

Spectral and Extraction Study of Cd DTC Chelates

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Received 16 September 2000

The absorption spectra in the range of $\lambda = 200\text{--}350$ nm and IR spectra in the range of $\tilde{\nu} = 200\text{--}1700$ cm^{-1} of cadmium(II) dithiocarbamate chelates are described. The values of the molar absorptivity of the absorption bands of chelates with ligands derived from diethyl-, dipropyl-, diisopropyl-, dibutyl-, diisobutylamine and piperidine around 260 nm and 280 nm were determined in the range $24\,900\text{--}32\,000$ $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$ or $13\,500\text{--}21\,400$ $\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$. On the basis of spectral properties there is a dependence of the values of ϵ and λ_{max} at about 265 nm (this wavelength is recommended for the spectrophotometric determination of cadmium) on alkyl substituents in the dithiocarbamate ligand. The influence of the solvent polarity on the shift of λ_{max} , the influence of alkyl substituents in the dithiocarbamate ligands on the values of wavenumber of their normal vibrations, and the influence of the central atom on the intensity of the absorption band at approximately 265 nm and the efficiency of the extraction are discussed. Chloroform extraction curves of Cd(II) chelates under investigation are drawn in the range of pH 1–11. The optimal pH values for determination of Cd(II) in the form of dithiocarbamate complexes and detection limits of Cd spectrometric determination are given.

In previous papers the spectral properties of the alkali salts of dithiocarbamide acids [1] and their chelates with Ni(II) [2], Cu(II), and Zn(II) [3] were described, and the influence of alkyl substituent and the solvent polarity on the absorption band shift was also studied. The possibility of the analytical use of different ligands of the DTC alkali salts for the spectrometric determination of Ni, Cu, Zn after extraction into chloroform [4, 5] was evaluated and IR spectra of DTC chelates of the presented metals were correlated with their crystal structure [6, 7].

The alkali salts of dithiocarbamic (DTC) acids (Table 1) form with Cd(II) pentacoordinated chelates (a trigonal pyramid or tetragonal pyramid) presented in Table 2 having the general formula $\text{Cd}(\text{R}-\text{C}-\text{S}_2)_2$, where R is a rest of dialkylamine. The aim of this work is to study the UV and IR absorption spectra of Cd(II) DTC chelates and the extraction conditions from the viewpoint of the possibility to use them for the spectrometric determination of Cd(II).

The absorption spectra of ethanol solutions of $\text{Na}(\text{Et}_2\text{DTC})$ and $\text{Cd}(\text{Et}_2\text{DTC})_2$ are presented in Fig. 1. The spectra of Cd(II) DTC chelates in chloroform solutions are shown in Fig. 2. The wavelength maxima of the important absorption bands are in Table 3.

According to the shape and intensity of the ab-

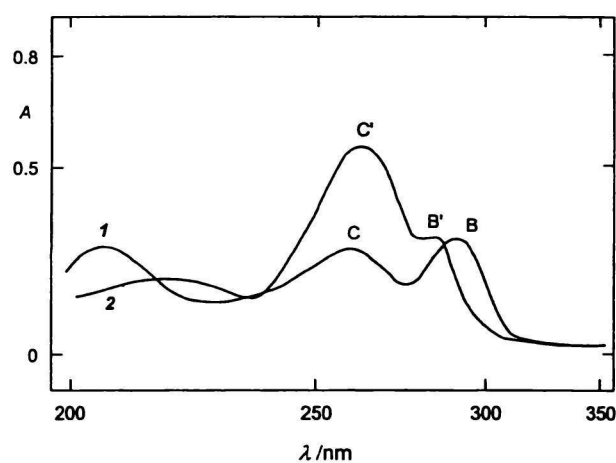


Fig. 1. Absorption spectra of ethanol solutions of 1. NaEt_2DTC and 2. $\text{Cd}(\text{Et}_2\text{DTC})_2$ in the UV range.

