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Characterization of Binuclear μ -Peroxo and μ -Superoxo Cobalt(III) Amine Complexes from Raman Spectroscopy

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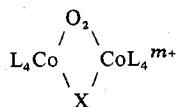
The Raman spectra of a range of binuclear μ -peroxo and μ -superoxo cobalt(III) complexes with principally amine donor ligands in other coordination sites have been measured in the characteristic O—O stretching regions. Monobridged μ -peroxo complexes exhibit a strong resonance Raman band in solution or as solid-state pressed disks at $800 \pm 10 \text{ cm}^{-1}$ and monobridged μ -superoxo complexes a band at $1120 \pm 10 \text{ cm}^{-1}$ in solution. These ν_{O_2} are generally far stronger than other vibrations of the complexes. Binuclear dicobalt complexes with a second μ -hydroxo or μ -amido bridge in addition to the μ -peroxo or μ -superoxo bridge exhibit relatively weak and generally broad ν_{O_2} bands. Dibridged μ -peroxo complexes exhibit the O_2^{2-} stretch at $812 \pm 5 \text{ cm}^{-1}$ in solution and $820 \pm 10 \text{ cm}^{-1}$ in the solid state, while dibridged μ -superoxo complexes exhibit the O_2^- stretch at $1075 \pm 10 \text{ cm}^{-1}$. The observation of strong Raman bands near 795 cm^{-1} for complexes of the macrocyclic tetraamines 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene ($\text{Me}_6[14]\text{diene}$) and 5,12-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene ($\text{Me}_2[14]\text{diene}$) supports their characterization as monobridged μ -peroxo-dicobalt(III) complexes and indicates that Raman spectroscopy is useful in the characterization of new binuclear dioxygen complexes.

Introduction

Reports of the presence of coordinated peroxide (O_2^{2-}) or superoxide (O_2^-) in several oxygen-transport proteins detected by the application of Raman and infrared (IR) spectroscopic techniques have appeared in recent years.¹⁻³ Suggestions of oxygen bridging of metal centers in hemocyanin and heme-rythrin⁴ has prompted investigations of the vibrational spectra of readily prepared binuclear cobalt(III) amine complexes with peroxo and superoxo bridges, since these may be appropriate simple model compounds for complex biological systems.

Assignment of the O—O stretching frequency has not been clearly established in the IR spectra of μ -peroxo-dicobalt complexes⁵⁻⁷ but is generally accepted to lie in the 800–900- cm^{-1} range. Subsequently, however, strong characteristic frequencies in the Raman spectra of both μ -peroxo- (near 800 cm^{-1}) and μ -superoxo- (near 1100 cm^{-1}) dicobalt compounds with ammine, polyamine, and cyanide ligands have been reported.⁸⁻¹⁰ Further, we have recently reported the observation of a strong O—O stretch in the Raman spectrum near 800 cm^{-1} of a μ -peroxo-dicobalt complex with a macrocyclic tetraamine.¹¹

The reactivity of molecular oxygen with cobalt(II) complexes has been extensively studied and reviewed.¹²⁻²¹ Solutions of simple cobalt(II) salts and amine ligands readily oxidize at room temperature producing characteristically brown μ -peroxo binuclear cobalt(III) complexes. A wide range of monobridged complexes $\text{L}_5\text{Co}-\text{O}_2-\text{CoL}_5^{n+}$ ($n = 4$ for neutral ligands L) and dibridged complexes



($m = 3$ for neutral ligands L) with additional μ -hydroxo or

μ -amido bridges have been reported. Further oxidation of these diamagnetic μ -peroxo-dicobalt complexes with oxidants such as Cl_2 or Ce^{4+} produces an analogous range of paramagnetic μ -superoxo-dicobalt complexes.

Despite the extensive chemistry reported for these complexes, only a limited number of dioxygen complexes have been studied by Raman spectroscopy.⁸⁻¹¹ Since bridged dioxygen complexes would seem to be readily characterized by the observation of an O—O stretch in their Raman spectra, we have measured the Raman spectra of a large number of amine-dioxygendicobalt complexes in the characteristic O—O stretching regions in both solution and solid states. We present the results of our investigation in this report.

Experimental Section

Preparation of Complexes. Monobridged μ -peroxo-dicobalt complexes of the general formula $\text{L}_5\text{Co}-\text{O}_2-\text{CoL}_5^{n+}$ were prepared by previously published methods for $\text{L}_5 = (\text{NH}_3)_5$,²²⁻²⁴ $(\text{NH}_3)_2(\text{dien})$,²⁵ $(\text{NH}_3)(\text{pn})_2$,²⁵ $(\text{NH}_3)(\text{tn})_2$,²⁵ $(\text{NH}_3)(\text{bn})_2$,²⁵ $(\text{pn})(\text{dien})$,^{25,26} $(\text{tn})(\text{dien})$,²⁵ $(\text{dien})_2$,²⁵ $(\text{bn})(\text{dien})$,²⁵ $(\text{NH}_3)(\text{trien})$,²⁶ $(\text{NH}_3)(\text{en})_2$,²⁷ (tetren) ,²⁷ $(\text{OH}_2)(\text{Me}_2[14]\text{diene})$,²⁵ $(\text{SCN})(\text{Me}_2[14]\text{diene})$,²⁵ $(\text{NH}_3)(\text{Me}_6[14]\text{diene})$,²⁵ $(\text{DMF})(\text{salen})$,²⁸ $(\text{his})_2$,²⁹ and $(\text{hm})_2$.^{9,30} Common ligand abbreviations are used.³¹

Dibridged μ -hydroxo- μ -peroxo complexes of the general formula $\text{L}_4\text{Co}-(\text{O}_2)(\text{OH})-\text{CoL}_4^{3+}$ were prepared by previously published methods for $\text{L}_4 = (\text{NH}_3)_4$,³² $(\text{en})_2$,³³ $(\text{pn})_2$,²⁵ and $(\text{tn})_2$.²⁵

The μ -superoxo analogues of several of the μ -peroxo-dicobalt complexes were prepared in solution but not isolated, as previously described,²⁵ by oxidation in dilute perchloric acid solution with chlorine.

Measurement of Raman Spectra. Raman spectra were measured with a Spex Ramalog 5 laser spectrophotometer using Ar^+ excitation generally at the 5145-Å excitation over the region 700–1200 cm^{-1} . The sample as either a pressed disk or an aqueous solution was spun at approximately 1200 rpm in a rotating disk holder or glass solution cell, respectively, to minimize decomposition by the laser beam.

