Synthesis and Coordination Chemistry of Novel Binucleating Macrocyclic Ligands with Amine-thioether and Amine-thiophenolate Donor Functions

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Macrocyclic Ligands, Nitrogen, Sulfur

The ability of the aromatic tetraaldehyde 1,2-bis(4-*tert*-butyl-2,6-diformylphenylsulfanyl)ethane (1) to function as a precursor in the preparation of binucleating hexaamine-dithiolate ligands has been investigated. Reductive amination of compound 1 with bis(aminoethyl)amine under medium-dilution conditions affords the macrobicyclic hexaamine-dithioether compound L¹. Deprotection of the [1+2] condensation product gives the corresponding 24-membered hexaamine-dithiophenol ligand H₂L². The formulation of L¹ as a macrobicyclic amine-thioether was confirmed by an X-ray crystal structure determination of the tetranuclear nickel(II) complex of L¹, [{(L¹)Ni₂Cl₂}₂(μ -Cl)₃](BPh₄) (**2b**). The formulation of the doubly deprotonated form (L²)²⁻⁷ of H₂L² as a 24-membered amine-thiophenolate ligand was confirmed by an X-ray crystal structure determination of the dinuclear cobalt(III) complex, [(L²)Co^{III}(μ -OH)](ClO₄)₂ · Cl (**3**). The preparation and the crystal structures of the new compounds are described.

Introduction

In recent years much effort has been put in the synthesis and the investigation of binuclear transition metal complexes. The pronounced interest in these compounds is due to both their biological relevance as simple model compounds for the active sites of certain metalloenzymes [1] and their intriguing magnetic and electronic properties [2]. Macrocyclic ligands are particularly suited for the synthesis of such complexes as they are more stable than their acyclic counterparts and the two metal ions are fixed in close proximity which has important implications for the metal-metal interactions [3] and the binuclear metal reactivity [4]. In the past most of the pertinent studies had focused on phenolatebased ligands [5 - 8] and it is only recently that the coordination chemistry of the corresponding thiophenolate-based macrocycles has been investigated [9 - 12].

Recently, we reported on a novel synthesis of macrocyclic amine-thiophenolate ligands [12, 13]. Our approach makes use of the air-stable precursor 1,2-bis(4-*tert*-butyl-2,6-diformylphenylsul-fanyl)ethane (1) which can be readily condensed



Scheme 1. Synthesis of L^1 and H_2L^2 : (*i*) HN(CH₂CH₂-NH₂)₂, CH₂Cl₂, C₂H₅OH, 12 h; then NaBH₄, r. t.; (*ii*) Na, liq. NH₃, THF, -78 °C; conc. HCl, H₂O.

with α, ω -diamines (see Scheme 1). In initial studies focused on condensation reactions with ethylenediamine and propylenediamine, however, only [2+4] condensation products could be obtained, not the desired [1+2] macrocycles. As the NH₂-functions in ethylenediamine and propylenediamine are separated by C₂ and C₃ alkyl chains, we have investigated the possibility of generating the [1+2] condensation product by using bis(aminoethyl)amine, where the two NH₂ functions are separated by a longer -CH₂CH₂NHCH₂CH₂- alkyl chain. We report here on our findings.

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Results and Discussion

Ligand syntheses

For the synthesis of the thiophenol ligand H_2L^2 (Scheme 1) the tetraaldehyde 1 was used as starting material. Earlier attempts to obtain a [2+1] product from the condensation of 1 with either ethylenediamine or propylenediamine had failed and only [4+2] products had been obtained [12, 13]. Despite these findings the condensation of 1 with diethylenetriamine under medium-dilution conditions was carried out and afforded, after subsequent sodium borohydride reduction of the tetraimine-dithioether intermediate, a single compound L^1 in 95% yield. On the basis of the elemental analysis and the NMR data the assignment of a [2+1] or [4+2] constitution for the isolated compound was not possible due to the fact that both possible products would give rise to identical analytical data. However, the formulation of L¹ as a macrobicyclic amine-thioether could be unambiguously confirmed by single crystal X-ray structure analysis of one of its metal complexes (vide infra). Removal of the protecting ethylene group was achieved with sodium in liquid ammonia followed by acidic work-up. This gave the bis-thiophenol ligand H_2L^2 as the hexa-hydrochloride in 63% yield [14].

