

264. *Infrared Spectra (1000—200 cm^{-1}) of Some Transition-metal Complexes with Tertiary Arsine Oxides.*

By G. A. RODLEY, D. M. L. GOODGAME, and F. A. COTTON.

The infrared spectra, in the region 1000—200 cm^{-1} , of complexes of the type ML_2X_2 , where $\text{L} = \text{Ph}_3\text{AsO}$ or Ph_2MeAsO , $\text{X} = \text{Cl}$ or Br , and M is a bivalent ion of the series Mn to Zn , are reported and discussed. The As—O stretching frequencies are in the range 910—840 cm^{-1} . The bands due to the metal—donor atom stretching vibrations are assigned, and occur as follows: $\nu(\text{M—O})$ 440—370, $\nu(\text{M—Cl})$ 325—270, and $\nu(\text{M—Br})$ 245—200 cm^{-1} . These results are discussed in relation to the structures of the complexes. The compounds $\text{M}(\text{Ph}_3\text{AsO})_2\text{Cl}_2$, where $\text{M} = \text{Co}$ or Zn , exist in two forms with differing infrared spectra and X-ray powder photographs.

The electronic spectra of the complexes $\text{Cu}(\text{Ph}_3\text{AsO})_2\text{X}_2$, where $\text{X} = \text{Cl}$ or Br , in the range 10,000—4000 cm^{-1} are reported, and the natures of these compounds, and also of the blue and the brown cuprous—cupric chloride complexes with Ph_2MeAsO , are discussed.

DURING the past few years, a variety of first-series transition-metal complexes has been prepared with tertiary phosphine oxide or arsine oxide ligands.¹ With bivalent metal ions these complexes are generally of the types ML_2X_2 or ML_4X_2 , where $\text{L} = \text{R}_3\text{PO}$ or R_3AsO , and X is a univalent anion. Apart from the compound $\text{Co}(\text{Me}_3\text{PO})_2(\text{NO}_3)_2$, the structure of which has been determined by a single-crystal X-ray study,² information concerning the stereochemical arrangement of the ligands around the metal ions in these complexes has been obtained mainly from studies of the electronic absorption spectra and magnetic susceptibilities, supplemented by X-ray diffraction data concerning isomorphism of crystals.

The effect of complex-formation on the P—O stretching frequencies of trimethyl- and triphenyl-phosphine oxide has been reported, and discussed in terms of the change in the P—O bond order.³ Some experimental results for the As—O stretching frequencies of complexes with triphenylarsine oxide have also been given.^{4,5} However, an investigation of the metal—oxygen stretching frequencies, and the correlation of these with the As—O stretching frequencies, seemed desirable. A study has now been made of the spectra in the region 1000—200 cm^{-1} of a number of complexes of bivalent metal ions with triphenylarsine oxide and methyldiphenylarsine oxide, and in this Paper the results are reported for those of the type $\text{M}(\text{R}_3\text{AsO})_2\text{X}_2$; results for complexes of the type $\text{M}(\text{R}_3\text{AsO})_4\text{X}_2$ will be reported separately.⁶

Before discussing the infrared spectra, it is helpful to summarise the information available concerning the structures of the complexes we have studied. For the series $\text{M}(\text{Ph}_3\text{AsO})_2\text{X}_2$, where $\text{X} = \text{Cl}$ or Br , and $\text{M} = \text{Mn}$ to Zn , the electronic spectra and the magnetic susceptibilities show that the complexes of manganese(II),^{4b} iron(II),⁷ cobalt(II),¹ and nickel(II)⁸ have essentially tetrahedral structures. The chloro-complexes of $\text{Mn}(\text{II})$, $\text{Fe}(\text{II})$, $\text{Co}(\text{II})$, and $\text{Zn}(\text{II})$ are isomorphous, as are the bromo-complexes of $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, and $\text{Zn}(\text{II})$. The compounds $\text{M}(\text{Ph}_2\text{MeAsO})_2\text{Cl}_2$, where $\text{M} = \text{Mn}(\text{II})$, $\text{Co}(\text{II})$, $\text{Ni}(\text{II})$, and

¹ D. M. L. Goodgame, M. Goodgame, and F. A. Cotton, *Inorg. Chem.*, 1962, **1**, 239, and references therein.

² F. A. Cotton and R. H. Soderberg, *J. Amer. Chem. Soc.*, 1963, **85**, 2402.