Solution samples of μ -peroxo-dicobalt complexes of typically 5-mM concentration were prepared and chilled in ice prior to spectroscopic

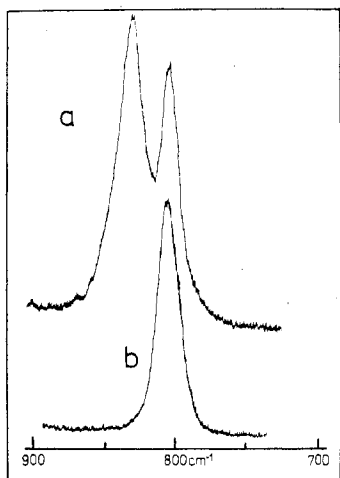


Figure 1. Solid-state Raman spectra of $[(\text{NH}_3)_5\text{Co}-\text{O}_2-\text{Co}(\text{NH}_3)_3](\text{SO}_4)_2$ dispersed in (a) KBr and (b) Na_2SO_4 .

measurement. The depolarization ratio (ρ_1) for each complex was measured as the ratio of parallel and perpendicular polarized spectrum intensity (I_{\parallel}/I_{\perp}). The parallel-polarized and perpendicular-polarized spectrum was measured in turn, followed again by the parallel-polarized spectrum as a check for decomposition. Peak size was estimated by both peak height and peak area, the value of ρ_1 calculated by each process being in agreement to less than 5%. To allow for any observed decomposition an estimate of peak size under parallel polarization was obtained by averaging the two measurements obtained. Since decomposition was usually not marked, it was estimated that ρ_1 is generally correct to within 10%. Spurious reflections from the solution cell were eliminated by first aligning the cell and recording a baseline with water only present. Spectra of complexes containing coordinated ammonia were measured in concentrated 7 or 15 M aqueous ammonia to limit ammine hydrolysis.

Solid samples of μ -peroxo-dicobalt complexes were prepared as pressed disks with either KBr or a simple salt of the anion of the complex under study as dispersant. A ratio of dispersant to complex of approximately 1:2 by weight was commonly employed. For selected compounds, a pseudo ρ_1 was measured in a like manner to that described above for solution samples.

Spectra of relatively unstable μ -superoxo complexes in solution (5 mM) were measured in 0.3-M perchloric acid solution to prevent decomposition to peroxo complexes. All solutions were chilled in ice prior to spectroscopic study.

Results

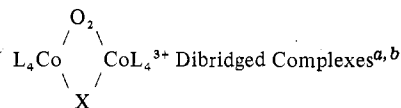
μ -Peroxo Complexes. All dicobalt amine complexes known to contain a single peroxo bridge exhibited a strong Raman band in the solid-state spectra in the region $800 \pm 15 \text{ cm}^{-1}$ (Table I), assigned to O_2^{2-} stretching,^{9,11} which was by far the strongest observed band for all complexes studied. The recently prepared dicobalt complexes of the macrocyclic tetraamine ligands $\text{Me}_2[14]$ diene and $\text{Me}_6[14]$ diene exhibit strong Raman bands at 795 cm^{-1} , consistent with their earlier formulation²⁵ as monobridged μ -peroxo-dicobalt complexes.

The solid-state spectrum of μ -peroxo-decaamminedibicobalt(III) in the O_2^{2-} stretching region exhibits a remarkable dependence on dispersant. The sulfate salt dispersed in KBr exhibits two strong bands at 808 and 833 cm^{-1} (Figure 1), although only a single band at 808 cm^{-1} has been reported for the isolated solid.⁹ However, the sulfate salt dispersed in Na_2SO_4 shows only one band at 808 cm^{-1} . This behavior was also observed for the nitrate and perchlorate salts dispersed in KBr or NaNO_3 and KClO_4 , respectively, and implies a specific interaction in the KBr environment. No similar dispersant dependence was observed for other amine complexes.

Measurement of peak area of the O_2^{2-} stretch relative to $\nu_1(\text{SO}_4^{2-})$ for added Na_2SO_4 in the disk spectrum of complexes with $L_5 = (\text{NH}_3)_5$, $(\text{NH}_3)(\text{en})_2$, $(\text{NH}_3)(\text{trien})$, and $(\text{OH}_2)-$

Table I. Solid-State Raman O_2^{2-} Stretching Frequency of μ -Peroxo Cobalt(III) Amine Complexes

$L_5\text{Co}-\text{O}_2-\text{Co}L_5^{4+}$ Monobridged Complexes ^{a,b}			
L_5	anion	dispersant	O-O str, cm^{-1}
$(\text{NH}_3)_5$	$(\text{SO}_4)_2 \cdot 2\text{H}_2\text{O}$	KBr	808, 833
		Na_2SO_4 solid ^c	808
$(\text{NH}_3)_5$	$(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$	KBr	808, 830 sh
		NaNO_3	802 ^d
$(\text{NH}_3)_5$	$(\text{NO}_3)_4$	NaNO_3	806
$(\text{NH}_3)_5$	$(\text{ClO}_4)_4$	KBr	810 sh, 829
		KClO_4	808 ^d
$(\text{NH}_3)_5$	$(\text{SCN})_4$	KBr	786
$(\text{NH}_3)_2(\text{dien})$	$(\text{ClO}_4)_4$	KBr	811
$(\text{NH}_3)(\text{pn})_2$	$(\text{ClO}_4)_4$	KBr	813
		KClO_4	815
$(\text{NH}_3)(\text{en})_2$	$(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$	KBr	805 ^d
		KClO_4	805
$(\text{NH}_3)(\text{en})_2$	$(\text{NO}_3)(\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$	KBr	809
$(\text{NH}_3)(\text{tn})_2$	$(\text{ClO}_4)_4$	KBr	808
		KClO_4	804
$(\text{NH}_3)(\text{bn})_2$	$(\text{ClO}_4)_4 \cdot x\text{H}_2\text{O}$	KBr	810
		$(\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$	803
$(\text{pn})(\text{dien})$	$(\text{ClO}_4)_4$	KBr	800
		KClO_4	800
$(\text{en})(\text{dien})$	$(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$	KBr	805
		KClO_4	803
$(\text{tn})(\text{dien})$	$(\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$	KBr	803
		KClO_4	800
$(\text{bn})(\text{dien})$	$(\text{ClO}_4)_4 \cdot x\text{H}_2\text{O}$	KBr	805
		$(\text{ClO}_4)_4$	800
$(\text{dien})_2$	$(\text{ClO}_4)_4 \cdot \frac{1}{2}\text{NaClO}_4 \cdot \text{H}_2\text{O}$	KBr	801 ^d
		$(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$	806
$(\text{NH}_3)(\text{trien})$	$(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$	KBr	803
		$(\text{ClO}_4)_4 \cdot 2\text{H}_2\text{O}$	803
(tetren)	$(\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$	KBr	795 ^d
		KClO_4	795
$(\text{OH}_2)-$ ($\text{Me}_2[14]$ diene)	$(\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$	KBr	796
		$(\text{ClO}_4)_2 \cdot \text{H}_2\text{O}$	795
$(\text{SCN})-$ ($\text{Me}_2[14]$ diene)	$(\text{ClO}_4)_4 \cdot x\text{H}_2\text{O}$	KBr	795
		$(\text{ClO}_4)_4$	795
$(\text{NH}_3)-$ ($\text{Me}_6[14]$ diene)	$(\text{ClO}_4)_4 \cdot \text{H}_2\text{O}$	KBr	800 br
		$(\text{ClO}_4)_4$	803
$(\text{DMF})(\text{salen})$	$(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$	KBr	803
$(\text{his})_2$	$(\text{NO}_3)_3 \cdot 2\text{H}_2\text{O}$	KBr	803



