The interaction of some metal dichlorides (Ca, Cr, Mn, Fe, Co, Ni, Zn) with dinitrogen

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The dichlorides of Ca, Cr, Mn, Fe, Co, Ni and Zn have been isolated in argon and nitrogen matrices and examined by infrared spectroscopy in the range 4000-200 cm⁻¹. The results obtained are discussed in relation to the behaviour of the difluorides and the monoxides. Both CoCl₂ and NiCl₂ show anomalous shifts in the frequency of ν_3 between argon and nitrogen matrices. Isotopic substitution shows that these molecules are strongly bent in nitrogen matrices, in contrast to their behaviour in argon matrices. It is likely that the primary interaction between the host nitrogen matrix and the guest dichloride is ion-induced-dipole rather than the formation of a discrete MCl₂·N₂ species.

1. Introduction

An understanding of how small molecules interact with metal centres is a major area of research and central to many industrial processes. The interest in such interactions ranges from the development of intermolecular potentials through solvation, sorption and complex formation to areas as diverse as catalysis and inclusion compounds. The first-row transition element dihalides represent an almost unique series for the systematic study of the interaction between species such as carbon monoxide or dinitrogen and a *molecular* dihalide.

Isolating a metal dihalide in a matrix is in many ways analogous to dissolving a molecular species in a solvent. Matrices have the added advantage that polymerization can be minimised, "solubility" is not a problem and a wide range of simple solvents from the rare gases to HCN, for example, can be studied. For diatomic molecules, a survey of matrix shifts gave the sequence $Ne < Ar < Kr < Xe < N_2$ [1]. Previous work on the infrared frequencies of guest molecules in host matrices suggested that N₂ and CO are comparable "solvents", with CO giving rather larger matrix shifts and broader bands, presumably due to the asymmetry of this molecule [2]. For MCl₂ in nitrogen matrices or nitrogen-doped argon matrices, it is usually possible to resolve isotopic fine structure from both the metal centre and the chlorine. This is not true of those species isolated in carbon monoxide matrices. In view of these factors, coupled with the fact that CO and N_2 are isoelectronic, have the same molecular weight, condense to give liquids with almost identical molar volumes and have similar molecular sizes and crystal structures, we have studied the chlorides of Ca, Cr, Mn, Fe, Co, Ni and Zn isolated in nitrogen matrices. A subsequent paper will deal with the more complex systems found in carbon monoxide matrices.

2. Results

The infrared spectra of the dichlorides in nitrogen were of high quality and (except in the cases of Ca, Cr and Mn) showed well resolved chlorine isotope fine structure modified (where applicable) by the effects of the metal isotopes. In fig. 1, the force constants calculated from ν_3 of the most abundant isotopomer (assuming a linear molecule and a Simple Valence Force Field) are plotted against atomic number for both argon and nitrogen matrices. The data for argon matrices are well documented in the literature [3]^{*1} and are used in the absence of suit-

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*1 For ZnCl<sub>2</sub> see ref. [4].
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Fig. 1. SVFF force constants $(10^2 N m^{-1})$ of MO (gas); MF₂ in argon; MCl₂ in argon; MCl₂ in nitrogen.

able gas-phase spectra. The result for TiCl₂ in a nitrogen matrix is taken from the work of Hastie et al. [5], where the isotopic splitting identifies the presence of the dichloride of titanium. CuCl₂ loses chlorine on sublimation in vacuo with formation of the copper (I) chloride. The point for CuCl₂ in fig. 1 was therefore interpolated from that of CuF₂ in argon giving a frequency fortuitously close to the gas-phase value [6] of 496 ± 20 cm⁻¹. (Where more than one matrix site is present, the higher frequency has been used in the force constant calculation, the lower frequency usually corresponding to a site which decreases in intensity on annealing.)

Although very subtle bonding effects are operative across this transition series, the trend of increasing force constant from Ca to Zn (as found in argon matrices) is to be expected on the basis of considerations (which are not independent) such as increasing nuclear charge, decreasing radius and increasing electronegativity (from the very electro-positive calcium to the less electropositive nickel and, to a lesser extent, zinc). At the beginning of the series, there are few d electrons and $d\pi$ -p π bonding from the ligand to the metal is expected to be significant and would be expected to raise the force constant. Presumably, the very high stretching frequencies of the diatomic oxides ScO, TiO and VO (see fig. 1) are to be attributed to this π -bonding ^{#2}. This would be less significant in the fluorides and weaker still in the chlorides.

