^{1}H NMR Relaxation Rate and Coordination Number in High Spin Cobalt(II) Complexes

I. BERTINI, G. LANINI and C. LUCHINAT

Istituti di Chimica Generale ed Inorganica dell'Università di Firenze, Florence, Italy

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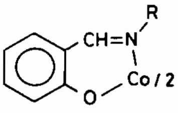
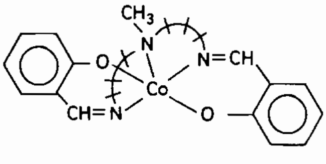
^{1}H T_1^{-1} values were measured for bis-salicylaldiminate cobalt(II) complexes with overall coordination numbers of four, five and six. It was found that the nuclear relaxing capabilities decrease in the order four- > five- > six-coordinate complexes. A semi-quantitative analysis of the various contributions to the proton relaxation rates was performed. The data are discussed in terms of their relevance for determining the coordination number of cobalt(II) substituted zinc proteins.

Introduction

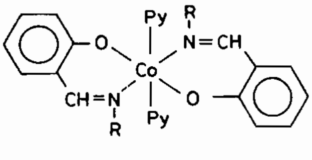
Cobalt(II) substituted zinc proteins have shown considerable variability in the proton relaxation rates of protons close to the paramagnetic center [1–3]. It has been proposed that cobalt(II) chromophores with different coordination geometries relax at different rates. With this in mind we investigated by ^{1}H NMR T_1 studies four-, five- and six-coordinate cobalt(II) chromophores with a common moiety. The following bis-salicylaldiminate cobalt(II) complexes were suitable for this study:



R = Phenyl (I)
R = i-propyl (II)



(III)



(IV)

R = phenyl Py = pyridine

Compounds *I* and *II* are tetracoordinated [4, 5], *III* is five-coordinated [6] and *IV*, which is the bis-pyridine adduct of *I*, is six-coordinated [5].

Experimental

Compounds *I*, *II* and *III* were prepared as described elsewhere, [4–6], and satisfactorily analyzed for C, H and N. Samples for NMR measurements were prepared by dissolving the crystals in chloroform-d$_1$. The bis-pyridine adduct of compound *I* was obtained by dissolving it in pyridine-d$_5$. The complete formation of the bis-pyridine adduct was checked by adding increasing amounts of pyridine-d$_5$ to a $CDCl_3$ solution of compound *I*. 60 MHz ^{1}H NMR measurements were performed with an instrument based on a Bruker CXP 100 console and a Varian DA 60 1.41 T electromagnet, equipped with an external lock unit giving a ± 1 Hz long-term stability. 200 and 300 MHz measurements were made on Bruker CXP 200 and CXP 300 instruments at Bruker A.G., Karlsruhe. All measurements were performed at room temperature. T_1 measurements were performed using the inversion recovery method.

Results and Discussion

The observed T_1^{-1} values at 60, 200 and 300 MHz for the ^{1}H NMR signals of the investigated compounds are reported in Table I, together with the isotropic shifts. The assignment for the tetracoordinated compound *I* was performed by analogy with the previously investigated compound *II*. The five-coordinate compound *III* was assigned by analogy, whereas the assignment of the six-coordinate complex *IV* was performed by adding increasing amounts of pyridine-d$_5$ to a chloroform-d$_1$ solution of complex *I*, the equilibrium between the pseudotetrahedral complex *I* and the six coordinate complex *IV* being fast on the NMR time scale.

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TABLE I. ^{1}H NMR Isotropic Shifts (ppm) and T_1^{-1} (s^{-1})[a] Values at Various Magnetic Field Strengths for the Salicylaldiminate Ring Protons of Complexes *I–IV* and for the Phenyl Ring Protons of Complexes *I* and *IV*.

Proton Signal:	3 H				4 H				5 H				6 H				ortho H		meta H		para H	
Compound:	*(I)*	*(II)*	*(III)*	*(IV)*	*(I)*	*(II)*	*(III)*	*(IV)*	*(I)*	*(II)*	*(III)*	*(IV)*	*(I)*	*(II)*	*(III)*	*(IV)*	*(I)*	*(IV)*	*(I)*	*(IV)*	*(I)*	*(IV)*
Isotropic Shift:	6.4	18.4	10.6	−71.2	−51.6	−47.4	−37.9	−54.8	3.4	12.2	18.0	−1.0	−43.2	−38.5	−6.6	−13.8	29	50.1	−10	−6.9	13	−3.6
Frequency (MHz)																						
60	861	1180	614	542	279	250	91	106	161	140	69	33	575	530	200	118	2950	818	147	68	111	39
200	769	840	562	392	229	227	60	73	135	108	51	34	485	498	154	88	2800	658	131	51	94	34
300	752	805	571	386	204	214	56	67	115	86	45	33	460	474	141	87	2439	637	118	50	81	33

[a] The experimental error is estimated to be within ±10%.

