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Metal Complexes with two Different Sulfur Containing Ligands. Electron Transfer Series of the $[M\text{-}S'_2S''_2]^z$-type

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*An electron transfer series of complexes of the $[M\text{–}S'_2S''_2]^z$–type has been investigated, using maleonitrile dithiolate and N,N–di–*n*–butyldithiocarbamate as the ligands (M = Ni, Cu, and Au). Monoanionic (z = –1) M(mnt)(dtc)$^-$ with M = Ni, Cu, and neutral (z = 0) (M(mnt)(dtc) with M = Cu, Au complexes have been prepared. Voltammetric data show these complexes to exist as part of a two membered series z = 0 or –1, the members being convertible by reversible one electron steps. The $E_{1/2}$ values are intermediate between those for the complexes with unmixed ligands.*

Introduction

Much interest has been shown in the square-planar metal complexes formed by bidentate sulphur-donor ligands. In particular the metal complexes derived from dithiolenes[1] and dithiocarbamates[2] have received considerable attention. These complexes exist in several oxidation states which are related by one electron-transfer reactions. It is therefore of interest to extend these studies with the characterization of metal complexes containing both types of ligands.

An iron complex with composition $Fe(Et_2dtc)(S_2C_2(CF_3)_2)$ has been reported[3] recently and some complexes with two different dithiolene ligands[1] and other sulphur containing ligands have also been studied.[4]

In a previous communication[5] we have reported the reaction of $Br_2Au(dtc)$ with Na(dtc) in which the ionic complex $[Au(dtc)_2]^+Br^-$ was formed.[6] This reaction stimulated us to a further study of the possibility of the substitution of the bromine atoms in $Br_2Au(dtc)$ and $Br_2Cu(dtc)$ by dithiolenes, forming complexes with two different sulphur containing ligands.

Results and Discussion

The reaction of disodium 1,2-dicyanoethylene-1,2-dithiolate ($Na_2(mnt)$) with solutions of $Br_2M(dtc)$ (M = Cu, Au) in dichloromethane afforded the green crystalline diamagnetic complexes Cu(mnt)(dtc) and Au(mnt)(dtc) resp. Voltammetric measurements indicated that reduction of Cu(mnt)(dtc) could readily be accomplished by a weakly basic solvent as has been pointed out by Davison and Holm.[7] n–$Bu_4NCu(mnt)(dtc)$ could indeed be obtained from an acetone solution. As has been shown[1] dithiolene complexes from the nickel group easily undergo ligand exchange reactions. From a reaction of $(n\text{–}Bu_4N)_2Ni(mnt)_2$ with $Ni(dtc)_2$ in boiling acetonitrile a yellow solution was formed from which n–$Bu_4NNi(mnt)(dtc)$ was obtained.

For n–$Bu_4NNi(mnt)(dtc)$ and n–$Bu_4NCu(mnt)(dtc)$ an equivalent conductance $\Lambda_e = 18.9$ and 20.0 cm^2 ohm^{-1} mole^{-1} was found in nitrobenzene (5.10^{-4} molar solutions), indicating them to be 1:1 electrolytes.

The molar magnetic susceptibility of solid n–$Bu_4NCu(mnt)(dtc)$ was 1676.10^{-6} (c.g.s.u. mole^{-1}) at room temperature. After correction for diamagnetism the effective magnetic moment was calculated to be 2.2 BM. This result is in agreement with the esr measurements for Cu(mnt)(dtc)$^-$ in DMF: $A(^{63}Cu) = 77.5$ gauss with $g = 2.0437$ and in acetone: $A = 79.0$ gauss with $g = 2.0445$.

The complexes were investigated by voltammetric techniques in dichloromethane solutions using a rotating platinum electrode. The results of these and some other related complexes are summarised in Table I. A comparison of the half-wave potentials obtained for the mixed complexes showed that these values are intermediate between $E_{1/2}$ values for the dithiolenes and the dithiocarbamato complexes, but a distinct quantitative relationship could not be found. The anion Ni(mnt)(dtc)$^-$ exhibited a reversible one electron oxidation step as could be concluded from the value of the slope of plot log $i(i_d - i)^{-1}$ *vs.* E and the magnitude of i_d/C, being about equal to the value of $Ni(mnt)_2^{2-}$ for which a one electron transfer reaction has been confirmed by synthetic results. A one electron transfer reaction is also observed for the reduction of Cu(mnt)(dtc), which is confirmed by the successful synthesis of Cu(mnt)(dtc)$^-$. Voltammetric data show that $Cu(dtc)_2$ could be oxidized in a one electron step to $Cu(dtc)_2^+$. Although the oxidation potential seems too positive for an oxidation with iodine, the reaction

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(1) J.A. McCleverty, *Progr. Inorg. Chem.*, *10*, 49 (1968).

