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UV–Vis–NIR spectroscopy and colour of bis(*N*-phenylsalicylaldiminato)cobalt(II) in a variety of solvents

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Abstract

Cobalt(II) complex with Schiff base obtained by condensation aniline with salicylaldehyde cobalt(II) complex, was studied in variety of solvents. The product i.e. salicylidene-anilinecobalt(II) ([Co(salan)$_2$]) complex is a red crystalline compound easily soluble in common solvents like chloroform (CHCl$_3$), benzene (Bz), toluene (MBz), dioxane (DX), dimethylformamide (DMF), dimethyl sulfoxide (DMSO), and acetonitrile (ACN) that is a necessary condition to observe solvatochromism. It has been characterised by elemental analyses, molar conductivities, ultraviolet (UV) and visible (Vis) spectroscopy. The molar conductivities indicate their non-electrolytic properties in all the solvents. Electronic spectra have been used to postulate the tetrahedral geometry for the species in solutions and to determine the coordination properties of ligators and their bonding abilities (ligand-field parameters), as well as their solvatochromism. The results obtained show fine colour changes. For discrimination of colour changes we applied CIE and CIELAB colour spaces.

Keywords: Cobalt(II) complexes; Schiff base; Salicylideneaniline; Solutions; Ligand-field parameters; Electronic spectra; Chromaticity; Solvatochromism

1. Introduction

This paper is a continuation of our studies on interpretation of the electronic spectra of the cobalt(II) complexes with Schiff bases derived from salicylaldehyde and amines in various solvents [1]. It is known that, variation of the size and nature of substituent of the salicyclaldimine ligand can be responsible for changes in the coordination geometry around metal ion. Because the electronic absorption spectra of the complexes depend on these changes, it is sensibly to calculate the ligand-field parameters.

The main aim of this work is explanation of solvent effect. It should be considered in two ways: (1) solvation effect on the structure and stability of complex, (2) solvatochromic effects on UV–Vis–NIR spectra. Because we are looking for an answer for the following question: are the geometry around metal ion and its bonding properties connected with chromaticity, we have extended this paper including results on solvatochromism and chromaticity for the bis(salicylidene-aniline)cobalt(II) complex ([Co(salan)$_2$]), which was investigated in a variety of solvents. It has been known that wavenumbers for absorption maximum correlate well with the solvent parameters such as Dimroth and Reichardt's E_T and Kosower's Z for charge transfer bands in the spectra of bis(2,2′dipyridyl)bis-cyanoiron(II) and analogous complexes containing Schiff base [2]. The position and intensity of d–d bands also have been correlated with some success with different solvent parameters [3–5]. In this paper we report similar correlation for the bis(*N*-phenyl-salicylaldiminato)cobalt(II) complex. The solvent parameters considered in this work are Kosower's Z, Dimroth and Reichardt's E_T, Kamlet and Taft's α, β, π^*, dielectric constant ε and Gutman's donor DN, and acceptor numbers AN. These values are directly obtainable from literature [6–11].

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The solvent effects can be the cause of both energetic shifts of absorption bands and change of solution colour. The latter effect can be difficult to observe by human eye. To precisely characterise the colour one usually uses tristimus colorimetry [12–18]. Colours of solutions and solid are reported in CIE and CIELAB colour space in our work.

2. Experimental

2.1. Measurements

The molar conductances were measured using a microcomputer pH/conductivity meter CPC-551 (Elmetron, Poland) and platinum dip electrode CD-2. The ultraviolet (UV) spectra were recorded on a SPECORD M40 (Zeiss Jena) spectrophotometer digitally (20 cm^{-1} step) after dissolving the sample for concentration $c \sim 5.0 \times 10^{-4}$ M. The near infrared (NIR) and visible (Vis) spectra (both solutions and solid state) were carried out (digitally 1 nm step) on a Cary 5E (Varian) spectrophotometer. The conductivities were measured for the concentration $c \sim 1.0 \times 10^{-2}$ M at room temperature. The NIR–Vis and UV spectral data at selected approximately 2500 wavenumbers, i.e. 1500 over the range 5000–18 900 cm^{-1} (NIR) and 1000 over the range 18600–40 000 cm^{-1} (UV), were resolved into the Gaussian components. These spectra were used for calculations of ligand-field (CFP/AOM) parameters (in NIR–Vis region) and chromaticity coordinates (in Vis region). The measurement conditions for the spectra in Vis region were as follows: $c = 1.0 \times 10^{-3}$ M, $l = 0.1$ cm.

2.2. Chemicals

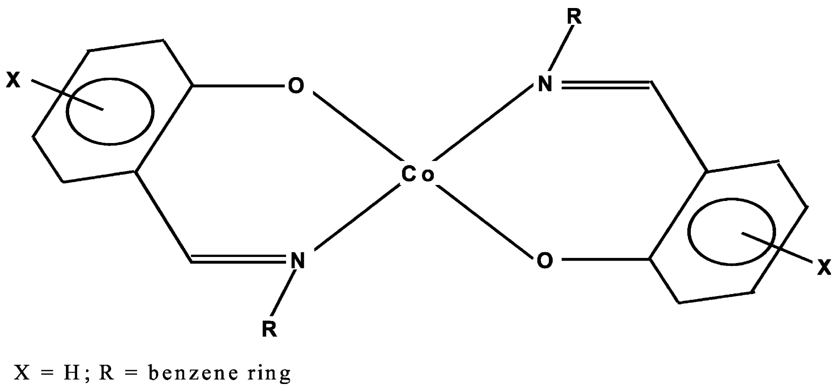
Complex [Co(salan)$_2$] was prepared according to Sacconi et al. [19] by reaction of bis-(salicylaldehyde)cobalt(II) dihydrate with aniline in ethanol. The solid complex was precipitated rapidly and the pure compound was obtained as red crystals. The complex is insoluble in water but easy soluble in variety of solvents: the non-polar with weak donor strengths like chloroform ($CHCl_3$), benzene (Bz), toluene (MBz), and polar with intermediate donor strengths like acetonitrile (ACN), dioxane (DX), and polar with strong donor strengths like dimethylformamide (DMF), and dimethyl sulfoxide (DMSO).

The complex was analysed for purity by elemental analysis. Cobalt analyses were performed by EDTA titration using murexide as an indicator. The results agreed with the expected composition. Analytical data of the complex are as follows: yield 80%. *Anal.* Calc. for [Co(salan)$_2$]–$C_{24}H_{18}N_4O_2Co$: C, 69.18; H, 4.47; N, 6.21; Co, 13.06. Found: C, 68.12; H, 4.52; N, 5.88; Co, 13.09%. M.p. 190 °C.

