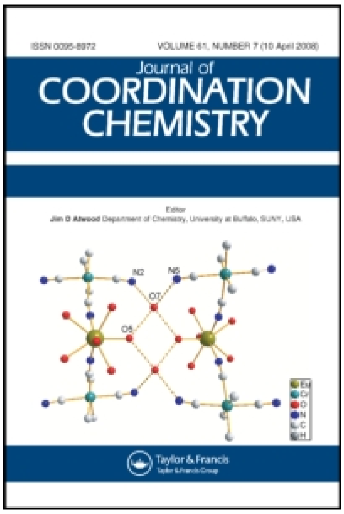

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

THE VIBRATIONAL SPECTRA OF COBALT AND IRON CYCLIDENE DIOXYGEN COMPLEXES AND THEIR RELATION TO MOLECULAR GEOMETRY

Mohamad Masarwa[a]; Alexandra Sauer-masarwa[a]; Naidong Ye[a]; Daryle H. Busch[a]
[a] Department of Chemistry, University of Kansas, Lawrence, Kansas, U.S.A.

To cite this Article Masarwa, Mohamad , Sauer-masarwa, Alexandra , Ye, Naidong and Busch, Daryle H.(1993) 'THE VIBRATIONAL SPECTRA OF COBALT AND IRON CYCLIDENE DIOXYGEN COMPLEXES AND THEIR RELATION TO MOLECULAR GEOMETRY', Journal of Coordination Chemistry, 28: 3, 355 — 364

To link to this Article: DOI: 10.1080/00958979308037117

URL: http://dx.doi.org/10.1080/00958979308037117

J. Coord. Chem. 1993, Vol. 28, pp. 355–364
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THE VIBRATIONAL SPECTRA OF COBALT AND IRON CYCLIDENE DIOXYGEN COMPLEXES AND THEIR RELATION TO MOLECULAR GEOMETRY

MOHAMAD MASARWA, ALEXANDRA SAUER-MASARWA,
NAIDONG YE and DARYLE H. BUSCH

Department of Chemistry, University of Kansas, Lawrence, Kansas 66045, U.S.A.

(Received 23 April 1992; in final form 2 June 1992)

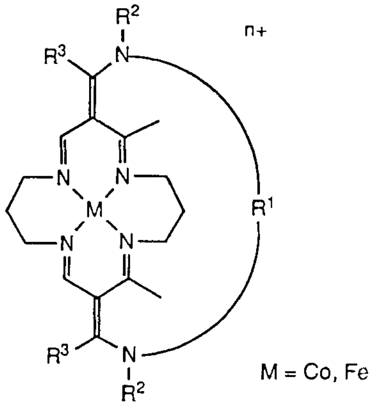
Infrared spectra were obtained for dioxygen adducts of a series of cobalt(II) and iron(II) cyclidene complexes with 1-methylimidazole as the axial base. The $\nu_{O\text{-}O}$ bands were located in the range 1137–1163 cm^{-1}, and their identity was confirmed by $^{18}O_2$ isotopic substitution. The frequency was found to be insensitive of the metal ion but dependent on both the σ and π electron donating properties of the cyclidene ligands. There is no apparent correlation between $\nu_{O\text{-}O}$ and the oxygen affinity; $\nu_{O\text{-}O}$ alternates with the even or odd number of carbon atoms in the bridging polymethylene group because of a symmetry effect on the π electron system of the ligand.

KEY WORDS: Cobalt, iron, cyclidenes, macrocycles, infrared, oxygen adduct, molecular mechanics.

INTRODUCTION

In recent years, several new families of synthetic dioxygen carriers have been designed and synthesized,[1–10] providing an expanded array of compounds which mimic the reversible dioxygen binding of the natural metalloproteins hemoglobin and myoglobin. The so-called cyclidenes[2,11] (**1**) are among the most successful ligand families discovered so far, giving in some cases reversible dioxygen binding in partially aqueous solution at room temperature, with high dioxygen affinity, and sufficient stability with respect to autoxidation for both the iron and cobalt complexes.[2,10–13] The generalized lacunar cyclidene ligand has an intrinsic cavity into which small molecules may enter and bind to the metal. The opposite, open axial metal-coordination position is usually occupied by a solvent molecule or by a nitrogenous base, such as 1-methylimidazole, which has been added to the solution in excess.

