Pyrazoles and Imidazoles as Ligands, XIX*

Complex Formation Between Imidazole and Nickel(II) Salts

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(Z. Naturforsch. **29b**, 527–531 [1974]; received May 16, 1974)

Pyrazole, Imidazole, Nickel(II)salts, Ligands

Coordination compounds of formula $Ni(Iz)_nX_2(H_2O)_m$, in which Iz = imidazole, n = 1, 2, 4, 6, m = 0–4, and X = Cl^-, Br^-, I^- and NCS^-, are described. The anhydrous compounds are prepared from ethanolic solutions of Iz and nickel(II) salts in stoichiometric amounts in the presence of the dehydrating agent triethylorthoformate. Without this dehydrating agent hydrates are isolated for n = 2,4 and 6 with X = Cl, Br.

The compounds were identified by means of infrared spectra (4000–25 cm^{-1}), ligand-field spectra (35000–4000 cm^{-1}) and X-ray powder diagrams. Compounds of formula $[Ni(Iz)_6]X_2$ all contain octahedrally coordinated Ni^{2+}, for which the spectrochemical parameters were obtained. Tetragonal Ni^{2+} ions occur in $[Ni(Iz)_4X_2]$ in which X = Cl and NCS, and in $[Ni(Iz)_4(H_2O)_2]X_2$ in which X = Cl and Br. These compounds are paramagnetic and the crystal-field parameters for tetragonal symmetry have been calculated. In $[Ni(Iz)_4]X_2$ with X = I and Br, the Ni^{2+} ions are square-planar coordinated with anions in the second coordination sphere, resulting in orange-coloured diamagnetic compounds.

Anion-bridged distorted octahedrally coordinated Ni^{2+} ions probably occur in the compounds of formula $Ni(Iz)_2X_2$, in which Iz takes the axial positions. Similar structures are suggested for the mono-imidazole compounds, $NiIzX_2$.

It is well known that complex formation between imidazole groups and metal ions plays an important role in several cell processes[1]. Especially the role of magnesium and calcium ions in such processes is hardly known[1,2]. We are currently investigating this field by preparing and characterizing model compounds containing Ca(II) and Mg(II) coordinated by imidazole (abbreviated Iz).

Since magnetic and spectroscopic techniques that are usually applied for characterization of coordination compounds and for information about the geometry, are not very useful for the study of Ca and Mg compounds, we decided to compare the properties of imidazole complexes of Ca and Mg with those of Ni(II). Ni(II) complexes have the advantage of easy spectroscopic and magnetic characterization[3], and in addition Ni(II) and Mg(II) behave as ions of similar size[4].

We will report in this paper our results for some Ni(II) imidazole compounds, since we found a few conflicting and erroneous literature reports on nickel-imidazole halides. For comparison the system $Ni(NCS)_2$-imidazole has also been studied, which has not been described in the literature.

Extensive studies of spectroscopic properties have been reported for $Ni(Iz)_6X_2$, with X = ClO_4, BF_4[5–7] and NO_3[6,8,9]. For the latter compound a crystal-structure determination has appeared[9].

Experimental

Syntheses

Nickel(II) salts were commercially available as the hydrates, as was imidazole (Aldrich).

Compounds of formula $Ni(Iz)_n(anion)_2(H_2O)_m$ were obtained by mixing stoichiometric amounts of imidazole and Ni(II) salts in ethanol. Crystals of the compounds appeared upon cooling or addition of diethylether. Metal analyses showed that the number of water molecules was about 2, although thermogravimetric analyses[10] indicated that values

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* Part XVIII. H. Okkersen, W. L. Groeneveld, and J. Reedijk, Rec. Trav. Chim. **92**, 945 [1973].

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from 1.0–2.5 may occur, depending upon the particular sample.

In addition compounds of formula $Ni(Iz)_6(anion)_2(H_2O)_4$, with Cl^- and Br^- as anions, were obtained from aqueous ethanol solutions.

