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Structure and bonding in metal sulfoxide complexes

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Abstract

Structural parameters of free and coordinated sulfoxides are comprehensively reviewed and average values derived. Principal component analyses have been performed in order to evidence the deformation pathways of sulfoxides upon coordination. Electronic and steric factors affecting the bonding mode of sulfoxides are discussed.

Keywords: Metal sulphoxide complexes

Abbreviations

AEPSO	aminoethylpyridyl sulfoxide
BMSP	1,3-bis(methylsulfinyl)propane
BMSE	1,2-bis(methylsulfinyl)ethane
BESE	1,2-bis(ethylsulfinyl)ethane
BPSE	1,2-bis(propylsulfinyl)ethane
BPSO	1,2-bis(phenylsulfinyl) ethane
BPESO	1,2-bis(phenylsulfinyl) ethylene
CASO	cysteamine sulfoxide
DBSO	dibenzyl sulfoxide
DESO	diethyl sulfoxide
DHSO	2,5-dihydrothiophene 1-oxide
DMSO	dimethyl sulfoxide
DiBSO	di-*i*-butyl sulfoxide
DnBSO	di-*n*-butyl sulfoxide
DiPSO	di-*i*-propyl sulfoxide
DnPSO	di-*n*-propyl sulfoxide
DTCSO	1,5-dithiacyclooctane 1-oxide
DTSO	2,5-dihydrothiophene 1-oxide
DPSO	diphenyl sulfoxide
EPSS	bis(3-(ethylsulfinyl)propyl sulfide
ETPSO	3-(ethylthio)-1-((3-(ethylthio)propyl)sulfinyl)propane
ETSO	dimethylene sulfoxide

MBSO	methylbenzyl sulfoxide
MCSO	methylcysteine sulfoxide
MESO	methylethylsulfoxide
MetSO	methionine sulfoxide
MPASO	3-methyl sulfinyl propylammine
MPSO	methylphenyl sulfoxide
MTSO	methyl-*p*-tolyl sulfoxide
PMSO	pentamethylene sulfoxide
tBMSO	*t*-butylmethyl sulfoxide
TMSO	tetramethylene sulfoxide

1. Introduction

After the first few reports on transition metal complexes with sulfoxides in the early sixties [1], the chemistry of this class of compounds has increased both quickly and widely.

The interest in these compounds stemmed, in part from the fact that they are useful starting materials for the synthesis of new organometallic and coordination compounds [2] and, in part from their role as possible intermediates in homogeneous catalytic processes [2,3]. In addition, special interest was aroused about the potential applications of ruthenium complexes in medicinal chemistry, both as antitumor agents [4], and as radiosensitizers [5]. Further, they have been studied widely in basic coordination chemistry, for the ambidentate nature of sulfoxides, and their cis and trans effects [2].

All these studies are related, in some way, to the strength and nature of the metal–sulfoxide bond. Therefore, the understanding of the parameters affecting the bonding mode of sulfoxides in metal complexes is a fundamental aspect of their coordination chemistry.

In 1981 Davies surveyed the chemistry of transition metal complexes with sulfoxides up to 1979, with particular reference to the sulfoxide bonding mode, including a discussion of the different physical methods applied [2].

More recently, the chemistry of sulfoxides has been reviewed, including theoretical and structural aspects of gaseous sulfoxides [6]. Some aspects of their coordination chemistry to transition metals have also been reported recently [7].

Since Davies's review was not intended to provide an exhaustive listing of all known sulfoxide complexes, and a great many new and more accurate X-ray structural determinations appeared in the last decade, we thought it could be of interest to collect the available structural data, in order to evaluate average geometries of free and coordinated sulfoxides.

The evaluation of the mean molecular dimensions, together with the investigation of the stereochemistry of the metal–sulfoxide bonds, can contribute to the understanding of the electronic and steric basis of such bonds.

In addition, average molecular dimensions may provide reliable 'standard' bond lengths and angles for model building applications, as well as for MO and semiempirical molecular energy calculations.

In order to elucidate the deformation pathways of sulfoxides, upon coordination, principal component analyses (PCA) have been carried out. In fact, the use of PCA in structure correlation studies is by now a well established tool [8]. A brief outline of the method is given in Appendix 2.

For the sake of clarity, we will first discuss the geometry of free sulfoxides and their interaction with hydrogen ions, providing relevant average dimensions, and their chemical interpretation. Then, we will discuss the structure and bonding in metal complexes, with particular regard to the electronic and stereochemical aspects.

Tables of supplementary material are available on request from the authors.

1.1. Treatment of data

It has been shown that, for crystallographic data, the best estimate of the mean value of n observations, x_i, is provided by the 'semi-weighted' mean, which takes into account both experimental errors and 'environmental' effects, like those derived from crystal packing [9]. Relevant expressions are given in Appendix 1.

Since it is well known that the ESDs derived from least-squares techniques are usually underestimated, it has been suggested that they should be multiplied by a factor in the range 1.3–2.0, to reflect the true experimental uncertainties in the observations [9]. In this article, the individual ESDs (quoted in parentheses) are multiplied by 1.3.

Disordered structures or structures of very low accuracy have not been taken into account. Bond distances with quoted $\sigma(x_i) > 0.01$ Å, and bond angles with $\sigma(x_i) > 1°$, even if listed, are not included in the calculation of the means, as well as values without ESDs. Data not included, for the above or any other reason, in the statistics are printed in italics. In PCA, structures were rejected when $\sigma(x_i)$ of one of its structural parameters was >0.01 Å, for bond lengths, or $>1°$, for bond angles.

A bibliographic search has been performed through the Cambridge Structural Database up until 1991 [10]. Further references have been searched in the main journals and should cover publications up to 1994, with a few quotations in 1995. We apologize for all the structures that we have unwillingly omitted.

2. Molecular structure of uncoordinated sulfoxides

2.1. Estimation of mean molecular dimensions

The crystal structure of the dimethyl sulfoxide (DMSO) (I) has been determined in 1966 at −60 °C [11] and +5 °C [12], yielding quite different S–O bond distances (Table 1). According to Bennett et al. [13], many authors have assumed that the reference value of the S–O bond length, for comparison between coordinated and uncoordinated DMSO, should be that of 1.531(5) Å, reported for the second structure determination. This, in fact, is nearer to room temperature (at which the vast majority

Table 1
Bond lengths (Å) and angles (°) of uncoordinated DMSO[a]

State	S–O	S–C	C–S–C	O–S–C	Ref.
Gas	*1.485(6)*	*1.799(5)*	*96.57(3)*	*106.65(3)*	[60]
−60 °[b]	*1.471*	*1.812*	*97.86*	*107.04*	[11]
		1.801		*107.43*	
+5 °	1.513(5)	1.771(8)	98.2(4)	106.7(4)	[12]
		1.81(1)		107.5(4)	
Solvate	1.488(5)	1.764(9)	98.0(4)	105.7(3)	[14]
		1.732(8)		106.8(4)	
Solvate	1.483(4)	1.775(3)	98.4(1)	107.8(2)	[15]
		1.776(3)		106.1(2)	
	1.502(3)	1.777(3)	98.6(1)	105.6(2)	
		1.775(3)		105.2(2)	
Solvate	*1.44(2)*	*1.78(2)*	99(1)	108(1)	[16]
		1.78(2)		105(1)	
Solvate[b]	*1.495*	*1.735*	*98.3*	*108.6*	[17]
Solvate	1.494(4)	1.766(5)	97.8(2)	105.5(2)	[18]
		1.759(6)		106.2(3)	
Solvate	1.493(4)	1.794(7)	97.8(5)	107.3(3)	[19]
		1.768(8)		104.7(3)	
Solvate	1.494(7)	1.75(1)	96.3(5)	106.8(5)	[20]
		1.78(1)		105.4(4)	
Solvate	*1.499(5)*[c]	1.76(1)	100.1(4)	103.7(4)	[21]
		1.756(9)		105.9(4)	
Solvate	*1.503(1)*[c]	1.731(6)	96.9(2)	104.9(2)	[22]
		1.812(4)		105.2(2)	
Solvate	*1.504(4)*[c]	1.796(8)	95.5(4)	105.2(3)	[23]
		1.778(7)		107.5(3)	
Solvate	*1.508(2)*[c]	1.776(2)	99.5(1)	105.1(1)	[24]
		1.769(3)		104.5(1)	
Solvate[b]	*1.52*[c]	*1.73*	*100*	*105*	[25]
		1.74		*104*	
Solvate	*1.526(4)*[c]	1.73(1)	97.6(5)	105.6(4)	[26]
		1.80(1)		104.5(5)	
Solvate	*1.529(8)*[c]	1.80(1)	98.8(5)	104.1(5)	[27]
		1.789(9)		104.4(5)	
n	7	26	14	28	
σ	0.010	0.022	1.2	1.2	
$\langle x\rangle_s$	1.495	1.773	98.0	105.7	
$\sigma(\langle x\rangle_s)$	0.004	0.004	0.3	0.2	

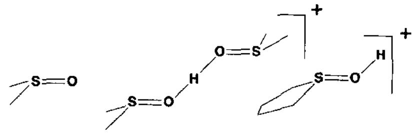
[a] Figures in italics are not included in the calculation of the mean. [b] ESDs not reported. [c] S–O involved in hydrogen bonding.

of structures have been solved) and seems better refined. However, it should be noted that the value of 1.531 Å has been obtained after correction for thermal motion, while most of the S–O bond lengths reported for metal complexes refer to uncorrected values. Thus, the uncorrected value of 1.513(5) Å [12] would appear more appropriate in this regard. At any rate, it is worth noting that the structure determination accuracy was not very high ($R = 0.074$).

Further, this value appears slightly longer than the S–O bond distances in DMSO solvates (Table 1), where the ligand is involved in weak intermolecular interactions, resembling free DMSO (range, 1.483(4)–1.502(3) Å) [14–20]. The average value of the S–O bond length in DMSO solvates is 1.495(4) Å. Table 1 shows that slightly longer distances (up to 1.529(8) Å) occur when the oxygen atom of the sulfoxide is involved in strong and/or multiple hydrogen bonds [21–27].

Further, the S–O bond distances in other free sulfoxides (Table 2) are markedly below 1.53 Å, ranging from 1.478(4) to 1.508(3) Å, with an average value of 1.492(1) Å [28–41]. As for DMSO, a lengthening is observed when strong hydrogen bonds are present (1.517(3)–1.521(3) Å) [42–44]. A similar trend is observed in the solid state structures of cyclic sulfoxides (Table 3) [45–48].

Markedly longer values (1.528(4)–1.559(2) Å) are found (Table 4) when the interaction with hydrogen becomes much stronger, as in the protonated dimers $[(DMSO)_2H]^+$ (II) [49–53] and $[(DnPSO)_2H]^+$ [54]. Even longer distances are found in the monomers, up to 1.585(8) Å in $[(DMSO)H]^+$ [27], and 1.589(3) Å in $[(TMSO)H]^+$ (III) [55].



I II III

Shorter values, such as 1.408(5) [56] and 1.46 Å [57], have been found in $[(DMSO)H][trans\text{-}MCl_4(DMSO)_2]$ compounds (M = Ru, Rh), but they correspond to disordered dimethylsulfoxonium structures.

In $[(DMSO)_2H]^+$ the hydrogen ion is usually shared by the two oxygen atoms forming "symmetrical" hydrogen bonds. However, in the tellurium derivative, $[(DMSO)_2H][TeCl_6 \cdot 2(DMSO)]$ [27], H^+ was found to be bound to the oxygen of only one DMSO molecule showing the presence of $[(DMSO)H]^+$ species, hydrogen bonded to the second one. This is in agreement with one long S–O bond distance (1.585(8) Å), comparable to that of 1.589(3) Å in $[(TMSO)H]^+$.

It is interesting to observe that the S–O bond distances reported in the H-bonded species are not too far from the value of 1.524 Å calculated for sulfinyl carbanions, $[R'\text{-}S(O)\text{–}R'']^-$ [58], which is further lengthened up to 1.58(1) Å in the lithium complex, α-(phenylsulfinyl)-α-methylbenzyllithium-tetramethylenediamine [59], resembling the hydrogen ion behavior.

Averaging the S–O bond distances of Tables 1, 2 and 3, with the exclusion of the values of the low temperature and gas phase determinations and of the compounds involved in strong hydrogen bonds, we obtain the mean value of 1.492(1) Å. The standard deviation of the set of data used is 0.009 Å (Table 5). It is interesting to observe that this average value compares well to that of 1.485(6) Å, obtained by gas phase microwave spectroscopy on various isotopically substituted DMSO species

Table 2
Bond lengths (Å) and angles (°) of uncoordinated sulfoxides R′R″SO, different from DMSO

R′	R″	S–O	S–C(R′)	S–C(R″)	C–S–C	O–S–C(R′)	O–S–C(R″)	Ref.
Ph	Ph	1.47(2)	1.76(2)	1.76(2)	97(1)	106(1)	106(1)	[28]
Ph	$PhS(O)(CH_2)_2$[b]	1.487(2)	1.798(3)	1.814(4)	98.5(1)	107.2(1)	106.6(1)	[29]
Ph	$PhS(O)(CH_2)_2$[c]	1.489(6)	1.789(6)	1.822(6)	98.2(3)	106.9(3)	105.6(3)	[30]
		1.494(6)	1.806(5)	1.828(7)	98.6(3)	106.7(3)	105.7(3)	
Ph	R-1-heptanyl[d]	1.495(1)	1.804(2)	1.822(2)	98.3(1)	106.2(1)	106.5(1)	[31]
		1.497(3)	1.789(5)	1.829(4)	96.7(2)	106.8(2)	106.6(2)	
Ph	2-Ph-1-R-vinyl[e]	1.484(2)	1.794(3)	1.801(3)	97.6(1)	107.0(1)	106.0(1)	[32]
Ph	norbornenyl[f]	1.508(3)	1.796(4)	1.823(4)	97.7(2)	106.0(2)	109.0(2)	[33]
Ph	norbornenyl[g]	1.492(3)	1.809(4)	1.825(4)	97.6(2)	107.2(2)	106.7(2)	[33]
		1.498(3)	1.801(4)	1.830(4)	98.0(2)	106.4(2)	106.2(2)	
Ph	norbornenyl[h]	1.500(2)	1.796(3)	1.816(2)	97.6(1)	107.1(1)	105.2(1)	[33]
		1.498(2)	1.794(3)	1.811(2)	98.4(1)	107.1(1)	105.0(1)	
Ar[i]	R-cyclopropyl[j]	1.487(6)	1.783(8)	1.783(9)	101.9(3)	106.8(4)	109.6(4)	[34]
Me	R-l-heptanyl[d]	1.496(3)	1.791(4)	1.823(2)	95.8(1)	106.9(2)	106.5(1)	[35]
Me	R-l-heptanyl[k]	1.492(9)	1.81(1)	1.84(1)	97.8(5)	104.2(6)	105.6(5)	[36]
Me	$MeS(O)(CH_2)_2$[b]	1.499(2)	1.786(2)	1.801(2)	97.0(1)	106.8(1)	106.3(1)	[37]
Me	2-I-l-thienyl	1.486(5)	1.808(9)	1.774(6)	97.6(4)	106.1(4)	105.7(3)	[38]
		1.499(5)	1.791(7)	1.757(6)	98.3(4)	106.2(3)	105.9(3)	[38]
Me	3-I-2-thienyl	1.50(2)	1.78(2)	1.78(2)	99(1)	105(1)	104.8(8)	[38]
Me	1-Br-3-I-2-thienyl	1.47(2)	1.79(2)	1.79(3)	99(1)	106(1)	107(1)	[38]
Me	3-I-2-furyl	1.50(1)	1.81(2)	1.77(1)	98.2(6)	104.6(7)	104.6(7)	[38]
Me	1-I-2-furyl	1.507(7)	1.77(1)	1.754(8)	98.8(5)	106.8(5)	106.1(4)	[38]
Me	2,3-F-Ph	1.486(2)	1.792(3)	1.798(2)	96.9(1)	105.9(1)	105.7(1)	[39]
Me	3,4-F-Ph	1.478(3)	1.789(6)	1.786(4)	97.0(2)	105.6(3)	107.4(2)	[39]
		1.478(4)	1.779(6)	1.800(4)	98.6(2)	107.6(2)	105.7(2)	[39]
Me	2,5-F-Ph	1.485(2)	1.793(3)	1.797(2)	97.1(1)	106.7(1)	106.0(1)	[39]
Me	3,5-F-Ph	1.498(4)	1.785(8)	1.788(6)	96.4(3)	106.6(3)	107.1(3)	[39]
Me	2,4,6-F-Ph	1.492(3)	1.782(6)	1.788(4)	97.7(2)	107.6(2)	107.5(2)	[39]
Me	2,6-Cl-Ph	1.48(1)	1.78(2)	1.82(2)	98.4(7)	108.0(7)	108.5(6)	[39]
Me	$2\text{-}NO_2\text{-}Ph$	1.499(3)	1.803(4)	1.820(3)	95.7(2)	104.2(2)	105.3(1)	[39]
Me	4-MePh[l]	1.493(6)	1.796(6)	1.797(6)	97.6(3)	105.5(3)	106.5(3)	[40]
Me	$2\text{-}CO_2MePh$	1.494(2)	1.801(3)	1.816(2)	97.2(2)	104.7(2)	105.0(2)	[41]
Ar[m]	$2\text{-}CO_2MePh$	1.491(1)	1.828(1)	1.828(1)	96.6(1)	104.1(1)	104.1(1)	[41]
Ar[m]	$2\text{-}NO_2\text{-}Ph$	1.490(1)	1.820(2)	1.822(2)	97.0(1)	104.8(1)	104.0(1)	[41]
Ar[n]	$2\text{-}NO_2\text{-}Ph$	1.481(2)	1.824(2)	1.825(2)	95.8(2)	104.2(1)	104.4(2)	[41]
Ar[n]	$2\text{-}CH_2CO_2MePh$	1.487(1)	1.808(1)	1.820(1)	98.5(1)	104.0(1)	104.7(1)	[41]
Me	2,2-Ph-Ar-vinyl[o]	*1.521(3)*[a]	1.827(4)	1.772(8)	96.5(2)	103.7(2)	104.3(2)	[42]
Me	$2\text{-}CO_2H\text{-}Ph$[p]	*1.517(2)*[a]	1.788(5)	1.800(3)	97.8(2)	104.6(2)	103.1(1)	[43]
Me	$2\text{-}CO_2H\text{-}Ph$[l]	*1.517(3)*[a]	1.782(6)	1.800(5)	98.8(2)	104.4(2)	103.7(2)	[44]
n		33	32[q]	18[r]	39	39	39	
σ		0.008	0.019	0.016	1.1	1.2	1.4	
$\langle x\rangle_s$		1.492	1.805	1.790	97.7	106.0	105.9	
$\sigma(\langle x\rangle_s)$		0.001	0.003	0.004	0.2	0.2	0.2	

[a] Figures in italics are not included in the calculation of the mean, because of hydrogen bonding. [b] (*R*,*S*) isomer. [c] (*S*,*S*) isomer. [d] R = 3,3,5,5-Tetramethyl-7-oxabicyclo[4.1.0]. [e] R = COOMe. [f] Exo-(2*R*,8*S*)-isomer. [g] Exo-(2*RS*,8*RS*)-isomer. [h] Endo-(2*SR*,8*SR*)-isomer. [i] Ar = *p*-Tolyl. [j] R = Ethyl(2*R*,3*R*,5*R*)-3-(ethoxycarbonyloxy)-1-pyrrolidinecarboxylate. [k] R = 3,3,5,5-Tetramethyl-7-oxabicyclo[4.1.0]-2-ol. [l] Optically active form (+). [m] Ar = $2\text{-}CO_2Me\text{-}Ph$. [n] Ar = $2\text{-}NO_2\text{-}Ph$. [o] Ar = 3′,4′-dimethylphenyl. [p] Racemic form. [q] S–C(sp^3). [r] S–C(sp^2) in groups different from substituted phenyls, for which (n = 19, σ = 0.015) $\langle x\rangle_s$ = 1.809(3) Å.

Table 3
Bond lengths (Å) and angles (°) of uncoordinated cyclic sulfoxides R′R″SO

State	Size[a]	S–O	S–C(R′)	S–C(R″)	C–S–C	O–S–C(R′)	O–S–C(R″)	Ref.
Gas[1]	4	1.484(3)	1.828(4)[b]		92.0(3)	110.0(4)		[61]
Gas[2]	6	1.483(3)	1.816(4)[b]		91.1(7)	108.1(3)		[62]
Crystal[3]	5	1.49(1)	1.86(2)[b]	1.84(2)[b]	88(1)	106(1)	104(1)	[45]
Crystal[4]	5	1.487(5)	1.82(1)[b]	1.879(6)[b]	92.5(4)	106.3(4)	108.6(3)	[46]
Crystal[5]	5	*1.512(5)*[d]	*1.786(5)*[c]	1.815(6)[b]	91.2(3)	106.4(2)	106.4(3)	[47]
Solvate[1]	5	*1.53(2)*[d]	1.79(3)[b]	1.82(3)[b]	93(1)	106(1)	106(1)	[48]

[a] No. of atoms in the sulfinyl ring. [b] $C(sp^3)$. [c] $C(sp^2)$. [d] S–O involved in hydrogen bonding.
[1] Tetramethylene sulfoxide. [2] Hexamethylene sulfoxide. [3] Cloxacillin sulfoxide. [4] (*E*)-2-Methylthio-2-(3-oxobutyl)thiolane 1-oxide. [5] 2,3-Dihydro-3-(2-hydroxyethylthio)-1-benzo[*b*]thiophene 1-oxide.

(Table 1) [60]. It is remarkable that similar values (1.484(3) and 1.483(3) Å) were determined by electron diffraction for tetra- and hexa-methylene sulfoxides (Table 3) [61,62].

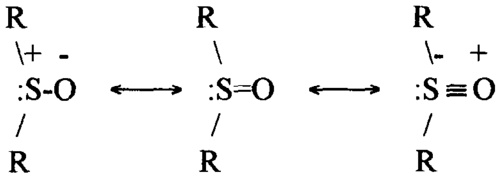
2.2. Electronic and conformational properties of free sulfoxides

The average value of 1.492 is consistent with a considerable double bond character in the S–O bond, being markedly shorter than 1.66 Å [12] or 1.68 Å [63], expected for a single S–O bond. As reported by Davies, X-ray spectroscopy has shown that free sulfoxide molecules are polarized, with a net positive charge localized on the sulfur atom [2]. Polarized structures, with a net positive charge on sulfur, are also predicted by MO calculations [39].

These observations, together with the relatively short S–O bond distance, indicate that in the valence bond representation of the sulfoxide structure as a resonance hybrid of three canonical forms, the first two are largely predominant.

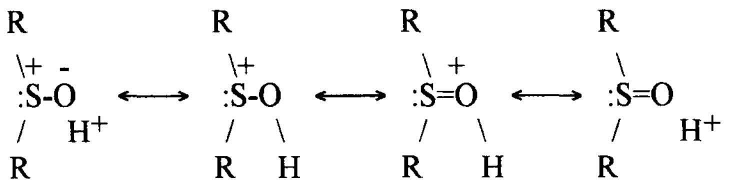
This bonding scheme is also in agreement with the observed lengthening of the S–O bond distance in hydrogen bonded and, specially, in protonated species. In this case, in fact, single bond forms become more important, reducing the bond order.

The weakening of the S–O bonds in protonated species is shown clearly by the decrease of the S–O stretching frequency, from 1022 cm^{-1} in free TMSO to 897 cm^{-1} in [(TMSO)H]$^+$, and from 1055 cm^{-1} in free DMSO to 869 and 865 cm^{-1} in [(DMSO)H]$^+$, for ruthenium and rhodium anionic complexes, respectively [64].



$$R_2\ddot{S}^{+}\text{–}O^{-} \longleftrightarrow R_2\ddot{S}{=}O \longleftrightarrow R_2\ddot{S}^{-}{\equiv}O^{+} \qquad (1)$$

Structure 1


(2)

Structure 2

Table 4
Bond lengths (Å) and angles (°) in protonated sulfoxides

Cation	S–O	S–C	C–S–C	O–S–C	Ref.
$[(DMSO)_2H]^+$	[1] 1.538(2)	1.771(3)	98.6(1)	103.7(1)	[49]
		1.773(3)		104.1(1)	
	1.550(2)	1.759(2)	100.0(1)	103.5(1)	
		1.771(3)		103.0(1)	
	[2] 1.531(4)	1.760(5)	100.5(2)	105.2(2)	[50]
		1.776(5)		105.7(2)	
	1.536(4)	1.743(5)	100.7(3)	102.6(3)	
		1.758(5)		103.2(3)	
	[3] 1.528(4)	1.766(6)	100.2(3)	105.8(3)	[51]
		1.764(5)		105.5(2)	
	1.536(6)	1.748(5)	101.9(3)	101.8(3)	
		1.749(6)		103.2(3)	
	[3] 1.536(3)	1.761(5)	100.1(2)	105.3(2)	[52]
		1.769(5)		105.8(2)	
	1.541(3)	1.747(5)	101.6(3)	102.1(3)	
		1.754(5)		103.0(2)	
	[4] 1.537(5)	1.769(7)	100.9(4)	105.5(3)	[53]
		1.783(8)		105.4(3)	
	1.548(5)	1.756(8)	100.6(5)	104.0(4)	
		1.744(8)		102.2(4)	
$[DPSO)_2H]^+$	[5] 1.559(2)[a]	1.784(4)	99.9(2)	102.3(2)	[54]
		1.779(4)		103.5(2)	
$[(DMSO)H]^+$	[6] *1.585(8)*[a]	1.77(1)	100.7(6)	102.5(6)	[27]
		1.76(2)		101.6(6)	
$[(TMSO)H]^+$	[7] *1.589(3)*[a]	1.780(4)	*93.5(2)*	*98.9(2)*	[55]
		1.781(4)		*100.5(2)*	
n	11	25	12	24	
σ	0.009	0.013	0.8	1.4	
$\langle x \rangle_s$	1.541	1.765	100.4	103.8	
$\sigma(\langle x \rangle_s)$	0.003	0.002	0.2	0.3	

[a] Figures in italics are not included in the calculation of the mean, which refers to half-protonated sulfoxides.

[1] $[(DMSO)_2H][7,8-C_2B_9H_{12}]$.

[2] $[(DMSO)_2H][RhCl_4(DMSO)_2]$.

[3] $[(DMSO)_2H][RuCl_4(DMSO)_2]$.

[4] $[(DMSO)_2H][IrCl_4(DMSO)_2]$.

[5] $[(DnPSO)_2H][RuCl_4(DnPSO)_2]$.

[6] $[(DMSO)_2H][TeCl_6 \cdot 2(DMSO)]$.

[7] $[(TMSO)H][RuCl_4(TMSO)_2]$.

Table 5
Average bond lengths (Å) and angles (°) in uncoordinated not cyclic sulfoxides

	S–O	S–C(sp^3)	S–C($sp2$)[b]	S–C(sp^2)[c]	C–S–C	O–S–C
Min	1.470	1.730	1.754	1.786	95.5	103.1
Max.	1.513	1.840	1.809	1.828	101.9	109.6
Range	0.043	0.110	0.055	0.042	6.4	6.5
n[a]	40	58	18	19	53	106
Median	1.493	1.790	1.794	1.808	97.8	106.0
σ	0.009	0.026	0.016	0.015	1.2	1.3
$\langle x\rangle_s$	1.492	1.791	1.790	1.809	97.8	105.9
$\sigma(\langle x\rangle_s)$	0.001	0.003	0.004	0.003	0.2	0.1
$\langle x\rangle_u$	1.492	1.790	1.788	1.809	97.8	105.9
$\sigma(\langle x\rangle_u)$	0.001	0.003	0.004	0.003	0.2	0.1
$\langle x\rangle_w$	1.4914	1.7977	1.796	1.8175	97.68	105.67
$\sigma(\langle x\rangle_w)$	0.0005	0.0007	0.001	0.0005	0.03	0.02

[a] Number of data from Tables 1 and/or 2, 3. [b] S–C distances from groups different from substituted phenyls. [c] S–C distances in ortho-substituted phenyls.

In spite of the dramatically short S–O distance (1.408 Å) found by Rudnitskaya et al. in a $[(DMSO)H]^+$ complex [56], the ν(S–O) value is of 870 cm^{-1}, supporting the hypothesis that the bond distance is not correct. A less pronounced decrease of ν(S–O) is expected in 'half protonated' sulfoxides, like $[(DMSO)_2H]^+$ and $[(DnPSO)_2H]^+$, but unfortunately, the peak is covered by the broad band, 900–600 cm^{-1}, typical of O·H·O systems [49–53].

It is worth noting that a significant decrease of ν(S–O) is also observed in the O-bonded metal complexes, where the average S–O bond distance is 1.529(1) Å (see Table 10). If the S–O bond length in uncoordinated sulfoxides were of 1.531 Å, as often erroneously assumed, this trend of the stretching frequencies could not be explained. In the S-bonded complexes, an increase of about 35 cm^{-1} compared to free sulfoxides is observed, together with a shortening of the S–O bond length (av. 1.472(1)Å, Table 10). As a matter of fact, the ν(S–O) bands in IR spectra are generally used to distinguish between the S- and O-bonding of sulfoxides [2].

The electronic structure of DMSO, both in the ground and in the excited states, has been studied by electronic energy loss and photoabsorption spectroscopies [65]. These studies show that the LUMO (17.21 eV above the HOMO) has largely σ*(C–S) character with some contribution from π*(S–O). The next virtual orbital (0.811 eV above the LUMO) has mainly σ*(S–O) character, while another (2.264 eV above the previous one) has both σ*(S–O) and σ*(C–H) characters.

An investigation of the conformational properties of methyl sulfinyl derivatives of aromatic and heteroaromatic rings, variously substituted with halogen atoms, has shown that the methyl group is always highly twisted in relation to the ring plane, while the S–O bond assumes different orientations, depending on the position of the halogen atoms [38,39]. The conformation found in the solid state is close to that of the most stable conformer(s), predicted by ab-initio MO calculations [39].

2.3. Principal component analysis of uncoordinated sulfoxides

A more accurate description of the molecular structure of the sulfoxides and of the effects of protonation on the molecular structure may be achieved by means of multivariate statistical analyses of the available structural data [9].

In order to characterize the data set, the three bond distances, S–O, S–C1, S–C2, and bond angles, C1–S–C2, O–S–C1, O–S–C2, have been chosen as the PCA variables. It is worth noting that six variables are enough to completely describe the non-linear C–S(O)–C fragment. The C1 and C2 labels were permuted, because of the intrinsic C_s symmetry of the four atom group [66].

