METAL COMPLEXES WITH TWO DIFFERENT SULFUR CONTAINING LIGANDS—II*

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Abstract—The synthesis and characterization of a series of mixed 1,1-1,2-dithiolene complexes, \(M[S_2C_2(CN)_2][S_2CNR_2]\) with \(z = -1\), \(M = \text{Ni, Cu, Pd, Pt}\) and with \(z = 0\), \(M = \text{Ni, Cu, Au}\), \(M[S_2C_2(CN)_2][S_2CNCN]^{2-}\), \(M = \text{Ni, Pd, Au}\), and \(\text{Ni}[S_2C_2(CN)_2][S_2COC_2H_5]^-\) are reported. Voltammetric studies in dichloromethane revealed that the mixed complexes could be oxidized in a one electron step, the half-wave potentials of which were generally in the middle between those for the unmixed complexes. The C—N stretching frequencies observed in the i.r. spectra of the \(M[S_2C_2(CN)_2][S_2CNR_2]\) complexes are reported.

INTRODUCTION

There is a growing interest in metal complexes containing two different sulfur donor ligands, especially those with the 1,1- and 1,2-dithiolato ligand systems. Nickel bis-complexes with two different 1,2-dithiolato ligands were reported[1], and the exchange reactions of these and related 1,2-dithioleines were studied with voltammetric techniques[1, 2].

Tris complexes with mixed 1,1- and 1,2-dithiolenic ligands were also prepared and investigated recently[3, 4].

In the course of investigating mixed metal bis-complexes we found electron transfer series in Ni, Cu and Au complexes containing an 1,2- as well as an 1,1-dithiolato ligand, \(M[S_2C_2(CN)_2]_2[S_2CNbu_2]^z\), with \(z = -1\) and 0[5].

The present paper describes the results of the voltammetric studies made on a series of mixed complexes derived from the same and some related sulfur donor ligands[6].

RESULTS AND DISCUSSION

Preparations

Analytical data for the newly prepared complexes correspond with the formulas given (Table 1). Colours, melting points and conductances are given in Table 2.

*Part—I. Ref. [5].

6. The following abbreviations are used:
   - \(mnt\) = maleonitrile dithiolate = \(S_2C_2(CN)_2\)
   - \(R_2dtc\) = \(N,N\)-di-alkyl(aryl)dithiocarbamate = \(S_2CNR_2\)
   - \(etxan\) = O-ethylxanthate = \(S_2COet\)
   - \(cdc\) = N-cyanodithiocarbimate = \(S_2CNCN\)
The reported[5] ligand exchange reaction between nickel bis-(1,2-dithiolato) and nickel bis-(dithiocarbamato) complexes have now been extended to prepare the compounds \( \text{M(mnt)(R}_2\text{dtc)}^- \) with \( \text{M} = \text{Cu, Pd and Pt} \). Also \( \text{Ni(exan)}_2 \)

<table>
<thead>
<tr>
<th>Complex</th>
<th>Colour</th>
<th>m.p. °C</th>
<th>( \Lambda^\dagger ) (cm(^2) Ω(^{-1}) M(^{-1}))</th>
<th>( \nu_{\text{CN}} ) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{bu}_4\text{NNi(mnt)(et}_2\text{dtc)} )</td>
<td>green</td>
<td>137</td>
<td>20-2</td>
<td>1520</td>
</tr>
<tr>
<td>( \text{bu}_4\text{NNi(mnt)(bu}_2\text{dtc)}^* )</td>
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<td>121</td>
<td>18-9</td>
<td>1512</td>
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<tr>
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<td>18-9</td>
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<td>( \text{Ni(mnt)(bu}_2\text{dtc)} )</td>
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<tr>
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<td>1420</td>
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<tr>
<td>( \text{et}_4\text{Ni(mnt)(exan)} )</td>
<td>green</td>
<td>151</td>
<td>28-2</td>
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<tr>
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<td>&gt;360</td>
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<tr>
<td>( \text{bu}_4\text{NPd(mnt)(bu}_2\text{dtc)} )</td>
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<tr>
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<td>114</td>
<td>53-8</td>
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<td>122</td>
<td>22-8</td>
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<tr>
<td>( \text{Au(mnt)(et}_2\text{dtc)} )</td>
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<tr>
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<td>1555</td>
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<tr>
<td>( \text{Au(mnt)(ph}_2\text{dtc)} )</td>
<td>green</td>
<td>310</td>
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<td>1438</td>
</tr>
</tbody>
</table>

*Ref. [5].

