Chemical Shift Parametrization for Metal-ion Nuclear Magnetic Resonance Spectroscopy of d^6 Transition Metal Complexes

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Metal-ion chemical shifts in cobalt(III), ruthenium(II), rhodium(III), and platinum(IV) complexes have been parametrized into metal and ligand contributions. The resulting metal-ion chemical shifts are calculated with a fair accuracy that allows analytical applications. Apparently diverse trends in the metal-ion chemical shifts for complexes of class A and B metal ions have been accommodated in a single scheme. An analysis of the ligand parameters shows that ligands including first-period ligating atoms can be ordered according to the increasing shielding of the metal ion into a magnetochemical series.

The amount of n.m.r. data available for metal ions in transition-metal complexes has rapidly increased in recent years,[1-4] to the extent that comparative studies for various metal ions are quite feasible.[5,6] A number of general trends have been noted,[1-7] and I felt that a more quantitative treatment of these trends, especially in isoelectronic complexes with identical ligand systems but different metal centres, would be of value. Of primary interest is the possibility of predicting metal-ion chemical shifts by devising a parametrization scheme for the metal and ligand contributions to the shift. In this respect octahedral d^6 spin-paired complexes seem to provide the best starting point because of the amount of information available for analogous complexes of cobalt(III), rhodium(III), and platinum(IV).

The parametrization of spectroscopic properties of transition-metal complexes into metal-only and ligand-only contributions seems to work extremely well, an example of such regularity being the arrangement of metal ions and ligand groups in the spectrochemical and the nephelauxetic series.[8] For the metal-ion chemical shifts of d^6 transition-metal complexes, especially for the ^{59}Co chemical shifts in cobalt(III) complexes, the correlation with the spectrochemical properties of ligands,[9,10] as well as with nephelauxetic properties,[11,12] is well documented. On this basis, I have already suggested that a magnetochemical series of ligands may exist,[11] *i.e.* that ligands could be arranged according to the magnitude of their influence on metal chemical shifts irrespective of the metal ion. Although this idea has proved to be only partially true it led to the parametrization scheme presented here.

Results and Discussion

Parametrization of the Paramagnetic Shielding Term.— Parametrization of chemical shifts in d^6 transition metal complexes may be reduced to the parametrization of the metal-ion paramagnetic shielding term, since this term is responsible for the observed large chemical shift variations.[9] In a recent ^{59}Co n.m.r. study of cobalt(III) complexes [12] it was established that the paramagnetic shielding term (σ^p) may be expressed as in equation (1). All specific influences of the metal–ligand

$$\sigma^p = -32\mu_B^2 \langle r^{-3} \rangle_{d_F}(\eta/\Delta E) \qquad (1)$$

bond on the paramagnetic shielding are contained in two (mainly mutually independent) quantities: the circulation-removing ratio (η) and the $^1T_{1g} \leftarrow {}^1A_{1g}$ electronic transition energy (ΔE). Therefore, the parametrization of these two quantities into metal-only and ligand-only contributions seems to be the best approach to the parametrization of the paramagnetic shielding term.

Parametrization of the electronic transition energy is straightforward, *i.e.*, it is analogous to the parametrization for the spectrochemical series, as the product of the metal and ligand parameters [equation (2)]. How such parametrization

$$\Delta E = ml \qquad (2)$$

works is shown in Figure 1. It enables the transition energy to be predicted in complexes for which this transition is usually not observable, *e.g.* platinum(IV) complexes.

It has been found that the circulation-removing ratio may be correlated with metal–ligand bond ionicities.[12] Therefore, it was assumed that the circulation-removing ratio is proportional to the difference between metal and ligand parameters: $\eta \propto \chi_L - \chi_M$. It follows then that the paramagnetic shielding term depends on four parameters [equation (3)].