Anhydrous compounds $Ni(Iz)_n(anion)_2$ were prepared from stoichiometric amount of imidazole and Ni(II) salts in ethanol in the presence of triethylorthoformate for dehydration[11]. However, for the preparation of $Ni(Iz)_6(NSC)_2$ a molar ratio of 8 : 1 was necessary, whereas $Ni(Iz)_4Cl_2$ was best prepared by dehydration of its dihydrate *in vacuo* (1 mm Hg) at 100 °C.

It appeared difficult to obtain pure samples of $Ni(Iz)_2I_2$ and $NiIzI_2$; most samples appeared to be contaminated with the – very stable – $Ni(Iz)_4I_2$, as concluded from spectral measurements.

All compounds were analysed for Ni(II) by complexometric titration with EDTA[12]. In a few cases also halogen, carbon, hydrogen and nitrogen determinations were carried out.

Spectral measurements

Infrared spectra were recorded as Nujol mulls between sodium chloride plates on a Hilger and Watts spectrophotometer (4000–650 cm^{-1}) and between polythene plates on a Perkin Elmer 521 spectrophotometer (700–250 cm^{-1}).

Ligand field spectra were performed on a Beckman DK-2 ratio recording spectrometer, furnished with a reflectance attachment (35,000–4000 cm^{-1}).

X-ray powder diagrams were taken with Guinier-de Wolff cameras using Cu–Kα radiation. The samples were mulled with vaseline.

Results and Discussion

General

All compounds thus far found in the system Ni(II)–Iz–X, with X = Cl, Br, I, NCS and their stable hydrates are listed in Table I, together with their colours, melting points, analytical data and X-ray powder-diffraction types. The division into these X-ray types was made according to the line patterns, that are similar in *d*-values and relative intensities.

It appeared that the compounds $Ni(Iz)_6X_2$, with X = Cl, Br and NCS, easily take up water from the atmosphere in non-stoichiometric amounts, *i.e.* varying from 1–2.5 moles per Ni. Only for X = Cl such a compound has been included in Table I. The fact that these water molecules are weakly bound in the lattice is illustrated by the X-ray line patterns, which do not differ markedly from the anhydrous compounds, and by the thermogravimetric behaviour of these compounds[10], which in-

Table I. Nickel(II) imidazole compounds and their hydrates, with colours, melting points and analytical data.

Compound	Colour	Melting point [°C]	X-ray type	%M		Remarks
				Found	Calcd	
$Ni(Iz)_6Cl_2$	violet	260	A	11.0	10.9	a, b, d
$Ni(Iz)_6Cl_2(H_2O)_1$	violet	260	A	10.7	10.6	f
$Ni(Iz)_6Cl_2(H_2O)_4$	violet	260	B	9.61	9.69	g
$Ni(Iz)_6Br_2$	violet	270	A′	9.30	9.36	a, b, d
$Ni(Iz)_6Br_2(H_2O)_4$	violet	270	B′	8.50	8.49	h
$Ni(Iz)_6I_2$	violet	273	A′	8.12	8.14	a
$Ni(Iz)_6(NCS)_2$	violet	126	–	10.3	10.1	k
$Ni(Iz)_4Cl_2$	blue-green	255	–	14.2	14.6	b, c, d
$Ni(Iz)_4(NCS)_2$	violet	230	–	13.3	13.1	–
$Ni(Iz)_4Br_2$	orange-brown	235	C	12.2	12.0	b, c, d
$Ni(Iz)_4I_2$	orange-brown	230	C	10.2	10.0	b, c, d
$Ni(Iz)_4(H_2O)_2Cl_2$	blue	255	D	13.4	13.4	d
$Ni(Iz)_4(H_2O)_2Br_2$	blue	235	D	11.3	11.1	d
$Ni(Iz)_2(H_2O)_2Cl_2$	green	>300	–	19.7	19.6	l
$Ni(Iz)_2(H_2O)_2Br_2$	green	>300	–	15.5	15.2	–
$Ni(Iz)_2Cl_2$	yellow-green	>300	–	21.2	22.1	c
$Ni(Iz)_2Br_2$	yellow	>300	–	16.3	16.5	c, e
$Ni(Iz)_2I_2$	brown	>300	–	13.3	13.1	c, e
$Ni(Iz)_2(NCS)_2$	blue-green	>300	–	19.1	18.9	–
$NiIzCl_2$	yellow	>300	–	29.2	29.7	c, d
$NiIzBr_2$	yellow-orange	>300	–	19.7	20.5	c, d
$NiIzI_2$	brown	>300	–	15.4	15.4	c, e
$NiIz(NCS)_2$	olive green	>300	–	24.3	24.2	

