Absorption Spectra of Cobalt(II) and Cobalt(III) Diethyldithiophosphates

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Whereas Co dtp_2(dtp^- = $(C_2H_5O)_2PS_2^-$) occurs as a tetrahedral non-solvated form in carbon tetrachloride, an indigo-blue solvate of different symmetry is formed in ethanol. Application of the method of continuous variations demonstrates the presence of a 2 dtp^-: 1 Co complex, among others, in ethanolic solutions. The nearly regularly octahedral Co dtp_3 can be formed by oxidation of such solutions with hydrogen peroxide and the absorption spectrum is compared with those of Rh dtp_3 and Ir dtp_3 and discussed in terms of the spectrochemical and nephelauxetic series and the variation of optical electronegativities derived from electron transfer bands.

The absorption spectra of inner-complexes of the ligand dtp^- = $(C_2H_5O)_2$ PS_2^- forming M dtp_3 and M dtp_2 have been studied [1] of a variety of central ions M. The M.O. treatment of the trigonally distorted, octahedral $M(S_2P)_3$ was given in a paper [2] on the similar selenium-containing complexes $M(Se_2P(OC_2H_5)_2)_3$. In most cases, these inner-complexes form readily and in great yield, and in a way comparable to the preparation of the acetylacetonates.

However, in a few cases, the chemistry is considerably more complicated. Malatesta and Pizzotti [3] prepared a dark blue solution of Co dtp_2 by extraction from an aqueous solution containing $Co(H_2O)_6^{2+}$ and dtp^- into an organic solvent. These authors reported the preparation of diamagnetic Co dtp_3 in small quantities by oxidation of such a solution. In a recent description [4] of Cr dtp_3, it is shortly reported that Co dtp_3 has been prepared from cobalt(III) fluoride. This does not leave the impression that Co dtp_3 is a very accessible material. Actually, it can easily be made in large quantities, as we shall see.

An aqueous solution of 0.3 M cobalt(II) nitrate or perchlorate and 0.6 M ammonium diethyldithiophosphate has nearly the same spectrum as when no dtp^- is present. This is analogous to the behaviour of aqueous solutions containing $Ni(H_2O)_6^{2+}$ and dtp^- in large concentrations. However, in the latter case [1], purple crystals of Ni dtp_2 may precipitate. Such crystallization has not been observed of the cobalt(II) solutions, and they show hardly any tendency to oxidation in the air.

In the presence of an immiscible organic solvent, this oxidation is cata-lyzed strongly. The mechanism is that sky-blue Co dtp_2 is extracted into the solvent and then, in the course of some hours, oxidized by oxygen entering at the phase separation. The colour changes to green and finally to brown. By dilution, a clear yellow colour is observed.

As we shall see below, this corresponds to the compound Co dtp_3. In mix-tures of a little water and much ethanol, cobalt(II) nitrate or perchlorate pro-duce an indigoblue colour with dtp^- comparable to that of cobalt(II) chloride alone in the same solvent. The indigo-blue solutions are rather resistant to air oxidation and turn green or brown only in the course of several days.

The simplest way to produce Co dtp_3, however, is to prepare the indigo-blue solution in 80 or 90 % ethanol and oxidize under rapid stirring with the stoichiometric amount of aqueous 30 % hydrogen peroxide. A dark brown powder separates. This can be recrystallized from ethanol and it is completely soluble in chloroform or dichloroethane. It can be syncrystallized with the colourless [1] In dtp_3.

In the following, we shall discuss the absorption spectra of the tetrahedral Co dtp_2, the one or more species occurring in the indigoblue ethanol solutions, and the octahedral Co dtp_3.

Co dtp_2 in carbon tetrachloride solutions. CCl_4 was chosen as solvent because it does not contain hydrogen atoms with subsequent high vibrational frequen-cies. On the Cary 14 recording spectrophotometer, it is actually possible to compare two 2 cm cells with CCl_4 readily out to 2200 mμ, whereas the slit-
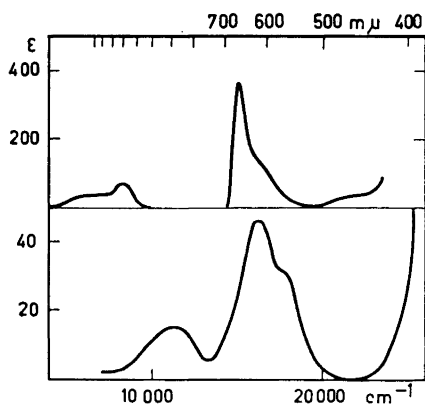