³ F. A. Cotton, R. Barnes, and E. Bannister, *J.*, 1960, 2199.

⁴ D. M. L. Goodgame and F. A. Cotton, *J.*, 1961, (a) 2298; (b) 3735.

⁵ D. J. Phillips and S. Y. Tyree, *J. Amer. Chem. Soc.*, 1961, **83**, 1806.

⁶ J. Lewis, R. S. Nyholm, and G. A. Rodley, to be published.

⁷ D. Forster and D. M. L. Goodgame, *J.*, 1965, 454.

⁸ D. M. L. Goodgame and F. A. Cotton, *J. Amer. Chem. Soc.*, 1960, **82**, 5774.

Zn(II), and $\text{M}(\text{Ph}_2\text{MeAsO})_2\text{Br}_2$, where $\text{M} = \text{Mn(II), Fe(II), Co(II), and Zn(II)}$, are also tetrahedral, and are isomorphous within each of the two series.^{7,9}

For the complexes $\text{M}(\text{R}_3\text{AsO})_2\text{X}_2$, the infrared bands of interest in the present study are those due to the As—O stretch, $\nu(\text{As—O})$, and those arising from the metal—donor atom stretching vibrations. On the basis of C_{2v} site-symmetry for the metal ions, four infrared-active metal—donor atom stretching vibrations would be expected, which may be designated symmetric and antisymmetric combinations of $\nu(\text{M—O})$, and the two corresponding $\nu(\text{M—X})$ modes, though these may not involve pure M—O or M—X stretching modes.

The bands due to $\nu(\text{As—O})$ can be assigned very readily for the triphenylarsine oxide complexes. Previous assignments^{4,5} of the strong band at 880 cm^{-1} , in the spectrum of triphenylarsine oxide, as $\nu(\text{As—O})$ have been confirmed¹⁰ by isotopic substitution studies, using ^{18}O , which also indicated that this band is a virtually pure group frequency in triphenylarsine oxide itself. The $\nu(\text{As—O})$ bands for the metal complexes with this ligand occur in the range $910\text{—}840 \text{ cm}^{-1}$ (see Table 1) and are sometimes split into two components.

TABLE 1.

Arsenic—oxygen, metal—oxygen, and metal—halogen stretching frequencies (cm^{-1}) of some arsine oxide complexes.^a

Ph ₃ AsO Complexes	$\nu(\text{As—O})$	$\nu(\text{M—O})$	$\nu(\text{M—Hal})$	
Ph ₃ AsO (= L)	880	—	—	
MnL ₂ Cl ₂ *	894	370	311, 287	
FeL ₂ Cl ₂ *	874	384	315, 288	
CoL ₂ Cl ₂ * (A)	889	382	325, 302	
(B)	886, 867	404, 392	323, 288	
NiL ₂ Cl ₂	865, 845	432	310, 284	
"CuL ₂ Cl ₂ "	844	440mw	270m, ^b 262m	
ZnL ₂ Cl ₂ * (A)	891	382	312, 286	
(C)	892, 873	396, 388	306, 284	
MnL ₂ Br ₂	910, 880	405mw, 393mw	230br	
FeL ₂ Br ₂	896, 851	403m, 395m	225br	
CoL ₂ Br ₂ †	870	405	243, 220	
NiL ₂ Br ₂ †	868	412	234br	
"CuL ₂ Br ₂ "	847	435mw	225mw	
ZnL ₂ Br ₂ †	874	400, 390	230br	
Ph ₂ MeAsO Complexes	$\rho(\text{As—Me})$ ^c	$\nu(\text{As—O})$ ^c	$\nu(\text{M—O})$	$\nu(\text{M—Hal})$
Ph ₂ MeAsO (= L')	875, 866sh	—	—	—
MnL' ₂ Cl ₂ †	896mw, 881sh, 874sh	865, 847sh	395br	298, 272
CoL' ₂ Cl ₂ †	875	851	418	315, 287
NiL' ₂ Cl ₂ †	874	859, 844	425, 414	312, 282
ZnL' ₂ Cl ₂ †	882, 875	858	408	305, 287
MnL' ₂ Br ₂ §	880, 873	859	397	236br
FeL' ₂ Br ₂ §	876	849	401	235
CoL' ₂ Br ₂ §	877	855, 840	425, 416	240, 222
ZnL' ₂ Br ₂ §	880, 873	858	407	233br
(CuL' ₄)(CuCl ₂) ₂	870sh	844	434mw	410m

^a Nujol mulls; all bands are strong unless designated otherwise. ^b Ligand absorption in same region. ^c See discussion in the text concerning assignment of these bands. *, †, ‡, § Isomorphous groups of compounds.