According to this procedure the new ligand is obtained in good overall yield without the need of metal templates. The bis-thiophenol H_2L^2 can be isolated and stored as the hydrochloride and reacted with metal ions. As their nitrogen donors are no longer imine functions these ligands are more flexible, stable towards hydrolysis and ring size alterations cannot occur. Moreover, as the thiophenol functions are masked during the synthesis and liberated only in the last step the formation of disulfides and other by-products arising from the oxidation of the sulphur atoms is avoided.

Preparation of metal complexes

In order to confirm the macrocyclic nature of the new ligands the metal complexes $[\{(L^1)Ni_2Cl_2\}_2(\mu-Cl)_3](BPh_4)$ (**2b**) and $[(L^2)Co^{III}_2(\mu-OH)](ClO_4)_2Cl$ (**3**) were prepared and characterized by single crystal X-ray structure determination. The reaction of L^1 with two equivalents of NiCl₂ · 6 H₂O in methanol at ambient temperature takes place readily to give a pale blue solution. Upon stirring for 15 min the



complex $[\{(L^1)Ni_2Cl_2\}_2(\mu-Cl)_3]Cl$ (2a) was obtained as a blue powder in 82% yield (eq. (1a)). The tetraphenylborate salt $[\{(L^1)Ni_2Cl_2\}_2(\mu-Cl)_3]$ -(BPh₄) (2b) was prepared by addition of NaBPh₄ to a solution of 2a in acetonitrile (eq. (1b)). Complex 2b exhibits excellent solubility in dichloromethane, while it is virtually insoluble in methanol. Thus, slow evaporation of a solution of the complex in a mixed CH₂Cl₂ / CH₃OH solvent system produced large single crystals of 2b · 8 MeOH.

The reaction of $H_2L^2 \cdot 6$ HCl, $CoCl_2 \cdot 6 H_2O$ and NEt₃ in methanol in a 1:2:8 molar ratio initially produced a pale-red solution, which can be attributed to the formation of a dicobalt(II) complex. Upon exposure to air the color of the solution quickly changed from red to brown. The dicobalt(III) complex [(L²)Co^{III}(μ -OH)](ClO₄)₂Cl (**3**) was isolated by adding an excess of LiClO₄ (eq. (2)). Complex **3** is diamagnetic and exhibits good solubil-



Fig. 1. Structure of the complex $[{(L^1)Ni_2Cl_2}_2(\mu-Cl)_3]^{1+}$ in crystals of **2b** · 8 MeOH with thermal ellipsoids drawn at the 50% probability level. *tert*-Butyl groups and hydrogen atoms are omitted for clarity.

Table 1. Selected bond lengths [Å] and angles $[\circ]$ in **2b**.

Table 1 (continued).

