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ON THE OXIMINE COMPLEXES OF TRANSITION METALS
Part CXIX. Thermal and spectral studies on Ni(Diox.H)$_2$ type chelate compounds

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Fourteen chelates of the type [Ni(II)(Diox.H)$_2$], ((Diox.H)$_2$: various α-dioximes) have been studied by means of FTIR, NMR, MS data and various thermoanalytical methods (TG, DTA, DTG, DSC). In some cases kinetic parameters of the thermal decomposition of the complexes were also calculated using Zsakó's 'nomogram method'. The mechanism of the decomposition processes was characterised on the basis of mass spectra.

Keywords: *chelate compounds, oximine complexes, Schiff bases, spectral data, thermal stability, transition metal complexes*

Introduction

Thermal behavior of the transition metal derivatives with azomethines (Schiff bases, hydrazones, oximes) stand also in the present, in the attention of the researcher in various branches of theoretical and technical chemistry [1–4].

Nickel(II) chelates of monodeprotonated dioximes: R–C(=NOH)–C(=NOH)–R^x, $R=R^x$ and $R\neq R^x$, R, R^x=H, alkyl, aryl-alicyclic, heterocyclic groups find extensive use in analytical chemistry, especially in the gravimetric and spectrophotometric determination of this metal in various alloys, minerals, rocks, industrial products, waste waters, etc.

Some physico-chemical properties of these compounds have been studied also from the analytical point of view [5–7].

The complexes with alkyl- or aryl-substituted glyoximes have been prepared by the reaction of nickel(II) salts with the appropriate ligand in aqueous or ethanolic solution or in aqueous alcoholic mixtures. In most cases the reaction is promoted by addition of ammonia or base and/or refluxing at a suitable temperature [8–10].

The complexes are always square with general formulas [Ni(Diox.H)$_2$] (Diox.H: monodeprotonated α-dioxime). In the crystal structure the Ni(Diox.H)$_2$ molecules generally stack one over the other to give rise of polydimensional structure which renders the complexes highly insoluble, especially in aqueous solutions [11, 12].

Preparative organic chemistry produces yearly a number of these 1igands (symmetric and asymmetric mixed aliphatic-, aromatic-, alicyc1ic- and heterocyclic α-dioximes) for investigations. Various properties (solubility, thermal stability, spectral data, etc.) of these chelating agents can be influenced by the nature of the groups linked to the –C(=NOH)–C(=NOH)– moiety [13, 14].

Experimental

Chelating agents

The symmmetric α-dioximes were obtained from the corresponding α-dicarbonyl compounds (glyoxal, alicyclic-diketones with NH_2–OH·HCl neutralized with NaOH, or pyridine in alcoholic solution by refluxing.

The asymmetric dioximes are formed by isonitrozation of the R–CO–CH_2–R^x monoketones with gaseous ethyl nitrite at 0...+5°C, followed by oximation of the keto-oximes with NH_2–OH. The crude products were recrystallized from alcohol.

Ni(Diox.H)$_2$

10 mmoles $NiCl_2$ (or $NiSO_4$) in 200 mL water were treated with 20–30 mmoles of NH_3 or CH_3–COONa. 20 mmoles of α-dioxime in 100–150 mL ethanol were added and warmed on a water bath (70–80°C) 30–40 min. The coloured slightly soluble products were filtered off, washed with warm water and dried in air (24–48 h). Note: Ni(*n*-decan-2,3-dione-diox.H)$_2$ was obtained from 96% ethanol [14, 15]. Analysis: Ni% was determined complexometrically after the digestion of 50–60 mg samples with conc. H_2SO_4+some cryst. KNO_3.

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Methods

Infrared spectra

The far IR spectra were recorded with a Bio-Rad-Ninn spectrophotometer in polyethylene pellets, while the middle FTIR ones with a PerkinElmer 2000 apparatus in KBr pellets.

Thermal analysis

The thermal measurements were carried out on a DuPont Instruments thermal analysis system in argon and nitrogen atmospheres. Sample mass 5–10 mg; heating rate: 10 K min^{-1}.

Mass spectra

The mass spectra were recorded with a VG ZAB-2 SEQ apparatus by direct introduction of the samples. Ionization: EI.

