261. *Low-frequency Infrared Spectra of Some Octahedral Metal Diarsine Chloro-complexes.*

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The infrared spectra in the region 450—200 cm.$^{-1}$ have been examined for a series of transition-metal complexes * (MD_2Cl_2) and (MD_2Cl_2),X where X is Cl^-, ClO_4. The metal-chlorine antisymmetric stretching frequency has been assigned. A *trans*-configuration has been established for all the complexes, with the exception of one form of (CoD_2Cl_2)ClO_4 which as, on the basis of infrared spectral values, the *cis*-configuration, in agreement with the assignment from the ultraviolet and visible spectrum. The variation of the metal–chlorine frequency with the mass, oxidation state, and electron configuration of the metal is discussed and related to measurements on other compounds. The major factor that appears to influence the metal–chlorine frequency is [1] the electron-configuration change d_ϵ^6 to $d_\epsilon^6 d_\gamma$, and is presumably associated with occupation of the antibonding orbitals.

INFRARED (i.r.) measurements have been of considerable utility in determining the stereochemistry of inorganic molecules by the use of symmetry arguments. These have been particularly useful, for instance, with metal carbonyl derivatives, as the co-ordinated CO group in these complexes [1,2] absorbs in a convenient range of the spectrum. Comparable studies with halogeno-complexes have been restricted because of the low range in which metal-halogen vibrations occur. However, recent developments in spectrometers now make this range available, and studies have been reported on some octahedral [3,4] and tetrahedral [5] metal complexes of the halogens. We report observations on some octahedral halogen complexes. During the past ten years, a wide range of halogeno-transition-metal complexes of the ligand *o*-phenylenebisdimethylarsine (diarsine = D) have been reported. The majority of these are six-co-ordinate derivatives of the type $[MD_2X_2]^{n+}$, and can have either *cis*- or a *trans*-configuration. However, the only complexes for which geometrical isomerism has been definitely established [6] are $[CoD_2X_2]ClO_4$, where X = Cl or Br. *cis,trans*-Isomerism may also occur in the complexes, RuD_2I_2, $[MoD_2(NCS)_2]NCS$, and $[IrD_2Cl_2]Cl$ as two forms have been isolated in each case.

RESULTS AND DISCUSSION

Three series of complexes have been investigated.

(*a*) MD_2Cl_2,M(II) = Mo, Tc, Re, Fe, Ru, Os, Co, and Ni.
(*b*) $[MD_2Cl_2]Cl$, M(III) = Re, Co, Rh, Ir, and Ni.
(*c*) $[MD_2Cl_2]ClO_4$, M(III) = Cr, Tc, Re, Fe, Ru, Os, Co, Rh, Ir, and Ni.

The Table contains the frequencies that have been assigned to metal–chlorine vibrations and fall in the range reported for tetrachloro and hexachloro metal complexes.

The i.r. absorptions of the metal–chlorine groups have been assigned by comparison of the spectra with that of the free diarsine, and in several cases with the spectra of the corresponding bromide complexes (metal–bromine absorptions normally fall below 300 cm.$^{-1}$). A set pattern of strong diarsine absorption bands occur in the ranges 436 ± 3, 372 ± 5, 366—329, and 266—245 cm.$^{-1}$.

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* For convenience, Diarsine is referred to throughout this paper as D.

[1] Cotton, " Modern Coordination Chemistry," ed. by Lewis and Wilkins, Interscience, London, 1960.

[2] Nakamoto, " Infra-red Spectra of Inorganic and Coordination Compounds," Wiley, New York, 1962.

[3] Adams, Chatt, Davidson, and Gerratt, *J.*, 1963, 2189.

[4] Beattie, McQuiltan, Rule, and Webster, *J.*, 1963, 1514.

[5] Clark and Dunn, *J.*, 1963, 1198.

[6] Dunn, Nyholm, and Yamada, *J.*, 1962, 1564.