2.3. Method of calculations

The convenient approach has been presented for the tetragonally distorted Cr(III) complexes in work [20]. In the present work the matrix elements of the excited states presented in paper [20], given as a function of the orbital energies and Racah parameters, were used for cobalt(II) complexes, assuming hole-formalism. The total one-electron orbital energy equations given by Kurzak [20] were applied and reduced for complex with O_h (T_d) symmetry. All the band maxima reported in this work are determined from Gaussian analysis of the experimental spectral contours. Absorption spectra were fitted with Gaussian components using CFP computer program [21] (and references herein), based on the Slavič [22] algorithm, which for the last few years has been successfully applied by us to the resolution of d–d (ligand-field) spectra. The Lorentz (Cauchy), Gauss, and also sum and product combination of the both may be used to approximate the contours of the individual unperturbated bands. The problem of the choice of the band shapes function has been determined for some time. In IR spectroscopy [23] (vibration spectra) the bands are well approximated by the Lorentz function, while for the bands broadened in Vis–UV region (electronic spectra) the Gauss function is a good approximation. Theoretical treatment of the UV band shapes [24] for the solutions systems and experimental measurements indicated that isolated absorption bands are of the Gaussian form. The ligand-field parameters (CFM) were calculated using the LFP computer program [25] (CFM/AOM). The assignment of bands is based on fitting the resolved band maxima (from Gaussian analysis) with the calculated transition energies (eigenvectors) using the d^3 quadrate energy levels with full configuration interactions and without spin–orbit coupling. In this work the ligand-field (d–d) spectrum of [Co(salan)$_2$] has been assigned by application of ligand-field and T_d symmetry. The AOM parameters, i.e. separate values for e_σ and e_π, cannot report as these are linearly related to Dq in this geometry ($10\ \mathrm{Dq} = 3e_\sigma - e_\pi$).

The CIE, CIELAB, and CIELUV systems were applied for a quantitative description of sample colour. The chromaticity coordinates have been calculated from the absorption spectra (in region 380–780 nm) by the method described in Refs. [14,26,27] for non-uniform (CIE) and two uniform (CIELAB and CIELUV) spaces. The calculation of these coordinates has been accomplished using CIEC computer program [28]. This one is designed to calculate the colour parameters for the solution, solid (reflectance) and simulated spectra. The CIE tristimulus values (X, Y, Z) expressed as integrals (or sums) [14,27] are calculated as well as chromaticity coordinates (x, y, z) and two space parameters: CIELAB (L^*, a^*, b^*) and CIELUV (L^*, u^*, v^*). The



Scheme 1. Cobalt(II) complex with salicylideneamine derivatives.

standard data [12,13,29] are built in the routine i.e. colour matching functions taken every 5 (or 1 nm) in the range 780–380 (or 830–360 nm), as well as standard illuminant D_{65}. Absorption spectrum is transformed into equivalent transmission spectrum. In the case of reflectance spectrum one can use the Kubelka–Munk function [30] for preliminary data transformation.

3. Results and discussion

The solutions of [Co(salan)$_2$] were prepared by dissolving a weigh amount of the complex in: $CHCl_3$, Bz, MBz, ACN, DX, DMF, and DMSO. The complexes with similar bidentate Schiff bases were studied by spectroscopy [19,31–33] previous. The electronic spectra as well as magnetic moments [34,35] of cobalt(II) complexes depend upon the geometry of the complexes. The differences in the band positions and magnetic moments may be regarded as diagnostic of stereochemistry of the cobalt(II) complexes. In fact, those are rather straightforward way, in many cases, to determine the geometry of a cobalt(II) complex. Typical electronic spectrum for Co(II) with bidentate Schiff base complex [36] in pyridine (octahedral) shows maxima at about 10 000, 26 000, 33 100 cm^{-1} and a shoulder at 17 000 cm^{-1}. Tetrahedral complexes show maxima at about 7700, 11 200, 25 000 and 34 100 cm^{-1}, and shoulders at 17 000 and 28 000 cm^{-1}. The magnetic moments for the tetrahedral cobalt(II) complexes are in the range 4.2–4.7 whereas for octahedral: 1.7–2.0 or 4.4–5.5 μ_B.

Electronic absorption spectra of the complex studied by us in all solutions show maxima at approximately 7700, 11 000, 25 800 and 34 000 cm^{-1} and shoulder at 17 100 cm^{-1}. Moreover, the solid-state spectrum of this complex is characterised by maxima at approximately 7400, 10 500, 20 700, 27 600, 35 600 and 44 200 cm^{-1}. This, as well as high band intensities in the d–d region, indicates the tetrahedral geometry of [Co(salan)$_2$] complex in all solutions studied.

The cobalt(II) complexes of salicylideneamine derivatives (Scheme 1), where R = alkyl, aryl and cyclohexyl, are red crystalline solids. They are stable on dry air, while in solution they are easily converted into the corresponding oxidation product [37]. Slow oxidation of the cobalt(II) complexes causes colour change. This process strongly depends on the solvents [38], steric factor, temperature, and ligand-field strength [39]. It is attained with Schiff bases predicting a stronger ligand-field, e.g. *N*-alkyl-salicylideneiminates. The *N*-aryl-salicylideneiminate presented in our studies characterises weaker ligand-field strength, rather. Red [Co(salan)$_2$] in polar solvents is slowly oxidised in air, or more rapidly by hydrogen peroxide, to brown. Spectrophotometric studies exclude the oxidation of the cobalt(II) ions in all solutions studied upon time elapsed up to 4 h (no spectral changes were observed), similar as in our earlier investigations on bis(5-bromosalicylidene-*o*-aminopyridine)cobalt(II) [1].