Results and discussion

In the present study, 14 nickel(II) oximine derivatives were obtained. The compounds are characterized in Table 1, $Ni_2(TrioxH_2)_3$ is also included in this table.

The symmetric derivatives (R=R^x) are generally insoluble in water and methanol or ethanol. They are soluble in apolar solvents CCl_4, $CHCl_3$, benzene, etc. The asymmetric ones with longer carbon chains in R^x (-butyl, -hexyl, etc.) are soluble in alcohol, too.

Infrared spectra

In the FTIR spectra of the free oximes and the mentioned coordination compounds the most important absorption bands belong to the various vibration frequencies of the oxime groups (Table 2).

$\nu_{O–H}$: 3400–3100 cm^{-1} (2–3 strong, broad bands); $\nu_{C=N}$: 1680–1650 cm^{-1} (by the non-conjugated systems), 1650–1610 cm^{-1} (by the conjugated ones); $\nu_{N–O}$: 950–980 cm^{-1} (a single band).

Table 1 $Ni(Diox.H)_2$ type complexes

No.	Formula	Molecular mass calcd.	Aspect	Analyis		
					calcd./%	found/%
I	$[Ni(Glyox.H)_2]\cdot H_2O$	250.8	red microcryst.	Ni H_2O	23.3 7.2	23.1 6.8
II	$[Ni(DMG.H)_2]$	288.9	red-violet microcryst.	Ni	20.3	20.2
III	$[Ni(Me\text{-}Et\text{-}Diox.H)_2]$	316.9	red-brown microcryst.	Ni	18.5	18.7
IV	$[Ni(Propox.H)_2]$	345.0	orange-brown microcryst.	Ni	17.0	17.2
V	[Ni(*n*-Decan-2,3-dion diox.H)$_2$]	456.7	orange red irreg. prisms	Ni	12.85	12.75
VI	$[Ni(Diamino\text{-}glyox.H)_2]$	292.9	orange-brown microcryst.	Ni	20.0	20.15
VII	$[Ni(Cpdox.H)_2]$	312.9	tile red cryst.	Ni	18.75	18.5
VIII	$[Ni(Niox.H)_2]$	340.9	red-violet gelatinous mass	Ni	17.2	17.35
IX	$[Ni(Heptox.H)_2]$	369.0	orange-brown microcryst.	Ni	15.9	16.1
X	$[Ni(Octox.H)_2]$	397.0	orange-brown microcryst.	Ni	14.8	14.7
XI	$[Ni(Triox.H)_2]_{1.5}$	255.2	red-violet gelatinous mass	Ni	18.7	18.5
XII	$[Ni(Phenil\text{-}glyox.H)_2]$	385.0	red-brown microcryst.	Ni	15.24	15.4
XIII	$[Ni(Benzyl\text{-}Me\text{-}glyox.H)_2]$	445.1	orange-brown microcryst.	Ni	13.2	13.1
XIV	$[Ni(Furox.H)_2]$	497.1	red-violet	Ni	11.8	11.6

I – $(Glyox.H)_2$: HC(NOH)CH(=NOH); II – $(DMG.H)_2$: $CH_3–C(=NOH)–C(=NOH)–CH_3$; III – $(Me\text{-}Et\text{-}Diox.H)_2$: $CH_3–C(=NOH)–C(=NOH)–C_2H_5$; IV – $(Propox.H)_2$: $CH_3–C(=NOH)–C(=NOH)–C_3H_3$; V – (*n*-Decan-2,3-dion diox.H)$_2$: $CH_3–C(=NOH)–C(=NOH)–(CH_2)_6–CH_3$; VI – $(Diamino\text{-}glyox.H)_2$: $H_2N–C(=NOH)–C(=NOH)–NH_2$; VII – $(Cpdox.H)_2$: $C_5H_6(=NOH)_2$; VIII – $(Nyox.H)_2$: $C_6H_8(=NOH)_2$; IX – $(Heptox.H)_2$: $C_7H_{10}(=NOH)_2$; X – $(Octox.H)_2$: $C_8H_{12}(=NOH)_2$; XI – $(Triox.H)_3$: $C_6H_6(=NOH)_3$; XII – $(Phenil\text{-}glyox.H)_2$: $C_6H_5–C(=NOH)–C(=NOH)–H$; XIII – $(Benzyl\text{-}Me\text{-}glyox.H)_2$: $C_6H_5–CH_2–C(=NOH)–C(=NOH)–CH_3$; XIV – $(Furox.H)_2$: $C_4H_3O–C(=NOH)–C(=NOH)– C_4H_3O$

