THE THERMOCHEMISTRY OF TRANSITION METAL SULPHOXIDE COMPLEXES

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ABSTRACT

The thermochemistry of oxygen-bonded and sulphur-bonded sulphoxide complexes of the *d*-block and *f*-block metals is discussed. The modes of thermal decomposition of such complexes are described in the light of structural data where such data are available. Areas worthy of further study, including several unique thermal isomerization processes, which remain unconfirmed to date, are outlined.

INTRODUCTION

Sulphoxides are an important class of ambidentate ligand capable of coordinating to transition metal ions through either sulphur or oxygen (Fig. 1). In terms of Pearson's classification [1], sulphoxides may act as either hard bases (coordinating via oxygen) or as soft bases (coordinating via sulphur) and are thus potential ligands for the entire transition metal series. As a result of the extraordinary coordinating ability of sulphoxides, much attention has been paid to the utilization of these readily available compounds in solvent extraction processes [2]. Additionally, transition metal sulphoxide complexes have assumed an important role as intermediates in preparative coordination chemistry and in homogeneous catalytic systems. The chemistry of transition metal sulphoxide complexes has been reviewed [3–6], the most recent article [7] covering literature through 1979.

Research on the thermochemistry of transition metal sulphoxide complexes and on the application of thermal analytical methods to this area of coordination chemistry in general has led to a greater understanding of a number of fundamental processes. This is particularly evident in studies of square-planar, d^8, platinum(II) sulphoxide complexes, which have contributed much to our understanding of the factors governing geometric isomeri-
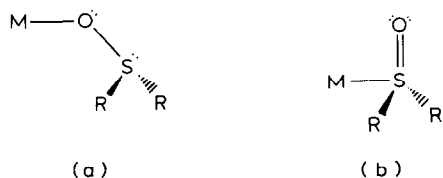
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Fig. 1. Coordination modes of simple sulphoxides. (a) Bonding via oxygen. (b) Bonding via sulphur.

zation reactions and the role of the *cis* and *trans* effects in controlling such processes. Conversely, thermochemical studies of sulphoxide complexes of the lanthanides and actinides are, at best, qualitative in nature due largely to the paucity of structural data of such complexes, making meaningful interpretation of thermal studies difficult and of uncertain value. This situation is particularly undesirable since sulphoxides may have an important role to play in the separation of these elements in the future [2].

This article summarizes and discusses the thermochemistry of transition metal sulphoxide complexes, considering first the very large class of complexes in which the sulphoxide is coordinated via oxygen and then the far smaller group in which metal–sulphur bonding is involved.

OXYGEN-BONDED SULPHOXIDE COMPLEXES OF THE *d*-BLOCK ELEMENTS

The majority of the transition metals form sulphoxide complexes in which the sulphoxide is coordinated via oxygen [7]. The only exceptions to this generality are low-valent, electron-rich, late transition metals, which tend to act as "soft" Lewis acids. The differences in bonding between the two cases have been explained by a valence-bond model [7].

Perhaps the most important point to note in connection with the thermochemistry of sulphoxide complexes is that considerable dangers do exist in examining certain classes of complex at high temperatures. In particular, salts of oxidizing anions such as nitrate and, especially, perchlorate tend to undergo explosive thermal decomposition. In fact, sulphoxide complexes of the *p*-block and *d*-block metals have been patented as explosives [8,9], having properties similar to those of nitroglycerine or TNT. The explosive complexes are prepared by replacing some or all of the water from a hydrated nitrate or perchlorate salt by a sulphoxide. In the case of aluminum perchlorate, the reaction is represented by

$$[Al(H_2O)_6][ClO_4]_3 + 6\ Me_2SO \rightarrow [Al(Me_2SO)_6][ClO_4]_3 + 6\ H_2O \qquad (1)$$
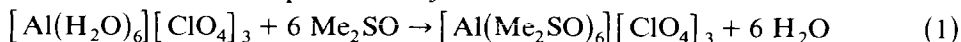
The oxygen-rich sulphoxide complex may be used as an explosive or an explosive admixture; the equation

$$[Al(Me_2SO)_6][ClO_4]_3 \rightarrow AlCl_3 + 12\ CO + 6\ H_2O + 6\ S + 12\ H_2 \qquad (2)$$
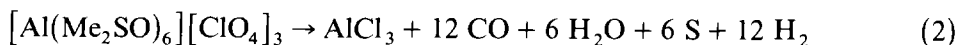
is believed to represent the reaction upon detonation. Similar chemistry occurs with iron(III) nitrate and perchlorate complexes and may be general for sulphoxide complexes containing oxidizing anions. Accordingly, due caution should be exercised in handling such materials.

The thermochemistry of a series of dimethylsulphoxide complexes of transition metal nitrates and perchlorates has been studied by TG and DTA [10]. The perchlorate complexes studied, $M(ClO_4)_2 \cdot nMe_2SO$ (M = Ni, Co, $n = 6$; M = Mn, $n = 6$; M = Cu, $n = 9$) and $Cr(ClO_4)_3 \cdot 6\ Me_2SO$, all formed only labile intermediates, with $Co(ClO_4)_2 \cdot 7\ Me_2SO$ alone being well-defined. The actual structures of these complexes cannot be simply inferred from their formulae, since the sulphoxide moieties may be coordinated or present as lattice-held solvent of crystallization and the anions may be coordinated or present as non-coordinated counterions. All of the perchlorate complexes were found to explode in the temperature range 200–235°C.

Three classes of nitrate complex were studied, $AgNO_3 \cdot Me_2SO$, $M(NO_3)_2 \cdot nMe_2SO$ (M = Mn, $n = 3$, 6; M = Ni, Co, $n = 8$) and $M(NO_3)_3 \cdot nMe_2SO$ (M = Fe, Cr, $n = 6$). All of the M(II) complexes were labile, allowing the identification of intermediates in three cases: $Mn(NO_3)_2 \cdot 2\ Me_2SO$ from $Mn(NO_3)_2 \cdot 3\ Me_2SO$, $Ni(NO_3)_2 \cdot 3\ Me_2SO$ from $Ni(NO_3)_2 \cdot 8\ Me_2SO$, and $Co(NO_3)_2 \cdot 3\ Me_2SO$ from $Co(NO_3)_2 \cdot 8\ Me_2SO$. The silver(I), iron(III) and chromium(III) complexes were thermally stable below 200°C and above this temperature all of the nitrate complexes, with the exception of $AgNO_3 \cdot Me_2SO$, showed exothermic effects attributed to the oxidation of dimethylsulphoxide by the nitrate anion.