\( \dagger \) In nitrobenzene at roomtemperature (5·10\(^{-4}\) molar solutions). For a 1:1 electrolyte \( \Lambda \sim 15-30 \), for a 2:1 electrolyte \( \Lambda \sim 45-65 \) cm\(^2\) Ω\(^{-1}\) M\(^{-1}\).
Metal complexes

reacted readily with Ni(mnt)$_2^{2-}$ forming Ni(mnt)(etxan)$^-$. Not only with these dithioiocacid complexes but also with 1,1-dithiolato complexes the $M$(mnt)$_2^{2-}$ complexes showed these ligand exchange reactions. In this way the $M$(mnt)(cdc)$_2^{2-}$ complexes ($M = $ Ni and Pd) were obtained. The platinum complexes however, Pt(mnt)$_2^{2-}$ and Pt(cdc)$_2^{2-}$, showed no exchange reaction, even after boiling in acetonitrile for 5 days. This is in agreement with observations made for platinum dithiolenes, which showed no scrambling reactions even after 30 days [2]. The exchange reactions between metal complexes both derived from dithioacids i.e., Ni(R$_2$dtc)$_2$ and Ni(etxan)$_2$ proceeded so slowly, that no mixed complex could be isolated so far.

Voltammetric measurements indicated (vide infra) that oxidation of some of the herein described complexes could be successful, in consequence of the reported half-wave potential for the oxidation of Cu(dtc)$_2$ (0.47 V vs. SCE) and the successful synthesis of Cu(dtc)$_2$I$_3$[7].

The oxidation of Ni(mnt) (R$_2$dtc)$^-$ led to green black products analysing as Ni(mnt)(R$_2$dtc)$^0$ ($R = $ bu or ph). Both complexes showed in the esr spectrum a single line as can be expected for paramagnetic nickel (I = 0) compounds. The high values observed for the C—N stretching frequencies in the i.r. spectrum (Table 2) indicated also compounds with the metal in a high oxidation state. This is generally observed for oxidized dithiocarbamato complexes[8].

The brown [pr$_3$Ni$_3$Ni(mnt) (cdc) could be oxidized with iodine to red products, which also showed a one-line e.s.r. spectrum, but no analytically pure sample was obtained so far. Further investigations on these nickel(III) complexes are in progress.

The C—N stretching absorption, usually found in the range 1570–1400 cm$^{-1}$ is a much discussed property of dithiocarbamato complexes. The values of $v_{CN}$ for $M$(mnt) (R$_2$dtc)$_2$ compounds, given in Table 2, decreased in the order $R = $ me $>$ et $>$ bu $>$ ph, also observed previously for bis(chelates)[9].

Voltammetric Study

The measured half-wave potentials are summarised in Table 3. The measurements are carried out in dichloromethane solutions, using a rotating platinum electrode as the indicator electrode and a saturated calomel electrode as the reference. As a reversibility criterion the values of $E_{3/4} - E_{1/4}$ were taken. The half-wave potentials obtained for the mixed complexes are generally in the middle between those for the unmixed complexes.

The influence of the alkyl(aryl) group in the bis(dtc) complexes on the $E_{1/2}$ values is small but significant. It is remarkable that the sequence for $E_{1/2}$ values phenyl $>$ et $>$ bu is reversed for the Ni(R$_2$dtc)$_2$ compounds, compared with the other bis(dtc) complexes. In this group of bis(dtc) complexes only the copper compounds showed a reversible behaviour. This is reflected in a remarkable way in the preparative oxidation of dtc complexes, only the copper complex giving a

