Reaction of β-diketiminate copper(II) complexes and Na_2S_2†

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Reaction of β-diketiminate copper(II) complexes and Na_2S_2 resulted in formation of (μ-η^2:η^2-disulfido)dicopper(II) complexes (adduct formation) or β-diketiminate copper(I) complexes (reduction of copper(II)) depending on the substituents of the supporting ligands. In the case of sterically less demanding ligands, adduct formation occurred to provide the (μ-η^2:η^2-disulfido)dicopper(II) complexes, whereas reduction of copper(II) took place to give the corresponding copper(I) complexes with sterically more demanding β-diketiminate ligands. Spectroscopic examinations of the reactions at low temperature using UV-vis and ESR as well as kinetic analysis have suggested that a 1 : 1 adduct LCu^{II}–S–SNa with an end-on binding mode is initially formed as a common intermediate, from which different reaction pathways exist depending on the steric environment of the metal-coordination sphere provided by the ligands. Thus, with the sterically less demanding ligands, rearrangement of the disulfide adduct from end-on to side-on followed by self-dimerisation occurs to give the (μ-η^2:η^2-disulfido)dicopper(II) complexes, whereas such an intramolecular rearrangement of the disulfide co-ligand does not take place with the sterically more demanding ligands. In this case, homolytic cleavage of the Cu^{II}–S bond occurs to give the reduced copper(I) product. The steric effects of the supporting ligands have been discussed on the basis of detailed analysis of the crystal structures of the copper(II) starting materials.

Introduction

The reaction of copper(I) complexes and elemental sulfur S_8 has been given much recent attention as an efficient method for the preparation of several Cu/S clusters.[1] So far, disulfido-bridged dicopper(II) complexes both with an end-on and a side-on binding mode (**A** and **B** in Chart 1, respectively)[2–7] and a bis(μ_3-sulfido) mixed valent trinuclear copper(II,II,III) complex **C**[8] as well as a bis(μ-1,2-$S_2^{\bullet-}$)dicopper(II) complex **D**[9] have been prepared by this method using several nitrogen donor ligands. For instance, tetradentate N_4 ligands such as TPA [tris(2-pyridylmethyl)amine] and its derivatives provide the end-on disulfido dicopper(II) complex **A**, whereas tridentate N_3 ligands such as PY2 {bis[2-(2-pyridyl)ethyl]amine} afford the side-on disulfido dicopper(II) complex **B**. The core structures obtained in these reactions are similar to those obtained in the reactions between O_2 and the copper(I) complexes supported by the same ligands.[10,11] Namely, the tetradentate N_4 ligands afforded the end-on type (*trans*-μ-1,2-peroxo)dicopper(II) complexes, whereas the tridentate N_3 ligands mainly gave the side-on type (μ-η^2:η^2-peroxo)dicopper(II) complexes. Formation of the mixed valent trinuclear copper complex **C** involving the bis(μ_3-sulfido) unit in the ethylenediamine N_2 didentate ligand system is also analogous to the formation of the mixed valent bis(μ_3-oxo)tricopper(II,II,III) complex in the oxygenation reaction of copper(I) complex of the same ligand.[10–12]

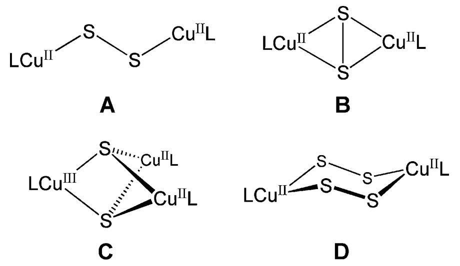

Chart 1

More recently, the reaction of copper(II) complexes and sulfides (reduced sulfur) has also been examined as an alternative method for the preparation of Cu/S clusters. Tolman and coworkers recently reported the formation of novel Cu/S cluster complexes of varying nuclearity (Cu_{2-6}) in the reaction of $Cu^{II}X_2$ (X = $CF_3SO_3^-$ or Cl^-) and Li_2S or Na_2S_2 in the presence of *N*,*N*,*N*′,*N*′-tetramethyl-*trans*-(1*R*,2*R*)-diaminocyclohexane (Me_4chd).[13] We have also demonstrated that the reaction of copper(II) acetate complexes supported by β-diketiminate ligands and Na_2S_2 afforded the disulfido dicopper(II) complexes with the side-on binding mode **B**.[14] The reaction can be regarded as a sulfur version of the copper(II)-H_2O_2 reaction, which affords various types of Cu_2/O_2 complexes.[15] However, little is known about the mechanistic details of the reaction between copper(II) complexes and sulfides. Thus, in this study, we have investigated the reaction of a series of

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† Electronic supplementary information (ESI) available: Fig. S1: ESR spectrum of **3a**. Fig. S2: ESR spectrum of **1c**. CCDC reference numbers 688667 (**3a**) and 688668 (**4a**). For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b808678h

β-diketiminate copper(II) complexes and Na_2S_2 in order to shed light on the reaction mechanism and ligand effects on the reaction.

