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On the Complexes of Tetramethyl- and Tetraethyl-Dithiooxamide with Manganese(II), Iron(II), Cobalt(II), Nickel(II) and Copper(II)

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The complexes of the ligands (L): tetramethyldithiooxamide (Met$_4$D) and tetraethyldithiooxamide (Et$_4$D) with the metals (M): Mn^{II}, Fe^{II}, Co^{II}, Ni^{II}, and Cu^{II}, were investigated in various media; the complexes identified by the Job method have the same metal: ligand ratios and the same electronic spectra (except those of Cu) as the corresponding solids, having the general formulae ML$_3$A$_2$ (A = ClO$_4^-$, FeCl$_4^-$) and CuLX$_2$ (X = Cl, Br); copper perchlorate gives with Met$_4$D only the 1:2 complex Cu(Met$_4$D)$_2$(ClO$_4$)$_2$. I.R. and far I.R. spectra and magnetic susceptibilities, in the range 100-300°K, were also investigated. The octahedral, high-spin, sulphur-coordinated ML$_3$A$_2$ complexes show a greater deformation for the Met$_4$D- than for the Et$_4$D-derivatives. CuLX$_2$ complexes have a cis configuration. All d–d bands were assigned, and the Dq, B, and β values were evaluated; the spectrochemical series Ni > Co > Fe > Cu was obtained. The lower Dq-values for the Et$_4$D-complexes are attributed to a greater steric effect of the Et$_4$D-ligand.

Introduction

In neutral or alkaline media dithiooxamide and partially substituted dithiooxamides with divalent transition ions generally give neutral inner complexes of the type (M . Dithiox)$_n$.[1-3]

We have already demonstrated[4,5] that in strong acid media dithiooxamide and partially substituted dithiooxamides form complexes of the type M^{II}(Dithiox)$_2$(ClO$_4$)$_2$ (M = Ni, Cu) or Co^{III}(Dithiox)$_3$(ClO$_4$)$_3$ without losing protons upon complexation. From strong acid media we also prepared the Et$_4$D-complexes: M^{II}(Et$_4$D)$_3$(ClO$_4$)$_2$ (M = Co, Ni, Cu) and Cu(Et$_4$D)Cl$_2$.[5] These results demonstrated that the removal of amidic hydrogens or their absence in the dithiooxamide are not essential for the complexation.

Recently Hart *et al.*,[6] considering it likely that a tetrasubstituted dithiooxamide could form transition metal complexes more easily in non-coordinating media, prepared the same type of Et$_4$D-complexes from neutral anhydrous media and partially studied them by physical methods.

We had in the meantime extended our investigations to (a) the influence of the medium on the complexation, (b) the type of complexes existing in several solutions, (c) a comparative study of the parent ligand tetramethyldithiooxamide (Met$_4$D) and to (d) a more complete analysis of their spectroscopic and magnetic properties.

Experimental Section

Both tetramethyl- and tetraethyl-dithiooxamide were prepared by the method described by R.N. Hurd *et al.*,[7] for tetraethyl-dithiooxamide. The yield of Met$_4$D (47%) is greater than that obtained with a different method by Klöpping (36%).[8] The acids were used at the concentrations: HAc = glacial, HClO$_4$ = 60%, HCl = 37%, HBr = 48%. All reagents were of the best pure chemical grade.

For the preparation of the complexes, the metal salts and the ligand were separately dissolved in the media summarized in Table I without any dehydration. Only in the two cases indicated were Mn and Fe perchlorates dehydrated with 2,2′-dimethoxypropane (DMP). Most of the solutions were prepared at 70-80°; the crystalline complexes were obtained by mixing the two solutions with the metal: ligand ratio indicated and then cooling. The copper complexes were prepared at room temperature in order to avoid the reduction of copper. No manganese complex of Met$_4$D was obtained in HAc or acetone even when the manganese perchlorate was dehydrated with dimethoxypropane; only in the HAc + HClO$_4$ solution, at high concentration, is an orange complex formed in solution. In all cases, however, only Met$_4$D recrystallizes. The Fe(Me$_4$D)$_3$(ClO$_4$)$_2$ complex was obtained by dehydrating Fe(ClO$_4$)$_2$. 6H$_2$O in DMP at 50°, adding Met$_4$D dissolved in boiling acetone (solvent ratio 1:1.5), evaporating the mixture to 1/3 of the volume, adding 3 volumes of HAc, concentrating to 1/2 volume, and cooling the solution. In the com-

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Table I. Reagents and solvents used; Metal: Ligand ratios (M: L) obtained in solution by the Job method and in the solid complexes.

