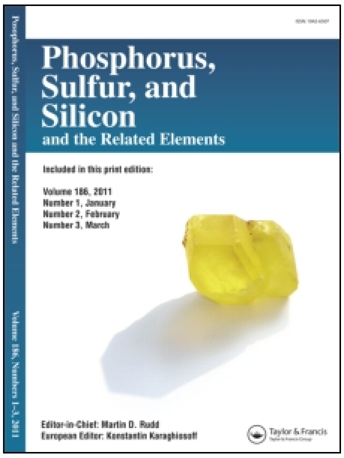


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

THE COMPLEXING INTO METAL-CONTAINING GELATIN-IMMOBILIZED MATRICES AS NOVEL PERSPECTIVE METHOD OF COORDINATION POLYMERS SYNTHESIS. UNCHELATED COORDINATION POLYMERS OF NICKEL (II) AND COPPER(II) WITH DITHIOOXAMIDE

Oleg V. Mikhailov[a]
[a] Inorganic Chemistry Department, Kazan State Technological University, Kazan, Russia

To cite this Article Mikhailov, Oleg V.(1997) 'THE COMPLEXING INTO METAL-CONTAINING GELATIN-IMMOBILIZED MATRICES AS NOVEL PERSPECTIVE METHOD OF COORDINATION POLYMERS SYNTHESIS. UNCHELATED COORDINATION POLYMERS OF NICKEL (II) AND COPPER(II) WITH DITHIOOXAMIDE', Phosphorus, Sulfur, and Silicon and the Related Elements, 126: 1, 129 — 136

To link to this Article: DOI: 10.1080/10426509708043552

URL: http://dx.doi.org/10.1080/10426509708043552

Phosphorus, Sulfur and Silicon, 1997, Vol. 126, pp. 129-136
Reprints available directly from the publisher
Photocopying permitted by license only

THE COMPLEXING INTO METAL-CONTAINING GELATIN-IMMOBILIZED MATRICES AS NOVEL PERSPECTIVE METHOD OF COORDINATION POLYMERS SYNTHESIS. UNCHELATED COORDINATION POLYMERS OF NICKEL (II) AND COPPER(II) WITH DITHIOOXAMIDE

OLEG V. MIKHAILOV

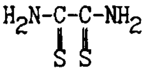
Inorganic Chemistry Department, Kazan State Technological University, K. Marx Street 68, 420015 Kazan, Russia

(Received 15 October, 1996; In final form 4 Februry, 1997)

The novel unchelates coordination polymers of Ni(II) and Cu(II) with dithiooxamide have been synthesized under specific complexing conditions which have not been used in coordination chemistry before,namely into a nickel(II)- and copper(II)hexacyanoferrate(II) gelatin-immobilized matrices in contact with the aqueous solution of above organic compound.

Keywords: Complexing; Immobilized matrix; Dithiooxamide; Ni (II), Cu (II) coordination polymers.

INTRODUCTION

It is known that dithiooxamide  $H_2N-C(=S)-C(=S)-NH_2$ forms with Ni(II) and Cu(II) chelate complexes having metal ion/singly deprotonated ligand form ratio of 1: 2[1-8]. It was noted in[1-3, 7-8] that both these chelates are coordination polymers. This circumstance deserves attention since in spite of rather considerable investigators' interest to complexing in the Ni (II)-dithiooxamide system and Cu (II)-dithiooxamide one in a solution or a solid phase an existence of other coordination compounds in these systems could not be found. We investigated the possibility of synthesis of various coordination polymers in the complexing processes proceeding in specific conditions, namely into nickel(II)- and copper(II)hexacyanoferrate(II) gelatin-immobilized matrix systems(GIM) have found that unchelated coordination polymers of Ni(II) and Cu(II) with dithiooxamide, which are unknown up to now, can be obtained.