Table 2 Some FTIR spectral data of $Ni(Diox.H)_2$ type complexes

ν/cm^{-1}	III	IV	VIII	IX	X	XI	XII	XIII
ν_{O-H}	–	–	–	–	–	3240–3160vs	–	–
$\delta_{O-H..O}$	1750–1790m	1730–1760m	1720–1800w	1740–1790m	1760–1820m	1700–1800m	1700–1800m	1720–1800m
$\nu_{C=N}$	1564vs	1562vs	1575vs	1570vs	1565vs	1610s 1575s	1544s	1559vs
$\nu_{C-C_{(arom)}}$	–	–	–	–	–	–	1495vs	1494vs
ν_{N-O}	1235vs	1234vs	1240vs	1235vs	1245vs	1235vs	1260vs	1241vs
ν_{N-O}	1110vs	1077s	1090vs	1095vs	1105vs	1050vs	1074s	1063vs
$\nu_{N-O_{(free)}}$	–	–	–	–	–	985s	–	–
ν_{Ni-N}	513vs	516vs	520s	518vs	520vs	530s	512s	515s
δ_{N-Ni-N}	202m	205m	205m	210m	206m	–	205m	207m

vs – very strong, s – strong, m – medium, w – weak; ν – vibration

The above frequencies of the free ligands are modified by coordination to the transition metals.

In the spectra of the Ni(II) complexes the ν_{O-H} bands disappear, and the azomethine stretching vibrations are shifted to lower frequencies (1550–1570 cm^{-1}).

The N–O band is splitted in two parts and shifted to higher frequencies (1100–1250 cm^{-1}). The $\nu_{C=N}$ and ν_{N-O} shifts prove the strong covalent character of the Ni–N bonds. The weak band at 1700–1800 cm^{-1} can be assigned to the $\delta_{O-H...O}$ deformation vibrations of the very short intramolecular hydrogen bonds, which stabilize the molecule.

In the far infrared region appear the ν_{Ni-N} stretching vibration and various δ_{N-Ni-N} deformation vibrations, as well as skeleton vibrations of the chelate rings, generally overlapping by other deformation vibrations $\delta_{(CH_3)_t}$, $\delta_{(C=N)_t}$, δ_{CNO}, etc.) [16–17].

^1H and ^{13}C NMR spectral data

In the ^1H NMR spectra of all Ni(II) chelates the proton resonance signal of the intramolecular hydrogen bridge appears at 17.5–18.2 ppm. This chemical shift is very great, higher than the values observed in the spectra of the enoles, aldehydes and carboxylates (12–15 ppm).

The value observed proves the high stability of this hydrogen bridge and the coplanar geometric configuration of the chelate molecules. The splitting of this signal is due to the *cis–trans* izomerism of the complexes with asymmetric α-dioximes.

The ^{13}C NMR resonance signal of the azomethine group appears at 145–170 ppm, influenced by the neighbouring groups of the molecule. In the case of the mentioned nickel(II) derivatives this signal can be observed at 151–154 ppm, generally splitted [18, 19].

Thermal behaviour of the [Ni(Diox.H)$_2$] complexes

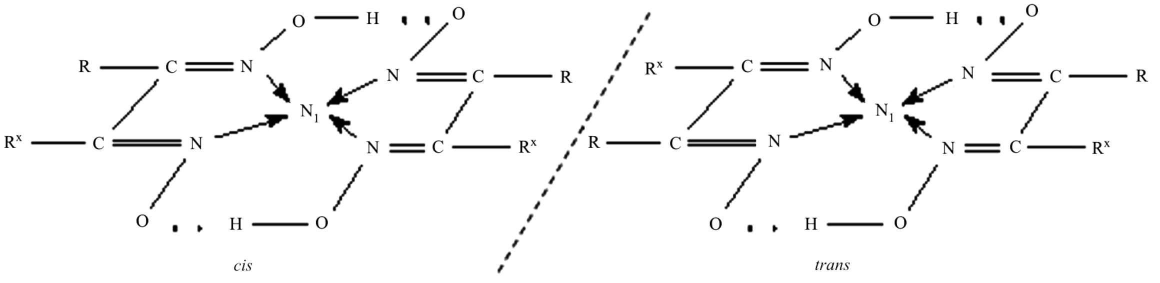
The description of the thermal decomposition of the oximine complexes of some transition metals is necessary from the analytical chemical point of view. Using TG measurements, one can determine the temperature range of the thermal stability, where the above mentioned complexes can be dried without decomposition.