The dioxygen affinities of the cobalt and iron cyclidene complexes depend on the ligand substituents R^1, R^2, R^3, (**1**). The dependence on R^1 is in response to cavity size, specifically to the width of that opening.[14] The influences of R^2 and R^3 appear to be of electronic origin.[2d,15] Recent investigations with the cyclidenes and other dioxygen carriers have been directed toward a better understanding of how various molecular parameters determine the dioxygen binding behaviour. In particular, there remains considerable interest about the nature of the bound dioxygen and how it is influenced by and, in turn, how it influences the cyclidene ligand.[14b,16] A systematic



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study of the $\nu_{O\text{-}O}$ stretching mode was undertaken. In particular, the cobalt cyclidenes were studied to evaluate how the frequency of that vibration responds to the length of the bridging group R^1. For this study, the cobalt cyclidenes with the substituents $R^1 = (CH_2)_n$, n = 5 to 12, $R^3 = CH_3$, $R^2 = CH_3$, C_6H_5, were examined. A series of iron cyclidenes were studied to examine the influence of R^2 and R^3 (R^1 = *m*-xylylene, $R^2 = CH_3$, $CH_2C_6H_5$, $R^3 = CH_3$, C_6H_5), as well as the effect of changing the metal ion from cobalt to iron, $R^1 = (CH_2)_6$, $R^2 = CH_3$, $R^3 = CH_3$, C_6H_5, on the O-O stretching frequency.

EXPERIMENTAL

The cobalt and iron cyclidene complexes were prepared as described previously.[2,17,18] All manipulations prior to exposure to dioxygen (or air) were performed in a nitrogen filled inert atmosphere box (Vacuum Atmospheres). Infrared spectra were obtained using a demountable solution cell (Spectra Tech, NaCl windows, 0.05 mm path length), and a Perkin Elmer 1600 FTIR spectrometer. A typical experimental procedure involved filling the cell and measuring the infrared spectrum with half of the volume of a solution of metal cyclidene (~ 3 mg/0.1 cm^3 of 1.5 M 1-methylimidazole in acetonitrile) in the absence of dioxygen. The procedure was then repeated with the oxygenated second half of the solution, and the two spectra were compared. The assignment of the dioxygen stretching frequency was confirmed by repeating the experiment using 95% enriched $^{18}O_2$ for selected complexes and comparing the frequency shift with the expected value.

For cobalt complexes with a long R^1 bridge, n = 11,12, the rate of autoxidation is appreciable at room temperature and, therefore, the spectra were recorded for these materials near 0°C. Experiments with the complex $R^1 = (CH_2)_6$, and $R^2 = R^3 = CH_3$ gave identical results at both 0°C and room temperature (25°C). At longer times and higher temperatures the $\nu_{O\text{-}O}$ stretching bands for the longer bridges (n = 11,12) slowly disappeared as autoxidation took its toll ($t_{1/2} = 2$ min, 25°C).

Due to their faster rates of autoxidation, and in some cases low dioxygen affinities, samples of iron cyclidenes were oxygenated at −40°C and transferred to a thermostattable, demountable solution cell (NaCl windows, 0.05 or 0.1 mm path length). When oxygenated samples were allowed to warm to room temperature, only the bands assigned to $\nu_{O\text{-}O}$ became weaker, due to dissociation of the oxygen adduct or autoxidation, but the frequencies of the bands did not shift.

Molecular mechanics calculations were performed with Lin's modification of the MM2/MMP2 program of Allinger,[16,19] running on a VAX 9000–210VP computer. The calculated results were visualized in the SYBYL program of TRIPOS Associates, Inc. of St. Louis, Missouri.

