spectrum as well as the Mössbauer spectrum of the brown compound resembled that of Fe$_2$O$_3$.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 [Fe(NH$_3$)$_3$NO]Cl$_3$, 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 $\chi_b$ of the brown destruction product prepared from the black compound by exposure to the air. We found $\chi_b = 24.7 \times 10^{-4}$, which is approx. 1.5 times the value we find for $\chi_b$ for the best samples of the black compound. A contamination with the brown destruction product will therefore increase the measured value for $\chi_b$ 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 [Fe(NH$_3$)$_3$NO]Cl$_3$ has a magnetic moment $\mu_{\text{eff}}$ 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 “browning”-complex, [Fe(H$_2$O)$_5$NO]$^{2+}$, by Griffith, Lewis, and Wilkinson and in [Fe(sal)_2(py)NO] by Nast and Rückemann. It is therefore probable, that the bonding of NO is similar in these compounds and in [Fe(NH$_3$)$_3$NO]Cl$_3$, which accordingly may be considered as an iron (I)-complex with NO coordinated as NO$^2-$. [Fe(NH$_3$)$_3$NO]Cl$_3$.

*Experimental.* The preparations and the analyses of the compound were all carried out as described earlier. The compound was prepared in an N$_2$-chamber, packed in a Gouy-tube and sealed off without beeing 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.


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Organic Selenium Compounds

VIII. Electronic Spectra of Diselenocarbamide Complexes

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

Sodium N,N-diethylselenocarbamate, 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 R$_n$N=C(So)$_3$ 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 diethylselenocarbamates are very similar to those of the corresponding dithiocarbamates.\(^4,5\) The difference in wave numbers of corresponding bands of dithiocarbamates and selenocarbamates 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\(^2\)-transitions. Octahedral low-spin d\(^4\)-systems such as Co(III) and Rh(III), and approximately quadratic d\(^2\)- and d\(^4\)-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 Cr(S\(_2\)P(\(\text{OEt}\))\(_3\)\(_2\)) 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, \(^2P\), \(^2T_{\text{lg}}\), and \(^2T_{\text{lg}}\) as classified in O\(_4\) 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 \(\beta_{\text{na}}=0.42\). These values are slightly larger than \(\alpha=13.7\) kK, \(B=340\) K and \(\beta_{\text{na}}=0.37\) previously reported \(^4\) for Cr(S\(_2\)P(OEt)\(_3\))\(_2\).

Similarly, for the corresponding sulfur compounds \(B\) is slightly smaller for Cr(III) diethyldithiophosphosphate \((B=420)\) 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 \(B=400\) K\(^2\) and \(380\) K\(^3\), respectively. Similar results have recently been reported by Galsbøl.\(^1\)

### Table 1. Absorption maxima\(^a\) of electronic spectra of diethylselenocarbamate complexes (L=\((\text{C}_4\text{H}_9)_2\text{NCSe}_{\text{Et}}\)) and bis(\(O\)-ethylselenocarbonato)nickel(II). (Shoulders in parentheses).

<table>
<thead>
<tr>
<th>(\lambda, \text{nm})</th>
<th>(\nu, \text{kK})</th>
<th>(\text{log}\ e)</th>
<th>(\lambda, \text{nm})</th>
<th>(\nu, \text{kK})</th>
<th>(\text{log}\ e)</th>
</tr>
</thead>
<tbody>
<tr>
<td>TIL</td>
<td>(400)</td>
<td>25.0</td>
<td>2.54</td>
<td>318</td>
<td>31.5</td>
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<tr>
<td></td>
<td>285</td>
<td>35.1</td>
<td>4.53</td>
<td>287</td>
<td>34.8</td>
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<tr>
<td></td>
<td>258</td>
<td>35.8</td>
<td>4.64</td>
<td>328</td>
<td>31.0</td>
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<td>NiL(_2)</td>
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<td>2.00</td>
<td>288</td>
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</tr>
<tr>
<td></td>
<td>470</td>
<td>21.3</td>
<td>2.47</td>
<td>(350)</td>
<td>28.6</td>
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<tr>
<td></td>
<td>(428)</td>
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<td>3.79</td>
<td>280</td>
<td>35.7</td>
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<tr>
<td></td>
<td>358</td>
<td>27.9</td>
<td>4.61</td>
<td>(500)</td>
<td>20.0</td>
</tr>
<tr>
<td></td>
<td>(275)</td>
<td>36.4</td>
<td>4.43</td>
<td>(315)</td>
<td>31.8</td>
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<tr>
<td>Ni(\text{EtOCSe}_{\text{Et}})(_2)</td>
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<td>18.0</td>
<td>3.20</td>
<td>293</td>
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<td></td>
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<td>(695)</td>
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<td>(355)</td>
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<td>327</td>
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<td>4.82</td>
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<td></td>
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<td>4.60</td>
<td>298</td>
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<tr>
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<td>(265)</td>
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<td>4.79</td>
<td>(450)</td>
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<tr>
<td>PtL(_2)</td>
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<td>4.01</td>
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<td>CuL(_2)</td>
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<td></td>
<td>(610)</td>
<td>16.4</td>
<td>3.31</td>
<td>FeL(<em>2)(</em>{\text{NO}})</td>
<td>670</td>
</tr>
</tbody>
</table>

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

\(^b\) 1 kK = cm\(^{-1}\) × \(10^4\).

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

The first spin-allowed transition, $^1A_{1g} \rightarrow ^1T_{1g}$, of rhodium(III) diethyl diselenocarbamate occurs at 22.5 kK.

In the case of low-spin $d^8$-complexes the main discrepancies between our spectra and those reported by Furlani et al. are, firstly, that our Ni(II) compound does not show bands at 18.4 and 38.5 kK nor a shoulder at 31.5 kK, and secondly, that we find $\log_{\text{mol}}=2.82$. 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 for the absolute evaluation of $\lambda_{opt}$ since the difference between the wave number of the first spin-allowed $d^8$- or $d^8$-transition ($\nu_1$) and the first electron transfer transition ($\nu_0$) is a linear function of the optical electron negativity of the ligand for a given central atom. Using the data for halogeno complexes, dithiocarbamates, dithiophosphates and diselenophosphates we get:

for Co(III): $\lambda_{opt} = \frac{(\nu_0 - \nu_1 + 70)}{30}$
for Rh(III): $\lambda_{opt} = \frac{(\nu_0 - \nu_1 + 71)}{30}$
for Pd(II): $\lambda_{opt} = \frac{(\nu_0 - \nu_1 + 74)}{30}$

With $\nu_0 = 22.2$ kK for the cobalt(III) complex and $\nu_0 = 29.0$ kK for the Rh(III) complex (Table 1) we get $\lambda_{opt} = 2.6$. For the diethyl dithiocarbamates there is a minor discrepancy, the $\lambda_{opt}$ 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 $\lambda_{opt} = 2.6$ 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 $\nu_0 = 23.4$ or 27.9 kK.

The comparatively weak shoulder at 28.8 kK of indium(III) diethyl diselenocarbamate seems to be comparable to the band at 34.0 kK of $\text{In(S}_2\text{P}^\text{Et}_2)_3$. 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 oligomer 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 Luciani for dithiobenzoate complexes.

Schmidtke 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 Ti 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 $\pi$ back-donation in the selenium ligands.


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