Metal salt	Ligand	M: L used**	Solvent	M: L (solution) (Job)	M: L (solid)
$Mn(ClO_4)_2 . 6H_2O$	Met_4D	1: 3	HAc or HAc+$HClO_4$ or DMP+Acetone(1: 2) or DMP+HAc(1: 1)	...	(a)
	Et_4D	1: 4.5	HAc	...	$ML_3(ClO_4)_2$
$Fe(ClO_4)_2 . XH_2O$	Met_4D	1: 1	HAc or Acetone	...	(b)
	»	1: 2	DMP+Acetone+HAc	...	$ML_3(ClO_4)_2$*
	Et_4D	1: 2.5	HAc	...	$ML_3(ClO_4)_2$
$FeCl_3 . 6H_2O$	Met_4D	1: 3	HAc	...	$ML_3(FeCl_4)_2$*
	Et_4D	1: 3	HAc	...	$ML_3(FeCl_4)_2$*
$CoAc_2 . 4H_2O$	Met_4D	1: 3	HAc+$HClO_4$(9: 1)	1: 3	$ML_3(ClO_4)_2$*
	Et_4D	1: 3	HAc+$HClO_4$(9: 1)	1: 3	$ML_3(ClO_4)_2$
	»	...	HAc or HAc+HCl(9: 1)	no reaction	...
$NiAc_2 . 4H_2O$	Met_4D	1: 2	HAc+$HClO_4$(9: 1)	1: 3	$ML_3(ClO_4)_2$*
	»	...	HAc+HCl(19: 1)	1: 3	(c)
	Et_4D	1: 2	HAc+$HClO_4$(9: 1)	1: 3	$ML_3(ClO_4)_2$
	»	...	HAc+HCl(19: 1)	1: 3	(c)
$CuAc_2 . H_2O$	Met_4D	1: 3	HAc+$HClO_4$(8: 2)	1: 2	$ML_2(ClO_4)_2$*
	»	1: 2	HAc+HCl(19: 1)	1: 1	$MLCl_2$*
	Et_4D	1: 3	HAc+$HClO_4$(9: 1)	1: 3	$ML_3(ClO_4)_2$
	»	2: 1	HAc+HCl(19: 1)	1: 1	$MLCl_2$*
	»	2: 1	HAc+HBr(9: 1)	...	$MLBr_2$*
	»	...	MetOH or MCS	no reaction	...
$Cu(ClO_4)_2 . 6H_2O$	Met_4D	1: 3	MetOH or MCS	1: 2	$ML_2(ClO_4)_2$*
	Et_4D	...	MetOH	1: 2	...
	»	...	MCS	1: 3	...
	»	1: 3	EtOH or EtOH+$HClO_4$	...	$ML_3(ClO_4)_2$
$CuCl_2 . 2H_2O$	Et_4D	...	MetOH	no reaction	...
	»	1: 1	EtOH	...	$MLCl_2$*
$CuBr_2 . 2H_2O$	Met_4D	1: 1	MetOH+Et_4NBr	...	$MLBr_2$*

(**) For the preparation of the solids. (*) New compounds. (a) Solid Met_4D is obtained. (b) Solid $Met_4D . HClO_4$ is obtained (For $C_6H_6N_2S_2$, S: calcd 23.18%, found 21.87%; N: calcd 10.12%, found 9.87%; Cl: calcd 12.81%, found 12.25%). (c) Solid $NiCl_2$ is obtained.

Table II. Analytical results.

Compound	Color	% Metal Found	% Metal Calcd	% Sulphur Found	% Sulphur Calcd	% Halogen Found	% Halogen Calcd	% Nitrogen Found	% Nitrogen Calcd
$Fe(Met_4D)_3(ClO_4)_2$	Red	7.39	7.13	23.95	24.56	8.77	9.05	10.99	10.73
$Fe(Met_4D)_3(FeCl_4)_2$	Red-brown	16.91	17.10	19.50	19.63	29.07	28.95	8.67	8.58
$Fe(Et_4D)_3(FeCl_4)_2$	Red-brown	13.96	14.59	16.57	16.76	24.79	24.71	7.40	7.32
$Co(Met_4D)_3(ClO_4)_2$	Red-brown	7.60	7.49	23.78	24.45	8.30	9.01	...	...
$Ni(Met_4D)_3(ClO_4)_2$	Red-brown	7.37	7.46	23.19	22.46	8.87	9.02	...	...
$Cu(Met_4D)_2(ClO_4)_2$	Black	10.16	10.33	21.24	20.85	10.69	10.85	...	...
$Cu(Met_4D)Cl_2$	Black	20.41	20.45	21.08	20.64	22.66	22.82	...	...
$Cu(Met_4D)Br_2$	Black	16.21	15.90	16.35	16.05	...	...	...	...
$Cu(Et_4D)Cl_2$	Black	17.18	17.32	17.39	17.48	19.49	19.33	7.77	7.64
$Cu(Et_4D)Br_2$	Black	13.83	13.94	13.50	14.07	...	...	...	...

plexes $Fe . L_3 . (FeCl_4)_2$ the Fe^{II} ion is produced by reduction of Fe^{III} by the dithiooxamides. The complex $Cu(Met_4D)Br_2$ was obtained only from neutral solutions in MetOH with an excess of Et_4NBr, since in HAc+HBr solution copper is partially reduced giving heterogeneous solid products. The compounds were analysed by conventional methods (Table II).

The electronic spectra were recorded from 200 to 2000 mμ with a Beckman DK-1 spectrophotometer. The solids were homogeneously distributed on a filter paper or in nujol mulls. The solution spectra were measured in 1.0, 0.5, and 0.1 cm quartz cells. The metal: ligand ratio for the complexes of Co, Ni, Cu existing in various media was determined by the Job method[9] of continuous variations. I.R. spectra were recorded on KBr pelletts with a Perkin Elmer 521 spectrophotometer from 4000 to 250 cm^{-1} and the far infrared spectra in nujol mulls with a Perkin Elmer FIS3 spectrophotometer from 400 to 60 cm^{-1}. Magnetic susceptibilities were measured on the solid complexes at room temperature or from 100 to 300°K by the Gouy method using a stabilized electromagnet and $HgCo(CNS)_4$[10] or $Nien_3S_2O_3$[11] as calibrants. Molar susceptibilities were corrected using tabulated diamagnetic corrections.[12,13] Four independent measurements were made at room temperature for each com-

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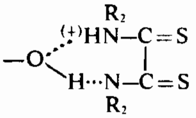
pound, and the mean value of susceptibilities was used to calculate the given B.M. value. The conductivities of the complexes in nitromethane or DMF solution were measured with a WTW conductivity bridge at 25°C.

