Metal Complexes of Some Hybrid Bidentate Ligands Containing Tertiary Arsine and Primary Amine Donor Groups. II. Compounds of Nickel and Copper

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Some first transition series metal complexes of the three new tertiary arsine-primary amine bidentate ligands, o-dimethylarsinoaniline (MAA), o-diphenylarsinoaniline (PAA), and 1-amino-2-(diphenylarsino)ethane (APE), have been prepared, and their structures elucidated by physico-chemical studies.

Octahedral high spin complexes of the type Ni(ligand)₂X₂ (where X = halogen, NCS or NO₃) were obtained for all three ligands. Only in the case of the weakly coordinating perchlorate ion were low spin four-coordinate compounds of formula [Ni(ligand)₂](ClO₄)₂ isolated.

The products from the reactions of the ligands with copper(II) salts were (i) complexes of copper-(II); (ii) complexes of copper(I); (iii) complexes of the corresponding arsine oxide with copper(II). In the case of MAA, examples of each of the three types of product were obtained. The complexes, [Cu(ligand)₂](ClO₄)₂ (where ligand = MAA or PAA), which are stable as solids, apear to be the first known examples of complexes of tertiary arsines with copper(II).

Introduction

Previous papers[1,2,3] have described the preparation, and certain of the transition metal complexes, of the «hybrid» bidentate ligands, o-dimethylarsinoaniline (MAA, I), o-diphenylarsinoaniline (PAA, II) and 1-amino-2-diphenylarsinoethane (APE, III). This paper reports work on the nickel and copper compounds of these ligands which contain a «hard» nitrogen and a «soft» arsenic donor atom.
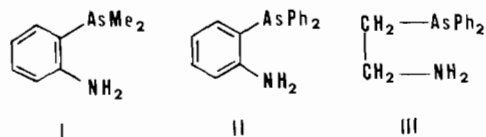
Nickel Compounds. Bidentate ligands, possessing an arsenic and nitrogen donor atom, exhibit relatively weak overall ligand fields, and in almost all cases form high spin complexes with nickel(II) salts. The 1:1 complexes formed by 1-(2'-pyridyl)-2-(diphenylarsino)ethane (AEP, IV, n = 2) with nickel(II) salts are paramagnetic with either tetrahedral or polymeric octahedral bridged structures. The 2:1 complexes, [Ni(AEP)₂X₂] (where X = I or NCS), are diamagnetic but the ligand in this instance is coordinating as a substituted pyridine with the arsenic donors uncoordinate; [Ni(AEP)₂](ClO₄)₂ is diamagnetic with a bis-chelate structure.
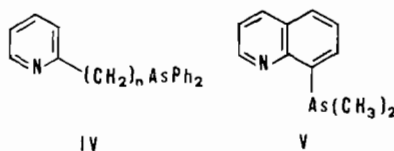
1-(2'-pyridyl)-2-(diphenylarsino)methane (AMP, IV, n = 1) forms a high spin octahedral 2:1 complex with nickel(II) thiocyanate.[5]

8-dimethylarsinoquinoline (8-dmaq, V) forms only high spin complexes with nickel(II) salts. The complexes are of general formulae [Ni(8—dmaq)₂X₂] (where X = Cl, Br, I, NCS, or NO₃) and [Ni(8—dmaq)₃]X₂ (where X = ClO₄ or BPh₄).[6]

The different stereochemistries and spin states displayed by the 2:1 complexes of the bidentate ligands with nickel(II) salts can easily be explained qualitatively. The field strengths of the diphosphine, diarsine, and many of the mixed donor bidentate ligands, are sufficiently high to favour the formation of four-coordinate planar diamagnetic complexes of the type ([Ni(ligand)₂]X₂, when X is a anion with weak coordinating ability *e.g.* ClO₄⁻ or BPh₄⁻. In the case of more strongly coordinating anions (X = Cl, Br, I, or NCS) there will be a tendency to form six-coordinated complexes [Ni(ligand)₂X₂]. Provided that the in-plane field of the bidentate ligands is much greater than the axial field of the anionic ligands, the structure will be tetragonally distorted and the singlet ground state will be retained. The coordination of the anions in these complexes is weak, and in solution dissociation may occur with the formation of five-coordinate

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Table I. Magnetic Susceptibility measurements.

	Method	$10^6\chi_g$	$10^6\chi_M$	$10^6\chi'_M$	T(K)	μ_{eff} B.M.
Ni(MAA)₂Cl₂	Faraday 10 amp magnet current	7.644	4004	4378	291.4	3.19
	20 amp magnet current	7.676	4021	4395	291.4	3.20
Ni(MAA)₂Br₂	Gouy	6.346	3890	4282	296	3.20
Ni(MAA)₂I₂	»	4.810	3399	3823	301	3.04
Ni(MAA)₂(NCS)₂	»	6.800	3870	4255	296	3.19
Ni(MAA)₂(NO₃)₂	»	6.664	3846	4207	296	3.17
Ni(MAA)₂(ClO₄)₂	»	0.358	—233	154	296	0.61
Ni(APE)₂Br₂	Gouy	4.358	3334	3702	296	2.97
Ni(APE)₂I₂	»	3.754	3225	3660	296	2.96
Ni(PAA)₂Br₂	Gouy	3.831	3299	4116	295	3.13
Ni(PAA)₂I₂	»	3.797	3626	4510	294	3.27
	Faraday 10 amp	2.0866	1370	1757	291.4	2.02
	20 amp	1.8700	1228	1615	291.4	1.94
[Cu(MAA)₂](ClO₄)₂	Gouy	1.697	1115	1502	301	1.91
[Cu(PAA₂)](ClO₄)₂	Faraday 10 amp	1.0470	947.5	1794	291.2	2.04
	20 amp	0.8368	757.3	1604	291.2	1.93
Cu(MAAO)₂(ClO₄)₂ · EtOH	Faraday 10 amp	1.7042	1252	1744	292.1	2.02
	20 amp	1.6578	1218	1710	292.1	2.00
[Cu(APEO)₂](ClO₄)₂	Gouy	1.305	1097	1557	296	1.93

diamagnetic species, which it is possible to isolate in certain cases as the salts of large non-coordinating anions e.g. [Ni(ligand)₂X]BPh₄. For the six-coordinate complexes where the in-plane field is reduced, e. g. in P–N bidentates, the tetragonal distortion is decreased and the ground state may become a triplet particularly in the case of the higher field anionic ligands, e.g. N-bonded thiocyanate. The effect of decreasing tetragonal distortion leads to a decreasing separation between the $d_{x^2-y^2}$ and d_{z^2} levels until electron pairing no longer occurs and the triplet ground state, as in regular octahedral symmetry, becomes fundamental.[7]

o-Dimethylarsinoaniline (MAA) reacts with nickel-II) salts in ethanol or other suitable organic solvents giving a series of 2:1 complexes. Attempts to isolate complexes of other stoichiometry were unsuccessful. Some 2:1 complexes with the ligands o-diphenylarsinoaniline (PAA) and 1-amino-2-(diphenylarsino)-ethane (APE) were also isolated. The complexes of PAA and APE were less stable and more difficult to prepare than those of MAA. Whilst PAA complexes of some nickel(II) salts would crystallize when concentrated solutions in very dry alcohol were used, APE showed no tendency to complex with nickel(II) in polar organic solvents. The method used for the preparation of the APE and PAA complexes was to add the ligand dissolved in a large volume of benzene to a relatively concentrated solution of the nickel(II) salt in ethanol. Water and ethanol were then removed from the reaction mixture by distillation of their benzene azeotropes, whereupon the complexes crystallized.

