Oxygen-18 Isotopic Infrared Study of Dioxygen–Transition Metal Complexes

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Abstract: An ^{18}O isotopic infrared study of various dioxygen complexes, $Pt(O_2)(PPh_3)_2$, $M(O_2)(\textit{tert}\text{-}BuNC)_2$ (M = Ni, Pd), and $RhX(O_2)L_2(\textit{tert}\text{-}BuNC)$ (X = Cl, Br; L = PPh_3, $AsPh_3$) prepared with a heavy dioxygen mixture ($^{16}O_2$, $^{16}O{-}^{18}O$, and $^{18}O_2$) revealed the geometry of the O_2 coordination to be a side-on isosceles structure except in the Pd complex, where deviation from the isosceles structure was inferred. Approximate force constants of O–O (a_1) as well as M–O stretching vibrations (a_1 and b_1) were calculated on the simple triatomic isosceles local model (C_{2v}). The results indicate a marked reduction in the O–O stretching force constant upon coordination (3.0–3.5 mdyn/Å) relative to that of the free gaseous dioxygen (11.5 mdyn/Å). The M–O stretching force constants (2.1–3.2 mdyn/Å) were correlated with the reactivity of the dioxygen ligand. The effect of various auxiliary ligands on the metal–oxygen vibrations is examined for the Rh complexes, $RhXO_2L_2(RNC)$ (R = *tert*-Bu, cyclohexyl, $p\text{-}CH_3C_6H_4$), and the nature of the metal–oxygen bond is discussed.

Although there has been continuing interest in metal–dioxygen complexes, no definite infrared assignment has been made of the metal–oxygen vibration which is valuable to an understanding of the nature of the bond.[3] Here we report isotopic ir studies of various metal–oxygen complexes, $PtO_2(PPh_3)_2$, $MO_2(\textit{tert}\text{-}BuNC)_2$[4] (M = Ni, Pd), and $RhCl(O_2)(PPh_3)_2(\textit{tert}\text{-}BuNC)$, leading to the assignment of metal–oxygen as well as oxygen–oxygen stretching vibrations. Also included are stretching frequency data for a series of complexes, $RhX(O_2)L_2(RNC)$ (X = Cl, Br, I; L = PPh_3, $AsPh_3$; R = *tert*-Bu, $c\text{-}C_6H_{11}$, $p\text{-}CH_3C_6H_4$). The study provides information such as (a) geometry of dioxygen coordination, (b) approximate strengths of metal–oxygen and oxygen–oxygen bonds, and (c) influence of the metal and the auxiliary ligand on the bond strengths. The O–O stretching force constants of coordinated dioxygen may be compared with those of the free oxygen molecule in excited states, affording information relevant to discussion of the bonding. Furthermore, the metal–oxygen stretching data, as a function of the metal and the auxiliary ligands, relate to the reactivity of the dioxygen ligand, which has been a subject of general interest to chemists in various fields.

After completion of our ^{18}O isotopic infrared study, Horn, Weissberger, and Collman[5] reported ^{18}O isotopic infrared shifts for dioxygen complexes. In addition to Vaska's iridium complexes, these authors examined the phosphine–platinum complex $PtO_2(PPh_3)_2$, but report only the isotopic shift of the O–O stretching vibration at 822 cm^{-1}. Their results indicated a good agreement between the observed shifts in the 800–900 cm^{-1} region with the calculated shifts based on a simple diatomic oscillator as we have already shown before[4,6] on the palladium and nickel dioxygen complexes. Hayward, *et al.*,[7] have also briefly examined the same platinum complex over a lower frequency region, tentatively assigning the two bands at 496 and 475 cm^{-1} to the metal–oxygen stretching vibrations, in accord with the isosceles coordination model. The assignment, however, was not confirmed by isotopic data.

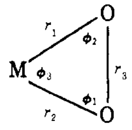
Experimental Section

The infrared spectra were measured on a Hitachi Perkin-Elmer Model 225 (4000–200 cm^{-1}) or a Hitachi Model FIS-1 (400–80 cm^{-1}) in Nujol mulls between KRS-5, CsI, or polyethylene plates. Calibration of frequency was performed with gaseous carbon monoxide, water vapor, or polystyrene film. Solution spectra of the rhodium and platinum complexes were obtained in dichloromethane in KRS-5 cells.

Preparation of dioxygen complexes was done according to the literature.[6,8,9] The detailed description of the preparation and properties of the rhodium–dioxygen complexes will be reported separately. Incorporation of heavy oxygen into complexes was carried out in ordinary vacuum systems. The heavy oxygen in various concentrations,[10] prepared by thermal diffusion, was kindly supplied by Professor K. Hirota, the Faculty of Science, Osaka University. The relative concentrations of the isotopic species are as follows (% overall ^{18}O, % $^{16}O_2$, % $^{16}O{-}^{18}O$, % $^{18}O_2$): sample 1 56.4, 17.9, 51.4, 30.7; sample 2 50.0, 25.0, 50.0, 25.0; sample 3 28, 58.3, 32.4, 9.3.

Calculation Procedure. (a) Monodentate Model. Calculation of force constants was performed by assuming that O–O and $M(O_2)$ behave as simple diatomic oscillators.

(b) Isosceles Model. The number of internal coordinates of the isosceles model depicted in I exceeds the number of fundamental



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[1] Osaka University.

