

Aerial oxidation of tetrahydrofuran to 2-hydroxytetrahydrofuran in the presence of a trimeric Cu^I complex [Cu₃L₃] (HL = *t*BuNHC(S)NHP(S)(OiPr)₂) and trapping of the unstable product at recrystallization†

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The reaction of the potassium salt of *N*-thiophosphorylated thiourea *t*BuNHC(S)NHP(S)(OiPr)₂ (HL) with Cu(NO₃)₂ in aqueous EtOH leads to the trinuclear [Cu₃(*t*BuNHC(S)NP(S)(OiPr)₂-S,S')₃] ([Cu₃L₃]) complex. It was established that [Cu₃L₃] provokes the aerobic oxidation of tetrahydrofuran to 2-hydroxytetrahydrofuran and traps the latter at crystallization.

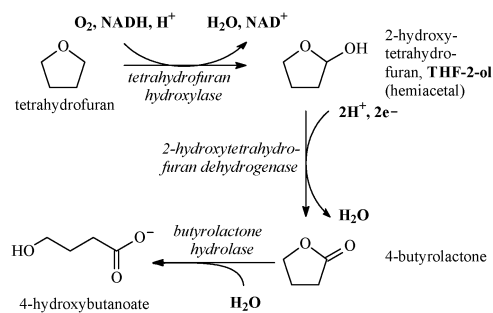
Introduction

Polynuclear Cu^I complexes are of great interest due to their luminescent properties,¹ their use as catalysts,² as precursors for chalcogenide nanoparticles³ and as models for biological systems.⁴ There is a growing family of ligands based on dithio(seleno)phosphinic acids RR'P(X)YH (X, Y = S, Se) and imidodithio(seleno)diphosphate R₂P(X)NHP(X)R'₂ (IDP), forming polynuclear aggregates with Cu^I.^{3a,5} In contrast to the previously mentioned ligands, there is a lack of information about the structures of polynuclear Cu^I complexes containing *N*-thiophosphorylated thioureas and thioamides, RC(S)NHP(S)R'₂ (R = R'₂N, alkyl, aryl), which are asymmetrical analogues of IDPs, containing a thiocarbonyl group instead of one of the thiophosphinic units. The molecular structures of only five polynuclear Cu^I complexes, namely the cyclic trimers [Cu₃{Et₂NC(S)NP(S)(OPh)₂}₃],⁶ [Cu₃{morpholyn-*N*-ylC(S)NP(S)(OiPr)₂}₃] ([Cu₃Q^I]),⁷ the hexanuclear aggregate [(Cu₃{PhNHC(S)NP(S)(OiPr)₂}₃)₂] ([Cu₃Q^{II}]),⁸ the supramolecular “honeycomb” aggregate [(Cu₆(H₂NC(S)NP(S)(OiPr)₂)₆){Cu₃(H₂NC(S)NP(S)(OiPr)₂)₃·4Me₂CO}]⁹ and an ionic aggregate [Cu₁₀{PhNHC(S)NP(S)(OEt)₂}₉]ClO₄,¹⁰ have been reported. Data available in the literature demonstrate that complexes of coinage metal cations with 1,3- and 1,5-bidentate ligands derived from sulfur- or selenium-containing phosphines exhibit a clear propensity to form oligo- and polynuclear assemblies with structural features that depend on the conditions employed for their preparation and the nature of the ligand. The investigation of

the structure of such compounds, as a rule, is impossible without the use of single crystal X-ray diffraction techniques.

On the other hand, THF is important in biology. Several actinomycetes, including *Rhodococcus ruber* strain 219,¹¹ *Pseudonocardia dioxanivorans*,¹² *P. tetrahydrofuranoxydans* strain K1,¹³ and *Pseudonocardia* strains M1¹⁴ and ENV478¹⁵ can utilize THF as the sole source of carbon and energy under aerobic conditions. The pathway of THF degradation by these organisms involves an initial mono-oxygenation of THF to generate the unstable hemiacetal, 2-hydroxytetrahydrofuran (THF-2-ol). This intermediate is then rapidly dehydrogenated to form 4-butyrolactone, a cyclic ester that subsequently undergoes an esterase-catalyzed hydrolytic cleavage to form 4-hydroxybutyrate (Scheme 1).

This hydroxyacid is further oxidized to succinate *via* succinate semialdehyde, which enters the tricarboxylic acid cycle. Another potential product of the abiotic dissociation of 2-hydroxytetrahydrofuran, 4-hydroxybutyraldehyde, may also be involved in THF degradation by *R. ruber* strain 219 but it is more likely to be an intermediate in the catabolism of 1,4-butanediol, another precursor to 4-hydroxybutyrate.¹¹ Based on gene expression studies, it appears that the putative aldehyde dehydrogenase responsible for oxidizing 4-hydroxybutyraldehyde in *P. tetrahydrofuranoxydans* K1 is expressed during growth on 1,4-butanediol but not during growth on THF.



Scheme 1 Mono-oxygenation of THF.