3.1. Ultraviolet spectra

The Schiff bases have been studied previously spectrochemically [40–43]. The Hsalan ligand spectra have been presented previously in methanol solution [42,44–46] and studied by us [47] in a wide variety of solvents. Houlden et al. [47] have synthesised the Schiff bases derived from benzalaldehyde and aniline, and quantitative interpreted their electronic spectra in heptane solution and UV region. They resolved the spectra into 13 Gaussian components in 25 000–47 000 cm^{-1} region. Based on the literature data [48] we have resolved the ligand spectra into ten Gaussian component bands in the 20 000–40 000 cm^{-1} region [47]. These have been used for analysis of complex spectra in UV region. West [49] has compared absorption spectra of [Co(salan)$_2$] (in absolute EtOH and 10% aqueous EtOH) with ligand (in 10% aqueous EtOH). In his experiment the electronic spectrum of [Co(salan)$_2$] (in 10% EtOH) is closely related to the ligand spectrum. The author suggests that disappearance of the band at approxi-

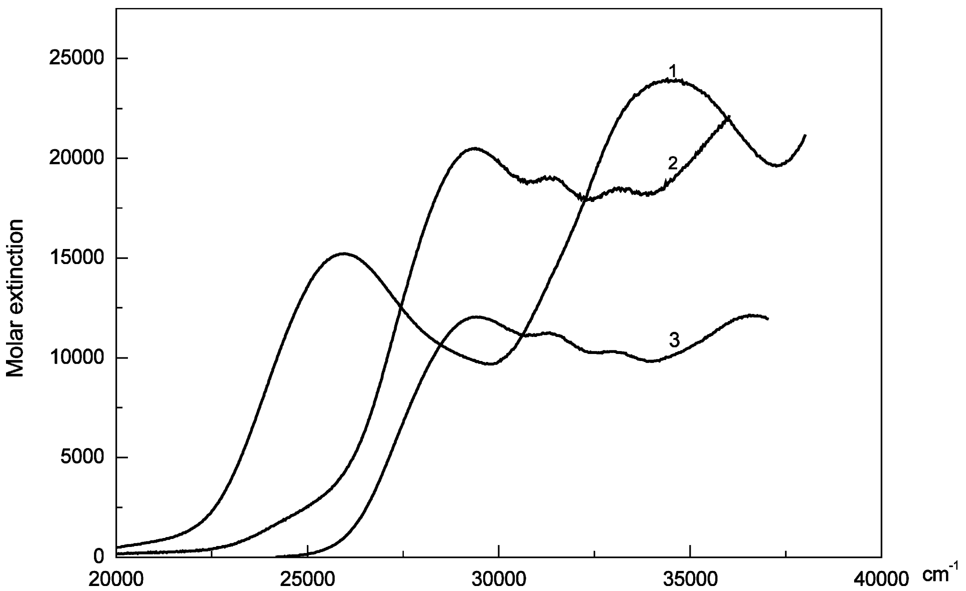


Fig. 1. Electronic spectra of [Co(salan)$_2$]: **1**, $c = 4.8 \times 10^{-4}$; **2**, $c = 1.0 \times 10^{-4}$ and ligand (Hsalan) **3**, $c = 1.0 \times 10^{-4}$ M in DMSO solution.

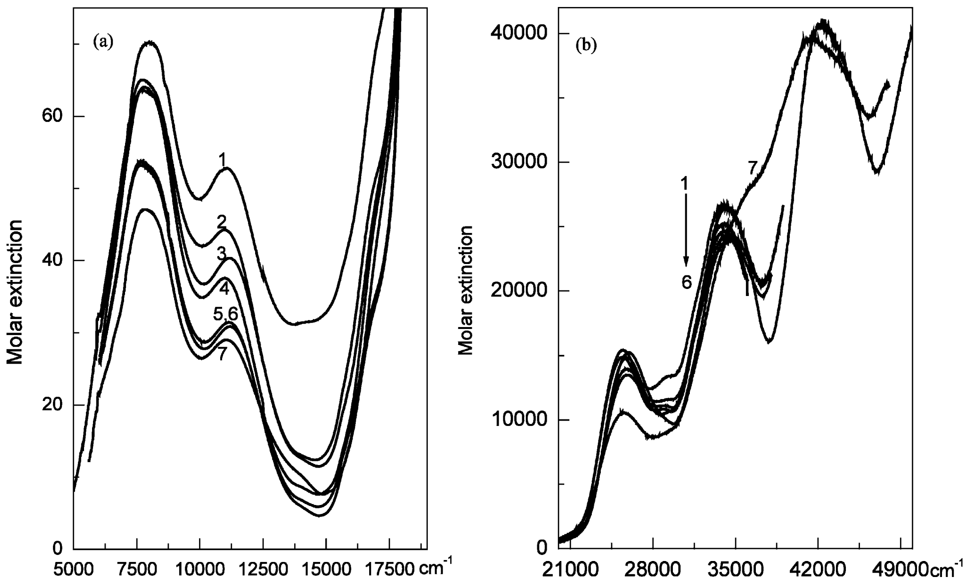


Fig. 2. Electronic spectra of [Co(salan)$_2$] at room temperature in solvents: 1, ACN; 2, CHCl$_3$; 3, DMF; 4, DX; 5, Bz; 6, MBz and 7, DMSO, in NIR–Vis region (a); 1, CHCl$_3$; 2, ACN; 3, Bz; 4, MBz; 5, DMF; 6, DMSO and 7, DX, in UV region (b).

mately 35 000 cm^{-1} in 10% EtOH solution is due to dissociation of complex. In our study we have not used mixed solvents, but when the complex concentrations in 'pure' solvents were less then $c = 5 \times 10^{-4}$ M such effect has been observed. Fig. 1 shows the electronic spectra of [Co(salan)$_2$] in DMSO, measured for different concentrations in comparison with Hsalan in the same solvent. As seen, the spectrum of diluted solution of [Co(salan)$_2$] has similar shapes as Hsalan spectrum and the positions of their observed bands are very close together (q.v. spectra 2 and 3 in Fig. 1). Because of ionisation of [Co(salan)$_2$] in diluted solutions highest concentrations as possible were used for further studies of the spectra.

In our previous studies on bis(5-bromosalicylidene-*o*-aminopyridine)cobalt(II) complex [1] we displayed that changes in complex spectra in UV region are not connected with coordination change. We do not observe any changes in [Co(salan)$_2$] spectra for concentrations $\sim 5 \times 10^{-4}$ M in UV region. Nevertheless, the interpreting spectra were recorded as rapidly as possibly.