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[3] (a) D. M. Adams, "Metal-Ligand and Related Vibrations," Edward Arnold, London, 1967, p 240; (b) W. P. Griffith, *J. Chem. Soc.*, 5345 (1962); 5345 (1963); 5248 (1964).

[4] A preliminary study of these two complexes has been published; see K. Hirota, M. Yamamoto, S. Otsuka, A. Nakamura, and Y. Tatsuno, *Chem. Commun.*, 533 (1968).

[5] R. Horn, E. Weissberger, and J. P. Collman, *Inorg. Chem.*, **9**, 2347 (1970).

[6] S. Otsuka, A. Nakamura, and Y. Tatsuno, *Chem. Commun.*, 836 (1967); *J. Amer. Chem. Soc.*, **91**, 6994 (1969).

[7] P. J. Hayward, D. M. Blake, G. Wilkinson, and C. J. Nyman, *ibid.*, **92**, 5873 (1970).

[8] S. Takahashi, K. Sonogashira, and N. Hagihara, *J. Chem. Soc. Jap.*, **87**, 610 (1966).

[9] G. Wilke, H. Schott, and P. Heimbach, *Angew. Chem.*, **79**, 62 (1967).

[10] M. Yamamoto, M. Takahashi, M. Imaoka, T. Hashioka, and K. Hirota, *J. Chem. Soc. Jap.*, **89**, 839 (1968).

Table I. ^{18}O Isotopic Infrared Data Obtained by Use of Heavy-Oxygen Mixtures[a]

	ν_1	$\Delta\nu_1$	ν_2	$\Delta\nu_2$	Overall ^{18}O concn, %
$Pt(^{16}O_2)(PPh_3)_2$	828	0	472	0	
			462	0	
$Pt(^{16}O{-}^{18}O)(PPh_3)_2$	805.5	−22.5	462	−10	56.4
			451	−9	
$Pt(^{18}O_2)(PPh_3)_2$	782	−46	451	−21	
			441	−19	
$Pd(^{16}O_2)$(*tert*-BuNC)$_2$	893	0	484	0	
$Pd(^{16}O{-}^{18}O)$(*tert*-BuNC)$_2$	869	−24	478	−6	56.4
$Pd(^{18}O_2)$(*tert*-BuNC)$_2$	837	−56	471	−13	
$Rh(^{16}O_2)Cl(PPh_3)_2$(*tert*-BuNC)	892	0	576	0	
$Rh(^{16}O{-}^{18}O)Cl(PPh_3)_2$(*tert*-BuNC)	868	−24	567	−9	50
$Rh(^{18}O_2)Cl(PPh_3)_2$(*tert*-BuNC)	842	−50	556	−20	
$Ni(^{16}O_2)$(*tert*-BuNC)$_2$	898	0	552	0	
$Ni(^{16}O{-}^{18}O)$(*tert*-BuNC)$_2$	873	−25	542	−10	28
$Ni(^{18}O_2)$(*tert*-BuNC)$_2$	848	−50			

[a] Spectra measured in Nujol mull; frequencies in cm^{-1}.

Table II. Approximate Force Constants

	Force constants, mdyn/Å		Frequencies, cm^{-1}				
			Calcd			Obsd	
	f_{M-O}	f_{O-O}	ν_{O-O}	$\nu_{MO(a_1)}$	$\nu_{MO(b_1)}$	ν_1	$\nu_{2,3}$
$PtO_2(PPh_3)_2$	2.1[a]	3.0	827[a]	470[a]	488	828	472
	2.2[b]		825[b]	461[b]	477		462
NiO_2(*tert*-BuNC)$_2$	2.4	3.5	897	560	523	898	552
$RhO_2Cl(PPh_3)_2$(*tert*-BuNC)	3.2	3.3	890	581	595	892	576
[PdO_2(*tert*-BuNC)$_2$[c]	2.1	3.5	901	477	482	893	484]

[a] Calculated on the assumption that the observed 462-cm^{-1} band is assigned as $\nu_{MO(a_1)}$. [b] Calculated on the assumption that the observed 472-cm^{-1} band is assigned as $\nu_{MO(a_1)}$. [c] Included for comparison assuming the palladium complex has the isosceles (C_{2v}) structure.

vibrations by three. Therefore, three redundant conditions exist. As it is more convenient to utilize Δr_{1-3} for internal coordinates, the following symmetry coordinates were used for the calculation.

$$R_1 = (\Delta r_1 + \Delta r_2)/\sqrt{2} \qquad a_1 \text{ M–O stretching}$$

$$R_2 = \Delta r_3 \qquad a_1 \text{ O–O stretching}$$

$$R_3 = (\Delta r_1 - \Delta r_2)/\sqrt{2} \qquad b_1 \text{ M–O stretching}$$

The G matrix was constructed by the Decius formula[11] and factored by symmetry (C_{2v}). The number of force constants to be determined being small, the simple valence force field[11] was adopted. As a preliminary computation showed a reasonable fit to the observed frequencies, off-diagonal elements of force constants were not included for all the later refinements. The potential energy distribution for the a_1 modes was calculated to reveal mixing of variable degrees. The platinum complex is the least in the mixing; ν_1 consists of 90% genuine O–O stretching and ν_2 also of 90% M–O stretching. The mixing seems to increase with an increase in the metal–oxygen stretching force constant; thus, the mixing is 85:15 in the nickel and 75:25 in the rhodium complex.