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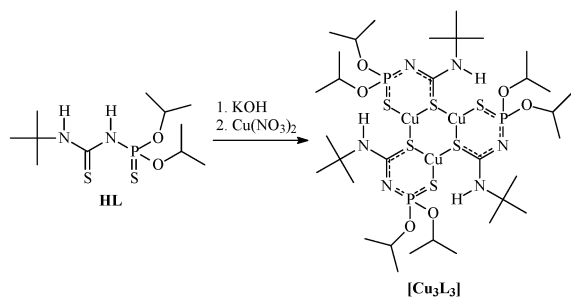
In this work, we describe the complete structural and spectroscopic characterization of the recently described trinuclear Cu^{I} complex $[\text{Cu}_3\text{L}_3]$, containing the thiourea ligand $t\text{BuC}(\text{S})\text{NHP}(\text{S})(\text{O}i\text{Pr})_2$ (**HL**).¹⁶ The complex was prepared by an alternative method and characterised by multinuclear NMR, IR, UV-vis spectroscopy and ESI-MS. Single crystals for a XRD experiment were obtained from a THF solution (in air), and contained the complex entity $[\text{Cu}_3\text{L}_3]\cdot\text{THF}\cdot 2\text{-ol}$, with co-crystallized 2-hydroxytetrahydrofuran. Motivated by this finding, we also carried out catalytic experiments for the aerobic oxidation of THF to THF-2-ol in the presence of $[\text{Cu}_3\text{L}_3]$.

Results and discussion

Reaction of the potassium salt **KL** with $\text{Cu}(\text{NO}_3)_2$ in aqueous EtOH leads to the trinuclear $[\text{Cu}_3\text{L}_3]$ complex (Scheme 2). The complex obtained is a colorless crystalline powder. ^1H , $^{31}\text{P}\{^1\text{H}\}$ NMR and IR spectroscopy data indicate that the deprotonated thiourea L^- coordinates in a 1,5- S,S' fashion. Recently, this complex was alternatively synthesized from Cu^{I} .¹⁶ With this and other related experiments, we have also demonstrated the equivalence of the structures of the formed polynuclear Cu^{I} complexes, irrespective of the copper “source”.^{7,9,16}

The IR spectrum of $[\text{Cu}_3\text{L}_3]$ shows a weak band at 605 cm^{-1} , assigned to the $\text{P}=\text{S}$ groups. It is shifted to lower wavenumbers relative to that in the spectrum of the parent ligand **HL** (648 cm^{-1}) due to coordination to the metal cation.¹⁷ The broad and strong band at 1563 cm^{-1} is assigned to the conjugated SCN group,¹⁸ proving the formation of an S,S' -chelate. A unique band at 3271 cm^{-1} , related to the $t\text{BuNH}$ group, was also observed in the spectrum. No signal was observed for the PNH group.

The UV-vis absorption spectrum of $[\text{Cu}_3\text{L}_3]$ was recorded in CH_2Cl_2 at 25°C and is characterized by an absorption band at 348 nm ($\epsilon = 4097\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$). Absorption bands for the free ligands $\text{RC}(\text{S})\text{NHP}(\text{X})(\text{O}i\text{Pr})_2$ ($\text{X} = \text{O}, \text{S}$) are rather high in energy ($\lambda_{\text{max}}^{\text{abs}} < 250\text{ nm}$) and thus fall into the region of intraligand transitions.^{16,19} However, it is more reasonable to compare the absorption spectrum of $[\text{Cu}_3\text{L}_3]$ and the corresponding potassium salt **KL**, and not the spectrum of the parent ligand **HL**. Under the same measurement conditions, the spectrum of **KL** shows a weak absorption band at 298 nm ($\epsilon = 186\text{ dm}^3\text{ mol}^{-1}\text{ cm}^{-1}$). The band can be attributed to intraligand transitions in the deprotonated form L^- . Recently, it was established that complexes of Ni^{II} , Zn^{II} and Cd^{II} with



Scheme 2 Preparation of $[\text{Cu}_3\text{L}_3]$.

$\text{RC}(\text{S})\text{NHP}(\text{X})(\text{O}i\text{Pr})_2$ ($\text{X} = \text{O}, \text{S}$) ligands show absorption bands at $380\text{--}420\text{ nm}$, which were assigned to ligand-to-metal (LMCT) transitions.¹⁹ Thus, we assign the long-wavelength absorption band of $[\text{Cu}_3\text{L}_3]$ to an LMCT transition.²⁰

In the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Cu}_3\text{L}_3]$ in CDCl_3 , a singlet signal appears at 50.2 ppm . The signal is in the region characteristic for deprotonated N -thiophosphorylated thioamides and thioureas.²¹ The ^1H NMR spectrum of $[\text{Cu}_3\text{L}_3]$ in CDCl_3 contains a set of signals for the $i\text{Pr}$ protons: a doublet for the CH_3 protons at 1.32 ppm and a doublet of septets for the CH protons at 4.75 ppm . The signal of the $t\text{Bu}$ protons is found at 1.40 ppm . The NH proton signal is observed at 6.63 ppm .

