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High-Spin Five-Coordinate $[ML_5]^{2+}$ and $[ML_4(ClO_4)]^+$ Complexes with Trimethylphosphine Oxide and Trimethylarsine Oxide

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The preparation of high-spin five-coordinate complexes of composition, $[ML_5]^{2+}$ and $[ML_4(ClO_4)]^{2+}$, L=Me_3PO and Me_3AsO, is reported for a number of first row divalent transition metal ions. The spectra of these compounds can best be correlated with a basically square pyramidal structure. Five-coordination is considered to be stabilised by the packing requirements of these ligands. The particular sensitivity to moisture of the Me_3PO complexes is related to the attainment of six-fold coordination with the formation of $[ML_5(H_2O)]^{2+}$ complexes. Low-frequency infrared data are presented and comparisons made with data for related $[ML_4]^{2+}$ tetrahedral complexes.

Introduction

Although examples of five-coordinate bivalent first row transition metal complexes with polydentate ligands are becoming increasingly common, examples of corresponding complexes with monodentate ligands are few and ML_5 complexes with identical ligands are limited to low-spin species such as $Fe(CO)_5$, $[Ni(CN)_5]^{3-}$ and $[Co(CNCH_3)_5]^+$.[1] We have now prepared a range of high-spin $[ML_5]^{2+}$ complexes with the oxo ligands Me_3PO and Me_3AsO (Table I) and a related series of $[ML_4(ClO_4)]^+$ complexes has also been isolated. All of these complexes are readily obtained under anhydrous conditions—$[ML_5]^{2+}$ using a slight excess of the ligand in acetone while $[ML_4(ClO_4)]^+$ are favoured using a deficiency of ligand and ethanol as solvent. The compounds are generally sensitive to atmospheric moisture though with the $[ML_5]^{2+}$ series the trimethylarsine oxide derivatives are less sensitive than their phosphine oxide analogues. The complexes are all decomposed in solution except for $[Ni(Me_3AsO)_5](ClO_4)_2$ which is relatively stable in acetone. The range of five-coordinate complexes of both types extends from manganese to nickel, with the exception that it has not been possible to obtain the $[FeL_5]^{2+}$ and $[CoL_4(ClO_4)]^+$ compounds (Table I). An X-ray structure analysis of $[Ni(Me_3AsO)_5](ClO_4)_2$ is now being attempted in these laboratories.

Results and Discussion

X-ray powder photographs show that all the $[ML_5](ClO_4)_2$ complexes have the same structure, and electronic reflectance spectra for the cobalt and nickel compounds (Table II) indicate a structure approximating that of a square pyramid. The spectra more closely resemble those obtained for other complexes known from X-ray analysis to have this configuration rather than those from complexes of the trigonal bipyramidal class.[2] Representative spectra from the present series are shown with those of $[Co(Me_5dien)Cl_2]$ and $[Ni(Me_5dien)Cl_2]$[3] in Figure 1. The same basic structure is also suggested for the $[ML_4(ClO_4)]^+$ complexes. The spectra of $[Ni(Me_3AsO)_4(ClO_4)]ClO_4$ and $[Ni(Me_3AsO)_4(ClO_4)]BPh_4$ are very similar to that of $[Ni(Me_3AsO)_5](ClO_4)_2$ (Figure 1) and the iron(II) and manganese(II) $ML_4(ClO_4)_2$ compounds (L=Me_3PO and Me_3AsO) can reliably be formulated in the same manner in view of the close similarity of their X-ray powder photographs to that of $[Ni(Me_3AsO)_4(ClO_4)]ClO_4$. The isolation of the tetraphenylboron complexes, for Fe^{II} and Ni^{II} (Table I) in itself also provides

Table I. Five-Coordinate Complexes from Trimethylphosphine Oxide and Trimethylarsine Oxide