Results and Discussion

The influence of various media on the formation of complexes in solution or in the solid state is shown in Table I. In solution either the complexes were identified only by their spectra or, as in the cases indicated, their M:L ratio was determined by the Job method.

In none of the systems investigated, except in the case of the formation of the solid $Fe(Met_4D)_3(ClO_4)_2$ complex, does water, even if present in a large extent, seem to be a determining factor against the formation of complexes in solution or in the solid state. Other components of the systems have a greater influence: $CoAc_2 . 4H_2O$ and Et_4D do not react in the anhydrous glacial acetic acid, but they do react when $HClO_4$ is added to the solution; $Ni(ClO_4)_2 . 6H_2O$ or $NiCl_2 .6H_2O$ and Et_4D react in methylcellosolve only when $HClO_4$ or HCl respectively, were added and the solid $Ni(Et_4D)_3(ClO_4)_2$ complex may be obtained; Et_4D does not react with $CuAc_2 . H_2O$ in methanol or methylcellosolve (MCS), but it does react in these solvents with $Cu(ClO_4)_2 . 6H_2O$ giving 1:2 and 1:3 complexes, respectively. Thus the solvent and the anion show a competitive action which is different from metal to metal and in many cases vanishes by adding strong mineral acids.

A protonation of the amidic nitrogen of the dithiooxamide may occur with strong acids. On the one hand, this protonation should reduce the availability for complexation of the nitrogen atom, since it is protonated, and of the sulphur atom, because of a reduction of the resonance form $R_2N^+=C-S^-$; on the other hand, this protonation could break some hydrogen bonds between the hydroxylated solvents and the nitrogen atoms of the molecule, thus making possible a free rotation of its groups, and could favour the formation of bridged hydrogen bonds of the type:



favourable to the complexation of both sulphur atoms.

Halide ions also show a different behaviour toward the various metal ions. In the $FeL_3(FeCl_4)_2$ complexes Fe^{II} is entirely bonded to the dithiooxamide while Fe^{III} is cordinated only by the chloride ions. $CoCl_2$ whether in HAc-HCl solution or in MCS, does not react with Et_4D, yielding only the spectrum of $(CoCl_4)^{2-}$. Ni^{II} reacts in HAc-HCl solution with both Met_4D and Et_4D to form the 1:3 complex, but yields only $NiCl_2$ on evaporation. $CuLX_2$ complexes contain halide ions coordinated to the metal. The competitive action of the halide ions against these dithiooxamides seems therefore to be greater for Fe^{III} and Co^{II}, intermediate for Ni^{II} and Cu^{II} and lower for Fe^{II}.

The complexes identified in solution by the Job method have the same metal: ligand ratio and the same spectra (except those of Cu^{II}) as the solids obtained from the same solutions. Also, the spectra of the 1:3 complexes given by Ni^{II} with both the ligands in HAc+HCl solution are identical to those of the corresponding perchlorate complexes. The form of the Job triangles indicates that these complexes do not appreciably dissociate in solution and do not interact with the solvents in which they can be formed.

The molar conductance values, in nitromethane, of the ML_3A_2 complexes ($A=ClO_4$ or $FeCl_4$), and of $Cu(Met_4D)_2(ClO_4)_2$ ($\lambda_m=138\text{-}184$ cm^2 Ω^{-1} mole^{-1}) fall in the correct range for a 1:2 electrolyte,[14] while the $CuLX_2$ complexes ($\lambda_m=15\text{-}38$ cm^2 Ω^{-1} mole^{-1}) behave like non-electrolites.[15]

Magnetic susceptibilities. The magnetic moments (Table III) of the $Cu(Met_4D)_2(ClO_4)_2$ and $CuLX_2$ complexes at room temperature are all within the range characteristic of a tetragonal coordination. Those of the $ML_3(ClO_4)_2$ complexes and of the FeL_3^{2+} ion in the $FeL_3(FeCl_4)_2$ complexes are within the range expected for spin-free weak-field octahedral complexes.[6,16,18]

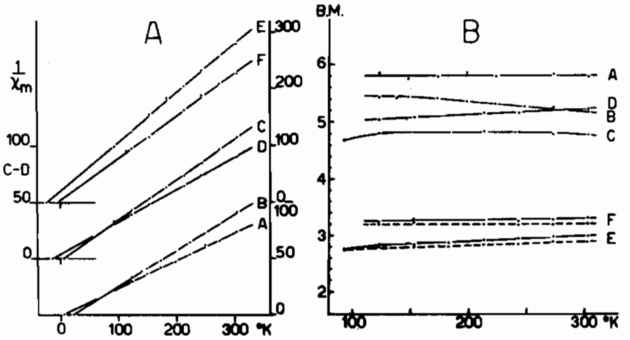


Figure 1. A) Plots of $1/\chi_m$ versus T (°K) and B) Plots of μ_{eff}(B.M.) versus T (°K) for the complexes: (A) $Mn(Et_4D)_3(ClO_4)_2$; (B) $Fc(Et_4D)_3(ClO_4)_2$; (C) $Co(Met_4D)_3(ClO_4)_2$; D) $Co(Et_4D)_3(ClO_4)_2$; (E) $Ni(Met_4D)_3(ClO_4)_2$; (F) $Ni(Et_4D)_3(ClO_4)_2$. Dashed lines correspond to the μ_{eff} values corrected for the temperature independent paramagnetism (t.i.p.).

