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Characterization of Cobalt Dioxygen Complexes by Means of High Field ^{59}Co NMR

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A large number of compounds formed by the reaction of Co(II) complexes with molecular oxygen are known. They have been widely studied as models for biological oxygen carrying molecules and several recent reviews [1–3] of the area have been published. They are generally of two types – those with a Co:O_2 stoichiometry of 1:1 and those with a 2:1 Co:O_2 ratio. The former are paramagnetic and ESR studies [4] have provided a useful probe for their electronic and molecular structure. The latter are diamagnetic and ^{59}Co NMR should be applicable but NMR spectra have not been previously reported.

Table I presents ^{59}Co chemical shift and line width data for six cobalt/oxygen complexes with 2:1 Co:O_2 stoichiometries. Such compounds are usually regarded as Co(III) complexes of the peroxy anion. This formulation is consistent with the molecular structure of compound 1 as determined by X-ray crystallography [5]. The chemical shift supports this structure. It has been suggested on the basis of the increased ligand lability [6] that the metal ion is intermediate in oxidation state between Co(II) and Co(III). If this were the case an anomalously large positive chemical shift would be anticipated. It is well established [7, 8] that ^{59}Co chemical shifts are inversely related to the energies of the first allowed electronic transition of the complex and are therefore determined by the position of the ligands in the spectrochemical series. The chemical shift of compound 1 may be compared with those of several other complexes of the type $Co(NH_3)_5X$ given in Table I. These data indicate that the position of the peroxy anion in the spectrochemical series is intermediate between N_3^- and Br^- with a crystal field splitting similar to I^-. This is a reasonable position and confirms the formulation of these compounds as simple Co(III) complexes. Comparisons of the chemical shifts of the remaining oxygen complexes with those of other complexes containing the same ligands support this conclusion.

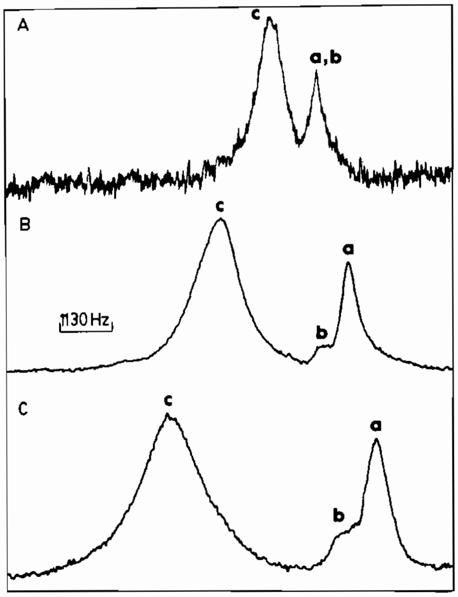

Fig. 1. ^{59}Co NMR spectra of $[Co(dien)(en)]_2O_2^{4+}$. A) 21.252 MHz, B) 59.035 MHz, C) 94.457 MHz. The assignments correspond to the structures of Fig. 3.

Compounds 2–6 in Table I can all exist in several isomeric forms. We have been interested in identifying the isomers present in solution with the intent of correlating structure with the case of reduction of the peroxy bridge. Either ^{13}C NMR or ^{59}Co NMR could be used for this purpose. The spectra of Fig. 1 illustrate the advantages of using high field ^{59}Co NMR. For compound 2 three isomers are possible as shown in Fig. 3. At a field of 2.114T only two can be clearly observed but at higher fields the third is unambiguously resolved. Assignments can be made on the basis of line widths and chemical shifts. The theory of ^{59}Co chemical shifts [9] combined with the crystal field expressions for the electronic transitions of low symmetry complexes [10] predicts that complexes with essentially *trans* geometry will have more positive chemical shifts than those with *cis* geometry and a point charge model for quadrupole coupling predicts that *trans* isomers will have broader lines than *cis* isomers [11]. The assignments indicated in Figs. 1 and 3 have been made on this basis. A quantitative scheme for assigning isomers in low symmetry compounds will be presented in a future publication. In the ^{13}C spectrum 4 lines are predicted for isomer a, 4 lines for isomer b and 3 lines for isomer c. The ^{13}C spectrum of Fig. 2 demonstrates that several isomers are present but is not useful in making assignments. The ^{59}Co line widths tend to

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TABLE I. ^{59}Co Chemical Shifts and Line Widths of Co(III) Complexes.