Ni(1)-N(1)	2.107(5)	Ni(3)-N(7)	2.113(5)	N(1)-Ni(1)-N(2)	84.8(2)	N(7)-Ni(3)-N(8)	85.0(2)
Ni(1)-N(2)	2.068(5)	Ni(3)-N(8)	2.064(5)	N(1)-Ni(1)-N(3)	96.7(2)	N(7)-Ni(3)-N(9)	98.3(2)
Ni(1)-N(3)	2.134(5)	Ni(3)-N(9)	2.140(5)	N(1)-Ni(1)-Cl(5)	92.99(14)	N(7)-Ni(3)-Cl(6)	92.80(14)
Ni(1)-Cl(5)	2.378(2)	Ni(3)-Cl(5)	2.461(2)	N(1)-Ni(1)-Cl(6)	172.56(15)	N(7)-Ni(3)-Cl(5)	173.69(13)
Ni(1)-Cl(6)	2.446(2)	Ni(3)-Cl(6)	2.382(2)	N(1)-Ni(1)-Cl(7)	89.44(15)	N(7)-Ni(3)-Cl(7)	90.16(13)
Ni(1)-Cl(7)	2.504(2)	Ni(3)-Cl(7)	2.520(2)	N(2)-Ni(1)-N(3)	82.9(2)	N(8)-Ni(3)-N(9)	82.8(2)
Ni(2)-N(4)	2.126(5)	Ni(4)-N(10)	2.092(5)	N(2)-Ni(1)-Cl(5)	174.8(2)	N(8)-Ni(3)-Cl(5)	95.44(15)
Ni(2)-N(5)	2.043(5)	Ni(4)-N(11)	2.061(5)	N(2)-Ni(1)-Cl(6)	95.2(2)	N(8)-Ni(3)-Cl(6)	172.7(2)
Ni(2)-N(6)	2.059(5)	Ni(4)-N(12)	2.042(5)	N(2)-Ni(1)-Cl(7)	89.7(2)	N(8)-Ni(3)-Cl(7)	89.0(2)
Ni(2)-S(1)	2.384(2)	Ni(4)-S(3)	2.426(2)	N(3)-Ni(1)-Cl(5)	102.08(14)	N(9)-Ni(3)-Cl(5)	87.99(13)
Ni(2)-Cl(1)	2.459(2)	Ni(4)-Cl(3)	2.457(2)	N(3)-Ni(1)-Cl(6)	90.64(14)	N(9)-Ni(3)-Cl(6)	104.41(14)
Ni(2)-Cl(2)	2.529(2)	Ni(4)-Cl(4)	2.527(2)	N(3)-Ni(1)-Cl(7)	169.82(14)	N(9)-Ni(3)-Cl(7)	167.61(14)
Ni(1)Ni(3)	3.070(2)			Cl(5)-Ni(1)-Cl(6)	86.44(6)	Cl(5)-Ni(3)-Cl(6)	86.00(6)
				Cl(5)-Ni(1)-Cl(7)	85.60(6)	Cl(5)-Ni(3)-Cl(7)	83.55(6)
ity in polar solvents such as methanol acetonitrile				Cl(6)-Ni(1)-Cl(7)	83.11(6)	Cl(6)-Ni(3)-Cl(7)	84.06(6)
ity in point s		as memanon, a		N(4)-Ni(2)-N(5)	83.3(2)	N(10)-Ni(4)-N(11)	83.6(2)
and dimethyl	formamide. A	A thoroughly dri	ed sample	N(4)-Ni(2)-N(6)	160.7(2)	N(10)-Ni(4)-N(12)	161.5(2)

and dimethylformamide. A thoroughly dried sample showed a strong, but broad infrared absorption band at 3142 cm⁻¹, which was assigned to the ν (O-H)stretching frequency of the bridging OH group. Recrystallization from ethanol afforded $\mathbf{3} \cdot 2$ EtOH as dark-brown crystals, which were subjected to single crystal X-ray structure analysis.

Description of the crystal structure of 2b · 8 MeOH

Crystallographic characterization of complex **2b** \cdot 8 MeOH confirmed the crystal structure to consist of tetranuclear [{(L¹)₂NiCl₂}₂(μ -Cl)₃]¹⁺ cations, tetraphenylborate anions and methanol solvent molecules of crystallization. The asymmetric unit consists of one formula unit. Fig. 1 shows the structure of the tetranuclear nickel complex. Two binuclear {(L¹)Ni₂Cl₂}²⁺ subunits are connected via three chloro bridges to generate the tetranu-

Cl(5)-Ni(1)-Cl(7)	85.60(6)	Cl(5)-Ni(3)-Cl(7)	83.55(6)
Cl(6)-Ni(1)-Cl(7)	83.11(6)	Cl(6)-Ni(3)-Cl(7)	84.06(6)
N(4)-Ni(2)-N(5)	83.3(2)	N(10)-Ni(4)-N(11)	83.6(2)
N(4)-Ni(2)-N(6)	160.7(2)	N(10)-Ni(4)-N(12)	161.5(2)
N(4)-Ni(2)-S(1)	98.97(14)	N(10)-Ni(4)-S(3)	100.30(14)
N(4)-Ni(2)-Cl(1)	99.5(2)	N(10)-Ni(4)-Cl(3)	98.71(14)
N(4)-Ni(2)-Cl(2)	82.5(2)	N(10)-Ni(4)-Cl(4)	84.71(14)
N(5)-Ni(2)-N(6)	84.6(2)	N(11)-Ni(4)-N(12)	84.0(2)
N(5)-Ni(2)-S(1)	177.5(2)	N(11)-Ni(4)-S(3)	175.9(2)
N(5)-Ni(2)-Cl(1)	83.0(2)	N(11)-Ni(4)-Cl(3)	82.66(15)
N(5)-Ni(2)-Cl(2)	94.5(2)	N(11)-Ni(4)-Cl(4)	96.37(15)
N(6)-Ni(2)-S(1)	93.53(14)	N(12)-Ni(4)-S(3)	92.60(14)
N(6)-Ni(2)-Cl(1)	93.87(14)	N(12)-Ni(4)-Cl(3)	93.21(15)
N(6)-Ni(2)-Cl(2)	83.53(14)	N(12)-Ni(4)-Cl(4)	83.13(14)
S(1)-Ni(2)-Cl(1)	95.60(6)	S(3)-Ni(4)-Cl(3)	95.27(6)
S(1)-Ni(2)-Cl(2)	86.85(6)	S(3)-Ni(4)-Cl(4)	85.46(6)
Cl(1)-Ni(2)-Cl(2)	176.54(6)	Cl(3)-Ni(4)-Cl(4)	176.30(6)
Ni(1)-Cl(5)-Ni(3)	78.74(5)	Ni(1)-Cl(6)-Ni(3)	78.97(5)
Ni(1)-Cl(7)-Ni(3)	75.34(6)		

