Synthesis and Spectroscopic Characterization of Triphenylphosphine Oxide Adducts of Uranyl Dithiocarbamates

C. C. HADJIKOSTAS, G. A. KATSOULOS and M. P. SIGALAS

Department of General and Inorganic Chemistry, Aristotelian University, Salonica 54006, Greece

(Received April 7, 1987)

Abstract

A new series of uranyl complexes with dithiocarbamato ligands and triphenylphosphine oxide has been synthesized and characterized by analytical and spectroscopic techniques. These mixed complexes with sulfur-donor bidentate ligands are monomeric species of the general formula $UO_2(R_2dtc)_2(Ph_3PO)$. Consequently, the coordination of the compounds here reported is concluded to be similar to that of the previously studied analogous dithio compounds, the uranium atom being in a seven-coordinate, pentagonal-bipyramidal environment.

Introduction

A very wide variety of metal complexes of dithiocarbamic acids is known and the general chemistry of this important class of coordination compounds is very well documented [1–3]. Moreover the chemistry of uranium coordination compounds has been extensively studied and still constitutes an active field of research. Uranyl dialkyldithiocarbamates were mentioned as early as 1908 by Delepine [4] and were reported by Malatesta [5]. This work was later extended [6] to the preparation of a variety of compounds of the general formula $UO_2(R_2dtc)_2$. Furthermore, it was found [7, 8] that the coordination number of the uranyl group in complexes with sulfur-containing ligands could be increased by interaction with a Lewis base, the affinity for adduct formation as well as the molecular structures of the products being closely related to the nature of the ligands already bound to the metal [9–11]. Actually, it has been concluded [11] that when the uranyl ion is bonded by dithio groups in complexes with neutral unidentate ligands a five-coordinate configuration should be preferred; this is different from the acetato analogs [10]. However, the effect of substituted terminal alkyl or aryl groups on the properties of $UO_2(R_2dtc)_2(Ph_3XO)$ complexes [X = P, As] has not been studied in detail so far. Therefore, in this work considerable emphasis has been directed toward a systematic study of the change in properties of triphenylphosphine oxide complexes of uranyl dithiocarbamates, induced by the substituents attached to the nitrogen of the dithiocarbamate moiety. Consequently, this paper reports the synthesis and characterization of a new series of $UO_2(R_2dtc)_2(Ph_3PO)$ adducts together with a detailed interpretation of the corresponding IR and electronic spectra.

Experimental

Physical Measurements

IR spectra were recorded in the 4000–250 cm^{-1} region on a Perkin-Elmer 1430 spectrophotometer using KBr pellets or Nujol mulls. Electronic spectra in acetonitrile solutions were obtained on a Cary 17DX spectrophotometer. Mass spectra were measured on a RMU-6L Hitachi Perkin-Elmer mass spectrometer with ionisation source of T-2p type operating at 70 eV. Conductivity measurements were carried out in a Wheatstone bridge Model RC $216B_2$ using 10^{-3} M solutions in nitromethane. Melting points were determined with a Büchi apparatus and are uncorrected. Molecular weights were determined using a Perkin-Elmer molecular weight apparatus, Model 115, in acetone solutions. The elemental analysis of carbon, nitrogen and hydrogen was performed on a Perkin-Elmer 240B elemental analyzer.

Preparation of the Complexes

The bis(*N,N*-dialkyldithiocarbamato)dioxo(triphenylphosphine oxide)uranium(VI) complexes were prepared in one step by the general procedure described below. A solution of 1 mmol of uranyl nitrate hexahydrate in 30 ml of methanol–DMSO (1:1) was treated with 1 mmol of triphenylphosphine oxide and 2 mmol of the appropriate sodium dialkyldithiocarbamate salt and the mixture was left for 30 min at room temperature under continuous magnetic stirring. In the resulting bright red solution a crystalline precipitate of sodium nitrate was formed, which was removed by filtration. On addition of 100 ml of water to the filtrate an orange precipitate was formed, which was filtered by suction, washed with water several times and dried over $CaCl_2$ under vacuum. Purification was achieved by dissolving the solid

