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Dedicated to Professor Ferenc Paulik on the occasion of this 75th birthday

ON THE OXIMINE COMPLEXES OF TRANSITION METALS

106. Spectroscopic and DSC study of some complexes of the types $[Cu(DioxH)_2]$ and $[CuX_2{\cdot}DioxH_2]$

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Abstract

Several new complexes of the types $[Cu(DioxH)_2]$ and $[CuX_2{\cdot}DioxH_2]$ ($DioxH_2$: aliphatic or alicyclic α-dioxime) were obtained and characterized by means of near and far Fourier transformation IR spectroscopy. The thermal decompositions of seven complexes of these types were studied by using DSC measurement data. For several decomposition stages, apparent kinetic parameters were derived by means of the nomogram method.

Keywords: copper(II)-oxime complexes, DSC, kinetic parameters

Introduction

The oximes of various types, such as α-dioximes, α-keto-oximes, α-hydroxy-oximes, amino-oximes, etc., generally form coloured soluble or very slightly soluble chelates with copper(II) salts, which can be used for different analytical purposes [1–6]. Unlike the sparingly soluble nickel(II), palladium(II) and platinum(II) chelates of the type $[M(DioxH)_2]$, the analogous copper(II) derivatives have been isolated in pure form from aqueous alcoholic solution in only a few cases, and with considerable difficulty.

The X-ray measurements show a dimeric structure for $[Cu(DioxH)_2]$, with pentacoordinated central copper(II) atoms ($DioxH_2$=dimethylglyoxime) [7, 8].

The dimeric structure breaks down in aqueous solution and the monomeric hexacoordinated species $[Cu(DioxH)_2{\cdot}(H_2O)_2]$, $[Cu(DioxH)_2(OH){\cdot}(H_2O)]^-$ and $[Cu(DioxH)_2(OH)_2]^{2-}$ are formed, to extents depending on the pH of the system.

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It is interesting that the interactions of $CuCl_2$ and $CuBr_2$ with some aliphatic dioximes in acetone lead to the formation of $[CuX_2DioxH_2]$ with a single coordinated ligand [9]. These compounds readily decompose in contact with water and the hexacoordinated $[Cu(DioxH)_2{\cdot}(H_2O)_2]$ are formed via a very complicated mechanism. This phenomenon is not observed with other halides or pseudohalides of copper(II) (X=F^-, NO_3^-, N_3^-, NCO^-, NCS^- or $NCSe^-$).

In a previous paper [13], the formation of copper(II) complexes with alicyclic α-substituted oximes {1,2,3-cyclohexanetrione dioxime (1,3), 1,2,3-cyclohexane trione trioxime, 1,2,3-cyclohexanetrione dioxime, 1,3,2-semicarbazone, 1,2,3-cyclohexanetrione dioxime(1,3)-2-thiosemicarbazone} in aqueous solution was studied.

Results and discussion

We observed that the solubility in water of the complexes $[Cu(DioxH)_2]$ is determined by the nature of the groups R, R^* in the ligand:

$$\begin{array}{cc} R-C & C-R^* \\ \| & \| \\ HO-N & N-OH \end{array}$$

With higher alicyclic α-dioximes and O- or N-heterocyclic ones, $[Cu(DioxH)_2]$ can easily be isolated from aqueous solution. Some new derivatives are characterized in Table 1. From the class $[CuX_2{\cdot}Diox]$, seven compounds are summarized in Table 2. The latter compounds also have dimeric structures containing pentacoordinated copper(II).

In the complexes $[CuX_2{\cdot}DioxH_2]$, each copper(II) is bonded to two N atoms of the dioxime and to two chloride ions. The fifth coordination site is occupied by the neighbouring $CuCl_2$·oxime group in a Cl–Cu–Cl linkage bonding.

