Journal of Organometallic Chemistry, 391 (1990) 131–137
Elsevier Sequoia S.A., Lausanne – Printed in The Netherlands
JOM 20755

Raman spectra of copper(I) and silver(I) complexes with 1,5-cyclooctadiene and the nature of metal–olefin bonds. Possibility of a copper(I)–olefin bond in cytochrome oxidase

Hideki Masuda *

Institute for Molecular Science, Myodaiji, Okazaki 444 (Japan)

Megumu Munakata, Susumu Kitagawa,

Department of Chemistry, Faculty of Science and Technology, Kinki University, Kowakae, Higashi-Osaka, 577 (Japan)

(Received February 13th, 1989; in revised form January 30th, 1990)

Abstract

The Raman spectra of copper(I) and silver(I) complexes with 1,5-cyclooctadiene (cod), $[Cu(cod)_2]ClO_4$ and $[Ag(cod)_2]ClO_4$, have been examined to determined the nature of the d^{10} metal ion–olefin bonding. Judging from the slight lowering of ν(C=C) stretching frequencies upon coordination of olefin to metal ions, the nature of the metal–olefin bonds in $[Cu(cod)_2]ClO_4$ and $[Ag(cod)_2]ClO_4$ seems to be predominantly by σ-bonding from the olefin π-orbital to the metal $d\sigma$ orbital. The two strong vibrations that appear in the range from 420 to 350 cm^{-1} are assigned to metal–olefin bond stretching and their lower wavenumbers compared with those in the isoelectronic series of d^8 and d^{10} metal complexes with cod also support the σ-bonding nature of the metal–cod bond. Similar lowering of ν(C=C) stretching region (1650–1600 cm^{-1}) upon reduction of oxidized cytochrome oxidase probably indicates that the peripheral 1-hydroxy-5,9,13-trimethyl-4,8,12-*trans,trans*-tetradecatrienyl substituent (trienyl group) on the heme *a* probably form part of the copper(I) ligation environment in the reduced copper–heme binuclear center.

Introduction

Structural studies on the metal–olefin complexes have been of interest in order to determine the nature of metal–olefin bonding, because Dewer [1] and Chatt and Duncanson [2] have suggested that the bonding of olefin to metal involves both a σ- and a π-bond; the σ-bond is formed by donation of electrons from the π-orbital of the olefin to a $d\sigma$-orbital of the metal, and the π-bond by back-donation from a filled $d\pi$-orbital of the metal to the empty π^*-ortibal of the olefin. Our group [3]

0022-328X/90/$03.50

and Thompson et al. [4] have previously reported the structures of the copper(I) complexes with olefin. They suggested that σ-donation predominates in the Cu^I–olefin bonding in their complexes, judging from the insignificant lengthening of the C=C double bond on coordination to Cu^I ion.

Vibrational spectroscopy has been shown to be an effective tool for the study of the nature of the metal–olefin bond. The bonding of the olefin to the metal is more sensitively reflected in the vibrational spectra of these complexes; in particular the two Raman bands, ν(C=C) and $\delta(CH_2)$, are significantly shifted upon coordination to a metal ion. Although there is considerable intermingling with each other and both bands are shifted to lower frequencies when such bonding occurs, in substituted olefins there is seemingly less mixing and the band having the higher population of ν(C=C) character is shifted most. Powell et al. have reported [5a,b] the relation between the degree to which ν(C=C) is lowered for the series of d^8 or d^{10} metal complexes of cod, $M(cod)X_n$ ($M = d^8$ or d^{10} metal ion; $X = Cl^-$ or BF_4^-), and their metal–olefin bonding nature. The metal–cod bond strengths consequently fall in the order $Rh^I > Pt^{II} > Pd^{II}$ for d^8 metal complexes and $Au^I \sim Cu^I > Ag^I$ for d^{10} metal complexes. In addition they have suggested that the amount of π back-bonding from the metal to the olefin is less in a d^{10} metal than in an incompletely filled-d^8 metal; the σ-bond formed between the olefin and the d^{10} metal is likely to make a much higher contribution to the total bond order of the metal–olefin bonding.