TABLE 1

Intermediates formed in the thermal degradation of some halo-transition metal complexes of Me_2SO

Complex	Intermediates
$CrCl_3 \cdot nMe_2SO$ ($n = 3, 4, 5$)	$CrCl_3 \cdot 3\ Me_2SO$
$MnI_2 \cdot 6\ Me_2SO$	$MnI_2 \cdot 3\ Me_2SO$
$CoI_2 \cdot nMe_2SO$ ($n = 6, 3$)	Labile
$FeCl_3 \cdot 4\ Me_2SO$	$FeCl_3 \cdot 2.5\ Me_2SO$
$MnCl_3 \cdot 3\ Me_2SO$	$MnCl_2 \cdot nMe_2SO$ ($n = 1, 0.5$)
$CoCl_2 \cdot 3\ Me_2SO$	Labile
$CuCl_2 \cdot 2\ Me_2SO$	Labile
$CrBr_3 \cdot 6\ Me_2SO$	Labile
$MnBr_2 \cdot 6\ Me_2SO$	$MnBr_2 \cdot nMe_2SO$ ($n = 2, 3$)
$CoBr_2 \cdot nMe_2SO$ ($n = 8, 3$)	Labile
$NiI_2 \cdot nMe_2SO$ ($n = 8, 6, 5$)	$NiI_2 \cdot 2\ Me_2SO$
$NiBr_2 \cdot 8\ Me_2SO$	$NiBr_2 \cdot nMe_2SO$ ($n = 1, 3, 6$)
$CuBr_2 \cdot 3\ Me_2SO$	$CuBr_2 \cdot 2\ Me_2SO$

A related study [11] of halo-complexes by TG and DTA demonstrates that the oxidation process mentioned above results from the presence of the oxidizing anions. Table 1 shows the classes of intermediates that were observed during thermal degradation of a series of halo-complexes. In most cases, dimethylsulphoxide was lost below 100°C, although the chromium(III) complex was inert up to 200°C. In the case of the copper(II) complexes $CuBr_2 \cdot 3\ Me_2SO$ and $CuCl_2 \cdot 2\ Me_2SO$, the copper ion appears to cause catalytic combustion, forming copper(II) sulphide, which is ultimately oxidized to copper sulphate.

To interpret these data meaningfully, it is necessary to know the actual structures of the complexes involved. In many cases, this information is simply not available. Of all of the complexes listed in table 1, X-ray crystallographic data are available [12,13] only for $[CuCl_2(Me_2SO)_2]$. The nickel(II) chloride system has been studied in the greatest depth and the transformations upon heating may be represented [14] by

$$NiCl_2 \cdot 8\ Me_2SO \xrightarrow{-5Me_2SO} NiCl_2 \cdot 3\ Me_2SO \xrightarrow{-2Me_2SO} NiCl_2 \cdot Me_2SO \qquad (3)$$

The initial complex must contain lattice-held solvent of crystallization, since the maximum coordination number of nickel(II) is six, and hence probably has the formula $[Ni(Me_2SO)_6][Cl]_2 \cdot 2\ Me_2SO$. The intermediate formed can be tentatively assigned the structure $[Ni(Me_2SO)_6][NiCl_4]$ by analogy with a related iron complex whose X-ray crystal structure has been determined [15,16]. The final product has been studied by infrared and electronic spectroscopy and, along with magnetic susceptibility measurements, these data suggest a halide bridged species where each nickel(II) center maintains an octahedral environment through spin–spin interactions [17]. The bond energy determinations for the final nickel(II)–dimethylsulphoxide bond by DTA (23.6 ± 0.5 kcal mole^{-1}, determined in air; 21.2 ± 1.1 kcal mole^{-1}, determined in vacuum) and by direct calorimetry [17] (24.06 ± 0.04 kcal mole^{-1}) are in close agreement.

Of all of the d-block elements, the sulphoxide complexes of Groups IV (Ti, Zr, Hf) and V (V, Nb, Ta) have been examined thermochemically in most detail. This may well be the result of interest in the solvent extraction and separation of Zr and Hf [18,19] and of Nb and Ta [20,21] employing sulphoxides as extractants.

Profound structural effects on the thermal stability of O-bonded sulphoxide complexes of the d-block elements are illustrated by comparing complexes of titanium with those of its horizontal and vertical neighbors in the periodic table, vanadium and zirconium. The titanyl, vanadyl and zirconyl complexes, $MO(ClO_4)_2 \cdot nPh_2SO$ (M = Ti, V, $n = 5$; M = Zr, $n = 6$) have been studied [22] by DTA, the presence of the perchlorate anion once again resulting in explosions during analysis. The initial decomposition temperatures are shown in Table 2. Clearly, the initial decomposition temperatures
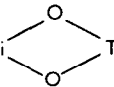
TABLE 2

Thermal decomposition of titanyl, vanadyl and zirconyl sulphoxide complexes

Complex	$T_{dec}/°C$	Ref.
$TiO(ClO_4)_2 \cdot 5\ Ph_2SO$	215	14
$ZrO(ClO_4)_2 \cdot 6\ Ph_2SO$	280	14
$VO(ClO_4)_2 \cdot 5\ Ph_2SO$	162	14
$VOCl_2 \cdot 3\ Ph_2SO$	234	14
$ZrO(ClO_4)_2 \cdot 8\ Me_2SO$ $(ZrO(ClO_4)_2 \cdot 6\ Me_2SO)$	185(270) [a]	17 [b]

[a] Endothermic loss of Me_2SO occurs at 185°C producing $ZrO(ClO_4)_2 \cdot 6\ Me_2SO$, which undergoes an explosion at 270°C.

[b] DTA performed using mixtures of complex and alumina (1:10 by weight) to minimize explosion and retain products in the cuvette.

indicate an order of thermal stability zirconyl > titanyl and titanyl > vanadyl. These results may be partially rationalized by considering the nature of the different "MO^{2+}" units and how these will affect the remaining ligands. Although the X-ray crystal structure of $VO(ClO_4)_2 \cdot 5\ Ph_2SO$ has not been reported, by analogy with other vanadyl complexes it is likely that the "VO^{2+}" moiety exists as a true $V{=}O$ double bond [23] and that the complex is monomeric in the solid state. It is also noteworthy that in the related species $VO(H_2O)_5^{2+}$, the H_2O ligand *trans* to the vanadyl oxygen has been shown [24] to be labile by [17]O-labeling studies. Accordingly, it seems likely that $VO(ClO_4)_2 \cdot 5\ Ph_2SO$ will have an octahedral structure, $[VO(Ph_2SO)_5][ClO_4]_2$, with a moderately labile Ph_2SO ligand *trans* to the vanadyl oxygen. Infrared studies support the presence of ionic perchlorate and oxygen-bonded R_2SO ligands in this and the analogous Me_2SO complex [22,25]. In the case of the titanyl complex, $TiO(ClO_4)_2 \cdot 5\ Ph_2SO$, the existence of a true $Ti{=}O$ moiety is problematic. The infrared spectrum shows neither the sharp band at 825 cm^{-1}, indicative of a polymeric $(Ti{-}O)_n$ structure, nor the broad band at 900–1100 cm^{-1}, indicative of a true $Ti{=}O$ moiety, but rather a sharp band at 825 cm^{-1}. This band was assigned to a

vibration of a $Ti\underset{O}{\overset{O}{\diamondsuit}}Ti$ unit and, accordingly, a dimeric bridged structure

was proposed [22]. It seems that the conclusion here is that the titanyl has a dimeric or higher oligomeric structure, whilst the vanadyl is monomeric. These factors may thus explain the enhanced thermal stability of the titanyl over the vanadyl.

   The zirconyl complex $ZrO(ClO_4)_2 \cdot 6\ Ph_2SO$ is derived from $ZrO(ClO_4)_2 \cdot 8\ Ph_2SO$ by heating at 185°C. The latter may be comparable with $ZrOCl_2 \cdot 8\ H_2O$, which in fact crystallizes as $[Zr_4(OH)_8(H_2O)_{16}]^{8+}$, where each

zirconium is coordinated to eight oxygens in a distorted octahedron [26]. The question of whether the zirconyl sulphoxide complex $ZrO(ClO_4)_2 \cdot 6 \, Ph_2SO$ has a monomeric or polymeric structure is unresolved. Cryoscopy indicates a monomeric structure in solution, but of course this cannot be taken to imply a monomeric structure in the solid state. Infrared data [22] indicated that a true $Zr{=}O$ exists by a vibration at 925 cm^{-1}, which implies that the solid is monomeric. In this context, it is interesting to note that zirconium's vertical neighbor in the period table, niobium, forms a polymeric sulphoxide complex, $NbOCl_2 \cdot 2 \, Me_2SO$, as ascertained by infrared studies [27].

