Dimethylsulphoxide Complexes of Vanadium(III)

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ABSTRAK

Garam kompleks dimetilsulfoksida (DMSO) dari vanadium(III) yang mempunyai formula empirik $VCl_3.6DMSO$ dan $VBr_3.6DMSO$ telah disintesis dan dikaji. Kedudukan jalur infra-merah dari regangan $v(S=O)$ menunjukkan bahawa ligan adalah terkoordinat kepada ion vanadium melalui oksigen. Keputusan dari spektra infra-merah jauh merumuskan bahawa tiada ion halida yang terkoordinat kepada ion logam. Spektra pantulan baur adalah konsisten dengan vanadium berada di sekitaran oktahedron. Berikutan dari itu, garam klorida dan bromida diformulakan sebagai $[V(DMSO)_6]Cl_3$ dan $[V[DMSO]_6]Br_3$ masing-masing.

ABSTRACT

Dimethylsulphoxide (DMSO) complex salts of vanadium(III) with the empirical formulae $VCl_3.6DMSO$ and $VBr_3.6DMSO$ were synthesized and investigated. The observed infra-red band positions of the $v(S=O)$ stretch indicate that the ligand is coordinated to vanadium ion via oxygen. Far-infra-red spectra lead to the conclusion that none of the halide ions are coordinated to the metal ion. Diffuse reflectance spectra are consistent with vanadium in an octahedral environment. Accordingly, the chloride and bromide salts are formulated as $[V(DMSO)_6]Cl_3$ and $[V[DMSO]_6]Br_3$, respectively.

INTRODUCTION

This research has been carried out as part of a general study of vanadium(III) with oxygen donor ligands (Sirat *et al.* 1985, 1988). The compounds to be reported here are the new complexes of vanadium(III) with dimethylsulphoxide (DMSO) ligands.

Dimethylsulphoxide has often been employed as a non-aqueous solvent for the preparation of anhydrous coordination compounds. However, the solvent is sometimes found to coordinate to the metal ion producing, for example, complexes such as $[Cr(DMSO)_6]^{3+}$ and $[PdCl_2(DMSO_2)]$ but in other cases no coordination occurs (Berney and Weber 1968). The coordination of DMSO molecules to metal ions may occur either through sulphur or

oxygen atoms, as in *Fig. 1*.

A dimethylsulphoxide complex of vanadium(III) with the formula $[V(DMSO)_6](ClO_4)_3$ has been reported (Langford *et al.* 1970). Kinetic studies of the reactions of this compound with thiocyanate ion, sulfosalicylic acid and 2,2-bipyridine
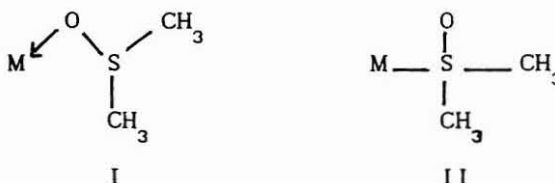

Fig. 1: Coordination modes of DMSO

were investigated. The salt was prepared by addition of excess DMSO to an aqueous solution of

vanadium(II) perchlorate without exclusion of air. The green crystals were obtained by evaporation of the solvent and purified by several recrystallizations from DMSO under vacuum. However, no physical properties of this compound such as magnetic and spectral data were obtained.

One other DMSO-vanadium(III) compound, $V_2(DMSO)_{12}(S_2O_7)_3$ has been reported (Harrison *et al.* 1979; Jeffreys *et al.* 1985). The compound was prepared from the reaction of V_2O_5 in DMSO solvent saturated with sulphur dioxide. After two days a green crystalline solid of metal disulphate with the above formula separated from solution. The product was characterized by infra-red spectroscopy, thermogravimetric studies and elemental analyses.

Based on the preparative method of $[V(DMSO)_6](ClO_4)_3$ it appeared possible to isolate anhydrous DMSO-V(III) complexes from aqueous vanadium(III) solutions. Therefore, in this study the reactions between aquavana-dium(III) halides and dimethylsulphoxide solvent in alcoholic media were investigated. As expected, water-free compounds of vanadium(III)-DMSO complexes isolated as green crystals of regular shapes were obtained. These salts with the general formula $VX_3.6DMSO$ (X = Cl and Br) were found slightly hygroscopic on exposure to air. Details of the preparative work are located in the experimental section below. The characterisation of these compounds based on the elemental analyses, electronic and infra-red spectra are described in this paper.