0020-1693/87/$3.50

in methanol–DMSO solution (1:1) and reprecipitating with water. The yields in this procedure were about 85%

Results and Discussion

Reaction of uranyl nitrate with triphenylphosphine oxide and sodium dithiocarbamates afforded compounds of stoichiometry $UO_2(R_2dtc)_2(Ph_3PO)$ which were found to be quite stable both in the solid state and in solution. These mixed uranyl complexes are microcrystalline solids, moderately soluble in acetone, methylene chloride, acetonitrile and nitromethane. The low values of the molar conductivity in nitromethane (7–12 ohm^{-1} cm^2 mol^{-1}) indicate the non-electrolyte character of the complexes, whereas osmometric molecular weight measurements in acetone show them to be monomeric. Data from elemental analyses, decomposition temperatures and molecular weights of the new compounds are reported in Table I. The coordination of the studied compounds is expected to be similar to that of $UO_2(Et_2dtc)_2(Ph_3PO)$, whose molecular structure was resolved by X-ray diffraction analysis [7]. Thus, the uranium should have coordination number seven, realized by four sulfur atoms from the chelated dithiocarbamato groups and one oxygen atom from the triphenylphosphine oxide, all lying in a plane normal to the linear uranyl ion. This prediction has been further corroborated on the basis of spectral properties of these compounds.

The most important IR peaks of the complexes are reported in Table II. The thioureide band near 1470 cm^{-1} indicates considerable double bond character in the $C\overset{\cdots}{-}N$ bond. This behavior may be attributed to the electron-releasing ability of the amines which forces high electron density towards the sulfur atoms via the π system [12]. Apparently, this band is found at lower energies when the R groups on nitrogen are aryls [13, 14]. The absorption around 1000 cm^{-1} is attributed to the stretching vibration of the $C\overset{\cdots}{-}S$ bonds. The presence in the complexes under study of only one strong band in this region strongly supports bidentate coordination of the dithio ligand, a doublet being expected in the 1000 ± 70 cm^{-1} region for unidentate behavior [15–17]. Further confirmation comes from the analysis of the position of the $\nu(C\overset{\cdots}{-}N)$ mode which undergoes a blue shift in all the complexes with respect to the value of the corresponding free dithiocarbamate salt [18]. This stretching would be shifted towards lower wavenumbers or remain unchanged in the case of unidentate coordination. The P–O bond stretching frequency, observed at ~1190 cm^{-1} in the free ligand, suffers a negative shift of the order of 50–60 cm^{-1} in the IR spectra of the complexes, in close agreement with previous studies on

TABLE I. Analytical Data[a], Melting Points (°C)[b] and Molecular Weights for the New Complexes[c]