The study of the physical properties of these complexes has been limited mainly to those measurements, such as magnetic susceptibility, infrared spec-

tra and electronic reflectance spectra, which can be made in the solid state. Most of the complexes are either insoluble or decompose in organic solvents.

The magnetic moments of the series of complexes: Ni(MAA)₂X₂ (where X = Cl, Br, I, NO₃, or NCS), Ni(APE)₂X₂ (where X = Br or I), and Ni(PAA)₂X₂ (where X = Br or I), lie in the region 3.0-3.3 M.M. (Table I). These values are consistent with six-coordinate octahedral structures.

Nickel(II) complexes with octahedral or tetrahedral stereochemistry are always paramagnetic and some five-coordinate complexes of nickel(II) may also have high spin electronic configurations. Magnetic susceptibility measurements alone do not provide a definite diagnosis of stereochemistry since the octahedral, and five-coordinate nickel(II) complexes frequently have similar magnetic moments.

Experimentally, the magnetic moments for octahedral nickel(II) complexes are found to lie in the range 2.9-3.3 B.M. The predominant contribution to the moment is the spin only term, however a small orbital contribution, temperature independente paramagnetism and covalent metal-ligand bonding also make small contributions.[7] In tetrahedral nicekl(II) complexes a temperature dependent orbital contribution to the magnetic moment is expected, and the orbital contribution may be reduced by covalent metal-ligand bonding. The observed magnetic moments for tetrahedral nickel(II) complexes vary from about 3.2 to 4.1 B.M., whilst high spin five-coordinate nickel(II) complexes have moments in the range 3.2-3.4 B.M.[7]

Since the magnetic moments of the high spin [Ni-(MAA)₂X₂], [Ni(APE)₂X₂] and [Ni(PAA)₂X₂] complexes mostly lie in the 3.0-3.2 region, it seems most probable that they have six-coordinate octahedral structures. This conclusion was substantiated by the result obtained from the study of the infrared and

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Table II. Infrared assignments for nickel(II) complexes.

(a) Compound	N—H stretching frequencies, cm^{-1}				
MAA	3440s		3355s		
Ni(MAA)$_2$(NO$_3$)$_2$	3240		3180m,	3140m,	3110m.
Ni(MAA)$_2$Br$_2$	3220,	3205sh,	3170,	3130,	3100.
Ni(MAA)$_2$Cl$_2$	3245,	3215,	3275,	3135,	3105.
Ni(MAA)$_2$(NCS)$_2$	3220,	3200sh,	3175,	3135,	3105.
Ni(MAA)$_2$I$_2$	3205,	3190sh,	3165,	3125,	3090.
Ni(MAA)$_2$(ClO$_4$)$_2$	3230,	3205, 3195,	3165,	3140, 3130,	3100.
APE	3375m,br		3290w,br.		
Ni(APE)$_2$Cl$_2$	3340m,	3300m,	3200m,	3245s,	3160w.
Ni(APE)$_2$I$_2$	3300,	3270,	3225,	3215,	3140.
PAA	3445s,	3360s.			
Ni(PAA)$_2$Br$_2$	3380s,br,	3260s,	3200w,	3170w,	3130w.
Ni(PAA)$_2$I$_2$	3400,	3265, 3240,	3220,	3200,	3140.

(b) Compound	N—H bending cm^{-1}	C—N stretching cm^{-1}
MAA	1615 (approx)	1290 s
Ni(MAA)$_2$Cl$_2$	1555 s	1272 m
Ni(MAA)$_2$Br$_2$	1552 s	1270 m
Ni(MAA)$_2$(NO$_3$)$_2$	1555 s	—
Ni(MAA)$_2$(SCN)$_2$	1555 s	1270 m
Ni(MAA)$_2$(ClO$_4$)$_2$	1565, 1560sh, 1555sh.	1275 m

(c) Compound	CH$_3$ rocking		As—(CH$_3$)$_2$ stretching	
MAA	890 m	850 m	585 m,	575 sh
Ni(MAA)$_2$Cl$_2$	895 m	862 m	612,	595
Ni(MAA)$_2$Br$_2$	895 m	870 m	610,	590
Ni(MAA)$_2$(NCS)$_2$	900 m	855 m	605	575
Ni(MAA)$_2$(NO$_3$)$_2$	905 m	862 m	610,	
Ni(MAA)$_2$(ClO$_4$)$_2$	930 m	875 m	—	—

Abbreviations: s = strong; m = medium; w = weak; sh = shoulder; br = broad.

electronic spectra. The diamagnetism of [Ni(MAA)$_2$](ClO$_4$)$_2$ and [Ni(PAA)$_2$](ClO$_4$)$_2$ is indicative of four-coordinate planar coordination and this conclusion is also supported by the infrared and electronic spectra.

Infrared Spectra of Nickel(II) Complexes. Infrared assignments provided evidence for the coordination of the polyatomic anions in [Ni(MAA)$_2$(NCS)$_2$] and [Ni(MAA)$_2$(NO$_3$)$_2$]. Characteristic shifts in some of the infrared bands of MAA were regarded as diagnostic of coordination of MAA as a bidentate chelating group and shifts in the NH$_2$ stretching frequencies indicated coordination of the amino groups of PAA and APE.

The N—H stretching frequencies of primary amines are shifted to lower frequencies on coordination in some cases by as much as 200 cm^{-1}.[8] MAA has two bands in the N—H stretching region at 3440 and 3355 cm^{-1}, which correspond to the ν_{asym}(N—H) and ν_{sym}(N—H) modes. In the complexes of MAA with nickel-(II), the N—H stretching modes were shifted to lower frequencies by about 200 cm^{-1}, and usually four or five bands were resolved (see Table IIa). The splitting may be caused by hydrogen-bonding effects, or by Fermi interaction with the first overtone of the N—H bending mode, which is expected to lie at about 3120 cm^{-1}; or both effects may be operative. In the complexes of PAA and APE with nickel(II) the N—H stretching frequencies are lowered by about 70 cm^{-1}, and they also appear as well resolved multiple bands

(see Table IIa). In the MAA complexes, the N—H bending mode and C—N stretching modes are shifted to lower frequencies in comparison to their positions in the spectrum of «free» MAA (see Table IIb).

