Spectroscopic Studies on Matrix-isolated Molybdenum Pentachloride

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Matrix-isolation studies have been carried out on molybdenum pentachloride. In a nitrogen-matrix, prominent i.r. bands are observed at *ca.* 473 and 408 cm^{-1}, which on the basis of isotope studies are assigned as the A_1(axial) and E Mo–Cl stretching modes of monomeric $MoCl_5$ (C_{4v}). Argon matrices yielded essentially the same spectroscopic features. Corresponding u.v.–visible spectra were obtained and assigned on the basis of a square-pyramidal geometry. Attempts to prepare and characterise $MoCl_6$ were unsuccessful.

Molybdenum pentachloride is the commonest binary halide of the element, and is a widely used starting material for the preparation of inorganic and organometallic molybdenum compounds. In the solid state the structure consists of edge-sharing bioctahedra [$Cl_4Mo(\mu\text{-}Cl)_2MoCl_4$] with the Mo ··· Mo separation (3.84 Å) indicating no significant interaction.[1] Mass spectrometric studies[2] are consistent with the presence of monomers in the vapour, and several electron-diffraction studies[3–5] were interpreted in terms of a D_{3h} geometry. However, a more recent electron-diffraction study[6] claimed that the molecular scattering curve could not be fitted to a simple trigonal-bipyramidal monomer, and that optimum fitting indicated the presence in the vapour of both D_{3h} and C_{4v} monomers and possibly also a D_{4d} dimer (*i.e.* $Cl_5Mo–MoCl_5$ with an unbridged Mo–Mo bond).

Spectroscopic data on the vapour-phase material are sparse. A Raman study by Beattie and Ozin[7] and a photoelectron spectroscopy study by Egdell and Orchard[8] both used a D_{3h} model, whilst u.v.–visible data[9,10] have been variously interpreted in either C_{4v} or D_{3h} symmetry. We have recently reported[11] a matrix-isolation i.r. and u.v.–visible study of WCl_5 and WBr_5, which showed evidence for only a single geometry (D_{3h}) in each case, and in view of the controversy over the nature of $MoCl_5$ vapour we now report the results of a similar study on the latter. During this study we also sought evidence for the existence of $MoCl_6$. Although WCl_6 and WBr_6 are well established,[11–13] the only report of molybdenum hexachloride is in a preliminary communication some twenty years ago[14] which has not subsequently been confirmed.

Experimental

Molybdenum(v) chloride was made by two routes. In the first, molybdenum powder (Alfa Inorganics) was heated at *ca.* 300 °C in a stream of dry chlorine, whereupon the pentachloride was obtained as a dark sublimate on cooler parts of the apparatus. This product was carefully resublimed in chlorine, the most volatile fraction being discarded, and the remainder sublimed into break-seal ampoules (Found: Cl, 64.8. Calc. for Cl_5Mo: Cl, 64.9%).

Alternatively, MoF_6 (*ca.* 0.4 g) was condensed at 77 K into a glass ampoule on a vacuum line, followed by boron trichloride (*ca.* 10 cm^3). The trap was cautiously allowed to warm in an ethyl acetate slush-bath. When the contents liquified a vigorous reaction ensued with the production of a dark solution. The boron halides were removed in vacuum, and the black product sublimed in vacuum into break-seal ampoules. The preparation was also conducted by diluting the MoF_6 with $CFCl_3$ (*ca.* 20 cm^3) which moderated the energetic reaction to yield an identical final product.

In marked contrast to the reaction of [$W(CO)_6$] with Cl_2 which produces WCl_6, we found that the analogous reaction between [$Mo(CO)_6$] and Cl_2 produced several products, and was not a viable route to $MoCl_5$.

Details of our matrix-isolation equipment and spectroscopic instrumentation are described elsewhere.[15,16] For the present work all sample manipulations were carried out in glass vacuum lines fitted with greaseless taps and joints [poly(tetrafluoroethylene), J. T. Young]. During deposition, samples were heated in break-seal ampoules at *ca.* 65 °C and condensed with high-purity (BOC 99.999%) nitrogen or argon.