For all the Mn, Fe, Co, Ni perchlorate complexes the Curie law is obeyed over the whole temperature range 100-300°K. The plots of $1/\chi_m$ versus T (Figure 1A) gave straight lines, where the intercepts θ $\{$in the formula μ $(\theta)=2.83$ $[\chi_m(T-\theta)]^{1/2}\}$ are, for the Met_4D-complexes, Co=+5°, Ni=−24° and for the Et_4D-complexes, Mn=+3°, Fe=+21°, Co=−16°, Ni =−7°. These values of Curie-Weiss temperature are in the range of other values given in the literature.[19,20a] The magnetic moments ($\mu_{eff}=2.83$ $[\chi_m T]^{1/2}$)

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Table III. Infrared bands (cm^{-1}) and magnetic moments (B.M.)

Compound	ν(CN)	ν(CS)	ν(MX)	ν(MS)	def.(MSC)	δ (XMX) δ (MX)	Ligand bands								μ_{eff} B.M.**
Met_4D	1528vs.b	828m	...	...	...	...	520w	434m	373m	310vs	225w	176m	108m	72s	...
$Fe(Met_4D)_3(ClO_4)_2$	1558vs.b	813m	...	334s 267s	182-163vs.b	...	513w	428m	378m	312vs	...	...	115mb	80s	5.25
$Fe(Met_4D)_3(FeCl_4)_2$	1550vs.b	818s	380vs	334m 268w	166s	139s	514w	430m	...	318m	...	...	100w	75s	5.74*
$Co(Met_4D)_3(ClO_4)_2$	1565vs.b	813m	...	339m 265w	167s	...	518w	436m	377m	314m	...	...	80-100mb		4.77
$Ni(Met_4D)_3(ClO_4)_2$	1561vs.b	813m	...	335m 270m	194-175vs.b	...	518w	434m	374m	317s	...	...	107s	89s	2.96
$Cu(Met_4D)_2(ClO_4)_2$	1573vs.b	814m	...	367m 340s 246m	186s	...	508w	431m	377m	310s	224w	...	80-115sb		1.86
$Cu(Met_4D)Cl_2$	1576vs.b	814m	300s.b 290s.b	362m 335sh	152ms	125ms	508w	431m	378w	318s	226w	...	105w	85ms	1.95
$Cu(Met_4D)Br_2$	1560vs.b	808w 822w	236s	360w 340m	155m	110m	503w	423m	378w	317s	...	...	111m	86m	1.76
Et_4D	1499vs.b	870m	...	...	...	...	485w	407s	365m	343m	292ms	197ms	...	77ms	...
$Mn(Et_4D)_3(ClO_4)_2$	1544vs.b	858ms	...	254s	175s	...	498w	407s	374m	348m	298m	...	...	80ms	5.78
$Fe(Et_4D)_3(ClO_4)_2$	1544vs.b	858ms	...	256s	150s	...	498w	406s	374m	348m	301m	...	...	80mb	5.17
$Fe(Et_4D)_3(FeCl_4)_2$	1532vs.b	855ms	378vs	258m	165s	137s	493w	...	...	...	296m	...	...	80mb	5.31*
$Co(Et_4D)_3(ClO_4)_2$	1546vs.b	859ms	...	254s	156s	...	498w	405s	373m	347m	302m	...	...	80mb	5.21
$Ni(Et_4D)_3(ClO_4)_2$	1545vs.b	860ms	...	254s	185s	...	500w	404s	367m	345m	300m	...	...	80mb	3.29
$Cu(Et_4D)_3(ClO_4)_2$	1545vs.b	861ms	...	250s	200w	...	498w	404s	352m	348m	302m	...	...	90mb	1.87
$Cu(Et_4D)Cl_2$	1563vs.b	853ms	309vs.b	320sh	153m	136m	502w	405s	363w	...	290sh	...	...	90mb	1.86
$Cu(Et_4D)Br_2$	1558vs.b	851ms	230s	303s	156m	122m	506w	406s	360w	...	...	...	...	...	1.84

(**) General μ(B.M.) range for high spin octahedral complexes (16): $Mn^{II}=5.8\text{-}6.1$; $Fe^{II}=5.2\text{-}5.8$; $Co^{II}=4.6\text{-}5.4$; $Ni^{II}=2.8\text{-}3.4$; $Cu^{II}=1.7\text{-}2.0$. (*) Values obtained by correcting the susceptibility of the complexes for $\chi_m FeCl_4^- = 14500$ (17).

