

## An Unusual Cu<sup>II</sup>-promoted Desulphurisation of Thiourea: Synthesis and Crystal Structure of Di- $\mu$ -hydrogencyanamido(1-)-bis[(*N,N',N''*-trimethyl-1,4,7-triazacyclononane)copper(II)] Di-perchlorate Monohydrate

Phalguni Chaudhuri,<sup>\*a</sup> Karl Wieghardt,<sup>a</sup> Bernhard Nuber,<sup>b</sup> and Johannes Weiss<sup>b</sup>

<sup>a</sup> Lehrstuhl für Anorganische Chemie I der Ruhr-Universität, D-4630 Bochum, West Germany

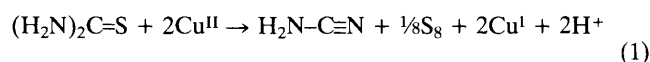
<sup>b</sup> Anorganisch-chemisches Institut der Universität, D-6900 Heidelberg, West Germany

The complex  $[\text{Cu}_2(\text{C}_9\text{H}_{21}\text{N}_3)_2(\mu\text{-HNCN})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  has been synthesized by reaction of  $[\text{Cu}(\text{C}_9\text{H}_{21}\text{N}_3)(\text{H}_2\text{O})_2]^{2+}$  with thiourea in the presence of oxygen in aqueous solution with concomitant formation of elemental sulphur; the complex has been characterized by X-ray crystallography, showing that two Cu<sup>II</sup> centres are connected *via* two bridging hydrogencyanamido(1-) ligands.

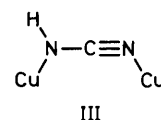
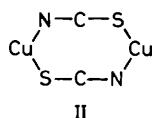
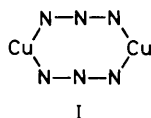
The ligating properties of the cyanamide dianion,<sup>1</sup>  $\text{NCN}^{2-}$ , and of the neutral cyanamide,<sup>2-4</sup>  $\text{H}_2\text{NCN}$ , towards transition metals have been studied in some detail. In contrast, only three complexes containing the monoanion hydrogen cyanamide(1-),  $\text{HNCN}^-$ , have been reported, by Beck *et al.*,<sup>1</sup> all of which contain monodentate, amido-N-bound ligands. Since  $\text{HNCN}^-$  is isoelectronic with the azide and thiocyanate anions, binuclear complexes with bidentate bridging  $\text{HNCN}^-$  ligands should also exist in accordance with well characterized structures I and II of copper(II).<sup>5-7</sup> The magnetic properties of such complexes have recently attracted much interest, since the unpaired electrons of the two Cu<sup>II</sup> centres are intramolecularly coupled (antiferromagnetically or ferromagnetically). Molecular orbital considerations, currently emerging, improve our understanding of the mechanisms of the magnetic superexchange on a structural basis.<sup>8,9</sup> We report here the first example of such a binuclear complex of copper(II) containing two bridging hydrogencyanamido(1-) ligands.

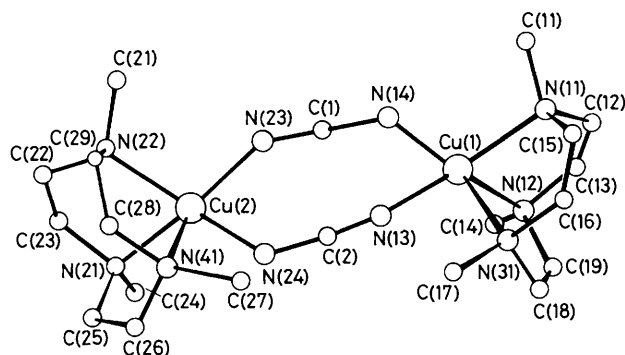
This complex has been obtained by an unusual, copper(II) promoted, desulphurisation reaction of thiourea. An aqueous

solution (30 ml) of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (1.9 g) was treated with the cyclic triamine *N,N',N''*-trimethyl-1,4,7-triazacyclononane<sup>10</sup> (7.5 mmol) dissolved in methanol (7.5 ml) at 20 °C. To the clear deep-blue solution of  $[\text{Cu}(\text{C}_9\text{H}_{21}\text{N}_3)(\text{H}_2\text{O})_2]^{2+}$ , thiourea (0.76 g) was added with stirring which afforded a deep-green solution. Within 20 min a green solid and elemental sulphur precipitated. The solid was filtered off and washed several times with  $\text{CS}_2$  (to remove  $\text{S}_8$ ). X-Ray quality crystals of the complex  $[\text{Cu}_2(\text{C}_9\text{H}_{21}\text{N}_3)_2(\mu\text{-HNCN})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$  were grown by slow diffusion of benzene into an acetone solution of the complex. The u.v.-visible spectrum of the complex in acetone exhibits absorption bands at 633 nm ( $\epsilon$  307 l mol<sup>-1</sup> cm<sup>-1</sup>) and 1023 nm (93). Thus the redox reaction in equation (1) is believed to occur. In the presence of



air Cu<sup>I</sup> is reoxidized and the mono deprotonated form of cyanamide is co-ordinated to two Cu<sup>II</sup> centres. Desulphurisa-