In the case of methyl-diphenylarsine oxide and its complexes the situation is complicated by the methyl rocking mode, which, in related arsine molecules, gives rise to a band (or bands) in the region $800\text{—}900 \text{ cm}^{-1}$.⁹ For example, in the spectrum of methyl-diphenylarsine the methyl rock occurs at 837 cm^{-1} . Methyl-diphenylarsine oxide shows one strong band in this region, at 875 , and a shoulder at 866 cm^{-1} . This absorption is presumed to arise from modes involving mixtures of As—O stretching and methyl rocking; that is, no pure $\nu(\text{As—O})$ group frequency exists. As would be expected, the complexes of Ph_2MeAsO show more than one band in this region (see Table 1). The situation is reminiscent of that

⁹ G. A. Rodley, Thesis, London University, 1963.

¹⁰ J. Bernstein, M. Halmann, S. Pinchas, and D. Samuel, *J.*, 1964, 821.

found in complexes of dimethyl sulphoxide,¹¹ and gives rise to a similar ambiguity in interpretation. It seems likely, however, that the stronger bands in the spectra of the complexes have the greater $\nu(\text{As-O})$ component, and these, which are always the lower-frequency ones, have been denoted as $\nu(\text{As-O})$ in Table 1, and have been used for comparisons.

The bands due to $\nu(\text{M-O})$ and $\nu(\text{M-X})$, where $\text{X} = \text{Cl}$ or Br , were assigned as follows. Those due to $\nu(\text{M-X})$ were identified by the intercomparison of the spectra of analogous pairs of halogeno-complexes, the M-X stretching frequency being lowered on replacement of Cl by Br . The ligand bands were essentially unaltered by this replacement. The $\nu(\text{M-Cl})$ bands were found in the range 325—270, and the $\nu(\text{M-Br})$ bands in the range 245—200 cm^{-1} . In the chloro-complexes, except for those of copper(II) which will be discussed later, both antisymmetric and symmetric $\nu(\text{M-Cl})$ bands were observed, and were separated by 20—30 cm^{-1} . However, with the bromo-complexes two $\nu(\text{M-Br})$ bands were found only for the cobalt(II) complexes. The other bromo-complexes had only one rather broad band in this region.

If the symmetric and antisymmetric $\nu(\text{M-Br})$ modes in these compounds are separated by $\sim 30 \text{ cm}^{-1}$ the lower frequency bands would be just below the range of the measurements. It is also possible, however, that the bands are broad, separated by less than about 20 cm^{-1} , and are thus unresolved.

The M-O stretches were assigned to those bands which appeared in addition to ligand and $\nu(\text{M-X})$ absorptions, and were found as strong bands in a clear region of the spectrum at 440—370 cm^{-1} (see Table 1). Although some of the complexes had two $\nu(\text{M-O})$ bands, usually only a single band was observed. When two $\nu(\text{M-O})$ bands were present a splitting of the $\nu(\text{As-O})$ band was also found.

The results of this infrared study have been correlated with the structures of the complexes in two main ways. First, the frequencies of $\nu(\text{As-O})$, $\nu(\text{M-O})$, and $\nu(\text{M-X})$ may be compared for the compounds which are known to be isomorphous, and then with those complexes which, though not isomorphous, have very similar structures. These are discussed in Section (1). Secondly, we have found that these studies have provided more information concerning some arsine oxide complexes of copper(II), which appear to have more complicated structures [Section (2)].

(1) *Tetrahedral $\text{M}(\text{R}_3\text{AsO})_2\text{X}_2$ Complexes.*—The P-O stretching frequencies of triphenyl- and trimethyl-phosphine oxide are lowered by $\sim 50 \text{ cm}^{-1}$ on co-ordination.³ In the metal complexes with these ligands the kinematic increase in $\nu(\text{P-O})$ due to the coupling of the oscillators P-O and M-O is more than offset by a lowering of the force constant k_{PO} , due to a decrease in the P-O bond order on co-ordination. The $\nu(\text{As-O})$ bands in the triphenylarsine oxide complexes behave rather differently. Although in some complexes $\nu(\text{As-O})$ is lower than in free triphenylarsine oxide, in others it is higher. The values of $\nu(\text{As-O})$ range from the average value, 895 cm^{-1} , of the two bands observed for the complex with manganese(II) bromide to the average value, 855 cm^{-1} , of those found for the nickel chloride complex.