	Complex		21.252 MHz		59.035 MHz		94.457 MHz		Ref. (Syntheses)
			δ/ppm	$\Delta\nu_{1/2}$/Hz	δ/ppm	$\Delta\nu_{1/2}$/Hz	δ/ppm	$\Delta\nu_{1/2}$/Hz	
1	$Co(NH_3)_5CN^{2+}$		6641 ± 20	3260 ± 200	6646 ± 20	8662 ± 300	6645 ± 20	14385 ± 1000	13
	$Co(NH_3)_5NO_2^{2+}$		7576 ± 5	440 ± 20					14
	$Co(NH_3)_5N_3^{2+}$		8671 ± 5	172 ± 10					This work
	$(Co(NH_3)_5)_2O_2^{4+}$/6M NH_4OH		8759 ± 5	1172 ± 25					18
	$Co(NH_3)_5I^{2+}$		8760*						14, 16
	$Co(NH_3)_5Br^{2+}$		8820*						16
	$Co(NH_3)_5Cl^{2+}$		8887 ± 5	1146 ± 100	8890 ± 5	1914 ± 50	8890 ± 5	2997 ± 50	15
	$Co(NH_3)_5H_2O^{2+}$		9122 ± 20	4005 ± 200	9130 ± 20	3977 ± 100	9114 ± 20	4405 ± 100	14
2	abf,de,c-$(Co(dien)(en))_2O_2^{4+}$		7555 ± 5	760 ± 30	7552 ± 10	846 ± 20	7554 ± 10	1282 ± 50	17
	ebf,ad,c-$(Co(dien)(en))_2O_2^{4+}$		7572 ± 10	850 ± 50	7569 ± 20	924 ± 20	7568 ± 20	1661 ± 50	
	bcf,ad,c-$(Co(dien)(en))_2O_2^{4+}$		7652 ± 10	1453 ± 50	7654 ± 20	2231 ± 50	7650 ± 20	3560 ± 100	
3	b,e(adf),c-$(Co(NH_3)(trien))_2O_2^{4+}$/pH 10.5		7655 ± 10	1913 ± 50					17
	pH 4.75		7672 ± 10	1766 ± 50					
4	$(Co(tetraen))_2O_2^{4+}$	a	7447 ± 10	777 ± 50	7479 ± 5	967 ± 100			
			7484 ± 5	364 ± 20	7508 ± 2	753 ± 100			
			7504 ± 10	485 ± 50	7520 ± 5	1721 ± 150			
			7527 ± 10	485 ± 50	7539 ± 5	1721 ± 150			
		b	7408 ± 50	2354 ± 200	7417 ± 50				
			7569 ± 10	1311 ± 50	7584 ± 20	4087 ± 200			
			7614 ± 50	2985 ± 200	7720 ± 50				
5	ae,df,b,c-$(Coen_2SCN)_2O_2^{2+}$				8385 ± 10	1266 ± 50	8391 ± 10	2500 ± 20	This work
	ab,df,e,c-$(Coen_2SCN)_2O_2^{2+}$				8502 ± 20	4700 ± 200	8499 ± 20	6163 ± 300	
6	$(Co(salen))_2O_2(DMSO)_2$		8369 ± 100	12854 ± 1500			8367 ± 50	13287 ± 1000	18

*Values obtained from Ref. 19. [a]Tentatively assigned as μ-peroxo-O_2 Complexes. [b]Tentatively assigned as μ-peroxo-O_2 Complexes with bridging terminal ethylenediamine chains.