**Figure 1.** A perspective view of the binuclear cation (H atoms are omitted). Selected bond distances (Å) and angles (°) are: Cu(1)–N(14) 2.017(6), Cu(1)–N(13) 1.964(5), Cu(1)–N(11) 2.082(5), Cu(1)–N(12) 2.066(5), Cu(1)–N(31) 2.221(6), C(1)–N(14) 1.27(1), C(1)–N(23) 1.15(1), C(2)–N(13) 1.15(1), C(2)–N(24) 1.29(1), Cu(2)–N(24) 1.977(6), Cu(2)–N(23) 1.962(5); Cu(2)–N(23)–C(1) 146.6(8), N(23)–C(1)–N(14) 178.3(6), C(1)–N(14)–Cu(1) 120.9(5), N(14)–Cu(1)–N(13) 89.6(3), Cu(1)–N(13)–C(2) 144.6(8), N(13)–C(2)–N(24) 175.4(8), C(2)–N(24)–Cu(2) 124.5(5), N(11)–Cu(1)–N(12) 84.8(3), N(11)–Cu(1)–N(14) 92.5(3), N(11)–Cu(1)–N(13) 170(1), N(12)–Cu(1)–N(13) 91.8(3).

tion of thiourea in aprotic media by the superoxide ion under drastic conditions has recently been reported to yield dicyanamide.<sup>11</sup> In living cells this type of oxidative desulphurisation of thioamides such as ethionamide is known.<sup>12</sup>

The structure<sup>†</sup> consists of binuclear cations of  $[\text{Cu}_2(\text{C}_9\text{H}_{21}\text{N}_3)_2(\mu\text{-HNCN})_2]^{2+}$ , unco-ordinated perchlorate

<sup>†</sup> Crystal data for  $[\text{Cu}_2(\text{C}_9\text{H}_{21}\text{N}_3)_2(\text{HN}_2\text{C})_2](\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$ .  $M = 768.626$ , monoclinic, space group  $P2_1/n$ ,  $a = 16.458(4)$ ,  $b = 11.914(3)$ ,  $c = 16.646(4)$  Å,  $\beta = 92.90(3)^\circ$ ,  $D_c = 1.56 \text{ g cm}^{-3}$ ,  $Z = 4$ , crystal dimensions  $0.4 \times 0.4 \times 0.3 \text{ mm}^3$ ,  $R = 0.071$  and  $R_w = 0.070$  for 4496 reflections with  $I > 2.5 \sigma(I)$  collected at  $20^\circ\text{C}$  on an AED-Siemens diffractometer ( $\theta$ – $2\theta$  scan,  $3 < 2\theta < 50^\circ$ ), an empirical absorption correction has been carried out. The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

anions, and water of crystallization. Each copper ion is in a pseudo-trigonal-bipyramidal environment of the tridentate cyclic amine, two nitrogens of which occupy positions in the plane, the two hydrogencyanamido(1–) bridging ligands occupying two of the remaining sites (Figure 1). The hydrogencyanamido ligands are co-ordinated *via* both nitrogens to  $\text{Cu}^{\text{II}}$  (structure III). Although the positions of the hydrogen atoms of the bridges have not been located unambiguously by X-ray crystallography, the hydrogens are most likely bound to the amido-nitrogen atoms N(14) and N(24). The C–N bond distances of  $\mu\text{-HNCN}$  support the description as  $\mu\text{-hydrogencyanamido}(1-)$ . A strong  $\nu(\text{C}\equiv\text{N})$  stretching frequency at  $2140 \text{ cm}^{-1}$  and  $\nu(\text{N-H})$  at  $3250 \text{ cm}^{-1}$  in the i.r. spectra are also in agreement with this view.<sup>1</sup> The  $\text{ClO}_4^-$  ions are not co-ordinated to  $\text{Cu}^{\text{II}}$ .

From measurements of the magnetic susceptibility of powdered samples of the complex between 93 and 298 K it is concluded that the spins of the copper(II) centres are intramolecularly antiferromagnetically coupled [ $\mu_{\text{eff}} = 0.66 \mu_{\text{B}}$  (98 K) and  $\mu_{\text{eff}} = 1.35 \mu_{\text{B}}$  (298 K) per dimeric cation].

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