Synthesis and Spectral Studies of some New Palladium(II) and Platinum(II) Dithiocarbimato Complexes. Reactions of Bases with the Corresponding *N*-Alkyldithiocarbamates

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Abstract

A new series of Pd(II) and Pt(II) *N*-alkyldithiocarbamato complexes has been prepared and characterized by analytical, magnetic and spectroscopic techniques. These complexes on reaction with strong bases form novel anionic metal(II) dithiocarbimates which have also been isolated and studied. On the basis of spectroscopic and magnetic data all complexes adopt the square-planar configuration.

Introduction

Recently, we reported that the reaction of various tertiary phosphines with bis(*N*-monosubstituted-dithiocarbamato)platinum(II) or palladium(II) complexes (1:1 molar ratio) gave the four-coordinate square-planar $[M(S_2CNHR)_2(PR'_3)]$ complexes which exhibit unidentate/bidentate bonding mode of the dithiocarbamato groups [1–4]. Moreover, we have found that the behaviour of the $RHNCS_2^-$ ligands is similar to that of the isoelectronic xanthate ones, since reacting the *N*-alkyldithiocarbamato complexes with excess tertiary phosphine [4] nucleophilic attack by anionic $RHNCS_2^-$ on a coordinated bidentate dithio-ligand can occur to give the corresponding dithiocarbimato complexes, $[M(S_2C{=}NR)(PR'_3)_2]$. The mechanism of these reactions has been fully investigated by EHMO-SCCC quantum chemical calculations based on the frontier molecular orbital interactions which are the main factor controlling the nucleophilic substitution reactions under consideration [5]. In contrast, the reaction between nickel(II) dithiocarbamates and most of the nitrogen- or phosphorus-donor ligands (L) affords either five-coordinate $[Ni(S_2CNR_2)_2L]$ and/or six-coordinate $[Ni(S_2CNR_2)_2L_2]$ adducts, depending on the nature of the ligand used [6]. However, it has been demonstrated [7–10] that in the case of $[Ni(S_2CNHR)_2]$ complexes, strong bases not only may interact with the metal but they may also remove a proton on the nitrogen atom to form the anionic nickel(II) dithiocarbimates. In continuation of our investigations on the chemical and electronic properties of the various coordination geometries obtainable within the dithioacid system using substituents of varying electronic effects, we report herein preparation and structural studies of a new series of Pt(II) and Pd(II) *N*-alkyldithiocarbamates. The deprotonation reactions of these complexes with strong bases, affording the corresponding anionic metal(II) dithiocarbimates, are also discussed in an attempt to provide more evidence for the substantial differences in chemistry exhibited by nickel on the one hand and palladium and platinum on the other.

Experimental

Physical Measurements

IR spectra were recorded in the 4000–250 cm^{-1} region on a Perkin-Elmer 467 spectrophotometer using KBr pellets or Nujol mulls. Electronic spectra were obtained on a Cary 17DX spectrophotometer using freshly prepared chloroform solutions. Mass spectra were measured on a RMU-6L Hitachi Perkin-Elmer mass spectrometer with ionisation source of T-2p type operating at 70 eV. Magnetic susceptibility measurements in solid state were done by the Faraday technique using $Hg[Co(SCN)_4]$ as the calibrant. Molecular weights were determined using a Perkin-Elmer molecular weight apparatus Model 115 in $CHCl_3$ solutions. Melting points were determined with a Büchi apparatus and are uncorrected. The elemental analysis of carbon, nitrogen and hydrogen was performed on a Perkin-Elmer 240B Elemental Analyzer. Platinum and palladium were determined according to published methods [11].

Starting Materials

All solvents were of reagent grade and were used without further purification in synthetic work. The ammonium [*N*-(n-butyl)dithiocarbamate] was prepared by running 0.2 mol of CS_2 into an ice cold mixture of 0.2 mol of n-butylamine and 0.2 mol of

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concentrated aqueous ammonia with vigorous stirring during 30 min. The temperature of the reaction mixture was maintained between 0–5 °C. After about 1 h a white crystalline product separated out, which was filtered, washed first with a little ice cold water, then several times with small portions of ether, and finally suction dried. A similar method was also employed for the preparation of ammonium (*N*-cyclohexyldithiocarbamate) and ammonium (*N*-phenyldithiocarbamate). The yields in this procedure were about 90%. These compounds are not very stable and decompose on keeping. All the other reagents were obtained commercially.

