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LEWIS ACIDITY OF COORDINATIVELY UNSATURATED BIS(2-MERCAPTOBENZOTHIAZOLATO)NICKEL(II) TOWARDS AZOLES AND MORPHOLINE.

Application of thermal equations to the decomposition of the products

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The reactions of bis(2-mercaptobenzothiazolato)nickel(II) with some azoles and morpholine afforded the corresponding mixed ligand complexes. The studied azoles were 2-aminothiazole, benzothiazole, benzoxazole, 2-methylbenzoxazole and 2-mercapto-benzoxazole. The formation of new compounds was confirmed from the spectral data. The thermal decompositions of the compounds together with some related compounds reported in the literature, for comparison, were studied. The activation energies and other kinetic parameters were calculated from the Coats-Redfern and Horowitz-Metzger equations.

2-Mercaptobenzothiazole(merBTz) exhibits biological activity in the sense that it can cause inhibition of tumour tissue [1]. Metal chelation is most probably involved in this effect. Further, the compound is used as a precipitant for gravimetric analysis of many metals [2]; it has found applications in the vulcanization of rubber [3] and as a corrosion inhibitor [4]. Several metal complexes of merBtz have been reported in the literature [5]. These complexes could form mixed ligand complexes with nitrogen-containing ligands [6].

Due to the above-mentioned particular importance of merBtz and because oxazole and thiazole derivatives are being used as analytical reagents in both industry and medicine [7, 8], we embarked on a study of the interaction of Ni(merBtz)$_2$ with a number of azoles and morpholine (morph).

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Results and discussion

The complexes were prepared from the reactions of Ni(merBtz)$_2$ with 2-aminothiazole (2-amtz), benzothiazole (Btz), benzoxazole (Boz), 2-methylbenzoxazole (2-MeBoz), 2-mercaptobenzoxazole (2-merBoz) and morph. The complexes decompose in most organic solvents; they are fairly soluble in DMSO and DMF. The analytical data, colours and melting points of the complexes are tabulated in Table 1.

The electronic spectra of the complexes show the typical bands of six-coordinate nickel(II). A band appearing in the range 14.084 - 14.388 cm^{-1} is assigned to the transition $^3A_{2g} \rightarrow {}^3T_{1g}$ (F). The intense charge transfer band observed between 23.529 and 24.691 cm^{-1} obscures other *d-d* bands expected in this region. The previously reported [9] isostructural complexes of Co(merBtz)$_2$ and Ni(merBtz)$_2$ with pyridine, CoL$_2$py$_2$ and NiL$_2$py$_2$, were proved to contain two coordinated thiazole nitrogen atoms in cis positions, two exocyclic sulphur atoms (trans), and two pyridine nitrogen atoms (cis). On the basis of previous data [10–12] that the azoles most probably coordinate through their nitrogen atom, we assume that the azoles in our complexes coordinate through the nitrogen atom (except for 2-amtz, which coordinates through its exocyclic nitrogen) and that the resulting complexes have a similar structure to that of CoL$_2$py$_2$ and NiL$_2$py$_2$. Due to the similarity of the electronic spectrum of the morph complex, Ni(merBtz)$_2$(morph)$_2$, to those of the azole complexes, it is suggested that the morph complex is isostructural.

The IR spectra of the complexes indicate that the merBtz ligand retains its mode of coordination as NS donor in the mixed ligand complexes; the bands of νC=N (1580-1590 cm^{-1}) and the thioamide group, νN-C=S (1430-1520 cm^{-1}) have comparable intensities and wavenumber values as for the parent Ni(merBtz)$_2$. Bands located in the regions 360-370 and 240-320 cm^{-1} are assigned to νNi-S and νNi-N, respectively.

In some compounds, the coordinated azoles and morph give extra characteristic bands. Thus, Ni(merBtz)$_2$(2-amtz)$_2$ exhibits νNH$_2$ at 3330 cm^{-1}; Ni(merBtz)$_2$(Btz)$_2$ and Ni(merBtz)$_2$(Boz)$_2$ show a band in the range 1550-1575 cm^{-1}, which is assigned to νC=N; Ni(merBtz)$_2$(morph)$_2$ displays a band at 3180 cm^{-1}, corresponding to νNH of the morph in the complex.

