

Mild template synthesis of nickel(II) and copper(II) chelates with an (N,N,S,S)-tetradentate ligand in metal hexacyanoferrate(II)-immobilised matrix systems

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Mild template synthesis of polydentate coordination compounds of nickel(II) and copper(II) with 2,8-dithio-3,7-diaza-5-oxanonane-1,9-dithioamide in gelatine-immobilised matrices has been carried out for the first time.

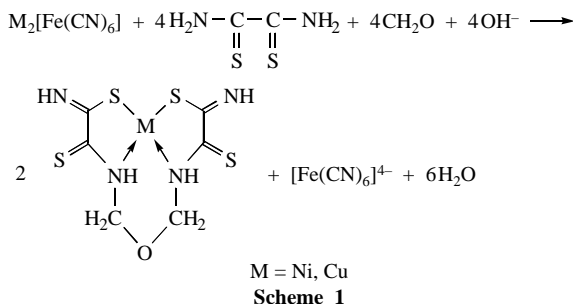
It is known that the processes of template synthesis, which afford the possibility of constructing coordination compounds of d-elements with polydentate ligands from simpler fragments (so-called 'ligand synthons'), mostly occur only under rather drastic conditions in solution and in the solid phase. However, it might be believed that specific conditions formed upon complexation in 3d metal-containing gelatine-immobilised matrices (GIM)¹⁻⁷ would enable at least certain template processes to occur under mild conditions, primarily at room temperature.

We report here that we have been able to perform such syntheses involving $\text{Ni}_2[\text{Fe}(\text{CN})_6]\text{-GIM}$, $\text{Cu}_2[\text{Fe}(\text{CN})_6]\text{-GIM}$ and such ligand synthons as dithiooxamide $\text{H}_2\text{N-C(=S)-C(=S)-NH}_2$ and formaldehyde CH_2O to give coordination compounds of nickel(II) and copper(II) with a new polydentate ligand, viz., 2,8-dithio-3,7-diaza-5-oxanonane-1,9-dithioamide.[†] The resulting compounds colour the polymeric bulk of the GIM, which becomes brown (Ni) or greenish-brown (Cu). The UV-VIS spectra of these compounds contain only a shoulder due to the intense charge transfer band, whose maximum is in the UV region. It should be noted specifically that at other concentrations of the reagents or in the absence of formaldehyde, a violet compound ($\lambda_{\text{max}} = 580 \text{ nm}$) with spectral characteristics similar to those of the $\text{NiL}(\text{OH})_2$ complex^{1,3,5,8} is formed in the system in the case of nickel(II). In the case of copper(II), a dark-blue compound with spectral characteristics similar to those of the known $[\text{Cu}(\text{HL})_2]_n$ chelate^{2,9} (where H_2L is dithiooxamide) is formed. It is apparent that both dithiooxamide and formaldehyde participate in the complexation that occurs under these specific conditions. Decomposition of the polymeric binder of GIM by enzymes according to the known procedure^{5,9} allowed us to isolate dark-brown compounds of molecular formula $\text{MC}_6\text{S}_4\text{N}_4\text{OH}_8$ according to elemental analysis [for nickel(II), found (%): Ni, 17.5; C, 21.3; S, 37.5; N, 16.5; O, 4.8; H, 2.4; calc. (%): Ni, 17.32; C, 21.25; S, 37.83; N, 16.52; O, 4.72; H, 2.36; for copper(II): found (%): Cu, 18.5; C, 20.9; S, 37.3; N, 16.1; O, 4.8; H, 2.4; calc. (%): Cu, 18.45; C, 20.96; S, 37.21; N, 16.34; O, 4.69; H, 2.35]. These compounds are almost insoluble in water, ethanol, acetone, chloroform, benzene and tetrachloromethane; and poorly soluble in dimethylformamide, dimethyl sulfoxide and hexamethylenephosphotriamide. The UV-VIS spectra of their solutions in dimethyl sulfoxide are almost identical to those of their source polymeric matrices indicating that the immobilised compound is the same as that isolated from GIM in the case of both Ni and Cu. The DTA data indicate that both compounds are very heat-resistant and do not undergo pyrolysis even at 600 °C. The IR spectra of both compounds have a wide $\nu(\text{NH})$ band in the 3400–3500 cm^{-1} region typical of NH groups uncoordinated to a metal ion. Hence, at least a portion of the N