are rather independent of temperature, in the range explored (Figure 1B), except for the complexes of Fe^{II} and Co^{II}, having T ground terms; for these ions a still more marked temperature dependence is expected at lower temperatures.[20a,b] Their μ(θ) values are much more constant in the temperature range explored. For the nickel complexes the susceptibilities measured at different temperature were corrected for the temperature independent paramagnetism, t.i.p. $= 8N\beta^2/10Dq$,[21] by using the Dq values obtained for the solids (Table IV). The calculated values of the t.i.p. are: 232×10^{-6} and 241×10^{-6} c.g.s. $mole^{-1}$ for the Met_4D- and Et_4D-complex respectively. The new intercepts in the plots of $1/\chi_m$ versus T are $\theta = -16°$ and 0° for the two complexes respectively. The plot of the corresponding new values of μ_{eff} versus T are given for comparison as dashed lines in Figure 1B. The copper perchlorate complexes do not follow the Curie law in the temperature range 100-300°K.

The large difference in the μ values of cobalt Met_4-D- ($\mu_{eff} = 4.77$, $\mu(\theta) = 4.74$ B.M.) and Et_4D-complex ($\mu_{eff} = 5.21$, $\mu(\theta) = 5.34$ B.M.) could be due to the greater deformation from the octahedral symmetry in the Met_4D complex. An axial distortion will produce lower magnetic moments for T terms, since the splittings are of the same order of magnitude as those due to spin-orbit coupling.[21] The low μ value of the (Met_4D, Co) complex cannot be ascribed to spin isomerism since its susceptibility follows the Curie law.

Infrared Spectra (Table III). The very strong band in the region of 1500 cm^{-1} and the medium band at about 800 cm^{-1} in thioamide ligands were considered to correspond predominantly to ν(CN) and ν(CS) frequencies, respectively.[22,23,24] Subsequent to a mesomeric delocalization of the type $\overset{\curvearrowright}{N}-C\overset{\curvearrowright}{=}S$ the ν(CN) and ν(CS) frequencies are increased and decreased, respectively. The formation of metal-sulphur bonds results in an increase of such delocalization.

From the observed values of these frequencies it appears that Met_4 D (ν(CN) = 1528, ν(CS) = 828 cm^{-1}) has a greater electron delocalization from nitrogen to sulphur than Et_4D (ν(CN) = 1499, ν(CS) = 870 cm^{-1}). Met_4D seems, therefore, to be a stronger sulphur-coordinating ligand; it gives the presumably planar four-coordinated complex $Cu(Met_4D)_2(ClO_4)_2$, while Et_4D gives the corresponding octahedral complex $Cu(Et_4D)_3ClO_4)_2$. The increasing of ν(CN), (30-60 cm^{-1}) and the decreasing of ν(CS) (10-20 cm^{-1}) frequencies observed in all the complexes confirm a metal-sulphur coordination.[6]

The difference (16 cm^{-1}) between the ν(CN) frequencies observed for the chloro- and bromo- $CuMet_4DX_2$ complexes could depend on the more electronegative character of chlorine, according to the mesomeric shift $R_2N=C-S-M—X$. The presence of only the ν_3 (1070-1100 cm^{-1}) and ν_4 (611-622 cm^{-1}) bands in all the perchlorate complexes confirms that this ion is not coordinated to the metal.[6,25]

In the infrared spectra, below 500 cm^{-1}, almost all the bands of the ligands are observed in the complex and the very few distinct new bands can be assigned to complex modes.

The strong bands of $M(Et_4D)_3(ClO_4)_2$ and the medium band of the $Fe(Et_4D)_3(FeCl_4)_2$ complexes observed at 258-250 cm^{-1} may be assigned to ν(MS) modes, as were those observed at 227-205 cm^{-1} for the octahedral complexes $NiTu_6(NO_3)_2$ and MTu_4X_2 (M = Mn, Fe, Co, Ni).[26] An increased frequency in this band seems likely as the chelating ligand Et_4D is stronger than the thiourea; moreover, this frequency in octahedral complexes must be lower than those (>300 cm^{-1}) observed in planar or tetrahedral complexes with other stronger ligands.

The two weaker and broader bands, observed at 339-334 and 270-265 cm^{-1} for the $M(Met_4D)_3(ClO_4)_2$, $Fe(Met_4D)_3(FeCl_4)_2$ and $Cu(Met_4D)_2(ClO_4)_2$ complexes, can be assigned to two different ν(MS) modes. In the $Cu(Met_4D)_2(ClO_4)_2$ complex the two ligand mole-

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Table IV. Electronic spectra of Mn^{II}, Fe^{II}, Co^{II}, Ni^{II} and Cu^{II} complexes of Met$_4$D and Et$_4$D *

