Linear Primary Polyamines as Building Blocks for Coordination Polymers, 1

Ligand Synthesis and Metal Complex Formation of 1,2,3-Triaminopropane

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A series of linear primary polyamines $H_2N–CH_2–(CH–NH_2)_n–CH_2–NH_2$ ($1 \leq n \leq 3$) was prepared from the corresponding polyalcohols. The polyamines were isolated as HCl adducts and the acidity constants in aqueous solution were determined. The crystal structure of the fully protonated tetraamine ($n = 2$) was elucidated by an X-ray diffraction study. Complex formation of the triamine ($n = 1$) with Ni^{2+}, Cu^{2+}, Zn^{2+}, Cd^{2+} was re-investigated in aqueous solution. The pH-dependent formation of a variety of species $M_xL_yH_z$ was established by potentiometric titrations and was compared with previous reports. The crystal structure of the Cu complex $[CuL_2]Cl_2$ exhibited a chain structure with a five-coordinate Cu^{II} centre in which two amino groups of the triamine ligands are coordinated to one Cu centre, while the third amino group of one of the ligands is bonded to a neighbouring Cu atom. The compound shows weak antiferromagnetic coupling interactions between the Cu^{II} centres within the chain.

Introduction

Aggregation of metal complexes has turned out to be a powerful concept for the design and preparation of extended polymeric structures[1]. Such molecular arrays have been discussed in the context of crystal engineering and supramolecular chemistry[2]. Different types of interactions have been used to connect the monomeric precursors to the polymeric forms. Zaworotko and coworkers exploited hydrogen bonding for the synthesis of a variety of indefinite coordination polymers[3]. Interconnection of metal centres by bridging counterions is another well-known strategy for the generation of such polynuclear structures. Hydrolytic polymerisation (where the metal centres are connected by bridging OH^- or O^{2-} ligands) is a prominent representative in this type of interaction[4]. In addition, a variety of tailored chelating ligands has been developed, where the binding of more than one metal cation is promoted by the specific steric characteristics of the ligand[5]. A series of multidentate chelators, based on the bipyridyl entity, has been developed by Lehn and coworkers[6]. These ligands allowed the systematic design of one-dimensional chains and helices, two-dimensional grids, and three-dimensional networks. The coordination chemistry of poly(ethyleneimines) with transition metal cations in aqueous solution has been investigated by Schläpfer et al., who suggests that these ligands have a considerable potential for technical applications[7]. The ability of polyalcohols such as the sugar alcohols or the tripodal tris(hydroxymethyl)aminoethane to act as sequestering agents, preventing formation of solid metal oxides or hydroxides in alkaline aqueous solution, has been well known for many years[8]. The linear polyalcohols $HO–CH_2–[CH–OH]_n–CH_2–OH$, $n > 1$ (sugar alcohols), are of particular interest with respect to the formation of polynuclear complexes. For steric reasons, it is not possible to bind all donor groups of one ligand molecule to a single metal centre and consequently these compounds could potentially serve as interesting building blocks for polymeric structures[9].

Although the sugar alcohols represent a well-known group of compounds that is widespread in nature, the corresponding linear polyamines $H_2N–CH_2–[CH–NH_2]_n–CH_2–NH_2$ have not been investigated to a great extent or are even completely unknown. This is of course, not true for 1,2-diaminoethane (en), the first member of

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this series ($n = 0$), for which innumerable reports of the coordinating properties have appeared in the literature[10]. In most of these reports, 1,2-diaminoethane acts as a simple, bidentate ligand. However, a bridging coordination mode of the diamine, where the two nitrogen donors are coordinated to two different metal centres, has also been established[11]. For 1,2,3-triaminopropane (trap), there have only been a limited number of reports describing the coordinating properties[12−17]. A tridentate coordination mode of trap has been established in the bis-complex of Co^{III}[14]. For the tetraamines, two different stereoisomers must be considered. Both isomers (the *threo* and the *erythro* form) have been prepared as intermediates in the synthesis of tetraazadecalins, but the free amines have not been isolated[18][19]. To the best of our knowledge, the pentaamine has not been described at all.

By analogy with the corresponding polyalcohols, linear primary polyamines could serve as novel building blocks for coordination polymers, since for $n > 1$ it is not possible to coordinate the complete donor set to one single metal centre. We have therefore initiated a comprehensive investigation of the coordination chemistry of this class of compounds and intend to publish a series of papers, where the interactions of these ligands with a variety of metal cations will be described. In the first contribution, we present the synthesis and characterisation of the ligands and we describe the coordination chemistry of the triamine with divalent metal centres in aqueous solution and in the solid state.

Results and Discussion

Preparation and Characterisation of the Ligands

1,2,3-Triaminopropane (trap, $n = 1$), *meso*-1,2,3,4-tetraaminobutane (tab) and 1,2*R*,3,4*S*,5-pentaaminopentane (pap) were prepared by a classical procedure from the corresponding polyalcohols, with the poly(benzenesulphonates) and polyazides as intermediates[20]. Conversion of the polyazides to the corresponding polyamines could be achieved either by reduction with $LiAlH_4$ or by hydrogenation in an autoclave[14][18]. The latter method proved to be more convenient and gave slightly higher yields. Due to the potential hazards of polyazides, a procedure was developed that did not require the isolation of these intermediates as pure substances. The solutions of the azides were rather transferred directly into the autoclave and hydrogenated to give the polyamines, which were finally isolated as the corresponding hydrochlorides trap . 3HCl, tab · 4HCl and pap · 5HCl. Chromatography on a strongly acidic cation exchange resin proved to be a very efficient procedure to remove any by-products, and the pure, linear polyamines could readily be isolated in their fully protonated form ($H_2N-CH_2-[CH-NH_2]_n-CH_2-NH_2)\cdot(n+2)HCl$[21]. This procedure was particularly helpful for the recovery of the amines after the titration experiments, where a large excess of salts such as KCl or KNO_3 had been added to the sample solutions. The synthetic method reported here thus represents a convenient, two-step procedure, allowing the preparation of these compounds in multi-gram quantities.