Most complexes gave a strong additional band in this region, which was assigned to the metal–chlorine vibration. For the complex $[CrD_2Cl_2]ClO_4$, three additional bands at 294, 310, and 375 cm.$^{-1}$ were observed. Low frequency values have not been obtained for the corresponding bromide complex, and the ν (Cr–Cl) frequency has been tentatively assigned at 375 cm.$^{-1}$, since many of the complexes have one or two weak or medium bands in the region 330—285 cm.$^{-1}$, and the 294 and 310 cm.$^{-1}$ bands are therefore assigned to diarsine absorption.

The complex $[RhD_2Cl_2]ClO_4$ does not give any bands that are not normally observed for co-ordinated diarsine. However, for the complexes $[MD_2Cl_2]ClO_4$, with M = Re, Ir, and Ni the M–Cl absorption occurs at 8—22 cm.$^{-1}$ higher than in the corresponding $[MD_2Cl_2]Cl$ complex. For the complex $[RhD_2Cl_2]Cl$, the ν (Rh–Cl) is assigned at 349 cm.$^{-1}$, and it is assumed that the corresponding vibration in the perchlorate complex coincides with a diarsine band at 358 cm.$^{-1}$. The complexes $[MD_2Cl_2]ClO_4$ (M = Cr or Fe) also have ν (M–Cl) absorption in the same region as the diarsine grouping. However, the relative intensities of the absorption indicate quite clearly that the metal–chlorine band is superposed on a ligand absorption; this was confirmed for the iron complex by comparison with the corresponding bromide complex.

Metal–chlorine bands are usually strong and broad,[5] but for the complexes reported here the absorption was found to be strong, whilst the bands were comparatively sharp. For the complexes $[CoD_2Cl_2]ClO_4$, $[CoD_2Cl_2]Cl$, $[FeD_2Cl_2]$, $[RuD_2Cl_2]$, and OsD_2Cl_2, however, the absorption assigned as ν (M–Cl) was quite weak. In the cobalt and ruthenium complexes, the assignment was confirmed by comparison with the corresponding bromide complex; for the osmium and iron compounds, however, the assignments must be considered more tentative, as weak absorption due to diarsine occurs in this region of the spectrum.

M–Cl stretching frequencies (cm.$^{-1}$) for octahedral diarsine complexes.

Complexes of the type MD_2Cl_2						
	M(II)	(M–Cl)	M(II)	(M–Cl)	M(II)	(M–Cl)
d^6	Fe	349	Ru*	316	Os*	288(?)
d^5			Tc*	304	Re*	279
d^4			Mo	299		
Complexes of the type MD_2Cl_2Cl						
	M(III)	(M–Cl)	M(III)	(M–Cl)	M(III)	(M–Cl)
d^7	Ni	238				
d^6	Co*	384 ± 4	Rh	349	Ir	320
d^4			Tc (hydrated)	335	Re	313
					Re (hydrated)	317
Complexes of the type $MD_2Cl_2{\cdot}ClO_4$						
	M(III)	(M–Cl)	M(III)	(M–Cl)	M(III)	(M–Cl)
d^7	Ni*	260				
d^6	Co*	388	Rh	358(?)	Ir	335
d^5	Fe*	373	Ru	340	Os	322
d^4			Tc	343	Re*	325
d^3	Cr	375(?)				

* Corresponding bromide complex also studied.

Coates and Parkin [7] have assigned metal–phosphorus frequencies to the region 347—391 cm.$^{-1}$, and also report metal–arsenic frequencies in two palladium trimethylarsine complexes at 276 and 269 cm.$^{-1}$. No attempt has been made to assign metal–arsenic frequencies in this work, but additional absorption occurred in the region 200—250 cm.$^{-1}$ in complexes of the type MD_2Cl_2. It is difficult to say whether these are metal–chlorine bending vibrations or metal–arsenic vibrations, and a simpler type of arsenic complex must be used to establish these frequencies.