a Also reported by EILBECK[6]; b From literature spectral data some of these compounds appear to be hydrated; c Also described by TAYLOR[13]; d Also described by GOODGAME[8]; e Literature spectra of these compounds indicate contamination with $Ni(Iz)_4X_2$; f %Cl: 12.8 (calcd 12.8); g %Cl: 11.2 (calcd 11.8); h %Br: 22.5 (calcd 23.1); k %C: 41.3 (calcd 41.2); %H: 4.3 (calcd 4.2); %N: 33.4 (calcd 33.6); l %Cl: 24.1 (calcd 23.8).

dicates that water molecules are removed at 50–80 °C from the lattice.

The compounds $Ni(Iz)_6X_2(H_2O)_4$, with X=Cl and Br, prepared from aqueous ethanol solutions, also contain water molecules not directly bound to the Ni(II) ion *(vide infra)*, but now the influence upon the imidazole molecules seems larger, as concluded from the different X-ray type (Table I). It is found, however, that already at about 35 °C a phase transition occurs to the other structure, accompanied with the loss of some water.

As already indicated in Table I, it appeared that some of the literature products were in fact hydrates, as can be concluded from the published spectral data *(vide infra)*. The fact that some of the compounds mentioned in Table I were not obtained by previous workers, can also be explained by the hygroscopic properties of these compounds. Only when sufficient dehydrating agent is present, anhydrous compounds of formula $Ni(Iz)_4X_2$, $Ni(Iz)_2X_2$ and $NiIzX_2$ can be isolated, with the exception of $Ni(Iz)_4Cl_2$ which can only be prepared pure by dehydration of its dihydrate *in vacuo*. Melting together anhydrous Ni(II) salts and imidazole in the desired ratio always results in mixtures of compounds or hydrated products.

Infrared spectra

For a first characterization of the compounds infrared spectra were recorded and compared with literature data for other imidazole compounds[5]. The absence or presence of water was easily determined from the IR spectra, although sometimes overlap occurs between the N–H stretch of imidazole and the O–H stretch of water. We found however, that definite evidence for the absence or presence of water comes from an IR combination band at about 5000 cm^{-1} (OH stretching + OH bending), which is observed in the solid-state diffuse reflectance spectrum.

The possible interference between O–H stretching and N–H stretching around 3400 cm^{-1} may be the origin of some discrepancies in the literature[8, 13].

In addition to the X-ray isomorphism, we found that within a group of powder-isomorphous compounds (see Table I) very similar infrared spectra are observed, with regard to line patterns (splittings and relative intensities).

Infrared spectra of the thiocyanate compounds give direct information about the manner of binding to the metal ion[14]. Some data of our compounds are listed in Table II. The occurrence of free, uncoordinated NCS^- ions in $Ni(Iz)_6(NCS)_2$ can be directly concluded from the bands around 2020 and 485 cm^{-1}. Nitrogen-coordinated NCS^- ions in $Ni(Iz)_4(NCS)_2$ are recognized from bands at 2100 and 475 cm^{-1}. The fact that the 2100 cm^{-1} band occurs sharp and unsplit agrees with a *trans*-geometry for the two NCS^- ions. The IR absorptions due to NCS for the remaining compounds are in agreement with coordination *via* both nitrogen and sulfur, as is expected from ligand-field spectra (see below). Unfortunately, the C–S stretching vibrations which are also indicative of the manner of coordination, cannot be distinguished among the numerous imidazole bands from 700–900 cm^{-1}.

