

Studies on Some Oxozirconium Dithiocarbamates

(Mrs) P R SHUKLA* & SANJAY KUMAR SRIVASTAVA

Department of Chemistry, Lucknow University, Lucknow 226 007

Received 17 February 1986; revised and accepted 12 September 1986

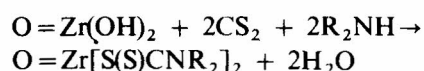
Several new oxozirconium dithiocarbamates and their bimetallic derivatives with Hg(II), Cd(II) and Ag(I) have been prepared and their structures established through physicochemical data. Bimetallic derivatives are formed through the coordination from the sulphur atom of the oxozirconium dithiocarbamate to the soft acceptors i.e. Hg(II), Cd(II) and Ag(I).

In the past two decades a large number of dithiocarbamates¹, carbamates², monothiocarbamates³ and xanthates⁴ of transition metals have been investigated. However, the reports on the corresponding derivatives of oxometals are limited to a few oxomolybdenum and oxovanadium dithiocarbamates⁵⁻⁷. In continuation of our studies on oxometal dithiocarbamates⁸, we report in this note the synthesis and characterisation of some oxozirconium dithiocarbamates. Their interaction with soft lewis acids such as Hg(II), Cd(II) and Ag(I) has yielded new bimetallic dithiocarbamates.

Oxozirconium chloride (BDH) was converted into $O = Zr(OH)_2$ by reaction with aqueous ammonium hydroxide. Carbon disulphide (BDH), amines (Aldrich), 2,2'-dimethoxypropane (Aldrich) and triethyl orthoformate (Aldrich) were distilled/recrystallized before use. The solvents were purified by standard methods.

Preparation of oxozirconium bis-(dithiocarbamates)

The title compounds were prepared by the interaction of CS_2 with oxozirconium hydroxide and amines using 2,2'-dimethoxypropane or triethyl orthoformate as the solvent according to the following general equation,



In a representative experiment, to a mixture of freshly prepared hydrated oxozirconium hydroxide (10 mmol) and carbon disulphide (20 mmol), suspended in 25 ml of 2,2'-dimethoxypropane, was added morpholine (20 mmol) in 10 ml of the same solvent at $-20^\circ C$ with constant stirring. The reaction mixture was stirred for six hr. The precipitated oxozirconium bis-(morpholine dithiocarbamate) was filtered, washed with diethyl ether and dried over P_4O_{10} *in vacuo*.

Table 1— Analytical Data and Characteristic IR Bands(cm^{-1}) of Oxozirconium Bis-(dithiocarbamates)

Complex (m.p., °C; yield,%)	Found (Calc.),%				IR absorption (cm^{-1}) (KBr)	
	Zr	C	H	N	$\nu(C \equiv N)$	$\nu(C = S)$
$O = Zr[S(S)CN(C_2H_5)_2]_2$ (> 240,80)	22.4 (22.5)	29.6 (29.7)	4.9 (4.9)	6.9 (6.9)	1430m	1020s
$O = Zr[S(S)CNHC_4H_9]_2$ (214d,84)	22.4 (22.5)	29.6 (29.7)	4.9 (4.9)	6.9 (6.9)	1435m	1020s
$O = Zr[S(S)CN(C_4H_9)_2]_2$ (192d,80)	17.5 (17.6)	41.7 (41.9)	6.8 (6.9)	5.3 (5.4)	1435m	1015s
$O = Zr[S(S)CN(C_6H_5)_2]_2$ (> 240,85)	15.2 (15.2)	52.3 (52.4)	3.3 (3.3)	4.6 (4.7)	1430m	1015s
$O = Zr[S(S)CN(CH_2C_6H_5)_2]_2$ (> 240,85)	13.8 (13.9)	55.2 (55.2)	4.2 (4.3)	4.2 (4.3)	1425m	1020s
$O = Zr[S(S)CNHC_6H_5]_2$ (> 240,84)	20.4 (20.5)	37.8 (37.9)	7.6 (7.7)	6.3 (6.3)	1430m	1025s
$O = Zr[S(S)CNC_4H_8O]_2$ (> 240,96)	21.1 (21.1)	27.8 (27.8)	3.6 (3.7)	6.3 (6.4)	1430m	1020s
$O = Zr[S(S)CNC_4H_8]_2$ (127d,90)	22.7 (22.8)	30.0 (30.0)	4.0 (4.0)	6.8 (7.0)	1435m	1020s
$O = Zr[S(S)CNC_5H_{10}]_2$ (> 240,88)	21.2 (21.3)	33.6 (33.7)	4.6 (4.6)	6.5 (6.5)	1430m	1020s
$O = Zr[S(S)CNC_4H_8CNC_6H_5]_2$ (193d,96)	15.6 (15.6)	45.3 (45.4)	4.3 (4.4)	9.5 (9.6)	1430m	1020s