MATERIALS AND METHODS

Preparations
All materials were handled under nitrogen atmosphere using standard vacuum equipment.

Dimethylsulphoxide
Dimethylsulphoxide, dehydrated by storage over 4 Å without further purification, was employed in the preparation of the compounds.

Hexaquavanadium(III) halide, $VX_3.6H_2O$ (X= Cl and Br)
Both hydrated vanadium(III) halides were prepared by dissolving pure vanadium metal powder (Aldrich Chemical Co. Ltd.) in the corresponding hydrohalic acid (concentrated) under reflux. The resulting solution was then evaporated to dryness.

Hexakis(dimethylsulphoxide)vanadium(III) chloride, $[V(DMSO)_6]Cl_3$
The compound was prepared by dissolving the hexaquavanadium(III) chloride $VCl_3.6H_2O$ in a minimum volume of methanol. Then an excess of dimethylsulphoxide solvent was added to the green solution. The green crystals of regular shape separated from the solution at room temperature. The compound is slightly hygroscopic on exposure to air and is stored under nitrogen.

Hexakis(dimethylsulphoxide)vanadium(III) bromide, $[V(DMSO)_6]Br_3$
For the preparation of the title compound, the same method as described above was applied but the starting material was hexaquavanadium(III) bromide. The bromide salt separated more rapidly than the chloride analogue. This compound is relatively more stable than the chloride complex.

Elemental analyses
Vanadium analysis was carried out according to the standard methods. Microanalytical results for the C, H, Cl, Br and S were obtained from AMDEL, (Australian Microanalytical Service, Port Melbourne).

TABLE 1

Analytical data for the $(V[DMSO]_6)^{3+}$ salts

	$[V(DMSO_6)]Cl_3$		$[V(DMSO)_6]Br_3$	
Colour	Green		Green	
Element	Found (%)	Calc. (%)	Found (%)	Calc. (%)
V	8.00	8.15	6.80	6.72
C	21.83	23.02	18.80	18.97
H	5.52	5.75	5.01	4.74
Cl	17.10	17.03	–	–
Br	–	–	27.60	31.62
S	29.50	30.70	25.50	25.30

Instrumentation
Infra-red spectra were recorded at room temperature using a fourier transform infra-red spectrometer (Digilab FT S 20 E) at a resolution of 4 cm^{-1}. The samples were prepared in the form of KBr pellets. Far-infra-red spectra were obtained on the same spectrometer. The samples were prepared as nujol mulls and were measured between polythene plates.

Diffuse reflectance spectra were measured using a Zeiss PMQ II with double monochromator.

RESULTS AND DISCUSSION

Far-Infra-red Spectra
Far-infra-red spectra of the DMSO complexes between 450-100 cm^{-1} are as shown in *Fig. 2* and the data are presented in Table 2. The assignments of the observed bands are based on the data for the free ligand and some reported DMSO-metal

TABLE 2
Far-infra-red data for $[V(DMSO)_6]X_3$ (X= Cl or Br)
salts band positions and assignments (cm^{-1})

Free DMSO[d,e]	$[V(DMSOo)_6]Cl_3$	$[V(DMSO)_3]Br_3$	Assignment
382	369 s	370 s	$\delta_s(C-S-O) + \rho_r(CH)_3$
335	352 sh	350 sh	
333	3344 s	345 s	$\delta_s(C-S-O) + \rho_r(CH)_3$
309	335 sh	330 sh	$\delta(C-S-C) + \rho_r(CH)_3$
	288 m	285 m	$\delta(M-O-S)$ angle deform[f]
277	275 m	275 m	$\tau(CH_3)$
248	205, 202 m	203 m	
214			
	132 sh	112 sh	lattice vibrations
	127 sh		
	121 sh, 177 s	103 s	
	100 s		

d : Tranquille *et al.* 1971.

e : Safford *et al.* 1969

f : Berney and Weber 1968.

complexes (Tranquille *et al.* 1971; Tranquille and Forel 1972; Safford *et al.* 1969). The main purpose in examining the region was to provide information on whether halide ions exist as free ions or are coordinated to vanadium. Complexes of palladium containing both coordinated DMSO and coordinated halide (Cl and Br) have been examined by Tranquille *et al.* (1971).