The six principal components (PCs), that is the six unique couples of eigenvectors and eigenvalues, are listed in Table 6, together with the percentage of the overall variance they describe. All the PCs should be considered as primary, on the basis of the χ^2 criterion [9a]. PC1, PC2, PC3, and PC5 are linear combinations of the symmetry coordinates of A′ symmetry (S1, S2, S4, and S5). Among the other two PCs, PC4 is substantially the S3 (A″) symmetry coordinate, and PC6 the S6 (A″) one.

The first principal component, which describes one half of the overall variance, is the only one discriminating the degree of protonation of the sulfoxides. In fact, only for the PC1 scores does the χ^2 test of homogeneity [67] clearly reject the hypothesis that the three groups of data (free, hydrogen bonded, protonated) come from the same population. A scatter plot of the PC2 scores versus the PC1 ones is shown in Fig. 1, and the distribution of the PC1 scores is reported in Fig. 2. Although no sound clustering takes place, it is apparent that in moving towards negative values of the PC1 score, the degree of protonation increases. Free sulfoxides have PC1 scores ranging between −1.034 and 8.431 (with mean value of 1.787 and standard deviation of the distribution of 1.872); hydrogen bonded sulfoxides have PC1 scores

Table 6
Principal component analysis of uncoordinated sulfoxides: summary of the principal components: eigenvectors, eigenvalues, and percentage of the overall variance they describe

	PC1	PC2	PC3	PC4	PC5	PC6
Eigenvectors						
S–O	−0.459	−0.248	−0.317	0.000	0.792	0.000
S–C1	0.382	−0.428	0.347	0.707	0.226	0.016
S–C2	0.382	−0.428	0.347	−0.707	0.226	−0.016
C1–S–C2	−0.354	0.449	0.782	0.000	0.248	0.000
O–S–C1	0.432	0.430	−0.154	−0.016	0.323	0.707
O–S–C2	0.432	0.430	−0.154	0.016	0.323	−0.707
Eigenvalues	3.292	1.255	0.528	0.437	0.284	0.235
Variance percentage	54.9	20.4	8.8	7.3	4.7	3.9
Cumulative variance percentage	54.9	75.3	84.1	91.4	96.1	100.0

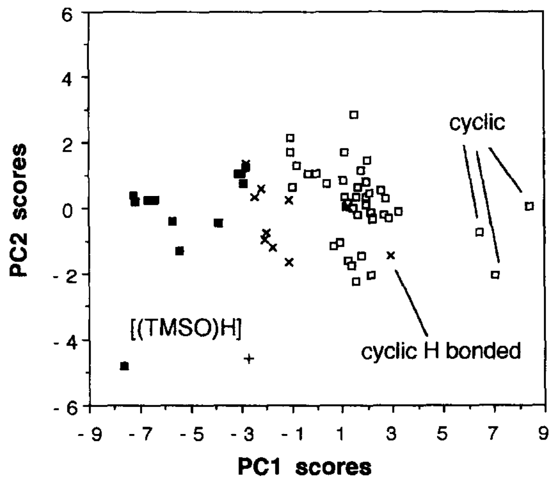


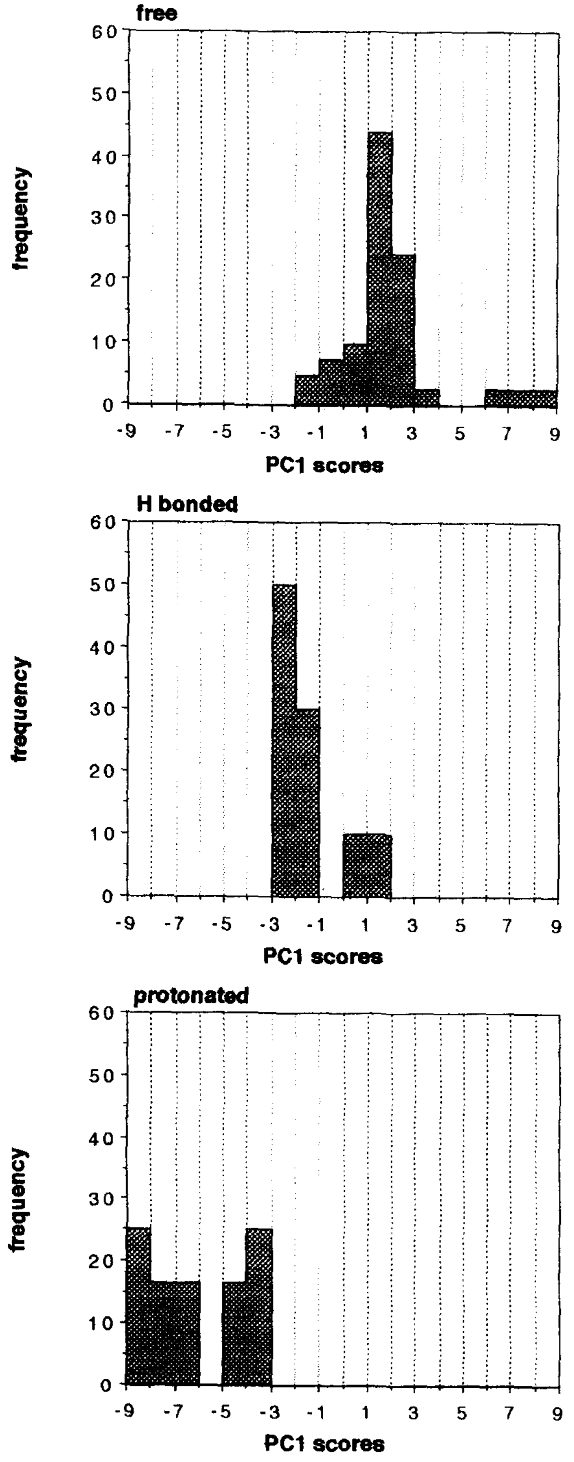
Fig. 1. Principal component analysis of the uncoordinated sulfoxides. PC2 versus PC1 scores for the free (□), hydrogen bonded (x) and protonated (■) sulfoxides.

ranging between −2.804 and 2.943 (with mean value of −1.137 and standard deviation of the distribution of 1.737); finally, the PC1 scores of the protonated sulfoxides range between −7.614 and −2.764 (with mean value of −5.158 and standard deviation of the distribution of 1.832).

Stereochemical reification of the PC1 eigenvector perfectly agrees with the dependence of the S–O bond length on the protonation degree described in the previous paragraphs 2.1 and 2.2; in fact, the S–O bond lengthens if its oxygen atom interacts with a proton. Moreover, the PC1 eigenvector shows that, by increasing the degree of protonation, the S–C bond distances shorten, the C–S–C bond angle widens, and the O–S–C bond angles tighten. This deformation pathway may be explained in terms of the VSEPR theory [68]. In fact, sulfoxides present a pyramidal geometry (I), and the C–S–C bond angle is always narrower than the O–S–C bond angles, independently of the nature of the side groups. This is probably the result of the repulsion between the bulkier S–O bonding double pair and the S lone-pair and the S–C electron bonding pairs. When the oxygen atom interacts with a proton, the reduced double bond character in the S–O bond weakens the repulsion of the S–O and the S–C bond pairs, causing a reduction of the O–S–C angles, under the compression effect of the S lone pair.

It is also interesting to observe in Fig. 1 that at the extreme right side there are the free cyclic sulfoxides. Presumably ring closure hinders the widening of the C–S–C bond angle, therefore causing high PC1 scores. As a consequence, the two known cases of hydrogen bonded cyclic sulfoxides have PC1 scores lower than those of the

Fig. 2. Principal component analysis of the uncoordinated sulfoxides. Distribution of the PC1 scores for the free, hydrogen bonded and protonated sulfoxides.


free
H bonded
protonated
frequency
0
10
20
30
40
50
60
-9
-7
-5
-3
-1
1
3
5
7
9
PC1 scores

free analogues, but considerably higher than those of the other hydrogen bonded non-cyclic sulfoxides.

Another interesting feature of Fig. 1 is that the lowest PC1 scores correspond to the case of protonated sulfoxides in which the proton is not shared with a second sulfoxide molecule. This supports the interpretation that the protonation of the oxygen atom is the driving force of the molecular deformation described by PC1.

The PC1 eigenvector allows one also to foresee the real space variations. The data set here analyzed is characterized by the following standard deviations: 0.023 Å (S–O), 0.026 Å (S–C1 and S–C2), 2.25° (C1–S–C2), and 1.74° (O–S–C1 and O–S–C2). This implies that a shortening of 0.049 Å of the S–O-bond length (i.e. 0.459·0.023, where 0.459 is the PC1 eigenvector term corresponding to S–O, and 0.023 the standard deviation) is accompanied by a lengthening of 0.045 Å of the S–C bond distances, a tightening of −3.56° of the C–S–C bond angle, and a widening of 3.34° of the O–S–C bond angles. These values are quite far from those expected from the mean values of the raw data. In fact, in the same data set submitted to PCA, the S–O bond length goes from 1.492(1) Å (free sulfoxides) to 1.541(3) Å (protonated sulfoxides), the S–C bond lengths from 1.791(3) (free) to 1.765(2) Å (protonated), the C–S–C bond angle from 97.8(2)° (free) to 100.4(2)° (protonated), and the O–S–C bond angles from 105.9(1)° (free) to 103.8(3)° (protonated). From these limit values, it is possible to calculate that a shortening of 0.049 Å of the S–O bond length would be accompanied by a lengthening of 0.026 Å of the S–C bond lengths, a tightening of 2.6° of the C–S–C bond angle, and by a widening of 2.1° of the O–S–C bond angles. This result confirms that PC1 is not the only primary component, or, in other words, that the protonation of the sulfoxides is not the only statistically significant reason for structural variations in the C–S(O)–C fragment.

All the other five PCs reported in Table 6 are independent of the protonation degree of the sulfoxide molecule. PC2, which describes a considerable amount of the overall variance (20%), can be related to the variation of pyramidalicity of the C–S(O)–C fragment. In fact, movements of the sulfur atom from (or towards) the plane defined by the oxygen and carbon atoms would produce a lengthening (or shortening) of all the bond distances, and a tightening (or widening) of all the bond angles. The remaining four PCs are clearly less important, since they only describe 9%, 7%, 5%, and 4% of the overall variance. PC3 has no sound stereochemical reification: if the S–O bond distance shortens, the O–S–C bond angles tighten, the S–C bond distances lengthen, and the C–S–C bond angle widens. PC4 and PC6 correspond to antisymmetric (A″) symmetry coordinates. PC5, in which all the variables increase, is probably the result of uncorrected thermal motion or to inhomogeneity of the sample. However, no sound relations between some chemical information and the PC2–PC6 scores can be found.

An indication of the inhomogeneity of the sample can be also found directly from inspection of the raw data of Table 2. The S–C bond distances span a rather wide range, from 1.754(8) to 1.84(1) Å, including S–C(sp^3) and S–C(sp^2) distances. It is interesting to observe that long distances are also found in the S–C(sp^2) case, where they are expected to be shorter. This is probably due to intramolecular steric interactions, particularly strong when R is a phenyl group with bulky substituents in positions 2 or 2, 6. When C(sp^2) refers to a less steric demanding vinyl or five-membered ring or an unsubstituted phenyl group, the average S–C(sp^2) distance is 1.790(4) Å.

3. Structure of metal complexes with sulfoxides

3.1. X-ray structures

Before discussing the bond distances in sulfoxide metal complexes and their statistical and chemical meaning, we will first present the compounds, so far structurally characterized by X-ray analysis, for metals from Group I to Group VIII of the Periodic Table, gathering A and B subgroups. Some average data for the transition metal complexes are presented in Tables 8 and 9. Structural details of the coordinated sulfoxides are given in Tables S1–S24 as Supplementary Material available from the authors.

3.1.1. Group I metal complexes

Few crystal structures exist of sulfoxide complexes of alkali metal ions. Most of them (Table 7) consist of DMSO or TMSO anionic transition metal complexes having lithium, sodium or potassium as counterions [69–74]. In this kind of

Table 7
Bond lengths (Å) and angles (°) in alkaline and alkaline-earth metal complexes with sulfoxides

Compound	S–O	M–O[a]	M–O–S[b]	Ref.
$[\mathrm{Li(DMS}\mathit{O}\mathrm{)(benzoate)}]$[c]	1.506(5)[d] 1.481(6)[d]	1.92(1)–1.96(1)	125.3(5)–135.8(5)	[69]
$[\mathrm{Li_2(TMS}\mathit{O}\mathrm{)_2}][\mathrm{Ru_2Br_6(TMSO)_6}]$	1.517(7)[d] 1.495(6)[e] 1.491(7)[e] 1.465(7)[f]	1.85(2)–2.05(2)	123.2(6)–137.6(6)	[70]
$[\mathrm{Na(DMS}\mathit{O}\mathrm{)_2}][\mathrm{RuCl_4(DMSO)(NH_3)}]$	1.542(4)[d] 1.508(3)[d] 1.479(3)[e]	2.272(4)–2.363(3)		[71]
$[\mathrm{Na(H_2O)(Me_2CO)}][\mathrm{RuCl_4(DM}\mathit{SO}\mathrm{)(Im)}]$[g]	1.487(2)[e]	2.370(2)–2.418(2)		[71]
$[\mathrm{Na_2(DMS}\mathit{O}\mathrm{)(Me_2CO)_2}][\mathrm{NiL_2}]$[h]	1.50(1)[d]	2.270(9)–2.374(8)	119.8(5)–139.2(5)	[72]
$[\mathrm{K(DMS}\mathit{O}\mathrm{)_2}][\mathrm{CoL_2}]$[i]	1.54(2)[d]	2.73(2)		[73]
$[\mathrm{K_2(H_2O)L}]_2[\mathrm{PtCl_3(DM}\mathit{SO}\mathrm{)}]_2$[j]	1.42(3)[e]	2.85(4)		[74]
$[\mathrm{Sr_2(H_2O)_2(N_3)_4(DMS}\mathit{O}\mathrm{)_2}]$[k]	1.517(3)	2.566–2.639	125.6–135.9	[99]

[a] Range of alkali metal to O-sulfoxide distances. [b] Range of alkali metal–O–S bond angles. [c] Two crystallographically independent molecules. [d] Crystallization sulfoxide bonded to the alkali ion. [e] Transition metal S-bonded sulfoxide coordinated to the alkali ion. [f] Ruthenium coordinated sulfoxide. [g] Im = imidazole. [h] L = *cis*-2-mercaptostilbene-1-sulfinato. [i] L = 3-phenylbiuretato. [j] L = tetrakis(hydroxymethyl)ethylene. [k] Data from C.S.D., unweighted mean with σ in parentheses.

Table 8
Average dimensions for O-bonded metal sulfoxide complexes: $\langle x \rangle_s$ with $\sigma(\langle x \rangle_s)$ in parentheses, σ with number of averaged values in square brackets

M	M–O	M–O–S	S–O
Ag(I)	2.43(4)	127(4)	1.509(5)[a]
	0.081[4]	8.7[4]	0.007[2]
Cu(I)[b]	2.223(3)	117(2)	1.57(6)
Cu(II)	2.05(3)	121(1)	1.527(4)
	0.15[29]	7.0[25]	0.023[26]
Zn(II)	2.11(1)	120(2)	1.495(5)[a]
	0.0914[2]	2.9[2]	0.007[2]
Cd(II)	2.309(9)	124(1)	1.527(1)
	0.055[38]	7.3[45]	0.016[32]
Hg(II)	2.47(9)	122(2)	1.524(6)
	0.25[8]	6.1[9]	0.017[7]
Ln(III)[b]	2.37(2)	137(4)	1.514(3)
	0.081[11]	11[8]	0.009[11]
U(VI)	2.376(9)	131(3)	1.528(4)
	0.026[5]	8.1[8]	0.013[8]
In(III)	2.18(1)	123.8(3)[a]	1.535(3)
	0.026[5]	0.75[7]	0.006[4]
Tl(III)[c]	2.42(2)	124(1)	1.49(2)
Zr(IV)	2.203(7)	127.3(8)	1.541(2)[a]
	0.015[5]	1.7[4]	0.004[5]
Sn(IV)	2.28(3)	126(1)	1.533(4)
	0.15[21]	6.4[22]	0.020[22]
Pb(II)	2.40(3)	128(2)	1.527(8)
	0.091[9]	6.8[9]	0.022[7]
V(IV)[d]	2.04[a]	125[a]	1.52[a]
	0.01	1.0	0.02
Mo(II)	2.134(6)	130(1)	1.521(3)[a]
	0.009[2]	1.8[2]	0.004[2]
Mo(VI)	2.27(2)	125(2)	1.524(3)
	0.062[8]	5.1[8]	0.009[8]
Mn(II)	2.149(8)	130(5)	1.509(3)[a]
	0.017[4]	11[4]	0.007[4]
Re(III)[c]	2.302(6)	129.7(4)	1.540(6)
Fe(II)	2.13(1)	122(1)	1.525(7)
	0.024[3]	1.8[3]	0.012[3]
Fe(III)	2.05(2)	125(2)	1.527(7)
	0.043[3]	2.9[3]	0.013[3]
Ru(II)	2.131(4)	122.4(9)	1.538(3)
	0.016[15]	3.6[15]	0.012[15]
Ru(III)	2.09(1)	121.6(8)	1.535(4)
	0.032[11]	2.5[11]	0.014[11]
Os(III)[c]	2.130(8)	123.5(3)	1.517(6)
Co(II)	2.084(5)	121(1)	1.52(1)
	0.014[7]	3.6[8]	0.027[7]
Co(III)[c]	1.91(1)	137.4(7)	1.52(1)
Rh(II)[e]	2.236(3)	132.4(2)	1.525(3)
Rh(III)	2.06(2)	121(1)	1.548(2)
	0.038[4]	2.4[4]	0.003[3]

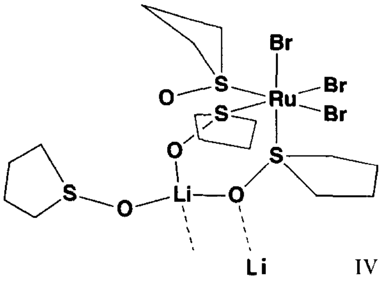
Table 8 (*continued*)

M	M–O	M–O–S	S–O
Pd(II)	2.05(1)	120(2)	1.541(8)
	0.022[5]	4.1[5]	0.019[5]
Pt(II)	2.046(6)[a]	122(1)	1.55(2)
	0.008[2]	1.7[2]	0.022[2]

[a] Unweighted mean. [b] Ln = La, Nd, Eu, and Er. [c] Data from one structure only. [d] Data calculated from C.S.D., for the −70 °C structure [190]. [e] Dirhodium complexes with a metal–metal bond.

compound, sulfoxides can be simple terminal ligands (η^1-O or η^1-S) or act as μ_2-O,S and μ_3-O,O,S bridging ligands.

This is well illustrated by the structure of $[Br_6(TMSO)_2Ru_2(\mu_2\text{-}TMSO)_2](\mu_3\text{-}TMSO)_2Li_2(TMSO)_2]$ (schematically represented in IV) [70].



IV

As will be shown later, when sulfoxides are S-bonded to a transition metal atom, the S–O bond length is markedly shortened with respect to free sulfoxides (av. 1.472(1) Å, Table 10). Inspection of Table 7 shows that coordination to alkali metal ions causes a significant lengthening of the S–O distances, which increase from η^1-S to μ and η^1-O sulfoxides. This is well exemplified by complex IV, where the S–O bond distance passes from 1.465(7) Å, when the sulfoxide is only S-bonded to Ru, to 1.493(2) Å when an S-bonded sulfoxide interacts with Li^+, up to 1.517(7) Å when the crystallization sulfoxide interacts only with the alkali ion [70].

In the potassium derivative $[K_2(H_2O)\{tetrakis(hydroxymethylene)ethylene\}_2][PtCl_3(DMSO)]_2$ [74], the S–O distance of 1.42(3) Å is comparable, within experimental errors, to that of 1.467(2) Å found in Pt(II) complexes containing one S-bonded sulfoxide (Table 9). Besides the scarce significance of this value, it seems likely that, in this case, a very slight lengthening should be expected because of the high coordination number (10) of K^+ and hence its lower polarizing effect.

For Group IB, only one structure is known for copper(I), $[\{Cu(DMSO)(\mu\text{-}CN)\}_2]_\infty$ (V) [97], while several X-ray structures have been reported for copper(II) complexes: *trans*-$CuCl_2(DMSO)_2$ [75], $[CuCl_2(DMSO)]_\infty$ [76], $[Cu(TMSO)_4][Cu_2Br_6]$ and $[Cu(TMSO)_4][Cu_2Cl_6]$ [77], $CuBr_2(DMSO)_2$ [78], $[\{Cu(DMSO)\}_4(\mu_4\text{-}O)(\mu_2\text{-}Cl)_6]$ [79], $[\{Cu(DESO)\}_4(\mu_4\text{-}O)(\mu_2\text{-}Cl)_6]$ [80], $CuBr_2(\mu\text{-}Br)_2(TMSO)_2$ [81], $Cu_2Cl_4(TMSO)_4$ [82], $[Cu_2(\mu_2\text{-}nitrobenzoato)_4$

Table 9
Average dimensions for S-bonded metal sulfoxide complexes: $\langle x \rangle_s$ with $\sigma(\langle x \rangle_s)$ in parentheses, σ with number of averaged values in square brackets

M	M–S	M–S–O	M–S–C	S–O
Cr(O)[a]	2.331(1)	114.6(1)	117.0(6)	1.486(3)
			0.85[2]	
Tc(III)	2.289(3)[b]	119.3(4)[b]	112(1)	1.475(7)[b]
	0.0000[2]	0.42[2]	2.0[4]	0.0007[2]
Re(II)	2.349(1)	118.5(3)	111(2)	1.462(4)
			2.1[2]	
Fe(II)	2.25(5)	116(2)	114.0(8)	1.464(7)[c]
	0.076[2]	3.1[2]	1.6[4]	0.009[2]
Ru(II)[d]	2.265(3)	117.6(3)	113.1(2)	1.478(1)
	0.026[74]	2.2[71]	2.6[139]	0.010[63]
Ru(II)[e]	2.330(4)	116.7(4)	111.8(6)	1.475(2)
	0.024[30]	2.5[30]	4.2[56]	0.013[30]
Ru(III)[d]	2.315(9)	116.1(6)	113.0(3)	1.474(2)
	0.038[17]	2.3[17]	1.9[34]	0.009[17]
Ru(III)[e]	2.323(3)	116.1(3)	111.9(2)	1.464(5)
	0.010[11]	0.9[11]	0.7[19]	0.015[11]
Os(II)	2.34(1)	115(1)	114(2)	1.47(1)
	0.019[2]	1.5[2]	3.8[3]	0.018[2]
Rh(II)	2.45(2)	123.0(9)	108.7(3)	1.476(5)
	0.076[11]	2.8[11]	1.5[21]	0.016[11]
Rh(III)[d]	2.271(6)	115.2(3)	112.2(3)	1.467(2)
	0.022[13]	1.2[12]	1.4[24]	0.008[12]
Rh(III)[e]	2.323(3)	116.1(3)	111.9(2)	1.464(5)
	0.010[11]	0.9[11]	0.7[19]	0.015[11]
Ir(III)	2.30(2)	117.2(7)	111.8(6)	1.467(2)[c]
	0.064[8]	1.9[8]	2.3[15]	0.004[5]
Pd(II)[f]	2.22(1)	115.6(7)	110(1)	1.47(1)
	0.027[5]	1.6[5]	3.9[10]	0.022[5]
Pd(II)[d]	2.243(5)	116(3)	109(1)	1.461(1)[c]
	0.010[4]	4.2[2]	2.1[4]	0.002[3]
Pd(II)[e]	2.297(3)	113(1)	112(1)	1.476(5)
	0.006[2]	1.8[2]	2.0[4]	
Pt(I)	2.170(4)[c]	121.1(3)[c]	110(2)	1.49(2)
	0.008[5]	0.69[5]	4.3[8]	0.028[2]
Pt(II)[f]	2.207(3)	116.2(2)	110.9(2)	1.467(2)
	0.022[62]	1.5[62]	2.5[113]	0.014[50]
Pt(II)[d]	2.226(3)	116.4(3)	110.5(3)	1.466(2)
	0.021[49]	2.3[31]	2.6[96]	0.012[37]
Pt(II)[e]	2.292(2)	116.7(3)	111(2)	1.473(7)
			2.8[2]	
Pt(IV)	2.33(1)	110(1)		1.54(3)

[a] Data from one structure only. [b] Weighted mean. [c] Unweighted mean. [d] S-bonded sulfoxides not trans to S. [e] S-bonded sulfoxides trans to S. [f] One S-bonded sulfoxide.

Table 10
Average bond lengths (Å) and angles (°) in metal coordinated sulfoxides

S-bonded sulfoxides:

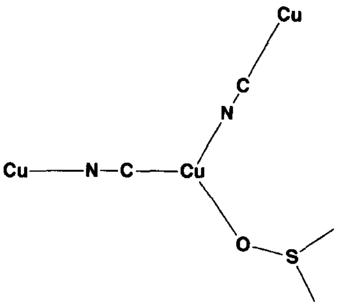
	S–O	S–C(sp^3)	M–S–O	M–S–C	C–S–C	O–S–C
Min.	1.422	1.717	109.4	100.4	92.9	99.5
Max.	1.512	1.911	129.5	120.3	108.0	114.8
Range	0.090	0.194	20.1	19.9	15.1	15.3
n	252	400	289	548	263	538
Median	1.470	1.781	116.7	111.8	100.1	107.4
σ	0.013	0.020	2.5	2.9	2.4	1.7
$\langle x\rangle_s$	1.4723	1.785	116.9	111.7	100.2	107.43
$\sigma(\langle x\rangle_s)$	0.0008	0.001	0.1	0.1	0.1	0.07
$\langle x\rangle_u$	1.4714	1.785	116.9	111.6	100.2	107.49
$\sigma(\langle x\rangle_u)$	0.0008	0.001	0.1	0.1	0.1	0.07
$\langle x\rangle_w$	1.4757	1.7849	116.84	112.36	99.97	106.99
$\sigma(\langle x\rangle_w)$	0.0003	0.0003	0.01	0.01	0.02	0.01

O-bonded sulfoxides:

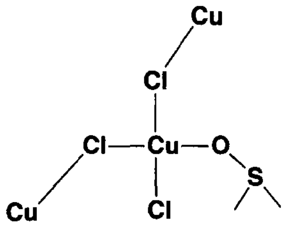
	S–O	S–C(sp^3)	M–O–S	C–S–C	O–S–C
Min.	1.470	1.540	112.0	86.0	97.0
Max.	1.578	1.915	158.6	122.0	115.9
Range	0.108	0.375	46.6	36	18.9
n	196	260	214	184	400
Median	1.528	1.780	123.0	99.0	104.2
σ	0.018	0.028	7.1	2.4	1.9
$\langle x\rangle_s$	1.529	1.780	124.7	99.0	104.32
$\sigma(\langle x\rangle_s)$	0.001	0.002	0.5	0.2	0.09
$\langle x\rangle_u$	1.528	1.781	124.7	99.0	104.34
$\sigma(\langle x\rangle_u)$	0.001	0.002	0.5	0.2	0.09
$\langle x\rangle_w$	1.5308	1.7792	124.06	99.13	104.01
$\sigma(\langle x\rangle_w)$	0.0003	0.0005	0.02	0.03	0.02

$(\mathrm{DMS}O)_2]$ [83], $[\mathrm{Cu}(\mu\text{-benzoato})_2(\mathrm{DMS}O)]$ [84], $[\mathrm{Cu}_2(\text{methoxymethyl-}\alpha\text{-methyl-2-naphthalene-acetato})_4(\mathrm{DMS}O)_2]$ and $[\mathrm{Cu}_2(\text{methyl-}p\text{-toluoyl-1}H\text{-pyrrole-2-acetato})_4(\mathrm{DMS}O)_2]$ [85], $[\mathrm{CuCl}_2(\mathrm{C}_5\mathrm{H}_5\mathrm{NO})(\mathrm{DMS}O)]_2$ [86], $[\{\mathrm{Cu}(\text{tetraazabicyclononanyl-ethanolato})(\mathrm{DMS}O)\}_2][\mathrm{ClO}_4]_2$ and $[\{\mathrm{Cu}(\text{methoxymethyl-tetraazabicyclononanyl-ethanolato})(\mathrm{DMS}O)\}_2][\mathrm{ClO}_4]_2$ [87], $\mathrm{MnCu}\{(o\text{-phenylenebis (oxamato)}\}(\mathrm{DMS}O)_3$ [88], $\mathrm{Cu}(\mathrm{UO}_2)(\text{diaminoethane-}o\text{-acetoacetyl phenolato}) (\mathrm{DMS}O)_2$ [89], $[\mathrm{Cu}(\mathrm{DMS}O)(\text{L-phenylalaninato})_2]$ [90], $[\mathrm{Cu}(\mathrm{DMS}O)(\text{4,4,4-trifluoro-1-(2-thienyl) butane-1,3-dionato})_2]$ [91], $[\mathrm{Cu}(\text{salicylidene-hydroxy-bromobenzylamine})(\mathrm{DMS}O)]_2$ [92], $[\mathrm{Cu}(\mathrm{DMS}O)_6]$ $[\mathrm{W}_6\mathrm{O}_{19}]$ [93], $[\mathrm{Cu}_2(\mathrm{DMS}O)_2(\mu\text{-pyridinato})]$ [94] and $\mathrm{Cu}(\mathrm{AEPS}O)_2$ [95], and $[\mathrm{Cu}_2(\mu\text{-hydroxobenzoato})_4 (\mathrm{DMS}O)_2\cdot\mathrm{DMSO}]$ [96].

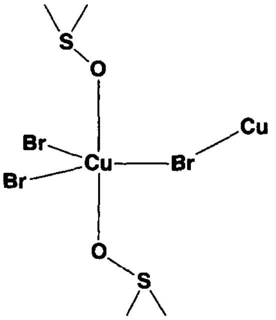
In the Cu(II) complexes, the metal atom has been found in different coordination environments, from square planar, as in $[CuCl_2(DMSO)]_n$ (VI) [76], to more or less distorted square pyramidal, e.g. $CuBr_2(DMSO)_2$ (VII) [78], and $[Cu(\mu\text{-benzoato})_2(DMSO)]_2$ (VIII) [84], as well as to octahedral, as in the $[Cu(DMSO)_6]^{2+}$ cation (IX) [93]. In the Cu(I) complex the metal atom displays a trigonal coordination.