Table 1 New complexes of type $[Cu(DioxH)_2]$

No.	Formula	Mw/ calc.	Appearance	Analysis calc.		found
1	$[Cu(HeptoxH]_2{\cdot}H_2O$	391.7	irregular, brown prisms	Cu	16.4	16.8
2	$[Cu(OctoxH_2)_2]$	401.9	irregular, brown prisms	N	14.5	14.9
3	$[Cu(TrioxH_2)_{1.5}]$	318.7	brown crops	Cu	15.8	16.2
				N	13.9	13.7
				Cu	19.9	20.1
				N	19.7	19.4

$HeptoxH_2$=1,2-cycloheptanedione dioxime
$OctoxH_2$=1,2-cyclooctanedione dioxime
$TrioxH_2$=1,2,3-cyclohexanetrione trioxime

Table 2 Complexes of type $CuX_2 \cdot$Dioxime

No.	Formula	Mw/ calc.	Appearance (microscopic)	Analysis		
					calc.	found
4	$CuCl_2 \cdot DH_2$	250.5	sparkling deep-green rhombic plates	Cu	25.4	25.1
				Cl	28.3	28.6
5	$CuBr_2 \cdot DH_2$	339.5	olive-green rhombic	Cu	18.7	18.9
				Br	47.1	46.8
6	$CuCl_2 \cdot GlyoxH_2$	222.5	yellow-green rhombic prisms	Cu	28.5	28.9
				Cl	31.9	31.7
7	$CuBr_2 \cdot GlyoxH_2$	311.4	olive-green short prisms	Cu	20.4	20.6
				Br	51.3	51.9
8	$CuCl_2 \cdot$Diamino glyoxime	252.6	dark-green cryst. crops	Cu	25.2	24.6
				Cl	28.1	27.8
9*	$CuCl_2 \cdot PropoxH_2$	278.6	irregular dark-green prisms (sol. in acetone)	Cu	22.8	22.2
				Cl	25.4	24.8
10*	$CuCl_2 \cdot HeptoxH_2$	290.6	sparkling dark-green square plates	Cu	21.9	22.3
				Cl	24.4	23.8

9* and **10*** are new compounds.
DH_2=dimethylglyoxime; $GlyoxH_2$=glyoximes; $PropoxH_2$=methyl-isopropyl-2,3-dione dioxime

The dimeric structure has been confirmed by ESR measurements, revealing a weak ferromagnetic coupling between the two copper(II) spins in the case of [$CuCl_2 \cdot DioxH_2$] ($DioxH_2$=dimethylglyoxime, glyoxime or propoxime) [10–12]. In dioxan solution, all these complexes are transformed into hexacoordinated monomers [12].

The near and far FT IR spectra of the copper(II)-dioxime complexes were recorded. Some important spectral data are presented in Table 3.

As in the case of [M(II)(DioxH)$_2$] [(*M*(II)=nickel, palladium or platinum] and [M(III)(DioxH)$_2$L$_2$]^n [*M*(III)=cobalt, rhodium or iridium], the frequencies ν_{O-H} of the free oximes are shifted from 3300–3100 cm^{-1} to 2300–2400 cm^{-1}, indicating strong intramolecular O–H...O hydrogen-bonding, which stabilizes the coplanar moiety [M(DioxH)$_2$] in the octahedral structure.

In the case of [Cu(HeptoxH)$_2$] besides ν_{O-H} at 2360 cm^{-1}, a strong band appears at 3400 cm^{-1} (cryst. water). The IR spectrum of [Cu(TrioxH$_2$)$_{1.5}$], with three oxime groups, and probably with a macromolecular structure, is more complicated and some overlapping can be observed.

In the spectra of [CuX_2DioxH_2], two strong bands may be observed at 3300–310 cm^{-1} (associated ν_{O-H} vibrations). The $\nu_{C=N}$ bands of the free dioximes appear at 1630–1650 cm^{-1}.

