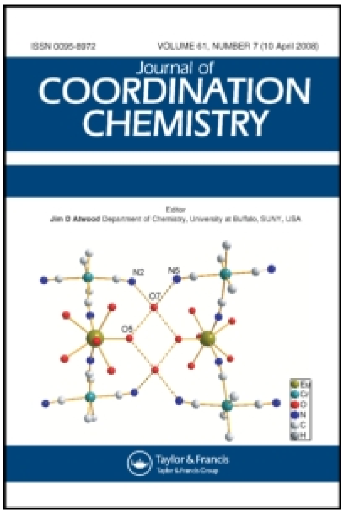

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THE MOLYBDENUM(V) CHELATES FORMED BY THE REACTION OF MOLYDBDENUM HEXACARBONYL OR MOLYBDENUM PENTACHLORIDE WITH SALICYL(2-PYRIDYL)ALDAZINE

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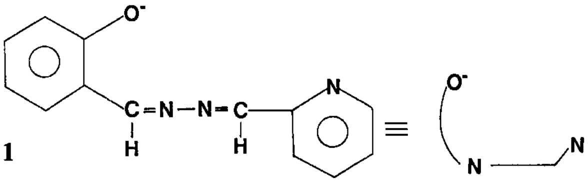
Reaction of molybdenum hexacarbonyl with salicyl(2-pyridyl)aldazine leads to the formation of the dinuclear compound tetra(salicyl(2-pyridyl)aldazineato)-μ-oxodioxodimolybdenum(V). Reaction of the ligand with molybdenum pentachloride gives tris(salicyl(2-pyridyl)-aldazineato)oxomolybdenum(V) which reacts with thionyl chloride to form dicholortris(salicyl(2-pyridyl)aldazineato)molybdenum(V). The dicholoride undergoes a hydrogen chloride elimination reaction with aniline to give tris(salicyl(2-pyridyl)aldazineato)-bis(anilineato)molybdenum(V). Spin Hamiltonian parameters and e.s.r spectral linewidths have been determined from the e.s.r. spectra due to the molybdenum(V)chelates. Computer simulations of the S-band e.s.r. spectrum due to the dichlorotris(salicyl(2-pyridyl)aldazineato)molybdenum(V) points to a cis configuration of the chloride anion about the molybdenum(V) centre with one chloride anion in the of the predominantly 4dxy ground molybdenum(V) centre and the other chloride anion out of that plane.

Key words: molybdenum, aldazine, e.s.p., structure, complexes

INTRODUCTION

The aldazines formed by the water elimination reaction of aldehydes with a hydrazone allow an element of design in the synthesis of ligands for the chelation of metal ions. An example is the aldazine formed by reaction of pyridine-2-carboxaldehyde with the hydrazone of salicylaldehyde, salicyl(2-pyridyl)aldazine (sapyal) which is capable of modes or coordination involving its ionized hydroxyl group, 1, pyridyl nitrogen and



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aldazine nitrogen. Indeed, it has been found that sapyal is capable of forming chelates with a variety of transition and non-transition metal ions. Oxidative decarbonylation has proven to be a useful route in the synthesis of chelate compounds, particularly those containing milybdenum and chromium.[1,2] The coordination chemistry of molybdenum has assumed an important role due to the occurrence of molybdenum in the enzymes nitrate reductase, sulphite oxidase, xanthine oxidase and formate dehydrogenase[3-6] where the molybdenum is capable of two-electron oxidation changes and formation of a cis-dioxomolybdenum centre. The biochemical function of the molybdenum containing enzymes has been the subject of chemical modelling,[8-10] which has largely involvedf the use of sulphur containing compounds. To expand further knowledge of the chemical properties of the oxomolybdenum group some molybdenum compounds of sapyal have been studied and we disclose here the occurence and properties of oxomolybdenum chelates of sapyal formed by reaction of the ligand under suitable conditions with molybdenum hexacarbonyl and molybdenum pentachloride. The synthesis, properties and biological activity of the furaldazine chelate of molybdenum pentachloride has been described.[11]

EXPERIMENTAL

The e.s.r. spectra, recorded as the first derivatives of absorption, were obtained using a Varian E-12 spectrometer with an E101 microwave bridge at X-band (*ca* 9.15 GHz) and an S-band microwave bridge, assembled from commercially available components, operating at *ca* 2.3 GHz. Low temperatures were achieved by means of a Varian E-257 temperature accessory (above *ca* 100K) or at liquid nitrogen temperature using narrow tail quartz Dewar flasks. Magnetic fields were calibrated against proton n.m.r. frequencies measured using a Hewlett Packard HP 5254L frequency counter. Microwave frequencies were measured using a direct reading EIP 548A frequency counter.

Computer simulations were carried out using a Burroughs 136700 computer. Absorption spectra in the UV and visible regions were recorded on a Varian 635 spectrophotometer at room temperature using 1cm glass and silica cuvettes.

Microanalyses were carried out by the C.S.I.R.O. Microanalytical Service, Melbourne.

Preparation of salicyl(2-pyridyl)aldazine

Pyridine-2-carbozaldehyde (10.7g, 0.1M) was added to salicylaldehyde hydrazone (13.6g, 0.1M) dissolved in dmf (100 cm^3) and the reaction mixture heated to reflux distillation for one hour. After cooling to room temperature, ice-cold water (100 cm^3) was added to precipitate the orange-yellow product which, after filtration, was washed with an ethanol/water mixture (50% v/v) (Yield 18.5g, 82%).