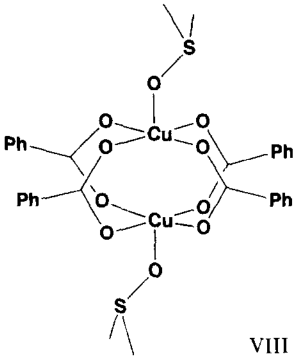
V



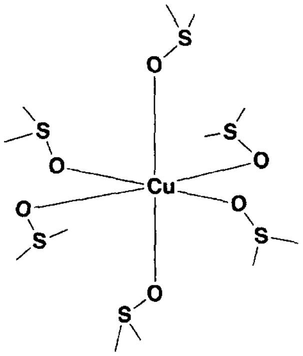
VI



VII

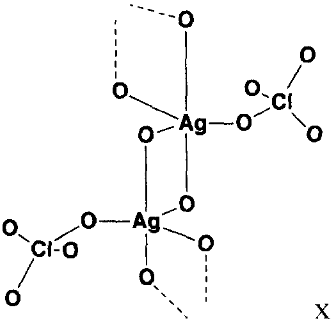


VIII



IX

For silver, the crystal structure of $Ag(DMSO)_2(ClO_4)$ (X) has been determined [98]. It consists of infinite chains, in which the Ag(I) atoms are joined by doubly bridging DMSO oxygens. Including a long Ag–O(perchlorate) distance, the coordination polyhedron can be described as a distorted trigonal bipyramid.

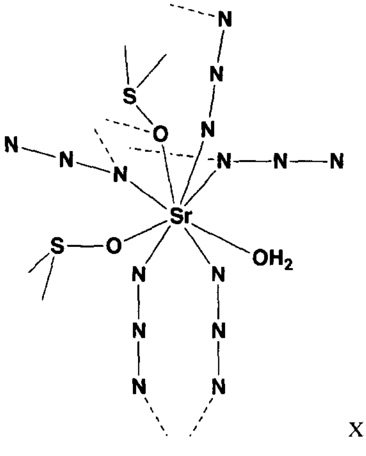


X

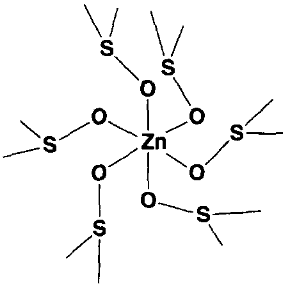
3.1.2. Group II metal complexes

To our knowledge there are no structural studies for alkaline-earth metals, with the exception of the X-ray structure determination of the strontium complex, *catena*-$[Sr\{(H_2O)(\mu_3\text{-}N_3)(\mu_2\text{-}N_3)(\mu_2\text{-}DMSO)\}_2]$ (XI) (see Table 7) [99].

Two structures have been determined for zinc [100,101], but three-dimensional coordinates are only available for $[Zn(DMSO)_6][ClO_4]_2$ (XII) [100].



XI

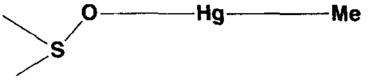


XII

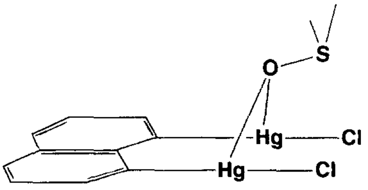
Several structures have been reported for Cd(II) [102–108], and Hg(II) [109–116]. Besides mononuclear complexes such as $[\mathrm{Cd(DMS}\mathit{O})_6][\mathrm{ClO_4}]_2$ [102,103], a binuclear complex of formula $[\mathrm{Cd(Ph(SCH_3)C{=}C(S)Ph)_2(DMS}\mathit{O})]_2$ has been described, where each Cd atom, related to the other by a centre of symmetry, is coordinated to five sulfur atoms of the ligand and one oxygen atom of DMSO [104]. A structure consisting of approximately octahedrally coordinated Cd^{2+} species, interconnected by chlorine bridges to form a one-dimensional polymer, has been also presented: [*catena*-Cd(DMS*O*)(9-methyladenine)(μ-Cl)$_2$] [105].

Various cadmium complexes have been obtained by reaction of $\mathrm{CdBr_2}$ with DMSO to produce a series of complexes ranging from a layer-lattice type, $[\mathrm{CdBr_2(DMS}\mathit{O})]_\infty$, to slab, $[\mathrm{CdBr_2(DMS}\mathit{O})]_\infty\cdot\mathrm{H_2O}$, $[(\mathrm{CdBr_2})_3(\mathrm{DMS}\mathit{O})_2\ (\mathrm{H_2O})]_\infty\cdot n\mathrm{H_2O}$, and chain structures, such as $[(\mathrm{CdBr_2})_2(\mathrm{DMS}\mathit{O})_3]_\infty$ and $[(\mathrm{CdBr_2})_3(\mathrm{DMS}\mathit{O})_4]_\infty$ [106], or $[\mathrm{CdBr_2(DMS}\mathit{O})(\mathrm{MeOH})]_\infty$ [107]. Chain structures of formula $[(\mathrm{CdCl_2})_5(\mathrm{DMS}\mathit{O})_7]_\infty$ [106] and $[\mathrm{CdCl_2(DMS}\mathit{O})(\mathrm{MeOH})]_\infty$ [107] have been obtained from $\mathrm{CdCl_2}$. From $\mathrm{CdI_2}$, polymeric chains $[\mathrm{CdI_2(DMS}\mathit{O})]_\infty$ have been obtained, as well as the binuclear complex $[(\mathrm{CdI_2})_2(\mathrm{DMS}\mathit{O})_4]$ and the ionic derivatives, $[\mathrm{Cd(DMS}\mathit{O})_6]\ [\mathrm{CdI_3(DMS}\mathit{O})]\cdot\mathrm{EtOH}$, and $[\mathrm{Cd(DMS}\mathit{O})_6][\mathrm{CdI_4}]$ [108].

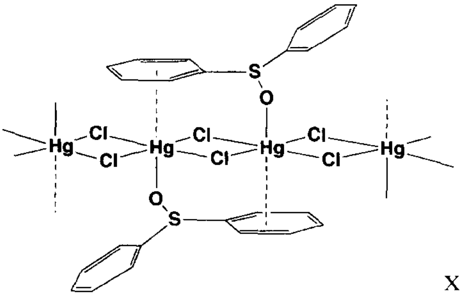
For Hg(II) simple structures are known, from $[\mathrm{Hg(Me)(DMS}\mathit{O})][\mathrm{BF_4}]$ (XIII) [109], and [(HgCl)$_2$(naphthalenedyl)(μ-DMS*O*)] (XIV) [110], to the octahedral complex $[\mathrm{Hg(DMS}\mathit{O})_6]\ [\mathrm{ClO_4}]_2$ [111].



XIII



XIV

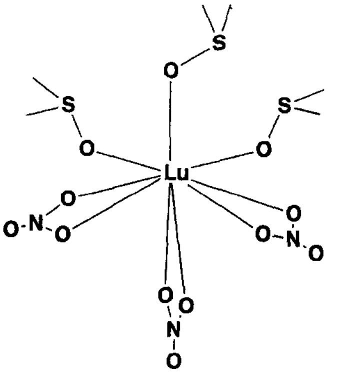


XV

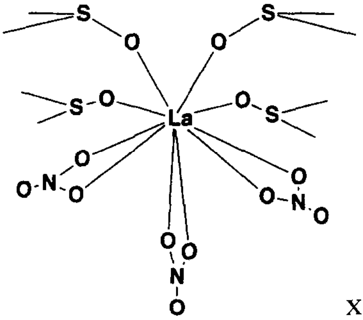
Complex structures have been obtained from $HgCl_2$ as adducts of various sulfoxides. In the 1 : 1 adduct, $HgCl_2$(DPS*O*) (XV), chains are formed, where the coordination around the metal atom involves the oxygen atom of the sulfoxide, and two pairs of chlorine atoms [112]. It has been proposed that the octahedral coordination is completed by a phenyl ring at 3.51 Å, trans to O [112]. In the 1 : 1 adduct with di-*n*-butyl sulfoxide, $HgCl_2$(DnBS*O*), similar chains are formed in the solid state, but here the mercury atoms display a distorted tetragonal-pyramidal coordination [113]. In the 3 : 2 adduct with DMSO, the crystal structure is composed of $HgCl_2$ molecules and centrosymmetric dimeric groups $[(HgCl_2)(DMSO)]_2$, with DMSO oxygen bridges [114]. Other structures concern the dimeric complex $[Hg_2(DMSO)_8][ClO_4]_4$ [115] and [24-pyrimidinium crown-6]$[(Hg(DMSO)I_3)(HgI_4)]$ [116].

3.1.3. Group III metal complexes

For Group IIIA, the structure of one yttrium complex, $[Y(NO_3)_3(DMSO)_3]$, has been reported [117]. Similar structures have been found for the heaviest lanthanide ions (Ln^{3+}), such as Ln = Er [118,119], Yb [120], and Lu [121], (XVI) while for Ln = La [122] (XVII), Ce [123], Pr [124], Nd [125], and Sm [126] the coordination number is greater, yielding compounds of formula $Ln(NO_3)_3(R_2SO)_4$.



XVI



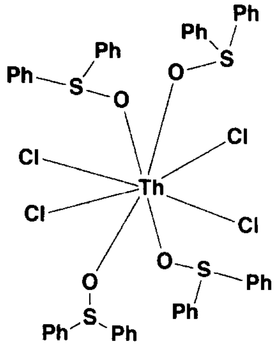
XVII

This is in agreement with the proposal that, as the size of the Ln^{3+} ion decreases, the repulsion between the ligands in the coordination sphere increases, reducing the Ln:sulfoxide ratio from 1:4 to 1:3 [120].

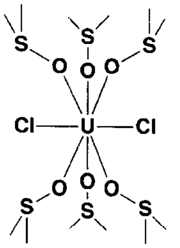
Relatively accurate structures concern $Er(NO_3)_3(DPSO)_3$ [119], $[La(\{(C_2H_5O)_2PS_2\}_3(DBSO)_2]$ [128], $[La(C_3H_7O)_3(DMSO)_2]$ and $[Eu(C_3H_7O)_2(DMSO)_3][Eu(C_3H_7O)_2PS_2]$ [129], and $[Nd_3(ClCH_2CO_2)_9(DMSO)_4]$ [130].

Several other structures have been determined [131–142], but unfortunately most of them are of very low accuracy with respect to the sulfoxide moiety and are not reported. In any case, all of them contain O-bonded sulfoxides, confirming the high affinity of lanthanide ions for oxo-ligands, in agreement with their Lewis hard-acid character [143].

For actinide–sulfoxide complexes, only two X-ray structures seem to have been determined for Th(IV), $Th(8\text{-quinolinolato})_4(DMSO)\cdot DMSO$ [144], and $ThCl_4(DPSO)_4$ (XVIII) [145], as well as for U(IV), $UCl_2(DMSO)_6][UCl_6]$ (XIX) [146], and *trans*-$UCl_4(DiBSO)_2$ [147].

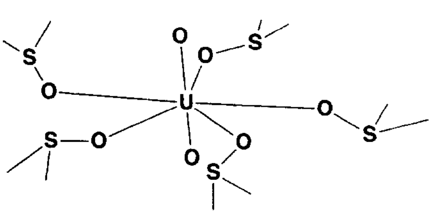


XVIII



XIX

In contrast, several X-ray structures are reported for U(VI) [89,148–159], that is for the dioxouranium derivatives. Besides the already seen Cu complex [89], other structurally characterized complexes are: $[UO_2(DMSO)_5][BF_4]_2$ [148], $[UO_2(DMSO)_5][ClO_4]_2$ [149], $[UO_2(DMSO)(pyOS)_2]$ [150], $[UO_2(DMSO)$(benxoyldihydromethylphenyl pyrazolonato)$_2]$ [151], $[UO_2(DMSO)$(benxoyldihydromethylphenylpyrazolthionato)$_2]$ [152], [*catena*-$UO_2(DMSO)(\mu\text{-}F)_2]$ [153], $[(UO_2)_2(DMSO)$(bis(dihydroxybenzaldehyde) diimino-azapentane)] [154], $[UO_2(DMSO)$ (oxyphenylsalicyaldiminato)] [155], $[(UO_2(DMSO))_2$(ethoxycarbonylthioureatopyridinyl)$_2$(biureato)] [156], $[UO_2(DMSO)(H_2O)$(phosphito)] [157], $[UO_2(DMSO)$(benzoato)$_2]$ [158], and $[UO_2(DMSO)(\mu_3$-succinato)] [159]. In all these compounds U displays a pentagonal bipyramidal geometry, as examplefied by $[UO_2(DMSO)_5][BF_4]_2$ (XX) [148].

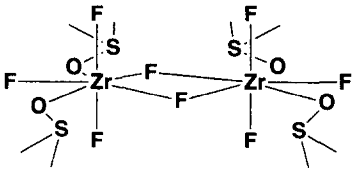


XX

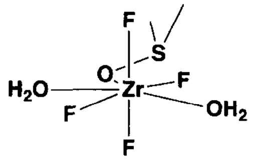
As to Group IIIB, oxygen bonding has been proposed for the 1:1 adduct $(DMSO)BF_3$ [160]. For In(III), complexes of general formula $[InX_n(DMSO)_{6-n}]^{3-n}$ ($n=0$ [161]; $n=2$, X=I [162]; $n=3$, X=Cl and Br [163]), have been characterized. A phenanthroline derivative has been also reported, $InCl_3$(phen)(DMSO) [164]. One crystal structure is also known for Tl(III), $[TlCl_5(DMSO)][Hpy]$ [165].

3.1.4. Group IV metal complexes

X-ray structural investigation of zirconium sulfoxide complexes is limited to three compounds: $[Zr(DMSO)_8][Cl]_4 \cdot DMSO$ [166], $[ZrF_4(DMSO)_2]_2$ (XXI) [167,168], and $[ZrF_4(DMSO)(H_2O)_2] \cdot 2H_2O$ (XXII) [167].



XXI

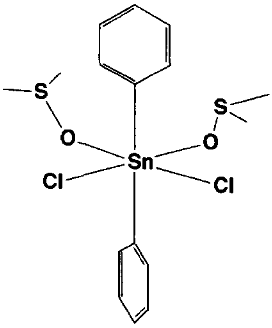


XXII

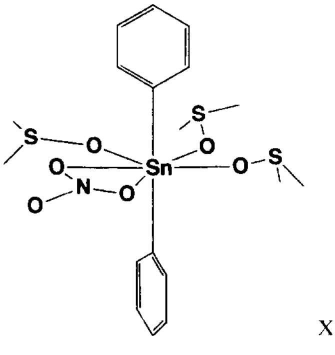
In the last two, the metal coordination polyhedron is represented by a pentagonal bipyramid with O-bonded sulfoxides in the basal plane.

Some more structures are available for tin(IV): *cis,trans,cis*-$SnCl_2Ph_2(DMSO)_2$ [169,170], *cis,trans,cis*-$SnCl_2Me_2(DMSO)_2$ [171,172], $[Sn(Ph)_3NC(O)C_6H_4SO_2$-$(DBSO)]$ [173], [*trans*-$SnPh_2(DMSO)_3(NO_3)][NO_3]$ [174], $[Sn_2(CH_2)Me_2Cl_4$-$(DMSO)_2]$, $[Sn_2(CH_2)Me_3Cl_3(DMSO)]$, and $[Sn_2(CH_2)Cl_6(DMSO)_4]$ [175], *cis*-$Sn(DMSO)_2Cl_4$ [176], *cis*-$Sn(DMSO)_2Br_4$ [177], *cis*-$Sn(DMSO)_2Cl_2Br_2$ [178], *cis*-$Sn(DPSO)_2Br_4$ [179], *cis*-$Sn(DPSO)_2I_4$ and *cis*-$Sn(DPSO)_2EtI_3$ [180], $[SnMe_2Cl_2(DBSO)]$ [181], [*trans*-$SnMe_2(DMSO)_4][N(SO_2Me)_2]_2$ [182], *trans,cis,cis*-$SnMe_2Cl_2(ETSO)_2$ [183], $[(SnMeCl_2)_2(CHCH_2EtSO)]$ [184], $[Sn_2$-$(C_{10}H_6)_2Me_2Cl_4(DMSO)]$ [185], and $[(SnPh(DnPSO))_2(NO_3)(\mu$-oxalato$)]$ [186].

In some compounds, the tin atom has an octahedral environment, e.g. [*cis,trans,cis*-$SnCl_2Ph_2(DMSO)_2$] (XXIII) [169], while in others the coordination is pentagonal bipyramidal, e.g. [*trans*-$SnPh_2(NO_3)(DMSO)_3][NO_3]$ (XXIV) [174].

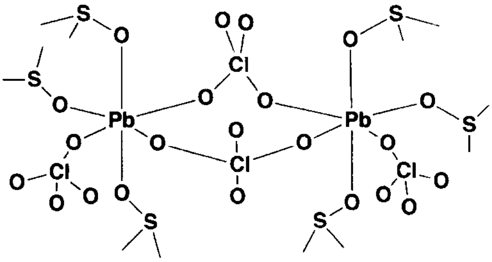


XXIII

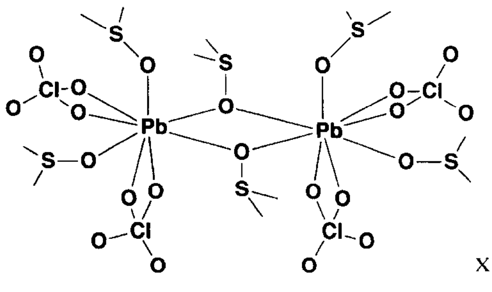


XXIV

Crystallization of $Pb(ClO_4)_2$ from aqueous ethanolic solutions containing various amounts of DMSO has resulted in the isolation of three distinct solvates with a Pb(II):DMSO stoichiometry of 1:3, 1:5, and (probably) 1:6 [187]. The X-ray structures of the first two complexes have been solved, showing the presence in the 1:3 adduct of $[Pb(DMSO)_5(O_2ClO_2)][ClO_4]$ and of two different dimers [187]. In one dimer (XXV), the two lead atoms are bridged by a pair of O,O′-perchlorate groups, the remainder of the lead coordination sphere is made up by one ClO_4^- and three DMSO ligands, all unidentate. In the other (XXVI), a compact PbO_2Pb central ring is found with bridging DMSO ligands, the remainder of the lead coordination sphere consisting of a pair of unidentate DMSO ligands and a pair of bidentate ClO_4^- ligands.



XXV



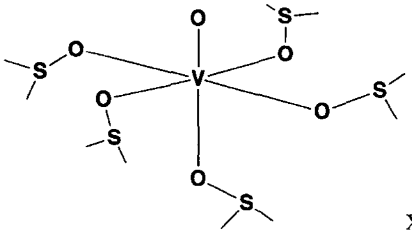
XXVI

The 1:5 adduct consists of $[Pb(DMSO)_5(O_2ClO_2)][ClO_4]$ molecules [187]. The structure of the 1:6 adduct has not been solved yet. It is suggested to contain $[Pb(DMSO)_6]^{2+}$ species [187].

Other structures concern the adducts $PbBr_2 \cdot 2DMSO$ [188], $PbI_2 \cdot 2DMSO$ [189], and $Pb(NCS)_2 \cdot 2DMSO$ [190].

3.1.5. Group V metal complexes

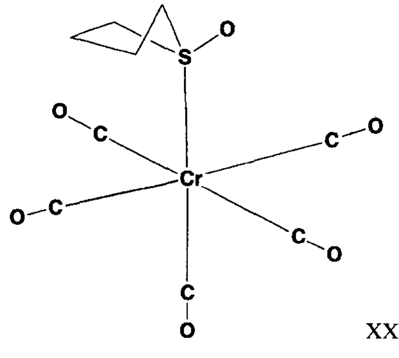
To our knowledge, the only X-ray structures available for this group concern oxovanadium(IV) complexes, containing the cation $[VO(DMSO)_5]^{2+}$ (XXVII), and $[ClO_4]^-$ [191], $[ReO_4]^-$ [192], and $[Pt(SCN)_6]^{2-}$ [193], as anions. Bond lengths and angles may be calculated from the C.S.D. data. Considering the most accurate structure (−70 °C) [191], unweighted average values, with σ in parentheses, are: V–O(sulfoxide), 2.04(1) Å; S–O, 1.52(2) Å; S–C, 1.80(1) Å; V–O–S, 125(1)°; C–S–C, 98.8(7)°; O–S–C, 104(2)°.



XXVII

3.1.6. Group VI metal complexes

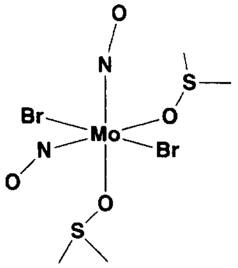
To the best of our knowledge, the only X-ray structure reported for chromium is that of the Cr(0) complex, $Cr(CO)_5(TMSO)$ (XXVIII), characterized by a metal to sulfur bond [194].



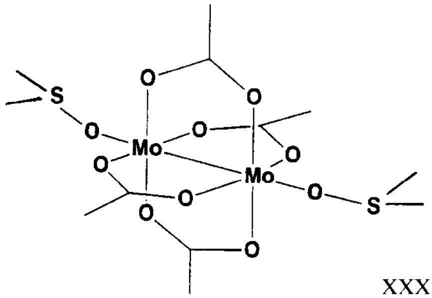
XXVIII

Other structures concern molybdenum, in different oxidation states: Mo(II): *trans,cis,cis*-$MoBr_2(NO)_2(DMSO)_2$ (XXIX) [195], $[Mo_2(\eta^5\text{-}C_5H_4CO_2)Fe(\eta^5\text{-}C_5H_5)\text{-}(MeCN)(DMSO)] \cdot 2DMSO$ [196], $[Mo_2(DMSO)_2(\mu_2\text{-formato})_4]$ (XXX) [197]; Mo(VI): $[MoO_2(DMSO)(C_{15}H_{12}O_2N_4S)]$ and $[(MoO_2)_2(DMSO)_2(C_{15}H_{10}O_3N_4)] \cdot 0.5DMSO$ [198], $[\{Mo_3CuS_4\}\{S_2P(OEt)_2\}_3(I)(\mu_2\text{-}OOCMe)(DMSO)]$ [199], $[MoO_2(\mu\text{-}O)(\text{pentanetrionato})(DMSO)_2]$ [200], $[Mo_3O_9 \cdot 4DMSO]$ [201,202], $[\{MoO_2(OEt)_2\ (DMSO)\}_2]$ [203], $[\{(MoO_2)(NCS)(DMSO)_2\}_2O]$ (XXXI) [204], $[MoO_2\{C_5H_3N\text{-}2,6\text{-}(CH_2S)_2\}(TMSO)]$ [205], and $[MoO_2\{$diphenyl-

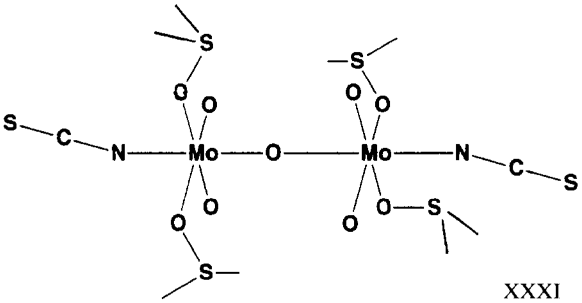
(ethanolato)pyridine}(DMSO)] [206]. All of these compounds contain unidentate O-bonded sulfoxides.



XXIX



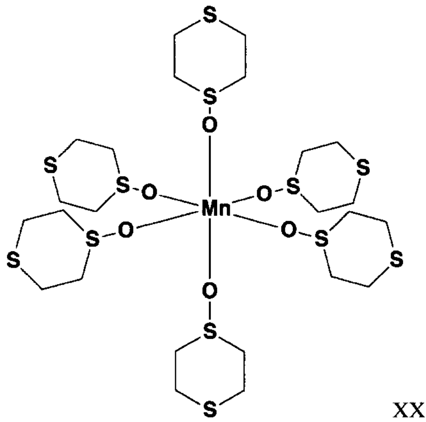
XXX



XXXI

3.1.7. Group VII metal complexes

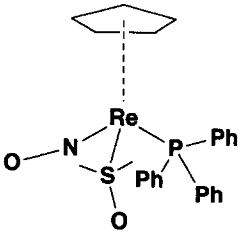
To the best of our knowledge, for this group only three X-ray structures have been reported for Mn(II), MnCu[o-phenylenebis(oxamato)](DMSO)$_3$ [88], [Mn{(SC$_4$H$_8$)SO}$_6$][ClO$_4$]$_2$ (XXXII) [207] and [Mn(DMSO)$_6$][W$_2$O$_{19}$] [208] all with the manganese atom in an octahedral environment.



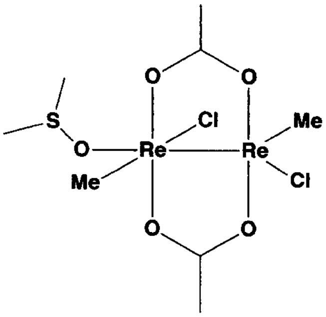
XXXII

One structure is reported for technetium(III), Tc(tetramethylbenzenethiolate)(MeCN)(DMSO), in which the metal coordination sphere is trigonal bipyramidal, with the S-bonded DMSO and acetonitrile molecules in the apical positions [209].

One rhenium(II), $[(C_5H_5)Re(NO)(PPh_3)(DMSO)][BF_4]$ (XXXIII) [210], and two dirhenium(III) complexes, $[Re_2Cl_4(\mu\text{-acetato})_2(DMSO)_2]$ [211], and $[Re_2Me_2Cl_2(\mu\text{-acetato})_2(DMSO)]$ (XXXIV) [212], have been structurally characterized. The Re(II) complex displays one S-bonded sulfoxide, while the others have O-bonded sulfoxide ligands.



XXXIII



XXXIV

3.1.8. Group VIII metal complexes

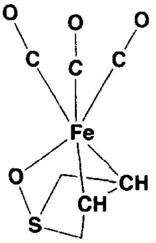
Most of the crystallographic investigations of metal–sulfoxide complexes concern elements in this group, particularly of the second and third transition series.

Structures will be presented following the transition series order. Palladium structures will be described together with those of platinum at the end of the section.

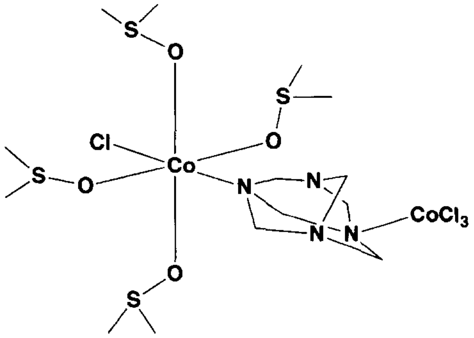
3.1.8.1. *Fe, Co and Ni complexes*

For iron, several structures have been reported for the different oxidation states: for Fe(0): $Fe(CO)_3(DHSO)$ (XXXV) [213]; for Fe(II): [*trans*-$Fe(DMSO)_2$ (phthalocyaninato)·2DMSO] [16], $[(Ph_3P)_2N][(Ph_3SnCl)_2(\mu\text{-}NC)_2Fe(CN)_2(DMSO)_2]$ [214] and $[Fe(DMSO)_6][Cl_2FeMoS_4]$, $[Fe(DMSO)_6][Cl_2FeMoOS_3]$ [216]; for Fe(III): complexes containing cations of formula $[FeCl_x(DMSO)_{6-x}]^{3-x}$, with $x=1$ [216,220] and $x=2$ [217–220]. For Fe(III) the structure of a tetraphenylporphyrin (TPP) derivative has been also determined, [*trans*-$Fe(TMSO)_2(TPP)][ClO_4]$ [221].

For cobalt(II), the structures of $[Co(DMSO)_6][CoCl_4]$ [222], and $[CoHg(SCN)_4(DMSO)_2]$ [223] have been reported; for Co(III) that of [Co(ethylenediamine)$_2$(CASO)][I]·H_2O [224]. A mixed Co(I)–Co(III) complex has also been reported, CoCl(DMSO)$_4$(μ_2-hexamethylenetetramine)$CoCl_3$ (XXXVI) [225].



XXXV



XXXVI

For nickel(II), five DMSO complexes have been structurally characterized, some in a square pyramid, [Ni(tetra-azamacrocycle)(DMSO)]$[ClO_4]_2$ [226], and [Ni(trifluoro-thienylbutanodionato)$_2$(DMSO)] [227], and some in an octahedral environment, [*trans*-$Ni(NCS)_2$(4-phenylpyridine)$_2$(DMSO)$_2$] [228], [*trans*-Ni(NCS)$_2$(4-benzylpyridine)$_2$ (DMS*O*)$_2$] and [*trans*-NiCl$_2$(4-benzylpyridine)$_2$(DMS*O*)$_2$] [229].

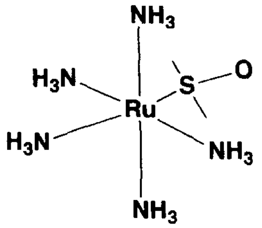
3.1.8.2. Ru and Rh complexes

Since Davies's review [2], significantly larger sets of structural data have become available, both for ruthenium and rhodium sulfoxide complexes.