$$\sigma^p \propto \eta/\Delta E \propto (\chi_L - \chi_M)/ml \qquad (3)$$

These parameters were adjusted in a fitting procedure that sought a linear correlation between metal-ion chemical shifts and the term $(\chi_L - \chi_M)/ml$. Cobalt, ruthenium, rhodium, and platinum chemical shifts in spin-paired d^6 complexes were considered. The fitting procedure was essentially a trial-and-error method involving adjustment of the parameters to provide a simultaneous maximization of the correlation coefficients of the correlations for all four metals. Adjustment of the parameters was greatly facilitated by holding the product ml close to the experimental value of ΔE (as may be concluded from Figure 1 where the final l values have been plotted against transition energies) and by holding χ_L closely related to the electronegativity of the ligating atom. The fitting has been quite successful (Figures 2—4) and it was found that χ_M may be put equal to m, thus reducing the number of parameters. The corresponding parameters for each metal and ligand considered are given in Tables 1 and 2. Some ligand parameters are less reliable than others, depending on the number of ML_6 type complexes available for their calculation. The least reliable values, given in parentheses in Table 2- were obtained when only mixed-ligand complexes were available for the derivation of ligand parameters.

From the linear plots in Figures 2—4, it follows that the metal chemical shifts in complexes of octahedral ligand-field symmetry may be calculated by the expression (4). For mixed-

$$\delta = A + B(\chi_L - m)/ml \qquad (4)$$

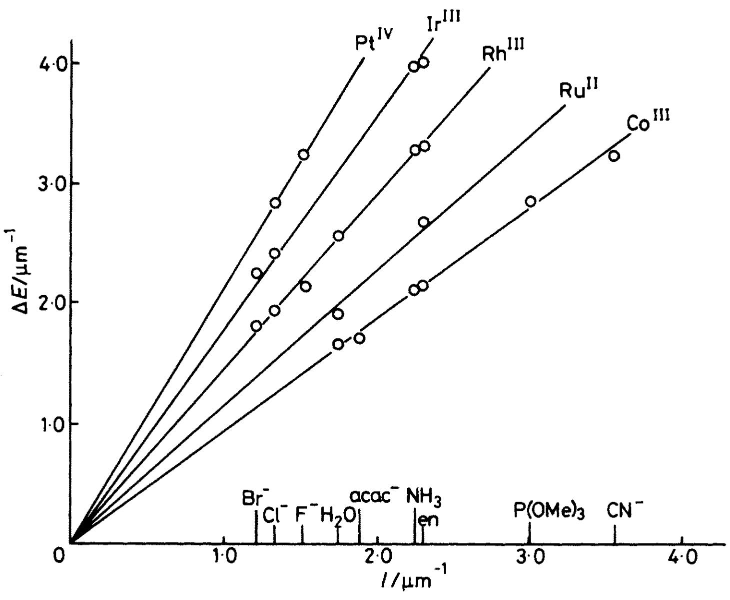

Figure 1. Parametrization of the $^1T_{1g} \leftarrow {}^1A_{1g}$ electronic transition energy. The l values are from Table 2. The experimental transition energies are taken from refs. 8 and A. B. P. Lever, 'Inorganic Electronic Spectroscopy,' Elsevier, Amsterdam, 1968. Hacac = Pentane-2,4-dione; en = 1,2-diaminoethane

Table 1. Metal parameters of the chemical shift parametrization according to equations (4) and (5)

Metal	m	A/p.p.m.	10^{-4} B/p.p.m. μm^{-1}
Co^{III}	0.931	−7 577	1.456
Ru^{II}	1.119	−6 733	1.745
Rh^{III}	1.439	−4 660	1.818
Pt^{IV}	2.103	−1 104	2.346

Table 2. Ligand parameters of the chemical shift parametrization according to equations (4) and (5)

Ligand	l/μm^{-1}	χ_L
F$^-$	1.517	3.860
H_2O	1.750	3.468
acac$^-$	1.890	3.385
NH_3	2.250	3.198
en	2.295	3.082
CN$^-$	3.571	2.662
CNMe	(3.62)	(2.66)
CO	(4.83)	(2.50)
Cl$^-$	1.328	2.769
PMe_3	(2.84)	(2.34)
$P(OMe)_3$	3.000	2.325
Br$^-$	1.228	2.520
I$^-$	0.810	2.072

ligand complexes, that is for complexes of lower ligand-field symmetry, the expression was modified since it was necessary to find values of the paramagnetic shielding along all three principal axes of the complex, and use the mean value of the shielding.[10] In doing this, the mean values for the parameters of the ligands involved in the shielding along a particular axis were used [equation (5), where i, j, or k can

