at higher frequency than found for the nitrates. This vibration has been assigned as the metal–oxygen stretching vibration to the coordinated nitrate in the nitrates [5]: The occurrence of this vibration at a higher frequency for the carbonates, may be a reflection of the stronger complexation occurring with the carbonates. The magnitude of splitting of ν_3, and the trend with Z, for the carbonates is similar to that found for the nitrates [8].

Some X-ray crystallographic data are available for the hydrated carbonates [9–13], and apparently none exist for the anhydrous materials. The site symmetry of the carbonate in the hydrated salts is C_{2v}, C_2 or C_1. The effect of causing the E vibration to split, v_1 to appear, the appearance of a low frequency vibration, which may be ascribed to a metal–oxygen stretching vibration to the carbonate, are consistent with several superimposing effects. Contributing causes are the perturbation of the anion by water molecules, interaction with the metal (either through coordination or by interaction with a highly polarizing cation) and crystal effects. In the case of the anhydrous salts the water effects are eliminated. The low frequency absorption remains in the anhydrous salts since the coordination effect exists, and presumably also the crystal effects. The similar split of E vibrations for the hydrated salts and for the anhydrous salts may possibly be explained by the fact that the predominant perturbing effect in both salts is caused by the interaction with the metal. The trend with Z for both salts is expected, since interaction with the metal exists in both classes of salts.

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Electron transition in dodekahedral crystal field — III
8-coordinated complexes of pentavalent rhenium

THE PENTAVALENT state of rhenium is established in a number of eight coordinated complexes in which rhenium may exist either as cationic or anionic complexes. All these complexes are diamagnetic and the i.r. spectra of the eight coordinated cyanocomplexes are very similar to corresponding molybdenum complex [1, 2]. So by analogy, it has been assumed that the geometry of the eight coordinated rhenium complexes is dodekahedral as is the case with eight coordinated cyano-complexes of molybdenum [1, 2]. In two previous communications [3, 4] the electronic spectra of the eight coordinated cyanocomplexes of molybdenum have been interpreted in terms of a d-orbital level scheme

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in a dodekahedral crystal field. The object of the present investigation was to measure the absorption spectra of two cationic and two anionic 8-coordinated complexes of pentavalent (d^2) rhenium in solution and where possible, in crystalline state, and see how far they conform to a d-orbital energy level scheme in a dodekahedral crystal field.

EXPERIMENTAL

All the complexes were prepared from reagent quantity chemicals of E. Merck and Co. and B.D.H., Ltd. $K_3[Re(CN)_8]$ and $K_3[Re(OH)_4(CN)_4]$ were prepared by the method of Lock and Wilkinson[1], while $[Re(py)_4(OH)_4]Cl$ and $[Re(en)_2(OH)_4]Cl$ (where py and en stands for pyridine and ethylene diamine respectively) were prepared by the method of Johnson, Lock and Wilkinson[2]. All these compounds were found to be diamagnetic.

The absorption spectra in aqueous solution were measured in a Beckman spectrophotometer Model DU, while the spectra of polycrystalline materials were measured in a crystal spectrophotometer described and used by Chakraborty and Basu[5]. The extinction coefficients on crystalline material were measured by approximate method of Tsuchida[6]. Since sufficiently big single crystals could not be grown, no polarization selectivity measurements could be made.

RESULTS AND DISCUSSIONS

$K_3[Re(CN)_8]$ complex was a brown crystalline substance, fairly soluble in water. The cyanide stretching frequencies in this complex were almost the same as those found in $K_3[Mo(CN)_8]$. Lock and Wilkinson[1] has concluded that this compound has a dodekahedral geometry. In aqueous solution the compound shows three absorption peaks at 340 mμ ($\epsilon = 50$), 420 mμ($\epsilon = 50$) and 520 mμ ($\epsilon = 10$) (Fig. 1a). Evidently the first two bands should be associated with singlet crystal field transitions, while the longest wavelength band must be a triplet one. If we associate the 420 mμ(23,809 cm^{-1}) and 520 mμ(19,230 cm^{-1}) bands with $A_1 \rightarrow B_1$ singlet and triplet transitions in a dodekahedral crystal field, then we calculate[4] the crystal field parameters as $D_q = 6526$ cm^{-1}; $F_2 = 355$ cm^{-1}; and $F_4 = 85$ cm^{-1} with these parameters we locate the singlet $A_1 \rightarrow E$ transition at 33,297 cm^{-1} which agrees reasonably well with the experimental value of 29,300 cm^{-1} (340 mμ).

Under high resolution the band at 420 mμ shows well defined fine structure (Fig. 2) which can be interpreted in terms of the ground (ν) and excited state (ν') vibrational frequencies of 581 cm^{-1} and 362 cm^{-1} respectively.

Vibrational assignment of 420 mμ band of $K_3[Re(CN)_8]$

λ(mμ)	ν(cm^{-1})	$\Delta\nu$	Assignment
398	25,125	735	$\nu_0 - 2\nu'$
404	24,752	362	$\nu_0 - \nu'$
410	24,390	0	ν_0
420	23,809	581	$\nu_0 + \nu$
430	23,255	1135	$\nu_0 + 2\nu$

These vibrational frequencies may be associated with stretching frequency of metal–carbon bond which appears in the range of 550–650 cm^{-1} in the cyanocomplexes of transition elements[7].

The electronic spectral data therefore suggests a dodekahedral geometry for $K_3[Re(CN)_8]$.

The complex $K_3[Re(CN)_4O_2]2H_2O$ has been formulated as $K_3[Re(CN)_4(OH)_4]$ by analogy with the corresponding molybdenum complexes[1]. In aqueous solution the orange coloured complex shows three bands (Figs. 1b and 3) with peaks at 300 mμ($\epsilon = 100$), 420 mμ($\epsilon = 30$) and 480 mμ($\epsilon = 10$). If we associate 420 mμ(23,809 cm^{-1}) and 480 mμ(20,833 cm^{-1}) bands with $A_1 \rightarrow B_1$ singlet and

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