Results and discussion

Structural characterisation of copper(II) acetate complexes (starting materials)

The mononuclear copper(II) acetate complexes (starting materials) **1a**, **2a**, **3a** and **4a** supported by β-diketiminate ligands $L1^-$, $L2^-$, $L3^-$ and $L4^-$ (deprotonated form of L1H–L4H, see Chart 2), respectively, were prepared by treating the ligands and $Cu(OAc)_2{\cdot}H_2O$ in refluxing methanol or ethanol for 48 h as reported previously.[14,16,17] The crystal structures of complexes **3a** and **4a** have been determined in this study, and those of **1a** and **2a** have already been reported in our previous papers.[16,17] The ORTEP drawings of the cationic parts of **3a** and **4a** are shown in Fig. 1, and their crystallographic data are summarised in Table 1.

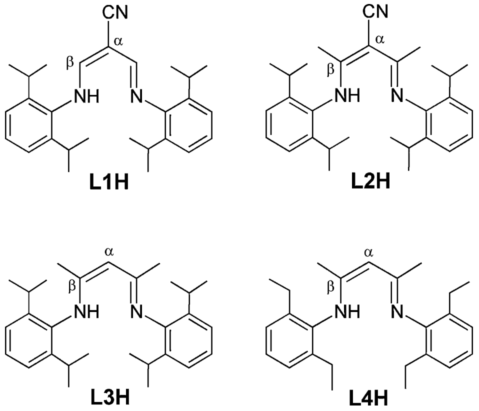


Chart 2

Overall structures of **3a** and **4a** look similar to those of **1a** and **2a**, exhibiting a mononuclear square planar geometry with the N_2O_2 donor set, where two nitrogen atoms and two oxygen atoms are provided by the β-diketiminate ligand and the didentate acetate co-ligand, respectively.[18] However, more detailed inspection of the X-ray structures revealed notable structural differences among the complexes as described below.

Table 1 Summary of X-ray crystallographic data of the Cu^{II}-complexes **3a** and **4a**

Compound	**3a**	**4a**
Empirical formula	$C_{31}H_{44}CuN_2O_2$	$C_{27}H_{36}CuN_2O_2$
M_r	540.25	484.14
Crystal system	Monoclinic	Triclinic
Space group	$C2/c$ (no. 15)	$P\bar{1}$ (no. 2)
a/Å	13.943(5)	8.015(6)
b/Å	14.355(4)	8.546(7)
c/Å	16.170(5)	19.929(17)
α/°		88.52(2)
β/°	106.237(7)	83.23(2)
γ/°		67.57(2)
V/Å^3	3107.3(16)	1252.8(17)
Z	4	2
F(000)	1156.00	514.00
D_c/g cm^{-3}	1.155	1.283
T/°C	23	−160
Crystal size/mm	0.38 × 0.28 × 0.24	0.32 × 0.23 × 0.03
μ(Mo-Kα)/cm^{-1}	7.297	8.968
R_{int}	0.048	0.077
No. reflns measd	15213	9984
No. reflns obsd	2331 [$I > 2.0\sigma(I)$]	3586[$I > 3.0\sigma(I)$]
No. variables	193	325
R^a; wR^b	0.0543; 0.1403	0.0866; 0.1944
GOF	1.003	1.048

[a] $R = \sum\|F_o| - |F_c\|/\sum|F_o|$. [b] $Rw = [\sum w(|F_o|^2 - |F_c|^2)^2/\sum wF_o^2]^{1/2}$.

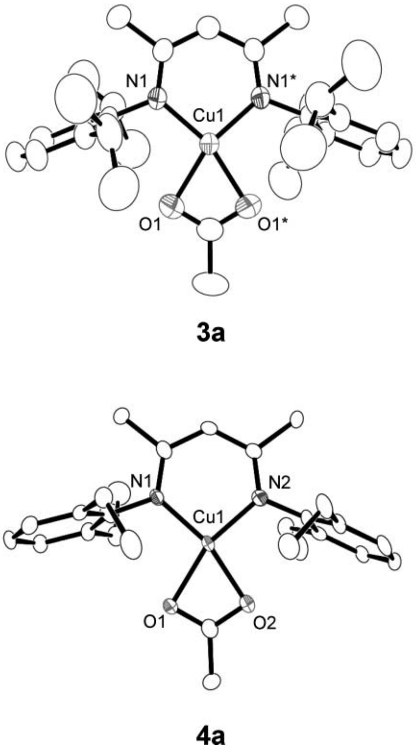


Fig. 1 ORTEP drawings of copper(II) acetate complexes **3a** and **4a** showing 50% probability thermal ellipsoids. The hydrogen atoms are omitted for simplicity.

