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 $Fe(ClO_4)_3$. 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 [Fe-(-O-N-$CH_3)_6$]$(ClO_4)_3$.

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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9. Complexes of these pyridine N-oxides with iron(III) did not form in water.
10. W. Byers, A. B. P. Lever and R. V. Parish, *Inorg. Chem.* **7**, 1835 (1968).
11. C. J. Popp, J. H. Nelson and R. O. Ragsdale, *J. Am. chem. Soc.* **91**, 611 (1969).
12. L. A. Woodward and M. J. Taylor, *J. chem. Soc.* 4473 (1960).

J. inorg. nucl. Chem., 1969, Vol. 31, pp. 3667 to 3669. Pergamon Press. Printed in Great Britain

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-

1. J. A. Goldsmith and S. D. Ross, *Spectrochim Acta* **22**, 1069 (1966).
2. J. A. Goldsmith and S. D. Ross, *Spectrochim Acta* **23A**, 1909 (1967).

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	$\Delta\nu^*$ Hydrate	$\Delta\nu^+$ Anhydrous	$\Delta\nu^*$ Hydrate	$\Delta\nu^+$ Anhydrous	Low frequency vibrations in annhydrous Salt
	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. Δv_1 = high frequency band 1-low frequency band; Δv_2 = high frequency band-low frequency band.

§ For $Sm_2CO_3 \cdot 8H_2O$ the water liberational 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

3. C. Postmus and J. R. Ferraro, *J. chem. Phys.* **48**, 3605 (1968).
4. L. Basile, D. Gronert and J. R. Ferraro, *Solvent Extraction Chemistry* (Edited by A. S. Kertes and Y. Marcus). Interscience, New York (1969).
5. J. R. Ferraro, S. S. Mitra and C. Postmus, *Inorg. nucl. chem. Lett.*, **2**, 269 (1966).
6. E. E. Angino, *Am. Mineralogist* **52**, 137 (1967).
7. A. Walker and J. R. Ferraro, *J. chem. Phys.* **43**, 2689 (1965).