Preparation of tetra(salicyl(2-pyridyl)aldazineato)-μoxodioxodimolybdenum(V)

A solution of salicyl-2-pyridylaldazine (2.3g) in methanol (100 cm^3) was added to a solution of molybdenum hexacarbonyl (1.0g) in toluene (50 cm^3) under dried nitrogen atmosphere. The reaction mixture was heated to reflux (1½ hr) under nitrogen, during which time the solution became purple in colour. Most of the solvent was removed by rotary evaporation at diminished pressure and the product precipitated by addition of *n*-hexane and washed with ethanol. The analytical results and magnetic susceptibility measurements are summarized in Table I. (Yield 3.1g, 55%).

Preparation of tris(salicyl(2-pyridyl)aldazineato)oxomolybdenum(V)

Under an atmosphere of dried nitrogen molybdenum pentachloride (1.0g) was added to a dmf solution (50 cm^3)of salicylpyridylaldazine (2.3g). The reaction mixture was heated to reflux under nitrogen for one hour, during which time the solution turned a reddish brown colour. Most of the solvent was removed by rotary evaporation at diminished pressure. Ethanol (50cm^3) was added to the product which was isolated by filtration. (Yield 2.0g, 77%).

Preparation of dichlorotris(salicyl(2-pyridyl)aldazineato)molybdenum(V)

A dmf solution (10 cm^3) containing thionylchloride (1 cm^3) was added dropwise under nitrogen atmosphere to a dmf solution (50 cm^3) of tris(salicyl(2-pyridyl)aldazineato)-oxomolybdenum(V) (1.0g). The addition of reagent effects a darkening of the colour of the reaction mixture. Most of the solvent was removed by distillation at diminished pressure and the product isolated after addition of dried chloroform (50 cm^3) and filtration under nitrogen atmosphere. The product was hygroscopic. (Yield 0.9g, 64%).

Preparation of tris(salicyl(2-pyridyl)aldazineato)bis(anilinato)molybdenum(V)

A dmf solution (10 cm^3) of aniline (0.2g) was added under nitrogen atmosphere to a dmf solution (25 cm^3) containing tris(salicyl(2-pyridyl)aldazineato)molybdenum(V) dicholoride (0.5g). The reaction mixture was refluxed for 1 hour and most of the solvent removed by heating at diminished pressure. The product was isolated by the addition of ethanol (50 cm^3) and filtration under nitrogen atmosphere with washing by hot ethanol (2 × 25 cm^3). (Yield 0.4g, 70%).

The analytical results for each of the products is summarized in Table I.

TABLE I

Analytical data for various molybdenum(V) chelates of salicylpyridylaldazine

Compound	Expected (%)				Found (%)				μ_{eff} (B.M.)
	C	H	N	Cl	C	H	N	Cl	
HL	69.33	4.89	18.67		69.00	4.85	18.70		
[MoOL$_2$]$_2$O	54.94	3.52	14.79		55.72	3.45	14.70		0.78
MoOL$_3$	59.69	3.83	16.07		60.10	3.85	16.12		1.63
MoCl$_2$L$_3$	55.78	3.57	15.02	8.46	55.85	3.65	14.95	8.55	1.68
Mo(anil)$_2$L$_3$	63.23	4.62	16.11		63.64	4.60	16.25		1.65

HL = salicyl(2-pyridyl)aldazine. L = anion of salicyl(2-pyridyl)aldazine.

RESULTS

Heating a dimethylformamide (dmf) solution containing molybdenum hexacarbonyl and sapyal under reflux and dinitrogen atmosphere leads to the formation of a reddish-brown product which was isolated after addition of *n*-hexane. The element analysis of the product is consistent with the empirical formula $[\mathrm{Mo(V)O(sapyal)_2}]_2\mathrm{O}$. The infra-red spectrum of the chelate in addition to showing absorptions due to the ligand has absorptions at 905 cm^{-1} and 930 cm^{-1} attributable to Mo-O terminal stretching frequencies, while an absorption at 762 cm^{-1} is assigned to one of the bridging antisymmetric of symmetric stretching frequencies of the molybdenum oxygen group.[12] The chelate is soluble in a variety of non-polar (benzene, toluene) or coordinating (dimethylformamide, dimethysulphoxide) solvents and Figure 1 shows the electronic spectra due to solutions of the chelate in toluene, acetonitrile and dmf. The magnetic moment of the chelate is therefore paramagnetic with a reduced magnetic moment possibly due to exchange coupling. The e.s.r. spectrum observed at high instrumental gain due to a frozen solution of the chelate in dmf is depicted in Figure 2 and confirms the chelate is paramagnetic.

