Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry

Publication details, including instructions for authors and subscription information:
http://www.tandfonline.com/loi/lsrt19

Carbodithioates of Oxozirconium(IV) and Dioxourantum(VI) Ions

B. S. Manhas [a] & S. B. Kalia [b]

[a] Department of Chemistry , Punjabi University , Patiala, 147002, India

[b] Department of Chemistry , Himachid pradesh University , Shimla, 171005, India

To cite this article: B. S. Manhas & S. B. Kalia (1998) Carbodithioates of Oxozirconium(IV) and Dioxourantum(VI) Ions, Synthesis and Reactivity in Inorganic and Metal-Organic Chemistry, 28:3, 415-422, DOI: 10.1080/00945719809349365

To link to this article: http://dx.doi.org/10.1080/00945719809349365

SYNTH. REACT. INORG. MET.-ORG. CHEM., 28(3), 415–422 (1998)

CARBODITHIOATES OF OXOZIRCONIUM(IV) AND DIOXOURANIUM(VI) IONS

B. S. Manhas
Deaprtment of Chemistry, Punjabi University, Patiala-147002, India

and

S. B. Kalia*
Department of Chemistry, Himachal Pradesh University, Shimla-171005, India

ABSTRACT

New carbodithioate complexes of the oxozirconium(IV) and dioxouranium(VI) ions of the general formulae $MO_x(L)_2.(H_2O)_n$ (NaL = sodium 4-MPipzcdt and sodium 4-PPipzcdt and x = 2 and n = 0 for M = U(VI); NaL = sodium 4-MPipzcdt and x = 1 and n = 2 for Zr(IV)) have been prepared and studied by elemental analyses, IR spectral and magnetic susceptibility measurements. The carbodithioate ligands, 4-methylpiperazine-1-carbodithioate (4-MPipzcdtH) and 4-phenylpiperazine-1-carbodithioate (4-PPipzcdtH), were derived from saturated heterocyclic secondary amines. The complexes exhibit diamagnetic behaviour.

INTRODUCTION

Zirconium and uranium dithiocarbamates are generally prepared in the oxidation states +4[1,2] and +6[3], respectively. The presently synthesized oxozirconium(IV) and dioxouranium(VI) carbodithioates with the carbodithioate ligands (Fig. 1) have the stoichiometric formulae $ZrO(4\text{-}MPipzcdt)_2.2H_2O$, $UO_2(4\text{-}MPipzcdt)_2$ and

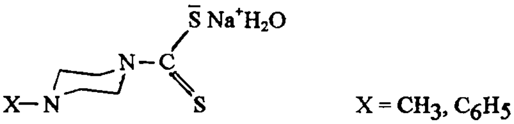


Fig. 1. Sodium Carbodithioate Monohydrate, NaL.H_2O

UO_2(4-PPipzcdt)$_2$. The solid ZrO(4-MPipzcdt)$_2$.2H_2O complex is stable for only 2-3 days and if it is kept for a longer period of time its elemental analysis results are not found to be reliable. Though uranyl complexes with oxygen-containing ligands, like acetate or nitrate ions acting as bidentate chelating groups, are quite common, the UO_2^{2+} ion has a weak tendency to form complexes with ligands of low electronegativity. Despite the weaker tendency of the dioxo cation to form complexes with sulfur-containing ligands, which are less electronegative than the acetate, the two synthesized carbodithioates are quite stable for two to three months. In general, the electronic spectral and magnetic properties of the complexes of these oxocations are less useful to the chemist because the zirconium(IV) ion of the oxocation ZrO^{2+} is large, highly charged, and spherical with no partly filled shell to give it stereochemical preferences and the uranium ($5f^3$ $6d^1$ $7s^2$) in its +6 oxidation state present in its dioxocation UO_2^{2+} has no d or f electrons. Hence, the complexes of these cations lack informative magnetic and electronic spectral characteristics.

EXPERIMENTAL

Synthesis

Sodium 4-methylpiperazine-1-carbodithioate monohydrate and sodium 4-phenylpiperazine-1-carbodithioate monohydrate were prepared as described previously[4].

