Inorganica Chimica Acta, 69 (1983) 25–28

The Metal Centre Dependence of Inversion at Coordinated Sulphur

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Received June 30, 1982

A series of dithiahexane complexes with the metal ions Ru(II), Rh(III), Ir(III), Pd(II), Pt(II), Pt(IV) and Au(III) have been studied by variable temperature ^{1}H NMR. Coalescence temperatures and $\Delta G^{\ddagger}$ values have been obtained for the dynamic process of inversion about coordinated sulphur. The results indicate that this process is metal ion dependent and is dependent on the ligand trans *to sulphur only in certain cases.*

Introduction

Although the nature of the dynamic process which occurs with coordinated thioethers, commonly called inversion, is now well established [1], the majority of the studies have dealt with complexes of Pd(II) and Pt(II) [2–5]. For these the rate of inversion varies Pd > Pt and for ligands *trans* to sulphur, R_2S > I > Br > Cl. We recently reported [6] that the inversion rate in the higher oxidation state Pt(IV) complexes is slower than in Pt(II) analogues but the *trans* ligand effect was the same. We also showed [3] that rate of inversion was markedly affected by the backbone in a series of bidentate ligands and this has recently been confirmed for two of our series of backbones [7]. Data for other normal [8] oxidation state transition metals is fragmentary [9, 10] and thus we have examined a series of 2,5-dithiahexane complexes with a range of transition metal ions as reported below.

Experimental

The following complexes were prepared by literature methods and were analytically pure: $[Pt(dth)_2](ClO_4)_2$ [3], $[Ru(dth)_2X_2]$ [11] (X = Cl, Br), $[Me_4N][Rh(dth)X_4]$ [6] (X = Cl, Br), $[Rh(dth)_2X_2]Y$ [12] (X = Y = Cl; X = Y = Br; X = Cl, Y = BF_4), $[Me_4N][Ir(dth)Cl_4]$ [6], $[Au(dth)Cl_2][AuCl_4]$ [6] and $[Au(dth)Br_2]Br$ [6]. The dimer, $[Rh_2(dth)_2Cl_6]$ was prepared by reaction of $[Me_4N][Rh(dth)Cl_4]$ with an equimolar quantity of $AgClO_4$ in dimethylsulphoxide as solvent.

The NMR spectra were recorded on a Perkin-Elmer R32 90 MHz spectrometer. Many of the complexes were poorly soluble in common NMR solvents and only d^6-dmso was generally suitable. Spectra were obtained below the freezing point of dmso (18 °C) using a d^6-dmso/$CDCl_3$ mixture. Several complexes employed in this study decomposed in dmso, *viz.*; $[Rh(dth)_2X_2]X$, $[Me_4N][Ir(dth)Br_4]$ and $[Au(dth)Cl_2][AuCl_4]$. $[Rh(dth)_2Cl_2]Cl$ had sufficient solubility in D_2O and spectra were obtained in this solvent.

The $\Delta G^{\ddagger}$ values were calculated from NMR spectra parameters using the expression for calculating k [13] and substitution into the Eyring equation.

Results and Discussion

The results of the variable temperature NMR studies are shown in Table I together with selected data for Pd(II), Pt(II) and Pt(IV) complexes for comparison.

For the complexes containing a single dithiahexane (dth) ligand, $[Me_4N][M(dth)X_4]$ M = Rh, X = Cl, Br; M = Ir, X = Cl, the ^{1}H NMR spectra exhibit two SMe resonances due to the *meso* and DL isomers [3, 4] of the coordinated ligand below coalescence temperature. As the temperature is increased these signals broaden and then coalesce. A typical example is shown in Fig. 1. In the case of $[Me_4N][Rh(dth)Cl_4]$ it is necessary to record the variable temperature spectra up to coalescence rapidly to obtain data on this complex. The doublet due to the

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TABLE I. ^{1}H NMR Data on Selected Dithiahexane Complexes.

Complex	$^3J_{M-H}$ (Hz)	T °C[a]	$\Delta G^{\dagger}$ [b]	Solvent
$[Pt(dth)Cl_4]$[c]	36.0	>150	–	d^6 dmso
$[Pt(dth)Br_4]$[c]	36.0	+120	89.6	d^6 dmso
$[Pt(dth)Cl_2]$[d]	46.8	+102	81.6	d^6 dmso
$[Pt(dth)Br_2]$[d]	46.8	+92	79.7	d^6 dmso
$[Pd(dth)Cl_2]$[d]	–	+40	69.6	d^6 dmso
$[Pd(dth)Br_2]$[d]	–	<20	–	d^6 dmso
$[Pt(dth)_2](ClO_4)_2$	–	0	–	d^6 dmso/$CDCl_3$
$[Ru(dth)_2Cl_2]$	–	40, 50	–	d^6 dmso
$[Ru(dth)_2Br_2]$	–	45, 60	–	d^6 dmso
$[Me_4N][Rh(dth)Cl_4]$	1	110	87.3	d^6 dmso
$[Me_4N][Rh(dth)Br_4]$	1	105	85.5	d^6 dmso
$[Rh_2(dth)_2Cl_6]$	1	105	85.3	d^6 dmso
$[Rh(dth)_2Cl_2]Cl$	1	80, 90	–	D_2O
$[Me_4N][Ir(dth)Cl_4]$	–	10	63.0	d^6 dmso/$CDCl_3$
$[Au(dth)Br_2]Br$	–	90	82.6	d^6 dmso

