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Metal Complexes of some Hybrid Bidentate Ligands Containing Tertiary Arsine and Primary Amine Donor Groups. I. Compounds of Mn, Fe and Co

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Some first transition series metal complexes of the two new tertiary arsine - primary amine bidentate ligands, o—dimethylarsinoanilline (MAA) and 1—amino—2—(diphenylarsino)ethane (APE), have been prepared, and their structure ellucidated by physico-chemical studies.

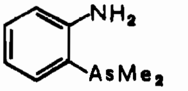
Octahedral manganese(II) compounds of the type $Mn(MAA)X_2$ *(where* $X = Br$ *or* ClO_4*), and manganese(I) compounds of formula* $[Mn(lig)_2(CO)Br]$ *(where lig = MAA or APE) have been isolated, while the octahedral iron(II) compound* $[Fe(MAA)_3](ClO_4)_2$ *was obtained. Values of the ligand field parameters Dq and B have been calculated from the absorption spectrum of this compound.*

Cobalt(II) complexes of MAA could be obtained from preparations carried out under dry nitrogen, but in the presence of air cobalt(III) compounds could be isolated.

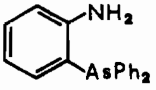
Introduction

Much work has been carried out upon bidentate ligands of the so-called «hybrid» type, in which one of the donor atoms is of the «soft» variety and the other a «hard» donor. Examples of such ligands are those containing two group V elements *e.g.* N and P or N and As.

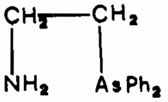
Due to problems in synthesis, bidentate ligands of the N—As variety have previously been prepared in which the nitrogen atom is either secondary or tertiary rather than primary. Recently we reported the synthesis of three new ligands of the N—As variety in which the N donor is a nitrogen of a primary amine, *viz.* *o*—dimethylarsinoaniline (MAA; I), *o*—diphenylarsinoaniline (PAA; II) and 1—amino—2—(diphenylarsino)ethane (APE; III). In this paper we report upon complexes of some first transition series metals with these ligands.



I



II



III

Manganese Compounds. Manganese(II) in its coordination compounds exhibits a marked preference for donor atoms of high electronegativity. Tertiary phosphine and tertiary arsine ligands display only a weak ability to complex with manganese(II) salts and the complexes dissociate readily in the presence of polar solvents. Difficulties encountered in preparing and preserving such complexes are so great that only a small number have been reported in the literature.[2]

o-phenylenebis(bimethylarsine) forms a series of high spin octahedral complexes $Mn(diars)_2X_2$ (where $X = Cl$, Br, I). These complexes were prepared under anhydrous conditions in dioxan.[3] Triphenylarsine and triphenylphosphine have been reported to form high spin four coordinate complexes with manganese(II) halides of the type $MnX_2(EPh_3)_2$ and $[Mn(EPh_3)_4]X_2$ (where $E = P$ or As).[4] However when these preparations were repeated, only complexes of triphenylphosphineoxide or triphenylarsineoxide were obtained.[5] (2'—pyridylamino)diphenylphosphine forms a 3:1 complex with manganese(II) bromide but the magnetic moment of the complex was not reported.[6]

Some manganese(II) complexes have been obtained from the oxidation of manganese(0) or manganese (I) carbonyl derivatives. Both $[Mn(CO)_3(diars)Br]$ and $[Mn(CO)_3(diars)]$ are oxidized by bromine with the formation of the manganese(II) complex, $[MnBr_2(CO)_2(diars)]$.[7] Nitric acid and other oxidizing agents have been used to oxidize $[Mn(diphos)_2(CO)_2]Br$ to $[Mn(diphos)_2(CO)_2](ClO_4)_2$, (where diphos = 1,2—bis (diphenylphosphino)ethane). These manganese(II) carbonyl derivatives are of the low spin type with one unpaired electron.[8]

Complexes of *o*—dimethylarsinoanaline with manganese(II) bromide and manganese(II) perchlorate were obtained by adding MAA dissolved in benzene to a concentrated solution of the hydrated manganese(II) salt in ethanol, and then removing the ethanol and water from the reaction mixture by distilling their azeotropic mixtures with benzene. A nitrogen atmosphere was necessary to protect the complexes from moist air. The colourless crystalline complexes Mn-

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(4) L. Naldini, *Gazz., Chim. Ital.*, 90, 1337 (1960).
(5) B. Chiswell, unpublished results.
(6) W. Seidel and H. Scholer, *Z. Chem.*, 7, 431 (1967).
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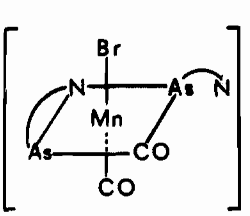
$(MAA)Br_2$, and $Mn(MAA)_2(ClO_4)_2$ were thus obtained. $Mn(MAA)_2(ClO_4)_2$ was hydrolysed particularly rapidly in air and its physical properties were not investigated. It is most likely a high spin six coordinate complex with coordinated perchlorate groups.

The magnetic moment of $Mn(MAA)Br_2$ at room temperature was 5.78 B.M. High spin manganese(II) complexes are expected to show magnetic moments close to the spin only value of 5.92 B.M. irrespective of the stereochemistry and independent of temperature. A polymeric six-coordinate structure with bromide bridges can be envisaged for the $Mn(MAA)Br_2$ complex. It is possible that a weak antiferromagnetic interaction via the bromide bridges produces a magnetic moment which is slightly less than the spin only value. Anhydrous manganese(II) bromide itself has $\mu_{eff} = 5.75$ at 300°K but the magnetic susceptibility is only slightly field dependent at low temperatures.[9] Antiferromagnetic exchange between manganese(II) ions across bromide bridges is therefore very weak.

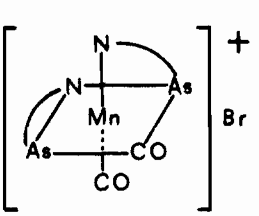
The reactions of *o*–dimethylarsinoaniline and 1–amino–2–diphenylarsinoethane with bromopentacarbonylmanganese(I) were also investigated. It was found that, in each case, three carbonyl groups were replaced by two ligand molecules. The yellow complexes $Mn(MAA)_2(CO)_2Br$ and $Mn(APE)_2(CO)_2Br$ were diamagnetic and almost insoluble in common organic solvents.

Assuming that the manganese(I) is six coordinate, it is necessary to distinguish two possible structures for these complexes: one in which both ligands are chelating and the bromide is ionic and the other which has one ligand chelating, one ligand coordinated as a monodentate and the bromide coordinated. Because of the low solubilities of both complexes infrared spectra of the compounds in the solid (Table I) provide the only data with which it might be possible to distinguish the two structures.

In the C–O stretching region both complexes have two strong sharp bands which are diagnostic of a *cis*-arrangement of the carbonyl groups. It is therefore necessary to distinguish between the non-ionic(IV) and ionic structures (V).

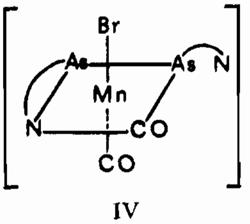


VI

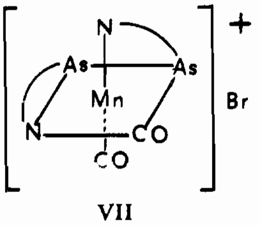


V

In addition a geometric isomer is possible for both structures in which the arsenic atoms are *cis* to each other *viz.* VI and VII.



IV



VII

Table I. Infrared Spectra of Manganese Compounds.

Compound	Peaks (cm^{-1})
(a) In the Carbonyl Stretching Region	
$Mn(MAA)_2(CO)Br$	1930(v.s.), 1828(v.s.)
$Mn(APE)_2(CO)_2Br$	1928(v.s.), 1848(v.s.)
(b) In the N–H Stretching Region	
$Mn(MAA)_2(CO)_2Br$	3310(s), 3215(m), 3180(m) 3150(m), 3120(m), 3020(s)
$Mn(APE)_2(CO)_2Br$	3310(m), 3240(m), 3195(m) 3115(s), 3085(s)

Intensities: v = very, s = strong, m = medium.