Cytochrome oxidase is the terminal enzyme of the mitochondrial respiratory chain [6] and exists as dimers containing two heme a(Fe)–copper and heme a_3(Fe)–copper binuclear centers per unit. Each metal center occurs in a distinctly different environment, and the enzyme can be prepared in a variety of oxidation and ligation states [7]. In view of the existence of the Cu^I state and the role of the peripheral trienyl substituent on heme a, the possibility has been raised that the trienyl substituents may form part of the Cu^I coordination environment in the reduced (heme $a(Fe^{2+})–Cu^+$), and semioxidized (heme $a(Fe^{3+})–Cu^+$) forms of the oxidase.

In this paper the Raman spectra of the copper(I) and silver(I) complexes with cod, $[Cu(cod)_2]ClO_4$ and $[Ag(cod)_2]ClO_4$, are reported and the nature of the metal–cod bonding in binary d^{10} metal complexes with two cod molecules is discussed. In addition, we describe the possibility of the bonding between Cu^I and the peripheral trienyl substituent on heme a.

Experimental

Preparation. $[Cu(cod)_2]ClO_4$ was prepared by the addition of a 10-fold excess of cod to a methanol solution of copper diperchlorate–copper powder mixture under argon in a glass tube [3d]. $[Ag(cod)_2]ClO_4$ was prepared by the addition of a ten-fold excess of cod to a methanol solution of $AgClO_4$ under argon in a glass tube. From both mixtures were obtained white cubic crystals in the glass tube after several days at −20 °C. The purities of the complexes were checked by elemental analysis.

$[Cu(cod)_2]ClO_4$. Found: C, 50.37; H, 6.17. $C_{16}H_{24}O_4ClCu$ calcd.: C, 50.66; H, 6.38%.

$[Ag(cod)_2]ClO_4$. Found: C, 45.04; H, 5.57. $C_{16}H_{24}O_4ClAg$ calcd.: C, 45.36; H, 5.71%.

Spectroscopy. Raman spectra were recorded with the JEOL S-1 laser Raman Spectrometer by use of the 4880 Å line of a Coherent Radiation 52G Ar$^+$ laser (70mW at the sample position) as the exciting source. The slit width was 3.4–14