If we assume that there will be only a small difference between the M-O bond-stretching force constants for the phosphine oxide and the arsine oxide complexes, then the kinematic raising of $\nu(\text{As-O})$ due to the coupling of As-O and M-O would be expected to be greater than that of $\nu(\text{P-O})$ from a similar process. In approximate calculations, taking the relevant force constants to be $k_{\text{PO}} \sim 8.85$, $k_{\text{AsO}} \sim 6.0$, and $k_{\text{MO}} \sim 1.2$ millidynes \AA^{-1} , the increase in $\nu(\text{As-O})$ due to the mechanical effect of coupling the As-O oscillator to the M-O oscillator would be $\sim 50 \text{ cm}^{-1}$ more than the corresponding increase in $\nu(\text{P-O})$. Thus, if the changes in k_{PO} and k_{AsO} are about the same, the net lowering in $\nu(\text{As-O})$ would be $\sim 50 \text{ cm}^{-1}$ less than for $\nu(\text{P-O})$. On the average, then, $\nu(\text{As-O})$ in the complexes would be expected to differ relatively little from $\nu(\text{As-O})$ in triphenylarsine oxide itself, as is observed.

¹¹ F. A. Cotton, R. Francis, and W. D. Horrocks, *J. Phys. Chem.*, 1960, **64**, 1534; R. S. Drago and D. W. Meek, *ibid.*, 1961, **65**, 1446.

Thus, the somewhat different behaviour of the $\nu(\text{As-O})$ bands, compared to the $\nu(\text{P-O})$ bands, does not, in fact, imply any major difference in the effects of co-ordination upon the electronic structure of the As-O bonds as compared to the P-O bonds, nor any qualitative difference in the nature (*i.e.*, π - and σ -components) of the As-O and P-O bonds. A more detailed comparison within the series does not seem warranted in view of the unknown variations in M-O σ - and π -bonding and in the M-O-As bond angles. However, it was observed that the variations in the $\nu(\text{As-O})$ values for related complexes, on changing M^{2+} , were generally in the opposite sense to the variations observed for $\nu(\text{M-O})$, although there were some exceptions.

For a series of closely related compounds it might be hoped that a rough comparison of the relative strengths of the metal-ligand bonds would be obtained from the values of $\nu(\text{M-X})$, where X is the donor atom concerned. From the values of $\nu(\text{M-O})$, $\nu(\text{M-Cl})$, and $\nu(\text{M-Br})$ (average values being taken where two bands were observed) for the isomorphous series of complexes the following observations may be made:

(i) For the complexes ML_2Cl_2 , the values of $\nu(\text{M-O})$ are generally greater for $\text{L} = \text{Ph}_2\text{MeAsO}$ than for $\text{L} = \text{Ph}_3\text{AsO}$, while for $\nu(\text{M-Cl})$ the reverse is true. In the case of the bromo-complexes the values of $\nu(\text{M-O})$ and $\nu(\text{M-Br})$ are generally rather similar for the two arsine oxide ligands.

(ii) Within each of the isomorphous series of compounds the highest $\nu(\text{M-O})$ or $\nu(\text{M-X})$ values are generally found for the cobalt(II) and nickel(II) complexes, although $\nu(\text{M-O})$ for $\text{Fe}(\text{Ph}_3\text{AsO})_2\text{Cl}_2$ is larger than that of the form of $\text{Co}(\text{Ph}_3\text{AsO})_2\text{Cl}_2$ with which it is isomorphous. Conversely, the manganese(II) complexes tend to have the lowest $\nu(\text{M-O})$ and $\nu(\text{M-X})$ values. Clark and Dunn found¹² that the ν_3 frequency for the tetrahalogenoions MX_4^{2-} , where $\text{M} = \text{Mn to Zn}$, reached a maximum at cobalt(II).