The enhanced thermal stability of the zirconyl over the titanyl is thus difficult to assess, since a definite structure for the zirconyl has not been determined spectroscopically and only preliminary X-ray data are available [28]. It is possible that the thermal stabilities reflect the abilities of the metal ions to maintain a high coordination number and thus the sequence Zr > Ti is to be expected (estimated ionic radii are $Zr^{4+} = 0.74$ Å, $Ti^{4+} = 0.68$ Å [29]).

The case of zirconyl sulphoxide complexes is further complicated by a postulated isomerization [30] believed to occur during heating of the dimethylsulphoxide complex $ZrO(ClO_4)_2 \cdot 6 \, Me_2SO$. In this case, the initially formed complex, $ZrO(ClO_4)_2 \cdot 8 \, Me_2SO$, is converted to $ZrO(ClO_4)_2 \cdot 6 \, Me_2SO$ by an endothermic loss of Me_2SO at 185°C (the boiling point of Me_2SO is 187°C, for reference) followed by an explosion at 270°C. Just prior to the explosion, very small endothermic effects were noted which were attributed to an endothermic breaking of an $M{-}OSMe_2$ bond plus an exothermic formation of an $M{-}S(O)Me_2$ bond. Analysis of the $\nu(S{=}O)$ region of the infrared spectrum at this point indicated that the complex may contain sulphur-bonded Me_2SO. Undoubtedly, this type of isomerization is worthy of further study, since the formation of a hard acid–soft base complex by isomerization of a hard acid–hard base complex is almost without precedent in coordination chemistry.

While a limited number of reports of thermal studies of other sulphoxide complexes of the *d*-block elements involving oxygen-bonding do exist, these do not provide data for which meaningful comparisons can be made. Quite clearly, it is necessary for future studies to concentrate on well-defined complexes without structural ambiguities. Those complexes whose X-ray crystal structures have been reported are tabulated in a review [7].

OXYGEN-BONDED SULPHOXIDE COMPLEXES OF THE *f*-BLOCK ELEMENTS

Many examples of the thermal degradation of oxygen-bonded sulphoxide complexes are available from studies of actinide chemistry, no doubt prompted by the importance of non-aqueous solvents in the extraction of these elements. An early study was that of Bagnall et al. [31] who examined

the reactions of thorium(IV) and uranium(IV) halides with dimethylsulphoxide (Me_2SO). The isolated products had the empirical formulae $ThCl_4 \cdot 5$ Me_2SO, $ThBr_4 \cdot 6$ Me_2SO, $UCl_4 \cdot 3$ Me_2SO and $UBr_4 \cdot 6$ Me_2SO. The compounds were not completely characterized and there are many questions as yet unanswered in these formulations. Thus, as the actinide elements exhibit variable coordination numbers, it is not clear how many of the sulphoxide molecules are covalently bound to the metal and how many are present as lattice-held solvent of crystallization, nor, indeed, how many of the halides are covalently bound and how many are present as uncoordinated counterions. Unfortunately, standard solution techniques are of little use in the study of such systems since it has been shown that uranium(IV) halide–sulphoxide mixtures exist as a very complicated series of equilibria between both ionic and neutral species [32]. The initial decomposition temperatures of the complexes were determined by heating in air (Table 3) and vacuum TG was used to demonstrate that Me_2SO was lost from each sample below 100°C, with the exception of $UCl_4 \cdot 3$ Me_2SO which started to decompose at 125°C. The final products were oxides (Table 3) and only in the case of $UBr_4 \cdot 6$ Me_2SO could an intermediate containing dimethylsulphoxide be observed. This complex showed loss of Me_2SO above 50°C and underwent oxidation to a yellow uranyl complex, $UO_2Br_2 \cdot Me_2SO$, between 125 and 170°C. The ultimate products (Table 3) were obtained by heating above 400°C. Later work showed that complexes of empirical formulae $UCl_4 \cdot 7$ Me_2SO [33] and $UCl_4 \cdot 4$ Me_2SO [34] could also be isolated from UCl_4–Me_2SO systems. The former is degraded to $UCl_4 \cdot 3$ Me_2SO in vacuum; data on the latter complex are not available. In the case of the UCl_4 complexes, at least, the available data indicate that three molecules of Me_2SO are strongly bound, suggesting covalent bonding, whilst any further Me_2SO is less strongly bound, indicative of lattice-held solvent of crystallization. The bromide analogue, $UBr_4 \cdot 6$ Me_2SO, begins to lose Me_2SO at only 50°C by vacuum TG, implying that all six molecules may not be functioning as covalently bonded ligands.

TABLE 3

Thermal decomposition of Th(IV) and U(IV) sulphoxide complexes

Complex	$T_{dec}/°C$ [a]	$T/°C$ for initial loss of Me_2SO [b]	Final products ($T/°C$ of formation)
$ThCl_4 \cdot 5$ Me_2SO	145	< 100	$ThOCl_2$ (> 450)
$ThBr_4 \cdot 6$ Me_2SO	142–144	< 100	$ThOBr_2$ (> 400)
$UCl_4 \cdot 3$ Me_2SO	169	ca. 125	Oxides of U (> 475)
$UBr_4 \cdot 6$ Me_2SO	133–135	50–100	$UO_2Br_2 + U_3O_8$ (> 400)

[a] Initial decomposition temperature in air.
[b] By vacuum TG.

In a separate study, it was found [35] that hydrated $ThBr_4$ reacted with Me_2SO to yield a series of complexes of general formula $ThBr_4 \cdot nMe_2SO \cdot mH_2O$ ($n = m = 4$; $n = 6$, $m = 3$; $n = 8$, $m = 0$; $n = 10$, $m = 4.5$). Thermal analysis showed that the hydrates lost water in the temperature range 80–100°C and that the non-hydrated complex, $ThBr_4 \cdot 8\ Me_2SO$, had an initial decomposition temperature of 150–160°C, slightly higher than that of $ThBr_4 \cdot 6\ Me_2SO$ (Table 3). All of the complexes examined underwent major mass loss in the temperature range 170–300°C, which was complete by 500–600°C when ThO_2 was formed in each case. The formation of $ThOBr_2$, as detected in the thermal analysis [31] of $ThBr_4 \cdot 6\ Me_2SO$ above 400°C, was not described. There is evidently some confusion as to the true nature of the $ThBr_4$ complexes, as varying compositions have been described. A second study by the Russian group [35a] reports a series of complexes with different empirical formulae from their earlier study, i.e. $ThBr_4 \cdot nMe_2SO \cdot mH_2O$ ($n = 1$, $m = 4$; $n = 10$, $m = 1$; $n = 8$, $m = 1$; $n = 6$, $m = 0$). Thermal analysis of these and other structurally ill-defined complexes of Me_2SO with $ThCl_4$, ThI_4, $Th(NO_3)_4$, $Th(C_2O_4)$ and $Th(SO_4)_2$ suggest that the bromide and nitrate complexes initially lose water of hydration followed by a simultaneous decomposition of both neutral and anionic ligands in the temperature range 200–300°C. ThO_2 is ultimately formed at 500–600°C. The sulphate and oxalate salts have initial decomposition temperatures in the range 400–800°C, indicating an enhanced thermal stability, possibly a result of bidentate coordination of the anionic ligands to the metal center.