RESULTS AND DISCUSSION

At the contact of **$Ni_2[Fe(CN)_6]$–GIM** with an alkaline solution of dithiooxamide at $C_F<1.0$ mol/dm^3, C_L^o ~ ($1.0\ 10^{-3} - 2.0\ 10^{-2}$) mol/L and t>2 min,the substance **I**, colouring the gelatin layer pink-violet, is obtained. At $C_F>1.0$ mol/dm^3, C_L^o ~ ($2.0\ 10^{-2}$–$5.0\ 10^{-2}$)mol/L, t=4–10 min,the substance **II** which colours the gelatin layer violet,is formed.The results of mathematical processing of D = f(C_F, C_L^o, t) kinetic curves in the ranges of (C_F, C_L^o, t) indicated according to[9] that the addition of two dithiooxamide molecules per one $Ni_2[Fe(CN)_6]$ fragment takes place in the formation of both these substances.According to chemical analysis data of substances isolated from the corresponding GIM, each of them has the stoichiometric formula $NiL(H_20)_2$(H_2L is dithiooxamide). It should be noted that the gelatin layer containing **II** changes its colour neither on addition of acid or alkaline solutions, whereas the gelatin layer containing **I** changes its colour from pink-violet to ultramarine at the addition of acid solutions having pH<5. The transition of colours (pink-violet → ultramarine) is irreversible. The substance **III** having ultramarine colour and stoichiometric formula $Ni(HL)_2$, can be isolated from the corresponding GIM. The spectral characteristics of **III** are similar to those of the only known chelate of Ni(II) with dithiooxamide with a nickel(II) ion:ligand=1:2[1-5].

At the contact of **$Cu_2[Fe(CN)_6]$–GIM** with an alkaline solution of dithiooxamide at C_F=(0.1–0.8) mol/dm^3, C_L^o ~ ($5.0\ 10^{-4}$–$5.0\ 10^{-3}$) mol/L and t=1-6 min, the compound **I'**, colouring the polymer layer brown-green, is formed. At higher C_L^o ($1.0\ 10^{-2}$–$4.0\ 10^{-2}$)mol/L, the compound **II'** colouring the gelatin layer dark-green, is obtained in the matrix. The data of mathematical processing of D=f(C_F, C_L^o, t) kinetic curves in the ranges of (C_F, C_L^o, t) indicated, as it has been showed in[9], that the addition of two dithiooxamide molecules in the case of **I'** formation and four ones in the case of **II'** formation per one $Cu_2[Fe(CN)_6]$ fragment takes place. The obtained metal-chelate matrices containing **I'** and **II'** do not change their colour and spectral characteristics at the influence of acid or alkaline solutions. According to chemical analysis data of substances isolated from the corresponding GIM, these compounds have stoichiometric formulas $CuL(H_20)_2$ and $Cu(HL)_2$, respectively.

Some characteristics of these compounds have been presented in Table I.

TABLE I Some properties of Ni(II) and Cu(II) coordination polymers with dithiooxamide synthesized into metalhexacyanoferrate(II) GIM

Coordination polymer	*Average molar mass*	*l_{max}. in UV-VIS-spectra nm*	*$\lambda_{max.}$ of bands (C-S) (S=C-N) (C=N) (N-H) in IR-spectra cm^{-1}*	*μ_{eff} at 298K μ_B*	*The chemical analysis data: Found, % (Calculated for the given formula,%)*			
					Ni (Cu)	*C*	*N*	*H*
$(NiC_2S_2N_2H_60_2)_n$ $([NiL(H_20)_n])$ **(II)**	6000	570	975 - 1660 3430	0.0	28.1 (27.69	11.4 11.26	12.8 13.14	3.2 2.82
$(NiC_4S_4N_4H_6)_n$ $([Ni(HL)_2]n)$ **(III)**	7000	640	985 1510 1655 3430	0.0	19.5 (19.76	16.0 16.17	19.2 18.85	2.2 2.04
$(CuC_2S_2N_2H_60_2)_n$ $([CuL(H_20)_n])$ **(I')**	8500	520–620 (shoulder) 680–690	990 – 1660 3420	1.92	29.8 (29.85	11.3 11.01	13.1 12.85	2.6 2.75
$(CuC_4S_4N_4H_6)_n$ $([Cu(HL)_2]_n)$ **(II')**	11000	510–680 (shoulder)	970 1515 1680 3425	1.85	21.0 (21.19	15.7 15.89	18.7 18.55	2.1 1.98