[a] More than one value indicates distinctly different coalescence processes. [b] kJ mole^{-1}, values given where calculations are possible from the spectra parameters. [c] Ref. 6. [d] Ref. 3.

meso and DL isomers of this moiety centered at 2.18 ppm decreases in intensity with a concomitant appearance of two doublets of equal intensity downfield at 2.24 and 2.39 ppm when heated in d^6-dmso for about 30 minutes. This behaviour is explained by the formation of a second species $[Rh_2(dth)_2Cl_6]$. The conversion can be rationalised by invoking a solvolysis of a chloride ligand *trans* to a sulphur donor. Two of these solvento intermediates then form a stable halide bridged species as shown.

$$2[Me_4N][Rh(dth)Cl_4] \xrightarrow{dmso}$$

$$2[Rh(dth)(dmso)Cl_3] + 2[Me_4N]Cl$$

$$\downarrow$$

$$[Rh_2(dth)_2Cl_6]$$

This type of behaviour is already documented [14] and this particular dimeric species has been proposed independently [12]. As further proof we have confirmed that this species prepared by halide abstraction from $[Me_4N][Rh(dth)Cl_4]$ with silver perchlorate has identical ^{1}H NMR parameters as the signals which appear on heating the anionic complex in d^6-dmso. The bromo analogue does not undergo this solvolysis reaction.

With complexes of the type *trans*-$[M(dth)_2X_2]$ five isomers are possible as shown in Fig. 2. The complexity of the spectra obtained for $[Rh(dth)_2X_2]$ X = Cl, Br and $[Rh(dth)_2Cl_2]Cl$ precludes detailed

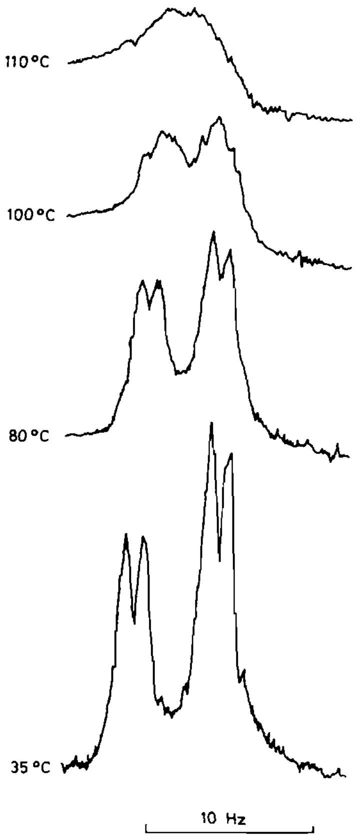

Fig. 1. Variable temperature ^{1}H NMR spectra of $[Et_4N][Rh(dth)Br_4]$.

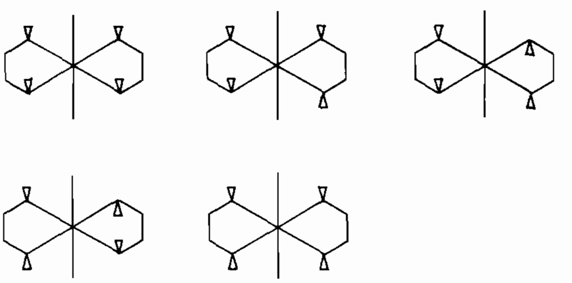

Fig. 2. Possible isomers for *trans*-[M(dth)$_2$X$_2$].

analysis, however, it is possible to obtain approximate coalescence temperatures and these are quoted in Table I. The spectra obtained for [Rh(dth)$_2$Cl$_2$]Cl are reproduced in Fig. 3.