$[Mn(Me_3PO)_5](ClO_4)_2$	[a]	$[Co(Me_3PO)_5](ClO_4)_2$ [b]	$[Ni(Me_3PO)_5](ClO_4)_2$	[a]
$[Mn(Me_3AsO)_5](ClO_4)_2$	[a]	$[Co(Me_3AsO)_5](ClO_4)_2$ [b]	$[Ni(Me_3AsO)_5](ClO_4)_2$ [c]	[a]
	$[Fe(Me_3PO)_4(ClO_4)]ClO_4$	[a]		$[Cu(Me_3PO)_4(ClO_4)]ClO_4$
$[Mn(Me_3AsO)_4(ClO_4)]ClO_4$	$[Fe(Me_3AsO)_4(ClO_4)]ClO_4$	[a]	$[Ni(Me_3AsO)_4(ClO_4)]ClO_4$	$[Cu(Me_3AsO)_4(ClO_4)]ClO_4$ [d]
	$[Fe(Me_3AsO)_4(ClO_4)]BPh_4$		$[Ni(Me_3AsO)_4(ClO_4)]BPh_4$	

[a] Complexes could not be isolated. [b] With these ligands cobalt also forms tetrahedral complexes $[CoL_4](ClO_4)_2$, isomorphous with their zinc analogues (refs. 5 and 6). [c] Corresponding compounds $[Ni(Me_3AsO)_5]X_2$, with X=NO_3^- or BF_4^- were obtained. [d] A tetraphenylborate analogue could not be prepared.

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Table II. Band Maxima (kK) for Diffuse Reflectance Spectra

$[Fe(Me_3PO)_4(ClO_4)]ClO_4$	9.8 w br
$[Fe(Me_3AsO)_4(ClO_4)]ClO_4$	11.0 w br
$[Co(Me_3PO)_5](ClO_4)_2$	20.2 sh, 19.65 s, 18.4 s, 16.9 s, 10.5 m, 7.6 m br
$[Co(Me_3AsO)_5](ClO_4)_2$	19.6 s, 18.7 s, 17.0 s, 11.0 m, 8.5 m br
$[Ni(Me_3PO)_5](ClO_4)_2$	22.2 s, 19.4 sh, 17.3 w, 13.95 w, 10.8 m, 8.3 w br ^{a}
$[Ni(Me_3AsO)_5](ClO_4)_2$	22.2 s, 19.2 m, 17.15 w, 13.6 sh, 11.3 m, 8.6 w br ^{a}
	22.2 (120), 19.2 sh, 17.2 sh, 13.6 (5), 11.3 (20), 8.6 sh ^{b}
$[Ni(Me_3AsO)_5](BF_4)_2$	22.1 s, 19.1 m, 17.15 w, 13.5 sh, 11.3 m, 8.7 w br ^{a}
$[Ni(Me_3AsO)_5](NO_3)_2$	22.2 s, 19.1 m, 17.15 w, 13.55 sh, 11.3 m, 8.6 w br ^{a}
$[Ni(Me_3AsO)_4(ClO_4)]ClO_4$	22.3 s, 19.4 m, 17.2 sh, 15.6 w, 13.5 sh, 11.2 m, 8.6 w br ^{a}
$[Ni(Me_3AsO)_4(ClO_4)](BPh_4)$	22.3 s, 19.4 sh, 17.2 sh, 15.4 w, 13.4 sh, 11.3 m, 8.6 w br ^{a}
$[Cu(Me_3PO)_4(ClO_4)]ClO_4$	16.7 sh, 11.4 m br
$[Cu(Me_3AsO)_4(ClO_4)]ClO_4$	17.0 sh, 14.5 m br
$[Co(Me_3PO)_5(H_2O)](ClO_4)_2$ ^{c}	20.5 sh, 18.45 m, 13.25 w, 8.5 mw, 7.0 m
$[Co(Me_3PO)_4(H_2O)_2](ClO_4)_2$ ^{c}	20.5 sh, 18.45 m, 13.25 w, 10.0 mw, 8.5 mw, 7.0 mw
$[Ni(Me_3PO)_5(H_2O)](ClO_4)_2$ ^{c}	23.2 m, 14.5 sh, 12.2 m, 7.1 m br
$[Ni(Me_3AsO)_4(NO_3)](BPh_4)$ ^{c}	23.4 m, 13.7 sh, 12.3 m, 7.2 w br

[a] For the five-coordinate nickel complexes there is also evidence of a band with maximum below 5kK. [b] Acetone solution (2.16×10^{-3} *M*), with molar extinction coefficients in parentheses. [c] Octahedral complex.