<table>
<thead>
<tr>
<th>Complex</th>
<th>Process</th>
<th>$E_{1/2}$ (V)</th>
<th>$E_{204} - E_{114}$ (mV)</th>
<th>Complex</th>
<th>Process</th>
<th>$E_{1/2}$ (V)</th>
<th>$E_{204} - E_{114}$ (mV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni(etxan)$_2$</td>
<td>0 $\rightarrow$ +1</td>
<td>0.88</td>
<td>80</td>
<td>Cu(ph$_2$dtc)$_2$</td>
<td>0 $\rightarrow$ +1</td>
<td>0.52</td>
<td>62</td>
</tr>
<tr>
<td>Ni(mnt)(etxan)$^-1$</td>
<td>-1 $\rightarrow$ 0</td>
<td>0.86</td>
<td>109</td>
<td>Cu(et$_2$dtc)$_2$</td>
<td>0 $\rightarrow$ +1</td>
<td>0.50</td>
<td>62</td>
</tr>
<tr>
<td>Ni(bu$_2$dtc)$_2$</td>
<td>0 $\rightarrow$ +1</td>
<td>0.79</td>
<td>152</td>
<td>Cu(bu$_2$dtc)$_2$</td>
<td>0 $\rightarrow$ +1</td>
<td>0.47</td>
<td>60</td>
</tr>
<tr>
<td>Ni(et$_2$dtc)$_2$</td>
<td>0 $\rightarrow$ +1</td>
<td>0.77</td>
<td>148</td>
<td>Cu(mnt)(ph$_2$dtc)</td>
<td>0 $\rightarrow$ -1</td>
<td>0.34</td>
<td>84</td>
</tr>
<tr>
<td>Ni(ph$_2$dtc)$_2$</td>
<td>0 $\rightarrow$ +1</td>
<td>0.75</td>
<td>200</td>
<td>Cu(mnt)(bu$_2$dtc)</td>
<td>0 $\rightarrow$ -1</td>
<td>0.33</td>
<td>68</td>
</tr>
<tr>
<td>Ni(mnt)(ph$_2$dtc)$^-1$</td>
<td>-1 $\rightarrow$ 0</td>
<td>0.48</td>
<td>84</td>
<td>Cu(mnt)(et$_2$dtc)</td>
<td>0 $\rightarrow$ -1</td>
<td>0.33</td>
<td>68</td>
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<tr>
<td>Ni(mnt)(bu$_2$dtc)$^-1$</td>
<td>-1 $\rightarrow$ 0</td>
<td>0.46</td>
<td>68</td>
<td>Au(ph$_2$dtc)$_2^+$</td>
<td>+1 $\rightarrow$ 0</td>
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<td>81</td>
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<tr>
<td>Ni(mnt)(et$_2$dtc)$^-1$</td>
<td>-1 $\rightarrow$ 0</td>
<td>0.46</td>
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<td>Au(me$_2$dtc)$_2^+$</td>
<td>+1 $\rightarrow$ 0</td>
<td>-0.22</td>
<td>75</td>
</tr>
<tr>
<td>Ni(mnt)(cdc)$^-2$</td>
<td>-2 $\rightarrow$ -1</td>
<td>0.38</td>
<td>58</td>
<td>Au(et$_2$dtc)$_2^+$</td>
<td>+1 $\rightarrow$ 0</td>
<td>-0.26</td>
<td>72</td>
</tr>
<tr>
<td>Pd(bu$_2$dtc)$_2$</td>
<td>0 $\rightarrow$ +1</td>
<td>1.21</td>
<td>140</td>
<td>Au(pr$_2$dtc)$_2^+$</td>
<td>+1 $\rightarrow$ 0</td>
<td>-0.28</td>
<td>77</td>
</tr>
<tr>
<td>Pd(mnt)(bu$_2$dtc)$^-1$</td>
<td>-1 $\rightarrow$ 0</td>
<td>0.71</td>
<td>56</td>
<td>Au(bu$_2$dtc)$_2^+$</td>
<td>+1 $\rightarrow$ 0</td>
<td>-0.29</td>
<td>78</td>
</tr>
<tr>
<td>Pd(mnt)(cdc)$^-2$</td>
<td>-2 $\rightarrow$ -1</td>
<td>0.60</td>
<td>58</td>
<td>Au(mnt)(ph$_2$dtc)</td>
<td>0 $\rightarrow$ -1</td>
<td>-0.41</td>
<td>60</td>
</tr>
<tr>
<td>Pt(bu$_2$dtc)$_2$</td>
<td>0 $\rightarrow$ +1</td>
<td>0.92</td>
<td>240</td>
<td>Au(mnt)(bu$_2$dtc)</td>
<td>0 $\rightarrow$ -1</td>
<td>-0.456</td>
<td>66</td>
</tr>
<tr>
<td>Pt(mnt)(bu$_2$dtc)$^-1$</td>
<td>-1 $\rightarrow$ 0</td>
<td>0.56</td>
<td>56</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

*Vs. SCE using approx. $5 \times 10^{-4}$ molar solution with $0.1 \text{ M} \text{Bu}_4\text{NClO}_4$ as the supporting electrolyte.
reaction product of the same stoichiometry Cu(dtc)$_2^+$, nickel[10], palladium and platinum[11] giving tris-complexes, $M$(dtc)$_3^+$, with the metal in the oxidation state +4.