It has been observed that the methyl rocking and As—(CH$_3$)$_2$ stretching modes of *o*-phenylenebisdimethylarsine are shifted to higher frequencies on coordination.[9] The corresponding vibrational modes of MAA were assigned and similar shifts were observed in the infrared spectra of the nickel(II) complexes (see Table IIc). From the shifts in these frequencies it was concluded that the —As(CH$_3$)$_2$ group is coordinated in the Ni(MAA)$_2$X$_2$ complexes but no criterion was developed to diagnose coordination of the —AsPh$_2$ groups in the Ni(PAA)$_2$X$_2$ and Ni(APE)$_2$X$_2$ complexes.

The C—N stretching mode of the thiocyanate ion occurs near 2060 cm^{-1} but is shifted to higher frequencies on coordination and such shifts are characteristic of the type of coordination. Thus it is claimed that N—bonded thiocyanates usually show C—N stretching frequencies in the range 2040-2080 cm^{-1}, while for the S—bonded thiocyanates, the C—N stretching mode appears in the range 2080-2120 cm^{-1},[10] and for bridging thiocyanates the C—N stretching mode occurs at about 2150 cm^{-1}. In the infrared spectrum of Ni(MAA)$_2$(NCS)$_2$ the C—N stretching mode occurs at 2105 cm^{-1}. Although this value is rather high for an N—bonded thiocyanate, the C—S stretching mode and the N—C—S bending modes were observed at 788 cm^{-1} and 470,490 cm^{-1} respectively,

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(9) Deacon G.B. and Green J.H.S., *Spectrochim. Acta,* **24A,** 959 (1968).
(10) Norbury and A.I.P. Sinha, *Quart. Rev.,* **24,** 82 (1970).

Table III. Electronic Spectra Nickel(II) Complexes.

	Solid state or solution	$\nu_1, {}^3A_{2g} \to {}^3T_{2g}$	$\nu_2, {}^3A_{2g} \to {}^3T_{1g}(F)$	$\nu_3, {}^3A_{2g} \to {}^3T_{1g}(P)$.
Ni(MAA)₂Cl₂	solid	— cm⁻¹	17,000 cm⁻¹	— cm⁻¹
Ni(MAA)₂Br₂	solid	—	17,100	—
Ni(MAA)₂I₂	solid	—	17,400	—
Ni(MAA)₂(NCS)₂	solid	—	18,800	—
Ni(MAA)₂(NO₃)₂	solid	—	18,100(br.)	—
Ni(APE)₂Cl₂	solid	—	14,400	24,100
Ni(APE)₂Br₂	solid	—	16,300	—
Ni(APE)₂I₂	solid	—	16,600	—
Ni(PAA)₂Br₂	solid	—	15,100	—
Ni(PAA)₂Br₂	soln.CH₂Cl₂	8000(br.)($\varepsilon_o=24$)	14,300 ($\varepsilon_o=22$)	—
Ni(PAA)₂I₂	solid	—	17,500(sh)	—
Ni(PAA)₂I₂	soln.CH₂Cl₂	9.600 ($\varepsilon_o=35$)	16,500(sh) $\varepsilon_o=250$	—
Ni(MAA)₂(NO₃)₂	soln.CH₃OH	—	{ 14,900($\varepsilon_o=3.5$) / 13,000 ($\varepsilon_o=3.7$)	25,000 ($\varepsilon_o=10$)
Ni(MAA)₂(ClO₄)₂	solid		23,800 cm⁻¹	
Ni(PAA)₂(ClO₄)₂	solid		22,000 cm⁻¹	

		Band maxima (cm⁻¹)
Ni(MAA)₂(NO₃)₂	soln.CH₃OH	33,800 cm⁻¹ ($\varepsilon_o=2,200$ for MAA concentration)
Ni(MAA)₂Cl₂	soln.CH₃OH	33,800 cm⁻¹ ($\varepsilon_o=2,400$ for MAA concentration)
Ni(MAA)₂(ClO₄)₂	soln.CH₃OH	33,800 cm⁻¹ ($\varepsilon_o=2,500$ for MAA concentration)

Copper(II) Complexes (Reflectance spectra in the region 12,000—27,000 cm⁻¹).

Band maxima (cm⁻¹)

Cu(MAA)₂(ClO₄)₂	20,400 cm⁻¹
Cu(PAA)₂(ClO₄)₂	20,000 cm⁻¹ (sh)
Cu(MAAO)₂(ClO₄)₂ . EtOH	13,800 cm⁻¹
Cu(APEO)₂(ClO₄)₂	14,900 cm⁻¹; 16,300 cm⁻¹ (sh)

sh = shoulder

indicative of N—bonded thiocyanates[10] which are normally observed for nickel(II). The presence of only one C—N stretching frequency in Ni(MAA)₂(NCS)₂ is indicative of a trans arrangement of the thiocyanate groups about the nickel(II).

The coordination of the nitrate group is indicated by the splitting of the degenerate NO₂ stretching vibration of the free ion which occurs at about 1380 cm⁻¹, and also by the appearance of the N—O stretching vibration at 1050 cm⁻¹ which is infrared inactive for the free nitrate ion.[12] The bands which are observed at 1420 cm⁻¹, 1310 cm⁻¹ and 1040⁻¹ thus establish the coordination of the nitrate groups in Ni(MAA)₂(NO₃)₂.

The perchlorate band at 1080 cm⁻¹ in the infrared spectrum of Ni(MAA)₂(ClO₄)₂ shows some structure. This is at least partly due to underlying MAA vibrations at about 1130, 1100, and 1060 cm⁻¹. Is is possible that the perchlorate ion may be weakly associated above and below the Ni(MAA)₂ plane, but there is definitely no strong covalent interaction.[13]

Electronic Spectra o fNickel(II) Complexes. Octahedral nickel II complexes exhibit a simple spectrum involving three spin-allowed transitions for the ³T₂g, ³T₁g(F) and ³T₁g(P) excited states. These occur in the regions 7000-13,000 cm⁻¹ (ν_1), 11,000-20,000 cm⁻¹ (ν_2) and 19,000-27,000 (ν_3) respectively, with comparatively low intensities.

