THE ELECTRONIC SPECTRA OF NICKEL(II) BIS(DITHIOCARBAMATE) CHELATES

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The synthesis and electronic spectra of the chelates of nickel(II) dithiocarbamates with ligands derived from dimethyl-, diethyl-, dipropyl, dibutyl-, dipentyl-, dihexyl-, diheptyl-, dioctyl-, diisopropyl, methylisopropylamine, piperidine, morpholine and piperazine are discussed. The absorption bands in the chelate spectra around 220 and 245 nm are assigned to absorption localized primarily in the S—C=S and N—C=S ligand groups. The analytically most important band with λ_{max} around 330 nm assigned to M—L charge transfer is affected by alkyl substituents on the nitrogen atom and by the solvent polarity. The lengthening of the alkyl chain causes the increase in the intensity of the band and a red-shift of its λ_{max}; the increase of the polarity of the solvent leads to an increase in the band intensity and a blue shift.

The electronic spectra of the metal chelates of DTC* have several very intensive absorption bands which can be used for the spectrophotometric determination of metals and ligands.

In the regions around 625 and 400 nm (ref.[1-7]) in the Ni(II) DTC spectra weak bands were observed and assigned to $d-d$ transitions of the central atom, a band at 430 nm assigned to charge transfer[7] or a $d-d$ transition[1-6] and a very intense band around 395 – 385 nm, which, similar to the most intense band around 330 nm, is assigned to charge transfer[1-7]. It was originally felt that the bands of the internal ligand transitions of the Ni(II) chelate with DTC lie in the region around 240 – 320 nm (ref.[1-2]), but calculations by the LCAO MO method indicated that these bands for $Ni(EtDTC)_2$ lie at 226 and 246 nm (*cf.*[3,4]). These assignments have been confirmed repeatedly[8-11].

Previous works were not devoted to the study of the absorption spectra of the Ni(II) DTC chelates considering the analytical importance of the bands and the effect of the ligand and solvent on the character of the spectra. This work deals with the study of the absorption spectra of these substances in the UV region from the

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* DTC designates dithiocarbamates (*i.e.* the salts and chelates of dithiocarbamidic acids and dithiocarbamate ligands.

point of view of their interpretation and studies the effect of the length of the hydrocarbon chain on the nitrogen atom and of the polarity of the solvent on the position and intensity of the analytically important bands with λ_{max} around 330 nm.

EXPERIMENTAL

Chemicals

Chloroform solutions were prepared using chloroform *p.a.*, which was, when necessary, redistilled and does not give any absorption in the wavelength region above 255 nm.

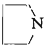
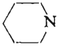
In the study of the DTC absorption spectra in the UV region, ethanol and methanol for the UV spectroscopy from Lachema were employed.

The bis(dithiocarbamate) chelates of nickel(II) are given in Tables I and II and were prepared in the following general manner:

TABLE I

Nickel Chelates of Dithiocarbamidic Acid of the Ni(R—C—S)$_2$ Type Described in This Work

Me methyl, Et ethyl, Pr propyl, Bu butyl, Pe pentyl, Ge hexyl, Hp heptyl, Oc Octyl, iPr isopropyl, Pl 1-pyrrolidinyl, Pp 1-piperidyl, Mo 4-morpholinyl.

Number	R	Chelate
I	$(CH_3)_2N$	$[Ni(Me_2DTC)_2]$
II	$(C_2H_5)_2N$	$[Ni(Et_2DTC)_2]$
III	$(C_3H_7)_2N$	$[Ni(Pr_2DTC)_2]$
IV	$(C_4H_9)_2N$	$[Ni(Bu_2DTC)_2]$
V	$(C_5H_{11})_2N$	$[Ni(Pe_2DTC)_2]$
VI	$(C_6H_{13})_2N$	$[Ni(He_2DTC)_2$
VII	$(C_7H_{15})_2N$	$[Ni(Hp_2DTC)_2]$
VIII	$(C_8H_{17})_2N$	$[Ni(Ok_2DTC)_2]$
IX	$(CH_3, iC_3H_7)N$	$[Ni(Me, iPrDTC)_3]$
X	$(iC_3H_7)_2N$	$[Ni(iPr_2DTC)_2]$
XI		$[Ni(PlDTC)_2]$
XII		$[Ni(PpDTC)_2]$
XIII		$[Ni(MoDTC)_2]$

An amount of 0·05 mol of nickel chloride dissolved in 50 ml of distilled water was added to 0·1 mol of the alkali or ammonia salt of DTC acid[12] dissolved in 100 ml of distilled water at constant stirring (650 rpm) at 15—20°C. The mixture was stirred for further 3 hours at this temperature and then the reaction mixture was continually stirred, cooled to 0°C. The precipitated solid substance was filtered off, washed with ice cold water and dried in the air. The raw products