L_4	X^-	anion	dispersant	O-O str, ^e cm^{-1}
$(\text{NH}_3)_4$	OH^-	$(\text{NO}_3)_3 \cdot \text{NH}_4\text{NO}_3 \cdot \frac{1}{2}\text{H}_2\text{O}$	KBr	826
$(\text{NH}_3)_4$	NH_2^-	$(\text{NO}_3)_3 \cdot \text{H}_2\text{O}$	solid ^c	793, 820
$(\text{en})_2$	OH^-	$(\text{S}_2\text{O}_8)(\text{NO}_3) \cdot \text{H}_2\text{O}$	KBr	785, 820
			$\text{Na}_2\text{S}_2\text{O}_8$	794 sh, 828

^a Ar⁺ 5145-Å excitation line. ^b sh = shoulder; br = broad.

^c Data from ref 9. ^d Measured also with 4880-Å excitation line.

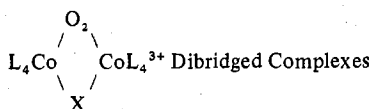
^e Absorbances relatively weak and broad.

($\text{Me}_2[14]$ diene) for spectra recorded at both 5145 and 4880 Å indicates the peroxo stretching mode undergoes intensity enhancement as the excitation wavelength is decreased from 5145 to 4880 Å. For each complex the relative intensity of the peak at 4880-Å excitation lies in the range 1.2–1.5 (± 0.1) relative to unit intensity at 5145-Å excitation. Minor decomposition during measurement does not allow for accurate enhancement ratios to be determined. This enhancement behavior has been reported previously for $L_5 = (\text{NH}_3)_5$ and suggests that the O_2^{2-} stretching mode is in resonance with the $\text{O}_2^{2-} \rightarrow \text{Co}(\text{III})$ charge-transfer absorption band observed²⁵ near 300 nm for monobridged complexes.

Solution Raman spectra of μ -peroxo-dicobalt complexes exhibit a strong band in the region $800 \pm 10 \text{ cm}^{-1}$ for monobridged complexes and a relatively weak broad band in the

Table II. Solution Raman O_2^{2-} Stretching Frequency of μ -Peroxo Cobalt(III) Amine Complexes

$L_5Co-O_2-CoL_5^{4+}$ Monobridged Complexes ^a				
L_5	anion	O-O str, cm^{-1}	ρ_1	
(NH ₃) ₅	NO ₃ ⁻	800 ^b	0.40	
(NH ₃) ₅	SO ₄ ²⁻	802 ^b		
(NH ₃) ₅	SCN ⁻	800 br ^b		
(NH ₃) ₂ (dien)	ClO ₄ ⁻	800 ^b	0.37	
(NH ₃)(pn) ₂	ClO ₄ ⁻	790 br ^b	0.32	
(NH ₃)(en) ₂	ClO ₄ ⁻	802 ^b	0.30	
(NH ₃)(tn) ₂	ClO ₄ ⁻	810 ^b	0.34	
(pn)(dien)	ClO ₄ ⁻	800	0.39	
(en)(dien)	ClO ₄ ⁻	799	0.37	
(tn)(dien)	ClO ₄ ⁻	802	0.32	
(dien) ₂	ClO ₄ ⁻	808	0.35	
(tetren)	ClO ₄ ⁻	800 ^c	0.37 ^c	
(OH ₂)(Me ₂ [14]diene)	ClO ₄ ⁻	796	0.35	
(his) ₂	NO ₃ ⁻	807	0.30	
(hm) ₂	Cl ⁻	800	0.30	

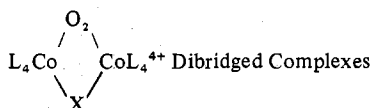


L_4	X^-	anion	O-O str, cm^{-1}	ρ_1
(en) ₂	OH ⁻	ClO ₄ ⁻	810 br	~0.5
(pn) ₂	OH ⁻	(S ₂ O ₆ ²⁻)(NO ₃ ⁻)	812 br ^d	
(tn) ₂	OH ⁻	ClO ₄ ⁻	815 br	~0.5
(NH ₃) ₄	NH ₂ ⁻	Cl ⁻	810 v br ^e	

^a Measured at 5145-Å excitation in aqueous solution. ^b Aqueous concentrated ammonia solution. ^c Also measured at 4880-Å excitation with equivalent results. ^d Fluorescence interference did not permit measurement of ρ_1 . ^e Very broad resonance did not permit measurement of ρ_1 .

Table III. Raman O_2^- Stretching Frequency of μ -Superoxo Cobalt(III) Amine Complexes

$L_5Co-O_2-CoL_5^{5+}$ Mononuclear Complexes ^a				
L_5	anion	O-O str, cm^{-1}	ref	
(NH ₃) ₂ (dien)	ClO ₄ ⁻	1124	<i>b</i>	
(NH ₃)(pn) ₂	ClO ₄ ⁻	1125	<i>b</i>	
(en)(dien)	ClO ₄ ⁻	1120	<i>b</i>	
(tn)(dien)	ClO ₄ ⁻	1123 ($\rho_1 = 0.33$)	<i>b</i>	
(tetren)	ClO ₄ ⁻	1121	<i>b</i>	
(his) ₂	NO ₃ ⁻	1118	<i>b</i>	
		1120	9	
(NH ₃) ₅	NO ₃ ⁻	1122 ^c	8	
(NH ₃) ₅	SO ₄ ²⁻	1110 ^c	8	
(hm) ₂	Cl ⁻	1125	<i>b</i>	



L_4	X^-	anion	O-O str, cm^{-1}	ref
(NH ₃) ₄	NH ₂ ⁻	SO ₄ ²⁻	1080 ^c	8
(NH ₃) ₄	NH ₂ ⁻	Cl ⁻	1072 ^c	8
(en) ₂	OH ⁻	ClO ₄ ⁻	<i>d</i>	<i>b</i>

^a Measured with 5145-Å excitation in 0.3-M aqueous HClO₄ generally. ^b This work. ^c Solid-state spectrum. ^d No resonance peak detected in attempted solution spectrum.

region $812 \pm 5 \text{ cm}^{-1}$ for dibridged complexes with a hydroxo or amido bridge in addition to the peroxo bridge. The monobridged complexes show a ρ_1 between 0.3 and 0.4, while a higher value is obtained in the case of the dibridged complexes of approximately 0.5. Data for the solution spectra are collected in Table II.