The data shown in Table 3 demonstrate that the initial decomposition temperatures of the U(IV) complexes vary with anion, chloride > bromide, while for the thorium(IV) complexes, these values are approximately equal. At this stage, these data cannot be satisfactorily explained, since the exact compositions (i.e. coordination number, geometry, etc.) of the complexes are not known. Further anion effects are demonstrated by studies of uranium(VI) complexes of diphenylsulphoxide (Ph_2SO). The complexes $UO_2(ClO_4)_2 \cdot 4\ Ph_2SO$ and $UO_2X_2 \cdot 2\ Ph_2SO$ (X = Cl, NO_3, CH_3COO) have been studied [22] by DTA and shown to decompose exothermally. The initial decomposi-

TABLE 4

Thermal decomposition of U(VI) sulphoxide complexes

Complex	$T_{dec}/°C$	Reaction type
$UO_2(ClO_4)_2 \cdot 4\ Ph_2SO$	322	Very violent
$UO_2Cl_2 \cdot 2\ Ph_2SO$	320	Controlled
$UO_2(OOCCH_3)_2 \cdot 2\ Ph_2SO$	328	Violent
$UO_2(NO_3)_2 \cdot 2\ Ph_2SO$	367	Violent

tion temperatures are shown in Table 4. Empirically, it is of interest to note that the perchlorate complex decomposes with great violence, the nitrate and acetate somewhat less violently and the chloride in a controlled fashion. The empirical formula of the perchlorate complex differs from that of the chloride, nitrate and acetate, no doubt because the perchlorate ions (members of the class known as "classically non-coordinating anions") are not covalently bonded to the metal center, whereas, in all likelihood, the other anions are. Conductivity measurements confirm this for these complexes in solution. In reality, the data in Table 4 thus describe two different types of complex, $[UO_2(Ph_2SO)_4][ClO_4]_2$ and $[UO_2(Ph_2SO)_2X_2]$. There appears to be little difference in the thermal stabilities of the chloride and acetate complexes, using the initial decomposition temperatures as a guide, despite the fact that the acetate anion is capable of bidentate coordination. The nitrate, which is also capable of bidentate coordination, forms a complex with a substantially higher initial decomposition temperature, however. Infrared studies confirm that the acetate and nitrate groups are coordinated to the metal in a bidentate fashion.

The analogous perchlorate complex of dimethylsulphoxide has also been studied [36] and an isomerization of the bonding mode proposed. The initially prepared complex, $[UO_2(Me_2SO)_4][ClO_4]_2 \cdot Me_2SO$, was identified as containing both oxygen-bonded and lattice-held Me_2SO by infrared spectroscopy. Heating to 170°C caused loss of the lattice-held sulphoxide and allowed isolation of $[UO_2(Me_2SO)_4][ClO_4]_2$. The infrared spectrum showed a change in the position of the $\nu(S{=}O)$ mode to that typically found in sulphur-bonded complexes and on this basis the authors propose an isomerization of the bonding mode of the Me_2SO ligand. A further complication is, however, apparent upon close examination of the infrared spectra, which shows that the ν_3 mode of the ClO_4^- ion in the proposed sulphur-bonded complex is, in fact, a split band. A free ClO_4^- ion has tetrahedral symmetry and exhibits a single ν_3 band, but coordination to a metal center lowers the symmetry to approximately C_{3v}, resulting in split bands in the infrared spectrum. The proposed formulation is thus incompatible with the spectroscopic data. Further heating of the complex results in an explosion at 330°C.

The extreme violence with which perchlorate complexes undergo thermal decomposition has also been noted in a study [30] comparing the thermochemistry of $ThCl_4$ and $Th(ClO_4)_4$ complexes of Me_2SO. Interestingly, the empirical formula of the chloride complex was reported to be $ThCl_4 \cdot 6$ Me_2SO, compared with $ThCl_4 \cdot 5$ Me_2SO previously reported [31] by Bagnall et al. Differential thermal analysis of $ThCl_4 \cdot 6$ Me_2SO is reported to result in an explosion at 485°C, yielding ThO_2 as the only solid product. Detection of $ThCl_4 \cdot 5$ Me_2SO or $ThOCl_2$, as described in Bagnall et al.'s analysis [31], was not mentioned. The perchlorate complex obtained preparatively was $Th(ClO_4)_4 \cdot 12$ Me_2SO, which lost six molecules of Me_2SO endothermically

at 180°C followed by an explosion at 290°C (compared with 485°C for the chloride).

In contrast to the actinides, few thermochemical studies of lanthanide perchlorate complexes have been reported. A series of tetramethylene sulphoxide (TMSO) complexes, $M(ClO_4)_3 \cdot 8$ TMSO, has been studied [37] by TG/DTA, both in air and in vacuum. The complexes themselves are rather unusual since the empirical formula is constant across the lanthanide series, despite the fact that the coordination number of the lanthanides normally decreases across the series, a result of the lanthanide contraction. Heating the complexes in vacuum causes the rapid onset of decomposition with the lighter metals losing two molecules of TMSO and the heavier metals (Er, Tm, Yb) losing approximately three molecules of TMSO in more than one step. A plot of the initial decomposition temperatures against the reciprocal ionic radii of the metals is horizontal up to Sm and then decreases rapidly. Conversely, a plot of the main peak temperatures (when the second or third molecule of TMSO is lost) against the reciprocal ionic radii shows a linear increase. Accordingly, it is proposed that loss of the first molecule of TMSO is governed by steric factors and thus is most favored for the smaller lanthanides, whereas loss of further TMSO is dependent upon the M–O bond strength and thus is most favorable for the heavier lanthanides, which form weaker bonds. The TG/DTA studies under nitrogen show shifts of the initial decomposition temperatures to higher temperature by approximately 50°C. The separate steps of decomposition were less well-defined under nitrogen. A phase transition at 73°C was noted for the samarium complex. In connection with this study, it is important to note that other workers [38] have isolated TMSO complexes of empirical formulae $M(ClO_4)_3 \cdot n$ TMSO (M = La, Ce, Pr, Nd, Sm, Eu, Gd, $n = 8$; M = Tb, Dy, Ho, Er, Y, $n = 7.5$; M = Tm, Yb, Lu, $n = 7$) in which the coordination number of the metals does indeed vary as predicted by the lanthanide contraction.

A study of the corresponding series of dimethylsulphoxide complexes, $M(ClO_4)_3 \cdot n$ Me$_2$SO (M = La to Gd, $n = 8$; M = Tb to Lu, $n = 7$) [39] shows no systematic relationship between the initial decomposition temperature and the inverse ion size, but the main peak temperatures show a linear increase with the reciprocal ionic radii, as for the TMSO complexes. The steric effects do not appear to be observed with the Me$_2$SO complexes because of the changing coordination number across the series, but the bond strength effects are, of course, still observed. Once again, other workers have reported series of $M(ClO_4)_3 \cdot n$ Me$_2$SO complexes with conflicting empirical formulae [40,41] for which explosive decomposition has been noted [40].

As with oxygen-bonded complexes of the d-block elements, the studies of lanthanide and actinide sulphoxide complexes are hindered by the lack of structural data and the proliferation of unsubstantiated and widely differing formulae for complexes isolated by similar, and sometimes identical, routes. Concerted thermochemical and structural studies would be of great value in this area.