Table 3 FTIR spectral data on some copper(II)-Dioximine complexes

Assignment/	**1**	**2**	**3**	**4**	**5**	**6**	**7**
ν_{O-H}	3419vs	–	3432vs	3302.5vs	3271.7vs	3300vs	3278vs
	3161	3250	3300m	3218.4vs	3227.5vs	3068vs	3185s
ν_{C-H}	2920vs	2933vs	2948m				
	2885vs	2859vs	2880w				
ν_{O-H}	2360vs	2361m	2360m				
(H-bond)	2341vs						
δ_{O-H-O}	1780–1830w	1780–1830w	1780–1830m				
δ_{OH}	1631s			1394vs	1391vs	1406vs	1405vs
$\nu_{C=N}$	1566vs	1536s	1589s	1631.2vs	1630m	1600–1650w	1650s
δ_{CH}	1445vs	1461vs	1430s				
δ_{CH}	1342vs	1357s	1360m				
ν_{N-O}	1222vs	1225s	1257s	1194s	1191s	1252s	1249m
	1187vs	1163vs	1127vs	1088s	1084s	1117s	1110s
γ_{-OH}	952vs	952vs	962s	951w	950w	1001m	998.1m
						906m	
γ_{-C-H}	731m	743s		812m	811m	741m	759m
ν_{Cu-N}	480–490s			476vs	473vs	481s	480s
ν_{Cu-X}				314s	252s	299s	240s
				298s	224s	274s	217s
δ_{N-Cu-N}				228.2m	154m	236.2m	161–145m
δ_{X-Cu-X}				144m 133m	115m 103m	142m 137m	114m 103m

The numbering of complexes is as in the text.

In the IR spectra of $[Cu(DioxH)_2]$, a shift can be observed to 1550–1570 cm^{-1}, similarly as in the case of the mentioned transition metal complexes (strong, covalent $M-N_{oxime}$ bond).

In the spectra of $[CuX_2 \cdot DioxH_2]$, only the band characteristic of the free ligand (1630–1660 cm^{-1}) appears.

The vibrations ν_{N-O} display analogous behaviour.

In both cases, the bands in the region 900–1000 cm^{-1} were overlapped by the vibrations γ_{O-H}. In the spectra of $M(DioxH)_2$, the ν_{N-O} band is split and shifted $\nu_{s(N-O)}$ 1240–1260 cm^{-1} (*vs.*) and $\nu_{as(N-O)}$ 1090–1120 cm^{-1} (*vs.*) (strong, covalent

Cu–N_{oxime} bonds). These spectral data reveal an important difference in the structure of the mentioned copper(II) dioximine complexes.

In the far IR region, the stretching vibrations ν_{Cu-N}, ν_{Cu-Cl} and ν_{Cu-Br} were identified [14].

Because of the appearance of Cu–X and X–Cu...X bridging, ν_{Cu-Cl} and ν_{Cu-Br} are split [15, 16].

In consequence of the lack of information, δ_{N-Cu-X} and δ_{X-Cu-X} and the lattice vibrations can not be identified with the desired precision.

Thermal decomposition of the complexes

A DSC study revealed the existence of 2 or 3 decomposition stages for both $[Cu(DioxH)_2]$ and $[CuX_2{\cdot}[DioxH_2]$. As an example, one TG-DSC curve pair is depicted in Fig. 1. In Table 4, these stages are characterized by the temperature