The crystal structure of the complex $[\text{Cu}_3\text{L}_3]\cdot\text{THF}\cdot 2\text{-ol}$ was determined by single crystal X-ray diffraction. X-Ray suitable crystals of the complex were obtained by slow evaporation of the solvent from solutions in THF in air. Obviously, and to our astonishment, $[\text{Cu}_3\text{L}_3]$ provokes the formation of THF-2-ol and traps it at recrystallization in THF.

Complex $[\text{Cu}_3\text{L}_3]\cdot\text{THF}\cdot 2\text{-ol}$ is a cyclic trimer (Fig. 1), in which the $\text{Cu}\text{--}\text{S}\text{--}\text{Cu}$ bridging bonds are formed by the sulfur atoms of the $\text{C}=\text{S}$ groups. The Cu_3S_3 cyclic backbone is in a chair conformation and the copper atoms are in an S_3 trigonal-planar environment. The distance $\text{Cu}(2)\cdots\text{Cu}(3)$ $2.764(4)$ (Table 1) is shorter than the sum of the van der Waals radii of Cu^{I} .²³ The other distances $\text{Cu}(1)\cdots\text{Cu}(2)$ $2.900(2)\text{ \AA}$ and $\text{Cu}(1)\cdots\text{Cu}(3)$ $3.062(2)\text{ \AA}$ indicate the lack of any distinct $\text{Cu}\cdots\text{Cu}$ interactions.¹⁰ This variation in $\text{Cu}\cdots\text{Cu}$ distances leads to an increase of the $\text{Cu}(1)\text{--}\text{S}(6)\text{--}\text{Cu}(3)$ bond angle relative to the $\text{Cu}(1)\text{--}\text{S}(2)\text{--}\text{Cu}(2)$ and $\text{Cu}(2)\text{--}\text{S}(4)\text{--}\text{Cu}(3)$

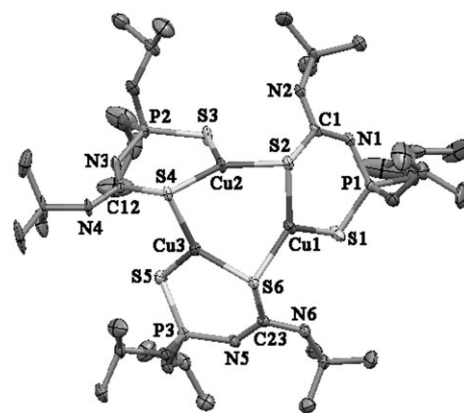


Fig. 1 A thermal ellipsoid representation of $[\text{Cu}_3\text{L}_3]\cdot\text{THF}\cdot 2\text{-ol}$ (THF-2-ol and hydrogen atoms were omitted for clarity). Ellipsoids are drawn at the 50% probability level.

Table 1 Selected bond lengths [\AA] and bond angles [$^\circ$] for $[\text{Cu}_3\text{L}_3]\cdot\text{THF}\cdot 2\text{-ol}$

Bond lengths			
$\text{Cu}(1)\cdots\text{Cu}(2)$	2.900(2)	$\text{Cu}(2)\cdots\text{Cu}(3)$	2.764(2)
$\text{Cu}(1)\cdots\text{Cu}(3)$	3.062(2)		
Bond angles			
$\text{S}(1)\text{--}\text{Cu}(1)\text{--}\text{S}(2)$	114.25(5)	$\text{S}(3)\text{--}\text{Cu}(2)\text{--}\text{S}(4)$	116.08(5)
$\text{S}(1)\text{--}\text{Cu}(1)\text{--}\text{S}(6)$	120.89(5)	$\text{S}(4)\text{--}\text{Cu}(3)\text{--}\text{S}(5)$	120.45(5)
$\text{S}(2)\text{--}\text{Cu}(1)\text{--}\text{S}(6)$	124.58(5)	$\text{S}(4)\text{--}\text{Cu}(3)\text{--}\text{S}(6)$	123.35(5)
$\text{S}(2)\text{--}\text{Cu}(2)\text{--}\text{S}(3)$	119.96(5)	$\text{S}(5)\text{--}\text{Cu}(3)\text{--}\text{S}(6)$	115.91(5)
$\text{S}(2)\text{--}\text{Cu}(2)\text{--}\text{S}(4)$	123.94(5)		

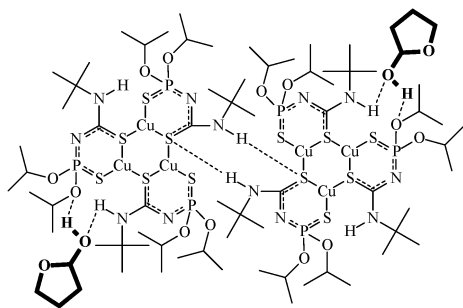


Chart 1 A simplified line diagram of hydrogen bonding in the molecular structure of $[\text{Cu}_3\text{L}_3]\cdot\text{THF-2-ol}$.