$\mathrm{Mn(Et_4D)_3(ClO_4)_2}$			$^6A_{1g}\rightarrow{}^4T_{1g}(G)$	$\rightarrow{}^4T_{2g}(G)$			Dq	B	β
	Solid	...		22220 (0.04)	...	...	...	...	...
	Solution	...	18520sh(0.15)		...	...	...	...	...
$\mathrm{Fe(Met_4D)_3(ClO_4)_2}$			$^5T_{2g}\rightarrow{}^5E_g$	$\rightarrow{}^3T_{1g}$		C.T.			
	Solid	6730sh(0.16)	7940 (0.19)	11630 (0.01)	...	20000 (0.78)	790	750	0.81
	Solution	6760sh(12)	7940 (16)	11760 (3)	...	21740 (445)	790	...	...
$\mathrm{Fe(Met_4D)_3(FeCl_4)_2}$									
	Solid	6620sh(0.15)	7840 (0.21)	...	...	20000 (0.79)	780	...	...
	Solution	...	8130 (14)	13700sh(8)	...	21280sh(950)	810	...	...
$\mathrm{Fe(Et_4D)_3(ClO_4)_2}$									
	Solid	6330sh(0.23)	7410 (0.31)	11770 (0.03)	...	18870 (0.94)	740	740	0.81
	Solution	6450sh(13)	7810 (19)	11770 (2)	...	22990sh(1050)	780	...	...
$\mathrm{Fe(Et_4D)_3(FeCl_4)_2}$									
	Solid	6620sh(0.26)	7810 (0.33)	...	...	19610sh(0.58)	780	...	...
	Solution	6450sh(14)	7870 (20)	13610sh(11)	...	21510sh(1067)	790	...	...
$\mathrm{Co(Met_4D)_3(ClO_4)_2}$		$^4T_{1g}\rightarrow{}^4T_{2g}(\nu_1)$	$\rightarrow{}^4A_{2g}(\nu_2)$	$\rightarrow{}^4T_{1g}(P)(\nu_3)$		C.T.			
	Solid	7250 (0.31)	...	15870 (0.56)	16810sh(0.56)	21280sh(0.93)	820	640	0.66
	Solution	7020 (24)	14840sh(67)	15550 (96)	16980sh(83)	22990sh(2000)	790	630	0.65
$\mathrm{Co(Et_4D)_3(ClO_4)_2}$									
	Solid	6850 (0.29)	...	15460 (0.50)	16810sh(0.38)	21510sh(1.10)	770	630	0.65
	Solution	6940 (29)	14710sh(60)	15480 (107)	16670 (77)	22990sh(2550)	790	630	0.65
$\mathrm{Ni(Met_4D)_3(ClO_4)_2}$			$^3A_{2g}\rightarrow{}^3T_{2g}(\nu_1)$		$\rightarrow{}^3T_{1g}(\nu_2)$	C.T.			
	Solid	7910sh(0.20)	9010 (0.27)	...	13790 (0.25)	23810 (0.62)	900	560	0.54
	Solution	7690sh(38)	8770 (54)	12200sh(30)	13510(65)	24390sh(4720)	880	560	0.54
$\mathrm{Ni(Et_4D)_3(ClO_4)_2}$									
	Solid	7140sh(0.28)	8480 (0.39)	...	13070 (0.29)	22990sh(1.18)	850	540	0.52
	Solution	7690sh(45)	8700 (70)	12200sh(40)	13420 (70)	24390 (5500)	870	560	0.54
$\mathrm{Cu(Met_4D)_2(ClO_4)_2}$	**		ν_2	$\nu_1+\nu_3$		C.T.			
	Solid	...	13330sh(0.45)	17240sh(0.69)	...	22220 (1.15)	730	...	...
	Solution	13330 (249) (d-d)		...	...	23870 (11870)	...	...	...
$\mathrm{Cu(Et_4D)_3(ClO_4)_2}$		ν_2	ν_1	ν_3		C.T.			
	Solid	7350 (0.10)	12350 (0.38)	16260 (0.43)	...	22220 (1.27)	710	...	...
	Solution	13330sh(351) (d-d)		...	...	23820 (13770)	...	...	...
$\mathrm{Cu(Met_4D)Cl_2}$		ν_2	ν_1	ν_3	C.T.	C.T.			
	Solid	11490 (0.56)	14710sh(0.56)	18520sh(1.24)	21280 (1.28)	25640 (1.22)	880	...	...
	Solution	13700 (216) (d-d)		...	22880 (2330)	...	...	...	...
$\mathrm{Cu(Met_4D)Br_2}$		ν_2	ν_1	ν_3	C.T.	C.T.			
	Solid	11110 (0.48)	15870 (0.97)	18620 (1.10)	22220 (1.39)	25000sh(1.13)	830	...	...
	Solution	13330 (231) (d-d)		...	20000 (852)	...	...	...	...
$\mathrm{Cu(Et_4D)Cl_2}$			ν_2	$\nu_1+\nu_3$	C.T.	C.T.			
	Solid	...	14490 (0.43)	17860sh(0.64)	21510 (1.06)	24100sh(1.11)	780	...	...
	Solution	13700 (204) (d-d)		...	22940 (2410)	...	...	...	...
$\mathrm{Cu(Et_4D)Br_2}$			ν_2	$\nu_1+\nu_3$	C.T.	C.T.			
	Solid	...	14290 (0.44)	17540sh(0.65)	19610sh(0.76)	23530 (0.90)	770	...	...
	Solution	13330 (349) (d-d)		...	20040 (1230)	...	...	...	...

* Wave numbers, Dq and B values are given in cm^{-1}. The relative absorbances for the solids and the extinctions for the solutions are given in parenthesis. Assignments given for the first also refer to the following complexes of the same metal. Manganese complex was in solution of DMF; the other complexes were in solution of nitromethane. The relative solid state « extinctions » are only valid and comparable for one single compound. ** Copper transitions are $^2B_1\rightarrow{}^2A_1(\nu_1);\rightarrow{}^2B_2(\nu_2);\rightarrow{}^2E(\nu_3)$ (27).

cules should be planarly bonded to the metal, probably with weaker axial interactions with other ligand groups of other molecules. It seems likely that such a tetragonal distortion also takes place for the M(Met$_4$D)$_3^{2+}$ complexes, thus giving two different M–S distances, those in plane being shorter and corresponding to a higher ν(MS) frequency, while the other two correspond to longer distances and lower frequencies.