Compound **1a** exhibits the C_β–N–C_{Ar} angles (C_{Ar} = C_1 carbon of the 2,6-disubstituted phenyl group) as 116.9(2)° and the Cu–N bond length as 1.944(2) Å (see Fig. 2 and Table 2). Introduction of methyl groups into the β-position of the carbon framework to give complex **2a** resulted in an increase of the C_β–N–C_{Ar} angle to 120.° (average value, see Table 2), whereas the average Cu–N bond length decreased to 1.910 Å. The structural change in going from **1a** to **2a** may be due to a steric repulsion between the β-methyl groups and the 2,6-diisopropylphenyl groups of L2. Namely, the nitrogen atoms are enforced to move inward of the six-membered chelate ring in order to reduce the steric repulsion between the *N*-aromatic substituent and the β-methyl group. Such an enhanced steric repulsion between the substituents in **2a** is also reflected in the larger torsion angle consisting of C_β–N–C_{Ar}–C_o(*o*-position of Ar group) of 83.1° (average value) in **2a** as compared to those in **1a** (average value 73.3°). The dihedral angle defined by N(1)–Cu(1)–N(2) and O(1)–Cu(1)–O(2) planes of the N_2CuO_2 core in **2a** is 7.0°, which is also larger than that of **1a** (0.0°). The structural features of **3a** are similar to those of **2a**. Namely, complex **3a** has a larger C_β–N–C_{Ar} angle of 119.2(2)°, a shorter Cu–N bond length of 1.905(2) Å, a larger torsion angle C_b–N–C_{Ar}–C_o

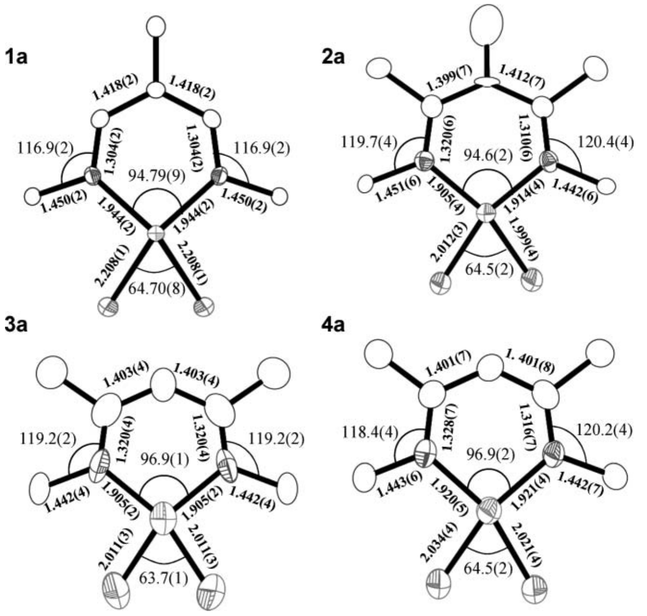


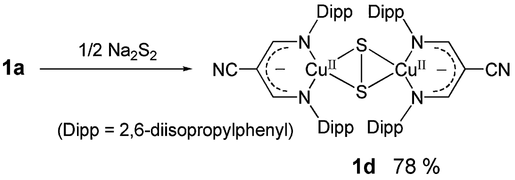
Fig. 2 ORTEP drawings around the N_2CuO_2 core of **1a**, **2a**, **3a** and **4a** showing 50% probability thermal ellipsoids. The ORTEP drawings of **1a** and **2a** are generated by using the reported data.[16,17]

of 80.5° and a larger dihedral angle between N(1)–Cu(1)–N(1)* and O(1)–Cu(1)–O(1)* planes of 10.1°, as compared with the respective values of **1a** (Table 2).

On the other hand, replacement of the 2,6-diisopropylphenyl (Dipp) groups in **3a** by 2,6-diethylphenyl (Dep) groups to give **4a** resulted in an increase of the Cu–N bond length to 1.921 Å (average value) (compare the structural parameters between **3a** and **4a** in Fig. 2). Although the torsion angle of C_β–N–C_{Ar}–C_o of 82.7° (average value) and the C_β–N–C_{Ar} angle of 119.2° (average value) are similar to those of **2a** and **3a**, the dihedral angle between N(1)–Cu(1)–N(2) and O(1)–Cu(1)–O(2) planes is much smaller (5.0°) as in the case of **1a**. These data clearly indicate that the steric repulsion between the β-methyl group and the 2,6-disubstituted phenyl group is reduced by changing the substituents from isopropyl to ethyl. Overall, it can be concluded that $L1^-$ and $L4^-$ are sterically less demanding ligands as compared with $L2^-$ and $L3^-$. These structural features are reflected to the differences in reactivity of the complexes toward Na_2S_2 as described below.

