

POSSIBLE LIGAND FIELD EFFECTS IN METAL-OXYGEN VIBRATIONS OF SOME FIRST-ROW TRANSITION METAL ALKOXIDES*

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Although metal alkoxides, particularly alkyl titanates and their hydrolysis products, have been the subject of several infrared studies,¹⁻⁵ little is known of the vibrational spectra of transition metal alkoxides in the far infrared region. Kriegsmann and Licht¹ have assigned Ti-O vibrational modes in titanium(IV) alkoxides in the range 400–650 cm⁻¹ and similar assignments have been made by Barraclough *et al.*⁴ for Ti(OEt)₄.

We report here far infrared spectra of the methoxides of chromium(II), manganese(II), iron(II), cobalt(II), nickel(II), copper(II), and zinc(II) within the region 600–200 cm⁻¹ (Table 1). Two bands, separated by 40–140 cm⁻¹, are found for

TABLE 1

Methoxide	$\nu(\text{M-O})$ (cm ⁻¹)	Methoxide	$\nu(\text{M-O})$ (cm ⁻¹)
Cr(OMe) ₂	515, 470(?)	Ni(OMe) ₂	425, 375
Mn(OMe) ₂	360, 307	Cu(OMe) ₂	520, 435
Fe(OMe) ₂	370, 330, 420(?)	Zn(OMe) ₂	465, 325
Co(OMe) ₂	491, 412, 340		

all the compounds except Co(OMe)₂, where a third band is observed. For Pb(OMe)₂⁶ and some alkyl tin methoxides, R₂Sn(OMe)₂,⁷ the two metal-oxygen vibrations have been assigned to asymmetric and symmetric stretching modes, $\nu_{\text{as}}(\text{M-O})$ and $\nu_{\text{s}}(\text{M-O})$. The pairs of bands listed in Table 1 can likewise be assigned to asymmetric and symmetric stretching modes although they may equally well arise from distortions of the MO₆ octahedra which produce more than one M-O bond distance. The two (Cu-X) bands in copper(II) halide pyridinates are believed to be due to distortions of this kind.⁸ Whichever interpretation is correct, it is likely that within the present

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¹ Kriegsmann, H., and Licht, K., *Z. Electrochem.*, 1958, **62**, 1163.

² Bradley, D. C., and Westlake, A. H., *Nature*, 1961, **191**, 273.

³ Zeitler, V. A., and Brown, C. A., *J. phys. Chem.*, 1957, **61**, 1174.

⁴ Barraclough, C. G., Bradley, D. C., Lewis, J., and Thomas, I. M., *J. chem. Soc.*, 1961, 2601.

⁵ Brini, M., and Deluzarche, A., *Bull. Soc. chim. Fr.*, 1961, 535.

⁶ Amberger, E., and Honigschmid-Grossich, R., *Chem. Ber.*, 1965, **98**, 3795.

⁷ Butcher, F. K., Gerrard, W., Mooney, E. F., Rees, R. G., and Willis, H. A., *Spectrochim. Acta*, 1964, **20**, 51.

⁸ Goldstein, M., Mooney, E. F., Anderson, A., and Gebbie, H. A., *Spectrochim. Acta*, 1965, **21**, 105.

series of methoxides the observed bands will have similar origins since their electronic spectra and magnetic properties indicate that the central metal atom is surrounded by six oxygen atoms in an approximately octahedral environment⁹ in each case.

Although the spectra are not always well resolved (half-widths of 100 cm^{-1} or more characterize the spectra of $\text{Mn}(\text{OMe})_2$, $\text{Fe}(\text{OMe})_2$, and $\text{Ni}(\text{OMe})_2$), the relative positions of the band maxima appear to provide evidence for a well-defined dependence on the d -shell population (Fig. 1). The pair of M-O stretching frequencies for the

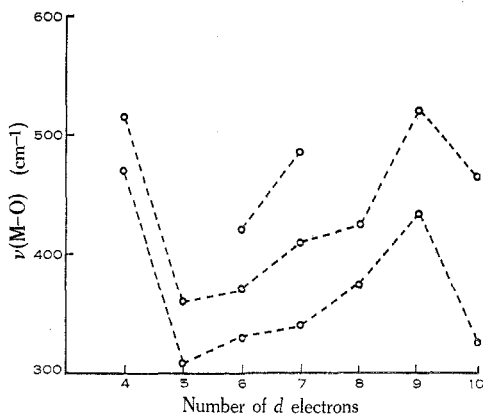


Fig. 1.—Dependence of $\nu(\text{M-O})$ on d -shell populations.

configurations ($t_{2g}^3 e_g^1$) and ($t_{2g}^6 e_g^3$) are highest, those for ($t_{2g}^3 e_g^2$) and ($t_{2g}^6 e_g^4$) are lowest, and a steady increase occurs from $\text{Mn}(\text{OMe})_2$ through to $\text{Cu}(\text{OMe})_2$. This correlation between metal-ligand stretching modes and d -orbital population of the high-spin complexes accords well with the expectations of ligand field theory, and parallels closely the trend in radii of divalent metal ions found in their binary oxides and halides.¹⁰ Unfortunately, the insolubility of the present compounds precludes the desirable study of their vibrational spectra in solution. Furthermore, in the absence of detailed structural information, it is not possible to differentiate those M-O modes which involve terminal alkoxide groups from those which involve bridging alkoxide groups. The additional band at 491 cm^{-1} in $\text{Co}(\text{OMe})_2$, and the poorly resolved shoulder at about 420 cm^{-1} in $\text{Fe}(\text{OMe})_2$, may well be reflecting just such a difference in ligand coordination. Even so, the general features of the trend seem to be unambiguous and corresponding trends in other series of compounds are to be expected.

Experimental

Materials

The chromium(II), manganese(II), iron(II), cobalt(II), nickel(II), and copper(II) methoxides were prepared as described previously.⁹ The $\text{Zn}(\text{OMe})_2$ was kindly prepared for us by Dr T. Mole from dimethylzinc and methanol.

Spectra

The spectra were obtained from Nujol mulls between polythene plates using a Perkin-Elmer 421 spectrophotometer.

⁹ Adams, R. W., Bishop, E. A., Martin, R. L., and Winter, G., *Aust. J. Chem.*, 1966, 19, 207.

¹⁰ Pryce, M. H. L., *J. chem. Phys.*, 1958, 28, 244.