Fig. 1. Absorption spectra of tetrahedral Co dtp_2 in CCl_4 (upper half) and of the in-digoblue form in ethanol (presumably con-taining Co dtp_2 $(C_2H_5OH)_2$) (in the lower part).
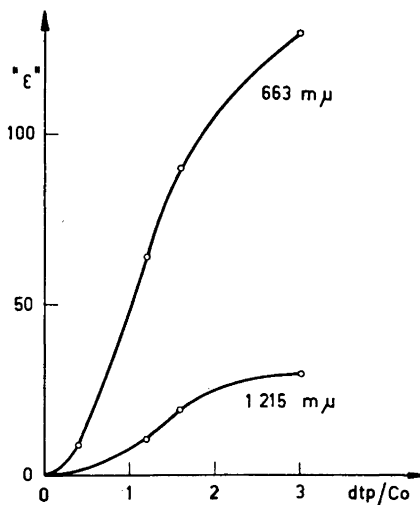
Fig. 2. Effective molar extinction coeffi-cient "ε" by extraction experiments of aqueous solutions containing various ratios of total dtp^-/Co^{2+} concentrations into CCl_4 (where Co dtp_2 alone is extracted) as discussed p. 2019.

Table 1. Absorption bands of the tetrahedral form Co dtp$_2$ in carbon tetrachloride, the indigo-blue form in alcohol (presumably Co dtp$_2$ (C$_2$H$_5$OH)$_2$) and of Co dtp$_3$. Wavelengths λ in mμ, wavenumbers σ in cm^{-1} and molar extinction coefficients ε are given of maxima, and of shoulders in parentheses. The half-widths $\delta(-)$ towards smaller and $\delta(+)$ towards larger wavenumbers are indicated.

	λ	σ	ε	$\delta(-)$	$\delta(+)$
Co dtp$_2$	∼1 600	6 700	∼ 40	—	—
	1 215	8 200	∼ 60	—	900
	663	15 100	∼ 360	350	600
	(590)	(16 900)	∼ 80	—	800
Co dtp$_2$(C$_2$H$_5$OH)$_2$(?)	870	11 500	15	2 200	1 400
	616	16 200	46	1 100	—
	(565)	(17 700)	32	—	—
Co dtp$_3$	(738)	13 550	450	1 200	1 400
	(526)	(19 000)	480	1 600	—
	406	24 600	6 500	2 200	—
	335	29 900	18 000	2 600	2 600
	233	43 000	9 500	3 900	—

width increases irregularly at longer wavelengths and makes the comparison slightly irreproducible. Small quantities of hydrogen-containing molecules such as ethanol produce very strong lines at 1400, 1690, 1730 and 2095 mμ and cut off longer wavelengths.

In each experiment, 0.5 ml of an aqueous solution (0.2 M Co(ClO$_4$)$_2$, and with the ratios NH$_4$ dtp/Co 0.4, 1.2, 1.6, or 3, respectively) was shaken with 10 ml CCl$_4$. When the phases were satisfactorily separated, the spectra were measured within a few minutes, avoiding the effects of air oxidation. In all cases, the spectra had the same form, as given in Fig. 1 and Table 1. The most characteristic feature is the narrow band at 663 mμ, having the half-width towards smaller wavenumbers $\delta(-) = 350$ cm^{-1}. This remarkably low figure suggests very strongly a tetrahedral micro-symmetry of Co(S$_2$P(OC$_2$H$_5$)$_2$)$_2$. The stoichiometric composition of this compound is also supported by the relative height of the 663 mμ peak as given in Fig. 2. At low values of dtp/Co in the aqueous phase, the intensity of the sky-blue colour in the CCl$_4$ phase increases more rapidly with this ratio than the first power. If only one dtp group were present in the complex extracted, the intensity would necessarily increase less than the first power if the mass-action law in concentration units is approximately valid in the aqueous phase and for the extraction

Table 2. Values of the sub-shell energy difference $-\Delta$ and Racah's parameter of interelectronic repulsion B in various tetrahedral cobalt(II) complexes.

	$-\Delta$	B
CoCl$_4^{2-}$ (Ref.[5])	3000 cm^{-1}	730 cm^{-1}
CoI$_4^{2-}$ (Ref.[5])	2690	640
Co(II)in ZnS (Ref.[6])	3750	610
Co(II)in CdS (Ref.[6])	3300	610
» (Ref.[7])	3160	665
Co(S$_2$P(OC$_2$H$_5$)$_2$)$_2$	4000	665

coefficient. Furthermore, well known arguments lead to the conclusion that entities such as Co dtp(H$_2$O)$_2$$^+$ or Co dtp(H$_2$O)(ClO$_4$) would not be extracted in carbon tetrachloride.