Results

Table I summarizes the results of the ^{18}O isotopic infrared study. The force constants calculated by use of a model and approximations described below are listed in Table II. The effect of auxiliary ligands on some important infrared frequencies are compared in Table III. Figures 1–3 illustrate some of the representative patterns of the isotopic spectra. The solution spectra were obtained for the platinum and rhodium complexes which are fairly stable in solution, and are shown in Table IV; this table also contains ν_{NC} data for the parent complexes.

Table III. Effect of Auxiliary Ligands

	Stretching, cm^{-1}			
	ν_{Rh-O}	ν_{O-O}	ν_{Rh-Cl}	ν_{NC}
$RhCl(O_2)(PPh_3)_2$(*tert*-BuNC)	576	892	291	2149
$RhCl(O_2)(PPh_3)_2(C_6H_{11}NC)$	579	893	293	2170
$RhCl(O_2)(PPh_3)_2$(*p*-$CH_3C_6H_4NC$)	590	889	300	2145
$RhBr(O_2)(PPh_3)_2$(*tert*-BuNC)	572	893		2152
$RhBr(O_2)(PPh_3)_2(C_6H_{11}NC)$	581	892		2165
$RhI(O_2)(PPh_3)_2$(*tert*-BuNC)	565	893		2151
$RhCl(O_2)(AsPh_3)_2$(*tert*-BuNC)	579	884	295	2145

Structure of Oxygen Complexes. There are several possible modes of coordination of an oxygen molecule to a metal,[12–15] *e.g.*, end on (bent or linear) and side

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(11) (a) E. B. Wilson, Jr., J. C. Decius, and P. C. Cross, "Molecular Vibrations," McGraw-Hill, New York, N. Y., 1955, p 174; (b) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," 2nd ed, Wiley-Interscience, New York, N. Y., 1970, p 55.

(12) N. Kasai, T. Kashiwagi, N. Yasuoka, M. Kakudo, S. Takahashi, and N. Hagihara, *Chem. Commun.*, 743 (1969).

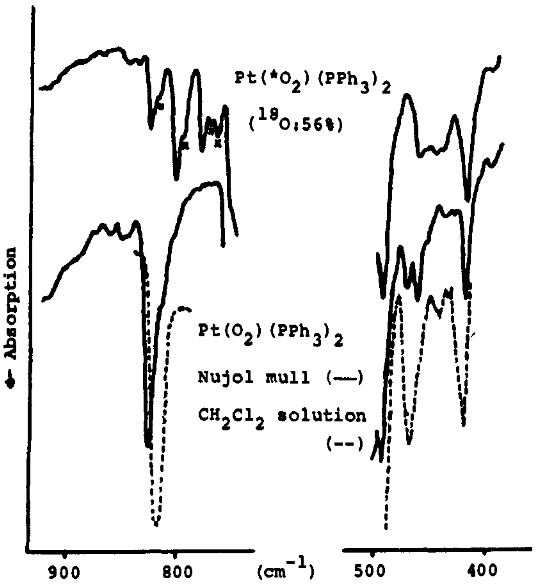


Figure 1. Isotopic infrared spectra of $Pt(O_2)(PPh_3)_2$ (only the important part of the spectral pattern is shown here). Peaks indicated by × are due to impurities.

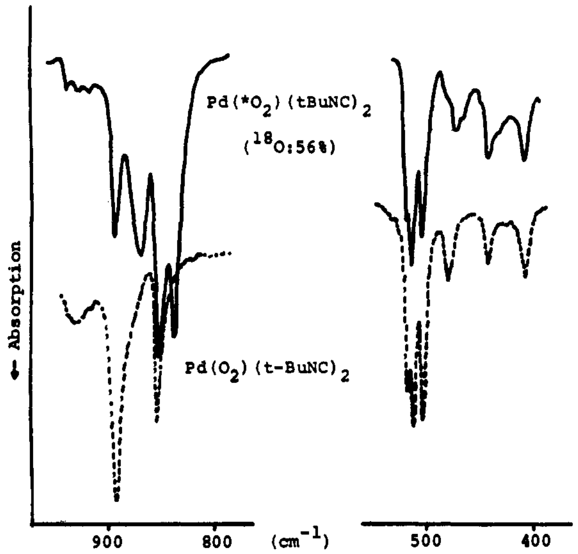


Figure 2. Isotopic infrared spectra of $Pd(O_2)$(*tert*-BuNC)$_2$.

on (isosceles or acute triangular), apart from bridging coordination as a bidentate.

In mononuclear species, the infrared study using ^{18}O isotopic substitution will distinguish between isosceles coordination and other types of coordination.

(a) Phosphine–Dioxygen Complexes. Two preliminary X-ray structural studies[12,13] are available for the platinum complex, but the results differ in the most important O–O distance. We adopt the value of Kasai, *et al.* (Pt–O, 2.01 Å; O–O 1.45 Å), for it is in the expected range of O–O distances reported for irreversible dioxygen complexes. The platinum complex seems the best selection for the isotopic infrared study among various metal–dioxygen complexes because of its large mass, good thermal stability, irreversibility of dioxygen addition, and discrete monomeric character.