Table 2 Hydrogen bond lengths [Å] and angles [°] for $[\text{Cu}_3\text{L}_3]\cdot\text{THF-2-ol}^a$

D–H...A	<i>d</i> (D–H)	<i>d</i> (H...A)	<i>d</i> (D...A)	∠(DHA)
N(4)–H(25)...S(4)′	0.88	2.68	3.500(5)	155
N(6)–H(49)...O(8)	0.88	2.24	3.120(6)	175
O(8)–H(80)...O(2)	0.84	2.14	2.971(6)	168

^a Symmetry transformations used to generate the S(4)′ atom: (1 – *x*, 2 – *y*, –*z*).

bond angles (Table 1). The three CuSCNPS six-membered chelate rings are similar to that in the mononuclear analogue, which adopts a distorted boat conformation. In these chelate rings, the C=S and P=S bonds are lengthened, while the C–N and P–N bonds are shortened in comparison to typical values for *N*-thiophosphorylated thioureas and thioamides.²¹ In the polynuclear complex $[\text{Cu}_3\text{L}_3]\cdot\text{THF-2-ol}$, the C=S bonds, participating by the formation of bridges, are especially lengthened to values of 1.781(5), 1.785(5) and 1.807(5) Å, characteristic for single bonds.²⁴

$[\text{Cu}_3\text{L}_3]\cdot\text{THF-2-ol}$ contains, in the crystal, two intermolecular N–H...S=C hydrogen bonds between two neighboring molecules (Chart 1, Table 2). As a result of the intermolecular interactions, a dimer is formed. There are also intermolecular O–H...O–*i*Pr and N–H...O–H hydrogen bonds between the hydroxy group of co-crystallized THF-2-ol, and the NH and *Oi*Pr groups of the trinuclear molecule $[\text{Cu}_3\text{L}_3]\cdot\text{THF-2-ol}$ (Chart 1). To the best of our knowledge, the complex $[\text{Cu}_3\text{L}_3]\cdot\text{THF-2-ol}$ is the second example, showing the crystal structure of THF-2-ol. A polynuclear Co^{III} complex with *t*BuCOO[–], containing solvated THF-2-ol, has been published.²⁵ Although the preparation method of THF-2-ol was described, no discussion of a mechanism of formation was given by the authors.

Attempts to record NMR spectra of the trapped THF-2-ol in $[\text{Cu}_3\text{L}_3]\cdot\text{THF-2-ol}$ unfortunately failed. However, when dissolving bulk $[\text{Cu}_3\text{L}_3]$ in THF-*d*₈, the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum revealed two singlet signals at 49.1 and 54.6 ppm with relative intensities of 7.3:1 for the high-field signal. Recently it was reported that the Cu^{I} complex fragment $[\text{Cu}(\beta\text{-diketiminato})]$ (depicted in Chart 2) is able to bind dioxygen in a side-on fashion.²⁶ At the same time, nitriles RCN and THF can be bound either alternatively to O_2 or at the same time as, for example, in the calculated species $[\text{Cu}(\beta\text{-diketiminato})(\text{THF})(\text{O}_2)]$. This complex exhibits an

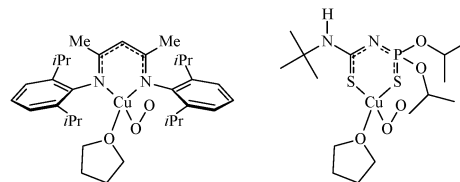


Chart 2 The structures of $[\text{Cu}(\beta\text{-diketiminato})(\text{THF})(\text{O}_2)]^{26}$ and the proposed $[\text{Cu}(\text{THF})(\text{O}_2)\text{L}]$.

intriguing end-on bound dioxygen (Chart 2). This complex is considered to be a key species in the observed oxygenation of THF.^{26b} Therefore, it is reasonable to assume the formation of comparable complex species $[\text{Cu}(\text{THF})\text{L}]$ and $[\text{Cu}(\text{THF})(\text{O}_2)\text{L}]$ in our case (Chart 2). Due to the smaller steric strain of our system, two THF molecules might also coordinate to form $[\text{Cu}(\text{THF})_2\text{L}]$. The species detected at $\delta_{\text{P}} = 54.6$ ppm in the $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum of $[\text{Cu}_3\text{L}_3]$ in THF is thus assigned to one of the three above-mentioned species, while the signal at 49.1 ppm corresponds to $[\text{Cu}_3\text{L}_3]$.