From the spectra obtained here, no absorp-tion assignable to the V-X stretching mode is observed. All the bands in this region where $v(V-X)$ is often found (380-310 cm^{-1}) are basically identical in both complex salts. (*Fig. 2*). If the $v(V-X)$ bands were present, the $v(V-Br)$ absorption would be shifted by 20-50 cm^{-1} to lower wavenumbers as compared to the $v(V-Cl)$. Since no such shift is exhibited, this provides evidence that the halide ions are not directly bonded to the metal ion.

The peak at around 285 cm^{-1} is assigned for the M-O-S angle deformation as reported for the $[Cr(DMSO)]_6^{3+}$ species (Berney and Weber 1968) and the bands at 275-205 cm^{-1} region to CH$_3$ torsion modes. Although bands below 100 cm^{-1}, assigned to coordinated DMSO have been reported by Tranquille *et al.* (1971), for the spectra discussed here the strong absorptions which occur at around 120 cm^{-1} for chloride and at about 100 cm^{-1} for bromide salts are best assigned as lattice vibrations. Lattice vibrations can be distinguished from internal vibrations by their inverse dependence on mass. As seen from the spectra in *Fig. 2*, the bands for the bromide salt lie at lower energy than the chloride, in the order as expected because of the greater masses of bromine over the chlorine atom.

Infra-red Spectra - Fundamental Region

The infra-red spectral data for both salts of hexakis−(dimethylsulphoxide)vanadium(III) trihalides recorded in the region 4000-400cm^{-1} and the assignments are presented in Table 3. In general,
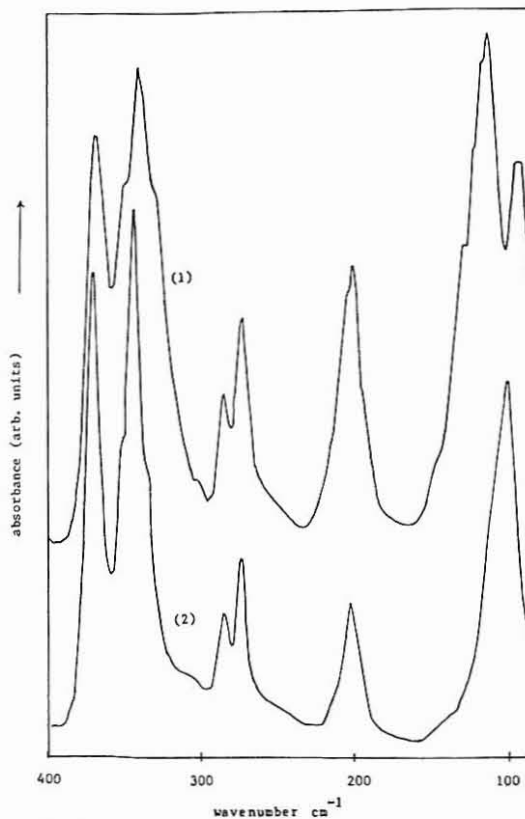

Fig 2: Far-infra-red spectra of $[V(DMSO)_6]Cl_3$ (1) and $[V(DMSO)_6]Br_3$ (2)

the spectra of the chloride and the bromide compounds are identical in this region.

A thorough normal coordinate analysis of a free DMSO ligand, reported by Horrocks and Cotton (1961), together with other spectral data of some DMSO-metal complexes have been used as a guide to assign the spectra of the DMSO-V(III) salts. The bonding nature of DMSO ligand to the metal ion can be determined from such data. The assignments of coordination through either oxygen or sulphur can be made on the basis of the different band positions of S=O stretching frequency in the two cases.

The S=O stretching frequencies of DMSO complexes with some metal ions are listed in Table 4. These data show that the $v(S=O)$ stretch for O-bonded DMSO compounds are found at lower frequencies, whereas for the S-coordinated compounds the $v(S=O)$ bands are observed at higher frequencies than those of free ligand.