RESULTS AND DISCUSSION

A typical IR spectrum for the dioxygen adduct of a cobalt cyclidene complex appears in Figure 1, which shows the oxygen-free spectrum, both the $^{16}O_2$ and $^{18}O_2$ oxygenated spectra, and the $^{18}O_2$-$^{16}O_2$ difference spectrum. The results are summarized in Table 1. The cobalt and iron complexes of the cyclidene ligand, $R^1 = (CH_2)_6$, $R^2 = R^3 = CH_3$, both have a $\nu_{O\text{-}O}$ stretch at 1141 cm^{-1}, a value that is similar to those reported for the dioxygen adducts of other ligand families, in the range for end-on bent, superoxide-type systems.[20] For example, the dioxygen adduct of cobalt tetraphenylporphyrin, [Co(TPP)(O$_2$)(MeIm)] has a $\nu_{O\text{-}O}$ of 1144 cm^{-1},[21] the Schiff base complex [Co(J-en)(py)(O$_2$)], where [H$_2$(J-en) = *N*,*N*′-ethylenebis(2,2-diacetylethylideneamine)], has a $\nu_{O\text{-}O}$ stretch at 1143 cm^{-1}.[22] A review of the vibrational spectra of dioxygen adducts has recently been published, and the reader is referred there for further details.[20]

The observed isotopic shift of the dioxygen stretching mode for the $R^2 = Me$, $R^3 = Me$ complexes is also similar to values observed for related complexes.[20] Further, the frequency shifts compare reasonably well with those predicted by a simple

Table 1 O-O stretching frequency of cobalt and iron cyclidene dioxygen adducts

R^3, R^2, R^1	$\nu^{16}O_2$/cm^{-1}	$\nu^{18}O_2$/cm^{-1}	$\Delta\nu$/cm^{-1}	K_{O_2}/torr^{-1} 20°C	(ref)
Cobalt complex					
CH_3, CH_3, $(CH_2)_5$	1137.0 ± 0.2			0.0094	(11)
CH_3, CH_3, $(CH_2)_6$	1141.3 ± 0.2	1070.0	71.3	0.155	(11)
CH_3, CH_3, $(CH_2)_7$	1139.0 ± 0.2			0.62	(11)
CH_3, CH_3, $(CH_2)_8$	1142.5 ± 0.2	1071.5	71.0	0.65	(11)
CH_3, CH_3, $(CH_2)_9$	1139.9 ± 0.2			0.59	(17)
CH_3, CH_3, $(CH_2)_{10}$	1139.6 ± 0.2			0.17	(17)
CH_3, CH_3, $(CH_2)_{11}$	1140.5 ± 0.2			0.144*	(17)
CH_3, CH_3, $(CH_2)_{12}$	1140.5 ± 0.2			0.08*	(17)
Ph, CH_3, $(CH_2)_6$	1157.5 ± 0.2	1067.9	89.6		
Ph, CH_3, $(CH_2)_8$	1151.0 ± 0.2				
Iron complex					
CH_3, CH_3, $(CH_2)_6$	1141.4 ± 0.2				
Ph, CH_3, $(CH_2)_6$	1157.1 ± 0.2				
CH_3, CH_3, mxyl	1140.1 ± 0.2				
CH_3, Bz, mxyl	1149.0 ± 0.2				
Ph, CH_3, mxyl	1162.0 ± 0.2				
Ph, Bz, mxyl	1163.1 ± 0.2				

*Extrapolated values; all values in MeCN + 1.5 M 1-methylimidazole.

