prepared by the method of Fanshawe and Blackman.^[15] We preferred the preparation outlined in ref.^[16] since the free ligand and not the hydrochloride is initially obtained in this preparation. For the present study, the synthesis of **2** was slightly modified compared to the published procedure.^[16a]

Modified Preparation of Bis(2-aminoethyl)(3-aminopropyl)amine (2**):** Ligand **2** has previously been obtained by Michael addition of acrylonitrile to ammonia followed by a Strecker synthesis to yield the dinitrile HN(CH₂CN)(CH₂CH₂CN). The addition of a second –CH₂CN group to the central nitrogen atom using glyconitrile (HOCH₂CN) proved more difficult and very often failed due to reasons not yet fully understood. However, reaction of the dinitrile HN(CH₂CN)(CH₂CH₂CN) with TsOCH₂CN^[23] in DMF at 50 °C over a period of 5 d yielded the salt of the desired trinitrile, [HN(CH₂CN)₂(CH₂CH₂CN)]OTs. On addition of an excess of aqueous sodium carbonate and cooling the resulting mixture to 5 °C, colorless crystals of N(CH₂CN)₂(CH₂CH₂CN) separated within a few days. The crude product could be recrystallized from hot chloroform. Reduction of the trinitrile with AlH₃ as described previously^[16a] gave bis(2-aminoethyl)(3-aminopropyl)amine (**2**) in 64% yield.

Preparation of Nickel Complexes from Ni(NO₃)₂·6H₂O: The preparation of **5a** is described as an example. Ni(NO₃)₂·6H₂O (290 mg, 1 mmol) was dissolved in acetonitrile (5 mL) and then ligand **1** (146 mg, 1 mmol) was added dropwise by means of a syringe. The blue solution thus obtained was stirred at room temperature for 30 min, filtered, and concentrated to a volume of 3 mL. Slow diffusion of diethyl ether into the flask led to the deposition of dark-blue crystals of **5a**, which proved to be suitable for X-ray crystallography without the need for recrystallization. The air-stable crystals were collected by filtration, washed with diethyl ether, and carefully dried. This procedure could also be carried out in methanol.

5a: Yield 263 mg [80% based on Ni(NO₃)₂·6H₂O]. – C₆H₁₈N₆NiO₆ (329.0): calcd. C 21.91, H 5.52, N 25.55; found C 22.18, H 5.40, N 24.93. – MS (FAB, positive ions, DMSO/glycerol): *m/z* (%) = 266 (83) [Ni(**1**)(NO₃)⁺], 203 (100) [Ni(**1**) – H]⁺, 58 (6), 44 (53).

5b: Yield 255 mg [74% based on Ni(NO₃)₂·6H₂O]. – C₇H₂₀N₆NiO₆ (343.0): calcd. C 24.51, H 5.88, N 24.50; found C 24.31, H 5.80, N 24.38. – MS (FAB, positive ions, DMSO/glycerol): *m/z* (%) = 280 (100) [Ni(**2**)(NO₃)⁺], 217 (90) [Ni(**2**) – H]⁺, 58 (13), 44 (60).

5c·CH₃CN: Yield 278 mg [78% based on Ni(NO₃)₂·6H₂O] of slightly air-sensitive (loss of solvent) crystals. – C₁₀H₂₅N₇NiO₆ (398.1): calcd. C 30.18, H 6.33, N 24.63; found C 30.25, H 6.37, N 24.39. – MS (FAB, positive ions, DMSO/glycerol): *m/z* (%) = 294 (84) [Ni(**3**)(NO₃)⁺], 232 (100) [Ni(**3**) – H]⁺, 174 (48), 143 (30), 58 (37), 44 (48).