The bands observed at 362-303 cm^{-1} for the CuLX$_2$ complexes can also be assigned to ν(MS) and not to ν(MN) modes, since the ν(MN) bands generally appear at lower frequencies. For instance, in the case of CuX$_2$ complexes with substituted pyridines 1–2–4 triazole and phenazine,[27] which have stronger Cu—N bonds, the ν(CuN) frequencies lie in the region of 261-234 cm^{-1}. Moreover, this assignment agrees with a planar coordination of CuLX$_2$ complexes, with shorter Cu–S bonds like those responsible, in the Met$_4$D-complexes, for the ν(MS) bands in the region of 339-334 cm^{-1}. The strong band observed at 200-150 cm^{-1} for all the complexes may be assigned to (MSC) deformation modes, as were those observed for the octahedral thiourea complexes[26] at 180-172 cm^{-1}.

In the spectra of the FeL$_3$(FeCl$_4$)$_2$ complexes the very strong band at 380 cm^{-1} and the band at 138 cm^{-1} are, respectively, the γ(FeCl) and δ(ClFeCl) frequencies observed at 388 and 137 cm^{-1} for the FeCl$_4$ ion.[28] This ion is not coordinated in these complexes.

The strong band of the CuLX$_2$ complexes observed at 310-290 cm^{-1} for the chlorides and at 236-230 cm^{-1} for the bromides may be assigned to ν(CuX) frequencies, as were those observed for the thiosemicarbazide (tsc) complexes Cutsc$_2$X$_2$ (Cl = 312, Br = 251 cm^{-1}) by Campbell *et al.*[29] The splitting of the ν(CuCl) band, clearly observable in the CuMet$_4$DCl$_2$ complex, corresponds to a *cis* configuration.[30] The bands observed at 136-110 cm^{-1} could correspond to δ(CuX) frequencies.[29]

The bands assigned to ν(MS) modes do not show a great variation as a function of the metal ion for the same ligand. Very similar ν(MS) frequencies have been observed for the octahedral ethyl- and methyl-xanthates of metals of the first transition series: Cr(etxn)$_3$ = 361,340 cm^{-1}; Co(etxn)$_3$ = 358,340 cm^{-1}; Cr(mexn)$_3$ = 376,338 cm^{-1}; Co(mexn)$_3$ = 361,342 cm^{-1}. The ν(MS) frequencies of Ni(etxn)$_2$ = 383,351 cm^{-1}; Ni(mexn)$_2$ = 383, 360 cm^{-1} are greater because these complexes are square planar, but of the same

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order of magnitude.[31] Moreover the complexes here described do not show other bands which could be assigned to ν(MS) modes.

Electronic Spectra (Table IV). The spectra of the complex $Mn(Et_4D)_3(ClO_4)_2$ show a well defined band at 22200 cm^{-1} for the solid and at 18520 cm^{-1} for its solution in DMF. As all the spectra of the complexes of this series show a great similarity both in the solid state and in solution the values of Dq (880 cm^{-1}) and B (770 cm^{-1}) may be calculated from the bands of the solid and the solution (Table IV) by using the Tanabe-Sugano[17] d^5 diagram; these values are in good agreement with other values given[17,32] for octahedral Mn-complexes.

The electronic spectra of the $FeL_3(ClO_4)_2$ and $FeL_3(FeCl_4)_2$ complexes are very similar, both in the solid state and in nitromethane solution. Assuming an octahedral symmetry, the two bands in the region of 6000-8000 cm^{-1} may be considered[17,33] to be two components of the same band with a doublet structure, representing transitions from the $^5T_{2g}$ to the ^5E_g state, the degeneracy of which has been lifted by the Jahn-Teller effect. The very weak band in the region 11000-14000 cm^{-1} may, on the basis of the d^6-Tanabe-Sugano diagram, be assigned to the forbidden $^5T_{2g} \rightarrow {}^3T_{1g}$ transition. Since in the $FeL_3(FeCl_4)_2$ complexes the band at 13500 cm^{-1} is disturbed by those of the $FeCl_4^-$ ion, the values of B were calculated, from the d^6-Tanabe-Sugano diagram, only for the two perchlorate complexes. The Dq values were obtained for all the Fe-complexes from $10\,Dq = \nu(^5T_{2g} \rightarrow {}^5E_g)$. The bands at 19000-23000 cm^{-1} in the $FeL_3(FeCl_4)_2$ complexes can be attributed to C.T. bands or to the $FeCl_4^-$ ion bands.[33]

In nitromethane solution both the $CoL_3(ClO_4)_2$ complexes show four bands in the region of the d–d transitions. Only the ν_1 and the more intense[33,34] ν_3 bands were already assigned for the Et_4D complex.[6] The weaker shoulder at 14840 for the Met_4D-and at 14710 cm^{-1} for the Et_4D-complex, not given by Hart *et al.*[6] but easily distinguishable in the nitromethane solution spectra, may be assigned to the ν_2 transition, owing to the fact that this band is generally very weak[33]. The frequencies calculated for ν_2 transitions (14910 and 14730 cm^{-1}) from the ratio ν_3/ν_1, using the method described by Lever,[35] correspond satisfactorily to the observed values. The weak band observed at 16600-17000 cm^{-1} in both solids and solutions may be assigned to spin-forbidden transitions as pointed out by Lever.[33] The values of Dq and B were calculated by Lever's method.[35]