It was expected that the infrared spectra in the NH stretching region would enable free amino groups and coordinated amino groups to be distinguished. $Mn(MAA)_2(CO)_2Br$ has six bands ranging in frequency from 3310 to 3020 cm^{-1}. The wide frequency range suggests two overlapping sets of NH_2 stretches and this would be expected for the «chelate and monodentate» structure (IV) or (VI). However since a trans effect has been noted for octahedral manganese(I) complexes of this type,[10] it is likely that structure (VII) with one amino group trans to arsenic and the other trans to a carbonyl group would also display two sets of $-NH_2$ stretching frequencies. In $Mn(MAA)_2(CO)_2Br$ the highest frequency band at 3310 cm^{-1} represents a shift to lower frequency of 130 cm^{-1} when compared to the highest frequency (ν asym. band) of MAA at 3440 cm^{-1}.[1] Coordination of MAA as a monodentate ligand through the arsenic atoms will result in reduced electron density on the arsenic which will in part be transmitted by the aromatic ring to the ortho-amino group and the N–H stretching frequencies should be decreased slightly. In the platinum(II) and palladium(II) complexes where MAA is coordinated as a monodentate ligand the NH stretching frequencies of the «free» amino group are shifted to lower frequencies by 35-37 cm^{-1}. In (*o*–aminophenyl)trimethylarsonium iodide the shift to lower frequency of the N–H stretching vibrations is about 100 cm^{-1}. In $[Cu(MAA)_2][CuCl_2]$, where MAA is coordinated as a chelate to a monovalent metal ion, the low frequency shift in the N–H stretching vibrations is about 155 cm^{-1}.

The above comparisons suggest the «bis-chelate» structure (V) or (VII) for $Mn(MAA)_2(CO)_2Br$, but since N–H stretching frequencies are effected by H–bonding and other effects in the solid state, the conclusion must be regarded as tentative.

The situation is similar for the $Mn(APE)_2(CO)_2Br$ complex where a number of bands are observed in the region between 3310 and 3085 cm^{-1}. The highest frequency band at 3310 cm^{-1} represents a shift to lower frequency of 65 cm^{-1} from ν asym NH_2 of APE itself. For a monodentate NAS group there should be very little change in the N–H stretching frequencies, at least in the absence of H–bonding effects. In the complex $[Cu(APE)_2][CuI_2]$, the low frequency

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shift in the N—H stretching frequencies is about 115 cm^{-1}. Even smaller shifts were observed in the complex of APE with nickel(II). Again the infrared data favour a bis-chelate structure in $Mn(APE)_2(CO)_2Br$. The conductivities of the complexes, $Mn(MAA)_2(CO)_2Br$ and $Mn(APE)_2(CO)_2Br$ in nitromethane were measured. The maximum solubility of these complexes is about 10^{-3} *M* and conductances of solutions at this concentration were much less than expected for 1:1 univalent electrolytes, the values being 26.6 and 30.3 r.o. respectively. This may indicate that there is an equilibrium between the structural isomers (IV) and (V) in solution. Alternatively (V) may not be completely dissociated due to ion-pairing being enhanced by a hydrogen bonding interaction between the bromide ion and the amino groups in the cation. Abnormally low conductivities of amine complexes due to the association of cation and anion by hydrogen bonding have previously been reported.

Iron Compounds. The complexes formed by monodentate phosphine and arsine ligands with iron(II) or iron(III) salts are generally of low stability and dissociate readily, particularly in the presence of hydroxylic solvents.

Complexes of iron(II) and iron(III) salts with bidentate phosphine and arsine ligands are more stable and have been more throughly characterized. The 2:1 complexes in all cases have *trans*—octahedral structures and are diamagnetic. Examples are $[Fe(diarsine)_2X_2]$ and $[Fe(diphosphine)_2X_2]$ (where X=halide; diarsine=*o*—phenylenebis(dimethylarsine)(diars),[12] *cis*-bis(dimethylarsino)ethylene (*cis*—edas),[13] 1,2—bis(dimethylarsino)—3,4,5,6—tetrafluorobenzene (F—diars)[14] and diphosphine= *o*—phenylenebis(dimethylphosphino)ethane.[15] The 3:1 complexes $[Fe(diars)_3](ClO_4)_2$[16,17] and $[Fe(cis\text{—}edas)_3](ClO_4)_2$[13] have also been described. The electronic spectra of these complexes have been assigned using an octahedral ligand field model.[13,17] The spectra of the $[Fe(diars)_2X_2]$ (where X=Cl, Br, I), complexes can be explained in terms of a tetragonal D_{4h} ligand field model.[17]

Bidentate phosphine and arsine ligands also form low spin (S=½) octahedral complexes with iron(III), salts of the type $[Fe(diphosphine)_2X_2]^+$[15] and $[Fe(cis\text{—}edas)_3](ClO_4)_3$ have recently been prepared.[18] The electronic spectra of these two complexes and the corresponding tris- complexes of iron(III) with the bidentate ligands, 8—dimethylarsinoquinoline, 2,2′—bipyridyl and 1,10—phenanthroline have been compared. The spectra of these complexes have been interpreted using ligand field theory, and similar values for the ligand field parameters, Dq, B and C, were obtained for the series of complexes.[18] 8—dimethylarsinoquinoline and (2—pyridylamino)diphenylphosphine appear to be the only mixed group V donor bidentate ligands for which complexes with iron salts have been obtained. 8—dimethylarsinoquinoline forms low spin 3:1 complexes with both iron(II) and iron(III) salts.[19] The preparation of 3:2 and 3:1 complexes of (2—pyridylamino)diphenylphosphine with iron(II) salts has been reported.[6]

While some examples of iron complexes with multidentate arsine ligands are known,[20,21] there appears to have been no emphasis placed on the study of iron complexes with multidentate «hybrid» ligands.

Complex formation did not occur when *o*—dimethylarsinoaniline was added to iron(II) salts in ethanol but when *o*—dimethylarsinoaniline in excess benzene was added to iron(II) perchlorate hexahydrate in ethanol and the ethanol and water in the reaction mixture subsequently removed by distillation of their azeotropic mixtures with benzene, a crystalline purplish-red precipitate of tris(*o*—dimethylarsinoaniline) iron(II) perchlorate, $[Fe(MAA)_3](ClO_4)_2$, was formed. The complex was slowly hydrolysed in moist air with the liberation of some MAA and the formation of a brown powder. Freshly prepared $[Fe(MAA)_3](ClO_4)_2$ is apparently considerably less stable than the analogous complex with 8—dimethylarsinoquinoline which has been prepared in hydroxylic solvents.[19] The reaction of MAA with iron(II) chloride tetrahydrate and iron(III) chloride was also investigated, but stable complexes could not be isolated.

Six coordinate octahedral iron(II) complexes may have either high spin ($^5T_{2g}$) or low spin ($^1A_{1g}$) ground states. The low spin complexes are formed only by relatively high field ligands. Examples of such complexes are $[Fe(phen)_3]^{2+}$, $[Fe(diars)_3]^{2+}$ and $[Fe(CN)]^{2-}$. Actually the iron(II) tris(1,10—phenanthroline) system seems to lie close to the crossover point between high and low spin ground states because the tris(2—methyl—1,10—phenanthroline)iron(II) complex is high spin. Furthermore, the physical properties of some bis(1,10—phenanthroline)iron(II) complexes show a marked temperature dependence which can be ascribed to an equilibrium between singlet and quintet ground states. Probably the best known example is the complex $[Fe(phen)_2(NCS)_2]$ in which the magnetic moment drops sharply at about 170°K from 5.2 (430°K) to 0.65 (77°K).[22]

The complex $[Fe(MAA)_3](ClO_4)_2$ is weakly paramagnetic with $\mu_{eff}=1.09$ B.M. at room temperature. Magnetic moments of this order are commonly observed for low spin iron(II) complexes.[23] Magnetic moments of about 1.0 B.M. are equivalent to molar susceptibilities of about 500×10^{-6} which are too high to be ascribed entirely to temperature independent paramagnetism. High spin iron(II) or iron(III) complexes have molar susceptibilities of about $10{,}000\times10^{-6}$ and 15.000×10^{-6} respectively and the presence of only 2-3% of such complexes as impurities can add about 300×10^{-6} to the molar susceptibility.