The free bases trap, tab and pap could be obtained in CO_2-free water by the simple action of a strongly basic anion resin in the OH^- form. Concentration of the resulting solution yielded the corresponding polyamines as hygroscopic and CO_2-sensitive oils. Since the crystalline polyhydrochlorides can be handled and stored without problems, the free amines were only prepared in situ in solution and were usually not isolated. Prolonged storage of tab · 4HCl and pap · 5HCl resulted in some loss of HCl (1−2%) and recrystallisation from conc. HCl was required to obtain a pure sample.

According to NMR-spectroscopic measurements and an X-ray diffraction analysis, the configuration of the ligands is retained during this synthetic procedure: conversion of erythritol yielded the corresponding *meso* isomer of the tetraamine. The ^{13}C-NMR spectrum of tab. 4 HCl exhibited a total of two signals, and the crystal structure depicted in Figure 1, showing two crystallographically independent ligand molecules, established the expected *erythro* configuration. It is noteworthy that the conformations of the two H_4tab^{4+} cations are distinctly different from a structure that would be assumed, for an isolated molecule, to be of lowest energy[13]. Only one N−C−C−N substructure exhibited a torsional angle of 161° and thus corresponds to a staggered orientation. All the other N−C−C−N torsional angles fall in the range of 66−93°, corresponding to conformations intermediate between a synclinal and an anticlinal orientation. This may be attributed to strong anion-cation interactions within the crystal lattice, with the H_4tab^{4+} cations binding several Cl^- counter ions in a bidentate mode by N−H···Cl hydrogen bonding.

The acidity constants (pK_a values) of the three ligands have been determined by potentiometric measurements (Table 1). Inspection of corresponding ΔpK_a values clearly indicates that the two positive charges of the doubly protonated species are located at the terminal amino groups. For H_3pap^{3+}, the data are consistent with a protonation in the 1-, 3- and 5-positions. These findings are in agreement with simple electrostatic considerations, where a maximal distance between the positive charges is achieved. For the fully protonated species trap · 3HCl, tab · 4HCl and pap · 5HCl an increasing acidity is observed in this order in aqueous solution (Table 1). The pK_a values (25°C, 0.1 M KCl) are 3.63 for H_3trap^{3+} and 1.4 ± 0.3 for H_4tab^{4+}. H_5pap^{5+} behaves as a strong acid in water and the pK_a for the first deprotonation step could not be determined by the potentiometric method.

Complex Formation with trap in Aqueous Solution

A variety of potentiometric measurements using total M/total L ratios of 1 and 0.5 was performed to elucidate the compositions of the different species and to determine their formation constants. Some of these systems have previously been investigated by Prue and Schwarzenbach[12],

Figure 1. Molecular structure of the two crystallographically independent cations of tab·4HCl·H_2O; the thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are shown as spheres of arbitrary size; range of bond lengths [pm]: C−N: 147.6(2)−149.7(2), C−C: 151.7(2)−153.7(2)

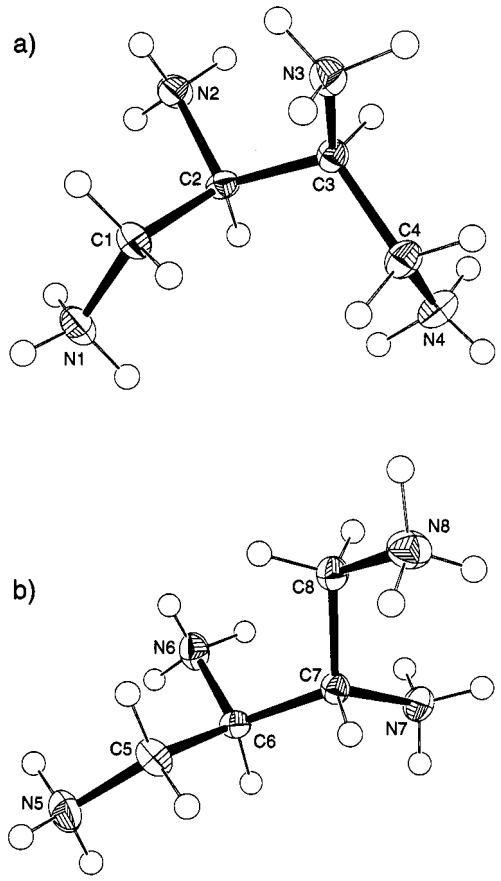


Table 1. Potentiometric data (25°C, 0.1 M KCl) and pK_a[a] values of the protonated polyamines

Experimental data			
Compound L	trap·3HCl	tab·4HCl	pap·5HCl
Total L [mol dm^{-3}]	1.0×10^{-3}	1.0×10^{-3}	1.0×10^{-3}
Evaluated pH range	3.43−10.80	3.03−10.20	2.82−10.83
Data points	41	40	59
pK_a (= $-\log K_a$)			
pK_1	9.59	9.65	9.72
pK_2	7.91	8.40	8.60
pK_3	3.63	5.03	6.26
pK_4		1.4(1)	2.62
pK_5			< 1
σ_{pH}[b]	0.0016	0.0023	0.0017

[a] The estimated standard deviations are less than 0.01 unless otherwise noted. − [b] $\sigma_{pH} = [\Sigma w(pH_{obsd.} - pH_{calcd.})^2/\Sigma w]^{1/2}$, $w = [pH_{i+1} - pH_{i-1}]^{-2}$.

