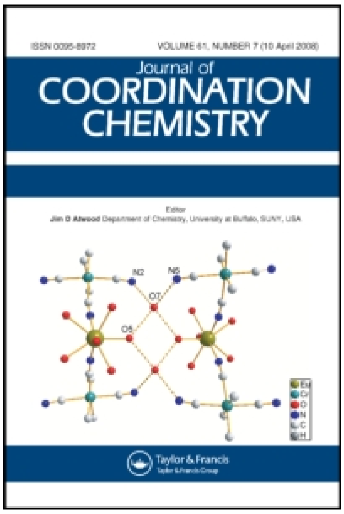

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# REACTIONS OF 1,3-OXAZOLIDINE-2-THIONE WITH ZINC(II), CADMIUM(II) AND MERCURY(II) HALIDES[†]

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The reactivity of 1,3-oxazolidine-2-thione towards II B group metals is considered. Cadmium halides, mercury chloride and bromide react to give coordination compounds, whose stereochemistry is tentatively assigned by their i.r. spectra.

Otherwise zinc halides and mercury iodide induce a ring opening.

## INTRODUCTION

Metal ions play an important role both in cyclization and in polymerization reactions. 1,3-Oxazolidine-2-thione, for example, can be prepared by reaction in basic medium between 2-hydroxyethylcarbamate and lead(II), according to Ettlinger:[1]

$$\mathrm{HO{\cdot}(CH_2)_2{\cdot}NH{\cdot}CS_2{}^- + OH^- + Pb^{++} \rightarrow}$$
$$\mathrm{H\overline{N{\cdot}(CH_2)_2{\cdot}O{\cdot}C}{=}S + PbS + H_2O} \qquad (1)$$

On the other hand it undergoes a ring-opening polymerization in the presence of cationic catalyst $A^+$ with the mechanism:[2]

$$\mathrm{H\overline{N{\cdot}(CH_2)_2{\cdot}O{\cdot}C}{=}S \xrightarrow{A^+} [H\overline{N{\cdot}(CH_2)_2{\cdot}O{\cdot}C}{\cdot}S{\cdot}A]^+}$$
$$\mathrm{\rightleftarrows -CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}S{\cdot}A \xrightarrow{monomers}}$$
$$\mathrm{\rightarrow (CH_2{\cdot}CH_2{\cdot}NH{\cdot}CO{\cdot}S)_n} \qquad (2)$$

Consequently we consider it useful to investigate 1,3-oxazolidine-2-thione in order to clarify the influence of metal ions on the ring stability. The present work deals with the behaviour of 1,3-oxazolidine-2-thione toward the IIb group metal halides.

## RESULTS AND DISCUSSION

By reaction of 1,3-oxazolidine-2-thione (oxt) with Zn(II), Cd(II) and Hg(II) halides in absolute ethanol, the complexes $Cdoxt_2X_2$ (X = Cl, Br, I) and $Hgoxt_2X_2$ (X = Cl, Br) were obtained, while Zn(II) halides do not give well defined products.

All compounds are white and diamagnetic, consistent with a $d^{10}$ configuration.

In Table I some analytical data for cadmium and mercury complexes are reported. The i.r. bands, attributed to the –NH•CS•O– group, are listed in Table II (4000–350 $cm^{-1}$) and all those present in the 400–100 $cm^{-1}$ range are reported in Table III.

### *Cadmium Complexes*

Completely insoluble in non polar solvents, the cadmium complexes are sparingly soluble in $H_2O$, $CH_3OH$ and acetone and the solubility decreases in the order I > Br > Cl. The molar conductivities in acetone (see Table I) indicate that all the complexes are non-electrolytes, ruling out the ionic formulations, $[Cdoxt_4]^{2+}[CdX_4]^{2-}$ and $[Cdoxt_2]^{2+}2X^-$.