It is interesting that the MCl_2 and MF_2 series show similar trends [8]. The dip at chromium (and copper) may be associated with contributions from M⁺ states. Similarly, the drop in *bond strength* from VO to CrO has been attributed [9] to the addition of an electron to an antibonding orbital.

The results in nitrogen matrices from Ca to Fe are unexceptional, being some 15% lower than those in argon. However, for Co and Ni there is a much greater change between argon and nitrogen, while Zn is again unexceptional. We therefore carried out isotopic enrichment experiments on the Fe, Co, Ni and Zn dichlorides in argon and nitrogen matrices. In the case of Fe, Co and Ni *3, the M ³⁵Cl₂ and M ³⁷Cl₂ isotopically enriched compounds were simultaneously vapourized from identical adjacent tubes placed symmetrically in the furnace and the vapours cocondensed with either argon or nitrogen. In this way, the M³⁵Cl³⁷Cl component (the position of which may be affected by interaction with other modes) was effectively eliminated, enabling the ³⁵Cl-³⁷Cl isotope shift to be determined more accurately. The results of these experiments are summarized in table 1 and fig. 2 shows the spectrum of $CoCl_2$ in nitrogen,

^{#3} The results on NiCl₂ in N₂ have been reported in a preliminary communication [10].

^{*2} For a summary of the ground state bond lengths, vibrational frequencies and symmetries for the gaseous 3d transition element monoxides see ref. [7].

Compound	Argon (ν_3/cm^{-1})	Nitrogen (ν_3 /cm ⁻¹)	Bond angle (N ₂) ^{b)}
⁵⁶ Fe ³⁵ Cl ₂	493.24	<u>447.5</u> 0	
⁵⁶ Fe ³⁵ Cl ³⁷ Cl	490.4 ₁	444 .7 ₅	
⁵⁶ Fe ³⁷ Cl ₂	487.2 ₃ (487.2 ₈) ^c	441.85 (442.09)	1 50°
59Co 35Cl2	<u>493.1</u> 7	438 .7 ₂	
⁵⁹ Co ³⁵ Cl ³⁷ Cl	490.2,	435.96	
⁵⁹ Co ³⁷ Cl ₂	487.0 ₁ (487.0 ₄)	432.90 (433.26)	1 40 °
⁵⁸ Ni ³⁵ Cl ₂	520.94	428.44	
58Ni 35Cl 37Cl	517.74	425.6 ¹ d)	
58Ni 37Cl ₂	514.3, (514.52)	422.5, (423.16)	1 30°
60Ni 35Cl ₂	516.2	425.07 ^d	
⁶⁰ Ni ³⁵ Cl ³⁷ Cl	513.0, ^d	=	
⁶⁰ Ni ³⁷ Cl ₂	509.63 (509.73)	419.0 ₅	[125°]
64Zn 37Cl ₂	510.13	488.54	
66Zn 37Cl ₂	506.07 (505.97)	484.63 (484.54)	
⁶⁸ Zn ³⁷ Cl ₂	502.1 ₈ (502.0 ₂)	480.92 (480.77)	[157°]

Table 1 Infrared spectra of Fe, Co, Ni and Zn dichlorides in argon or nitrogen matrices ^{*)}

^{a)} Frequencies (cm⁻¹ in nitrogen) for: CaCl₂, 373.8; CrCl₂, 426.3; MnCl₂, 431.9.

b) Bond angles calculated from ³⁵Cl/³⁷Cl isotope shifts. Angles in square brackets are calculated from metal isotope shifts for M ³⁷Cl₂.

^{c)} Values in parentheses are calculated from underlined frequencies assuming a bond angle of 180°.

⁴⁾ Results obtained from other spectra, not simultaneous vapourization of ³⁵Cl₂ and ³⁷Cl₂ species. Not used in angle calculations.