The *X*-ray powder photographs indicate that the complexes within each of the above

[7] Coates and Parkin, *J.*, 1963, 421.

series, (a), (b), (c) are isostructural. For series (a) all the compounds, except M = Co and Ni, are isomorphous. However, the cobalt and nickel complexes have a similar powder pattern, which suggests that they have the same molecular configuration as the other complexes. The complexes of series (b) and (c) are isomorphous; although differences, due to the variable scattering powers of the metal, are observed in the relative intensities of powder lines. With $[NiD_2Cl_2]ClO_4$ there are features of the powder patterns that indicate some small changes in the molecular structure.

Single-crystal *X*-ray studies have provided evidence for the *trans*-configuration in each series. The space group and cell dimensions of NiD_2Br_2, isomorphous with NiD_2Cl_2, have been determined. The space group $P2_1/c$, with two molecules per unit cell can accommodate either six-co-ordinate *trans*-molecules or planar $[NiD_2]^{2+}$ and Br^- ions. The close similarity of the powder photograph with those of MD_2Cl_2, where M = Mo, Tc, Re, Ru, and Os, for which octahedral co-ordination has been definitely established, and also the similarity with the powder photograph of NiD_2I_2 (which has a *trans*-octahedral * structure [8]) strongly suggests the six-co-ordinate *trans*-structure for NiD_2Br_2. The complex CoD_2Cl_2,Cl has the space group $P2_1/c$ and with two molecules per unit cell must have the *trans*-centrosymmetric structure. A complete *X*-ray structural study of the green isomer $CoD_2Cl_2ClO_4$ [isomorphous with the other complexes of series (c)] has shown that this complex also has the *trans*-structure.

Two points of interest arise from these results, (i) the number of metal–chlorine frequencies and (ii) the position of the absorption. For a *cis*-octahedral distribution, on the assumption of C_2 symmetry, there should be two infrared-active (A,B) metal-chlorine stretching frequencies; whilst for a *trans* structure, with D_{2h} symmetry only one frequency (B_{1u}) would be expected. The sharpness of the bands observed in these complexes may be associated with the single degeneracy of the vibrations. In the majority of studies on metal–halogen vibrations, the complexes have potentially had a much higher symmetry (T_d or O_h) so that the vibration active in the infrared will be of a high degeneracy (T_{1u} or T_2). The broadness of the band in these circumstances may be a reflection on the local asymmetry in the molecule, as these complexes are studied in the solid state, which may remove this degeneracy to give two or more closely spaced bands.

Only one established *cis*-diarsine complex, $[CoD_2Cl_2]ClO_4$, has been studied and, as expected, two metal–chlorine frequencies were observed. In the *cis*- and *trans*-complexes $[Co\ en_2Cl_2]X$, X = Cl, ClO_4, en = ethylenediamine, two metal–chlorine frequencies were also observed for the *cis*-complexes, whilst one was observed for the *trans*-complexes. For the remainder of the complexes studied, only one metal–chlorine vibration was observed. This is in agreement with a *trans*-configuration for the complexes and agrees with the crystallographic data available for these compounds.

The position of the absorption band appears to depend upon the atomic weight, valency, and electron configuration of the metal and, for the complexes $[MD_2Cl_2]X$, the nature of the anion X. These effects will be considered in increasing order of magnitude of the metal–halogen stretching frequency.

