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Syntheses and characterization of copper complexes of the ligand (2-aminoethyl)bis(2-pyridylmethyl)amine (uns-penp) and derivatives

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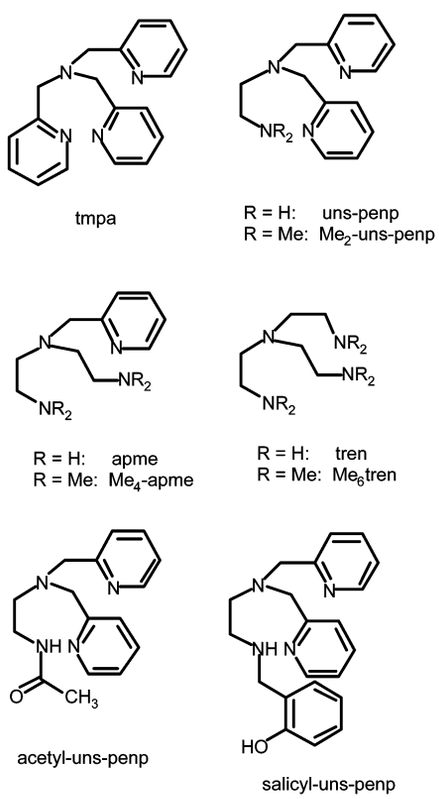
Synthesis and structural characterization of the copper(I) and copper(II) complexes of the tripodal tetradentate ligand (2-aminoethyl)bis(2-pyridylmethyl)amine (uns-penp) are reported as well as the reactivity of the copper(I) uns-penp complex towards dioxygen. Uns-penp can be easily modified and two copper(II) complexes of these derivatives have been structurally characterized. In the copper(II) complex of an amide derivative of uns-penp, [Cu(acetyl-uns-penp)Cl]ClO_4, it is evident that the amide nitrogen is no longer truly sp^2 hybridised, a consequence of a weak interaction with the copper(II) ion.

Introduction

Copper ions are found in the active sites of a large number of proteins involved in redox processing of molecular oxygen.[1–8] Low molecular weight model complexes for such enzymes have been synthesized and their reactions with dioxygen investigated.[1,4,9–14] These model compounds not only provide better understanding of the biological molecules but furthermore, they assist in the development of new homogeneous catalysts for selective oxidations under mild conditions.[5,6,9,10,13–17] A whole variety of copper dioxygen adducts can form when copper(I) complexes are reacted with dioxygen.[12,13] The course of these reactions depends on temperature, ligand and solvent.[12,13] Therefore, it is of great interest to elucidate the factors that govern the (reversible) binding and activation of dioxygen with copper(I) complexes.

The first example of a structurally characterized copper peroxo complex was obtained by Karlin and coworkers from the reaction of [Cu(tmpa)(CH_3CN)]PF_6 (tmpa = tris[(2-pyridyl)-methyl]amine, Scheme 1) with O_2 at low temperatures.[18–20] A detailed kinetic investigation of the reversible reaction of [Cu(tmpa)(CH_3CN)]$^+$ with O_2 was performed in propionitrile which allowed the spectroscopic observation of a superoxo complex prior to formation of the peroxo complex.[21] Furthermore, the influence of sterical hindrance as well as different donor atoms on the formation of the peroxo complexes was studied.[21–24] More recently we have investigated the effect of chelate ring size on the properties of these complexes.[25,26]

To further elucidate the factors that influence the reactions of dioxygen with Cu(I) complexes we have started to use tripodal ligands derived from the parent compound tris(2-aminoethyl)amine (tren, Scheme 1).[13] Tren is a versatile tetradentate ligand, known to form trigonal bipyramidal complexes with copper(II) ions in the solid state as well as in solution (similar to copper(II) tmpa complexes).[27–29] One of the axial coordination sites around the copper(II) ion is occupied by the tertiary amine nitrogen, the other by water or some other monodentate ligand.[13,28] In contrast to [Cu(tmpa)(CH_3CN)]$^+$ the copper(I) tren complex does not form a stable dioxygen adduct on O_2 exposure.[13,30] However, if the fully methylated form of tren, tris(2-dimethylaminoethyl)amine (Me_6tren, Scheme 1) is used the formation of a copper superoxo and peroxo complex at low temperatures is observed in a similar manner to tmpa.[30,31]



Scheme 1

Therefore, we became interested in investigating how a ligand incorporating both amine as well as pyridine arms would influence the reactivity of its copper(I) complexes towards dioxygen (Scheme 1). Both the amines (2-aminoethyl)bis(2-pyridylmethyl)amine (uns-penp, Scheme 1) and bis[2-aminoethyl-(2-pyridylmethyl)]amine (apme, Scheme 1) as well as some

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derivatives have been described in the literature, but have been used only recently in a few cases for the syntheses of metal complexes.[32–42]

The respective methylated forms of these ligands, Me_2-uns-penp and Me_4-apme have not been reported prior to our work.[43,44] Herein we describe the syntheses, properties and reactions of copper complexes of the ligand uns-penp and some of its derivatives.

Results and discussion

The ligand uns-penp

Amines are versatile ligands in coordination chemistry because they can be readily derivatised, thus allowing the introduction of further functional groups. For example amines react with aldehydes to form imines which can be subsequently reduced to secondary or tertiary amines. With tren a whole series of new ligands has been described where all three 'arms' have been modified (only some examples are given in the references).[13,30,45–52] It is possible to chemically derivatise only one 'arm' of tren but often ligand mixtures are obtained.[53,54] This can be avoided if a tren derivative is used that has only one modifiable amine group available. Therefore, a ligand such as uns-penp (Scheme 1) has much potential for incorporating further donor atoms or for the formation of dinucleating ligands with various spacer groups.[13]

