

metal ion conforms with the normal coordination number of the given metal ion. In the case of iron(III) a 6 : 1 ratio of N-oxide to metal ion was reported [1, 2].

For our initial studies we chose to examine some alkyl substituted pyridine N-oxides [9]. The compounds were prepared by the method of Byers *et al.* [10], using FeCl_3 instead of $\text{Fe}(\text{ClO}_4)_3$. The i.r. absorbances and the elemental analyses are shown in Table 1. I.r. spectra were obtained as KBr discs on a Beckman IR 12 Recording Spectrophotometer. The analyses were performed by the Galbraith Laboratories, Knoxville, Tennessee.

Since the elemental analyses indicate a ratio of 2 : 1, N-oxide to iron(III), the normal octahedral structure is unlikely. The compounds of iron(III) previously reported [1, 2] all had a 6 : 1 N-oxide to iron(III) ratio. In order to get the normal octahedral case, either solvent molecules or chloride ions would have to occupy four coordination positions which is inconsistent with the analyses.

Other possibilities for the structures of these compounds are (a) tetrahedral and (b) bridged octahedral. In case (b) either chloro-bridging or oxygen-bridging N-oxide ligands similar to those found for other transition metals [5, 11] are possible. We suggest structure (a) although not many tetrahedrally coordinated Fe(III) complexes besides FeCl_4^- have been reported. This is probably due to their instability in aqueous solution with respect to octahedrally coordinated Fe(III). In (b) one would expect N-O stretching bands at two different frequencies, with the bridging type lower than the normally coordinated N-oxide. The absorbance assigned to the N-O stretching frequency is a symmetrical, sharp peak indicating one type of N-oxide coordination. The shift predicted for the N-O stretching frequency upon coordination to Fe(III) is of the same magnitude as reported [1, 8]. Note that as substitution occurs at the 2- and 6- positions of the heterocyclic ring, there is a further decrease in the N-O stretching frequency. This is attributed to steric effects. These same steric effects appear to decrease the other i.r. absorbances shown in Table 1. Based on the same argument we would also expect more than one Fe-O stretching frequency. This was not observed. The assignment of the single i.r. band in the 290 cm^{-1} region to the Fe-Cl stretching frequency was made on the following basis: in FeCl_4^+ this Fe-Cl stretching frequency is at 330 cm^{-1} [12]. Because of the greater donor ability of an N-oxide ligand, it should appear at a position less than 330 cm^{-1} . Further, no absorbance in this region was observed for $[\text{Fe}(-\text{O}-\text{N}(\text{C}_5\text{H}_4\text{CH}_3)_6)](\text{ClO}_4)_3$.

All of the iron(III) coordination complexes prepared decompose instantly when dissolved in water. For this reason and the fact that no temporary color formation was observed, the 'ferric chloride test' often used to test for the presence of an N-oxide group is unsuitable for these compounds. However, pyridine N-oxides substituted in the 2-position with a group bearing an unshared pair of electrons do give color reactions in aqueous solution. We are presently investigating this type of compound.

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Department of Chemistry
Central Michigan University
Mt. Pleasant
Mich. 48858

D. X. WEST
T. J. DELIA
T. M. WILCOX

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The symmetry of rare-earth carbonates*

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RECENTLY, Goldsmith and Ross [1, 2] studied the factors which affect the i.r. spectra of several planar anions with D_{3h} symmetry. Among those compounds studied were the anhydrous and octa-

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hydrated rare-earth carbonates [2]. The appearance of ν_1 and the splitting of the *E*-type vibrations (ν_3 and ν_4) were consistent with a site symmetry for the carbonate group of C_{2v} , C_2 or C_1 . Certain considerations concerning the spectra of these compounds have been apparently overlooked. Additionally, the low frequency region has not been investigated. This note is an extension of the previous study [2], and as a consequence, the following points of interest are presented:

- (1) The magnitude of splitting of ν_3 and ν_4 is of the same order of magnitude for the anhydrous and hydrated salts.
- (2) The splitting of ν_3 appears to increase as *Z* increases. No trend is apparent for ν_4 .
- (3) The forbidden frequency, ν_1 , appears for both the hydrates and anhydrous salts.
- (4) Additional bands observed in the spectra of hydrated salts are due to coordinated water librational modes [3-4].
- (5) A broad intense band is observed at 300-400 cm^{-1} in the anhydrous salts, which is not shifted under high pressures as are lattice modes in compressible ionic solids [5]. This band diminishes only slightly in intensity with an increase in hydration. No other vibrations are found at lower frequencies (to 70 cm^{-1}). Table 1 summarizes these data.