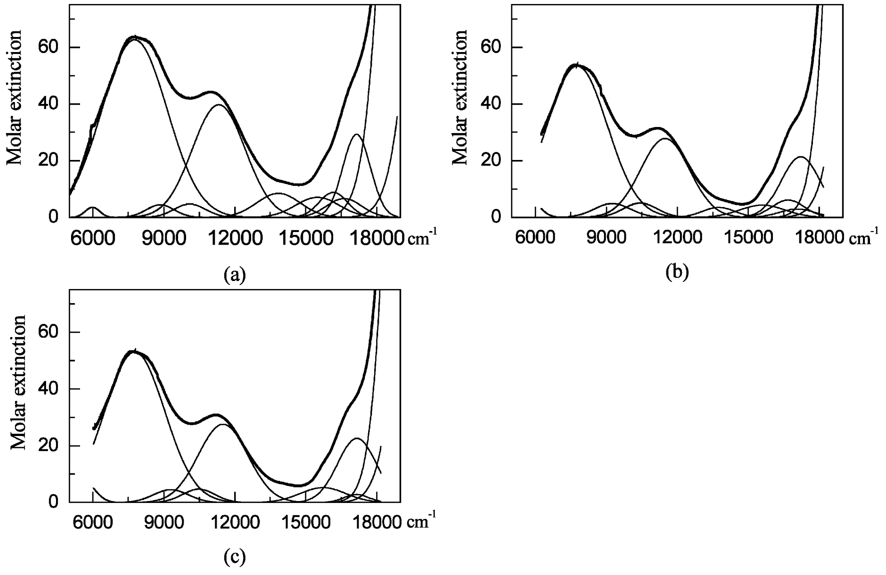
Fig. 2 shows the electronic absorption spectra of [Co(salan)$_2$] in various solvents in NIR–Vis (a) and UV region (b). All the spectra in UV region are similar and exhibit two bands at about 25 800 and 34 500 cm^{-1} except DX solution where latter is observed as a shoulder, only. Additional band characterises the spec-

Table 1
Parameters of the component bands resulting from Gaussian analysis of the electronic spectrum of *trans*-[Co(salan)$_2$] in CHCl$_3$ solution, and NIR–Vis and UV region; T_d symmetry

Band number	ε (M^{-1} cm^{-1})	ν_0 (cm^{-1})	$\delta_{1/2}$ (cm^{-1})	f	Assignment [a]
NIR–Vis: number of points 1471, range 5000–18 868 cm^{-1}					
1	3.6	5980	720	1.2×10^{-05}	unassigned (not d–d)
2	62.6	7760	3250	9.4×10^{-04}	d–d, s-a
3	4.4	8850	1410	2.9×10^{-05}	d–d
4	4.7	10 100	1560	3.4×10^{-05}	d–d
5	39.7	11 320	2630	4.8×10^{-04}	d–d, s-a
6	8.5	13 850	2160	8.4×10^{-05}	d–d
7	7.1	15 500	2170	7.1×10^{-05}	d–d
8	8.8	16 170	1410	5.8×10^{-05}	d–d
9	6.6	16 620	1750	5.3×10^{-05}	d–d
10	29.3	17 150	1370	1.8×10^{-04}	d–d, s-a
11	558.6	20 160	2610	6.7×10^{-03}	IM [b]
12	453.0	21 530	2780	5.8×10^{-03}	IM [b]
RMS%	0.64				
UV: number of points 1023, range 18 600–39 040 (cm^{-1})					
1	520	20 150	2460	5.9×10^{-03}	IM
2	540	21 350	1670	4.2×10^{-03}	IM
3	2640	23 330	2320	2.8×10^{-02}	IM
4	4540	24 330	1930	4.0×10^{-02}	IM
5	8930	25 580	2350	9.7×10^{-02}	CT
6	4140	26 880	2530	4.8×10^{-02}	IM
7	11 370	29 060	3960	2.1×10^{-01}	IM
8	1780	31 260	1240	1.0×10^{-02}	IM
9	1430	32 380	1920	1.3×10^{-02}	IM
10	10 090	33 420	4580	2.1×10^{-01}	IM
11	15 920	34 170	4540	3.3×10^{-01}	CT
12	2430	35 790	1910	2.1×10^{-02}	IM
13	1940	39 030	1370	1.2×10^{-02}	IM
14	14 140	38 010	3710	2.4×10^{-01}	IM
15	32 860	41 470	4070	6.1×10^{-01}	IM
RMS%	0.24				

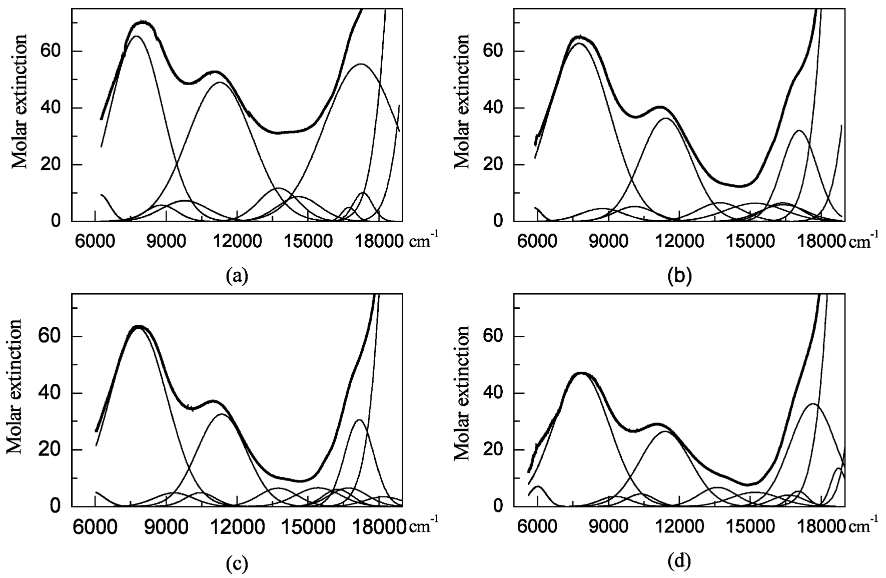
[a] IM, intramolecular band; CT, charge transfer band; s-a, spin-allowed transition (another d–d transitions are spin forbidden).

[b] Gaussian arms of the first and second band from UV region (1, 2).



(a) (b) (c)

Fig. 3. Electronic spectra and the Gaussian line-shapes of [Co(salan)$_2$] at room temperature in NIR–Vis region in non-polar solvents: CHCl$_3$ (a), Bz (b) and MBz (c).



(a) (b) (c) (d)

Fig. 4. Electronic spectra and the Gaussian line-shapes of [Co(salan)$_2$] at room temperature in NIR–Vis region in polar solvents: ACN (a), DX (b), DMF (c) and DMSO (d).