The diffuse reflectance spectrum of $[Fe(MAA)_3](ClO_4)_2$ in the region 12,000-27,000 cm^{-1} shows two

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(21) G.A. Barclay and R.S. Nyholm, *Chem. Ind. (London)*, 378 (1953).

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moderately intense maxima at 18,300 and 25,400 $\mathrm{cm^{-1}}$. Most likely these are ligand field bands and can be assigned as the two spin allowed ${}^1A_{1g}\rightarrow{}^1T_{1g}$ and ${}^1A_{1g}\rightarrow{}^1T_{2g}$ transitions expected for the low spin d^6 configuration in an octahedral field. The departure from regular octahedral symmetry in $Fe(MAA)_3(ClO_4)_2$ apparently is not sufficient to produce observable band splittings in low resolution spectra. If the departure from octahedral symmetry can be ignored and the assignments given above are correct, then it is possible to calculate approximate values for the ligand field parameter Dq and B in the $[Fe(MAA)_3](ClO_4)_2$ complex.

The difference in the energies of the transitions ${}^1A_1\rightarrow{}^1T_1$ and ${}^1A_1\rightarrow{}^1T_2$ is given approximately by 16B. (The term 8.4 $B^2/10$ Dq has been ignored. This term should be relatively small compared with 16B when Dq is large.[24])

$$16B = 25{,}400 - 18{,}300$$

$$B = 444\ \mathrm{cm^{-1}}$$

$$\text{with}\quad B = 444\ \mathrm{cm^{-1}}$$

$$\frac{\Delta E(A_1\rightarrow{}^1T_1)}{B} = \frac{18{,}300}{444} = 41.2$$

$$\text{and}\quad \frac{\Delta E({}^1A_1\rightarrow{}^1T_1)}{B} = \frac{25{,}400}{444} = 57.2$$

Referring to the Tanabe-Sugano diagram for the d^6 configuration and extrapolating slightly, these E/B values are found to correspond to a mean Dq/B value of 4.5.

whence $Dq = 2{,}000\ \mathrm{cm^{-1}}$

$$\text{Alternatively, the ratio}\quad \frac{\Delta E({}^1A_1\rightarrow{}^1T_2)}{\Delta E({}^1A_1\rightarrow{}^1T_1)} = \frac{25{,}400}{18{,}300} = 1.39$$

and referring to the Tanabe-Sugano diagram again, this ratio for the ${}^1A_1\rightarrow{}^1T_2$ and ${}^1A_1\rightarrow{}^1T_1$ transitions occurs at $Dq/B = 3.8$ which corresponds to E/B values for the transitions of 49.7 and 35.9.

$$\text{thus}\ B = \frac{25{,}400}{49.7}\ \text{or}\ \frac{18{,}300}{35.9} \simeq 510\ \mathrm{cm^{-1}}$$

$$\text{and}\ Dq = 510 \times 3.8 = 1940\ \mathrm{cm^{-1}}.$$

The discrepancies in the results of the two calculations are fairly small and the mean values are taken as estimates of Dq and B

$$\textit{i.e.}\quad Dq \approx 1970\ \mathrm{cm^{-1}}$$

$$B \approx 470\ \mathrm{cm^{-1}}$$

$$\text{and}\ \beta = B/_{B_0} \simeq 0.45$$

Only a few Dq values for other ligands in low spin iron(II) complexes aret available for comparison:

For $[Fe(CN)_6]^{4-}$: $Dq = 3140\ \mathrm{cm^{-1}}$, $B = 400\ \mathrm{cm^{-1}}$(24)

$[Fe(diars)_3]^{2+}$: $Dq = 2490\ \mathrm{cm^{-1}}$, $B = 325\ \mathrm{cm^{-1}}$(26)

and for $[Fe(bipy)_3]^{2+}$ it has been estimated that Dq lies in the range 1650-1900 $\mathrm{cm^{-1}}$.[25] The Dq value estimated for MAA in $[Fe(MAA)_3](ClO_4)_2$ cannot be compared directly with that of ethylenediamine ($Dq \approx 1{,}100\ \mathrm{cm^{-1}}$) or *o*–phenylenediamine ($Dq \approx 1{,}000\ \mathrm{cm^{-1}}$) in the complexes $[Fe(en)_3]^{2+}$ or $[Fe(opda)_3]Br_2$ since these are high spin.[26,27] The ligand field splitting parameters would be greater in a low spin iron(II) complex because the e_g orbitals are now empty allowing closer-ligand approach.[24] The Dq value of 2,320 $\mathrm{cm^{-1}}$ for ethylenediamine in the low spin d^6 complex, $[Co(en)_3]^{3+}$,[23] cannot be used for comparison either because of the higher charge on this complex. In the hypothetical low spin $[Fe(en)_3]^{2+}$ complex, Dq should be roughly 60-70% of the value in $[Co(en)_3]^{3+}$. A value of about 1,500 $\mathrm{cm^{-1}}$ can be taken as an estimate of the Dq parameter in the hypothetical low spin iron(II) diamine complexes.

It can readily be seen, then, that the Dq value obtained for MAA is intermediate between that of diamine ligands and *o*–phenylenebis(dimethylarsine). This result would be predicted from the rule of average environment.

According to Jørgensen the nephelauxetic ratio β can be factorized to a good approximation into a ligand function and central metal ion function, *viz.*,

$$1-\beta = h(\text{ligands}) \,.\, k(\text{central ion}).^{6}$$

A value of $h = 4.0$ has been calculated for *o*–phenylenebis(dimethylarsine). Since $\beta = 0.36$ has been found from spectroscopic data for $Fe(diars)_3{}^{2+}$,[17] k for iron(II) can be obtained from the equation above. The result is $k\ (Fe^{II}) = 0.16$. This result is used to calculate $h = 3.4$ for MAA. For ethylenediamine $h = 1.5$.[26] Thus the nephelauxetic effect of MAA is intermediate between that of a diarsine ligand and a diamine ligand.

From the consistencies in these comparisons, it is concluded that the band assignments and estimates of Dq and B in $[Fe(MAA)_3](ClO_4)_2$ are basically correct.

Cobalt Compounds. The cobalt(II) complexes formed by *o*–phenylenebis(dimethylarsine) of general formula $Co(diars)_2X_2$ (where X = Cl, Br, I, or NCS) were first reported in 1950. They are all low spin with magnetic moments in the range 2.0-2.4 B.M.[28] The complexes behave as electrolytes in solution but probably have six-coordinate structures in the solid state.[29] Evidence based on infrared spectra has been obtained to show that the anions in $Co(diars)_2(NO_3)_2$ and $Co(diars)_2(ClO_4)_2$ are coordinated.[29] The latter complex exists in two forms for which X-ray structural data have been obtained. The orthorhombic form has weakly associated perchlorate ions, while in the monoclinic form the perchlorate groups are covalently

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Table II. Magnetic susceptibility data of complexes of MAA with cobalt(II).