clear complex cation. Although the complex does not possess crystallographically imposed symmetry, its idealized symmetry is C_2 . Table 1 shows that the bond lengths and angles of the two binuclear subunits are more or less identical.



The dimerization of the two $\{(L^1)Ni_2Cl_2\}^{2+}$ -subunits is due to the specific coordination mode of L^1 (Fig. 2). Only one nickel ion (Ni(2)) resides within the cavity of the amine-thioether ligand. It is pseudo-octahedrally coordinated by three secondary nitrogen atoms and one thioether sulfur atom of L^1 and two chloro ligands. The three nitrogen atoms are arranged in a meridional fashion. The two halide ions are found in *trans* dispositions. The thioether sulfur atom is in a *trans* position to N(5). The second lateral bis(aminoethyl)amine unit of L¹ coordinates facially. Remarkably, the second thioether atom of L¹ does not participate in coordination to the metal atoms. Thus, the complexes dimerize via three chloro-briges between Ni(1) and Ni(3) to generate a $N_3 Ni^{II} (\mu - Cl)_3 Ni^{II} N_3$ core with a pseudo-confacial bioctahedral geometry. The average metal-ligand bond lengths (Ni-N 2.087(5) Å, Ni-S 2.405(2) Å, Ni-(μ -Cl) 2.449(2), Ni-Cl 2.493(2) show no unusual features and compare well with those of other octahedral nickel(II) complexes [15].

Description of the crystal structure of $3 \cdot 2$ EtOH

The crystal structure of **3**·2EtOH was found to consist of discrete, dinuclear $[(L^2)Co^{III}_2(\mu$ -OH)]^{3+} trications. The asymmetric unit contains one trication, two perchlorate anions, a chloride anion, and two ethanol molecules of solvent of crystallization. Fig. 3 shows the structure of the dinuclear cobalt(III) complex, Table 2 lists selected bond lengths and angles.

Although the complex does not possess crystallographically imposed symmetry, its idealized symmetry is C_s , where one half of the molecule is related Fig. 2. Structure of the binuclear $\{(L^1)Ni_2Cl_2\}^{2+}$ -subunit in crystals of **2b** · 8 MeOH with thermal ellipsoids drawn at the 50% probability level. *tert*-Butyl groups and hydrogen atoms are omitted for clarity. The other subunit is connected *via* the three bridging chloride ligands Cl(5)-Cl(7).



Fig. 3. Structure of the μ -OH complex in crystals of 3 · 2 EtOH with thermal ellipsoids drawn at the 50% probability level. *tert*-Butyl groups and hydrogen atoms are omitted for clarity.

to the other by a mirror plane that passes through the two bridging thiolate sulfur atoms and the oxygen atom of the OH unit. Thus the two cobalt(III) ions are symmetrically bridged by the hydroxide group. The Co-OH bond length of 1.927(5) Å is normal for hydroxo-bridged Co^{III} complexes [16]. Likewise, the average Co-N- and Co-S-distances at 1.979(5) and 2.271(2) Å, respectively, show no

Table 2. Selected bond lengths [Å] and angles $[\circ]$ in 3.