μ -Superoxo Complexes. Raman spectra of a number of monobridged μ -superoxo-dicobalt complexes prepared in solution exhibit a moderately strong resonance assigned to the

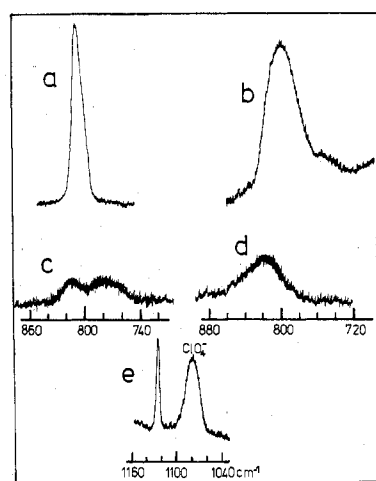


Figure 2. Raman spectra of (a) [(dien)(en)Co-O₂-Co(en)(dien)]-(ClO₄)₄ dispersed in a KBr disk, (b) [(dien)(pn)Co-O₂-Co(pn)(dien)](ClO₄)₄ in aqueous solution, (c) [(en)₂Co-(O₂)(OH)-Co(en)₂](S₂O₆)(NO₃) dispersed in a KBr disk, (d) [(tn)₂Co-(O₂)(OH)-Co(tn)₂](ClO₄)₃ in aqueous solution, and (e) [(dien)(tn)Co-O₂-Co(tn)(dien)](ClO₄)₅ superoxo complex in aqueous 0.3 M HClO₄.

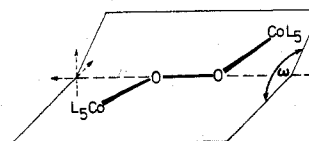


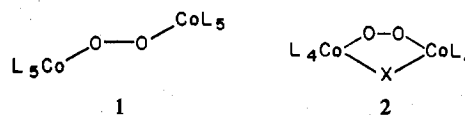
Figure 3. The dihedral angle ω in dioxygendicobalt complexes.

O_2^- stretching mode at $1120 \pm 10 \text{ cm}^{-1}$. Dibridged complexes exhibit a relatively weak resonance in the region $1075 \pm 5 \text{ cm}^{-1}$ in the solid state, although the resonance could not be readily detected in solution due partly to fluorescence interference. Data for the spectra of the μ -superoxo complexes studied are collected in Table III.

Marked differences in the average position of the O_2^- stretch for monobridged (1120 cm^{-1}) and dibridged (1075 cm^{-1}) μ -superoxo-dicobalt complexes as well as for the O_2^{2-} stretch for monobridged (800 cm^{-1}) and dibridged (812 cm^{-1}) μ -peroxo-dicobalt complexes occur. Moreover, the intensity of the O_2^- or O_2^{2-} stretch is markedly reduced when a second hydroxo or amido bridge is present generally. Typical Raman spectra of both μ -superoxo and μ -peroxo complexes are illustrated in Figure 2.

Discussion

Dioxygendicobalt complexes generally adopt configuration 1 for monobridged complexes and configuration 2 for dibridged



complexes in both peroxo and superoxo forms. Crystal structure determinations of a range of such complexes have been reported and confirm these general configurations.^{22,24,33-43} From the determined structures of the simple monobridged μ -peroxo- and μ -superoxo-decaamminedicobalt(III) sulfate complexes,^{22,41} certain obvious differences are apparent. The Co-O and O-O bond lengths vary from 188.2 and 147 pm, respectively, in the peroxo complex to 189.4 and 131 pm, respectively, in the superoxo complex. The observed dihedral angle ω , defined as the angle between the Co-O-O and O-O-Co' planes (Figure 3), is 146° in the peroxo complex and 175° in the superoxo complex. The Co-O-O angle is similar for both monobridged complexes, however, being 112°

Table IV. Crystallographic Data for Binuclear Dioxygenaminocobalt(III) Complexes

	Co-O ₂ , pm	O-O, pm	ω , deg	\angle Co-O-O, deg	ref
μ -Peroxo Complexes					
$\{[(\text{NH}_3)_5\text{Co}]_2\text{O}_2\}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$	188	147	145.8	112	22
$\{[(\text{NH}_3)_5\text{Co}]_2\text{O}_2\}(\text{SCN})_4$	183	147	180	112	24
$\{[(\text{en})(\text{dien})\text{Co}]_2\text{O}_2\}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$	190	149	180	110	34
$\{[(\text{DMF})(\text{salen})\text{Co}]_2\text{O}_2\}$	191	134	110.1	120	35
$\{[(\text{dipsalen})\text{Co}]_2\text{O}_2\} \cdot \text{C}_6\text{H}_5\text{CH}_3$	193	145	149	118	36
$\{[(\text{OH}_2)(\text{F-salen})\text{Co}]_2\text{O}_2\} \cdot \text{CHCl}_3 \cdot \text{C}_5\text{NH}_{11}$	196	131	122	118	37
$\{[(\text{en})_2\text{Co}]_2\text{O}_2(\text{NH}_2)\}(\text{SCN})_3 \cdot \text{H}_2\text{O}$	187	146	62.7	110	38
$\{[(\text{en})_2\text{Co}]_2\text{O}_2(\text{OH})\}(\text{NO}_3)(\text{S}_2\text{O}_6) \cdot 2\text{H}_2\text{O}$	186	147	60.7	110	33
$\{[(\text{tren})\text{Co}]_2\text{O}_2(\text{OH})\}(\text{ClO}_4)_3 \cdot 3\text{H}_2\text{O}$	187	146	60.7	109	39
μ -Superoxo Complexes					
$\{[(\text{NH}_3)_5\text{Co}]_2\text{O}_2\}(\text{NO}_3)_5$	189	132	180	117	40
$\{[(\text{NH}_3)_5\text{Co}]_2\text{O}_2\}(\text{SO}_4)(\text{HSO}_4)_3 \cdot 3\text{H}_2\text{O}$	189	131	175	117	41
$\{[(\text{NH}_3)_4\text{Co}]_2\text{O}_2(\text{NH}_2)\}(\text{NO}_3)_4$	187	132	0	121	42
$\{[(\text{en})_2\text{Co}]_2\text{O}_2(\text{NH}_2)\}(\text{NO}_3)_4 \cdot \text{H}_2\text{O}$	188	135	23.4	119	43
$\{[(\text{en})_2\text{Co}]_2\text{O}_2(\text{OH})\}(\text{NO}_3)_4 \cdot \text{H}_2\text{O}$	187	134	22.0	120	33

Table V. General Absorption Spectral Data for Binuclear Dioxygenaminocobalt(III) Complexes^a

complex type	absorption maxima ^b
monobridged μ -peroxo	300 \pm 5 (3.8 \pm 0.2), 430 \pm 20 (2.8 \pm 0.1) ^c
dibridged μ -peroxo	352 \pm 5 (3.7 \pm 0.1), 500 \pm 20 (2.6 \pm 0.1) ^c
monobridged μ -superoxo	306 \pm 8 (4.2 \pm 0.15), 468 \pm 8 (2.6 \pm 0.1), 705 \pm 15 (3.05 \pm 0.15)
dibridged μ -superoxo	ca. 300, 485 \pm 8 (2.6 \pm 0.1), 680 \pm 20 (2.6 \pm 0.15)

^a Data from ref 19 and ref 25 and references therein.^b Averaged band maxima (nm) with averaged extinction coefficients (log ϵ , M⁻¹ cm⁻¹). ^c Shoulder.

in the peroxo complex and 117° in the superoxo complex. Structural information available for dioxygenicobalt amine complexes is collected in Table IV.

