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, $M[S_2C_2(CN)_2][S_2CNR_2]^z$ with $z = -1$, $M = Ni, Cu, Pd, Pt$ and with $z = 0$, $M = Ni, Cu, Au$, $M[S_2C_2(CN)_2][S_2CNCN]^{2-}$, $M = Ni, Pd$, and $Ni[S_2C_2(CN)_2][S_2COC_2H_5]^-$ 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 $M[S_2C_2(CN)_2][S_2CNR_2]^z$ 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-dithiolenes were studied with voltammetric techniques [1, 2].

Tris complexes with mixed 1,1- and 1,2-dithiolene 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, $M(S_2C_2(CN)_2)(S_2CNbu_2)^z$, 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].

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6. The following abbreviations are used:
mnt = maleonitrile dithiolate = $S_2C_2(CN)_2$
 R_2dte = N,N-di-alkyl(aryl)dithiocarbamate = S_2CNR_2
etxan = O-ethylxanthate = S_2COEt
cdc = N-cyanodithiocarbamate = S_2CNCN

Table 1. Analytical data

Complex	%C		%H		%N		%S		% Metal	
	found	calc.	found	calc.	found	calc.	found	calc.	found	calc.
$\text{bu}_4\text{NNi}(\text{mnt})(\text{et}_2\text{dtc})$	51.0	50.93	7.9	7.86	9.5	9.50			10.0	9.95
$\text{bu}_4\text{NNi}(\text{mnt})(\text{ph}_2\text{dtc})$	57.6	57.80	6.6	6.76	8.2	8.17			8.7	8.56
$\text{Ni}(\text{mnt})(\text{bu}_2\text{dtc})$	38.8	38.72	4.5	4.50	10.3	10.42			14.9	14.58
$\text{Ni}(\text{mnt})(\text{ph}_2\text{dtc})$	44.5	46.07	2.3	2.27	8.5	9.48	26.6	28.94	13.3	13.25
$\text{et}_4\text{NNi}(\text{mnt})(\text{etxan})$	40.3	40.01	5.6	5.60	9.4	9.33	27.8	28.48	13.5	13.04
$[\text{pr}_4\text{N}]_2\text{Ni}(\text{mnt})(\text{cdc})$	52.2	52.38	8.2	8.20	12.0	12.20	18.3	18.60	8.4	8.54
$\text{bu}_4\text{NCu}(\text{mnt})(\text{et}_2\text{dtc})$	49.5	50.51	7.8	7.79	9.3	9.43				
$\text{bu}_4\text{NCu}(\text{mnt})(\text{ph}_2\text{dtc})$	57.0	57.40	6.8	6.71	8.7	8.11				
$\text{Cu}(\text{mnt})(\text{et}_2\text{dtc})$	30.2	30.71	2.8	2.86	11.5	11.96				
$\text{Cu}(\text{mnt})(\text{ph}_2\text{dtc})$	46.2	45.57	2.4	2.25	8.0	9.38				
$\text{bu}_4\text{NPd}(\text{mnt})(\text{bu}_2\text{dtc})$	50.4	50.23	7.7	7.85	8.2	8.08	18.3	18.93	15.3	15.34
$[\text{bu}_4\text{N}]_2\text{Pd}(\text{mnt})(\text{cdc})$	54.7	53.84	8.2	8.56	10.0	9.91			12.4	12.55
$\text{bu}_4\text{NPt}(\text{mnt})(\text{bu}_2\text{dtc})$	44.8	44.53	7.0	6.95	7.4	7.16			25.2	24.94
$\text{Au}(\text{mnt})(\text{et}_2\text{dtc})$	22.4	22.27	2.2	2.07	8.8	8.66	26.4	26.25	40.4	40.58
$\text{Au}(\text{mnt})(\text{ph}_2\text{dtc})$	35.2	35.11	1.7	1.73	7.3	7.23				