Co(1)-O(1)	1.924(4)	Co(2)-O(1)	1.930(5)
Co(1)-N(1)	1.977(5)	Co(2)-N(4)	1.958(5)
Co(1)-N(2)	1.986(5)	Co(2)-N(5)	1.976(5)
Co(1)-N(3)	1.978(5)	Co(2)-N(6)	1.996(6)
Co(1)-S(1)	2.275(2)	Co(2)-S(1)	2.268(2)
Co(1)-S(2)	2.271(2)	Co(2)-S(2)	2.271(2)
$Co(1)\cdots Co(2)$	2.7936(12)		
O(1)-Co(1)-N(1)	176.3(2)	O(1)-Co(2)-N(4)	87.0(2)
O(1)-Co(1)-N(2)	94.4(2)	O(1)-Co(2)-N(5)	92.6(2)
O(1)-Co(1)-N(3)	86.2(2)	O(1)-Co(2)-N(6)	175.0(2)
O(1)-Co(1)-S(1)	81.22(14)	O(1)-Co(2)-S(1)	81.26(13)
O(1)-Co(1)-S(2)	81.74(13)	O(1)-Co(2)-S(2)	81.60(13)
N(1)-Co(1)-N(2)	85.8(2)	N(4)-Co(2)-N(5)	85.6(2)
N(1)-Co(1)-N(3)	97.6(2)	N(4)-Co(2)-N(6)	97.8(2)
N(1)-Co(1)-S(1)	95.1(2)	N(4)-Co(2)-S(1)	167.5(2)
N(1)-Co(1)-S(2)	98.2(2)	N(4)-Co(2)-S(2)	91.3(2)
N(2)-Co(1)-S(2)	174.7(2)	N(5)-Co(2)-N(6)	86.6(2)
N(2)-Co(1)-S(1)	100.5(2)	N(5)-Co(2)-S(1)	99.2(2)
N(2)-Co(1)-N(3)	84.9(2)	N(5)-Co(2)-S(2)	173.5(2)
N(3)-Co(1)-S(1)	166.6(2)	N(6)-Co(2)-S(1)	94.0(2)
N(3)-Co(1)-S(2)	91.2(2)	N(6)-Co(2)-S(2)	99.4(2)
S(1)-Co(1)-S(2)	82.57(7)	S(1)-Co(2)-S(2)	82.69(7)

unusual features and compare well with those of related $Co^{III}N_3S_3$ complexes [17].

Conclusions

By means of a straightforward procedure we were able to obtain the new 24-membered macrocyclic bis-thiophenol ligand H_2L in good overall yield. In comparison to the conventional route applied for the synthesis of binucleating macrocyclic ligands the necessity of using metal templates has been eliminated. The new ligands are stable and isolable and can be stored and used for complexation reactions.

Experimental Section

Materials and methods: 2-Bromo-5-tert-butylbenzene-1,3-dicarbaldehyde was prepared as described in the literature [18]. Compound 1 was prepared according to a modified literature procedure [12]. All syntheses were carried out under a protective atmosphere of argon. Melting points were determined in open glass capillaries and are uncorrected. NMR spectra were recorded on a Bruker AVANCE DPX-200 spectrometer at 300 K. Chemical shifts refer to solvent signals. Infrared spectra were recorded on a Bruker VECTOR 22 FT-IR-spectrometer and electronic absorption spectra on a Jasco V-570 UV / VIS / NIR spectrophotometer. Elemental analyses were carried out by the microanalytical laboratory of this university. CAUTION! Perchlorate salts are potentially explosive and should therefore be prepared only in small quantities and handled with appropriate care.

Preparation of tetraaldehvde (1): To a suspension of anhydrous potassium carbonate (20.73 g, 150.0 mmol) in N.N-dimethylformamide (150 cm³) was added 1.2ethanedithiol (4.71 g, 50.0 mmol) and 2-bromo-5-tertbutylbenzene-1,3-dicarbaldehyde (26.91 g, 100.0 mmol) and the reaction mixture was stirred at 50 °C for 24 h. After dropwise addition of water (500 cm³), the resulting precipitate was filtered off and washed with water. Drving in vacuo gave 1 as a pale vellow solid (22.44 g. 95%). - M. p. 176 - 178 °C (dichloromethane / cyclohexane). $-{}^{1}$ H NMR (200 MHz, CDCl₃): $\delta = 1.31$ (s, 18 H, ArC(CH₃)₃), 2.96 (s, 4 H, ArSCH₂), 8.11 (s, 4 H, s, ArH), 10.67 (s, 4 H, CHO). – ¹³C{¹H} NMR (50 MHz, CDCl₃): $\delta = 30.9, 35.2, 38.5, 131.3, 136.9, 138.3, 153.9, 191.0. -$ C₂₆H₃₀O₄S₂ (470.65): calcd. C 66.37. H 6.72. S 13.53: found C 66.58, H 6.60, S 13.33.