The observed dihedral angle ω in solid H₂O₂ is 90° (C₂ symmetry), consistent with the calculated minimum conformational energy of the O₂²⁻ bridge.³⁴ The calculated maximum conformational energy in H₂O₂ occurs for $\omega = 180^\circ$, but this latter conformation appears to be preferred for ionic dicobalt complexes (Table IV). This observation has been interpreted as indicating that electrostatic repulsion of the highly charged metal chromophores is the dominant effect,³⁴ since reduction of effective charge about each cobalt center when anionic ligands are present³⁵ or when extensive hydrogen bonding occurs²² allows the adoption of a structure with ω approaching 90°. For dibridged complexes, the angle ω is reduced below 90° as a result of conformational restrictions from inclusion of a second hydroxo or amido bridge.

A decrease in bond order and a corresponding increase in bond length are observed from dioxygen (O₂) to superoxide (O₂⁻) and peroxide (O₂²⁻).²⁰ The O₂ molecule of bond order 2 has a bond length of 121 pm, and the O-O stretching frequency occurs at 1580 cm⁻¹. The O₂⁻ superoxide has a bond order of 1.5 and a bond length of 133 pm in KO₂ with an O-O stretching frequency at 1097 cm⁻¹ in LiO₂. For the peroxide (O₂²⁻) of bond order 1, the bond length in BaO₂ is 149 pm with the O-O stretch in Li₂O₂ observed at 802 cm⁻¹. For ionic binuclear cobalt dioxygen complexes, the average bond length in the μ -superoxo-dicobalt complexes is 132 pm compared with 147 pm in the μ -peroxo-dicobalt complexes. Assigned O-O stretching frequencies lie near 1100 and 800 cm⁻¹, respectively.⁸⁻¹¹

The resonance Raman effect suggests that the O₂²⁻ stretch is vibronically coupled with the O₂²⁻ \rightarrow Co(III) charge-transfer absorption in the monobridged complexes. For a wide range

of monobridged μ -peroxo-dicobalt amine complexes, the O₂²⁻ \rightarrow Co(III) charge-transfer absorption maximum is observed at 300 \pm 5 nm, while dibridged complexes generally have maxima at 352 \pm 5 nm.^{19,25} Average band positions and extinction coefficients of complexes of the type reported here are collected in Table V. A molecular orbital description for the analogous copper-oxygen complexes has been given⁴⁴ and the likely vibronic interaction discussed. The depolarization ratio of 1/3 observed for the O₂²⁻ stretching frequency is consistent with the idea of a mechanism such as vibronic coupling greatly increasing one component of the polarizability tensor.

The standard formula for ρ_1 is⁴⁵

$$\rho_1 = 3\beta^2 / (45\bar{\alpha}^2 + 4\beta^2) \quad (1)$$

where

$$\bar{\alpha} = 1/3(\alpha_{xx} + \alpha_{yy} + \alpha_{zz}) \quad (2)$$

and

$$\beta^2 = 1/2[(\alpha_{xx} - \alpha_{yy})^2 + (\alpha_{yy} - \alpha_{zz})^2 + (\alpha_{zz} - \alpha_{xx})^2 + 6(\alpha_{xy}^2 + \alpha_{yz}^2 + \alpha_{zx}^2)] \quad (3)$$

in which α_{ij} = ij th component of the polarizability tensor. It can be seen that, if one of the diagonal tensor components, say α_{zz} , is made very large relative to all other α_{ij} , then $\rho_1 \rightarrow 1/3$. This expression for ρ_1 is for normal Raman scattering. The possibility of an antisymmetric Raman scattering tensor for the resonance Raman spectra cannot be ignored but there is no sign of an inverse polarization ratio.

Because of the available structural data for μ -peroxo-dicobalt complexes in the solid state, pseudo ρ_1 values for several complexes dispersed in pressed disks were measured in an attempt to seek some correlation of measured ω and ρ_1 values. It has been suggested that polarization data for polycrystalline samples was not useful due to reflections and other optical effects,⁴⁶ although the possibility of obtaining quantitative polarization data from very fine powders has been suggested.⁴⁷ For the finely ground pressed disks studied, pseudo ρ_1 values in the range 0.48–0.84 were measured. Effects of reflections, which lead to values of $\rho_1 > 3/4$ in certain cases, were assumed constant since several measurements of each compound in different dispersants produced practically identical ρ_1 values. No apparent relationship of ω and ρ_1 was observed. For example, the sulfate and thiocyanate salts of (NH₃)₅Co-O₂-Co(NH₃)₅⁴⁺ exhibited similar pseudo ρ_1 values of 0.84 and 0.78 for measured ω of 146 and 180°, respectively, while (en)(dien)Co-O₂-Co(dien)(en)⁴⁺ with ρ_1 of 0.65 did not differ from (en)₂Co-(O₂)(OH)-Co(en)₂³⁺ with ρ_1 of 0.67, though ω varied from 180 to 63°, respectively. The solid-state ρ_1 values

are high compared with those measured in solution and indicate that attempts to elucidate structural information from solid-state polarization data in this case are invalid.

Small but significant differences in peak maxima of μ -peroxo and μ -peroxo- μ -hydroxo or μ -peroxo- μ -amido complexes are observed in both solution and solid-state Raman. The dibridged complex band in the O-O stretching region was generally relatively weak and broad, with two distinct maxima apparent in certain solid-state spectra (Table I). Previously, the O_2^{2-} stretch for dibridged complexes was assigned as occurring near 790 cm^{-1} on the basis of a peak at 793 cm^{-1} for $(\text{NH}_3)_4\text{Co}-(\text{O}_2)(\text{NH}_3)_4\text{Co}(\text{NH}_3)_4^{3+}$ and a peak at 790 cm^{-1} for a solution believed to contain $(\text{hm})_2\text{Co}-(\text{O}_2)-(\text{OH})-\text{Co}(\text{hm})_2^{3+}$. From IR deuteration studies of similar complexes, however, an O_2^{2-} stretch was assigned in the $820\text{--}830\text{-cm}^{-1}$ region.³² The observation in the solution spectra of one peak near 812 cm^{-1} and of a peak in the $820\text{--}830\text{-cm}^{-1}$ region in the solid state for dibridged complexes reported here suggests that the O_2^{2-} stretch can be best assigned near 820 cm^{-1} . The band sometimes observed near 790 cm^{-1} is presumably an amine ligand band.