Results and Discussion

Vibrational Spectroscopy.—As indicated above, the earlier electron-diffraction and Raman studies on $MoCl_5$ were interpreted on the basis of a D_{3h} monomer, but the most recent electron-diffraction report indicates that three different structures might co-exist in the vapour. The initial aim of our matrix-isolation studies was therefore to establish, if possible, which form(s) could be isolated in low-temperature matrices, using the established strategy of i.r. and Raman vibrational selection rules. In principle, this approach can provide an unequivocal distinction between D_{3h} and C_{4v} geometries for the monomer from a consideration of the stretching region only.

Thus for the D_{3h} structure, $\Gamma_{str} = 2A_1' + A_2'' + E'$, and the Raman spectrum should show three stretching fundamentals, $2A_1' + E'$, two of them being polarised. The i.r. spectrum should show two bands, A_2'' and E', and thus have one coincidence with the Raman. The alternative C_{4v} structure gives $\Gamma_{str} = 2A_1 + B_1 + E$. All modes are now Raman active, and the i.r. spectrum should exhibit a maximum of three bands: $2A_1 + E$. However, simple band counting in the i.r. is not expected to be conclusive, since for many square-pyramidal molecules the A_1 stretch associated with the basal plane has a very small dipole change, and such species often show only two prominent i.r. stretches. Nevertheless the presence of a stretching mode in the i.r. which is not found in the Raman is indicative of D_{3h} symmetry, whereas a coincidence between a polarised Raman band and an i.r. absorption would suggest C_{4v}. There are no published i.r. data on vapour-phase $MoCl_5$, but in their Raman study on this system Beattie and Ozin[7] assign features at 390 (p), 313 (p), and 418 cm^{-1} as the stretching modes $2A_1' + E'$ of the D_{3h} model.

A second point of distinction concerns the relative intensities of the two most prominent i.r.-active stretches. If one assumes

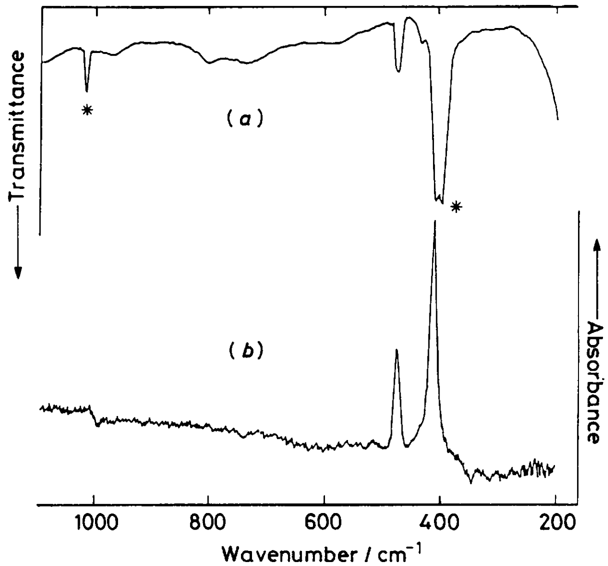

Figure 1. (*a*) Typical i.r. spectrum obtained after deposition of MoCl$_5$ in a nitrogen matrix. The features denoted * are due to MoOCl$_4$. (*b*) Difference spectrum obtained from consecutive spray-ons at a later stage of sample deposition