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 $M(\text{mnt})(\text{R}_2\text{dtc})^-$ with $M = \text{Cu}$, Pd and Pt . Also $\text{Ni}(\text{etxan})_2$

Table 2. Physical properties of the prepared complexes

Complex	Colour	m.p. °C	$\Lambda^\dagger$ ($\text{cm}^2 \Omega^{-1} \text{M}^{-1}$)	ν_{CN} (cm^{-1})
$\text{bu}_4\text{NNi}(\text{mnt})(\text{et}_2\text{dtc})$	green	137	20.2	1520
$\text{bu}_4\text{NNi}(\text{mnt})(\text{bu}_2\text{dtc})^*$	green	121	18.9	1512
$\text{bu}_4\text{NNi}(\text{mnt})(\text{ph}_2\text{dtc})$	green	163	18.9	1377
$\text{Ni}(\text{mnt})(\text{bu}_2\text{dtc})$	blackgreen	230		1530
$\text{Ni}(\text{mnt})(\text{ph}_2\text{dtc})$	black	> 360		1420
$\text{et}_4\text{NNi}(\text{mnt})(\text{etxan})$	green	151	28.2	
$[\text{pr}_4\text{N}]_2\text{Ni}(\text{mnt})(\text{cdc})$	brown	207	52.4	
$\text{bu}_4\text{NCu}(\text{mnt})(\text{et}_2\text{dtc})$	darkbrown	110	20.3	1502
$\text{bu}_4\text{NCu}(\text{mnt})(\text{bu}_2\text{dtc})^*$	brown	93	20.0	1480
$\text{bu}_4\text{NCu}(\text{mnt})(\text{ph}_2\text{dtc})$	brown	110 dec	22.3	1370
$\text{Cu}(\text{mnt})(\text{et}_2\text{dtc})$	darkgreen	> 360		1570
$\text{Cu}(\text{mnt})(\text{bu}_2\text{dtc})^*$	darkgreen	> 360		1550
$\text{Cu}(\text{mnt})(\text{ph}_2\text{dtc})$	darkbrown	> 360		1390
$\text{bu}_4\text{NPd}(\text{mnt})(\text{bu}_2\text{dtc})$	yellow	117	21.8	1518
$[\text{bu}_4\text{N}]_2\text{Pd}(\text{mnt})(\text{cdc})$	brownyellow	114	53.8	
$\text{bu}_4\text{NPt}(\text{mnt})(\text{bu}_2\text{dtc})$	brown	122	22.8	1523
$\text{Au}(\text{mnt})(\text{et}_2\text{dtc})$	green	267		1545
$\text{Au}(\text{mnt})(\text{bu}_2\text{dtc})^*$	green	188		1555
$\text{Au}(\text{mnt})(\text{ph}_2\text{dtc})$	green	310		1438

*Ref. [5].

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

reacted readily with $\text{Ni}(\text{mnt})_2^{2-}$ forming $\text{Ni}(\text{mnt})(\text{etxan})^-$. Not only with these dithioacid complexes but also with 1,1-dithiolato complexes the $M(\text{mnt})_2^{2-}$ complexes showed these ligand exchange reactions. In this way the $M(\text{mnt})(\text{cdc})^{2-}$ complexes ($M = \text{Ni}$ and Pd) were obtained. The platinum complexes however, $\text{Pt}(\text{mnt})_2^{2-}$ and $\text{Pt}(\text{cdc})_2^{2-}$, 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., $\text{Ni}(\text{R}_2\text{dtc})_2$ and $\text{Ni}(\text{etxan})_2$ 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 $\text{Cu}(\text{dtc})_2$ (0.47 V vs. SCE) and the successful synthesis of $\text{Cu}(\text{dtc})_2\text{I}_3$ [7].