and more recently by Cini et al.[17]. The authors of the latter paper investigated complex formation at 25°C and in 0.15 M NaCl. We performed the measurements at 25°C in 0.1 M KNO_3 or 0.1 M KCl (Table 2), which have become standard conditions for the determination of stability constants[22]. This allows a direct comparison with corresponding formation constants of other ligands that were measured under the same conditions[23]. Considering the difference in the media, the agreement between our values and the results of Cini et al. is good. However, we also noted some characteristic differences that led us to draw different conclusions. The most significant disagreement is the fact that we could not find an unambiguous indication for the formation of a complex of composition $[CuL]^{2+}$. In the titration experiments with a total Cu/total trap ratio of 1:2, a protonated complex of composition $[Cu(HL)]^{3+}$ is formed in the acidic range. At higher pH, coordination of an additional ligand occurred rather than the deprotonation of the coordinated HL^+ entity (Figure 2). The titration experiments, where a total L/total Cu ratio of 1:1 was used, could not be evaluated in the alkaline range because precipitation of solid $Cu(OH)_2$ was observed. This was in contrast to the Ni^{2+} system, where the formation of both $[NiL]^{2+}$ and $[NiL_2]^{2+}$ could be established unambiguously. Cini et al. performed calorimetric measurements and they deduced a tridentate coordination mode for trap in $[CuL]^{2+}$. However, a comparison of the formation constants of trap with the bidentate en does not support this interpretation: the overall protonation constants κ_2 (= $[H_2L]\cdot[L]^{-1}\cdot[H]^{-2}$) for the generation of the diprotonated H_2en^{2+} and H_2trap^{2+} are in close agreement (en: log κ_2 = 17.00; trap: log κ_2 = 17.50)[23], indicating that the formation of H_2trap^{2+} is slightly favoured. The Ni^{2+} complexes of trap are, however, of significantly higher stability (en: log β_1 = 7.3, log β_2 = 13.4; trap: log β_1 = 9.5, log β_2 = 17.3). This is not the case for Cu^{2+} where log β_2 is 19.6 for the en complex and 19.5 for the trap complex. The value for log β_1 of $[Cu(trap)]^{2+}$ in 0.15 M NaCl has been reported to be 10.4, once again showing no further increase in stability on going from the diamine to the triamine ligand (en: log β_1 = 10.50 at 25°C in 0.1 M KNO_3)[23]. Furthermore, these considerations are supported by the favoured formation of the protonated species $[Cu(HL)]^{3+}$, $[CuL(HL)]^{3+}$ and $[Cu(HL)_2]^{4+}$ and by the results of our X-ray diffraction study (see next section), where a tridentate coordination mode of trap was also not observed for Cu^{2+}.

Figure 2. Species distribution plot for an equilibrated aqueous solution with total Cu 0.5×10^{-3} mol dm^{-3} and total trap (= L) 1×10^{-3} mol dm^{-3}; only metal-containing species are shown; the charges of the different species are omitted for clarity; the equilibrium constants listed in Tables 1 and 2 were used for the calculations

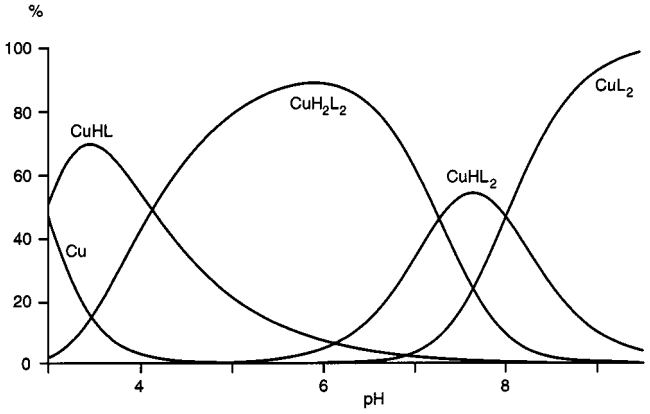


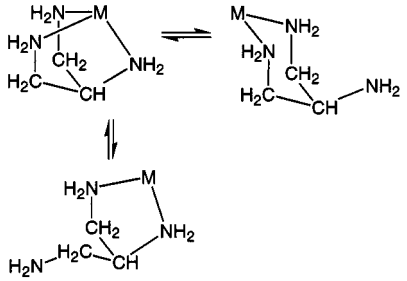
Table 2. Potentiometric data (25°C, 0.1 mol dm^{-3} KNO_3 or KCl) and evaluated formation constants[a] for trap complexes with divalent metal cations

Experimental data									
Metal			Ni[b]	Ni[b]	Cu[c]	Cu[c]	Zn[c]	Zn[c]	Cd[c]	Cd[c]
Tot.M [mol dm^{-3}]			0.5	1.0	0.5	1.0	0.5	1.0	0.5	1.0
Tot. L [mol dm^{-3}]			1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0
pH range			3.43−7.43	4.18−6.92	3.15−9.41	3.06−3.96	6.10−10.43	5.85−8.02	5.47−10.74	5.31−9.09
Data points			28	20	61	35	58	52	60	40
Formation constants log β_{xyz}[d]										
x	*y*	*z*								
1	1	0	9.58(5)	9.52(4)			6.50(2)	6.47(1)	5.99(2)	5.90(1)
1	1	1	15.45(4)	15.58(6)	18.07(3)	18.11(1)	13.75(1)	13.77(2)	13.60(3)	13.61(1)
1	1	−1					−2.89(6)		−4.39(4)	−4.22(7)
1	1	−2					−12.80(2)			
1	2	0	17.35(3)		19.55(5)		11.42(1)		10.39(3)	
1	2	1	23.87(11)		27.54(5)		19.08(8)			
1	2	−1					0.81(8)			
1	2	2			34.83(3)	34.58(6)				
σ_{pH}[e]			0.0046	0.0051	0.0015	0.0013	0.0018	0.0081	0.0069	0.0071

[a] The uncertainties, given in parentheses, correspond to the evaluated standard deviations calculated by SUPERQUAD multiplied with a factor of 3. − [b] KCl. − [c] KNO_3. − [d] $\beta_{xyz} = [M_xL_yH_z] \times [M]^{-x} \times [L]^{-y} \times [H]^{-z}$. − [e] $\sigma_{pH} = [\Sigma w(pH_{obsd.} - pH_{calcd.})^2/\Sigma w]^{1/2}$, $w = [pH_{i+1} - pH_{i-1}]^{-2}$.