Monobridged complexes containing ammonia ligands are known to undergo hydrolysis with the formation of an additional μ -hydroxo bridge.²⁶ When several μ -peroxo complexes of this type were dissolved in water and their Raman spectra recorded at discrete time intervals, a decrease in peak intensity and a shift to higher frequency of the maxima initially near 800 cm^{-1} was observed. This is consistent with μ -hydroxo bridge formation and with assignment of the O_2^{2-} stretch in the dibridged complexes in the region near 820 cm^{-1} .

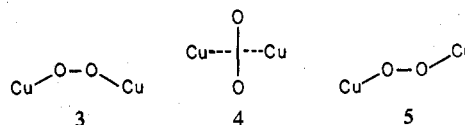
The μ -superoxo complexes also exhibited characteristic stretching regions for the monobridged (1120 cm^{-1}) and dibridged (1080 cm^{-1}) species. The hm complex prepared in solution as a μ -peroxo complex exhibited a relatively strong peak near 800 cm^{-1} , most consistent with its formulation as a monobridged rather than a dibridged compound. Oxidation to a μ -superoxo complex produced a compound exhibiting an O_2^{2-} stretch at 1125 cm^{-1} , analogous to a range of characterized monobridged compounds, supporting assignment of the initial μ -peroxo complex as a monobridged rather than dibridged species.

The unique behavior of the μ -peroxo-decaamminedicovalent(III) cation's pressed-disk Raman spectrum may be interpreted in two ways. Crystal structural evidence indicates that the symmetry of the complex can be dependent on the counteranion.^{22,24} Criteria for anion-exchange reactions in solid pressed disks have been investigated recently⁴⁸ and it is reasonable to suppose that bromide ion could supplant the original anion of the polycrystallites partially. The subsequent generation of two different dioxygen environments in the disk could then produce two different resonances. Alternatively, bromide ion may partially replace labile ammine ligands directly in the first coordination sphere. The resultant change in charge of the dicobalt complex cation may influence the O_2^{2-} stretching frequency. It has been observed that the peak at higher frequency increases at the expense of the peak at lower frequency as the relative amount of KBr in the disk increases, but this would be consistent with both proposals. The observations for this complex highlight the fact that the ν_{O_2} is not derived from a "pure" O-O stretching vibration and that the mass of the metal and other ligands, as well as the overall symmetry of the complex, must play some role in determining the observed frequency.²⁰ No doublet peaks in KBr disks were observed for other amine complexes even where some coordinated ammonia was present.

The characterization of new μ -peroxo and μ -superoxo complexes of cobalt which are monobridged from the observation of a strong resonance Raman band near 800 and

1120 cm^{-1} , respectively, has been illustrated in the case of the μ -peroxo macrocyclic complexes with $\text{Me}_2[14]$ diene or $\text{Me}_6[14]$ diene ligands reported in this study. The O-O stretch is generally far stronger than other bands of the monobridged complexes. Known dibridged complexes exhibit weaker and generally broader Raman bands which do not seem to be vibronically coupled as they do not exhibit a detectable resonance Raman effect. While they can be readily distinguished from monobridged complexes, making structural assignments of dibridged complexes on the basis of a weak or undetectable Raman O-O stretch alone is hazardous. However, the dibridged dicobalt amine complexes also usually exhibit a strong charge-transfer absorbance near 350 nm , significantly different from the maxima near 300 nm for monobridged amine complexes (Table V).

The monobridged μ -peroxo complexes appear to adopt an analogous structure to that in the dioxygen complex containing copper protein oxyhemocyanin. Three structures have been considered for dioxygen bridging in oxyhemocyanin, **3**, **4**, or **5**.⁴⁹⁻⁵¹ Structure **4** was discounted on the basis of excessive



steric interaction and structure **3** because it was not consistent with the observation of a resonance Raman effect in the protein O-O stretch.⁵¹ The favored structure (**5**) is analogous to that known in the dicobalt complexes and supports their value as possible structural models for certain dioxygen-complexing proteins.