Fig. 3 represents the resonance hybrids of a dialkylsulphoxide molecule (Johnson and Walton 1966). If DMSO is coordinated through oxygen the contribution of structure IV is decreased. As a result

the $v(S=O)$ stretch is shifted to a lower frequency compared with that for free dimethylsulphoxide. In contrast, the contribution of structure III decreases for S-coordinations, and this results in an overall increase of $v(S=O)$ value. Free DMSO exhibits

TABLE 3

Infra-red spectral data for $[V(DMSO)_6]X_3$
(X = Cl and Br) salts.
Band positions (cm^{-1}) and assignments

$[V(DMSO)_6]Cl_3$	$[V(DMSO)_6]Br_3$	Assignment
3180 m	3175 m	$v(CH_3)$
2980 m	2980 m	
1445 m	1410 m	
1425, 1410 m	1400 m	$\delta_a(CH_3)$ and
1330 m	1320 m	$\delta_s(CH_3)$
1310 m	1300 m	
1060 m	1050 m	?
1010 s	1000 s	$\rho_r(CH_3)$
975 s	980 s	
940 sh, 923 s	940 sh, 930 s	$v(S=O)$
		for O-bonded
700 w	700 w	$v(C–S)$
510 s, 500 sh	500 s, 490 sh	$v(V–O)$

TABLE 4
S=O and M–O stretching frequencies of some DMSO complexes;
band positions (cm^{-1}) and assignment

Compound	$v(S=O)$	Donor atom	$v(M–O)$	Ref.
Reported compounds				
Free DMSO	1070	–	–	g
	1100-1055	–	–	h
trans – $[Pd(DMSO)_2Cl_2]$	1116	S	–	i
$[Ru(NH_3)_5 (DMSO)] (PF_6)_3$	1045	S	–	j
$[NH_2 Me_2][RuCl_3(DMSO)_3]$	1100	S	–	k
$RuCl_2 (DMSO)_4$	1120, 1090	S	–	–
	915	O	479	l
$[Cr(DMSO)_6](ClO_4)_3$	928	O	529	m
$[Al(DMSO)_6]X_3$				
X=Cl	1008	O	545	n
X=Br	1006	O	542	n
X=I	1000	O	540	n
$[Mn(DMSO)_6](ClO_4)_3$	915, 960	O	?	o
This study				
$[V(DMSO)_6]X_3$				
X=Cl	923, 940	O	500, 510	
X=Br	930, 940	O	490, 500	

g : Tranquille and Forel 1972.
h : Nakamoto 1978.
i : Kitching *et al.* 1970.
j : Senoff *et al.* 1971.
k : McMillan *et al.* 1975.
l : Evans *et al.* 1973.
m: Berney and Weber 1968.
n : Fuentes and Patel 1970.
o : Prabhackaran and Patel 1972.

Fig. 3: Resonance hybrid of dialkylsulphoxide

v(S=O) stretch at about 1100-1055 cm^{-1} (Nakamoto 1978).

For the DMSO-vanadium(III) complex salts reported here, the bands at 940 and 923 cm^{-1} for chloride and 940 and 930 cm^{-1} for bromide are attributed to v(S=O) for the coordinated DMSO molecules. As these absorptions are found at lower frequencies than those of a free ligand, this shows that in both cases, the DMSO ligand is bonded to vanadium ion via oxygen. The appearance of a shoulder on the v(S=O) band may indicate the existence of two different bond strengths amongst the coordinated DMSO molecules. These metal-ligand bonding differ-ences may occur due to the Jahn-Teller distor-tion. The splitting of this S=O stretching band through the Jahn-Teller effect has also been reported for [Mn(DMSO)$_6$]$^{3+}$ compound, at 960 and 915 cm^{-1} (see Table 6). In this case, the v(S=O) band at 915 cm^{-1} corresponds to the strongly bonded ligands in the equatorial plane and the less intense band at 960 cm^{-1} to weakly bonded DMSO molecules in axial positions.