Assuming a bidentate coordination mode for trap in the bis-complexes of Cu, a free amino group would be present in an alkaline medium (Scheme 1), and thus the formation of polynuclear, trap-bridged species must also be considered. As shown in the next section, such bridging interactions can indeed be observed in the solid state. However, careful evaluation of the potentiometric data provided no evidence for the formation of polynuclear species in dilute solutions such as those used in the present investigation. This may, however, be different for more concentrated solutions of complexes, where such aggregation processes are more likely to occur.

Scheme 1



Crystal Structure and Magnetic Properties of $[Cu(trap)_2]Cl_2$

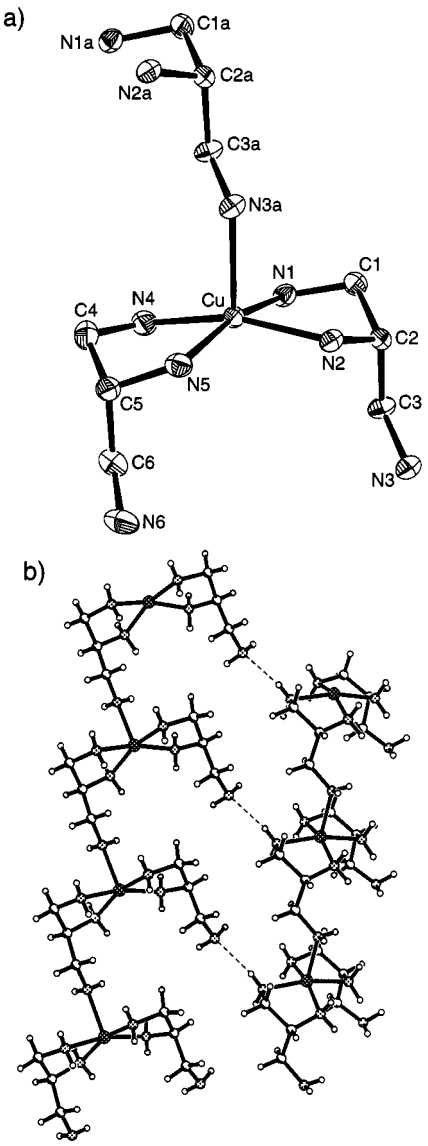
The dichloride salt of the bis-complex crystallises in the polar space group *Cc*. A view of the molecular structure is presented in Figure 3.

Both trap ligands coordinate the Cu^{II} centre in a bidentate mode, forming five-membered chelate rings. The four nitrogen donors of the two ligands form a slightly distorted square. The two ligands differ, however, with respect to the orientation of the third amino group. In the first ligand, the third amino group is coordinated to a neighbouring Cu atom. This bridging interaction of one of the trap ligands generates an infinite chain structure with five coordinate Cu^{II} cations. The coordination sphere of the Cu^{II} centre can be described as a slightly distorted tetragonal pyramid with the amino group of the bridging ligand in the apex. The Cu−N distances of the four amino groups of the square basis (2.02−2.05 Å) and of the apical amino group (2.27 Å) all fall within the expected ranges[24]. The third amino group of the second trap ligand is engaged in a weak hydrogen bond of the type N−H···Cl. This is a remarkable result since this amino group is not protonated and only minor internal rearrangements would be required to bring it into a position where coordination to the Cu centre would be possible (the Cu···N distance to this non-coordinating amino group is 4.60 Å).

A tridentate coordination mode of trap has been observed for $[Co^{III}(trap)_2]^{3+}$ and this has been confirmed by crystal structure analysis[14]. This is not surprising since Co^{III}, with its low-spin d^6-electron configuration, has a strong preference for a regular octahedral CoN_6 coordination. However, molecular mechanics calculations showed that this tridentate coordination mode causes some degree of strain in the ligand backbone, due to the formation of a six-membered chelate ring having an unfavourable boat conformation (Scheme 1)[15].

Due to the Jahn−Teller effect, Cu^{II}-hexaamine complexes usually exhibit strong tetragonal distortion[25], and the facial coordination of a triamine such as trap to Cu^{II} is particularly disfavoured. The X-ray structural analysis together with the potentiometric measurements supports indeed a bidentate coordination mode for the Cu^{II} complexes of trap. Similar conditions could be expected for Pd^{II}, Pt^{II}, or Ag^{I}, where a tridentate binding mode is also unfavourable. In such complexes, additional free amino groups must be present and trap could thus serve as an interesting build-