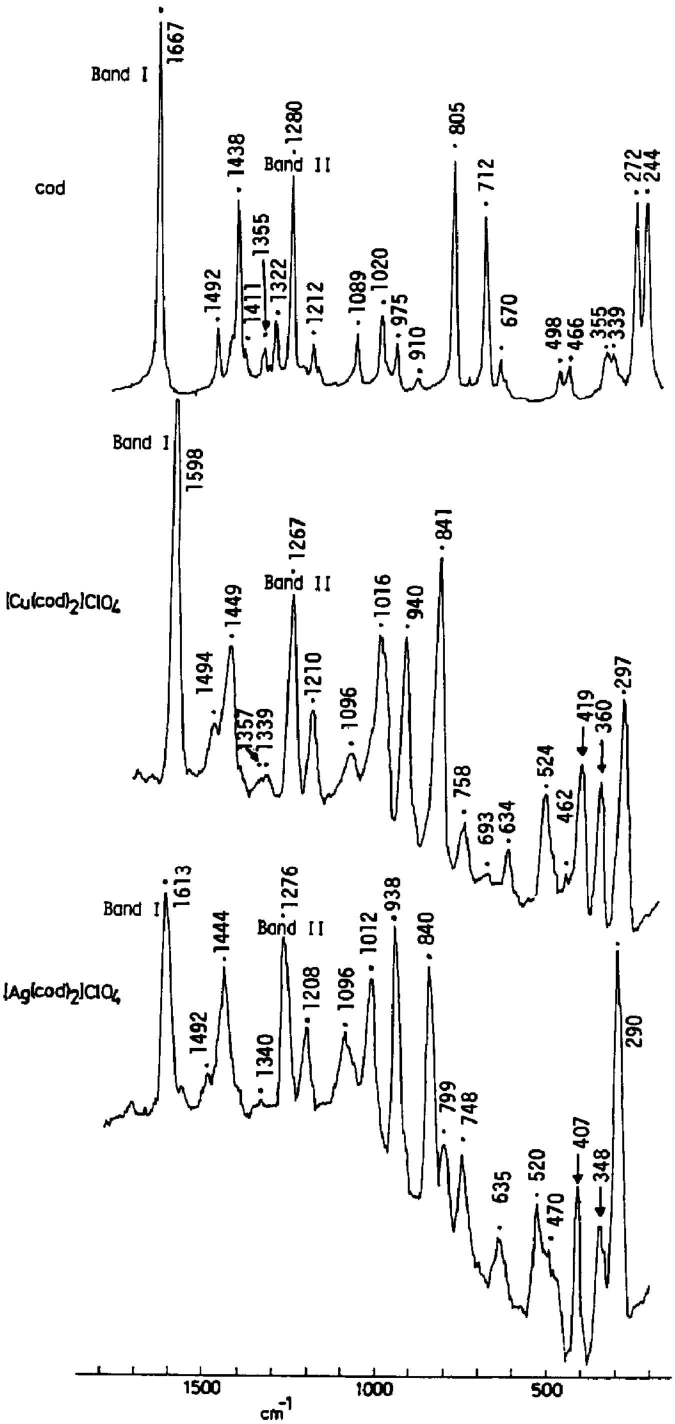

Fig. 1. Raman spectra of cod (liquid) and the complexes with Cu(I) and Ag(I) (crystal).

cm^{-1} in the region 2000–200 cm^{-1}. The samples were placed in Pyrex capillary tubes. The observed frequencies were calibrated by the standard Raman shifts of liquid indene [8].

Results and discussion

The Raman spectra of $[Ag(cod)_2]ClO_4$ and $[Cu(cod)_2]ClO_4$ complexes (solid) are shown in Fig. 1 and compared with that of metal-free cod (liquid). In the region between 1700 and 500 cm^{-1}, the number of observed peaks for the copper and the silver complexes is essentially the same as that for free cod. Their spectra were tentatively assigned (Table 1) from comparison with those for metal-free cod and Rh^I, Pd^{II} and Pt^{II} complexes of cod [5c], in which cod possesses the C_{2v} tub configuration.

Upon complexation, the two bands shift markedly to lower wavenumbers (Table 2). The two bands consist of mixed fractions of $\nu(C{=}C)$ and $\delta(CH_2)$, the higher

Table 1

Correlation of the vibrational modes of cod in the free state and in its complexes [a]

cod	$Cu(cod)_2ClO_4$	$Ag(cod)_2ClO_4$	Vibrational mode
1667(vs)	1598(vs)	1613(vs)	a_1 $\nu(C{=}C)$
1492(w)	1494(w)	1492(w)	
1438(2)	1449(s)	1444(s)	a_1
1411(vw)			
1355(w)	1357(w)		
		1340(vw)	
1322(w)	1339(w)		
1280(s)	1267(s)	1276(s)	a_1 $\delta(CH_2)$
1212(w)	1210(m)	1208(m)	a_1
	1096(m)	1096(m)	ClO_4
1089(w)			
1020(w)	1016(s)	1012(s)	a_1
	940(s)	938(vs)	ClO_4
975(w)			$\rho_w(C-H)$
910(vw)			
805(s)	841(vs)	840(vs)	a_1 $\rho(C-C-C)$
		799(m)	
712(s)	758(m)	748(m)	a_1 $\rho_r(C-H)$
670(w)	693(vw)		$\rho_r(C-H)$
	634(w)	635(m)	ClO_4
498(w)			
	524(m)	520(m)	
	460(vw)	470(vw)	ClO_4
	419(s)	407(s)	$\nu(M-C)$
	360(s)	348(s)	$\nu(M-C)$
355(w)			
339(w)			
272(s)	297(vs)	290(vs)	
244(s)			