$$\delta = A + \frac{B}{3}\sum_i \frac{(\bar{\chi}_L)_{j,k} - m}{m(\bar{l})_{j,k}} \qquad (5)$$

be any of x, y, or z provided that $i \neq j \neq k$]. Application of equation (5) may not seem straightforward, and will be demonstrated by using the complex *mer*-$[RhCl_3(PMe_3)_3]$ as an example. If the principal axes of the complex are assigned as x(P–Rh–Cl), y(Cl–Rh–Cl), and z(P–Rh–P), then equation (5) becomes (6). Using the numerical values from Tables 1 and 2, equation (6) gives the δ value in (7). At this point one may

$$\delta = A + \frac{B}{3}\left[\frac{\frac{1}{4}(2\chi_P + 2\chi_{Cl}) - m_{Rh}}{m_{Rh} \times \frac{1}{4}(2l_P + 2l_{Cl})} + \frac{\frac{1}{4}(3\chi_P + \chi_{Cl}) - m_{Rh}}{m_{Rh} \times \frac{1}{4}(3l_P + l_{Cl})} + \frac{\frac{1}{4}(\chi_P + 3\chi_{Cl}) - m_{Rh}}{m_{Rh} \times \frac{1}{4}(l_P + 3\,l_{Cl})}\right] \qquad (6)$$

$$\delta = -4\,660 + 1.818 \times 10^4 \times 1.155/3 = 2\,339 \text{ p.p.m.} \qquad (7)$$

also note that equation (5) predicts different chemical shifts for the geometric isomers of mixed-ligand complexes.

For the metals and ligands considered here the parametrization reproduces metal chemical shifts in octahedral ligand-field complexes with a standard deviation of about 20 p.p.m. For lower symmetries (mixed-ligand complexes) the deviation is much larger, *ca.* 250 p.p.m. The parametrization for mixed-ligand complexes is less successful because of the specific mutual influences of the ligands. Nevertheless, equations (4) and (5) reproduce chemical shifts with sufficient accuracy that in most cases one is able to determine the chromophore of the complex by measuring the shift. Moreover, equation (5) correctly predicts the sign of the difference between the chemical shifts for geometrical isomers in all cases considered here.

Trends of the Metal and Ligand Parameters.—As expected, the metal parameter m in the electronic transition-energy expression follows closely the trend observed in the spectrochemical series of metal ions.[8] It would not be expected, however, that the same parameter would appear in the term proportional to the circulation-removing ratio. In this term