For distorted octahedral complexes the degenerate

T states undergo further splitting, so that a larger number of transitions is expected. However the spectra of pseudooctahedral nickel(II) complexes frequently retain the simple form observed for regular octahedral symmetry. If splittings are observed they are usually most prominent in the ν_1 band.[7,14] In the spectra of the *o*-methylthioaniline complexes, [Ni(NH₂SMe)₂X₂] (where X = Br or I), splitting of the ν_1 band was reported.[8] Splitting of both the ν_1 and ν_2 bands is prominent in the *o*-phenylenediamine complexes [Ni(opda)₂X₂] (where X = Cl, Br, I, NCS, or NO₃).[15] However, in the 8-dimethylarsinoquinoline complexes, [Ni(8—dmaq)₂X₂] (where X = Cl, Br, I, NCS, or NO₃), the low symmetry ligand field is reflected only in a broadening of the ν_1 band.[6]

The reflectance spectra of the high spin six-coordinated nickel(II) complexes of MAA, APE, and PAA were obtained in the 12,000-27,000 cm⁻¹ region. Ni(PAA)₂I₂ and Ni(PAA)₂Br₂ were soluble in dichloromethane and their spectra were obtained down to 7,000 cm⁻¹, but the high frequency region of the spectra of these complexes was obscured by charge transfer bands. Observation of the entire d—d spectrum could not be made for any one complex, but it appeared that the spectra could be most readily assigned on the basis of an octahedral ligand field. The proposed assignments of the spectra are given in Table III.

The spectrum of Ni(PAA)₂I₂ could alternatively be assigned on the basis of a tetrahedral structure in so-

(11) Chatt J. and Duncanson L.A., *Nature*, *181*, 43 (1958).
(12) Gatehouse B.M., Livingstone S.E., and Nyholm R.S., *J. Chem. Soc.*, 4222 (1957).
(13) Hathaway B.J. and Underhill A.E., *J. Chem. Soc.*, 3091 (1961).

(14) Lever A.B.P. Lever in Inorganic Electronic Spectroscopy, pp. 333-357 and references therein (1968). Elsevier; Amsterdam.
(15) Kakazai B.J.A. and Nelson G.A., *Inorg. Chim. Acta*, 2, 186 (1968).

Table IV. Molar Conductance Measurements at 25°C.

Complex	Solvent	Molar concentration	Λ_M
Ni(MAA)₂(NO₃)₂	99% methanol	$1.09 \times 10^{-2} M$	108
»	»	2.19×10^{-4}	207
Ni(MAA)₂(ClO₄)₂	»	2.80×10^{-4}	172
Ni(MAA)₂Cl₂	»	2.31×10^{-4}	165
Ni(MAA)₂(ClO₄)₂	CH₃NO₂	1.04×10^{-3}	188
Ni(MAA)₂Cl₂	PhNO₂		0.3
Cu(APEO)₂(ClO₄)₂	nitromethane	$1.04 \times 10^{-3} M$	161
Cu(MAAO)₂(ClO₄)₂ · EtOH	nitromethane	$1.03 \times 10^{-3} M$	174*

* Decomposes, the solution is initially yellow.

lution with the $^3T_1 \to {}^3A_2$ and $^3T_1 \to {}^3T_1(P)$ transitions[7,14] at 9,600 and 16,500 cm^{-1} respectively, but the high intensity of the 16,500 cm^{-1} band ($\varepsilon_o = 250$) may be simply due to its close proximity to the charge transfer absorption. Both the bands in the spectrum of [Ni(PAA)₂Br₂] at 8000 cm^{-1} and 14,300 cm^{-1} have low intensities characteristic of octahedral complexes.

For the series of APE complexes, [Ni(APE)₂X₂] (where X = Cl, Br, or I), the relative position of the ν_2 band is the opposite to that expected from the positions of Cl, Br, and I in the spectrochemical series. This could mean that the ligand field exerted by APE increases as the polarizability of the anionic ligand increases. It is also observed from the position of the band maxima for the complexes with the same anion, that the field strengths of the ligands increase in the order PAA<APE<MAA, i.e. with decreasing aryl substitution on the arsenic atom.

The spectrum of the complex Ni(MAA)₂(NO₃)₂ in methanol differs from the solid state spectrum and is similar to that reported for [Ni(MeOH)₆]²⁺ or [Ni(H₂O)₆]²⁺.[14] Solutions of the complexes in methanol also have spectra similar to MAA itself in the near-ultraviolet region. These observations are consistent with the assumption that the complexes are dissociated in this solvent.

The spectra of square planar nickel(II) complexes largely depends on the nature of the ligands, and no general assignment can be given to cover all cases. This is because the relative order of the energies of the non-bonding levels e$_g$, b$_{2g}$, and a$_{1g}$ in D$_{4h}$ symmetry depends on the bonding requirements of the ligands, and the position of the a$_{1g}$ level is also determined by the extent of any axial interaction that may be present.[7,14] The spectra of [Ni(PAA)₂](ClO₄)₂ and [Ni(MAA)₂](ClO₄)₂ (which most likely have a NiAs₂N₂ chromophore with D₂ₕ symmetry), showed only one band in the region examined, at 22,000 and 23,800 cm^{-1} respectively. The spectra are thus similar to those observed for planar complexes with nitrogen ligands, which show one band that probably contains several transitions of similar energy from the e$_g$, b$_{2g}$, and a$_{1g}$ levels. Planar complexes with high field ligands usually show additional bands because of larger differences in the energies of the a$_{1g}$, b$_{2g}$, and e$_g$ levels.

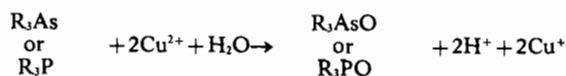*Conductance Measurements on Nickel(II) Complexes.* Nearly all the complexes were insoluble in solvents suitable for conductance measurements, such as nitromethane or nitrobenzene. Ni(MAA)₂Cl₂ was

sufficiently soluble to determine that it was a non-electrolyte in nitrobenzene. The yellow colour of Ni(MAA)₂(ClO₄)₂ was retained for a short period in nitromethane and the molar conductivity was in the range expected for a bi-univalent electrolyte. The complexes [Ni(MAA)₂(NO₃)₂], [Ni(MAA)₂Cl₂] and [Ni(MAA)₂](ClO₄)₂ dissolved in 99% methanol on warming and the solutions had molar conductivities in the range expected for bi-univalent electrolytes in this solvent (Table IV). It is obvious that decomposition according to the equation:

$$Ni(MAA)_2X_2 \rightleftarrows Ni^{2+}(\text{solvated}) + 2X^- + 2MAA$$
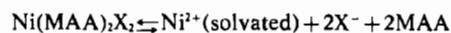
has occurred This was confirmed by measuring the absorption spectra of the solutions which were found to have a spectrum similar to that reported for [Ni(H₂O)₆]²⁺ with a doublet at 13,600 cm^{-1}, 14,900 cm^{-1} ($\varepsilon_o = 3.5$) (Table III).