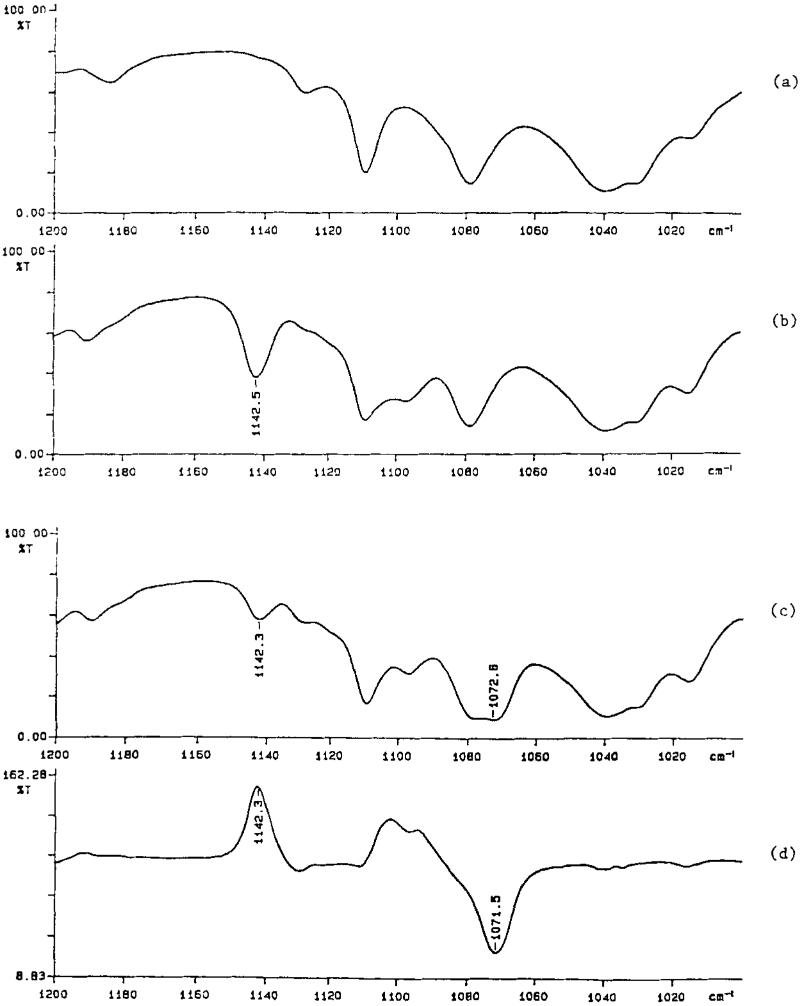


Figure 1 Infrared spectrum of the cobalt cyclidene complex having $R^2 = R^3 = CH_3$, $R^1 = (CH_2)_8$, at room temperature in acetonitrile + 1.5 M 1-methylimidazole (a): under nitrogen; (b): air saturated; (c): $^{18}O_2$; (d): difference spectrum (c-b).

harmonic oscillator model $[(\nu^{18}O_2) = (\nu^{16}O_2)\cdot(16/18)^{1/2}]$. The isotopic shift for the cobalt cyclidene complex ($R^1 = (CH_2)_6$, $R^2 = Me$, $R^3 = Ph$) showed an appreciable deviation from the expected value, which might suggest the possibility of vibrational coupling with either internal modes of the axial ligand, the molecule core or the solvent.

Further confirmation of the $\nu_{O\text{-}O}$ assignment was provided by the observation that the band for $^{18}O_2$ disappeared upon bubbling $^{16}O_2$ through the solution, with the concomitant formation of the expected $^{16}O_2$ band.

The cobalt and iron oxygen stretching vibrations that were predicted[20] to occur at *circa* 500–520 and 560–580 cm^{-1}, respectively, were not observed due to strong absorbance by the deoxy-complex, solvent system or window material in this region of the infrared spectrum. Those frequencies are routinely observed only by RR techniques.