Two peculiar characteristics of these spectra are that *III* shows splitting of several signals owing to the lack of any symmetry, as observed in the nickel(II) analogue [7], and the 3H signal in the six-coordinate complex *IV* moves about 80 ppm downfield from the position in the tetracoordinated complex *I*. The latter shift change indicates a change in spin density delocalization, and possibly mechanism, with coordination number.

From a first glance at Table I, it appears that the longitudinal relaxation rates at all frequencies investigated decrease from tetra- to penta- to esa-coordination, well outside the experimental error, and in a fashion apparently independent of the value of the isotropic shift. The only exception is the 4H proton in compound *IV*.

The differences in proton relaxation rates with coordination number encouraged us to analyse them in terms of the available theory. Proton relaxation rates are related through several constants to the distance of the resonating proton from the paramagnetic center, r, the unpaired π spin density on the attached carbon atom, ρ_c^π, the hyperfine constant $A/\hbar$, and functions of the correlation time, τ_e.

$$T_{1M}^{-1} = K\frac{1}{r^6}f(\tau_e) + K\rho_c^{\pi^2}\Delta f(\tau_e) + K'\left(\frac{A}{\hbar}\right)^2 f'(\tau_e) \quad (1)$$

The above simplified equation holds for nuclei more than 4 Å away from the metal [8, 9]. The electronic correlation time τ_e for fast relaxing systems, where the Redfield approximation [10] breaks down, is related to the actual electronic relaxation time through a constant K ($K\tau_e = \tau_s$) not much larger than unity [11]. The explicit form of $f(\tau_e)$ and $f'(\tau_e)$ may be rather complex if zero field splitting and g anisotropy are considered. Qualitatively, however, since all the complexes investigated contain high spin cobalt(II) (S = 3/2) ion, we can assume that the forms of $f(\tau_e)$ and $f'(\tau_e)$ will be similar for all of them. The first term in eqn. (1) represents metal centered dipolar contributions, the second term ligand centered dipolar contributions, and the third the contact contributions. An estimate of the relative magnitude of the three terms can be made by taking the values for K and K′ (1.2×10^{-31} and 2.5 respectively) and the forms of $f(\tau_e)$ and $f'(\tau_e)$ predicted by the simple approach of Solomon and Bloembergen [12]:

$$f(\tau_e) = \frac{3\tau_e}{1+\omega_I^2\tau_e^2} + \frac{7\tau_e}{1+\omega_s^2\tau_e^2};\quad f'(\tau_e) = \frac{\tau_e}{1+\omega_s^2\tau_e^2} \quad (2)$$

Within this frame $f'(\tau_e) = 1/10\ f(\tau_e)$ in the low field limit ($\omega_s\tau_e \ll 1$) and $f'(\tau_e) \ll 1/10\ f(\tau_e)$ in the high field limit; in general $f'(\tau_e) \leqslant 1/10 f(\tau_e)$.

With this in mind, the relative contributions of the three terms of eqn. 1) are obtained by comparing the expressions:

TABLE II. Cobalt–Proton Distances (pm) for the Salicylaldiminate Ring Protons.

	I, II[a]	*III*[b]	*IV*[c]
3H	445	450	460
4H	625	630	635
5H	660	660	670
6H	525	530	540

[a] Average values from refs. 13, 14. [b] Average values from refs. 15, 16. [c] Estimated from ref. 17.

TABLE III. Calculated Values of Expressions (3) (s^{-2}) for Metal Centered Dipolar Contributions, Ligand Centered Dipolar Contributions and Contact Contributions (see text).

	$1.2 \times 10^{-31}\ 1/r^6$	$3.3 \times 10^{16}\ \rho_c^{\pi^2}$	$0.25\ (A/\hbar)^2$
3H	1.5×10^{13}	2.0×10^{12}	2.6×10^{11}
4H	2.0×10^{12}	6.6×10^{12}	8.6×10^{11}
5H	1.5×10^{12}	2.3×10^{12}	3.0×10^{11}
6H	5.7×10^{12}	8.8×10^{11}	1.2×10^{11}

$$1.2 \times 10^{-31}\frac{1}{r^6}\,;3.3 \times 10^{16}\,\rho_c^{\pi^2};0.25\left(\frac{A}{\hbar}\right)^2 \tag{3}$$

where Δ has been taken [8, 9] as 2.762×10^{47} cm^{-6}. From the structural data available for these and related complexes, the r values can be obtained to a reasonable degree of accuracy (Table II); $A/\hbar$ could be calculated from the contact part of the isotropic shifts if the dipolar contributions are factorized out; ρ_c^{π} can be estimated from $(A/\hbar)$ and the McConnell eqn. (4) in the further assumption that the sp in delocalization is π in origin [18]:

$$\rho_c^{\pi} = \frac{A}{\hbar}\,\frac{S}{\pi Q} \tag{4}$$

where Q is a proportionality constant equal to $\cong -63$ MHz.