The presence of metal-oxygen stretching vibrations at 510 and 500 cm^{-1} assigned to v(V-O) is further evidence of oxygen-bonded DMSO ligands. A similar band-splitting has also been reported for [Fe]DMSO)$_6$]$^{2+}$ where Berney and Weber (1968) have suggested from their studies of several metal-DMSO complexes that all the v(M–O) bands are in fact split since the observed bands are broad but only in the case of Fe(II) compound is the band resolved. Such splitting may be explained as follows. If the [V(DMSO)$_6$]$^{3+}$ complex is regarded as a [V(O)$_6$]$^{3+}$ entity, this chromophore belongs to the points group O$_h$. The vibrational representation of this type of molecule is given by:

$$\Gamma_{vib} = A_{1g} + E_g + T_{2g} + 2T_{1u} + T_{2u}$$

with only T$_{1u}$ symmetry infra-red active. However, when the structure of the ligand is considered, the actual point group of [V(DMSO)$_6$]$^{3+}$ is unlikely to be O$_h$, even if the six DMSO ligands are octahedrally coordinated to vanadium ion. From other spectral evidence for [Cr(DMSO)$_6$]$^{3+}$, (Berney and Weber 1968), it has been shown that the actual symmetry in this case is S$_6$. Accordingly, the lowering of symmetry splits the degenerate T$_{1u}$ vibration into A$_u$ + E$_u$ infra-

red active species. Therefore, the splitting of this M–O stretching band is most probably due to the effect of reducing the symmetry of the complex from O$_h$ to that of S$_6$.

The spectra of DMSO-V(III) salts exhibit a sharp band at 1060 cm^{-1} and 1050 cm^{-1} for chloride and bromide, respectively. At first, this absorption was assigned as v(S=O) of the free ligand, as this is normally found at about 1100-1055 cm^{-1}. However, the information obtained from far-infra-red spectra indicates that none of the halide ions are directly coordinated to vanadium ion. Therefore, this rules out the possibility of a complex cation of the type [V(DMSO)$_4$Cl$_2$]$^+$ and accordingly that all six DMSO molecules must be coordinated to form [V(DMSO)$_6$]$^{3+}$ complex as reported for the chromium(III) (Berney and Weber 1968). This formulation is further discussed in relation to electronic spectra later. Therefore, the above absorptions are unassigned but could be due to a methyl rocking mode.

Since O-bonding in DMSO complexes has been reported in the cases of Cr(III) and Al(III) (Fuentes and Patel 1970; Evans *et al.* 1973), it might be expected that this would also apply for V(III). Further, in general vanadium(III) appears to show little tendency to form complexes with S-donor ligands. Apart from this, steric consider-ations of the DMSO ligands favour the formation of O-bonded complexes with vanadium ion. Six ligand molecules in the [V(DMSO)$_6$]$^{3+}$ species cannot fit around the metal ion when coordination occurs through sulphur because of steric hindrance from the CH$_3$- and O- groups. However, for the O-bonded DMSO the steric effect caused by (CH$_3$)$_2$S- "tails" is less. It has also been observed that a decrease in the size of the metal ion would increase the steric influence and favour the formation of O-bonded complexes. This has been noted, for example, in comparisons between DMSO complexes of the iron and ruthenium, in which the iron is O-bonded whereas the latter is both S- and O-bonded (Mercer and Trotter 1975).

Finally, as regards the possibility of [V(DMSO)$_6$]$^{3+}$ complex containing water, no infra-red bands due to water molecules either coordinated or uncoordinated are observed even though the salts are prepared from the aqua-halovanadium(III) salts. These results are in agreement with the elemental analyses.

Electronic Spectra

Room temperature diffuse reflectance spectral data of the DMSO-V(III) salts are presented in Table 5. The spectra show two well-defined peaks which are

TABLE 5
Diffuse reflectance spectra of $[V(DMSO)_6]^{3+}$

| Compound | Observed Bands (cm^{-1}) and Assignments | | | | |
	$^3T_{1g}(F) \to {}^3T_{2g}$	$^3T_{1g}(F) \to {}^3T_{1g}(P)$	10 Dq	B	Ref
$[V(DMSO)_6]Cl_3$	16600	24300	17860	600	p
$[V(DMSO)_6]Br_3$	16500	23800	17710	570	p
$[V(urea)_6]^{3+}$	16200	24200	17400	610	q

p = This work
q = Dingle *et al.* 1969.

typically those of V(III) in an octahedral environment. The ligand field splitting parameter, 10 Dq and the Racah parameter, B are calculated. The perturbation expected from Jahn-Teller distortion is not observed, probably because for the d^2 case this will be small and not easily detected in the broad bands exhibited in the powder spectra obtained by reflectance method.

The observed band positions in both DMSO-V(III) compounds are comparable to those of $[V(urea)_6]^{3+}$ (Table 5). Using the approach adopted by Jorgensen (1962), the ligand field parameter, Dq of any complexes can be estimated by multiplying a ligand field factor, f, and a metal ion factor, g.