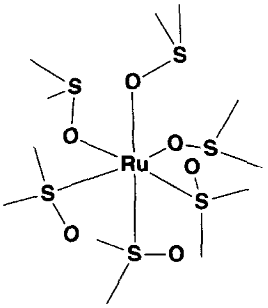
For Ru(II), the following compounds have so far been structurally characterized by X-ray analyses: [Ru(DM*S*O)(NH$_3$)$_5$][PF$_6$]$_2$ [230], [Ru(pyrazolyl)$_2$(pyrazole)$_3$(DM*S*O)] [231], [*trans*-Ru(2,2′-bipyridine)$_2$(4-ethylpyridine)(DM*S*O)][PF$_6$]$_2$·0.5DMF [232], [Ru$_2$Cl$_4$(diphenylbutanediphosphine)$_2$(DM*S*O)]·0.76Et$_2$O·0.33CH$_2$Cl$_2$ [233], [RuCl(tetrahydrothiophene)(1,5-dithiacyclooctane)(DTC*S*O)][BPh$_4$] and *trans*-RuCl$_2$(DTC*S*O)$_2$ [234], [(η^5-C$_5$H$_5$)Ru(CO)(PPh$_3$)(tBM*S*O)][SbF$_6$]·MeOH [235], *cis*-RuCl$_2$(DM*S*O)(CO)(*o*-phenylenebis{methyl(phenyl)phosphine}) [236], Ru$_2$Cl$_4$(DM*S*O)$_5$ [237], *cis*-RuCl$_2$ (DM*S*O)$_2$(trimethylbenzimidazole)$_2$ [238], *cis*-RuCl$_2$(DM*S*O)$_2$(trimethylbenzimidazole)(pyridine) [239], *cis*-RuCl$_2$(DM*S*O)$_2$(3,5-lutidine)$_2$, *trans,cis,cis*-RuCl$_2$(DM*S*O)$_2$(benzimidazole)$_2$, and *trans,cis,cis*-RuCl$_2$(DM*S*O)$_2$(trimethylbenzimidazole)$_2$ [240], *cis,-cis,trans*-RuCl$_2$(DM*S*O)$_2$(DMS*O*)(CO), *trans,trans,trans*-RuCl$_2$(DM*S*O)$_2$(DMS*O*)(CO), and *cis,trans,cis*-RuCl$_2$(DM*S*O)$_2$(CO)$_2$, and *cis,fac*-RuCl$_2$(CO)$_3$(DMS*O*) [241], *cis*-RuBr$_2$(DM*S*O)(ETP*S*O) [242], *trans,cis,cis*-RuCl$_2$(DM*S*O)$_2$(NH$_3$)$_2$ and *cis,fac*-RuCl$_2$(DM*S*O)$_3$(NH$_3$) [243], *trans,cis*-RuCl$_2$(pyrazole)$_2$(DM*S*O)$_2$ and *cis,fac*-RuCl$_2$(DM*S*O)$_3$(pyrazole) [244], *cis*-RuBr$_2$(DM*S*O)$_3$(DMS*O*) [245], *trans*-RuCl$_2$(DM*S*O)$_4$ [52,245], *cis*-RuCl$_2$(DM*S*O)$_3$(DMS*O*) [245–247], [*fac*-Ru(DM*S*O)$_3$(DMS*O*)$_3$][BF$_4$]$_2$ [248], [NH$_2$Me$_2$][*fac*-RuCl$_3$(DM*S*O)$_3$] [249], [NEt$_4$][*fac*-RuBr$_3$(DM*S*O)$_3$]·0.5MeOH [250], *trans*-RuBr$_2$(TM*S*O)$_4$, *cis*-RuCl$_2$(BE*S*E)$_2$, *cis*-RuCl$_2$(BM*S*P)$_2$, *trans*-RuCl$_2$(BM*S*E)$_2$, and *trans*-RuCl$_2$(BP*S*E)$_2$ [54], *cis*-RuCl$_2$(TM*S*O)$_4$ [55,251], *cis*-RuBr$_2$(tetrahydrothiophene)(EP*S*S) [252], *trans*-RuBr$_2$(DM*S*O)$_4$ [253], and *trans*-RuCl$_2$(DM*S*O)$_2$ (imidazole)$_2$ [254].

For Ru(III), X-ray structures are available for the following compounds: *mer,trans*-RuCl$_3$(DM*S*O)$_2$(DMS*O*) [51], [(DMSO)$_2$H][*trans*-Ru(DM*S*O)$_2$Cl$_4$] [51,52], *mer,trans*-RuCl$_3$(DP*S*O)(DPS*O*)(MeOH) [54], [(TMSO)H][*trans*-Ru(TM*S*O)$_2$Cl$_4$] [55], Na[*trans*-RuCl$_4$(DM*S*O)(NH$_3$)]·2DMSO, Na[*trans*-RuCl$_4$(DM*S*O)(imidazole)]·H$_2$O, Me$_2$CO and *mer,cis*-RuCl$_3$(DM*S*O)(DMS*O*)(NH$_3$) [71], [(acridine)H][*trans*-Ru(DM*S*O)$_2$Cl$_4$] [255], *mer*-RuCl$_3$(DM*S*O)(1-methylimidazole)$_2$, and [(4-ethylpyridine)H][RuCl$_4$(DM*S*O)(4-ethylpyridine)] [256], *mer,cis*-RuCl$_3$(DM*S*O)$_2$(NH$_3$), and *mer,cis*-RuCl$_3$(DPS*O*)$_2$(DP*S*O) [257], *mer,cis*-RuCl$_3$(DMS*O*)$_2$(CO), and [(DMSO)$_2$H][*trans*-RuCl$_4$(DMS*O*)(CO)] [258], *mer, trans*-RuBr$_3$(DES*O*)(NO)(Et$_2$S) [259].

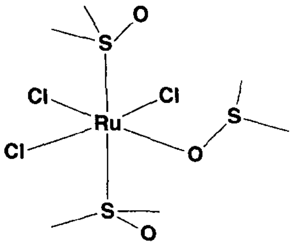
Most of the compounds are mononuclear octahedral complexes containing halide ligands. With the exception of a few Ru(II) cationic species [230,232,248], such as [Ru(DM*S*O)(NH$_3$)$_5$]$^{2+}$ (XXXVII) [230], and [Ru(DM*S*O)$_3$(DMS*O*)$_3$]$^{2+}$ (XXXVIII) [248], and two anionic, [*fac*-RuX$_3$(DM*S*O)$_3$]$^{2-}$, X = Cl [249], X = Br [250], all the other Ru(II) compounds are neutral. For Ru(III) both neutral and monoanionic species have been characterized, e.g. *mer*-RuCl$_3$(DM*S*O)$_2$(DMS*O*) (XXXIX) and [(DMSO)$_2$H][*trans*-RuCl$_4$(DM*S*O)$_2$] (XL) [51].



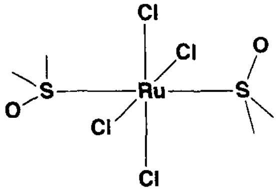
XXXVII



XXXVIII

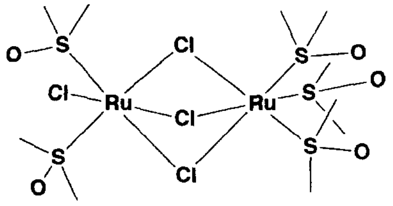


XXXIX



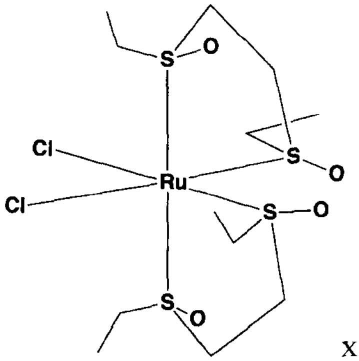
XL

One binuclear structure has also been reported, $[Ru_2Cl_4(DMSO)_5]$ (XLI) [237].



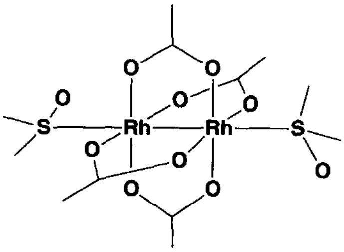
XLI

Chelating sulfoxides such as BMSE, BESE, BPSE, and BMSP have been used, yielding several cis and trans dichloro complexes, e.g. (XLII) [54].



XLII

For rhodium(II), the structures of several dirhodium DMSO complexes have been reported: $Rh_2(DMSO)_2$(acetato)$_4$ [260], $Rh_2(DMSO)_2$(propionato)$_4$ and $Rh_2(DMSO)_2$(trifluoroacetato)$_4$ [261], $Rh_2(DMSO)$(6-fluoro-2-oxypyridinate)$_4$ [262], $Rh_2(DMSO)_2$(benzoato)$_4$·toluene [263], $Rh_2(DMSO)_2(MeCONH)_4$ [264], $Rh_2(DMSO)_2(MeCOO)(MeCONH)_3 \cdot 2H_2O$ [265], $Rh_2(DMSO)(PhNOCMe)_4$ and $Rh_2(DMSO)_2(PhNOCMe)_4$ [266]. All these are characterized by a metal–metal bond and a trans arrangement of the S- and O- bonded sulfoxides, e.g. (XLIII).



XLIII

Rhodium(III) gives sulfoxide complexes analogous to those of Ru(III). The available data refer to the following compounds: [(DMSO)H][*trans*-$RhCl_4(DMSO)_2$] [57], *mer,cis*-$RhCl_3$(pyridine)$_2$(DMSO) [267], *mer,cis*-$RhCl_3(DMSO)_2$(1-methylbenzimidazole)·DMSO [14], *mer,cis*-$RhCl_3(DMSO)_2$(dimethylformamide) [268], *mer,cis*-$RhCl_3(DMSO)_2(DMSO)$ [269], [*trans,cis,cis*-$RhCl_2(DMSO)_2(DMSO)_2$]-[BF_4] [270], [NEt_4][*cis*-$RhCl_4(DMSO)_2$] [271], *mer,cis*-$RhCl_3(DMSO)_2$-(CH_2CHNEt_2) [272], [NEt_2H_2][*trans*-$Rh(DMSO)_2Cl_4$] [273], [Me_2SCH_2C-(O)Me][*trans*-$RhCl_4(DMSO)_2$] [274], and *mer,trans*-$RhCl_3(DMSO)_2$ (DMSO) [275].

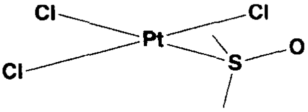
3.1.8.3. Os and Ir complexes

For osmium only a few compounds seem to have been structurally characterized, two containing S-bonded sulfoxides, (η^6-*p*-cymene)$OsCl_2$(DMSO) [276] and *trans*-$OsBr_2(DMSO)_4$ [277], and two containing O-bonded sulfoxides, [*trans*-Os(NO)(DESO)(Et_2S)Br_3] and [$^nBu_4N$][*trans*-$Os(CO)(DMSO)Cl_{2.68}Br_{1.32}$ [278,279]. All but the last one, Os(III), are Os(II) complexes, with the metal atom with an approximately octahedral coordination, if in the first one we consider the *p*-cymene ligand occupying three coordination sites.

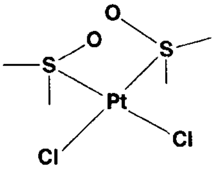
For iridium, one X-ray structure concerns Ir(I) in the trinuclear cation, $[AgIr_2(1,8\text{-diisocyanomenthane})_4(DMSO)_2]^{3+}$ [280], while for Ir(III), six structures are reported: $[(DMSO)_2H]$[*trans*-$Ir(DMSO)_2Cl_4$] [53], Ir(benzylacetophenone) $Cl_2(DMSO)_2$ [281], $(C_5Me_5)Ir(CPh{=}CHCO{-}O)(DMSO)$ [282], $(C_5Me_5)Ir(O_2CC_6H_4)(DMSO)$ [283], [Ir(octaethylporphyrine)(C_3H_7)(DMSO)] [284], and $IrCl(C_5Me_5)(DMSO)$(thyminato) [285].

3.1.8.4. Pt and Pd complexes

Available structural data for sulfoxide platinum complexes refer to two types of compound: [PtLXY(sulfoxide)]^n [74,286–333] and *cis*- [313,334–348] and *trans*- [349] $PtLX(\text{sulfoxide})_2$. *n* varies from −1 to +1, according to the nature of the ancillary ligands, e.g. $[PtCl_3(DMSO)]^-$ (XLIV) [307], and *cis*-$PtCl_2(DMSO)_2$ (XLV) [334].

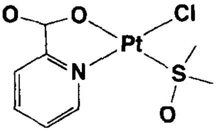


XLIV

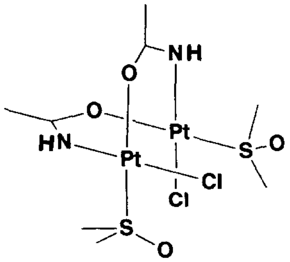


XLV

L and X, besides single ligands, may also represent the donors of chelate or bridging ligands. In this last case, binuclear compounds are formed, e.g. PtCl(DMSO)(pyridine-2-carboxilato) (XLVI) [287], and Cl(DMSO)Pt(μ-acetamido)$_2$Pt(DMSO)Cl (XLVII) [292].

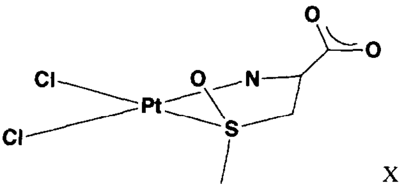


XLVI



XLVII

Y may also be the atom of a side group of the sulfoxide ligand itself, as in $PtCl_2(MCSO)$ (XLVIII) [293].



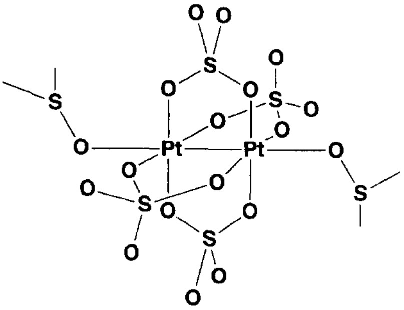
XLVIII

The following compounds have been characterized structurally: $[K_2(H_2O)L_2][PtCl_3(DMSO)]_2$ [74], [μ-(oxo-5prolinato)]$_2$[PtCl(DMSO)]$_2\cdot H_2O$ [286], PtCl(DMSO)(pyridine-2-carboxilato) [287], [μ-(oxo-5-prolinato)]$_2$ [PtCl(DMSO)]$_2\cdot 3H_2O$ [288], PtCl(DMSO)(sarcosine) [289], bis(μ-acetamido) dichlorobis(DMSO)diplatinum(II) [290], K[PtCl(DMSO)](oxo-5-prolinato)·oxo-5-proline·H_2O [291], [{PtCl(DMSO)}$_2$(μ-C_4H_8NO)$_2$] and [{PtCl(DMSO)}$_2$(μ-$C_5H_{10}NO$)$_2$] [292], *cis*-$PtCl_2(MCSO)\cdot H_2O$ [293], *cis*-$PtCl_2(DMSO)(NH_3)$ [294], *cis*-$PtCl_2$(MetSO) [295], *cis*-$PtCl_2$(DMSO)(2-picoline) [296], *cis*-$PtCl_2$(MPASO) [297], *cis*-$PtCl_2$(DMSO)(pyridine) [298], *cis*-$PtCl_2$(DMSO)(*tert*-butylamine) [299], *cis*-$PtCl_2(DMSO)(PhCH_2CN)$ and *cis*-$PtCl_2$(DMSO)(ethylene) [300], $[PtCl(DMSO)(C_6H_4NO_2)]$ [301], *cis*-$PtCl_2$(DMSO)(MeCN) [290, 302], *cis*-$PtBr_2$(DMSO)(MeCN) [302], *cis*-$PtCl_2(DMSO)(H_2O)$, Pt(DMSO)Cl(hexachloro diacetamido) and $PtCl(DMSO)(C_4NO_2Cl_6)$ [303], [Pt(DESO)(μ-Cl)Cl]$_2$ [304], [Pt(propanediamine)$_2$][$PtCl_3$(DMSO)] [305], [(2-carboxypyridine)H][$PtCl_3$ (DMSO)] [306], K[$PtCl_3$(DMSO)] [307], $[Ph_3PCH_2Ph][PtCl_3(DMSO)]$ [308], K[$PtCl_3$(DESO)] [309], $[Pt(NH_3)_4][PtCl_3(DMSO)]$ [310], [$PtCl_3$-(2-ammonioethylmethyl sulfoxide)] [311], $[Et_4N][PtCl_3(DPSO)]$ [312], K[$PtCl_3$(DPSO)]·Me_2CO [313], [*trans*-$Pt(NH_3)_2(DMSO)Cl]Cl$ [314], [*trans*-$Pt(NH_3)_2(DMSO)Cl][(ClO_4)_{0.8}Cl_{0.2}]$ [315], *cis*-$PtCl_2$(DMSO)(dimethylsulfide) [316], *cis*-$PtCl_2$(MTSO)(3-methyl-1-butene) [317], *cis*-$PtCl_2$(MTSO)[(R)-styrene] [318], K[$PtBr_3$(DESO)] [319], *trans*-$PtCl_2(DMSO)(NH_3)$ [320], *trans*-$PtCl_2$(DMSO)(2-picoline) [321], *trans*-$PtCl_2$(DMSO)(piperidine) [322], *trans*-$PtCl_2$(DMSO)(isopropylamine) [323], *trans*-$PtCl_2$(DMSO)(cytidine) [324], *trans*-$PtCl_2$(DMSO)(pyridine) [325], *trans*-$PtCl_2$(DiPSO)(1-methyl-cytosine-N) [326], [μ-(9-methyladenine-N1,N7)]-bis[*trans*-$PtCl_2$(DiPSO)]·H_2O [327], *trans*-$PtCl_2$(DMSO)(tenonitrozolato) [328], [Pt(DMSO)(1,4-diaminobutane)Cl]Cl [329], Pt_2Cl_2(3-methyl-4-acetyl-5-aminopyrazolate)(DMSO)$_2$ [330], [PtCl(DMSO) (tetramethylenediaminoethane)][BPh_4] [331], [η^5-{PtCl(DMSO)Me_2N $CH_2C_5H_3$}$_2$Fe] [332], *trans*-PtI_2(DMSO)(3,5-dimethylpyridine) [333], *cis*-$PtCl_2(DMSO)_2$ [334,335], *cis*-$PtCl_2(MESO)_2$ and *cis*-$PtCl_2(DnPSO)_2$ [336], *cis*-$PtCl_2(TMSO)_2$ [337], *cis*-$PtCl_2(MPSO)_2$ [313,338], *cis*-$PtCl_2(MBSO)_2$ [338], *cis*-$PtCl_2$(*meso*-BPESO) and *cis*-$PtCl_2$(*rac*-BPESO) [339], *cis*-$PtCl_2$(*rac*-*cis*-BPESO) [340], $[Pt(DMSO)_2(\mu\text{-}OH)]_2[ClO_4]_2$ [341], $[Pt(DMSO)_2(\mu\text{-}OH)]_2[BF_4]_2$ and $[Pt(DMSO)_2(\mu\text{-}OH)]_2[CF_3SO_3]_2\cdot 2H_2O$ [342], $[PtCl_2(TMSO)_2(\mu\text{-}OH)]_2[NO_3]_2$ [343], $[Cl_2Pt_2{}^{I}(DMSO)_2(\mu_3\text{-}O)_2Pt_2{}^{II}(DMSO)_4]\cdot 2H_2O$, $[Cl_2Pt_2{}^{I}(DMSO)_2(\mu_3\text{-}O)_2\text{-}Pt_2{}^{II}(DMSO)_4]\cdot H_2O\cdot DMF$, and $[Cl_2Pt_2{}^{I}(DMSO)_2(\mu_3\text{-}O)_2Pt_2{}^{II}(DMSO)_4]\cdot CH_2Cl_2$

[344], [*cis*-Pt(DMSO)$_2$(DMS*O*)$_2$] [CF_3SO_3]$_2$ [345], *cis*-Pt(DMSO)$_2$(NO_3)$_2$ [346], [*cis*-Pt(DMSO)$_2$(ethylenediamine)][PF_6]$_2$ [347], *cis*-Pt(DMSO)$_2$(phenyl)$_2$ [348], and *trans*-$PtCl_2$(DnPSO)$_2$ [349].

Inspection of the above list shows that almost all of the compounds are square planar platinum(II) complexes, with sulfoxide ligands S-bonded to the metal atom. In the bis-sulfoxide complexes the cis arrangement is largely prevalent over the trans one.

The only compound having O-bonded sulfoxides is represented by a binuclear Pt(III) complex K_2[Pt_2(DMS*O*)$_2$(SO_4)$_4$]·4H_2O (XLIX) [350]. This is characterized by a Pt(III)–Pt(III) bond (2.471(1) Å) and by the O-bonding of the two trans DMSO molecules. O-bonding in Pt(II) complexes has been found only in [*cis*-Pt(DMSO)$_2$(DMS*O*)$_2$][CF_3SO_3]$_2$ [345].



XLIX

As to platinum complexes in oxidation states less than 2, mixed valence tetranuclear Pt(I,II) complexes, [$Cl_2Pt_2^{I}$(DMSO)$_2$(μ_3-O)$_2$$Pt_2^{II}$(DMSO)$_4$]·X, with X = 2$H_2O$, H_2O·DMF, CH_2Cl_2, have been structurally characterized [344]. The Pt(I) atoms are linked by metal–metal bonds (2.579(1), 2.605(1), and 2.569(3) Å, in the three solvates). A distorted square planar geometry around the metal atoms is achieved by μ_3-oxo bridges and coordination of one Cl and one DMSO to each Pt(I) atom and two DMSOs to each Pt(II) atom. All the sulfoxides are S-bonded and trans to oxygen atoms [344].

The X-ray structure of an octahedral Pt(IV) complex, [Et_4N][$PtCl_5$(DMSO)], has also been reported, showing S-bonding of DMSO [351].

Far fewer structures have been determined for palladium compounds. These are of the same type as the Pt(II) derivatives: [PdLXY(sulfoxide)]^n [351–356] and *cis*- [357,358] and *trans*- [13] PdLX(DMSO)$_2$: [NEt_4][Pd(DMSO)Cl_5] [351], [*cis*-$PdCl_2$(MCSO)]·H_2O [352], *trans*-Pd(DMSO)(DMS*O*)(trifluoroacetato)$_2$ [353], [($PhCH_2$)PPh_3][*cis*-$PdCl_2$(2,4,6-trinitrophenyl)(DMSO)] [354], [Pd(μ-trifluoroacetato){($CH_2C_6H_5$)($CH_2C_6H_4$)SO}]$_2$ [355], [PdCl(DMSO)(ethylenediamine)][ClO_4] and [Pd(DMS*O*)(2,2′-bipyridyl)Cl][BF_4] [356], *cis*-Pd(DMS*O*)$_2$(NO_3)$_2$ [357], [*cis*-Pd(DMSO)$_2$(DMS*O*)$_2$][BF_4]$_2$·DMSO [358], and *trans*-$PdCl_2$(DMSO)$_2$ [13].

3.2. Stereochemistry of O-coordination

Oxygen coordination of sulfoxides to metal ions can be stereochemically classified into different categories, depending on the mutual orientation of the metal–oxygen (M–O) and S–C bonds around the S–O bond.

As shown in Fig. 3, it is possible to have trans and cis arrangements, which can be defined as follows, according to the torsion angles M–O–S–C1 (ψ_1) and M–O–S–C2 (ψ_2): (i) *trans-trans*, when both ψ_1 and ψ_2 are between 90° and 270°; (ii) *cis-cis*, when ψ_1 and ψ_2 are less than 90° or greater than 270°; (iii) *cis-trans* (cis to C1, trans to C2), if ψ_1 is either less than 90° or greater than 270°, while ψ_2 is between 90° and 270°; (iv) *trans-cis* (trans to C1, cis to C2), if ψ_1 is between 90° and 270°, and ψ_2 is either less than 90° or greater than 270°.

Fig. 4 shows the bivariate distribution ψ_1 and ψ_2. It appears that the *trans-trans* arrangement is markedly preferred (72%). Only a few structures adopt the *cis-trans* (11%), *trans-cis* (7%), or *cis-cis* (11%) geometries. It is also evident that in both the *trans-trans* and *cis-cis* conformations, the metal ion tends to lie in the plane bisecting the C1–S–C2 angle. In fact, the mean values of the M–O–S–C1 and M–O–S–C2 torsion angles are 223(2)° and 128(2)°, respectively, in the *trans-trans* case, and 51(4)° and 306(4)° in the *cis-cis* case.

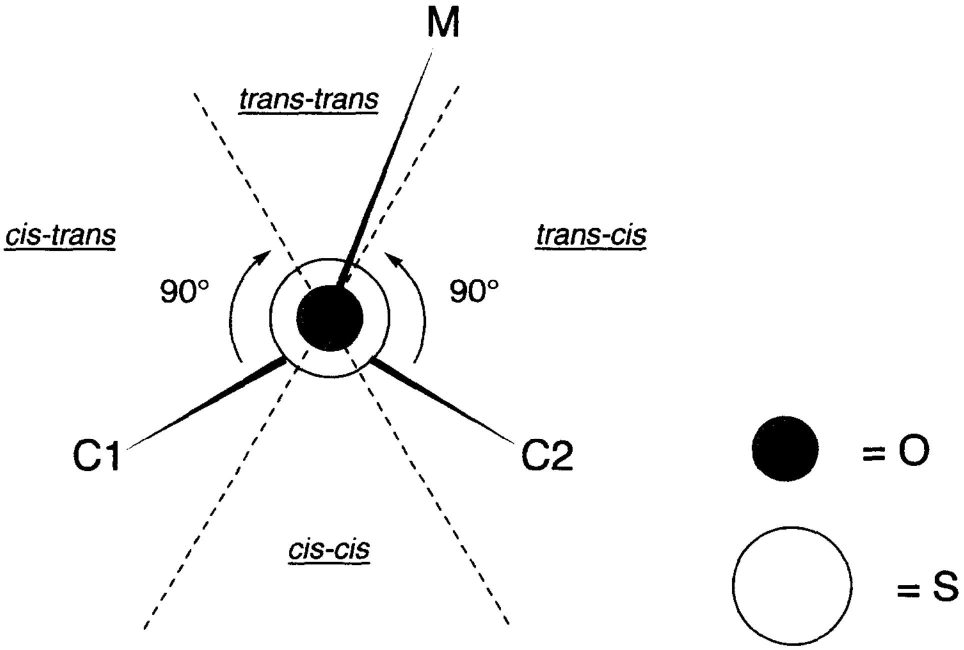


Fig. 3. Scheme of the *trans*, *cis* arrangements of the metal cation M with respect to the O-bonded sulfoxide ligand.

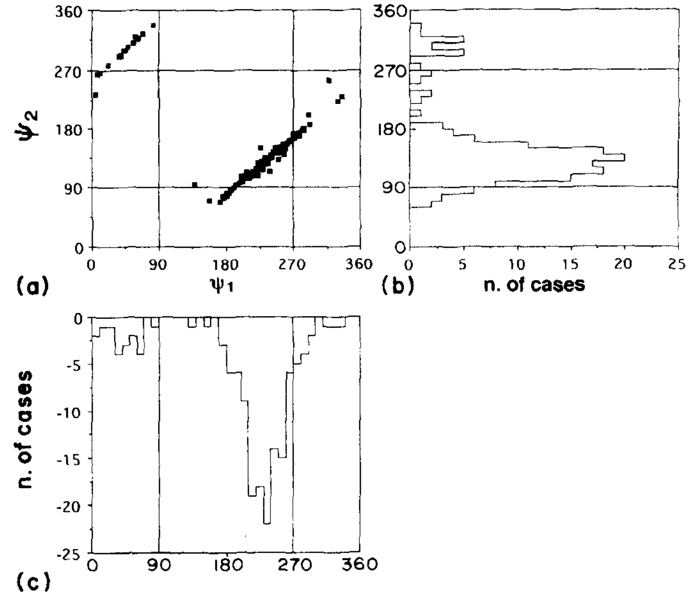


Fig. 4. Bivariate (a) and monovariate (b and c) distributions of the M–O–S–C1 and M–O–S–C2 torsional angles in the O-bonded sulfoxide complexes.

The above trend can be explained easily in terms of steric interactions with the sulfoxide side groups. In fact, as shown in Fig. 5, the distribution of the M–O–S bond angles is rather skewed and the plots of M–O–S vs. ψ_1 and ψ_2 (Fig. 6) suggest that the M–O–S bond angle tends to widen if the metal cation is cis to C1 or C2

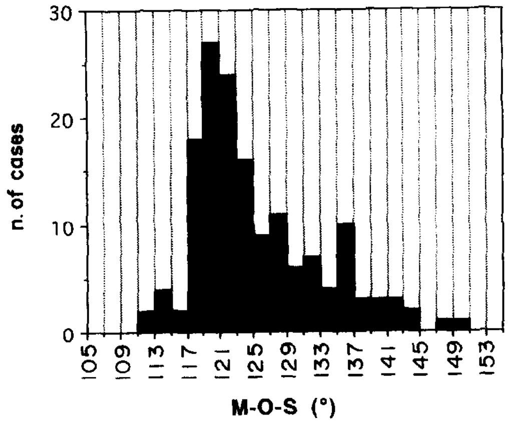


Fig. 5. Distribution of the values of the M–O–S bond angle in the O-bonded sulfoxide complexes.

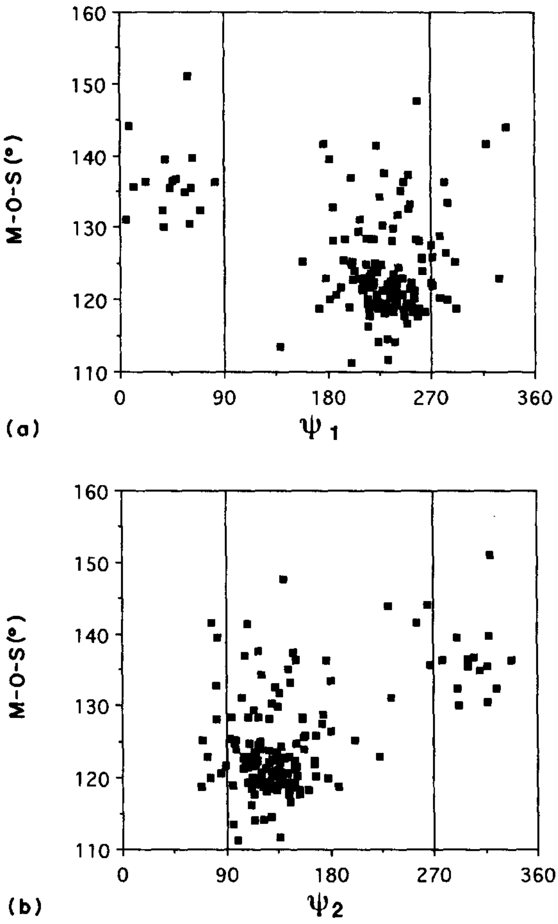


Fig. 6. Dependence of the M–O–S angle values on the torsional M–O–S–C1 (a) and M–O–S–C2 (b) angle values. When M–O–S–C1 (or M–O–S–C2) is lower than 90° or greater than 270°, the metal cation is *cis* to C1 (or to C2). In between 90° and 270° the metal cation is *trans*.

or both. As a matter of fact, while in the *trans-trans* cases the mean value of the M–O–S angle is 125.4(6)°, in the *cis-trans* cases it is 127.2(2)°, in the *trans-cis* cases it is 129.0(2)°, and in the *cis-cis* cases it is 136(1)°.

Moreover, the M–O–S angle varies in a wider range (118.2(2)–150.9(2)°) when M is cis to C atoms, than in the *trans-trans* geometry (111.3(2)–137.6(6)°).

Finally, we can observe that in the crystal structures of O-bonded sulfoxides, the sulfur atom is often disordered, while the other atoms occupy fixed positions. This kind of disorder implies a movement of the sulfur atom which inverts the pyramid, with consequent interconversion of the cis and trans isomers.

3.3. *Stereochemistry of S-coordination*

The stereochemistry of the S coordination of sulfoxides to metal atoms is essentially characterized by the twisting around the coordinative metal–sulfur (M–S) bond. Possible rotation around this bond will depend upon the nature of the M–S bond (and hence on the nature of M) and upon the steric hindrance, determined by the number and bulkiness of the coordinated ligands. Because of the many factors involved it is preferable to discuss selected typical cases separately.