The reaction of molybdenum pentachloride with sapyal in refluxing dmf gives rise to

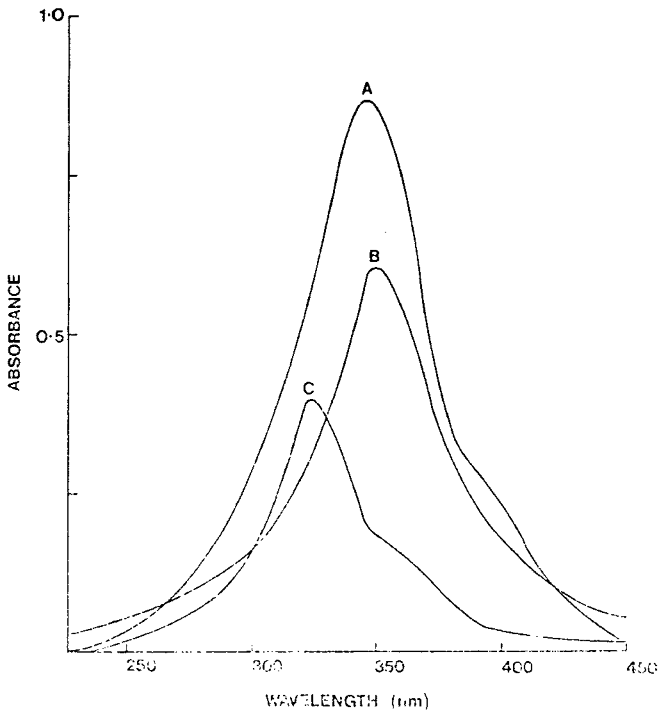


FIGURE 1 Absorption spectra in the ultraviolet and visible region of tetra(salicyl(2-pyridyl)aldazineato)-μ-oxo-oxomolybdenum(V) (5.0×10^{-3}) in different solvents. (1): Dimethylformamide, (2): Acetonitril, (3): Toluene. (Using 1cm quartz cells.)

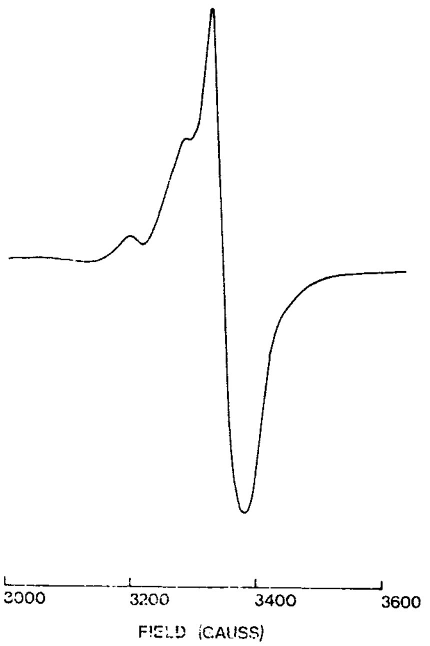


FIGURE 2 First derivative X-band e.s.r. spectrum at 77K of a frozen dmf solution containing tetra(salicyl(2-pyridyl)aldazineato)-μ-oxo-oxomolybdenum(V) (5.0×10^{-3} mol dm^{-3}). Microwave frequency 9.108 GHz.

the formation of a dark brown product which was isolated from solution after subsequent addition of ethanol. The elemental analysis of the product indicates an empirical formula Mo(V)O.(sapual)$_3$. The electronic spectrum due to the product dissolved in dmf is shown in Figure 3 while its e.s.r. spectrum recorded in frozen dmf is depicted in Figure 4A and its room temperature e.s.r. spectrum is illustrated by Figure 4B.

The tris(salicyl(2-pyridyl)aldazineato)oxomolybdenum(V) complex reacts readily in refluxing dmf with thionyl chloride. The product, a dark brown solid, was isolated by addition of ethanol to the reaction mixture. Elemental analysis indicates the empirical formula Mo(V)Cl$_2$(sapyal)$_3$. In the infra-red spectrum of the product to the spectral features due to the aldazine ligand the peaks at 905 cm^{-1} and 950 cm^{-1}, attributed to molybdenum-oxygen (terminal) stretching frequencies present in the infra-red spectrum of the reactant, are absent. On the other hand, a new band in the infra-red spectrum of the product occurs at 340cm^{-1} and is assignable to a molybdenum-chloride vibration.

The electronic spectrum due to a dmf solution of the product, dichlorotris(salicyl-(2-pyridyl)aldazineato)molybdenum(V) is shown in Figure 3 while its X-band e.s.r. spectrum recorded using a frozen dmf solution of the chelate is shown in Figure 5A. The integrated intensity of the e.s.r. spectrum is same as that due to tris(salicyl-(2-pyridyl)aldazineato)oxomolybdenum(V). The S-band (2.28 GHz) e.s.r. spectrum due to dichlorotris(salicyl(2-pyridyl)aldazineato)molybdenum in frozen dmf is illustrated by Figure 5B. Here, at high instrumental gain, in addition to the hyperfine interactions which give rise to the major peaks in the spectrum, superhyperfine lines with a spacing of about 7 Gauss are observable in the 800 Gauss region, which arise from the interaction of the unpaired electron of the central metal ion with the nuclei of the chloride anions (Cl, I = 3/2).

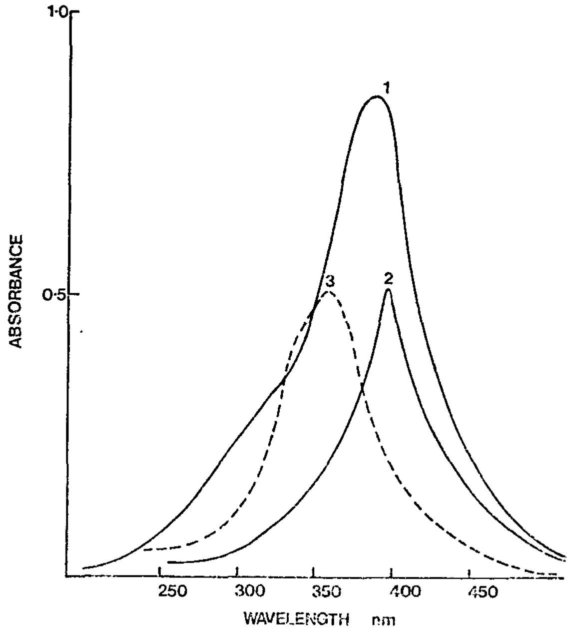


FIGURE 3 Absorption spectra in the ultra-violet and visible region of a dmf solution 3.0 × 10^{-1} mol dm^{-3} of (1) Tris(salicyl(2-pyridyl)aldazineato)molybdenum(V) dichloride, (2) Tris(salicyl(2-pyridyl)aldazineato) oxomolybdenum(V), and (3) Tris(salicyl(2-pyridyl)-aldazineato)bis(anilato)-molybdenum(V).