The ESI spectrum of the positive ions of complex $[\text{Cu}_3\text{L}_3]$ in THF contains the characteristic peaks for the ions $[\text{CuL}]^+$, $[\text{Cu}_2\text{L}_2]^+$ and $[\text{Cu}_3\text{L}_3]^+$. The molecular ion $[\text{Cu}_3\text{L}_3 + \text{H}]^+$ ($m/z = 1125.1$) is stable under the measurement conditions and was found in the mass spectrum of the complex. However, the ion has intensity of 17%. The most intense peak corresponds to the ion $[\text{Cu}_4\text{L}_3]^+$ ($m/z = 1187.6$). Recently the Cu^{I} complexes $[\{\text{Cu}_4\text{Q}^{\text{III}}_3\}\{\text{CuCl}_2\}]\cdot\text{CCl}_4$ and $[\text{Cu}_4\text{Q}^{\text{III}}_3]\cdot\text{I}_3$ ($\text{Q}^{\text{III}} = [\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{PPh}_2]^-$) were described.^{5a,g} It was established that the tetrahedral complex core $[\text{Cu}_4\text{Q}^{\text{III}}_3]^+$ (Chart 3) is rather stable, even in the presence of acids.^{5g} It is noteworthy that the second intense peak corresponds to the ion $[\text{Cu}(\text{THF})(\text{O}_2)\text{L} + \text{H}]^+$ (m/z (%) = 480.1 (93)). Furthermore, the ion $[\text{Cu}(\text{THF})\text{L} + \text{H}]^+$ was also assigned, while no ions with a mass characteristic of the species $[\text{Cu}(\text{THF})_2\text{L}]$ were determined.

The ESI spectrum of the complex $[\text{Cu}_3\text{L}_3]$ using negative ionisation contains characteristic peaks for the ions $[\text{L}]^-$ and $[\text{CuL}_2]^-$. The $[\text{CuL}_2]^-$ backbone was previously found by us in the polynuclear Cu^{I} complex $[\text{KCuQ}^{\text{IV}}_2]_n$ ($\text{Q}^{\text{IV}} = [\text{PhC}(\text{S})\text{NP}(\text{S})\text{P}(\text{O}i\text{Pr})_2]^-$).²² The most intense peak observed in the spectrum corresponds to the ion $[\text{Cu}_2\text{L}_3 + \text{THF}]^-$ ($m/z = 1132.7$).

Trying to find further evidence for the dioxygen-containing complex $[\text{Cu}(\text{THF})(\text{O}_2)\text{L}]$, we carried out resonance Raman spectroscopy (rR) in the region 500–1500 cm^{-1} . We found a number of bands corresponding to L^- but no band

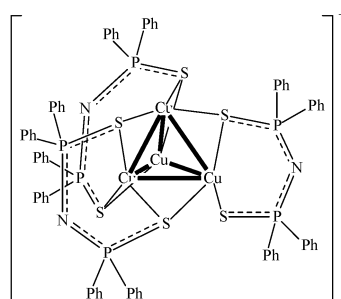


Chart 3 The structure of $[\text{Cu}_4\text{Q}^{\text{III}}_3]^+$ ($\text{Q}^{\text{III}} = [\text{Ph}_2\text{P}(\text{S})\text{NP}(\text{S})\text{PPh}_2]^-$).^{5a,g}

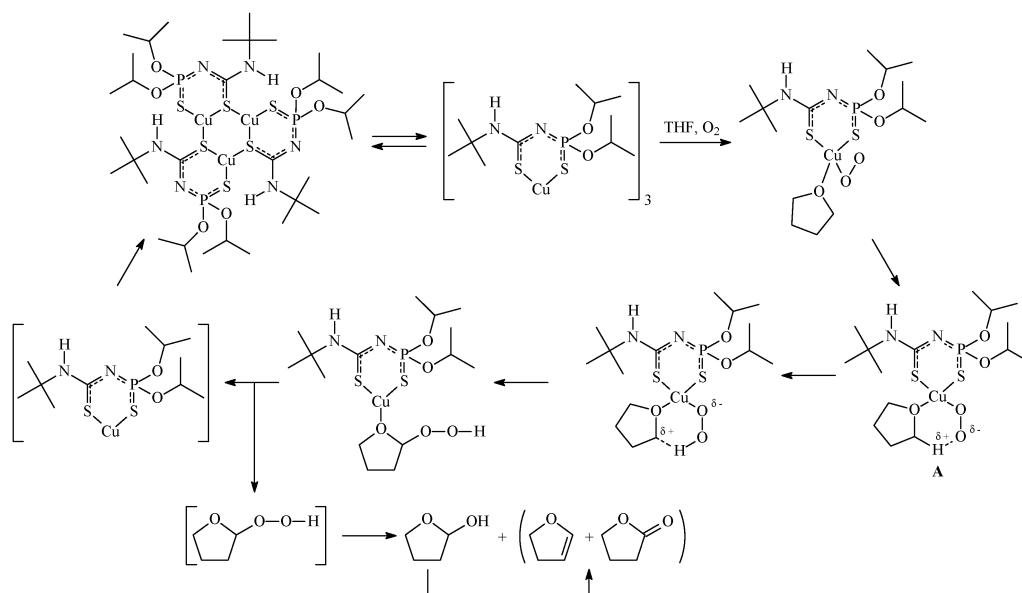
unambiguously attributable to the dioxygen ligand, which might exist in a neutral, anionic (superoxide) or dianionic (peroxide) form, was detected. Thus, ESI mass spectrometry is not only a promising technique for the structure determination of polynuclear Cu^{I} complexes with $\text{RC}(\text{S})\text{NHP}(\text{S})\text{R}'_2$ ligands, but in the present case has also allowed us to establish the formation of $[\text{Cu}(\text{THF})\text{L}]$ and $[\text{Cu}(\text{THF})(\text{O}_2)\text{L}]$, and to exclude the formation of $[\text{Cu}(\text{THF})_2\text{L}]$.