Substitution of iron for cobalt had no measurable effect on $\nu_{O\text{-}O}$ for the two pairs of complexes studied; $\nu_{O\text{-}O}$ is 1141 cm^{-1} for cobalt and iron cyclidene ($R^1 = (CH_2)_6$, $R^2 = Me$, $R^3 = Me$) and 1157 cm^{-1} for cobalt and iron cyclidene ($R^1 = (CH_2)_6$, $R^2 = Me$, $R^3 = Ph$). However, for porphyrin model systems, a metal ion effect has been noted on substitution of iron for cobalt, with a shift to lower wave numbers for cobalt complexes; it was also pointed out that the magnitude of that shift depends on the nature of the porphyrin and the other axial ligand. The shift is smaller (6 *vs* 15 cm^{-1}) on going from simple unprotected porphyrins to the picket fence porphyrin.[20] For the capped porphyrin, the reported trend is in the opposite direction, with $\nu_{O\text{-}O}$ for the iron derivative being 4 cm^{-1} lower than that of the corresponding cobalt complex. The relatively small shifts found for the hindered complexes would seem to indicate that $\nu_{O\text{-}O}$ is insensitive to the amount of electron transfer between O_2 and the metal ion (assuming that these are different for Fe^{II} and Co^{II}), and that the non-polar pockets provided by those complexes insulate the dioxygen from the solvent influences that have been observed in the cases of simpler porphyrins.[23]

The findings for our cyclidene complexes, which also provide a non-polar cavity, agree well with those observations in showing no measurable distinction in $\nu_{O\text{-}O}$ for the iron and cobalt complexes. This is also an additional example in support of the disputed close correspondence between iron and cobalt reconstituted analogues in natural systems, although the situation in those systems is admittedly much more complicated as indicated by splitting of $\nu_{O\text{-}O}$.[20,23,24,25]

Comparison of the series of iron cyclidenes having different R^2 and R^3 substituents reveals that the more electron withdrawing power these groups provide, the higher the $\nu_{O\text{-}O}$ values for their complexes (1140 to 1163 cm^{-1}). The cobalt complexes show the same trend; upon replacement of $CH_3 = R^3$ by C_6H_5, $\nu_{O\text{-}O}$ increases slightly. These results are consistent with a weakening of the metal-oxygen bond by the electron withdrawing substituent. The electron withdrawing ability of phenyl substituents at R^3 in cyclidene complexes is well documented; for example, in the nickel complex for which $R^1 = (CH_2)_6$, $R^2 = CH_3$, this is reflected in the reduction potentials for the Ni(III)/(II) couple ($R^3 = CH_3$, $E° = 0.775$ V;[27] $R^3 = C_6H_5$, $E° = 0.92$ V[28] *vs* Ag/Ag^+ (0.1 M)). However, it has been pointed out that although this structural feature exerts a significant effect on the dioxygen binding constant, this thermodynamic trend does not necessarily correlate with measurable changes in the Fe-O bond strength. Specifically, for conventional model porphyrin complexes, there is no strong dependence on the electronic properties of substituents.[26] Another possible explanation for the shift in $\nu_{O\text{-}O}$ that has been observed for cyclidenes might be the increasing bulk these substituents provide, leading to a more protected cavity. It has been indicated that the more polar the cavity, the higher the $\nu_{O\text{-}O}$.[23]

It is clear from the graph in Figure 2 that there is a marked dependence of the $\nu_{O\text{-}O}$ stretching frequency on the cyclidene bridge length R^1. As the bridge length varies from $(CH_2)_5$ to $(CH_2)_8$, $\nu_{O\text{-}O}$ generally shows an overall small increase, a result that is consistent with a small increase in O-O double bond character. This change parallels an inferred decrease in repulsion between the bound dioxygen and the walls of the cavity, as evidenced by dioxygen equilibrium constant measurements[11] and molecular mechanics studies.[16] This is not expected in terms of a simple model based on increasing charge transfer in conjunction with increasing Co-O bond strength.