In addition, an X-ray analysis carried out on the chloride shows that the asymmetric unit is a formula unit, thus excluding the $[Cdoxt_4]^{2+}[CdX_4]^{2-}$ structure and the displacements of the principal i.r. bands of the coordinated ligand (see later) will discard the $[Cdoxt_2]^{2+}2X^-$ formulation. The high conductivity values in water may be largely ascribed to solvolytic equilibria, since the solutions, after evaporation of the solvent, give the starting complexes.

Therefore, the cadmium compounds must have monomeric tetrahedral or polymeric octahedral

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TABLE I
Analytical data and some physical properties

| | Calcd% | | | Found% | | | M.p.(°C) | $\Lambda_M(\Omega^{-1}\,cm^2\,mol^{-1})$ at 25°C | |
|---|---|---|---|---|---|---|---|---|---|
| Compound | M | C | H | M | C | H | (dec.) | $H_2O$ | acetone |
| $Cdoxt_2Cl_2$ | 28.87 | 18.48 | 2.57 | 29.00 | 18.67 | 2.71 | 132 | 183 | 7.5 |
| $Cdoxt_2Br_2$ | 23.50 | 15.28 | 2.12 | 23.41 | 15.05 | 2.09 | 133 | 189 | 7.1 |
| $Cdoxt_2I_2$ | 19.64 | 12.62 | 1.75 | 19.48 | 12.98 | 1.90 | 133 | 180 | 10.5 |
| $Hgoxt_2Cl_2$ | 42.01 | 15.09 | 2.11 | 41.95 | 14.81 | 2.19 | 295 | – | – |
| $Hgoxt_2Br_2$ | 35.42 | 12.72 | 1.78 | 35.33 | 12.40 | 1.86 | 103 | – | 15 |

TABLE II
Shifts of the most important bands in the region 4000–350 $cm^{-1}$ in the Cd(II) and Hg(II) complexes

| Compound | $\nu NH$ | $\nu C\overset{\cdot\cdot}{=}N + \delta NH$ | $\nu C{-}O$ | $\nu C{=}S$ | $\omega NH$ | $\Delta CS$ |
|---|---|---|---|---|---|---|
| oxt† | 3210vs | 1530vs | 1171vs | 1110m | 695sbr | 350w |
| $Cdoxt_2Cl_2$ | 3315vs | 1545vs | 1185vs | – | 568s | 356m |
| $Cdoxt_2Br_2$ | 3310vs | 1540vs | 1187vs | – | 568s | 369m |
| $Cdoxt_2I_2$ | 3315s | 1538vs | 1183vs | – | 565vs | 366m |
| $Hgoxt_2Cl_2$ | 3290m – 3140s | 1540vs | 1190vs – 1185vs | – | 695m – 570m | 374mw |
| $Hgoxt_2Br_2$ | 3280ms – 3130ms | 1540vs | 1190vs – 1183vs | – | 695m – 570m | 368w |

†For the i.r. assignments – see Ref. 10.

TABLE III
I.r. bands in the range 400 – 100 $cm^{-1}$

| | |
|---|---|
| oxt | 350w, 284w, 178s, 146w, 102ms |
| $Cdoxt_2Cl_2$ | 356m, 210vsbr, 150w, 118w |
| $Cdoxt_2Br_2$ | 369m, 277vw, 207m, 188s, 172s, 110m |
| $Cdoxt_2I_2$ | 366m, 244vw, 202m, 167s, 154s, 98m |
| $Hgoxt_2Cl_2$ | 374mw, 333mbr, 200s, 170sbr, 118w |
| $Hgoxt_2Br_2$ | 368w, 346w, 210s, 198s, 168s, 148vs, 120w |

stereochemistry. Because of the insolubility in convenient solvents, it was not possible to verify the molecular weights in solutions. Attempts with the Rast method using camphor or naphtalene were also unsuccessful.

However useful information about the coordination can be obtained by comparing the i.r. spectra of the complexes with that of the ligand (Table II).

The increase of the $\nu$NH vibration of about 100 $cm^{-1}$ and the simultaneous reenforcing of the $C\overset{\cdot\cdot}{-}N$ bond, shown by the shifts of $\nu$CN + $\delta$NH of *ca.* 10 $cm^{-1}$ towards higher wavenumbers, exclude the nitrogen as coordinating atom.