The synthesis of uns-penp as well as the copper(II) complex of the protonated form uns-Hpenp were reported by Mandel and co-workers.[32,55] Unfortunately, the ligand uns-penp was described as a "new ligand" ten years later by Matouzenko *et al.* using a different synthetic route.[33] A slightly modified synthesis has been described recently by Girerd and coworkers as well as by Rheingold, Bosnich and coworkers.[37,56] A different approach for the preparation of uns-penp was employed by Nagano and co-workers.[57] All authors have failed to acknowledge the original reports by Mandel *et al.* These recent synthetic routes described in the literature allow uns-penp to be prepared in acceptable yields. The ligand can be routinely purified by chromatography or by distillation.[56,57]

We have developed a facile two-step synthesis for the preparation of uns-penp, which is based upon a modified version of the original synthesis described by Mandel *et al*. *N*-Acetyl-uns-penp was synthesized in high yield by the *in situ* reductive alkylation of *N*-acetylethylenediamine with 2-pyridylcarbaldehyde using $NaBH(OAc)_3$.[58] Our synthetic route obviates the need of using the unpleasant chemical picolyl chloride and is one step shorter than the more recently reported procedures for the synthesis of uns-penp which employ *N*,*N*-bis(2-pyridylmethyl)-amine.

Copper(II) complexes

[Cu(uns-penp)Cl]ClO_4 (1). The copper(II) complex [Cu(uns-penp)Cl]ClO_4 (**1**) was prepared by reacting stoichiometric amounts of $Cu(ClO_4)_2$, $CuCl_2$ and uns-penp. Crystals suitable for structural characterization were obtained and an ORTEP plot of the cation of **1** is shown in Fig. 1 (crystallographic data are reported in Tables 1 and 2).

The geometry around the copper(II) centre is best described as trigonal bipyramidal with the chloride ion and the tertiary nitrogen atom occupying the axial coordination sites, and the pyridine nitrogen atoms together with the primary amine nitrogen atom in the equatorial positions. This is analogous to the structures of the respective copper(II) complexes of tmpa and Me_6tren.[30,59] In contrast, and as discussed previously, the structure of [Cu(Me_2-uns-penp)Cl]ClO_4 is better described as distorted square pyramidal.[43]

[{Cu(uns-Hpenp)Cl}$_2$Cl]$(ClO_4)_3$ (2). In the original work on the synthesis of uns-penp the ligand was isolated as the hydrochloride salt. At the beginning of our work we observed that it was quite difficult to obtain uns-penp (as well as its derivatives, see below) in a pure form because this amine had the tendency to strongly bind one proton. Therefore our efforts to synthesize **1** resulted first in the isolation of a copper(II) compound with the protonated ligand (uns-Hpenp). The complex [{Cu(uns-Hpenp)Cl}$_2$Cl]$(ClO_4)_3$ (**2**) was prepared by reacting stoichiometric amounts of copper(II) salts and the ligand in a mixture of methanol and water. **2** crystallizes in the monoclinic space group *C*2/*c* with $Z = 8$; a summary of crystal structure parameters and refinement results for this compound is given in Table 1, selected bond distances and angles in Table 2. An ORTEP plot of the cation of **2** is shown in Fig. 2.

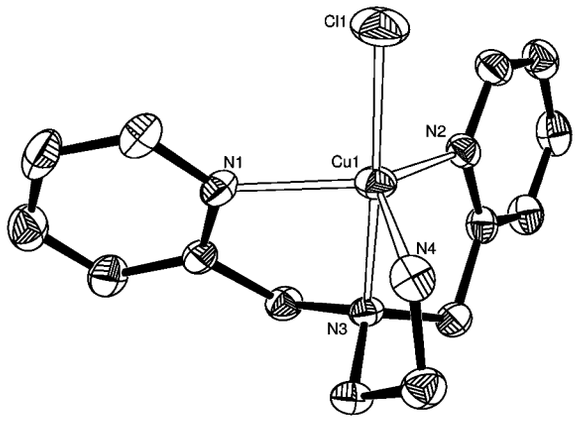

Fig. 1 ORTEP representation (50% thermal probability ellipsoids) of the crystal structure of the cation of **1**.

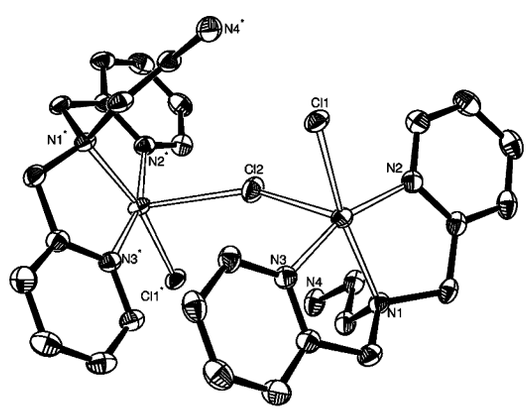

Fig. 2 ORTEP representation (50% thermal probability ellipsoids) of the crystal structure of the cation of **2**.

This complex crystallizes in a dimeric form where each copper(II) ion is ligated by the two aromatic nitrogen atoms of the pyridyl groups, the nitrogen atom of the tertiary amines and a chloride ion. Furthermore the two copper(II) ions are bridged by a chloride ion. The aliphatic primary amine arms of uns-penp, which are protonated do not coordinate to the copper(II) ions. The coordination geometry around the copper(II) centres is best described as square pyramidal. Our crystal structure is clearly different from the one reported earlier by Mandel and Douglas which is monomeric and in which the coordination geometry around the copper(II) centre is distorted trigonal bipyramidal.[55] Two pyridyl groups of uns-Hpenp are found to occupy the axial coordination positions around the copper(II) centre. The equatorial plane consists of the two chloride ions and the tertiary amine nitrogen of the ligand. The reason for obtaining different crystals most likely is a consequence of the slightly different crystallisation conditions employed.

