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Short Communication

The electronic spectra of liquid ruthenium and molybdenum pentafluorides

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The absorption spectra of liquid RuF_5 and MoF_5 have been recorded between 4000 cm^{-1} and 26 000 cm^{-1}. Possible assignments are discussed.

The X-ray structures of transition metal pentafluorides have thus far depicted a bridged pseudo-octahedral environment for the transition metal[1]. The electronic spectra of two MF_5 compounds, RuF_5 and MoF_5, are presented here for the liquid phase with a discussion of the spectral assignments.

Experimental

The ruthenium pentafluoride and molybdenum pentafluoride samples were prepared by direct fluorination of the metals in a flow apparatus[2, 3]. Purification was accomplished by repeated distillations *in vacuo*. The quartz cells were filled under an active vacuum by heating the whole apparatus except for a Pyrex U-trap attached to the neck of the cell which was cooled to 0°. After sealing under a vacuum or under one atmosphere of nitrogen, the pentafluoride was warmed and allowed to flow into the spectroscopic cell. (Caution must be exercised here so that the pentafluoride does not crystallize thus causing the narrow cell to crack.) The spectra were recorded immediately on a Unicam SP 700 spectrophotometer using an electrically-heated metal block to maintain the correct temperature and to hold the cell. The spectrum of the empty cell was recorded before and after use, the pentafluoride spectra being appropriately modified.

Discussion

The spectrum of the ruthenium pentafluoride melt shows peaks distinctly characteristic of d^3 octahedral transition metal compounds. The assignment of this spectrum to spin-forbidden transitions is given in Table 1. The ligand field parameters of $B = 400$ cm^{-1}, $\lambda = 1200$ cm^{-1}* have been used to calculate the

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* λ is taken as 80% of the free ion value as given by Dunn[4].

energies of the transitions. The value of 10 Dq cannot be obtained since no spin-allowed transition was observed. Any inaccuracy of the fit probably reflects expected distortions of the pseudo-octahedral environment.

TABLE 1

SPECTRUM OF THE RuF_5 MELT

Observed bands[a] (cm^{-1})	Intensity[a] (Absorbance)	Assigned transition	Calculated energy (cm^{-1})
8,600	0.20	$\Gamma_8(^4A_1) \rightarrow \Gamma_8'(^2E)$ $\rightarrow \Gamma_8''(^2T_1)$	8,500 8,700
9,000 (sh)	0.17	$\rightarrow \Gamma_6(^2T_1)$	9,100
13,500	0.16	$\rightarrow \Gamma_7(^2T_2)$ $\rightarrow \Gamma_8'''(^2\mathrm{T}_2)$	14,300 14,400
13,700 (sh)	0.17		
14,200	0.05		
15,000	0.12		
15,700 (br)	0.11		

[a] At ~ 90°C with 0.1 mm path length.

The spectrum of molten molybdenum pentafluoride at 66° (and of a solution of the pentafluoride in molybdenum hexafluoride at 25°) presents more difficulties in interpretation. Between 4000 and 26 000 cm^{-1} there is one symmetric band centred at 7500 cm^{-1} with an absorbance of 0.28 and a path length of 0.1 mm. This transition is too low in energy to arise from the d^1 octahedral 10 Dq transition, $^2E_g \rightarrow {}^2T_{2g}$. In addition, the transition between spin-orbit states is predicted at a much lower energy (*i.e.* $^3/_2\ \lambda = 1236$ cm^{-1})[4]. It is therefore unlikely that distortion of a d^1 pseudo-octahedral structure could account for this transition. A square-pyramidal structure is also unlikely, since the energies of the predicted transitions would be very similar to those for a distorted octahedral structure. However, some justification may be found for assigning the absorption to a trigonal-bipyramidal configuration. The results of calculations[5] on $CuCl_5^{3-}$ can be extended to the present system by a series of approximations. The $^2A'_1 \rightarrow {}^2E'$ transition in $CuCl_5^{3-}$ was predicted at 3800 cm^{-1}; using the ligand field strengths for central metal ions and ligands[6,7], the predicted value for MoF_5 is 9100 cm^{-1} compared with the observed absorption at 7500 cm^{-1}; this difference is probably within the limits of accuracy of the extrapolation. Although infrared and Raman spectroscopic measurements on liquid molybdenum pentafluoride were originally interpreted in terms of a trigonal bipyramidal configuration for the molecule[8], subsequent studies on the very similar niobium and tantalum pentafluorides suggest strongly that in all these compounds a polymeric unit is retained[9].

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