ZrO(4-MPipzcdt)$_2$.2H_2O (a) (b)

To a solution of sodium 4-methylpiperazine-1-carbodithioate monohydrate (0.50 g, 2.31 mmol) in absolute alcohol (100 mL) was added with stirring an ethanolic solution (100 mL) of $ZrOCl_2.8H_2O$ (0.372 g, 1.15 mmol). Stirring was continued at room temperature for 10 min. during which time a white solid separated out. The resulting insoluble product was filtered under vacuum, washed several times with ethanol and diethyl ether and finally dried under vacuum over P_4O_{10}. Anal. Found: C, 28.6; H, 5.4; N, 11.7; S, 25.7; Zr, 19.0. Calc. for $C_{12}H_{26}N_4S_4O_3Zr$ (493.2): C, 29.0; H, 5.3; N, 11.4; S, 25.9; Zr, 18.5. Yield: 0.54 g, 95%. Decomposition temperature, 300°C.

UO_2(4-MPipzcdt)$_2$ (c)

Uranyl acetate dihydrate (0.49 g, 1.15 mmol) in methanol (10mL) was added with stirring to a solution of sodium 4-methylpiperazine-1-carbodithioate monohydrate (0.50 g, 2.31 mmol) in methanol (10 mL). Stirring was continued at room temperature during which time an orange solid separated out. The resulting insoluble product was filtered, washed with small amounts of methanol (the product has a slight solubility in methanol) and diethyl ether and was air-dried. Final drying of the product was done under vacuum over P_4O_{10}. Anal. Found: C, 22.9; H, 4.0; N, 9.7; S, 20.2; U, 38.2. Calc. for $C_{12}H_{22}N_4S_4O_2U$ (620) : C, 23.2; H, 3.8; N, 9.2; S, 20.6; U, 38.3. Yield: 0.65 g, 90%. Decomposition temperature, 300°C .

UO_2(4-PPipzcdt)$_2$ (c)

Uranyl chloride (0.50 g, 1.46 mmol) dissolved in water (20 mL) was added with stirring to an aqueous-ethanolic solution (20 mL : 10 mL) of a stoichiometric amount of sodium-4-phenylpiperazine-1-carbodithioate prepared in situ (0.82 g, 2.93 mmol). Stirring was continued at room temperature during which time an orange solid separated out. The resulting insoluble product was filtered, washed with water, methanol and diethyl ether and finally dried under vacuum over P_4O_{10}. Anal. Found: C, 35.2; H, 3.6; N, 7.90; S, 16.9; U, 32.0. Calc. for $C_{22}H_{26}N_4S_4O_2U$ (744): C, 35.5; H, 3.5; N, 7.5; S, 17.2; U, 31.9. Yield: 0.98 g, 90%. Decomposition temperature, 310°C.

Elemental Analyses and Physical Measurements

The zirconium and uranium contents of the complexes were determined gravimetrically as ZrO_2 or U_3O_8. C, H, N and S determinations, IR and magnetic susceptibility measurements were made as described earlier[4].

RESULTS AND DISCUSSION

Oxozirconium(IV) and dioxouranium(VI) carbodithioates have been prepared by mixing stoichiometric amounts of aqueous or ethanolic solutions of zirconyl or uranyl salts and sodium carbodithioates. The synthesis follows the following general reaction:

$$MO_xX_n + 2NaL.H_2O \rightarrow MO_x(L)_2 + nNaX + 2H_2O$$

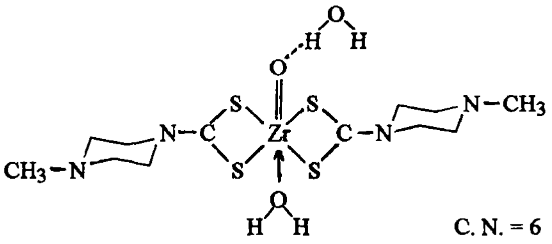
L = 4-MPipzcdt, X = Cl, x = 1 and n = 2 for M = Zr(IV)
L = 4-MPipzcdt, X = OAc, x = 2 and n = 2 for M = U(VI)
L = 4-PPipzcdt, X = Cl, x = 2 and n = 2 for M = U(VI)

The complexes (Fig. 2) separated immediately after combining the reactants.