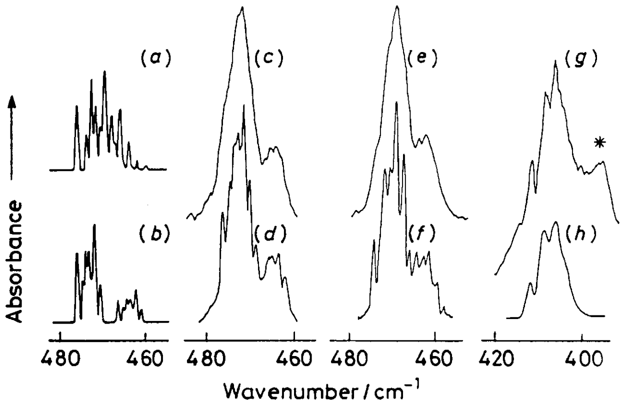

Figure 2. (*a*) Calculated vibrational isotope pattern for the antisymmetric stretch of linear MoCl$_2$. (*b*) Calculated vibrational isotope pattern for diatomic MoCl. The spectral band widths for both (*a*) and (*b*) are 0.5 cm^{-1}. (*c*) I.r. spectrum (460—480 cm^{-1}) obtained at a resolution of 2.0 cm^{-1} for MoCl$_5$ isolated in a nitrogen matrix. (*d*) As (*c*), but recorded at a resolution of 0.5 cm^{-1}. (*e*), (*f*) I.r. spectra obtained for MoCl$_5$ isolated in an argon matrix: conditions identical to (*c*) and (*d*) respectively. (*g*) I.r. spectrum obtained in the region 390—420 cm^{-1} for MoCl$_5$ isolated in argon. The feature at *ca.* 395 cm^{-1} denoted * is due to MoOCl$_4$. (*h*) Spectral simulation of (*g*)

the validity of the bond-dipole model for a C_{4v} structure in which the axial–equatorial bond angles are close to 90°, then it may be shown[17] that the intensities of the axial A_1 stretch and the equatorial E stretch are in the approximate ratio 1:4. For a D_{3h} model, similar considerations indicate the intensity ratio of the A_2'' and E' modes should be *ca.* 2:3.

Finally, it is possible to distinguish between D_{3h} and C_{4v} geometries for pentachlorides on the basis of isotope patterns.[18] For a species MCl$_5$ in which the central atom M is monoisotopic the chlorine isotope structure expected for the A_2'' (axial) and E' (equatorial) stretching modes in D_{3h} symmetry should consist of a triplet and a quartet respectively. In contrast, the two most prominent i.r. absorptions in the C_{4v} structure should appear as a doublet (A_1 axial stretch) and a triplet (E equatorial stretch).

Matrix I.R. Spectra and Assignments.—Figure 1(*a*) shows a typical nitrogen-matrix spectrum obtained during an early stage of an experiment in which a sample of black MoCl$_5$ was heated to *ca.* 65 °C during deposition. Four bands are observed at 1 017, 473, 408, and 395 cm^{-1}. Further deposition at this sample temperature results in continued growth of the features at 473 and 408 cm^{-1}, but little further increase in the bands at 1 017 and 395 cm^{-1}, indicating that at least two species are present. The two bands at 1 017 and 395 cm^{-1} which effectively cease to grow are readily identified[19] as fundamentals of MoOCl$_4$, whilst the bands at 473 and 408 cm^{-1} are attributed to MoCl$_5$, and are most clearly displayed after spectral subtraction [Figure 1(*b*)]. When argon is used as the matrix gas corresponding new features are observed at *ca.* 470 and 405 cm^{-1}.

The assignment of these features to MoCl$_5$ is supported by mass spectrometric studies carried out under identical vaporisation conditions on the same sample, which yielded a weak multiplet corresponding to [MoCl$_5$]$^+$ in addition to the fragments [MoCl$_n$]$^+$ (n = 0—4) as had been reported previously.[2]

Despite repeated and careful attempts, it proved very difficult to obtain primary spectra which were free of MoOCl$_4$, but this impurity could be greatly minimised by flaming the spray-on system prior to deposition, and by pretreatment with MoCl$_5$ vapour.

The observation of only two prominent i.r. bands in the Mo–Cl stretching region clearly points to the presence of only one structural form, and both bands lie in the terminal region, indicating that the trapped species is monomeric. The absorption at 473 cm^{-1} has no close counterpart in the gas-phase Raman, and this therefore suggests a D_{3h} structure, assuming there is no change in shape between the two environments. On this basis the band at 473 cm^{-1} is the A_2'' whilst that at 408 cm^{-1} is E', matrix shifted by *ca.* 10 cm^{-1} from the Raman band at 418 cm^{-1}. The D_{3h} symmetry thus seems established.