The thermal behaviour of three of the complexes i.e. Ni(merBtz)$_2$(Btz)$_2$, Ni(merBtz)$_2$(Boz)$_2$ and Ni(merBtz)$_2$(morph)$_2$, was studied; for the sake of comparison, the thermal decomposition of three mixed ligand complexes known in the literature [6] was carried out: Ni(merBtz)$_2$(*o*-phen), Ni(mer-

Table 1 Analytical data and physical properties of the complexes

Compound	Colour	C, % (Calc.)	H, % (Calc.)	N, % (Calc.)	S, % (Calc.)	*m.p.*, °C
$Ni(merBtz)_2(2\text{-}amtz)_2$	light	39.8	2.4	13.8	32.2	148
	green	(40.6)	(2.7)	(14.2)	(32.5)	(dec.)
$Ni(merBtz)_2(Btz)_2$	light	51.1	2.6	8.4	28.8	155
	green	(50.8)	(2.7)	(8.5)	(29.1)	(dec.)
$Ni(merBtz)_2(Boz)_2$	green	53.1	2.8	8.7	20.2	120
		(53.4)	(2.9)	(8.9)	(20.4)	(dec.)
$Ni(merBtz)_2(2\text{-}MeBoz)_2$	green	54.9	2.8	8.4	19.7	140
		(54.8)	(3.1)	(8.5)	(19.5)	(dec.)
$Ni(merBtz)_2(2\text{-}merBoz)_2$	dark	49.0	2.3	8.0	27.9	180
	brown	(49.2)	(2.6)	(8.2)	(28.1)	(dec.)
$Ni(merBtz)_2(morph)_2$	light	46.8	4.9	10.1	22.5	170
	green	(46.7)	(4.6)	(9.9)	(22.7)	(dec.)

Table 2 IR and electronic spectra of the complexes, cm^{-1}

Compound	IR spectra, cm^{-1}							Electronic spectra, cm^{-1}	
	$\nu(C{=}N)$	$\nu(N{-}C{=}S)$	$\nu(C{=}S)$ $\nu N{-}C{=}S$	$\nu C{-}S$	$\nu M{-}S$	$\nu M{-}N$	$\nu N{-}H$	$^3A_{2g} \rightarrow {}^3T_{1g}(F)$	Charge transfer
Ni(merBtz)$_2$(2-amtz)$_2$	1590	1470 1520	1265	690	370	240	3330	14.285	23.809
Ni(merBtz)$_2$(Btz)$_2$	1580 1550	1460(sh)	1280	670	370	290	-	14.380	23.809
Ni(merBtz)$_2$(Boz)$_2$	1575 1590	1520	1290	670	370	290	-	14.285	23.809
Ni(merBtz)$_2$(2-MeBoz)$_2$	-	1520	1275	680	360	320	-	14.184	24.096
Ni(merBtz)$_2$(2-merBoz)$_2$	1590	1470 1505	1250	735	370	-	-	14.388	23.529
Ni(merBtz)$_2$(morph)$_2$	1580	1430	1240	670	370	290	3180	14.084	24.691

Btz)$_2$(py)$_2$ and Ni(merBtz)$_2$(α-pic)$_2$. The decomposition patterns of these complexes can be summarized as follows:

Two decomposition stages are observed in the TG curves of the complexes (Fig. 1). The first correlates with the evolution of the coordinated bases, leaving the parent Ni(merBtz)$_2$, which decomposes in the second step. Table 3 gives the temperature range of each step.

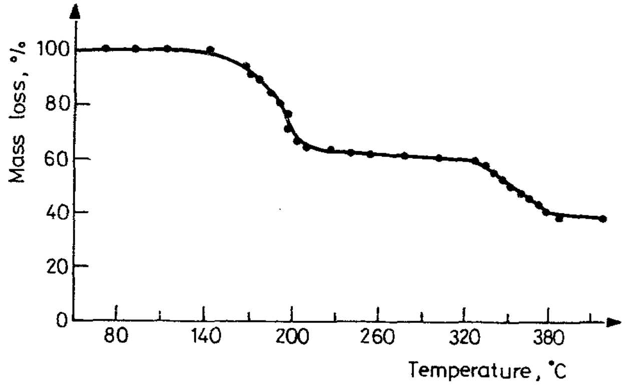

Fig. 1 TG curve of Ni(merBtz)(Btz)$_2$

From the thermogravimetric data, the activation energies of decomposition were evaluated by adopting the following two equations, assuming first-order decomposition reactions:

a) Coats-Redfern equation [13]