3.3.1. *Platinum complexes with one sulfoxide*

The known structural data can be analyzed with reference to the geometrical scheme depicted in Fig. 7, considering the modulus of the lowest torsion angle X–Pt–S–O or Y–Pt–S–O, ψ. As shown in Fig. 8, the sulfoxide ligand cannot rotate freely around the Pt–S bond, the most frequent rotamer being found around $\psi = 0$.

3.3.2. *Platinum complexes with two cis sulfoxides*

The orientation of each S–O bond, with respect to the metal coordination plane, is described by the relative S–Pt–S–O torsion angle (ψ), while their mutual disposition is given by the O1–S1–S2–O2 pseudo torsion angle (Fig. 9).

The distribution of ψ (Fig. 10) is quite similar to that observed in platinum complexes with only one sulfoxide ligand (Fig. 8), showing again hindered rotation around the Pt–S bonds. The most frequent rotamer is again that at ψ near 0° or 180°.

The distribution of the O1–S1–S2–O2 torsion angles (Fig. 11), indicates that the two cis sulfoxides tend to assume staggered conformations, the frequency maxima being around 60–70° and 180°. It is worth noting that the anomalous case with O1–S1–S2–O2 near 20°, that is with nearly eclipsed S–O bonds, corresponds to a bidentate chelate sulfoxide, $PhS(O)CH_2CH_2(O)SPh$.

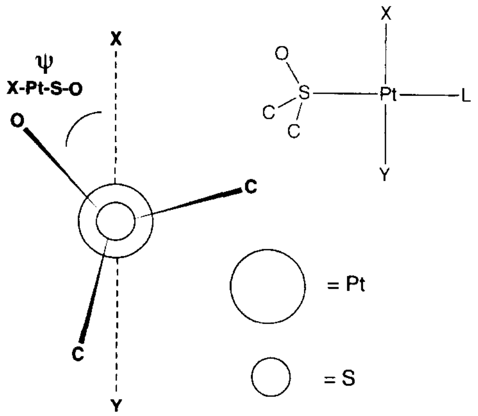


Fig. 7. Scheme of the square planar Pt^{2+} complexes with one S-coordinated sulfoxide. The absolute values of the torsional angles X–Pt–S–O and Y–Pt–S–O are considered to describe the stereochemistry of S-coordination. Among them, for simplicity, only that with the lowest absolute value is taken into account, the other one being nearly supplementary.

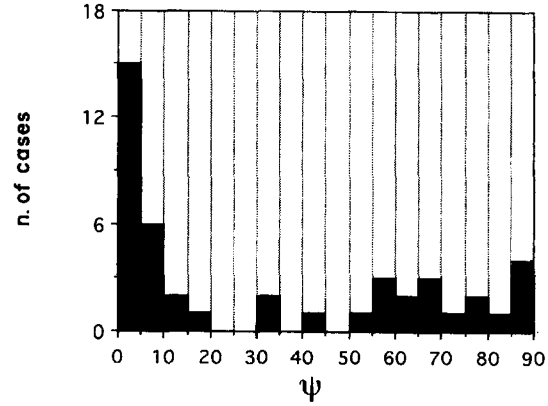


Fig. 8. Distribution of the X–Pt–S–O torsional angles as defined in Fig. 7.

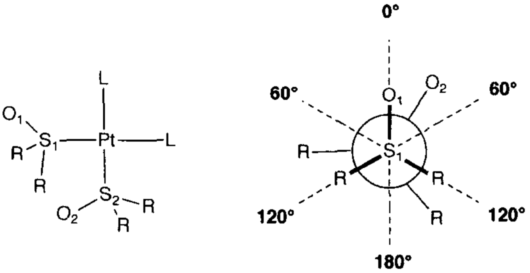


Fig. 9. Scheme of the square planar Pt^{2+} complexes with two *cis* S-coordinated sulfoxides. The absolute values of the torsional angles S1–Pt–S2–O2 and S2–Pt–S1–O1 are considered to describe the stereochemistry of S-coordination.

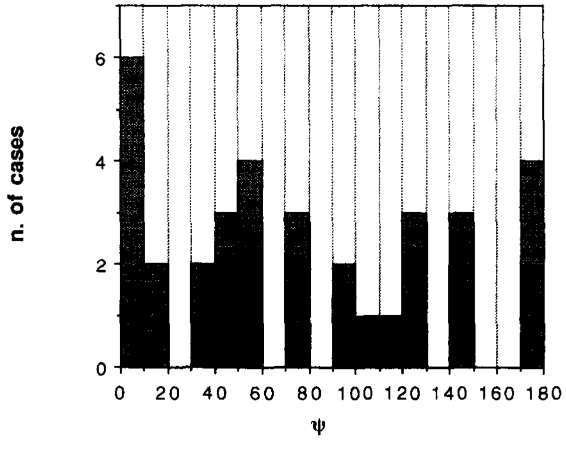


Fig. 10. Distribution of the absolute values of the S1–Pt–S2–O2 (or S2–Pt–S1–O1) torsional angle as defined in Fig. 9.

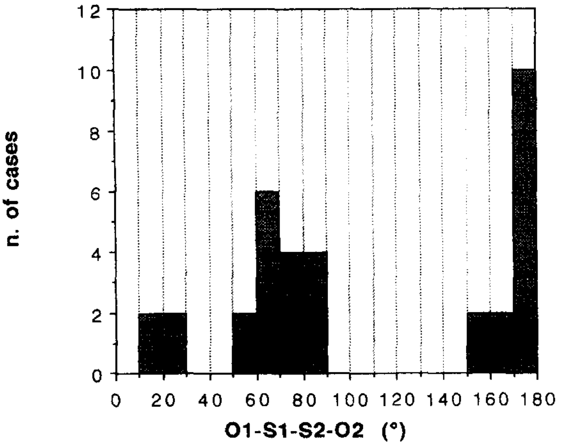


Fig. 11. Distribution of the absolute values of the O1–S1–S2–O2 (or O2–S2–S1–O1) torsional angle as defined in Fig. 9.

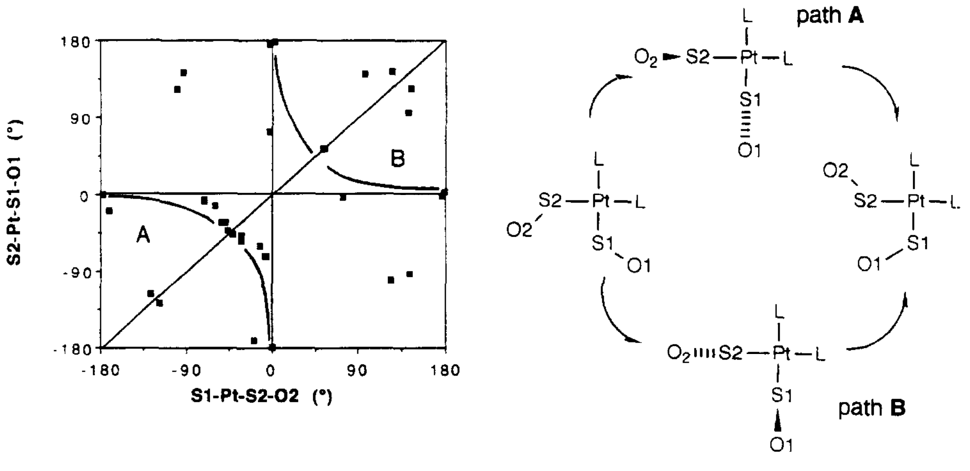


Fig. 12. Dependence of the S2–Pt–S1–O1 torsional angle upon the S1–Pt–S2–O2 one.

Fig. 12 shows the dependence of S2–Pt–S1–O1 on S1–Pt–S2–O2. The two torsion angles appear to be strongly correlated, indicating that both sulfoxide ligands tend to rotate clockwise (or anti-clockwise) around the Pt–S bonds. If S1–Pt–S2–O2 is close to 0°, S2–Pt–S1–O1 can be either −180° (pathway A) or +180° (pathway B). Moreover, if S1–Pt–S2–O2 becomes negative, S2–Pt–S1–O1 decreases from 180° (pathway B). Finally, if S1–Pt–S2–O2 approaches −180° (pathway A) or +180° (pathway B), S2–Pt–S1–O1 approaches 0°. The only cases with marked deviations from these pathways correspond to the chelating sulfoxides $PhS(O)CH_2CH_2(O)SPh$ and $PhS(O)CH{=}CH(O)SPh$.

Fig. 13 shows the dependence of O1–S1–S2–O2 on S1–Pt–S2–O2 and S2–Pt–S1–O1. It appears that the two cis sulfoxides tend to be staggered, with

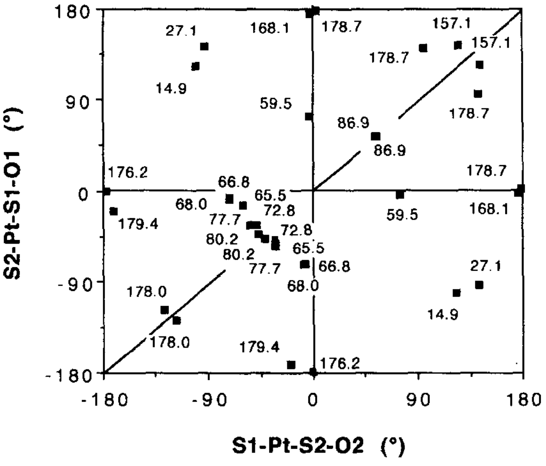


Fig.13. Dependence of the O1–S1–S2–O2 torsional angle upon S1–Pt–S2–O2 and S2–Pt–S1–O1. For sake of clarity only absolute values are reported for each point.

O1–S1–S2–O2 near 60°, unless S1–Pt–S2–O2 and S2–Pt–S1–O1 approach either 0° and 180° or 180° and 0°, respectively. Again the only deviation occurs for the bidentate sulfoxides $PhS(O)CH_2CH_2(O)SPh$ and $PhS(O)CH{=}CH(O)SPh$.

3.3.3. Ruthenium and rhodium complexes with one or two trans sulfoxides

For these octahedral complexes (Fig. 14), the torsion angle X–M–S–O can be used to monitor the geometry of the S-coordination, X being the cis donor giving the smallest absolute value of the X–M–S–O angle. The pseudo torsion angle O–S–S′–O′ monitors the possible reciprocal influence of two trans sulfoxides.

The distribution of the X–M–S–O torsion angles is given in Fig. 15. A frequency maximum is again found near 0°, indicating that the most frequent conformation

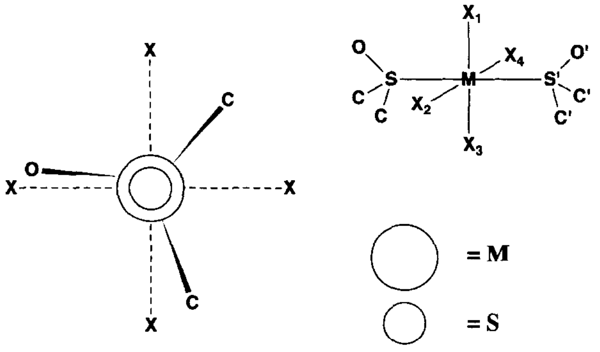


Fig. 14. Scheme of the octahedral complexes without *cis* S-coordinated sulfoxide. The absolute values of the torsional angle X–M–S–O are considered to describe the stereochemistry of S-coordination. The O–S–S′–O′ torsional angle is considered to describe the possible reciprocal influence of two *trans* sulfoxides.

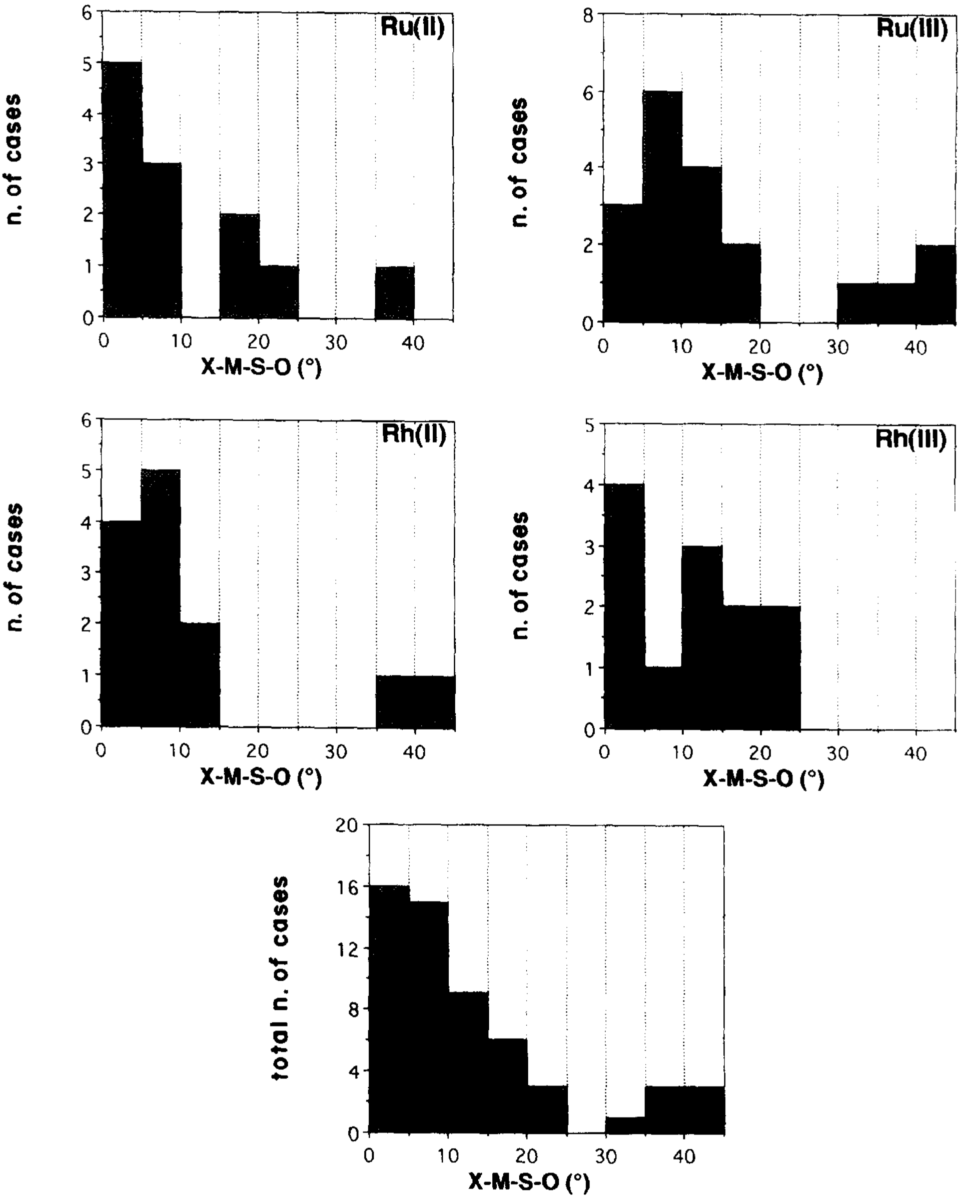


Fig. 15. Distribution of the X–M–S–O torsional angles, as defined in Fig. 14, in the cases of Ru(II), Ru(III), Rh(II), Rh(III), and all complexes.

has the S–O bond coplanar with the M–X bond. Because of the small number of cases, it would be unwise to compare ruthenium and rhodium complexes or different oxidation states. However, although this could be a simple coincidence, it appears

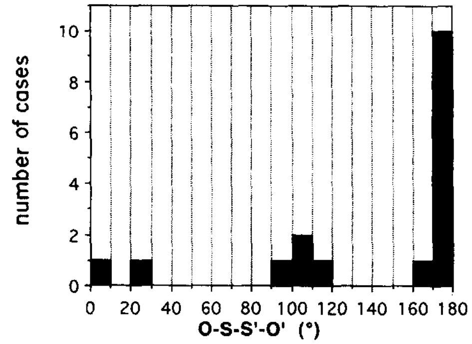


Fig. 16. Distribution of the O–S–S′–O′ torsional angles, as defined in Fig. 14.

that the eclipsed conformation seems to be preferred by ruthenium rather than by rhodium complexes, and by the +2 oxidation state.

In the subset of cases with two trans sulfoxides, O–S–S′–O′ is quite strictly confined to values close to 0–30°, 90–120°, and 160–180°, with a marked preference for this last value (Fig. 16). It seems likely that this is the consequence of the preference for the eclipsed conformation of the S–O bonds and the presence, in most cases, of a crystallographic inversion center on the metal atom.

4. Molecular structure of coordinated sulfoxides

4.1. Estimation of mean molecular dimensions

Average values for coordinated sulfoxides are collected in Table 10. Unlike those reported previously [2], the average structural parameters show that the geometry of sulfoxides is significantly affected by coordination, whether they are bonded via sulfur or oxygen atoms.

In the case of S-coordination, we have a shortening of 0.020 Å of the S–O bond distance with respect to free sulfoxides (1.4723(8) vs. 1.492(1) Å), and a widening of 2.4° and 1.5°, respectively, of the C–S–C and O–S–C bond angles (100.2(1)° and 107.43(7)° in S-bonded complexes vs. 97.8(2)° and 105.9(1)° in free sulfoxides). This trend of the average bond angles is actually that expected from the tetrahedral environment of the metal coordinated sulfur atom, in which the M–S bonding pair exerts a repulsive effect less than that of the S lone-pair in the free sulfoxide [2].

In contrast, in the case of O-coordination, the S–O distance is lengthened by 0.037 Å, becoming 1.529(1) Å, and again the average C–S–C angle increases slightly (1.2°), while the O–S–C angle decreases (1.6°), being 99.0(2)° and 104.32(9)°, respectively.

A more marked contraction (3.1°) of the O–S–C bond angle is evident going from S- to O- bonded complexes, again as a consequence of the change from a tetrahedral to a pyramidal structure of the sulfoxide sulfur atom. A smaller change is observed for the C–S–C bond angle, from 100.2(1)° to 99.0(2)°, passing from S to O bonding.

As to the S–C bond lengths, inspection of Table 10 shows that in S-bonded complexes the S–C distances are scarcely longer than those in O-bonded complexes (1.785(1) vs. 1.780(2) Å), so that it is possible to average all the values, giving $n=660$, $\sigma=0.023$ Å, median = 1.780 Å, $\langle x \rangle_s = 1.7834$ Å, $\sigma(\langle x \rangle_s) = 0.0009$ Å. Finally, we can observe that this value is only slightly shorter than that of 1.791(3) Å calculated for free sulfoxides, confirming the previous observation that the S–C distances are practically unaffected by coordination.

The trend in the S–O distances will be discussed later (Section 6). In any case, these show a larger double bond character for the S-bonded sulfoxides, which is strongly reduced in the O-bonded complexes, just like in the protonated species seen above (Section 2.2).

As expected, in the TMSO complexes, the C–S–C bond angle is narrower compared to DMSO ($\langle x \rangle_s = 92.9(2)°$, $\sigma = 0.97°$ for $n=24$), while the other bond angles, as well as the S–C bond distances, are close to those of the non-cyclic coordinated sulfoxides, allowing overall averages.

4.2. Principal component analysis of coordinated sulfoxides

A more comprehensive analysis of the molecular structure of sulfoxides coordinated to metal atoms can be performed by the principal component analysis of S–O, S–C1, S–C2, C1–S–C2, O–S–C1, and O–S–C2. As in the case of free sulfoxides, the labels of C1 and C2 have been permutated in order to take into account the intrinsic C_s symmetry of the C–S(O)–C group. For comparison purpose, the data of both uncoordinated and coordinated sulfoxides have been considered together.

If the whole set of data are analyzed, no chemically significant results are obtained. As shown in Fig. 17, no clear clustering appears, but if the data are classified into

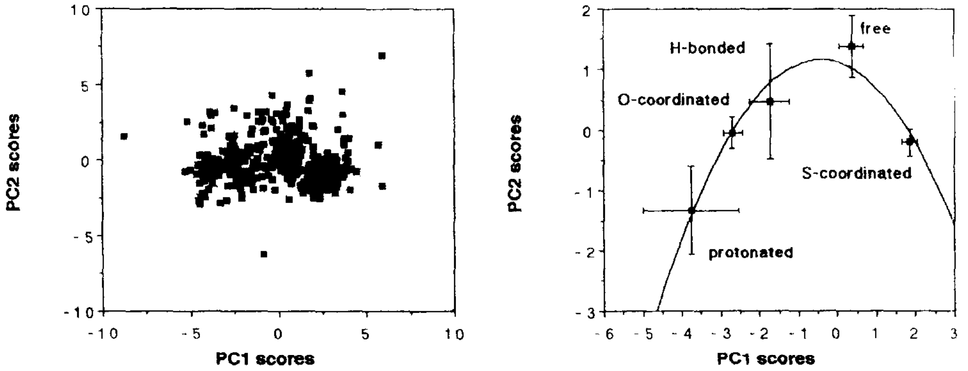


Fig. 17. Principal component analysis of coordinated sulfoxides. Interdipendence of the PC1 and PC2 scores. On the right side, the mean values of the PC1 and PC2 scores, and the triple of their standard deviations, are considered for the five classes of "free", "H-bonded", "protonated", "O-coordinated", and "S-coordinated" sulfoxides.

the five classes "free", "H-bonded", "protonated", "O-coordinated", and "S-coordinated", interesting features can be observed. The "free" sulfoxides can be considered at the origin of two reaction pathways, one going towards the "S-coordinated" sulfoxides, and the other going towards the "protonated" sulfoxides, passing through the intermediate steps of the "H-bonded" and "O-coordinated" ligands.

Such results suggest that application of an appropriate rotation algorithm could produce new chemically significant eigenvectors [8a]. However, a simpler approach consists in performing the PCA on the free and O-bonded sulfoxides on one side, and on the free and S-bonded sulfoxides on the other.

4.2.1. *Principal component analysis of O-coordinated sulfoxides*

Eigenvectors and corresponding eigenvalues are reported in Table 11. Four PCs (PC1, PC2, PC3, and PC6) have A′ symmetry, the other two (PC4 and PC5), A″ symmetry.

On the basis of the χ^2 test criterion [67], all the PCs are primary, but only the first two (which describe complexively 60% of the overall variance) have a sound chemical meaning.

PC1 indicates that if S–O shortens, S–C1 and S–C2 lengthen, C1–S–C2 tightens, and O–S–C1 and O–S–C2 widen. This trend is analogous to that observed in the PCA of uncoordinated sulfoxides, and can be simply interpreted on the basis of the VSEPR theory [68], as reported above (Section 2.3). PC2 indicates that when the bond distances increase, the bond angles tighten. This corresponds to an increase of the pyramidalicity of the sulfur atom, which moves out from the plane of the O, C1, and C2 atoms.

In the PC1–PC2 plot (Fig. 18), there is no clear clustering, but considering the mean values of the PC1 and PC2 scores for "free", "H-bonded", "protonated", and

Table 11

Principal component analysis of uncoordinated and O-coordinated sulfoxides: summary of the principal components: eigenvectors, eigenvalues, and percentage of the overall variance they describe

	PC1	PC2	PC3	PC4	PC5	PC6
Eigenvectors						
S–O	−0.521	0.344	0.000	−0.012	0.781	0.000
S–C1	0.301	0.438	−0.637	0.472	0.015	−0.301
S–C2	0.301	0.438	0.643	0.460	0.015	0.301
C1–S–C2	−0.312	−0.583	0.005	0.748	0.060	0.000
O–S–C1	0.474	−0.281	0.300	−0.059	0.440	−0.640
O–S–C2	0.474	−0.281	−0.301	−0.053	0.440	0.640
Eigenvalues						
	2.509	1.121	0.895	0.668	0.503	0.303
Variance percentage						
Cumulative variance percentage						
	41.8	18.7	14.9	11.1	8.4	5.1
	41.8	60.5	75.4	86.5	94.9	100.0

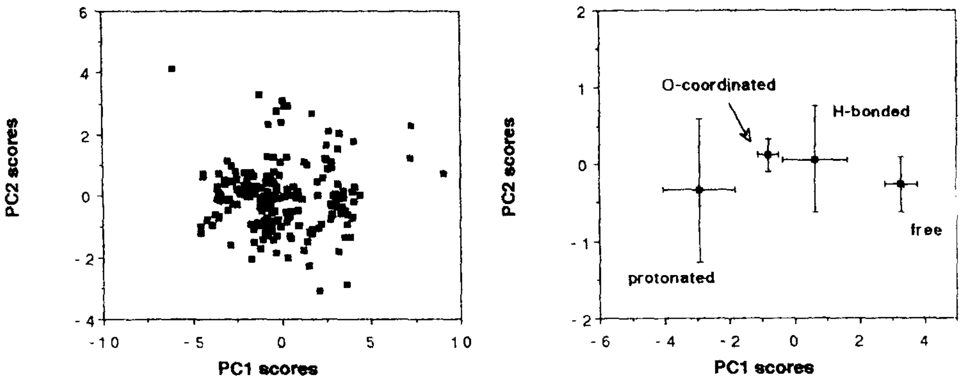


Fig. 18. Principal component analysis of coordinated sulfoxides (without S-coordinated). Interdipendence of the PC1 and PC2 scores. On the right side, the mean values of the PC1 and PC2 scores, and the triple of their standard deviations, are cosidered for the four classes of "free", "H-bonded", "protonated", and "O-coordinated" sulfoxides.

"O-coordinated" species, we can observe, as expected, that the "H-bonded" and the "O-coordinated" sulfoxides are structurally intermediate in a reaction from "free" to "protonated" sulfoxides.

It is particularly worth noting that only PC1 discriminates the four classes of ligands, supporting the hypothesis that the principal structural deformation due to protonation is that described by Schemes 1 and 2 of Section 2.2.

Further, it is important to stress that the O-coordinated sulfoxides behave as intermediates between "H-bonded" and "protonated" ligands. As a consequence, O-coordination to a metal cation is interpretable as the formation of a strong electrostatic interaction.

The translation of the PC1 eigenvector into real space, indicates that a shortening of 0.048 Å of the S–O bond distance implies a lengthening of 0.035 Å of S–C1 and S–C2, a tightening of 3.0° of the C1–S–C2 bond angle, and a widening of 3.5° of the O–S–C bond angles. These values differ from those expected from the mean values, where a shortening of 0.048 Å of S–O is accompanied by a tightening (1.5°) of C1–S–C2, and a widening (1.6°) of the O–S–C bond angles angles. This inconsistency is due to the fact that PC1 does not consider the overall variance of the data, but only the part involved directly in the O-coordination.

4.2.2. *Principal component analysis of S-coordinated sulfoxides*

Eigenvectors and corresponding eigenvalues are reported in Table 12. Four of them (PC1, PC2, PC3 and PC4) have A′ symmetry, and two (PC5 and PC6), A″ symmetry.

On the basis of the χ^2 criterion [67], all of them are principal, but only the first two are chemically meaningful. They describe only 61% of the overall variance, but analogous results with a higher percentage (82%) can be obtained limiting the PCA to DMSO complexes.

PC1 indicates movements of the S atom from (or towards) the plane defined by

Table 12
Principal component analysis of uncoordinated (without protonated and H-bonded) and S-coordinated sulfoxides: summary of the principal components: eigenvectors, eigenvalues, and percentage of the overall variance they describe

	PC1	PC2	PC3	PC4	PC5	PC6
Eigenvectors						
S–O	0.470	−0.216	−0.418	0.747	0.000	0.000
S–C1	0.416	0.405	0.396	0.077	0.470	0.529
S–C2	0.416	0.405	0.396	0.077	−0.470	−0.529
C1–S–C2	−0.418	−0.316	0.658	0.540	0.000	0.000
O–S–C1	−0.359	0.513	−0.198	0.263	0.529	−0.470
O–S–C2	−0.359	0.513	−0.198	0.263	−0.528	0.470
Eigenvalues						
	2.285	1.408	0.688	0.604	0.556	0.406
Variance percentage						
Cumulative variance percentage						
	38.1	23.5	11.5	10.1	9.3	7.5
	38.1	61.6	73.1	83.2	92.5	100.0

O, C1, and C2. PC2 indicates that shortening of S–O implies lengthening of S–C1 and S–C2, tightening of C1–S–C2, and widening of O–S–C1 and O–S–C2. Inspection of Table 12 shows that PC1 corresponds to PC2 in the PCA of O-coordinated sulfoxides.

The scatter plot of the PC2 scores vs. the PC1 scores (Fig. 19) does not present any evident clustering. However, if the mean values of the PC1 and PC2 scores are considered, a significant difference appears between “free” and “S-coordinated” sulfoxides.

Since only PC1 is able to discriminate these two classes of compounds, it may be

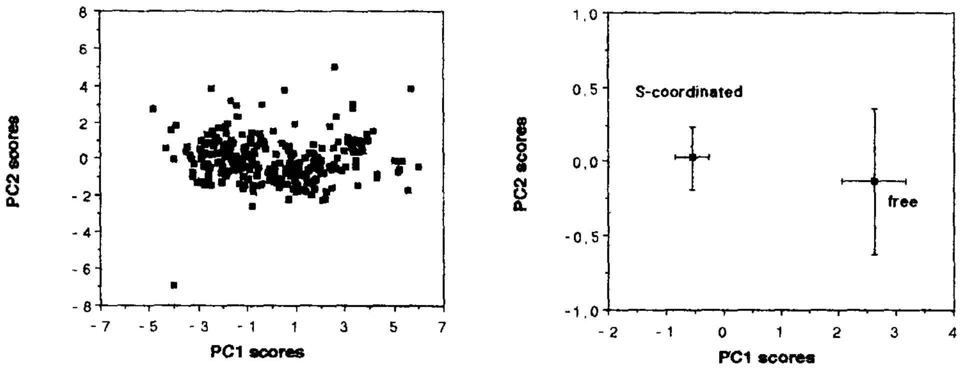


Fig. 19. Principal component analysis of coordinated sulfoxides (without O-coordinated, protonated, or H-bonded). Interdependence of the PC1 and PC2 scores. On the right side, the mean values of the PC1 and PC2 scores, and the triple of their standard deviations, are considered for the two classes of “free” and “S-coordinated” sulfoxides.

concluded that S-coordination implies a displacement of S towards the plane of C1, C2, and O. In other words, S-coordination causes a decrease of the pyramidalicity of the sulfur atom and a distortion towards a tetrahedral environment.