Unfortunately, we do not have further evidence for the assumed species $[\text{Cu}(\text{THF})(\text{O}_2)\text{L}]$ at the moment, and therefore we cannot tell anything about the oxidation state of the copper or the dioxygen ligand. Tolman *et al.* showed that their complexes exhibited significant Cu^{III} -peroxo character.²⁶ Efforts to clarify the situation for our system by vibrational spectroscopy and XAS will be made in the near future.

Inspired by the crystallization of $[\text{Cu}_3\text{L}_3]\cdot\text{THF-2-ol}$, we have studied the formation of THF-2-ol in THF under different conditions (Table S1 in the ESI†). In a typical procedure, complex $[\text{Cu}_3\text{L}_3]$ was dissolved in freshly distilled and de-gassed THF, and the samples were further analyzed by GC-MS. The following observations were made (Table S1†). In the absence of O_2 (under argon), very small amounts of THF-2-ol and 4-butyrolactone were always found (1–2%), which were probably due to traces of O_2 in the THF solution. The absence or presence of $[\text{Cu}_3\text{L}_3]$ had no impact on this. The presence of $[\text{Cu}_3\text{L}_3]$ accelerated the formation of THF-2-ol, while the 4-butyrolactone concentration remained largely the same and generally small in all the experiments. After 24 h, about 15% of THF-2-ol and after 60 h about 25% of THF-2-ol were found. After an initiation period of about 6–10 h, appreciable amounts of 2,3-dihydrofuran were observed and reached a maximum concentration of about 7% after 60 h. We assume that the latter is the product of dehydration of THF-2-ol. Under this assumption, we may add this 7% to the 25% of THF-2-ol formed after 60 h. Furthermore, according to the obtained data, we may assert that the influence of UV

irradiation in the presence of the copper complex is practically negligible (Table S1†). Summing up, all the products lead to conversions of about 30–35%, which corresponds to approximately 0.01 mmol of the starting THF amount. Thus, no unequivocal proof for a catalytic reaction is supplied by our experiments. After 2 d stirring the reaction mixture under an ambient atmosphere, the formation of THF-2-ol is practically stopped; we suppose that complex decomposition is the main reason. Solutions containing $[\text{Cu}_3\text{L}_3]$ became greenish-blue and we assumed that Cu^{II} compounds were formed. In an experiment to elucidate the underlying species, such a solution was left standing for 3 d, after which the solvent was removed by vacuum. The residue was extracted using toluene and analyzed by EPR spectroscopy. It was established that the EPR spectra were similar to the spectra of the previously described Cu^{II} complexes $[\text{Cu}\{\text{RNHC}(\text{S})\text{NP}(\text{O})(\text{O}i\text{Pr})_2\text{-N,S}\}_2]$ ($\text{R} = \text{Ph}, \text{c-hex}$).²⁷

Furthermore, we examined complexes $[\text{Cu}_3\text{Q}^{\text{I}}_3]$ ⁷ and $[(\text{Cu}_3\text{Q}^{\text{II}})_3]$ ⁸ to see if they also provoked the aerobic oxidation of THF to THF-2-ol. Surprisingly, both complexes were extremely unstable under the experimental conditions (bubbling O_2 through a catalyst solution in THF). Solutions containing the catalyst $[\text{Cu}_3\text{Q}^{\text{I}}_3]$ or $[(\text{Cu}_3\text{Q}^{\text{II}})_3]$ also became greenish-blue after a few minutes of bubbling due to the formation of Cu^{II} species, which were detected by EPR spectroscopy.²⁷ Thus, we postulate that the starting complex $[\text{Cu}_3\text{L}_3]$ decomposes with the formation of the Cu^{II} complex $[\text{Cu}\{t\text{BuNHC}(\text{S})\text{NP}(\text{O})(\text{O}i\text{Pr})_2\text{-N,S}\}_2]$, which is unstable in solutions and further decomposes. A signal for $(i\text{PrO})_2\text{P}(\text{O})\text{OH}$ at 2–3.5 ppm ($\delta_{\text{P}} = 2.98 \text{ ppm}$)²⁸ was observed in $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of reaction mixtures, though complex $[\text{Cu}_3\text{L}_3]$ could be isolated quantitatively in a shorter time, e.g. 1.5 d (yield 98%). We also examined the formation of THF-2-ol in the *vice versa* procedure: complex $[\text{Cu}_3\text{L}_3]$ was treated with oxygen (bubbling O_2 through the solid material) for 1 d and then THF was added. First, it is noteworthy that the solid material $[\text{Cu}_3\text{L}_3]$ did not decompose under the



Scheme 3 The supposed catalytic mechanism of THF-2-ol formation in the presence of $[\text{Cu}_3\text{L}_3]$.

influence of oxygen, and secondly the obtained yields of THF-2-ol were very similar to those listed in the entry 7 of Table S1.† Furthermore, using morpholine or 1,4-dioxane instead of THF as a substrate did not lead to the corresponding oxygenation products. Further investigation of the formation of THF-2-ol under an $^{18}\text{O}_2$ atmosphere (using GC-MS) proved dioxygen activation.

