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Metal Complexes of 1,3-Dimethylimidazolium-2-dithiocarboxylate

LONDA L. BORER*, JEANIE V. KONG, PATRICIA A. KEIHL and DAVID M. FORKEY
California State University, Sacramento, Sacramento, Calif. 95819, U.S.A.

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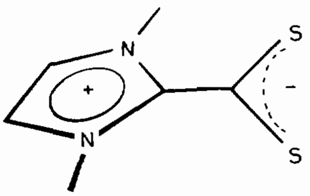
Abstract

Complexes containing the soft acid metals Pt, Pd, Ag, and Au, with the ligand 1,3-dimethylimidazolium-2-dithiocarboxylate (L) have been synthesized and characterized by analytical data and infrared and electronic spectroscopy. The data suggest that the ligand acts as a bidentate ligand with Pt and Pd, a monodentate ligand with Ag and a bridging ligand between two Au atoms.

Introduction

Dithiocarboxylates have been less widely investigated as ligands than other well known dithio anions such xanthates, dithiocarbamates, and dithiophosphates. Several recent reviews [1–3] have discussed a variety of metal complexes of the 1,1-dithiolato ligands. Nickel triad metals react with aliphatic dithioacids, for example, to form dithioacetates and phenyldithioacetates [4]. Two aromatic dithioacids have been employed in preparing dithiobenzoates and cyclopentadienyldithiocarboxylates [5]. To our knowledge no complexes of a zwitterionic dithiocarboxylate have been reported. We report here the preparation and characterization of some metal complexes of the heterocyclic dithiocarboxylate zwitter ion, 1,3-dimethylimidazoliumdithiocarboxylate (**1**). This has a dithiocarboxylate group joined to the 2-position of an orthogonally oriented dimethylimidazolium cation.



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Experimental

Preparation of Bis(1,3-dimethylimidazolium-2-dithiocarboxylate)platinum(II) Hexafluorophosphate, (PtL$_2$)(PF$_6$)$_2$

The ligand was prepared by the general procedure of Forkey and Kiehl [16]. Polymeric PtCl$_2$ (0.47 g, 1.8 mmol) in 25 ml of acetonitrile was allowed to reflux approximately 15 min to form PtCl$_2$(CH$_3$CN)$_2$. The ligand (0.62 g, 3.6 mmol), dissolved in 25 ml of acetonitrile, was added to the refluxing solution. This mixture was refluxed for 45 min. A brown precipitate was collected and air dried. The product was extremely soluble in water and gave an electrical conductivity measurement in water at 25 °C and 10^{-1} M dilution of $\Omega = 41$ ohm^{-1} cm^2 mol^{-1}. Analysis of this product was indefinite. The precipitate was dissolved in water and a stoichiometric amount of KPF$_6$ was added. A finely divided black precipitate was collected and washed several times with water, melting point (m.p.) > 300 °C. *Anal.* Calc. for [Pt(C$_6$H$_8$N$_2$S$_2$)$_2$](PF$_6$)$_2$: C, 17.37; H, 1.95; N, 6.75; S, 15.46; P, 7.47. Found: C, 17.22; H, 2.07; N, 6.61; S, 15.67; P, 7.10%.

Preparation of Dichloro(1,3-dimethylimidazolium-2-dithiocarboxylate)palladium(II), PdLCl$_2$

Anhydrous PdCl$_2$ (0.19 g, 1.1 mmol) was refluxed with the ligand (0.19 g, 1.1 mmol) in 25 ml of acetonitrile. A brown precipitate was collected by vacuum filtration and washed with acetonitrile, m.p. > 300 °C. *Anal.* Calc. for Pd(C$_6$H$_8$N$_2$S$_2$)Cl$_2$: C, 20.61; H, 2.31; N, 8.01; S, 18.34; Cl, 20.28. Found: C, 20.67; H, 2.44; N, 8.11; S, 18.52; Cl, 20.45%. Molecular weight determination in methanol: calc. for monomeric PdLCl$_2$, 349, found, 336.