$$\log F(\alpha)/T^2 = \log ZR/\beta E\,(1-2RT/E) - E/2.303RT$$

where Z, R, β and E are the pre-exponential factor, gas constant, rate of heating and activation energy, respectively. The function $F(\alpha) = -\log(1\text{-}\alpha)$ and the plot of $-\log[-\log(1-\alpha)/T^2]$ *vs.* $\frac{1}{T}$ resulted in a straight line of slope = $-E/2.303\,R$. The expression $\log ZR/\beta$E (1-2 RT/E) was constant for the temperature range over which reactions generally occur. Thus, the E and Z values were calculated from the slopes and intercepts, respectively, of the straight lines. The activation enthalpy ΔH^* was calculated from $\Delta H^* = E-RT$, while the activation entropy ΔS^* was obtained from

$$\Delta S^* = R\,[\ln(Zh/kT) - 1]$$

where k is the Boltzmann constant, and h is the Plank constant, assuming the transmission coefficient to be 1.

b) Horowitz-Metzger equation [14]

$$\log\log\left(\frac{W_0 - W_f}{W - W_f}\right) = \frac{E\theta}{2.303RT_s^2} - \log 2.303$$

where W_0 and W_f are the initial and final masses, respectively, and W is the mass at temperature T. $\theta = T\text{-}T_s$ is the temperature at the DTG peak; R is the gas constant in kJ deg^{-1} mol^{-1} and E is the energy of activation in kJ mol^{-1}. The plot of log log $\left(\frac{W_0 - W_f}{W - W_f}\right)$ *vs.* θ gives a straight line, from the slope of which the activation energy E of decomposition can be determined. The activation energies of the first and second decomposition steps are recorded in Table 3. The near-unity values of the correlation coefficients for the least square plots indicate good agreement between the observed points and the linear square plots.

The kinetic parameters log Z, ΔS^* and ΔH^* calculated with the Coats-Redfern equation, are tabulated in Table 4.

The activation enthalpy values, ΔH^* have the same trend as those of the activation energy. The negative values of the activation entropies ΔS^* in these complexes indicate that the activated complex has a more ordered structure than the reactants, and that the reactions are slower than normal [15].

Taking the activation energy of the first step as a criterion, the following thermal stability sequence can be deduced:

$$\mathrm{Ni(merBtz)_2(morph)_2} > \mathrm{Ni(merBtz)_2(\mathit{o}\text{-}phen)_2} > \mathrm{Ni(merBtz)_2(Boz)_2} >$$
$$\mathrm{Ni(merBtz)_2(Btz)_2} > \mathrm{Ni(merBtz)_2(py)_2} > \mathrm{Ni(merBtz)_2(\alpha\text{-}pic)_2}.$$

Boz and Btz are much weaker bases than py [11], so that the σ-component of the metal-nitrogen bond is expected to be weaker for Boz and Btz than for py. However, the activation energy values (Table 3) of the Boz and Btz compounds are greater than that of the py complex, behaviour which can be explained on the basis that the π-bonding in the Boz and Btz complexes is enhanced, which reverses the expected trend in the above sequence [11].

Table 3 Thermal data of the complexes

Compound	First step		Second step	Coats-Redfern equation		Horowitz-Metzger equation	
	Mass loss, % (theoretical)	Temp. range, °C	Temp. range, °C	E_1 (1st step), kJmol^{-1}	E_2 (2nd step), kJmol^{-1}	E_1 (1st step), kJmol^{-1}	E_2 (2nd step), kJmol^{-1}
Ni(merBtz)$_2$(Boz)$_2$	39.2 (37.7)	150-230	310-370	82.4	27.5	76.7	18.9
Ni(merBtz)$_2$(Btz)$_2$	42.0 (40.7)	170-250	330-370	67.7	32.7	66.7	21.7
Ni(merBtz)$_2$(morph)$_2$	32.0 (30.7)	170-270	310-370	98.4	34.9	-	27.5
Ni(merBtz)$_2$(o-phen)$_2$	32.5 (31.4)	210-270	320-370	94.4	-	90.4	31.3
Ni(merBtz)$_2$(pyz)$_2$	29.0 (28.7)	170-270	320-370	55.6	21.3	49.3	25.4
Ni(merBtz)$_2$(α-pic)$_2$	34.0 (32.1)	130-230	290-370	29.9	19.4	20.9	16.5

The low thermal stability of the complex Ni(merBtz)$_2$(α-pic)$_2$ may be attributed to the steric hindrance by the methyl group at the α-position of the py ring.