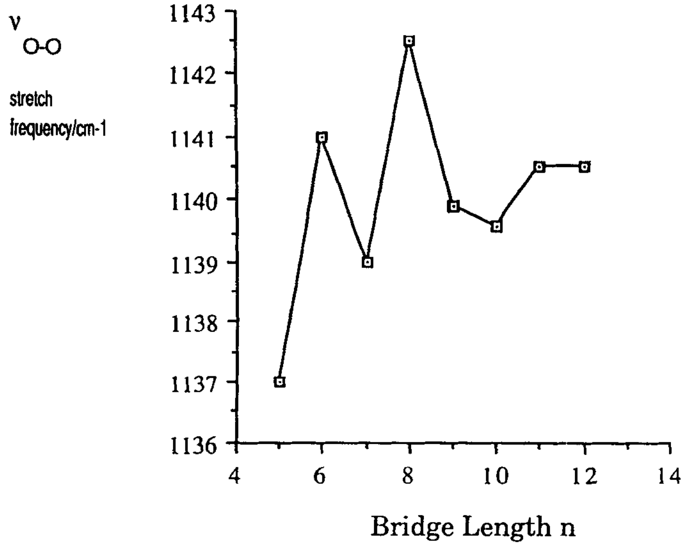


Figure 2 Graph of O-O stretching frequency *versus* bridge length for cobalt cyclidene dioxygen adducts with $R^2=R^3=CH_3$, $R^1=(CH_2)_n$, n=5–12.

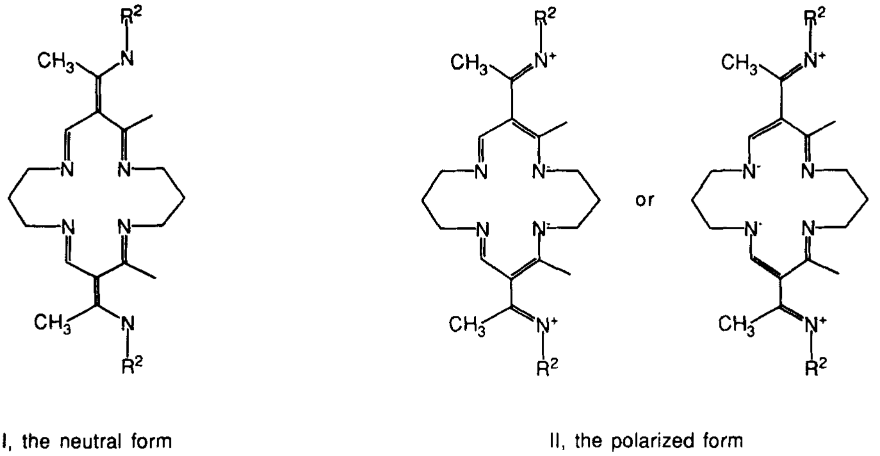


Figure 3 Two resonance forms for a cyclidene ligand.

Possibly, as the complexes become more relaxed, their σ skeletons become more stable, thus leading to an increase in $\nu_{O\text{-}O}$.

The most striking feature is the large oscillatory function of the $\nu_{O\text{-}O}$ stretching frequency with changing cyclidene bridge length. Similar behaviour has been observed for other physical parameters; e.g., the first ligand oxidation potential of this series of cyclidene complexes[29] and certain of the ^{13}C NMR chemical shifts of the corresponding nickel complexes.[30] A molecular mechanics study suggests that this oscillatory pattern reflects changes in the conjugated π systems in cyclidene ligands, and that those changes are traceable to variations in the conformational strain energy of the bridge group upon adding -CH_2- units.[14,16] For a cyclidene ligand, two resonance forms permit rationalization of these observations; they represent neutral and polarized structures, respectively (Figure 3). There is no doubt that the relative contributions of resonance forms of these kinds will be affected by the conformations of the complexes. The question is how this derives from alternating between even and odd numbered polymethylene chains. ^{13}C NMR data for the nickel cyclidene complexes[30] suggest that the relative contribution of the polarized form is greater for odd-chain complexes than for even-chain complexes. On the basis of electron shielding theory for NMR, complexes in the polarized form will display larger differences between the chemical shifts of Carbon A and Carbon B, $\Delta\delta_{AB}$, and similarly for $\Delta\delta_{AC}$ values. Figures 4 and 5 (from reference 30) clearly show that odd-chain