Table II. Infrared spectral data for thiocyanate compounds.

Compound	ν_{CN} stretching*	ν_{CNS} bending**
$Ni(Iz)_6(NCS)_2$	2020	480, 488
$Ni(Iz)_4(NCS)_2$	2100	470, 475
$Ni(Iz)_2(NCS)_2$	2120	460 br
$NiIz(NCS)_2$	2125, 2155	450, 460, 470sh

* Band positions are accurate to 5 cm^{-1}; sh=shoulder; br=broad;

** bands due to the C–S stretching could not be assigned unambigiously, due to the presence of numerous imidazole absorptions in the 700–900 cm^{-1} region.

The far-IR spectra of all compounds, except the yellow-orange diamagnetic $Ni(Iz)_4X_2$ compounds with $X=Br^-$ and I^-, show a broad band around 265 cm^{-1} which is split in some cases. This band can be assigned to Ni–N vibrations in six-coordinate Ni(II) compounds[5, 8]. The diamagnetic, square-planar coordinated compounds, on the other hand, have a much stronger Ni–N bond, as reflected by the absorption at about 390 cm^{-1} which is assigned to a Ni–N stretching[8]. A second band in these compounds, at 330 cm^{-1}, is tentatively assigned to a Ni–N bending or a Ni-ligand wagging. We observed that impurities in the compounds $NiIzX_2$ and $Ni(Iz)_2X_2$ are readily recognized by the absorptions at 390 and 330 cm^{-1} and are ascribed to $Ni(Iz)_4X_2$.

Since the products reported by TAYLOR *et al.*[13] show these bands, we conclude that those products are contaminated with $Ni(Iz)_4X_2$.

Ligand-field spectra

Solid coordination compounds are easily studied by the diffuse reflectance technique, and a lot of

Table III. Diffuse reflectance spectra of Ni(II) imidazole compounds; band maxima are in kK. Ligand-field maxima are assigned according to refs. 3 and 16; calculated parameters are in cm^{-1} and are accurate 10 cm^{-1}.