Table 2 — Analytical Data and Characteristic IR Bands (cm^{-1}) of Oxozirconium Bis-(morpholine-dithiocarbamate). $2\text{M}'\text{X}_2$ or 2MX

Complex (m.p., °C)	Found (calc.), %					IR absorption (cm^{-1})	
	Zr	Hg/Cd/Ag	C	H	N	$\nu(\text{C}=\text{N})$	$\nu(\text{C}=\text{S})$
$\text{O}=\text{Zr}[\text{S}(\text{S})\text{CNC}_4\text{H}_8\text{O}]_2 \cdot 2\text{HgCl}_2$ (> 240)	9.3 (9.3)	41.0 (41.1)	12.3 (12.3)	1.6 (1.6)	2.84 (2.80)	1470m	1005s
$\text{O}=\text{Zr}[\text{S}(\text{S})\text{CNC}_4\text{H}_8\text{O}]_2 \cdot 2\text{Hg}(\text{SCN})_2$ (176d)	8.5 (8.5)	37.6 (37.6)	15.6 (15.8)	1.4 (1.5)	7.8 (7.9)	1465m	1005s
$\text{O}=\text{Zr}[\text{S}(\text{S})\text{CNC}_4\text{H}_8\text{O}]_2 \cdot \text{CdCl}_2$ (> 240)	10.5 (10.6)	26.2 (26.3)	14.0 (14.0)	2.2 (2.2)	3.2 (3.2)	1475m	1005s
$\text{O}=\text{Zr}[\text{S}(\text{S})\text{CNC}_4\text{H}_8\text{O}]_2 \cdot 2\text{AgSCN}$ (178d)	11.8 (11.9)	28.2 (28.3)	18.8 (18.8)	2.0 (2.0)	7.2 (7.3)	1470m	1005s
$\text{O}=\text{Zr}[\text{S}(\text{S})\text{CNC}_4\text{H}_8\text{O}]_2 \cdot 2\text{Hg}(\text{OCOCF}_3)_2$ (130d)	7.0 (7.0)	31.1 (31.1)	—	—	—	1470m	1005s
$\text{O}=\text{Zr}[\text{S}(\text{S})\text{CNC}_4\text{H}_8\text{O}]_2 \cdot 2\text{Hg}(\text{OCIO}_3)_2$ (*)	7.3 (7.4)	32.4 (32.5)	—	—	—	1465m	1005s
$\text{O}=\text{Zr}[\text{S}(\text{S})\text{CNC}_4\text{H}_8\text{O}]_2 \cdot 2\text{AgOCIO}_3$ (*)	10.7 (10.7)	25.3 (25.3)	—	—	—	1468m	1005s
$\text{O}=\text{Zr}[\text{S}(\text{S})\text{CNC}_4\text{H}_8\text{O}]_2 \cdot 2\text{AgOCOCF}_3$ (194d)	9.3 (9.3)	22.0 (22.0)	—	—	—	1475m	1005s

*Explode at their m.p.

Identical product was obtained by the reaction of oxozirconium chloride with ammonium morpholine dithiocarbamate in methanol at room temperature.

Reaction of oxozirconium bis-(morpholinedithiocarbamate) with Hg(II), Cd(II) and Ag(I) salts

In a typical experiment, to a stirring methanolic solution of oxozirconium bis-morpholine dithiocarbamate (10 mmol) was added HgCl_2 (20 mmol) in acetone-methanol mixture. The reaction mixture was stirred for about 10 hr. The precipitated product was washed several times with acetone-methanol mixture and dried over P_4O_{10} *in vacuo*. Similar adducts were prepared using $\text{Hg}(\text{SCN})_2$, $\text{Hg}(\text{OCOCF}_3)_2$, $\text{Hg}(\text{OCIO}_3)_2$, CdCl_2 , AgSCN , AgOCIO_3 and AgOCOCF_3 as acceptors. The analytical data are given in tables 1 and 2.

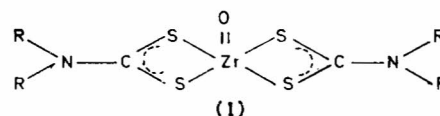
Zr and Hg were determined gravimetrically by reported methods. Analytical data for C, H, N at semimicro and infrared spectra in the range $4000\text{--}200\text{ cm}^{-1}$ using Perkin-Elmer 577 spectrophotometer were obtained from the CDRI, Lucknow. The molar conductances were measured at room temperature by a Phillips magic eye conductivity bridge PR9500 using dip-type conductivity cell. TG analysis was carried out using a manual balance supplied by FCI, India, in a self-produced atmosphere using platinum crucible.