Copper Compounds. A redox reaction takes place between copper(II) salts and tertiary phosphine or arsine ligands, and consequently simple copper(II) tertiary phosphine or arsine complexes cannot usually be characterized.[16,17]

$$\begin{matrix} R_3As \\ \text{or} \\ R_3P \end{matrix} + 2Cu^{2+} + H_2O \to \begin{matrix} R_3AsO \\ \text{or} \\ R_3PO \end{matrix} + 2H^+ + 2Cu^+$$

When the ligand is used in excess a tertiary arsine or phosphine complex of copper(I) is often isolated, and when the copper(II) salt is used in excess the usual product is a tertiary phosphineoxide or arsineoxide complex of copper(II).

The ability to reduce copper(II) is also evident in the bidentate ligands containing tertiary phosphine and arsine donors. Thus, the reaction of 1-diethyl-amino-2-(diphenylphosphino)ethane with excess copper(II) chloride gives the dichlorocuprate(I) salt of the quaternized and oxidized ligand 2-(diphenylphosphineoxide)ethyldiethylammonium chloride(VI).[18]

$$\left[\overset{\overset{\|}{O}}{Ph_2P}CH_2CH_2\overset{\overset{+}{N}}{\underset{H}{N}}Et_2 \right] \left[CuCl_2 \right]^-$$

VI
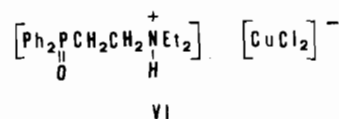
(16) Both G. in « Advances in Inorganic Chemistry and Radiochemistry », 6, pp. 47-49, (1964), Academic Press New York.
(17) Matfield W.E. and Whyman R. in « Transition Metal Chemistry », 5, pp. 138-141, (1969). Marcel Dekker, New York. London.
(18) Coughman H.D. and Taylor R.G., *Inorg. Nucl. Chem. Letters*, 6, 623 (1970).

Although a copper(II) complex may initially form in solution, only a phosphineoxide complex of copper(I) has been isolated from the reaction of o-diphenylphosphinobenzoic acid and copper(II) chloride(VII).[19]
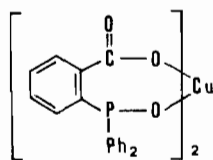
VII

In the original study of the o-phenylenebisdimethylarsine complexes of copper, it was observed that a transient dark-brown colouration formed immediately on adding the diarsine to a copper(II) salt,[10] and recently it has been reported that o-phenylenebisdimethylarsine complexes of copper(II) may be isolated for short periods.[21] However, the diarsine cis-1,2-bis-(dimethylarsino)ethylene (cis-edas) reduces copper(II) perchlorate and forms the copper(I) complex [Cu-(cis-edas)₂](ClO₄) without any evidence for an intermediate copper(II) complex.[21] The mixed arsenic-nitrogen and arsenic-sulphur ligands, 8-dimethylarsinoquinoline,[22] 3-thiomethylpropyldimethylarsine[24] and (o-diphenylarsinophenyl)diphenylphosphinesulphide[25] have been reported to reduce copper(II) sulphate with the subsequent formation of [Cu(ligand)₂]⁺ complexes.

(2-pyridyl)dimethylarsinomethane also reduced copper(II) salts but the product isolated was the arsineoxide complex of copper(I).[26] (n=1 in VIII).
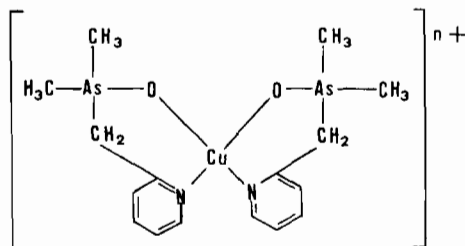
VIII

The complex can be oxidized by air and the corresponding copper(II) arsineoxide complex (VIII, n=2) was also obtained.

Copper(I) complexes can also be prepared from the direct reaction of diphosphines, diarsines or the mixed donor bidentate ligands with copper(I) salts. Most of these derivatives contain the cation [Cu(ligand)₂]⁺ with a tetrahedral disposition of the donor groups about the copper(I). Frequently the complexes have been isolated with [CuX₂]⁻ (where X=Cl, Br

or I) as the counter anion. The ligands from which [CuX₂] complexes have been prepared include o-phenylenebisdimethylarsine,[20] 1-(2 pyridyl)-2-(diphenylarsinomethane,[26] dimethyl(o-methylthiophenyl)arsine,[23] 3-dimethylarsinopropylmethylthiol,[24] and (o-diethylphosphinophenyl)diethylarsine.[27]

The 1:1 complexes formed by the ligands 8-dimethylarsinoquinoline[22] and 1-(2 pyridyl)-2-(diphenylphosphino)ethane[28] with copper(I) appear to have halide bridged dimeric structures with tetrahedral coordination about each copper atom.

The reaction of MAA with copper(II) perchlorate in ethanol yields the crystalline red-brown complex [Cu(MAA)₂](ClO₄)₂. When dry, and sealed under vacuum, this complex appears to be stable indefinitely. With the exception of a recent report which states that copper(II) complexes of o-phenylenebisdimethylarsine can be isolated for short periods,[21] no other examples of tertiary arsine complexes with copper(II) salts have been described in the literature. The exceptional stability of [Cu(MAA)₂](ClO₄)₂ is limited to the solid state because the dark red-brown colour of its solutions is discharged within about ten minutes at room temperature owing to the reduction of the copper to the monovalent state by the tertiary arsine group of MAA.

The presence of divalent copper in [Cu(MAA)₂]-(ClO₄)₂ was confirmed by magnetic susceptibility measurements (Table I). The magnetic moment is approximately 1.9 B.M. at room temperature. It was observed that the moment is slightly dependent on field strength, but the reason for this is not known. The infrared spectrum of [Cu(MAA)₂](ClO₄)₂ is similar to that of the MAA complexes with other metal ions. In particular no additional bands are observed in the As—O stretching region between 800 and 900 cm⁻¹. These results rule out the possibility of a copper(I) complex of MAA or a copper(II) complex of the arsineoxide of MAA.

The solid state reflectance spectrum (Table III) of [Cu(MAA)₂](ClO₄)₂ in the region 12,000-27,000 cm⁻¹ shows a broad maximum at 20,400 cm⁻¹ with strong absorption at higher frequency. The maximum is most likely a ligand field band and can be compared with the broad maxima at 18,800 cm⁻¹ and 19,500 cm⁻¹ that are observed in the electronic spectra of the corresponding complexes of ethylenediamine and o-phenylenediamine, Cu(en)₂(ClO₄)₂ and Cu(opda)₂(ClO₄)₂, respectively.[29,30] These complexes are considered to have a square planar arrangement of the chelating diamine ligand around the copper(II) ion with unidentate perchlorate ions coordinated weakly above and below the plane giving a six-coordinate tetragonal structure. In the bis-ethylenediamine complexes of copper(II) the broad band centered at about 18,000 cm⁻¹ has been assigned to the three unresolved transitions $^2B_{1g} \rightarrow ^2A_{1g}$, $^2B_{2g}$, ^2E_g expected under D_{4h} symmetry.[29]

A four-coordinate planar or tetragonal six-coordin-

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Table V. Infra-red spectra, N—H stretching frequencies for copper(II) complexes.