Complex	method	$10^6\chi_g$	$10^6\chi_m$	$10^6\chi'_m$	T°K	μ_{eff}
	Faraday					
$Co(MAA)_2(NO_3)_2$	10 amp	15.003	8659	9022	291.3	4.58
	20 amp	14.986	8649	9013	291.3	4.58
	Faraday					
$[Co(MAA)_2I_2]$	10 amp	1.575	1114	1538	297.0	1.92
	20 amp	1.652	1168	1592	297.0	1.95
$[Co(MAA)_3](ClO_4)_2$	Gouy	1.356	1153	1695	296.0	2.0
$[Co(MAA)_2][CoCl_4]$	Faraday					
	10 amp	14.740	9645	10074	296.0	3.47*
	20 amp	14.878	9729	10158	296.0	3.49*
	Faraday					
$[Co(MAA)_2][CoBr_4]$	10 amp	11.370	9457	9931	296.7	3.45*
	20 amp	11.527	9504	9978	296.7	3.46*
$[Co(MAA)_2Cl_2]_2[CoCl_4]$	Gouy	6.380	7968	8828	296.0	4.57

* μ_{eff} calculated per cobalt atom.

bonded to the cobalt.[30] The magnetic moment of the monoclinic form is 2.00 B.M. which is in the range expected for six coordinate low spin cobalt(II) complexes. The 3:1 complex $[Co(diars)_3](ClO_4)_2$ with $\mu_{eff} = 1.92$ B.M. has also been obtained.[16]

The cobalt(III) complexes of formula $[Co(diars)_2X_2]^+$, (where X = Cl, Br, or I) have been obtained in *cis* and *trans* isomeric forms which have been differentiated by means of their electronic absorption spectra.[31] Studies of the reaction kinetics of these complexes have recently been carried out.[32]

1,2–bis(dimethylarsino)–3,4,5,6–tetrafluorobenzene (F–diars) forms cobalt(II) complexes which are similar to those of diarsine but the F–diars complexes are exceedingly readily oxidized to the cobalt(III) complexes.[33]

Only cobalt(III) complexes of *cis*–bis(dimethylarsino)ethylene (*cis*–edas) have been described in the literature to the present time *e.g.* *trans*$[Co(cis\text{–}edas)_2Br_2]ClO_4$.[13]

8–dimethylarsinoquinoline forms low spin planar 2:1 complexes with cobalt(II) perchlorate. The high orbital contributions to the magnetic moment, μ_{eff} 2.8 B.M., supports the postulated planar stereochemistry.[19]

Tertiary arsines with more than one aryl substituent have only a weak ability to complex with cobalt(II) salts. 1–(2′–pyridyl)–2–diphenylarsinoethane forms high spin 2:1 complexes with cobalt(II) halides but the coordination number is only four with tetrahedral stereochemistry. In these complexes the ligand does not act as a chelate and coordinates only through the pyridyl nitrogen atom.[34]

The 2:1 complex formed by (2–pyridyl)diphenylarsinomethane with cobalt(II) thiocyanate exists in two forms. Both have high spin electronic configurations, one form being octahedral and the other tetrahedral with the arsenic atoms of the ligands not involved in coordination.[35]

The reaction of *o*–dimethylarsinoaniline (MAA) with cobalt(II) salts in ethanol under nitrogen yields crystalline complexes of either 1:1, 2:1, or 3:1 stoichiometry as determined by the particular cobalt(II) salt. For cobalt(II) perchlorate only a 3:1 complex was isolated irrespective of the ligand to metal ratio used in the preparation. Similarly, cobalt(II) chloride and cobalt(II) bromide gave only 1:1 complexes, whilst cobalt(II) iodide and cobalt(II) nitrate gave only 2:1 complexes. The products obtained from the reactions of MAA with cobalt(II) thiocyanate were of indefinite composition. When the preparations were carried out in air, cobalt(III) complexes containing the cations trans $[Co(MAA)_2X_2]^+$ were obtained.

The complexes formed by *o*–diphenylarsinoaniline with cobalt(II) salts were unstable and none were definitely characterized. All attempts to prepare cobalt(II) complexes of 1–amino–2–diphenylarsinoethane were unsuccessful.

1:1 Cobalt(II) Complexes. Complexes of empirical formula $Co(MAA)Cl_2$ and $Co(MAA)Br_2$ were obtained as dark green-blue and dark brown-green crystalline precipitates on treating the appropriate cobalt(II) salt with MAA in ethanol under nitrogen. The complexes were only slightly soluble in polar organic solvents producing blue solutions under nitrogen which, however, were oxidized rapidly in the presence of air. As crystalline solids the complexes appeared to be stable in air.

Table III. Reflectance spectra for MAA complexes of cobalt(II).

Complex	Band frequencies (cm^{-1})
$[Co(MAA)_2][CoCl_4]$	13,900, 14,600, 15,100(sh), 15,800
$[Co(MAA)_2][CoBr_4]$	13,300, 13,900, 14,400(sh), 14,900, 15,400
$Co(MAA)_2(NO_3)_2$	17,500(sh), 19,000(sh), 20,500, 22,500(sh)
$Co(MAA)_2I_2$	14,100, 21,500.

The magnetic moments calculated assuming the formulae $Co(MAA)Cl_2$ and $Co(MAA)Br_2$ were 3.48 and 3.46 B.M. respectively (Table II). These results do not compare with those expected for either high spin

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(31) T.M. Dunn, R.S. Nyholm, and S. Yamada, *J. Chem. Soc.* (*A*), 1564 (1962).

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Table IV. Some infrared band assignments for the MAA complexes of cobalt (II)

(a) N—H stretching frequencies (cm^{-1})

$[Co(MAA)_2][CoCl_4]$	3240, 3195, 3150, 3140(sh), 3120, 3100(sh).
$[Co(MAA)_2][CoBr_4]$	3235, 3195, 3155, 3140(sh), 3120.
$Co(MAA)_2(NO_3)_2$	3270, 3235, 3190, 3140, 3110.
$Co(MAA)_2I_2$	3225, 3165.
MAA	3440, 3355.

(b) CH_3 rocking frequencies and As—$(CH_3)_2$ stretching frequencies.

Compound	CH_3 rocking		As—$(CH_3)_2$ stretching
$[Co(MAA)_2][CoCl_4]$	860	915	632, 620, 612, 605, 595.
$[Co(MAA)_2][CoBr_4]$	860	920	620, 610, 605, 595.
$Co(MAA)_2(NO_3)_2$	870	905	612, 598.
$Co(MAA)_2I_2$	860	920	605, 590.
MAA	850	890	585, 575(sh).

(3 unpaired electrons) or low spin (1 unpaired electron) cobalt(II) complexes. Furthermore, the reflectance spectra of the solids show strongly structured bands near 15,000 cm^{-1} (Table III) which agree closely with the known spectra of $[CoCl_4]^{2-}$ and $[CoBr_4]^{2-}$ in this region.[36] Taking 4.50-4.70 and 4.63-4.77 as the established ranges of the magnetic moments for the $[CoCl_4]^{2-}$ and $[CoBr_4]^{2-}$ anions respectively,[37] the calculated ranges for the magnetic moments of the cobalt in the cation of $[Co(MAA)_2][CoCl_4]$ and $[Co(MAA)_2][CoBr_4]$ are 1.49-2.01 and 1.08-1.57 respectively. The μ_{eff} calculated for the cation depends critically on the μ_{eff} value assumed for the anion, since a small change in the assumed value of μ_{eff} (anion) produces a considerably larger change in the value calculated for μ_{eff} (cation). It is therefore difficult to determine μ_{eff} (cation) precisely, but the results suggest a value which is close to the spin only value for one unpaired electron. It has been postulated that in the methylisonitrile complexes $[Co(CNCH_3)_4][CoX_4]$ (where X=Cl or Br), the $[CoX_4]^{2-}$ ion functions as a bridging group so that the cobalt in the cation is in an essentially octahedral environment and has $\mu_{eff}=1.82$ B.M. It appears likely that the situation in the $[Co(MAA)_2][CoX_4]$ complexes is similar because the magnetic moment for the cobalt in the cation must be close to the spin only value of 1.73 B.M. suggesting octahedral rather than planar coordination.

