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Stabilisation of High Oxidation States by Strong Electron Donors: the Crystal Structure of Tetra-n-butylammonium o-Phenylenebisbiuretatocuprate(III)–Chloroform

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Summary The *X*-ray crystal structure of $Bu^n_4N[Cu\text{-}o\text{-}C_6H_4(NCONHCONH)_2].CHCl_3$ shows that the Cu atom is formally tervalent and is co-ordinated by four deprotonated amide nitrogen atoms; the Cu^{III}–N bonds (1·82—1·89 Å) are shorter than those found in related Cu^{II} complexes.

IT was shown earlier[1,2] that oxidation of Co^{II}, Ni^{II}, and Cu^{II} complexes of biuret and substituted biurets results in the formation of stable complexes in which the central metal atom is formally tervalent. Strong electron donation by the deprotonated amide nitrogen atoms of the ligands accounts for the relatively low redox potentials of these complexes and is consistent with 4-co-ordination of the metal atoms. The Cu^{III} complexes are diamagnetic and isoelectronic with the analogous Ni^{II} complexes.

Metal binding to deprotonated amide groups in metal–peptide complexes is well known[3] and Cu^{III}– and Ni^{III}–peptide complexes of this type have been reported.[4] The possibility therefore exists that biologically important molecules may provide donor groups and co-ordination geometries which stabilise high oxidation states. Evidence for the involvement of Cu^{III} as a catalytically intermediate oxidation state in galactose oxidase has recently been published.[5] The present work provides the first structural data for an N_4-co-ordinated Cu^{III} complex.

The structure of the title compound consists of discrete $Bu^{n}_{4}N^{+}$ and $[Cu\text{-}o\text{-}C_6H_4(NCONHCONH)_2]^{-}$ ions and chloroform molecules. The co-ordination of the Cu atom by four deprotonated nitrogen donor atoms is approximately square planar (see Figure). The Cu–N distances are significantly shorter than those found in Cu^{II} complexes of biuret and peptides[3] and are comparable with Ni^{II}–N(deprotonated amide) bond-lengths in a planar Ni^{II}–peptide complex[6] (see Table). This observation indicates that oxidation of the metal centre has occurred and supports the description of the Cu atom as Cu^{III} (d^8). The dimensions of the biuret ligands are, within the limits of precision, equal to those found in Cu^{II} and Co^{III} biuret complexes.[7,8]

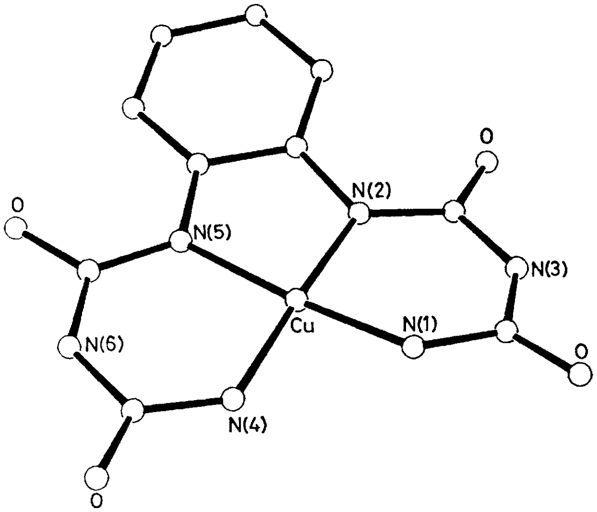

FIGURE. Structure of o-phenylenebisbiuretatocuprate(III) anion.

TABLE. Comparison of Cu^{II}–N, Cu^{III}–N, and Ni^{II}–N bond lengths in planar peptide and biuret complexes. Standard deviations in parentheses.

Complex	d(M–N)/Å[a]
$Na_2Cu(H_{-3}gggg).10H_2O$[b]	1·923(4), 1·912(4), 1·944(4)
$K_2Cu(biu)_2.4H_2O$	1·93(1), 1·94(1)
Present complex	1·82(1) [N(4)], 1·85(1) [N(1)] 1·86(1) [N(2)], 1·89(1) [N(5)]
$Na_2Ni(H_{-3}gggg).8H_2O$[d]	1·83(1), 1·84(1), 1·87(1)

[a] d(M–N) = metal–N(deprotonated amide) bond-length. [b] Disodium triglycylglycinatocuprate(II).$10H_2O$ (ref. 8). [c] $biuH_2$ = biuret, $H_2NCONHCONH_2$; H. C. Freeman, J. E. W. L. Smith, and J. C. Taylor, *Acta Cryst.*, 1961, **41**, 407. [d] Disodium triglycylglycinatonickelate(II).$8H_2O$ (ref. 6).

o-Phenylenebisbiuret was prepared as described earlier.[2] The Cu^{III} complex precipitated when a mixture of $CuCl_2.2H_2O$ (0·34 g), ligand (0·56 g), and 10 ml of $Bu^{n}_{4}NOH$ (20% in water) in 20 ml of Me_2SO was oxidised with I_2 (0·35 g in 2 ml of Me_2SO). Crystals (from Me_2SO–$CHCl_3$) are triclinic, space group $P\bar{1}$, $a = 9{\cdot}68(1)$, $b = 10{\cdot}75(1)$, $c = 16{\cdot}64(4)$ Å, $\alpha = 93{\cdot}4(1)$, $\beta = 105{\cdot}2(1)$, $\gamma = 94{\cdot}32(5)^\circ$, $U = 1660(8)$ Å^3, $D_m = 1{\cdot}44(2)$ g cm^{-3}, $D_c = 1{\cdot}403$ g cm^{-3} for $Z = 2$. Hydrogen atoms were included at calculated positions. Refinement by full-matrix least-squares with anisotropic temperature factors for Cu and Cl resulted in a final residual R of 0·079 for 3075 reflections (measured on a Nonius CAD4/F automatic diffractometer using Mo-K_α radiation).†

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† 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.

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