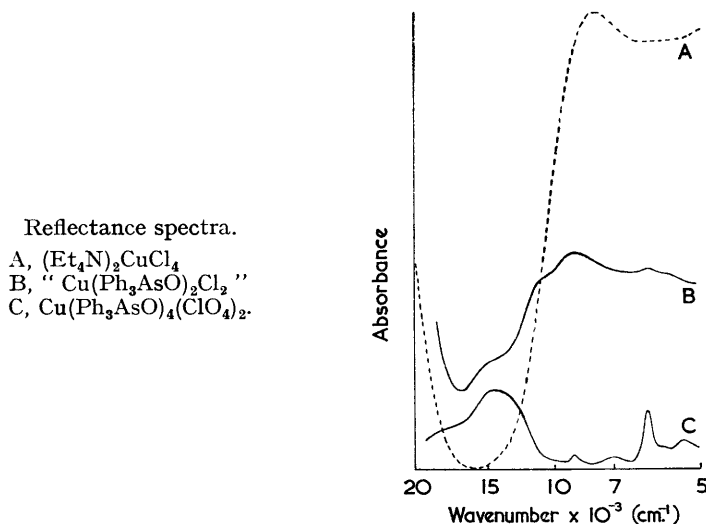
Some of the compounds studied are not members of isomorphous series, although they have essentially tetrahedral structures. Two of these, $\text{Mn}(\text{Ph}_3\text{AsO})_2\text{Br}_2$ and the corresponding iron(II) compound, have $\nu(\text{M-O})$ values which differ little from those of the analogous complexes which do form an isomorphous series. However, the value of $\nu(\text{M-O})$ for the compound $\text{Ni}(\text{Ph}_3\text{AsO})_2\text{Cl}_2$ was found to be considerably larger than those of the other $\text{M}(\text{Ph}_3\text{AsO})_2\text{Cl}_2$ complexes which are isomorphous one with another. It appears, therefore, that relatively small changes in molecular configuration or crystal packing, which are not evident from magnetic or electronic spectral studies, may sometimes produce shifts in metal-donor atom stretching frequencies which are quite large compared with the variations found within an isomorphous series.

The complexes $\text{Co}(\text{Ph}_3\text{AsO})_2\text{Cl}_2$ and $\text{Zn}(\text{Ph}_3\text{AsO})_2\text{Cl}_2$ each appear to exist as two solid forms, with differing values of $\nu(\text{As-O})$, $\nu(\text{M-O})$, and $\nu(\text{M-Cl})$. In the case of the cobalt complexes the form denoted as A in Table I is that reported previously¹ and is a member of the isomorphous series. Form B has a powder pattern rather similar to that of A. The $\nu(\text{As-O})$ values reported by Phillips and Tyree⁵ for $\text{Co}(\text{Ph}_3\text{AsO})_2\text{Cl}_2$, 882 and 862 cm^{-1} , indicate that they prepared form B. From their magnetic moments and electronic spectra both forms appear to contain tetrahedrally co-ordinated cobalt(II). One of the zinc complexes, A, is isomorphous with form A of the analogous cobalt(II) compound, but the other form, C, has a powder pattern which differs from those of both the cobalt(II) isomers. The infrared spectrum of form C of the zinc compound in the solid state also shows two shoulders at 861 and 847 cm^{-1} in addition to the main bands at 894 and 873 cm^{-1} listed in Table I. We have not investigated in detail the experimental conditions necessary to favour the formation of each of these isomers. Preparations of the cobalt complex carried out according to the methods outlined in references 1 and 5 usually gave form A, but occasionally B was obtained. In the case of the zinc complexes, form A was obtained by addition of a cold ethanolic solution of the neutral ligand to a 25% excess over the calculated quantity of zinc chloride, also in cold ethanol, whereas form C was prepared by adding zinc chloride to excess triphenylarsine oxide under similar conditions.

¹² R. J. H. Clark and T. M. Dunn, *J.*, 1963, 1198.

The existence of two forms appears to be a solid-state effect since both forms of the zinc complex have identical spectra in the As-O stretching region when dissolved in chloroform, with $\nu(\text{As-O}) = 875 \text{ cm.}^{-1}$. The spectrum, in the region $1000\text{--}800 \text{ cm.}^{-1}$, of the solid obtained by spontaneous evaporation of a chloroform solution of form C of $\text{Zn}(\text{Ph}_3\text{AsO})_2\text{Cl}_2$ was identical with that of the original solid. However, evaporation of a chloroform solution of the A isomer yielded a solid which, from its infrared spectrum, appeared to be a mixture of A and C forms.