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Registry No. $\{[(\text{NH}_3)_5\text{Co}]_2\text{O}_2\}(\text{SO}_4)_2$, 23103-43-7; $\{[(\text{NH}_3)_5\text{Co}]_2\text{O}_2\}(\text{NO}_3)_4$, 16632-71-6; $\{[(\text{NH}_3)_5\text{Co}]_2\text{O}_2\}(\text{ClO}_4)_4$, 67393-25-3; $\{[(\text{NH}_3)_5\text{Co}]_2\text{O}_2\}(\text{SCN})_4$, 18496-85-0; $\{[(\text{NH}_3)_2(\text{dien})\text{Co}]_2\text{O}_2\}(\text{ClO}_4)_4$, 67421-42-5; $\{[(\text{NH}_3)(\text{pn})_2\text{Co}]_2\text{O}_2\}(\text{ClO}_4)_4$, 36502-63-3; $\{[(\text{NH}_3)(\text{en})_2\text{Co}]_2\text{O}_2\}(\text{ClO}_4)_4$, 36573-37-2; $\{[(\text{NH}_3)(\text{en})_2\text{Co}]_2\text{O}_2\}(\text{NO}_3)(\text{ClO}_4)_3$, 49736-97-2; $\{[(\text{NH}_3)(\text{tn})_2\text{Co}]_2\text{O}_2\}(\text{ClO}_4)_4$, 67393-27-5; $\{[(\text{NH}_3)(\text{bn})_2\text{Co}]_2\text{O}_2\}(\text{ClO}_4)_4$, 67393-29-7; $\{[(\text{pn})(\text{dien})\text{Co}]_2\text{O}_2\}(\text{ClO}_4)_4$, 49728-66-7; $\{[(\text{en})(\text{dien})\text{Co}]_2\text{O}_2\}(\text{ClO}_4)_4$, 36502-65-5; $\{[(\text{tn})(\text{dien})\text{Co}]_2\text{O}_2\}(\text{ClO}_4)_4$, 49728-67-8; $\{[(\text{bn})(\text{dien})\text{Co}]_2\text{O}_2\}(\text{ClO}_4)_4$, 67421-40-3; $\{[(\text{dien})_2\text{Co}]_2\text{O}_2\}(\text{ClO}_4)_4$, 67393-18-4; $\{[(\text{NH}_3)(\text{trien})\text{Co}]_2\text{O}_2\}(\text{ClO}_4)_4$, 36502-64-4; $\{[(\text{tetren})\text{Co}]_2\text{O}_2\}(\text{ClO}_4)_4$, 36502-66-6; $\{[(\text{OH})_2(\text{Me}_2[14]\text{diene})\text{Co}]_2\text{O}_2\}(\text{ClO}_4)_4$, 58880-98-1; $\{[(\text{SCN})_2(\text{Me}_2[14]\text{diene})\text{Co}]_2\text{O}_2\}(\text{ClO}_4)_2$, 67393-20-8; $\{[(\text{NH}_3)(\text{Me}_6[14]\text{diene})\text{Co}]_2\text{O}_2\}(\text{ClO}_4)_4$, 67393-22-0; $\{[(\text{DMP})(\text{salen})\text{Co}]_2\text{O}_2\}$, 36300-65-9; $\{[(\text{his})_2\text{Co}]_2\text{O}_2\}(\text{NO}_3)_3$, 37238-70-3; $\{[(\text{NH}_3)_4\text{Co}(\text{O}_2)(\text{OH})\text{Co}(\text{NH}_3)_4]\}(\text{NO}_3)_3$, 67393-24-2; $\{[(\text{NH}_3)_4\text{Co}(\text{O}_2)(\text{NH}_2)\text{Co}(\text{NH}_3)_4]\}(\text{NO}_3)_3$, 31085-11-7; $\{[(\text{en})_2\text{Co}(\text{O}_2)(\text{OH})\text{Co}(\text{en})_2]\}(\text{S}_2\text{O}_6)(\text{NO}_3)_3$, 58692-02-7; $\{[(\text{hm})_2\text{Co}]_2\text{O}_2\}\text{Cl}_4$, 67393-13-9; $\{[(\text{en})_2\text{Co}(\text{O}_2)(\text{OH})\text{Co}(\text{en})_2]\}(\text{ClO}_4)_3$, 24925-38-0; $\{[(\text{pn})_2\text{Co}(\text{O}_2)(\text{OH})\text{Co}(\text{pn})_2]\}(\text{S}_2\text{O}_6)(\text{NO}_3)_3$, 67393-15-1; $\{[(\text{tn})_2\text{Co}(\text{O}_2)(\text{OH})\text{Co}(\text{tn})_2]\}(\text{ClO}_4)_3$, 67393-16-2; $\{[(\text{NH}_3)_4\text{Co}(\text{O}_2)(\text{NH}_2)\text{Co}(\text{NH}_3)_4]\text{Cl}_3$, 67393-17-3; $\{[(\text{NH}_3)_2(\text{dien})\text{Co}]_2\text{O}_2\}(\text{ClO}_4)_5$, 12556-79-5; $\{[(\text{NH}_3)(\text{pn})_2\text{Co}]_2\text{O}_2\}(\text{ClO}_4)_5$, 67478-44-8; $\{[(\text{en})(\text{dien})\text{Co}]_2\text{O}_2\}(\text{ClO}_4)_5$, 12563-59-6; $\{[(\text{tn})(\text{dien})\text{Co}]_2\text{O}_2\}(\text{ClO}_4)_5$, 67478-45-9; $\{[(\text{tetren})\text{Co}]_2\text{O}_2\}(\text{ClO}_4)_5$, 12568-13-7; $\{[(\text{hm})_2\text{Co}]_2\text{O}_2\}\text{Cl}_5$, 67421-36-7; $\{[(\text{en})_2\text{Co}(\text{O}_2)(\text{OH})\text{Co}(\text{en})_2]\}(\text{ClO}_4)_4$, 67478-43-7.

References and Notes

- (1) J. S. Loehr, T. B. Freedman, and T. M. Loehr, *Biochem. Biophys. Res. Commun.*, **56**, 510 (1974).
- (2) C. H. Barlow, J. C. Maxwell, W. J. Wallace, and W. S. Caughey, *Biochem. Biophys. Res. Commun.*, **55**, 91 (1973).
- (3) J. B. R. Dunn, D. F. Shriver, and I. M. Klotz, *Proc. Natl. Acad. Sci. U.S.A.*, **70**, 2582 (1973).
- (4) H. B. Gray, *Adv. Chem. Ser.*, No. 100, 365 (1971).
- (5) S. Bagger and K. Gibson, *Acta Chem. Scand.*, **26**, 3788 (1972).
- (6) A. G. Sykes and J. A. Weil, *Prog. Inorg. Chem.*, **13**, 1 (1970).
- (7) M. Mori, J. A. Weil, and M. Ishiguro, *J. Am. Chem. Soc.*, **90**, 615 (1968).
- (8) T. Shibahara, *J. Chem. Soc., Chem. Commun.*, 864 (1973).