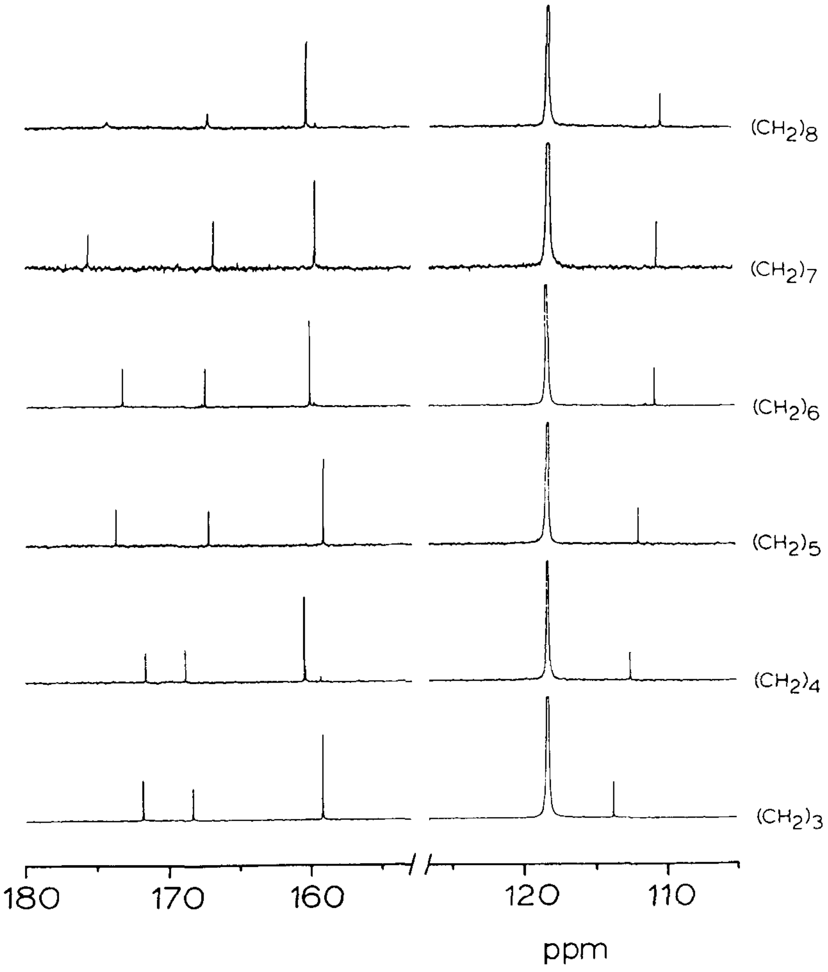


Figure 4 ^{13}C NMR spectra for the Ni(II) complexes, $R^2=R^3=CH_3$.

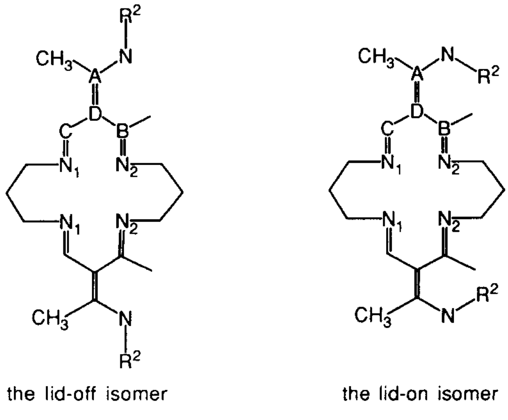
complexes have larger $\Delta\delta_{AB}$ and $\Delta\delta_{AC}$ values than their adjacent even-chain counterparts. The present molecular mechanics study suggests that the underlying reason for this interesting phenomenon is the improbability of producing a symmetrical structure for the species having even-numbered bridges, since such a structure would require the middle two methylene groups to be completely eclipsed. The compounds with odd-umbered bridges do not have this problem.