Fig. 2. Infrared spectrum in the region of ν_3 for CoCl₂ isolated in a nitrogen matrix using simultaneous independent vapourization of ³⁵Cl and ³⁷Cl enriched samples: (a) experimental; (b) calculated.

together with a simulated spectrum. In the case of $ZnCl_2$, isotopically enriched $Zn^{37}Cl_2$ was synthesized and the zinc isotopes in the naturally abundant material used to determine the bond angle. The results are summarized in the table. Formally, the use of the chlorine isotopes leads to an upper limit for the true bond angle, while central atom substitution leads to a lower limit.

In the case of the argon matrix experiments, our results on FeCl₂, CoCl₂ and NiCl₂ agree closely with those of Green et al. [11] and give an apparent bond angle in the region of 160°. Because of the nature of the sine function, a change of bond angle from 180° to 160° only results in a difference between the two calculated isotope shifts of the order of 1.0 cm^{-1} (for either central atom or terminal atom substitution). As has been pointed out previously [12] for the diatomic molecule, NiO, the discrepancy between calculated and observed frequencies [13] is 0.12 cm^{-1} . We assume that for: FeCl₂ (Ar and N₂); CoCl₂ (Ar); NiCl₂ (Ar); and ZnCl₂ (Ar and N_2) we cannot reliably distinguish the isotope shifts from those which would be given by a linear molecule. By contrast, NiCl₂ and CoCl₂ are strongly bent molecules in nitrogen matrices, central atom and chlorine isotopic substitution leading to a bond angle of $129^{\circ} \pm 1^{\circ}$ in the case of NiCl₂. It must be emphasized that in these calculations, no allowance has been made for anharmonicity or for change in effective mass of the atoms due to interaction with the surrounding matrix.

3. Discussion

In none of our spectra were we able to identify a $\nu_{\rm NN}$ stretching frequency in the infrared spectrum. Previous workers have studied a variety of dihalides in nitrogen-doped argon matrices or in pure nitrogen matrices: MgF₂ [14,15], MgCl₂ [14], PbF₂ [16], SnCl₂ [16], HgF₂ [17], NiF₂ [18] and NiCl₂ [18]. For NiF₂ and NiCl₂ in a pure nitrogen matrix, a very weak band at 2327 cm⁻¹ was found in both cases, effectively coincident with the formally infrared-inactive N=N stretch of the matrix. However, it is well known [19] that impurities can account for the activation of infrared absorption by N₂ matrices. In all other cases, except those of the two magnesium dihalides, no $\nu_{\rm NN}$ frequency was reported.

In a very extensive study Lesiecki and Nibler [14] report v_{NN} at 2344 cm⁻¹ (MgF₂, Raman only) and 2341 or 2340 cm⁻¹ (MgCl₂, Raman and infrared) when these molecules are isolated in a nitrogen matrix. The spectra are convincing and the main problem is the possibility of impurities causing these bands. The authors refer specifically to H_2O , N_2 , O_2 , CO and CO_2 . In view of the high temperatures necessary for volatilisation, HF and HCl might also be considered. The following species have been observed in doped argon matrices (N₂ in an argon matrix having been observed [20] in the Raman effect at 2327.5 cm⁻¹) ^{#4}: N₂-HF [21] 2332.1 cm⁻¹ (weak); N₂-HCl [20,21] 2330.7 cm⁻¹ (weak), 2330.5 cm⁻¹ (R); N₂-H₂O [21] 2329.0 cm⁻¹ (very weak); CO_2 -HCl [22] (observed on ¹³CO₂ 2 cm⁻¹ to high frequency of the ¹³CO₂ fundamental. ¹²CO₂ in argon gives two bands [23] 2344.5 and 2338.8 cm^{-1}); CO₂-HF [24] 2354.4 cm⁻¹. It should also be noted that CO_2 in a nitrogen matrix gives only one intense band [23], a very weak band being observed close to $\nu_{\rm NN}$ of the matrix (2328.1 cm⁻¹). In the absence of studies in ¹⁵N₂ and ¹⁵N¹⁴N it is difficult to be sure whether the bands observed by Lesiecki and Nibler were due to $\nu_{\rm NN}$ of a "complex" MgX₂·N₂ or to an artefact. The shift in frequency for MgF₂ from an argon matrix to a nitrogen matrix is 58 cm⁻¹ for ν_3 (in about 800 cm⁻¹). This may be compared with the shift of ν_3 of NiCl₂ from 521 cm⁻¹ in argon to 428 cm⁻¹ in nitrogen, i.e. nearly 100 cm⁻¹.