Table 1

Complex	**1**	**2**	**3**	**4**	**5**
Molecular formula	$C_{14}H_{18}Cl_2CuN_4O_4$	$C_{14}H_{19}Cl_3CuN_4O_{6.50}$	$C_{16}H_{20}Cl_2CuN_4O_5$	$C_{42}H_{57}Cl_6Cu_2N_8O_{24.50}$	$C_{30}H_{37}Cl_2N_9O_8Cu_2$
M_r	440.77	517.22	482.80	1405.74	849.67
Temperature/K	298(2)	200(2)	200(2)	200(2)	173(2)
Radiation used (λ/Å)	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Mo-Kα (0.71073)	Mo-Kα (0.71073)
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$C2/c$	$P2_1/n$	$C2$	$C2/c$
a/Å	9.101(4)	14.3876(13)	12.4114(11)	24.686(2)	12.6284(2)
b/Å	13.133(5)	20.6906(18)	11.7813(10)	10.4701(8)	16.8880(2)
c/Å	15.199(5)	14.8827(13)	13.7910(12)	24.507(2)	34.5479(5)
β/°	101.91(3)	108.8280(10)	105.5720(10)	114.146(2)	92.8550(6)
V/Å^3	1778(2)	4193.3(6)	1942.5(3)	5780.0(8)	7358.83(18)
Z	4	8	4	4	8
D_c/g cm^{-3}	1.647	1.639	1.651	1.615	1.534
μ/mm^{-1}	1.556	1.465	1.436	1.100	1.361
Crystal size/mm	0.58 × 0.45 × 0.20	0.35 × 0.25 × 0.20	0.3 × 0.3 × 0.04	0.5 × 0.3 × 0.6	0.30 × 0.30 × 0.20
Reflections measured	4797	22039	20630	30211	11855
Unique reflections, R_{int}	3898, 0.0332	5135, 0.0265	4787, 0.0796	13756, 0.0431	6935, 0.0222
Refined parameters	317	311	265	759	460
$R(F, F^2 > 2\sigma)$	0.0418	0.0508	0.0377	0.0477	0.0458
$R_w(F^2$, all data)	0.0917	0.1802	0.0829	0.1333	0.1523
Abs. structure parameter[76]				0.045(10)	
Max./min. el. dens./e Å^{-3}	0.420, −0.376	1.555, −0.726	0.356, −0.325	0.616, −0.671	0.707, −0.438

Table 2 Selected bond lengths (Å) and angles (°)

1		**3**		N(7)–Cu(2)–N(6)	165.0(2)
Cu(1)–N(1)	2.129(3)	Cu(1)–N(1)	2.031(2)	N(7)–Cu(2)–N(5)	82.3(2)
Cu(1)–N(2)	2.054(3)	Cu(1)–N(2)	1.985(3)	N(6)–Cu(2)–N(5)	83.3(2)
Cu(1)–N(3)	2.047(3)	Cu(1)–N(3)	1.979(2)	N(7)–Cu(2)–Cl(1)	97.2(1)
Cu(1)–N(4)	2.059(4)	Cu(1)–Cl(1)	2.235(1)	N(6)–Cu(2)–Cl(1)	96.0(1)
Cu(1)–Cl(1)	2.241(2)			N(5)–Cu(2)–Cl(1)	168.7(1)
		N(1)–Cu(1)–N(2)	83.8(1)	N(7)–Cu(2)–O(3)	94.2(2)
N(1)–Cu(1)–N(2)	118.4(2)	N(1)–Cu(1)–N(3)	82.5(1)	N(6)–Cu(2)–O(3)	93.1(2)
N(1)–Cu(1)–N(3)	80.2(2)	N(1)–Cu(1)–Cl(1)	179.0(1)	N(5)–Cu(2)–O(3)	101.6(2)
N(1)–Cu(1)–N(4)	108.9(2)	N(2)–Cu(1)–N(3)	165.9(1)	Cl(1)–Cu(2)–O(3)	89.8(1)
N(1)–Cu(1)–Cl(1)	97.6(1)	N(2)–Cu(1)–Cl(1)	97.1(1)	Cu(2)–Cl(1)–Cu(1)	96.1(1)
N(2)–Cu(1)–N(3)	81.8(2)	N(3)–Cu(1)–Cl(1)	96.6(1)		
N(2)–Cu(1)–N(4)	127.0(2)			**5**	
N(2)–Cu(1)–Cl(1)	99.3(1)	**4**		Cu(1)–N(1)	2.282(3)
N(3)–Cu(1)–N(4)	84.1(2)	Cu(1)–N(2)	1.981(3)	Cu(1)–N(20)	2.030(3)
N(3)–Cu(1)–Cl(1)	177.7(1)	Cu(1)–N(3)	1.984(3)	Cu(2)–N(2)	2.319(3)
N(4)–Cu(1)–Cl(1)	96.9(2)	Cu(1)–N(1)	2.056(3)	Cu(1)–N(10)	2.058(3)
		Cu(1)–Cl(2)	2.255(1)	Cu(1)–N(7)	2.017(3)
2		Cu(1)–Cl(1)	2.688(1)	Cu(2)–N(3)	1.999(3)
Cu(1)–N(1)	2.068(3)	Cu(2)–N(7)	1.967(3)	Cu(2)–N(30)	2.031(3)
Cu(1)–N(2)	1.970(3)	Cu(2)–N(6)	1.983(4)	Cu(2)–N(40)	2.047(3)
Cu(1)–N(3)	1.972(3)	Cu(2)–N(5)	2.066(3)		
Cu(1)–Cl(1)	2.288(1)	Cu(2)–Cl(1)	2.293(1)	N(1)–Cu(1)–N(7)	132.6(2)
Cu(1)–Cl(2)	2.683(1)	Cu(2)–O(3)	2.357(3)	N(1)–Cu(1)–N(10)	80.5(2)
Cu(1)–Cl(2)*	2.683(1)			N(1)–Cu(1)–N(20)	79.9(2)
		N(2)–Cu(1)–N(3)	165.0(2)	N(7)–Cu(1)–N(10)	113.6(2)
N(2)–Cu(1)–N(1)	83.0(2)	N(2)–Cu(1)–N(1)	82.9(2)	N(7)–Cu(1)–N(20)	123.1(2)
N(2)–Cu(1)–N(3)	163.6(2)	N(3)–Cu(1)–N(1)	82.2(2)	N(10)–Cu(1)–N(20)	117.5(2)
N(1)–Cu(1)–N(3)	82.9(2)	N(2)–Cu(1)–Cl(2)	97.3(1)	N(2)–Cu(2)–N(3)	132.2(2)
N(1)–Cu(1)–Cl(1)	166.6(1)	N(3)–Cu(1)–Cl(2)	97.3(1)	N(2)–Cu(2)–N(30)	79.4(2)
N(2)–Cu(1)–Cl(1)	96.0(1)	N(1)–Cu(1)–Cl(2)	173.7(1)	N(2)–Cu(2)–N(40)	79.1(2)
N(3)–Cu(1)–Cl(1)	95.9(1)	N(2)–Cu(1)–Cl(1)	87.9(1)	N(3)–Cu(2)–N(30)	124.6(2)
N(1)–Cu(1)–Cl(2)	104.4(1)	N(3)–Cu(1)–Cl(1)	93.9(1)	N(3)–Cu(2)–N(40)	122.2(2)
N(2)–Cu(1)–Cl(2)	95.9(1)	N(1)–Cu(1)–Cl(1)	90.1(1)	N(30)–Cu(2)–N(40)	105.8(2)
N(3)–Cu(1)–Cl(2)	95.6(1)	Cl(2)–Cu(1)–Cl(1)	96.2(1)		
Cl1(1)–Cu(1)–Cl(2)	89.0(1)				