Table 2
Intensities (M^{-1} cm^{-1}) and positions (cm^{-1}) of CT bands resulting from Gaussian analysis of UV region in variety of solvents

Solvent	$CT_{Co \rightarrow O}$		$CT_{Co \rightarrow N}$	
	ε_{max}	ν_{max}	ε_{max}	ν_{max}
$CHCl_3$	9830	25 580	15 920	34 170
Bz	11 220	25 570	16 030	34 350
MBz	10 750	25 560	15 470	34 390
ACN	10 850	25 630	17 300	34 230
DX	8220	25 630	14 520	34 320
DMF	8850	25 580	15 470	34 280
DMSO	10 700	25 640	15 250	34 240

tra in DX and ACN solvents at 41 500 and 43 000 cm^{-1}, respectively. This band is not observed in others solvents because of their no transmittance above 40 000 cm^{-1}. All the UV spectra were resolved and the component bands for Gaussian analysis of the complex spectra have been assumed from the analysis of the Hsalan ligand spectra and additional CT bands predicted for complex. Table 1 shows, as representative example, the results of the Gaussian analysis, parameters of the component bands, their oscillator strength values and relative root mean squares error (RMS%), for the full spectral range: the NIR–Vis and UV regions, in $CHCl_3$ solution. The digital spectra $\varepsilon_i = f(\nu_i)$ and dull Gaussian analysis results of all spectra (NIR–Vis and UV) are available from the authors on request. The background absorption from the strong IM bands was included by two the last Gaussian arms (band 11 and 12 of first part of Table 1, q.v. Figs. 3 and 4) that have the maxima at 20 000 and 21 000 cm^{-1}, i.e. out of low energy part of the experimental curve. These affect the band above 15 000 cm^{-1}. No effect of higher energy UV bands (e.g. CT) on Vis region was observed that affect the band above 19 000 cm^{-1}. Usually, the observed absorption bands at 25 000 and 35 000 cm^{-1} are attributed to the charge transfer transitions [50,51]. Based on our previous studies [1] and literature data [51,52] we assigned the band at about 25 000 cm^{-1} to MLCT i.e. Co → O, and at higher energy to MLCT (Co → N) transitions. The positions and intensities of both the CT bands (from Gaussian analysis) for all the solutions studied are given in Table 2. Both the $CT_{Co \rightarrow O}$ and $CT_{Co \rightarrow N}$ have the same position in all solvent studied.

3.2. *Visible spectra and ligand-field analysis*

No crystallographic data of [Co(salan)$_2$] are available. Elerman et al. [53–55] have synthesised two similar complexes: (**1**) bis(*N*-2-propyl-salicylideneamino-*N*,*O*)cobalt(II) and (**2**) bis(*N*-4-bromophenylsalicylaldiminato)cobalt(II) and presented X-ray data. In both the complexes Co(II) ions adopt tetrahedral coordination geometries. The Co–N distances are 2.00 and Co–O 1.90 Å in both the complexes. The N–Co–O angles (α bite angle) are similar (96.4° and 96.7°), and N–Co–N (O–Co–O) angles are 120°.

The spectra of bis(salicylaldehyde-aniline)cobalt(II) complex in Bz and pyridine solutions as well as in solid state have been presented in literature [19,31]. Authors [19] have reported that spectra in Bz solution and in the solid state show maxima at approximately 7700, 11 200, 25 000 and 34 100 cm^{-1} and shoulders at about 17 000 and 28 000 cm^{-1}, but in pyridine solution maxima at 10 000, 26 000, 33 100 cm^{-1} and a shoulder at about 17 000 cm^{-1}. The latter spectrum is very similar in shape

Table 3
Assignments, transition energies and ligand-field parameters (cm^{-1}) for the [Co(salan)$_2$] complex in variety of solvents; symmetry T_d, ground term $^4A_2$

Assignments	Solvent						
	$CHCl_3$	Bz	MBz	ACN	DX	DMF	DMSO
$^4T_2$[F]	7760	7760	7770	7750	7760	7820	7860
^2E[G]	8850	9250	9300	8800	8740	9340	9300
$^2T_1$[G]	10 100	10 430	10 470	9790	10 110	10 420	10 360
$^4T_1$[F]	11 320	11 480	11 500	11 270	11 420	11 360	11 400
$^2T_2$[G]	13 840	13 750	13 880	13 760	13 720	13 800	13 620
$^2A_1$[G]	15 490	15 600	15 730	14 600	15 200	15 420	15 210
$^2T_2$[H]	16 170	16 690	16 580	16 730	16 370	16 310	16 610
$^2T_1$[H(1)]	16 620	17 060	17 150	17 320	16 380	16 700	17 030
$^4T_1$[P]	17 150	17 220	17 170	17 230	17 070	17 150	17 650
RMS%	350	270	300	370	370	340	280
Dq	1660 (30)	1670 (30)	1670 (30)	1650 (40)	1660 (30)	1640 (30)	1660 (30)
B	410 (40)	420 (30)	420 (30)	440 (40)	420 (40)	430 (30)	460 (30)
C	2120 (70)	2170 (60)	2200 (60)	2050 (80)	2080 (70)	2130 (60)	2070 (50)
C/B	5.2	5.2	5.2	4.7	5.0	5.0	4.5

to the reflectance spectrum of six-coordinated adduct [Co(salan)$_2$(pyridine)$_2$]. Kogan et al. [31] presented magnetic moment values for [Co(salan)$_2$] in solid state and in Bz, DX and $CHCl_3$ solutions in 294 K, and Sacconi et al. [19] in solid state (over the range 91–293 K), and in Bz and pyridine solutions (both in 297 K). The μ_{eff} values are similar (over the range 4.2–4.4 μ_B) and a tetrahedral structure of [Co(salan)$_2$] for solid and non-donor solvents indicate. In pyridine solution the value is significantly higher and equals to 4.9 μ_B. Based on the electronic spectra, magnetic moments and high dipole moment values [31] (for planar complexes those should be close to zero) authors confirm the tetrahedral structure of [Co(salan)$_2$] in solid state and in non-donor solvents.

We have confirmed lack of complex dissociation in various solutions by conductance measurements. The conductance values of all the [Co(salan)$_2$] solutions are 0.0, 0.0, 0.0, 0.1, 0.0, 0.6 and 0.9 S mol^{-1} cm^2 for $CHCl_3$, Bz, MBz, ACN, DX, DMF and DMSO, respectively. They show their nonelectrolytic properties and the predominance of an electrically neutral species in solutions. Thus, the assumed geometrical model (T_d) is adequate for our calculations of the ligand-field parameters for the solution systems.