This behaviour may well be related to the expected non-linearity of the As-O-M grouping,^{2,13} which, in the solid state, could permit more than one orientation of the two Ph_3As groups relative to each other. Therefore, more than one overall crystal structure might be possible, with no appreciable change in the geometry of the primary co-ordination sphere of the metal ion. The small differences observed for $\nu(\text{As-O})$, $\nu(\text{M-O})$, and $\nu(\text{M-Cl})$ could arise either from differences in the intermolecular forces expected for the various crystal modifications, which would cause small changes in the lengths or angles of the



metal-donor atom bonds, or changes in coupling between different oscillators, or both. It is possible that some of the other complexes of the type $\text{M}(\text{R}_3\text{AO})_2\text{X}_2$, where $\text{A} = \text{As}$ or P , and $\text{X} = \text{Cl}$ or Br , also exist in more than one form, although we have found no evidence for this.

(2) *Copper Complexes*.—It was previously shown^{4a} that the complexes $\text{Cu}(\text{Ph}_3\text{PO})_2\text{X}_2$, $\text{X} = \text{Cl}$ or Br , had electronic spectra consistent with their formulation as monomers with pseudotetrahedral structures. However, the analogous complexes with triphenylarsine oxide appeared to have different structures, since their reflectance spectra contained bands in the visible region. Moreover the magnetic moment of the bromo-complex was only 1.56 B.M. at 301°K . The low-frequency infrared study has now provided more information concerning the structures of these complexes.

Except for the presence of additional bands at 270 and 262 cm.^{-1} , the spectrum of the complex of empirical formula $\text{Cu}(\text{Ph}_3\text{AsO})_2\text{Cl}_2$ closely resembles that of the compound $\text{Cu}(\text{Ph}_3\text{AsO})_4(\text{ClO}_4)_2$, which is believed to contain a planar arrangement of four arsine oxide ligands around the copper atom.^{6,14} For example, the frequencies of $\nu(\text{M-O})$, 440 cm.^{-1} , and $\nu(\text{As-O})$, 844 cm.^{-1} , for the chloro-complex are very similar to those found for the perchlorate complex, 436 and 845 cm.^{-1} , respectively. These infrared results suggest the formulation $[\text{Cu}(\text{Ph}_3\text{AsO})_4][\text{CuCl}_4]$ for the chloro-complex. The bands at 270 and 262 cm.^{-1}

¹³ C. Brändén, *Acta Chem. Scand.*, 1963, **17**, 1363.

¹⁴ E. Bannister and F. A. Cotton, *J.*, 1960, 1878.

could be assigned to the ν_3 mode of the tetrachlorocuprate(II) anion, and may be compared with the values of 289sh, 268, and 247 cm^{-1} for $(\text{Et}_4\text{N})_2\text{CuCl}_4$, 283 cm^{-1} for $(\text{MePh}_3\text{As})_2\text{CuCl}_4$, and 288 and 256 cm^{-1} for Cs_2CuCl_4 .¹²

Further evidence for the presence of the tetrakis(triphenylarsine oxide)copper(II) cation in " $\text{Cu}(\text{Ph}_3\text{AsO})_2\text{Cl}_2$ " is provided by the reflectance spectrum of this compound, shown in the Figure. The pronounced shoulder at $\sim 14,800 \text{ cm}^{-1}$ corresponds to the band at 14,500 cm^{-1} in the spectrum of the complex $\text{Cu}(\text{Ph}_3\text{AsO})_4(\text{ClO}_4)_2$. The sharp bands in the near-infrared region for the perchlorate complex were also found in the reflectance spectrum of triphenylarsine oxide and are presumably overtones or combinations of vibrational modes of the neutral ligands.