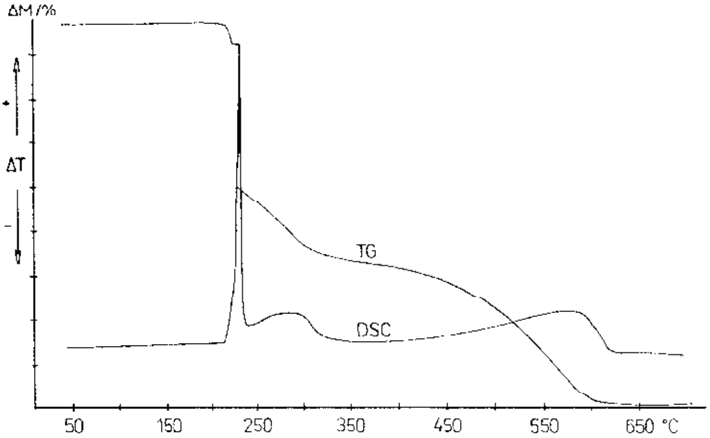

Fig. 1 TG–DSC curves of $CuCl_2$·diaminoglyoxime. Measurements were performed under an argon atmosphere (mass. 6.14 mg)

Table 4 $T_{0.1}$ and ΔM values for different thermal decomposition stages

No.	Stage	a	a	b	b	c	c
	M	$T_{0.1}$/°C	ΔM	$T_{0.1}$/°C	ΔM	$T_{0.1}$/°C	ΔM
1	391.7	113	16.5	208	270	430	23.6
2	401.9	–	–	210	300	450	24.0
4	250.5	227	104	–	–	470	–
5	339.5	224	110	250	46	525	–
6	222.5	184.5	86.5	215	23	454	–
7	311.4	149	43.6	225	74.5	503	–
8	252.6	216	93.4	230	44.2	442	–

$T_{0.1}$ at which the transformation degree is 10%, and by the mass loss ΔM during the whole stage, expressed in molar mass units (Table 4).

In the case of $[Cu(HeptoxH)_2]\cdot H_2O$, stage **a** corresponds to the loss of crystallization water. By taking into account the ΔM values in stages **b** and **c**, for both $[Cu(HeptoxH)_2]$ and $[Cu(OctoxH)_2]$, one may presume that stage **b** corresponds to the transformation

$$2Cu(DioxH)_2 \rightarrow Cu_2CO_3 \tag{1}$$

and stage **c** to the reaction

$$Cu_2CO_3 \rightarrow Cu_2O \tag{2}$$

Theoretical ΔM values corresponding to this scheme would be 280 and 310 ΔM in stage **b** for compound 1 and 2, respectively, and ΔM=22 in stage **c**.

The decomposition of $[CuX_2\cdot DioxH_2]$ seems to occur in the following way. In stage **a**, the organic ligand is lost:

$$CuX_2\cdot DioxH_2 \rightarrow CuX_2 \tag{3}$$

while stage **b** corresponds to $CuX_2 \rightarrow CuX$ (4) and stage **c** consists of the volatilization of CuX. The experimentally found ΔM values are generally consistent with this general scheme, but reactions (3) and (4) are not complete, e.g. for compound **7** the mass loss in stage **a** is only half of the theoretical one. The same behaviour is observed in stage **b**, which is absent for compound **4**, while for **5** the ΔM value is only about 60% of the theoretical one.

As concerns the influence of the ligands X and $DioxH_2$, one may observe that the thermal stability for $X=Cl^-$ is higher that with $X=Br^-$, as shown by the $T_{0.1}$ values of stage **a**. The thermal stabilities of $GlyoxH_2$ derivatives are much lower than those of the DH_2 and $DiaminoglyoxH_2$ complexes.

The integrated DSC curves allowed calculation of the reaction heats of different stages. The results are presented in Table 5.

Since the DSC measurements were performed in an argon atmosphere, the exothermal character of stage **b** for compounds **1** and **2** shows that step (1) is due to a complicated redox reaction. In a similar way, reaction (3) must be a complex formation process since in stage **a** for **4** and **7** two peaks are observed for a single TG step. The endothermal character of this stage is quite surprising for compound **4**, in contrast with the exothermal nature for the analogous complexes. The reason for the endothermal character of stage **b** for compound **7** is not yet clear.

Derivation of kinetic parameters

From the TG curves, apparent kinetic parameters were calculated: reaction order n, activation energy E and pre-exponential factor A. Some decomposition stages occur so rapidly that the TG curve is practically vertical (1b, 2b, 5a and 8a), and consequently no kinetic parameter may be derived.

