THE ELECTRONIC SPECTRA OF THE BIS(DITHIOCARBAMATE) CHELATES OF Cu(II) AND Zn(II)

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This work deals with the synthesis of dithiocarbamate chelates of Cu(II) and Zn(II) with ligands derived from dimethyl-, diethyl-, dipropyl-, dibutyl- and methylisopropylamine, piperidine and morpholine and the electronic spectra of these substances in the UV and visible regions. The absorption spectra of the cupric (and zinc(II)) chelates contain a single analytically important band around 270 (260) nm, assigned to the $\pi-\pi^*$ transition within the ligand, that is affected by the substituent on the nitrogen atom and the solvent polarity. Lengthening of the alkyl chain leads to increased intensity of the bands and a red shift of their λ_{max}, increased solvent polarity leads to increased intensity of the bands and a blue shift.

The simple preparation and suitable analytical properties of DTC* have long led to its use in the analysis of various substances[1]. The analytical use of dithiocarbamates has been surveyed in reviews[2,3]. Because of the characteristic, intense absorption bands in the electronic spectra of DTC metal complexes[4], spectrophotometric methods of determination are frequently used, both for determining the metals and for determining DTC ligands[3].

DTC complexes of Cu(II) and Zn(II) have been known since 1907 (ref.[5]) and since then their chemical, magnetic and spectral properties have been studied intensely; these are listed in a book[6] and in reviews[4,7,8]. Works published on the electronic spectra of the DTC complexes of Cu(II) and Zn(II) have been concerned with assignment of the absorption bands of electronic transitions[9-18] and on the use of the DTC complexes of Cu(II) and Zn(II) in spectrophotometric determinations[3].

This work deals with the study of the electronic spectra of the listed complexes in the UV region, considering the effect of the length of the hydrocarbon chain on the nitrogen atom and the solvent polarity on the position and intensity of analytically important bands with λ_{max} around 275 nm (Cu) and 265 nm (Zn). The work discusses the advantages of using various DTC ligands for the trace analysis of copper and zinc in the UV and visible spectral regions.

* DTC dithiocarbamates (*i.e.* salts and chelates of dithiocarbamic acids) and dithiocarbamate ligands.

EXPERIMENTAL

Chemicals

Chloroform solutions were prepared using *p.a.* chloroform that was freshly redistilled and passed through an SiO_2 column and that did not exhibit absorption in the wavelength region above 255 nm.

The absorption spectra of DTC in the ultraviolet region were studied using ethanol and methanol for UV spectroscopy from Lachema, Czechoslovakia.

The bis-dithiocarbamate chelates of copper(II) and zinc(II) listed in Tables I to III were prepared in the following manner: To 0·1 mol of alkali or ammonium salt of DTC acid[19] dissolved in 100 ml of distilled water with constant stirring (650 rpm) was added 0·05 mol of copper(II) or zinc(II) chloride dissolved in 50 ml of distilled water at a temperature of 15—20°C. Stirring was continued for 3 hours at this temperature and then the reaction mixture was cooled to 0°C. The precipitated solid substance was filtered off; the precipitate was washed with ice water and dried in the air. The raw product was purified by crystallization from ethanol, from a chloroform–methanol mixture or from a chloroform–pyridine mixture.

The chelates of Cu(II) and Zn(II) with dihexyldithiocarbamate ligands were prepared in the same manner. After completion of the reaction, 15 ml of chloroform were added to the reaction mixture and the solid chelate was extracted into the chloroform phase. The chloroform layer was separated, rinsed twice with distilled water and dried over anhydrous Na_2SO_4. The chloro-

TABLE I

Cu(II) and Zn(II) chelates with dithiocarbamic acids of the $M(R\text{–}\underset{\displaystyle S}{\overset{|}{C}}\text{–}S)_2$ type. Me — methyl, Et — ethyl, Pr — propyl, Bu — butyl, Pe — pentyl, He — hexyl, iPr — isopropyl, iBu — isobutyl, Me,iPr — methylisopropyl, Pp — piperidyl, Mo — morpholinyl