The elemental analyses indicate 1:2 (metal:dithiocarbamate) stoichiometry for the oxozirconium dithiocarbamates. The compounds are white to light grey in colour, inert towards atmospheric oxygen and moisture. They are insoluble in common organic

solvents, sparingly soluble in methanol and soluble in DMSO and DMF. The conductance data ($10\text{--}20\text{ ohm}^{-1}\text{cm}^2\text{mol}^{-1}$) show their non-electrolytic nature in DMSO.

The TG analysis of a few representative samples at a heating rate of 5°C min^{-1} indicated their slow decomposition at 100°C resulting in the formation of CS_2 and organic matter. At 160° , a mixture of $\text{O}=\text{Zr}=\text{S}$ and ZrO_2 was obtained which ultimately changed to ZrO_2 at 440°C .

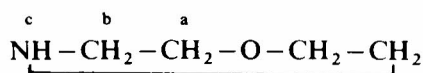
The dithiocarbamate group can act as a monodentate or a bidentate ligand. The nature of bonding can be distinguished on the basis of the $(\text{C}=\text{S})$ stretching mode of vibration. The presence of only one strong $\nu\text{C}=\text{S}$ absorption at $1020 \pm 5\text{ cm}^{-1}$ in the present complexes suggests the chelating behaviour of the dithiocarbamate group. A doublet is expected at $1000 \pm 70\text{ cm}^{-1}$ in case of unidentate dithiocarbamate groups¹⁰. The absorption at $1430 \pm 5\text{ cm}^{-1}$, assigned to $\nu(\text{C}=\text{N})$, is characteristic of thioureide bond having partial double bond character¹¹. A band at $980 \pm 2\text{ cm}^{-1}$ has been assigned to $\nu(\text{Zr}=\text{O})$ mode of vibration¹². Conclusive evidence of sulphur to metal bonding is provided by a band occurring at $355 \pm 2\text{ cm}^{-1}$ which has been assigned to $\nu(\text{Zr}-\text{S})$ mode. Structure(I) may be proposed for oxozirconium bis(dithiocarbamates) in the solid state.



In the IR spectra of bimetallic complexes, oxozirconium bis-(morpholine dithiocarbamate). $2M'X_2$ or $2MX(M' = \text{Hg, Cd; } M = \text{Ag; } X = \text{Cl, SCN, OClO}_3, \text{OCOCF}_3)$, absorptions due to $\nu\text{C}=\text{S}$ and $\nu\text{C}\equiv\text{N}$ are observed at 1005 cm^{-1} and $1470 \pm 5\text{ cm}^{-1}$, respectively. Two separate absorptions for $\nu\text{C}=\text{S}$ and $\nu\text{C}-\text{S}$ could not be identified since due to coordination from sulphur atom to soft metal acceptor, the $\text{C}=\text{S}$ bond is significantly weakened and approximately corresponds to $\text{C}-\text{S}$ bond order. Due to the formation of new coordinated bond an electron drift from R takes place resulting in an increase in double bond character of $(\text{C}=\text{N})$ and decrease in $(\text{C}=\text{S})$ bond order. The former, therefore, shows a distinct positive shift, while the latter is lowered. $\nu\text{Zr}=\text{O}$ and $\nu\text{Zr}-\text{S}$ modes of vibration remain unaltered in the adducts. The $\nu\text{Hg}-\text{S}$ mode could not be identified since it lies beyond the recording range of the spectrophotometer. The thiocyanate group is S-bonded, since $\nu\text{C}\equiv\text{N}$, $\nu\text{C}=\text{S}$ and δNCS appear at 2060 , 730 and 460 cm^{-1} respectively¹³. The trifluoroacetate groups are unidentate¹⁴ since $\nu_{\text{as}}\text{OCO}$ and $\nu_{\text{s}}\text{OCO}$ appear at 1690 and 1430 cm^{-1} , respectively, with $-\Delta\nu = 260\text{ cm}^{-1}$. The perchlorate group is unidentately coordinated as $\nu_{\text{s}}\text{Cl}-\text{O}$, $\nu_{\text{s}}\text{ClO}_3$, $\delta_{\text{as}}\text{Cl}-\text{O}$, $\delta_{\text{s}}\text{Cl}-\text{O}_3$ and $\delta_{\text{as}}\text{ClO}_3$ are located at 910 , 1040 , 1130 , 690 and 620 cm^{-1} , respectively¹⁵.