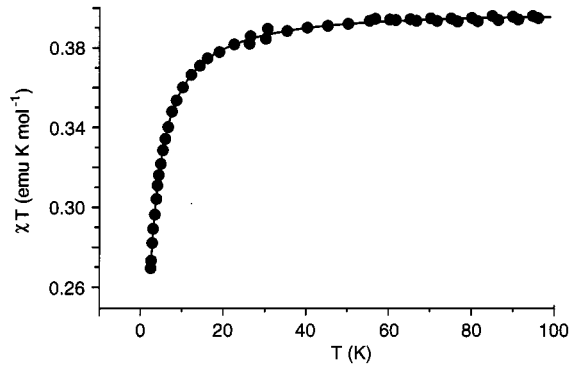
Figure 3. Molecular structure of $[Cu(trap)_2]Cl_2$; (a) the $[Cu(trap)_3]^{2+}$ cation, (b) section of the infinite chain structure; the thermal ellipsoids are drawn at the 50% probability level; hydrogen atoms are omitted (a) or shown as spheres of arbitrary size (b), the Cl^- counter ions are omitted for clarity; selected bond lengths [pm] and angles [°]: Cu−N(1) 201.6(3), Cu−N(2) 204.5(3), Cu−N(4) 202.7(3), Cu−N(5) 204.6(3), Cu−N(3a) 226.8(3); N(1)−Cu−N(2) 84.1(1), N(1)−Cu−N(3a) 97.6(1), N(1)−Cu−N(4) 92.9(1), N(1)−Cu−N(5) 166.4(1), N(2)−Cu−N(3a) 93.9(1) N(2)−Cu−N(4) 162.7(1), N(2)−Cu−N(5) 94.9(1), N(4)−Cu−N(3a) 103.3(1), N(4)−Cu−N(5) 84.0(1), N(5)−Cu−N(3a) 96.0(1); symmetry-related atoms were generated by the symmetry operation (a): $x + 1, y, z$



ing block for the synthesis of polymeric complexes of these metal cations.

Coordination polymers of paramagnetic cations are of particular interest with regard to their magnetic properties[26]. It is to be expected that interactions between the cations within the polymeric structure would result in antiferromagnetic coupling. Magnetic susceptibility measurements of $[Cu(trap)_2]Cl_2$ established Curie−Weiss behaviour with $\Theta = 1.1$ K and $C = 0.40$ emu K mol^{-1}. Since significantly different Cu···Cu distances are observed for the neighbouring Cu atoms within the chain (6.14 Å) and between two different chains (7.81 Å), the Bonner and Fisher equation for antiferromagnetic coupling interactions of paramagnetic centres within a linear infinite chain was used to fit the data (Figure 4)[27]. The experimental findings could be well reproduced with $g = 2.07$ and $J = 0.82$ cm^{-1}. The g value determined by this method was in good agreement with $g_{\parallel} = 2.19$, $g_{\perp} = 2.07$ observed in the EPR spectrum of a powder sample at room temperature.

Figure 4. Temperature dependence of $\chi \times T$ for $[Cu(trap)_2]Cl_2$; observed data are shown as squares, a theoretical behaviour, calculated for $g = 2.07$ and $J = 0.82$ cm^{-1} is shown as a solid line



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Experimental Section

General: ^{1}H- and ^{13}C-NMR spectra were measured in $CDCl_3$ or D_2O at 28°C with a Bruker DRX 500-MHz NMR spectrometer. Chemical shifts (on the δ scale) are given relative to sodium (trimethylsilyl)propionate (D_2O) or tetramethylsilane ($CDCl_3$) as internal standard ($\delta = 0$). C, H and N analyses were performed by H. Feuerhake, Institut für Anorganische Chemie, Universität des Saarlandes. 1,2,3-Propanetriol, benzenesulphonyl chloride, NaN_3, $LiAlH_4$, 5% Pd/C, *meso*-erythritol, xylitol, $CuCl_2 \cdot 2H_2O$ and the organic solvents were commercially available products of reagent-grade quality. They were used without further purification. Dowex 50 W-X2 (100−200 mesh, H^+ form) and Dowex 2-X8 (50−100 mesh, Cl^- form) were from Fluka. The OH^- form of the anion resin was obtained from the Cl^- form by elution with 0.3 M NaOH, followed by extended rinsing with CO_2-free water until a neutral eluent was observed. The temperature dependence of the static magnetic susceptibility was measured with a Metronique Ing. MS02 SQUID magnetometer at 1.0 T operating in the range of 2−250 K. The data were corrected for the contribution of the sample holder and for the diamagnetism using Pascal's constants. The EPR spectrum of a polycrystalline powder sample of $[Cu(trap)_2]Cl_2$ was recorded at room temperature at the X-band frequency with a Varian ESR9 spectrometer.

1,2,3-Propanetriyl Tribenzenesulphonate: A solution of propane-1,2,3-triol (2.30 g, 25 mmol) in 50 ml of dry pyridine was cooled to 0°C using an NaCl/ice bath. Benzenesulphonyl chloride (26.49 g, 150 mmol) was added dropwise over a 1-h period. During that

time, the colour turned to red and a white precipitate appeared. The resulting mixture was stirred overnight at room temperature and then filtered. The red solution was poured with stirring into a mixture of ice (75 g) and concentrated HCl (25 ml). An oily product was obtained from which the aqueous layer was decanted. The oil was dissolved in a mixture of methanol (75 ml) and acetone (12.5 ml) and heated until a yellow solution was obtained. The volume of the solution was reduced to 50% and the product was allowed to crystallise. It was then separated by filtration and washed with 0.5 M HCl and then hot EtOH. After drying in vacuo (12 h, 25°C), the product was obtained as a white solid (7.84 g, 61%). − $C_{21}H_{20}O_9S_3$ (512.6): calcd. C 49.21, H 3.93; found C 49.48, H 3.91. − ^{1}H NMR ($CDCl_3$): δ = 4.13 (d, 4 H, CH_2, *J* = 5 Hz), 4.75 (quint, 1 H, CH), 7.53−7.58 (m, 6 H, aryl-H), 7.67−7.71 (m, 3 H, aryl-H), 7.81−7.83 (m, 6 H, aryl-H). − ^{13}C NMR: δ = 66.4, 74.6, 128.0, 129.5, 134.3, 134.9.