2:1 Cobalt(II) Complexes. A pink-coloured 2:1 complex was isolated from the reaction of MAA with cobalt(II) nitrate under nitrogen. Solutions of the complex were readily oxidized in air and the solid compound was also oxidized slowly in the presence of moist air.

In the infrared spectrum of $Co(MAA)_2(NO_3)_2$ the N–H stretching frequencies, the As–$(CH_3)_2$ stretching frequencies, and the CH_3 rocking frequencies are shifted from their positions in MAA (Table IV) and it is concluded that MAA is coordinated as a bidentate ligand in $Co(MAA)_2(NO_3)_2$. In addition, asymmetric and symmetric NO_3 stretching vibrations were observed in the infrared spectrum at 1430 and 1320 cm^{-1} with no absorption band at 1390 cm^{-1}, which indicates that both nitrate groups are coordinated.[38] Thus $Co(MAA)_2(NO_3)_2$ has a six coordinate structure with an $As_2N_2O_2$ donor set.

The room temperature magnetic moment of the complex was 4.58 B.M. (Table II). This result was reproducible for samples obtained from several preparations. The moment is somewhat lower than that usually obtained for high spin octahedral cobalt(II) complexes. (4.8-5.2 B.M.)[39] Since the complex $Co(MAA)_2I_2$, donor set $As_2N_2I_2$ is of the low spin type, the donor set of $As_2N_2O_2$ must lie close to the crossover point between the quartet and doublet ground states and it is posible that the separation between the quartet and doublet ground states for the field of $As_2N_2O_2$[17] is small enough to allow a partial thermally dependent population of both states; thus accounting for the low room temperature magnetic moment of 4.58 B.M. If such a situation did exist then the magnetic moment should show a strong temperature dependence. For example, the bis complex of 2,6–pyridinedialdihydrazone with cobalt(II) iodide, for which a quartet-doublet equilibrium has been proposed, has $\mu_{eff}=3.69$ at 373°K and $\mu_{eff}=1.90$ at 80°K.[39] The magnetic moments of $Co(MAA)_2(NO_3)_2$ were measured over a temperature range but only a small variation was observed (Table V). The low room temperature moment of $Co(MAA)_2(NO_3)_2$ therefore apparently arises from a loss of orbital degeneracy of the $^4T_{1g}$ ground state due to the low symmetry of the ligand field.

A theoretical account of the behaviour of the ma-

Table V. Magnetic moments of $Co(MAA)_2(NO_3)$ at various temperatures.

μ_{eff}(B.M.)	Temp. K	$\frac{kT}{\lambda_o}$
4.62	291.9	—0.93
4.62	231.4	—0.70
4.58	173.4	—0.45
4.48	111.6	—0.31
4.13	77.0	—1.17

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gnetic properties of the $^4T_{1g}$ ground term under simultaneous spin orbit coupling and an axial ligand field has been given, and values of μ_{eff} as a function of kT/λ have been calculated for various selected values of the parameter A, k and ν,[40] (where ν is proportional to the splitting of the $^4T_{1g}$ level by the axial ligand field component, k is a reduction factor for the t_{2g} orbitals, and A is a factor that allows for mixing of the upper $^4T_{1g}(P)$ state with the ground term). The effect of increasing distortion is to bring μ_{eff} closer to the spin only value at room temperature and to decrease the variation with temperature. It was not possible to determine a value for A in Co(MAA)$_2$(NO$_3$)$_2$ because the complete electronic spectrum was not obtained, consequently, estimation of values for the other parameters could not be made. But it was noted that the values of μ_{eff} calculated for certain combinations of A, k, and ν agree closely with the experimental μ_{eff} value for Co(MAA)$_2$(NO$_3$)$_2$ (Table VI). The set $A=1.4$, $k=0.8$, and $\nu=10$ probably are the most appropriate to the situation in Co(MAA)$_2$(NO$_3$)$_2$. The solid state reflectance spectrum of Co(MAA)$_2$(NO$_3$)$_2$ in the visible region shows a very broad, weak, structured band centered near 20,000 cm^{-1}. For octahedral high spin cobalt(II) complexes a multiple absorption band is usually observed in the vicinity of 20,000 cm^{-1} and is assigned principally to the $^4T_{1g}\rightarrow{}^4T_{1g}(P)$ transition. The structure of the band is generally attributed to superposed spin forbidden transitions to doublet states. For certain values of the ligand field parameters, *viz.* $Dq/B\approx1.3$, it is possible that a component of the visible absorption band can be assigned to the weak two-electron transition $^4T_{1g}\rightarrow{}^4A_{2g}$.[41] The structure in the absorption band in the spectrum of Co)MAA)$_2$(NO$_3$)$_2$ is not well resolved but it appears that there may be four components at 17,500, 19,000, 20,500, and 22,500 cm^{-1}. The low energy component may be attributed to the transition to the $^4A_{2g}$ level and the other components to transitions to he $^4T_1(P)$ level, which is split because of the low symmetry ligand field present in Co(MAA)$_2$(NO$_3$)$_2$.

Table VI. Comparison of experimental μ_{eff} of Co(MAA)$_2$(NO$_3$)$_2$ with some calculated values from reference 40

kT λ_o	—1.0	—0.8	—0.6	—0.4	—0.3
Experimental μ_{eff} for Co(MAA)$_2$(NO$_3$)$_2$	4.62	4.60	4.55	4.41	4.09
A=1.0 K=1.0 ν=2.0	4.64	4.62	4.56	4.41	4.26
A=1.2 K=0.8 ν=0	4.63	4.58	4.47	4.25	4.08
A=1.4 K=0.8 ν=10	4.63	4.62	4.57	4.45	4.36
A=1.5 K=0.6 ν=—5	4.62	4.58	4.51	4.38	4.26

Brown crystals of Co(MAA)$_2$I$_2$ were obtained from the reaction of MAA with cobalt(II) iodide in ethanol under nitrogen. Solutions of Co(MAA)$_2$I$_2$ were readily oxidized in the presence of air, but in the solid state the compound appears to be stable in air for a long period.

The infrared spectrum of Co(MAA)$_2$I$_2$ (Table IV) indicates that the MAA is coordinated as a bidentate chelate. The magnetic moment of Co(MAA)$_2$I$_2$ is 1.95 B.M., which is in the range normally observed for six coordinate low spin cobalt(II) complexes. Most of the bis- complexes formed by bidentate phosphine and arsine ligands with cobalt(II) iodide have higher moments in the range 2.2-2.5 B.M. These complexes usually dissociate in solution to give five-coordinate species, but both iodides may be weakly coordinated in the solid state. Examples of complexes of this type with their reported magnetic moments are given in Table VII. The complexes Co(ligand)$_2$I$_2$ formed by the disecondary phosphines R(H)P–CH$_2$–CH$_2$–P(H)R (where R=Et or Ph) have lower magnetic moments, 1.77 and 1.86 B.M. respectively, consistent with the six coordinate structures proposed for them.[42] The reflectance spectrum of Co(MAA)$_2$I$_2$ in the region 12,000-27,000 cm^{-1} exhibits two bands at 14,000 cm^{-1} and 21,500 cm^{-1}. The highest energy band at 21,500 cm^{-1} may correspond to the $^2E_g\rightarrow{}^2A_{1g}$ transition for octahedral symmetry and the lower energy band to a component of the $^2E_g\rightarrow{}^2T_{1g}$, ^2T_g transition. It would be necessary to obtain the spectrum in the region 5,000-12,000 cm^{-1} in order to make a complete assignment.