Both the $NiL_3(ClO_4)_2$ complexes, in nitromethane solution, show only the ν_1 and ν_2 bands. The shoulder observed in both nitromethane solutions at 7690 cm^{-1} cannot be considered to be suggestive of dissociation, as was indicated by Hart *et al.*[6] for the Et_4D complex in nitromethane solution, because it also appears in the solid spectra of both complexes. The ν_2 band also has a shoulder at 12200 cm^{-1}, observable in both solutions. The splitting of ν_1 and ν_2 bands is not due to infrared overtone of the ligands, as shown by their spectra, and may be explained as being due to a distortion of the octahedral symmetry, as was observed in $Nipy_4Cl_2$ ($\nu_1 = 8500$ and 10900 cm^{-1}; $\nu_2 = 14300$ and 15800 cm^{-1}).[36] The ν_3 bands ($^3A_{2g} \rightarrow {}^3T_{1g}(P)$), calculated by Lever's method[35] at 21220 cm^{-1} for the Met_4D- and at 21060 cm^{-1} for the Et_4D-complex, are masked by the very intense C.T. band at 23000-24000 cm^{-1}. With the same method the Dq, B were calculated. The low values of Dq and B for Co and Ni complexes may be attributed to sulphur coordination.[6,33,37]

The d–d bands observed in the copper complexes may be tentatively assigned by using the energy level diagram given by Billing and Underhill,[27] which relates the reciprocal position of the ν_1, ν_2, and ν_3 bands to the increasing tetragonal distortion of the copper complexes. The relative position of the three observed bands seems to indicate that the methyl derivative has a tetragonal distortion greater than that of the ethylderivative. From the band assignment given in Table IV an approximate value of Dq may be obtained from the expression $10\,Dq = \nu_3 - \frac{1}{2}\nu_1 - 1/3(\nu_3 - \nu_2)$. The Dq values of 732 and 712 cm^{-1} obtained for the two perchlorate complexes are in good agreement with the values of 700-770 cm^{-1} found by Billing and Underhill[27] for CuX_2 complexes with substituted pyridines. The Dq values calculated for the $CuLX_2$ complexes seem to be reasonable, because for both methyl- and ethyl-derivatives they are greater for the chloride than for the bromide, and because, as for all the other complexes, the Dq values are greater for the Met_4D- than for the Et_4D-complexes.

In the nitromethane solutions all the copper complexes give only one band which has a higher frequency for the chloride (13700 cm^{-1}) than for the bromide and perchlorate derivatives (13330 cm^{-1}). This constancy of values, irrespective of the nature of the ligand and of the composition of the solution, seems to indicate the formation of similarly coordinated species in solution.

Conclusions

The following spectrochemical series results from the Dq values obtained for the perchlorate complexes of Fe, Co, Ni, Cu.

		Ni>	Co>	Fe>	Cu	
(Met_4D)	solid	900	820	790	730	Dq (cm^{-1})
	solution	880	790	790	...	»
(Et_4D)	solid	850	770	740	710	»
	solution	870	790	780	...	»

The values of the Racah parameter B_o, given by Cole and Garrett,[38] were used to calculate $\beta = \frac{B}{B_o}$. From the β values the following nephelauxetic series may be obtained:

	Co >	Ni	
(Met_4D)	0.66	0.54	β
(Et_4D)	0.65	0.52	»

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Neither series corresponds to those reported by Figgis.[17]

The value $\beta = 0.81$ for Fe was calculated from spin-forbidden bands, while the other β values (Co, Ni) were obtained from spin-allowed bands, and therefore is not included.

From all observed Dq values the spectrochemical sequence of the ligands proves to be $Met_4D > Et_4D$, while their nephelauxetic position is practically the same. It has been observed by Pavchovic and Meek[39] that the nephelauxetic effect seems to be less sensitive to steric effects than the Dq values. Although the ethyl group is more electron-releasing than the methyl group, this effect is often offset by its larger steric requirements. As pointed out by Nykerk, Elman and Smith,[40] in six-coordinated complexes steric effects predominate in determining the metal ligand interaction.

Ligand to metal and metal to ligand charge transfer may be distinguished by the way in which their energy changes when the metal or the ligands is altered.[33] The observed charge-transfer bands for the solid perchlorate complexes decrease in energy in the sequence:

	Ni	>	Co	>	Fe	
(Met_4D)	23.800		21.300		20.000	cm^{-1}
(Et_4D)	23.000		21.500		18.900	

According to Lever,[33] this sequence should correspond to a metal to ligand charge-transfer band. Since the M→L C.T. band for Cu^{II} should have higher energy than Ni^{II} in that sequence it may be that this Cu^{II} band appears at frequencies greater than 24000 cm^{-1} and is masked by halogen→metal or L→L* transition bands. The Cu^{II} band at 20000-23000 cm^{-1} could, in this case, be interpreted as an L→M C.T. band, owing to the greater reductibility of Cu^{II} with sulphur compounds.

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