TABLE II

Characteristic Data on Nickel(II) Chelates of Dithiocarbamidic Acids

Chelate	General formula (m.w.)	Calculated/Found			Solubility g/100 g MeOH (EtOH)	Melting point °C
		% C	% H	% N		
I	$C_6H_{12}N_2NiS_4$ (299·1)	24·09 24·21	4·04 3·92	9·36 9·17	traces (traces)	>340
II	$C_{10}H_{20}N_2NiS_4$ (355·2)	33·81 33·20	5·68 6·11	7·89 7·53	0·025 (0·013)	83—83·5
III	$C_{14}H_{28}N_2NiS_4$ (411·3)	40·88 40·22	6·86 7·07	6·81 7·10	0·051 (0·028)	122—123
IV	$C_{18}H_{36}N_2NiS_3$ (467·4)	46·25 46·11	7·75 7·82	5·99 5·88	0·079 (0·066)	83—84
V	$C_{22}H_{44}N_2NiS_4$ (523·5)	50·47 50·67	8·47 8·70	5·35 5·34	0·063 (0·054)	87·5—88
VI	$C_{26}H_{52}N_2NiS_4$ (579·6)	53·87 54·11	9·04 8·94	4·83 4·79	0·042 (0·049)	45—46
VII	$C_{30}H_{60}N_2NiS_4$ (635·5)	— —	— —	— —	— —	waxy substance
VIII	$C_{34}H_{68}N_2NiS_4$ (691·6)	— —	— —	— —	— —	viscous liquid
IX	$C_{10}H_{20}N_2NiS_4$ (355·2)	33·81 33·97	5·68 5·85	7·89 7·42	0·078 (0·076)	170·5—171
X	$C_{14}H_{28}N_2NiS_4$ (411·4)	40·88 39·92	6·80 6·50	6·81 6·47	0·007 (0·038)	>340
XI	$C_{10}H_{16}N_2NiS_4$ (351·1)	34·20 33·96	4·59 4·67	7·98 8·12	traces (traces)	>340
XII	$C_{12}H_{20}N_2NiS_4$ (379·1)	38·01 37·81	5·32 5·33	7·39 7·22	traces (traces)	>340
XIII	$C_{10}H_{16}N_2NiO_2S_4$ (382·2)	31·34 31·25	4·21 4·25	7·31 7·18	traces (traces)	>340

were purified by recrystallization from ethanol, from a chloroform methanol mixture or from a chloroform–pyridine mixture respectively.

The stability of the Ni(II) chelate with DTC was studied by recording the absorption spectra of chloroform and ethanol solutions of the substances at 20 minute intervals at room temperature (20°C). It was found that the structure of the spectra does not change over 8 hours and that the intensity of the absorption band does not change, indicating that the absorbing system is stable. As the band of carbon disulphide at 207 nm (ref.[12]) was not observed in any system, it follows that a decomposition of the substances producing CS_2 does not occur under the experimental conditions. The spectrophotometric control of the chloroform solutions of the dithiocarbamate Ni(II) chelates indicated that they are stable for 14 days in this solvent.

The aqueous solution of $[NiPz(DTC)_2]$, formed in spectrophotometric titration of $NiCl_2$ with $K_2Pz(DTC)_2$, was produced by adding 20 ml of water and the required amounts of $1 . 10^{-3}$M-$K_2Pz(DTC)_2$ solution to the 0·5 ml of an aqueous $1 . 10^{-3}$M solution of $NiCl_2$ in a 25 ml volumetric flask at continual constant stirring; the resulting solution was then diluted to 25 ml with water. In this way, $[NiPz(DTC)_2]$ did not precipitate.

Recording of Absorption Spectra

$1 . 10^{-3}$M and $1 . 10^{-4}$M solutions of the dithiocarbamate chelate in chloroform, ethanol and methanol respectively were prepared by dissolving the required amounts of substance, as given in Table II, in 250 ml of the solvent. The stock solutions were stable for 5 to 14 days. The absorption spectra were studied using $2 . 10^{-5}$—$8 . 10^{-5}$M chloroform, ethanol and methanol solutions prepared from the stock solutions. The absorption spectra were recorded on a Specord UV VIS recording spectrophotometer from Carl Zeiss, Jena, in 0·2, 0·5, 1·0 and 3·0 cm quartz cells. The λ_{max} values of the studied absorption bands were confirmed using a VSU-1 instrument from the same firm with an accuracy of ±1 nm.

RESULTS AND DISCUSSION

Fig. 1 depicts the absorption spectra of ethanol solutions of some bis(dithiocarbamate) chelates of Ni(II) in the UV region.

