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Compound 28 was converted mainly to the phthalide either with (Ph,P)PdCl$_2$ (cat.), Cul (cat.), Et,N in benzene at room temp. for 20 h, or (Ph,P)PdCl$_2$ (cat.), NaHCO$_3$ in DMF at 60°C for 12 h, or, (Ph,P)PdCl$_2$ (cat.), CuI (cat.), EuN$_3$ in benzene at room temp, for 20 h. 19-Phthalide was obtained in low yields by palladium-assisted cyclization of 2-vinylbenzoic acid and 2-(2-methyl-2-propenyl)benzoic acid, D. E. Korte, L. S. Hegedus and R. K. Wirth, J. Org. Chem. 1977, 42, 1329. The thallation-olefination of benzoic acid in the presence of palladium reagents usually led to isocoumarins, although phthalides were obtained in a few cases. R. C. Larock, S. Varaparthi, H. H. Lau and C. A. Fellows, J. Am. Chem. Soc. 1984, 106, 5274.


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) monoazacrown 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-$eta$-hydroxylase. The former protein is responsible for dioxygen 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(i) complexes that reduce to the copper(i) state. We present here a novel dinuclear copper(i) crown ether-dimethylpyrazole complex 1, which in methanol solution is reduced to the copper(ii) 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-azin-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 two equiv. (for 1) and 1 equiv. (for 2) of CuCl₂·H₂O 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(i) complex. The homogeneous solution of 1, however, decolorized rapidly, indicating the formation of a copper(i) complex. Proof that 1 indeed had reduced to the copper(i) state was obtained by the addition of alkali metal ions.

The following parameters were obtained: forward reaction 

\[ \text{Cu}^{2+} + \text{Cu}^{2+} \rightleftharpoons 2 \text{Cu}^{+} \]

\[ \Delta G^\circ = -88 \text{kJ mol}^{-1} \]

\[ \Delta H^\circ = 84 \text{kJ mol}^{-1} \]

\[ \Delta S^\circ = -120 \text{J} \text{K}^{-1} \text{mol}^{-1} \]

The progress of the reduction of 1 (2.5 mmol dm⁻³, acetoniitrile–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

\[ \Delta G^\circ = -88 \text{kJ mol}^{-1} \]

\[ \Delta H^\circ = 84 \text{kJ mol}^{-1} \]

\[ \Delta S^\circ = -120 \text{J} \text{K}^{-1} \text{mol}^{-1} \]

The rate constants k₁ and k₂ follow from the equilibrium constant

\[ K = k_1/k_2 \]

and from k₁ = k₃ + k₄. The latter k is obtained by fitting absorbance (A) = time (t) data points to the equation

\[ A_t = [A_0/(K + 1)] \times [1 + (K \times \exp(-k \times t))] \]
positive value of $\Delta S^\circ$. This can be rationalized from the fact that during the reduction solvent molecules surrounding the CuII 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(e)] and influence the reduction of the copper(II) 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).\textsuperscript{10} We indeed observed that the addition of potassium picrate increased the reduction rate of 2 and caused a shift in the OX $\equiv$ Red equilibrium in the direction of the CuI species. An optimum was found for a K$^+$ to 2 ratio of 0.5–1. The increase in $K_{eq} = k_1/k_{-1}$ was fivefold (see Fig. 2).

Alkali metal ions are known to control the aggregation of the subunits of haemocyanin to form the active protein.\textsuperscript{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.\textsuperscript{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 $\beta_1$ on the molecular conjugation length.\textsuperscript{3} Many donor–acceptor conjugated organic molecules reported in the literature fall into the following categories: substituted benzenes, biphenyls, stilbenes, azobenzenes and Schiff bases.\textsuperscript{4–7} In all these classes, benzene ring(s) with or without the JT-bridges have been employed as the conjugating moieties to connect donor and acceptor functional groups. However, optical studies on compounds containing more than two benzenoid 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.

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.\textsuperscript{1} These materials have potential applications in areas such as telecommunications, optical information processing and data storage.\textsuperscript{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.\textsuperscript{3} Many donor–acceptor conjugated organic molecules reported in the literature fall into the following categories: substituted benzenes, biphenyls, stilbenes, azobenzenes and Schiff bases.\textsuperscript{4–7} In all these classes, benzene ring(s) with or without the x-bridges have been employed as the conjugating moieties to connect donor and acceptor functional groups. However, optical studies on compounds containing more than two benzenoid 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.