Compounds	IR-overtones[a]		Ligand-field maxima and assignments[b]						Absorbing species	Ligand-field parameters			
Octahedral Ni:	N–H	O–H		$^3T_{2g}\leftarrow$	$^1E_g\leftarrow$	$^3T_{1g}$ (F)$\leftarrow$		$^3T_{1g}$ (P)$\leftarrow$		Dq	B	Ds	Dt
$Ni(Iz)_6X_2$[c]	6.5			10.7	13.2 vw	17.4		27.8	NiN_6	1070	870		
$Ni(Iz)_6X_2(H_2O)_4$[d]	6.5	5.05	6.8	10.7	13.1 vw	17.4		27.8	NiN_6	1070	870		
$Ni(Iz)_4(NCS)_2$	6.5			10.5	13.1 vw	17.3		27.4	NiN_6	1050	880		
$Ni(Iz)_2(H_2O)_2Cl_2$	6.5	5.05	6.7	8.6	13.1	15.0	24.1 sh	25.9	$NiN_2O_2Cl_2$	860	890[e]		
$Ni(Iz)_2(H_2O)_2Br_2$	6.5	5.05	6.7 7.6	9.0 sh	12.6 sh	14.8	23.8 sh	25.8	$NiN_2O_2Br_2$	760	850[e]		
$Ni(Iz)_2Cl_2$	6.4			8.1	12.1	13.8		23.4	NiN_2Cl_4	810	840		
$Ni(Iz)_2Br_2$	6.5		6.0 br	7.5	11.3	12.5		21.7	NiN_2Br_4	750	790[e]		
$Ni(Iz)_2I_2$	6.5			7.4	11.4 sh	f		f	NiN_2I_4	740	—		
$NiIzCl_2$	6.3		6.4 br	7.6	12.0	13.4		22.5	$NiNCl_5$	760	800		
$NiIzBr_2$	6.3		6.0 br	7.4	11.1	12.4		21.4	$NiNBr_5$	740	760		
$NiIzI_2$	6.3		6.0 br	7.2	11.0	11.6		21.6	$NiNI_5$	720	740		
$NiIz(NCS)_2$	6.4			8.4 br		15.4 br		22.8 br	NiN_3S_3	840	860[e]		
Tetragonal elongated Ni:			$^3E_g\leftarrow$	$^3B_{2g}\leftarrow$	$^3A_{2g}$, $^1E_g\leftarrow$	$^3E_g\leftarrow$	$^3A_{2g}\leftarrow$	$^3E_g\leftarrow$					
$Ni(Iz)_4Cl_2$	6.3		6.8	10.7	11.7	15.0	g	25.0	NiN_4Cl_2	1070	840	1050	370
$Ni(Iz)_2(NCS)_2$	6.4		7.4	11.6	13.1	16.3	h	h	NiN_4S_2	1160	860	920	420
$Ni(Iz)_4(H_2O)_2Cl_2$	6.4	5.0 6.7	8.8	11.4	14.1	16.8	g	27.6	NiN_4O_2	1140	880	840	250
$Ni(Iz)_4(H_2O)_2Br_2$	6.4	5.0 6.7	8.9	11.4	14.0	16.9	g	27.6	NiN_4O_2	1140	880	850	240
Square planar Ni:					$^1B_{1g}\leftarrow{}^1A_{1g}$								
$Ni(Iz)_4Br_2$	6.5				21.6				NiN_4				
$Ni(Iz)_4I_2$	6.5				21.5				NiN_4				

[a] All compounds have imidazole combination bands and overtones at 4.05, 4.25, 4.45, 4.65(sh), 5.4 vw and 6.2 kK; additional near IR bands assigned to N–H and O–H are listed; [b] ground states are assigned $^3A_{2g}$ (octahedral case) and $^3B_{1g}$ (tetragonal case); [c] X=Cl, Br, I, NCS; [d] X=Cl, Br; [e] inaccurate parameters due to too large deviations from octahedral geometry; [f] bands obscured due to strong bands caused by small amounts of free iodine and/or $Ni(Iz)_4I_2$; [g] unresolved; [h] not observed due to charge-transfer Ni–S band.

information can be obtained for paramagnetic octahedral and distorted octahedral Ni(II) compounds[3, 15].

Ligand-field maxima of our compounds are listed in Table III, together with some important infrared overtones, and with calculated ligand-field parameters. It is seen from this table that the octahedral hexakis solvates all yield similar parameters within experimental error, in agreement with the proposed structure and with literature values for $Ni(Iz)_6^{2+}$ [5, 6]. The hydrates of these compounds are only different with respect to the near-IR overtones and combination bands, in agreement with second-sphere bonding of the water ligands. The tetragonal compound $Ni(Iz)_4(NCS)_2$ yields parameters very similar to $Ni(Iz)_6^{2+}$, confirming the nitrogen coordination of the NCS^- ion.

The other tetragonal compounds yield different spectra, from which two additional spectral parameters can be derived[15, 16]. From the spectral data it is clear that in both the hydrates $[Ni(Iz)_4(H_2O)_2]X_2$ the water molecules are coordinated to Ni(II), whereas the anions are held in the second coordination sphere.

Since the band maxima of these latter compounds are the same as those reported by Taylor and Underhill[13] for the "anhydrous" compounds, we conclude that the compounds of Taylor, obtained by fusing the reagents, are at least highly contaminated with the hydrates.

