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Redox Behaviour of Novel Copper(II) Crown Ether-Pyrazole Complexes

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A novel dinuclear copper(II) diazacrown ether complex reduces in solution to the copper(I) state; the related mononuclear copper(II) monoaza crown ether complex undergoes reduction, when K⁺-ions are added.

One of the most challenging themes in bioinorganic chemistry is the mimicking of the dinuclear copper sites in copper proteins such as haemocyanin and dopamine-ß-hydroxylase. The former protein is responsible for oxygen transport in arthropods and molluscs, the latter enzyme is vital for the biosynthesis of noradrenaline. The binding of dioxygen to haemocyanin occurs through the cooperative action of both copper ions present in the active centres and can be influenced by pH, anions and cations. Model systems mimicking this behaviour could provide insight into the mechanistic action of these biomolecules.

In the literature only a few examples are known of dinuclear
copper(II) complexes that reduce to the copper(I) state. We present here a novel dinuclear copper(II) crown ether-dimethylpyrazole complex 1, which in methanol solution is reduced to the copper(I) state, even in the presence of air. The related complex 2 undergoes a much slower reduction under these conditions. This process can be enhanced and controlled by the addition of alkali metal ions.

The ligands from which 1 and 2 are derived were synthesized by treating α-bromo-α′-[bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amino]m-xylene with the corresponding diaza- and azan-crown ethers in dimethylformamide (DMF). The yield after column chromatography (silica 60H, eluent CHCl₃-MeOH-triethylamine, 97.5:2:0.5, v/v/v) for both ligands was approximately 55%. The ligands were mixed with 2 equiv. (for 1) and 1 equiv. (for 2) of CuCl₂·2H₂O in methanol to give the di- and mono-nuclear complexes 1 and 2 in 77 and 80% yield, respectively. During the synthesis of 2 a dark-green colour developed, typical for this type of copper(II) complex. The homogeneous solution of 1, however, decolorized rapidly, indicating the formation of a copper(II) complex. Proof that 1 indeed had reduced to the copper(I) state came from electrochemical experiments on samples of the complex. The chemical reduction amounted to 1/2, which in methanol solution is 1/2, indicating that 1 indeed is a Cu(I) complex. Complex 1 also showed a reversible wave at approximately the same potential (E₁/₂ = 0.31 V, iₚ/iₚ’ = 0.18 V, iₚ/iₚ’ = 1) as found for 2. The equilibrium potential (Eeq) of the solution was 0.15 V, clearly indicating that 1 was present in the form of a reduced complex. In view of the broad forward oxidation peak and the presence of two copper atoms, it is clear that 1 can be oxidized in two consecutive one-electron steps following an EE-reaction path. The half-wave potentials of these steps were calculated by the method of Richardson and Taube and amounted to E₁/₂ (1) = 0.29 V and E₁/₂ (2) = 0.32 V.

For the reaction Cu(I) + Cu(I) → 2Cu(II) we can calculate from the ΔE₁/₂ (30 mV) a proportionation constant K₆ = 4.8. This value suggests that there is hardly any interaction between the two copper centres in the electrochemical reduction of 1. This is not unexpected in view of the large metal–metal distance [18 Å from Corey–Pauling–Kolm (CPK) models] in the complex. The chemical reduction reaction follows a pathway different from the electrochemical oxidation/reduction of 1. We assume that in the former case a cooperative action between the two copper(II)-centres is necessary to achieve the observed reduction of complex 1. This is based on our observation that formaldehyde is produced during the reaction (fuchsine test): a two electron oxidation of methanol requires two copper(II) ions as electron acceptors. This reaction probably takes place in a μ-alkoxo (or μ-hydroxo) bridged complex, as described by Nelson and Drew. Subsequent electron transfer and liberation of the aldehyde will yield the dinuclear copper(II) complex.

The progress of the reduction of 1 (2.5 mmol dm⁻³, acetonitrile–methanol 1:1, v/v) was followed by UV–VIS spectroscopy, measuring the decrease of the d-d absorption band at 700 nm as a function of time and temperature. Rate constants and equilibrium constants were obtained by standard procedures assuming the equilibrium Ox -> Red.

The following parameters were obtained: forward reaction ΔG* = 87.4 kJ mol⁻¹, ΔH* = 48 kJ mol⁻¹, ΔS* = −14.2 kJ mol⁻¹ K⁻¹, E₁/₂ = 50.6 kJ mol⁻¹; ΔG* = −4.5 kJ mol⁻¹, ΔH* = 17 kJ mol⁻¹ and ΔS* = 63 J mol⁻¹ K⁻¹. The negative entropy of activation points towards a highly ordered transition state, thus supporting our proposed mechanism. The overall reaction is entropy driven as can be seen from the selected spectral data for complex 1: UV–VIS (MeCN–MeOH, 1:1, v/v) λ max (m, nm): 450 (1400), 695 (1400), 733 (1400), 1110 (1400); FAB-MS: m/z (m-nitrobenzylalcohol) 1414 (M⁺-ClO₄⁻), 1314 (M⁺-2 ClO₄⁻); IR (Csl, cm⁻¹) 1552 (pyrazole), 1097, 624 (ClO₄⁻); satisfactory elemental analyses was obtained. For complex 2: UV–VIS (MeCN–MeOH, 1:1, v/v) λ max (m, nm): 591 (80); FAB-MS: m/z (m-nitrobenzylalcohol) 645 (m, 20%, M+1); IR (Csl, cm⁻¹) 1553 (pyrazole), 1097 (ClO₄⁻). No reproducible elemental analysis could be obtained for oil 2.