However, matrix isolation frequently permits the observation of vibrational isotope structure which would be difficult to obtain in the vapour phase, and in the case of MoCl$_5$ such structure could be used to confirm molecular symmetry.[18] In particular, if the band at 473 cm^{-1} is correctly assigned as the A_2'' mode in D_{3h} MoCl$_2$, it should show isotope structure appropriate for a linear MoCl$_2$ unit. In contrast, the observation of structure characteristic of diatomic MoCl would point strongly towards its assignment as the axial Mo–Cl stretch (A_1) of the C_{4v} model.[18] Several calculations were therefore carried out on the isotope patterns expected for MoCl$_2$ and MoCl units, and the absorption at 473 cm^{-1} was studied under high resolution.

Molybdenum in natural abundance has seven isotopes (^{92}Mo, 15.8; ^{94}Mo, 9.0; ^{95}Mo, 15.7; ^{96}Mo, 16.5; ^{97}Mo, 9.5; ^{98}Mo, 23.5; and ^{100}Mo, 9.6%) and it is evident that when combined with the two isotopes of chlorine (^{35}Cl, 75; and ^{37}Cl, 25%), the antisymmetric stretch of linear MoCl$_2$ should show twenty-one components. Figure 2(*a*) shows the expected isotope pattern, assuming that the frequency of the lightest isotopomer lies at 476.0 cm^{-1}, and that the corresponding symmetric stretch (inactive) lies at 350 cm^{-1}. The resulting pattern is complex, and not immediately identifiable as a 9:6:1 triplet of septets owing to extensive overlap between molybdenum and chlorine isotopic components. However, it is quite distinctive, with several intense components. Additional calculations in which different values were assumed for the inactive symmetric stretch showed that the computed pattern was not sensitive to the position of this mode over the wavenumber range 350—400 cm^{-1}. Figure 2(*b*) shows the isotope pattern computed for diatomic MoCl. In contrast to Figure 2(*a*), this is now easily recognisable as a 3:1 doublet of

Table 1. Observed and calculated vibration frequencies (cm^{-1}) for isotopic components of the band at 473 cm^{-1} of $MoCl_5$ isolated in a nitrogen matrix

Observed[a]	Calculated[b]	Assignment [ν(Mo–Cl)]
476.0	476.0	92–35
474.5	474.6	94–35
c	473.9	95–35
472.8	473.3	96–35
c	472.6	97–35
471.3	472.0	98–35
469.8	470.7	100–35
468.3	466.6	92–37
c	465.2	94–37
c	464.5	95–37
c	463.8	96–37
c	463.1	97–37
463.1	462.5	98–37
461.6	461.2	100–37

[a] Accuracy ±0.5 cm^{-1}. [b] Calculated for diatomic MoCl. [c] Feature not clearly resolved.

septets. The wavenumber of the lightest isotopic unit, $^{92}Mo^{35}Cl$, has again been taken as 476.0 cm^{-1}.

Figure 2(*c*) shows the $MoCl_5$ absorption at 473 cm^{-1} (nitrogen matrix) under medium resolution. It can be seen to consist of a partially resolved 3:1 doublet. Under higher resolution both components of this doublet yield further structure [Figure 2(*d*)], and this absorption may be seen to resemble Figure 2(*b*) rather than 2(*a*). Qualitatively, this indicates a Mo–Cl vibration, and thus C_{4v} geometry.

Detailed comparison between the observed molybdenum and chlorine isotope shifts and those predicted for diatomic MoCl (Table 1) reveals that in $MoCl_5$ the molybdenum isotope effect is somewhat larger than predicted for MoCl, and the chlorine isotope effect somewhat smaller. The net result is thus to reduce the separation between the two septets. However, since it is primarily the number and relative intensities of the isotopic components rather than their precise frequencies which afford the distinction between D_{3h} and C_{4v} geometries,[18] these small frequency perturbations are not important here. Indeed, they are to be expected, since there will be a small vibrational coupling between the two A_1 stretching modes of the C_{4v} model, and this will lead to small differential isotope shifts of the magnitude observed. A small anharmonic contribution would also affect isotope shifts at this level of precision. Figure 2(*e*) shows the band at 470 cm^{-1} in argon matrices under medium resolution, and it is evident that a 3:1 doublet is again observed consistent with C_{4v} geometry. Under higher resolution this band again shows molybdenum isotope structure, but the basic septet patterns are complicated by what we believe to be the presence of two trapping sites.