Overlapping low energetic and more intensive charge transfer and intramolecular spectral bands complicates the d–d spectra in Vis region. Fig. 2(a) presents the electronic spectra of [Co(salan)$_2$] in various solutions in NIR–Vis region. All the spectra exhibit two maxima at 7750–7850 (50–65) and 10 970–11 150 (30–45), and shoulder at about 17 100 cm^{-1} (50 cm^{-1} M^{-1}). As seen, the hipochromic effect is especially visible for observed bands at 10 900–11 100 cm^{-1}. The spectra were resolved into twelve component bands. Figs. 3 and 4 show the experimental spectra in the NIR–Vis region in all the solvents studied along with Gaussian analysis. In general, the unique procedure (see Section 2), which starts with Gaussian analysis, through assignment of the bands, to calculation of the chemically useful parameters, is based on two assumptions: the symmetry of compound is known, and theoretical model (e.g. ligand-field model for the complexes) is adequate for the calculation of the spectral parameters. Because of this, our calculations (and Gaussian analysis of the ligand-field spectra) take into account all the d–d transitions that are given by ligand-field theory, even those strong overlapped. In this region all the bands may be attributed to d–d transitions, except one band at approximately 6000 cm^{-1} which has been omitted in parameters estimation as not predicted by ligand-field theory, i.e. not d–d transition. The spectra in 15 000–20 000 cm^{-1} region are more complicated, because of variety of the bands (d–d, charge transfer, and intramolecular transitions) in this region, which differ significantly in intensities. Usually, ligand-field analysis of spectra of the transition metal complexes has been made for the d–d isolated bands [20,21,56,57]. Transition energies, their assignments, values of the crystal field (CFM) parameters, and RMS are collected in Table 3. The best fit of the calculated and experimental data was obtained for these results. RMS error values are about 300 for the nine transitions fitted (q.v. Table 3). It follows that the experimental (Gaussian analysis) and calculated energies of the parameter set optimised are unusually close together. It can be seen that the Dq parameter values for all studied solutions are very close together and are equal to 1660 cm^{-1}. The similar effect is observed for the Racah B parameter where the values of the B parameters are 410–460 cm^{-1}. Insignificantly

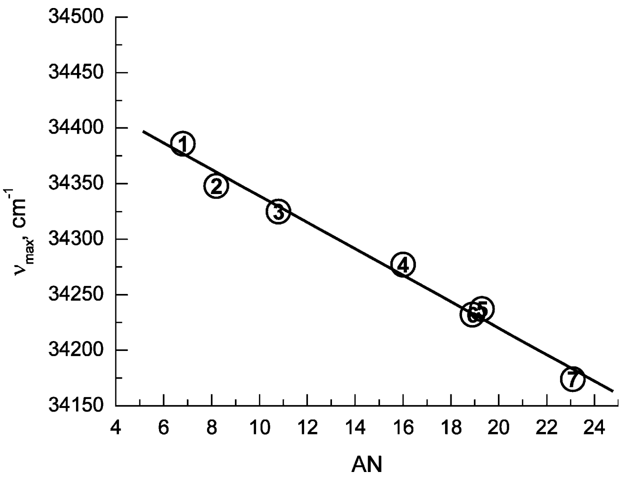


Fig. 5. Correlation between wavenumbers of absorption maximum of $CT_{Co \rightarrow N}$ and AN in solvents: 1, MBz; 2, Bz; 3, DX; 4, DMF; 5, DMSO; 6, ACN and 7, $CHCl_3$.

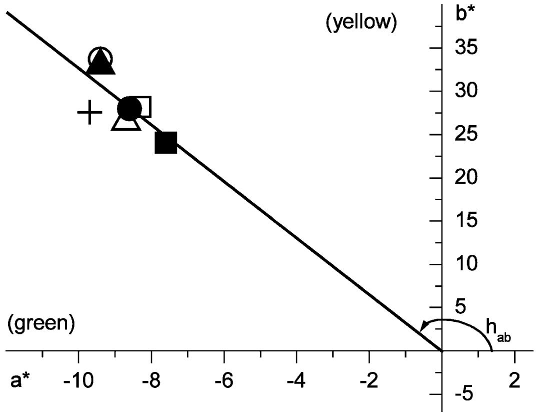


Fig. 6. The CIELAB plane. The colour points correspond to $[Co(salan)_2]$ in solvents: □, $CHCl_3$; ○, Bz; ▲, MBz; ■, ACN; +, DX; ●, DMF and △, DMSO.

changes are observed for C parameter that has values in the range 2050–2200 cm^{-1}. It suggests that the interactions of donor atoms are independent on solvents used, contrary to analogous copper(II) complexes that are very sensitive for these type interactions [47,58,59].

3.3. Solvatochromism

As mentioned above, the spectra studied display four bands. From these two bands are assigned to CT transitions. Their intensities and wavenumbers of absorption maximum in variety of solvents are reported in Table 2. The positions of absorption maxima of the $CT_{Co \rightarrow O}$ band are very similar, i.e. the band shifts are lower than 50 cm^{-1} and they will not further discuss for solvent effects. Position differences of the higher energy $CT_{Co \rightarrow N}$ band are significant. As known, the most of the solvents show solvatochromism, i.e. meant us absorption maxima changes dependent on various solvent parameters. All these parameters considered in this work are directly obtainable from literature. In Fig. 5 positions of $CT_{Co \rightarrow N}$ absorption maximum are plotted against the acceptor number AN. This plot shows a roughly linear correlation, with increasing hydrogen bonding ability of solvents associated with decreasing wavelength. The correlation equation has form: $\nu_{max} = (34\,458.1 \pm 10.4) - (11.905 \pm 0.659)$ AN with correlation coefficient $r = -0.992$. We also compared positions of absorption maximum of $CT_{Co \rightarrow N}$ band with other solvent parameters i.e. Dimroth and Reichardt's, Gutman's (donor number) and Kamlet and Taft's. However, no other correlations between positions of $CT_{Co \rightarrow N}$ band and solvent parameters could be find for solutions studied. The results show that $CT_{Co \rightarrow N}$ band position does clearly depend on AN only whereas $CT_{Co \rightarrow O}$ band position does not depend on any solvent parameters.