The square-planar coordinated compounds $Ni(Iz)_4X_2$ yield ligand-field maxima that are in the usual region for a square-planar $Ni–N_4$ species[17, 18].

This bis- and mono-imidazole compounds yield spectral data that agree with less-distorted octahedral coordination, although in $Ni(Iz)_2(NCS)_2$ clear splittings occur, allowing assignment on a tetragonal basis. It appeared that the spectral maxima of the other compounds could be interpreted in terms of octahedral symmetry, allowing the parameters Dq and B to be calculated[3], which are also listed in Table III. It must be noticed however, that these parameters are less accurate due to the rather broad ligand-field absorptions, caused by deviations from octahedral geometry.

Considering the available spectral data the spectrochemical series was determined to be $\mathrm{Iz} > \underline{\mathrm{N}}\mathrm{CS}^- > \mathrm{H_2O} > \underline{\mathrm{S}}\mathrm{CN}^- \geqslant \mathrm{Cl}^- > \mathrm{Br}^- > \mathrm{I}^-$, which agrees with literature[19].

Final remarks

From the results discussed above a few remarks are appropiate:

1. The diamagnetism of the tetrakis solvates $\mathrm{Ni(Iz)_4X_2}$ with X = Br, I is surprising, since diamagnetic square-planar Ni is only known for very strong ligands (*e.g.* $\mathrm{CN^-}$), for chelates (*e.g.* bipyridyl) or for sterically hindered ligands (*e.g.* 2-methylimidazole). The origin for this geometry in our compounds may have something to do with hydrogen bonding, since in the corresponding pyridine compounds $\mathrm{Ni(py)_4X_2}$ the Ni(II) ions are distorted octahedrally coordinated and paramagnetic[15]. With stronger ligands than $\mathrm{Br^-}$, and $\mathrm{I^-}$, *i.e.* $\mathrm{Cl^-}$, $\mathrm{NCS^-}$ and $\mathrm{H_2O}$, six-coordinate paramagnetic compounds $\mathrm{Ni(Iz)_4X_2}$ are formed, similar to pyridine.
2. In the present work these square-planar compounds are prepared directly from $\mathrm{NiX_2}$ and Iz, while a former investigation[8] needed high-temperature dehydration of $\mathrm{Ni(Iz)_4(H_2O)_2X_2}$. The direct synthesis in the presence of triethylorthoformate allows preparation of large crystals, which are excellent diamagnetic hosts for ESR studies.
3. The occurrence of $\mathrm{Ni(Iz)_6(NCS)_2}$ is rather unique, since no compounds of Ni(II) with monodentate ligands are known to the authors in which $\mathrm{NCS^-}$ is not coordinated to the cation.
4. It is found that two types of hydrates occur; the first type contains water molecules not attached to Ni(II), but held in the second coordination sphere, probably hydrogen bonded to the anions and to the Iz ligands; the second type contains water molecules directly bound to Ni(II). Water molecules of the first type are easy removed by heating the products to 80–100 °C or drying *in vacuo* at room temperature. Removal of water molecules from compounds of the second type needs drying *in vacuo* at 60–150 °C. This thermal decomposition behaviour will be the subject of a separate study.
5. The compunds $\mathrm{Ni(Iz)}_n\mathrm{X_2}$ with $n = 1$, 2, 4 prepared by TAYLOR[13], by fusing the reactants appear to contain hydrated products and also mixtures of compounds with different n, as concluded from their magnetic data and ligand-field and far-IR spectral data.

The authors are indebted to Mr. C. F. VERMEULEN and Mrs. V. 'T HART- DE KLEYN for assistance with the metal and halogen analyses. The assistance of dr. ir. J. M. A. BAAS with the far-IR spectra and of Mr. N. M. V. D. PERS with the X-ray powder diffraction measurements is gratefully acknowledged.

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