Attempts to resolve isotope structure on the lower-frequency absorption at *ca.* 400 cm^{-1} were not as successful, and generally produced a relatively broad, asymmetric band. However, this asymmetry was reproducible, and consistent with the band envelope computed for the Mo–Cl *E* stretch. A typical argon-matrix spectrum of this absorption is shown in Figure 2(*g*), together with a computed band envelope.[18]

On the basis of the isotopic structure on the higher-frequency band, we therefore believe that in low-temperature matrices $MoCl_5$ adopts a square-pyramidal geometry, with the axial A_1 stretch lying at *ca.* 473 cm^{-1} and the equatorial *E* mode at *ca.* 408 cm^{-1}. This model is also consistent with the observed intensity ratio, for which we estimate $I(A_1)/I(E)$ to be *ca.* 1:4.4. Our studies do not, of course, establish the *vapour* phase geometry of monomeric $MoCl_5$, but the observation that the i.r. spectra in both argon and nitrogen are so similar suggests perhaps that specific co-ordination at the vacant site of the square pyramid may not be an important factor in determining the low-temperature geometry.

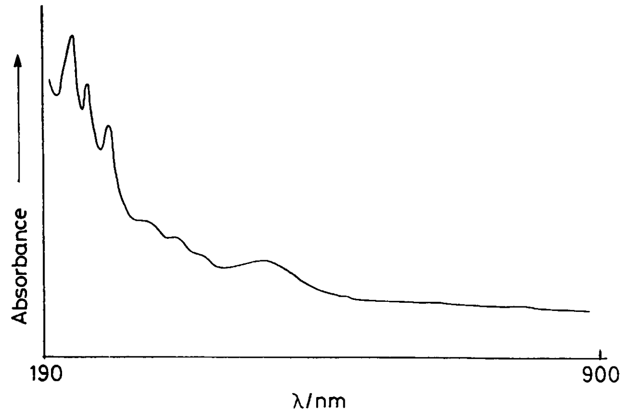

Figure 3. U.v.–visible spectrum obtained for $MoCl_5$ isolated in a nitrogen matrix

U.V.–Visible Studies.—Spectra were obtained for several samples of $MoCl_5$ trapped in nitrogen matrices. As discussed in the i.r. studies (above), initial depositions always showed the characteristic features of the spectrum of $MoOCl_4$,[19] resulting from the extreme sensitivity of $MoCl_5$ to traces of moisture in those parts of the apparatus that could not be flamed before use. However, if the apparatus was first passivated with $MoCl_5$ before deposition onto the central window of the cryostat, subsequent spectra were found to be essentially free of this impurity. Spectra obtained from samples of $MoCl_5$ made by the two routes were found to be identical, and the band positions and relative intensities showed good reproducibility over a large number of runs. We are thus confident that the spectrum reported is that of a single species and in particular is free from halide oxide contamination. A typical spectrum is shown in Figure 3 and the band maxima are listed in Table 2, along with literature data on this system.

The spectrum of $MoCl_5$ shows a broad feature at 21 700 cm^{-1}, three overlapping features at *ca.* 26 000, 29 000, and 32 700 cm^{-1}, and more intense bands at 37 000, 40 300, and 43 750 cm^{-1}. Based upon the C_{4v} structure proposed above, one would predict the *d*-orbital ordering to be d_{yz}, d_{xz} (e) < d_{xy} (b_2) < d_{z^2} (a_1) < $d_{x^2-y^2}$ (b_1), with the ground-state configuration $(e)^1$. The broad band at 21 700 cm^{-1} is assigned as the $e \longrightarrow b_1$ transition. The other three bands predicted were not observed in our experiments, and probably lie in the near-i.r. region. The higher-energy features are likely to be charge-transfer (ligand to metal) transitions. In marked contrast to the spectra of molybdenum(VI) and tungsten(VI) oxide[19] or thio[20] halides, heavy-metal hexafluorides,[21] and WCl_6,[11] none of these bands showed any vibrational fine structure which would have supported the assignment. In C_{4v} symmetry a large number of transitions are possible and specific assignments are impractical on the basis of the information available and the much smaller number of transitions observed. The alternative assignment ($b_2 < e$) is also possible and would result in a structure which was free from Jahn–Teller distortion.