[a] Frequencies in cm^{-1}, $\rho_r(C-H)$: out-of-plane olefinic C–H rocking; $\rho_w(C-H)$: in-plane olefinic C–H wagging; $\rho(C-C-C)$: C–C–C scissoring; $\nu(C{=}C)$: C=C stretching; $\delta(CH_2)$: CH_2 scissoring; $\nu(M-C)$: M–C stretching.

Table 2

Olefin frequencies in cod and its complexes

Compound	Frequency/cm^{-1}		$\Delta\nu$ ^{a}/cm^{-1}		Reference
	Band I	Band II	Band I	Band II	
cod	1667 vs	1280 s			this work
[Cu(cod)$_2$]ClO$_4$	1598 vs	1267 s	69	13	this work
[Cu(cod)Cl]$_2$	1490 s	1265 s	177	15	[5b]
[Ag(cod)$_2$]ClO$_4$	1613 vs	1276 s	54	4	this work
[Ag(cod)]BF$_4$	1605 vs	1276 s	62	4	[5b]

^{a} Frequency shift from metal free cod.

frequency band has been called Band I and the lower Band II. These frequencies are essentially similar to the analogous copper and silver complexes [5b], [Cu(cod)Cl]$_2$ and [Ag(cod)BF$_4$], previously reported. In the present complexes the fractional ν(C=C) character appears to be greater in Band I than in Band II since it is the more perturbed upon coordination to metal ion. The degree to which the lowering of Bands I for [Ag(cod)$_2$]ClO$_4$ (54 cm^{-1}) and [Cu(cod)$_2$]ClO$_4$ (69 cm^{-1}) upon complexation is small compared with analogous complexes having one cod molecule, [Ag(cod)BF$_4$] (59 cm^{-1}) [5b] and [Cu(cod)Cl]$_2$ (174 cm^{-1}) [5b], [Rh(cod)Cl]$_2$ (197 cm^{-1}) [5c], [Pt(cod)Cl$_2$] (164 cm^{-1}) [5c] and [Pd(cod)Cl$_2$] (135 cm^{-1}) [5c]; the lowering of Band I for [Ag(cod)$_2$]ClO$_4$ is the smallest shift found up to now for several metal complexes with cod [5]. The degree to which the frequency of Band I is lowered upon complexation reflects the strength of the C=C double-bond character in olefin coordinated to metal ion; the C=C frequency in alkanes is at ca. 1600 cm^{-1} and the C–C frequency in alkanes at ca. 990 cm^{-1} [9]. A comparison of the frequencies of Bands I for [Ag(cod)$_2$]ClO$_4$ and [Cu(cod)$_2$]ClO$_4$ with those for other metal–olefin complexes [5] indicates that the perturbations for the olefinic bond on coordination to metal ions are very weak and that the metal–olefin bond is stronger for Cu^{I} than for Ag^{I}.

In the region 500 to 350 cm^{-1} assigned to the metal–olefin stretching vibrations [3,9], two new strong vibrations appear (Table 3). From the vibrations of Pd(cod)Cl$_2$ (352, 413 cm^{-1}), Pt(cod)Cl$_2$ (385, 461 cm^{-1}) and Rh(cod)Cl$_2$ (393, 480 cm^{-1}) [5a], two stretching vibrations are assigned to the symmetric and asymmetric stretching vibrations, respectively. Their stretching frequencies fall in the order Cu^{I} > Ag^{I}, and their metal–olefin bonds are weaker than those in the Rh^{I}, Pd^{II} and Pt^{II} complexes with cod [5a,c].