For species such as MAr⁺ (where M is a first-row transition element) binding energies of the order of half an electronvolt have been determined [25]. Where several noble gases were studied the binding energy increased with polarizability [26] (as expected for charge-induced-dipole bonding). An interesting comment [27] is that "the potential well depth of VAr⁺ is strong enough as to be similar to the more chemically relevant solvent water". This suggests that in the case of MCl₂ isolated in a matrix there will be strong interactions between $M^{\delta+}$ and the surrounding host. The primary interaction will be electrostatic, polarization of the host atom or molecule by the positively charged metal ion of the guest leading to an ion-induced-dipole interaction. In addition, there may be some charge transfer where the wave functions of partners overlap [28].

It would be naive to expect that one could predict the behaviour of these many-electron systems. However, it is reasonable that bringing up "equatorial ligands" to a linear MCl₂ molecule could cause a considerable reorganisation of the electron density, notably where the d shell is incomplete. This could be more significant for the members to the right-hand side of the first-row transition series which are electron rich. Again, it is reasonable to assume that this could reduce the M–Cl stretching frequency, although it must be emphasized that this is not necessarily directly related to the bond strength. In the case of ZnCl₂, which is a d¹⁰ system, a stronger ligand than N₂ may be necessary to cause a significant reorganization of the electrons in the closed shell.

4. Conclusions

The major frequency shifts and changes in geometry for $CoCl_2$ and $NiCl_2$ between argon and ni-

⁴⁴ Only Raman bands are marked R, all others are infrared observations.

trogen matrices mean that characterization of such molecules as intercalates (for example) by vibrational spectroscopy must be treated with caution. Such changes in shape are not unknown and have previously been reported for ThCl₄ between krypton and neon matrices [29]. Recently, it has been shown [30] that the shapes of some pentachlorides are matrix dependent.

It is also interesting to note that fluorescence and d-d absorption spectra for $CoCl_2$ are not observable in the same matrix gas [31]. Thus absorption (4000–25000 cm⁻¹) is found in a nitrogen matrix; fluorescence in an argon matrix. Clearly, if our results are correct, $CoCl_2$ in a nitrogen matrix is of C_{2v} symmetry and, in particular, does not have a centre of symmetry. Further, the strong interactions with the nitrogen matrix could give a route for the quenching of fluorescence.

A major point of interest is whether our results should be interpreted in terms of the formation (for Co and Ni) of species of the type $MCl_2 \cdot N_2$. In the case of NiCl₂ we have preliminary EXAFS data for this molecule isolated in a nitrogen matrix. There is no clear evidence for a short Ni...N distance from our spectra. Similarly, the lack of an N-N stretching vibration shifted from ν_{NN} of the matrix does not suggest the formation of an $MCl_2 \cdot N_2$ type of species. We thus conclude that the primary interaction is via ion-induced-dipole terms. A figure in a recent paper [32] demonstrates the substantial effects which can occur on bringing up "non-bonding" atoms to a charged metal centre.

5. Experimental

CaCl₂ (Aldrich 99.99%) or MnCl₂·4H₂O (BDH Analar) were oven dried at $\approx 120^{\circ}$ C, followed by drying in vacuo at $\approx 250^{\circ}$ C. Dichlorides of Cr, Fe, Co, Ni, Zn were prepared from reaction of high purity metals with AgCl precipitated from aqueous solutions of AgNO₃ and NaCl. The AgCl after drying at 200°C in vacuo was mixed with the metal in tenfold excess and heated in argon (≈ 400 Torr) until reaction was complete. The tube was cooled, evacuated and the product sublimed out. Isotopic Ag ^{35,37}Cl was synthesized from enriched ³⁵Cl or ³⁷Cl NaCl (Monsanto). After degassing in vacuo, the dichlorides were sublimed from silica or alumina $(CaCl_2)$ tubes and co-condensed with BOC high purity (99.998%) argon or nitrogen (oxygen free). Sublimation temperatures were (°C) about: 900 (Ca); 650 (Cr); 520 (Mn); 450 (Fe); 450 (Co); 450 (Ni); 300 (Zn). The matrix head (Air Products DE204SL) was at ≈ 8 K and a Perkin Elmer 983G plus data station was used to examine the range 4000 to 200 cm⁻¹.

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