atoms in these compounds are not bound to nickel(II) or copper(II). In addition, the IR spectra of the compounds under study contain $\nu(\text{C}=\text{S})$ [680 cm^{-1} (Ni), 650 cm^{-1} (Cu)] (usually recorded at 705–570 cm^{-1}) and $\nu(\text{C}=\text{N})$ bands (1640 cm^{-1}) (usually observed at 1690–1625 cm^{-1})^{10,11} indicating the presence of C=S and C=N groups, respectively. Unfortunately, the IR spectra obtained in the region < 1000 cm^{-1} , where $\nu(\text{M}-\text{S})$ and $\nu(\text{M}-\text{N})$ (M = Ni, Cu) frequencies should be observed,¹⁰ do not allow us to reliably assign the bands they contain to the stretching vibrations indicated above. It should be especially noted that two medium-intensity peaks at ca. 2940 and 2865 cm^{-1} (Ni) and at ca. 2910 and 2860 cm^{-1} (Cu) belonging to $\nu(\text{CH}_2)$ (according to the literature data,^{10,11} these bands lie within the 2945–2915 and 2870–2845 cm^{-1} ranges, respectively) and a band due to the stretching vibrations of the bridging C–O–C group at 1120–1100 cm^{-1} (usually observed in the 1200–1100 cm^{-1} range)^{10,11} is also present in these spectra. These bands are absent in the IR spectra of dithiooxamide and in any of the coordination compounds of nickel(II) and copper(II) with this ligand known to date.⁴ Thus, one may conclude that both of the brown compounds isolated contain $\text{H}_2\text{C}-\text{O}-\text{CH}_2$ structural groups. Since such groups are not present either in dithiooxamide [and in any of its chelates with nickel(II) and copper(II)] or in formaldehyde, it is quite evident that the formation of coordination compounds of nickel(II) and copper(II) with some new ligand, which is 'assembled' from dithiooxamide and formaldehyde fragments, occurs during complexation in the M^{II} -dithiooxamide-formaldehyde systems (M = Ni, Cu). It is noteworthy that the UV-VIS absorption spectra of aqueous solutions of dithiooxamide of any concentration in the 400–700 nm region at pH > 10 do not change even on addition of significant amounts of formaldehyde for at least 2 days, and no indication of a chemical reaction between these compounds is observed. Therefore, we have no doubt that the reaction between the reagents mentioned above does not take place at all in the absence of a metal ion. A similar phenomenon is possible only in template synthesis¹²⁻¹⁴ where dithiooxamide and formaldehyde act as ligand synthons. The analysis of kinetic curves of complexation, $D = f(c_{\text{P}}, c_{\text{L}}, t)$ [where D is the optical density of the metal-chelate GIM corresponding to the concentration of hexacyanoferrate(II) of metal(II) in the matrix (c_{P}), dithiooxamide in solution (c_{L}) and the duration of the process t], according to the reported procedure,¹⁵ provides clear evidence that the addition of exactly two dithiooxamide molecules and two formaldehyde molecules per M^{II} ion takes place in the course of the process, in complete agreement with route (2). On this basis, the template synthesis in the systems under study can be presented by Scheme 1.

The compound synthesised by us, (2,8-dithio-3,7-diaza-5-oxanonandithioamido-1,9)nickel(II), like all known⁴ complexes of nickel(II) with dithiooxamide, is diamagnetic and does not give an EPR signal. This indicates a coordination number of 4 and a planar coordination of the ligand donor centres to nickel(II), which is also in complete agreement with its structure according to Scheme 1. Such a conclusion agrees completely with its UV-VIS spectrum and its brown colour typical of coplanar nickel(II) chelates. The structurally similar copper(II)

[†] This synthesis occurs on contact of $\text{M}_2[\text{Fe}(\text{CN})_6]\text{-GIM}$ (M = Ni, Cu) with alkaline solutions (pH > 10) containing dithiooxamide and formaldehyde. The concentration of $\text{M}_2[\text{Fe}(\text{CN})_6]$ in the matrix was 0.1 to 0.2 mol dm^{-3} . The concentration of dithiooxamide in the solution was 3.0×10^{-3} – 5.0×10^{-1} mol dm^{-3} , and the molar ratio of dithiooxamide to formaldehyde was 0.5–2.0. The duration of the process was 10–12 min at 18–20 °C.



Scheme 1

compound is paramagnetic ($\mu_{\text{eff}} = 1.92 \mu\text{B}$) and gives an EPR signal with $g_{\parallel} = 2.21$ and $g_{\perp} = 2.05$, which is also typical of planar coordination of ligand donor centres to copper(II) and the N_2S_2 composition of these centres. This agrees with the structure of the copper complex according to Scheme 1. In this connection, it should be specially mentioned that that process occurs only in GIM, and we failed to obtain these coordination compounds in the reaction of $Ni[Fe(CN)_6]$ or $Cu_2[Fe(CN)_6]$ [as nickel(II) or copper(II)] with dithiooxamide and formaldehyde in solution or in the solid phase at room temperature. This fact indicates the specific role of gelatine-immobilised matrix systems in template synthesis *via* Scheme 1. Unfortunately, we have not yet been able to carry out X-ray diffraction studies of the metal-polydentate compounds synthesised by us, since the method of their isolation from GIM affords extremely small crystals hardly usable for these studies at the contemporary technical level. For this reason, we leave the question of their steric structure open, and additional studies are required to clarify this aspect.

This work was financially supported by the Russian Foundation for Basic Research (grant no. 96-03-32112).

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Received: Moscow, 22nd October 1997

Cambridge, 8th April 1998; Com. 7/07976A