Anion and Mass Effects.—As noted above in the discussion on the frequency assignments for metal–chlorine vibrations, in the complexes $[MD_2Cl_2]X$ the metal–chlorine vibrations of the perchlorate complexes occur at 8 to 22 cm.$^{-1}$ above those of the corresponding chloride complexes. The effect of the counter-ion on metal–halogen frequencies has been observed previously; different cations affect the M-Hal spectra of a series of tetrachloro- and tetrabromo-metal complexes.[5] In any comparisons between complexes, it is thus important to consider isostructural series in the same counter-ion. This effect must reflect various solid-state interactions, and is equivalent to the solvent effects observed for measurements in solution.[9]

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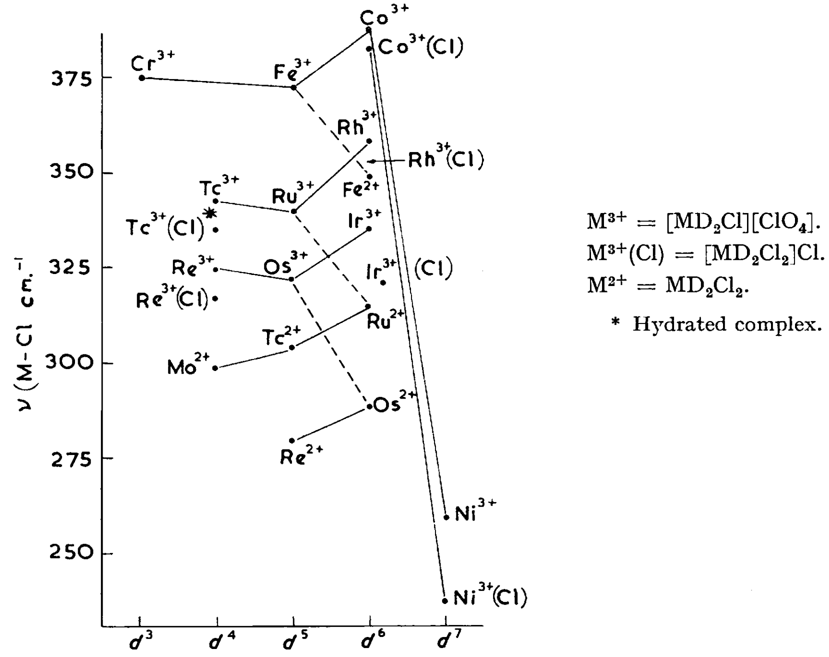
* Strictly speaking, tetragonal.

[8] Harris, Nyholm, and Stephenson, *Nature*, 1956, **177**, 1127.

[9] Barraclough, Lewis, and Nyholm, *J.*, 1961, 2582.

The effect of the variation in mass of the metal on the metal–chlorine frequency may be seen from the Figure. For complexes involving metals of the same charge and electron configuration, the frequency of the band falls as the mass of the metal increases. For a given force-constant for a bond, the frequency of the vibration will be proportional to the square root of the inverse of the reduced mass of the system. We should therefore expect the frequency of the vibration to fall with increase in mass of the metal. However, the changes (~60 cm.$^{-1}$) are less than those calculated for a simple diatomic system, but it is not possible, without allowing for all the interactions present, to say if there has been a change in force-constant for the bonds.

Valency of Metal.—If the complexes $[MD_2Cl_2]ClO_4$ are compared with the $[MD_2Cl_2]$ group (M = Tc, Re, Fe, Ru, and Os), a drop in the ν (M–Cl) varying from 23 to 45 cm.$^{-1}$ is observed when the charge on the metal ion is reduced. Some change in the ν (M–Cl) frequency may occur because of differences in secondary interaction of the type discussed above. With the tetrahedral chloro-complexes of iron a difference of 100 cm.$^{-1}$ was observed between the Fe(III) and Fe(II) complexes.[5] An increase in formal charge on the metal would be expected to increase the frequency of the metal–ligand vibration, ν (M–Cl). However, two additional factors must be considered:



$M^{3+} = [MD_2Cl][ClO_4]$.
$M^{3+}(Cl) = [MD_2Cl_2]Cl$.
$M^{2+} = MD_2Cl_2$.
* Hydrated complex.