Preparation of the Complexes

The bis(*N*-alkyldithiocarbamato)palladium(II) and platinum(II) complexes were prepared according to the following synthetic route: Metal(II) chloride was suspended in dimethylsulfoxide (DMSO) and treated with 1:2 mole ratio of the appropriate ammonium dithiocarbamate dissolved in the same solvent. To the resulting clear solution ethanol–aqua solution (1:1) was added and an orange precipitate was formed which was filtered off, washed several times with water and dried in vacuum over P_2O_5. Recrystallization was carried out by dissolving the solid in acetone–DMSO mixture and reprecipitating with water (yield 85%).

The di(tetrakis-n-butylammonium) bis(*N*-alkyldithiocarbimato)palladium(II) and platinum(II) complexes were prepared according to the following general method: 1 mmol of the appropriate $[M(S_2CNHR)_2]$ complex was treated with an aqueous solution containing an excess of NaOH and the mixture was left at room temperature under continuous magnetic stirring. A clear solution was obtained which, on addition of 2 mmol of Bu^n_4NBr dissolved in ethanol, precipitated a yellow product which was filtered off, washed with water and dried in vacuum over P_2O_5. Recrystallization was carried out from acetone (yield 70%).

Results and Discussion

Reaction of DMSO solutions of the freshly prepared ammonium dithiocarbamates with MCl_2 (M = Pd or Pt) in a 2:1 mole ratio rapidly gave clear solutions from which solid compounds of stoichiometry $M(S_2CNHR)_2$ were isolated by precipitation with water. These are non-conducting, diamagnetic, and quite stable both in solid and solution state. The bis(*N*-alkyldithiocarbamato)metal(II) complexes when treated with aqueous solutions containing an excess of NaOH afford in most cases the corresponding dithiocarbimate complex anions, $[M(S_2C{=}NR)]^{2-}$, which can be isolated as tetrabutylammonium salts. These new dithiocarbimato complexes are some of the few examples in the chemistry of the *N*-alkyliminodithiocarbonato ligands. Until recently only the bis-nickel complex of the $(PhN{=}CS_2)^{2-}$ ligand [6] and the binuclear complexes of type $[Ni(S_2C{=}NR)(PPh_3)]_2$ had been reported [9]. Moreover, the formation of dithiocarbimato complexes of the general formula $[M(S_2C{=}NR)(PR'_3)_2]$ (M = Pd or Pt) by the reaction of coordinated *N*-alkyldithiocarbamates with excess tertiary phosphine had also been reported [4, 12]. These new compounds are diamagnetic and 2:1 electrolytes in nitromethane. They are pale yellow crystals soluble in most of the common organic solvents, such as chloroform, acetone, methylene chloride and DMSO, but insoluble in ethanol, diethylether, carbon tetrachloride and water. Protonation of these compounds with trifluoroacetic acid in benzene affords yellow crystalline complexes formulated as $[M(S_2CNHR)_2]$. This result is consistent with the evidence presented elsewhere [4, 5] on the electrophilic reactions of dithiocarbimato ligands. The analytical data for the new compounds, decomposition temperatures, and the most relevant absorption bands in their IR spectra are shown in Table I.

The IR spectra of the Pd(II) and Pt(II) *N*-alkyldithiocarbamates show one broad band in the 3100–3300 cm^{-1} region due to the N–H stretching frequency [13]. In contrast, no such band appears in the spectra of the various dithiocarbimato complexes, as a consequence of deprotonation of the S_2CNHR system. The strong band found between 1380 and 1550 cm^{-1} in these complexes was assigned to the $C\overset{\cdots}{-}N$ stretch, according to spectral evidence presented by Chatt *et al.* [14, 15] and a normal coordinate treatment of $[Pt(S_2CNH_2)_2]$ complex [16]. An increase of the double bond character of the $C\overset{\cdots}{-}N$ bond results in higher frequencies for this vibration [17]. Apparently, this band is found at lower energies [8, 18] when R groups on nitrogen are aryls. A reduction in the electron releasing ability of the NHR group due to the presence of electron withdrawing R groups is a plausible explanation. Moreover, the position of this band is affected by the nature of the central atom and is shifted to lower frequencies in the Pd(II) complexes. This is a reflection of the higher electron acceptor ability of Pt(II) than Pd(II). By protonation of the dithiocarbimato complexes the $\nu(C\overset{\cdots}{-}N)$ band is shifted to lower frequencies and its position is the same as that of the corresponding *N*-alkyldithiocarbamates. Furthermore, a new broad band in the 3300 cm^{-1} region appeared, which is also characteristic of the monalkyldithiocarbamates. The band at 920 to 1010 cm^{-1} in the metal complexes is assigned to asymmetric stretching modes of the CSS group. This band must be highly coupled with other modes and is very sensitive to environmental change [16, 19]. Accordingly, this band has