The above observations are also supported by bond length data; the C=C bond lengths for [Cu(cod)$_2$]ClO$_4$ (1.33(1) Å) [3d] and [Ag(cod)$_2$]BF$_4$ (1.34(2) Å) [10] show no significant deviations from that for free olefin molecule (1.337(6) Å) [11] and are

Table 3

Metal–olefin vibrations (cm^{-1})

Compound	Asymmetric stretching	Symmetric stretching
[Ag(cod)$_2$]ClO$_4$	407	348
[Cu(cod)$_2$]ClO$_4$	419	360

short compared with those for [Ni(cod)$_2$] (1.39(3) Å) [12a], [Pt(cod)$_2$] (1.398(9) Å) [12b] and [Rh(cod)Cl]$_2$ (1.44(7) Å) [5c], which were reported to have predominantly π-bonding from metal $d\pi$-orbital to the olefin π^*-orbital; the M–C bond lengths for [Cu(cod)$_2$]ClO$_4$ (2.27(1) Å) [3d] and [Ag(cod)$_2$]BF$_4$ (2.50(2) Å) [10] are longer than those with cod (2.12(2) Å for [Ni(cod)$_2$] [12a], 2.211(7) Å for [Pt(cod)$_2$] [12b] and 2.12(3) Å for [Rh(cod)Cl]$_2$ [5c]). An increase in the π component in the metal–olefin bound is usually manifested in the elongation of the C=C bond and the shortening of the M–C bond. Since the molecular orbital formed by the electron donation from the $d\pi$-orbital of the metal to the empty π^*-orbital of the olefin is an antibonding orbital for the C=C bond and a bonding orbital for the M–C bond, the increased population of the olefin π^*-orbital and increased M–olefin bonding show a decrease in the C=C bond order and an increase in the M–C bond order, respectively. These features are manifested in the observed decrease in the ν(C=C) stretching frequency and increase in the ν(M–C) stretching frequency, respectively. However, the ν(C=C) stretching vibration did not show a large decrease and the ν(M–C) stretching frequency was observed at lower frequency. Consequently, the nature of the metal–olefin bond in [Cu(cod)$_2$]ClO$_4$ and [Ag(cod)$_2$]ClO$_4$ reported here seems to be dominated by σ-bonding from the olefin π-orbital to the metal $d\sigma$-orbital.

Cu^I-coordination surroundings in reduced cytochrome oxidase

Heme a and a_3 in cytochrome oxidase have a trienyl group with three olefinic bonds to the peripheral groups. The π-orbitals in these olefinic bonds are electronically localized in analogy with cod used in this study. These olefinic stretching modes have not been assigned [13], because other bands overlap in the region 1650–1573 cm^{-1} and it is difficult to confidently assign them. However, the vibrations that appear in the region 1650–1573 cm^{-1} shift slightly to the lower frequency region (1611–1574 cm^{-1}) when the enzyme is reduced. The behaviour is

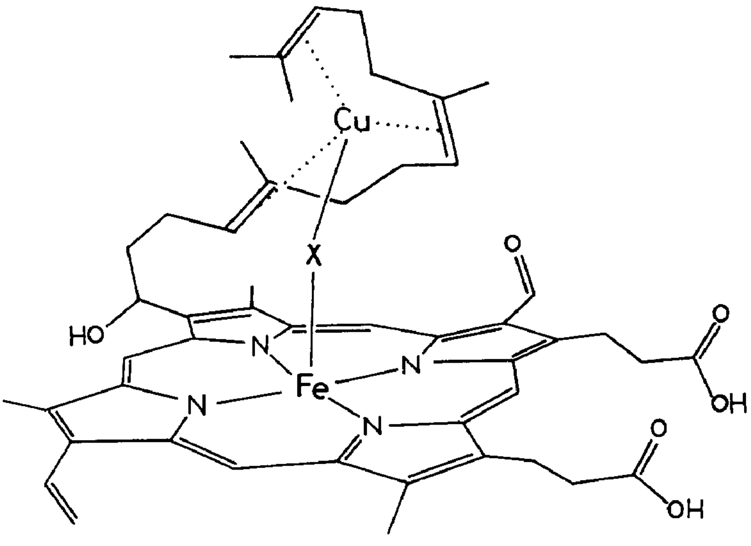

Fig. 2. Proposed structure for heme a–Cu environment in reduced and semioxidized forms of cytochrome oxidase.