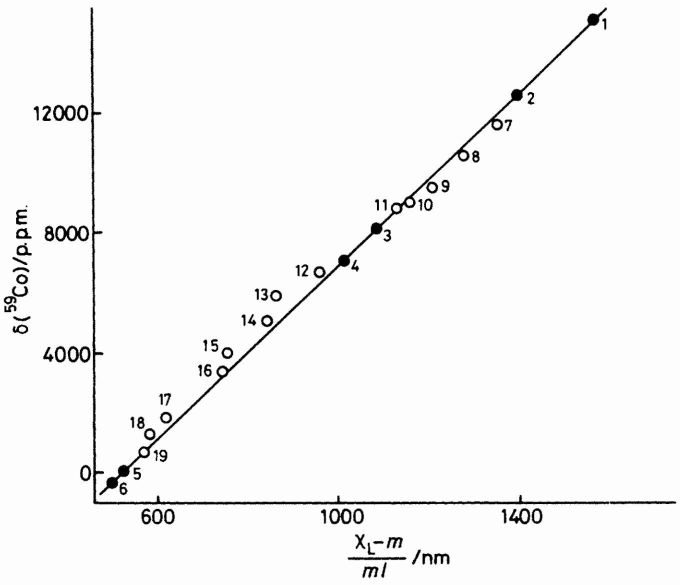

Figure 2. Linear dependence of ^{59}Co chemical shifts in cobalt(III) complexes on the parametrized paramagnetic shielding term. Complexes: 1, $[Co(OH_2)_6]^{3+}$; 2, $[Co(acac)_3]$; 3, $[Co(NH_3)_6]^{3+}$; 4, $[Co(en)_3]^{3+}$; 5, $[Co(CN)_6]^{3-}$; 6, $[Co\{P(OMe)_3\}_6]^{3+}$; 7, *fac*-$[CoCl(OH_2)_3(NH_3)_2]^{2+}$; 8, *fac*-$[CoCl(OH_2)_2(NH_3)_3]^{2+}$; 9, $[CoF(NH_3)_5]^{2+}$; 10, $[Co(OH_2)(NH_3)_5]^{3+}$; 11, $[CoCl(NH_3)_5]^{2+}$; 12, $[Co(CN)(NH_3)_5]^{2+}$; 13, *trans*-$[Co(CN)_2(NH_3)_4]^+$; 14, *cis*-$[Co(CN)_2(NH_3)_4]^+$; 15, *mer*-$[Co(CN)_3(NH_3)_3]$; 16, *fac*-$[Co(CN)_3(NH_3)_3]$; 17, $[Co(CN)_5(OH_2)]^{2-}$; 18, $[CoBr(CN)_5]^{3-}$; 19, $[CoI(CN)_5]^{3-}$. Chemical shift data are taken from refs. 1, 12, and N. Juranič, M. B. Ćelap, D. Vučetić, M. J. Maliner, and P.N. Radivojša, *Spectrochim. Acta*, 1979, **35**, 997. In Figures 2—4 filled symbols indicate complexes with identical ligands and open circles complexes with mixed ligands

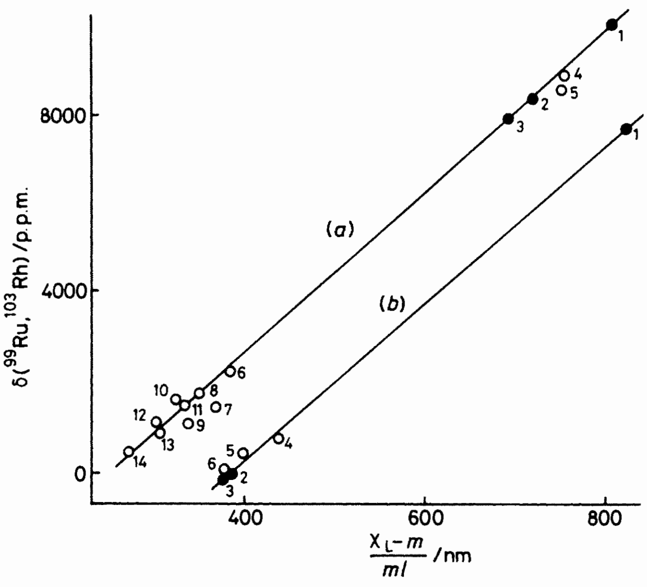

Figure 3. Linear dependence of (*a*) ^{103}Rh chemical shifts in rhodium(III) complexes, and (*b*) ^{99}Ru chemical shifts in ruthenium(II) complexes on the parametrized paramagnetic shielding terms. Complexes: (*a*), 1, $[Rh(OH_2)_6]^{3+}$; 2, $[Rh(acac)_3]$; 3, $[RhCl_6]^{3-}$; 4, *mer*-$[RhCl_3(OH_2)_3]$; 5, *fac*-$[RhCl_3(OH_2)_3]$; 6, *mer*-$[RhCl_3(PMe_3)_3]$; 7, *fac*-$[RhCl_3(PMe_3)_3]$; 8, *mer*-$[RhBr_3(PMe_3)_3]$; 9, *fac*-$[RhBr_3(PMe_3)_3]$; 10, *trans*-$[RhCl_2(PMe_3)_4]^+$; 11, *mer-trans*-$[RhCl_3(CO)(PMe_3)_2]$; 12, *trans*-$[RhBr_2(PMe_3)_4]^+$; 13, *mer*-$[RhI_3(PMe_3)_3]$; 14, *trans*-$[RhI_2(PMe_3)_4]^+$; (*b*), 1, $[Ru(NH_3)_6]^{2+}$; 2, $[Ru(CN)_6]^{4-}$; 3, $[Ru(CNMe)_6]^{2+}$; 4, *fac*-$[RuCl_3(CO)_3]^-$; 5, *mer*-$[RuI_3(CO)_3]^-$; 6, *fac*-$[RuI_3(CO)_3]^-$. Chemical shift data are taken from ref. 1 and B. E. Mann and C. Spencer, *Inorg. Chim. Acta*, 1982, **65**, 57 for ^{103}Rh and R. W. Dykstra and A. M. Morrison, *J. Magn. Reson.*, 1982, **46**, 338 for ^{99}Ru