Preparation of macrobicyclic thioether L^1 : Solutions of 1 (7.06 g, 15.0 mmol) in dichloromethane (150 cm³) and of diethylenetriamine (3.10 g, 30.0 mmol) in ethanol (150 ml) were added simultaneously over a period of 6 h to a mixture of dichloromethane (450 cm^3) and ethanol (150 cm³). After complete addition, the reaction mixture was stirred at room temperature for 18 h. The dichloromethane was then removed at reduced pressure and a solution of sodium borohydride (4.54 g, 120.0 mmol) in ethanol (150 cm³) was added. After stirring at room temperature for 2 h, the reaction mixture was acidified to pH 1 with conc. hydrochloric acid and the resulting colourless suspension was evaporated to dryness. Water (150 cm³) and dichloromethane (300 cm³) were added to the residue, the pH of the aqueous phase was adjusted to 13 with 3 M aqueous potassium hydroxide and the heterogeneous mixture was stirred vigorously for 30 min. The layers were separated and the aqueous phase was extracted with dichloromethane $(5 \times 50 \text{ cm}^3)$. The combined organic fractions were dried over anhydrous sodium sulphate. Evaporation of the solvent gave L^1 as a yellowish foamy solid (8.80 g, 95%). - M. p. 223 - 225 °C (dichloromethane / methanol). - ¹H NMR (200 MHz, $CDCl_3$): $\delta = 1.24$ (s, 18 H, $ArC(CH_3)_3$), 2.34 (s, 6 H, NH), 2.81 - 2.91 (m, 16 H, N(CH₂CH₂)₂), 3.15 (s, 4 H, ArSCH₂), 3.87 (s, 8 H, ArCH₂N), 7.21 (s, 4 H, ArH). -¹³C{¹H} NMR (50 MHz, CDCl₃): δ = 32.2, 35.5, 38.1, $49.9, 50.4, 55.0, 128.4, 131.0, 145.1, 153.1 - C_{34}H_{56}N_6S_2$ (612.99): calcd. C 66.62, H 9.21, N 13.71, S 10.09; found C 66.28, H 8.97, N 14.01, S 10.30.

Preparation of the bis-thiophenol ligand $H_2L^2 \cdot 6$ HCl: To a solution of sodium (3.45 g, 150.0 mmol) in liquid ammonia (150 cm³) was added a solution of L¹ (3.06 g, 5.00 mmol) in tetrahydrofuran (50 cm³) dropwise at -78 °C. The resulting blue reaction mixture was

Brought to you by | New York University Bobst Library Technical Services Authenticated Download Date I 7/28/15 8:52 PM stirred at -78 °C for 1 h before solid ammonium chloride (8.02 g, 150.0 mmol) was added in small portions at -78 °C to destroy excess reducing agent. The resulting colourless suspension was allowed to warm to room temperature. After 12 h, the remaining solvent was distilled off at reduced pressure. The residue was taken up in water (50 cm³), conc. hydrochloric acid (5 cm³) was added and the mixture was evaporated to dryness. To remove sodium chloride and ammonium chloride from the product, the residue was triturated with methanol $(3 \times 50 \text{ cm}^3)$ and filtered. Evaporation of the solvent gave the product as a colourless solid (2.54 g, 63%). - M.p. > 300 °C (methanol). $-{}^{1}$ H NMR (20 0 MHz, D₂O): $\delta = 1.13$ (s, 18 H, ArC(CH₃)₃), 3.33 - 3.45 (m, 16 H, N(CH₂CH₂)₂), 4.46 (s, 8 H, ArCH₂N), 7.52 (s, 4 H, ArH). - ${}^{13}C{}^{1}H$ NMR (50 MHz, D_2O): $\delta = 30.6, 34.5, 42.4, 44.3, 51.5,$ 131.3, 133.7, 152.4, one carbon signal was not observed. -C₃₂H₆₀Cl₆N₆S₂ (805.72) calcd. C 47.70, H 7.51, N 10.43, S 7.96; found C 47.41, H 7.25, N 10.07, S 7.56.