The oxidation of $\text{Ni}(\text{mnt})(\text{R}_2\text{dtc})^-$ led to green black products analysing as $\text{Ni}(\text{mnt})(\text{R}_2\text{dtc})^0$ ($R = \text{bu}$ 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 $[\text{pr}_4\text{N}]_2\text{Ni}(\text{mnt})(\text{cdc})$ 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 ν_{CN} for $M(\text{mnt})(\text{R}_2\text{dtc})^z$ compounds, given in Table 2, decreased in the order $R = \text{me} > \text{et} > \text{bu} > \text{ph}$, 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 $\text{Ni}(\text{R}_2\text{dtc})_2$ 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

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Table 3. Voltammetric data in dichloromethane solutions*

Complex	Process	$E_{1/2}$ (V)	$E_{3/4} - E_{1/4}$ (mV)	Complex	Process	$E_{1/2}$ (V)	$E_{3/4} - E_{1/4}$ (mV)
Ni(<i>etxan</i>) ₂	0 → +1	0.88	80	Cu(<i>ph₂dtc</i>) ₂	0 → +1	0.52	62
Ni(<i>mnt</i>)(<i>etxan</i>) ⁻	-1 → 0	0.86	109	Cu(<i>et₂dtc</i>) ₂	0 → +1	0.50	62
Ni(<i>bu₂dtc</i>) ₂	0 → +1	0.79	152	Cu(<i>bu₂dtc</i>) ₂	0 → +1	0.47	60
Ni(<i>et₂dtc</i>) ₂	0 → +1	0.77	148	Cu(<i>mnt</i>)(<i>ph₂dtc</i>)	0 → -1	0.34	84
Ni(<i>ph₂dtc</i>) ₂	0 → +1	0.75	200	Cu(<i>mnt</i>)(<i>bu₂dtc</i>)	0 → -1	0.33	68
Ni(<i>mnt</i>)(<i>ph₂dtc</i>) ⁻	-1 → 0	0.48	84	Cu(<i>mnt</i>)(<i>et₂dtc</i>)	0 → -1	0.33	68
Ni(<i>mnt</i>)(<i>bu₂dtc</i>) ⁻	-1 → 0	0.46	68	Au(<i>ph₂dtc</i>) ₂ ⁺	+1 → 0	-0.19	81
Ni(<i>mnt</i>)(<i>et₂dtc</i>) ⁻	-1 → 0	0.46	62	Au(<i>me₂dtc</i>) ₂ ⁺	+1 → 0	-0.22	75
Ni(<i>mnt</i>)(<i>cdc</i>) ²⁻	-2 → -1	0.38	58	Au(<i>et₂dtc</i>) ₂ ⁺	+1 → 0	-0.26	72
Pd(<i>bu₂dtc</i>) ₂	0 → +1	1.21	140	Au(<i>pr₂dtc</i>) ₂ ⁺	+1 → 0	-0.28	77
Pd(<i>mnt</i>)(<i>bu₂dtc</i>) ⁻	-1 → 0	0.71	56	Au(<i>bu₂dtc</i>) ₂ ⁺	+1 → 0	-0.29	78
Pd(<i>mnt</i>)(<i>cdc</i>) ²⁻	-2 → -1	0.60	58	Au(<i>mnt</i>)(<i>ph₂dtc</i>)	0 → -1	-0.41	60
Pt(<i>bu₂dtc</i>) ₂	0 → +1	0.92	240	Au(<i>mnt</i>)(<i>et₂dtc</i>)	0 → -1	-0.45	60
Pt(<i>mnt</i>)(<i>bu₂dtc</i>) ⁻	-1 → 0	0.56	56	Au(<i>mnt</i>)(<i>bu₂dtc</i>)	0 → -1	-0.456	66

* Vs. SCE using approx. $5 \cdot 10^{-4}$ molar solution with 0.1 M bu_4NClO_4 as the supporting electrolyte.

reaction product of the same stoichiometry $\text{Cu}(\text{dtc})_2^+$, nickel[10], palladium and platinum[11] giving tris-complexes, $M(\text{dtc})_3^+$, with the metal in the oxidation state +4.