Table 5 Heat flow and peak temperatures for various decomposition stages

No.	Stage **a**		Stage **b**	
	HF/kJ mol^{-1}	T_m/°C	HF/kJ mol^{-1}	T_m/°C
1	–	–	44.1	196.9
2	–	–	160.6	213.0
4	–35.6	222	–	–
	–6.3	230		
5	78.1	223.2	–	–
7	3.8	153.3	–2.8	196.1
	19.8	178.9	–54.2	264
8	64.4	217.6	–	–

Kinetic parameters were derived by using our nomogram method [17, 18]. The results are presented in Table 6, in which τ denotes the position parameter $\tau = 10^3\, T_{0.1}^{-1}$, where $T_{0.1}$ is the absolute temperature corresponding to the conversion α=0.1.

Inspection of this Table shows that the apparent activation energy E is generally highest for stage **a**, lower for **b** and lowest for **c**. With decreasing E, the log A values also decrease, which is a manifestation of the 'kinetic compensation effect'. As shown earlier [19], this apparent effect obeys a non-linear law:

$$\log A = (RT_{0.1}\ln 10)^{-1}E + \log(qET_{0.1}^{-2}) - 1.85 \qquad (5)$$

In the above relation, E must be given in J and q is in $K\,s^{-1}$.

Equation (5) may also be written in the following form:

$$\log A = 0.0522\tau E + \log(qE\tau^2) - 5.628 \qquad (6)$$

These 'theoretical values' calculated by means of Eq. (6) are given in Table 6 as log$A$. It may be observed that there is excellent agreement between the calculated logA' and the log$A$ values obtained directly from the nomogram.

Experimental

Preparation of [Cu(HeptoxH)$_2$]·H$_2$O, [Cu(OctoxH)$_2$] and [Cu(TrioxH$_2$)$_{1.5}$]

10 mmoles $CuSO_4$ in 150 cm^3 aqueous solution was treated with 20 mmoles oxime in 100 cm^3 alcohol. After standing for 48 h, the brown crystalline hept-

Table 6 Apparent kinetic parameters of thermal decomposition stages

No. stage	τ	*n*	*E*/kJ	log*A*	log*A′*
1a	2.5907	0.95	191.23	23.10	23.14
1c	1.4225	1.22	93.51	3.60	3.60
4a	2.0000	3.16	537.34	53.95	53.93
5b	1.9120	1.24	116.58	8.60	8.65
6a	2.1858	–0.39	173.26	17.05	17.08
6c	1.3755	0.25	80.46	2.30	2.34
7a	2.3697	0.55	102.45	9.82	9.82
7b	2.0080	0.26	50.81	2.03	2.02
7c	1.2887	0.09	93.21	2.82	2.84
8b	1.9881	1.58	135.1	11.14	11.14
8c	1.3986	0.53	86.57	2.85	2.93

oxime and octoxime derivatives were filtered off, washed with water (0°C) and dried in air. [Cu(TrioxH$_2$)$_{1.5}$] was separated after only 20–30 min.

CuX$_2$·Dioxime

10 mmoles CuCl$_2$ or CuBr$_2$ in 50–100 cm^3 acetone was treated with 10 mmoles α-dioxime in 50–100 cm^3 acetone. The crystalline product that separated out was filtered off after standing for 1–6 h, and washed with cold acetone.

Observation

The 1,2,3-cyclohexanetrione trioxime can not be synthesized by the above procedure.

Analysis

Copper(II) contents were determined complexometrically after destruction of the samples with boiling H$_2$SO$_4$ in the presence of a few crystals of KNO$_3$.

Cl and Br contents wer determined potentiometrically in 0.1 M HNO$_3$ solution.

DSC measurements were performed in an argon atmosphere, at a heating rate of 10 K min^{-1}.

* * *

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