TABLE I. Analytical Data[a], Melting Points (°C)[b], and Relevant IR Frequencies (cm^{-1}) of the New Pd(II) and Pt(II) Dithio-complexes[c] with their Assignments (KBr discs)[d]

Compound	Melting point	Analysis (%)				ν(N–H)	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$	$\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{S})$	ν(M–S)
		C	N	H	M[e]				
$[Pd(S_2CNHBu^n)_2]$	165–167d	29.72 (29.81)	6.89 (6.95)	5.03 (5.00)	26.43 (26.41)	3220s	1536vs	923m	328m
$[Pd(S_2CNHCx)_2]$	237–239d	36.91 (36.96)	6.10 (6.16)	5.29 (5.32)	23.32 (23.38)	3245s	1510vs	978m	332m
$[Pd(S_2CNHPh)_2]$	226–228d	37.95 (37.96)	6.35 (6.32)	2.66 (2.73)	24.00 (24.02)	3165m	1388vs	985m	335w
$[Pt(S_2CNHBu^n)_2]$	196–198d	24.39 (24.43)	5.62 (5.70)	4.11 (4.10)	39.61 (39.68)	3219s	1538vs	921m	324w
$[Pt(S_2CNHCx)_2]$	280–282d	30.71 (30.93)	5.14 (5.15)	4.48 (4.45)	35.80 (35.88)	3225s	1516vs	978m	325w
$[Pt(S_2CNHPh)_2]$	258–260d	31.55 (31.63)	5.23 (5.27)	2.20 (2.28)	36.52 (36.70)	3160m	1394vs	986m	332w
$(Bu^n{}_4N)_2[Pd(S_2C{=}NBu^n)_2]$	158–160d	56.92 (56.94)	6.19 (6.32)	10.21 (10.24)	12.06 (12.01)		1554vs	926m	334m
$(Bu^n{}_4N)_2[Pd(S_2C{=}NPh)_2]$	168–170d	59.66 (59.68)	6.10 (6.05)	8.96 (8.93)	11.39 (11.49)		1479vs	921s	333m
$(Bu^n{}_4N)_2[Pt(S_2C{=}NBu^n)_2]$	182–184d	51.70 (51.76)	5.74 (5.75)	9.27 (9.31)	20.28 (20.20)		1558vs	930m	325m
$(Bu^n{}_4N)_2[Pt(S_2C{=}NPh)_2]$	185–187d	54.27 (54.46)	5.49 (5.52)	8.12 (8.15)	19.12 (19.23)		1520vs	935m	322w

[a] Figures in parentheses are the calculated values. [b] d = decomposition. [c] Abbreviations used throughout: Bu^n = n-butyl, Cx = cyclohexyl, Ph = phenyl. [d] vs = very strong, s = strong, m = medium, w = weak, br = broad. [e] M = Pd or Pt.

TABLE II. Electronic Spectral Data of the New Pd(II) and Pt(II) Dithio-complexes in $CHCl_3$

Compound	Band I $L(\pi^*) \leftarrow L(\pi)$	Band II $L(\pi^*) \leftarrow L(\pi)$	Band III $L(\pi^*) \leftarrow L(n)$	Band IV $M(d) \leftarrow L(\pi)$	Band V $L(\pi^*) \leftarrow M(d)$
$[Pd(S_2CNHBu^n)_2]$	41.0[a](4.51)[b]	33.4(4.86)	29.0sh[c](4.05)	24.0sh(2.62)	21.5sh(2.50)
$[Pd(S_2CNHCx)_2]$	38.9(4.69)	34.5sh(4.18)	28.8(4.30)	25.6sh(3.58)	
$[Pd(S_2CNHPh)_2]$	41.0(4.46)	32.0(4.84)	29.1sh(4.59)	26.5sh(3.91)	22.0(2.56)
$[Pt(S_2CNHBu^n)_2]$	39.1(4.70)	35.1sh(4.20)	28.8(4.28)	25.6(3.46)	
$[Pt(S_2CNHCx)_2]$	38.8(4.63)	34.6sh(4.16)	28.7(4.28)	25.6sh(3.46)	
$[Pt(S_2CNHPh)_2]$	37.7(4.67)	34.8sh(4.43)	32.5sh(4.21)	26.1(4.40)	23.3sh(3.52)
$(Bu^n{}_4N)_2[Pd(S_2C{=}NBu^n)_2]$	41.5(4.44)	39.1sh(4.26)	33.3(4.91)	28.6sh(4.08)	21.8(2.70)
$(Bu^n{}_4N)_2[Pd(S_2C{=}NPh)_2]$	41.7(4.41)	37.0(4.15)	25.4(4.27)	24.4sh(3.61)	
$(Bu^n{}_4N)_2[Pt(S_2C{=}NBu^n)_2]$		38.1(4.70)	28.6(4.12)	26.9sh(3.85)	
$(Bu^n{}_4N)_2[Pt(S_2C{=}NPh)_2]$		38.5(4.47)	31.2(4.84)		22.6(2.70)