sorption bands of the spectra of chloroform or ethanol solutions of Cd(II) DTC chelates the most significant band for the Cd determination is the C band with λ_{max} at approximately 265 nm. This band is intensive enough, symmetrical and located in the range of wavelengths where the used solvents do not absorb. It is sufficiently sensitive to changes of the Cd concen-

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Table 1. Alkali Salts of Dithiocarbamic Acids

Formula		Denotation
$(C_2H_5)_2NCS_2 Na$	sodium diethyldithiocarbamate (cupral)	Na Et ₂ DTC
$(C_3H_7)_2NCS_2 K$	potassium dipropyldithiocarbamate	K Pr ₂ DTC
$(C_4H_9)_2NCS_2 Na$	sodium dibutyldithiocarbamate	Na Bu ₂ DTC
$(iC_3H_7)_2NCS_2 Na$	sodium diisopropyldithiocarbamate	Na iPr ₂ DTC
$(iC_4H_9)_2NCS_2 Na$	sodium diisobutyldithiocarbamate	Na iBu ₂ DTC
$C_5H_{10}N K$	potassium 1-piperidinocarbodithioate	K PpDTC

Table 2. Elemental Analysis of DTC Chelates of Cd(II)

DTC Cd(II)	$w_i(\text{calc.})/\%$			$w_i(\text{found})/\%$		
	C	H	N	C	H	N
Cd(Et ₂ DTC) ₂	29.37	4.93	6.85	29.33	5.02	6.92
Cd(Pr ₂ DTC) ₂	36.15	6.07	6.02	35.74	6.15	5.96
Cd(iPr ₂ DTC) ₂	36.15	6.07	6.02	35.94	6.05	6.22
Cd(Bu ₂ DTC) ₂	41.48	6.96	5.38	40.93	7.03	5.98
Cd(iBu ₂ DTC) ₂	41.48	6.96	5.38	41.43	7.17	5.50
Cd(PpDTC) ₂	34.49	1.21	6.70	33.39	1.68	6.73

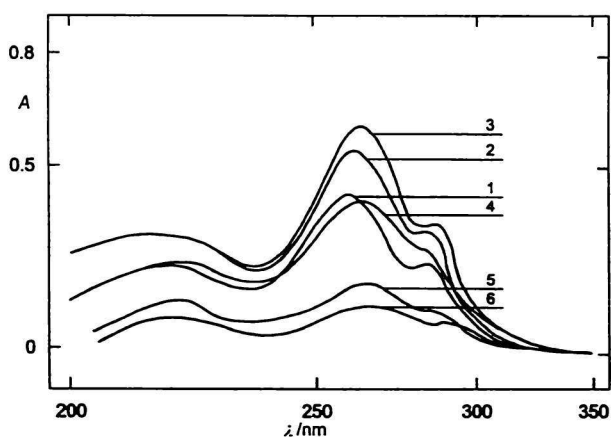


Fig. 2. Absorption spectra of chloroform solutions of 1. Cd(Et₂DTC)₂, 2. Cd(Pr₂DTC)₂, 3. Cd(Bu₂DTC)₂, 4. Cd(PpDTC)₂, 5. Cd(iPr₂DTC)₂, 6. Cd(iBu₂DTC)₂ in the UV range.

tration and so the further experiments were devoted to the study of the spectral characteristics from the analytical point of view.

From the ethanol solutions spectra it is clear that the B band of chelates shifts to the shorter wavelengths with respect to the B band of alkali salts of DTC [1] and its intensity decreases. On the other hand, the wavelengths of the maximum absorption bands C and C' with DTC ligands [8–10] and chelates derived from the same diaalkylamine are very similar but after formation of the chelate there can be observed a significant growth of absorption attributed to the original atomic configuration of S—C=S ligand. This fact can be explained by incorporating Cd into chelate, which causes a larger original absorp-

tion system. The data summarized in the first column of Table 3 (chloroform solutions) indicate the dependence between the position of $\lambda_{\max} = 265$ nm and the kind of the substituent on the nitrogen atom. A significant growth of the value λ_{\max} in the order of ethyl-, propyl-, butyl-, isobutyl-, isopropyl- is evident whereas an enormous growth of the value at the isopropyl derivative in comparison with the propyl derivative can be explained by the hyperconjugative effect, which confirms the previous data [2, 3].