Some metal complexes with organic ligands have been studied by means of TG, DTG and DTA measurements [1–3], especially for gravimetrical purposes.

Our thermoanalytical results are summarised in Table 3. We observed that the majority of the oximine complexes do not have a reproducible melting point and decompose to a dark resinous mass, accompanied with evolution of gaseous products.

The TG, DTA measurements show that the thermal stability of the $Ni(Diox.H)_2$ complexes is higher than that of the free, non-coordinated α-dioximes, since the free =C=NOH groups participate in some internal redox decomposition processes. The electron donor properties of the =C=N– groups are influenced by the nature of *R* and R^x radicals. For this reason the force constants of Ni–N (oxime) bonds and the temperature ranges of the decomposition depend on chemical composition.

The following empirical stability order was established for the studied complexes:



cis *trans*

Table 3 Thermoanalytical data of Ni(Diox.H)$_2$ type complexes

Method	I	II	III	IV	VI	VII	VIII	IX	X	XI	XII[*]	XIII	XIV
TG – thermal stability													
T/°C	20–80	20–280	20–210	20–192	20–50	20–180	20–190	20–190	20–200	20–140	20–225	20–235	20–230
$-\Delta m$/%	0	0	0.5	0	0	0	20	0	0	0	0.5	0	0
I. step													
T/°C	90–120	285–290	220–280	195–275	55–80	200–250	190–230	250–260	270	150–180	228–275	240–265	240–270
$-\Delta m$/%	6–7	42	20	38	25	43	43	41–42	42–43	60	12.9	27.9	35
II. step													
T/°C	185–200	300–480	282–284	278–315	120–250	260–400	250–400	280–400	290–400	200–350	280–313	268–325	300–400
$-\Delta m$/%	8–73	37	36.5	14.1	50	38	40	32–34	33–35	20	10	11.4	38
III. step													
T/°C	–	–	–	315–318	–	–	–	–	–	–	315–318	–	–
$-\Delta m$/%	–	–	–	20	–	–	–	–	–	–	27	–	–
–(Diox.H) calcd.%	34.7	40	40.7	41	40	40.6	41.5	42	42.6	54	42.3	43	44
(Diox.H) calcd.%	69.3	79.8	81.4	82.4	80	81	83	84	85.2	81	84.5	86.5	88
DTA													
T/°C (peak)	endo: 75, 312 exo: 245, 345	exo: 260, 320, 430, 535	exo: 258	endo: 153, 228, 274 exo: 307, 420	endo: –550 exo: 341	exo: 240, 320, 420, 530	exo: 260, 320, 430	exo: 265, 320, 430 endo: 563	exo: 270, 320, 440	exo: 110, 140, 400 endo: 190	exo: 267, 313	exo: 262, 314	exo: 283, 313
DTG													
T/°C (peak)	100, 190	310	286	275, 307	–	250	260	270	280	–	231.4	166, 257, 313	–
DSC													
T/°C (peak)	endo: 215, 312 exo: 250, 345	311	–	280, 297	277	endo: 260	endo: 290	–	290, 307	–	–	–	exo: 283, 315, 759 J g^{-1}

[*] example: Fig. 1

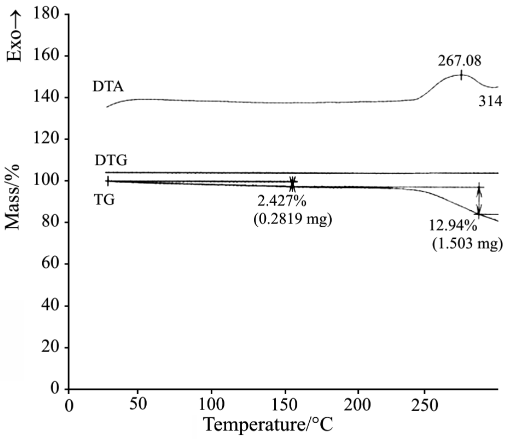


Fig. 1 Thermoanalytical curves for [Ni(monophenyl-glyox.H)$_2$] complex

- with aliphatic dioximes: II>III>IV>VI>V
- with oximes of various types:

II>III>XIV>XIII>XII>XI>X>IX>VIII>VII

The symmetric derivatives have higher stability than the asymmetric ones. The decomposition temperature decreases with increasing –C–C– chain length in the R^x group. The majority of the Ni(II) complexes of the mentioned type decompose suddenly (steep steps on the TG-curves) and in some cases also with explosion (bifurcate steps). On the TG curves in some cases one or two steps can be observed by stoichiometric ratios: Diox.H/Ni(Diox.H)$_2$=0.85–1.1 corresponding to the loss of the two Diox.H ligands in subsequent steps. The reaction probably starts with the dissociation Ni(Diox.H)$_2$→Ni(Diox)$^+$+Diox.H$^-$.

The TG and DTA measurements in inert gas atmosphere exclude the participation of air in the decomposition processes.

The TG curves of the studied compounds only in a few cases are suitable for the evaluation of decomposition kinetics. Kinetic parameters of the thermal decomposition of [Ni(Propox.H)$_2$] (No. IV) and [Ni(Diamino-glyox.H)$_2$] (No. VI) have been calculated using Zsakó's 'Nomogram method' [20–22]. The results are summarized in Table 4.

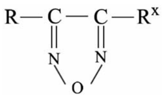
The shape and position parameters (τ, Δ, ∇) were calculated from the $T_{0.1}$, $T_{0.5}$, and $T_{0.9}$. The approximate kinetic parameters n_1, E_1 and $\log A_1$ obtained in the first approximation from the nomogram [16] are shown in the upper part of the table. From the reduced shape and position parameters (∇^x, Δ^x, τ^x) obtained with an iterative procedure, the apparent kinetic parameters (n, E and $\log A$) were calculated. The results are shown in the lower part of the table.

Mass spectra

In the mass spectra of the complexes the peak of the Ni(Diox.H)$_2$ molecule ion (M$^+$) appears with high intensity ratios (60–l00%). The metal containing fragments, Ni(DioxH)NO, Ni(Diox.H) show an intensity of only 3–40% and 3–30%, respectively (Table 5).

The isotopic effect of ^{58}Ni(67%), ^{60}Ni(26%), ^{63}Ni(3.7%) can be also observed in the case of Ni containing molecule ions.

In the majority of the mass spectra one can observe the peaks of the free ligands, the 3,4-substituted furazans (dehydration products of the dioximes):



various nitrils, alkyl- and aryl-, and $C_nH_m^+$ ions, intermediary products with –C–C– chains (1–50–70% values, the latter having very short lifetimes) [22–24].

On the basis of the mass spectra the following thermal decomposition mechanism can be proposed:

Ni(Diox.H)$_2$→Ni(Diox.H)(Furazan)→
Ni(Diox.H)NO→Ni(Diox.H)

Ni(Diox.H)→Ni(Furazan)→Ni(nitrile)+various free and deprotonated dioximes, furazans, and other fragment ions.

These MS results confirm the assumptions based on the thermogravimetrical curves, i.e., that the first step in the sequence of reactions is the dissociation of the chelate: Ni(Diox.H)$_2$ = Ni(Diox.H)$^+$ + Diox.H$^-$

A similar phenomenon was observed also in the case of Pd(Diox.H)$_2$ and Pt(Diox.H)$_2$ derivatives (results to be published in following papers).