[a] ν (kK). [b] $\log_\epsilon$ mol. [c] sh = shoulder.

been used to distinguish between disulfur and unisulfur chelation. With disulfur chelation a single band is usually found [20], whereas when unisulfur chelation occurs, this band is split. The asymmetric band in our case is unsplit, indicating the bidentate mode of the dithio-ligands. Further confirmation comes from the analysis of the position of the $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{N})$ mode. This band undergoes a blue shift in all the dithiocarbamato complexes while for unidentate coordination this stretching would be shifted towards lower wavenumbers or remain unchanged at the value of the free dithiocarbamate ammonium salt [21]. In addition, the coordination of the gem-disulfide ligands is further confirmed by the M–S stretching frequencies observed in the 300–400 cm^{-1} region.

The IR data, the diamagnetic nature of the complexes under investigation and their stoichiometry allowed us to suggest a square-planar configuration. This structure was further supported by the electronic spectral data.

The electronic spectral bands and their assignments are listed in Table II. Taking into consideration that sulfur as a donor atom has a profound influence on the electronic structure of the planar d^8 metal dithio-complexes, mainly due to strong π nature of the metal–sulfur link [22–24], assignments were made on the basis of molecular orbital calculations for some PtS_4 systems [5], as well as the results of previously published electronic spectral data on metal dithiocarbamato complexes [25, 26]. The most intense band I is due to an intraligand $\pi^* \leftarrow \pi$ transition located on the $N\stackrel{\cdots}{-}C\stackrel{\cdots}{-}S$ group [25, 27]. This band, in the case of dithiocarbimato complexes, shows an hypsochromic shift relative to the corresponding band of the *N*-alkyldithiocarbamates, due to the localisation of the π-electron system in the *N*-alkyliminodithiocarbonato ligands. Band II, which appears as a shoulder, is attributed to a second transition of the type $\pi^* \leftarrow \pi$ in the $S\stackrel{\cdots}{-}C\stackrel{\cdots}{-}S$ group [28]. Band III may be due to a $\pi^* \leftarrow n$ transition located on the sulfur atoms [28]. Finally, bands IV and V are due to charge transfer (CT) transitions of the types $M \leftarrow L$ and $L \leftarrow M$, respectively. These bands are analogous to the CT bands observed in the square-planar Pt(II) and Pd(II) complexes of D_{2h} symmetry and are assigned to ${}^1B_{2u}$, ${}^1B_{3u} \leftarrow {}^1A_g$ and ${}^1B_{1u}$, ${}^1B_{2u}$, ${}^1B_{3u} \leftarrow {}^1A_g$ transitions, respectively [22].

The molecular ion corresponding to the species $[M(S_2CNHR)_2]^{+\cdot}$ was always observed in the mass spectra although usually at an intensity of only about 2% of the base peak. This molecular ion showed the characteristic mass distribution expected for the isotopic composition of platinum or palladium. Apart from an m/e value corresponding to the formula $[(S_2CNHR)_2HNCS]^+$ observed in all complexes, the remainder of the spectrum consisted of peaks corresponding to the $[M(S_2CNHR)]^{+\cdot}$ ion and its subsequent fragmentation. That is, $[M(S_2CNHR)_2]^{+\cdot}$ breaks down to $[M(S_2CNHR)]^{+\cdot}$ and $[RHNCS_2]^+$, with the remaining breakdown pattern being that expected from $[RHNCS_2]^+$. The fragmentation pattern for the ligand $RHNCS_2^-$ is similar to that previously reported [3, 29]. On the contrary, in the case of the deprotonated derivatives, no molecular ions were detected in the mass spectra. This absence of molecular ions can be attributed either to pyrolytic decompositon, in the direct inlet, under the high temperature which was used (200–280 °C), or to electron impact. However, in all spectra the ion $[M(S_2C{=}NR)]^{+\cdot}$ is present and can be regarded as a direct fragment of the molecular ion upon elimination of one dithiocarbimato moiety. This is further supported by the detection of a peak with a variable relative intensity (85–100%) due to $[RN{=}CS_2]^{+\cdot}$ ion.

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