Among the complexes investigated a factorization of the isotropic shifts has been performed only for compound *II* [19] using the ratio method and the factorization available for the analogous nickel(II) complex [20]. The reported contact shift values are: +21.5 (3H), −38.8 (4H), +22.8 (5H) and −14.2 (6H). Attempts to use the ratio method to obtain the contact shifts for the other complexes gave no reliable values, either on account of different spin delocalization mechanisms in the nickel(II) analogues and/or non axial symmetry of the magnetic susceptibility tensor. According to the values calculated for complex *II*, the three expressions in (3) for the salycylaldiminate ring protons can be calculated as shown in Table III. The figures indicate that the contact term is sizeably smaller than both the metal and ligand centered dipolar term for all the protons; since the estimated contact contribution is actually an upper limit (being calculated in the low field limit) we may try to proceed in the analysis by neglecting it throughout the following discussion. This consideration will also hold for the other complexes for which the contact shifts could not be factorized out, judging from the overall values of the isotropic shifts and keeping in mind that the ligand centered contributions are likely to be larger anyway, being also proportional to the square of the contact coupling constant within the limits of validity of the McConnell equation.

We are then left with the relative importance of the metal and ligand centered contributions: the two effects estimated for complex *II* are comparable, the ligand centered being even higher than the metal centered for the 4H and 5H nuclei which are relatively far from the paramagnetic center. However, as mentioned before, the estimate of the ligand centered contribution relies heavily on the hypothesis that electron spin density delocalization occurs only through the π electrons systems; the simple observation that the ratio method does not give satisfactory results for complexes *III* and *IV*, and that the 3H proton isotropic shift changes dramatically from complex *I* to *IV* indicate that the above hypothesis may be rather rough. As a consequence, the numbers in Table III may have little meaning besides indicating the possible relevance of ligand

TABLE IV. Comparison between Experimental and Theoretical T_1^{-1} Ratios Assuming Purely Metal Centered Dipolar Relaxation. The Range of Experimental Values Reflects the Differences Observed at Different Magnetic Fields.

Proton	r_i^{-6}/r_3^{-6}	*I*	*II*	*III*	*IV*
3	1	1	1	1	1
4	0.14	0.27–0.32	0.21–0.27	0.10–0.15	0.17–0.19
5	0.10	0.15–0.19	0.11–0.13	0.08–0.11	0.06–0.09
6	0.38	0.61–0.67	0.47–0.59	0.25–0.32	0.22

centered relaxation. The only criterion we can use to go further is to compare the experimental T_1^{-1} values for the various protons in each system and check whether a qualitative $1/r^6$ dependence is followed; for dominant ligand centered contributions the order 3H > 6H > 4H > 5H is not likely to hold in all instances. In Table IV the experimental T_1^{-1} ratios are shown, together with the theoretical ratios for a purely metal centered dipolar relaxation. Although the agreement is not excellent, the relative order is maintained in all cases, suggesting that the metal centered contribution is, on average, still a relevant part of the metal nucleus interaction.

From the above considerations, a comparison of the T_1^{-1} values of the same proton in different complexes is expected to give an estimate of the relative magnitude of $f(\tau_e)$ in the various stereochemistries, since the r values are almost unchanged on passing from one complex to another. Using the data of Table I we can estimate that $f(\tau_e)_{I,II}/f(\tau_e)_{III} \cong 1.5$–$3.0$ and $f(\tau_e)_{I,II}/f(\tau_e)_{IV} \cong 2.5$–$5.0$. In the frame of the Solomon equation, at high magnetic field these ratios directly reflect the ratios among the τ_e themselves.

Data obtained from water ^{1}H NMR of cobalt(II) enzymes containing exchangeable water in the coordination sphere have been found to span a larger range of τ_e *i.e.* even in a ratio of 1:10 [1–3]. Slow relaxing samples have been attributed to five-coordinated species and fast relaxing to four-coordinate species. The theoretical background of this observation is that the electron spin relaxation mechanisms are quite efficient in the former complexes because there are low lying excited states. In the present case the observed pattern of $f(\tau_e)$ is consistent with the expectation, *i.e.* six-coordinate < five-coordinate < four-coordinate. However, the ratio between the $f(\tau_e)$ is somewhat smaller and depends on the particular proton position; probably this is due to variable contributions of ligand centered effects. Unfortunately the variable frequency study has not detected a different frequency dependence of $f(\tau_e)$, probably because the measurements are affected by the error introduced by the change of instruments when changing frequency. However, although the absolute figures of $f(\tau_e)$ are not suitable for a deep analysis, the general trend of the relaxation properties of cobalt(II) complexes emerges and provides a semiquantitative estimate of the well known qualitative observation that four-coordinate complexes provide proton linewidths larger than five- or six-coordinate complexes.

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