Absorption Spectrum of Ruthenium (III) diethyldithiophosphate

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The absorption spectra of a series of complexes $Mdtp_3$ with $dtp^- = (C_2H_5O)_2PS_2^-$ and M = Cr, Fe, Rh, In, Ir, and Bi were recently described [1] and a more detailed theoretical discussion attempted [2]. In the case of a few elements, such as cobalt (shortly to be discussed) and ruthenium, the reactions with dtp^- are complicated and yield several products. However, the Ru dtp_3 expected can be isolated from the reaction mixture and the absorption spectrum is studied here.

The actual Ru dtp_3 gives a strong raspberry colour (and not strawberryred as when brown impurities occur) in organic solvents such as ethanol, chloroform and dichloroethane. The absorption bands (wavelength λ in mμ, wavenumber σ in cm^{-1}, molar extinction coefficient ε, half-widths $\delta(-)$ and $\delta(+)$, with shoulders in parentheses) in ethanol are given in Table 1.

Table 1.

λ	σ	ε	$\delta(-)$	$\delta(+)$
511	19 550	2 250	1 650	1 800
421	23 700	2 000	1 800	–
(400)	(25 000)	1 850	–	2 000
280	35 700	10 500	3 200	–
240	41 700	20 000	–	–

The positions of electron transfer bands of this low-spin $4d^5$-system are obviously interesting for comparison with the other diethyldithiophosphates and for a determination [3,4] of the optical electronegativity x_{opt} of the ligand. It is not believed that the first three bands are internal $\gamma_5 \rightarrow \gamma_3$ transitions though they have only twice the intensity of such bands [1] in Rh dtp_3 and Ir dtp_3. However, a comparison with other metals [1] and also a comparison of the weaker bands of $RuCl_6^{3-}$ relative to $RhCl_6^{3-}$ would suggest that the two former compounds are rather exceptional. A very slightly pronounced shoulder at 550–575 mμ observed here of Ru dtp_3 (see Fig. 1) might represent such a transition.

Since $x_{opt} = 2.1$ of Ru(III), the value $x_{opt} = 2.7$ of dtp^- is substantiated by the identification to the band at 19 550 cm^{-1} as the first electron transfer band. The detailed structure of the group of the first three bands may be explained along the lines previously exposed [2].

The high band at 35 700 cm^{-1} is presumably an electron transfer band to the empty γ_3 sub-shell and can be compared to the similar band [1] at 31 200 cm^{-1} of Rh dtp_3 which would be expected to occur at somewhat smaller wavenumber than in

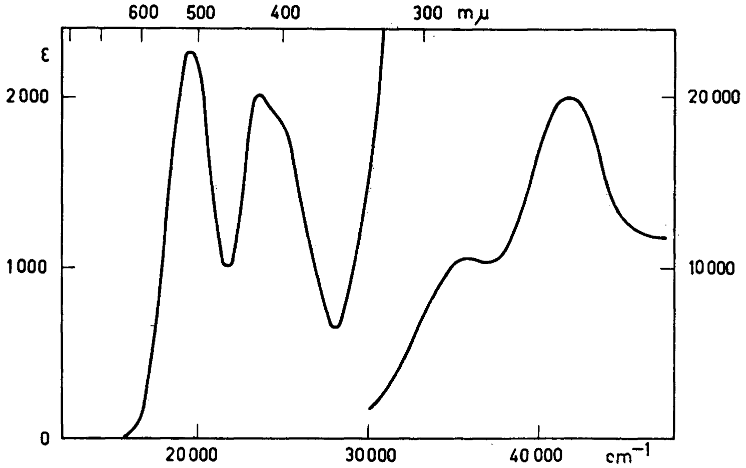

Fig. 1. Absorption spectrum of Ru dtp_3 in ethanol.

Ru dtp_3. However, the band is considerably broader in the latter case ($\delta(-)$ is only 2000 cm^{-1} in Rh dtp_3) as may be explained by the more complicated structure of the excited configuration $\pi^{-1}\,\gamma_5{}^5\gamma_3$ of the Ru(III) complexes. Similar remarks apply to the highest band observed at 41 700 cm^{-1} of Ru dtp_3 which may be compared to the band of Rh dtp_3 at 38 800 cm^{-1}.