[Cu(acetyl-uns-penp)Cl]ClO$_4$ (3). Following the original synthetic report, the acetyl-protected form of the ligand was isolated as an intermediate product during the synthetic procedure.[32] Therefore, we decided to synthesize and characterize a copper(II) complex of this ligand, in order to ascertain whether or not the amide nitrogen was coordinated to the copper(II) centre. Mixing stoichiometric amounts of $Cu(ClO_4)_2$, $CuCl_2$ and acetyl-uns-penp in aqueous methanol lead to the formation of [Cu(acetyl-uns-penp)Cl]ClO_4 (**3**). This complex crystallizes in the monoclinic space group $P2_1/n$ with $Z = 4$ and an ORTEP plot of the cation of **3** is presented in Fig. 3 (a summary of crystal parameters, selected bond distances and angles are given in Tables 1 and 2).

The copper(II) centre is four coordinate, being ligated by the two pyridine groups, the aliphatic tertiary amine nitrogen and a chloride ion. The amide nitrogen atom does not coordinate to the copper(II) centre [Cu(1)–N(4) 2.640(2) Å]. The amide nitrogen atom N(4) does however form a weak electrostatic interaction with the copper(II) centre. Analysis of the torsional angles around the amide unit according to Winkler and Danitz allows the degree of "pyramidalization" at the amide nitrogen atom to be calculated.[60,61] From this analysis it is evident that

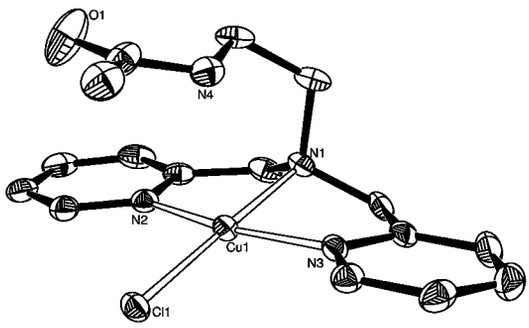

Fig. 3 ORTEP representation (50% thermal probability ellipsoids) of the crystal structure of the cation of **3**.

the nitrogen atom N(4) is no longer truly sp^2 hybridised. The geometry around the copper(II) centre is distorted square planar, as is evident from the following angles [N(1)–Cu(1)–Cl(1) 179.01(7)°, N(2)–Cu(1)–N(3) 165.93(11)°]. In contrast, no interaction between the copper(II) ion and the amide nitrogen was reported (distance 2.827(4) Å) for the copper(II) complex of the *N*-benzyl-uns-penp analogue, structurally characterized by Nishida and coworkers.[62]

N-acetyl-uns-penp resembles the amino acid derivatised bispicolylamine ligands prepared by Alsfasser and coworkers[63,64] However, in such metal complexes the amide oxygen atom is found to be coordinated to the respective metal centres (Cu(II), Ni(II), Zn(II)). The motivation for such research is in preparing small molecule model complexes that mimic the metal-coordination by peptide frameworks, which is hypothesised as playing a crucial role in key biological metal-induced pathogenic events.[65]

[(H_2O)(salicyl-uns-Hpenp)Cu(Cl)Cu(salicyl-uns-Hpenp)Cl]-(ClO_4)$_4$ (4). As discussed above, uns-penp has the advantage to readily allow the introduction of further functional groups starting with a Schiff base condensation. This approach was demonstrated successfully by Girerd and coworkers who employed salicylaldehyde and subsequently reduced the imine to the according amine.[37] However, during the attempted synthesis of the manganese complex of salicyl-uns-penp (Scheme 1) it turned out that dehydrogenation of the ligand had occurred and only crystals of the manganese imine complex were obtained. This observation is quite similar to the formation of an imine copper(II) complex (here subsequent hydrolysis occurred additionally) during the reaction of [Cu(Bz_3tren)Cl](ClO_4) (Bz_3tren = tris(2-benzylaminoethyl)-amine) or [Cu(Bz_3tren)H_2O](ClO_4)$_2$ with dioxygen described recently by us.[52]

Related to salicyl-uns-penp is the ligand pyridyl-uns-penp that can be prepared in a similar manner. However, pyridyl-uns-penp and its derivatives have been synthesized in a different way and the ligands are abbreviated in the literature as trispic or tpen.[39–42] They proved to be quite useful in the understanding of the formation of iron peroxo species.[39–42]

At the beginning of our own work we were unaware of the difficulties to remove the strongly bound proton in this kind of amine ligands (see discussion above). Therefore, the product from the synthesis of salicyl-uns-penp was mainly salicyl-uns-penp·*x*HCl. The reaction of this protonated amine with $Cu(ClO_4)_2$ in a mixture of methanol and water lead to the formation of [(H_2O)(salicyl-uns-Hpenp)Cu(Cl)Cu(salicyl-uns-Hpenp)Cl](ClO_4)$_4$ (**4**). It crystallizes with 5.5 water molecules in the asymmetric unit. The positions of the hydrogen atoms of the non-coordinated water molecules could not be located and therefore were omitted for the refinement. An ORTEP plot of the cation of **4** is shown in Fig. 4 (a summary of crystal parameters, selected bond distances and angles are given in Tables 1 and 2).