Reaction of the copper(II) complexes and Na_2S_2

Treatment of **1a** with 0.5 equivalent of Na_2S_2 in CH_3CN under Ar atmosphere gave dark reddish solid material in a 78% yield, which was identified as the (μ-η²:η²-disulfido)dicopper(II) complex **1d** by the X-ray crystallographic analysis as previously reported [eqn (1)].[14] Compound **1d** exhibited two intense absorption bands at 333 (ε = 24 000 M^{-1} cm^{-1}) and 432 (12 500), attributable to the ligand based π–π* and/or S_2^{2-} to Cu^{II} LMCT transitions, together with a weak d–d band at 867 nm (150 M^{-1} cm^{-1}).[14] The resonance-Raman spectrum of **1d** newly obtained in the present study showed an isotope sensitive band at 446 cm^{-1}, which shifted to 431 cm^{-1} upon ^{34}S-substitution using $Na_2{}^{34}S_2$ instead of $Na_2{}^{32}S_2$ (Fig. 3). The peak position and its associated isotope shift are fully consistent with those of the reported (μ-η²:η²-disulfido)dicopper(II) complexes.[6] Thus, the band can be assigned to a S–S stretching vibration ν_{S-S} of the side-on disulfido ligand. The additional peaks at 509 and 605 cm^{-1} also shifted to 506 and 603 cm^{-1}, respectively. Judging from their small isotope shifts, these Raman bands can be assigned to the stretching vibrations arising from the β-diketiminate ligand backbone, which may also be affected slightly by the isotope substitution of the disulfide moiety. Furthermore, compound **1d** was ESR silent and exhibited a sharp ¹H NMR spectrum,[14] indicative of the existence of strong antiferromagnetic coupling interaction between the two Cu^{II} ions through the side-on disulfido bridging ligand.



(1)

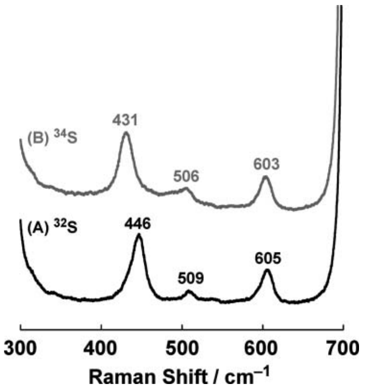


Fig. 3 Resonance-Raman spectra of **1d** generated by using $Na_2{}^{32}S_2$ (A) and $Na_2{}^{34}S_2$ (B) in CH_2Cl_2 obtained with an excitation wavelength of 441.6 nm at room temperature.

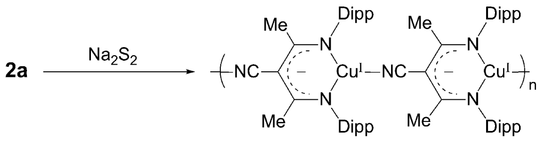
The reaction of **2a** having β-methyl groups in addition to the α-cyano group on the carbon framework with Na_2S_2 under the same experimental conditions resulted in precipitation of yellow solid material, which was insoluble to ordinary organic solvents. The IR spectrum of the isolated product was identical to that of the

Table 2 Structural parameters of Cu^{II}-complexes **1a**, **2a**, **3a** and **4a**

Structural parameter	1a	2a	3a	4a
Cu–N/Å	1.944(2)	1.914(4), 1.905(4) (1.910)[c]	1.905(2)	1.920(5), 1.921(4) (1.921)[c]
C_β–N–C_{Ar}/°	116.9(2)	119.7(4), 120.4(4) (120.1)[c]	119.2(2)	118.2(4), 120.2(4) (119.2)[c]
Torsion angle[a,c]/°	73.3	83.1	80.5	82.7
Dihedral angle[b]/°	0.0	7.0	10.1	5.0

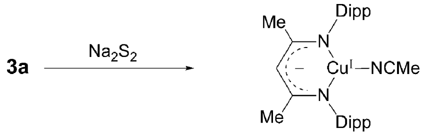
[a] Torsion angle consisting of C_β–N–C_{Ar}–C_o(*o*–position of Ar). [b] Dihedral angle between N–Cu–N′ and O–Cu–O′ planes. [c] Average value.