1,2,3-Triazidopropane: Caution: Organic polyazides are highly explosive. They should only be handled in dilute solutions and should not be isolated as pure substances. 1,2,3-Propanetriyl tribenzenesulphonate (15.36 g, 30 mmol), NaN_3 (9.75 g, 150 mmol) and dry DMF (350 ml) were heated at 100°C for 4 h and stirred at room temperature for additional 14 h. The mixture was cooled to 10°C and diluted with 130 ml H_2O. The orange solution was extracted with Et_2O (6 × 100 ml) and the combined ether extracts were washed with water (2 × 100 ml). The ether solution was dried with $MgSO_4$. For characterisation, only a small sample (5 ml) was separated and set aside until the solvent had evaporated, and a solution of the residual brown oil in $CDCl_3$ was used to measure the NMR spectra. − ^{1}H NMR: δ = 3.40−3.48 (m, 4 H, CH_2), 3.65 (quint, 1 H, CH). − ^{13}C NMR: δ = 51.8, 60.4. − For the preparation of the triamine by method A, the solution of the azide in Et_2O was immediately used without further manipulations, while for method B, the volume of the Et_2O solution was reduced to one half by evaporation at reduced pressure and the resulting solution was then diluted by adding 150 ml of EtOH.

1,2,3-Triaminopropane·3HCl. − Method A: To a suspension of $LiAlH_4$ (8.33 g, 220 mmol) in 500 ml of dry Et_2O, the azide solution obtained from 29.3 mmol of 1,2,3-propanetriyl tribenzenesulphonate was added slowly under gentle reflux, and the mixture was then heated under reflux for another 18 h. After cooling and addition of water (10 ml), 15% NaOH (10 ml) and water (30 ml), the resulting precipitate was extracted for 18 h from a Soxhlet thimble using refluxing isopropyl alcohol (500 ml). After removing the solvent under reduced pressure, EtOH was added to the resulting oil. An excess of 6 M HCl was added to the cooled solution with stirring. The white solid which precipitated was collected by filtration and redissolved in 500 ml of H_2O. The resulting solution, having a pH ≈ 2, was sorbed onto Dowex 50 W-X2. The column was washed with water and eluted with 1 M HCl. The second fraction was concentrated to dryness under reduced pressure yielding 2.59 g (45%) of a white solid. − $C_3H_{14}Cl_3N_3$ (198.5): calcd. C 18.15, H 7.11, N 21.17; found C 18.34, H 6.90, N 20.99. − ^{1}H NMR (D_2O, pD < 2): δ = 3.34−3.40 (m, 1 H, CH), 3.21−3.25 (dd, 2 H, CH_2), 2.95−2.30 (dd, 2 H, CH_2); (pD > 12): δ = 2.68−2.73 (m, 2 H), 2.65−2.66 (m, 1 H), 2.48−2.51 (m, 2 H). − ^{13}C NMR (pD < 2): δ = 45.3, 50.0; (pD > 12): δ = 47.1, 57.1. − *Method B:* The solution of the triazide (obtained from 40.2 mmol of 1,2,3-propanetriyl tribenzenesulphonate) in EtOH/Et_2O and 885 mg of 5% Pd/C were placed in an autoclave. The mixture was hydrogenated at 4.0 bar under vigorous stirring until TLC did not show any remaining starting material. The solution was filtered twice and then cooled. An excess of 6 M HCl was added with stirring. The protocol reported for method A was then used for the isolation of the trihydrochloride. Elution from a Dowex 50 W-X2 column with 1 M HCl yielded 4.42 g (55%) of a white solid. The product was further characterised as $[Co(trap)_2]Cl_3$: trap·3HCl (602.5 mg; 3.04 mmol) was dissolved in water (60 ml) and NaOH (15%) was added until pH = 8 was reached. $CoCl_2·6H_2O$ (0.361 g; 1.52 mmol), dissolved in 60 ml of water, was added and oxygen was passed through the solution at 80°C for 24 h. The mixture was filtered, acidified to pH = 1 (HCl) and diluted with 100 ml of water. The solution was sorbed onto a column of Dowex 50W-X2. Elution with 3.0 M HCl yielded a yellow fraction which was concentrated to dryness. The brown residue (440 mg) was dissolved in water again and sorbed onto a column of SP-Sephadex. Elution with 0.2 M trisodium citrate gave two well-separated bands. A minor red band was discarded. The major orange fraction was desalted on Dowex 50W-X2 and concentrated to dryness. Yield: 272.4 mg (52%). − $C_6H_{22}Cl_3CoN_6$ (343.6): calcd. C 20.98, H 6.45, N 24.46; found: C 20.67, H 6.33, N 22.98. − Single crystals were grown from H_2O/EtOH. A single-crystal analysis revealed the same structure as reported by Henrick et al.[14].

[Cu(trap)$_2$]Cl$_2$: trap·3HCl (400 mg, 2.01 mmol) was dissolved in 25 ml of water and deprotonated using Dowex 2-X8 (OH^- form). The solution was concentrated to dryness under reduced pressure. The oily residue was dissolved in 5 ml of water and a solution of $CuCl_2·2H_2O$ (153.4 mg, 0.9 mmol) in 5 ml of water was then added. Deep blue crystals were grown by layering the solution with EtOH. − $C_6H_{22}Cl_2CuN_6$ (312.7): calcd. C 23.04, H 7.09, N 26.87; found C 23.04, H 6.93, N 26.48.