The position of the lowest-energy charge-transfer band, $E_{obs.}$, may be estimated using the optical electronegativity formula[22] (1). Taking $\chi_{opt}(Cl) = 3.0$ and $\chi_{opt}(Mo^V) = 2.0$, and *D*, the spin-

$$E_{obs.} = 30\,000[\chi_{opt}(Cl) - \chi_{opt}(Mo^V)] - 2D/3 \quad (1)$$

Table 2. U.v.–visible data for $MoCl_5$[a]

$MoCl_5$ vapour			Solid Mo_2Cl_{10}[b]	$MoOCl_4$ (vapour)
Ref. 9 Gas	Ref. 10 Gas	This work N_2 matrix		Ref. 19 N_2 matrix
1 009				
15 200			*ca.* 14 300	15 380w
				15 770w
21 300	*ca.* 20 600	21 700	*ca.* 18 500	20 790
27 800		26 000	*ca.* 25 000	
		29 000		
	ca. 32 000	32 700		31 250
35 700	*ca.* 36 000	37 000		36 630
		40 300		
42 600		43 750		
	ca. 48 000			48 780

[a] Transition energies in cm^{-1}. [b] B. J. Brisdon, D. A. Edwards, D. J. Machin, K. S. Murray, and R. A. Walton, *J. Chem. Soc. A*, 1967, 1825.

pairing energy, to be *ca.* 2 500 cm^{-1},[22] the lowest-energy charge-transfer band ($E_{obs.}$) is predicted to lie at 27 500 ± 3 000 cm^{-1} which is in reasonable agreement with the observed transition at 26 000 cm^{-1}. The $\chi_{opt}(Mo^V)$ value is that appropriate to octahedral systems, since our previous studies[19,20] have indicated that the values for the same oxidation state of the metal differ little between five- and six-co-ordinate environments.

Comparison of our matrix spectra with the literature data for the gas phase (Table 2) shows rather poor agreement. We believe this may be due to the presence of $MoOCl_4$ in the samples used to obtain gas-phase spectra. In Bader and Westland's[9] spectrum a band at 1 009 cm^{-1} was assigned as a metal-centred electronic transition, whilst in practice it corresponds closely to the A_1(Mo–O) vibration mode of $MoOCl_4$, and the profile of the spectrum at higher energies is quite similar to that of $MoOCl_4$.[16] Topol *et al.*'s[10] spectrum is of lower resolution than the one reported in the present work and the band at *ca.* 21 000 cm^{-1} is relatively very intense which would again suggest substantial $MoOCl_4$ contamination. In view of the difficulties we experienced in obtaining chloride oxide-free spectra in the present work, it would seem that gas-phase samples free of this impurity might similarly be difficult to achieve.

Molybdenum Hexachloride.—Molybdenum hexachloride has been reported as a minor product of the reaction of molybdic acid with thionyl chloride which could be separated from other products by careful sublimation.[14] We have carried out many reactions of MoO_3 with $SOCl_2$ or BCl_3 under a wide variety of conditions.[23] The major volatile product in every case was $MoOCl_4$, and minor products detected were MoO_2Cl_2 and $MoCl_5$. In a few cases some other minor products were detected, but combined mass spectrometric and matrix-isolation i.r. studies showed these to be WCl_6 and $WOCl_4$ arising from impurities in the molybdenum starting materials, which had become concentrated on sublimation because of their greater volatility. Reaction of MoF_6 with BCl_3 gave exclusively $MoCl_5$ (*cf.* ref. 24). Despite these many attempts we have no evidence for the existence of $MoCl_6$ as a volatile species, although we cannot absolutely rule out the possibility that it may exist as a solid at low temperatures, which decomposes before vaporising.