Preparation of $[\{(L^1)Ni_2Cl_2\}_2(\mu-Cl)_3]Cl(\mathbf{2a})$: To a solution of L¹ (613 mg, 1.00 mmol) in methanol (20 cm³) was added a solution of nickel(II) chloride hexahydrate (475 mg, 2.00 mmol) in methanol (5 cm³) and the reaction mixture was stirred at room temperature for 15 minutes. The resulting blue precipitate was filtered off and washed with little methanol and diethyl ether. Drying *in vacuo* gave **2a** as a blue powder (719 mg, 82 %), which decomposes without melting. – UV/vis (CH₃CN): λ_{max} (lg ε) = 370 nm (2.28), 586 (2.02), 1075 (1.70). – IR (KBr): ν = 3204, 2959, 2870, 1466, 1451, 1024, 959, 942 cm⁻¹. – C₆₈H₁₁₂Cl₈N₁₂Ni₄S₄ (1744.38): calcd. C 46.82, H 6.47, N 9.64, S 7.35; found C 46.21, H 6.41, N 10.20, S 7.08.

Preparation of $[{(L^1)Ni_2Cl_2}_2(\mu-Cl)_3]BPh_4$ (2b): To a solution of 2a (174 mg, 0.100 mmol) in acetonitrile (50 cm³) was added solid sodium tetraphenylborate (342 mg, 1.00 mmol). After the solvent volume had been reduced to approximately one fifth at reduced pressure, the resulting blue precipitate was filtered off, washed with little acetonitrile and diethyl ether. Drying *in vacuo* gave 2b as a pale blue powder (179 mg, 88%). – Single crystals of 2b · 8 CH₃OH suitable for X-ray crystal structure analysis were obtained by slow evaporation of a solution of 2b in CH₂Cl₂ / MeOH. Being stored in air at room temperature, these crystals decomposed within a short period of time with the loss of the solvent of crystallization.

Preparation of $[(L^2)Co^{III}_2(\mu-OH)]Cl(ClO_4)_2$ (3): A solution of cobalt(II) chloride hexahydrate (476 mg, 2.00 mmol) in methanol (10 cm³) was added dropwise to a suspension of $H_2L^2 \cdot 6 H_2O$ (806 mg, 1.00 mmol) in methanol (50 cm³) and the resulting bluish-green solution was stirred at room temperature for 30 min. A solution of triethylamine (810 mg, 8.00 mol) in methanol (5 cm³) was then added to give a red solution. Exposure of the

reaction mixture to air initiated a colour change to dark red-brown. After stirring for 2 h, the product was precipitated by the addition of solid lithium perchlorate (2.13 g, 20.0 mmol). The microcrystalline solid was filtered off and washed with little methanol and diethyl ether. Drying in vacuo gave 3 as a brown solid (580 mg, 60%). which decomposes without melting. – UV/vis (CH₃CN): λ (lg ε) = 428 (3.58), 538 (3.03). – IR(KBr): ν = 3431 (O-H), 3192, 1120, 1107, 1090 cm⁻¹. – ¹H NMR (200 MHz, DMSO-d₆): $\delta = 1.26$ (s, 9 H, CH₃), 1.29 (s, 9 H, CH₃), 4.30 - 2.50 (m, 20 H), 4.60 (m, 2 H), 4.90 (m, 2 H), 5.95 (m, 2 H), 7.13 (m, 2 H), 7.32 (s, 2 H, ArH), 7.46 (s, 2 H, ArH). $-{}^{13}C{}^{1}H$ NMR (50.3 MHz, DMSO-d₆): $\delta =$ 31.59, 31.71, 35.50, 35.66, 52.63, 53.07, 56.12, 56.99, 57.06, 57.11, 124.49, 127.58 (CH), 128.40 (CH), 131.64, 139.43, 142.85, 151.59, 152.01. $-C_{32}H_{53}Cl_3Co_2N_6O_9S_2$ (954.16) calcd. C 40.28, H 5.60, N 8.81, S 6.72; found C 39.06, H 5.72, N 8.72, S 6.45. - Single crystals of 3 \cdot 2 C₂H₅OH suitable for X-ray crystal structure analysis were obtained from a dilute solution of 3 in ethanol by slow evaporation of the solvent.