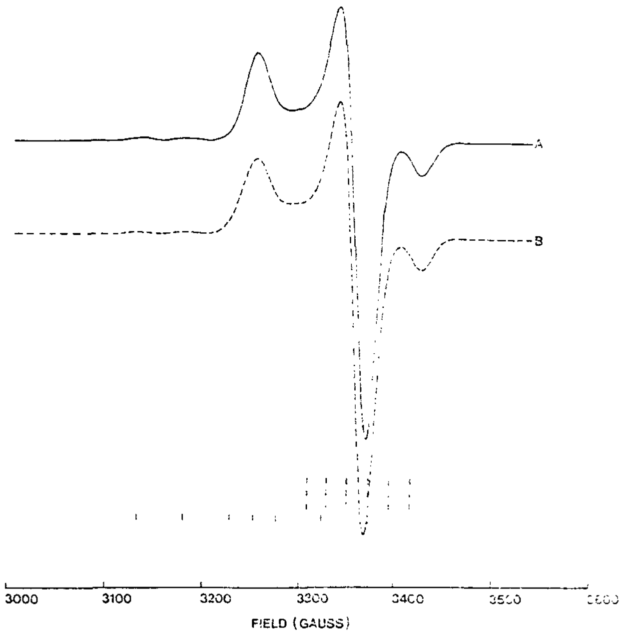


FIGURE 4A First derivative X-band e.s.r. spectrum at 77K of a frozen dmf solution containing tris(salicyl-(2-pyridyl)aldazineato)oxomolybdenum(V) (5.0 × 10^{-3} mol dm^{-3}). Microwave frequency 9.108 GHz. (A): Experimental result. (B): Computer simulation using spin Hamiltonian parameters given in Table IIA and linewidth terms in Table IIB.

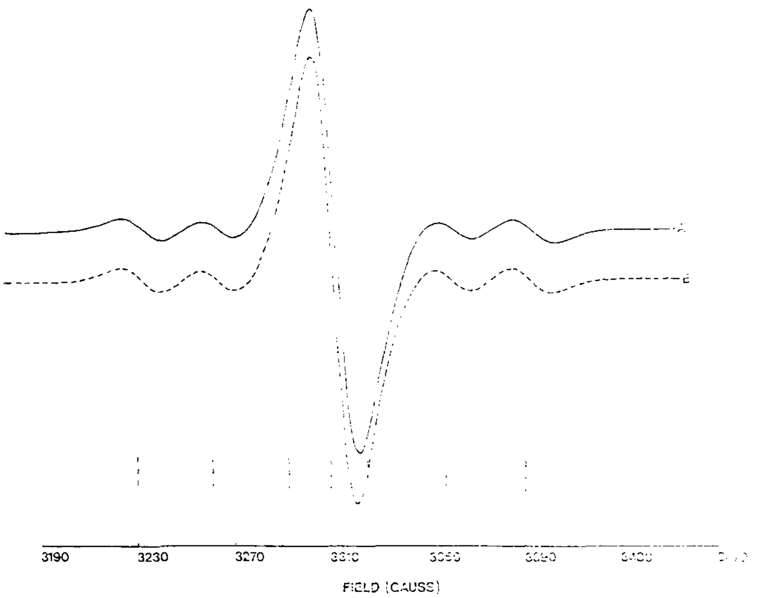


FIGURE 4B First derivative X-band e.s.r. spectrum at room temperature (298K) of a dmf solution containing tris(salicyl(2-pyridyl)aldazineato)oxomolybdenum(V) (5.0 × 10^{-3} mol dm^{-3}). Microwave frequency 9.108 GHz. (A): Experimental result. (B): Computer simulation using spin Hamiltonian parameters in Table IIA and linewidth terms in Table IIB.

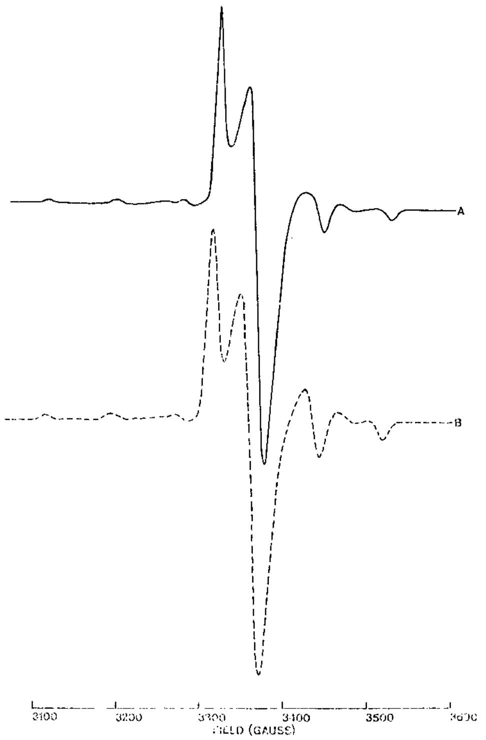


FIGURE 5A First derivative X-band e.s.r. spectrum at 77K of a dmf solution containing tris(salicyl-(2-pyridyl)aldazineato)molybdenum(V) dichloride (5.0×10^{-3} mol dm $^{-3}$).