Conclusions

These experiments indicate that when $MoCl_5$ is isolated in low-temperature argon or nitrogen matrices it adopts a C_{4v} geometry. Since argon in particular is not generally regarded as forming strong adducts, it is possible that this is also the ground-state geometry of the gas-phase molecule. However, at a higher temperature it is probable that this geometry would undergo interconversion with the alternative D_{3h} model by the well known Berry mechanism. This could account for the difficulties encountered in fitting the gas-phase electron-diffraction pattern to a single geometry, and might also account for the disagreement with the gas-phase Raman data.

Attempts to confirm the existence of $MoCl_6$ as a vapour-phase species were unsuccessful.

Acknowledgements

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References

1 D. E. Sands and A. Zalkin, *Acta Crystallogr.*, 1959, **12**, 723.
2 H. Preiss, *Z. Anorg. Allg. Chem.*, 1972, **389**, 280.
3 R. V. G. Evans and M. W. Lister, *Trans. Faraday Soc.*, 1938, **34**, 1358.
4 V. P. Spiridonov and V. G. Romanov, *Vestn. Mosk. Univ., Ser. II*, 1967, **22**, 98 (*Chem. Abstr.*, 1967, **67**, 15868w).
5 Yu. A. Ezhov and A. P. Sarvin, *Zh. Strukh. Khim.*, 1983, **24**, 57.
6 J. Brunvoll, A. A. Ischenko, V. P. Spiridonov, and T. G. Strand, *Acta Chem. Scand., Ser. A*, 1984, **38**, 115.
7 I. R. Beattie and G. A. Ozin, *J. Chem. Soc. A*, 1969, 1691.
8 R. G. Egdell and A. F. Orchard, *J. Electron Spectros. Relat. Phenom.*, 1978, **14**, 277.
9 R. F. W. Bader and A. D. Westland, *Can. J. Chem.*, 1961, **39**, 2306.
10 I. A. Topol, V. M. Kovba, and E. L. Orsina, *Theoret. Chim. Acta*, 1984, **64**, 217.
11 A. K. Brisdon, E. G. Hope, W. Levason, and J. S. Ogden, *J. Chem. Soc., Dalton Trans.*, 1989, 313.
12 J. C. Taylor and P. W. Wilson, *Acta Crystallogr., Sect. B*, 1974, **30**, 1216.
13 W. Willing and U. Muller, *Acta Crystallogr., Sect. C*, 1987, **43**, 1425.
14 M. Mercer, *Chem. Commun.*, 1967, 119.
15 E. G. Hope, P. J. Jones, W. Levason, J. S. Ogden, M. Tajik, and J. W. Turff, *J. Chem. Soc., Dalton Trans.*, 1985, 529.
16 E. G. Hope, W. Levason, and J. S. Ogden, *J. Chem. Soc., Dalton Trans.*, 1988, 997.
17 See, for example, E. B. Wilson, jun., J. C. Decius, and P. C. Cross, 'Molecular Vibrations,' McGraw-Hill, New York, 1955.
18 J. S. Ogden, W. Levason, E. G. Hope, J. T. Graham, D. M. Jenkins, and R. M. Angell, *J. Mol. Struct.*, in the press.
19 W. Levason, R. Narayanaswamy, J. S. Ogden, A. J. Rest, and J. W. Turff, *J. Chem. Soc., Dalton Trans.*, 1981, 2501.
20 P. J. Jones, W. Levason, J. S. Ogden, J. W. Turff, E. M. Page, and D. A. Rice, *J. Chem. Soc., Dalton Trans.*, 1983, 2625.
21 J. H. Holloway, G. Stanger, E. G. Hope, W. Levason, and J. S. Ogden, *J. Chem. Soc., Dalton Trans.*, 1988, 1341.
22 A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' 2nd edn., Elsevier, Amsterdam, 1984.
23 E. G. Hope and R. A. S. Mould, unpublished work, 1985—1987.
24 T. A. O'Donnell and D. F. Stewart, *Inorg. Chem.*, 1966, **5**, 1434.

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