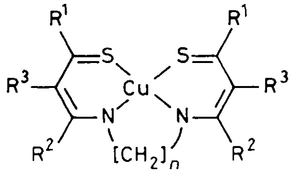
Copper(II)–N_2S_2 Complexes of Bidentate *N*-Substituted β-Aminothiones

Peter Beardwood and John F. Gibson*

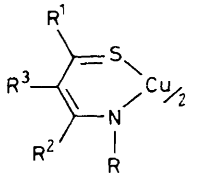
Department of Chemistry, Imperial College of Science and Technology, London SW7 2AY, U.K.

Bis(α,β-unsaturated *N*-substituted β-aminothione)Cu^{II} complexes, synthesised at low temperature, show intense S → Cu charge-transfer bands and have e.s.r. spectra with small $|A_z|$ (Cu) indicative of pseudo-tetrahedral CuN_2S_2 co-ordination similar to that found for the type 1 centres in blue copper proteins.

Although there have been several reports of copper(II) complexes involving quadridentate *N,N'*-substituted bis(β-aminothiones) (**1**),[1–3] corresponding complexes of the bidentate ligands (**2**) have not been described. Comparisons



(1)



Cu(R–NR^{2}R^{3}R^{1}S)$_2$

(2)

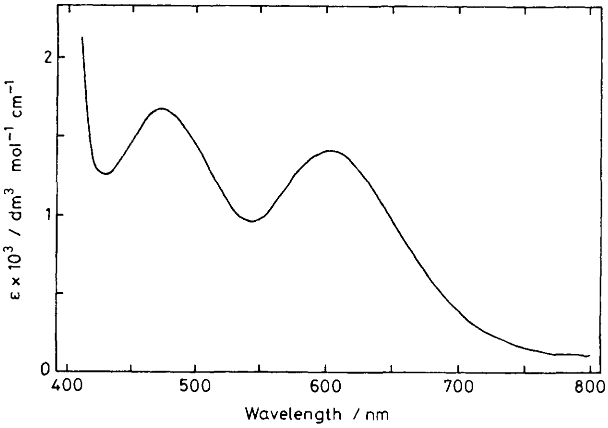


Figure 1. Electronic spectrum of Cu$^{\rm II}$(Bu$^{\rm i}$NMeHMeS)$_2$ in tetrahydrofuran at —50 °C.

have been made between the spectroscopic and redox properties of (**1**)[3] and those characteristic of type 1 blue copper protein centres for which low symmetry CuN$_2$S$_2$ co-ordination is known[4] or speculated to be present. The corresponding properties of (**2**), in which distortion from planar co-ordination could be controlled by varying the steric bulk of the amino substituent R, are of additional and surpassing interest for comparison with the distinctive features of the type 1 protein site. However, owing to a facile reduction of Cu$^{\rm II}$ by the bidentate β-aminothione ligand, orange diamagnetic Cu$^{\rm I}$ complexes are the product of attempted syntheses of (**2**) at room temperature. We report here that dark green/blue copper(II) complexes (**2**) may be isolated if the complexation reaction is undertaken at low temperature.

The ligands in (**2**) (R^1 = R^2 = Me, R^3 = H) were prepared by the method of Gerlach and Holm[5] and we employ a similar abbreviation to theirs; R–NMeHMeS = R–NR^{2}R^{3}R^{1}S. Cu$^{\rm II}$ complexes were synthesised by mixing methanolic solutions of ligand and copper(II) chloride at low temperatures (-30 to -70 °C depending on the bulk of R). The dark coloured solid produced on standing was collected by low-temperature filtration and drying. Satisfactory analytical data were obtained for R = Bu$^{\rm i}$ and R = p-MeC$_6$H$_4$. However, for the more bulky R = cyclohexyl group the less stable product was always contaminated by some Cu$^{\rm I}$(cyclohexyl–NMeHMeS) and attempts to purify the product by recrystallisation led only to further decomposition. The impurity does not, however, interfere with the present spectroscopic investigations.

Figure 1 shows the electronic absorption spectrum at -50 °C for Cu$^{\rm II}$(Bu$^{\rm i}$–NMeHMeS)$_2$ dissolved in tetrahydrofuran. The band maxima occur at 603 (1400) and 470 nm (1700) (the figures in brackets are extinction coefficients ϵ in dm^3 mol^{-1} cm^{-1}). The corresponding maxima for Cu$^{\rm II}$-(p-MeC$_6$H$_4$–NMeHMeS)$_2$ are observed at 620 (1600) and 540 nm (1600) and for Cu$^{\rm II}$(cyclohexyl–NMeHMeS)$_2$ at 678 and 504 nm. As judged from their high intensity these bands originate from S $\rightarrow$ Cu charge-transfer transitions, but their exact assignment is uncertain. Type 1 blue copper protein centres show bands of similar origin in the range 550—790 nm, with the most intense blue band at 600—630 nm.[6] Weaker absorption bands in the range 960—1200 nm observable in the reflectance spectra of the copper complexes (**2**) are assignable to d–d transitions and their low energy in comparison with the complexes of type (**1**)[1–3] is indicative of substantial distortion from square-planar toward tetrahedral co-ordination geometry.