- (9) T. B. Freedman, C. M. Yoshida, and T. M. Loehr, *J. Chem. Soc., Chem. Commun.*, 1016 (1974).
- (10) T. C. Streckas and T. G. Spiro, *Inorg. Chem.*, **14**, 1421 (1975).
- (11) C. G. Barraclough and G. A. Lawrance, *Inorg. Nucl. Chem. Lett.*, **12**, 133 (1976).
- (12) L. H. Voigt, H. Faigbaum, and S. Wimberley, *Chem. Rev.*, **63**, 269 (1963).
- (13) E. Bayer and P. Schretzmann, *Struct. Bonding (Berlin)*, **2**, 181 (1967).
- (14) S. Fallab, *Angew. Chem.*, **6**, 496 (1967).
- (15) E.-I. Ochiai, *J. Inorg. Nucl. Chem.*, **37**, 1503 (1975).
- (16) R. G. Wilkins, *Adv. Chem. Ser.*, No. **100**, 111 (1971).
- (17) F. Basolo, B. M. Hoffman, and J. A. Ibers, *Acc. Chem. Res.*, **8**, 384 (1975).
- (18) A. V. Savitskii and V. I. Nelyublin, *Russ. Chem. Rev. (Engl. Transl.)*, **44**, 110 (1975).
- (19) G. McLendon and A. E. Martell, *Coord. Chem. Rev.*, **19**, 1 (1976).
- (20) L. Vaska, *Acc. Chem. Res.*, **9**, 175 (1976).
- (21) M. R. Paris and D. Aymes, *Bull. Soc. Chim. Fr.*, 1431 (1976).
- (22) W. P. Schaefer, *Inorg. Chem.*, **7**, 725 (1968).
- (23) R. Davies, M. Mori, A. G. Sykes, and J. A. Weil, *Inorg. Synth.*, **12**, 197 (1970).
- (24) F. R. Fronczek, W. P. Schaefer, and R. E. Marsh, *Acta Crystallogr., Sect. B*, **30**, 117 (1974).
- (25) G. A. Lawrance and P. A. Lay, *J. Inorg. Nucl. Chem.*, in press.
- (26) Y. Sasaki, J. Fujita, and K. Saito, *Bull. Chem. Soc. Jpn.*, **44**, 3373 (1971).
- (27) D. L. Duffy, D. A. House, and J. A. Weil, *J. Inorg. Nucl. Chem.*, **31**, 2053 (1969).
- (28) C. Floriani and F. Calderazzo, *J. Chem. Soc. A*, 946 (1969).
- (29) M. Woods, J. A. Weil, and J. K. Kinnaud, *Inorg. Chem.*, **11**, 1713 (1972).
- (30) M. S. Michailidis and R. B. Martin, *J. Am. Chem. Soc.*, **91**, 4683 (1969).
- (31) Ligand abbreviations: en = 1,2-diaminoethane, tn = 1,3-diaminopropane, pn = 1,2-diaminopropane, bn = 1,4-diaminobutane, dien = diethylenetriamine, trien = triethylenediamine, tetren = tetraethylenepentamine, Me₂[14]diene = 5,7-dimethyl-1,4,8,11-tetraazacyclotetradeca-4,11-diene, Me₆[14]diene = 5,7,7,12,14,14-hexamethyl-1,4,8,11-tetraazacyclo-
- tetradeca-4,11-diene, salen = bis(salicylaldehyde)ethylenediimine, his = histidine, hm = histamine.
- (32) M. Mori, J. A. Weil, and M. Ishiguro, *J. Am. Chem. Soc.*, **90**, 615 (1968).
- (33) V. Thewalt and G. Strickmeier, *Z. Anorg. Allg. Chem.*, **419**, 163 (1976).
- (34) J. R. Fritch, G. C. Christoph, and W. P. Schaefer, *Inorg. Chem.*, **12**, 2170 (1973).
- (35) M. Calligaus, G. Nardis, L. Randaccio, and H. Ripamonti, *J. Chem. Soc. A*, 1069 (1970).
- (36) L. A. Lindblom, W. P. Schaefer, and R. E. Marsh, *Acta Crystallogr., Sect. B*, **27**, 1461 (1976).
- (37) B. C. Wang and W. P. Schaefer, *Science*, **166**, 1404 (1969).
- (38) U. Thewalt, *Z. Anorg. Allg. Chem.*, **393**, 1 (1972).
- (39) M. Zehnder, U. Thewalt, and S. Fallab, *Helv. Chim. Acta*, **59**, 2290 (1976).
- (40) R. E. Marsh and W. P. Schaefer, *Acta Crystallogr., Sect. B*, **24**, 246 (1968).
- (41) R. E. Marsh and W. P. Schaefer, *Acta Crystallogr.*, **21**, 246 (1966).
- (42) C. G. Christoph, R. E. Marsh, and W. P. Schaefer, *Inorg. Chem.*, **8**, 291 (1969).
- (43) U. Thewalt and R. E. Marsh, *Inorg. Chem.*, **11**, 351 (1972).
- (44) T. B. Freedman, J. S. Loehr, and T. M. Loehr, *J. Am. Chem. Soc.*, **98**, 2809 (1976).
- (45) T. G. Spiro and T. C. Streckas, *Proc. Natl. Acad. Sci. U.S.A.*, **69**, 2622 (1972).
- (46) E. Stager, *Raman Spectrosc.*, **2**, 200 (1970).
- (47) R. S. Tobias, *Raman Eff.*, **2**, 419 (1973).
- (48) J. W. Milne, *Spectrochim. Acta*, **22**, 1347 (1974).
- (49) T. J. Thaman, J. S. Loehr, and T. M. Loehr, *J. Am. Chem. Soc.*, **99**, 4187 (1977).
- (50) J. A. Larrabee, T. G. Spiro, N. S. Ferris, W. H. Woodruff, W. A. Maltese, and M. S. Kerr, *J. Am. Chem. Soc.*, **99**, 1979 (1977).
- (51) T. B. Freeman, J. S. Loehr, and T. M. Loehr, *J. Am. Chem. Soc.*, **98**, 2809 (1976).

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Volumes of Activation for Racemization of Mixed 1,10-Phenanthroline and 2,2'-Bipyridyl Complexes of Nickel(II) from High-Pressure Solution Kinetics

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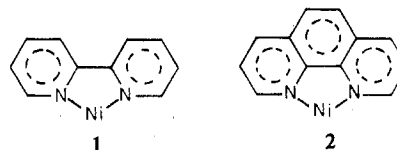
The effect of pressure on the rates of racemization of Ni(phen)₂(bpy)²⁺ and Ni(phen)(bpy)₂²⁺ in solution has been evaluated. Reactions of Ni(phen)₂(bpy)²⁺ exhibit only a minor pressure dependence of the rate, with a volume of activation (ΔV^\ddagger) of +0.6 cm³ mol⁻¹ and -0.1 cm³ mol⁻¹ for racemization in 0.01 and 1.0 M aqueous HCl, respectively. Aquation of Ni(phen)₂(bpy)²⁺ in 1.0 M aqueous HCl exhibits no measurable pressure dependence, with $\Delta V^\ddagger = 0.0$ cm³ mol⁻¹. Racemization of Ni(phen)(bpy)₂²⁺ proceeds with a minor acceleration upon the application of pressure, with $\Delta V^\ddagger = -1.9$ cm³ mol⁻¹ and $\Delta V^\ddagger = -5.2$ cm³ mol⁻¹ in 0.01 and 1.0 M aqueous HCl, respectively. Variation of ΔV^\ddagger with acidity observed suggests an acid-dependent pathway is the dominant mechanism at high acidity but is not important at low acidity. A common mechanistic pathway for racemization and aquation of these complexes is favored since reported rates, enthalpies, entropies, and volumes of activation are very similar. A one-ended dissociative mechanism via a half-bonded bpy ligand is consistent with experimental ΔV^\ddagger data.

Introduction

Kinetic studies of racemization and aquation reactions of nickel(II) complexes have attracted continuing interest.² Extensive kinetic studies of 1,10-phenanthroline (phen) and 2,2'-bipyridyl (bpy) complexes of nickel(II) and other metal ions have been reported.^{2,3} The rates of dissociation, racemization, and labeled ligand exchange in Ni(phen)₃²⁺ have been shown to be very similar,^{4,5} providing consistent evidence for an intermolecular mechanism with rate-determining release of a chelated phen ligand. In nonaqueous solvents, exchange rates are also the same as the rates of racemization in the same solvents for Ni(phen)₃²⁺,⁵ although rates of racemization and associated activation parameters show a solvent dependence,^{6,7} indicating that solvent-complex interactions may be significant.

While racemization of Ni(bpy)₃²⁺ also appears to proceed via an intermolecular mechanism, the rate of racemization and also aquation is much faster than that observed for Ni(phen)₃²⁺ and further exhibits acid-dependence and specific-ion effects.⁶⁻⁸

The mixed complexes Ni(phen)₂(bpy)²⁺ and Ni(phen)(bpy)₂²⁺ have also been subject to kinetic investigation,⁹ and racemization and aquation appear to proceed by a mechanism analogous to that proposed for Ni(bpy)₃²⁺, involving a half-bonded bpy molecule in the transition state. Chelated bpy (**1**) is capable of rotation about the internal C(2)-C(2') bond joining the pyridine residues, a process which is forbidden by the fused ring system in chelated phen (**2**).



One-ended dissociation in complexes with chelated bpy can readily proceed via rotation of one pyridine residue about the C(2)-C(2') bond while the second ring remains fixed. A one-ended dissociative process may occur for chelated phen,