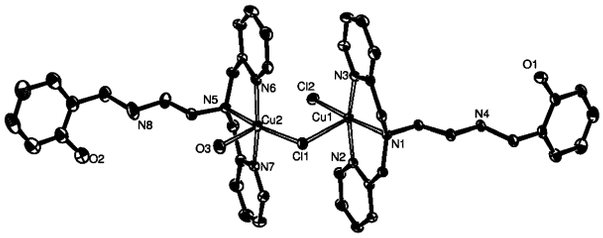

Fig. 4 ORTEP representation (50% thermal probability ellipsoids) of the crystal structure of the cation of **4**.

The structure is dimeric in the solid-state. Each copper(II) centre is ligated by the two nitrogen atoms from the bis(pyridylmethyl)amine-moiety and the tertiary amine nitrogen (for Cu(1); N(2) and N(3), and N(1), respectively). A chloride ion (Cl(2) and Cl(1)) completes the respective basal planes around each copper(II) centre. The coordination geometry around each copper(II) centre is best described as square pyramidal. The apical coordination position of Cu(1) is occupied by Cl(1), and for Cu(2) a water molecule O(3) occupies the apical site. Furthermore Cl(1) bridges the two copper(II) centres. Both the secondary amine nitrogens N(4) and N(8) are protonated and the two salicyl "arms" retain their phenol groups and are not coordinated to the copper(II) centres.

Efforts to obtain crystals of copper complexes with the unprotonated salicyl-uns-penp are in progress but all attempts so far have been unsuccessful.

Copper(I) complexes

Only the copper(I) complex of uns-penp could be prepared by mixing stoichiometric amounts of [Cu(CH_3CN)$_4$]ClO_4 with the amine in acetonitrile under argon. The syntheses of copper(I) complexes of the other ligands were unsuccessful. Crystals of the copper(I) complex of uns-penp suitable for structural characterization formed by slow diffusion of diethyl ether into an acetonitrile solution in the glove box. It is worth noting that we were able to obtain crystals of this complex because all our attempts to isolate crystals of the copper(I) tren complex in an analogous manner have been to date unsuccessful (most of the time disproportionation was observed [30]).

An ORTEP plot of the cation of [Cu_2(uns-penp)$_2$](ClO_4)$_2$ (**5**) is shown in Fig. 5 (a summary of crystallographic data and refinement parameters can be found in Table 1; selected bond lengths and angles are reported in Table 2).

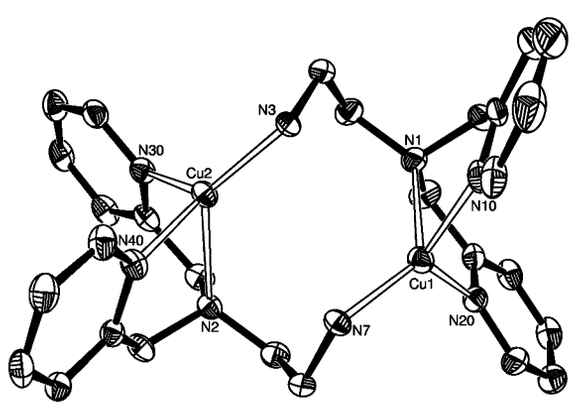

Fig. 5 ORTEP representation (50% thermal probability ellipsoids) of the crystal structure of the cation of **5**.

Fig. 5 illustrates that the complex crystallizes as a four-coordinate copper(I) dimer which incorporates two uns-penp ligands with the two copper(I) ions separated by 3.933(3) Å. Each copper(I) ion is ligated by two pyridyl moieties and the tertiary amine group from one uns-penp ligand unit. The fourth

donor, the nitrogen atom of the primary amine is supplied by the other ligand unit. The geometry around each copper(I) ion is best described as distorted tetrahedral. The tertiary amine nitrogen atoms [N(1) or N(2)] bind more weakly to the copper(I) ion [Cu(1)–N(1) 2.232(3) Å] compared to the other three nitrogen atoms [Cu(1)–N = 2.017(3)–2.058(3) Å]. There is another example of a similar dimeric copper(I) complex ($[Cu_2(BPIA)_2](CF_3SO_3)_2$, (BPIA = bis((2-pyridyl)methyl)((1-methylimidazol-2-yl)methyl)amine)) described in the literature that also shows coordination of two tripodal ligands.[23]

The observed dimeric structure of the above complex is different from that seen for other copper(I) complexes with similar tripodal tetradentate ligands, such as tmpa or Me_6tren, where only mononuclear complexes were isolated and characterized. This is furthermore demonstrated by the crystal structure of the related copper(I) complex of Me_2-uns-penp.[43] In contrast to **5**, this complex is mononuclear and the coordination geometry around the copper(I) ion is best described as slightly distorted trigonal bipyramidal, with an additional acetonitrile solvent molecule occupying an axial position.

Reactivity of 5 towards dioxygen

The reaction of dioxygen with copper(I) complexes with tripodal tetradentate ligands has been studied extensively by us and others.[1,6,13,21,25,30,31,52,66–68] It was noticed during this work that the presence of protons destabilized to a large extent the "dioxygen adduct" complexes that formed as intermediates during the oxidation reaction at low temperatures.[30] Protons could come from the solvent (*e.g.* methanol) or from the ligand itself. When tren is used as a tripodal ligand, only a very unstable "dioxygen adduct", most likely a superoxo complex, was observed during the reaction at low temperatures.[13] In contrast single alkylation of each 'amine arm' leading to Bz_3tren allowed the spectroscopic observation of a peroxo complex at low temperatures.[52] Full alkylation of each 'amine arm' leading to Me_6tren further increased the stability of the formed "dioxygen adduct" complexes.[13,30,31,68] To gain further insight into the reaction of dioxygen with copper(I) complexes with "proton rich" ligands we used the ligand uns-penp which in contrast to tren has only one primary 'amine arm'.