Complex	Absorption band maxima (cm^{-1})		
[Cu(MAA)$_2$](ClO$_4$)$_2$	3285 s	3245 s	3150 sh
[Cu(MAAO)$_2$](ClO$_4$)$_2$. EtOH	3270 sh	3225 s	3095 s,br
[Cu(MAA)$_2$][CuCl$_2$]	3280 s	3235 s	3150 m
[Cu(APEO)$_2$](ClO$_4$)$_2$	3330 m	3260 m	
[Cu(APE)$_2$][CuI$_2$]	3265 m	3230 m	3145 w

Relative intensities: s = strong; m = medium; w = weak; sh = shoulder; br = broad. Samples as mulls in nujol or hexachlorobutadiene.

Table VI. Analytical Results for nickel(II) complexes.

Complex	Description	C%		H%		N%		Ni%	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Ni(MAA)$_2$Cl$_2$	pale blue crystals	36.7	36.5	4.6	4.6	5.4	5.5	11.2	11.3
Ni(MAA)$_2$Br$_2$	greyish green crystals	31.4	31.4	4.0	4.2	4.6	4.3	9.6	9.7
Ni(MAA)$_2$I$_2$	yellow crystals	27.2	26.8	3.4	3.6	4.0	3.7	8.3	8.1
Ni(MAA)$_2$(NCS)$_2$	lilac crystals	38.0	37.9	4.3	4.7	9.8	9.7	10.3	10.3
Ni(MAA)$_2$(NO$_3$)$_2$	lilac crystals	33.3	33.4	4.2	4.3	9.7	9.6	10.2	10.2
Ni(MAA)$_2$(ClO$_4$)$_2$	orange-yellow crystals	29.5	29.7	3.7	3.8	4.3	4.1	9.0	9.1
Ni(APE)$_2$Cl$_2$	pale green crystals	49.8	50.3	4.8	5.0	4.1	4.0	8.7	8.7
Ni(APE)$_2$Br$_2$	blue crystals	44.0	45.3	4.2	4.4	3.7	3.4	7.7	7.5
Ni(APE)$_2$I$_2$	green crystals	39.2	40.4	3.8	3.8	3.3	3.0	6.8	6.6
Ni(PAA)$_2$Br$_2$	pale green crystals	50.2	51.5	3.7	4.0	3.3	3.0	6.8	6.6
Ni(PAA)$_2$I$_2$	brownish-yellow crystals	45.3	44.3	3.4	3.4	2.9	2.7	6.1	6.4
Ni(PAA)$_2$(ClO$_4$)$_2$	brownish-orange crystals	48.0	47.9	3.6	3.6	3.1	3.3	6.5	6.4

Table VII. Analytical Results for Copper(II) complexes.

Complex	Description	C%		H%		N%		Cu%		Cl%	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Cu(MAA)$_2$(ClO$_4$)$_2$	red-brown crystals	29.3	29.2	3.7	3.8	4.3	4.2	9.7	9.4	10.8	10.9
Cu(MAAO)$_2$(ClO$_4$)$_2$EtOH	green crystals	29.4	29.2	3.8	3.9	3.8	3.7	8.7	8.7	9.7	9.7
Cu(MAA)$_2$CuCl$_2$	colourless crystals	32.5	33.0	4.1	4.2	4.7	4.9	21.5	21.5		
Cu(MAA)$_2$CuBr$_2$	colourless crystals	28.2	28.3	3.6	3.6	4.1	4.0	18.7	18.6		
Cu(PAA)$_2$(ClO$_4$)$_2$	dark red crystals	47.8	47.2	3.6	3.7	3.1	3.3	7.0	7.0		
Cu(APEO)$_2$(ClO$_4$)$_2$	bright blue crystals	40.0	40.0	3.8	3.8	3.3	3.3	7.6	7.5		
Cu(APE)$_2$CuI$_4$	white micro-crystalline solid	36.3	36.2	3.5	3.6	3.0	3.0	13.7	13.4		

ate structure may be considered for [Cu(MAA)$_2$]-(ClO$_4$)$_2$ depending on the extent of any bonding interaction between the perchlorate ion and the central copper(II) ion. Weak coordination of polyatomic anions in the axial positions occurs in many apparently four-coordinate planar copper(II) complexes, and the term «semi-coordination» has been used to describe it. The infrared spectra of the polyatomic anions in such complexes are intermediate between those for the free and fully coordinated anions.[29,31] Examining the infrared spectrum of [Cu(MAA)$_2$](ClO$_4$)$_2$ for «semi-coordinated» perchlorate groups is made difficult by the fact that the strong bands at approximately 1160 cm^{-1}, 1130 cm^{-1}, and 1060 cm^{-1} of coordinated MAA will cause some structure to be observed in the ν_3 perchlorate band. A similar situation arises for the ν_4 perchlorate band near 620 cm^{-1} which is close to the As—CH$_3$ stretching frequencies of coordinated MAA. Also, the infrared inactive ν_1 ionic perchlorate band near 930 cm^{-1}, which is expected to occur with some intensity in the spectrum of «semi-coordinated» perchlorate ions, will possibly be obscured by the 920 cm^{-1} methyl rocking band of coordinated MAA. The ν_3 perchlorate band in the spectrum of [Cu(MAA)$_2$](ClO$_4$)$_2$ appears to be split to only a very small extent (1110 and 1070 cm^{-1}); much less than that reported in the case of Cuen$_2$(ClO$_4$)$_2$. It is therefore concluded that the perchlorate groups in [Cu(MAA)$_2$](ClO$_4$)$_2$ are either ionic or, at most, very weakly coordinated.

When MAA and copper(II) perchlorate were heated in ethanol the initial red-brown colour due to the copper(II) complex rapidly faded and a pale-brown coloured solution was obtained. Attempts to isolate from this solution a copper(I) complex of definite composition were unsuccessful, but if the solution was kept freely exposed to the atmosphere for about two days, a bright green crystalline precipitate formed. According to the sequence of reactions involved, this is likely to be a copper(II) complex of o-aminophenyldimethylarsineoxide, (MAAO).