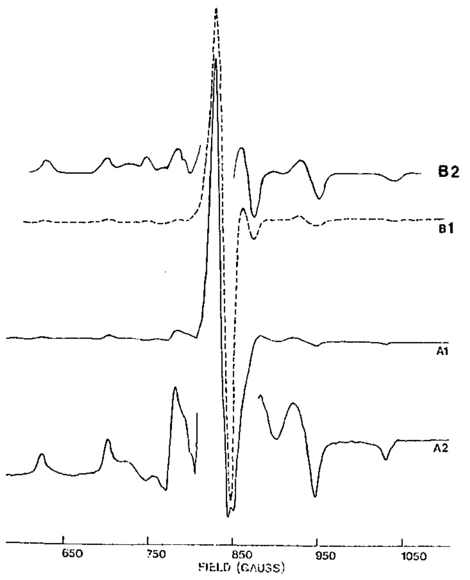


FIGURE 5B First derivative S-band e.s.r. spectrum at 77K of a frozen solution containing tris(salicyl-(2-pyridyl)aldazineato)molybdenum(V) dichloride (5.0×10^{-3} mol dm^{-3}). Microwave frequency 2.280 GHz. (A1): Experimental result. (A2): Experimental spectrum recorded at higher instrumental gain. (B1): Computer simulation using spin Hamiltonian parameters in Table IIA and linewidth terms in Table IIB. (B2): Resolution enhancement of computed lineshape.

Dichlorotris(salicyl(2-pyridyl)aldazineato)molybdenum(V) in dmf solution reacts with aniline to form a product whose elemental analysis corresponds to the empirical formula, $Mo(V)(C_6H_5NH)_2(sapyal)_3$. The infra-red spectrum of the product confirms the elimination of the metal-halide stretching frequency at 340 cm^{-1} and, apart from that portion of the spectrum attributable to the ligand, a new band at 1150 cm^{-1} attributable to a C-N stretch in the anilinato group appears. The e.s.r. spectrum of the chelate in frozen dmf solution in shown in Figure 6.

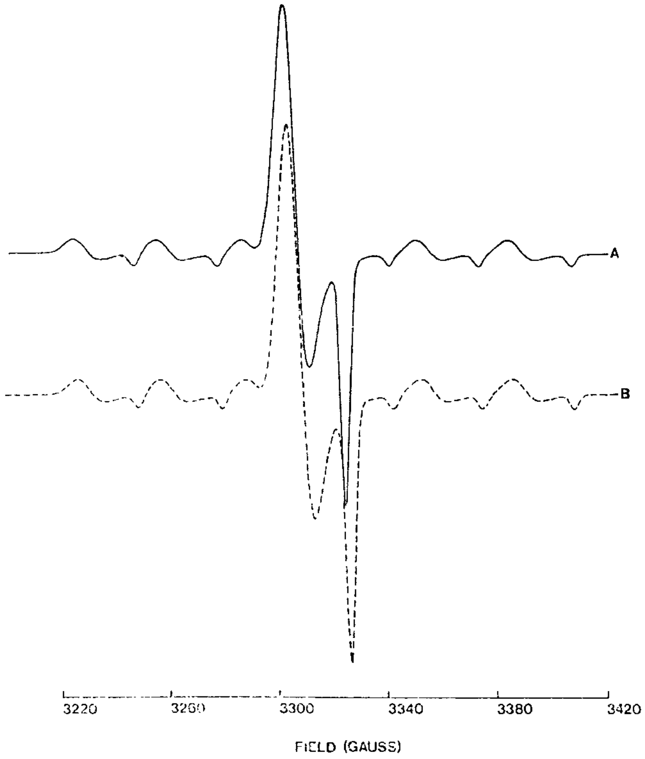


FIGURE 6 First derivative X-band e.s.r. spectrum at 77K of a frozen dmf solution containing tris(salicyl-(2-pyridyl)aldazineato)bisanilatomolybdenum(V) (5.0×10^{-3} mol dm^{-3}). Microwave frequency 9.108 GHz. (A): Experimental result. (B): Computer simulation using spin Hamiltonian parameters in Table IIA.

Interpretation of the e.s.r. spectral data: The spin Hamiltonian parameters

The e.s.r. spectral properties of the molybdenum(V) ($4d^1$, S = ½) centre of a variety of coordination compounds may be represented by the spin Hamiltonian

$$\mathcal{H} = \beta[g_\parallel B_z S_z + g_\perp(B_x S_x + B_y S_y)] + A_\parallel S_z I_z + A_\perp(S_x I_x + S_y I_y) \qquad (1)$$

where the parameters have their usual meaning. The hyperfine structure arises from the naturally occurring isotopes ^{95}Mo and ^{97}Mo which have almost identical nuclear magnetic moments and identical nuclear spins (I = 5/2). ^{98}Mo is also present; it has zero nuclear spin and therefore does not contribute any hyperfine structure.