Compound	Melting point	C (%)	N (%)	H (%)	Molecular weight
$UO_2(Pr^n{}_2dtc)_2(Ph_3PO)$	183–185d	42.43 (42.66)	3.05 (3.11)	4.76 (4.81)	820 (901.0)
$UO_2(Pr^i{}_2dtc)_2(Ph_3PO)$	253–255d	42.71 (42.66)	3.09 (3.11)	4.78 (4.81)	810 (901.0)
$UO_2(Bu^n{}_2dtc)_2(Ph_3PO)$	172–174d	45.16 (45.18)	2.84 (2.93)	5.31 (5.37)	910 (957.1)
$UO_2(Bu^i{}_2dtc)_2(Ph_3PO)$	101–103	45.11 (45.18)	2.82 (2.93)	5.46 (5.37)	900 (957.1)
$UO_2(Bz_2dtc)_2(Ph_3PO)$	233–235d	52.62 (52.74)	2.51 (2.56)	4.00 (3.96)	1130 (1093.1)
$UO_2(Pyrrdtc)_2(Ph_3PO)$	273–275d	39.75 (40.00)	3.19 (3.33)	3.62 (3.72)	780 (840.8)
$UO_2(Pipdtc)_2(Ph_3PO)$	268–270d	41.53 (41.47)	3.39 (3.22)	4.13 (4.06)	800 (868.9)
$UO_2(2\text{-}MePipdtc)_2(Ph_3PO)$	248–250d	42.77 (42.85)	3.15 (3.12)	4.27 (4.38)	810 (896.9)
$UO_2(Morphdtc)_2(Ph_3PO)$	275–277d	38.49 (38.53)	3.25 (3.21)	3.52 (3.58)	820 (872.8)
$UO_2(Me,Phdtc)_2(Ph_3PO)$	125–127d	44.65 (44.73)	3.09 (3.07)	3.55 (3.42)	860 (912.9)
$UO_2(Ph_2dtc)_2(Ph_3PO)$	270–272d	50.83 (50.96)	2.86 (2.70)	3.48 (3.40)	970 (1037.0)

[a] Figures in parentheses are the calculated values. [b] d = decomposition. [c] Abbreviations used throughout: Me = methyl, Pr^n = n-propyl, Pr^i = i-propyl, Bu^n = n-butyl, Bu^i = i-butyl, Ph = phenyl, Bz = benzyl, Pyrr = pyrrolidyl, Pip = piperidyl, 2-MePip = 2-methylpiperidyl, Morph = morpholinyl.

TABLE II. The most Relevant IR Frequencies (cm^{-1}) of the Investigated Compounds and their Assignments (KBr discs)[a]

Compound	$\nu(C\cdots N)$	$\nu(P-O)$	$\nu(CSS)$	$\nu_{as}(UO_2)$	$\nu_s(UO_2)$
$UO_2(Pr^n{}_2dtc)_2(Ph_3PO)$	1479s	1140s	998m	915s	828w
$UO_2(Pr^i{}_2dtc)_2(Ph_3PO)$	1478s	1140s	997w	912s	849w
$UO_2(Bu^n{}_2dtc)_2(Ph_3PO)$	1477s	1141s	998w	917s	820w
$UO_2(Bu^i{}_2dtc)_2(Ph_3PO)$	1480s	1138s	987m	914s	820w
$UO_2(Bz_2dtc)_2(Ph_3PO)$	1468s	1129s	997m	919s	825w
$UO_2(Pyrrdtc)_2(Ph_3PO)$	1466m	1133s	1005m	915s	830w
$UO_2(Pipdtc)_2(Ph_3PO)$	1483s	1130s	998m	911s	855w
$UO_2(2\text{-}MePipdtc)_2(Ph_3PO)$	1467m	1133s	999m	911s	863w
$UO_2(Morphdtc)_2(Ph_3PO)$	1468s	1135s	1002m	912s	875w
$UO_2(Me,Phdtc)_2(Ph_3PO)$	1364s	1133s	1003m	914s	868w
$UO_2(Ph_2dtc)_2(Ph_3PO)$	1337s	1140m	995m	914s	855w

[a] s = strong, m = medium, w = weak.