known copper(I) β-diketiminate coordination polymer complex, which was previously obtained in the reaction of L2H and $[Cu^I(CH_3CN)_4]PF_6$ in the presence of base.[19] Thus, the copper(II) complex **2a** was found to be reduced to the corresponding copper(I) complex **2e** in a 77% yield by the reaction with Na_2S_2 [eqn (2)]. Similarly, copper(II) complex **3a** without the α-cyano group but having the β-methyl groups on the carbon framework was reduced to copper(I) complex **3e** by the reaction with Na_2S_2 under the same experimental conditions [65% yield, eqn (3)]. The IR and MS spectra of **3e** were identical to those of $[Cu^I(L3)(CH_3CN)]$ in the literature.[20]



(2)

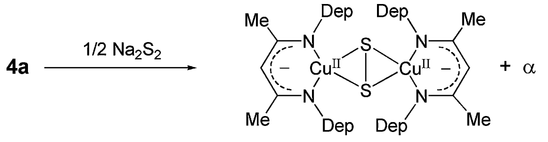
2e 77 %



(3)

3e 65 %

Interestingly, replacement of the 2,6-diisopropylphenyl (Dipp) groups of **3a** by 2,6-diethylphenyl (Dep) groups resulted in formation of the (μ-η^2:η^2-disulfido)dicopper(II) complex **4d** exhibiting similar spectral features to those of **1d** [eqn (4)],[14] although the yield was lower (39%).[21]



(4)

4d 39 %

Reaction pathway

In order to get insight into the ligand effects on the reactivity of the copper(II) complexes toward Na_2S_2 (adduct formation *vs.* reduction), the reactions of **1a** leading the adduct formation and **3a** causing the reduction of copper(II) were examined in more detail at low temperature. Fig. 4 shows the spectral change for the reaction of **1a** (2.0×10^{-4} M) and Na_2S_2 (1 equiv.) in CH_2Cl_2–CH_3OH (2 : 1) at −80 °C. At the initial stage of the reaction, intermediate **1b** exhibiting absorption bands at 520 nm ($\varepsilon = 1310$ M^{-1} cm^{-1}) and 640 (1210) immediately appeared (within a few seconds after mixing). Titration for the formation of this intermediate from **1a** with Na_2S_2 (inset of Fig. 4) clearly demonstrated that the intermediate **1b** is a 1 : 1 adduct between the copper(II) complex and Na_2S_2.

Intermediate **1b** was then gradually converted to another intermediate **1c** exhibiting absorption bands at 424 nm (ε = 3070 M^{-1} cm^{-1}) and 610 (845). Notably, the conversion of **1b** to **1c** obeyed *first-order* kinetics, and the first-order dependence of this process was confirmed by the fact that the first-order rate constants obtained from the reactions with different initial concentration of **1a** were nearly identical; $k_{obs} = 9.4 \times 10^{-3}$ s^{-1}, 9.0×10^{-3} s^{-1}, 9.5×10^{-3} s^{-1}, and 8.5×10^{-3} s^{-1}, at [**1a**] = 0.2, 0.4, 0.6 and 0.8 mM, respectively. The first-order dependence on the copper complex clearly demonstrates that the reaction from **1b** to **1c** is a *unimolecular* process with respect to the copper complex. Intermediate **1c** was further converted to the final product, (μ-η^2:η^2-disulfido)dicopper(II) complex **1d**, when the temperature of the reaction mixture was raised to room temperature, and the UV-vis spectrum of the final reaction mixture was identical to that of the isolated (μ-η^2:η^2-disulfido)dicopper(II) complex (the spectrum is not shown in Fig. 4).[14]

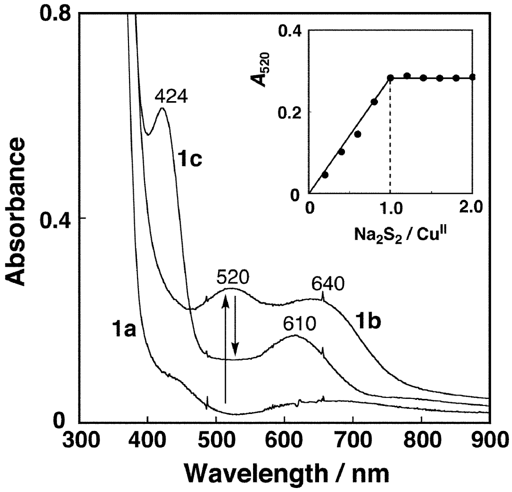


Fig. 4 UV-vis spectra of **1a**, **1b** and **1c** in CH_2Cl_2–CH_3OH (2 : 1) at −80 °C. Inset: Titration for the formation of **1b**.