In the near infra-red spectrum of Co dtp$_2$, a band at 1215 mμ and a broad plateau 1500—1700 mμ are observed. This is closely analogous to the spectra of other regularly tetrahedral cobalt(II) complexes [5]. If the centre of gravity of the near infra-red band is fixed to 1450 mμ, that is 6900 cm^{-1}, and if the excited level is a $^4\Gamma_4$ whereas the band at 15 100 cm^{-1} has b $^4\Gamma_4$, the secular determinants for d^7 in T_d are satisfied by the parameters $\varDelta = -4000$ cm^{-1} and $B = 665$ cm^{-1}. As discussed by Cotton, Goodgame and Goodgame [5], this choice of parameters is necessarily somewhat uncertain. Qualitatively, the values are very satisfactory when compared to the parameters compiled in Table 2. The spectrochemical position of dtp$^-$ corresponds to more negative value of $\varDelta$ than of Cl$^-$, whereas the nephelauxetic effect of dtp$^-$ is more pronounced and corresponds to a value intermediate between Br$^-$ and I$^-$.

The intensity is remarkably low. The extinction coefficients of the maxima (360 at 663 mμ and 60 at 1215) might be somewhat overestimated due to the indirect determination (based on the amount of cobalt *not* extracted in the organic solvent) but it is beyond all doubt that they are lower than in the corresponding tetrahalides [5]. This is in striking contrast to the octahedral complexes, where the tris (diethyldithiophosphates) have absorption bands some twenty times stronger than the corresponding hexahalides [1].

The indigo-blue solutions in ethanol. The effect of distortions of the tetrahedral symmetry to C_{3v} in CoX$_3$Y and to C_{2v} in CoX$_2$Y$_2$ have been studied by Cotton, Goodgame, Goodgame, and Sacco [8]. The extensive studies by Buffagni and Dunn [9] of CoCl$_2$ and CoCl$_4^{2-}$ in various organic solvents have
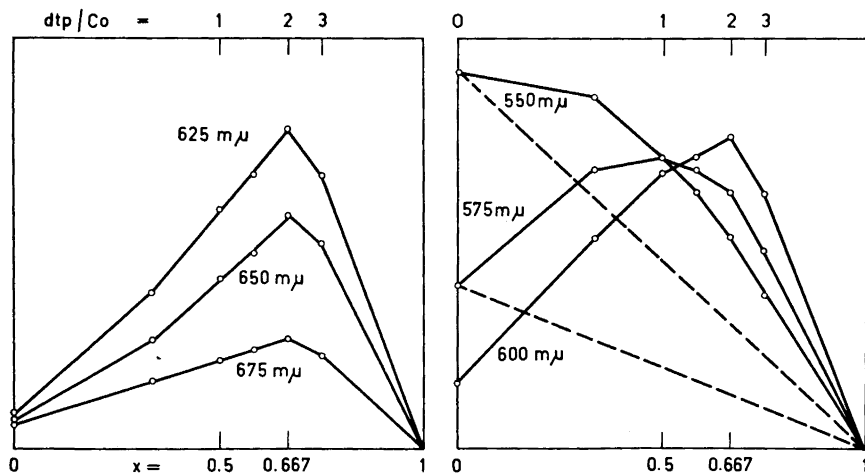

Fig. 3. Continous variation studies of the indigo-blue complex in ethanol 0.03(1—x) M Co(NO$_3$)$_2$ and 0.03x M NH$_4$dtp having optical densities measured at various wavelengths.

demonstrated the occurrence not only of a common $CoCl_4^{2-}$ without other ligands in the first coordination sphere, but also $CoCl_3X^-$ where X can be nitromethane or dimethyl formamide, and even the distorted $CoCl_2(CH_3NO_2)_2$. Hence, the indigo-blue solutions of Co(II) and dtp$^-$ in ethanol might possibly contain many different species. The comparatively low intensity of the bands at 565 and 616 mμ and the occurrence of a new band at 850—870 mμ might suggest that the main species are not at all tetrahedral but rather distorted octahedral such as Co dtp$_2(C_2H_5OH)_2$ or Co dtp$(C_2H_5OH)^+$ would be.

