^{18}O Isotopic Infrared Studies on Isocyanide–Oxygen–Metal Complexes

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RECENTLY several low-valent post-transition metal complexes have been found to absorb molecular oxygen forming mononuclear peroxycomplexes, *e.g.* $MO_2(PPh_3)_2$ ($M = Pt$,[1,2] Pd,[1,2] Ni[2]), $NiO_2(Bu^tNC)_2$,[3] $IrO_2Cl(CO)(PPh_3)_2$,[4] $RhO_2Cl(AsPh_3)_2$,[5] and $RhO_2Cl(Bu^tNC)(PPh_3)_2$.[6] A strong i.r. absorption band in the region of 800—900 cm.$^{-1}$ is universally bound for these peroxy-complexes. Although the absorption is ascribed to the peroxy-vibration, definite assignment has not yet been made.

We report a preliminary result on the i.r. studies of the simplest peroxy-complexes, $NiO_2(Bu^tNC)_2$ and $PdO_2(Bu^tNC)_2$.[6] The corresponding complexes containing heavy oxygen (25·5% as $^{18}O_2$) were prepared.[7] Their spectra in Nujol mull (Figure) show new bands at two regions, 800—900 and 480—550 cm.$^{-1}$, no other new band due to isotopic substitution was found between 3500—80 cm.$^{-1}$. The band at 898 cm.$^{-1}$ for the nickel complex splits into three, 898, 873, and 848 cm.$^{-1}$, and the band at 893 cm.$^{-1}$ for the palladium complex into three, 893, 868, and 837 cm.$^{-1}$. These three bands appear to be explicable in terms of O–O stretching since the oxygen contains three molecular species, ^{16}O–^{16}O, ^{16}O–^{18}O, and ^{18}O–^{18}O. Qualitatively the relative intensity of the three bands is that expected from the isotopic composition of oxygen gas ($^{16}O_2$:^{16}O–^{18}O:$^{18}O_2$ = 58·3 :

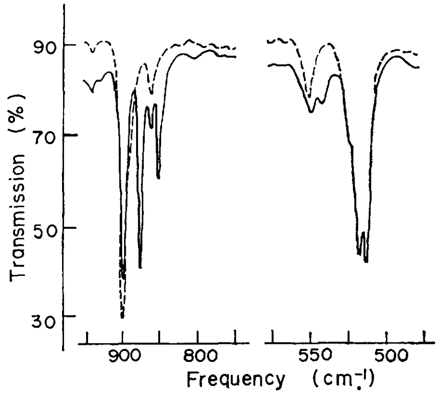
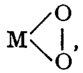


FIGURE 1. *Infrared spectra of the nickel–oxygen complex* (——) $Ni(O_2^*)L_2$; (- - -) $Ni(O_2)L_2$.

32·4 : 9·3). An excellent agreement is obtained between the empirical wave numbers and those calculated on the assumption of free diatomic molecules, *i.e.* 1 : 1·209 : 1·061. The ratio gives calculated wave numbers for the nickel complex as 898, 873, 846 and for the palladium complex as 893, 868, 842 cm.$^{-1}$. The implication is, of course, that the band near 900 cm.$^{-1}$ is assignable to the stretching vibration of the O–O bond. The agreement further implies that the two oxygen atoms coordinate to a metal as a peroxy-group (not as two independent oxygen atoms) forming an isosceles triangle as in Vaska's oxygen complex, , which was elucidated by *X*-ray analysis.[8] The fact that substitution of Ni by Pd has little effect on the stretching frequency (consistent with the isosceles structure), suggests that mixing with other vibrations is slight, or absent. A bent linear or bridged form is thus excluded.

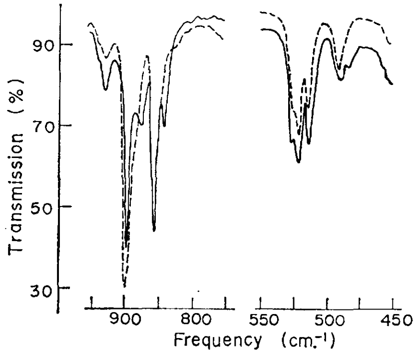


FIGURE 2. *Infrared spectra of the palladium-oxygen complex* (——) Pd (O_2^*) L_2; (- - -) Pd(O_2) L_2.

The marked decrease in frequency from the corresponding Raman mode of vibration (1555 cm.$^{-1}$) of the free oxygen molecule indicates reduction in the bond order. The origin of the isotropical bands near 500 cm.$^{-1}$ is not clear at present.

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