1,2,3,4-Butanetetrayl Tetrabenzenesulphonate: meso-Erythritol (6.12 g, 50 mmol) and benzenesulphonyl chloride (52.99 g, 300 mmol) were treated in dry pyridine (150 ml) as described above for the preparation of 1,2,3-propanetriyl tribenzenesulphonate. The precipitate was filtered and washed with 0.5 M HCl and then hot EtOH. After drying in vacuo (60°C, 14 h), a white solid was obtained (24.28 g, 71%). − $C_{28}H_{26}O_{12}S_4$ (682.8): calcd. C 49.26, H 3.84; found C 49.26, H 4.06. − ^{1}H NMR ($CDCl_3$): δ = 4.02−4.19 (m, 4 H, CH_2), 4.80 (m, 2 H, CH), 7.53−7.82 (m, 20 H, aryl-H). − ^{13}C NMR: δ = 66.2, 75.7, 128.1, 129.5, 134.3, 134.6.

1,2,3,4-Tetraazidobutane: Caution: Organic polyazides are highly explosive. They should only be handled in dilute solutions and should not be isolated as pure substances. 1,2,3,4-Butanetetrayl tetrabenzenesulphonate (12.16 g, 17.8 mmol) was treated with NaN_3 (6.95 g, 106.9 mmol) in dry DMF (200 ml) as described for 1,2,3-propanetriyl tribenzenesulphonate. The solution turned deep brown and was diluted with H_2O (150 ml), and extracted with ether (4 × 150 ml). The ether extract was washed with H_2O (2 × 200 ml). − ^{1}H NMR ($CDCl_3$): δ = 3.68−3.70 (m, 2 H, CH), 3.55−3.58 (m, 4 H, CH_2). − ^{13}C NMR: δ = 51.9, 61.4.

1,2,3,4-Tetraaminobutane·4HCl: Method B was used. A solution of the tetraazide (obtained from 17.8 mmol 1,2,3,4-butanetetrayl tetrabenzenesulphonate) in EtOH (150 ml) was hydrogenated at 4.0 bar using 300 mg of 5% Pd/C as catalyst. The mixture was worked up as described above and sorbed onto Dowex 50W-X2. Elution with 3 M HCl yielded 2.16 g (46%) of a white solid. − $C_4H_{18}Cl_4N_4$ (264.0): calcd. C 18.20, H 6.87, N 21.22; found C 18.15, H 6.73, N 21.02. − ^{1}H NMR (D_2O, pD < 2): δ = 3.17−3.22 (dd, 2 H, CH_2), 3.37−3.41 (dd, 2 H, CH_2), 3.50−3.54 (m, 2 H, CH); (pD > 12): δ = 2.53 (br., 2 H), 2.68 (br., 2 H), 2.76−2.78 (br., 2 H). − ^{13}C NMR (pD < 2): δ = 43.4, 54.0; (pD > 12): δ = 46.0, 58.3.

1,2,3,4,5-Pentanepentayl Pentabenzenesulphonate: Xylitol (7.61 g, 50 mmol) was treated with benzenesulphonyl chloride (88.31 g, 500 mmol) in dry pyridine (200 ml) as described above for the preparation of 1,2,3-propanetriyl tribenzenesulphonate. Traces of pyri-

dine were extracted with a mixture of ice (300 g) and concentrated HCl (100 ml) and the product was washed with MeOH (150 ml) and acetone (25 ml). Drying in vacuo at 60°C yielded 27.25 g (64%) of a white solid. – $C_{35}H_{32}O_{15}S_5$ (852.9): calcd. C 49.29, H 3.78; found C 49.20, H 3.83. – ^{1}H NMR: δ = 4.00–4.14 (4 H, CH_2), 4.81–4.92 (3 H, CH), 7.27–7.97 (25 H, aryl-H). – ^{13}C NMR: δ = 65.9, 74.0, 74.3 (3 C, aliphatic), 126.0–141.5 (12 C, aryl).

1,2,3,4,5-Pentaazidopentane: ***Caution:*** Organic polyazides are highly explosive. They should only be handled in dilute solutions and should not be isolated as pure substances. 1,2,3,4,5-Pentanepentayl pentabenzenesulphonate (27.25 g, 31.95 mmol) was treated with NaN_3 (16.6 g, 255.6 mmol) in dry DMF (400 ml) as described for 1,2,3-propanetriyl tribenzenesulphonate. The reaction mixture turned deep brown. The solution was diluted with H_2O (430 ml), and extracted with ether (8 × 200 ml). The ether extracts were combined and washed with H_2O (6 × 150 ml). – ^{1}H NMR ($CDCl_3$): δ = 3.60–3.68 (m, 7 H). – ^{13}C NMR: δ = 51.5, 61.1, 63.1.

1,2,3,4,5-Pentaaminopentane·5HCl: 1,2,3,4,5-Pentaaminopentane·5HCl was prepared using Method B. A solution of the pentaazide (obtained from 31.95 mmol of 1,2,3,4,5-pentanepentayl pentabenzenesulphonate) in EtOH (150 ml) was hydrogenated at 4.0 bar using 404 mg of 5% Pd/C as catalyst. The mixture was worked up as described above and sorbed onto Dowex 50W-X2. Elution with 3 M HCl yielded 2.27 g (22%) of a white solid. – $C_5H_{22}Cl_5N_5$ (329.5): calcd. C 18.22, H 6.73, N 21.25; found C 18.33, H 6.62, N 21.01. – ^{1}H NMR (D_2O, pD < 2): δ = 3.34–3.39 (2 H), 3.46–3.49 (2 H), 3.51–3.52 (1 H), 3.79–3.83 (2 H); (pD > 12): δ = 2.56 (br., 3 H), 2.76 (br., 4 H). – ^{13}C NMR (pD < 2): δ = 43.4, 53.2, 54.1; (pD > 12): δ = 47.2, 56.9, 57.1.