The translation of the PC1 eigenvector into real space shows that a shortening of 0.020 Å of the S–O bond distance implies a shortening of 0.026 Å of the S–C1 and S–C2 bond distances, a widening of 3.3° of the C1–S–C2 bond angle, and a widening of 1.6° of the O–S–C bond angles. These values differ from those expected from the mean values alone, where a shortening of 0.020 Å of S–O is accompanied by a widening of 2.4° of C1–S–C2, and of 1.5° of O–S–C1 and O–S–C2. This inconsistency depends on the fact that PC1 does not consider the overall variance of the data, but only the part directly involved in the coordination.

5. Trans and cis influence

The trans influence of sulfoxides has been investigated by several authors [2], mainly in platinum complexes, reaching different conclusions about the amount of such effect. In some cases, in fact, the difference between the bond distances examined is very small, at the limits of the statistical significance. Thus, Rochon et al. in 1990 concluded that the structures reported in the literature did not show any systematic lengthening of the Pt–Cl bonds, trans to DMSO [303]. On the other hand, Kukushkin and coworkers observed spectroscopically that DMSO and other sulfoxides strengthen trans Pt–N [359], and Pt–Cl bonds [360]. However, further structural investigations showed that in $[PtCl_3L]^-$ complexes the Pt–Cl bond trans to L becomes weaker in the order $PEt_3 > DMSO > ethylene > amines, Cl^-$ [308]. In any case, the trans influence of DMSO relative to the chloride ion is fairly weak [308].

When more extensive, and hence statistically more significant, sets of data are examined, it is confirmed that S-bonded sulfoxides display a fairly weak trans influence on Cl, as well as on N and O ligands.

In fact, from data in Table 13 it appears that on average, the Pt–Cl bond length is increased from 2.299(2) Å, when trans to Cl, O or N ligands, to 2.312(1) Å, when trans to S. A lengthening is also observed going from cis to trans S for Pt–N bond distances (2.034(6) vs. 2.067(8) Å), as well as for Pt–O distances (2.01(6) vs. 2.040(4) Å), even if the latter difference is not significant, because of the scarcity of data available. Interestingly, the same trend is observed for the Ru(II)–Cl, Ru(II)–N and Rh(III)–Cl, Rh(III)–N distances, as shown in Tables 14 and 15. Bonds trans to S appear slightly weakened, compared to the cis ones.

Kukushkin deduced, from IR data, that S-bonded DMSO displays a trans influence comparable to that of ethylene [366]. The few available structural data are in agreement with this observation. In fact, the average Pt–Cl bond length, trans to olefinic ligands, of 2.308(5) Å is very close to that trans to S (2.312(1) Å).

Inspection of the Pt–S bond distances, in compounds having only one S-bonded sulfoxide per metal atom (av. 2.207(3) Å), shows that they span a rather wide range, from 2.168(2) to 2.257(8) Å, depending on the nature of the coordinated ligands. It is interesting to observe that the longest values are found in complexes containing

Table 13
Average Pt(II)–X bond distances (Å) trans and cis to S-bonded sulfoxides

	Pt–Cl trans S	Pt–Cl cis S[a]	Pt–N trans S[b]	Pt–N cis S[b]	Pt–O trans S	Pt–O cis S
Min.	2.289(3)	2.216(7)	2.030(10)	1.983(6)	1.994(7)	1.950(5)
Max.	2.337(5)	2.376(1)	2.142(7)	2.067(13)	2.068(9)	2.076(16)
Range	0.048	0.160	0.112	0.084	0.074	0.126
n	51	71	15	20	22	2
Median	2.312	2.299	2.060	2.031	2.040	2.013
σ	0.010	0.018	0.032	0.027	0.019	0.089
$\langle x \rangle_s$	2.312	2.299	2.067	2.034	2.040	2.01
$\sigma(\langle x \rangle_s)$	0.001	0.002	0.008	0.006	0.004	0.06
trans-cis difference	0.013(3)		0.033(14)		0.03(6)	

[a] Cl trans to Cl, O, and N. [b] N(*sp*) distances excluded.

Table 14
Average Ru(II)–X bond distances (Å) trans and cis to S-bonded sulfoxides

	Ru–Cl trans S	Ru–Cl cis S[a]	Ru–N trans S	Ru–N cis S
Min.	2.392(2)	2.388(1)	2.100(6)	2.081(7)
Max.	2.467(3)	2.431(1)	2.156(2)	2.156(8)
Range	0.075	0.043	0.056	0.075
n	30	13	13	16
Median	2.426	2.413	2.142	2.107
σ	0.016	0.012	0.017	0.026
$\langle x \rangle_s$	2.426	2.411	2.138	2.113
$\sigma(\langle x \rangle_s)$	0.003	0.003	0.005	0.006
trans-cis difference	0.015(6)		0.025(11)	

[a] Cl trans to Cl, O, and N.

sulfoxides bulkier than DMSO, such as DiPSO (2.251(8), 2.257(8) Å) [327], or π accepting ligands in cis positions, like olefinic ligands (2.225(3)–2.252(2) Å) [300,317,318]. These data suggest the existence of steric effects and of a π cis influence on the Pt–S bond. A similar lengthening is also observed with organonitrile ligands (2.215(1)–2.233(5) Å) [290,300,302], generally assumed to possess rather weak π accepting properties.

Cis influence effects of L ligands have been revealed by Belsky et al. examining the trend of the Pt–S bond lengths in [*cis*-$PtCl_2$(DMSO)L] complexes, which decrease in the following order: DMSO > nitriles > pyridines > NH_3 [298].

In platinum complexes with two cis sulfoxides (Table 9), the mean Pt–S distance is longer (2.226(3) Å) than in complexes with one sulfoxide per metal atom. This lengthening could be ascribed to cis influence effects, similar to those seen above, exerted by weak π accepting ligands, such as olefins and possibly nitriles.

Again the longest values are found with substituted DMSO ligands, such as MESO (2.257(5)–2.272(5) Å) [336] and DnPSO (2.247(3), 2.263(3) Å) [336], presumably due to steric effects.

Strong trans influence effects appear in *trans*-$PtCl_2(DnPSO)_2$ [349], where the Pt–S bond distance of 2.292(2) Å is far longer than the mean value of 2.226(3) Å, found in the cis complexes. To our knowledge this is the only trans bis(sulfoxide) platinum complex, in agreement with the thermodynamic instability of such complexes, with respect to the cis isomers.

A more marked trans influence is evident in *cis*-$PtPh_2(DMSO)_2$ (Pt–S, 2.315(2) and 2.324(2) Å), as expected from the higher trans influence of the phenyl groups compared to chlorides [348].

As for platinum, ruthenium and rhodium complexes also show a significant lengthening of the M–S bond distances, trans to S-bonded sulfoxides, compared to those trans to halides or N, and O ligands, i.e. Ru(II), 0.065(8) Å; Ru(III), 0.068(12) Å; Rh(III), 0.052(9) Å.

In view of the π accepting properties of sulfoxides, the trans influence of S upon itself can be ascribed both to σ and π effects [2].

It is interesting to observe that the longest Ru–S bond distance is found in *cis*-$RuCl_2(CO)(DMSO)$[*o*-phenylenebis(methylphenylphosphine)] [236]. The Ru(II)–S bond, trans to phosphorus, lengthens up to 2.380(2) Å, confirming the trans influence of P on S, already observed in platinum complexes [308]. In any case, a small contribution to the lengthening could derive from the π cis influence of CO.

It is well known that the electron withdrawing ability of carbonyls leads to a shortening of the trans Pt–Cl bonds, attributable to the increase of the electrostatic interaction between the metal and the chloride ion [361]. A similar effect is clearly evident also in the Ru(II) octahedral complex *cis,cis,trans*-$RuCl_2(CO)_2(DMSO)_2$ [241], where the mean Ru–Cl distance of 2.399(3) Å is shorter than those trans or cis to S-sulfoxides, of 2.426(3) and 2.411(3) Å, respectively.

Of interest, in *mer,cis*-$RuCl_3(DPSO)_2(DPS\mathit{O})$ the Ru(III)–Cl bond distance (2.307(2) Å), trans to O, is significantly shorter than the mutually trans Ru(III)–Cl bond lengths (av. 2.331(9) Å) [258]. The same trend (2.301(1) vs. 2.328(16) Å) has been observed in *mer*-$RuCl_3(DPSO)(DPS\mathit{O})(MeOH)$ [54], showing that DPS*O* and MeOH have a similar trans influence and supporting the suggestion that this is weaker than that of Cl [54]. This is supported by the trend of the Rh–Cl distances in *mer,trans*-$RhCl_3(DMSO)_2(DMS\mathit{O})$ (2.312(1) Å, trans to O; 2.329(2) and 2.342(2) Å, trans to Cl) [275]. However as expected, the Ru(III)–O distance, trans to S, of 2.114(5) Å is longer than that of 2.091(6) Å, trans to Cl [258]. A similar situation (2.122(2) vs. 2.094(3) Å) was found in *mer*-$RuCl_3(DPSO)(DPS\mathit{O})(MeOH)$ [54]. These data are in agreement with a trans influence order O<Cl<S. No appreciable difference in trans influence between oxygen and chlorine is observable in Pt complexes.

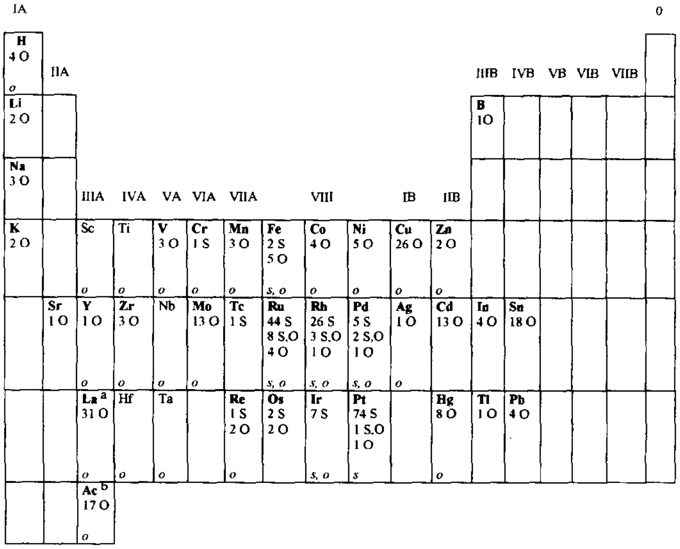
6. Metal–sulfoxide bonding

Fig. 20 shows a sketch of the Periodic Table reporting the number of known X-ray molecular structures containing O- and/or S-bonded sulfoxides, as well as the prevalence of O- and S-bonding, as inferred from IR spectroscopy in several other compounds [2].

Inspection of this table shows a general prevalence of O-bonded species. S-bonding appears to be preferred by elements of the 2nd and 3rd transition series in group VIII. This trend has been interpreted [2] on the basis of the Hard-Soft-Acid-Base principle [362]. However, it must be kept in mind that the "hardness" or "softness" of a metal ion can be dramatically modified by the nature of the coordinated ligands, depending on their σ donor or π accepting properties [241,257]. Further, steric effects can force a linkage isomerism, from S- to O-bonded species [258].

6.1. S-bonding

According to the HSAB theory, in soft metal ion complexes the orbital diffuseness of the acceptor atoms would be better matched by the diffuse sulfur donor orbitals, favoring S-coordination. However, it may be seen that for soft metal ions, such as Ag^+, Cd^{2+}, and Hg^{2+}, there is evidence of a prevalence of O-bonded species, even in the absence of π accepting or bulky ligands. This suggests that a particular electronic structure is required in order to favor the metal–sulfur bond over the



IA	IIA	IIIA	IVA	VA	VIA	VIIA	VIII			IB	IIB	IIIB	IVB	VB	VIB	VIIB	0
H 4 O *o*																	
Li 2 O												**B** 1O					
Na 3 O																	
K 2 O		Sc *o*	Ti *o*	**V** 3 O *o*	**Cr** 1 S *o*	**Mn** 3 O *o*	**Fe** 2 S 5 O *s, o*	**Co** 4 O *o*	**Ni** 5 O *o*	**Cu** 26 O *o*	**Zn** 2 O *o*						
	Sr 1 O	**Y** 1 O *o*	**Zr** 3 O *o*	Nb *o*	**Mo** 13 O *o*	**Tc** 1 S	**Ru** 44 S 8 S,O 4 O *s, o*	**Rh** 26 S 3 S,O 1 O *s, o*	**Pd** 5 S 2 S,O 1 O *s, o*	**Ag** 1 O *o*	**Cd** 13 O	**In** 4 O	**Sn** 18 O				
		La^a 31 O *o*	Hf *o*	Ta *o*		**Re** 1 S 2 O *o*	**Os** 2 S 2 O	**Ir** 7 S *s, o*	**Pt** 74 S 1 S,O 1 O *s*		**Hg** 8 O *o*	**Tl** 1 O	**Pb** 4 O				
		Ac^b 17 O *o*															

Fig. 20. Sketch of the Periodic Table showing, for elements in bold characters, the number of known X-ray molecular structures of sulfoxide complexes, containing only O-bonded (O), S-bonded (S) or both S- and O-bonded sulfoxides (S,O) (disordered structures are also included). *o* and *s* indicate prevalence of O- or S-bonded species, as suggested by IR spectroscopy. ([a]Lanthanides: La, Ce, Pr, Nd, Sm, Eu, Er, Yb, Lu. [b]Actinides: Th, U).

metal–oxygen one, probably through a π back-bonding from metal to sulfoxide orbitals. For the above species, the possibility of π bonding between the metal atom and the S-ligand is much lower compared to the *d*-transition elements [363].

As a matter of fact, for Ru(II)–DMSO complexes, it has been proposed that the metal–sulfur bond contains a partial double bond character, due to d_π–p_π back-donation from the metal to the sulfur atom [2]. This was essentially based on March's and Ferguson's observation that in $[Ru(NH_3)_5(DMSO)][PF_6]_2$, the Ru–S bond distance was particularly short (2.188(3) Å) and the S–O bond distance (1.527(7) Å) much longer than in other S-bonded metal complexes [230]. These features could be easily explained in terms of a π back-bonding contribution from Ru to S. Accordingly, it was also proposed that the trans arrangement of S-bonded ligands is unfavored, because of their competition for the metal π electrons [230,245,248,249]. This is in agreement with the thermodynamic instability of *trans*-$RuX_2(DMSO)_4$ with respect to *cis*-$RuX_2(DMSO)_3(DMSO)$ complexes (X = Cl, Br), but, as stated above, other factors, like the σ trans influence of S ligands and steric effects, could also play an important role [245].

The π bonding scheme in Ru(II) complexes is now further supported by the observation that the mean Ru–S bond length of 2.265(3) Å (Table 9) is significantly lower than the sum of the single bond covalent radii, of 2.37 Å. Furthermore, in the first five Ru(II) compounds listed above in Section 3.1.8.2, containing but one sulfoxide ligand, the Ru–S bond distance increases from 2.188(3) to 2.269(2) Å [230–234], following the decrease of the σ donor power of the coordinated atoms. The decrease of electron charge density on the metal atom decreases its π back donation ability, lengthening the Ru–S distance. Accordingly, the S–O bond length is reduced from 1.512(7) Å, in $[Ru(DMSO)(NH_3)_5][PF_6]_2$ [230], to 1.45(2) Å in the Cl,S_4 derivative [RuCl(tetrahydrothiophene)(1,5-dithiacyclooctane)(DTCSO)][BPh_4] [234]. This trend is confirmed by the S–O stretching frequency, which is of 1045 cm^{-1} in the pentaammino complex (~10 cm^{-1} less than in free DMSO) and of 1090, 1075 cm^{-1} in [Ru_2Cl_4(diphenylbutanediphosphine)$_2$(DMSO)] [233] and [RuCl(tetrahydrothiophene) (1,5-dithiacyclooctane)(DTCSO)][BPh_4] [234]. The observed weakening of the S–O bond suggests that π electrons are transferred from metal to sulfoxide orbitals having a marked S–O antibonding character.

In trans sulfoxide complexes, the mean Ru(II)–S bond length is markedly longer (2.330(4) Å) (Table 9), suggesting a reduction of the bond order, as expected from the metal π electron competition between the trans π accepting sulfoxide ligands. However, this lengthening is not paralleled by a significant decrease of the S–O bond distances. In fact, the mean value of 1.475(2) Å is hardly shorter than that of 1.478(1) Å in the non-trans compounds (Table 9). This may be explained considering the σ trans influence of S which, weakening the trans Ru–S bonds, reduces the S→M σ donation and hence the positive charge on the sulfur atom with consequent lengthening of the S–O bonds. Therefore, the thermodynamic instability of the trans arrangement of sulfoxide ligands should be due both to σ and π effects, which have nearly opposite effects on the S–O bond.

Indirect evidence of π effects in the Ru–S bonds has been deduced from the comparison of the Ru–Cl and Ru–S bond distances in Ru(II) and Ru(III) derivatives. In fact, while there is a significant decrease, passing from Ru(II) to Ru(III), of the Ru–N and Ru–O (~0.04 Å), as well as of the Ru–Cl bond lengths (~0.06 Å, trans to Cl; ~0.09 Å, trans to S), a slight increase is found in the Ru–S bond lengths in the two oxidation states (Ru(II), 2.330 Å, Ru(III), 2.343 Å, trans to S; Ru(II), 2.265 Å, Ru(III), 2.275 Å, cis to S) [51,55,256]. This trend has been interpreted in terms of a reduction of π back-bonding in the Ru(III)–S(DMSO) bonds, with respect to the Ru(II) analogues. The reduction of the bond length, passing from the +2 to the +3 oxidation state, would be counterbalanced by the decrease of the Ru–S bond order.

In any case, the average Ru(III)–S bond distance of 2.289(8) Å, in strictly related compounds having a N-ligand trans to DMSO (Na[*trans*-$RuCl_4$(DMSO)(imidazole)] [71], Na[*trans*-$RuCl_4$(DMSO)(NH_3)] [71], and [(4-ethylpyridine)H][$RuCl_4$(DMSO)(4-ethyl pyridine)] [256]) is shorter than that of 2.34(1) Å, found in compounds with two trans DMSO ligands ([$(DMSO)_2H$][*trans*-Ru$(DMSO)_2Cl_4$] [51,52], [(TMSO)H][*trans*-Ru$(TMSO)_2Cl_4$] [55], and [(acridine)H][*trans*-Ru$(DMSO)_2Cl_4$] [255]), while the average S–O bond distance goes from 1.482(5) to 1.466(5) Å. This trend is also reflected in the S–O stretching frequency that, for example, decreases from 1115 cm^{-1} in [$(DMSO)_2H$][*trans*-Ru$(DMSO)_2Cl_4$] to about 1090 cm^{-1} in Na[*trans*-$RuCl_4$(DMSO)(NH_3)] [71]. All these data are consistent with some π back-bonding even in Ru(III) complexes.

The role of π effects is further shown by the sulfoxide–carbonyl derivatives. In fact, the presence of such strong π accepting ligands, trans to DMSO, hinders any π back bonding from Ru(II) to the sulfoxide, and O-bonding is induced, as in *cis,cis,trans*-$RuCl_2(DMSO)_2$(DMSO)(CO) [240], *trans,trans,trans*-$RuCl_2(DMSO)_2$(DMSO)(CO) [240], and *cis,fac*-$RuCl_2(CO)_3$(DMSO) [241]. It is worth noting that in *cis,cis,trans*-$RuCl_2(DMSO)_2$(DMSO)(CO) [241] the reduction of charge density on the metal atom by CO causes a further lengthening of the two cis Ru–S bond distances, with respect to other *cis,cis*-$RuCl_2$(sulfoxide-*S*)$_2$ derivatives. A slight lengthening, with respect to the mean value, is also found in *trans,trans,trans*-$RuCl_2(DMSO)_2$(DMSO)(CO) [241].

In Ru(III)-DMSO complexes, the small π back-bonding ability is further reduced by the presence of CO or NO and only O-bonded sulfoxide complexes are found, such as *mer,cis*-$RuCl_3(DMSO)_2$(CO) [258], [$(DMSO)_2H$)][*trans*-$RuCl_4$(DMSO)(CO)] [258], and *mer,trans*-$RuBr_3$(DESO)(NO)(Et_2S) [259]. The structure of *cis,fac*-$RuCl_2(CO)_3$(DMSO) is of particular interest since its Ru–O bond distance of 2.090(5) Å is the lowest found in Ru(II)–O(DMSO) complexes, comparable to the mean value of the Ru(III)–O distances (Table 8). This is probably due to the combined withdrawing effect of the three carbonyl groups which increase the positive charge of the metal atom.

Similar π effects are also shown by osmium, which shows S-bonding in *trans*-$OsBr_2(DMSO)_4$, but O-bonding in [$^nBu_4N$][*trans*-Os(CO)(DMSO)Cl_xBr_{4-x}] [279], as well as in *mer*-$OsBr_3$(NO)(DESO)(Et_2S) [278].

The effect of the metal oxidation state is clearly shown by the Cr(0) complex, $Cr(CO)_5(TMSO)$, where, in spite of the five carbonyl groups, the metal atom displays a charge density great enough to yield to an S-bonded TMSO [193]. It is interesting to observe that the axial Cr–C bond distance, trans to TMSO, of 1.858(5) Å, is shorter than the average Cr–C(equat.) distance of 1.909(3) Å, clearly showing the lower π accepting properties of sulfoxides, with respect to carbonyls [193]. The lower competition of TMSO allows the strengthening of the axial Cr–C bond. Consequently, the axial C–O bond distance of 1.153(6) Å is longer than the equatorial ones, which average 1.141(4) Å.

Comparing the average Rh(III)–S and S–O bond distances in Table 9 (cis: Rh–S, 2.271(6); S–O 1.467(2) Å; trans: Rh–S, 2.323(3); S–O, 1.464(5) Å) we can see that the trans arrangement of the DMSO groups causes an increase of the Rh–S bond length of about 0.052 Å, while the S–O distance is virtually unchanged. The very short S–O bond distance, with respect to that of Ru(III) complexes (1.474(2) Å), is indicative of a strengthening of the S–O bond, and hence of a greater π bonding between O and S. This can be rationalized in terms of an increase of the positive charge on the sulfur atom acting as an essentially pure σ donor to Rh(III). The lengthening in the trans complexes should be then ascribed to σ trans influence effects.

The hypothesis that the Rh(III)–DMSO bond is essentially σ in character has already been proposed from the comparison of structural and spectroscopic data of Ru and Rh analogues, i.e. *mer,trans*-$MCl_3(DMSO)_2(DMSO)$, M = Ru(III), Rh(III) [275]. In fact, going from Ru to Rh, we have a shortening of about 0.030(8) Å, higher than that expected of 0.015 Å [364], accompanied by a slight contraction (av. 0.014(6) Å) of the S–O bond distance. Consistent variations in the M–S and S–O stretching frequencies are: M = Ru, ν(M-S) = 411, ν(S–O) = 1127, 1107 cm^{-1}; M = Rh, ν(M-S) = 415, ν(S–O) = 1140, 1120 cm^{-1} [275]. Further, it has been found that replacement of a DMSO with a σ donor ligand such as trimethylbenzimidazole induces a strengthening of both the Rh–S and S–O bonds (ν(Rh–S) = 432, ν(S–O) = 1136 cm^{-1}), while in the Ru derivative the strengthening of the Ru–S bond is followed by a weakening of the S–O bond (ν(Ru–S) = 425, ν(S–O) = 1094 cm^{-1}), due to the increase of π back-donation [275].

The minimum π back-bonding ability of Rh(III) is expected from the trend in the energy of the metal orbitals due to the increase of the effective nuclear charge going from Ru to Rh [275]. This is consistent with the values of the C–O stretching frequencies in $[M(CO)X_5]^{2-}$ complexes. For X = Cl, ν(CO) = 2117 cm^{-1} for Rh, vs. 2030 cm^{-1} for Ru, and similarly, for X = Br, ν(CO) = 2067 cm^{-1} for Rh, vs. 1996 cm^{-1} for Ru [365]. The higher values in the Rh derivatives imply less π back-donation from metal orbitals to antibonding C–O MOs.

The markedly longer Rh(II)–S distance of 2.45(2) Å in dirhodium(II) complexes (Table 9) is clearly determined by the particular electron configuration of the Rh_2^{4+} group and related to π back-bonding from Rh to S. As a matter of fact, the mean S–O bond distance of 1.476(5) Å is longer than that of the Rh(III) compounds, in agreement with the lower stretching frequency (1090 cm^{-1}) [261].

It is very interesting to observe that while in $[Rh_2(DMSO)_2(propionato)_4]$ the sulfoxide ligands are S-bonded, in the trifluoroacetato derivative they are O-bonded

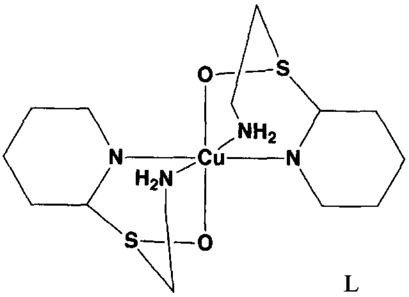
[261]. The introduction of highly electronegative substituents lowers the electron charge density on the metal atoms, favoring O-bonding.

6.2. *O-bonding*

As stated at the beginning of the section, O bonding is preferred by 'hard' metal ions or, in the case of softer metals, to avoid a trans arrangement of S-bonded sulfoxides or generally in the presence of strong π accepting ligands. With bulky ligands, steric effects (see next section) can also induce O-bonding.

The stereochemistry and average structural parameters have already been discussed. The *trans-trans* arrangement is the most favorable, and the mean S–O bond length and M–O–S bond angle are of 1.529(1) Å and 124.7(5)°, respectively.

In any case, the M–O–S bond angle varies in a rather wide range, because of intramolecular steric interactions or constraints imposed by particular sulfoxide ligands. Two interesting examples are represented by $[Cu(AEPSO)_2][ClO_4]$ (L) [95], and $Fe(CO)_3(DHSO)$ (XXXV) [213].



L

In both cases, the sulfoxide acts as a chelating ligand, imposing a narrow M–O–S bond angle, 106.7° in the copper complex, and 109.9° in the iron complex.

Very wide angles (126.0(3)–158.6(2)°) are found in lanthanide and actinide complexes, because of the overcrowding of ligands, determined by their high coordination numbers. Wide M–O–S angles are also found in bridging sulfoxide ligands. If the statistical analysis is limited to square planar and octahedral complexes of group VIII, the average value becomes $\langle x \rangle_s = 121.7(5)°$ with $\sigma = 3.2°$ for $n = 38$ observations.

This value of the M–O–S bond angle is consistent with a directional σ character of the M–O bond and suggests a trigonal geometry around the oxygen atom, with a lone-pair occupying the vacant site, available for further coordination.

7. Steric effects

In order to try to quantify the steric effects exerted by coordinated sulfoxides, cone-angles have been calculated from molecular models, for S- and O-bonded ligands [257]. Solid cone angles (Ω) and circular cone apertures (Θ), the latter representing Tolman's cone-angles, are listed in Tables 16 and 17 for the most common sulfoxides.

Inspection of the calculated cone angles for S-bonded sulfoxides (Table 16) shows that the smallest values are displayed by TMSO ($R=R'=CH_2$–; $\Omega=2.68$ ster rad, $\Theta=110.1°$) and DMSO ($R=R'=$ Me; $\Omega=2.75$ ster rad, $\Theta=111.6°$), and that they slightly increase with the introduction of bulkier groups, such as ethyl, phenyl, and propyl. The maximum value is shown by the di-*i*-propyl sulfoxide, $\Omega=4.16$ ster rad, $\Theta=140.6°$. Comparison of data in Tables 16 and 17 shows that cone angles for

Table 15
Average Rh(III)–X bond distances (Å) trans and cis to S-bonded sulfoxides

	Rh–Cl trans S	Rh–Cl cis S[a]	Rh–N trans S	Rh–N cis S
Min.	2.344(6)	2.314(5)	2.041(11)	2.028(13)
Max.	2.366(2)	2.351(1)	2.098(5)	2.053(13)
Range	0.022	0.037	0.057	0.025
n	6	36	3	2
Median	2.360	2.340	2.082	2.041
σ	0.008	0.012	0.029	0.018
$\langle x \rangle_s$	2.360	2.338	2.08	2.04
$\sigma(\langle x \rangle_s)$	0.003	0.001	0.02	0.01
trans-cis difference	0.022(4)		0.04(3)	

[a] Cl trans to Cl.

Table 16
Solid cone angles (Ω) and circular cone apertures (Θ) for metal S-bonded sulfoxides, M(RR′SO), with M–S = 2.28 Å

R	R′	Ω (ster rad)	Θ (°)
CH_2–	CH_2–	2.68	110.1
Me	Me	2.75	111.6
Me	Et	3.11	119.3
Me	^{n}Pr	3.13	119.8
Me	Ph	3.15	120.1
Ph	Ph	3.35	124.4
Me	^{i}Pr	3.41	125.6
Et	Et	3.46	126.6
Et	^{n}Pr	3.48	127.1
^{n}Pr	^{n}Pr	3.51	127.6
Et	Ph	3.64	130.2
Ph	^{n}Ph	3.64	130.2
Et	^{i}Pr	3.70	131.5
Ph	^{i}Pr	3.88	135.0
^{n}Pr	^{i}Pr	3.90	135.4
^{i}Pr	^{i}Pr	4.16	140.6

Table 17
Solid cone angles (Ω) and circular cone apertures (Θ) for metal O-bonded sulfoxides, M(RR'SO), with M–O = 2.10 Å

R	R'	Ω (ster rad)	Θ (°)
CH_2–	CH_2–	2.18	98.4
Me	Ph	2.23	99.6
Me	Me	2.26	100.4
Ph	^{n}Pr	2.28	100.8
Ph	Ph	2.53	106.7
Et	Ph	2.55	107.1
Me	Et	2.66	109.5
Me	^{n}Pr	2.66	109.5
Me	^{i}Pr	2.74	111.3
Ph	^{i}Pr	2.76	111.8
Et	Et	3.12	119.4
Et	^{n}Pr	3.12	119.5
^{n}Pr	^{i}Pr	3.14	119.9
^{n}Pr	^{n}Pr	3.20	121.2
Et	^{i}Pr	3.20	121.3
^{i}Pr	^{i}Pr	3.25	122.3

S-bonded sulfoxides are markedly larger than those of O-bonded sulfoxides, in spite of the shorter coordination bond distance, 2.10 Å vs. 2.28 Å. Again, the smallest and largest cone angles are shown, respectively, by the tetramethylene- ($\Omega = 2.18$ ster rad, $\Theta = 98.4°$) and di-*i*-propyl- ($\Omega = 3.25$ ster rad, $\Theta = 122.3°$) sulfoxides.

Because of the intrinsic lack of conic symmetry in sulfoxides, the 'ligand profiles' are rather distorted, with two or three bumps superimposed to the circle determined by the sulfur or oxygen atoms [257].