3.4. Trichromaticity colorimetry

All solutions of complex studied have reddish–orange colour and their electronic absorption spectra display only one maximum at approximately 25 800 cm^{-1} and shoulder at 17 100 cm^{-1} in the region 12 800–26 300 cm^{-1} that is a range commonly employed for specifying colours of compounds. Table 4 summarises the values of chromaticity coordinates calculated from the absorption spectra of $[Co(salan)_2]$ for all the solutions studied. In

Table 4
The chromaticity coordinates, h_{ab} hue-angle (°), and colours of $[Co(salan)_2]$ in variety of solvents ($c \approx 1 \times 10^{-2}$ M, $l = 0.2$ cm) and solid state

Solvent	x	y	Y	L^*	a^*	b^*	h_{ab} [b]	CIE colour [a]
$CHCl_3$	0.35	0.39	95.1	98.1	−8.3	28.2	106.5	yellow–green
Bz	0.36	0.40	94.8	97.9	−9.4	33.7	105.6	yellow–green
MBz	0.36	0.40	94.7	97.9	−9.4	33.0	105.9	yellow–green
ACN	0.34	0.38	95.6	98.3	−7.6	24.1	107.5	yellow–green
DX	0.35	0.39	92.9	97.2	−9.7	27.6	109.4	yellow–green
DMF	0.35	0.39	95.4	98.2	−8.6	28.0	107.1	yellow–green
DMSO	0.34	0.38	96.2	98.5	−8.7	26.5	108.2	yellow–green
Solid (R_F)	0.69	0.31	12.7	28.4	64.3	64.3	37.2	red

[a] Colour observed for solutions in 25 cm^3 flask: reddish-orange.

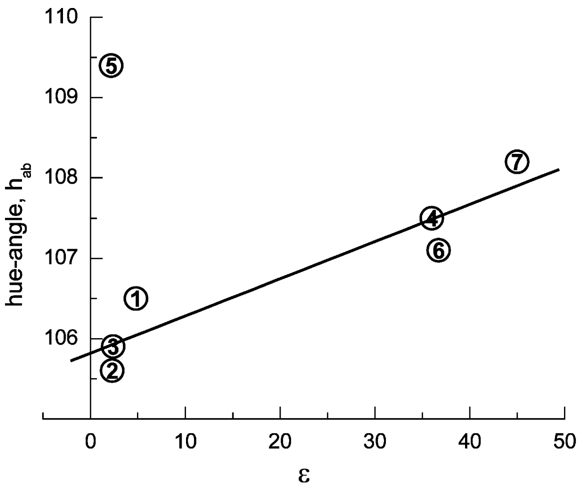


Fig. 7. Correlation between hue-angle h_{ab} and dielectric constant ε in solvents: 1, $CHCl_3$; 2, Bz; 3, MBz; 4, ACN; 5, DX; 6, DMF and 7, DMSO.

the case of reflectance spectra for solid sample the Kubelka–Munk theory has been used for preliminary data transformation (R_F coefficient). Colours of solutions are reported in CIE and CIELAB colour spaces. These chromaticity parameters characterise the solutions studied unambiguously and allow a comparison of colour changes. L^*, a^*, b^* colour space is uniform and recommended by CIE for the colour description. The L^* is psychometric lightness and corresponds to black ($L^* = 0$) and white ($L^* = 100$). The a^* and b^* are psychometric chromaticness. Positive values of a^* correspond to red colour negative ones to green whereas positive values of b^* correspond to yellow colour negative ones to blue. The position of colour points on the CIELAB plane is presented in Fig. 6. The colours of the solutions are represented by points on the chromaticity, positioned on the field of green–yellow hues. The h_{ab} values have been compared with some solvent parameters previously [60]. In our study we compared those values with solvent parameters, i.e. dielectric constant, Dimroth and Reichardt's, Kosower's, Gutman's (donor and acceptor numbers), and Kamlet and Taft's. The linear correlations between hue-angle (where $h_{ab} = \text{arc tg } (b^*/a^*)$) and above mentioned solvent parameters have been found for all the solvents except DX. Calculated values of hue-angle against the dielectric constant ε are plotted in Fig. 7. The plot shows a roughly linear correlation, with increasing ε values associated with increasing h_{ab} values. The data for all studied solvents can be correlated as: $h_{ab} = (105.8 \pm 0.2) + (0.046 \pm 0.008)\varepsilon$ (correlation coefficient $r = 0.939$). We have found that the hue-angle depends on Kosower's Z and Kamlet and Taft's π^* parameters. The resulting regression of the $h_{ab} = f(Z)$ is: $h_{ab} = (98.5 \pm 1.9) + (0.129 \pm 0.030)Z$, ($r = 0.929$), the result for the $h_{ab} = f(\pi^*)$ is: $h_{ab} = (103.6 \pm 0.8) + (4.460 \pm 1.144)\pi^*$ ($r = 0.890$). The linear correlations between hue-angle and other solvent parameters were not found for all the solvents studied. The results show that the hue-angle values mainly depend on the polarity of solvents, only.

Table 5
Bands parameters resulting from Gaussian analysis of $CoCl_2$ in *i*-propanol [a], and ligand-field parameters as a starting data for simulation spectra as a function of Dq; ε^{i}_{max}, $\delta^{i}_{1/2}$, B and C parameters are constants

Number	$\varepsilon_{max}{}^{i}$ (M^{-1} cm^{-1})	$\delta^{i}_{1/2}$ (cm^{-1})	ν^{i}_{max} (cm^{-1})
1	22.5	1950	5540
2	29.3	2400	7290
3	78.9	920	14 900
4	76.4	920	15 140
5	225.8	1900	16 020
6	72.2	1260	17 520
7	27.3	1830	18 320
8	7.6	1890	19 890
9	3.7	1950	20 410
10	6.0	1480	21 730
11	5.8	1510	23 040
12	5.4	1640	24 290
13	5.2	1930	25 690
14	10.3	3560	28 040
B		696	
C		3435	
Dq		1005	

[a] $[Co^{2+}] = 0.045$ M, path length = 0.1 cm; CIE chromaticity coordinates: $x = 0.182$, $y = 0.254$, $Y = 44.7$ (colour: greenish blue).

3.5. Simulation of optical spectra and colour quantitative characteristics

In the course of our studies on optical spectra of transition metal compounds it was shown that their colour quantitative characteristics expressed by chromaticity coordinates clearly correspond to properties and structure of the studied objects. Colour parameters yielded by CIE, CIELAB and CIELUV colour spaces are derived from the optical spectra and described in detail in many sources. Our main goal was to find out relations between the spectra and colorimetric data if such relations do exist at all. As a result of many investigations [14–18] it has been demonstrated that the ligand-field parameter, Dq, could create a basis for expressing such a relation with colour characteristic parameters. This would approximately be true when the colour of transition metal compound would be caused only by ligand-field spectra, i.e. d–d transitions (and not by e.g. CT transitions in the optical region). Hence using the Dq parameter one should be able to simulate the spectra and to predict the corresponding colour. Such simulations were carried out for many systems and described in literature [14–18]. The steps in using our model are as follows.