evidence for this formulation. The copper compounds of composition $CuL_4(ClO_4)_2$, $L = Me_3PO$ and Me_3AsO, give similar powder photographs to those from the other $[ML_4(ClO_4)]^+$ complexes (though with several additional lines in the case of the arsine oxide complex). They are therefore considered to have essentially the same configuration. A square planar structure has previously been assigned[4] to the complex of composition $Cu(Me_3PO)_4(ClO_4)_2$. With zinc only $[ZnL_4]^{2+}$ complexes, isomorphous with their tetrahedral cobalt analogues, could be isolated.[5,6] However, a lowering of the ν(M–O) mode from 430 cm^{-1} to about 400 cm^{-1} when excess ligand was added to a nitromethane solution of $[Zn(Me_3AsO)_4](ClO_4)_2$ may be taken as indication of the development of higher coordination (see below). It is of interest that crystalline five-coordinate $[ZnL_5]^{2+}$ and $[ZnL_4(ClO_4)]^+$ complexes can be obtained with the related diphenylmethylphosphine oxide and arsine oxide.[6,7]

Somewhat surprisingly the ν(Cl–O) absorptions do not give definite indication of perchlorate coordination for the $[ML_4(ClO_4)]^+$ complexes. There is no conspicuous splitting of the ν(Cl–O) band as is usually observed for anion coordination[8] although a shoulder appears at 1065 cm^{-1} for the BPh_4^- complexes. However, it is recognised that this is not a reliable criterion and anion coordination (ClO_4^- and BF_4^-) has been established for a number of compounds which do not show splitting of anion absorptions.[9,10,11] On the other hand correlations of the degree of splitting and the strength of coordination have been made[9] and on this basis the lack of splitting for these complexes indicates a weak association of perchlorate.

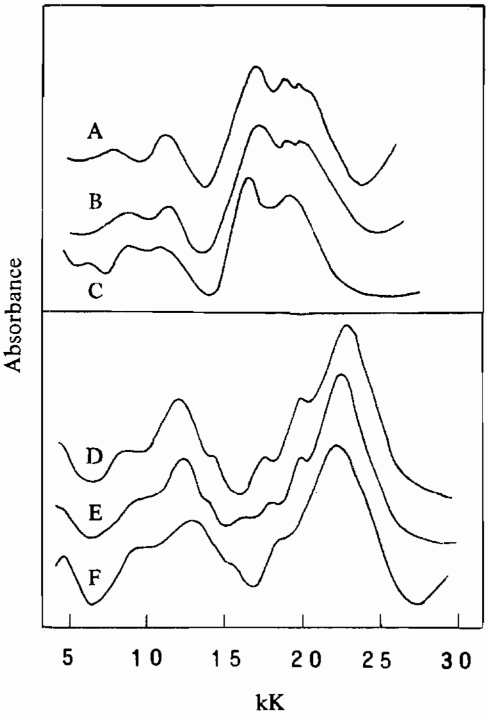

Figure 1. Electronic Reflectance Spectra: A, $[Co(Me_3PO)_5](ClO_4)_2$; B, $[Co(Me_3AsO)_5](ClO_4)_2$; C, $[Co(Me_5dien)Cl_2]$; D, $[Ni(Me_3AsO)_5](ClO_4)_2$; E, $[Ni(Me_3AsO)_4(ClO_4)]ClO_4$; F, $[Ni(Me_5dien)Cl_2]$.

With the ligands Ph_2MePO and Ph_2MeAsO complexes of the $[ML_4(ClO_4)]^+$ type (M=Mn, Co, Ni, and Zn) do by contrast show considerable splitting of ν(Cl–O) absorptions,[6,7] indicating stronger perchlorate coordination. From a steric point of view it is unlikely that the diphenylmethyl substituents provide a significantly more favourable arrangement for perchlorate coordination than the trimethyl analogues although the smaller steric requirement of trigonal than tetrahedral carbon may be helpful. In fact a limited examination has shown that with Ph_2MePO, $[ML_5]^{2+}$ compounds of iron, cobalt, nickel, and zinc can also be isolated[6] and this shows that the diphenylmethyl ligands are certainly not less favourable for the formation of five-coordinate complexes.