Table VII. Magnetic moments reported for Co(ligand)$_2$I$_2$.

ligand	μ_{eff}	reference
P–N	2.7	46
As–As	2.4	28
P–P	2.21 or 1.92	47, 48

3:1 Cobalt(II) Complexes. The reaction of MAA with cobalt(II) perchlorate yields a red-brown crystalline complex of composition Co(MAA)$_3$(ClO$_4$)$_2$. This complex was extremely sensitive to oxidation. Even in the solid state samples changed in colour from red-brown to green during a few minutes exposure to air. The brick red coloured solution of the complex obtained under nitrogen was changed in an instant to bright green when exposed to air. A magnetic susceptibility measurement of the complex was made by packing a Gouy tube in a nitrogen-filled glove-box. The complex is low spin with a magnetic moment of 2 0 B.M. (Table II), which is consistent with a six-coordinate tris-chelate structure for the complex.

The Cobalt(III) Complexes of o–dimethylarsinoaniline. The complexes of MAA with cobalt(II) were readily oxidized by air to cobalt(III) complexes. In fact oxidation takes place so readily that when MAA was reacted with cobalt(II) salts in the presence of

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[40] B.N. Figgis, M. Gerloch, and J. Lewis, P.E. Mabbs, G.A. Webb, *J. Chem. Soc.* (A), 2086 (1968).

[41] A.B.P. Lever in « Inorganic Electronic Spectroscopy », Elsevier, Amsterdam (1967) and references therein.

[42] K. Issleib and H. Weichmann, *Z. Anorg. Allgem. Chem.*, *362*, 33 (1968).

Table VIII. Lowest energy ligand field and for *cis-* and *trans-* $[Co(L—L)_2X_2]^+$ complexes (cm^{-1})

Complex	Lowest energy ligand field band *cis-* isomer	*trans-* isomer
$[Coen_2Cl_2]^+$	18,600 (log ε_o 1.95)	16,100 (log ε_o 1.61)
$[Coen_2Br_2]^+$	18,100	15,200
$[Co(diars)_2Cl_2]^+$	20,400 (logε_o 28.0)	16,400 (log ε_o 1.85)
$[Co(diars)_2Br_2]^+$	19,600	15,700
$[Co(diars)_2I_2]$	18,500	15,200

air, cobalt(III) complexes were the only products normally isolated. The complexes obtained were of the type *trans*$[Co(MAA)_2X_2]^+$, (where X = Cl, Br, I, or NCS), and are typical diamagnetic six coordinate cobalt(III) complexes. When preparing the cobalt(III) complexes it was necessary to use the cobalt(II) salt in excess otherwise the MAA decomposed with the formation of dark-coloured tarry products. This decomposition occurred most rapidly for cobalt(II) perchlorate.

A green complex with a composition corresponding approximately to the formula $[Co(MAA)_3](ClO_4)_3$ was obtained, but even in the solid state this complex slowly developed a black colour. Similar decomposition in the presence of certain metal ions of other ligands containing primary aromatic amine groups *e. g.* 8—aminoquinoline, *o*—phenylenediamine and *o*—methylthioaniline, have been observed by other workers.[43]

Because an excess of the cobalt(II) salt was used, the cationic complexes were isolated in the first instance with the counter anions $[CoX_4]^{2-}$ (where X= Cl, Br, or NCS) containing cobalt(II). The $[CoX_4]^{2-}$ anions were replaced by Cl^-, Br^-, or ClO_4 by treating a solution of the $[Co(MAA)_2X_2]_2[CoX_4]$ complex in an organic solvent with an excess of a dilute aqueous solution of the appropriate acid (HX or $HClO_4$. The complexes $[Co(MAA)_2Cl_2]Cl\,.\,2H_2O$, $[Co(MAA)_2Br_2]Br\,.\,2H_2O$, $[Co(MAA)_2Cl_2]ClO_4H_2O$ and $[Co(MAA)_2(NCS)_2]ClO_4$ were thus obtained. Solutions of these complexes in polar organic solvents or dilute aqueous acids were stable for long periods.

Complexes of the type $[Co(L—L)_2X_2]^+$ (where L—L is a symmetrical bidentate ligand such as ethylenediamine (en) or *o*—phenylenebis(dimethylarsine), (diars), can exist in *cis-* and *trans-* isomeric forms but in the case of an unsymmetrical bidentate ligand such as *o*—dimethylarsinoaniline (As—N), four geometric isomers are theoretically possible.

The study of the electronic spectra of the complexes $[Co(MAA)_2X_2]^+$ (where X=Cl, Br, or I) in the visible region leads to the conclusion that X^- ligands are in positions trans to each other, but no decision could be reached regarding the arrangement of the arsenic and nitrogen donor atoms. In the following discussion the complexes are referred to as trans, but the prefix applies only to the arrangement of the X^- ligands.

Electronic spectral measurements have been used to differentiate the *cis-* and *trans-* isomers of $[Co(en)_2X_2]^+$ and $[Co(diars)_2X_2]^+$. The differentiation is based on the fact that the $^1A_{1g}\rightarrow{}^1T_{1g}$ transition for a regular octahedral cobalt(II) complex is split to a greater degree under D_{4h} symmetry (trans) than under C_{2v} symmetry (*cis*). Thus a component of the $^1A_{1g}\rightarrow{}^1T_{1g}$ transition appears at lower energy in the case of the trans- isomers. This is illustrated in Table VIII, with data taken from references 17, 31, and 44.

It can also be seen that although ethylenediamine stands below *o*—phenylenebis(dimethylarsine) in the spectrochemical series, the positions of the band maxima in the corresponding ethylenediamine and *o*—phenylenebis(dimethylarsine) complexes do not differ greatly. Because of the similarity of the spectra for the amine and arsine complexes, the same argument, based on the electronic spectra, can be used to determine the *cis-* and *trans-* arrangement of the halide ligands in $[Co(MAA)_2X_2]^+$ complexes. The arrangement of the arsenic and nitrogen donor atoms can be expected to have a negligible effect on the spectra. The frequencies of the lowest energy band in the spectrum of the complexes, $[Co(MAA)_2X_2]^+$ are 15,800 cm^{-1} (log ε_o=2.22) for the chloride, 14,800 cm^{-1} for the bromide, and 14,200 cm^{-1} for the iodide. It is interesting to note that the intensity of the band in *trans*$[Co(MAA)_2Cl_2]^+$ is higher than that in either *trans*—$[Co(diars)_2X_2]^+$ or *trans*—$[Co(en)_2Cl_2]^+$.

Additional data derived from the electronic spectra of the cobalt(III) complexes of MAA is collected in Table IX. The $^4T_2\rightarrow{}^4T_1(P)$ transition for the tetrahedral $[CoX_4]^{2-}$ anion was observed in the reflectance spectra of $[Co(MAA)_2X_2]_2[CoX_4]$ (where X=Cl or Br). The solution spectrum of $[Co(MAA)_2Cl_2]_2[CoCl_4]$ in nitrobenzene was similar to the solid state spectrum. A second component of the $^1A_{1g}\rightarrow{}^1T_{1g}$ transition for $[Co(MAA)_2Cl_2]^+$ was observed as a shoulder near 23,000 cm^{-1}. The complex $[Co(MAA)_2(NCS)_2]^+$ has an absorption maximum at 18,300 cm^{-1} (log ε_o=2.99). It is not possible to determine from the spectrum whether it is the *cis* or *trans-* isomer. While the complexes $[Co(MAA)_2X_2]^+$ have their absorption maxima at only about 400 cm^{-1} lower than the corresponding *trans*—$[Co(en)_2X_2]^+$ complexes (where X=Cl, Br, or I), the difference in the frequencies of the absorption maxima for the $[Co(MAA)_2(NCS)_2]^+$ and $[Co(en)_2(NCS)_2]^+$ complexes (*cis-* 19,800, *trans-* 19,700)[49] is about 1,400 cm^{-1}. The anomaly is also evident for the $[Co(diars)_2(NCS)_2]^+$ complex which absorbs at lower instead of higher energy than the $[Co(en)_2(NCS)_2]$ complexes.[44] A possible explanation for these discrepancies is to postulate that the thiocyanate group is S—bonded in the complexes of MAA and diars. This postulate is in keeping with the observation that the presence of

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(44) S. Yamada, *Coord. Chem. Rev.*, *2*, 83 (1967).