In the mixed complexes, $M$(mnt)($R_2$dtc)$_z^+$, the influence of the alkyll(aryl) group vanished almost totally. The $M$(mnt)($R_2$dtc)$_z^+$ ($z = 0$ or $-1$, $M =$ Ni, Cu, Pd, Pt, Au) and $M$(mnt)(cdc)$_z^-$ ($M =$ Ni, Pd) complexes showed a reversible redox behaviour. This could be confirmed by the synthesis of Ni(mnt)($R_2$dtc) and Cu(mnt)($R_2$dtc).

A comparison of the oxidation waves for the mixed nickel complexes Ni(mnt)($L$)$_z^+$, showed that there was a significant effect arising from the ligand L. Thus the $E_{1/2}$ values became more positive in the sequence $L =$ cdc $< R_2$dtc $<$ etxan. A corresponding order was found shortly for cobalt and iron tris-complexes with the same and some related sulfur donor ligands[4].

The oxidation potentials for the mixed and unmixed complexes are dependent on $M$ (Table 4). The order of $E_{1/2}$ values for $M$(R$_2$dtc)$_2^+$ and $M$(mnt)($R_2$dtc)$_z^-$ complexes Cu $<$ Ni $<$ Pt $<$ Pd is however not valid for the oxidation potentials of $M$(mnt)$_2^-$ compounds.

<table>
<thead>
<tr>
<th>Table 4. Polarographic half-wave potentials for the reaction $ML_1L_2^{+} \rightarrow ML_1L_2^{+1} + e$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M$(bu$_4$N)$_2$M(mnt)$_2$</td>
</tr>
<tr>
<td>0.47</td>
</tr>
<tr>
<td>$M$(mnt)(bu$_4$N)$_2$</td>
</tr>
<tr>
<td>$M$(mnt)(cdc)$_z^-$</td>
</tr>
<tr>
<td>$M$(mnt)$_2^-$</td>
</tr>
</tbody>
</table>

In CH$_2$Cl$_2$ vs. SCE.

**EXPERIMENTAL**

**Starting materials**

The starting products were synthesised as described in the literature: (bu$_4$N)$_2$M(mnt)$_2$ with Ni, Cu, Pd, Pt[12], (bu$_4$N)$_2$M(cdc)$_2$ with $M =$ Ni, Pd, Pt[13], Ni(etxan)$_2^+$[14], Au(R$_2$dtc)$_2$Br[19]. $M$(R$_2$dtc)$_2$ were prepared by general known methods[15].

**Preparation of the complexes**

The (bu$_4$N)$_2$M(mnt)($R_2$dtc), (R$_2$N)$_2$M(mnt)(cdc) and (et$_4$N)Ni(mnt)(etxan) were synthesised from their unmixed bis(chelates) by a procedure similar to that described for bu$_4$NNi(mnt)(bu$_2$Ac)[5].

Cu(mnt)(R$_2$dtc), Au(mnt)(R$_2$dtc) were prepared from an equimolar mixture of Br$_2$M(R$_2$dtc) and Na$_2$mnt by a procedure similar to that described for Cu(mnt)(bu$_4$N)[5].

Ni(mnt)(bu$_4$N) was prepared by oxidation of the corresponding nickel(II) complex (2.0 g in 400 ml CH$_2$Cl$_2$) by adding in 15 min an excess iodine (1.6 g in 75 ml of the same solvent). The solvent was evaporated in vacuo and the residue was thoroughly washed with ethanol, until iodine free. The

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11. J. Willemse, personal communication, to be published.
product was dissolved in 30 ml hot chloroform, the solution was filtered, and to the filtrate 50 ml of diethyl ether was added. On cooling green black crystals were obtained in 70 per cent yield.

Ni(mnt)(Ph₃dtc) was obtained as a black precipitate from the oxidation of bu₄NNi(mnt)(Ph₃dtc) with iodine in CH₂Cl₂. The product was purified by repeated washing with acetone, and at least once with diethyl ether. After drying a black powder resulted. Yield 75 per cent.

**Physical measurements**

Voltammetric measurements in dichloromethane solutions were made with a Metrohm Polarecord E 261 with a Metrohm E 446 iR compensator equipped with three electrode geometry.

Conductivity measurements in nitrobenzene were carried out as described previously [16].

I.R. spectra were measured on a Perkin Elmer 257 spectrophotometer using the KBr disc technique.

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