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Table III. Infrared Spectra (cm^{-1})

Compound	ν(P—O), ν(As—O)	ν(M—O)	Other bands (500-200 cm^{-1})
Me_3PO	1166 s	—	375 sh, 365 m, 315 w, 242 vw
$[Mn(Me_3PO)_5](ClO_4)_2$	1146 s, 1135 s	404 m, 400 m	363 m, 320 w, 255 vw
$[Fe(Me_3PO)_4(ClO_4)]ClO_4$	[a]	423 m	366 m, 265 vw, 242 vw
$[Co(Me_3PO)_5](ClO_4)_2$	1145 s	409 m	365 m, 324 w, 258 vw
$[Ni(Me_3PO)_5](ClO_4)_2$	1141 s, 1132 s	420 m	366 m, 324 w, 258 vw
$[Cu(Me_3PO)_4(ClO_4)]ClO_4$	1120 sh	466 m, 454 m	363 m, 338 w, 261 vw
Me_3AsO	870 s	—	266 m
$[Mn(Me_3AsO)_5](ClO_4)_2$	869 s, 863 s	366 m	284 m
$[Mn(Me_3AsO)_4(ClO_4)]ClO_4$	868 s, 855 sh	368 m, br	306 w, 279 m
$[Fe(Me_3AsO)_4(ClO_4)]ClO_4$	861 s	402 m, br	307 m, 283 sh
$[Fe(Me_3AsO)_4(ClO_4)]BPh_4$	855 s	415 m, br	468 w,[b] 300 m, 279 m
$[Co(Me_3AsO)_5](ClO_4)_2$	867 s, 857 sh	407 m, 391 m	285 m
$[Ni(Me_3AsO)_5](ClO_4)_2$	866 s	407 m	290 m
$[Ni(Me_3AsO)_5](BF_4)_2$	866 s	407 m	291 m, 278 sh
$[Ni(Me_3AsO)_5](NO_3)_2$	866 s	408 m	290 m, 279 sh
$[Ni(Me_3AsO)_4(ClO_4)]ClO_4$	866 s	407 m, br	283 m
$[Ni(Me_3AsO)_4(ClO_4)]BPh_4$	864 s	410 m, br	468 w,[b] 293 m, 280 sh
$[Cu(Me_3AsO)_4(ClO_4)]ClO_4$	854 m, 833 s [c]	470 m	288 m, 268 sh

[a] Obscured by perchlorate band. [b] BPh_4^- band. [c] Contains methyl rocking mode normally observed at 840 cm^{-1}.

The infrared data are presented in Table III. The ν(P—O) and ν(As—O) modes are affected by coordination in the usual manner. The simplicity of the ligand spectra enabled additional bands for the complexes to be assigned as ν(M—O) modes. Only one such band was usually observed for each complex, although three would be expected for square pyramidal ML_5 structures[12] and an identifiable perchlorate ν(M—O) absorption for the $[ML_4(ClO_4)]^+$ complexes might be anticipated. It is significant that lower ν(M—O) values arise from the five-coordinate cobalt complexes as compared with values for the four-coordinate tetrahedral complexes (460, 448 cm^{-1} for $[Co(Me_3PO)_4](ClO_4)_2$; 442, 428 cm^{-1} for $[Co(Me_3AsO)_4](ClO_4)_2$).[5,13] Assuming the generality of this effect it may be used to distinguish between four- and five-fold coordination as mentioned above for zinc complexes. As has been generally observed for other oxo complexes low ν(M—O) values are found for manganese complexes and high values for copper.[14]

The magnetic moments show that all the complexes are of the high-spin type, the values lying within the ranges observed for other high-spin five-coordinate complexes. Those found for the nickel compounds (3.56-3.63 B.M.) are such as to exclude the possibility of octahedral coordination (range 2.9-3.3 B.M.).

From the wide range of complexes with oxo ligands now available it appears that the $[ML_5]^{2+}$ compounds are the first examples of five-fold coordination with identical oxo ligands. Edwards *et al.*[15] have studied oxo complexes in relation to coordination number and although a complex of composition $Cd(Me_2SO)_5(ClO_4)_2$ is reported no evidence for five-coordination, beyond the elemental analysis, is presented. The trimethylphosphine and arsine oxides are apparently sufficiently small to enable five-fold coordination but bulky enough to prevent six-coordination as found for other «smaller» oxo ligands such as pyridine-N-oxide[16] and dimethylsulphoxide.[17] This is further indicated by the fact that the spectrum of the one complex which was sufficiently stable to study in solution, $[Ni(Me_3AsO)_5](ClO_4)_2$, was unaffected by excess ligand.