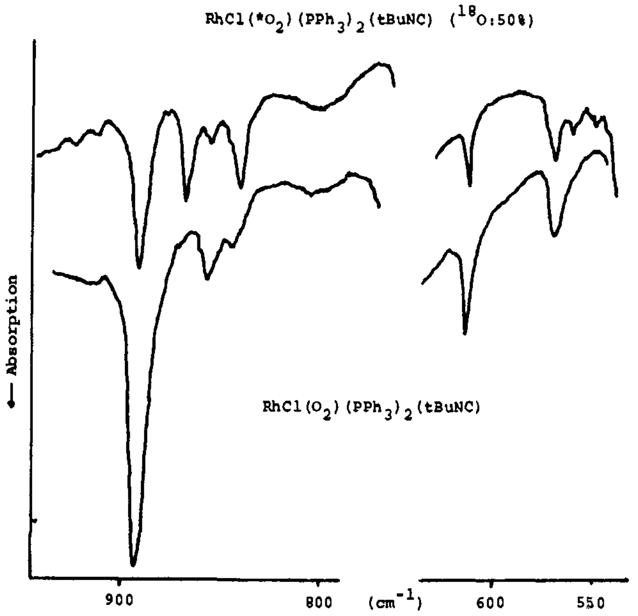
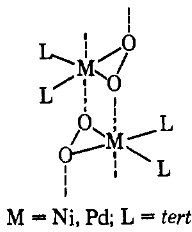


Figure 3. Isotopic infrared spectra of $RhCl(O_2)(PPh_3)_2$(*tert*-BuNC).

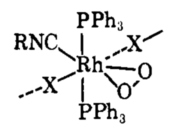
Table IV. Solution Spectra in CH_2Cl_2

	Obsd frequencies, cm^{-1}		
	ν_{M-O}	ν_{O-O}	ν_{NC}
$RhCl(O_2)(PPh_3)_2$(*tert*-BuNC)	580	881	2169
$RhCl(PPh_3)_2$(*tert*-BuNC)			2112
$RhCl(O_2)(PPh_3)_2(p\text{-}CH_3C_6H_4NC)$	585	888	2145
$RhCl(PPh_3)_2(p\text{-}CH_3C_6H_4NC)$			2083 2048 (weak)
$Pt(O_2)(PPh_3)_2$	470	819	

(b) Isocyanide–Dioxygen Complexes. At present, no X-ray analysis is available owing to difficulty in obtaining well-formed single crystals. However, a reasonable structure for the nickel and palladium complexes has already been proposed, which involves a coplanar arrangement of two carbon ligands and two oxygen atoms around the metal center.[6] For the rhodium complexes a structure analogous to Vaska's dioxygen complexes[14] seems probable (*vide infra*).



M = Ni, Pd; L = *tert*-BuNC



$RhX(O_2)(PPh_3)_2(RNC)$

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(13) C. D. Cook, P. T. Cheng, and S. C. Nyburg, *J. Amer. Chem. Soc.*, 91, 2123 (1969).

(14) S. J. LaPlaca and J. A. Ibers, *ibid.*, 87, 2581 (1965).

(15) A. L. Crumbliss and F. Basolo, *Science*, 164 (1969); *J. Amer. Chem. Soc.*, 92, 55 (1970); D. Klemente, B. M. Hoffman, and F. Basolo, *Chem. Commun.*, 467 (1970); *J. Amer. Chem. Soc.*, 92, 61 (1970).

Considering the approximate nature of our model, we have assumed bond lengths (M–O, 2.0 Å; O–O, 1.5 Å) for all of the isocyanide–oxygen complexes on the basis of the reported data.[12–16] It is to be noted that although the bond lengths will be somewhat different depending on the metal and auxiliary ligands a change of *ca.* 0.1 Å does not appreciably alter the resulting force constants.

Mechanical Models for Calculation. Two limiting mechanical local models have been considered for the oxygen complex, one being the monodentate model and the other the isosceles model.[17] Distinction between these two models can be made from the number of metal–oxygen stretching vibrations, one such vibration being expected for the monodentate model and two for the isosceles model. A similar situation would exist for the metal–olefin bond in Zeise's salt.

monodentate isosceles

If a significant reduction of the bond order of the oxygen molecule takes place owing to back-binding, the delocalized bonding would approach the isosceles model, for which a force constant of 3–5 mdyn/Å is anticipated. On the other hand, the monodentate model implies essentially multiply bonded oxygen, and the lowering of the force constant from that of ground-state oxygen (11.5 mdyn/Å) would be less than a few millidynes per ångström. Hence, in addition to the criterion solely based on the number of observed metal–oxygen stretching vibrations, the O–O stretching force constant also provides an important clue for the nature of bonding.

Monodentate Model. Grogan and Nakamoto[18,19] treated the platinum–ethylene vibration of Zeise's salt by assuming this mechanical model. Their treatment seems reasonable when the bond order of the coordinated double bond is high relative to that of the platinum–ethylene bond. Insignificant lowering of the C=C stretching force constant on coordination (from 7.4 to 6.0 mdyn/Å) also points to the relevance of the monodentate model for Zeise's salt. For the platinum–oxygen complex, the calculation of force constants is straightforward and results in values of $f_{O-O} = 3.1$ mdyn/Å and $f_{MO} = 3.6$ mdyn/Å if the 828- and 472-cm^{-1} bands are assigned to ν_{O-O} and ν_{Pt-O_2}, respectively. The lowering of f_{O-O} on coordination is substantial and does not favor the monodentate model as described above.