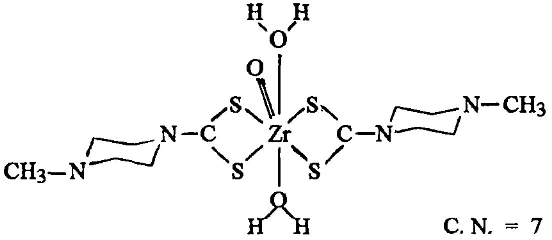
Infrared Spectra

Partial IR spectral data of the complexes are listed in Table I. The rise in the ν(C⩵N) frequency in all three complexes, in comparison to the free sodium carbodithioate ligands, is deemed to indicate that out of the two canonical forms of the ligands, $^{2-}S_2C{=}NR_2$ and $^{-}S_2C{-}NR_2$, the first one contributes to a greater extent in the complexes than in the free ligands[5]. The observation of the C⩵N stretching vibrational band at higher energy in the UO_2(4-MPipzcdt)$_2$ complex as compared to the UO_2(4-PPipzcdt)$_2$ complex further shows the higher inductive and hyperconjugative effects of the Me-N group than that of the Ph-N group. The band positions due to the antisymmetric ν_a(SCS) and symmetric ν_s(SCS) stretching vibration modes of the >NCS_2 group of the carbodithioate ligands (Table I) suggest a chelating bidentate mode of coordination to the metal ions[6] in the three complexes.

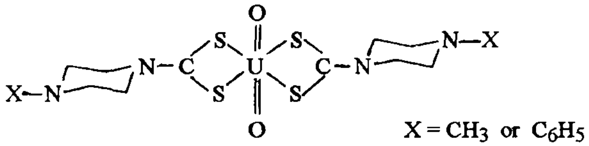
In the ZrO(4-MPipzcdt)$_2$.2H_2O complex the band due to ν(Zr=O) is found to overlap with the SCS antisymmetric stretching absorption[7] at 967 cm^{-1}. Nevertheless, the band is quite strong and sharp. A broad band is observed in the region 3500-3240 cm^{-1} due to the antisymmetric stretching frequency of the O-H band of water molecules present in this complex. The appearance of an absorption band at 823 cm^{-1}, assignable to the rocking vibrational mode of coordinated water, $\rho_r(H_2O)$, indicates that the water



(a) $ZrO(4\text{-}MPipzcdt)_2.2H_2O$



(b) $ZrO(4\text{-}MPipzcdt)_2.2H_2O$



(c) $UO_2(L)_2$ L = 4-MPipzcdt or 4-PPipzcdt

Fig. 2. Proposed Structures of the Complexes

Table I

Some Coordinatively Diagnostic Features of the IR Spectra (cm^{-1}) of Oxozirconium(IV) and Dioxouranium(VI) Carbodithioates

Complex	ν(O-H) [δ (OH)]	ν(C═N)	ν_a(SCS)	ν_s(SCS)	ν(M═O)	ν(M-S)
$ZrO(4\text{-MPipzcdt})_2.2H_2O$	3500- 3240 [1590]	1470	967	907	967	360
$UO_2(4\text{-MPipzcdt})_2$	-	1462	970	910	895	245
$UO_2(4\text{-PPipzcdt})_2$	-	1427	1010	915	895	315