Table XI. Visible and ultraviolet spectra of the cobalt(III) complexes of MAA

Complex	solid state or solution	band maxima (cm^{-1})
$[Co(MAA)_2Cl_2]_2[CoCl_4]$	solid	14,600, 15,100, 15,900, 23,000 (sh).
$[Co(MAA)_2Cl_2]_2[CoCl_4]$	soln. $PhNO_2$	14,400, 15,000, 15,900, (2.90)*.
$[Co(MAA)_2Br_2]_2[CoBr_4]$	solid	13,700, 14,100, 14,800, 15,400.
$[Co(MAA)_2Cl_2]Cl \cdot 2H_2O$	solid	15,900, 23,000.
$[Co(MAA)_2Cl_2]ClO_4 \cdot H_2O$	soln. CH_3OH	15,800 (2.22), 23,000 (2.52), 28,900 (3.52), 34,600 (4.26), 40,000 (4.31).
$[Co(MAA)_2Cl_2]ClO_4 \cdot H_2O$	soln. $PhNO_2$	16,000 (2.55).
$[Co(MAA)_2Br]Br \cdot H_2O$	solid	14,800.
$[Co(MAA)_2I_2]I$	solid	14,200.
$[Co(MAA)_2(NCS)_2]ClO_4$	soln. CH_3OH	18,300 (2.99), 29,300 (3.73), 40,000.

* (Figures in brackets are the log ε_o values).

Table X. Conductance measurements for the cobalt(III) complexes of MAA.

Complex	concentration	solvent	conductance per mole
$[Co(MAA)_2(NCS)_2]ClO_4$	$3.31 \times 10^{-3}M$	CH_3OH	86.7r.o.
$[Co(MAA)_2Cl_2]ClO_4 \cdot H_2O$	$3.89 \times 10^{-3}M$	CH_3OH	87.8r.o.
	$1.02 \times 10^{-3}M$	CH_3NO_2	84.0r.o.
	$0.936 \times 10^{-3}M$	$PhNO_2$	23.8r.o.
$[Co(MAA)_2Cl_2]_2[CoCl_4]$	$0.889 \times 10^{-3}M$	$PhNO_2$	5.8r.o.

ligands which are supposed to be capable of back π–bonding favours S–bonding of the thiocyanate group to cobalt(III).[39]

A comparison of the infrared spectrum of $[(Co(MAA)_2(NCS)_2]ClO_4$ and $[Co(MAA)_2Cl_2]ClO_4 \cdot H_2O$ enables the following assignments to be made for the thiocyanate vibrational modes: C–N stretch 2120 cm^{-1}, C–S stretch 840 cm^{-1} and NCS bend 462 cm^{-1}, while the frequency of the C–N strech is high, the frequencies of the other modes are indicative of N–bonded thiocyanate. Either some other factor is responsible for the anomaly in the electronic spectra or the infrared criterion of distinguishing N– and S–bonded thiocyanate groups breaks down in this instance. The presence of only one C–N stretching frequency in $[Co(MAA)_2(NCS)_2]^+$ indicates a trans arrangement of the thiocyanate groups.

In the cobalt(III) complexes of MAA, the N–H stretching frequencies occur as broad structured bands between 3250 and 3100 cm^{-1} and 870 cm^{-1} whilst the $As–(CH_3)_2$ stretches occur at 620 and 605 cm^{-1}. The features of the vibrational spectra are similar to those in the nickel(II) and cobalt(II) complexes and are in support of their use as a criterion for bidentate coordination of MAA.

The complexes $[Co(MAA)_2Cl_2]ClO_4 \cdot H_2O$ has molar conductivities in various solvents which are typical of di–univalent electrolytes. The complex $[Co(MAA)_2(NCS)_2]ClO_4$ likewise behaves as a di–univalent electrolyte in methanol (Table X). In nitrobenzene a solution of $[Co(MAA)_2]_2 [CoCl_4]$ is almost non–conducting. However the absorption spectrum of the solution is similar to the reflectance spectrum of the solid (at least in the region where nitrobenzene is transparent) and tends to rule out the possibility of decomposition. If there is no decomposition, it must be assumed then, that the cations and anions are strongly associated in the nitrobenzene solution of $[Co(MAA)_2Cl_2]_2 [CoCl_4]$. Hydrogen–bonding between the amino–hydrogens and the chloro–ligands in the $[CoCl_4]^{2-}$ anion probably provides a mechanism for this association. The magnetic moment of $[Co_2(MAA)_2Cl^2]_2[CoCl_4]$ (Table II) also provides evidence for the presence of the $[CoCl_4]^{2-}$ anion.

Experimental Section

Monganese Complexes. bis(o–dimethylarsinoaniline) dicarbonylmanganese (1) bromide. It is necessary to carry out the following preparations under an atmosphere of nitrogen otherwise only red tarry products are formed.

$Mn(MAA)_2(CO)_2Br$, once isolated, is stable in the solid state. Bromopentacarbonylmanganese(I) (0.30 g) and MAA (0.44 g) dissolved in absolute ethanol (total volume approximately 40 ml) were heated under reflux until a yellow crystalline precipitate just began to separate (approx. 3 hours). The solution was then filtered and the filtrate allowed to stand overnight under nitrogen. The yellow crystals were collected and washed with ethanol. The yield was 0.15 g. (Analysis: $C_{18}H_{24}N_2AsBrMnN_2O_2$ requires C, 37.0; H, 4.1; N, 4.8; Mn, 9,4. Found; C, 37.0; H, 4.2; N, 4.7; Mn, 9.6%).

bis(1–amino-2–diphenylarsinoethane) dicarbonylmanganese (I) bromide. This complex was prepared similarly to the above from bromopentacarbonylmanganese(I) (0.60 g) and 1–amino–2–diphenylarsinoethane (1.30 g) in absolute ethanol (100 ml) under nitrogen. The complex was obtained as yellow crystals. Yield, 0.94 g. (*Analysis*: $C_{30}H_{32}As_2BrMnN_2O_2$ requires C, 48.9; H, 4.4; N, 3.8; Mn, 7.5. Found: C, 48.7; H, 4.3; N, 3.8; Mn, 7.6%).

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(45) A.H. Norbury and A.I.P. Sinha, *Quar. Rev.*, *24*, 82 (1970).

Table XI. Analytical Results for cobalt(II) and cobalt(III) complexes.

Complex	Description	Analysis for Carbon		Analysis for Hydrogen		Analysis for Nitrogen		Analysis for Cobalt	
		Calcd. %	Found %	Calcd. %	Found %	Calcd. %	Found %	Calcd. %	Found %
$[Co(MAA)_2][CoCl_4]$	dark bluish green crystals	29.4	29.4	3.7	3.7	4.3	4.3	18.0	18.0
$[Co(MAA)_2][CoBr_4]$	dark brownish green crystals	23.1	23.1	2.9	2.9	3.4	3.3	14.2	14.1
$Co(MAA)_2I_2$	brown crystals	27.2	27.2	3.4	3.5	4.0	4.0	8.3	8.2
$Co(MAA)_2(NO_3)_2$	pink crystals	33.3	33.3	4.2	4.4	9.7	9.6	10.2	10.2
$Co(MAA)_3(ClO_4)_2$	reddish-brown crystals	34.0	34.4	4.3	4.4	5.0	4.5	7.0	6.8
$[Co(MAA)_2Cl_2]_2[CoCl_4]$	dark green crystals	30.8	31.0	3.9	3.9	4.5	4.6	14.2	13.9
$[Co(MAA)_2Cl_2]Cl.2H_2O$	green crystals	32.3	31.9	4.7	4.7	4.7	4.6	9.9	9.9
$[Co(MAA)_2Cl_2]ClO_4H_2O$	green crystals	30.0	29.8	4.1	1	4.4	4.4	9.2	9.3
$[Co(MAA)_2Br_2]Br.H_2O$	green crystals	27.0	27.1	3.7	3.8	3.9	3.8	8.3	8.3
$[Co(MAA)_2I_2]I$	deep red crystals with a greenish black metallic lustre	23.1	23.3	2.9	3.1	3.4	3.4	7.1	7.0
$[Co(MAA)_2(NCS)_2]_2[Co(NCS)_4]$	dark violet crystals	33.6	33.6	3.4	3.3	11.8	11.6	12.4	12.4
$[Co(MAA)_2(NCS)_2]ClO_4$	red crystals	32.3	32.3	3.6	3.6	8.4	8.2	8.8	8.9