However, the inference from the far-infrared studies that " $\text{Cu}(\text{Ph}_3\text{AsO})_2\text{Cl}_2$ " contains the tetrachlorocuprate anion is not unambiguously substantiated by the electronic spectrum in the near-infrared region. As may be seen from the Figure, the strong band at 8800 cm^{-1} agrees quite well with the highest-energy $d-d$ transition found for $(\text{Et}_4\text{N})_2\text{CuCl}_4$, and for other compounds which are known to contain the CuCl_4^{2-} ion.¹⁵ However, the shoulder at $\sim 11,200 \text{ cm}^{-1}$ cannot be explained on this basis. Both this shoulder and also the band ^{4a} at 20,800 cm^{-1} are close to the positions of the bands reported by Furlani and Morpurgo^{15a} as being characteristic of the solvolysed species $[\text{CuCl}_n\text{L}_{4-n}]^{(n-2)-}$, where $n = 1$ or 2, which are obtained when salts containing the CuCl_4^{2-} ion are dissolved in solvents such as nitromethane in the absence of excess chloride ion. It may also be noted in this context that the pseudo-tetrahedral complex $\text{Cu}(\text{Ph}_3\text{PO})_2\text{Cl}_2$ has an electronic spectrum very similar to that of the CuCl_4^{2-} ion. The highest energy $d-d$ band for the phosphine oxide complex occurs at 8150 cm^{-1} , and there are no bands between this and a charge-transfer band at 23,500 cm^{-1} . Thus, although both the far-infrared and the electronic spectra of " $\text{Cu}(\text{Ph}_3\text{AsO})_2\text{Cl}_2$ " suggest the presence of the $\text{Cu}(\text{Ph}_3\text{AsO})_4^{2+}$ cation, the true formulation of this compound may well be more complex than $[\text{Cu}(\text{Ph}_3\text{AsO})_4][\text{CuCl}_4]$.

The structure of the green complex of composition $\text{Cu}(\text{Ph}_3\text{AsO})_2\text{Br}_2$ also remains rather obscure. The values of $\nu(\text{As-O})$, 847 cm^{-1} , and $\nu(\text{M-O})$, 435 cm^{-1} , are close to those observed for the $\text{Cu}(\text{Ph}_3\text{AsO})_4^{2+}$ cation, and the $\nu(\text{M-Br})$ value, 225 cm^{-1} , is near that found¹² for the $\nu_3(\text{M-Br})$ stretch in CuBr_4^{2-} . The electronic spectrum of the complex in the visible region was reported previously.^{4a} A study of the reflectance spectrum in the region 10,000—4000 cm^{-1} reveals the presence of one additional band at 8460 cm^{-1} , apart from vibrational bands associated with triphenylarsine oxide. This band in the near-infrared region correlates well with those reported^{15,16} for the ${}^2B_2 \rightarrow {}^2A_1$ transition for the CuBr_4^{2-} ion. However, the electronic spectrum above 10,000 cm^{-1} is very similar to those of the green solutions containing solvolysed species derived from the CuBr_4^{2-} anion,^{15,16} and, therefore, a structure such as $[\text{Cu}(\text{Ph}_3\text{AsO})_4][\text{CuBr}_4]$ seems unlikely. Unfortunately we could not check for the presence of the tetrakis(triphenylarsine oxide)-copper(II) cation from the electronic spectrum since the relatively weak $d-d$ band expected at 14,500 cm^{-1} for this species would, in any case, be hidden by the strong, charge-transfer¹⁷ absorption in this region.

The reaction of cupric chloride with methyldiphenylarsine oxide is rather complex and requires further study. However, two of the products isolated correspond to the so-called " blue and brown cuprous-cupric " complexes originally made from methyldiphenylarsine as ligand,¹⁸ but later shown by Nyholm¹⁹ to be arsine oxide complexes. It was

¹⁵ (a) C. Furlani and G. Morpurgo, *Theor. Chim. Acta*, 1963, **1**, 102; (b) P. Day, *Proc. Chem. Soc.*, 1964, 18.

¹⁶ A. G. Karipides and T. S. Piper, *Inorg. Chem.*, 1962, **1**, 970; J. C. Barnes and D. N. Hume, *ibid.*, 1963, **2**, 444.

¹⁷ P. S. Braterman, *Inorg. Chem.*, 1963, **2**, 448.

¹⁸ G. J. Burrows and E. P. Sanford, *J. Proc. Roy. Soc., N.S.W.*, 1935, **69**, 182; D. P. Mellor and D. P. Craig, *ibid.*, 1941, **75**, 27.