On the other hand, the i.r. displacements are consistent with a coordination *via* sulphur atom. In fact, the S-coordination would delocalize the $\pi$ system with the following consequences: (i) increase of $\nu$NH vibration according to a higher $sp^2$ hybridization on the N atom;[3] (ii) increase of $C\overset{\cdot\cdot}{-}N$ $\pi$-bond order; (iii) increase of the $\nu$CO vibration and (iv) lowering of the $\nu$CS. All these statements are verified, apart from (iv); it is difficult to find the lowered $\nu$CS, because the region is very rich with bands.

In 1,3-oxazolidine-2-thione the carbon of the methylene group near the oxygen has a fractional positive charge available for a nucleophilic attack.[2] Consequently, the behaviour of the ligand as bidentate with the couple (S,O) would imply an increase of the positive charge on the carbon with an easier break of the $CH_2{-}O$ link. This fact and the experimental shifts of $\nu$CO exclude the oxygen as coordinating atom and the $[Cdoxt_2]^{2+}2X^-$ formulation.

Hence, the ligand uses only the sulphur atom to coordinate the metal. This is also supported by the shift towards higher wavenumbers of the band at

350 $cm^{-1}$, attributable to the out-of-plane deforming ΔCS, as found for the analogous band at 337 $cm^{-1}$ in ethylenthiourea under S-complexation.[4,5]

In a tetrahedral configuration, these complexes would have local $C_{2v}$ point-group symmetry; then two νCdX ($A_1 + B_1$) and two νCdS vibrations ($A_1 + B_2$), all i.r. and Raman active, would be expected. For the octahedral structure, the local symmetry of $CdX_4S_2$ is $D_{4h}$ which would decrease to $D_{2h}$ because of the polymeric chain (we assume no distortion). Then, one would expect two νCdS vibrations belonging to $A_{1g}(R)$ and $A_{2u}(IR)$ in $D_{4h}$ or $A_g(R)$ and $B_{1u}(IR)$ in $D_{2h}$. As far as the νCdX vibrations are concerned, there would be two Raman active vibrations ($A_{1g} + B_{1g}$ in $D_{4h}$ and $2A_g$ in $D_{2h}$) and a νCdX vibration i.r. active ($E_u$ in $D_{4h}$), which splits in $B_{2u}$ and $B_{3u}$ in $D_{2h}$ both i.r. active.

From the data reported on Table III, the two metal-halogen vibrations are tentatively located[6] at 188s and 172s $cm^{-1}$ for Br and at 167s and 154s $cm^{-1}$ for I derivative, while the two νCdCl are not identified in consequence of a very strong broad absorption with a middle point at 210 $cm^{-1}$. Two νCdS vibrations should appear in the i.r. spectrum for a tetrahedric structure. In contrast, only one vibration, attributable to a νCdS, was found in the range 200–210 $cm^{-1}$, in agreement with an octahedral environment. However, the identification of only one band νCdS does not exclude the presence of the other νCdS required for the tetrahedral structure, since it might be overlapped with some other vibrations. On the other hand, their solubilities and the high conductivity values in water support the tetrahedral stereochemistry.

### *Mercury Complexes*

The i.r. bands of the Hg(II) halide complexes (Table II) show that they are S-bonded. Unlike cadmium, mercury derivatives exhibit some split bands, i.e. νNH, νCO and ωNH. This could be due to different hydrogen bondings, occurring among NH and oxygen, sulphur or halogen. As seen for cadmium complexes, the out-of-plane ΔCS band moves towards higher wavenumbers.