5d·CH₃OH: Yield 269 mg [72% based on Ni(NO₃)₂·6H₂O] of slightly air-sensitive (loss of solvent) crystals. – C₁₀H₂₈N₆NiO₇ (403.1): calcd. C 29.80, H 7.00, N 20.85; found C 29.77, H 6.94, N

Table 4. Summary of crystallographic data for **5a**, **5b**, **5c**·CH₃CN, **5d**·CH₃OH, **6b**·2CH₃OH, **6c**, and **6d**·H₂O

	5a	5b	5c ·CH ₃ CN	5d ·CH ₃ OH	6b ·2CH ₃ OH	6c	6d ·H ₂ O
Empirical formula	C ₆ H ₁₈ N ₆ NiO ₆	C ₇ H ₂₀ N ₆ NiO ₆	C ₁₀ H ₂₅ N ₇ NiO ₆	C ₁₀ H ₂₈ N ₆ NiO ₇	C ₁₆ H ₄₈ Cl ₄ N ₈ Ni ₂ O ₂	C ₈ H ₂₄ Cl ₂ N ₄ NiO	C ₉ H ₃₀ Cl ₂ N ₄ NiO ₃
Molecular mass [amu]	328.97	343.00	398.08	403.09	643.84	321.92	371.98
<i>a</i> [Å]	8.284(2)	12.228(5)	8.946(3)	17.436(2)	8.3694(6)	10.283(3)	8.0390(10)
<i>b</i> [Å]	11.800(2)	15.742(4)	9.650(3)	12.605(2)	10.8197(9)	11.125(4)	14.698(2)
<i>c</i> [Å]	12.825(3)	13.730(5)	20.963(8)	18.056(3)	15.9196(9)	12.388(5)	14.574(6)
α [°]	90	90	99.71(3)	90	90	90	90
β [°]	90	90	98.11(3)	118.602(11)	100.135(5)	97.46(3)	94.44(3)
γ [°]	90	90	100.56(2)	90	90	90	90
<i>V</i> [Å ³]	1253.7(5)	2643(2)	1725.7(10)	3484.1(9)	1419.1(2)	1405.2(9)	1716.9(8)
<i>Z</i>	4	8	4	8	2	4	4
Space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁	<i>Pbca</i>	<i>P</i> $\bar{1}$	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>P</i> 2 ₁ / <i>c</i>	<i>Cc</i>
$\rho_{\text{calcd.}}$ [g/cm ³]	1.743	1.724	1.532	1.537	1.507	1.522	1.439
μ [mm ⁻¹]	1.583	1.506	1.167	1.159	1.732	1.749	1.450
Data collection temp. [K]	293(2)	150(2)	293(2)	173(2)	153(2)	293(2)	293(2)
2 θ range [°]	5–45	5–50	4–45	5–50	5–50	4–50	5–52
No. of unique data	1628	2320	4500	6104	2485	2462	1789
No. of obsd. data, <i>I</i> $\geq$ 2 σ (<i>I</i>)	1588	1651	2946	4557	2121	1842	1735
<i>R</i> (%) ^[a]	3.09	4.16	4.11	6.17	2.71	4.24	3.03
<i>wR</i> (%) ^[a]	7.67	9.89	9.10	16.42	7.00	10.30	7.34
No. of variables	173	243	434	434	242	144	173

^[a] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$, $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w|F_o|]^2$, all refinement parameters were calculated for observed data only.

20.70. – MS (FAB, positive ions, DMSO/glycerol): *m/z* (%) = 308 (38) [Ni(4)(NO₃)]⁺, 245 (56) [Ni(4) – H]⁺, 143 (26), 58 (75), 44 (38).

Preparation of Nickel Complexes from NiCl₂·6H₂O: The preparation of the previously synthesized^[2] **6a** is described as an example. To a solution of NiCl₂·6H₂O (236 mg, 1 mmol) in methanol (5 mL) was added **1** (146 mg, 1 mmol). After stirring for 30 min at room temperature, the mixture was concentrated to a volume of 3 mL. To initiate crystallization, 1 mL of acetonitrile and a few drops of diethyl ether were added to the concentrated mixture and the resulting purple-blue solution was cooled to 5 °C. After a few hours, needle-shaped crystals had formed, which were collected by filtration and washed with diethyl ether. Recrystallization from methanol by slowly concentrating the solution gave blue, plate-shaped crystals suitable for X-ray analysis.

6a: Yield 132 mg (45% based on NiCl₂·6H₂O). – C₆H₂₀Cl₂N₄NiO (only directly coordinated water was left after drying, 293.9): calcd. C 24.53, H 6.86, N 19.07; found C 24.68, H 6.79, N 18.91. – MS (FAB, positive ions, DMSO/glycerol): *m/z* (%) = 239 (75) [Ni(1)Cl]⁺, 203 (24) [Ni(1) – H]⁺.