As ν_{M-O} and ν_{O-O} are mutually orthogonal in the monodentate model, mechanical mixing between these two vibrations is not expected. Ibers, *et al.*,[20] however, have suggested considerable mixing of these vibrations on the basis of the inconsistency of information on the $M-O_2$ bond strength as judged from the infrared data and from the bond lengths of Vaska's various oxygen complexes. As will be described later in this paper, we have also observed a similar inconsistency of trend based on the ir frequency and reversibility of oxygen addition. In addition to the information on the O–O stretching force constant, the suggestion of considerable mixing therefore leads us to prefer the isosceles model.

Isosceles Local Model. In the present systems the separation of the metal–oxygen vibrations from the other metal–ligand vibrations is not as complete as in Zeise's salt.[18,19] However, the relatively heavy mass of the metal and the expected small force constants of the metal–ligand bond in the platinum complex would allow treatment using the local C_{2v} model. Appearance of a strong band near 830–900 cm^{-1} in most of the oxygen complexes having side-on coordination seems to support the "group frequency" of the metal–oxygen (MO_2) group. This frequency may be related to "ring breathing" of the triangle, characteristic of small-ring compounds such as cyclopropane[21,22a] or ethylene oxide.[22b]

Accepting isosceles side-on coordination of oxygen (C_{2v} local symmetry) regardless of the exact nature of the bonding, we have two fundamental a_1 modes of vibration and one b_1 mode. The a_1 modes are composed of genuine O–O stretching and symmetrical M–O stretching vibrations of different degree, while the b_1 mode is solely from the asymmetric M–O stretching vibrations. A similar triangular local model was assumed by Paradilla-Sorzano and Fackler[23] and also by Hiraishi[24] for the vibrational analysis of the platinum–ethylene group in Zeise's salt on the basis of three observed frequencies. However, Grogan and Nakamoto[18] observed only two frequencies assignable to the platinum–ethylene group vibration and assumed the monodentate model.

A complete vibrational analysis of even the simplest oxygen complex, such as NiO_2(*tert*-BuNC)$_2$, will require structural data and infrared and Raman assignments based on isotopic substitution with not only ^{18}O but also ^{62}Ni, ^{13}C, and ^{15}N. Here we confine ourselves to an approximate analysis, postulating a simple triangular local model, and leave the complete analysis of the whole molecule for future work.

Assignment of the Observed Bands and Their Isotopic Splitting. (a) O–O Stretching Band (ν_1). The strong infrared band (830–900 cm^{-1}) splits into a triplet when a "heavy" oxygen mixture is used (Figures 1–3).[25] Appearance of a single absorption for the $^{16}O-^{18}O$ species clearly indicates isosceles coordination of oxygen for the platinum and nickel complexes. Similar results have already been observed for Vaska's oxygen com-

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(16) (a) J. A. McGinnety, R. J. Doedens, and J. A. Ibers, *Inorg. Chem.*, **6**, 2243 (1967); (b) J. A. McGinnety and J. A. Ibers, *Chem. Commun.*, 235 (1968); (c) J. A. Ibers, J. A. McGinnety, and N. C. Page, *J. Amer. Chem. Soc.*, **91**, 6301 (1969).

(17) For discussion of the point, *cf.* L. Vaska, *Accounts Chem. Res.*, **1**, 335 (1968).

(18) M. J. Grogan and K. Nakamoto, *J. Amer. Chem. Soc.*, **88**, 5454 (1966).

(19) M. J. Grogan and K. Nakamoto, *ibid.*, **90**, 918 (1968).

(20) J. A. McGinnety, R. J. Doedens, and J. A. Ibers, *Science*, **155**, 709 (1967); *Inorg. Chem.*, **6**, 2243 (1967).

(21) R. C. Lord, and B. Nolin, *J. Chem. Phys.*, **24**, 656 (1956); L. J. Bellamy, "Advances in Infrared Group Frequencies," Methuen, London, 1968, p 18.

(22) G. Herzberg, "Infrared and Raman Spectra of Polyatomic Molecules," Van Nostrand, Princeton, N. J., 1945: (a) p 352; (b) p 340.

(23) J. Paradilla-Sorzano and J. P. Fackler, *J. Mol. Spectrosc.*, **22**, 80 (1967).

(24) J. Hiraishi, *Spectrochim. Acta, Part A*, **25**, 749 (1969).

(25) The absence of impurities, *e.g.*, Ph_3PO or *tert*-BuNCO, in the isotopic samples was confirmed by the ir spectra.

Table V. Observed and Calculated ^{18}O Splitting ($\Delta\nu_2$) of the Metal–Oxygen Stretching Vibration[a]

Compounds	$\Delta\nu_2$(obsd)		$\Delta\nu_2$(calcd) for the a_1 mode		$\Delta\nu_2$(calcd) for the b_1 mode	
	^{16}O–^{18}O	$^{18}O_2$	^{16}O–^{18}O	$^{18}O_2$	^{16}O–^{18}O	$^{18}O_2$
NiO_2L_2[b]	−10	*c*	−11	−23	−6	−12
PdO_2L_2[d]	−6	−12	−10	−20	−13	−26
$RhCl(O_2)(PPh_3)_2L$	−9	−20	−12	−25	−15	−31
$RhBr(O_2)(PPh_3)_2L$	−12	*c*	−12	−25	−14	−31
$RhCl(O_2)(AsPh_3)_2L$	−11	*c*	−12	−24	−15	−31

