

spectrum as well as the Mössbauer spectrum of the brown compound resembled that of $\text{Fe}_2\text{O}_3\text{,aq}$. The destruction of this sample is probably due to untight sealing of the tube.

From the magnetic results it is seen, that the compound is reasonably stable in the Gouy-tube, since the rate of decomposition is fairly small, so it is possible to make several measurements on the same sample.

As could be expected when dealing with an unstable compound as $[\text{Fe}(\text{NH}_3)_5\text{NO}]\text{Cl}_2$, the magnetic susceptibility of the freshly prepared samples has not always the same value. In order to get an impression of the effect of a beginning decomposition, we have measured the χ_g of the brown destruction product prepared from the black compound by exposure to the air. We found $\chi_g = 54.7 \times 10^{-8}$, which is approx. 1.5 times the value we find for χ_g for the best samples of the black compound. A contamination with the brown destruction product will therefore increase the measured value for χ_g of the black compound.

As a consequence of these considerations we consider the results found for the samples C, D, and E as the most reliable. Due to a rather heavy, thickwalled Gouy-tube used for sample C, these measurements have not the same degree of accuracy as the other measurements. We therefore conclude that Fe in the compound $[\text{Fe}(\text{NH}_3)_5\text{NO}]\text{Cl}_2$, has a magnetic moment μ_{eff} not exceeding 4.70 BM, which may be explained as due to three unpaired electrons and a contribution of an orbital moment. Approximately the same magnetic moment is found in the "brown-ring"-complex, $[\text{Fe}(\text{H}_2\text{O})_5\text{NO}]^{2+}$, by Griffith, Lewis, and Wilkinson² and in $[\text{Fe}(\text{sal})_2(\text{py})\text{NO}]$ by Nast and Rückemann.³ It is therefore probable, that the bonding of NO is similar in these compounds and in $[\text{Fe}(\text{NH}_3)_5\text{NO}]\text{Cl}_2$, which accordingly may be considered as an iron (I)-complex with NO coordinated as NO^+ .

Experimental. The preparations and the analyses of the compound were all carried out as described earlier.¹ The compound was prepared in an N_2 -chamber, packed in a Gouy-tube and sealed off without being exposed to the air. The quantitative analyses showed that the contents of Fe, NH_3 , and Cl within the limits of the experimental error were equal to the theoretical values. (Found, %: Fe 23.2; NH_3 35.0; Cl 28.4. Calc. Fe 22.8; NH_3 35.0; Cl 29.0).

The magnetic susceptibility was measured by means of the Gouy method as described by Asmussen and Soling.⁴

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Organic Selenium Compounds

VIII. Electronic Spectra of Diselenocarbamate Complexes

K. A. JENSEN and V. KRISHNAN

Chemical Laboratory II (General and Organic Chemistry), University of Copenhagen, The H. C. Ørsted Institute, DK-2100 Copenhagen, Denmark

and C. KLIXBÜLL JØRGENSEN

Laboratoire de Chimie Physique, Université de Genève, Switzerland

Jensen and Krishnan¹ have described the preparation of several diselenocarbamate complexes. Some of these were independently prepared by Furlani *et al.*² who also discussed their electronic spectra. This investigation gives supplementary information on the electronic spectra of these compounds.

Sodium *N,N*-diethyldiselenocarbamate, in ethanol solution, has a broad band with maximum at 290 nm (34.4 kK), but the Zn and Cd complexes (in chloroform) show two well-developed bands in this region (see Table 1). The spectral change in the ultraviolet region on going to complexes with partly filled *d*-shells is presumably due to a change in the electron distribution in the ligand, the structure $\text{R}_2\overset{+}{\text{N}}=\text{C}(\text{Se}^-)_2$ becoming more important. This is also

reflected in a shift of the strong infrared absorption band near 1500 cm^{-1} to higher frequencies.³

The visible spectra of the transition metal diethyldiselenocarbamates are very similar to those of the corresponding dithiocarbamates.^{4,5} The difference in wave numbers of corresponding bands of dithiocarbamates and diselenocarbamates is usually 2–3 kK in the case of the electron transfer bands, but only 0.5 to 1 kK in the case of internal d^q -transitions. Octahedral low-spin d^8 -systems such as Co(III) and Rh(III), and approximately quadratic d^8 - and d^9 -systems such as Ni(II), Pd(II), and Cu(II) accumulate both effects in the lowest electron transfer transition.