R	Number	Cu(II) Chelate	Number	Zn(II) Chelate
$(CH_3)_2N$	*I*	$[Cu(Me_2DTC)_2]$	*XII*	$[Zn(Me_2DTC)_2]$
$(C_2H_5)_2N$	*II*	$[Cu(Et_2DTC)_2]$	*XIII*	$[Zn(Et_2DTC)_2]$
$(C_3H_7)_2N$	*III*	$[Cu(Pr_2DTC)_2]$	*XIV*	$[Zn(Pr_2DTC)_2]$
$(C_4H_9)_2N$	*IV*	$[Cu(Bu_2DTC)_2]$	*XV*	$[Zn(Bu_2DTC)_2]$
$(C_5H_{11})_2N$	*V*	$[Cu(Pe_2DTC)_2]$	*XVI*	$[Zn(Pe_2DTC)_2]$
$(C_6H_{13})_2N$	*VI*	$[Cu(He_2DTC)_2]$	*XVII*	$[Zn(He_2DTC)_2]$
$(CH_3,iCH_7)N$	*VII*	$[Cu(Me,iPrDTC)_2]$	*XVIII*	$[Zn(Me,iPrDTC)_2]$
$(iC_3H_7)_2N$	*VIII*	$[Cu(iPr_2DTC)_2]$	*XIX*	$[Zn(iPr_2DTC)_2]$
$(iC_4H_9)_2N$	*IX*	$[Cu(iBu_2DTC)_2]$	*XX*	$[Zn(iBu_2DTC)_2]$
	*X*	$[Cu(PpDTC)_2]$	*XXI*	$[Zn(PpDTC)_2]$
	*XI*	$[Cu(MoDTC)_2]$	*XXII*	$[Zn(MoDTC)_2]$

form was distilled off under decreased pressure and the distillate was freed of chloroform at a temperature of 50°C and pressure of 26·6 Pa (0·2 Torr).

The time stability of the DTC chelates of Cu(II) and Zn(II) was studied by spectrophotometric recording of the absorption spectra of chloroform and ethanol solutions of the substances at 20 minute time intervals at laboratory temperature (20°C). It was found that the structure of the absorption spectra and the intensities of the absorption bands of the dithiocarbamate chelates of Zn(II) do not change over 5 hours and that the spectral structure and intensities of the bands of the chelates of Cu(II) do not change over 8 hours. As (except for methanolic solutions of $Zn(Me_2DTC)_2$) the carbon disulphide band at 207 nm[19,20] was not recorded, it is apparent that, under these conditions, the substances do not decompose to carbon disulphide, CS_2. Control

TABLE II

Characteristic data on the Cu(II) chelates of dithiocarbamic acids

Chelate	General formula (m.w.)	Calculated/Found			Solubility g/100 g	Melting point
		% C	% H	% N	MeOH (EtOH)	°C
I	$C_6H_{12}N_2S_4Cu$	23·71	3·98	9·22	0·013	>340
	(303·94)	24·05	3·82	9·01	(traces)	
II	$C_{10}H_{20}N_2S_4Cu$	33·36	6·60	7·78	0·030	262–263
	(360·05)	33·72	5·41	7·28	(0·013)	
III	$C_{14}H_{28}N_2S_4Cu$	40·40	6·78	6·73	0·164	89–90
	(416·15)	40·07	6·52	6·81	(0·161)	
IV	$C_{18}H_{36}N_2S_4Cu$	45·78	7·68	5·93	0·198	76·5–77
	(472·26)	44·93	7·59	5·80	(0·206)	
V	$C_{22}H_{44}N_2S_4Cu$	50·01	8·39	5·30	0·103	91·92
	(528·36)	50·27	8·12	5·21	(0·140)	
VI	$C_{26}H_{52}N_2S_4Cu$	—	—	—	—	viscous
	(584·26)	—	—	—	—	liquid
VII	$C_{10}H_{20}N_2S_4Cu$	33·36	5·60	7·78	0·047	242–243
	(360·05)	33·10	5·40	7·54	(0·153)	
VIII	$C_{14}H_{28}N_2S_4Cu$	40·40	6·78	6·73	0·014	>340
	(416·15)	40·27	6·38	6·59	(0·032)	
IX	$C_{18}H_{36}N_2S_4Cu$	45·78	7·68	5·95	0·314	205·5–206
	(472·26)	45·72	7·50	5·68	(0·167)	
X	$C_{12}H_{20}N_2S_4Cu$	37·52	5·25	7·29	0·024	333–334
	(384·07)	38·00	5·12	7·01	(0·012)	
XI	$C_{10}H_{16}N_2O_2S_4Cu$	30·95	4·16	7·22	0·012	337–339
	(388·02)	30·67	4·08	7·10	(0·010)	