¹⁹ R. S. Nyholm, *J.*, 1951, 1767.

proposed¹⁹ that the blue form had the composition $\text{Cu}(\text{Ph}_2\text{MeAsO})_4(\text{CuCl}_2)_2$, and that the brown form was of essentially the same composition but with 5–10% of cupric chloride present, probably as the polymerised CuCl_3^- ion. It has now been possible to confirm these conclusions by infrared and X-ray diffraction studies. Both forms have the same X-ray powder patterns, and have identical spectra in the region 2000–200 cm^{-1} . The presence of strong $\nu(\text{As}-\text{O})$ bands at 844 cm^{-1} , and the preparations from methyldiphenylarsine oxide confirm that they are arsine oxide complexes. Furthermore, the infrared spectra are identical with that of $\text{Cu}(\text{Ph}_2\text{MeAsO})_4(\text{ClO}_4)_2$, apart from the absorption due to the perchlorate ion in the latter, and a band at 410 cm^{-1} in the former complexes. The band at 410 cm^{-1} may be assigned as the antisymmetric $\nu(\text{Cu}-\text{Cl})$ mode of the CuCl_2^- ion.

EXPERIMENTAL

Preparation of the Complexes.—The preparations of the complexes with triphenylarsine oxide have been described elsewhere.^{1,7} The methyldiphenylarsine oxide complexes, and the triphenylarsine oxide complexes with the zinc halides, were prepared by the general methods outlined previously.¹ The analytical figures for the new compounds are given in Table 2. The compound $\text{Ni}(\text{Ph}_2\text{MeAsO})_2\text{Cl}_2$ could not be obtained pure.

When cupric chloride reacted with methyldiphenylarsine oxide, the blue and the brown cuprous–cupric compounds previously reported by Nyholm¹⁹ were obtained. They were identified by X-ray powder photographs. The blue form was obtained from aqueous alcoholic solutions, whereas the brown form was precipitated from alcoholic solutions of the reactants.

Physical Measurements.—The X-ray diffraction patterns were recorded photographically

TABLE 2.
Analytical results for some Ph_2MeAsO (= L) and Ph_3AsO (= L') complexes.

Compound	Found (%)				Required (%)			
	C	H	As	Cl or Br	C	H	As	Cl or Br
MnL_2Cl_2	47.7	4.0	23.5	11.0	48.3	4.0	23.2	11.0
CoL_2Cl_2	48.1	4.0	22.9	10.8	48.0	4.0	23.1	10.9
NiL_2Cl_2	46.85	4.25	—	—	48.0	4.0	—	—
ZnL_2Cl_2	47.1	4.3	—	—	47.5	4.0	—	—
MnL_2Br_2 *	42.4	3.6	—	—	42.5	3.6	—	—
FeL_2Br_2	42.6	4.0	—	—	42.25	3.5	—	—
CoL_2Br_2	42.3	3.6	20.0	21.9	42.2	3.5	20.3	21.7
ZnL_2Br_2 *	42.1	3.8	—	—	41.9	3.5	—	—
$\text{ZnL}'_2\text{Cl}_2$ (A)	54.9	4.0	—	—	55.4	3.9	—	—
(C)	55.1	4.0	—	—	—	—	—	—
$\text{ZnL}'_2\text{Br}_2$	49.3	3.5	—	—	49.7	3.5	—	—

* Prepared by Mr. D. Forster.

with a Philips Debye–Scherrer powder camera (diameter 11.483 cm.). Most of the infrared spectra for the region 1000–475 cm^{-1} were recorded on a Grubb–Parsons GS2A spectrometer, and the remainder with a Grubb–Parsons Spectromaster grating spectrometer. The spectra in the region 475–200 cm^{-1} were obtained with a Grubb–Parsons double-beam grating spectrometer type DM2, serial number 28. The reflectance spectra were obtained using a Beckman DK2 spectrometer.

One of us (G. A. R.) gratefully acknowledges the award of a Commonwealth Scholarship, during the tenure of which this work was carried out. Support from the U.S. Army Research Office (to F. A. C.) is also acknowledged.

(G. A. R.) WILLIAM RAMSAY AND RALPH FORSTER LABORATORIES, UNIVERSITY COLLEGE, GOWER STREET, LONDON W.C.1.

(D. M. L. G.) INORGANIC CHEMISTRY RESEARCH LABORATORIES, IMPERIAL COLLEGE OF SCIENCE AND TECHNOLOGY, LONDON S.W.7.

(F. A. C.) DEPARTMENT OF CHEMISTRY, MASSACHUSETTS INSTITUTE OF TECHNOLOGY, CAMBRIDGE 39, MASS., U.S.A.

[Present address (G. A. R.): CHEMISTRY DEPARTMENT, UNIVERSITY OF CANTERBURY, CHRISTCHURCH 1, NEW ZEALAND.] [Received, June 17th, 1964.]