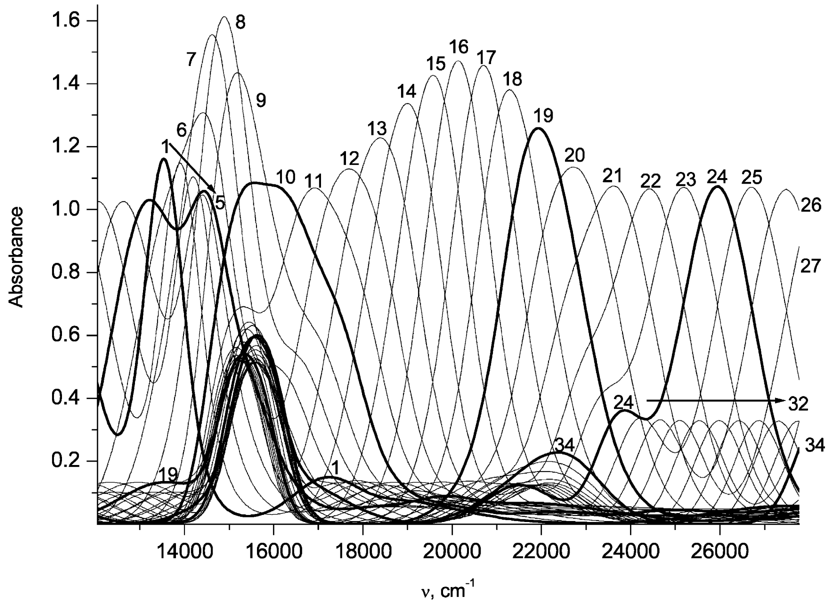


Fig. 8. Simulation of spectra for $CoCl_2$ in *i*-propanol as a function of Dq parameter: 1–100, … 34–3400 cm^{-1} (100 cm^{-1} step), with the experimental spectrum-10; all C.I. interaction is allowed and B and C parameters are constants.

1) The experimental optical spectrum of the proper metal compound is chosen, in this case a solution of anhydrous $CoCl_2$ in *i*-propanol ($c = 0.045$ M, $l = 0.5$ cm) that characterised 'pure' tetrahedral symmetry (T_d). Gaussian analysis results (component band parameters) and ligand-field parameters are being carried out. These for NIR–Vis region are shown in Table 5.
2) The set of resulting parameters is taken as constants: ε^{i}_{max}, $\delta^{i}_{1/2}$, B and C (see frame in Table 5), except ν^{i}_{max} set that depend on Dq values.
3) The last has been calculated for variety of Dq values that for simulation are varied within a broad range (50–3400, with step 50 cm^{-1}), i.e. the transitions energy diagram is generated using LFP program [25]. Proper energy matrices are applied, here for d^7 electronic configuration and T_d symmetry according to the surrounding of the Co(II) central ion in this solvent.
4) For each new Dq value the overall contour of the spectrum was calculated and the chromaticity coordinates determined applying the CIEC computer program [28].

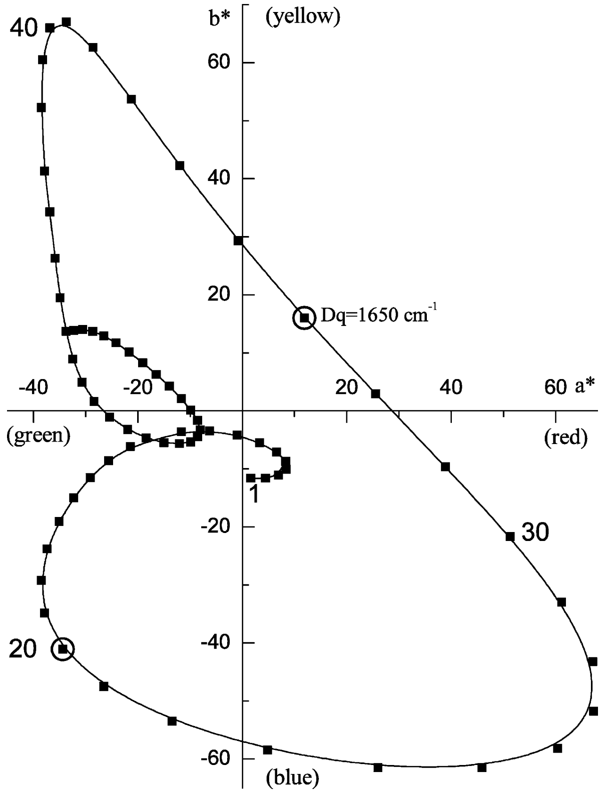


Fig. 9. The CIELAB plane. The colour points correspond to simulated spectra for $CoCl_2$ in *i*-propanol as a function of Dq parameter: 1–50, … 68–3450 cm^{-1} (50 cm^{-1} step), the point 20 corresponds to experimental spectrum.

The results of these simulations are demonstrated in Fig. 8 that shows the course of the spectra for a broad Dq range 100–3400 cm^{-1} (the step is 100 cm^{-1} because of graph clarity). Note that bands positions (transition energies) in spectra simulated as well as observed intensities are changed simultaneously. It is result that full energy matrices were used to allow for term interactions in our calculations (LFP program). Fig. 9 shows CIELAB colour parameters for assumed Dq range (the step is 50 cm^{-1}). The CIELAB data (the Vis part only) clearly shows that colour of the $CoCl_2$ solution, for instance in the solution creating a low ligand-field could change its hue from greenish–blue to purple or even red for higher Dq values. The kind of this behaviour is formally the same as predicted in the case of simulation of Cr(III) and presented in [14–18]. It is evident that the course of colour changes remains as predicted in our earlier investigations. Namely, applying a broad range of Dq values (as in this simulation) it is possible to reach at colour hues over the whole CIELAB plane.

The chromaticity coordinates of the [Co(salan)$_2$] solutions correspond to green–yellow hues and the colours of all solutions are nearly the same. Note that their Dq values are close together and equal about 1650 cm^{-1} (q.v. Table 3). As seen in Fig. 9, the spectrum simulated for tetrahedral Co^{2+} and Dq = 1650 cm^{-1} (point 34th in CIELAB plane) characterises the same colour.

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