of the chloroform solutions of the dithiocarbamate chelates of Cu(II) indicates that they are stable for up to 14 days.

Solutions of $1 . 10^{-3}$ and $4-10^{-4}$ mol l^{-1} dithiocarbamate chelates of Cu(II) and Zn(II) in chloroform, ethanol and methanol were prepared by dissolving the necessary amount of substance, as given in Tables II and III in 250 ml of the appropriate solvent. The absorption spectra were studied using chloroform, ethanol and methanol solutions with concentrations of $2 . 10^{-5}$ to $8 . 10^{-5}$ mol l^{-1}, prepared from stock solutions. The absorption spectra were recorded on a recording SPECORD UV VIS spectrophotometer (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 a precision of ± 1 nm.

TABLE III

Characteristic data on the Zn(II) chelates of dithiocarbamic acids

Chelate	General formula (m.w.)	Calculated/Found			Solubility g/100 g MeOH (EtOH)	Melting point °C
		% C	% H	% N		
XII	$C_6H_{12}N_2S_4Zn$ (305·75)	23·57 23·30	3·96 3·89	9·16 9·13	0·036 (traces)	317—318
XIII	$C_{10}H_{20}N_2S_4Zn$ (231·86)	33·19 33·23	5·57 5·63	7·74 7·95	0·123 (0·042)	228—229
XIV	$C_{14}H_{28}N_2S_4Zn$ (417·96)	40·23 40·21	6·75 6·75	6·70 6·79	0·111 (0·145)	142—143
XV	$C_{18}H_{36}N_2S_4Zn$ (474·07)	45·60 45·73	7·65 7·84	5·91 5·75	0·134 (0·138)	137·5—138
XVI	$C_{22}H_{44}N_2S_4Zn$ (530·17)	49·84 49·62	8·37 8·33	5·28 5·18	0·138 (0·214)	107—108
XVII	$C_{26}H_{52}N_2S_4Zn$ (586·10)	— —	— —	— —	— —	very viscous liquid
XVIII	$C_{10}H_{20}N_2S_4Zn$ (361·86)	33·19 33·00	5·57 5·60	7·74 7·85	0·095 (0·007)	244—245
XIX	$C_{14}H_{28}N_2S_4Zn$ (417·96)	40·23 40·31	6·75 6·70	6·70 6·68	0·044 (0·012)	287—288
XX	$C_{18}H_{36}N_2S_4Zn$ (474·07)	45·60 45·68	7·65 7·50	5·91 5·82	0·129 (0·169)	153—154
XXI	$C_{12}H_{20}N_2S_4Zn$ (385·88)	37·35 37·71	5·22 5·10	7·26 7·26	0·033 (0·027)	288—289
XXII	$C_{10}H_{16}N_2O_2S_4Zn$ (389·83)	30·81 30·67	4·14 4·19	7·19 7·25	(traces) (traces)	>340

RESULTS AND DISCUSSION

In Fig. 1 are depicted the absorption spectra in ethanol solutions of some bis(dithiocarbamate) chelates of Cu(II) in the UV spectral region. The spectra contain

TABLE IV

The molar absorption coefficients of chloroform solutions of dithiocarbamate chelates of Cu(II) in the UV and visible spectral regions