While ML_6 complexes could not be obtained with the Me_3XO ligands (X = P or As) an isomorphous series of six-coordinate $[M(Me_3PO)_5(H_2O)](ClO_4)_2$ derivatives (M = Mn, Co, and Ni) was obtained upon exposure of the $[M(Me_3PO)_5](ClO_4)_2$ compounds to atmospheric moisture, indicating that a sufficiently small ligand can increase the coordination to six. That only the Me_3PO complexes show this behaviour may be associated with the lower steric requirement of the phosphine oxide than the arsine oxide, although a higher electrophilicity of the metal atom (due to a smaller net charge transfer by the weaker Me_3PO donor[13]) may be an important factor. The tetrahedral complex $[Co(Me_3PO)_4](ClO_4)_2$ is also much more sensitive to moisture than its arsine oxide analogue, giving a six-coordinate dihydrate $[Co(Me_3PO)_4(H_2O)_2](ClO_4)_2$ (Table II). It is of interest however that trimethylarsine oxide in association with a small bidentate nitrate ligand does form a six-coordinate complex $[Ni(Me_3AsO)_4(NO_3)]BPh_4$. The electronic spectrum of this compound (Table II), characteristic of an octahedral complex, excludes the possibility of five-coordination (as found for the perchlorate $[Ni(Me_3AsO)_4ClO_4]BPh_4$) and establishes the bidentate role of the nitrate.

In view of its similar shape to the phosphine and arsine oxides trimethylamine oxide might also be expected to form five-coordinate complexes, but isolation of such compounds did not prove possible. The amine oxide usually gives four-coordinate complexes, but its ability to develop six-coordination, as in $[Cr(Me_3NO)_6](ClO_4)_3$,[18] indicates that an

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$[M(Me_3NO)_5]$ species might not be stabilised by steric interactions as was postulated for the trimethylphosphine and arsine oxide ligands. Although the addition of excess ligand to $[Co(Me_3NO)_4]^{2+}$ and $[Ni(Me_3NO)_4]^{2+}$ in nitromethane produces spectral changes indicating the attainment of a higher coordination than four, crystalline complexes could not be isolated from these solutions. Likewise it was not possible to isolate five-coordinate complexes with hexamethylphosphoramide which, like Me_3NO, produces both four- and six-coordinate compounds.[19]

Experimental Section

Preparation of Complexes. The $[ML_5]X_2$ complexes ($L = Me_3PO$, Me_3AsO; $X = ClO_4^-$, BF_4^-, NO_3^-) were obtained from reaction of the metal salt in anhydrous acetone with a slight excess of ligand. In the preparation of $[Ni(Me_3AsO)_5](ClO_4)_2$, for example, hydrated nickel perchlorate (0.22 g) in hot acetone (10 ml) containing ethyl orthoformate (1 ml) as dehydrating agent was added to the arsine oxide (0.42 g) in the same solvent. Orange crystals separated on cooling. As standard procedure the product was washed successively with solvent and ether, and dried under high vacuum. The $[ML_4(ClO_4)]ClO_4$ derivatives, on the other hand, separated from hot anhydrous ethanol (with ethyl orthoformate) following the addition of ligand (4 moles) to the metal perchlorate (1 mole). All samples were handled in a dry box, though this was not strictly necessary for the $[M(Me_3AsO)_5]^{2+}$ compounds whose reaction with atmospheric moisture was slow. Infrared spectra were examined routinely to confirm absence of water. It was checked by direct weighing that uptake of water by $[Co(Me_3PO)_5](ClO_4)_2$ and $[Co(Me_3PO)_4](ClO_4)_2$ corresponded to 1 and 2 moles respectively. The arsine oxide complexes of manganese are susceptible to atmospheric oxidation. They were therefore prepared and stored under nitrogen. Attempts to prepare $[ML_5]^{2+}$ complexes of iron, copper, and zinc using different solvents, temperatures, and conditions of crystallisation were unsuccessful.

In the preparation of $[Ni(Me_3AsO)_4(ClO_4)]BPh_4$ sodium tetraphenylborate (0.149 g) and arsine oxide (0.426 g) in hot anhydrous ethanol (15 ml) were added to hydrated nickel perchlorate (0.164 g) in hot ethanol (10 ml) with ethyl orthoformate. For the iron compound excess sodium tetraphenylborate was required.