Propionitrile or acetone solutions of **5** (formed in situ by mixing stoichiometric amounts of copper(I) salt and uns-penp) were reacted with dioxygen at low temperatures in a stopped-flow unit equipped with a diode array detector. A typical example of time resolved spectra for this reaction at −89.9 °C in propionitrile is shown in Fig. 6. During the mixing time an absorbance band at 410 nm has already formed that decreases while another band is formed with an absorbance maximum at 486 nm. An absorbance *vs.* time trace at 486 nm is shown as an insert in Fig. 6. Under the conditions employed this complex is completely formed in about 40 s but decomposition is observed shortly afterwards.

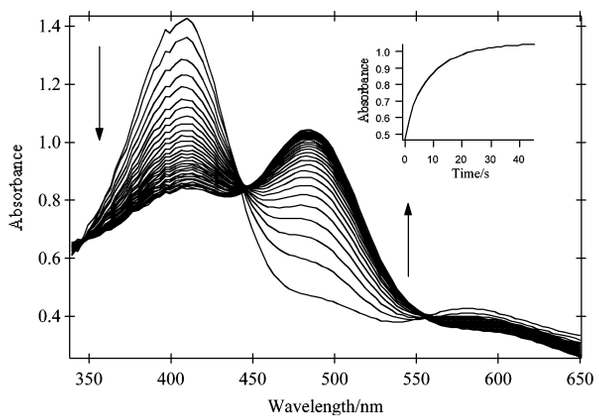

Fig. 6 Time resolved spectra of the reaction of **5** with dioxygen in propionitrile at −89.9 °C ([complex] = 0.4 mM, $[O_2]$ = 4.4 mM, total time = 46 s). Only every seventh spectrum is shown.

As described earlier the solvent can have a dramatic effect on the reaction of a copper(I) complex with dioxygen.[30,66] Here we observe a large rate increase when the oxidation of **5** is analyzed in acetone instead of propionitrile. In Fig. 7 time resolved spectra for this reaction at −89.9 °C in acetone are shown.

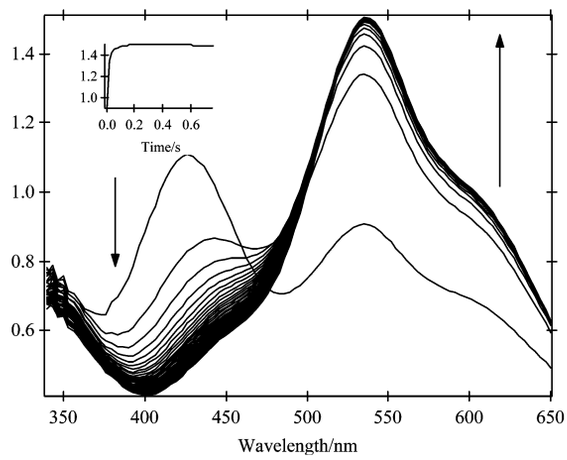

Fig. 7 Time resolved spectra of the reaction of **5** with dioxygen in acetone at −89.9 °C ([complex] = 0.4 mM, $[O_2]$ = 5.1 mM, total time = 0.77 s). Only every fifth spectrum is shown.

Here the absorbance maxima are clearly shifted to a large extent to longer wavelengths. The band at 426 nm decreases while the band at 535 nm increases. The insert shows that the reaction under these conditions is complete in less than 0.1 s in contrast to the 40 s that was observed in propionitrile.

The comparison of the UV-vis spectra with the spectral features of known "copper dioxygen" complexes indicates that superoxo (high energy band) and peroxo (low energy band) copper complexes are formed.[21,23,30,68] This is in accord with the behaviour observed in the two different solvents: in propionitrile the solvent is competing with dioxygen as a ligand and therefore equilibria are pushed to the side of the reactants in propionitrile while in acetone the formation of the peroxo complex is favoured. This is documented by the higher rates in acetone discussed above and also by a comparison of the relative absorptivities of the formed species: lower absorptivity for the superoxo complex in contrast to the higher absorptivity of the peroxo complex (in acetone). However, due to the decomposition reactions described above, a clear assignment of these species by Resonance Raman measurements was not possible. Furthermore, it is not clear what causes the large shift of the absorbance maxima going from propionitrile to acetone, an experimental result that was not observed for the corresponding copper complexes of tmpa and Me_6tren. An attempted kinetic analysis showed that the data could not be fitted to the same mechanistic model that was used for the copper complexes of tmpa and Me_6tren.[68] Additional reactions take place and the reaction behaviour is more complex, probably a consequence of the dimeric nature of **5**.

Although the reaction mechanism and the detailed nature of the superoxo and peroxo complexes could not be determined completely, a comparison with the oxidation of the copper(I) complex with the ligand Me_2-uns-penp, the methylated form of uns-penp, is quite useful. As described earlier $[Cu(Me_2\text{-uns-penp})(CH_3CN)]ClO_4$ reacts with dioxygen to form a peroxo complex that is persistent even at room temperature for a short time.[43] Therefore it is most likely that again the presence of the protons from the primary amine group in uns-penp destabilize the formed peroxo complex.

Conclusion

Uns-penp is an attractive ligand in that it can be readily synthesized and a variety of substituted functionalised derivatives are amenable. Due to such versatility, research groups now have started to employ uns-penp and its derivatized ligands in many diverse areas of bioinorganic chemistry. In this regard, we have modified an old synthesis for the facile preparation of the starting ligand uns-penp and its derivatives and have described some copper(I)/(II) complexes thereof.

The copper(II) complex of *N*-acetyl-uns-penp shows a weak copper(II)–amide nitrogen interaction as is evident from an analysis of the torsional angles around the amide unit.