analogous to that of the interaction between Cu^I and cod. In particular, the intense band at 1650 cm^{-1} which appears in the spectrum of the oxidized form disappears in the reduced form and a new intense band grows up at 1588 cm^{-1} in the spectrum of the reduced cytochrome oxidase. These two bands are similar to the intense $\nu(C{=}C)$ bands at 1667 and 1598 cm^{-1} appearing in cod and $[Cu(cod)_2]ClO_4$, respectively. This redox-dependent spectral behavior is unique to cytochrome oxidase. This probably suggests that the Cu^{II} ion in the oxidized form does not strongly interact with olefinic π-orbitals, and that the Cu^I ion in the reduced form is coordinated to the trienyl substituent. We suggest that Cu^I–olefin bonding could occur in the reduced and semioxidized cytochrome oxidase, and propose the possible structure for Cu^I environment in their oxidation states, as schematically shown in Fig. 2; the coordination about the Cu^I ion, involving three olefinic groups of trienyl substituent and the other ligand, is a four-coordinate tetrahedron.

References

1 M.J.S. Dewer, Bull. Soc. Chim. France, 18 (1951) C79.

2 J. Chatt and L.A. Duncanson, J. Chem. Soc., (1953) 2939.

3 (a) H. Masuda, N. Yamamoto, T. Taga, K. Machida, S. Kitagawa, and M. Munakata, J. Organomet. Chem., 322 (1987) 121; (b) M. Munakata, S. Kitagawa, H. Shimono, T. Emori, and H. Masuda, J. Chem. Soc., Chem. Commun., (1987) 1798; (c) H. Masuda, K. Machida, M. Munakata, S. Kitagawa, and H. Shimono, J. Chem. Soc., Dalton Trans., (1988) 1907; (d) M. Munakata, S. Kitagawa, H. Shimono, H. Masuda, and K. Machida, submitted for publication.

4 (a) J.S. Thompson and J.F. Whitney, J. Am. Chem. Soc., 105 (1983) 5488; (b) J.S. Thompson, R.J. Harlow and J.F. Whitney, ibid., 105 (1983) 3322; (c) J.S. Thompson and R.M. Swiatek, Inorg. Chem., 24 (1985) 110; (d) J.S. Thompson and J.F. Whitney, ibid., 23 (1984) 2813.

5 (a) D.B. Powell and T.J. Leedham, Spectrochim. Acta, 28A (1972) 337; (b) T.J. Leedham, D.B. Powell and J.G.V. Scott, ibid., 29A (1973) 559; (c) D.W. Wertz and M.A. Moseley, Inorg. Chem., 19 (1980) 705.

6 O. Warburg and H.S. Gewitz, Z. Physiol. Chem., 288 (1951) 1.

7 B.G. Malmston, in T.G. Spiro (Ed.), Metal Ion Activation of Dioxygen, Wiley, New York, 1980, p. 181–208.

8 P.J. Hendra and E.J. Loader, Chem. Ind. (London), (1968) 718.

9 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, 4th ed., Wiley, New York, 1986.

10 A. Albinati, S.V. Meille and G.J. Carturan, J. Organomet. Chem., 182 (1979) 269.

11 Y. Sasada in K. Hata (Ed.), Kagaku Binran, 3rd ed., The Chemical Society of Japan, Maruzen, Tokyo, 1984, Vol. II, p. 646–722.

12 (a) H. Dierks and H.Z. Dietrich, Kristallogr., 122 (1965) 1: (b) J.A.K. Howard, Acta Crystallogr. Sect B, 38 (1982) 2896.

13 S. Choi, J.J. Lee, Y.H. Wei and T.G. Spiro, J. Am. Chem. Soc., 105 (1983) 3692.