Dq = f (ligand) x g (central ion)

Since both DMSO and O-bonded urea possess the same value of f (f = 0.91), these ligands are placed at the same position in the spectrochemical series (Lever 1984). The fact that the DMSO-V(III) spectra show band maxima and the Dq values are very similar to those of $[V(urea)_6]^{3+}$, leads to the conclusion that $[V(DMSO)_6]^{3+}$, species also contains the $[V(O)_6]^{3+}$, chromophore. This result further supports the formulation proposed earlier from the infra-red spectra.

CONCLUSION

The reactions between hydrated vanadium(III) halide, $VX_3.6H_2O$ (X = Cl and Br) and dimethyl-sulphoxide (DMSO) have resulted in the preparation of new complexes of vanadium(III) with empirical formulae $VCl_3.6DMSO$ and $VBr_3.6DMSO$. The complex salts have been characterized by elemental analyses, infra-red and diffuse reflectance spectra. The most striking feature of the complexes is the lack of water molecules in their formulation, yet the compounds are obtained from hydrated vanadium(III) halide compounds.

The absence of v(V-X) band from far-infra-red spectra further supports the fact that none of the

halides are coordinated to the vanadium ion. Infra-red spectra in a fundamental region have indicated the coordination of DMSO molecules to vanadium via oxygen atoms. In additon, the diffuse reflectance electronic spectra at room temperature are interpreted in terms of an O_h field and suggest that this complex consists of $[V(O)_6]^{3+}$ entity. Based on the above evidence these salts are therefore formulated as $[V(DMS)_6]X_3$ (X = Cl and Br).

REFERENCES

BERNEY, C.V. and J.H. WEBER. 1968. Complexes of Sulfoxides II. Metal-Oxygen Stretching Vibrations in Complexes of Dimethyl Sulf-oxide and Dimethyl Sulfoxide-d_6 and the Point Group of the Cation. *Inorg. Chem.* **7(2)**: 283-287.

DINGLE, R., P.J. MCCARTHY and C.J. BALLHAUSEN. 1969. Crystal. Spectra of Hexaurea Complexes. III. Optical and Magnetic Properties of Crystals Containing the Hexaureavanadium(III) ion. *J. Chem. Phys.* **50(5)**: 1957-1962.

EVANS, I.P., A. SPENCER and G. WILKINSON. 1973. Dichlorotetrakis (dimethyl sulphoxide) Ruthenium(II) and its Use as a Source Material for Some New Ruthenium(II) Complexes. *J. Chem. Soc. Dalton Trans.*: 204-209.

FEELTHAM, R. D and R.G. HAYTER. 1964. The Electrolyte Type of Ionized Complexes. *J. Chem. Soc.*: 4587-4591.

FUENTES, C.G and S.J. PATEL. 1970. New Cationic Complexes of Hydrated Alumi-nium(III) Halides with Dimethyl Sulfoxide. *J. Inorg. Nucl. Chem.* **32(52)**: 1575-1577.

HARRISON, W. D., J. B. GILL and D.C. GOODALL. 1979. Reaction in Mixed Non-aqueous Systems Containing Sulphur Dioxide. Part 2. The Dissolution of Transition Metals in the Binary Mixture Dimethyl Sulphoxide-Sulphur Dioxide and Ion-pair Formation Involving the Sulphoxylate Radical Ion in Mixed Solvents Containing Sulphur Dioxide. *J. Chem. Soc. Dalton Trans.*: 847-850.

HORROCKS, Jr., W.D and F.A. COTTON. 1961. Infra-red and Raman Spectra and Normal Coordinate Analysis of Dimethyl Sulfoxide and Dimethyl Sulfoxide - d_6. *Spectrochim. Acta* 17:134-147.

JEFFREYS, B., J.B. GILL and D.C. GOODALL. 1985. Reactions in Mixed Nonaqueous Systems Containing Sulfur Dioxide. Part 6. The Reaction of Metal Oxides with Dimethyl Sulfoxide-Sulfur Dioxide. *J. Chem. Soc. Dalton Trans.* (1): 99-100.