TABLE III. Electronic Spectral Data of the New Compounds in CH_3CN

Compound	Band I $L(\pi^*) \leftarrow L(\pi)$	Band II $L(\pi^*) \leftarrow L(\pi)$	Band III $L(\pi^*) \leftarrow L(\pi)$ $M(f) \leftarrow L(\pi)$	Band IV $M(f) \leftarrow L(\pi)$
$UO_2(Pr^n{}_2dtc)_2(Ph_3PO)$	37.7[a] (4.63)[b]		32.6sh[c] (3.95)	26.1sh (3.50)
$UO_2(Pr^i{}_2dtc)_2(Ph_3PO)$	37.6 (4.58)	35.7sh (4.44)	32.2sh (3.98)	26.0sh (3.58)
$UO_2(Bu^n{}_2dtc)_2(Ph_3PO)$	37.9 (4.64)		32.8sh (4.01)	26.3sh (3.50)
$UO_2(Bu^i{}_2dtc)_2(Ph_3PO)$	37.5 (4.71)	35.1sh (4.29)		26.0sh (3.51)
$UO_2(Bz_2dtc)_2(Ph_3PO)$	37.7 (4.63)	35.6sh (4.52)	32.6sh (4.08)	26.8sh (3.51)
$UO_2(Pyrrdtc)_2(Ph_3PO)$	38.4 (4.49)		33.3sh (3.81)	25.8sh (3.22)
$UO_2(Pipdtc)_2(Ph_3PO)$	37.5 (4.61)	35.4sh (4.45)	33.3sh (4.09)	27.0sh (3.25)
$UO_2(2\text{-}MePipdtc)_2(Ph_3PO)$	37.5 (4.55)		32.8sh (3.92)	26.7sh (3.41)
$UO_2(Morphdtc)_2(Ph_3PO)$	37.7 (4.53)		32.8sh (3.91)	26.7sh (3.26)
$UO_2(Me,Phdtc)_2(Ph_3PO)$	37.4 (4.67)	35.2sh (4.55)	31.1sh (3.96)	26.1sh (3.54)
$UO_2(Ph_2dtc)_2(Ph_3PO)$	36.3 (4.66)	34.3sh (4.64)	30.5sh (4.16)	25.5sh (3.61)

[a] ν/kK. [b] $\log \epsilon_{mol}$. [c] sh = shoulder.

the coordination influence of the uranyl group on the P–O bond of triphenylphosphine oxide [19, 20]. This decrease in the phosphoryl stretching frequency upon binding the uranium through the oxygen atom is consistent rather with penta-coordination than with hexa-coordination [19]. Finally, the spectra of the studied complexes show two bands at ~915 and ~845 cm^{-1} which have been assigned to asymmetric and symmetric stretching frequencies of the O–U–O group, respectively [7, 11, 21]. The values of the $\nu_{as}(U-O)$ frequency are close to that of the diethyldithiocarbamato derivative, further confirming that the uranyl group is scarcely influenced by dithio ligands which differ only in the substituent [11].

The electronic absorption bands, together with their assignments for all complexes, are shown in Table III. Assignments were made on the basis of previously published electronic spectral data on metal dithiocarbamato complexes [22, 23]. The most intense band I is due to an intraligand $\pi^* \leftarrow \pi$ transition located on the $N\cdots C\cdots S$ group [22, 24]. Band II, which appears as a shoulder, is also due to an intraligand $\pi^* \leftarrow \pi$ transition located on the triphenylphosphine oxide ligand. Finally, bands III and IV, whose energy difference is about 6 kK [25], may be assigned to the expected charge-transfer transitions of the type f (uranium) $\leftarrow \pi$(ligand), arising from two molecular orbitals mainly localized on the sulfur atoms to the same empty molecular orbital of uranium f AO's character [7, 11]. However, band III may be alternatively attributed to an intraligand transition of the $\pi^* \leftarrow \pi$ type located in the $S\cdots C\cdots S$ group [26], which in that case apparently masks the expected LMCT band.

The molecular ions of the studied compounds were not detected in the mass spectra. The absence of molecular ions can be attributed either to pyrolytic decomposition, in the direct inlet, under the high temperature which was used (200–280 °C), or to electron impact. Apart from an *m/e* value corresponding to the $[UO_2]^+$ ion observed in all complexes, the remainder of the spectrum consisted of peaks corresponding to the $[S_2CNR_2]^{+\cdot}$ ion and the triphenylphosphine oxide moiety, as well as their subsequent fragmentations. In most cases the base peak of the spectra corresponds to the $[CS_2]^{+\bullet}$ ion.

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