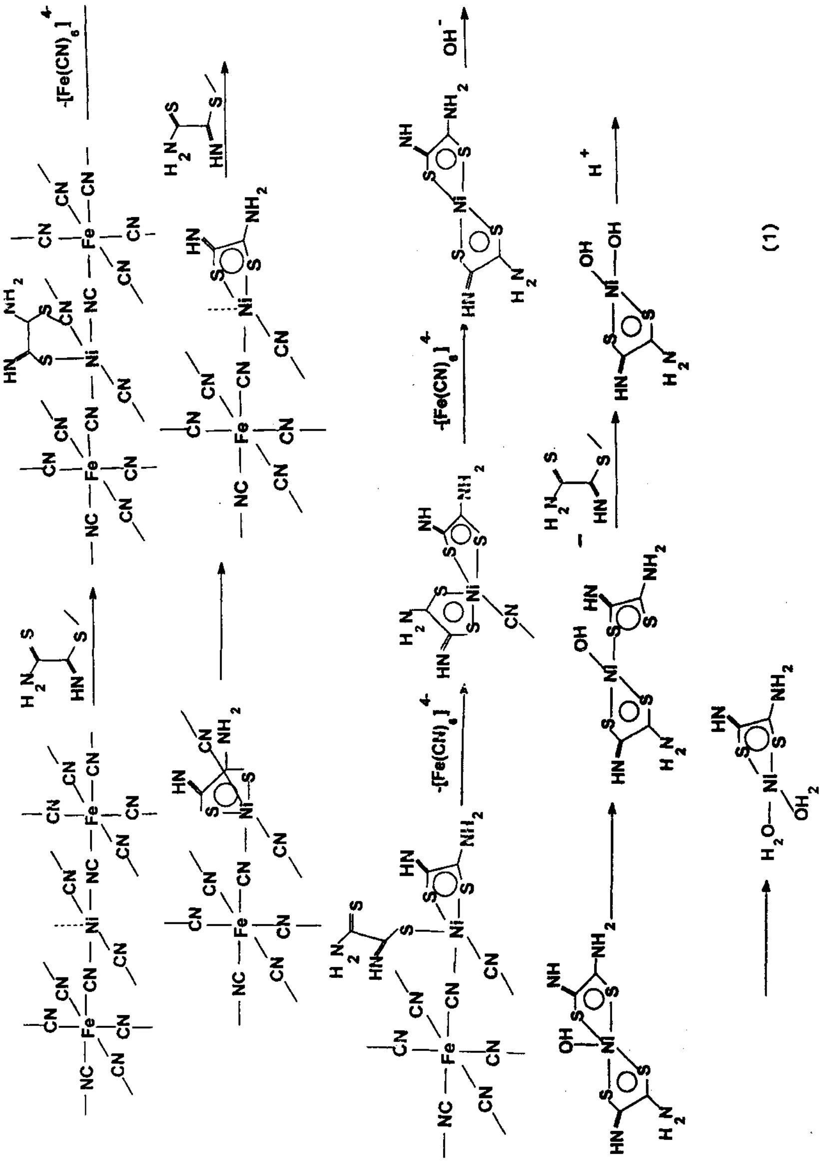
UV-VIS spectra of GIM containing the above-mentioned coordination polymers are typical for Ni(II) and Cu(II) complexes with coordination number 4 and donor centers in rhombic coordination around the central metal ion[11-15]. The diamagnetism of Ni(II) compounds **I-III** and μ_{eff} values of Cu(II) compounds **I'** and **II'** are in favour of this conclusion.Taking into account the stoichiometric metal ion: dithiooxamide ratios in the compounds under discussion, we postulate tha the ligand is bidentate in all these compounds.The IR spectra of these compounds exhibit an intense band at 3400–3500 cm^{-1} corresponding to ν(N-H) of uncoordinated NH- (NH_2-) groups[16]; the (NH) band of dithiooxamide(3455 cm^{-1}) also falls within this region.This makes it possible to conjecture,with a degree certainly, that in the Ni(II) and Cu(II) compounds the dithiooxamide is coordinated through two sulfur atoms. Furthermore,the IR spectra of these compounds exhibit pronounced ν(C-S) (970–990 cm^{-1}) and ν(C=N)(1660–1680 cm^{-1}) bands which are absent in the IR spectra of dithiooxamide. This fact indicates that singly (HL^-) and doubly (L^{2-}) deprotonated ligand forms occur in the inner sphere of these complexes. It is particularly remarkable that the spectra of **III** and **II'** exibit ν(S=C-N) bands at 1510 and 1515 cm^{-1}, respectively which is present in the IR spectra of the ligand(1520 cm^{-1}) but absent in the spectra **II** and **I'**. In connection with this,we propose that the inner sphere of **III** and **II'** contain the HL^--, the inner sphere of **II** and **I'**, the L^{2-} form of dithiooxamide. The rather weak absorbance of compounds **II** and **I'** allow to affirm that these compounds are unchelated coordination polymers.