m is subtracted from the ligand parameter χ_L, which is related to the ligand electronegativity, and therefore one might assume that it could be replaced by the metal-ion electronegativity. Yet the variation of *m* from 0.93 for cobalt(III) to 2.1 for platinum(IV) is very large in view of the nearly constant electronegativity values for these transition metals. It seems that the value of *m* properly reflects the difference in polarizability of the metal ions, being low for the ' hard ' (class A) metal ions and high for the ' soft ' (class B) metal ions.

For the ligand parameters it has already been stressed that the χ_L values follow the trend in electronegativity values for the ligating atoms. The other ligand parameter, *l*, shows similar trends to those observed in the spectrochemical series of ligands.[8] The magnetic shielding of the metal ion is affected by both ligand parameters. From equation (4) it may be concluded that the ligands having lower values of $1/l$ and χ_L will always exhibit a larger shielding of the metal ions (lower chemical shifts) irrespective of the metal ion (*i.e.* irrespective of the value of *m*). On this basis the correlation between $1/l$ and χ_L in Figure 5 shows that for all the ligands studied having first-period ligating atoms (C, N, O, or F) an ordering of the ligands according to the increasing shielding of the metal ion is possible (*i.e.* these ligands can be ordered in the magnetochemical series of ligands). For the higher-period ligating atoms studied, the parameter χ_L becomes progressively lower, and the position of these ligands in the magnetochemical series (with respect to the position of ligands having first-period ligating atoms) is uncertain, since it may vary greatly with the value of *m*. For instance, iodide anion is among the least-shielding ligands in cobalt(III) complexes, but

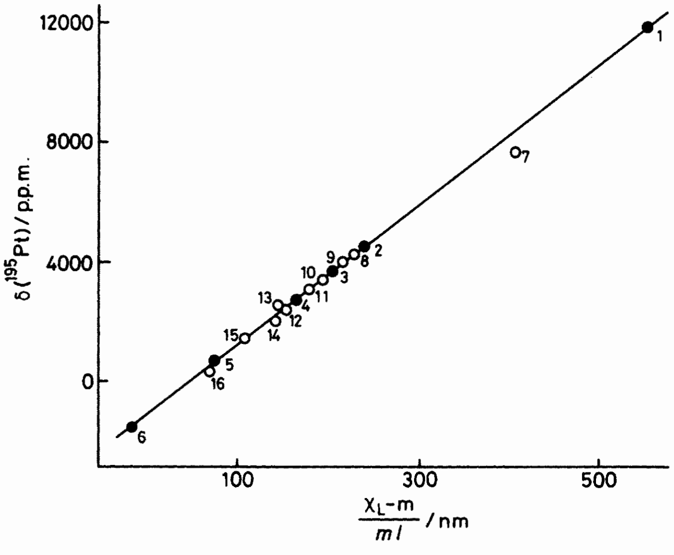

Figure 4. Linear dependence of ^{195}Pt chemical shifts in platinum(IV) complexes on the parametrized paramagnetic shielding term. Complexes: 1, $[PtF_6]^{2-}$; 2, $[PtCl_6]^{2-}$; 3, $[Pt(en)_3]^{4+}$; 4, $[PtBr_6]^{2-}$; 5, $[Pt(CN)_6]^{2-}$; 6, $[PtI_6]^{2-}$; 7, *fac*-$[PtCl_3F_3]^{2-}$; 8, $[PtBrCl_5]^{2-}$; 9, $[PtBr_2Cl_4]^{2-}$; 10, $[PtCl_5(CNMe)]^-$; 11, $[PtBr_5Cl]^{2-}$; 12, *cis*-$[PtCl_4(CNMe)_2]$; 13, *trans*-$[PtCl_4(PMe_3)_2]$; 14, *cis*-$[PtCl_4(PMe_3)_2]$; 15, *mer*-$[PtCl_3(PMe_3)_3]^+$; 16, $[PtI(CN)_5]^{2-}$. Chemical shift data are taken from ref. 1 and P. S. Pregosin, *Coord. Chem. Rev.*, 1982, **44**, 247