Fig. 5 shows the spectral change for the reaction of copper(II) complex **3a** and Na_2S_2 under the same experimental conditions, where formation of intermediate **3b** exhibiting two intense absorption bands at λ_{max} = 483 nm (ε = 3240 M^{-1} cm^{-1}) and 625 (3580) was observed at the initial stage of the reaction. The spectrum of **3b** is fairly close to that of intermediate **1b** shown in Fig. 4, suggesting that both intermediates **1b** and **3b** have a similar structure. In fact, the stoichiometry of Cu^{II} to Na_2S_2 for the formation of **3b** was also 1 : 1 (inset of Fig. 5) as in the case of the formation of **1b** (inset of Fig. 4). In contrast to the case of the adduct formation reaction of **1a** to give **1d**, intermediate **3b** was reduced to the copper(I) compound **3e** having a featureless UV-vis spectrum in the visible

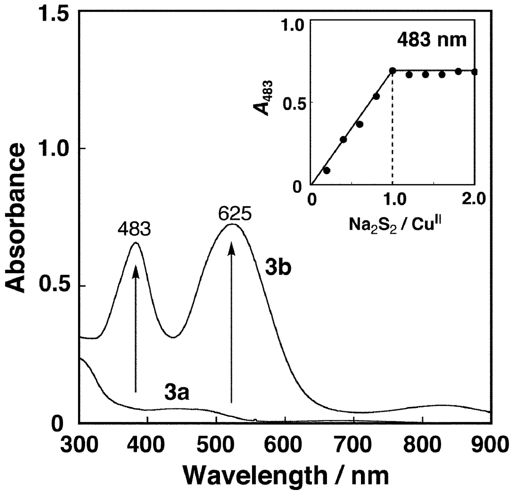
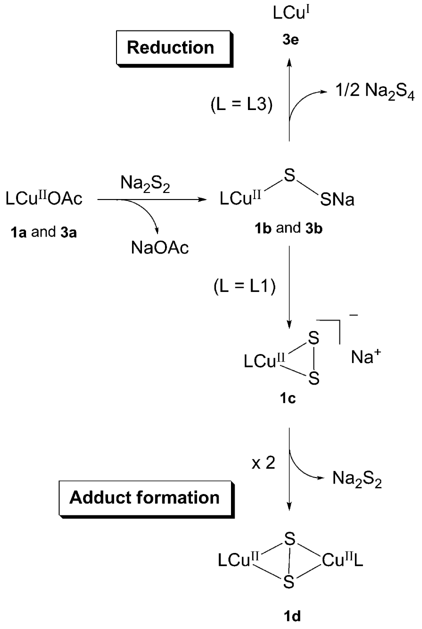


Fig. 5 UV-vis spectra of **3a** and **3b** in CH_2Cl_2–CH_3OH (2 : 1) at −80 °C. Inset: Titration for the formation of **3b**.

region at the elevated temperature (the spectrum is not shown in Fig. 5).

All these results can be interpreted by the reaction pathway shown in Scheme 1. In the initial stage of the reaction, both copper(II) starting materials **1a** and **3a** ($LCu^{II}OAc$) react with Na_2S_2 to form similar 1 : 1 adducts **1b** and **3b**, respectively. The ESR spectrum of **3b** shown in Fig. 6, which is different from that of starting material **3a** shown in Fig. S1 (see ESI†), is very close to that of Tolman's three-coordinate copper(II)-thiolate complex with β-diketiminate ligand L3⁻.[22] This strongly suggests that intermediate **3b** has a similar three coordinate structure with N_2S donor set, where disulfide co-ligand binds to the copper ion in an end-on fashion. Despite our great efforts, however, Raman data of intermediate **3b** has yet to be obtained.



Scheme 1

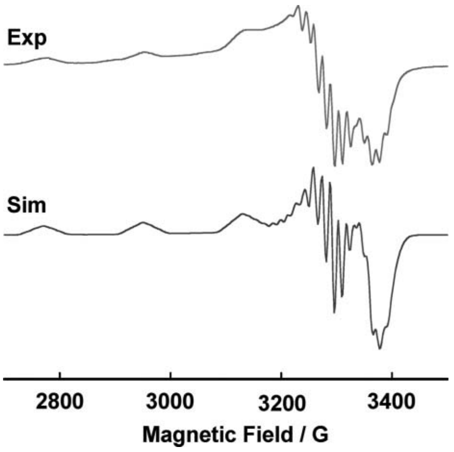


Fig. 6 Experimental ESR spectrum of **3b** in CH_2Cl_2 at −150 °C (Exp); microwave frequency 9.40 GHz, modulation frequency 100 kHz, modulation amplitude 5 G, microwave power 0.097 mW, and its computer simulation spectrum (Sim) with the ESR parameters $g_1 = 2.210$, $g_2 = 2.035$, $g_3 = 2.046$, $A_{Cu1} = 180$ G, $A_{Cu2} = 15$ G, $A_{Cu3} = 15$ G, $A_{N1} = 15$ G, $A_{N2} = 15$ G, $A_{N3} = 13.5$ G, $W_1 = 13$ G, $W_2 = 30$ G, $W_3 = 7$ G.