(2) D. Coucouvanis, *Progr. Inorg. Chem.*, *11*, 233 (1970).

(3) L.H. Pignolet and R.H Holm, *J. Am. Chem. Soc.*, 92, 1791 (1970).

(4) R.G. Pearson and D.A. Sweigart, *Inorg. Chem.*, 9, 1167 (1970).

(5) P.T. Beurskens, J.A. Cras, and J.G.M. van der Linden, *Inorg. Chem.*, 9, 475 (1970).

(6) In this paper the following abbreviations are used: mnt = maleonitriledithiolate = $S_2C_2(CN)_2^{2-}$, tdt = toluene-3,4-dithiolate = $S_2C_6H_3\text{-}CH_3^{2-}$, dtc = N,N-di-*n*-butyldithiocarbamate = $S_2CN(n\text{-}Bu)_2^-$. The use of the abbreviation $[M\text{-}S'_2S''_2]^z$ is intended to refer to a bis-substituted metal complex with two different sulphur ligands.

(7) A. Davison and R.H. Holm, *Inorg. Synth.*, *10*, 8 (1967).

Table I. Voltammetric data in dichloromethane solutions [a]

Complex	process	vs SCE			vs. AgI/Ag electrode		ΔE [c]
		$E_{1/2}$ (V)	slope [b] (mV)	i_d/C (μA/m*M*)	$E_{1/2}$ (V)	slope [b] (mV)	(V)
Ni(mnt)$_2^{2-}$	$-2 \rightarrow -1$	0.19	62	48	0.37 [d]	61	0.18
Ni(mnt)(dtc)$^-$	$-1 \rightarrow 0$	0.48	69	40	0.65	67	0.17
Ni(dtc)$_2$	$0 \rightarrow +1$				1.08	irrev.	
Cu(mnt)$_2^{2-}$	$-2 \rightarrow -1$				0.41 [d]		
Cu(mnt)(dtc)$^\circ$	$0 \rightarrow -1$	0.33	64	47	0.51	68	0.18
Cu(dtc)$_2^\circ$	$0 \rightarrow +1$	0.47	69	50	0.65	60	0.18
Au(mnt)$_2^-$	$-1 \rightarrow -2$	−0.61	64		−0.42 [d, e]	67	0.19
Au(mnt)(dtc)$^\circ$	$0 \rightarrow -1$	−0.46	66	50	−0.27	57	0.19
Au(dtc)$_2^+$	$+1 \rightarrow 0$	−0.29	78	61	−0.11	70	0.18
Au(tdt)$_2^-$	$-1 \rightarrow -2$				−1.95 [f]		
Au(tdt)(dtc)$^\circ$	$0 \rightarrow -1$	−0.87	67	57	−0.67	64	0.20

[a] Using approx. 5.10^{-4} molar solutions with 0.1 molar *n*-Bu$_4$NClO$_4$ as the supporting electrolyte. [b] Slope of plot of log $i(i_d - i)^{-1}$ *vs* E, which for a reversible reaction at 25° is 58/n mV. [c] Two different reference electrodes are used: an AgI/Ag electrode (ref. 11) and a saturated calomel electrode. The half-wave potentials are found to be related by $\Delta E = E_{1/2}(\text{AgI/Ag}) - E_{1/2}(\text{SCE}) = 0.18$ V. [d] A.L. Balch, I.G. Dance, R.H. Holm., *J. Am. Chem. Soc.*, *90*, 1144 (1968). These authors report the same value for the oxidation of Ni(mnt)$_2^{2-}$ and a well-defined wave for Au(mnt)$_2^-$ in CH$_2$Cl$_2$ solutions. [e] Also −0.42 V in CH$_3$CN *vs* SCE (ref. 2). [f] Measured in DMF solution, relative to a AgClO$_4$/Ag reference electrode: R. Williams, E. Billig, J.H. Waters, H.B. Gray, *J. Am. Chem. Soc.*, *88*, 43 (1966).