A comparison of the absorption spectra of nickel chelates of DTC and alkali salts of DTC indicates that the spectra of the chelates contain a band in the UV region with the maximum absorption around 330 nm, which is not observed in the spectra of alkali DTC, while the band at 207 nm assigned to carbon disulphide, produced by decomposition of alkali DTC (ref.[12]), is not present in the absorption spectra of the chelates. The change in the character of the absorption spectra and the shift of the absorption bands of the chelate compared with the bands of alkali DTC is depicted in Fig. 2, which gives the absorption spectra corresponding to the spectrophotometric titration of Ni(II) with an aqueous solution[12] of $K_2Pz(DTC)_2$. The bands can be assigned to the internal ligand transition of $[NiPz(DTC)_2]$ in the S—C=S and N—C=S groups.

Curves *1* to *5* in Fig. 2 correspond to the absorption spectra of an aqueous solution of $NiPz(DTC)_2$ formed during the titration, which is characterized by absorption bands *A'* (λ_{max} 328 nm), *B'* (λ_{max} 247 nm) and *C'* (λ_{max} 223 nm). The character of the spectrum changes on attaining the equivalence point, where the absorbing system begins to contain further component $K_2Pz(DTC)_2$, as can be seen in curves *6* to *9*. This component appears in the spectra as bands *D* and *B*, corresponding to

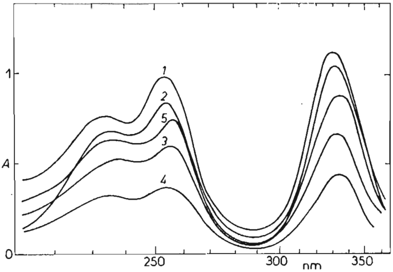


FIG. 1

The Absorption Spectra of Ethanol Solutions of the Ni(II) DTC

1 $[Ni(Me_2DTC)_2]$; *2* $[Ni(Et_2DTC)_2]$; *3* $[Ni(Pr_2DTC)_2]$; *4* $[Ni(Pe_2DTC)_2]$; *5* $[Ni(Bu_2DTC)_2]$.

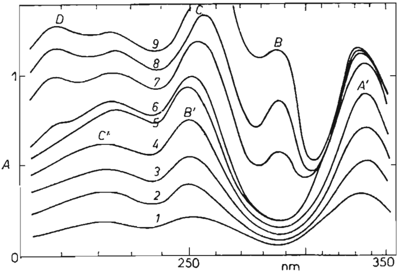


FIG. 2

Absorption Spectra at the Spectrophotometric Titration of an Aqueous Solution of $NiCl_2$ with an Aqueous Solution of $K_2Pz(DTC)_2$

1—*5* before the equivalent point; *6*—*9* after the equivalence point.

the N—C=S chromophor and in an increase in the intensity and deformation of band *B'* toward higher wavelengths, as band C (S—C=S chromophor) in the spectra of $K_2Pz(DTC)_2$ lies in the same wavelength region as band *B'*. The λ_{max} value of band *C* is only several nm higher than that of band *B'*. The blue shift of band *A'* can be assigned to a change in the ionic strength of the solution and to an increase in the pH after addition of excess $K_2Pz(DTC)_2$.

It is clear from the character of the absorption spectra of the solution before and after attaining the equivalence point that chelate formation results in a shift of the absorption bands corresponding to the N—C=S and S—C=S groups of the ligand to lower wavelengths. This is probably a result of a decrease on the band energies of the bonding or nonbonding orbitals of the ligand, while band *C* corresponding to ligand chromophor S—C=S becomes weaker and band *A'* characterizing the chelate appears. The weakening and blue shift of band *C* and simultaneous formation of band *A'* characterizing the chelate indicate that, in chelate formation, bonds to the nickel are formed primarily with the group orbitals of the S—C=S group, whose transitions in the chelate spectrum have a smaller effect than with the free $Pz(DTC)_2^{2-}$ anion. Chelate formation apparently also leads to strengthening of the bonds in the N—C=S group and is connected with increasing π-electron participation in the N—C bond, as is confirmed by data from analysis of the crystal structure of [Ni(Et$_2$.DTC)$_2$ (ref.[13], [Cu(Et$_2$DTC)$_2$] (ref.[14]), [Zn(Et$_2$DTC)$_2$] ref.[15]) and [Na$^+$Et$_2$DTC$^-$] (ref.[16]).

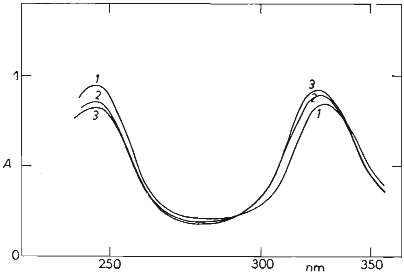


FIG. 3

The Effect of Ethanol and Methanol on Changes in the Absorption Spectra of $Ni(Bu_2DTC)_2$
1 Chloroform; *2* chloroform: ethanol = 1 : 4; *3* chloroform: methanol = 1 : 9; *c* 4 . 10^{-5}M; *d* 0·5 cm.