Experimental 3.8 g ”potassium chlororuthenite” (predominantly $K_2[RuCl_5(H_2O)]$ or K_2RuCl_5) from H. Drijfhout and Zoon, Amsterdam, was heated with 100 ml 0.5 M perchloric acid. An olive-brown precipitate (0.9 g) was filtered off, and the filtrate added 40 ml 1 M aqueous solution of ammonium diethyldithiophosphate (from American Cyanamid, Stamford, Conn.). By heating at 80° for 6 h, under stirring, a dark brown precipitate was formed. When boiled with ethanol, this precipitate left 0.6 g of a yellow-brown powder (believed possibly to be dtp_3 RuORu dtp_3, having nearly the same analysis as Ru dtp_3: C 20.93; H 4.39; P 14.79; S 32.67. It is nearly insoluble in ethanol. A solution in dichloroethane shows a broad band at 380 mμ but no maxima in the visible), and the hot filtrate deposited various fractions of dark red, nearly black, crystals. The latter fractions were mixed with small amounts of a brown substance, reversing the intensity ratio between the 420 and 400 mμ bands. On the other hand, the first fraction so prepared (only 0.1 g) was identified as genuine Ru dtp_3. This was not so much because of the analysis. (Found: C 21.50; H 4.52; P 15.18; S 32.95. Calc. for $C_{12}H_{30}O_6P_3S_6Ru$: C 21.92; H 4.66; P 14.14; S 29.27) as because of the fact that colourless In dtp_3, when recrystallized from boiling ethanol together with one of the mixed fractions, syncrystallized with a clear red colour, leaving an orange solution. The visible absorption spectrum of a solution of these In(III), Ru(III) containing crystals was identical with that given above. The reflection spectrum of the red crystals was measured on the attachment to the Cary 14 recording spectrophotometer (on which all solutions were also measured) and showed maxima of the optical density at 509 and 421 mμ and a shoulder at 400 mμ.

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”The Formation of Polynuclear Complexes”

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In a recent contribution to *Acta Chem. Scand.*[1] professor L. G. Sillén has critisized my paper ”The Formation of Polynuclear Complexes.”[2]

The display presented by Sillén clearly shows that I have drawn some wrong conclusions in the case of the hydrolysis of the $VO_2{}^+$-ion, but apart from this his criticism is rather surprising both in its form as well as in its examples as will be evident from the following.

It will be clear for readers of my paper that the analysis of experimental data by the method proposed by me is in its present form limited to cases where only two complexes exist simultaneously in major amounts. This is the cause why I did not intend to identify the mononuclear species being formed in the case of the hydrolysis of the vanadyl ion.

Sometimes, however, the trends in the limiting slopes may be of some aid in identifying the new species arising when new reactions start. Such a case do we in fact have in the hydrolysis of the VO^{2+}-ion.

Rosotti by curve-fitting methods claimed the monomeric hydrolysis product to be VO(OH) with a stability constant of $\beta_{11} = 10^{8.2} \pm {}^{0.1}$ and showed how well the calculated curve fitted the experimental data. In his contribution Sillén used this example to demonstrate the superiority of the treatment of experimental data used by him and his group.

By considering the trends shown by the limiting slopes in a log *Z versus* pH plot of the available data it is obvious that the monomeric species $VO(OH)_2$ might as well be the actual species being formed. From the limiting tangent the formation constant is estimated to $\beta_{21} \simeq 10^{19}$.

In Fig. 1 a plot of *Z versus* pH calculated by means of the following formula is compared with experimental data

$$(Z-1) = ((\beta_{21}[OH]^2-1)/(4C_B\beta_{22}[OH]^2)) \left(\sqrt{(\beta_{21}[OH]^2+1)^2 + 8\beta_{22}[OH]^2C_B} - (\beta_{21}[OH]^2+1)\right)$$

where C_B is the total concentration of vanadium and with $\beta_{21} = 10^{18.8}$ and $\beta_{22} = 10^{21.5}$.