6b·2CH₃OH: Yield 309 mg (48% based on NiCl₂·6H₂O). – C₁₆H₄₈Cl₄N₈Ni₂O₂ (643.8): calcd. C 29.85, H 7.51, N 17.40; found C 29.76, H 7.49, N 17.32. – MS (FAB, positive ions, DMSO/glycerol): *m/z* (%) = 253 (70.2) [(Ni(2)Cl)₂]²⁺, 217 (17.53) [Ni(2) – H]⁺.

6c: Yield 132 mg (41% based on NiCl₂·6H₂O). – C₈H₂₄Cl₂N₄NiO (321.9): calcd. C 29.85, H 7.51, N 17.40; found C 29.95, H 7.37, N 17.32. – MS (FAB, positive ions, DMSO/glycerol): *m/z* (%) = 267 (89) [Ni(3)Cl]⁺, 232 (47) [Ni(3)]⁺, 174 (36).

6d·H₂O: Yield 176 mg (50% based on NiCl₂·6H₂O). – C₉H₂₈Cl₂N₄NiO₂ (only directly coordinated water was left after drying, 353.9): calcd. C 30.54, H 7.97, N 15.83; found C 30.60, H 7.84, N 15.71. – MS (FAB, positive ions, DMSO/glycerol): *m/z* (%) = 281 (53) [Ni(4)(H₂O)(OH)]⁺, 246 (34) [Ni(4)]⁺, 188 (28).

Crystal Structure Analyses: Crystals of **5a–d** and **6b–d** obtained by crystallization from methanol were found to slowly decompose

in air, most probably due to loss of solvent of crystallization. However, those obtained by crystallization from acetonitrile proved to be more stable. Complexes **5c**, **5d**, **6b**, and **6d** were crystallized as solvates **5c**·CH₃CN, **5d**·CH₃OH, **6b**·2CH₃OH, and **6d**·H₂O. Suitable crystals were mounted on an Enraf–Nonius CAD-4 diffractometer at low temperature (**5b**, **5d**·CH₃OH, **6b**·2CH₃OH) or at room temperature. Salient crystal and data collection details are listed in Table 4. Routine search and autoindexing procedures yielded the dimensions of the unit cell for all seven compounds. Diffraction data were collected using ω –2 θ scans. Raw data were reduced to structure factors^[29] (and their e.s.d. values) by correcting for scan speed, Lorentz and polarization effects. No decay corrections were necessary. Empirical absorption corrections (based on Ψ scans) were applied to the raw data for **5b**, **5d**·CH₃OH, and **6b**·2CH₃OH. The structure solutions were found by standard Patterson methods. The positional parameters for all non-hydrogen atoms were refined by using first isotropic and then anisotropic thermal parameters. Difference Fourier maps calculated at this stage showed the positional parameters of the hydrogen atoms. However, hydrogen atoms were added to the structure models in calculated positions and were refined as riding atoms. No hydrogen positions were calculated for non-coordinated solvent molecules. Calculations were carried out with SHELXL-93^[30] (refinement on *F*²). ORTEP^[31] was used for all molecular drawings. The asymmetric unit for **5c**·CH₃CN and **5d**·CH₃OH contains two independent molecules, while **6b**·2CH₃OH possesses a crystallographic inversion center and the asymmetric unit contains 1/2 of the complex. Table 1 and Table 2 list selected bond lengths and angles for complexes **5** and **6**, respectively. Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-149397 (**5a**), -149398 (**5b**), -149399 (**5c**·CH₃CN), -149400 (**5d**·CH₃OH), -140401 (**6b**·2CH₃OH), -149402 (**6c**), and -149403 (**6d**·H₂O). Copies of the data may be obtained free of charge from the CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [Fax (internat.) + 44-1223/360-033; E-mail: deposit@ccdc.cam.ac.uk].

UV/Vis Spectra: The UV/Vis spectra of all the complexes were recorded from 250 nm (40000 cm⁻¹) to 1400 nm (7100 cm⁻¹) at room temperature in methanol solution. The

wavelengths of the absorption maxima and the molar extinction coefficients of the absorption bands are listed in Table 3.

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