From the data in Table 3 it is clear that the solution polarity influences the λ_{\max} shift of the bands of DTC chelates of Cd. It is evident that the higher polarity of the solvent caused the shift of both the bands to the shorter wavelengths while this effect is more significant at about 265 nm than with the band at about 285 nm. This fact can be caused by the significant influence of $n-\pi^*$ transfer on the absorption but on the other hand, the high band intensity indicates the $\pi-\pi^*$ transfer [11, 12]. It can be assumed that a chelate interaction of both ligand molecules through the central atom can occur and this phenomenon causes larger area of the absorption system.

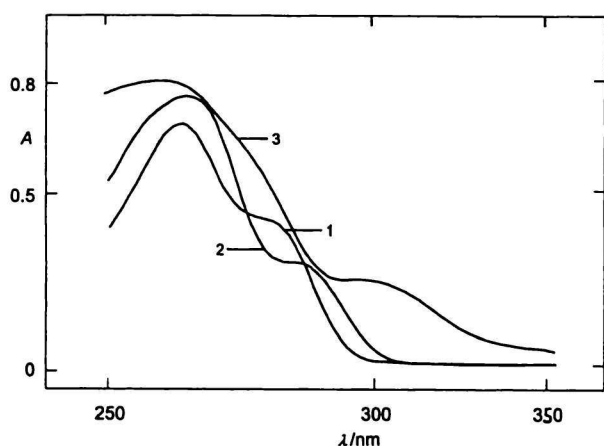
The influence of the central atom on the position and the shape of the absorption bands of DTC Cd in the UV range can be evaluated by comparing the absorption spectra of ethyl derivatives DTC Zn(II), Pb(II), and Cd(II). Fig. 3 shows that the growth of the central atom volume leads to the formation of the wider and more intensive C bands [7]. This fact can be explained on the basis of higher stability of the chelate structure which is indicated by the pH values shift of maximum chelate extraction in the acidity range in the order Zn(Et₂DTC)₂ at pH 4–10, Cd(Et₂DTC)₂ at pH 3–10, Pb(Et₂DTC)₂ at pH 2–6.

Table 3. Influence of the Solvent on the Shift of the λ_{\max} of the Absorption Bands B' and C' of Dithiocarbamate Chelates of Cadmium(II)

Chelate	Band	Chloroform	φ (chloroform—ethanol)	φ (chloroform—methanol)
		λ_{\max}/nm	1 : 4 λ_{\max}/nm	1 : 9 λ_{\max}/nm
Cd(Et ₂ DTC) ₂	B'	286	283	282.5
	C'	265	260.5	259
Cd(Pr ₂ DTC) ₂	B'	287	283	282.5
	C'	266	261.5	260.5
Cd(Bu ₂ DTC) ₂	B'	290	287	287
	C'	268	265	264
Cd(iPr ₂ DTC) ₂	B'	284	282.5	282.5
	C'	270	261.5	261.5
Cd(iBu ₂ DTC) ₂	B'	288	283	282.5
	C'	271	265.5	263.5
Cd(PpDTC) ₂	B'	284	281	280
	C'	268	263	262

Table 4. Wavenumbers of the $\nu(\text{C—N})$, $\nu(\text{C—S})$, and $\nu(\text{M—S})$ Vibrations of Dithiocarbamate Chelates of Cadmium(II)

Chelate	$\lambda_{\max}(\text{C—N})/\text{cm}^{-1}$	$\lambda_{\max}(\text{C—S})/\text{cm}^{-1}$	$\lambda_{\max}(\text{M—S})/\text{cm}^{-1}$
Cd(Et ₂ DTC) ₂	1503	986	392, 378
Cd(Pr ₂ DTC) ₂	1500	976	380, 363
Cd(Bu ₂ DTC) ₂	1490	975	372
Cd(iPr ₂ DTC) ₂	1485	940	315
Cd(iBu ₂ DTC) ₂	1490	975	368
Cd(PpDTC) ₂	1485	970	358

**Fig. 3.** Absorption spectra of chloroform solutions of Zn(Et₂DTC)₂ (1), Cd(Et₂DTC)₂ (2), Pb(Et₂DTC)₂ (3); $c = 4 \times 10^{-5} \text{ mol dm}^{-3}$.