It has been shown that the bulkiness of the DPSO is large enough ($\Omega = 3.35$ ster rad, $\Theta = 124.4°$) to hinder the formation of complexes of formula *mer*-$RuCl_3$(S-sulfoxide)$_2$(O-sulfoxide), as obtained in the case of DMSO, to give only a *mer*-$RuCl_3$(S-sulfoxide)(O-sulfoxide)$_2$ complex [257]. A conformational analysis and molecular mechanics calculations have suggested that the greater thermodynamic stability of *mer*-$RuCl_3$(DPSO)(DPS*O*)$_2$ with respect to other isomers is due to both enthalpic and conformational entropic factors. In fact, O-bonded sulfoxides not only have one more degree of freedom, but, because of their reduced steric hindrance, allow a great many more low energy geometries [257].

8. Conclusions

The whole set of structural data now available shows that the S–O bond distance of free sulfoxides is significantly modified upon coordination, passing from 1.492(1) Å to 1.4723(8) Å in S-bonded complexes and to 1.529(1) Å in O-bonded complexes. Minor changes are found for the S–C(sp^3) bond distances, whose average values are

1.791(3), 1.785(1), and 1.780(2) Å, in free, S-, and O- bonded complexes, respectively, with an overall average of 1.783(1) Å. The average C–S–C bond angle significantly increases from free (97.8(2)°) to O- (99.0(2)°) and S-bonded (100.2(1)°) complexes, while the O–S–C angle passes from 105.9(1)° in free sulfoxides to 104.3(1)° in O- and 107.4(1)° in S-bonded complexes.

Mean values for coordination bond angles are: M–O–S, 124.7(5)°; M–S–O, 116.9(1)°; M–S–C, 111.7(1)°.

Sulfoxides behave as weak π accepting ligands and exert a weak trans and cis influence.

Considering the whole Periodic Table, a prevalence of O-bonding is observed. S-bonding seems to be favored in d^6 and d^8 transition metal ion complexes, probably through π back-bonding contributions. The presence of other π accepting ligands, in the metal first coordination sphere, such as CO, NO, and even other sulfoxides increases the metal ion 'hardness', weakening the metal–sulfur bond or causing a linkage isomerism from S- to O-bonded species. O-bonding may be also induced by the ligand bulkiness, as measured by the sulfoxide cone-angle, so that the bonding mode of sulfoxides is the result of a delicate balance between electronic and steric factors. Preference of O-bonded species could also derive from entropic contributions, due to the increased number of degrees of freedom and ligand mobility which makes possible much more low energy conformers.

Such effects are to be further investigated, as well as the nature of the metal–sulfur bond through MO calculations, to analyze the nature of the metal and sulfoxide orbitals involved in the coordination bonding.

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Appendix 1. Calculation of the means

The semi-weighted mean, $\langle x\rangle_s$, is defined as:

$$\langle x\rangle_s=\sum_{1}^{n}{}_{i}\, W_i x_i/\sum_{1}^{n}{}_{i} W_i$$

where

$$W_i=1/[\sigma^2(\mu)+\sigma(x_i)]$$

$\sigma^2(\mu)$ and $\sigma^2(x_i)$ are, respectively, the variance of the overall mean and the variance of each observation x_i. The former is estimated as:

$$\sigma^2(\mu)=\sigma^2-\langle\sigma^2(x_i)\rangle$$
$$=\sum_{1}^{n}{}_i(x-\langle x\rangle_u)^2/(n-1)-\sum_{1}^{n}{}_i\sigma^2(x_i)/n$$

where $\langle x\rangle_u$ is the unweighted mean,

$$\sum_{1}^{n}{}_i\ x_i/n$$

The standard error of $\langle x\rangle_s$ is approximately given by:

$$\sigma(\langle x\rangle_s)=(1/\sum_{1}^{n}{}_i W_i)^{1/2}$$

Appendix 2. Principal component analysis

The data matrix D (d_{ij}), consisting of m rows (each row corresponds to a compound) and n columns (each column corresponds to a variable), is transformed into the normalized data matrix, DN (dn_{ij}), as:

$$dn_{ij}=(d_{ij}-\langle d_j\rangle)\cdot w_j$$

where $\langle d_j\rangle=\Sigma d_{ij}/m$ and $w_j=[\Sigma(\langle d_j\rangle-d_{ij})^2/(m-1)]^{-1/2}$.

The covariance matrix of DN, Z, which is the correlation matrix of D, is calculated as:

$$\mathbf{Z}=(\mathbf{DN}^{\mathrm{T}}\cdot\mathbf{DN})/(n-1)$$

The eigenanalysis of Z, $\mathbf{Z}\cdot\mathbf{e}_i=\lambda_i\cdot\mathbf{I}\cdot\mathbf{e}_i$, where I is the $n\times n$ identity matrix, produces n unique pairs of vectors e_i (eigenvectors) and scalars λ_i (eigenvalues). Each couple of eigenvector and eigenvalue is referred to as principal component (PC). The $m\times n$ score matrix S, which contains the coordinates of the m compounds within the n-dimensional space, spanned by the n eigenvectors, is obtained as:

$$\mathbf{S}=\mathbf{DN}\cdot\mathbf{F}$$

$$\mathbf{F}=\mathbf{C}\cdot\Lambda^{1/2}$$

where F is the $n\times n$ factor matrix, C is the $n\times n$ eigenvector matrix (in which each column is one of the eigenvectors e_i), and Λ is the $n\times n$ diagonal eigenvalue matrix (in which each element within the diagonal is one of the eigenvalues λ_i).

The cumulative variance percentage $\mathbf{V}_k$, described by the first k principal components is calculated as

$$\mathbf{V}_k=100\cdot(\Sigma\lambda_i)/n$$

Of course, the n PCs are able to describe the totality of the variance. However, it often occurs that a subset k, with $k<n$, of PCs are enough to describe the total variance. These k PCs are referred to as primary components, while the remaining $(n-k)$ PCs are the secondary ones. Among the possible criteria to discriminate between primary and secondary components [8a,367], we have used the χ^2 criterion [8a] which considers the variability of the errors from one data point to the next.

Once $\boldsymbol{S}$ is calculated, it is often important to verify the discriminatory power of the PCs. It may happen that the m compounds are clustered in two or more different regions of the space spanned by the eigenvectors. Therefore, appropriate cluster analysis algorithms can be used to analyze the two or more clusters [368]. However, it often happens that no evident clustering appears within the eigenvector space. Also in this case, it is worth estimating the discriminatory power of each PC, by using contingency table analysis [369].

In order to describe the structural variation of a series of compounds, it is also possible to define a set of symmetry coordinates [370], which are linearly independent and refer to some ideal geometry (e.g. C_s for R_2SO fragments). These symmetry coordinates can be used as components of the distortion vector, if their reference values are known.

Although this is not the case for sulfoxides, it is important to define the symmetry coordinates, in order to help the interpretation of the PCA results. Since PCA is performed on the bond distances and angles of the sulfoxide fragment C1–S(O)–C2, the symmetry coordinates, S_i, resulting from these variables are as follows:

$$S1(A')=(S\text{–}O)$$

$$S2(A')=(1/2)^{1/2}[(S\text{–}C1)+(S\text{–}C2)]$$

$$S3(A'')=(1/2)^{1/2}[(S\text{–}C1)-(S\text{–}C2)]$$

$$S4(A')=(C1\text{–}S\text{–}C2)$$

$$S5(A')=(1/2)^{1/2}[(O\text{–}S\text{–}C1)+(O\text{–}S\text{–}C2)]$$

$$S6(A'')=(1/2)^{1/2}[(O\text{–}S\text{–}C1)-(O\text{–}S\text{–}C2)]$$

As shown, four of them have A′ symmetry, and the remaining two have A″ symmetry.

References

[1] I. Lindquist and P. Einarsson, Acta Chem. Scand., 13 (1959) 420; F.A. Cotton and R.C. Elder, J. Am. Chem. Soc., 82 (1960) 2986; D.W. Meek, D.K. Straub and R.S. Drago, Bull. Chem. Soc. Japan, 33 (1960) 861; F.A. Cotton and R. Francis, J. Inorg. Nucl. Chem., 17 (1961) 62.

[2] J.A. Davies, Adv. Inorg. Chem. Radiochem., 24 (1981) 115.

[3] B.R. James, R.S. McMillan and K.J. Reimer, J. Mol. Catal., 1 (1976) 439; B.R. James and R.S. McMillan, Can. J. Chem., 55 (1977) 3927; D.P. Riley, Inorg. Chem., 22 (1983) 1965; D.P. Riley and R.E. Shumate, J. Am. Chem. Soc., 106 (1984) 3179; D.P. Riley and J. Lyon III, J. Chem. Soc., Dalton Trans., (1991) 157; R.S. Srivastava, B. Milani, E. Alessio and G. Mestroni, Inorg. Chim. Acta, 191 (1992) 15.

[4] G. Mestroni, E. Alessio, G. Sava, S. Pacor and M. Coluccia, in B.K. Keppler (ed.), Metal Complexes in Cancer Chemotherapy, VCH Verlag, Weinheim, 1994, p. 159.

[5] P.K.L. Chan, B.R. James, D.C. Frost, P.K.H. Chan and H.-L. Hu, Can. J. Chem., 67 (1989) 508.

[6] S. Patai, Z. Rappoport and C. Stirling (eds.), The Chemistry of Sulphones and Sulfoxides, J. Wiley & Sons, New York, 1988.

[7] H.B. Kagan and B. Ronan, Rev. Heteroatom Chem., 7 (1992) 92; V.Yu. Kukushkin, Coord. Chem. Rev., 139 (1995) 375.

[8] (a) E.R. Malinowski, Factor Analysis in Chemistry, Wiley, New York, 1991; (b) R. Taylor and F.H. Allen, in H.-B. Bürgi and J.D. Dunitz (eds.), Structural Correlation, VCH Verlag, Weinheim, 1994, pp. 111–161.

[9] R. Taylor and O. Kennard, Acta Crystallogr., B39 (1983) 517; R. Taylor and O. Kennard, Acta Crystallogr., B42 (1986) 112; W.G. Cochran, Biometrics, 10 (1954) 101.

[10] Cambridge Structural Database, 5.06 version, October 1993.

[11] K.K. Kannan and M.A. Viswamitra, Nature, 209 (1966) 1016.

[12] R. Thomas, C.B. Shoemaker and K. Eriks, Acta Crystallogr., 21 (1966) 12.

[13] M.J. Bennett, F.A. Cotton, D.L. Weaver, R.J. Williams and W.H. Watson, Acta Crystallogr., 23 (1967) 788.

[14] W.J.J. Smeets, A.L. Spek, F.G.M. Niele, C.F. Martens and R.J.M. Nolte, Acta Crystallogr., C43 (1987) 2330.

[15] A.J. Blake, J.A. Greig and M. Schröder, Acta Crystallogr., C46 (1990) 322.

[16] F. Calderazzo, G. Pampaloni, D. Vitali, I. Collamati, G. Dessy and V. Fares, J. Chem. Soc., Dalton Trans., (1980) 1965.

[17] M.N. Bell, A.J. Blake, M. Schröder, H.-J. Küppers and K. Wieghardt, Angew. Chem. Int. Ed. Engl., 26 (1987) 250.

[18] C. George and D.S. Dudis, Acta Crystallogr., C46 (1990) 650.

[19] Guang Wu, Pei-Ju Zheng, S.-Z. Zhu and Q.-Y. Chen, Acta Crystallogr., C47 (1991) 1227.

[20] J. Bernstein, A. Weissman, D. Britton, E.G. Rippie and J. Hedenstrom, Acta Crystallogr., C48 (1992) 214.

[21] D. Viterbo, A. Gasco, A. Serafino and V. Mortarini, Acta Crystallogr., B31 (1975) 2151.

[22] C. Dickinson and J.R. Holden, Acta Crystallogr., B34 (1978) 2361.

[23] J. Mizuguchi and G. Rihs, Acta Crystallogr., C48 (1992) 1279.

[24] B. Busetta, C. Courseille and M. Hospital, Acta Crystallogr., B29 (1973) 2456.

[25] J. Iball, C.H. Morgan and H.R. Wilson, Proc. Roy. Soc., A., 302 (1968) 225.

[26] F.H. Herbstein, M. Kapon and S. Wasserman, Acta Crystallogr., B34 (1978) 1613.

[27] B. Viossat, P. Khodadad and N. Rodier, J. Mol. Struct., 71 (1981) 237.

[28] S.C. Abrahams, Acta Crystallogr., 10 (1957) 417.

[29] G. Pelizzi, G. Michelon and M. Bonivento, Crystallogr. Struct. Comm., 5 (1976) 617.

[30] G. Pelizzi, L. Coghi, G. Michelon and M. Bonivento, Crystallogr. Struct. Comm., 5 (1976) 621.

[31] A. Leclaire, D. Barillier and M. Vazeux, Acta Crystallogr., C47 (1991) 148.

[32] K.A. Hellmund, S.G. Pyne, B.W. Skelton and A.H. White, Aust. J. Chem., 45 (1992) 1923.

[33] X. Ji, D. van der Helm, R.V. Williams and W.J. Ebey, Acta Crystallogr., B45 (1989) 93.

[34] P.D. Robinson, D.H. Hua, X. Wu, S. Wu Miao and M. Meled, Acta Crystallogr., C48 (1992) 2088.

[35] A. Leclaire, D. Barillier and M. Vazeux, Acta Crystallogr., C47 (1991) 146.

[36] A. Leclaire, D. Barillier and M. Vazeux, Acta Crystallogr., C47 (1991) 1758.

[37] T. Svinning, F. Mo and T. Bruun, Acta Crystallogr., B32 (1976) 759.

[38] U. Folli, D. Iarossi, A. Mucci, A. Musatti, M. Nardelli, L. Schenetti and F. Taddei, J. Mol. Struct., 246 (1991) 99.

[39] S. Ianelli, A. Musatti, M. Nardelli, R. Benassi, U. Folli and F. Taddei, J. Chem. Soc., Perkin Trans. 2 (1992) 49.

[40] U. de la Camp and H. Hope, Acta Crystallogr., B26 (1970) 846.

[41] A. Kucsman, I. Kapovits, I. Kövesdi, A. Kálmán and L. Párkányi, J. Mol. Struct., 127 (1985) 135.

[42] D. Tranqui and H. Fillion, Acta Crystallogr., B28 (1972) 3306.

[43] B. Dahlén, Acta Crystallogr., B29 (1973) 595.

[44] B. Dahlén, Acta Crystallogr., B30 (1974) 642.

[45] P. Blanpain and F. Durant, Crystallogr. Struct. Comm., 5 (1976) 89.
[46] J.-S. Brunck, J. Voss, F. Olbrich and H. Viebrock, Acta Crystallogr., C49 (1993) 934.
[47] D. Ginderow, J.-P. Mornon, I. Erdelmeier, P. Dansette and D. Mansuy, Acta Crystallogr., C48 (1992) 1808.
[48] R. Dodge, O. Johnson and W. Selig, Crystallogr. Struct. Commun., 1 (1972) 181.
[49] J. Buchanan, E.J.M. Hamilton, D. Reed and A.J. Welch, J. Chem. Soc., Dalton Trans., (1990) 677.
[50] B.R. James, R.H. Morris, F.W.B. Einstein and A. Willis, J. Chem. Soc., Chem. Commun., (1980) 31.
[51] E. Alessio, G. Balducci, M. Calligaris, G. Costa, W.M. Attia and G. Mestroni, Inorg. Chem., 30 (1991) 609.
[52] J.S. Jaswal, S.J. Rettig and B.R. James, Can. J. Chem., 68 (1990) 1808.
[53] P.S. Cartwright, R.D. Gillard, E.R.J. Sillanpaa and J. Valkonen, Polyhedron, 7 (1988) 2143.
[54] D.T.T. Yapp, Ph.D. Thesis, University of British Columbia, 1993.
[55] E. Alessio, B. Milani, G. Mestroni, M. Calligaris, P. Faleschini and W.M. Attia, Inorg. Chim. Acta, 177 (1990) 255.
[56] O.V. Rudnitskaya, I.V. Miroshnichenko, A.I. Stash and N.M. Sinitsyn, Russ. J. Inorg. Chem., 38 (1993) 1101.
[57] P. Faleschini, Ph.D. Thesis, University of Trieste, 1994.
[58] S. Wolfe, A. Stolow and L.A. LaJohn, Tetrahedron Lett., 24 (1983) 4071.
[59] M. Marsh, W. Massa, K. Harms, G. Baum and G. Boche, Angew. Chem. Int. Ed. Engl., 25 (1986) 1011.
[60] W. Feder, H. Dreizler, H.D. Rudolph and V. Typke, Z. Naturforsh. Teil A, 24 (1969) 266.
[61] G. Forgács, G. Schultz, I. Hargittai, I. Jalsovszky and Á. Kucsman, J. Chem. Soc., Faraday Trans. 2, 85 (1989) 303.
[62] G. Forgács, I. Hargittai, I. Jalsovszky and Á. Kucsman, J. Mol. Struct., 243 (1991) 123.
[63] V. Schomaker and D.P. Stevenson, J. Am. Chem. Soc., 63 (1941) 37, .
[64] E. Alessio, private communication.
[65] K.H. Sze, C.E. Brion, M. Tronc, S. Bodeur and A.P. Hitchcock, Chem. Phys., 121 (1988) 279.
[66] P. Murray-Rust, Acta Crystallogr., B38, 2765, 1982.
[67] S. Dowdy and S. Wearden, Statistics for Research, Wiley, New York, 1991, pp. 119–128.
[68] R.J. Gillespie and I. Hargittai, The VSEPR Model of Molecular Geometry, Allyn and Bacon, Boston, 1991.
[69] R.P. Mason and J.E. Harriman, J. Chem. Phys., 65 (1976) 2274.
[70] J.S. Jaswal, D.T.T. Yapp, S.J. Rettig, B.R. James and K.A. Skov, Inorg. Chim. Acta, 207 (1994) 97; J. Chem. Soc. Chem. Commun., (1992) 1528.
[71] E. Alessio, G. Balducci, A. Lutman, G. Mestroni, M. Calligaris and W.M. Attia, Inorg. Chim. Acta, 203 (1993) 205.
[72] G.N. Schrauzer, C. Zhang and R. Chadha, Inorg. Chem., 29 (1990 4104).
[73] P.J.M.W.L. Birker and P.T. Beurskens, Rec. Trav. Chim. Pays-Bas, 93 (1974) 218.
[74] D.M. Walba, R.M. Richards, M. Hermsmeier and R.C. Haltiwanger, J. Am. Chem. Soc., 109 (1987) 7081.
[75] R.D. Willett and K'un Chang, Inorg. Chim. Acta, 4 (1970) 447.
[76] D.D. Swank, D.D. Landee and R.D. Willett, Phys. Rev. B, Condens. Mat., 20 (1979) 2154.
[77] C.P. Landee, A. Djili, D.F. Mudgett, M. Newhall, H. Place, B. Scott and R.D. Willett, Inorg. Chem., 27 (1988) 620.
[78] R.D. Willett, F.H. Jardine and S.A. Roberts, Inorg. Chim. Acta, 25 (1977) 97.
[79] S. Brownstein, Nam Fong Han, E. Gabe and F. Lee, Can. J. Chem., 67 (1989) 551.
[80] J.T. Guy Jr., J.C. Cooper, R.D. Gilardi, J.L. Flippen-Anderson and C.F. Geoge Jr., Inorg. Chem., 27 (1988) 635.
[81] C.P. Landee and R.E. Greeny, Inorg. Chem., 25 (1986) 3771.
[82] D.D. Swank, G.F. Needham and R.D. Willett, Inorg. Chem., 18 (1979) 761.
[83] M. Klinga, M.R. Sundberg, M. Melník and J. Mrozinski, Inorg. Chim. Acta, 162 (1989) 39.
[84] M. Melník, M. Dunaj-Jurco and M. Handlovic, Inorg. Chim. Acta, 86 (1984) 185.
[85] C. Dendrinou-Samara, D.P. Kessissoglou, G.E. Manoussakis, D. Mentzafos and A. Terzis, J. Chem. Soc., Dalton Trans., (1990) 959.

[86] R.J. Williams, W.H. Watson and A.C. Larson, Acta Crystallogr., B31 (1975) 2362.
[87] N.F. Curtis, F.W.B. Einstein, K.R. Morgan and A.C. Willis, Inorg. Chem., 24, (1985) 2026.
[88] H.O. Stumpf, Y. Pei, O. Kahn, J. Sletten and J.P. Renard, J. Am. Chem. Soc., 115 (1994) 6738.
[89] R. Graziani, M. Vidali, U. Casellato and P.A. Vigato, Trans. Met. Chem., 3 (1978) 239.
[90] H. Muhonen and R. Hamalainen, Finn. Chem. Lett., (1983) 120.
[91] Li Zhong-De, You Xiao-Zeng, Yao Yuan-Gen, Huang Jing-Shun and Wang Man-Fang, Uaxue Xuebao (Acta Chim. Sin.), 45 (1987) 260.
[92] M. Mikuriya, Y. Kakuta, K. Kawano and T. Tokii, Chem. Lett., (1991) 2031.
[93] Chen Ming-Qin, Zhu Si-San and Gu Yi-Dong, Jiegou Huoaxue (J. Struct. Chem.), 9 (1990) 26.
[94] Show-Kei, Der-Shin Liaw and Shie-Ming Peng, Bull. Inst. Chem. Acad. Sin., 34 (1987) 49.
[95] K. Umakoshi, I. Kinoshita, K. Matsumoto and S. Ooi, Nippon Kagaku Kaishi (J. Chem. Soc. Jpn.), (1986) 1517.
[96] I. Bkouche-Waksman, C. Bois, G.A. Popovitch and P.L'Haridon, Bull. Soc. Chim. Fr., (1980) 69-1.
[97] T.A. Emokpae, A.C. Ukwueze, D.R. Walton and P.B. Hitchcock, Synth. R. Inorg. Met.-Org. Chem., 16 (1986) 387.
[98] N.-O. Björk and A. Cassel, Acta Chem. Scand., A30 (1976) 235.
[99] A. Taeb, H. Krischner and C. Kratky, Z. Kristallogr., 176 (1986) 97.
[100] I. Persson, Acta Chem. Scand., A36 (1982) 7.
[101] K.N. Zelenin, L.A. Khorseeva, M.T. Toshev, V.V. Alekseev and Kh.B. Dustov, Zh. Obshch. Khim., 60 (1990) 2549.
[102] M. Sandström, Acta Chem. Scand., A32 (1978) 519.
[103] T.Yu. Lyubeznova and V.I. Ponomarev, Kristallografiya, 34 (1989) 862.
[104] H.K. Reddy, Cheng Zhang, E.O. Schlemper and G.N. Schrauzer, Inorg. Chem., 31 (1992) 1673.
[105] E.A.H. Griffith, N.G. Charles and E.L. Amma, Acta Crystallogr., B38 (1982) 942.
[106] M. Nieuwenhuyzen and C.J. Wilkins, J. Chem. Soc., Dalton Trans., (1994) 2673.
[107] M. Nieuwenhuyzen, W.T. Robinson and C.J. Wilkins, Acta Crystallogr., C49 (1993) 1173.
[108] M. Nieuwenhuyzen, H. Wen and C.J. Wilkins, Z. Anorg. Allg. Chem., 615 (1992) 143.
[109] H. Schmidbaur, H.-J.Öller, S. Gamper and G. Müller, J. Organomet. Chem., 394 (1990) 757.
[110] H. Schmidbaur, H.-J.Öller, D.L. Wilkinson, B. Huber and G. Müller, Chem. Ber., 122 (1989) 31.
[111] M. Sandström and I. Persson, Acta Chem. Scand., A32 (1978) 95.
[112] P. Biscarini, L. Fusina, G.D. Nivellini, A. Mangia and G. Pelizzi, J. Chem. Soc. Dalton, (1973) 159.
[113] P. Biscarini, L. Fusina, G. Nivellini and G. Pelizzi, J. Chem. Soc. Dalton, (1981) 1024.
[114] P. Biscarini, L. Fusina, G.D. Nivellini, A. Mangia and G. Pelizzi, J. Chem. Soc. Dalton, (1974) 1846.
[115] M. Sandström, Acta Chem. Scand., A32 (1978) 527.
[116] R.E. Cramer and M.J.J. Carrié, Inorg. Chem., 29 (1990) 3902.
[117] Lin Yonghua, Hu Ninghai, Zhou Qinglian, Liu Shuzhen, Shi Endong and Wang Mingyi, Acta Phys. Sin., 32 (1983) 400.
[118] L.A. Aslanov, L.I. Soleva and M.A. Porai-Koshits, Z. Strukt. Khim., 13 (1972) 1101.
[119] Jiang Jiansheng, Hu Ninghai, Zhon Qinglian, Shen Cheng and Fan Yuguo, J. China Univ. Sci. Technol., 14 (1984) 154.
[120] K.K. Bhandary, H. Manohar and K. Venkatesan, J. Chem. Soc. Dalton, (1975) 288.
[121] L.A. Aslanov, L.I. Soleva, and M.A. Porai-Koshits, Z. Strukt. Khim., 14 (1973) 1064.
[122] K.K. Bhandary and H. Manohar, Acta Crystallogr., B29(1973), 1093.
[123] Yu Zhaolou, Guo Fang, Chen Benming, Liu Yuming, Zhu Naijue, Su Qiang and Lu Yuhua, Jiegou Huaxue (J. Struct. Chem.), 5 (1986) 101.
[124] Lin Yonghua, Hu Ninghai, Zhou Qinglian, Liu Shuzhen, Wu Shixue, Shi Endong and Wang Mingyi, Huaxue Xuebao (Acta Chim. Sin.), 42 (1984) 372.
[125] L.A. Aslanov, L.I. Soleva, M.A. Porai-Koshits and S.S. Goukberg, Z. Strukt. Khim., 13 (1972) 655.
[126] Chen Benming, Liu Yuming, Guo Fang, Zhu Naijue, Yu Zhaolou, Su Qiang and Lu Yuhua, Jiegou Huaxue (J. Struct. Chem.), 5 (1986) 105.
[127] E.E. Castellano, G. Oliva, L.B. Zinner and G. Vicentini, Inorg. Chim. Acta, 110 (1985) 77.
[128] T. Imai, M. Shimoi and A. Ouchi, Bull. Chem. Soc. Jpn., 59(1986), 669.
[129] T. Imai, M. Nakamura, K. Nagai, Y. Ohki, Y. Suzuki, M. Shimoi and A. Ouchi, Bull. Chem. Soc. Jpn., 59 (1986) 2115.

[130] Y. Sugita and A. Ouchi, Bull. Chem. Soc. Jpn., 61 (1988) 1607.
[131] J.M. Harrowfield, M.I. Ogden and A.H. White, Aust. J. Chem., 44 (1991) 1237.
[132] R.M. Wing, J.J. Uebel and K.K. Andersen, J. Am. Chem. Soc., 95(1973), 6046.
[133] Su Qiang, Lu Yuhua, Hu Ninghai, Liu Yongsheng and Jin Zhongsheng, Jiegou Huaxue, J. Struct. Chem., 6 (1987) 182.
[134] Y. Ohki, M. Nakamura, Y. Suzuki, K. Nagai, M. Shimoi and A. Ouchi, Bull. Chem. Soc. Jpn., 58 (1985) 1593.
[135] Zhu Naijue, Guo Fang, Su Qiang, Zhou Qinglian and Lu Yuhua, Jiegou Huaxue J. Struct. Chem., 4 (1985) 183.
[136] Guo Fang, Chen Benming, Liu Yuming, Zhu Naijue, Yu Zhaolou, Su Qiang, Zhou Qinglian and Lu Yuhua, Jiegou Huaxue, J. Struct. Chem., 5 (1986) 109.
[137] Guo Fang, Liu Yuming, Chen Benming, Zhu Naijue, Su Qiang and Lu Yuhua, Jiegou Huaxue, J. Struct. Chem., 6 (1987) 25.
[138] Su Qiang, Lu Yuhua, Hu Ninghai, Liu Yongsheng and Jin Zhongsheng, Jiegou Huaxue, J. Struct. Chem., 6 (1987) 182.
[139] M.A. Oliveira, J.M. Miranda, E.E. Castellano, E. Scoralick, L.B. Zinner and G. Vicentini, Lanth. Actin. Res., 1 (1986) 205.
[140] J.M. Miranda, M.A. Oliveira, E.E. Castellano, E. Scoralick, L.B. Zinner and G. Vicentini, Inorg. Chim. Acta, 139 (1987) 131.
[141] Z. Asfari, J.M. Harrowfield, M.I. Odgen, J. Vicens and A.H. White, Angew. Chem. Int. Ed. Engl., 30 (1991) 854.
[142] Huang Ling, Huang Chunhui and Xu Guangxian, Jiegou Xuaxue, J. Struct. Chem., 8 (1989) 1.
[143] L.C. Thompson, in K.A. Gschneidner Jr. and L. Eyring (eds.), Handbook on the Physics and Chemistry of Rare Earths, Vol. 3, North Holland, 1979, pp. 209–297; G.R. Choppin, in J.-C. Bünzli and G.R. Choppin (eds.), Lanthanide Probes in Life, Chemical and Earth Sciences, Elsevier, 1989, pp. 1–41.
[144] N. Singer, B.F. Studd and A.G. Swallow, Chem. Commun., (1970) 342.
[145] C.E.F. Rickard and D.C. Woollard, Acta Crystallogr., B36 (1980) 292.
[146] G. Bombieri and K.W. Bagnall, J. Chem. Soc. Chem. Commun., (1975) 188.
[147] J.F. de Wet and M.R. Caira, J. Chem. Soc., Dalton Trans., 2043 (1986); M.R. Caira and J.F. de Wet, Acta Crystallogr., A40 (1984) C223.
[148] L. Deshayes, N. Keller, M. Lance, M. Nierlich and D. Vigner, Acta Crystallogr., C48 (1992) 2209.
[149] J. McB. Harrowfield, D.L. Kepert, J.M. Patrick and A.H. White, J. Chem. Soc., Dalton Trans., (1983) 393.
[150] U. Casellato, P.A. Vigato, S. Tamburini, R. Graziani and M. Vidali, Inorg. Chim. Acta, 72 (1983) 141.
[151] R.R. Ryan and G.V. Jarvinen, Acta Crystallogr., C43 (1987), 1295.
[152] G.D. Jarvinen, R.R. Ryan, B.F. Smith and J.M. Ritchey, Inorg. Chim. Acta, 129 (1987) 139.
[153] J.C. Dewan, A.J. Edwards, D.R. Slim, J.E. Guerchais and R. Kergoat, J. Chem. Soc., Dalton Trans., (1975) 2171.
[154] U. Casellato, P. Guerriero, S. Tamburini, P.A. Vigato and R. Graziani, J. Chem. Soc., Dalton Trans., (1990) 1533.
[155] R. Graziani, U. Casellato, P.A. Vigato, O.A. Rajan and A. Chakravorty, Inorg. Chim. Acta, 49 (1981) 129.
[156] K.T. Potts, J.J.O'Brien and F.S. Tham, Inorg. Chim. Acta, 177 (1990) 13.
[157] V.E. Mistryukov, A.S. Kanishceva, T.G. Grevtseva and Yu.N. Mikhailov, Koord. Khim., 8 (1982) 1561.
[158] R.N. Shchelokov, Yu.N. Mikhailov, I.M. Orlova, A.V. Sergeev, Z.R. Ashurov, M.T. Tashev and N.A. Parpiev, Koord. Khim., 11 (1985) 706.
[159] R.N. Shchelokov, Yu.N. Mikhailov, I.M. Orlova, A.V. Sergeev, Z.R. Ashurov, M.T. Tashev and N.A. Parpiev, Koord. Khim., 11 (1985) 1010.
[160] E.L. McGandy, Diss. Abstr., 22 (1961) 754.
[161] J. MacB. Harrowfield, B.W. Skelton and A.H. Whiet, Austr. J. Chem., 43 (1990) 759.
[162] F.W.B. Einstein and D.G. Tuck, J. Chem. Soc. Chem. Commun., (1970) 1182.