In the case of **1b** supported by the sterically less demanding ligand L1⁻, intramolecular rearrangement of the disulfide co-ligand may occur from end-on to side-on to give another intermediate **1c**, from which (μ-η^2:η^2-disulfido)dicopper(II) complex **1d** can be generated by self-dimerisation. The first-order kinetics observed in the conversion of **1b** to **1c** is consistent with this mechanism. Furthermore, the ESR spectrum of **1c** shown in Fig. S2 (ESI†) supports the mononuclearity of **1c**. Another sterically less demanding ligand L4 may follow the same reaction pathway to give (μ-η^2:η^2-disulfido)dicopper(II) complex **4d**.

On the other hand, with sterically more demanding ligand L3⁻, such an intramolecular rearrangement of the sulfide co-ligand from end-on to side-on may be prohibited due to the steric congestion around the coordination sphere, thus Cu^{II}–S bond homolysis predominates to give the copper(I) product **3e**. Similarly, the reduction of copper(II) to copper(I) occurred in the case of another sterically demanding ligand L2⁻. The different reactivity between the **1a**/**4a**-system and the **2a**/**3a**-system could not be attributed to a difference in the reduction potential of the copper(II) complexes, since regardless of the presence or absence of the strong electron withdrawing substituent α-CN both the adduct formation and the reduction of copper(II) occur.[23]

In summary, we have demonstrated that the reaction of β-diketiminate copper(II) complexes and Na_2S_2 leads to formation of a mononuclear LCu^{II}–S–SNa end-on adduct as a key intermediate, from which both the (μ-η^2:η^2-disulfido)dicopper(II) complexes and the copper(I) complexes are generated depending on the substituents of supporting ligand. The results can be interpreted by taking into account of the steric congestion around the metal-coordination sphere as discussed above. Similar steric effects by the substituents of β-diketiminate ligand system have been reported in Cu(I)/O_2 chemistry.[24] Thus, the present results provide further insight into the ligand effects on the reactivity of the β-diketiminate complexes toward small molecules.

Experimental

General

The reagents and the solvents used in this study except the ligands and the complexes were commercial products of the highest available purity and were further purified by the standard methods, if necessary.[25] Na_2S_2 was prepared according to the reported procedures,[26] and the purity of the Na_2S_2 sample (~98%) was confirmed by the reported method.[26] The isotope labeled $Na_2{}^{34}S_2$ was prepared by the reaction of Na and $^{34}S_8$ (isotope content is 99%, purchased from Euriso-top) according to the reported procedures.[26] The ligand precursors L1H, L2H, L3H and L4H (see Chart 2) were prepared by the reported methods.[19,27–29] Copper(II) acetate complexes **1a**, **2a**, **3a** and **4a** were prepared according to the reported procedures.[14,17] FT-IR spectra were recorded on a Jasco FTIR-4100 and UV-visible spectra were taken on a Hewlett Packard 8453 photo diode array spectrophotometer equipped with a Unisoku thermostated cell holder USP-203. ^{1}H NMR spectra were recorded on a JEOL FT-NMR GX-400 spectrometer. Mass spectra were recorded on a JEOL JMS-700T Tandem MS-station mass spectrometer. Raman scattering was excited by a He/Cd laser (Kinmon Electrics, CDR80SG) and the resonance-Raman light was dispersed with a JEOL 400D Raman spectrometer equipped with a modified cryostat cell holder USP-203 for the Raman measurements. Elemental analyses were recorded with a Perkin-Elmer or a Fisons instruments EA1108 Elemental Analyzer.