The gelatin is known to be a "molecular ensemble" containing polypeptide units with a highly chaotic space orientation and voids sufficiently large to include different compounds[10]. Our studies,using electron microscopy,indicated that metalhexacyanoferrates (II) immobilized in the GIM, are of a quasi-molecular dispersion. Both in crystalline $M_2[Fe(CN)_6]$ (M=Ni, Cu) and in the gelatin-immobilized nickel (II) or copper (II)hexacyanoferrate(II) coordination polymer,a quantity of Ni (II) or Cu (II) with the 0_h symmetry of the coordination surrounding with one or two unoccupied positions always occurs which appears as a result of local disturbances in the process of the formation of the Ni(II) or Cu(II) hexacyanoferrate(II) structures.According to Langford and Gray[13], square-pyramidal(C_{4v}) or square-planar(D_{4h}) coordination of CN^- groups around 3d-element central ion formed in this case, are most favourable for the substituting of cyanide groups by the incoming ligand. In the case of $Ni_2[Fe(CN)_6]$ where the Ni-N bond energy is larger thant the Ni-O bond, the substitution of CN^- ions by donor centers of dithiooxamide will take place; in the case of $Cu_2[Fe(CN)_6]$ where the Cu-N bond energy is less than the Cu-O bond one, the substitution of CN^- ions by OH^- groups and formation of polymeric Cu(II) hydroxocomplexes takes place and only then their interaction with dithiooxamide will be observed. The fact that the colour of $Cu_2[Fe(CN)_6]$–GIM is changed rather quickly(~5 min) from red brown to greyish-blue corresponding to $[Cu(OH)_2]_n$ at the contact with solutions of KOH or NaOH (pH>10), whereas the colour of $Ni_2[Fe(CN)_6]$–GIM does not change in contact with the above-mentioned solutions, is evidence of this principle. Taking these circumstances into consideration, we can write for formation of Ni(II) and Cu(II) coordination polymers the Schemes 1 and 2, respectively.