Table 1. Various relationships existing in spectra of rare-earth carbonates (cm^{-1})

Anhydrous rare-earth carbonates	$\Delta\nu^*$	$\Delta\nu^+$	$\Delta\nu^*$	$\Delta\nu^+$	Low frequency vibrations in anhydrous Salt
	Hydrate	Anhydrous	Hydrate	Anhydrous	
	ν_3		ν_4		
La	95(75)‡	80	55(30)‡	61	320(s), broad
Nd	95	85	55	65	525(sh), 350(s), 275(sh)
Sm§	100	80	48	75	520 (sh), 375(s), 280(sh)
Dy	120	105	60	60	500(vvw), 420(m), 320(m) 285(m)
Yb	125	130	67	66	345(s), broad
Lu	115	140	55	60	450(s), 335(s)

* Taken from Ref. [2].

† Results are from this work.

‡ Three bands are observed. $\Delta\nu_1$ = high frequency band 1-low frequency band;
 $\Delta\nu_2$ = high frequency band-low frequency band.

§ For $\text{Sm}_2\text{CO}_3 \cdot 8\text{H}_2\text{O}$ the water librational modes are at 744 and 530 cm^{-1} .

The assignment of the low frequency vibrations between 300-400 cm^{-1} in the anhydrous salts is of interest. The choice as to whether these bands are due to lattice modes or to metal-oxygen stretching vibrations to the carbonate must be made. Lattice modes are cation and anion sensitive. Thus, it would be expected that CaCO_3 (calcite) should have lattice modes occurring at higher frequencies than the low frequency bands found in the rare-earth carbonates. Actually, calcite [6] shows lattice modes at 315, 228, 190 and 110 cm^{-1} , at positions equal to or lower than the heavier rare-earth carbonates. These results, in conjunction with the nonpressure dependency behavior of the low-frequency band in the anhydrous salts, lend support to the conclusion that these bands are not lattice modes, and may be metal-oxygen stretching modes to a coordinated carbonate.

A comparison of the behavior of the low frequency band in the anhydrous carbonates with that in the anhydrous rare earth nitrates [7] is worthy of comment. The low frequency band in the nitrates occurs at ~ 180 -270 cm^{-1} . Thus, the position of the low frequency band for the carbonates is

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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, ν_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.

Chemistry Division
Argonne National Laboratory
Argonne, Ill. 60439, U.S.A.

J. R. FERRARO
A. QUATTROCHI

Department of Chemistry
Indian Institute of Technology
Kanpur, India

K. C. PATIL
C. N. R. RAO

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

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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 $m\mu$ ($\epsilon = 50$), 420 $m\mu$ ($\epsilon = 50$) and 520 $m\mu$ ($\epsilon = 10$) (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 $m\mu$ (23,809 cm^{-1}) and 520 $m\mu$ (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 $m\mu$).

Under high resolution the band at 420 $m\mu$ 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 $m\mu$ band of $K_3[Re(CN)_8]$

$\lambda(m\mu)$	$\nu(cm^{-1})$	$\Delta\nu$	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 $K_3[Re(CN)_4O_2] \cdot 2H_2O$ 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 $m\mu$ ($\epsilon = 100$), 420 $m\mu$ ($\epsilon = 30$) and 480 $m\mu$ ($\epsilon = 10$). If we associate 420 $m\mu$ (23,809 cm^{-1}) and 480 $m\mu$ (20,833 cm^{-1}) bands with $A_1 \rightarrow B_1$ singlet and

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