bis(o–dimethylarsinoaniline)manganese(II) perchlorate MAA (0.50 g) dissolved in benzene (60 ml) was added to manganese(II) perchlorate hexahydrate (0.45 g) in ethanol (10 ml) under nitrogen. When about three quarters of the solvent was removed by distillation a mass of fibrous white crystals formed. The product was collected and washed with boiling benzene and boiling petroleum ether (40–50°C) under nitrogen. The complex was rapidly hydrolysed in moist air. (*Analysis*: $C_{16}H_{24}Cl_2MnN_2O_8$ requires Mn = 8.5%. Found Mn = 8.8%).

dibromo(o–dimethylarsinoaniline)manganese(II). This colourless crystalline compound was prepared similarly to the foregoing compound from anhydrous manganese (II) bromide (0.33 g) and MAA (0.65 g). Although the quantity of MAA used represents more than two equivalents, only the 1:1 complex formed. (*Analysis*: $C_8H_{12}AsBr_2MnN$ requires C, 23.3; H, 2.9; N, 3.4; Mn, 13.3. Found: C, 23.5; H, 3.2; N, 3.2; Mn, 13.6%).

Iron Compound. tris(o–dimethylarsinoaniline)iron (II) perchlorate. This preparation was carried out under nitrogen in a reaction flask fitted with a filter stick and still head. Freshly prepared iron (II) perchlorate solution (0.75 ml of 1.1 M aqueous solution) was diluted with ethanol (20 ml) and added to a solution of MAA (0.65 g) in benzene (75 ml). The solvents were distilled from the colourless solution until a reddish purple crystalline precipitate formed. The crystals were collected and washed thoroughly with boiling benzene and boiling petroleum ether (40-60°C), and dried in a stream of nitrogen. Samples were preserved by sealing in evacuated glass tubes. (*Analysis*: $C_{24}H_{36}As_3Cl_2FeN_308$ requires C, 34.1; H, 4.3; N, 5.0; Fe, 6.6%. Found: C, 34.7; H, 4.6; N, 4.7; Fe 6.7%). Magnetic Susceptibility Data for $Fe(MAA)_3(ClO_4)_2$: $10^6\chi_g = 0.0432$; $10^6\chi_M = 36.52$; $10^6\chi'_M, = 504.5$; T = 294.7°K whence $\mu_{eff} = 1.09$ B.M.

Cobalt Compounds. Cobalt (II) complexes of MAA are readily oxidized by air to cobalt (III) complexes, therefore all the preparations given below (i–v) were carried out under oxygen–free nitrogen in a reaction flask fitted with a "filter stick". The reaction products could then be collected washed and dried in an inert atmosphere. All solutions and solvents that were added to the reaction flask were added whilst they were boiling to eliminate any dissolved oxygen. Analytical results and the colours of the compounds are given in Table (XI)

(i) *bis(o–dimethylarsinoaniline)cobalt(II) tetrachlorocobaltate (II)*. A solution of MAA (0.25 g) in ethanol (25 ml) was added to a solution of cobalt (II) chloride hexahydrate (0.30 g) in ethanol (25 ml). After refluxing the deep–blue solution for a few minutes a dark bluish–green crystalline precipitate formed. The crystals were collected and washed successively with ethanol, 1:1 ethanol and petroleum ether, and petroleum ether. The complex was then dried with a stream of nitrogen for about twenty minutes.

(ii) *bis(o–dimethylarsinoaniline)cobalt(II) tetrachlorocobaltate (II)*. This compound was prepared similarly to (i) above using cobalt (II) bromide hexahydrate (0.40 g) and MAA (0.25 g).

(iii) *diiodobis(o–dimethylarsinoaniline)cobalt(II)*. This compound was prepared by a procedure similar to (i) and (ii) from cobalt(II) iodide hexahydrate (0.40 g) and MAA (0.37 g) in ethanol.

(iv) *dinitratobis(dimethylarsinoaniline)cobalt(II)*. MAA (0.47 g) in ethanol (30 ml) was added to cobalt (II) nitrate hexahydrate (0.35 g) in ethanol (25 ml). The pink solution was concentrated by distillation to about 10 ml and then petroleum ether was gradually added until two layers just began to form. After removal of some of the solvent mixture by distillation, a pink crystalline mass formed. The crystals were collected and washed firstly with a 1:5 ethanol and petroleum ether mixture and then with petroleum ether, and dried in a stream of nitrogen.

(v) *tris(o-dimethylarsinoaniline)cobalt(II) perchlorate.* This complex was prepared from MAA (0.50 g) and cobalt(II) perchlorate hexahydrate (0.30 g) in ethanol and petroleum ether by a procedure similar to that of (iv).

(vi) *bis[dichlorobis(dimethylarsinoaniline)cobalt (III)]tetrachlorocobaltate(II).* A solution of MAA (0.78 g) in ethanol was added to an ethanol solution of cobalt(II) chloride hexahydrate (1.2 g) acidified with a few drops of 10 *M* hydrochloric acid. A green crystalline precipitate gradually formed. The compound was recrystallized from ethanol containing some cobalt(II) chloride and hydrochloric acid.

(vii) *dichloro(o-dimethylarsinoaniline)cobalt(III) chloride dihydrate.* Compound (vi) was dissolved in hot dilute hydrochloric acid ($\sim$0.1 *M*). On cooling compound (vii) separated as green crystals. Long needle-like crystals several centimeters long were easily obtained.

(viii) *dichlorobis(o-dimethylarsinoaniline)cobalt(III) perchlorate monohydrate.* Compound (vi) was dissolved in hot dilute hydrochloric acid and added to an aqueous solution of perchloric acid. A green crystalline precipitate of (viii) formed.

(ix) *dibromobis(o-dimethylarsinoaniline)cobalt(III) bromide monohydrate.* The green precipitate formed by the reaction of cobalt(II) bromide hexahydrate (0.25 g), MAA (0.30 g), and 48% hydrobromic acid (0.10 g) in ethanol was dissolved in hot ethanol and added to an aqueous solution of hydrobromic acid. A green crystalline precipitate of (ix) formed.

(x) *diiodobis(o-dimethylarsinoaniline)cobalt(III) iodide.* This complex was prepared from MAA (0.20 g) cobalt(II) iodide hexahydrate (0.30 g) and hydriodic acid (0.2 g) of 55% solution in ethanol. The complex was recrystallized from ethanol and obtained as large crystals with a greenish black metallic lustre.

(xi) *bis[dithiocyanatobis(o-dimethylarsinoaniline)-cobalt(III)] tetrathiocyanatocobaltate(II).* A solution of cobalt(II) thiocyanate containing excess potassium thiocyanate was obtained by mixing ethanol solutions of cobalt(II) perchlorate hexahydrate (0.73 g) and potassium thiocyanate (0.60 g) and filtering off the precipitated potassium perchlorate. The solution of cobalt(II) thiocyanate was treated with MAA (0.38 g). A dark violet-blue crystalline precipitate of (xi) formed.

(xii) *dithiocyanatobis(o-dimethylarsinoaniline)cobalt-(III) perchlorate.* When compound (xi) was dissolved in hot methanol and added to excess perchloric acid a red crystalline precipitate of (xii) formed.

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