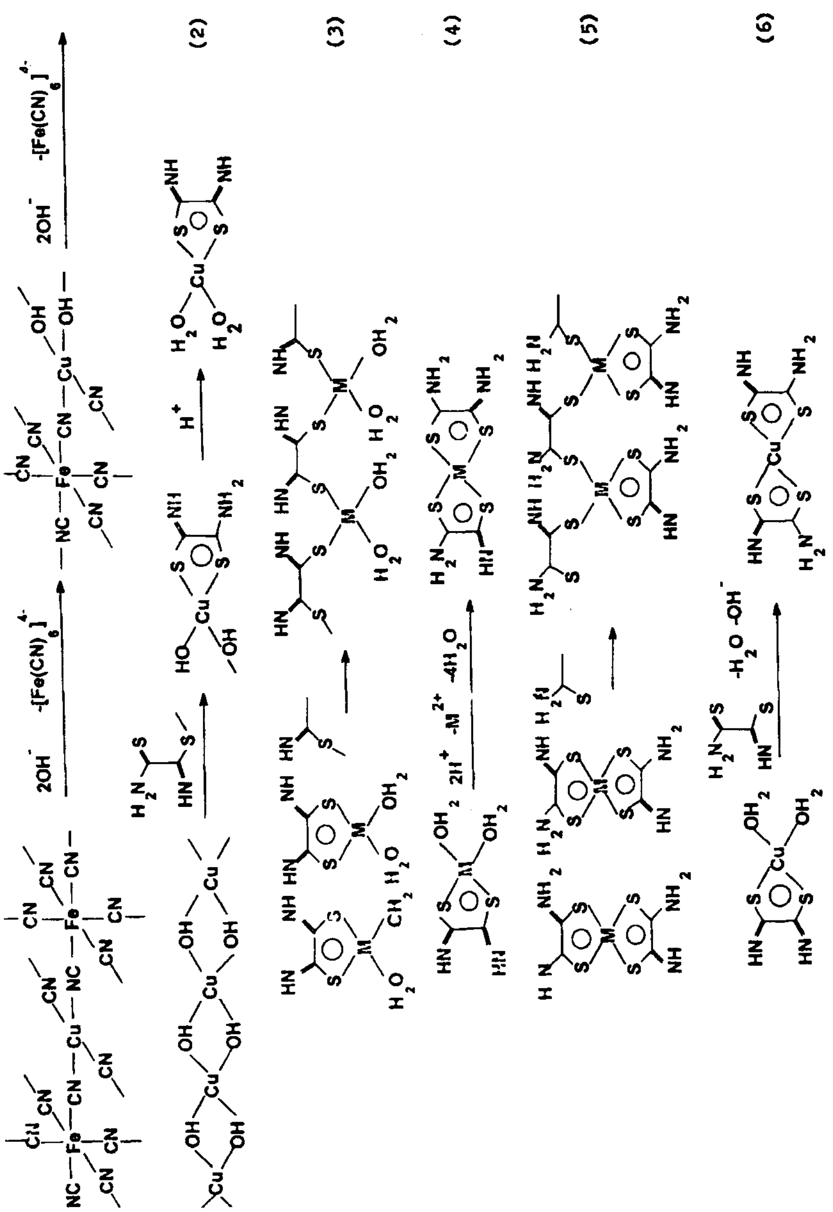
Unfortunatelly, we failed to perform X-ray diffraction analysis of the coordination polymers because, by the method of their isolation from the GIM used in this work, they were obtained in an amorphous state unsuitable for diffraction analysis. For this reason, the exact spatial structure of novel coordination polymers of Ni(II) and Cu(II) with dithiooxamide is still an open question which requires further investigation.

EXPERIMENTAL SECTION

In order to obtain the Ni(II)- and Cu(II)hexacyanoferrate(II) gelatin-immobilized matrix systems, the commercial AgHal-photographic mamaterial PT–12 (Tasma, Russia) was used. On the one hand, this material has a high surface AgHal concentration in photographic layer (up to 25 g/m^2 calculated on free silver); owing



(1)