Good agreement of the analytical data can only be

(31) Hathaway B.J. and Underhill A.E., *J. Chem. Soc.*, 3091 (1961).

obtained if the complex is formulated as an ethanol solvate, Cu(MAAO)₂(ClO₄)₂ · EtOH. The analytical results for C, H, N, Cu, and Cl (Table VII) are in good agreement with this formula, and were reproducible for samples from different preparations. Bands at 3625 cm⁻¹ and 3540 cm⁻¹ in the spectrum of this complex were assigned to O–H stretching frequencies. Normally only one O–H stretching vibration would be expected in EtOH, however, it is possible that a H–bonded interaction with the amino groups could account for the observed doublet. Another example of an ethanolate is provided by the complex, Pd(PAA)₂I₂ · EtOH. This complex also has two bands at 3665 and 3560 cm⁻¹ in its spectrum, and when the ethanol is removed by heating the bands disappear. If ethanol is present in the copper complex then it is not easily removed, as there is no change in the infrared spectrum after heating the complex at 80°C under vacuum.

The magnetic moment of the complex based on the formula Cu(MAAO)₂(ClO₄)₂ · EtOH was 2.02 B.M. at room temperature (Table I), and this establishes that only copper(II) is present.

The spectrum of Cu(MAAO)₂(ClO₄)₂ · EtOH was also obtained in the 800-900 cm⁻¹ region in order to check for the presence of bands due to the arsineoxide group. The medium intensity band at 895 cm⁻¹ is probably a methyl rocking vibration and corresponds to the band near 870 cm⁻¹ in the complexes of MAA. A moderately intense structured band with peaks at 825 cm⁻¹ and 810 cm⁻¹, and a shoulder at 845 cm⁻¹ was observed in the spectrum of Cu(MAAO)₂(ClO₄)₂ · EtOH. A weak broad band at 825 cm⁻¹ is found for MAA, and this occurs as a sharp peak near 815 cm⁻¹ in the complexes of MAA. Whilst it is apparent that there are additional features in the spectrum of Cu(MAAO)₂(ClO₄)₂ · EtOH, the assignment of an As–O stretching frequency cannot be made unambiguously.

The perchlorate band near 1100 cm⁻¹ in the spectrum of Cu(MAAO)₂(ClO₄)₂ · EtOH shows no sign of splitting, so it is likely that the copper(II) ion is four-coordinate. The solid state reflectance spectrum (Table III) in the region 12,000-27,000 cm⁻¹ shows only one maximum at 13,800 cm⁻¹. This is at somewhat lower energy than the absorption bands in the spectrum of [Cu(APEO)₂](ClO₄)₂, in which the cation appears to possess a planar structure. This could mean that the ligand field strength of MAAO is considerably less than that of APEO, or that Cu(MAAO)₂(ClO₄)₂ · EtOH may have a different structure to Cu(APEO)₂(ClO₄)₂.

The reactions of MAA with other copper(II) salts were also investigated. With copper(II) nitrate, a dark red copper(II) complex was the initial product, but reduction took place too readily to enable it to be characterized. MAA decomposes slowly in the presence of copper(II) nitrate and it was not possible to isolate an arsineoxide complex. Copper(II) chloride and copper(II) bromide are also easily reduced by MAA and the products of these reactions were the colourless crystalline 1:1 complexes of MAA with copper(I). These complexes were insoluble in nitromethane, nitrobenzene and other organic solvents and

it was not possible to carry out conductance measurements. It is most likely that they are salts, [Cu-(MAA)₂][CuX₂] (where X = Cl or Br), rather than three coordinate monomers or halide bridged dimers.

When o-diphenylarsinoaniline (PAA), dissolved in absolute ether, was added to copper(II) perchlorate hexahydrate, dissolved in a small volume of ethanol, a precipitate of the dark red copper(II) complex, [Cu(PAA)₂](ClO₄)₂, was obtained. In the solid state this complex appears to be stable indefinitely. The magnetic moment of [Cu(PAA)₂](ClO₄)₂ which is about 1.9 B.M. at room temperature, is dependent on the field strength to about the same extent as found for [Cu(MAA)₂](ClO₄)₂ (Table I).

The complex formed by 1-amino-2-(diphenylarsino)-ethane (APE) with copper(II) perchlorate was not stable enough to isolate and characterize. The only product that was isolated from the reaction of APE with copper(II) perchlorate was a bright blue compound which is a copper(II) complex of β-aminoethyldiphenylarsineoxide (APEO).

To obtain [Cu(APEO)₂](ClO₄)₂, it is necessary to keep a mixture of APE and copper(II) perchlorate exposed to the air for several hours. It is most likely that the APE is oxidized by copper(II) according to the equation:

$$2Cu^{2+} + Ph_2AsCh_2CH_2NH_2 + H_2O \rightarrow$$
$$2Cu^+ + Ph_2As(O)CH_2CH_2NH_2 + 2H^+$$
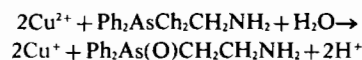
and that copper(II) is then regenerated by aerial oxidation.

[Cu(APEO)₂](ClO₄)₂ appears to possess a four-coordinate planar structure in which APEO functions as a bidentate ligand with oxygen and nitrogen donor atoms. Since APE complexes are usually free of infrared absorption bands between 800 and 900 cm⁻¹, a strong band at 858 cm⁻¹ in the spectrum of Cu(APEO)₂(ClO₄)₂ can be confidently assigned as the coordinated As–O stretching frequency. The As–O stretching frequency in tertiary arsine oxides usually lies in the range 870-910 cm⁻¹, and on coordination it is shifted to lower frequencies by about 40 cm⁻¹.[32] The ν_3 perchlorate band for [Cu(APEO)₂](ClO₄)₂ occurs at 1080 cm⁻¹ and there is no splitting evident, so it is concluded that the perchlorate groups are ionic.

The solid state reflectance spectrum of [Cu(APEO)₂](ClO₄)₂ shows a very broad band with a maximum at 14,900 cm⁻¹ and a shoulder at 16,300 cm⁻¹ (Table III). The spectrum is similar to those usually observed for planar or tetragonal copper(II) complexes in which the three transitions $^2B_{1g} \rightarrow {}^2A_{1g}$, $^2B_{2g}$, ^2E_g usually appear under one broad band envelop. The magnetic moment of [Cu(APEO₂](ClO₄)₂ is 1.93 B.M. at room temperature.

Attempts to prepare copper(I) complexes by reacting copper(II) salts with excess APE were unsuccessful, but the complex [Cu(APE)₂][CuI₂] was obtained from the reaction of APE with copper(I) iodide in aqueous potassium iodide solution. The «salt like» structure is proposed but no direct evidence can be given for it because of the extremely low solubility of the compound in all the common organic solvents.

(32) Goodgame D.M.L. and Cotton F.A., *J. Chem. Soc.*, 2298 (1961).

Experimental Section

Nickel(II) Complexes. (Analytical data are given in Table VI).