The special stereochemical consequences associated with disymmetry of the even-numbered bridges has profound effects on the π systems of the cyclidene complexes as it significantly alters the relative amounts of the polar and nonpolar resonant forms. Neutral resonant form I describes the N-A bond as a single bond and the A-D bond a double bond while polar resonant form II interchanges these bond orders. Analysis of the R^2N-AD and NA-DC dihedral angles (average of two values, Table 2; see Figure 5 for atom labelling) from the minimized structures of dioxygen adducts ($R^1 = R^3 = CH_3$) indicates that the odd-chain complexes indeed have larger contributions from the polarized resonant form II than do their even-chain counterparts.

The effects of this oscillatory pattern on the strengths of the O-O bonds can be rationalized as follows. Compared with a ligand having resonance form I, a ligand having resonance form II is a better π-donor and will donate more π-electron density to the cobalt centre. As a result, the cobalt centre will accept π back-bonding electron density from the dioxygen to a lesser degree in form II, effectively increasing the π anti-bonding electron density in dioxygen ad resulting in a lower O-O stretching frequency. Significantly, ∠NA-DC varies with bridge length in exactly the same way as $\nu_{O\text{-}O}$.

Table 2 Calculated dihedral angles associated with odd- and even-numbered bridged cobalt cyclidene complexes

	$(CH_2)_5$	$(CH_2)_6$	$(CH_2)_7$	$(CH_2)_8$	$(CH_2)_9$	$(CH_2)_{10}$	$(CH_2)_{11}$	$(CH_2)_{12}$
∠R^2-ND	178.8	176.6	179.0	175.3	1.3	2.4	1.4	2.4
∠NA-DC	148.4	158.1	152.3	164.4	153.7	153.0	153.0	152.6



the lid-off isomer the lid-on isomer

Figure 5 Atom labelling scheme.

A distinct break occurs in the oscillatory pattern of the graph for the $\nu_{O\text{-}O}$ stretching frequency *versus* chain length $R^1=(CH_2)_n$ for $n=9$ and 10. This change in behaviour coincides with a shift in the stereochemistry of attachment of the polymethylene chain to the bridging nitrogen, and involves an isomerization associated with structural variants that have been dubbed *lid-on* and *lid-off* isomers (Figure 5). All relatively short chain bridges ($n=3$–8) in cyclidene complexes exist exclusively in the lid-off form, in which the bridging group is displaced to one side of the metal ion as it traverses the coordination plane. For n larger than 10, the lid-on conformation dominates, placing the R^1 bridge directly above the cavity, with both conformations occurring for $n=9$ and 10.[31] In this series of complexes, $\angle$NA-DC shows little change; nor does $\nu_{O\text{-}O}$. The magnitude of the oscillatory changes in $\angle R^2$N-AD are also small when compared with those of the shorter chain complexes, and $\angle$NA-DC no longer has the same pattern as $\nu_{O\text{-}O}$.

For this series of cobalt complexes the dioxygen affinity is known to vary over about four orders of magnitude, and the change has been shown to be dependent on the cavity width.[11,17] In contrast, there is little change in the O-O stretching frequency. Apparently, the strengths of the O-O and Co-O bonds themselves do not vary much with bridge length. From a molecular mechanics point of view, van der Waals interactions between the bound dioxygen and the cavity seem to be very important in determining the dioxygen affinity of a cyclidene complex. The previously established steric effect attributed to cavity width is based on both X-ray crystal structure determinations and molecular mechanics calculations,[14,16] in which it is found that the bridge length establishes the cavity width, and it is the cavity width which determines the dioxygen affinity. However, it has been pointed out that this thermodynamic trend does not necessarily correlate with measurable changes in the Fe-O bond strength; thus the relationship between the binding affinity and the Fe-O stretching frequency is not necessarily straightforward.[26]

Acknowledgements

The financial support of the United States Science Foundation (NSF-CHE 8822822) and the United States National Institutes of Health (GM10040) is gratefully acknowledged.

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