Crystal structure determinations: Single crystals of 2b · 8 CH₃OH suitable for X-ray structure analysis were obtained by slow evaporation of a solution of the compound in a CH₂Cl₂/MeOH mixed solvent system. Single crystals of 3 · 2 EtOH were grown by recrystallization from ethanol. The crystals were mounted on glass fibers using perfluoropolyether oil. Intensity data were collected at 180(2) K, using a Bruker SMART CCD diffractometer. Graphite monochromated Mo- K_{α} radiation ($\lambda = 0.71073$ Å) was used throughout. The data were processed with SAINT [19] and corrected for absorption using SADABS [20] (transmission factors: 1.00 - 0.65 for **2b**, 1.00 - 0.92 for **3**). The structures were solved by direct methods by using the program SHELXS-86 [21] and refined by full-matrix least-squares techniques against F^2 using SHELXL-93 [22]. Platon was used to search for higher symmetry. Hydrogen atoms were assigned to idealized position and given a thermal parameter 1.2 times $(1.5 \text{ for CH}_3 \text{ groups})$ that of the atoms to which they are attached.

Crystal data for **2b** · 8 CH₃OH: C₁₀₀H₁₆₄BCl₇N₁₂Ni₄-O₈S₄ ($M_r = 2284.47$); crystal size 0.28 × 0.16 × 0.08 mm³; triclinic, space group $P\bar{1}$ (no. 2), with a = 13.516(3), b = 19.072(4), c = 23.997(5) Å, $\alpha = 73.54(3), \beta = 82.92(3), \gamma = 79.84(3)^{\circ}, Z = 2, V = 5821.7(22)$ Å³, $\rho_{calcd} = 1.303$ g·cm⁻³, $2\theta_{max} = 56.72^{\circ}, \mu$ (Mo-K_{α}) = 0.924 mm⁻¹, 52989 reflections measured, 27177 unique ($R_{int} = 0.0548$), 12113 observed reflections [$I > 2\sigma(I$]]. All non-hydrogen atoms were refined anisotropically except for the carbon atoms of the disordered *t*Bu groups and the oxygen and carbon atoms of the methanol molecules of solvent of crystallization. A split atom model was applied. The site occupancies of the respective orientations were refined as follows: 0.48(1) (for C30a, C31a, C32a) and 0.52(1) (for C30b, C31b, C32b); 0.47(1) (for C60a, C61a, C62a) and 0.53(1) (for C60b, C61b, C62b). No hydrogen atoms were calculated for the OH groups of the methanol molecules. Final residuals: R1 = 0.0753, wR2 = 0.2278 (for 5186 reflections with $I > 2\sigma(I)$), R1 = 0.1452, wR2 = 0.2650 (for all data); parameter 486; largest difference peak/hole 1.448 / -1.047 eA⁻³.

Crystal data for $3 \cdot 2$ EtOH: C₃₆H₆₅Cl₃Co₂N₆O₁₁S₂ ($M_r = 1046.27$); crystal size 0.45 × 0.38 × 0.25 mm³; monoclinic, space group C 2/c (no. 15), with a = 19.090(4), b = 20.219(4), c = 25.257(5) Å, $\beta = 110.23(3)^{\circ}$, Z = 8, V = 9147.3(32) Å³, $\rho_{calcd} = 1.519$ g·cm⁻³, $2\theta_{max} = 56.62^{\circ}$, μ (Mo-K_{α}) = 1.054 mm⁻¹, 28804 reflections measured, 10936 unique ($R_{int} = 0.0425$), 5186 observed reflections [$I > 2\sigma(I)$]. All non-hydrogen atoms were refined anisotropically except for the oxygen atoms of the ClO₄⁻ anions and the oxygen and carbon atoms of the ethanol molecules of solvent of crystallization. One ClO₄⁻ is disordered over two positions. The site occupancy factors for

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the two positions were fixed at 0.50 for Cl(2), O(6), O(7), O(6)', O(7)', and 0.50 for Cl(3), O(8), O(9), O(10), O(11). No hydrogen atoms were calculated for the bridging OH group. Final residuals: R = 0.0753, wR = 0.2278 (for 5186 reflections with $I > 2\sigma(I)$), R1 = 0.1452, wR2 = 0.2650 (for all data); parameter 486; largest difference peak/hole 1.448 / -1.047 eA⁻³. Crystallographic data (excluding structure factors) for the structure(s) reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-164431 (**2b**) and -164432 (**3**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223 336-033; e-mail: deposit@ccdc.cam.ac.uk).

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