It is well-known [10],[11] that the method of continuous variations (Job's principle) is open to severe criticism if more than one definite complex is formed in solution. However, in our particular case, it is nevertheless one of the best ways available for determining the composition of the species occurring if the necessary circumspection is exercized by the interpretation of the results.

Solutions containing $Co(NO_3)_2$ and NH_4dtp at a total concentration of 0.03 M in ethanol (and a water concentration of 0.2 M) were studied, as shown on Fig. 3. At this water concentration, cobalt(II) alone is present mainly as a nitrato complex $Co(NO_3)(C_2H_5OH)_5^+$, and there are good reasons to believe that co-ordination of water will only play a minor role in the complex equilibria [12]. Fig. 3 shows that at some wavelengths (675, 650, 625 and 600 mμ), the formation of a complex containing two dtp$^-$ per Co can be clearly demonstrated. The sharply triangular shape of the curves indicate that this bis-complex does not dissociate very much, $i.e.$ it has a formation constant higher than the reciprocal cobalt concentration used here [13]. Actually, this is confirmed by the approximate validity of Beer's law in the concentration range 0.005 to 0.02 M Co(II) containing a slight excess above 2 dtp$^-$/Co. It cannot be excluded that small amounts of a tris-complex Co dtp$_3^-$ are formed. In 0.1 M NH_4dtp in ethanol, the two first bands shift to 875 and 622 mμ. However, no conclusion will be drawn here.

On the other hand, it is completely certain that a mono-complex, perhaps Co dtp$(C_2H_5OH)_4^+$, is formed to some extent. This can be seen from the right-hand part of Fig. 3 where the curves for 575 and 550 mμ have a broad bell-shape. According to the method of continuous variations, it is actually the deviations from a linear variation (the dashed lines) as function of x which should be considered. If only these curves were known, the conclusion would be a rather ambiguous indication of a mixture of 1:1 and 2:1 among other possible complexes. Though the spectra of the 2:1 complex $\varepsilon_2(\lambda)$ and the dtp$^-$ free solution $\varepsilon_0(\lambda)$ are known, it is not very easy to determine the spectrum of the 1:1 complex $\varepsilon_1(\lambda)$ from the data available. What would be experimentally accessible is the deviation of the intermediate spectra at a given dtp$^-$:Co ratio n:1 from the average spectrum of the two known complexes $(\varepsilon_0 + \varepsilon_2)/2$. Unfortunately, it is not possible in general, without further information, to estimate the relative proportion of the complexes even under the assumption that only three coloured sepcies are present. Hence, we will here refrain from attempts to estimate ε_1 and only note that such a complex has been detected.

The strong difference in spectral characteristics of the tetrahedral Co dtp$_2$ in inert solvents and the bis-complex in ethanol can only be rationalized by
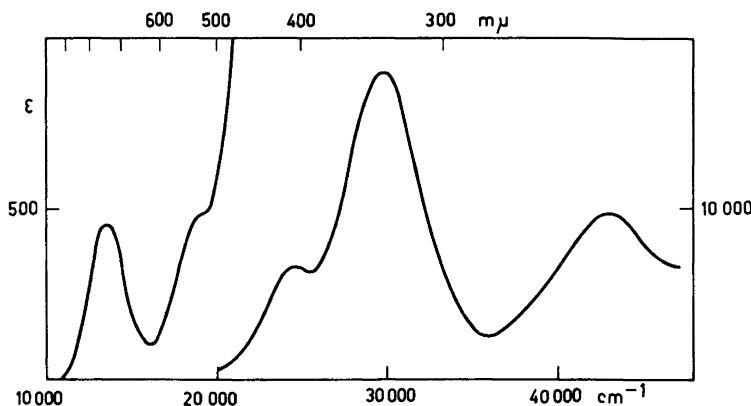
Fig. 4. Absorption spectrum of Co dtp$_3$ in ethanol.

solvation, forming, *e.g.*, Co dtp$_2$(C$_2$H$_5$OH)$_2$ of distorted octahedral symmetry (conceivably either low-spin or high-spin). Solutions of Co dtp$_2$ in CCl$_4$ or in dichloroethane change conspicuously (the 663 mμ peak decrease ε to the value 215 with 1.8 % ethanol, and disappears entirely at higher ethanol concentrations) with small amounts of ethanol. It is quite unexpected in this context that an aquated Co dtp$_2$(H$_2$O)$_2$ is not extracted from aqueous solutions in the inert solvents. Actually, one explanation of the relatively low intensity of the tetrahedral Co dtp$_2$ might involve the presence of such an aquated species in equilibrium. However, this is less probable when the absence of a band at 860 mμ is taken into account.