The influence of the ligand on electron effects can be studied by analyzing IR spectra of the series of DTC chelates of Cd(II) (Table 4). The results show that the longer chain of the alkyl substituent on the nitrogen atom causes decreasing of the value of $\nu(\text{C—N})$ and $\nu(\text{C—S})$ in the order ethyl to butyl until it reaches the minimum at Cd(iPr₂DTC)₂; this effect probably can be explained by increasing of the alkyl groups mass [7, 13] and by hyperconjugation. The va-

lent vibration wavenumber of the bond Cd—S shows a similar dependence on the alkyl length. The anomalous decreasing of the wavenumber of the isopropyl derivative in comparison with the propyl derivative can be explained by hyperconjugation as well as spherical effects.

The determination of Cd in the form of DTC chelate after extraction into chloroform required to find such experimental conditions in which the recovery of the extraction of DTC Cd chelates is in the range 98—100 % at a practically zero extractability [4] of DTC ligands. This is important from the point of view of the following spectrophotometrical determination because the ligand presence in the extract within a certain range [4] of the pH values (3—7) may strongly influence the Cd determination. In addition to factors influencing the formation of the chelate produced at a given ligand and metal concentration (the reaction time, pH of water phase) also factors influencing the extraction process itself were investigated (the extraction time, the organic phase volume, and the number of repeated extractions).

The most suitable reaction time is 4.5—5.0 min. It can be seen in Fig. 4 that the shorter time causes the lower extraction recovery and does not reach the desirable values. The longer time than 5 min has no influence on higher extraction recovery. The optimal extraction time is in the range 30—60 s with volumes of the organic and water phase presented in opera-

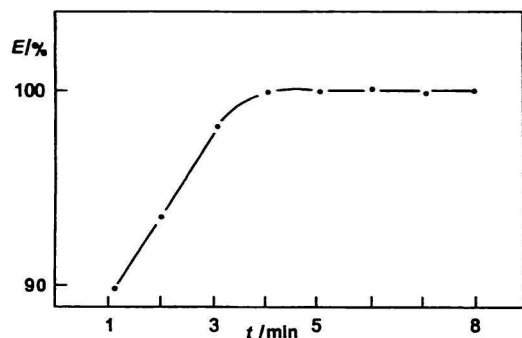


Fig. 4. The dependence of yield extraction of $\text{Cd}(\text{Et}_2\text{DTC})_2$ on reaction time t_R .

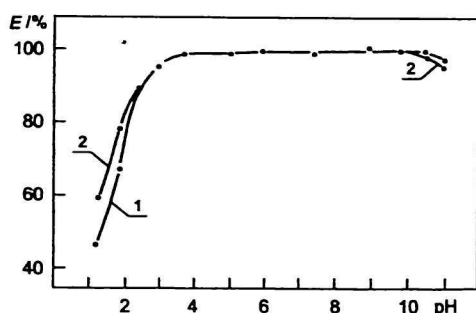


Fig. 5. The dependence of yield extraction by chloroform on pH of water phase of reaction mixture 1. $\text{Cd}(\text{Et}_2\text{DTC})_2$, 2. $\text{Cd}(\text{Bu}_2\text{DTC})_2$.

tion instructions described above. As seen from the extraction curves it is possible to reach 98–100 % of the extraction recovery. The extraction curves show

the dependence of the extraction recovery ($E/\%$) on the pH value of the water phase of the extraction mixture that was measured potentiometrically. A number of buffer solutions were recommended [2, 3], in this paper the ammonium acetate solutions were used because the interference caused by formation of other complexes of Cd^{2+} in the water phase is less probable. The dependences of the extraction recovery on the pH values of the water phase of extracts for DTC chelates $\text{Cd}(\text{Bu}_2\text{DTC})_2$ and $\text{Cd}(\text{PpDTC})_2$ are shown in Fig. 5. The pH values of the water phases which have the extraction recovery within the range of 98–100 % are in Table 5.