Stopped-flow measurements of the reaction of the copper(I) complex of uns-penp with dioxygen at low temperatures, allowed the spectroscopic detection of a copper superoxo and peroxo species. The corresponding copper(I) complex of the methylated version of uns-penp (Me_2-uns-penp) supports a more persistent copper peroxo complex, most likely a consequence of the absence of available protons in the ligand.

Experimental

General remarks

Reagents and solvents used were of commercially available reagent grade quality. The purification of acetonitrile and propionitrile was done according to literature procedures:[69] the nitriles were stirred first over K_2CO_3 and then over P_2O_5 for 24 h, and distilled first from P_2O_5 and then K_2CO_3. Acetone was distilled from dried B_2O_3. Diethyl ether was refluxed prior to distillation over sodium metal until added benzophenone showed a blue colour. $[Cu(CH_3CN)_4]^+$ salts were synthesized and characterized according to literature methods.[70,71] Preparation and handling of air-sensitive compounds was carried out in a glove-box filled with argon (Braun, Garching, Germany; water and dioxygen less than 1 ppm). The ^{1}H NMR measurements were recorded on a Bruker DXP 300 AVANCE spectrometer. Element analyses were performed on a Carlo Erba Element Analyzer (type 1106) at the University of Erlangen-Nürnberg. Time resolved spectra of the reactions of dioxygen with copper(I) complexes were recorded on a modified Hi Tech SF-3 L low temperature stopped-flow unit (HiTech, Salisbury, UK) equipped with a J&M TIDAS 16–500 diode array spectrophotometer (J&M, Aalen, Germany). Data fitting was performed using the integrated J&M software Kinspec or the program Specfit (Spectrum Software Associates, Chapel Hill, USA). Dioxygen saturated solutions for the kinetic measurements were obtained by bubbling dioxygen (Linde, Germany) through the solvent for 20 min as described earlier.[21]

The ligands uns-penp and N-acetyl-uns-penp were synthesized according to the published procedures discussed above or as described below. The ligand uns-Hpenp was obtained following the original synthesis for uns-penp.[32]

Synthesis of uns-penp

Step 1: Synthesis of *N*-Acetyl-uns-penp. *N*-Acetylethylenediamine (1.02 g, 10 mmol) and 2-pyridinecarbaldehyde (2.14 g, 20 mmol) were placed in 1,2-dichloroethane. $NaBH(OAc)_3$ (6.0 g, 28.3 mmol) was added and the cloudy solution was stirred at room temperature under nitrogen for 3 h. The reaction was quenched by the addition of a 2 M aqueous solution of NaOH (100 mL). The organic layer was separated and the aqueous layer was extracted with CH_2Cl_2 (2 × 100 mL). The organic fractions were combined and washed with a saturated aqueous solution of NaCl (100 mL). The organic fraction was dried over anhydrous Na_2SO_4. Filtration and removal of the solvent *in vacuo* yielded the title compound as a cream coloured solid (2.55 g, 8.97 mmol, 89%). $R_f = 0.51$ (EtOAc–MeOH, 95:5). Mp 104–106 °C. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.56 (d, 2H, py-H), 7.69 (br, 1H, N*H*$COCH_3$), 7.64 (dt, 2H, py-H), 7.36 (d, 2H, py-H), 7.17 (m, 2H, py-H), 3.89 (s, 4H, pyCH_2), 3.32 (q, 2H, CH_2NHCOMe), 2.75 (t, 2H, NCH_2), 2.03 (s, 3H, NHCOCH_3). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 170.0 (C=O), 159.2, 149.1, 136.5, 123.2, 122.2, 59.5, 52.5, 37.7, 23.4 (CH_3). IR (KBr disc)/cm^{-1}: 3249 (m), 3208 (m), 3055 (m), 2982 (m), 2940 (m), 2894 (m), 2821 (m), 2362 (m), 1712 (m), 1672 (s), 1591 (m), 1564 (s), 1473 (m), 1433 (m), 1396 (m), 1370 (m), 1284 (m), 1244 (m), 1152 (m), 1130 (w), 1111 (m), 1086 (w), 1046 (m), 984 (m), 937 (w), 889 (w), 764 (s), 671 (w), 600 (w), 523 (w), 470 (w), 456 (w), 408 (w).

Step 2: Removal of the acetyl protecting group. *N*-Acetyl-uns-penp (2.20 g, 7.74 mmol) was dissolved in 5 M aqueous hydrochloric acid (50 mL). The yellow solution was heated at reflux for 24 h. The solution was allowed to cool, and made basic (pH 10) by the careful addition of NaOH. An orange oil separated. The mixture was extracted with CH_2Cl_2 (3 × 50 mL). The organic fractions were combined and dried over anhydrous $MgSO_4$. The solution was filtered and concentrated *in vacuo*. The oil was then triturated with diethyl ether (60 mL). The yellow solution was decanted, and the solvent removed *in vacuo* to give the product as a pale yellow–orange oil (1.3 g, 5.36 mmol, 70%). Overall yield 62% (two steps). ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.45 (d, 2H, py-H), 7.58 (dt, 2H, py-H), 7.42 (d, 2H, py-H), 7.08 (m, 2H, py-H), 3.77 (s, 4H, pyCH_2), 2.71 (t, 2H, CH_2NH_2), 2.59 (t, 2H, $CH_2CH_2NH_2$), 1.77 (s, 2H, NH_2). ^{13}C NMR ($CDCl_3$, 75 MHz): δ 160.0, 149.0, 136.6, 123.3, 122.3, 61.0, 57.7, 40.0. IR (neat oil, NaCl disc)/cm^{-1}: 3687 (w), 3685 (m), 3649 (m), 3362 (s, br), 3290 (s, br), 3059 (s), 3010 (s), 2935 (s, br), 2825 (s), 2491 (m), 2195 (m), 1986 (m), 1917 (m), 1891 (m), 1770 (m), 1650 (s), 1590 (s), 1471 (s), 1436 (s), 1364 (s), 1307 (s), 1252 (s), 1147 (s), 1125 (s), 1090 (s), 1047 (s), 991 (s), 896 (s), 844 (s), 763 (s), 618 (s), 557 (s), 527 (m).