Provided that the formation of the complex $[\text{Cu}(\text{THF})(\text{O}_2)\text{L}]$ is one of the key steps for the oxygenation of THF, we can speculate that the $[\text{Cu}(\text{THF})(\text{O}_2)\text{L}]$ complex (Chart 1) is an intermediate in our system, while the hypothetical complexes $[\text{Cu}(\text{THF})(\text{O}_2)\text{Q}^{\text{I}}]$ and $[\text{Cu}(\text{THF})(\text{O}_2)\text{Q}^{\text{II}}]$ were not formed or were too unstable. The combination of the bulky *t*BuNH and *i*PrO substituents might be crucial in stabilizing the complex $[\text{Cu}(\text{THF})(\text{O}_2)\text{L}]$, while the less bulky systems $[\text{Cu}_3\text{Q}^{\text{I}}_3]$ and $[(\text{Cu}_3\text{Q}^{\text{II}}_3)_2]$ rapidly decompose.

At present, we cannot provide an exact mechanism for the oxygenation of THF with $[\text{Cu}_3\text{L}_3]$, but the virtual absence of 4-butyrolactone supposes that the reaction follows other mechanisms than those described in the biological systems mentioned above. The assumed catalytic mechanism is shown in Scheme 3. We suppose that the key role is played by H-bonded structure **A** (Scheme 3). It is noteworthy that the existence of the similar hydrogen bonded structures $[\text{Cu}(\beta\text{-diketiminate})(\text{X})(\text{O}_2)]$, where X is carbene, pyrazole, tetrazole and 2-pyridinamine, was described previously.^{26b}

Conclusions

In summary, the reaction of $\text{Cu}(\text{NO}_3)_2$ with the potassium salt of **HL** has allowed us to obtain the trinuclear complex $[\text{Cu}_3\text{L}_3]$. NMR and IR experiments have shown that the deprotonated thiourea L^- acts as a 1,5-*S,S'*-ligand. Single crystals obtained from THF solutions grown under aerial conditions revealed the complex $[\text{Cu}_3\text{L}_3]\cdot\text{THF}\cdot 2\text{-ol}$, which is a cyclic trimer, formed by bridging bonds with participation of the thio-carbonyl sulfur atoms, and two molecules are linked through two hydrogen bonds of the $\text{N-H}\cdots\text{S}=\text{C}$ type. The metal cations are in a trigonal planar S_3 environment. Surprisingly, the compound contains one equivalent of 2-hydroxytetrahydrofuran (THF-2-ol). Further experiments (NMR, ESI-MS) and catalytic studies established that $[\text{Cu}_3\text{L}_3]$ provokes the formation of 2-hydroxytetrahydrofuran and traps it by recrystallization from THF.

Experimental

General procedures

Elemental analysis was performed on a HEKAtech CHNS EuroEA 3000 microanalyser. NMR spectra (CDCl_3 or $\text{THF}-d_8$) were obtained on a Bruker Avance 300 MHz spectrometer at 25 °C. Infrared spectra (Nujol) were recorded with a Specord M-80 spectrometer in the range 400–3600 cm^{-1} . Electronic absorption spectra of 10^{-4} M solution in CH_2Cl_2 were measured on a Lambda-35 spectrometer in the range 200–1000 nm. Resonance Raman spectra were collected on an Acton AM-506 spectrometer using Kaiser Optical holographic super-notch filters with a Princeton Instruments

liquid N_2 -cooled CCD detector. EPR measurements were performed on Bruker ESP 300 spectrometer equipped with X-band 4110ST resonator and standard nitrogen flow accessory. The field was controlled by Bruker ER035 field meter and the microwave frequency measured with Hewlett–Packard 5255A frequency counter. Electrospray ionization mass spectra were measured using a Finnigan-Mat TCQ 700 mass spectrometer on 10^{-6} M solutions in THF. The speed of sample submission was 2 $\mu\text{L min}^{-1}$. The ionization energy was 4.5 kV. The capillary temperature was 200 °C. The GC-MS analysis was carried out using an Automass 150 instrument (Delsi Nermag, France) equipped with a 0.25 mm \times 25 m capillary column with 0.3 μm OV101 (helium as carrier gas, 0.6 atm; injector temperature 250 °C, divider 1 : 40, volume of the sample 0.2 μL , initial column temperature 50 °C (2 min), temperature programming to 250 °C at a rate of 10 °C min^{-1} , interface temperature 250 °C). UV irradiation experiments were performed using a CAMAG UV Lamp.