From the coalescence temperatures and calculated $\Delta G^{\ddagger}$ values it is significant that:

a) the values for [Rh(dth)X$_4$]$^-$ (X = Cl, Br) and [Rh$_2$(dth)$_2$Cl$_6$] are identical within experimental error,

b) the coalescence temperature for *trans*-[Rh(dth)$_2$Cl$_2$]Cl is lower than [Rh(dth)Cl$_4$]$^-$ having – SMe *trans* to S and Cl respectively, however, the difference is much smaller than between [Pt(dth)$_2$]-(ClO$_4$)$_2$ and [Pt(dth)Cl$_2$],

c) the values for [Ir(dth)Cl$_4$]$^-$ are lower than for [Rh(dth)Cl$_4$]$^-$ in contrast to [M(dth)Cl$_2$] (M = Pd, Pt) where the values are higher for the third row metal.

The observation noted in c) is in accord with data obtained on the complexes *mer*-[M{S(CH$_2$SiMe$_3$)$_2$}$_3$-Cl$_3$] (M = Rh, Ir) [9].

We are cautious of deducing trends from studies on a limited series of complexes, ideally a wide range of isostructural complexes should be studied. However, this aim is limited by the nature of thioether coordination chemistry. Attempts to prepare the unknown complexes [Os(dth)$_2$X$_2$], [Ir(dth)$_2$Cl$_2$]-Cl or [Ru(dth)X$_4$]$^{2-}$ have been unsuccessful, whilst known complexes of Os(IV), Ir(IV) and Ru(III) [6, 11] are paramagnetic and hence unsuitable for NMR studies.

On the basis of this study the following conclusions can be drawn. Dependence on the *trans* ligand is very significant for some metal ions *i.e.* Pd(II), Pt(II) and to a lesser extent Pt(IV) but unimportant for others such as Ru(II) and Rh(III). It also appears that ease of inversion is very metal dependent but there is no obvious trend within the periodic table nor in d^n configuration. Comparing Pd(II) and Pt(II), the third row metal has the higher coalescence temperature whereas for Rh(III) and Ir(III) inversion occurs more easily with Ir(III). The d^6 species of Ru(II), Rh(III), Ir(III) and Pt(IV) show no correlation nor do Pd(II), Pt(II) and Au(III), all d^8.

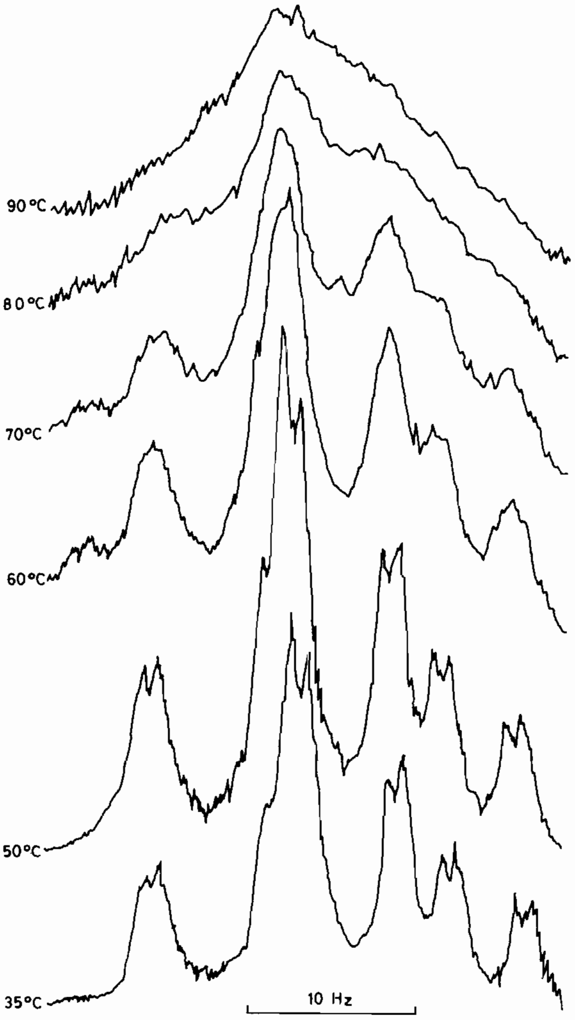

Fig. 3. Variable temperature ^{1}H NMR spectra of *trans*-[Rh-(dth)$_2$Cl$_2$]Cl.

One factor which may affect inversion is the M–S bond strength. For Pd(II) and Pt(II) the metal–thioether bond strengths are in the order Pd(II) < Pt(II) and ease of inversion Pd(II) > Pt(II) [15]. It has been noted that Ir(III) has a poor affinity towards thioether ligands [9] and this may well explain why ease of inversion in the order Ir(III) > Rh(III). One thing, however, is clear, that generalisations assumed in early work do not hold when metal ions other than Pd(II) and Pt(II) are used.

Acknowledgement

We thank Johnson-Matthey Ltd for the loan of precious metal salts and the S.E.R.C. for financial support.

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