It is evident that the minimum extraction pH range includes weak acid, neutral and alkali region approximately up to the pH value 10. As for the fact that in the alkali range DTC ligands are not extracted by chloroform, this range is the most recommended for the spectrophotometrical determination of Cd^{2+} . Table 6 summarizes the characteristic data of the spectrophotometrical determination of Cd^{2+} after its extraction into chloroform in the form of Cd DTC. The calibration dependences are linear within the range of 2×10^{-7} – 1×10^{-4} mol dm^{-3} . The detection limit was calculated from the value of absorbance of blank experiment for the ligands NaEt_2DTC , KPr_2DTC , NaIPr_2DTC , NaBu_2DTC , NaIBu_2DTC , and KPpDTC after extraction into chloroform at a given wavelength and pH value as a sum of triple of the standard deviation and the arithmetic mean of blank absorbance.

It is evident that the values of ϵ are sufficiently high and according to the value of the detection limits the trace concentrations of Cd^{2+} can be determined.

Table 5. pH Range of Aqueous Phase^a

Chelate	pH	Chelate	pH
$\text{Cd}(\text{Et}_2\text{DTC})_2$	4.0–10.7	$\text{Cd}(\text{PpDTC})_2$	3.3–8.5
$\text{Cd}(\text{Pr}_2\text{DTC})_2$	3.0–10.2	$\text{Cd}(\text{iPr}_2\text{DTC})_2$	3.0–9.0
$\text{Cd}(\text{Bu}_2\text{DTC})_2$	4.0–9.7	$\text{Cd}(\text{iBu}_2\text{DTC})_2$	3.5–9.8

a) The pH range in which the extraction yields of DTC chelates are above 98 % within the reaction time of 4.5 min.

Table 6. The Values of Molar Absorptivity and Detection Limits of Cd Determination as Cd DTC

Chelate	λ_{max}	ϵ	pH of extraction	Limit of Cd detection
	nm			$\text{mol}^{-1} \text{dm}^3 \text{cm}^{-1}$
$\text{Cd}(\text{Et}_2\text{DTC})_2$	265	29024	10.0	54.2
$\text{Cd}(\text{Pr}_2\text{DTC})_2$	266	30872	10.0	49.6
$\text{Cd}(\text{iPr}_2\text{DTC})_2$	270	26738	9.0	74.5
$\text{Cd}(\text{Bu}_2\text{DTC})_2$	268	30932	9.5	18.8
$\text{Cd}(\text{iBu}_2\text{DTC})_2$	271	31528	9.5	14.2
$\text{Cd}(\text{PpDTC})_2$	268	31956	8.5	22.5

Considering a low determination selectivity, however, it is necessary for real samples to consider Cd^{2+} separation from interfering elements at the given pH value for DTC chelates which can be also extracted into chloroform.

EXPERIMENTAL

The hydrochloric acid with anal. grade purity was purified from heavy metals by distillation in a glass equipment. The methanol and ethanol were spectrally pure, the chloroform used for extraction and preparation of the standard solutions of Cd(II) DTC chelates was always freshly distilled and there was not observed the absorbance at 255 nm. The deionized water used had the resistance of 18 M Ω or more. All the other chemicals used were of anal. grade. Acetate buffers according to Babko [14] were used for the preparation of extraction mixtures within a pH range of 3–11 and HCl solutions were used for the preparation of extraction mixtures within a pH range of 1–3. The pH values were controlled potentiometrically.

The chloroform or ethanol standard solutions (10^{-3} mol dm $^{-3}$) of the Cd(II) DTC chelates were prepared by diluting the compounds presented in Table 2. The stability of the standard solutions was controlled spectrophotometrically at laboratory temperature. The chloroform solutions were stable during 48 h while the ethanol solutions were stable only during 8 h. The two different compositions of the solvents of the Cd(II) DTC chelates were used for the study of the maximum wavelength shift: φ_r (chloroform—ethanol) 1:4 and 1:9. The spectra were measured within the time of 20 min. A spectrometer Specord M40, a Specord IR 80 (Zeiss), and an atomic absorption spectrophotometer AA 40 (Varian) were used for the measurement.