Potentiometric Measurements: Potentiometric titrations were carried out with a Metrohm 713 pH/mV meter and a Metrohm combined glass electrode with an internal Ag/AgCl reference. The sample solutions were titrated with 0.1 M KOH, using a Metrohm 665 piston burette. The ionic strength of the 50-ml sample solutions was 0.1 M KCl or 0.1 M KNO_3 and the stability of the electrode was checked by two calibration titrations prior to, and after, each measurement. All titrations were performed at 25.0°C under nitrogen (scrubbed with an aqueous solution of 0.1 M KCl or 0.1 M KNO_3). The measuring time per point was 2 min for the pK_a determinations, 5 min for the Cu complex solutions and 10 min for all other metal complexes. For the pK determination of trap, tab and pap, several alkalimetric titrations were carried out with analytically pure samples of the corresponding hydrochlorides (total concentration: 2×10^{-3} M or 1×10^{-3} M). Solutions for the titration experiments of $[M(trap)]^{2+}$ and $[M(trap)_2]^{2+}$ were prepared by dissolving trap·3HCl and $M(NO_3)_2$ (M = Cu, Zn, Cd) or $NiCl_2$ in a 1:1 and 1:2 molar ratio with total M = 1.0×10^{-3} or 0.5×10^{-3} M. The solutions were made up by using standardised aqueous stock solutions of $NiCl_2$, $Cu(NO_3)_2$, $Zn(NO_3)_2$ and trap·3HCl and solid $Cd(NO_3)_2·4H_2O$.

Calculations of Equilibrium Constants: All equilibrium constants were calculated as concentration constants. The pK_a values of the ligands and the formation constants of the metal complexes were calculated using the computer program SUPERQUAD[28] and double-checked with the computer program BEST[29]. The formation constants were evaluated with fixed values for the total concentrations of the reactants and for pK_w (13.79)[23]. For the evaluation of the titration experiments of the metal complexes, only the formation constants of the metal-containing species were varied and fixed values were used for the total concentrations of M, trap, and H, and the protonation constants of trap as obtained from the pK_a determination.

Crystal-Structure Determination of tab · 4HCl · H_2O[30]: Data were collected at 253 K with a Stoe IPDS diffractometer using monochromated Mo-K_α radiation. 220 exposures were taken in the 0–220° φ range with a crystal-to-detector distance of 72 mm and an exposure time of 2 min. Monitoring of control reflections during data collection indicated no crystal decay during the measurement. Corrections were made for Lorentz and polarisation effects. An absorption correction was not performed. The structure was solved using Direct Methods[31] and refined by full-matrix least-squares calculations[32] on F^2. All non-hydrogen atoms were refined using anisotropic displacement parameters. The hydrogen atoms were located in a difference Fourier map. Atomic coordinates and isotropic displacement parameters were refined free for all ammonium H atoms. All H atoms belonging to CH and CH_2 groups were refined riding on their C atom with isotropic displacement parameters set to 1.2 and 1.3 times the U_{eq} of the corresponding C atom, respecively. The coordinates and isotropic displacement parameters of the H atoms at the water molecule O1w were refined free, while the O–H distances in O2w had to be restrained to one common value. Further details are summarized in Table 3.

Crystal-Structure Determination of [Cu(trap)$_2$]Cl$_2$[33]: Data were collected with a Siemens P4 diffractometer using monochromated Mo-K_α radiation. Intensities were measured by ω scans. Monitoring of control reflections during data collection indicated no crystal decay during the measurement. Corrections were made for Lorentz and polarisation effects. An absorption correction was not performed. The structure was solved using Direct Methods[31] and refined by full-matrix least-squares calculations[32] on F^2. The value

Table 3. Crystallographic data for tab · 4HCl · H_2O and $[Cu(trap)_2]Cl_2$

Compounds	tab·4HCl·H_2O	$[Cu(trap)_2]Cl_2$
Empirical formula	$C_8H_{40}Cl_8N_8O_2$	$C_6H_{22}Cl_2CuN_6$
Formula weight	564.1	312.74
Temperature [K]	253	293
Radiation, λ [Å]	Mo-K_α, 0.71073	Mo-K_α, 0.71073
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$	Cc
a [Å]	8.228(2)	6.1428(9)
b [Å]	12.890(4)	14.367(2)
c [Å]	23.873(6)	15.215(2)
β [°]	99.41(3)	90.084(9)
V [Å^3]	2497.9(13)	1342.8(3)
Z	4	4
$D_{calcd.}$ [g cm^{-3}]	1.500	1.547
μ [mm^{-1}]	0.923	2.007
F[000]	1184	652
Crystal size [mm]	0.05 × 0.10 × 0.20	0.62 × 0.48 × 0.26
θ min and max	4.09 to 25.02	2.68 to 29.99
Data set	−9/9; −15/15; −28/28	0/8; 0/20; −21/21
Tot., uniq. data	17722, 4196	2119
Reflections with $I > 2\sigma(I)$	3177	1996
Structure solution	Direct methods	Direct methods
Refinement method	Full-matrix least squares on all F^2	Full-matrix least squares on all F^2
Parameters	371	173
Final R indices	R_1 = 0.0240	0.0314
[$I > 2\sigma(I)$]	wR_2 = 0.0423	0.0744
R indices	R_1 = 0.0364	0.0333
(all data)	wR_2 = 0.0431	0.0758
Largest diff. peak and hole [e/Å^3]	0.290 and −0.231	0.575 and −1.348
Max shift/error	0.090	0.001

of the Flack parameter[34] was 0.005(14) for the refined absolute structure (space group *Cc*). All non-hydrogen atoms were refined in the anisotropic mode. The hydrogen atoms were placed at calculated positions using a riding model. Further details are summarized in Table 3.

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