Analyses are given in Table IV. With $[Ni(Me_3PO)_5](ClO_4)_2$ which was particularly sensitive to uptake of moisture figures are given for the derived monohydrate.

The manganese compounds from both the phosphine and arsine oxides are white, the iron are buff, cobalt mauve, nickel $[NiL_5]^{2+}$ orange, nickel $[NiL_4(ClO_4)]^{2+}$ yellow, and copper pale blue. When dissolved in nitromethane the cobalt complexes $[CoL_5]^{2+}$ reverted to blue $[CoL_4]^{2+}$ derivatives. The analogous nickel compounds are more resistant to decomposition. The absorption spectrum of $[Ni(Me_3AsO)_5](ClO_4)_2$ in acetone, though showing some deviation from Beer's law, is essentially the same as that of the solid. The compound is a 2:1 electrolyte in this solvent. In nitromethane the compound shows spectral changes probably associated with partial development of octahedral coordination. The $[NiL_4(ClO_4)]^+$ compounds suffer more complete decomposition in solution and behave as 2:1 electrolytes.

Table IV. Analyses

Compound	Found % C	Found % H	Calculated % C	Calculated % H
$[Mn(Me_3PO)_5](ClO_4)_2$	25.0	6.2	25.2	6.3
$[Co(Me_3PO)_5](ClO_4)_2$	25.1	6.1	25.1	6.3
$[Ni(Me_3PO)_5(H_2O)](ClO_4)_2$	24.3	6.4	24.4	6.4
$[Fe(Me_3PO)_4(ClO_4)]ClO_4$	22.2	5.8	23.1	5.8
$[Cu(Me_3PO)_4(ClO_4)]ClO_4$	23.0	6.1	22.8	5.7
$[Mn(Me_3AsO)_5](ClO_4)_2$	19.3	4.8	19.3	4.8
$[Mn(Me_3AsO)_4(ClO_4)]ClO_4$	18.2	4.6	18.1	4.5
$[Fe(Me_3AsO)_4(ClO_4)]ClO_4$ [a]	17.5	4.6	18.0	4.5
$[Co(Me_3AsO)_5](ClO_4)_2$ [b]	19.4	4.9	19.2	4.8
$[Ni(Me_3AsO)_5](ClO_4)_2$ [c]	19.15	4.8	19.2	4.8
$[Ni(Me_3AsO)_5](BF_4)_2$	20.0	5.4	19.7	4.9
$[Ni(Me_3AsO)_5](NO_3)_2$	20.5	5.8	20.9	5.2
$[Ni(Me_3AsO)_4(ClO_4)]ClO_4$ [d]	18.0	4.6	18.0	4.5
$[Ni(Me_3AsO)_4(ClO_4)]BPh_4$	43.0	5.6	42.3	5.5
$[Ni(Me_3AsO)_4(NO_3)]BPh_4$	45.0	5.8	43.9	5.7
$[Cu(Me_3AsO)_4(ClO_4)]ClO_4$	17.9	4.7	17.9	4.5

[a] Fe, 7.3%; (calcd. 7.0). [b] Co, 5.9 (6.3). [c] Ni, 6.3 (6.3). [d] Ni, 7.6 (7.3).

Physical Measurements. Electronic spectra were run over the range 5-30 kK using a Beckman DK2A spectrophotometer with standard reflectance attachment for solid samples. Infrared spectra were obtained from nujol mulls using Perkin Elmer 337 (to 400 cm^{-1}) and Grubb Parsons DM4 (500-200 cm^{-1}) spectrophotometers. Calibrations were made with polystyrene and water vapour respectively.

Electrolytic conductivities were measured in anhydrous nitromethane at concentrations close to 10^{-3} *M*. Magnetic susceptibility measurements were made by the Gouy method at room temperature, using $[Nien_3]S_2O_3$ as calibrant.[20] Diamagnetic corrections from Pascal constants were made. Values (B.M.) obtained for trimethylarsine oxide complexes were: $[MnL_5](ClO_4)_2$, 6.05; $[FeL_4(ClO_4)]ClO_4$, 4.94; $[CoL_5](ClO_4)_2$, 4.80; $[NiL_5](ClO_4)_2$, 3.62; $[NiL_5](BF_4)_2$, 3.63; $[NiL_4(ClO_4)]ClO_4$, 3.56; $[CuL_4(ClO_4)]ClO_4$, 2.02.

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