[a] $\Delta\nu_2$ in wave numbers (cm^{-1}). [b] L stands for *tert*-BuNC. [c] Not observable owing to the low concentration (9%) of the $^{18}O_2$ species. [d] The isosceles model is assumed for the calculation.

plex.[26] As this band has the highest frequency among the bands split by isotopic substitution, assignment to an a_1 vibration, which has a larger contribution of genuine O–O stretching, seems correct. Therefore, this band is referred to hereafter as the O–O stretching (a_1) band. A comparison of the extent of the splitting with the theoretical value supports the assignment as described below. A calculation by use of the *G* matrix and "product and sum" rules[27] on the triatomic isosceles model does not unequivocally determine the splitting value for the O–O stretching (a_1) band because of mixing with the other a_1 vibration. Actually the ν_1 of the nickel complex was found to split according to the simple diatomic oscillator model of O–O; *i.e.*, the expected ratio of wave numbers for ^{16}O–^{16}O, ^{16}O–^{18}O, and ^{18}O–^{18}O species is 1:0.972:0.943.[28] This result is also predictable by the isosceles model with no motion of the metal in the O–O stretching mode. The diatomic splitting persists when the metal atom is varied, *e.g.*, nickel, platinum, rhodium, and iridium. This remarkable tendency suggests that the O–O stretching mode (a_1) does not appreciably involve the motion of the metal, and assumption of a metal of infinite mass readily leads to the same theoretical splitting.

(b) M–O Stretching Bands (ν_2 and ν_3). Two absorption bands, the a_1 mode (symmetric M–O stretching) and the b_1 mode (asymmetric M–O stretching), should appear in a region of longer wavelength than that of the O–O stretching. The bands at 472 and 462 cm^{-1} of $PtO_2(PPh_3)_2$ in the solid state both showed splitting upon isotopic substitution to result in the cluster of bands as shown in Figure 1. These two bands may at first sight be assigned to the expected M–O stretching vibrations (a_1 and b_1). Calculated values of expected splittings, as described below, were utilized in order to find the positions of these isotopic bands, on the assumption that each band splits into a triplet corresponding to the three isotopic species, $^{16}O_2$, ^{16}O–^{18}O, and $^{18}O_2$ (*cf.* Table I).

A solution spectrum of $Pt(O_2)(PPh_3)_2$ in CH_2Cl_2 showed, however, a single peak at 470 cm^{-1} (*cf.* Figure 1). The small separation of the bands in the solid state may be a result of the crystal field effect. A change of intensity or of band position on dissolution leading to an accidental degeneracy also cannot be excluded. The 498-cm^{-1} band, previously assigned as one of two possible metal–oxygen stretching vibrations by Hayward, *et al.*,[7] did not show any isotopic shift. Therefore, only one of the two bands of their assignment is due to ν_{Pt-O}. The weak bands at 552 and 484 cm^{-1} of the nickel and palladium complexes, respectively, appeared to split into two bands upon partial isotopic substitution[4] with heavy oxygen (26% ^{18}O). We were unable to explain the splitting when we published a previous communication.[4] The band at 570–580 cm^{-1} generally appearing on oxygenation of the rhodium complexes, $RhXL_2(RNC)$, also showed splitting on isotopic substitution. The expected splitting into three bands was now observed with concentrated "heavy" oxygen (50% ^{18}O) (*cf.* Figure 3).

The expected third band ν_3 (ν_{MO}) for the nickel, palladium, and rhodium complexes was sought carefully in the far-infrared region, 80 to 650 cm^{-1}; however, no splitting was observed. There is, however, the possibility that the expected band is hidden under the strong absorption of the coordinated isocyanide or triphenylphosphine.[29] The strong interferring bands due to the phosphine at 500–550 cm^{-1} were almost completely eliminated by use of the corresponding triphenylarsine complex without greatly affecting the metal–oxygen bond. Thus, isotopic shift (*cf.* Table V) of the metal–oxygen vibration of this complex was clearly observed without any interference at the expected point.

The extent of the observed isotopic splitting of the M–O stretching bands of the platinum complex ($\Delta\nu_{2,3} = -20$ cm^{-1}) can also be calculated from the isosceles model. The theoretical splitting depends on whether the observed band is assigned to the symmetric (a_1) or asymmetric (b_1) mode. For the platinum complex, the observed splitting for the $^{18}O_2$ species is in rough agreement with the calculated values of $\Delta\nu$, -23 cm^{-1} (for the a_1 mode) or -26.5 cm^{-1} (for the b_1 mode). In the absence of off-diagonal force constants, the higher frequency band (472 cm^{-1}) may be assigned to the b_1 mode and the lower one to the a_1 mode. In the presence of an off-diagonal force constant ($f_{MO.MO}$) of *ca.* $+0.1$ mdyn/Å, however, this assignment must be reversed. In any case, the diagonal force constant, f_{MO}, does not change appreciably (only ± 0.1 mdyn/Å).

The theoretical splitting of the "M–O" stretching of the isocyanide–oxygen complexes is compared in Table V for the two alternate assignments. The observed splitting is closer to the values calculated with the a_1 assignment than to those calculated with the b_1 assign-

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(27) (a) Reference 11b, 1st ed, 1963, p 62; (b) ref 11a, p 182.