It is thus concluded that one of the sulphur atoms of the dithiocarbamate group in $\text{O}=\text{Zr}(\text{dtc})_2$ is coordinated to soft metal atom giving rise to bimetallic dithiocarbamates which are new and are liable to possess significant biological importance.

In the ^1H NMR spectrum of morpholine, the methylene protons, viz., $\text{N}-\text{CH}_2$ and $\text{O}-\text{CH}_2$ are tentatively numbered as shown:

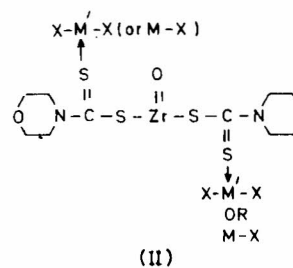


In the ^1H NMR spectrum, two multiplets centered at $\delta 2.74\text{ ppm}$ and $\delta 3.52\text{ ppm}$ correspond to $\text{N}-\text{CH}_2$ and $\text{O}-\text{CH}_2$ protons respectively. In the spectrum of oxozirconium bis-(morpholine dithiocarbamate) there is a slight upfield shift of $\text{N}-\text{CH}_2$ (b) and $\text{O}-\text{CH}_2$ (a) protons which now appear at $\delta 2.67\text{ ppm}$ and 3.45 ppm , respectively. It is thus concluded that due to $\text{Zr}-\text{S}$ bonding, there is a drift of electrons from $\text{N}-\text{CH}_2$ (b) and $\text{O}-\text{CH}_2$ (a) groups towards the metal.

In the bimetallic complex of oxozirconium bis(morpholine dithiocarbamate) the $\text{N}-\text{CH}_2$ protons appears at $\delta 2.52\text{ ppm}$ indicating considerable drift of

electrons from $-\text{N}-$ to the metal through carbon and sulphur atoms whereas the position of $\text{O}-\text{CH}_2$ protons remains more or less the same ($\sim 3.52\text{ ppm}$) as in morpholine, indicating little effect on the $\text{O}-\text{CH}_2$ protons.

On the basis of the above evidence, structure(II) may be proposed for oxozirconium bis-(morpholine dithiocarbamate). $2M'X_2$ or $2MX$.



In these adducts Hg(II) and Cd(II) are tri-coordinated¹⁶ while Ag(I) possesses the usual coordination number of two¹⁷.

The authors are thankful to Prof. T N Srivastava, Emeritus Scientist (CSIR) for valuable suggestions. The financial assistance from UGC is gratefully acknowledged.

References

- 1 Kowka W, Moyer R O & Lindsay R, *J inorg nucl Chem*, **39**(1975) 1889.
- 2 Calderazzo F, Dell'Amico G, Netti R & Pasquali M, *Inorg Chem*, **17** (1978) 471.
- 3 Steffen W L & Fay R C, *Inorg Chem*, **17**(8) (1978) 2120.
- 4 Coutts R S P, Wails P C & Kingston J V, *Aust J Chem*, **23** (1970) 469.
- 5 Casey A T, Mackey D J, Martin R L & White A M, *Aust J Chem*, **16**(2) (1971) 31.
- 6 Young C G, Broomhead J A & Boreham C J, *J chem Soc Dalton*, **9** (1983) 2135.
- 7 Forghieri F, Graziosi G, Preti C & Tosi G, *Trans Met Chem*, **8** (1983) 372.
- 8 Shukla P R & Srivastava S K, *Indian J Chem*, **25A** (1986) 741.
- 9 Nikolov G St, Jordanov N & Havezov I, *J inorg nucl Chem*, **33** (1971) 1055, 1059.
- 10 Bonati F & Ugo R, *J organomet Chem*, **10** (1967) 257.
- 11 Dix A H, Diesveld J W & Vanderlinden J G M, *Inorg chim Acta*, **L51** (1977) 24.
- 12 Madan S K & Donohue A M, *J inorg nucl Chem*, **28** (1966) 1303.
- 13 Norbury A H, *Adv inorg Chem Radiochem*, **17** (1975) 231.
- 14 Garner C D & Hughes B, *Adv inorg Chem & Radiochem*, **17** (1975) 1.
- 15 Hathway B J & Under Hill A E, *J chem Soc*, (1961) 3091.
- 16 Allman T & Geol R G, *Can J Chem*, **62** (1984) 615.
- 17 Das R N & Ramanarao D V, *Indian J Chem*, **11** (1973) 603.