The theoretical description of the ground state electronic structure for ions with electron configurations in a tetragonal crystal field leads to the following expressions for g- and A-values:[13–15]

$$g_{\parallel} = g_e(a^2 - b^2) - 2kb^2 \tag{2a}$$

and

$$g_{\perp} = g_e a^2 - 2\sqrt{2}\,kab \tag{2b}$$

$$A_{\parallel} = P\left(-\kappa - \frac{4}{7}a^2 - \frac{3}{7}b^2 + \frac{6\sqrt{2}}{7}ab - 2b^2\right) \tag{3a}$$

and

$$A_{\perp} = P\left(-\kappa + \frac{2}{7}a^2 - \frac{2}{7}b^2 - \frac{3\sqrt{2}}{7}ab - 2\sqrt{2}\,ab\right) \tag{3b}$$

where

$$P = 2g_n\beta\beta_n <r^{-3}> 3d \tag{4}$$

k is the orbital reduction factor and κ the S-electron hyperfine structure parameter due to core polarization. In equations (*2*) and (*3*), a and b are state mixing coefficients satisfying the condition (*5*).

$$a^2 + b^2 = 1 \tag{5}$$

When a 1 and b 0 corrections due to excited state mixing lead to g-values

$$g_{\parallel} = g_e - \frac{8\zeta}{\Delta} \tag{6a}$$

and

$$g_{\perp} = g_e - \frac{2\zeta}{\delta} \tag{6b}$$

where Δ is the energy above the ground state of the $d_{x^2-y^2}$ excited state and δ the first order splitting between dxy and degenerate d_{xz}, d_{yz} pair.

Under the same conditions ($a \approx 1$, $b \approx 0$) the hyperfine constants simplify to

$$A_{\parallel} \approx P\left(-\kappa - \frac{4}{7}\right) \tag{7a}$$

and

$$A_{\perp} \approx P\left(-\kappa + \frac{2}{7}\right) \tag{7b}$$

When it is necessary to consider three g-values and three hyperfine constants, relevant expressions have been described.[16]

The model so far outlined is based on crystal field theory, the orbital reduction factor k (equations (*2a*) and (*2b*)) providing some insight into the presence of covalency.

LCAO-MO theories have been used to modify the above equations[17–18] and used in further modified form by many authors.[19–22] The effect of the ligand contribution is to include the effect of ligand spin-orbit coupling and this particularly can modify the g-shifts from the free electron value.

Computer simulation of e.s.r. spectra: The linewidth terms

The usual approach to computer simulation of e.s.r. spectra due to powder or frozen solutions is to solve the spin Hamiltonian for the resonance field positions $B_r(\theta, \Phi, M_I)$ and to calculate the spectrum from the following equations:

$$S(B) = \sum_{\theta}\sum_{\phi}\sum_{\substack{M_I=-I \\ (I=0,5/2)}}^{I} a(I)\,\frac{\overline{g_1^2}}{\overline{g}}\; f(B-Br, \sigma_B)\Delta\cos\theta\,\Delta\phi \qquad (8)$$

In equation (*8*) the integration, approximated as a sum is over both polar angles Θ, Φ, which specify the orientation of the magnetic field relative to the g-principal axes, a(I) is the isotope weighting factor for ^{98}Mo and the sum of ^{95}Mo, g_1^2 the powder of frozen solution average value of the transition probability, σ_B the linewidth (in mT or Gauss) and f the lineshape function. The presence of g^{-1}, the reciprocal of the g-factor for a general orientation, is required to effect the transformation from frequency to field variable for symmetric lines.[24]

In the light of recent understanding of the nature of field-swept e.s.r. spectra their computer simulation can be considered as follows.[24,25] The spin Hamiltonian is solved at various frequencies and the resonance frequency difference, $\nu_0(B)$, as a function of the magnetic field, is determined at each point across a line where at the line centre $\nu_0(B_r) = \nu_c$, the constant applied frequency. Equation (*8*) then is more correctly written

$$S(B) = \sum_{\theta}\sum_{\phi}\sum_{\substack{M_I=-I \\ (I=0,5/2)}}^{I} a(I)\,\overline{g_1^2}\; f(\nu_c - \nu_o[B], \sigma_\nu) \qquad (9)$$

where the lineshape is defined in frequency space. Here the linewidth, σ_ν, which itself may vary over a given line is defined in frequency units.

It has been shown for copper(II) complexes that the linewidths may be written in the form similar to that of Froncisz and Hyde[26] but using frequency and field variables:

$$\sigma_{\nu i} = \sigma_{Ri}{}^2 + (C_{1i}\,\nu_o\,[B] - C_{2i}M_I)^2\ {}^{1/2} \qquad (10)$$

where i = // or ⊥, σ_{Ri} is the residual width due to spin spin interaction and unresolved ligand hyperfine structure,

$$C_{1i} = \sigma_{gi}/gi \qquad (11a)$$

and

$$C_{2i} = \sigma_{Ai} \qquad (11b)$$

In equation (*11*) σ_{gi} and σ_{Ai} should be considered to be the variances of the random distributions of g_i and A_i values treated as random variables. Froncisz and Hyde[26] found that $C_{1\parallel}$ and $C_{2\parallel}$ were strongly correlated. If imperfect correlation exists then in equation (*10*), $(C_{1i}\nu_o[B] - C_{2i}M_I)^2$ should be multiplied out and the cross term multiplied by a correlation coefficient, ρ_i where $|\rho_i| \leqslant 1$. In the case of molybdenum(V), the expression for g- and A-values do not necessarily imply as high a degree of correlation as for copper but the inclusion of more adjustable parameters in the program has not been considered justifiable at this point.