Chelate	λ_{max} nm	ε l/mol cm	λ_{max} nm	ε l/mol cm
$[Cu(Me_2DTC)_2]$	268	29 800	435	10 200
$[Cu(Et_2DTC)_2]$	272	33 000	437	10 600
$[Cu(Pr_2DTC)_2]$	273	33 400	436	11 200
$[Cu(Bu_2DTC)_2]$	274	33 800	435	11 500
$[Cu(Pe_2DTC)_2]$	274	34 100	435	11 000
$[Cu(iPr_2DTC)_2]$	276	32 800	439	9 800
$[Cu(iBu_2DTC)_2]$	276	34 900	437	10 300
$[Cu(Me,iPrDTC)_2]$	269	32 500	437	10 800
$[Cu(PpDTC)_2]$	273	35 500	435	10 000
$[Cu(MoDTC)_2]$	274	35 700	436	9 800

TABLE V

The molar absorption coefficients of chloroform solutions of dithiocarbamate chelates of Zn(II) in the UV spectral region

Chelate	λ_{max} nm	ε l/mol cm
$[Zn(Me_2DTC)_2]$	260	30 200
$[Zn(Et_2DTC)_2]$	263	32 800
$[Zn(Pr_2DTC)_2]$	265	35 000
$[Zn(Bu_2DTC)_2]$	266	35 200
$[Zn(Pe_2DTC)_2]$	266	35 500
$[Zn(iPr_2DTC)_2]$	267	32 200
$[Zn(iBu_2DTC)_2]$	268	37 000
$[Zn(Me,iPrDTC)_2]$	263	32 000
$[Zn(PpDTC)_2]$	267	36 500
$[Zn(MoDTC)_2]$	266	36 000

absorption bands at 273 and 290 nm, that were assigned to the $\pi - \pi^*$ transition within the ligands[10,12,15] and bands at 245 and 220 nm, assigned to charge transfer transitions[15].

The spectra of Zn(II) DTC and Cu(II) in the near UV region are very similar. The electronic spectra of the DTC chelates Zn(II) (Fig. 2) contain bands at 265 and 280 nm corresponding to transitions within the ligands[10,12,16,17]. The band around 207 nm was assigned[19] to carbon disulphide as a decomposition product of alkaline dithiocarbamates; this band is lacking in the chelate spectra, reflecting the stabilizing effect of the central atom on the DTC ligands, apparently connected with the dissociability of the DTC chelates.

From an analytical point of view, the absorption bands of copper(II) and zinc(II) chelates with λ_{max} in the regions around 273 nm and 260 nm (ε 33·000) are most important. The intensities of these bands are strongly dependent on the chelate concentration. The other absorption bands in the UV spectra of the bis-dithiocarbamate chelates of Cu(II) and Zn(II) are less intense or cannot be used in the spectrophotometric determination because of intereference, mostly from the solvent, in the absorption of radiation, Thus they were not studied further It can be seen

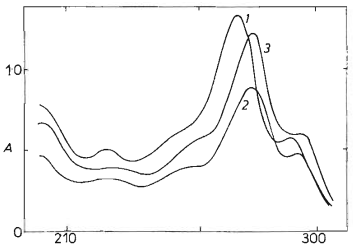

FIG. 1

Absorption spectra of ethanol solutions of Cu(II)DTC. *1* [$Cu(Me_2DTC)_2$], $c = 4 \cdot 10^{-5}$ mol l^{-1}, $d = 1$ cm; *2* [$Cu.(Pr_2DTC)_2$, $c = 2{\cdot}5 \cdot 10^{-5}$ mol l^{-1}, $d = 1$ cm; *3* [$Cu(Pe_2DTC)_2$], $c = 3{\cdot}5 \cdot 10^{-5}$ mol l^{-1}, $d = 1$ cm

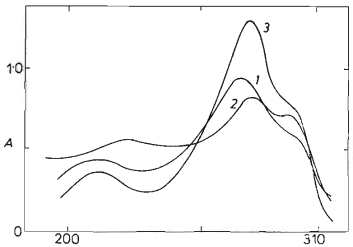

FIG. 2

The absorption spectra of ethanol solutions of Zn(II)DTC. *1* [$Zn(Me_2DTC)_2$], $c = 3 \cdot 10^{-5}$ mol l^{-1}, $d = 1$ cm; *2* [$Zn(Pr_2DTC)_2$], $c = 2 \cdot 10^{-5}$ mol l^{-1}, $d = 1$ cm; *3* [$Zn(Pe_2.DTC)_2$], $c = 3{\cdot}5 \cdot 10^{-5}$ mol l^{-1}, $d = 1$ cm