molecules present in the zirconium complex are coordinated to the metal ion[8]. Since the zirconium(IV) ion is larger than vanadium(IV) ion, the zirconium(IV) ion has a tendency to exhibit higher coordination numbers and a great variety of coordination polyhedra[9]. Compounds containing (a) octahedral $[ZrF_6]^{2-}$ ions, (b) $[ZrF_7]^{3-}$ ions with both pentagonal bipyramidal and capped trigonal prismatic structures are known. Since the coordination chemistry of Zr(IV) is not highly developed, it shows considerable variety. Acetylacetonates of six-coordinate $Zr(acac)_2X_2$ and seven-coordinate $Zr(acac)_3X$ types, as well as eight-coordinate $Zr(dik)_4$ and tetrakis-(thioacetylacetonato)zirconium(IV) complexes have been reported[9]. Here too, it may be possible that the two water molecules present in the complex are coordinated giving a total coordination number of seven to zirconium(IV) (structure (b) in Fig. 2). The broadness of the ν(O-H) band can be attributed to hydrogen bonding effects between the oxygen of the Zr=O group and the hydrogen of the water molecules. However, it may also be possible that only one of the two water molecules is coordinated to zirconium(IV), giving a total coordination number of six (structure (a) in Fig. 2). The presence of the second water molecule in the lattice may result in broadening of the ν(O-H) band due to the effect of hydrogen bonding. Because of the tendency of the zirconium(IV) ion to exhibit a great variety of coordination polyhedra, it is difficult to ascertain the preferred coordination number without the X-ray crystallographic studies.

In uranyl carbodithioates, infrared spectral behaviour similar to that of the acetato complexes[10] e.g., $UO_2(CH_3COO)_2[(C_6H_5)_3AsO]_2$, in regard to the antisymmetric stretching vibrational frequency of the UO_2 (uranyl) moiety can be seen. The groups attached to the nitrogen atom of the NCS_2 group are not found to affect the UO_2 absorption frequencies since the band ascribable to this vibrational mode[11] is observed at the same position (~ 895 cm^{-1}) in the UO_2(4-MPipzcdt)$_2$ and UO_2(4-PPipzcdt)$_2$ complexes. Generally, in uranyl dithiocarbamates the UO_2 group is linear and normal to the equatorial plane of sulfur atoms[12]. The additional bands, when compared with far-IR spectra of sodium carbodithioates, observed in the region 360-245 cm^{-1} have tentatively been assigned to ν(M-S) frequencies (Table I).

Magnetic Susceptibilities

The room temperature μ_{eff} values for ZrO(4-MPipzcdt)$_2$.2H_2O, UO_2(4-MPipzcdt)$_2$ and UO_2(4-PPipzcdt)$_2$ are 0.2, 0.1 and 0.4, respectively. This reveals diamagnetic behaviour of these complexes. A slight paramagnetism in these complexes may result from distortions due to steric hindrance of the ligand.

REFERENCES

1. D. C. Bradley, I. F. Randall and K. D. Sales, J. Chem. Soc. Dalton Trans., 2228 (1973).
2. D. C. Bradley and M. H. Gitlitz, J. Chem. Soc., A, 1152 (1969).
3. R. G. Jones, G. Karmas, G. A. Martin and H. Gilman, J. Am. Chem.. Soc., 79, 4921 (1957).
4. B. S. Manhas and S. Bala, Polyhedron, 7, 2465 (1988).
5. J. Chatt, L. A. Duncanson and L. M. Venanzi, Nature, 177, 1042 (1956).
6. F. Bonati and R. J. Ugo, J. Organometal. Chem., 10, 257 (1967).

7. C. C. Patel and V. V. Savant, J. Inorg. Nucl. Chem., 31, 2319 (1969).

8 I. Nakagawa and T. Shimanouchi, Spectrochim. Acta, 20, 429 (1964).

9. F. A. Cotton and G. Wilkinson, "Advanced Inorganic Chemistry", Wiley Sons, New York, Chichester, Brisbane, Toronto, 1980.

10. C. Panattoni, R. Graziani, G. Banodoli, B. Zarli and G. Bombieri, Inorg. Chem., 8, 320 (1969).

11. I. S. Ahuja and R. Singh, J. Inorg. Nucl. Chem., 35, 2075 (1973).

12. R. Graziani, B. Zarli, A. Cassol, G. Bombieri, E. Forsellini and E. Todello, Inorg. Chem., 9, 2116 (1970).

Received: 22 October 1996
Accepted: 31 October 1997

Referee I: D. Coucouvanis
Referee II: N. E. Shore