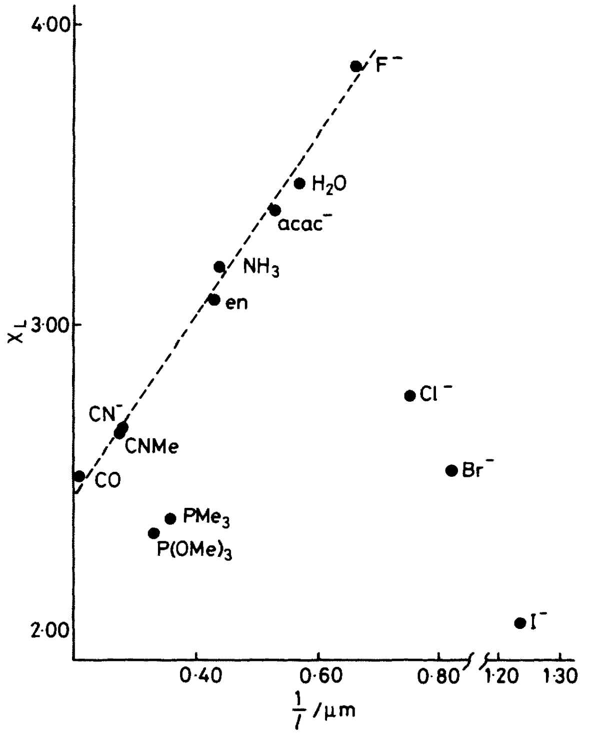

Figure 5. Correlation between $1/l$ (spectrochemical parameter of ligand) and χ_L (circulation-removing parameter of ligand). The broken line is drawn for the first-period ligating atoms

it is the most shielding ligand in platinum(IV) complexes. The position of the ligands studied in the magnetochemical series may be best represented as follows {where $\longleftarrow$[P(OMe)$_3$ > PMe$_3$]$\longrightarrow$ indicates that P(OMe)$_3$ is always > than PMe$_3$, but the position of both ligands can vary from en to beyond CO}:

$$\mathrm{CO > CNMe > CN^- > en > NH_3 > acac^- > H_2O > F^-}$$
$$\longleftarrow [\mathrm{P(OMe)_3 > PMe_3}] \longrightarrow \mathrm{> en}$$
$$\mathrm{CN^-} > \longleftarrow\!\!-\!\!-\!\!-\; \mathrm{Cl^-} \;-\!\!-\!\!-\!\!\longrightarrow \mathrm{F^-}$$
$$\mathrm{CO} > \longleftarrow\!\!-\!\!-\!\!-\!\!-\!\!-\; \mathrm{Br^-} \;-\!\!-\!\!-\!\!-\!\!-\!\!\longrightarrow \mathrm{F^-}$$
$$\longleftarrow\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\; \mathrm{I^-} \;-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!\longrightarrow \mathrm{F^-}$$

When m is small (as in the class A metal ions) changes in the excitation energies predominate. In contrast, the changes in the circulation-removing ratio predominate for metal ions with high m values (class B metal ions). However, 'normal halogen dependence'[1] of metal-ion shielding is always exhibited, *i.e.* I > Br > Cl > F.

The chemical shift parametrization reported here thus may provide a new, general approach to analytical applications of metal-ion n.m.r. spectroscopy in d^6 transition-metal complexes. It quantifies and accommodates in a single scheme the apparently diverse chemical shift trends of 'hard' and 'soft' metal ions. One important regular feature is apparent: the existence of the magnetochemical series for ligands containing first-period ligating atoms.

There is still a paucity of experimental data for metal-ion n.m.r. spectroscopy of d^6 transition-metal complexes and the metal and ligand parameters given here (obtained in a fitting procedure) are open to further changes and improvements. An extension of the parametrization scheme to d^6 complexes of early transition metals, *e.g.* complexes of $\mathrm{V^{-I}}$, $\mathrm{Cr^0}$, $\mathrm{Mo^0}$, and $\mathrm{Mn^I}$, is hampered by the relatively limited number of ligand types that stabilize the low oxidation states of these metals. However, recent advances in metal-ion n.m.r. spectroscopy of these complexes[4–6] are likely to provide the necessary data in the near future.

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