SULPHUR-BONDED SULPHOXIDE COMPLEXES OF THE d-BLOCK ELEMENTS

Coordination of sulphoxides via sulphur has been unambiguously confirmed for complexes of Ru, Rh, Ir, Pd and Pt. Claims of sulphur-bonding in complexes of Cr(0), Mo(0), Fe(II), Os(II) and Hg(II), in addition to those mentioned in the preceeding sections, have been reported and recently discussed [7]. The thermochemistry of this small group of compounds has been examined, with several studies of Rh(II) complexes and a great many studies of Pt(II) complexes having appeared in the literature.

In 1963, it was observed [42] that rhodium acetate formed a complex with Me_2SO of stoichiometry $Rh_2(OOCCH_3)_4 \cdot 2 \ Me_2SO$. In common with the many reported adducts of rhodium acetate, spectroscopic data indicate that this complex has the acetate-bridged structure shown in Fig. 2. At this time, it was noted that heating at 120°C in an oven caused the loss of the two sulphoxide ligands, yielding anhydrous rhodium acetate. Later [43], a series of complexes, $Rh_2(OOCCH_3)_4 \cdot 2 \ L$, was examined by DSC under a flowing nitrogen atmosphere and the heats of reaction for the loss of both terminal ligands, eqn. (4), were determined. The data are given in Table 5.

$$Rh_2(OOCCH_3)_4 \cdot 2 \ L \rightarrow Rh_2(OOCCH_3)_4 + 2 \ L \tag{4}$$

The majority of the adducts underwent an initial loss of both ligands in a single step, but the sulphoxide complex proved to be an exception. It is also noteworthy that a secondary process was observed in the case of amine complexes, whereby the thermally generated amine attacked the acetate cage. The reaction of $Rh_2(OOCCH_3)_4 \cdot 2 \ Me_2SO$ was examined in further detail [44] and found to proceed according to

$$Rh_2(OOCCH_3)_4 \cdot 2 \ Me_2SO_{(s)} \rightarrow Rh_2(OOCCH_3)_4 \cdot Me_2SO_{(s)} + Me_2SO_{(g)} \tag{5}$$
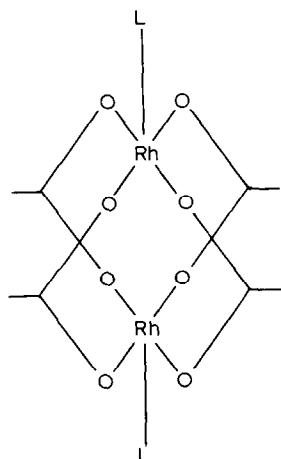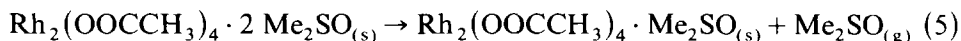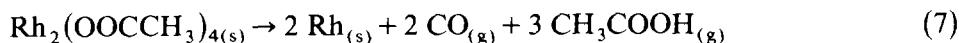

Fig. 2. The acetate-bridged structure of $Rh_2(OOCCH_3)_4 \cdot 2 \ L$.

TABLE 5

Heats of reaction and initial decomposition temperatures for the thermal decomposition of $Rh_2(OOCCH_3)_4 \cdot 2 L$

L	ΔH/kcal mole^{-1}	T_{dec}/°C
H_2O	23.2 ± 0.3	85
SEt_2	27.4 ± 0.6	84
Me_2SO	29.1 ± 0.8	147
NH_3	23.8 ± 0.4	130
$NHMe_2$	26.5 ± 0.5	135
NMe_3	24.7 ± 0.2	139
$NHEt_2$	33.1 ± 0.3	75
NEt_3	27.2 ± 0.5	76
pyridine	36.7 ± 0.5	170

$$Rh_2(OOCCH_3)_4 \cdot Me_2SO_{(s)} \rightarrow Rh_2(OOCCH_3)_{4(s)} + Me_2SO_{(g)} \qquad (6)$$

$$Rh_2(OOCCH_3)_{4(s)} \rightarrow 2\ Rh_{(s)} + 2\ CO_{(g)} + 3\ CH_3COOH_{(g)} \qquad (7)$$

The product $Rh_2(OOCCH_3)_4 \cdot Me_2SO$ was a new compound and could be isolated by heating $Rh_2(OOCCH_3)_4 \cdot 2\ Me_2SO$ in a N_2 atmosphere to 185°C, the temperature of final mass loss in the first stage of the reaction (by TG). The heat of reaction for eqn. (5) was determined by the difference between the heats of reaction for eqns. (4) and (6), yielding a value of ca. 10 kcal mole^{-1}. The initial decomposition temperatures of the $Rh_2(OOCCH_3)_4 \cdot 2\ L$ complexes, Table 5, follow the sequence $L = $ pyridine $> Me_2SO >$ amines $>$ EtS $\sim H_2O$. Whilst this sequence no doubt results from a combination of many factors, it is apparent that the steric and electronic properties of the ligands contribute to the observed order. Thus, taking electronically similar pairs of ligands, the order of the initial decomposition temperatures varies $NHMe_2 > NHEt_2$ and $NMe_3 > NEt_3$, relating to the increased steric bulk of the ethyl-substituted amines. The thioether and sulphoxide complexes exhibit very different initial decomposition temperatures, despite the fact that both complexes involve metal–sulphur bonding. Generally, it is observed [7] that analogous $M-S(O)R_2$ and $M-SR_2$ complexes have shorter $M-S$ bonds in the case of the sulphoxide than for the thioether when M is a late transition metal, indicating more favorable $M-S$ bonding in the former case.

The M–S bond strength is only one factor that must be taken into account when considering the thermal reactions of sulphoxide complexes. Another factor, which is particularly important in the chemistry of square-planar metal complexes, is the way in which one ligand can affect the lability of other ligands within the coordination sphere. It has long been known [45] that a certain ligand may affect the rate of substitution of a ligand *trans* to

itself in a metal complex. This is known as the *trans* effect and an approximate order of decreasing labilizing ability for some common ligands is [46, 47] $C_2H_4 \sim CO \sim CN^- > R_3P > R^- > SCN^- > I^- > Br^- > Cl^- > NH_3 > H_2O$. Theories based on both σ-bonding [48] and π-bonding [49,50] effects have been proposed to account for the *trans* effect. The *trans* effect is a kinetic phenomenon and a closely related ground-state property is referred to as the *trans* influence [51]. This is a property of a ligand that refers to its ability to lengthen (weaken) a bond *trans* to itself. Thus, in the case of a ligand such as carbon monoxide *trans* to a σ-donor such as Cl^-, the high degree of M–CO π-back bonding gives rise to a short metal to *trans*-ligand bond (i.e. a low *trans* influence) but promotes attack at the electron-poor region of the metal center (i.e. a high *trans* effect). Many authors use the terms *trans* effect and *trans* influence interchangeably, which can cause interpretational problems. A ligand's ability to affect a second ligand coordinated in a *cis* position is similarly governed by its *cis* effect and *cis* influence.

Much work has been done in order to elucidate the magnitudes of these properties for sulphoxides [52], largely by Kukushkin and co-workers. The square-planar geometry of most platinum(II) complexes makes them ideal candidates for the study of these properties and most work has centered on sulphoxide complexes of this metal. Added interest in the chemistry of platinum(II) sulphoxide complexes comes from their applications in homogeneous catalysis [7] and their potential as anticarcenogenic chemotherapeutic agents [52].