The angular variation is treated in the same manner as hyperfine structure so that, for axial symmetry

$$\sigma_\nu^2 = \sigma_{\nu\parallel}{}^2 \cos^2\theta + \sigma_{\nu\perp}{}^2 \sin^2\theta \tag{12}$$

Computer simulations of the e.s.r. spectra due to copper(II) and cobalt(II) compounds have been quite successful in reproducting the experimental linewidths though it has not been possible to use the same linewidth values to compute spectra obtained at S-band frequencies as well as X-band.[27–29]

The use of a more vigorously statistical model based on some recent work by Hagen *et al.*,[30,31] as well as earlier considerations[22,23] may make possible computer fits at widely different frequencies using a fixed set of linewidth parameters.

The spin Hamiltonian parameters obtained from computer simulation of the experimental e.s.r. spectra due to the various salicyl(2-pyridyl)aldazine molybdenum(V) chelates are summarized in Table IIA while the corresponding values of the linewidth terms used to obtain reasonable fits of the experimental spectra are outlined in Table IIB. The numerical values of $g_\parallel$, $g_\perp$, $A_\parallel$, and $A_\perp$shown in Table IIA are within the range usually found for molybdenum(V) compounds.[34]

TABLE IIA
Spin Hamiltonian parameters for the molybdenum(V) chelates (at X-band except where indicated). All g-values ± 0.001.

Compound		Hyperfine constants x 10^{-4} cm^{-1}					
		$g_\parallel$	$g_\perp$	$A_\parallel$	$A_\perp$	Cl_A	Cl_A
$MoOL_3$	RT	1.965	1.965	32±1	32±1		
	N_2	1.935	2.000	22±1	48±1		
$MoCl_2L_3$	X-band	1.934	1.963	34±1	82±2	7±0.5	0
	S-band	1.930	1.970	31±1	80±2	7±0.5	0
MoB_2L_3		1.969	1.957	32±1	33±1		

L = anion of salicyl(2-pyridyl)aldazine. B = anilide anion ($C_6H_4NH^-$).

TABLE IIB
Linewidth parameters for the molybdenum(V) chelates (at X-band except where indicated).

Compound		$\sigma_{R\parallel}$	$\sigma_{R\perp}$	$c_{1\parallel}$	$c_{1\perp}$	$c_{2\parallel}$	$c_{2\perp}$
$MoOL_3$	RT	12±1	6±1	0.0002	0.0002	1.2±0.5	1.2±0.5
	N_2	12±1	14±1	0.0002	0.0002	1.2±0.5	1.2±0.5
$MoCl_2L_3$	X-band	9±1	10±1	0.0025	0.0010	4.0±0.5	4.0±0.5
	S-band	4±1	4±1	0.0060	0.0100	3.0±0.5	3.0±0.5
MoB_2L_3		4±1	2±1	0.0003	0.0002	1.4±0.5	1.3±0.5

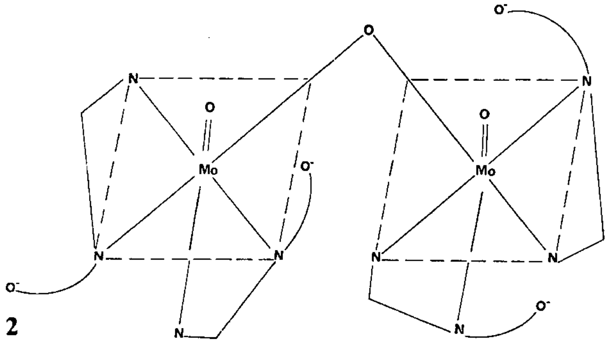
DISCUSSION

Coordination of molybdenum is a variety of oxidation states may involve the formation of oxo species with oxygen atoms bonded to the metal centre or bridging metal centres or the formation of clustered centres[35,36] and multiple bonds between molybdenum atoms.[37,38]. Molybdenum(V) derivatives have a di-μ-oxodioxo (M_2O_4) core when the ligand is terdentate so that six coordination is maintained,[39,41] though the dinuclear metalloporpohyrins containing the unit $M_2O_3^{4+}$ where the O=Mo–O–Mo= group is nearly linear, could be the prototype for compound of this type.[42] The reaction of molybdenum(V) compound with pyrrole-*N*-carbodithioate involves reduction to molybdenum(IV) and coordination.[43] In the present investigation the formation of the coordination compounds by the aldazine ligand may be related to the compounds formed by the starting materials in the solvent used. Thus it has been shown[44] that heating molybdenum hexacarbonyl in dmf leads to a compound isolated as $(N_2O)_3$.MoO.O.MoO.$(H_3O)_2$.dmf, which may be regarded as constituting the core of the compound formed by heating molybdenum hexacarbonyl with sapyal in dmf and formulated as tetreasalicyl(2-pyrid)aldazineato-μ-oxodioxodimolybdenum(V). Again the reaction of molybdenum pentachloride with diphenylsulphoxide leads to formation of complexes formulated as $MoOCl_3.[(C_6H_5)_2SO]_3$,[45] while the reaction of molybdenum pentachloride with pyridine[46] leads to the product represented as $MoOCl_3(NC_5H_5)_3$, although there was no obvious source of oxygen for incorporation into the product. Both of these materials closely resemble the product obtained by reaction of molybdenum pentachloride with sapyal formulated as tris(salicyl-(2-pyridyl)aldazineato)oxomolybdenum(V) where the organic ligand takes the place of the anionic charge of the chlorides and ligand nitrogren atoms those of the coordinating solvent molecules.