Preparation of Dibromo(1,3-dimethylimidazolium-2-dithiocarboxylate)palladium(II), PdLBr$_2$

The ligand (0.30 g, 1.7 mmol) was refluxed with anhydrous PdBr$_2$ (0.45 g, 1.7 mmol) for 45 min in acetonitrile. A dark green, finely divided precipitate was collected by vacuum filtration, m.p. > 300 °C. *Anal.* Calc. for Pd(C$_6$H$_8$N$_2$S$_2$)Br$_2$: C, 16.43; H, 1.84; N, 6.39; Br, 36.25. Found: C, 16.75; H, 1.88; N, 6.49; Br, 36.25%.

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*Author to whom correspondence should be addressed.

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Preparation of Bis(1,3-dimethylimidazolium-2-dithiocarboxylate)silver(I) Hexafluorophosphate, [AgL_2]PF_6

The ligand (0.30 g, 1.7 mmol) was dissolved in 30 ml of methanol and 4.4 ml of 0.2 M $AgNO_3$ solution was added. Solid KPF_6 was added immediately and a dark purple precipitate formed. The precipitate was collected by vacuum filtration and washed with water, m.p. 245 °C. If KPF_6 was not added immediately, silver(0) formed on the sides of the reaction container. *Anal.* Calc. for $[Ag(C_6H_8N_2S_2)_2]PF_6$: C, 24.13; H, 2.69; P, 5.18. Found: C, 24.16; H, 2.64; N, 5.30%.

Preparation of Dichlorobis(1,3-dimethylimidazolium-2-dithiocarboxylate)digold(I), Au_2LCl_2

The ligand (0.17 g, 0.10 mmol) and $NaAuCl_4 \cdot 2H_2O$ (0.40 g, 0.10 mmol) were dissolved in acetonitrile and heated for 15 min. A brown precipitate was collected, m.p. = 152 °C. *Anal.* Calc. for $Au_2(C_6H_8N_2S_2)Cl_2$: C, 11.30; H, 1.26; N, 4.40. Found: C, 11.54; H, 1.44; N, 4.48%.

Spectroscopy

All UV–Vis spectra were taken on a Beckman model 25 spectrophotometer. All IR spectra were obtained on a Perkin-Elmer model 598 spectrophotometer or Perkin-Elmer 1800 FTIR. Solid samples were run from 300–4000 cm^{-1} as KBr pellets and 200–400 cm^{-1} as mineral oil smears on polystyrene plates.

Electrical Conductivity

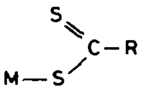
Electrical conductivity measurements were made using a Chemtrix type 60A pH meter and Lazar Cond-156 conductivity probe.

Cyclic Voltammetry

Cyclic voltammetry measurements were made on a BAS 100 Electrochemical system.

Results and Discussion

The neutral dithiocarboxylate zwitter ion can bind to a metal ion in one of the following ways:



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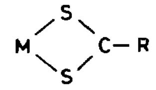

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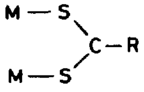

III

Various neutral ligands such as H_2S, RSH, thioethers, organic disulfides, and anionic ligands such as the xanthates, dithiocarbamates, and dithiophosphates form metal complexes with soft acid metals and are well characterized. It is therefore expected that this neutral ligand containing sulfur atoms would best react with soft acid metals such as platinum, palladium, silver and gold.

Infrared data has often been used to determine complexation of dithio ligands to a metal [7–11]. The infrared spectra of the metal complexes are compared to the ligand in Table I. The symmetric and assymetric stretch of the CSS unit shifts relative to the ligand, indicating sulfur chelation to the metal. This shift to higher frequency can be explained by M → L π bonding. The electron in the π orbital of the metal can overlap with the empty π^* orbital of the sulfur atom in the ligand. The π^* orbitals are relatively low in energy as shown by the fact that the zwitter ion is intensely colored. There are also electrons in nonbonding molecular orbitals on the sulfur atoms with proper symmetry to overlap with the empty $d_{x^2-y^2}$, for example on the Pt, thereby allowing L → M π bonding. In the $PdLCl_2$ spectrum, a stretch is observed at 300 cm^{-1} which disappears in the $PdLBr_2$ spectrum. This peak, therefore, is assigned to a Pd–Cl bond. A peak at 330 cm^{-1} in the gold complex spectrum is assigned to an Au–Cl bond.