Table II. Elemental Analyses and Melting Points

Complex	M.p.°C	C(%)		H(%)		N(%)		S(%)		Metal (%)	
		Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
n-Bu$_4$NMi(mnt)(dtc)	121	54.3	53.94	8.6	8.43	8.6	8.68			9.0	9.09
n-Bu$_4$NCu(mnt)(dtc)	93	53.5	53.54	8.4	8.37	8.4	8.61			9.7	9.77
Cu(mnt)(dtc)	>360	38.5	38.25	4.3	4.45					15.7	15.57
Au(mnt)(dtc)	188	28.7	28.83	3.3	3.35	7.7	7.76	23.3	23.68	36.4	36.38
Au(tdt)(dtc)	176	34.5	34.59	4.3	4.35			22.7	23.08	35.1	35.45

of Cu(dtc)$_2$ with I$_2$ yielded [Cu(dtc)$_2$]$^+$I$_3^-$.[8] As far as we know this is the first reversible one electron transfer reaction reported for a bis-dithiocarbamato complex. It is known from esr measurements that gold(II)-diethyldithiocarbamate only exists in solutions containing excess thiuram disulphide.[9] The voltammetric reduction of Au(dtc)$_2^+$ is clearly not a reversible one electron reaction. This is probably due to a further disproportionation of the Au$^{\text{II}}$(dtc). The mixed gold complexes on the other hand could be reduced in a reversible one electron step.

The observed one electron transfer series of the [M—S$_4$]^z—type and of the [M—S'$_2$S''$_2$]^z—type with dithiocarbamates and dithiolenes as the ligands, show that Schrauzer's[10] classification for sulphur containing ligands is not as clear as was proposed.

Experimental Section

Analyses. The results of the elemental analyses are given in Table II. Metals were analyzed by atomic absorption photometric methods. The other elemental analyses were carried out by the microanalytical department of this university.

All melting points are uncorrected.

Preparations. n—*Bu$_4$NNi*(*mnt*)(*dtc*). Equimolar amounts (2 mmoles) of Ni(dtc)$_2$ and [*n*—Bu$_4$N]$_2$[Ni(mnt)$_2$] were refluxed for 12 hours in 100 ml acetonitrile. The solution turns dark yellow-green. After the solvent was removed *in vacuo,* the residue was taken up in acetone and the solution filtered if necessary. To the hot acetone solution water was added untill the first cloudiness appeared. On cooling golden green crystals (1.2 g) were obtained.

n—*Bu$_4$NCu*(*mnt*)(*dtc*). Equimolar amounts (0.01 mol) of Cu(mnt)(dtc) and *n*—Bu$_4$NBr were dissolved in 100 ml acetone, giving a dark brown solution. The solvent was removed and the residue was taken up in hot ethyl alcohol. The solution was filtered hot. On cooling 0.6 g of dark brown crystals were obtained.

Cu(*mnt*)(*dtc*). A solution of 2.14 g Br$_2$Cu(dtc) in 30 ml methylene chloride was slowly added to a suspension of 0.93 g Na$_2$(mnt) in the same solvent. The solution turned dark green immediately. The solution was filtered and diethyl ether was slowly added to the filtrate until the first cloudiness. On cooling (0°) 1.0 g dark green crystals were obtained. These were recrystallized following the same procedure.

Au(*mnt*)(*dtc*). 0.19 g Na$_2$(mnt) was suspended in 15 ml chloroform. A solution of 0.56 g Br$_2$Au(dtc) in 15 ml chloroform was added slowly with intensive stirring. The colour of the solution changed from red to green. The solution was filtered and an equal amount of diethyl ether was added to the filtrate. The precipitate was recrystallized from aceton. 0.4 g of lustrous green crystals were obtained.

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(8) H.C. Brinkhoff, personal communication, submitted for publication.
(9) T. Vänngard and S. Åkerström, *Nature*, *184*, 183 (1959).
(10) G.N. Schrauzer, *Transition Metal Chem.*, *4*, 299 (1968).

Au(tdc)(dtc). To a solution of 0.56 g $Br_2Au(dtc)$ in 30 ml tetrahydrofuran an equimolar amount (0.16 g) of toluene-3,4-dithiol in 30 ml THF was added. The colour changed immediately from orange to green. To neutralize the acid solution an equimolar amount of potassium hydroxide in 30 ml ethanol was added. The green product was filtered, washed with diethyl ether and recrystallized from methylene-ethanol mixtures. Light green crystals were obtained in 70% yield.

Physical measurements. Voltammetric measurements in dichloromethane solutions were made using a Metrohm Polarecord E 261 with a Metrohm E 446 iR compensator equipped with three electrode geometry. A rotating platinum electrode served as the indicator electrode and a saturated calomel electrode or an AgI/Ag[11] electrode as the reference electrode. *n*—Bu_4ClO_4 (0.1 molar solutions) was used as the supporting electrolyte.

Conductivity measurements in nitrobenzene were carried out as described previously.[12]

Esr measurements were carried out on a Varian X-band spectrometer (V4502). The microwave frequency was measured with a HP 5246 L frequency counter. Magnetic field measurements were performed on a AEG magnetfeldmesser. Magnetic susceptibilities were measured with a standard Gouy-type balance at room temperature.

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