Table 4 Kinetic parameters of the complexes

Compound	log (*Z*)/*s*$^{-1}$	ΔS^*, kJ mol^{-1}	ΔH^*, kJ mol^{-1}
Ni(merBtz)$_2$(Boz)$_2$	4.379	–113.12	78.48
Ni(merBtz)$_2$(Btz)$_2$	1.231	–165.74	63.42
Ni(merBtz)$_2$(morph)$_2$	4.044	–111.83	94.16
Ni(merBtz)$_2$(o-phen)$_2$	4.149	–110.12	90.03
Ni(merBtz)$_2$(py)$_2$	2.534	–140.99	51.25
Ni(merBtz)$_2$(α-pic)$_2$	–1.877	–224.56	26.01

It is to be noted that the samples after decomposition in the temperature range 100-450° were heated at 700° for about one hour, and the residue in each case was identified as NiS.

Experimental

All chemicals used in the preparation of the complexes were of analytical grade. Bis(2-mercaptobenzothiazolato)nickel(II), bis(2-mercaptobenzothiazolato)(*o*-phenanthroline)nickel(II), bis(2-mercaptobenzothiazolato)-bis(pyridine)nickel(II), and bis(2-mercaptobenzothiazolato)bis(α-picoline)-nickel(II) were prepared according to literature according procedures [6]. The mixed ligand complexes were prepared as follows:

Bis(2-aminothiazole)bis(2-mercaptobenzothiazolato)nickel(II):

An EtOH solution (20 ml) of 2-aminothiazole (10 mmol) was added to bis(2-mercaptobenzothiazolato)nickel(II) (5 mmol). The mixture was warmed on a steam bath for 4 h, then allowed to stand for 7 days, when light-green crystals deposited, which were filtered off, washed with ether and dried in air.

Bis(benzothiazole)bis(2-mercaptobenzothiazolato)nickel(II):

Benzothiazole (20 mmol) in absolute EtOH (30 ml) was mixed with 10 mmol bis(2-mercaptobenzothiazolato)nickel(II); during stirring of the mixture, a yellow solution was obtained, from which green crystals began to deposit. After 3 days, the crystals were filtered off, washed with ether and dried in air.

Bis(benzoxazole)bis(2-mercaptobenzothiazolato)nickel(II) and bis(2-methylbenzoxazole)bis(2-mercaptobenzothiazolato)nickel(II):

These compounds were prepared by a similar procedure to that used for the benzothiazole compound.

Bis(2-mercaptobenzoxazole)bis(2-mercaptobenzothiazolato)nickel(II):

Upon the addition of 2-mercaptobenzoxazole (25 mmol) in 30 ml EtOH to bis(2-mercaptobenzothiazolato)nickel(II) (10 mmol), dissolution of the complex occurred to give a dark-brown solution. After 24 h, the dark-brown crystals were filtered off, washed with ether and dried in air.

Bis(morpholine)bis(2-mercaptobenzothiazolato)nickel(II):

Bis(2-mercaptobenzothiazolato)nickel(II) (5 mmol) was dissolved in excess morpholine; light-green crystals formed after about 5 h; they were filtered off, washed with ether and dried in air.

Physical measurements

The IR spectra of the complexes in KBr discs were recorded on a Perkin-Elmer 599 DB spectrophotometer. The electronic spectra were obtained with a Shimadzu UV-200S spectrophotometer. The thermogravimetric analyses were performed with an electrobalance of the type Sartorius 200 MP converted to a thermobalance by the addition of a small furnace and sample holder. The temperature was measured with a chromal-alumal thermocouple attached to a digital multimeter type Weston model 600; the heating rate was adjusted to 7 deg/min.

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Zusammenfassung — Die Reaktion von Bis(2-mercaptobenzothiazolato)nickel(II) mit einigen Azolen und Morpholin liefert die entsprechenden Mischligandenkomplexe. Die untersuchten Azole waren 2-Aminothiazol, Benzothiazol, Benzoxazol, 2-Methylbenzoxazol und 2-Mercaptobenzoxazol. Die Bildung neuer Verbindungen wurde anhand von Spektren festgestellt. Es wurde die thermische Zersetzung von einigen dieser Verbindungen sowie zum Vergleich auch von einigen in der Literatur beschriebenen verwandten Verbindungen untersucht. Anhand der Coats-Redfern- und der Horowitz-Metzger-Gleichung wurden die Aktivierungsenergien und andere kinetische Parameter errechnet.