1. In a complex with more than one type of ligand group, it is possible that any variation in covalent character, arising from a change in the formal charge of the metal ion, may be more effectively compensated by change in one of the metal–ligand bonds rather than the other. This will obviously be associated with the polarisability of the ligand groups. For the diarsine complexes investigated, it is probable that the metal-arsenic bonds will show the major variation in covalent character, and this may account for the smaller variation in the frequency of the metal–chlorine vibration in these complexes.
2. Although the observed frequency is considered to be mainly associated with the metal–chlorine vibration, this vibration will, in general, interact with other vibrations of the same symmetry in the molecule, the extent of this interaction being related to the

energy separation of interacting vibrations. Any discussion on the variation of the (M–Cl) frequency as a function of changes in the charge must make allowance for interaction of this type. For the complexes under consideration, as the molecular symmetry is D_{2h} the metal–arsenic stretching modes will have the symmetry A_g, B_{1g}, B_{2u}, B_{3u}, of which only two (B_{2u}, B_{3u}) will be infrared-active, the metal–chlorine stretching modes will be (A_g, B_{1u}) of which the B_{1u} mode will be infrared-active, whilst the bending modes for the metal–arsenic–chlorine system will have the symmetry A_g, A_u, B_{2g}, B_{3g}, $2B_{2u}$, $2B_{3u}$, B_{1u} of which three (B_{2u}, B_{1u}, and B_{3u}) will be infrared-active.

There will be no symmetry-allowed interactions between the metal–ligand stretching vibrations, but one of the bending modes will have the same symmetry as the metal–chlorine stretching mode, and coupling will occur. This will tend to raise the frequency of the metal–chlorine vibration, because the bending vibration will occur at lower frequencies. For the tetrahedral molecules, the infrared-active metal–chlorine stretching frequency (T_2) has the same symmetry as one of the bending modes, and hence there is the possibility of a similar type of interaction. It is possible, however, that the bending vibrations in the two classes of molecules may be influenced by variation in the metal charge to different degrees. This could then be reflected in a different degree of interaction between the metal–chlorine stretching and bending vibration in the two cases. It is thus not possible *a priori* to state whether the variation observed is a true reflection of the variation of the force-constant of the bond when the charge of the metal is changed.

Configuration of Metal.—As noted previously for some tetrahedral chloro and bromide complexes, there appears to be a significant correlation between the electron configuration and the metal–halogen stretching frequency.[5] From the Figure, it can be seen that, for related series of complexes, a maximum occurs at the d^6 configuration. However, it would be difficult to draw any conclusions from the changes in frequency for the d^3 — d^6 configurations apart from the fact that the maximum at d^6 is possibly significant. As observed from the studies on tetrahedral complexes, this maximum corresponds to the maximum crystal field stabilisation energy of the systems. In these octahedral complexes there is a very significant drop in the metal–chlorine frequency for the d^7 configuration. The metal–chlorine frequency was not detected in the complex [CoD_2Cl_2] down to 200 cm.$^{-1}$. However, M–Cl frequencies were observed in the isoelectronic Ni(III) complexes NiD_2Cl_2,X, $X = Cl$ and ClO_4 at 238 and 260 cm.$^{-1}$, respectively. It must be emphasised that, although the value of 238 cm.$^{-1}$ for NiD_2Cl_2,Cl is about 135 cm.$^{-1}$ lower than the ν (M–Cl) value for CoD_2Cl_2,Cl, both these complexes have the same powder patterns. The corresponding perchlorate complexes CoD_2Cl_2,ClO_4 and NiD_2Cl_2,ClO_4, which have ν (M–Cl) absorptions differing by 128 cm.$^{-1}$, give similar powder patterns and single-crystal *X*-ray photographs, which show that they have the same structure with a slight difference in one of the unit cell dimensions. No absorption associated with metal–chlorine frequencies was observed for the Ni(II) complexes studied, the pairs of complexes NiD_2Cl_2,NiD_2Br_2 and $NiD_2ClClO_4,NiD_2BrClO_4$ giving identical spectra above 200 cm.$^{-1}$. The complexes [NiD_2X_2][$X = Br, Cl$) are considered to be five-covalent in solution, and the formation of the perchlorate complex also suggests five-co-ordination for these complexes.[10] However, preliminary *X*-ray studies of [NiD_2Cl]ClO_4 indicate that the nickel is six-co-ordinate with *trans*-chlorine bridges between the nickel atoms.[11] The stretching frequency of a metal–chlorine–metal bridging group would be expected to be lower than for terminal groups, and the change from $M{-}Cl{\rightarrow}M$ to $M \cdots Cl^- \cdots M$ will also affect the result. Adams *et al.*[3] have shown that chlorine bridging frequencies occur at about 20 to 40 cm.$^{-1}$ below the terminal frequencies and, on this basis, terminal bridging frequencies would still be considerably less than for the d^3 — d^6 series of complexes.