Much chemical evidence and spectroscopic data point to sulphoxides having a moderate *trans* influence and a high *trans* effect [7,52] and this aids in the understanding of much thermochemical data. For example, the equations

$$\textit{trans-}\left[PtCl_2(Me_2SO)(amine)\right] \rightarrow \textit{cis-}\left[PtCl_2(Me_2SO)(amine)\right] \qquad (8)$$

$$\textit{trans-}\left[PtBr_2(Me_2SO)(amine)\right] \rightarrow \textit{cis-}\left[PtBr_2(Me_2SO)(amine)\right] \qquad (9)$$

$$\textit{cis-}\left[PtI_2(Me_2SO)(amine)\right] \rightarrow \textit{trans-}\left[PtI_2(Me_2SO)(amine)\right] \qquad (10)$$
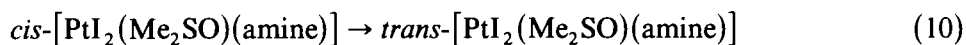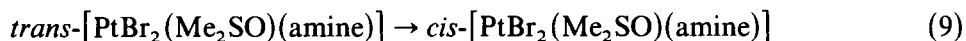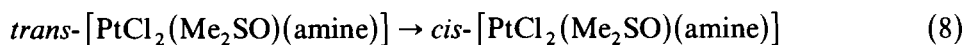
shows the isomerization reactions that occur [54] upon heating a series of $[PtX_2(Me_2SO)(amine)]$ complexes (X = Cl, Br, I; amine = ethanolamine).

These reactions are characterized by an endothermic effect, due to melting of the complex, followed by an exothermic effect due to the isomerization reaction and crystallization of the product from the melt. The course of the reaction is governed by the *trans* influences of the ligands coordinated to platinum. Series of ligands arranged according to their *trans* influence tend to vary slightly according to the probe used to estimate this property, but an accepted general order [51] (in this case derived from the magnitudes of NMR coupling constants) is carbon donors ($sp^3 \sim sp^2 > sp$) > phosphorus donors $\geqslant$ arsenic donors > sulphur donors > nitrogen donors > halides > oxygen donors. Among the halides, the order is $I^- > Br^- > Cl^-$ (from in-

frared studies) [51]. Thus, we would expect the ligands involved in eqns. (8)–(10) to be arranged in an approximate *trans* influence series $Me_2SO >$ $NH_3 > I^- > Br^- > Cl^-$. The thermal isomerization reactions will proceed such that the final product has the lowest and the highest *trans* influence ligands in mutually *trans* positions, thus relieving instability resulting from having two *trans* labilizing ligands *trans* to each other (i.e. having each trying to labilize the other); this arrangement frequently results when the kinetic product of a reaction is formed if a high *trans* effect ligand also has a high *trans* influence. In the case of the chloride and bromide complexes, eqns. (8) and (9), the *trans* complexes have the two highest *trans* influence ligands *trans* to each other (Me_2SO and NH_3) and hence isomerization occurs to produce a complex with NH_3 *trans* to Cl^- and Me_2SO *trans* to Cl^-, since Cl^- is the lowest *trans* influence ligand. Exactly the same explanation describes the bromide case. In eqn. (10), however, all of the ligands (I^-, NH_3 and Me_2SO) have a sizeable *trans* influence and the thermodynamic product has Me_2SO *trans* to NH_3, indicating that I^- has a higher *trans* influence than NH_3 and thus is reluctant to remain *trans* to the Me_2SO ligand. Accordingly, the approximate series mentioned above can be modified to the form $Me_2SO > I^- > NH_3 > Br^- > Cl^-$.

The *trans* effect and *trans* influence series have been used to explain many thermochemical and preparative results. For example, the reactions described [55] by eqns. (11) and (12) demonstrate that the *trans* effect series $Me_2SO > Cl^- > NH_3$ is operative.

$$
\begin{array}{ccc}
& \text{Cl} & \text{Cl} \\
& | & | \\
\text{Cl}-\text{Pt}-\text{S(O)Me}_2^- + \text{NH}_3 & \rightarrow & \text{H}_3\text{N}-\text{Pt}-\text{S(O)Me}_2 + \text{Cl}^- \\
& | & | \\
& \text{Cl} & \text{Cl}
\end{array} \tag{11}
$$

$$
\begin{array}{ccc}
& \text{Cl} & \text{Cl} \\
& | & | \\
\text{Cl}-\text{Pt}-\text{NH}_3^- + \text{Me}_2\text{SO} & \rightarrow & \text{Cl}-\text{Pt}-\text{NH}_3 + \text{Cl}^- \\
& | & | \\
& \text{Cl} & \text{S(O)Me}_2
\end{array} \tag{12}
$$
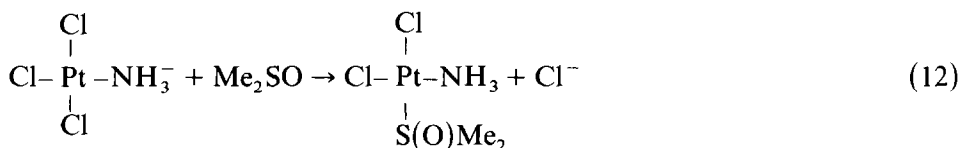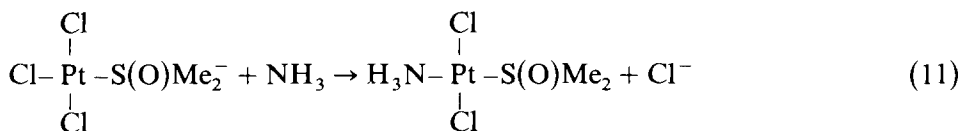
Subsequent DTA studies show that the *trans* isomer isomerizes to the *cis* form at 190°C, whereas the *cis* isomer undergoes no thermal isomerization processes. Accordingly, the *trans* influence series $Me_2SO > NH_3 > Cl^-$ is defined. The *trans* to *cis* isomerization of various $[PtCl_2(R_2SO)(amine)]$ complexes, and their bromo-analogues, has been noted on many occasions [57–61]. Some typical isomerization temperatures are given in Table 6.

The simple *trans*-$[MCl_2(Me_2SO)_2]$ (M = Pd, Pt) complexes do not undergo thermal isomerization [11,56], since decomposition occurs at the melting point (208°C for Pt, 187°C for Pd). The analogous *trans*-$[PtCl_2(R_2SO)_2]$ complexes (R = Et, *n*-Pr) similarly decompose without isomerization [61], although in chloroform solution, the *trans* to *cis* isomerization can be induced either thermally or photochemically [62]. In solution, the
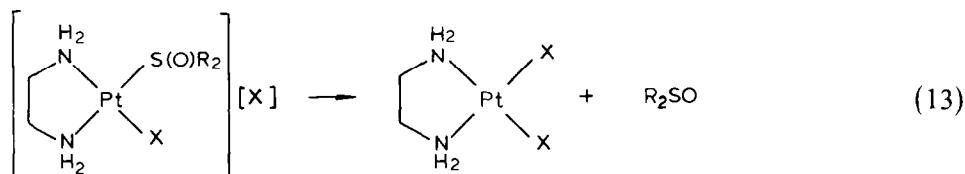
TABLE 6

Thermal isomerization temperatures of some *trans*-[PtX$_2$(R$_2$SO)(amine)] complexes

R$_2$SO	X	Amine	T_{isom}/°C	Ref.
Me$_2$SO	Cl	NH$_2$Me	172	56
Me$_2$SO	Cl	NH$_2$Et	168	56
Me$_2$SO	Cl	Piperidine	145	57
Me$_2$SO	Cl	Morpholine	a	57
Me$_2$SO	Br	Piperidine	130	57
Me$_2$SO	Br	Morpholine	a	57
TMSO	Cl	Pyridine	150	58
TMSO	Cl	NH$_3$	138	58
TMSO	Cl	NHEt$_2$	168	58
TMSO	Cl	NH$_2$Et	180	58
TMSO	Cl	Piperidine	160	58

a Decomposition without isomerization occurs at 165°C (chloride) and 185°C (bromide).

temperature dependence of the *trans / cis* equilibrium suggests that the *trans* isomer is enthalpy favored and the *cis* isomer is entropy favored [62].