Reaction of 1a and Na_2S_2[14]. To a CH_3CN solution (40 mL) of **1a** (165.5 mg, 0.30 mmol) was added Na_2S_2 (17.6 mg, 0.16 mmol) suspended in CH_3CN (5 mL), and the mixture was stirred for 60 min under anaerobic conditions (Ar). The resulting dark reddish solid was immediately collected by filtration and dried to give compound **1d** in a 78% yield (114.7 mg). ^{1}H NMR ($CDCl_3$, 400 MHz); δ 0.93 (d, J = 6.8 Hz, 24 H, CH_3), 1.04 (d, J = 6.8 Hz, 24 H, CH_3), 2.80 (q, J = 6.8 Hz, 8 H, CH), 6.98 (d, J = 8.0 Hz, 8 H, $H_{Ar\text{-}3}$), 7.18 (t, J = 8.0 Hz, 4 H, $H_{Ar\text{-}4}$), 7.37 (s, 4 H, CH); IR (KBr): 2207 cm^{-1} (C≡N), 1563 cm^{-1} (C=N); HRMS: m/z 1019.3955, calc. for $C_{56}H_{73}Cu_2N_6S_2$ 1019.4130; Anal. Calc. for $C_{56}H_{72}Cu_2N_6O_2\cdot H_2O$: C, 64.77; H, 7.18; N, 8.09. Found: C, 65.07; H, 7.01; N, 8.12%; UV-vis (THF); λ_{max}/nm (ε/M^{-1} cm^{-1}); 333 (24 000), 432 (12 500), 867 (150). Single crystals of **1d** were obtained by slow diffusion of methanol into a CH_2Cl_2 solution of **1d**.

Reaction of 2a and Na_2S_2. To a CH_3CN solution (5 mL) of **2a** (42.5 mg, 0.08 mmol) was added Na_2S_2 (4.6 mg, 0.04 mmol) suspended in CH_3CN (3 mL), and the mixture was stirred for 30 min under anaerobic conditions (Ar). The resulting yellow solid was immediately collected by filtration and dried to give compound **2e** in a 77% yield (29.2 mg). The IR and mass spectra of the product were identical with those of the authentic sample of **2e**.[19]

Reaction of 3a and Na_2S_2. To a CH_3CN solution (5 mL) of **3a** (99.1 mg, 0.18 mmol) was added Na_2S_2 (11.2 mg, 0.10 mmol) suspended in CH_3CN (3 mL), and the mixture was stirred for 30 min under anaerobic conditions (Ar). The resulting yellow solid was immediately collected by filtration and dried to give compound **3e** in a 65% yield (60.7 mg). The IR and mass spectra of the product were identical with those of the authentic sample of **3e**.[20]

Reaction of 4a and Na_2S_2[14]. To a CH_3CN solution (10 mL) of **4a** (248.8 mg, 0.51 mmol) was added Na_2S_2 (28.3 mg, 0.26 mmol) suspended in CH_3CN (5 mL), and the mixture was stirred for 30 min under anaerobic conditions (Ar). The resulting brown solid was immediately collected by filtration and dried to give compound **4a** in a 39% yield (92 mg). HRMS: m/z 912.3334, calc. for $C_{50}H_{66}Cu_2N_4S_2$ 912.3321; IR (KBr): 1577 cm^{-1} (C=N); UV-vis (THF): λ_{max}/nm (ε/M^{-1} cm^{-1}); 331 (20 500), 432 (8200), 541 (350), 804 (100). Further stirring of the filtrate gave a dark green solid as a hardly soluble (to CH_3CN, CH_3OH, acetone) unidentified byproduct.

Titration for the formation of 1b and 3b. To a CH_2Cl_2–CH_3OH (2 : 1) solution containing **1a** or **3a** (2.0×10^{-4} M) in a UV-vis quartz cell (1.0 cm path length) kept at −80 °C in a Unisoku thermostated cell holder USP-203 was added 0.2 equivalent of Na_2S_2 in the same solvent system through a microsyringe, and the spectrum was taken after a few seconds. Similarly, 0.4 equivalent of Na_2S_2 was added to a new CH_2Cl_2–CH_3OH (2 : 1) solution of the copper(II) complex, and the spectrum was measured. This procedure was continued with increasing the amount of Na_2S_2 (0.6–2.0 equivalent). For each addition of Na_2S_2, a new solution of the copper(II) complex was used.

X-Ray structure determination. The single crystals of **3a** and **4a** were obtained by solvent vaporization from a CH_3OH solution containing the complex in a glove-box ([O_2] <1 ppm, [H_2O] <1 ppm). A crystal suitable for X-ray analysis was mounted on a glass-fiber. Data of X-ray diffraction were collected by a Rigaku CCD area detector with graphite-monochromated Mo-Kα radiation (λ = 0.71070 Å) to $2\theta_{max}$ of 55°. All the crystallographic calculations were performed by using Crystal Structure software package of the Molecular Structure Corporation [Crystal Structure: Crystal Structure Analysis Package version 3.8.0, Molecular Structure Corp. and Rigaku Corp. (2005)].[30] The crystal structures were solved by the direct methods using SIR2002[31] and refined by the full-matrix least squares against F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located at calculated positions and not refined.

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