(28) The previous values for the ratio[4] should be replaced with the above values.

(29) A difference spectrum may reveal the hidden band, as suggested by a referee; instability of the solution and experimental difficulty prevented such measurements, however.

ment. For rigorous assignment, however, the Raman data are indispensable, but the thermal instability of the complexes has prevented their measurement. The splitting of ν_{M-O} (a_1 or b_1) calculated on the assumption of a metal of infinite mass does not agree well with the observed splitting, implying involvement in these normal modes of the metal vibration which will be coupled with the metal–auxiliary ligand vibrations. A heavy metal with heavy ligand atoms as in the platinum complex, $PtO_2(PPh_3)_2$, renders this coupling negligible, making the simple isosceles model tenable.

Nonisosceles Complex, PdO_2(*tert*-BuNC)$_2$. Our preliminary ^{18}O isotopic infrared study seemed to indicate the isosceles coordination.[4] However, when concentrated "heavy" oxygen (^{18}O, 56%) was used, the ν_{O-O} band (869 cm^{-1}, see Figure 2) due to the mixed isotopic species, $^{16}O-^{18}O$, was found to be very broad in comparison with the other ν_{O-O} bands. The broad absorption curve could be resolved into two bands of approximately equal intensity separated by *ca.* 4–5 cm^{-1}. The appearance of the two bands can be accounted for by a distortion of the isosceles coordination or a bent linear coordination of dioxygen. The isosceles structure of the nickel congener (*vide infra*) favors the distorted isosceles structure. The extent of distortion, however, cannot be predicted from the infrared data alone and requires an X-ray analysis. The ν_{O-O} value of the $^{18}O_2$ species also deviates from the value calculated assuming a regular isosceles structure. Besides the ν_{O-O} band mentioned above, only the 484-cm^{-1} band was split by the isotopic substitution. Splitting into a triplet was descernible, although heavy overlapping precludes precise measurement (Figure 2). The observed splitting (6 cm^{-1} for the $^{16}O-^{18}O$ species) is quite a bit less than the value (10 cm^{-1}) calculated by the regular isosceles model (Table V). The discrepancy is apparently due to inadequacy of the isosceles model (C_{2v}). Therefore, the force constants (Table II) for the palladium complex are included merely to give some measure of the bond strengths (*cf.* Table 2).

The reason for the deviation from the isosceles triangle is unknown.

Calculation of Approximate Force Constants. The approximate force constants, *viz.*, f_{O-O} and f_{M-O}, were calculated ignoring all the off-diagonal elements of the force constants. The calculation was done with the assignment of the observed two frequencies to the a_1 mode, and the results are shown in Table II. The calculation also predicts the position of the unobservable b_1 vibration which is shown in the Table II. The two frequencies (a_1 and b_1) of the "metal–oxygen" stretching are thus expected to be close, and accidental coincidence of the two bands is possible by inclusion of small off-diagonal force constants. The failure to observe the third band (ν_3, ν_{M-O}) for the nickel, palladium, or rhodium complexes may be due to the accidental degeneracy of the two metal–oxygen stretching vibrations or due to low intensity of one of the absorption bands. The accidental degeneracy has been observed for various metal–ligand vibrations in the far-infrared region.[30]

Discussion

Force Constants and the Nature of the Metal–Oxygen Bond. For discussion of the observed frequencies and the approximate force constants therefrom, we must restrict ourselves to a relative comparison of isostructural complexes. The greatly reduced O–O force constant of O_2 on complex formation (11.5 mdyn/Å for gaseous O_2) suggests the reduction of the bond order mainly *via* back-donation into antibonding molecular orbitals of the oxygen molecule. The value of 3.0–3.3 mdyn/Å is even lower than the force constant of O_2^{2-} ion ($f_{O-O} = 5.4$ mdyn/Å)[31] and close to that of O_2 in an excited state, $^3\Sigma_u^+$ ($f_{O-O} = 3.2$)[32] or $^3\Sigma_u^-$ ($f_{O-O} = 2.3$).[32] A similar reduction in the force constant (f_{C-C}) of acetylene on π-complex formation has recently been reported, and its resemblance to that of an excited state of acetylene was noted.[33] Attempts[34–37] were made to correlate electronic structures of coordinated small molecules such as oxygen, acetylene, or carbon disulfide with their electronically excited states on such a basis as bond lengths,[34,35] geometry,[34,36] or reaction products.[37] The ir force constant may also help to find such a correspondence.

The value of f_{M-O} can be compared with those of metal acetylacetonates where an increase in f_{M-O} was observed on increasing effective nuclear charge of the metal. Thus, bis(acetylacetonato)palladium ($f_{Pd-O} = 2.65$ mdyn/Å) has a stronger M–O bond than the nickel analog ($f_{Ni-O} = 2.05$ mdyn/Å).[38] The trend in f_{MO} in our oxygen complexes is, however, Ni > Pd. The contribution of σ-donating interaction seems dominant in the M–O bond of metal(II) acetylacetonates, as the trend of M–O force constants indicates. The reversed trend in the oxygen complexes apparently implies significant contribution of π back-donation. The force constants obtained for the rhodium complexes are quite different from those of the nickel triad. A combination of difference in the stereochemistry, metal oxidation state, auxiliary ligands, and also bonding orbitals prevents intelligent comparison between the rhodium and nickel complexes. However, the increased f_{M-O} value in the rhodium complexes is certainly caused by stronger σ-accepting ability of Rh(I) as compared with that of the formally zerovalent metal of the nickel triad (see the next section).