(i) *Nickel(II) Salts.* Nickel(II) bromide, nickel(II) iodide and nickel(II) perchlorate hexahydrate were obtained from the reaction of nickel(II) oxide with the appropriate acid. An ethanol solution of nickel-(II) thiocyanate was prepared by mixing ethanol solutions of nickel(II) perchlorate hexahydrate and potassium thiocyanate in equivalent amounts and filtering off the precipitated potassium perchlorate. Nickel(II) chloride hexahydrate and nickel(II) nitrate hexahydrate were commercial analytical grade reagents.

(ii) *General Method for the Preparation of Complexes $Ni(MAA)_2X_2$.* $X = Cl, Br, I, NCS, NO_3, ClO_4$. A solution of MAA (0.42 g; 0.0021 mole) in hot ethanol was added to a filtered solution of 0.001 mole of the appropriate nickel(II) salt in ethanol. The complexes which formed as crystalline precipitates were collected on a sintered glass filter, washed with ethanol and absolute ether, and dried under vacuum at room temperature. In the case of the very sparingly soluble $Ni(MAA)_2I_2$ complex, a more coarsely crystalline precipitate was obtained if dichloromethane was used as the solvent for the MAA.

(iii) *General Method for the Preparation of Complexes $Ni(APE)_2X_2$.* $X = Cl, Br, I$. The preparations were carried out under nitrogen in a reaction flask fitted with a filtering device so that the complexes could be prepared, collected, washed, and dried under nitrogen; avoiding contact with moist air.

A solution of APE (0.69 g; 0.0025 mole) in dry benzene (approx. 60 ml) was added to a filtered solution of 0.001 mole of the required nicekl(II) salt in ethanol (approx. 5 ml). The ethanol and water present in the reaction mixture were then removed by distillation of their benzene azeotropic mixtures. After most of the ethanol and water had been thus removed, the complexes crystallized out. The complexes were collected on the filter, washed with dry benzene and petroleum ether, and dried in a stream of nitrogen for twenty minutes. The complexes were stored in a dessicator, but they could be handled in the normal laboratory atmosphere for short periods without noticeable hydrolysis occurring.

(iv) *General Method for the Preparation of Complexes $Ni(PAA)_2X_2$.* $X = Br, I, ClO_4$. The preparations were carried out as described above under (iii) using 0.65 g (0.002 mole) of PAA and 0.0008 mole of the required nickel(II) salt. The complexes slowly hydrolysed in the presence of moist air with the formation of PAA and the hydrated nickel(II) salt.

Copper(II) Complexes. (Analytical data are given in Table VII).

Copper(II) Salts. Copper(II) perchlorate hexahydrate was obtained from the reaction of copper(II) oxide with aqueous perchloric acid. Copper(II)

chloride dihydrate and copper(II) bromide were commercial analytical grade reagents. Copper(I) iodide was prepared according to the procedure in Inorganic Syntheses.[33]

(i) *Bis(o-dimethylarsinoaniline)copper(II) perchlorate.* $[Cu(MAA)_2](ClO_4)_2$. A cold solution (about −20°C) of MAA (0.43 g) in dichloromethane (30 ml) was added to a cold solution (about −20°C) of copper(II) perchlorate hexahydrate (0.40 g) in ethanol (10 ml). Red-brown crystals of $[Cu(MAA)_2](ClO_4)_2$ slowly separated and the reaction mixture was kept at −20°C until crystallization appeared to be complete (about 30 minutes). The crystals were collected and washed with cold ethanol and absolute ether and dried under vacuum at room temperature. Samples were stored in sealed evacuated tubes.

$[Cu(MAA)_2](ClO_4)_2$ was also formed as an immediate red-brown microcrystalline precipitate on mixing solutions of MAA and $Cu(ClO_4)_2 \cdot 6H_2O$ in ethanol at room temperature.

(ii) *Bis[(o-aminophenyl)dimethylarsine oxide]copper(II) perchlorate ethanolate* $Cu(MAA)_2(ClO_4)_2 \cdot C_2H_5OH$. MAA (0.30 g) was added to excess copper-(II) perchlorate hexahydrate (1.40 g) in ethanol (total volume about 40 ml) and the combined solution was heated under reflux for about 20 minutes. After cooling, a small quantity of colourless crystals was removed by filtration. The filtrate was slightly acidified by adding 1 drop of 70% perchloric acid and then kept exposed to the air for about two days. The green crystalline complex which formed was collected and washed with ethanol. Attempts to recrystallize the complex resulted in its decomposition into tarry residues.

(iii) *Bis(o-dimethylarsinoaniline)copper(I) dichlorocuprate(I).* $[Cu(MAA)_2][CuI_2]$. An excess of MAA (0.48 g) was added to copper(I) chloride dihydrate (0.25 g) in ethanol (total volume about 60 ml). A dark red-brown colouration appeared for an instant then the solution became colourless and a colourless crystalline precipitate of the complex formed.

(iv) *Bis(o-dimethylarsinoaniline)copper(I) dibromocuprate(I).* $[Cu(MAA)_2][CuBr_2]$. This colourless crystalline precipitate was prepared from copper(II) bromide (0.30 g) and MAA (0.44 g) in ethanol by the use of a procedure similar to (iii) above.

(v) *Bis(o-diphenylarsinoaniline)copper(II) perchlorate.* $[Cu(PAA)_2](ClO_4)_2$. A solution of PAA (0.35 g) in absolute ether was added to a solution of copper(II) perchlorate hexahydrate (0.20 g) in the minimum volume of ethanol. The dark red crystalline precipitate which formed immediately was collected and washed with absolute ether.

(vi) *Bis(β-aminoethyldiphenylarsineoxide)copper(II) perchlorate.* $[Cu(APEO)_2](ClO_4)_2$. APE (0.55 g) was added to copper(II) perchlorate hexahydrate (0.37 g) in ethanol (total volume approx. 60 ml). A pale

(33) Kauffman G.B. and Pinnell R.P., *Inorg. Syntheses*, **6**, 3 (1960).

blue amorphous precipitate of indefinite composition formed immediately while $Cu(APEO)_2(ClO_4)_2$ crystallized slowly over a period of about 24 hours. The combined precipitates were collected and extracted with boiling ethanol (2×75 ml). $[Cu(APEO)_2](ClO_4)_2$ which dissolves in the hot ethanol separates on cooling as large royal blue crystals.

(vii) *Bis(1-amino-2-diphenylarsinoethane)copper(I) diiodocuprate(I).* $[Cu(APE)_2][CuI_2]$. A solution of APE (0.14 g) in ethanol was added to copper(I) iodide (0.10 g) dissolved in concentrated aqueous potassium iodide solution. The white microcrystalline precipitate which formed was collected and washed with water, ethanol and ether.