The change in the frequency observed for the tetrahedral complexes was not as large (>60 cm.$^{-1}$). The larger change for the octahedral diarsine complexes may be related

[10] Harris, Nyholm, and Phillips, *J.*, 1960, 4379.

[11] Stephenson, personal communication.

to two factors. First, for the tetrahedral complexes, the change occurred at the configurations $d_\gamma^4 d_\epsilon^3$ to $d_\gamma^4 d_\epsilon^4$, whilst for the octahedral complexes the corresponding change was d_ϵ^6 to $d_\epsilon^6 d_\gamma^1$. In the latter case, electrons are being added to an empty antibonding orbital (d_γ), whilst, for the tetrahedral complexes, it is merely the addition of an electron to already occupied antibonding orbital. Secondly, the d_γ shell in octahedral complexes is strictly σ-antibonding in character, whilst for tetrahedral molecules it is not possible to differentiate between the σ- and π-character of the d_ϵ-orbital on symmetry grounds. The difference in the frequency change may be of potential use as a means of differentiating between tetrahedral and octahedral stereochemistry for the d^7 configuration.

Infrared Absorption of Diarsine.—A very close similarity occurs in the spectra of the free and co-ordinated diarsine group. A detailed consideration of the spectra will not be undertaken here, but it is significant to note that the methyl rocking modes appear to be sensitive to the stereochemistry of the molecule. It has previously been shown that the methyl rocking modes are sensitive to steric interactions.[12] For *cis*- and *trans*-octahedral complexes, considerable splitting of the two As-CH_3 modes was observed, whereas for complexes with only diarsine of co-ordination in a tetrahedral disposition, *e.g.*, ($[CuD_2][CuI_2]$) a much smaller splitting was found. These results agree with the decrease in steric interaction observed when an octahedral arrangement changes to tetrahedral.

EXPERIMENTAL

The complexes were prepared as described previously, and their identity checked by carbon and hydrogen analyses, and *X*-ray powder patterns. Samples of the following complexes were obtained from previous workers in these laboratories: $[IrD_2Cl_2]Cl$, (D. J. Phillips); $[ReD_2Cl_2]Cl$, (W. J. Kirkman); $[TcD_2Cl_2]^\circ$; $[TcD_2Br_2]^\circ$; $[ReD_2Br_2]ClO_4$ (J. E. Fergusson) $[MoD_2Cl_2]^\circ$, (P. W. Smith) $[CoD_2Br_2]Br$, *cis*; $[CoD_2Cl_2]ClO_4$, *cis*; $[CoD_2Br_2]ClO_4$; (C. Yamada). The complex $[FeD_2Cl_2]$ was prepared by using a large excess of diarsine (Found: C, 34·20; H, 4·6. $C_{20}H_{32}Cl_2Fe$ requires C, 34·19; H, 4·6%).

The spectra for the region 200—475 cm.$^{-1}$ were recorded on a Grubb–Parsons double-beam grating spectrometer, type DM2 Serial number 28, which was calibrated with the spectrum of water vapour. The spectra were recorded as Nujol mulls between polythene plates.

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[12] Randle and Whiffen, *J.*, 1955, 3497.