† This compound was synthesized from 1 equiv. of bis[2-(3,5-dimethyl-1-pyrazolyl)ethyl]amine and 3.5 equiv. of m-α-α′-dibromo-m-xylene in tetrahydrofuran–benzene (1:1, v/v). Yield 51% after column chromatography (silica 60H, eluent 3% methanol in chloroform), Rf = 0.22. 1H NMR (CDCl₃) δ 2.1 (s, 6H, CH₃), 2.2 (s, 6H, CH₂), 2.9 (t, 6H, NCH₂CH₃), 4.5 (s, 2H, ArCH₂Br), 6.8 (s, 2H, Pyrazole H), 7.1–7.4 (m, 4H, ArH); Mass spectrometry (m/z) 364 (20%, M – Br).

‡ Selected spectral data for complex 1: UV–VIS (MeCN–MeOH, 1:1, v/v) λ max (m, nm): 695 (1400), 755 (1400), 88 (1400), 1110 (1400); FAB-MS: m/z (m-nitrobenzylalcohol) 1414 (M⁺-ClO₄⁻), 1314 (M⁺-2 ClO₄⁻); IR (Csl, cm⁻¹) 1552 (pyrazole), 1097, 624 (ClO₄⁻); satisfactory elemental analyses was obtained. For complex 2: UV–VIS (MeCN–MeOH, 1:1, v/v) λ max (m, nm): 691 (80); FAB-MS: m/z (m-nitrobenzylalcohol) 645 (m, 20%, M+1); IR (Csl, cm⁻¹) 1553 (pyrazole), 1097 (ClO₄⁻). No reproducible elemental analysis could be obtained for oil 2.

§ K₆ = exp[n₁/k₆(ΔE₁/₂)/RT] = exp[ΔE₁/₂/2.303RT] at 298 K with n₁ = n₂ = 1.9.
positive value of $\Delta S^\circ$. This can be rationalized from the fact that during the reduction solvent molecules surrounding the Cu$^{II}$ centres are liberated.

15-Crown-5 is able to form sandwich complexes with a K$^+$ ion. It was, therefore, tempting to investigate whether this ion could induce the aggregation of 2 [see Fig. 1(c)] and influence the reduction of the copper(n) centre. Titration of the ZnCl$_2$ derivative of 2 with potassium picrate confirmed the predominant existence of sandwich complexes at low K$^+ : 2$ ratios and 1:1 complexes at high ratios (see Fig. 2).10 We indeed observed that the addition of potassium picrate increased the reduction rate of 2 and caused a shift in the Ox $\rightleftharpoons$ Red equilbrium in the direction of the Cu$^{II}$ species. An optimum was found for a K$^+$ to 2 ratio of 0.5-1. The increase in $K_{eq} = k_r/k_i$, was fivefold (see Fig. 2).

Alkali metal ions are known to control the aggregation of the subunits of haemocyanin to form the active protein.11 We think that complexes of type 2 and the related pyridine complexes may be used to mimic this process. Work along this line is in progress.12

References
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Functionalized Thiophenes: Second-order Nonlinear Optical Materials
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It is shown experimentally that the complete replacement of benzene rings with thiophene rings in a donor–acceptor substituted stilbene significantly enhances its second-order nonlinear optical hyperpolarizability ($\beta$); results obtained with a series of thiophene-substituted donor–acceptor compounds with different conjugation lengths reveal a power law dependence of $\beta$ on the molecular conjugation length.

Organic materials with second-order nonlinear optical (NLO) properties have been the subject of intense investigations owing to their exceptionally large nonlinearity and ultrafast response times.1 These materials have potential applications in areas such as telecommunications, optical information processing and data storage.2 Major research efforts have focused on developing NLO chromophores possessing large molecular nonlinearity and good thermal stability as well as improved solubility and processability.

It is well-known that the second-order molecular nonlinear optical hyperpolarizability ($\beta$) increases with increasing donor and acceptor strengths and with increasing length of conjugation.3 Many donor–acceptor conjugated organic molecules reported in the literature fall into the following categories: substituted benzenes, biphenyls, stilbenes, azobenzenes and Schiff bases.4-7 In all these classes, benzene ring(s) with or without the a-bridges have been employed as the conjugating moieties to connect donor and acceptor functional groups. However, optical studies on compounds containing more than two benzene rings are limited. This could be attributed, in part, to the difficulty in the synthesis of extended conjugated compounds possessing more than two benzenoid rings as they are practically insoluble in most common organic solvents.