We find shoulders at 14.4 kK and 18.0 kK as well as a band at 38.5 kK in the spectrum of $\text{Cr}(\text{Se}_2\text{C}-\text{NEt}_2)_3$, which were not reported by Furlani *et al.*² On the other hand, because of less satisfactory resolution in the near infrared, we could

not confirm the shoulder at 12.7 kK. The additional shoulders found by Furlani *et al.*, *viz.* at 25.5 kK and 30.8 kK are presumably due to impurities. There is little doubt that the excited levels giving rise to the three shoulders at 12.7, 14.4, and 18.0 kK are, arranged according to increasing wave numbers, 2E_g , ${}^2T_{1g}$, and ${}^2T_{2g}$ as classified in O_h symmetry. We take the two spin-allowed transitions to occur at 14.6 kK and 18.6 kK corresponding to $B=390$ kK and the nephelauxetic ratio $\beta_{35}=0.42$. These values are slightly larger than $\Delta=13.7$ kK, $B=340$ K and $\beta_{35}=0.37$ previously reported⁶ for $\text{Cr}(\text{Se}_2\text{P}(\text{OEt})_2)_3$. Similarly, for the corresponding sulfur compounds B is slightly smaller for Cr(III) diethyldithiophosphate ($B=420$ K) than for the dithiocarbamate ($B=430$ K). The opposite order of dithiophosphates and dithiocarbamates in the nephelauxetic series is found for Co(III), with $B=400$ K⁷ and 380 K^{4,5}, respectively. Similar results have recently been reported by Galsbøl⁸

Table 1. Absorption maxima^a of electronic spectra of diethyldiselenocarbamate complexes ($L=(\text{C}_2\text{H}_5)_2\text{NCSe}_2^-$) and bis(*O*-ethyldiselenocarbonato)nickel(II). (Shoulders in parentheses).

	λ , nm	ν , kK ^b	log ϵ		λ , nm	ν , kK	log ϵ
TiL	(400	25.0	2.54)	ZnL ₂	318	31.5	4.08
	285	35.1	4.53		287	34.8	4.40
	258	38.8	4.64		323	31.0	4.06
NiL ₂	675	14.8	2.00	CdL ₂	288	34.7	4.47
	470	21.3	2.47		InL ₃	(350	28.6
	(428	23.4	3.79)	280		35.7	~5
	358	27.9	4.61	TiL ₂		(500	20.0
	(275	36.4	4.43)		(315	31.8	4.59)
Ni(EtOCSe ₂) ₂	555	18.0	3.20	CrL ₃	293	34.1	4.81
	472	21.2	3.43		(255	39.2	4.59)
	350	28.6	4.38		(695	14.4	2.52)
	286	35.0	4.24		675	14.8	2.55
	PdL ₃	488	20.5		2.60	(555	18.0
PtL ₃	(385	26.0	3.78)	RhL ₃	527	19.0	2.52
	326	30.7	4.82		357	28.0	4.07
	(285	35.1	4.60)		298	33.6	4.65
	(265	37.7	4.79)		(450	22.2	2.08)
	422	23.7	3.45		345	29.0	4.44
	370	27.0	4.01		275	36.4	4.68
	285	35.1	4.80		CoL ₂ NO	670	14.9
CuL ₂	(610	16.4	3.31)	FeL ₂ NO	670	14.9	2.77
	495	20.2	4.00				
	325	30.8	4.13				
	292	34.2	4.43				

^a Recorded on a Perkin-Elmer Model 137 UV spectrophotometer. Solvent: chloroform.