Chemical evidence supports the relative order of f_{M-O} among our isocyanide–dioxygen complexes. Thus, catalytic oxygenation of isocyanides occurs at room temperature with $Ni(O_2)$(*tert*-BuNC)$_2$ as catalyst and even at −20° with $Pd(O_2)$(*tert*-BuNC)$_2$.[6] Similar oxygenation of PPh_3 occurs at 110° in boiling toluene with $RhCl(O_2)(Ph_3P)_2$(*tert*-BuNC) as catalyst.[39] Hence, M–O force constants seem to be indicative of the lability of the O_2 ligand. In contrast, the O–O stretchings are poorly correlated with such a property (*vide infra*).

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Effect of Auxiliary Ligand. The frequency of the so-called "O–O" stretching band in various dioxygen or peroxy complexes has been discussed in the literature.[3,20] A slight variation of the frequency upon change of the halogen in Vaska's dioxygen complexes $IrX(O_2)(PPh_3)_2(CO)$, was interpreted to mean that this band is not a pure O–O stretching.[16] In our rhodium complexes the frequency is surprisingly constant when the anionic ligand is changed (*cf.* Table III). Substitution of PPh_3 with $AsPh_3$ also caused only a minor change of the frequency. A change of a substituent on the isocyanide again results in a very small change of the frequency in spite of the great influence on the reversibility of the oxygen addition (*cf.* Table III). The *tert*-butyl derivative irreversibly combines with oxygen, whereas the para tolyl derivative combines reversibly.[39] Thus, the O–O stretching vibration is little influenced by the electronic charge density of the metal coordination center. On the other hand, the "M–O" stretching frequency is more sensitive to these ligand effects and much more helpful for a better understanding of the metal–oxygen bond.

Although the data at hand are not sufficient to establish the effect of an auxiliary ligand, the following trend in the metal–oxygen stretching frequency (ν_{MO}) among the rhodium complexes is discernible: Cl > Br > I; $AsPh_3 > PPh_3$; *tert*-BuNC < c-C_6H_{11}NC < *p*-$CH_3C_6H_4$-NC. The trend in the halogen triad may not be reflecting the electronic effect only. The mass effect may be operative here. The same reservation should be borne in mind for comparison of the PPh_3 derivatives with the $AsPh_3$ complex. However, only the electronic effect will be operative on changing the substituent of the isocyanide ligand. The trend suggests that the frequency increases in the order of electron attraction of the substituent and thus of the increase in partial positive charge of the metal. Examination of Table III further indicates that ν_{RhO} and ν_{RhCl} are both increased by an increase in the electron-attracting nature of the isocyanide ligand, *i.e.*, *tert*-Bu < c-C_6H_{11} < *p*-$CH_3C_6H_4$. This trend implies a stronger bond between the more positive rhodium and the anionic ligand. Hence, in comparison with the bonding in the nickel triad, the σ-donating interaction of a partially anionic oxygen ligand with the metal seems more important than the π interaction. This is in contrast with what was observed for Vaska's dioxygen complexes, where irreversible dioxygen coordination was realized in the presence of electron-donating ligands, *e.g.*, $[Ir(O_2)(dp)_2]^+$ (dp = 1,2-bis-diphenylphosphinoethane).[14] Thus, it should be pointed out that the trend in *metal–oxygen stretching* is not in accord with the evaluation of bond strength based on the reversibility of dioxygen coordination.[40]

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(40) NOTE ADDED IN PROOF. Recent trends in nomenclature indicate that the ligand referred to in many places in this paper as "oxygen" should be called dioxygen throughout.

Studies on the Mechanism of Isotopic Oxygen Exchange and Reduction of Ferrate(VI) Ion (FeO_4^{2-})[1]

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Abstract: In basic media the rate of ^{18}O exchange between FeO_4^{2-} and water follows the law $R = k[FeO_4^{2-}]$, where $k = 1.62 \times 10^{-2}$ sec^{-1} at 25°, $\log A = 9.51 \pm 0.79$, and $E_a = 15.4 \pm 1.0$ kcal/mol. In aqueous media the ion of 6+ Fe is FeO_4^{2-} and all oxygens are kinetically equivalent. Both water exchange and water oxidation are accelerated by dilute acid. Stoichiometric, kinetic, and ^{18}O studies have been applied to the reaction of FeO_4^{2-} with H_2O, H_2O_2, and SO_3^{2-}, and the results are compared with other strong oxidizing agents. The reaction with H_2O_2 and SO_3^{2-} are quantitative and show simple stoichiometry. The reactions are first order in H_2O_2 and second order in SO_3^{2-}, but oxygen transfer from FeO_4^{2-} to the product (O_2 or SO_4^{2-}) occurs only in the latter case.

Methods for preparing and analyzing potassium ferrate, K_2FeO_4, of high purity (97–99%) have existed for some time, but little is known about its aqueous chemistry. K_2FeO_4(s) is usually prepared by OCl^- oxidation of freshly prepared iron hydroxide in strongly basic media and isolated from saturated KOH solution.[2-4] Electrolytic means may also be used.[5] Analysis consists of the oxidation of Cr(III) in basic media followed by titration of the Cr(VI) formed with

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