Studies of the thermal decomposition of [PtL(NH$_3$)$_3$][X]$_2$ (L = Me$_2$S, Et$_2$S, Me$_2$SO; X = Cl, Br) [63] illustrate the point that both bond strength and *trans* influence play a part in deciding the mode of a thermal reaction. In each of these complexes, the sulphur donor is the highest *trans* influence ligand, but the metal–amine bonds are stronger than the metal–sulphur. Accordingly, as no isomerization of these complexes is possible, the first step in the thermal decomposition will be evolution of either ammonia or the sulphur donor. Prediction of which will leave is not possible since the bond strength and *trans* influence factors are mutually opposed. In practice, loss of ammonia is never found to occur [63], illustrating that the bond strength considerations are dominant in this case. A probable pathway for these thermal reactions involves displacement of the neutral ligand by the counterion; this class of reaction being observed [64] in reactions of [PtX(R$_2$SO)(H$_2$NCH$_2$CH$_2$NH$_2$)][X] (R = Me, Et, *n*-Pr; X = Cl, Br) according to

$$\begin{bmatrix} \text{H}_2 \\ \text{N} \quad \text{S(O)R}_2 \\ \quad \text{Pt} \\ \text{N} \quad \text{X} \\ \text{H}_2 \end{bmatrix} [\text{X}] \longrightarrow \begin{matrix} \text{H}_2 \\ \text{N} \quad \text{X} \\ \quad \text{Pt} \\ \text{N} \quad \text{X} \\ \text{H}_2 \end{matrix} + \text{R}_2\text{SO} \qquad (13)$$

Since the thermal decomposition represented by eqn. (13) is a one-step process, the activation energy could be calculated by Piloyan and Novikova's method [65] and the order of the reaction by Kissenger's method [66]. These

TABLE 7

Kinetic parameters derived for eqn. (13)

PtX(L)(H$_2$NCH$_2$CH$_2$NH$_2$)]X		E (kcal mole^{-1})	Order	k (440 K) (s^{-1})
L	X			
Me$_2$SO	Cl	47 ± 4	1.2	7.1×10^{-4}
Et$_2$SO	Cl	41 ± 2	1.1	1.2×10^{-3}
Pr$_2$SO	Cl	38 ± 2	0.8	5.0×10^{-3}
Me$_2$SO	Br	57 ± 4	1.2	8.7×10^{-4}
Et$_2$SO	Br	53 ± 4	1.0	2.6×10^{-3}
Pr$_2$SO	Br	46 ± 4	0.9	1.2×10^{-2}

data, together with the Arrhenius rate constants are given in Table 7. The most prominent feature of these data is the increase in activation energy: n-Pr$_2$SO < Et$_2$SO < Me$_2$SO, a possible consequence of steric factors with the bulkier sulphoxides.

Characterization of the decomposition products of platinum(II) sulphoxide complexes, following any major mass loss, has rarely been performed. In one example [67] thermolysis of cis-[PtCl$_2$(CO)(Me$_2$SO)] was shown to yield a polymeric material, [PtCl(SCH$_3$)]$_n$, and the simple [PtCl$_2$(Me$_2$SO)$_2$] complex yields a product with the empirical formula [Pt$_2$Cl$_2$(SCH$_3$)$_3$]. Whilst sulphoxide deoxygenation reactions are well-known from solution studies [7], the accompanying dealkylation reactions described here are exceptional.

Only a few studies of the thermal isomerization of platinum(IV) sulphoxide complexes have been described. In the case of cis-[PtCl$_4$(Me$_2$SO)$_2$] [68], an exothermic isomerization to the *trans* isomer occurs without mass loss over the range 128–164°C. The difference in the initial and final isomerization temperatures allowed a value of $-\Delta H = 2$ kcal mole^{-1} to be estimated for the process. Interestingly, the corresponding Et$_2$SO and TMSO complexes of platinum(IV) undergo isomerization with no detectable exothermic effects [69], possibly due to masking by large endothermic fusion processes.

Whilst considerable effort has gone into the study of platinum(II) sulphoxide complexes and, to a lesser extent, rhodium(II) and platinum(IV) complexes, the thermochemistry of the remaining elements forming sulphur-bonded R$_2$SO complexes has been largely neglected, despite the particularly rich and varied coordination chemistry of these compounds [7].

CONCLUSIONS

Thermochemistry has clearly played an important role in the development of sulphoxide coordination chemistry and yet it is quite apparent that much

remains to be accomplished. The lack of correlation between structural and thermochemical data make the utility of some reports questionable. There is no doubt that there is commercial interest in many areas of sulphoxide coordination chemistry and yet our knowledge in such areas is limited. The chemistry described by eqn. (3), for example, represents the thermal conversion of $NiCl_2 \cdot 8\ Me_2SO$ into $NiCl_2 \cdot 3\ Me_2SO$ and, ultimately, $NiCl_2 \cdot Me_2SO$. The structures of all three of these compounds are unknown and yet $NiCl_2 \cdot Me_2SO$ has been patented [70] as a co-catalyst for olefin dimerization and $NiCl_2 \cdot Me_2SO$ as a co-catalyst specifically for the dimerization of propylene [71]. It is surprising that studies on such potentially important compounds are so limited and it is hoped that this review will help in providing a stimulus to correct these deficiencies.