A conductivity measurement carried out on $Hgoxt_2Br_2$ ($Hgoxt_2Cl_2$ is insoluble in all the solvents) in acetone shows to be a non-electrolyte. The great difference between solubilities and melting points (Table I) of the two derivatives suggests that they have no identical structures. We propose that $Hgoxt_2Cl_2$ is an octahedral polymer; in fact, the strong band at 200 $cm^{-1}$ (Table III) is attributable to the νHgCl with the chloride bridged[7] and the other expected νHgCl vibration for a $D_{2h}$ symmetry falls at 170 $cm^{-1}$, probably coupled with other vibrations. The νHgS in $Hgoxt_2Cl_2$ is attributed to the band at 333 $cm^{-1}$ in agreement with the literature.[8]

On the basis of the solubility and its melting point $Hgoxt_2Br_2$ should have a tetrahedral structure. One of the two expected νHgS vibrations could be the band at 346 $cm^{-1}$. However, its i.r. spectrum does not allow us to confirm this hypothesis without any doubt, in consequence of the presence of several bands which might be in agreement with a νHgBr both terminal and bridged.[6–9]

### *Reaction of 1,3-oxazolidine-2-thione with Zn(II) Halides and $HgI_2$*

All the attempts to obtain the zinc complexes were unsuccessful. The analyses of the white non-crystalline products obtained by reaction of the halides with oxt in ethanol solutions did not give products of well defined formulae. In every case the analyses showed higher carbon and hydrogen content than any calculated for the various trial ratios between metal and ligand.

All the i.r. spectra exhibit very broad bands with a strong peak at 1650 $cm^{-1}$ attributable to a νC=O vibration. Its presence shows unambigously the ring opening of the 1,3-oxazolidine-2-thione with the probable mechanism (2), where Zn(II) is the cationic catalyst.

This is not surprising, since Zn(II) is the most acid in the IIb group. The acidic properties of Cd(II) and Hg(II) are not enough to determine the ring opening, although in the case of $HgI_2$ it was not possible to obtain the corresponding complex $Hgoxt_2I_2$. This may be due to the nucleophilic attack of $I^-$ on the carbon near the oxygen atom as it occurs in the reaction between oxt and $CH_3I$.[2] Recently C. Preti and G. Tosi[9] prepared well defined complexes of zinc(II) with the benzoxazole-2-thione of general formula $Znbot_2X_2$ (where X = Cl, Br, I). There, the presence of the benzene ring stabilizes the heterocyclic system, preventing its opening.

To conclude, 1,3-oxazolidine-2-thione behaves differently towards Zn(II), Cd(II) and Hg(II) halides. This behaviour is attributable to a different acidity of the three ions. However, the ring-breaking always occurs on the $CH_2$–O linkage and it is aided by the presence of the strongly nucleophilic species.

## EXPERIMENTAL SECTION

### *Preparation of Ligand and Complexes*

1,3-Oxazolidine-2-thione was prepared according to Ettlinger,[1] by adding at low temperature $CS_2$ (0.1 moles) to an equimolecular solution of KOH and ethanolamine in $H_2O$/dioxane. After a further addition of 0.1 moles of KOH, an aqueous solution of lead nitrate (0.1 moles) was added and the solution was heated for half an hour. The PbS was eliminated by filtration and the solution was completely evaporated. The residue, extracted with boiling benzene, was recrystallized several times from benzene (m.p. 98–99°C).

All the complexes were obtained by boiling an absolute ethanol solution of the metal halide under reflux with the ligand in 1:2 ratio.

The reaction between mercury iodide and ligand was carried out in methanol, but it did not give the expected complex.

### *Reactions of Zinc(II) Halides with oxt*

The attempts to obtain the zinc(II) complexes were carried out both in the molten ligand and in ethanol solutions in different stoichiometrical ratio.
The former method has given the starting substances, while the latter always produced the ring opening.

### *IR Measurements*

The i.r. were recorded in the range 4000–100 cm$^{-1}$ with Perkin-Elmer 325 and Hitachi-Perkin-Elmer F153 spectrophotometers. The spectra in the range 4000–400 cm$^{-1}$ were measured for KBr discs.
Far i.r. spectra were recorded for Nujol mulls supported between polyethylene sheets. Atmospheric water was removed from the spectrophotometer housing by flushing with dry nitrogen.

### *Conductivity Measurements*

The measurements were carried out with a WTW bridge at 25°C.

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