The solutions with a concentration of 2×10^{-7} — 1×10^{-4} mol dm $^{-3}$ were used for the study of the absorption spectra of Cd(II) DTC chelates in the UV range. The concentration of the standard solutions of Cd(II) DTC chelates for the measurement of the absorbance was in the range of 2×10^{-7} — 1×10^{-4} mol dm $^{-3}$ to prepare the calibration curve. The calibration standard solutions were prepared from DTC chelates of Cd(II) shown in Table 2 by diluting in chloroform. The measurement was accomplished in quartz cells of the length 0.2 cm, 0.5 cm, 1.0 cm, and 5.0 cm. The absorption spectra of the Cd(II) DTC chelates in the IR range were measured within 400—4000 cm $^{-1}$ using KBr technique and within 200—600 cm $^{-1}$ by nujol technique after pressing of the emulsion into a polyethylene folio.

The concentration of Cd in the water and organic phase at the extraction was controlled by the flame AAS method under current conditions recommended by producers.

Cd(II) DTC Chelates

0.1 mol of the alkali salts of DTC acid was diluted in 100 cm 3 of distilled water and during mixing (1 h) 0.05 mol of cadmium chloride dehydrate (a solution of 10.9 g in 50 cm 3) was added at the temperature of 15—20°C. After adding the solution was mixed for 1 h. The precipitate was filtered, washed on a filter with cold water (4°C) and dried up. A mixture of ethanol—chloroform was used for recrystallization of the raw product and the organic elemental analysis was used for the determination of the purity of the product. The results of the elemental analysis are presented in Table 2 and it can be supposed that the products are sufficiently clear.

Dependence of Extraction Yields on the Reaction Time*

1 cm 3 of the aqueous solution of Cd^{2+} (10^{-3} mol dm $^{-3}$) was mixed in a separation funnel with 5 cm 3 of octane buffer solution having the pH values 3, 7, 11. 5 cm 3 of an aqueous solution of cupral (10^{-3} mol dm $^{-3}$) was added to the mixture and the resulting precipitate of the chelate $\text{Cd}(\text{Et}_2\text{DTC})_2$ was extracted during 30 s after different time intervals (t/min : 0, 0.5, 1.0, 2.0, 3.0, 4.0, 5.0, 6.0, 7.0, 8.0) with 20 cm 3 of chloroform. The extract containing the chelate of $\text{Cd}(\text{Et}_2\text{DTC})_2$ was put into a platinum bowl and evaporated. After adding of concentrated HNO_3 it was again evaporated and the rest was slightly heated. After leaching with the diluted nitric acid cadmium was determined by the flame AAS method.

The Dependence of the Extraction Yield on the pH Values of the Water Phase

The extraction funnels with a capacity of 50 cm 3 were used for the extraction of Cd(II) DTC chelates at the reaction time of 4.5 min in the range of the pH values 1—11. The extraction was carried out with a water phase containing 5 cm 3 of acetate buffer solution (or HCl solution), 1 cm 3 of 1×10^{-3} mol dm $^{-3}$ Cd^{2+} solution and 5 cm 3 of 1×10^{-3} mol dm $^{-3}$ alkali salt DTC solution. After 4.5 min the resulting precipitate was extracted with 15 cm 3 of chloroform during 0.5 min. The chloroform phase containing Cd(II) DTC chelate was separated and if it was not transparent the phase was filtered through a filter paper into a measuring flask for 25 cm 3 . The water phase was extracted again with 5 cm 3 of chloroform for 0.5 min. The extracts were put together and the next procedure continued in a platinum bowl as it was mentioned above.

*The reaction time is the time of DTC ligand with Cd^{2+} ion in an extraction funnel before adding chloroform.

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