Salicyl-uns-penp. To a solution of uns-penp (0.5 g, 2.1 mmol) in methanol (20 mL) salicylaldehyde (0.26 g, 2.1 mmol) was added. The resulting Schiff base was reduced *in situ* with $NaBH_4$ (0.14 g, 3.6 mmol) which was added in small portions and the solution was stirred for at least 2 h. The excess $NaBH_4$ was destroyed by the careful addition of HCl, until the solution had a pH value of 2. The methanol was removed *in vacuo* and the residue was re-dissolved in a 5 M aqueous solution of NaOH. The solution was extracted with CH_2Cl_2, the organic solution was dried over Na_2SO_4 and the solvent was removed *in vacuo* to yield salicyl-uns-penp. ^{1}H NMR ($CDCl_3$, 300 MHz): δ 8.32 (m, 2H, py-H), 7.56–6.60 (m, 10 H, aromatic), 4.25 (s, 2H, HNCH_2(2-hydroxybenzyl)), 3.73 (s, 4H, NCH_2py), 3.05 (m, 4H, NCH_2CH_2NH).

[Cu(uns-penp)Cl]ClO_4 (1). To a solution of uns-penp (0.5 g, 2.06 mmol) in methanol (15 mL) was added a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.38 g, 1.03 mmol) and $CuCl_2 \cdot 2H_2O$ (0.18 g, 1.03 mmol) in water (10 mL). The solution was stirred for 10 min and then filtered. Green crystals formed which were suitable for X-ray analysis by slow evaporation of a methanol solution. $C_{14}H_{18}Cl_2CuN_4O_4$: calc. C 38.15, H 4.12, N 12.71; found C 37.64, H 4.44, N 12.35%.

[{Cu(uns-Hpenp)Cl}$_2$Cl]$(ClO_4)_3$ (2). To a solution of H-uns-penp (0.54 g, 2.2 mmol) in methanol (15 mL) was added a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.42 g, 1.1 mmol) and $CuCl_2 \cdot 2H_2O$ (0.19 g, 1.1 mmol) in water (10 ml). The solution was stirred for 10 min and filtered. Green crystals formed which were suitable for X-ray analysis by slow evaporation of a methanol solution.

[Cu(acetyl-uns-penp)Cl]ClO_4 (3). To a solution of acetyl-uns-penp (0.6 g, 2.1 mmol) in methanol (15 ml) was added a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.46 g, 1.1 mmol) and $CuCl_2 \cdot 2H_2O$

(0.21 g, 1.1 mmol) in water (10 ml). The solution was stirred for 10 min and filtered. Blue crystals formed which were suitable for X-ray analysis by slow evaporation of a methanol solution. $C_{16}H_{20}Cl_2CuN_4O_5$: calc. C 39.80, H 4.18, N 11.60; found C 39.56, H 4.38, N 11.39%.

$[(H_2O)$(salicyl-uns-Hpenp)Cu(Cl)Cu(salicyl-uns-Hpenp)Cl]-$(ClO_4)_4$ (4). To a solution of salicyl-uns-penp (0.17 g, 0.48 mmol) in methanol (15 ml) was added a solution of $Cu(ClO_4)_2 \cdot 6H_2O$ (0.184 g, 0.49 mmol) in water (10 mL). The solution was stirred for 10 min and filtered. Blue crystals formed which were suitable for X-ray analysis by slow evaporation of a methanol solution.

$[Cu_2$(uns-penp)$_2](ClO_4)_2$ (5). $[Cu(CH_3CN)_4]ClO_4$ (0.23 g, 0.7 mmol) was added with stirring to a solution of uns-penp (0.17 g, 0.7 mmol) in a small amount of acetonitrile in a glove box. Diethyl ether was added to the orange solution until a precipitate was observed to develop. The solution was filtered through a medium porosity frit, and the solid was washed with diethyl ether. The yellow powder was dissolved in a small amount of acetonitrile. Yellow crystals suitable for X-ray characterization were obtained by diffusion of diethyl ether into this solution.

X-Ray crystallographic study. Single crystals were coated with polyfluoropolyalkylether oil and mounted on a glass fiber or sealed in a glass capillary. Data for $[Cu$(uns-penp)Cl$]ClO_4$ were collected on a Nicolet R3m/V diffractometer at 298(2) K and for $([Cu_2$(uns-penp)$_2](ClO_4)_2$, on a Nonius Kappa diffractometer with a CCD array detector at 173(2) K (graphite-monochromator). Lorentz, polarization, and empirical absorption corrections were applied. The structures were solved by direct methods and refined on F^2 using full-matrix least-squares techniques.[72] Non-hydrogen atoms were refined with anisotropic thermal parameters. Intensity data for all other complexes were collected on a Siemens SMART 1000 CCD-Diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71073 Å). The exposure time was 10 s per frame collected with the ω-scan technique ($\Delta\omega$ = 0.3°). The collected reflections were corrected for Lorentz, polarization and absorption effects. The structures were solved by direct methods and refined by full matrix least squares methods on F^2.[73–75]

CCDC reference numbers 186857 ($[Cu$(uns-penp)Cl$]ClO_4$ (**1**)), 186855 ($[\{Cu$(uns-Hpenp)Cl$\}_2Cl](ClO_4)_3$ (**2**)), 186854 ($[Cu$(acetyl-uns-penp)Cl$]ClO_4$ (**3**)), 186856 ($[(H_2O)$(salicyl-uns-Hpenp)Cu(Cl)Cu(salicyl-uns-Hpenp)Cl$](ClO_4)_4$ (**4**)) and 186634 ($[Cu_2$(uns-penp)$_2](ClO_4)_2$ (**5**)).

See http://www.rsc.org/suppdata/dt/b2/b208740e/ for crystallographic data in CIF or other electronic format.

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