Approximately octahedral Co dtp$_3$. After the necessary recrystallization from ethanol, the oxidation product of the indigo-blue solution with H$_2$O$_2$ has the spectrum expected of Co(S$_2$P(OC$_2$H$_5$)$_2$)$_3$ given in Table 1 and Fig. 4. This inner-complex has also been studied by Schäffer [14]. Table 3 illustrates the close analogy between this lowspin 3d^6 system and the analogous complexes [1] of the 4d-and the 5d-groups Rh dtp$_3$ and Ir dtp$_3$.

The spectrochemical development is quite ordinary [13,15] in the series Co(III), Rh(III) and Ir(III). The nephelauxetic effect is very pronounced in

Table 3. Wavenumbers in cm^{-1} and identification of absorption bands of cobalt(III), rhodium(III) and iridium(III) diethyldithiophosphates. Further on, parameters characterizing the transitions in the partly filled shell.

Assignment	Co dtp$_3$	Rh dtp$_3$	Ir dtp$_3$
$^1\Gamma_1 \rightarrow {}^1\Gamma_4$	13 550	21 300	26 200
$\rightarrow {}^1\Gamma_5$	19 000	24 400	28 600
$\pi_1 \rightarrow \gamma_3$	24 600	31 200	37 400
$\pi_2 \rightarrow \gamma_3$	29 900	38 800	45 700
M.O. energy difference Δ	14 200	21 900	26 700
Racah's parameter B	400	210	160
Nephelauxetic ratio β_{35}	0.36	0.29	(0.24)

all sulphur-containing complexes [14], and the nephelauxetic ratio β_{35} (between B derived from eqn. (1) below and the value in the corresponding gaseous ion) has the smallest values known of any complex of these central ions, except $Ir(Se_2P(OC_2H_5)_2)_3$ having a slightly smaller nephelauxetic ratio [2]. The quantities given in Table 3 are derived from Tanabe and Sugano's secular determinants with various assumptions [16], leading to the energy of the three lowest energy levels with zero total spin S:

$$
\begin{aligned}
&^1\Gamma_1 \; -120 \; B^2/\varDelta \\
&^1\Gamma_4 \; \varDelta - \; 4 \; B - 34 \; B^2/\varDelta \\
&^1\Gamma_5 \; \varDelta + 12 \; B - 118 \; B^2/\varDelta
\end{aligned}
\tag{1}
$$

where $\varDelta$ is the M.O. energy difference between the sub-shells γ_5 and γ_3.

It is remarkable that the intensity of the $\gamma_5 \rightarrow \gamma_3$ transitions between the levels given in eqn. (1) is less than half as large in Co dtp$_3$ as in [1] Rh dtp$_3$ and Ir dtp$_3$.

The electron transfer spectra were discussed in general for this type of complexes [1],[2]. It is seen from Table 3 that the optical electronegativity [17] x_{opt} of the γ_3-sub-shell is 1.8 of Co dtp$_3$, 1.6 of Rh dtp$_3$, and 1.4 of Ir dtp$_3$, if $x_{opt} = 2.7$ of the ligand dtp$^-$. When corrected for the highly varying values of $\varDelta$, the values of the optical electronegativity of the filled γ_5-sub-shell are seen to be about the same, 2.3 in all three complexes. The values of x_{opt} extrapolated from the behaviour of hexahalide complexes are 2.3 of Rh(III) and 2.2 of Ir(III). When a lower number of electrons are present in the γ_5-sub-shell, it is elsewise a general rule that the 4d-ions have x_{opt} 0.2 units higher than the corresponding 5d-ion.

EXPERIMENTAL

Stock solutions in water and in ethanol were made of AnalaR $Co(NO_3)_2,6H_2O$, of aqueous $Co(ClO_4)_2$ made from B.D.H. $CoCO_3$, and of NH_4dtp from American Cyanamid Laboratories, Stamford, Conn. The carbon tetrachloride used for the extraction experiments was p.a. Merck.

The absorption spectra were measured on a Cary 14 recording spectrophotometer.

The preparation of Co dtp$_3$ is discussed in the text above. The analysis. Found: C 23.42; H 4.93; P 15.98; S 33.99. Calc. for $C_{12}H_{30}O_6P_3S_6Co$: C 24.45; H 4.92; P 15.12; S 31.30.

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