Syntheses

*t*BuNHC(S)NHP(S)(*Oi*Pr)₂ (**HL**) was synthesized as described previously.¹⁷

$[\text{Cu}_3(\text{tBuNHC(S)NP(S)(OiPr)}_2\text{-S,S'})_3]$ ($[\text{Cu}_3\text{L}_3]$). A suspension of **HL** (0.936 g, 3 mmol) in aqueous ethanol (25 mL) was mixed with an ethanol solution of KOH (0.185 g, 3.3 mmol). The resulting mixture was added dropwise to a suspension of $\text{Cu}(\text{NO}_3)_2\cdot 6\text{H}_2\text{O}$ (0.474 g, 1.6 mmol) in aqueous ethanol (20 mL). The mixture was stirred at room temperature for 5 h and left overnight. The resulting complex was extracted using CH_2Cl_2 , and the combined extracts were dried over anhydrous MgSO_4 . The solvent was then removed in vacuum and the residue was recrystallized from THF. The complex was obtained as a colorless microcrystalline material. Yield: 0.821 g, 73%. M.p. 139 °C. ^1H NMR (CDCl_3): 1.32 (d, $^3J_{\text{H,H}} = 6.1$ Hz, 36 H, CH_3 , *i*Pr), 1.40 (s, 27 H, CH_3 , *t*Bu), 4.75 (d, sept, $^3J_{\text{H,H}} = 6.0$ Hz, $^3J_{\text{P,H}} = 10.5$ Hz, 6 H, OCH), 6.63 (d, $^4J_{\text{P,H}} = 9.2$ Hz, 3 H, NH) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (CDCl_3): 50.2 ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (THF): 49.1 (7.3 P), 54.6 (1 P) ppm. IR: 605 (P=S), 1000, 1009 (POC), 1563 (SCN), 3271 (NH) cm^{-1} . ESI-MS (positive ion): m/z (%) = 376.1 (11) $[\text{CuL} + \text{H}]^+$, 447.8 (18) $[\text{Cu}(\text{THF})\text{L} + \text{H}]^+$, 480.1 (93) $[\text{Cu}(\text{THF})(\text{O}_2)\text{L} + \text{H}]^+$, 519.4 (3) $[\text{Cu}(\text{THF})_2\text{L} + \text{H}]^+$, 749.5 (21) $[\text{Cu}_2\text{L}_2 + \text{H}]^+$, 885.2 (29) $[\text{Cu}_3\text{L}_2 + \text{THF}]^+$, 1125.1 (17) $[\text{Cu}_3\text{L}_3 + \text{H}]^+$, 1187.6 (100) $[\text{Cu}_4\text{L}_3]^+$. ESI-MS (negative ion): m/z (%) = 311.2 (39) $[\text{L}]^-$, 686.3 (22) $[\text{CuL}_2]^-$, 1132.7 (100) $[\text{Cu}_2\text{L}_3 + \text{THF}]^-$. Anal. calc. for $\text{C}_{33}\text{H}_{72}\text{Cu}_3\text{N}_6\text{O}_6\text{P}_3\text{S}_6$ (1124.91): C, 35.23; H, 6.45, N, 7.47. Found: C, 35.41; H, 6.39; N, 7.51.

Catalytic properties of $[\text{Cu}_3\text{L}_3]$ in the oxidation of THF

In a typical procedure, the complex $[\text{Cu}_3\text{L}_3]$ (0.01125 g, 0.01 mmol) was dissolved in freshly distilled and de-gassed THF (3 mL) at room temperature under an argon atmosphere in the dark or under UV irradiation. Further experimental conditions are summarized in Table S1 in the ESI.†

X-Ray crystallography

Data were collected on a Bruker SMART Apex CCD diffractometer with graphite monochromated Mo-K α

radiation ($\lambda = 0.71073 \text{ \AA}$).²⁹ Data reduction was carried out using SAINT.³⁰ Empirical absorption correction was performed with SADABS.³¹ The structure was solved by direct methods, while the remainder of the atomic positions were found using difference Fourier methods. All non-hydrogen atoms were refined anisotropically (with appropriate restraints using SIMU and ISOR) by blocked full-matrix least squares calculations on F² using SHELX-97³² within the X-seed environment. Hydrogen atoms were added to the structure model in calculated positions and were refined as rigid atoms. ORTEP-III for Windows was used to generate the figure at the 50% probability level.³³ C₃₃H₇₂Cu₃N₆O₆P₃S₆, C₄H₈O₂, $M = 1213.05$, monoclinic, space group $P2_1/n$, $a = 14.448(7)$, $b = 15.407(7)$, $c = 25.575(11) \text{ \AA}$, $\beta = 91.100(8)^\circ$, $V = 5692(5) \text{ \AA}^3$, $T = 100(2) \text{ K}$, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 1.462 \text{ mm}^{-1}$, $F(000) = 2544$, 32467 reflections measured, 11760 observed ($R_{\text{int}} = 0.067$). R indices (all data): $R_1 = 0.0696$, $wR_2 = 0.1550$.†

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