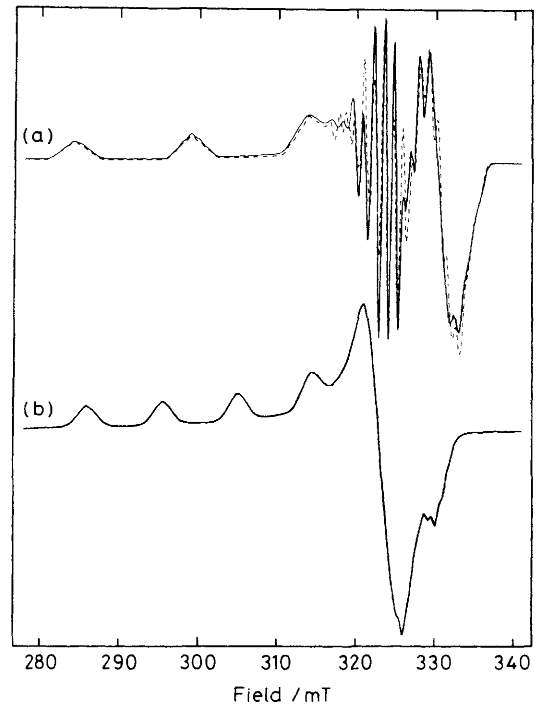


Figure 2. E.s.r. spectra of (a) ^{63}Cu$^{\rm II}$(Bu$^{\rm i}$–NMeHMeS)$_2$ in MeOH at 100 K (——) (microwave frequency, microwave power, modulation amplitude = 9.224 GHz, 2 mW, 0.25 mT) together with simulation according to the parameters given in the text (- - -); (b) ^{63}Cu$^{\rm II}$-doped Zn$^{\rm II}$(cyclohexyl–NMeHMeS)$_2$ at 100 K (9.229 GHz, 2 mW, 0.1 mT).

An e.s.r. spectrum of ^{63}Cu$^{\rm II}$(Bu$^{\rm i}$–NMeHMeS)$_2$ in MeOH at 100 K is shown in Figure 2(a) together with a simulation assuming a superhyperfine interaction with two nitrogens and employing the following parameters $g_x = 2.019$, $g_y = 2.041$, $g_z = 2.150$, A_x(Cu) $= A_y = -0.0021$ cm^{-1}, $A_z = -0.0148$ cm^{-1}, $|{}^NA_x| = 0.0012$ cm^{-1}, $|{}^NA_y| = |A^N{}_z| = 0.0011$ cm^{-1}. Corresponding spectra for (**2**) with R = p-MeC$_6$H$_4$ and R = cyclohexyl have $A_z = -0.0132$ cm^{-1}, $g_z = 2.139$ and $A_z = -0.0130$ cm^{-1}, $g_z = 2.173$ respectively. Compared with $A_z = -0.0177$ cm^{-1}, $g_z = 2.118$[2] for the essentially planar (**1**) with R^1 = R^2 = Me, R^3 = H, $n = 2$ the reduced magnitude of $|A_z|$ in the present complexes is indicative of their anticipated distortion toward tetrahedral co-ordination. The drop in $|A_z|$ on going from R = Bu$^{\rm i}$ to R = cyclohexyl is attributed to an increase in the extent of this distortion as a consequence of increased steric bulk. When doped into the analogous zinc complex ^{63}Cu(cyclohexyl–NMeHMeS)$_2$ shows a spectrum characteristic of further twisting of the chelate planes, Figure 2(b), with $A_z = -0.0097$ cm^{-1} and $g_z = 2.196$. These latter parameters closely approach those of $A_z = -0.0090$ cm^{-1} and $g_z = 2.190$ found for the type 1 centre in fungal laccase.[7] The other R = p-MeC$_6$H$_4$ and R = Bu^t copper-doped zinc complexes have higher $|A_z|$ parameters but show well resolved 1:2:3:2:1 superhyperfine splitting on the low field Cu hyperfine peaks confirming the expected co-ordination by two nitrogens.

The well established inverse $|A_z|$ *vs.* g_z relationship for Cu^{II} with varying degrees of tetrahedral distortion from square planar which has been extrapolated for CuN$_2$S$_2$ complexes from observations made on CuN$_4$ and CuS$_4$ species[8] is directly confirmed by the present results which also give additional confirmation of the need to assume low symmetry CuN$_2$S$_2$ co-ordination in the interpretation of type 1 blue copper protein spectra.

We hope in the future to report investigations on a more extensive series of these copper(II) complexes involving changes in the R and also the R^1 and R^2 substituents.

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