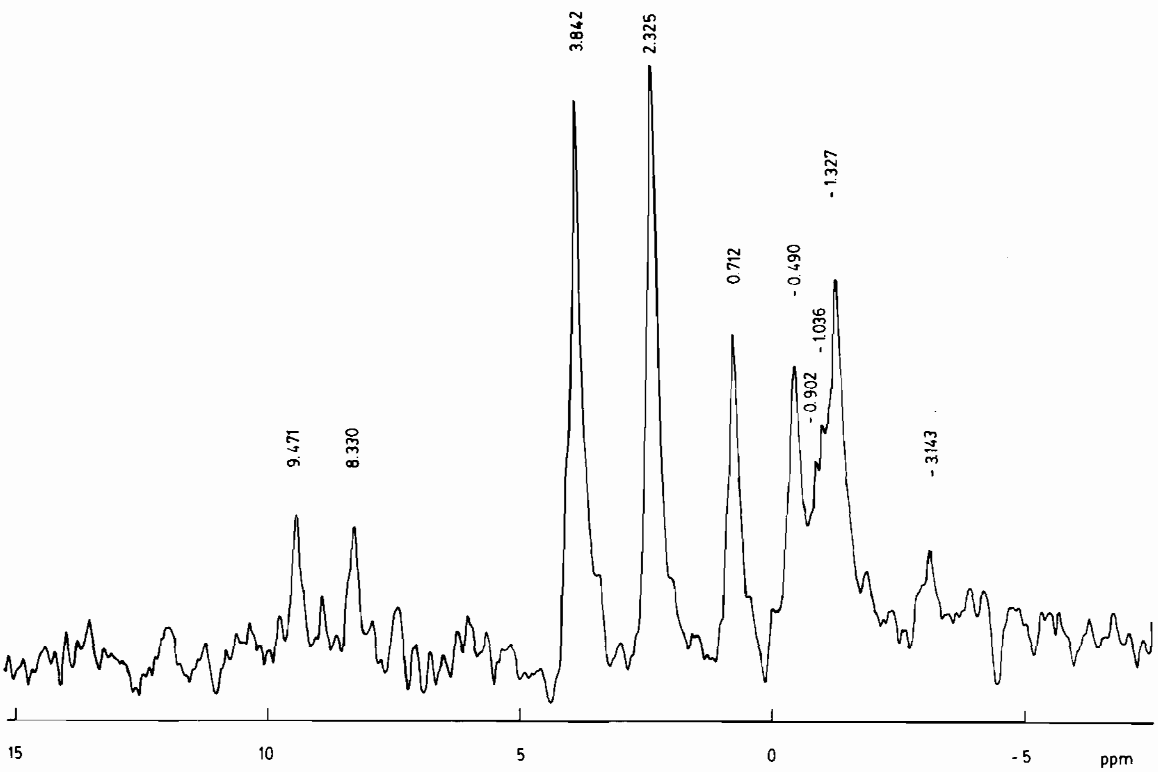

Fig. 2. ^{13}C NMR spectrum of $[Co(dien)(en)]_2O_2^{4+}$, 100.577 MHz.

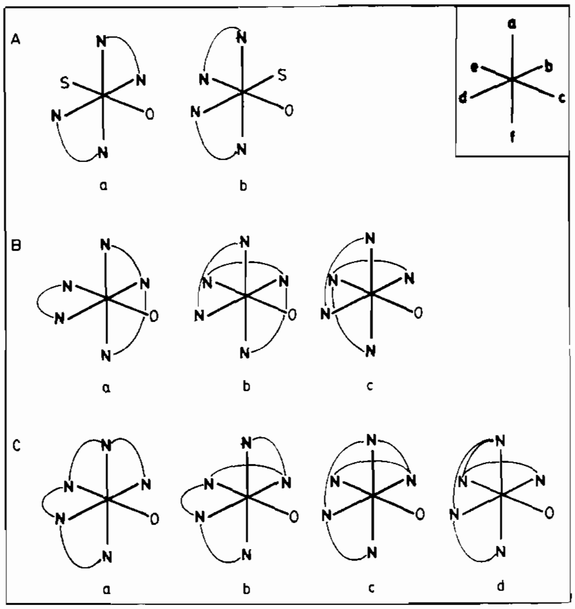

Fig. 3. Structures of Co/O$_2$ complexes. A, Compound 5; B, Compound 2; C, Compound 4.

increase with field so that the improvement in resolution on increasing the field from 5.872 T to 9.395 T is not dramatic as might be anticipated. Similar resolution of the isomers was achieved for compounds 4 and 5 but compound 6, which also has isomeric possibilities, showed only a single broad line at all fields indicating that this technique is not always applicable. This observation could result from either rapid chemical exchange between the isomers or excessive quadrupolar broadening. Compound 3 shows a single line which is assigned to b,e(adf),c isomer. Four isomers are predicted for compound 4 but additional lines are required to fit the spectrum. Nakon [12] has postulated bridging amine ligands in this type of complex. This would give an additional three isomers consistent with the seven lines found.

NMR measurements were made at frequencies of 21.252 MHz, 59.035 MHz and 94.457 MHz using Bruker WH90, WM250 and WM400 spectrometers respectively. Overlapping lines were resolved by means of a curve fitting programme. Chemical shifts are reported relative to $Co(CN)_6^{3-}$ (external) and line widths are the full width at half height. Spectra were obtained at ambient temperatures (24 °C for the WH90 and WM250 22 °C for the WM400) in aqueous solutions. Synthesis of all complexes except compound 5 followed literature procedures [13–18]. Compound 5, which does not appear to have been reported previously was obtained by the reaction of oxygen with an aqueous solution containing cobalt chloride, ethylene diamine and potassium thiocyanate in stoichiometric quantities. The orange crystals obtained from this reaction give a brown solution when redissolved in water.

Acknowledgements

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