TABLE VI

The effect of the solvent on the shift of λ_{max} of the absorption bands of dithiocarbamate chelates of Cu(II)

Chelate	$CHCl_3$[a] λ_{max}, nm	$CHCl_3$: EtOH[b] 1 : 4 λ_{max}, nm	$CHCl_3$: MeOH[c] 1 : 9 λ_{max}, nm
$[Cu(Me_2DTC)_2]$	268	266	265
$[Cu(Et_2DTC)_2]$	272	271	270
$[Cu(Pr_2DTC)_2]$	273	271	271
$[Cu(Bu_2DTC)_2]$	274	271	272
$[Cu(Pe_2DTC)_2]$	274	272	271
$[Cu(He_2DTC)_2]$	274·5	272	271·5
$[Cu(iPr_2DTC)_2]$	276	274	273
$[Cu(iBu_2DTC)_2]$	276	274	274
[Cu(Me,iPrDTC)$_2$]	269	268	267
[Cu(PpDTC)$_2$]	273	271	271
[Cu(MoDTC)$_2$]	274	272	272

[a] [a] $\varepsilon_r \sim 5{\cdot}0$; $\varepsilon_r \sim 20{\cdot}0$; $\varepsilon_r \sim 30{\cdot}0$.

TABLE VII

The effect of the solvent on the shift of the λ_{max} of the absorption bands of dithiocarbamate chelates of Zn(II)

Chelate	$CHCl_3$[a] λ_{max}, nm	$CHCl_3$: EtOH[b] 1 : 4 λ_{max}, nm	$CHCl_3$: MeOH[c] 1 : 9 λ_{max}, nm
$[Zn(Me_2DTC)_2]$	260	257	256
$[Zn(Et_2DTC)_2]$	263	261	260
$[Zn(Pr_2DTC)_2]$	265	263	262
$[Zn(Bu_2DTC)_2]$	266	263	263
$[Zn(Pe_2DTC)_2]$	266	265	264
$[Zn(He_2DTC)_2]$	266	265	264
$[Zn(iPr_2DTC)_2]$	267	265	264
$[Zn(iBu_2DTC)_2]$	268	266	265
[Zn(Me,iPrDTC)$_2$]	262	259	258
[Zn(PpDTC)$_2$]	267	264	264
[Zn(MoDTC)$_2$]	266	263	263

[a] $\varepsilon_r \sim 5{\cdot}0$; [b] $\varepsilon_r \sim 20{\cdot}0$; [c] $\varepsilon_r \sim 30{\cdot}0$.

from the results in Table IV that the UV region is preferable to the visible region for the trace analysis of Cu because the bands at 273 nm are much more intense than the bands in the visible region at 430 nm.

The effect of the length of the alkyl chain bonded to the nitrogen atom in the dithiocarbamate molecules on the intensity of the absorption bands of the Cu(II) chelates at 273 nm and the absorption bands of the Zn(II) chelates at 260 nm, as well as the shift of the λ_{max} of these bands are depicted in Figs 1 and 2 and in Tables IV and V. It can be seen that an increase in the size of the alkyl substituent leads to a red shift of the bands and to increased intensity, that, among other things, indicates that it is preferable to use DTC derivatives with higher alkyls in the trace analysis of Cu and Zn. The red shift and increase in the band intensity result from the induction effects[20,21] of the alkyl groups mentioned above, leading to electron delocalization towards the absorbing chromophores and thus to an increase in the length of the absorbing system. The highest λ_{max} values for DTC chelates of Cu(II) and Zn(II) derived from diisopropyl- and diisobutylamines can be explained by a combination of the induction and hyperconjugation effects[21] of the isopropyl and isobutyl groups, leading to an increase in the conjugation of the chelate electron system.

The effect of the solvent polarity of the λ_{max} of the bands at 273 nm or 260 nm is apparent from Tables VI and VII. It is evident from the results that an increase in the solvent polarity leads to an increase in the band intensities and a blue shift for all the studied substances, that can be connected with an increase in the electron density around the Cu–S and Zn–S bonds with increasing solvent polarity.

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