JOHNSON, B.F.G. and R.A. WALTON. 1966. A Far Infra-red Study of Transition Metal-dimethylsulphoxide Complexes. *Spectrochim. Acta.* 22: 1853-1858.

JONES, M.M. 1964. *Elementary Coordination Chemistry.* New Jersey: Prentice-Hall. p. 254.

JORGENSEN, C.K. 1962. *Absorption Spectra and Chemical Bonding in Complexes.* London: Pergamon p. 109-113.

KITCHING, W., C.J. MOORE and D. DODDRELL. 1970. Spectroscopic Studies of Alkyl Sulfoxide Complexes of Platinum (II) and Palladium (II). *Inorg. Chem.* 9: 541-549.

LANGFORD, C.H. and F.M. CHUNG. 1979. The Preparation and Kinetics of Complex Formation of Hexadimethylsulfoxido-vanadium (III) Perchlorate. *Can. J. Chem.* 48: 2969-2971.

LEVER, A. B. P. 1984. *Inorganic Electronic Spectroscopy.* 2nd ed. Amsterdam: Elsevier. p. 748.

MCMILLAN, R. S., A. MERCER, B.R. JAMES and J. TROTTER. 1975. Preparation, Characterization and Crystal and Molecular Structure of Dimethylammonium Trichlo-rotris (dimethylsuphoxide)-ruthenate (II) *J. Chem. Soc. Dalton Trans:* 1006-1010.

MERCER, A and J. TROTTER. 1975. Crystal and Molecular Structure of Dichlorotetrakis (dimethylsulph–oxide) ruthenium (II). *J. Chem. Soc. Dalton Trans.:* 2480-2483.

NAKAMOTO, K. 1978. *Infra-red and Raman Spectra of Inorganic and Coordination Compounds.* 3rd ed. New York: Wiley-Interscience. p. 344.

PRABHACKARAN, C.P and C.C. PATEL. 1972. Jahn-Taller Distortion in Monodentated Ligand Complexes of Manganese (III). *J. Inorg. Nucl. Chem.* 34(7): 2371-2374.

SAFFORD, G. J., P.C. SCHAFFER, P. S. LEUNG, G.F. DOEBBLER, G.W. BRADY and E.F.X. LYDEN. 1969. Neutron Inelastic Scattering and X-Ray Studies of Aqueous Solutions of Dimethylsulphoxide and Dimethy-sulphone. *J. Chem. Phys.* 50(5): 2140-2159.

SENOFF, C. V., E. MASLOWSKY, Jr. and R.G. GOEL. 1971. Dimethylsulfoxidepentaamineruthenium (II) Hexafluorophosphate. A Spectroscopic Study. *Can. J. Chem.* 15: 3585-3589.

SIRAT, K., P.W. SMITH, I.E. GREY and I.C. MADSEN. 1985. Structure of transDiaquabis (oxalato) vanadate (III) Complexes: A[V(C$_2$O$_4$)$_2$ (H$_2$O)$_2$].x H$_2$O, A = Cs (x=4) and A = CH$_3$NH$_3$ (x=4.5). *Acta Cryst.* C41: 681-683.

SIRAT, K, P.W. SMITH, R. STRANGER, I.E. GREY and I.C. MADSEN. 1988. Structure, Vibrational and Electronic Spectra and Bonding in trans-Diaquabis (oxalato) vanadate (III) Complex Salts, A[V(ox)$_2$ (H$_2$O)$_2$].xH$_2$O (A=Cs, K or NH$_3$Me) and X-Ray Crystral Structure of the Potassium Salt (x=3). *J. Chem Soc. Dalton Trans.:* 2245-2253.

TRANQUILLE, M., P. LARBARBE, M. FOUASSIER and M.T. FOREL. 1971. Determination des Champs de Forces de Valence et des Modes Normaux de Vibration des Molecules (CH$_3$)$_2$S et (CH$_3$)$_2$SO. *J. Mol. Structure* 8: 273-291.

TRANQUILLE, M. and M.T. FOREL. 1972. Etude des Spectres Infra-rouges et Raman des Composes de Coordination PdL$_2$X$_2$ trans (4000–40 cm^{-1}) L=(CH$_3$)$_2$S, (CD$_3$)$_2$S, (CH$_3$)$_2$SO, (CD$_3$)$_2$SO; X=Cl, Br. *Spectrochim. Acta.* 28A: 1305-1320.