(2)
(3)
(4)
(5)
(6)
2OH⁻
-[Fe(CN)6]4-
H+
2H+ -M2+ -4H2O
-H2O -OH⁻

to that the matrix systems having a wide range of Ni(II)- or Cu(II)hexacyanoferrate(II) concentrations in the gelatin layer may be obtained. On the other hand, any agents which are able to form stable complexes with Ni(II) or Cu(II) are absent in this material. The samples of PT–12 were exposed to hard ionizing radiation; the exposure dose was varied within (0.001–10) Röntgen. Then, the exposed samples were processed by water solutions containing(g/L): methol 2.2,hydroquinone 8.8,sodium sulphate 96.0, sodium carbonate 48.0, potassium bromide 4.5 (this composition is known as "D–19 developer") for 6 min, by 25% water solution of sodium thio-osulphate for 10 min and, finally, washed with running water for 15 min at 20°C. Then, silver-containing gelatin-immobilized matrices obtained were subjected to two-stage chemical processing. At the first stage, the elemental silver was transformed to AgCl by influence of water solution containin g (g/L): nickel(II) chloride hexahydrate 16.0, trisubstituted sodium citrate 88.0 and potassium hexacyanoferrate(III) 15.0 or $Ag_4[Fe(CN)_6]$ by influence of water solution containing copper(II) sulphate pentahydrate 7.0, trisubstituted sodium citrate 90.0 and potassium hexacyanoferrate(III) 6.0 (with simultaneous precipitation of $Ni_2[Fe(CN)_6]$ and $Cu_2[Fe(CN)_6$, respectively).This processing was carried out for 15-20 min. At the second stage which was realized after washing with running water(for 15 min), the removal of $Ag_4[Fe(CN)_6]$ or AgCl took place by influence of 25% water solution of sodium thiosulphate for 3 min owing to the formation of $Na_3[Ag(S_20_3)_2]$, water-soluble complex; $Ni_2[Fe(CN)_6]$ and $Cu_2[Fe(CN)_6]$ remained in the gelatin layer because they did not interact with $Na_2S_20_3$. The matrices obtained were thoroughly washed with running water for 15 min at 20°C. In order to realize the complexing on such matrices, they were processed with water-alkaline solutions of dithiooxamide having a concentration within (10^{-3}–10^{-1}) mol/L. The pH of these solutions and temperature in the system were kept constant (12.0 ± 0.1 and (20.0 ± 0.1) °C, respectively). The time of contact of matrices with dithiooxamide solution was varied from 1 to 10 min. Finally, the metalcomplex matrices obtained were washed in running water for 15 min and dried at room temperature for 2-3 hours. The gelatin layer thickness of these matrices was 15-25 μm depending on the kind of initial material. The dependences $D = f(C_F, C_L^o, t)$ in the coordinate sections [C_L^o =const, varied t,argument C_F] and [C_F=const, varied C_L^o, argument t] where D is the absorbance of the metalchelate matrix corresponding to metalhexacyanoferrate(II) concentration into gelatin layer (C_F), dithiooxamide concentration in the solution (C_L^o) and the process time(t), were used to describe the kinetics of th complexing. These dependences were analyzed according to a procedure described in.[9] In order to determine the empirical formulas of compounds formed in the matrices, these compounds were isolated from gelatin layers by treating them with solutions of proteolytic enzymes. In addition, the gelatin was split into low molar weight compounds and dissolved, whereas a complex contained in a matrix was precipitated and then isolated from the mother liquor. After washing and drying,the precipitates isolated from matrices were subjected to chemical analysis by a conventional procedure. Molar masses of compounds synthesized were determined by nefelometry. The optical densities of the GIM(D) were measured with a Macbeth TD 504 photometer in the 0.1 –5.0 absorbance units with an accuracy of ±2%. Electron absorption spectra of GIM were recorded using a PU 8710 spectrophotometer (Philips). For IR spectra recording, UR–20 spectrometer (Karl Zeiss) was employed.

Acknowledgements

The **Russian Foundation of Fundamental Researches (RFFR)** is acknowledged for the financial support, grant **N 96–03–32112**.

References

[1] P. Ray, J. Indian Chem Soc., **3,** 118 (1926)
[2] P. Ray, Z. anal.Chemie, **79,** 94 (1930)
[3] K.A. Jensen, Z. anorg allg Chemie, **252,** 227 (1944)
[4] L. Farady, A. Janosi, Magyar kem folyoirat, **63,** 19 (1957)
[5] D.P. Maluga, Zh. Analyt Khim., **10,** 107 (1955)
[6] J. Xavier, P. Ray, Science and Culture, **20,** 455 (1955)
[7] P.V. Marchenko, M.E. Vdovenko, B.I. Nabivanets, Zavod Lab., **27,** 638 (1961)
[8] J. Barcelo, Spectrochim Acta, **10,** 245 (1958)
[9] O.V. Mikhailov, Koord Khim., **18,** 1173 (1992)
[10] T.H. James, The Theory of the Photographic Process, Macmillan Publishing Co., Inc.; New York, Collier Macmillan Publishers, London, 1978.
[11] V.I. Tananaev, G.B. Seifer, V.G. Kouznetsov, A.P. Korol'kov, The Chemistry of Ferrocyanides, Nauka, Moscow, 1971 (in rus.)
[12] Yu.N. Koukoushkin, The Chemistry of Coordination Compounds, Vysshaya Shkola, Moscow, 1986. P.131 (in rus.)
[13] C.H. Langford, H.B.Gray, Ligand Substututed Processes, W.A. Benjamin, Inc., New York - Amsterdam, 1965.
[14] F.A. Cotton, G.W. Wilkinson, Advanced Inorganic Chemistry, Wiley New York - London - Sydney, 1990.
[15] A.B.P. Lever, Inorganic Electron Spectroscopy, Elsevier, Amsterdam - Oxford - New York - Tokyo, 1986.
[16] K. Nakamoto, Infrared Absorption Spectra of Inorganic and Coordination Compounds, Mir, Moscow, 1991.