Table 4 Kinetic parameters of the thermal decomposition of [Ni(Propox.H)$_2$] (No. IV) and [Ni(Diamino-glyox.H)$_2$] (No. VI)

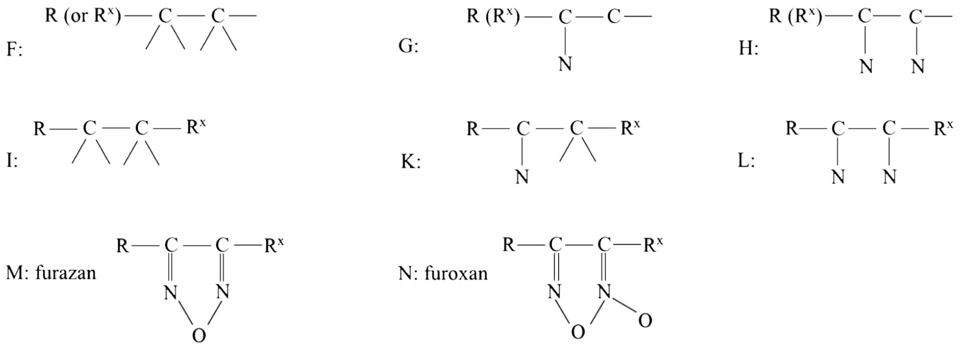
Complex	$T_{0.1}$	$T_{0.5}$	$T_{0.9}$	Δ^x	∇^x	n_1	Δ_1^x	E_1/kcal mol^{-1}	$\log A_1$
[Ni(Propox.H)$_2$]	498	523	535	96	0.309	0.380	90.369	33.04	11.07
[Ni(Diamino-glyoxime)$_2$]	326	340	350	126	0.398	1.120	105.625	24.810	7.88

Complex	∇^x	τ^x	Δ_2^x	n	E/kcal mol^{-1}	$\log A$	$\log A^x$
[Ni(Propox.H)$_2$]	0.309	1.965	91.383	0.313	32.758	12.312	11.54
[Ni(Diamino-glyoxime)$_2$]	0.398	3.013	107.379	1.068	28.364	16.044	16.44

Table 5 Mass spectral data of some [Ni(Diox.H)$_2$] type complexes

Formula	*m/z*
[Ni(DMG.H)$_2$]	28 (4%) A, 39 (12%) E, 41 (6%) B, 42 (7.5%) C, 53 (3%) F, 67 (5%) I, 68 (5%) K, 82 (2%)L, 99 (15%) M, 115 (30%) O, 116 (11%) P, 157 (3%) S, 174 (31%) U, 204 (26%) V, 272 (3%) W, 288 (100%) X, 290 (42%) X
[Ni(Me-Et-Diox.H)$_2$]	28 (12%) A, 30 (2%) B, 39 (23%) VI, 41 (37%) D, 55 (9%) D, 56 (12%) D, 67 (12%) G, 81 (4%) G, 99 (19%) M, 130 (24%) N, 169 (67%) S, 187 (17%) U, 299 (4%) Z, 316 (75%) X, 318 (30%) X
[Ni(Propox.H)$_2$]	28 (5%) A, 30 (25%) B, 41 (42%) D, 55 (6%) G, 68 (18%) F, 70 (19%) D, 81 (3%) G, 99 (30%) M, 127 (40%) M, 144 (32%) N, 184 (17%) T, 202 (26%) U, 232 (55%) V, 327 (8%) Z, 344 (100%) X, 346 (40%) X
[Ni(Phenyl-glyox.H)$_2$]	27 (3%) E, 28 (4%) A, 39 (13%) F, 77 (65%) R, 147 (95%) M, 164 (55%) R, 220 (3%) U, 222 (19%) U, 251 (30%) V, 351 (10%) W, 368 (8%) Z, 384 (55%) X, 386 (25%) X
[Ni(Me-benzyl-Diox.H)$_2$]	28 (5%) A, 30 (3%) B, 31 (3%) C, 41 (25%) D, 39 (15%) F, 67 (25%) H, 115 (10%) E, 117 (75%) –, 129 (5%) –, 130 (22%) I, 143 (15%) H, 144 (18%) K, 158 (43%) L, 174 (22%) M, 190 (2%) N, 192 (77%) P, 232 (12%) S, 249 (35%) U, 279 (35%) V, 407 (8%) W, 424 (8%) Z, 440 (60%) X, 442 (30%) X

Symbols: A: N_2 or CO, B: NO, C: NOH, D: R–CN, E: R^x–CN,



O: Diox.H, P:(Diox.H)$_2$, R: alkyl, aryl radicals, S: Ni(furazan), T: Ni(furoxan),
U: Ni(Diox.H), V: Ni(Diox.H).NO, W: Ni(furazan)$_2$, Z: Ni(Diox.H)furazan, X: Ni(Diox.H)$_2$

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