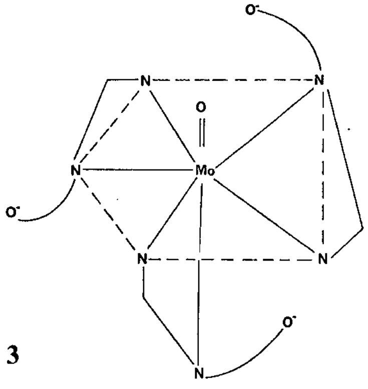
It has been shown that treatment of 5,10,15,20-tetra-μ-tolylporphyrinoxomolybdenum(IV) with gaseous hydrogen chloride leads to the formation of the corresponding dichloromolybdenum(IV) chelate where the formation of the corresponding dichloromolybdenum(IV) chelate where the chloride anions are trans with respect to the porphyrin ring.[47] Similarly, the treatment of tris(salicyl(2-pyridyl)aldazineato)-oxomolybdenum(V), which contains the strong Mo=0 bonding found in the porphyrin derivatives, with thionyl chloride affords dichlorotris(salicyl(2-pyridyl)aldazineato)-molybdenum(V). This reaction is similar to that used to prepare dichlorobis-(salicaldehydehydrazone)vanadium(IV)[48] which like the dichlorotris(salicyl-(2-pyridyl)aldazineato)molybdenum(V) leads to the formation of the corresponding dianilinato compounds after reaction with aniline and elimination of chloride. A replacement of the oxygen in the oxomolybdenum(V) centre be two chloride anions which requires minimal change to the coordination of the molybdenum is a cis arrangement of the chloride anions with one chloride anion in the x-y plane. Since the molybdenum(V) centre possesses a predominantly $4d_{xy}$ ground state a cis-arrangement of the chloride anions would be expected to lead to the observation of an e.s.r. spectrum showing superhyperfine components arising from the molybdenum centre unpaired electron interacting with the nucleus of one in-plane chloride anion. Such an interaction is accounted for by the spin Hamiltonian (*1*) supplemented by expressions for the chloride nuclear interactions. As shown by Figure 5B, the first derivative e.s.r. S-band spectrum recorded at high instrumental gain provides experimental evidence for the occurrence of superfine lines in the 800 Gauss region of the spectrum. A computer simulation of the S-band e.s.r. spectrum shown by curve (B) is shown in Figure 5B using the values of the spin Hamiltonian parameters as follows: $g_\parallel = 1.975$, $g_\perp = 1.913$ $^{Mo}A_\parallel = 81 \times 10^{-4}cm^{-1}$, $^{Mo}A_\perp = 32 \times 10^{-4}cm^{-1}$, $^{Cl}A_\parallel 7.0 \times 10^{-4}cm^{-1}$, $^{Cl}A_\perp = 0.1 \times 10^{-4}$ cm^{-1}.

These parameters give a simulation which is in reasonable overall agreement with the experimental e.s.r. spectrum, but does not reveal computed superhyperfine interactions. However, a resolution enhancement on the 600-800 Gauss region of the computed lineshape shows peaks which are due to computed superhyperfine effects and which bear a reasonable resemblance to the experimental e.s.r. spectrum recorded at high instrumental gain. Thus, the available data points to a cis-disposition of the chloride anions in dichlorotris(salicyl(2-pyridyl)aldazineato)molybdenum(V).

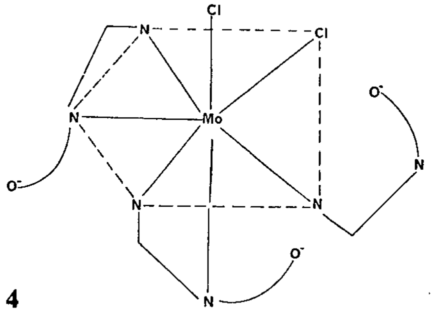
The composition and i.r. magnetic susceptibility and e.s.r. measurements served to characterize the compounds described here. In the absence of X-ray crystallographic evidence, which prove to be elusive due to the difficulties in obtaining suitable crystalline material, it is tentatively proposed that the chelates described possess the structural features shown by the structural formulae 2–4. Six-membered ring formation



2



3



4

may be achieved by bidentate coordination involving the ionized hydroxyl group and nitrogen atom of the aldazine bridge or by the pyridyl nitrogen and the same nitrogen atom of the nitrogen bridge of the ligand shown by Structure 1. Thus, assuming that coordination involves an N_4 donor set with a pendant ionized hydroxyl group, structure 2 represent tetra(salicyl(2-pyridyl)aldazineato)-μ-oxodioxo-dimolybdenum(V). Hexacoordination of the central molybdenum(V) can be preserved by the grouping of three aldazine ligands, provided one of them in unidentate, possibly involving coordination by the ionized hydroxyl group with a pendant pyridyl nitrogen. Alternatively, an expansion of the coordination number would allow bidentate coordination by all three aldazine ligands as shown by structure 3, which represents tris(salicyl(2-pyridyl)-aldazineato)oxomolybdenum(V). A small modification of structure 3 to structure 4 is required to form a cis arrangement of the chloride anions in dichlorotris(salicyl(2-pyridyl)aldazineato)molybdenum(V).

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