REFERENCES

1   R.G. Pearson (Ed.), Hard and Soft Acids and Bases, Dowden, Hutchinson and Ross, Stroudsberg, U.S.A., 1973.
2   Yu.E. Nikitin, Yu.I. Murinov and A.M. Rozen, Russ. Chem. Rev., 45 (1976) 1155.
3   J. Gopalakrishnan and C.C. Patel, J. Sci. Ind. Res., 27 (1968) 475.
4   W.L. Reynolds, Prog. Inorg. Chem., 12 (1970) 1.
5   A. Tenhunen, Suom. Kemistil, A, 46 (1973) 147.
6   Yu.N. Kukushkin, Usp. Khim. Koord. Soedin., (1975) 248.
7   J.A. Davies, Adv. Inorg. Chem. Radiochem., 24 (1981) 115.
8   H. Dehn, U.S. Pat. 3,463,684 (1969).
9   H. Dehn, U.K. Pat. 1,129,777 (1968).
10   M. Glavas and T. Skerlak, Glas. Hem. Tehnol. Bosne Hercegovine, 15 (1967) 41.
11   M. Glavas and T. Skerlak, Glas. Hem. Tehnol. Bosne Hercegovine, 15 (1967) 31.
12   K. Chang, Diss. Abstr. Int. B., 32 (1971) 2626.
13   K. Chang and R.D. Willet, Inorg. Chim. Acta, 4 (1970) 467.
14   M. Glavas and T. Skerlak, Glas. Hem. Drus. Beograd, 31 (1968) 439.
15   M.A. Bennett, F.A. Cotton and D.A. Weaver, Nature (London), 212 (1966) 286.
16   M.A. Bennett, F.A. Cotton and D.A. Weaver, Acta Crystallogr., 23 (1967) 581.
17   C.R. Kanekar, S.V. Nipankar and V.P. Marathe, Indian J. Chem., 8 (1970) 451.
18   P. Faugeras, G. Laurence, P. Michel and J. Talbot, Fr. Pat. 2,263,307 (1974).
19   A.M. Reznik, Yu.A. Tsylov and A.N. Turanov, Zh. Prikl. Khim., 49 (1976) 201.
20   V.G. Maiorov and A.I. Nikolaev, U.S.S.R. Pat. 479,734 (1973).
21   A.G. Babkin, V.G. Maiorov and A.I. Nikolaev, Khim. Tekhnol. Pererab. Redkomet. Syr'ya Kol'sk. Poluostrova, (1972) 111.
22   V.V. Savant and C.C. Patel, J. Inorg. Nucl. Chem., 31 (1969) 2319.
23   J. Selbin, Coord. Chem. Rev., 1 (1966) 293.
24   K. Wuthrich and R.E. Connick, Inorg. Chem., 7 (1968) 1377.
25   C.C. Patel and D.N. Sathyanaranyana, Indian J. Chem., 5 (1967) 360.
26   T.C.W. Mak, Can. J. Chem., 46 (1968) 3491.
27   D.B. Copley, F. Fairbrother, K.H. Grundy and A. Thompson, J. Less Common Met., 6 (1964) 407.
28   V. Krishnan and C.C. Patel, J. Inorg. Nucl. Chem., 27 (1965) 244.
29   F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Wiley, New York, 3rd edn., 1972, pp. 808, 927.
30   V. Krishnan and C.C. Patel, J. Inorg. Nucl. Chem., 26 (1964) 2201.

31 K.W. Bagnall, D. Brown, P.J. Jones and J.G.H. du Preez, J. Chem. Soc. A., (1966) 737.
32 J.G.H. du Preez and M.L. Gibson, J. Inorg. Nucl. Chem., 36 (1974) 1795.
33 K.W. Bagnall, D. Brown, D.H. Holah and F. Lux, J. Chem. Soc. A., (1968) 465.
34 J.D. Ortego, M. Schober and J. Selbin, J. Inorg. Nucl. Chem., 28 (1966) 1385.
35 O.M. Ivanova, K.I. Petrov, A.K. Molodkin, O.D. Saralidze and L.E. Kozina, Russ. J. Inorg. Chem., 13 (1968) 693.
35a A.K. Molodkin, O.M. Ivanova, Z.V. Belyakova and L.E. Kolesnikova, Russ. J. Inorg. Chem., 15 (1970) 1692.
36 V. Krishnan and C.C. Patel, Indian J. Chem., 2 (1964) 416.
37 K. Nagase, H. Yokobayashi, A. Iwase and K. Sone, Thermochim. Acta, 17 (1976) 335.
38 G. Vicentini and L.B. Zinner, Inorg. Nucl. Chem. Lett., 7 (1971) 967.
39 A. Iwase and S. Tade, Nippon Kagaku Kaishi, (1973) 60.
40 F. Kutek, Collect. Czech. Chem. Commun., 33 (1968) 1341.
41 V.N. Krishnamurthy and S. Soundararajan, J. Inorg. Nucl. Chem., 29 (1967) 517.
42 J. Kitchens and J.L. Bear, J. Inorg. Nucl. Chem., 2 (1963) 960.
43 J. Kitchens and J.L. Bear, J. Inorg. Nucl. Chem., 31 (1969) 2415.
44 J. Kitchens and J.L. Bear, J. Inorg. Nucl. Chem., 32 (1970) 49.
45 F. Basolo and R.G. Pearson, Prog. Inorg. Chem., 4 (1962) 381.
46 F. Basolo, Adv. Chem. Ser., 49 (1965) 81.
47 T.P. Cheeseman, A.L. Odell and H.A. Raethal, Chem. Commun., (1968) 1496.
48 A.A. Grinberg, Ann. Inst. Platine (USSR), 5 (1927) 109.
49 J. Chatt, L.A. Duncanson and L.M. Venanzi, J. Chem. Soc., (1955) 4456.
50 L. Orgel, J. Inorg. Nucl. Chem., 2 (1956) 137.
51 T.G. Appleton, H.C. Clark and L.E. Manzer, Coord. Chem. Rev., 10 (1973) 335.
52 Yu.N. Kukushkin, Chem. Zvesti, 25 (1971) 380.
53 C.J.L. Lock, R.A. Speranzini, G. Turner and J. Powell, J. Am. Chem. Soc., 98 (1976) 7865.
54 Yu.N. Kukushkin and V.F. Lobantsova, Russ. J. Inorg. Chem., 22 (1977).
55 Yu.N. Kukushkin, Yu.E. Vyaz' menskii and L.I. Zorina, Russ. J. Inorg. Chem., 13 (1968) 1573.
56 Yu.N. Kukushkin, Yu.E. Vyaz' menskii and E.S. Postnikova, Zh. Prikl. Khim., 42 (1969) 926.
57 Yu.N. Kukushkin and V.A. Yurinov, Russ. J. Inorg. Chem., 16 (1971) 601.
58 Yu.N. Kukushkin and Ts. Naidenova-Tolorova, Russ. J. Inorg. Chem., 17 (1972) 559.
59 Yu.N. Kukushkin, A.I. Stetsenko, S.G. Strelin and V.G. Duibanova, Russ. J. Inorg. Chem., 17 (1972) 561.
60 Yu.N. Kukushkin and E.D. Ageeva, Russ. J. Inorg. Chem., 17 (1972) 767.
61 Yu.N. Kukushkin and V.N. Spevak, Russ. J. Inorg. Chem., 18 (1973) 240.
62 J.H. Price, J.P. Birk and B.B. Wayland, Inorg. Chem., 17 (1978) 2245.
63 E.A. Andronov, Yu.N. Kukushkin, T.M. Lukicheva, V.P. Kotel'nikov and Yu.S. Shcherbakov, Russ. J. Inorg. Chem., 21 (1976) 1632.
64 Yu.N. Kukushkin, V.P. Kotel'nikov and V.N. Spevak, Russ. J. Inorg. Chem., 22 (1977) 1194.
65 G.O. Piloyan and O.S. Novikova, Russ. J. Inorg. Chem., 12 (1967) 313.
66 F.S. Freeman and B. Carrol, J. Phys. Chem., 62 (1958) 394.
67 I.V. Pakhomova, Yu.N. Kukushkin, Yu.N. Martynov and N.A. Gudova, Zh. Obshch. Khim., 51 (1981) 2292.
68 Yu.N. Kukushkin, G.N. Sedova, E.A. Andronov and T.M. Lukicheva, Russ. J. Inorg. Chem., 23 (1978) 1751.
69 Yu.N. Kukushkin, E.A. Andronov, G.N. Sedova and T.M. Lukicheva, Russ. J. Inorg. Chem., 26 (1981) 377.
70 G. Desgrandchamps, H. Hemmer and M. Haurie, Ger. Offen. 1,964,701 (1970).
71 G. Desgrandchamps, H. Hemmer and M. Haurie, Ger. Offen. 2,001,923 (1970).