In the mixed complexes, $M(\text{mnt})(\text{R}_2\text{dtc})^z$, the influence of the alkyl(aryl) group vanished almost totally. The $M(\text{mnt})(\text{R}_2\text{dtc})^z$ ($z = 0$ or -1 , $M = \text{Ni}, \text{Cu}, \text{Pd}, \text{Pt}, \text{Au}$) and $M(\text{mnt})(\text{cdc})^{2-}$ ($M = \text{Ni}, \text{Pd}$) complexes showed a reversible redox behaviour. This could be confirmed by the synthesis of $\text{Ni}(\text{mnt})(\text{R}_2\text{dtc})$ and $\text{Cu}(\text{mnt})(\text{R}_2\text{dtc})$.

A comparison of the oxidation waves for the mixed nickel complexes $\text{Ni}(\text{mnt})(\text{L})^z$, showed that there was a significant effect arising from the ligand L. Thus the $E_{1/2}$ values became more positive in the sequence $\text{L} = \text{cdc} < \text{R}_2\text{dtc} < \text{etxan}$. 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 $M(\text{R}_2\text{dtc})_2$ and $M(\text{mnt})(\text{R}_2\text{dtc})^-$ complexes $\text{Cu} < \text{Ni} < \text{Pt} < \text{Pd}$ is however not valid for the oxidation potentials of $M(\text{mnt})_2^{2-}$ compounds.

Table 4. Polarographic halve-wave potentials for the reaction
 $\text{ML}_1\text{L}_2^z \rightarrow \text{ML}_1\text{L}_2^{z+1} + e$

	Cu	Ni	Pt	Pd	Au
$M(\text{bu}_2\text{dtc})_2$	0.47	0.75	0.92	1.21	-0.29
$M(\text{mnt})(\text{bu}_2\text{dtc})^-$	0.33	0.46	0.56	0.71	-0.46
$M(\text{mnt})(\text{cdc})^{2-}$		0.38		0.60	
$M(\text{mnt})_2^{2-}$	0.23	0.19	0.20	0.41	-0.61

In CH_2Cl_2 vs. SCE.

EXPERIMENTAL

Starting materials

The starting products were synthesised as described in the literature: $(\text{bu}_4\text{N})_2M(\text{mnt})_2$ with Ni, Cu, Pd, Pt[12], $(\text{bu}_4\text{N})_2M(\text{cdc})_2$ with $M = \text{Ni}, \text{Pd}, \text{Pt}$ [13], $\text{Ni}(\text{etxan})_2$ [14], $\text{Au}(\text{R}_2\text{dtc})_2\text{Br}$ [19]. $M(\text{R}_2\text{dtc})_2$ were prepared by general known methods[15].

Preparation of the complexes

The $(\text{bu}_4\text{N})M(\text{mnt})(\text{R}_2\text{dtc})$, $(\text{R}_4\text{N})_2M(\text{mnt})(\text{cdc})$ and $(\text{et}_4\text{N})\text{Ni}(\text{mnt})(\text{etxan})$ were synthesised from their unmixed bis(chelates) by a procedure similar to that described for $\text{bu}_4\text{NNi}(\text{mnt})(\text{bu}_2\text{dtc})$ [5].

$\text{Cu}(\text{mnt})(\text{R}_2\text{dtc})$, $\text{Au}(\text{mnt})(\text{R}_2\text{dtc})$ were prepared from an equimolar mixture of $\text{Br}_2M(\text{R}_2\text{dtc})$ and Na_2mnt by a procedure similar to that described for $\text{Cu}(\text{mnt})(\text{bu}_2\text{dtc})$ [5].

$\text{Ni}(\text{mnt})(\text{bu}_2\text{dtc})$ was prepared by oxidation of the corresponding nickel(II) complex (2.0 g in 400 ml CH_2Cl_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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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*)(*ph₂dtc*) was obtained as a black precipitate from the oxidation of $\text{bu}_4\text{NNi}(\text{mnt})(\text{ph}_2\text{dtc})$ with iodine in CH_2Cl_2 . 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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