TABLE III

Molar Absorption Coefficients of Ni(II) Dithiocarbamate Chelates in the UV and Visible Spectral Regions

Chelate	λ_{max} nm	ε	λ_{max} nm	ε
$[Ni(Me_2DTC)_2]$	325	28 400	385	4 000
$[Ni(Et_2DTC)_2]$	327	33 400	388	6 700
$[Ni(Pr_2DTC)_2]$	328	34 200	390	6 600
$[Ni(Bu_2DTC)_2]$	328	35 000	391	6 400
$[Ni(Pe_2DTC)_2]$	329	35 600	390	6 300
$[Ni(He_2DTC)_2]$	329	36 500	389	6 300
$[Ni(Hp_2DTC)_2]$	329	35 600	388	6 300
$[Ni(Ok_2DTC)_2]$	329	36 500	388	6 300
$[Ni(iPr_2DTC)_2]$	332	35 200	395	4 900
$[Ni(Me, iPrDTC)_2]$	327	34 000	386	4 800
$[Ni(PpDTC)_2]$	328	36 000	389	6 500
$[Ni(MoDTC)_2]$	326	35 500	388	5 600

TABLE IV

Effect of Solvents on the Shift of the λ_{max} Absorption Bands of Nickel(II) Dithiocarbamate Chelates

Chelate	$CHCl_3$ λ_{max}, nm	$CHCl_3$: EtOH 1 : 4 λ_{max}, nm	$CHCl_3$: MeOH 1 : 9 λ_{max}, nm
$[Ni(Me_2DTC)_2]$	325	322	320
$[Ni(Et_2DTC)_2]$	327	324	324
$[Ni(Pr_2DTC)_2]$	328	325	324
$[Ni(Bu_2DTC)_2]$	328	325	324
$[Ni(Pe_2DTC)_2]$	329	326	326
$[Ni(He_2DTC)_2]$	329	327	326
$[Ni(iPr_2DTC)_2]$	332	329	326
$[Ni(Mi, iPrDTC)_2]$	327	325	323
$[Ni(PpDTC)_2]$	328	326	325
$[Ni(MoDTC)_2]$	326	325	321

From the analytical point of view, the strong absorption bands with λ_{max} around 330 nm ($\varepsilon \sim 33000$) and 395 nm ($\varepsilon \sim 6000$, Table III) are most important; these bands react very sensitively to changes in the chelate concentration. The remaining bands in the UV spectra of the Ni(II) bis(dithiocarbamate) chelates are unsymmetrical, weak or cannot be used in spectrophotometric determinations because of the interfering effect of most solvents on the absorbing substance. Thus they were not studied further. It is clear from the results in Table III that the bands at 330 nm are much more intense than those at 395 nm and thus they are more useful for trace analysis of Ni.

The effect of the length of the alkyl chain bonded to the nitrogen atom in the DTC molecule on the intensity of the absorption bands of the Ni(II) chelates at 330 nm and on the shift of these bands follows from the λ_{max} values and molar absorption coefficients given in Table III. It can be seen that a red shift of the bands and an increase in their intensity occur with increasing size of the alkyl substituent, indicating that DTC derivatives with larger alkyl groups are preferable for the analysis of nickel. The red shift and the increase in the band intensity are a result of the already mentioned induction effect of the alkyl group[12], resulting in delocalization of the electrons towards the absorbing chromophor and thus in an increase in the length of the absorbing system. The highest λ_{max} value for $Ni(iPr_2DTC)_2$ can be explained by a combination of induction and hyperconjugation effects in the isopropyl groups, resulting in an increase in the conjugation of the chelate electron system.

Fig. 3 depicts parts of the absorption spectra of $Ni(Et_2DTC)_2$ in chloroform and in a 1 : 4 mixture of chloroform and methanol or in 1 : 9 chloroform–methanol. The blue shift of the λ_{max} value of the band at 245 nm and the simultaneous decrease in the intensity of the band with increasing polarity of the solvent indicate that the interaction of the polar solvent with the chelate molecule, probably through the nitrogen atom, leads to a decrease in the electron density in the region around the N—C=S chromophor and to the conjugation of the electron system of the chelate. The effect of the solvent polarity on the λ_{max} value of the band at 330 nm for the other studied substances is clear from Table IV. It can be seen from the results that increasing solvent polarity results in an increase in the band intensity around 330 nm and a blue shift for all the studied substances. This observed increase in the intensity of the absorption bands at 330 nm and their blue shift as a result of increasing solvent polarity is connected with increasing of electron density in the area of the Ni—S bonds.

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