The UV–Vis absorptions (Table II) are observed in similar regions in the complexes and the ligand

TABLE I. Infrared Absorption (cm^{-1}) for Ligand, $[AgL_2]PF_6$, $PdLCl_2$, $PdLBr_2$, $[PtL_2](PF_6)_2$, Au_2LCl_2

Ligand	$[AgL_2]PF_6$	$PdLCl_2$	$PdLBr_2$	$[PtL_2](PF_6)_2$	Au_2LCl_2	Band assignment
1240s	1240s	1240s	1240s	1240s	1240s	Ar–CSS
1100m	1090sh	1100s	1100m	1100sh	1090s	
				1080m		
1050–1070(s.b.)		1050m	1050m	1050m		
900s	920s	960m	970m	920sh	970s	ν_aCSS
840s	870sh	945s	950s	885s.b.	750b	ν_sCSS
	820–860s.b.		800s.b.			PF_6
750s	750m	780s	775s			
700s	690s	680s	680s	690m	705s	
		300 cm^{-1}				Pd–Cl
					330	Au–Cl

s = strong, m = medium, b = broad, sh = shoulder.

TABLE II. UV–Vis Data

	n–π^* (CSS)	π–π^* (CSS)		π–π^* (aromatic ring)
Ligand	523 (2.26)	433 (2.51)	358 (4.44)	269 (4.45)
$[AgL_2]PF_6$	505 (2.98)		359 (4.54)	260 (4.55)
$[PtL_2](PF_6)_2$			358 (4.16)	260
$PdLBr_2$			350 (4.02)	268 (4.38)

λ is in nm and log E_{mol} is given in parentheses. Solutions are in acetonitrile.

indicating that the ligand charge transfer bands are not strongly affected by chelation. The n-π band at 520 nm in the dithiocarboxylate group is responsible for the intense red color of the ligand and the dark colors of the complexes.

Of the metals used in this work silver is the one which might be expected to form a complex with the metal binding to only one of the sulfur atoms of the ligand, such as represented by bonding mode I. The strong broad PF_6 band between 800–900 cm^{-1} in the IR masks the region of interest for the $-CS_2$ stretching, consequently, no definitive statement can be made about the structure of the silver complex from IR data only. The complex might be monomeric; however, it is more likely that the ligand acts as a bridge and a polynuclear species forms [12–14]. The ligand is expected to act in a bidentate manner as in bonding mode **II** with Pt and Pd, forming square planar complexes. $PdLCl_2$ is monomeric in solution as shown by the molecular weight determination in methanol. However, there is precedence for metal–metal interactions in linear arrays of Pt and Pd complexes [15–21]. Attempts to crystallize any of the Pt and Pd complexes were also unsuccessful. Consequently, polynuclear behavior could not be established. There is also precedence for partial oxidation of the metal in a platinum complex [15] or full oxidation to Pt(III) as in some dithiocarboxylate complexes [22]. The partial oxidation of $K[Pt(CN)_6]$ to $K_2[Pt(CN)_4]Br_{0.3}\cdot 3H_2O$, for example, has been well characterized [23]. An attempt was made to oxidize $[PtL_2](PF_6)_2$ in aqueous solution by electrolysis and chemically by reacting it with iodine or bromine. Addition of silver nitrate solution to the metal complex in aqueous solution produces reduced silver. No definitive product could be isolated from any of the reactions. It is unclear as to whether the metal or the ligand undergoes oxidation. The ligand is easily oxidized with $E_{ox} = -1.65$ V reversible and a second $E_{ox} = 0.4$ V irreversible. Oxidation of similar dithiolate ligands to form coupled dimers is well known [24, 25].

Gold(III) reacts with the zwitter ion forming an Au(I) complex. The low yield of complex suggests that there is oxidation of the ligand while the metal ion is reduced. Analytical results indicate a 2:1 metal-to-ligand ratio which is consistent with the ligand acting as a bridge between two metal atoms as denoted in bonding mode **III**. There are reports of polynuclear gold complexes of dithiocarbamates and other sulfur containing ligands [26–28]; however, without crystallographic data, we are unable to suggest a multinuclear d^{10} system. No solvent suitable for crystallization could be found which did not destroy the complex. This suggests that the ligand is not strongly held to the metal ions. In all instances, the ligand could be recovered from the solutions used in attempted crystallization.

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