^b 1 kK = $\text{cm}^{-1} \times 10^3$.

for diselenophosphinates, $\text{Cr}(\text{Se}_2\text{PEt}_2)_3$, having $A=12.9$ kK and $B=460$ K.

The first spin-allowed transition, ${}^1A_{1g} \rightarrow {}^1T_{1g}$, of rhodium(III) diethyl-diselenocarbamate occurs at 22.2 kK.

In the case of low-spin d^8 -complexes the main discrepancies between our spectra and those reported by Furlani *et al.*² are, firstly, that our Ni(II) compound does not show bands at 18.4 and 38.8 kK nor a shoulder at 31.5 kK, and secondly, that we find $\log \epsilon_{\text{mol}}=2.82$. The Pt(II) compound, not reported by Furlani, is included in Table 1.

It is possible to compare the reducing character of the ligands in such cases without introducing all the corrections needed^{9,10} for the absolute evaluation of χ_{opt} , since the difference between the wave number of the first spin-allowed d^8 - or d^8 -transition (ν_1) and the first electron transfer transition (ν_{et}) is a linear function of the optical electronegativity of the ligand for a given central atom. Using the data for halogeno complexes,¹¹ dithiocarbamates,⁵ dithiophosphates,^{5,7} and diselenophosphates⁶ we get:

$$\begin{aligned} \text{for Co(III): } \chi_{\text{opt}} &= (\nu_{\text{et}} - \nu_1 + 70)/30 \\ \text{for Rh(III): } \chi_{\text{opt}} &= (\nu_{\text{et}} - \nu_1 + 71)/30 \\ \text{for Pd(II): } \chi_{\text{opt}} &= (\nu_{\text{et}} - \nu_1 + 74)/30 \end{aligned}$$

With $\nu_{\text{et}}=22.2$ kK for the cobalt(III) complex² and $\nu_{\text{et}}=29.0$ kK for the Rh(III) complex (Table 1) we get $\chi_{\text{opt}}=2.6$. For the diethyl dithiocarbamates⁵ there is a minor discrepancy, the χ_{opt} value being calculated as 2.65 for the Co(III) compound, and as 2.75 for the Rh(III) compound. The former value seems more reliable because the electron transfer of the rhodium complex almost coincides with an internal transition in the ligands. The value $\chi_{\text{opt}}=2.6$ suggests that the first electron transfer band of the Pd(II) complex is the shoulder at 26.0 kK rather than the band at 30.7 kK. The evidence available for nickel(II) compounds is not sufficient for deciding between the two alternatives $\nu_{\text{et}}=23.4$ or 27.9 kK.

The comparatively weak shoulder at 28.6 kK of indium(III) diethyl diselenocarbamate seems to be comparable to the band⁶ at 34.0 kK of $\text{In}(\text{S}_2\text{P}(\text{OEt})_2)_3$. For a classification one should consult Refs. 12, 13.

The central atom Tl(III) is so oxidizing that the shoulder at 20 kK of the diselenocarbamate is an electron transfer band. The identification of the shoulder at 25 kK of the Tl(I) compound — if real — is

uncertain. Possibly this compound is an obligomer in solution.

The strong absorption bands of (O-ethyl)diselenocarbonato)nickel(II) in the visible region are comparable to the strong bands observed by Furlani and Luciani¹⁴ for dithiobenzoate complexes.

Schmidtke¹⁵ concluded that the difference in optical electronegativities between the sulfur and selenium containing ligands is only 0.05 to 0.1 unit, whereas the difference between Cl^- and Br^- is 0.2 unit. This observation is compatible with the fact that the electronegativity differences in the series B, C, N, O, F are very large, attenuate in the subsequent series Al to Cl and Ga to Br, and are almost negligible in the series Tl to At. Since the difference between Cl and Br is moderate, it is not surprising that S- and Se-containing ligands are not essentially different. Thus we cannot agree with Furlani *et al.* who argue that the very small spectrochemical difference between S and Se is unexpected and requires a special explanation in terms of a larger π back-donation in the selenium ligands.

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