[163] W.T. Robinson, C.J. Wilkins and Zhang Zeying, J. Chem. Soc., Dalton Trans., (1990) 219.

[164] Dong Nan, Wang Naidong, Dong Zhenchao and Hu Shengzhi, Jiegou Huaxue, J. Struct. Chem., 6 (1987) 145.

[165] B.D. James, M.B. Millikan and M.F. Mackay, Inorg. Chim. Acta, 77 (1983) L251.

[166] N.N. Kulikova, S.I. Troyanov, K.N. Nikitin and S.O. Gerasimova, Zh. Neorg. Khim., 34 (1989) 2693.

[167] Y. Gao, J. Guery and C. Jacoboni, Acta Crystallogr., C49 (1993) 963.

[168] N.W. Alcock, W. Errington, S.L. Golby, S.M.C. Patterson and M.G.H. Wallbridge, Acta Crystallogr., C50 (1994) 226.

[169] L. Coghi, M. Nardelli, C. Pelizzi and G. Pelizzi, Gazz. Chim. Ital., 105 (1975) 1187.

[170] L. Coghi, C. Pelizzi and G. Pelizzi, Gazz. Chim. Ital., 104 (1974) 873.

[171] N.W. Isaacs and C.H.L. Kennard, J. Chem. Soc. (A), (1970) 1257.

[172] L.A. Aslanov, V.M. Ionov, V.M. Attiya, A.B. Permin and V.S. Petrosyan, Zh. Strukt. Khim., 19 (1978) 109.

[173] Seik Weng Ng, Chen Wei and V.G. Kumar Das, Acta Crystallogr., C48 (1992) 2211.

[174] L. Coghi, C. Pelizzi and G. Pelizzi, J. Organometal. Chem., 114, 53.

[175] T.J. Karol, J.P. Hutchinson, J.R. Hyde, H.G. Kuivila and J.A. Zubieta, Organometallics, 2 (1983) 106; J.R. Hyde, T.J. Karol, J.P. Hutchinson, H.G. Kuivila and J.A. Zubieta, Organometallics, 1 (1982) 404.

[176] J.M. Kisenyi, G.R. Willey and M.G.B. Drew, Acta Crystallogr., C41 (1985) 700.

[177] M. Gregorkiewitz and D. Tudela, Acta Crystallogr., C46 (1990) 210.

[178] D. Tudela, V. Fernandez, J.D. Tornero and A. Vegas, Z. Anorg. Allg. Chem., 532 (1986) 215.

[179] A.V. Yatsenko, S.V. Medvedev, A.I. Tursina and L.A. Aslanov, Zh. Obshch. Khim., 56 (1986) 2330.

[180] A.V. Yatsenko, S.V. Medvedev, K.A. Paseshnitchenko and L.A. Aslanov, J. Organomet. Chem., 284 (1985) 181.

[181] Seik Weng Ng and A.L. Rheingold, J. Organomet. Chem., 378 (1989) 339.

[182] A. Blaschette, I. Hippel, J. Krahl, E. Wieland, P.G. Jones and A. Sebald, J. Organomet. Chem., 437 (1992) 279.

[183] W.A. Schenk, A. Khadra and C. Burschka, J. Organomet. Chem., 396 (1990) C4.

[184] K. Swami, J.P. Hutchinson, H.G. Kuivila and J.A. Zubieta, Organometallics, 3 (1984) 1687.

[185] R. Krishnamurti, H.G. Kuivila, N.S. Shaik and J. Zubieta, Organometallics, 10 (1991) 423.

[186] A. Mangia, C. Pelizzi and G. Pelizzi, J. Chem. Soc., Dalton Trans., (1973) 2557.

[187] J.M. Harrowfield, B.W. Skelton and A.H. White, J. Chem. Soc., Dalton Trans., (1994) 2011.

[188] A.D. Baranyi, M. Onyszchuk, Y. Le Page and G. Donnay, Can. J. Chem., 55 (1977) 849.

[189] H. Miyamae, Y. Numahata and M. Nagata, Chem. Lett., (1980) 663.

[190] A.D. Baranyi, M. Onyszchuk, S. Fortier and G. Donnay, J. Chem. Soc., Dalton Trans., (1976) 2301.

[191] T.S. Khodashova, M.A. Porai-Koshits, V.S. Sergienko, L.A. Butman, Yu.A. Uslaev, V.V. Kobalev and A.A. Kuznetsova, Koord. Khim., 4 (1978) 1909.

[192] T.S. Khodashova, M.A. Porai-Koshits, Yu.A. Buslaev, A.A. Kuznetsova and V.V. Kobalev, Koord. Khim., 3 (1977) 38.

[193] T.S. Khodashova, M.A. Porai-Koshits, V.S. Sergienko, Yu.A. Uslaev, A.A. Kuznetsova, V.V. Kobalev and L.A. Butman, Koord. Khim., 4 (1978) 941.

[194] A.L. Spek, Crystallogr. Struct. Commun., 6 (1977) 835; J.H. Eekhof, H. Hogeveen and R.M. Kellogg, J. Organomet. Chem., 161 (1978) 361.

[195] C. Schumaker, F. Weller and K. Dehnicke, Z. Anorg. Allg. Chem., 508 (1984) 79.

[196] F.A. Cotton, L.R. Falvello, A.H. Reid Jr. and J.H. Tocher, J. Organomet. Chem., 319 (1987) 87.

[197] P.A. Koz'min, M.D. Surazhskaya, T.B. Larina, A.S. Kotel'nikova and E.L. Akhmedov, Koord. Khim., 13 (1987) 627; E.L. Akhmedov, P.A. Koz'min, A.S. Kotel'nikova and S.A. Mektieva, Azerb. Khim. Zh., (1988) 110.

[198] C. Bustos, O. Burckhardt, R. Schrebler, D. Carrillo, A.M. Arif, A.H. Cowley and C.M. Nunn, Inorg. Chem., 29 (1990) 3996.

[199] Lu Shaofang, Zhu Nianyong, Wu Xintao, Wu Qiangjin and Lu Jiaxi, J. Mol. Struct., 197 (1989) 15.

[200] L.L. Borer and E. Sinn, Inorg. Chem., 29 (1990) 2514.

[201] E.M. McCarron III and R.L. Harlow I, J. Chem. Soc., Chem. Commun., (1983) 90.

[202] V. McKee and C.J. Wilkins, Acta Crystallogr., C40 (1984) 1678.
[203] V. McKee and C.J. Wilkins, J. Chem. Soc., Dalton Trans., (1987) 523.
[204] T. Shibahara, H. Kuroya, S. Ooi and Y. Mori, Inorg. Chim. Acta, 76 (1983) L315.
[205] J.M. Berg and R.H. Holm, Inorg. Chem., 22 (1983) 1768.
[206] J.M. Berg and R.H. Holm, J. Am. Chem. Soc., 107 (1985) 917; J. Am. Chem. Soc., 106 (1984) 3035.
[207] A.L. Spek, Cryst. Struct. Commun., 2 (1973) 331.
[208] Chen Ming-Qin, Zhu Si-San and Gu Yi-Dong, Jiegou Huaxue, J. Struct. Chem., 9 (1990) 26.
[209] N. de Vries, A.G. Jones and A. Davison, Inorg. Chem., 28 (1989) 3728.
[210] N. Quirós Méndez, A.M. Arif and J.A. Gladysz, Organometallics, 10 (1991) 2199.
[211] P.A. Koz'min, M.D. Surazhskaya and T.B. Larina, Koord. Khim., 5 (1979) 598.
[212] M.B. Hurtshouse and K.M.A. Malik, J. Chem. Soc., Dalton Trans., (1979) 409.
[213] F.A.J.J. van Santvoort, H. Krabbendam, G. Roelofsen and A.L. Spek, Acta Crystallogr., B33 (1977) 3000.
[214] C. Carini, C. Pelizzi, G. Pelizzi, G. Predieri, P. Tarasconi and F. Vitali, J. Chem. Soc. Chem. Commun., (1990) 613.
[215] A. Müller, H. Bögge, U. Schimanski, M. Penk, K. Nieradzik, M. Dartmann, E. Krickemeyer, J. Schimanski, C. Römer, M. Römer, H. Dornfeld, U. Wienböker, W. Hellmann and M. Zimmermann, Monatsh. Chem., 120 (1989) 367.
[216] V.I. Ponomarev, L.D. Arutyunyan and L.O. Atovmyan, Kristallografiya, 29 (1984) 910.
[217] M.J. Bennett, F.A. Cotton and D.L. Weaver, Acta Crystallogr., 23 (1967) 581.
[218] V.I. Ponomarev, O.S. Filipenko and L.O. Atovmyan, Koord. Khim., 8 (1982) 98.
[219] V.I. Ponomarev, O.S. Filipenko and L.O. Atovmyan, Koord. Khim., 1 (1975) 974.
[220] I.P. Lavrent'ev, L.G. Korableva, E.A. Lavrent'eva, G.A. Nifontova, M.L. Khidekel, I.G. Gusakovskaya, T.I. Larkina, L.D. Arutyunyan, O.S. Filipenko, V.I. Ponomarev and L.O. Atovmyan, Koord. Khim., 5 (1979) 1484.
[221] T. Mashiko, M.E. Kastner, K. Spartalian, W.R. Scheidt and C.A. Reed, J. Am. Chem. Soc., 100 (1978) 6354.
[222] A. Ciccarese, D.A. Clemente, A. Marzotto and G. Valle, J. Crystallogr. Spectr. Res., 23 (1994) 223.
[223] H. Kinoshita and A. Ouchi, Bull. Chem. Soc. Jpn., 61 (1988) 1169.
[224] G.J. Gainsford, W.G. Jackson and A.M. Sargeson, J. Am. Chem. Soc., 104 (1982) 137.
[225] I.A. Baidina, B.I. Imanakunov, T.A. Toktomatov and P.A. Stabnikov, Zh. Neorg. Khim., 36 (1991), 775.
[226] N.W. Alcock, P. Moore and H.A.A. Omar, J. Chem. Soc., Dalton Trans., (1987) 1107.
[227] Pei-Ju Zheng, Wang-Xi Liu, Zheng Xu, Jian-Zhong Zhou, Xiao-Zeng You, Yun-Peng Yu and Duo-Lin Zhu, Jiegou Huaxue, J. Struct. Chem., 11 (1992) 321.
[228] M.W. Taylor and L.R. Nassimbeni, A.C.A. (Winter), 14 (1986) 26.
[229] L.R. Nassimbeni, M.L. Niven and M.W. Taylor, Acta Crystallogr., B46 (1990) 354.
[230] F.C. March and G. Ferguson, Can. J. Chem., 49 (1971) 3590.
[231] M.M. Taqui Khan, P.S. Roy, K. Venkatasubramanian and N.H. Khan, Inorg. Chim. Acta, 176 (1990) 49.
[232] B.J. Coe, T.J. Meyer and P.S. White, Inorg. Chem., 32 (1994) 4012.
[233] A.M. Joshi, I.S. Thorburn, S.J. Rettig and B.R. James, Inorg. Chim. Acta, 198–200 (1992) 283.
[234] B.W. Arbuckle, P.K. Bharadwaj and W.K. Musker, Inorg. Chem., 30 (1991) 440.
[235] J.W. Faller and Y. Ma, Organometallics, 11 (1992) 2726.
[236] S.R. Hall, B.W. Skelton and A.H. White, Aust. J. Chem., 36 (1983) 271.
[237] M. Calligaris, P. Faleschini and E. Alessio, Acta Crystallogr., C49 (1994) 663.
[238] L.G. Marzilli, M. Iwamoto, E. Alessio, L. Hansen and M. Calligaris, J. Am. Chem. Soc., 116 (1994) 815.
[239] E. Alessio, M. Calligaris, M. Iwamoto and L.G. Marzilli, Inorg Chem., in press.
[240] E. Alessio, S. Geremia, F. Todone and P. Faleschini, Inorg. Chim. Acta, in preparation.
[241] E. Alessio, B. Milani, M. Bolle, G. Mestroni, P. Faleschini, F. Todone, S. Geremia and M. Calligaris, Inorg. Chem., 34 (1995) 4722.
[242] D.P. Riley and J.D. Oliver, Inorg. Chem., 25 (1986) 1821.
[243] M. Henn, E. Alessio, G. Mestroni, M. Calligaris and W.M. Attia, Inorg. Chim. Acta, 187 (1991) 39.

[244] M.M. Taqui Khan, N.H. Khan, R.I. Kureshy and K. Venkatasubramanian, Polyhedron, 11 (1992) 431.
[245] E. Alessio, G. Mestroni, G. Nardin, W.M. Attia, M. Calligaris, G. Sava and S. Zorzet, Inorg. Chem., 27 (1988) 4099.
[246] W.M. Attia and M. Calligaris, Acta Crystallogr., C43 (1987) 1426.
[247] A. Mercer and J. Trotter, J. Chem. Soc., Dalton Trans., (1975) 2480.
[248] A.R. Davies, F.W.B. Einstein, N.P. Farrell, B.R. James and R.S. McMillan, Inorg. Chem., 17 (1978) 1965.
[249] R.S. McMillan, A. Mercer, B.R. James and J. Trotter, J. Chem. Soc., Dalton Trans., (1975) 1006.
[250] E. Alessio, B. Milani, M. Calligaris and N. Bresciani-Pahor, Inorg. Chim. Acta, 194 (1992) 85.
[251] D.T.T. Yapp, J.S. Jaswal, S.J. Rettig, B.R. James and K.A. Skov, Inorg. Chim. Acta, 177 (1990) 199.
[252] D.P. Riley and J.D. Oliver, Inorg. Chem., 25 (1986) 1825.
[253] J.D. Oliver and D.P. Riley, Inorg. Chem., 23(1984) 156.
[254] B.K. Keppler, personal communication (1994).
[255] M. Calligaris, N. Bresciani-Pahor and R.S. Srivastava, Acta Crystallogr., C49 (1994) 448.
[256] S. Geremia, E. Alessio and F. Todone, Inorg. Chim. Acta, in press.
[257] M. Calligaris, P. Faleschini, F. Todone, E. Alessio and S. Geremia, J. Chem. Soc., Dalton Trans., (1995) 1653.
[258] E. Alessio, M. Bolle, B. Milani, G. Mestroni, P. Faleschini, S. Geremia and M. Calligaris, Inorg. Chem., 34 (1995) 4716.
[259] R.K. Coll, J.E. Fergusson, V. McKee, C.T. Page, W.T. Robinson and T.S. Keong, Inorg. Chem., 26 (1987) 106.
[260] F.A. Cotton and T.R. Felthouse, Inorg. Chem., 19 (1980) 323.
[261] F.A. Cotton and T.R. Felthouse, Inorg. Chem., 19 (1980) 2347.
[262] F.A. Cotton, S. Han and W. Wang, Inorg. Chem., 23 (1984) 4762.
[263] C.J. Simmons, A. Clearfield and Y. Sun, Inorg. Chim. Acta, 121 (1986) L3.
[264] M.Y. Chavan, X.Q. Lin, M.Q. Ahsan, I. Bernal, J.L. Bear and K.M. Kadish, Inorg. Chem., 25 (1986) 1281.
[265] M.Q. Ahsan, I. Bernal and J.L. Bear, Inorg. Chim. Acta, 115 (1986) 135.
[266] R.S. Lifsey, X.Q. Lin, M.Y. Chavan, M.Q. Ahsan, K.M. Kadish and J.L. Bear, Inorg. Chem., 26 (1987) 830.
[267] P. Colamarino and P. Orioli, J. Chem. Soc., Dalton Trans., (1976) 845.
[268] F.D. Rochon, P.C. Kong and R. Melanson, Can. J. Chem., 61 (1983) 1823.
[269] V.I. Sokol and M.A. Porai-Koshits, Koord. Khim., 1 (1975) 577.
[270] M. Calligaris, P. Faleschini and E. Alessio, Acta Crystallogr., C47 (1991) 747.
[271] E. Alessio, A. Sessanta o Santi, P. Faleschini, M. Calligaris and G. Mestroni, J. Chem. Soc., Dalton Trans., (1994) 1849.
[272] S.N. Gamage, R.H. Morris, S.J. Rettig and B.R. James, J. Organomet. Chem., 309 (1986) C59.
[273] S.N. Gamage, B.R. James, S.J. Rettig and J. Trotter, Can. J. Chem., 66 (1988) 1123.
[274] M. Calligaris and P. Faleschini, Acta Crystallogr., C51 (1995) 588.
[275] E. Alessio, P. Faleschini, A. Sessanta o Santi, G. Mestroni and M. Calligaris, Inorg. Chem., 32 (1994) 5756.
[276] J.A. Cabeza, H. Adams and A.J. Smith, Inorg. Chim. Acta, 114 (1986) L17.
[277] P.D. Robinson, C.C. Hinckley and A. Ikuo, Acta Crystallogr., C45 (1989) 1079.
[278] J.E. Fergusson, W.T. Robinson and R.K. Coll, Inorg. Chim. Acta, 181 (1991) 37.
[279] T.W. Johnson, S.M. Tetrin, P.E. Fanwick and R.A. Walton, Inorg. Chem., 30 (1991) 4146.
[280] A. Sykes and K.R. Mann, J. Am. Chem. Soc., 110 (1988) 8252.
[281] M. McPartlin and R. Mason, J. Chem. Soc. (A), (1970) 2206.
[282] G.J. Sunley, P. del C. Menanteau, H. Adams, N.A. Bailey and P.M. Maitlis, J. Chem. Soc., Dalton Trans., (1989) 2415.
[283] J.M. Kisenyi, J.A. Cabeza, A.J. Smith, H. Adams, G.J. Sunley, N.J.S. Salt and P.M. Maitlis, J. Chem. Soc. Chem. Commun., (1985) 770.
[284] K.M. Kadish, J.-L. Cornillon, P. Mitaine, Y.J. Deng and J.D. Korp, Inorg. Chem., 28 (1989) 2534.
[285] R. Krämer, K. Polborn and W. Beck, J. Organomet. Chem., 410 (1991) 111.

[286] B. Viossat, P. Khodadad and N. Rodier, Acta Crystallogr., C47 (1991) 179.
[287] G. Annibale, L. Cattalini, L. Canovese, B. Pitteri, A. Tiripicchio, M. Tiripicchio Camellini and M. Tobe, J. Chem. Soc., Dalton Trans., (1986) 1101.
[288] B. Viossat, P. Khodadad, N. Rodier and O. Guillard, Acta Crystallogr., C46 (1990) 894.
[289] L.E. Erickson, G.S. Jones, J.L. Blanchard and K.J. Ahmed, Inorg. Chem., 30 (1991) 3147.
[290] F.D. Rochon, P.C. Kong and R. Melanson, Inorg. Chem., 29 (1990) 1352.
[291] B. Viossat, A. Michelet, P. Khodadad and N. Rodier, Acta Crystallogr., C46 (1990) 1733.
[292] F.D. Rochon, R. Boughzala and R. Melanson, Can. J. Chem., 70 (1992) 2476.
[293] L.J. Nicholls and W.A. Freeman, Acta Crystallogr., B35 (1979) 2392.
[294] R. Melanson and F.D. Rochon, Acta Crystallogr., B34 (1978) 941.
[295] W.A. Freeman, Acta Crystallogr., B33 (1977) 191.
[296] R. Melanson and F.D. Rochon, Acta Crystallogr., B33 (1977) 3571.
[297] G.R. Champion, L.G. Marzilli, J.P. Hutchinson, K. Gebreyes and J. Zubieta, Acta Crystallogr., C40 (1984) 639.
[298] V.K. Belsky, V.E. Konovalov and V.Yu. Kukushkin, Acta Crystallogr., C47 (1991) 292.
[299] E.W. Neuse, A.G. Perlwitz, J.S. Field and N. Ramesar, Inorg. Chim. Acta, submitted for publication.
[300] V.Yu. Kukushkin, V.K. Belsky, V.E. Konovalov, G.A. Kirakosyan, L.V. Konovalov, A.I. Moiseev and V.M. Tkachuk, Inorg. Chim. Acta, 185 (1991) 143.
[301] E.N. Izakovich, L.M. Kachapina, R.P. Shibaeva and L. Khidekel, Izv. Akad. Nauk SSSR, Ser. Khim., (1983) 1389.
[302] V.K. Belsky, V.E. Konovalov, V.Yu. Kukushkin and A.I. Moiseev, Inorg. Chim. Acta, 169 (1990) 101.
[303] F.D. Rochon, P.C. Kong and R. Melanson, Inorg. Chem., 29 (1990) 2708.
[304] V.Yu. Kukushkin, V.K. Belsky, V.E. Konovalov, R.R. Shifrina, A.I. Moissev and R.A. Vlasova, Inorg. Chim. Acta, 183 (1991) 57.
[305] B. Viossat, P. Toffoli, P. Khodadad and N. Rodier, Acta Crystallogr., C44 (1988) 92.
[306] A. Cantoni, A. Tiripicchio, M. Tiripicchio Camellini and G. Annibale, Acta Crystallogr., C47 (1991) 701.
[307] R. Melanson, J. Hubert and F.D. Rochon, Acta Crystallogr., B32 (1976) 1914.
[308] S.S. Sotman, V.S. Fundamenskii, V.Yu. Kukushkin and E.Yu. Pankova, Zh. Obshch. Khim., 58 (1988) 2297.
[309] V.Yu. Kukushkin, V.K. Belski, V.E. Konovalov, E.A. Aleksandrova, E.Yu. Pankova and A.I. Moiseev, Phosphorus, Sulfur, and Silicon, 69 (1992) 103.
[310] P. Khodadad and N. Rodier, Acta Crystallogr., C43 (1987) 1690.
[311] E.C.H. Ling, G.W. Allen and T.W. Hambley, Acta Crystallogr., C48 (1992) 1197.
[312] V.Yu. Kukushkin, V.K. Belski, E.A. Aleksandrova, E.Yu. Pankova and V.E. Konovalov, Phosphorus Sulfur Silicon, 68 (1992) 253.
[313] S. Gama de Almeida, J.L. Hubbard and N. Farrell, Inorg. Chim. Acta, 193 (1992) 149.
[314] J.-M. Delafontaine, P. Khodadad, P. Toffoli and N. Rodier, Acta Crystallogr., C41 (1985) 702.
[315] W.I. Sundquist, K.J. Ahmed, L.S. Hollis and S.J. Lippard, Inorg. Chem., 26 (1987) 1524.
[316] K. Lövqvist, V.Yu. Kukushkin and Å.Oskarsson, XVI Congress I.U.C., Beijing, 21–29 August 1993, p. 224.
[317] R.G. Ball and N.C. Payne, Inorg. Chem., 16 (1977) 1871.
[318] R.G. Ball and N.C. Payne, Inorg. Chem., 15 (1976) 2494.
[319] V.K. Belsky, V.E. Konovalov and V.Yu. Kukushkin, Acta Crystallogr., C49 (1994) 751.
[320] B. Viossat, P. Khodadad and N. Rodier, Acta Crystallogr., C47 (1991) 1316.
[321] R. Melanson and F.D. Rochon, Acta Crystallogr., B34 (1978) 1125.
[322] K. Lövqvist and Å.Oskarsson, Acta Crystallogr., C48 (1992) 2073.
[323] R. Melanson and F.D. Rochon, Acta Crystallogr., C40 (1984) 793.
[324] R. Melanson and F.D. Rochon, Inorg. Chem., 17 (1978) 679.
[325] F. Caruso, R. Spagna and L. Zambonelli, Acta Crystallogr., B36 (1980) 713.
[326] C.J.L. Lock, R.A. Speranzini and J. Powell, Can. J. Chem., 54 (1976) 53.
[327] C.J.L. Lock, R.A. Speranzini, G. Turner and J. Powell, J. Am. Chem. Soc., 98 (1976) 7865.

[328] B. Viossat, Nguyen Huy Dung, J.-C. Lancelot and M. Robba, Chem. Pharm. Bull., 39 (1991) 3023.
[329] N. Bresciani Pahor, M. Calligaris, L. Randaccio and R. Romeo, Inorg. Chim. Acta, 26 (1978) L13.
[330] V.Yu. Kukushkin, E.A. Aleksandrova, V.M. Leovac, E.Z. Ivegeš, V.K. Belski and V.E. Konovalov, Polyhedron, 11 (1992) 2691.
[331] G. Alibrandi, R. Romeo, L. Monsù Scolaro and M.L. Tobe, Inorg. Chem., 31 (1992) 5061.
[332] C.E.L. Headford, R. Mason, P. Ramini Ranatunge-Bandarage, B.H. Robinson and J. Simpson, J. Chem. Soc. Chem. Commun., (1990) 601.
[333] T.T.B. Ha, F.L. Wimmer, J.-P. Souchard and N.P. Johnson, J. Chem. Soc., Dalton Trans., (1990) 1251.
[334] R. Melanson and F.D. Rochon, Can. J. Chem., 53 (1975) 2371.
[335] R.P. Shibaeva, Koord. Khim., 11 (1983) 129.
[336] R. Melanson and F.D. Rochon, Acta Crystallogr., C43 (1987) 1869.
[337] R. Melanson, C. de La Chevrotière and F.D. Rochon, Acta Crystallogr., C41 (1985) 1428.
[338] L. Antolini, U. Folli, D. Iarossi, L. Schenetti and F. Taddei, J. Chem. Soc., Perkin Trans. 2, (1991) 955.
[339] L. Cattalini, G. Michelon, G. Marangoni and G. Pelizzi, J. Chem. Soc., Dalton Trans., (1979) 96.
[340] C.A.L. Filgueiras, P.R. Holland, B.F.G. Johnson and P.R. Raithby, Acta Crystallogr., B38 (1982) 954.
[341] F.D. Rochon, P.C. Kong and R. Melanson, Acta Crystallogr., C41 (1985) 1602.
[342] V. Ericson, K. Lövqvist, B. Norén and Å.Oskarsson, Acta Chem. Scand., 46(1992), 854.
[343] F.D. Rochon and F. Guay, Acta Crystallogr., C43 (1987) 43.
[344] P. Betz and A. Bino, J. Am. Chem. Soc., 110 (1988) 602.
[345] L.I. Elding and Å.Oskarsson, Inorg. Chim. Acta, 130 (1987) 209.
[346] D. Boström, R. Strandberg, B. Norén and Å.Oskarsson, Acta Crystallogr., C47 (1991) 2101.
[347] G. Bruno, G. Bombieri, G. Alibrandi, S. Lanza and R. Romeo, Crystallogr. Struct. Comm., 11 (1982) 1369.
[348] R. Bardi, A. Del Pra and A.M. Piazzesi, Crystallogr. Struct. Comm., 10 (1981) 301.
[349] R. Melanson and F.D. Rochon, Acta Crystallogr., C44 (1988) 1893.
[350] F.A. Cotton, L.R. Falvello and S. Han, Inorg. Chem., 21 (1982) 2889.
[351] V.Yu. Kukushkin, V.K. Belski, E.A. Aleksandrova, E.Yu. Pankova, V.E. Konovalov, V.M. Yakovlev and A.I. Moiseev, Zh. Obshch. Khim., 61 (1991) 318.
[352] A. Allain, M. Kubiak, B. Jezowska-Trzebiatowska, H. Kozolowski and T. Glowiak, Inorg. Chim. Acta, 46 (1980) 127.
[353] D.P. Bancroft, F.A. Cotton and M. Verbruggen, Acta Crystallogr., C45 (1989) 1289.
[354] J. Vicente, A. Arcas, M.V. Borrachero, E. Molins and C. Miravitlles, J. Organom. Chem., 359 (1989) 127.
[355] R. Rüger, W. Rittner, P.G. Jones, W. Isenberg and G.M. Sheldrick, Angew. Chem. Int. Ed. Eng., 20 (1981) 382.
[356] G. Annibale, L. Cattalini, V. Bertolasi, V. Ferretti, G. Gilli and M.L. Tobe, J. Chem. Soc., Dalton Trans., (1989) 1265.
[357] D.A. Langs, C.R. Hare and R.G. Little, Chem. Commun., (1967) 1080.
[358] B.F.G. Johnson, J. Puga and P.R. Raithby, Acta Crystallogr., B37 (1981) 953.
[359] Yu.N. Kukushkin, N.V. Ivannikova and K.A. Khokhryakov, Russ. J. Inorg. Chem., 15 (1970) 1595.
[360] Yu.N. Kukushkin and V.N. Spevak, Russ. J. Inorg. Chem., 17 (1972) 1671.
[361] Lj. Manojlovic-Muir and R. Walken, Inorg. Chim. Acta, 10 (1974) 47.
[362] R.G. Pearson, Coord. Chem. Rev., 100 (1990) 403.
[363] F.A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, Interscience, New York, 1972, p. 1048.
[364] R.D. Shannon, Acta Crystallogr., A32 (1976) 751.
[365] M.J. Cleare, H.P. Fritz and W.P. Griffith, Spectrochim. Acta, 28A (1972) 2019.
[366] Yu.N. Kukushkin and V.N. Spevak, Russ. J. Inorg. Chem., 17 (1972) 1671.
[367] P. Murray-Rust and R. Bland, Acta Crystallogr., B34 (1978) 2527.
[368] B. Everitt, Cluster Analysis, Wiley, New York, 1980.
[369] S. Dowdy and S. Wearden, Statistics for Research, Wiley, New York, 1991, p. 119.
[370] P. Murray-Rust, H.-B. Bürgy and J.D. Dunitz, Acta Crystallogr., B34 (1978) 1787.