Effect of Geometrical Isomerism on Metal Nuclear Magnetic Resonance Chemical Shifts in Octahedral d^6 Transition-metal Complexes

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Experimental observation that metal n.m.r. chemical shifts for geometrical isomers in octahedral d^6 transition-metal complexes exhibit two, mutually opposite, trends in relation to their geometrical configurations has been rationalized in terms of a theoretical model for calculation of the shifts. Over 100 shifts, of more than 50 pairs of geometrical isomers, of vanadium(-I), ruthenium(II), cobalt(III), rhodium(III), and platinum(IV) complexes of the type $MA_{6-n}B_n$ were considered. It is shown that complexes whose metal shifts are mainly governed by the spectrochemical properties of the ligands generally exhibit negative deviations from the additivity of ligand contributions to the chemical shifts, and higher chemical shifts for *trans* than for *cis* isomers. Complexes whose metal shifts are mainly governed by the nephelauxetic properties of the ligands generally exhibit positive deviations from additivity and lower chemical shifts for *trans* than for *cis* isomers.

Metal n.m.r. chemical shifts in octahedral d^6 transition-metal complexes are sensitive to the geometrical configuration of the complexes. Therefore, these shifts may be used to determine the configuration if regularities applicable to the effect of geometrical isomerism on the shifts can be established.

In a study of cobalt(III) complexes by ^{59}Co n.m.r. spectroscopy, Yajima *et al.*[1] concluded that in complexes of the type $CoA_{6-n}B_n$ a *trans* configuration of the ligands always results in a larger shielding of the metal nucleus than does a *cis* configuration. Subsequently, the opposite behaviour was more often observed,[2,3] which led to a generalization according to which *cis* isomers in cobalt(III) complexes produce higher shielding than *trans* isomers.[3-5] However, if reported metal n.m.r. chemical shifts for geometrical isomers of d^6 complexes, from vanadium(−I) to platinum(IV),[6,7] are considered, then the existence of both the above trends in the effect of geometrical configuration on metal chemical shifts becomes evident. This fact requires a rationalization.

Therefore, in this paper, an investigation into the effect of geometrical configuration on metal n.m.r. chemical shifts, in mixed-ligand complexes of the type $MA_{6-n}B_n$, has been undertaken.

Results and Discussion

In octahedral, strong ligand-field, d^6 complexes the paramagnetic shielding term, which is the major cause of metal n.m.r. chemical shifts,[8] can be expressed as a function of the ligand-field parameters [equation (1)][9] where μ_O is the

$$\sigma^p = -\frac{8\mu_O\mu_B{}^2}{\pi}\langle r_d{}^{-3}\rangle_F\frac{\eta}{\Delta E} = -B_0\frac{\eta}{\Delta E} \qquad (1)$$

permeability of free space, μ_B the Bohr magneton, $\langle r_d{}^{-3}\rangle_F$ the radial parameter of a d electron in a free metal ion, ΔE the energy of the $^1A_{1g} \longrightarrow {}^1T_{1g}$ electronic transition, and η the covalency factor which has a value close to the nephelauxetic ratio β_{35}. In mixed-ligand complexes, which are of interest here, the paramagnetic shielding becomes anisotropic,[8,10,11] and should be specified along the principal axes of the complex [equation (2)]. The covalency factor η_{ii} and the excitation energy ΔE_{ii} involved in the paramagnetic shielding of the metal nucleus along any of the principal axes of a complex are determined by four ligands lying on the other two axes. According to the rule of average environment, one would expect that appropriate values of η_{ii} and ΔE_{ii} are obtained by averaging the values of the corresponding ligand parameters taken from ML_6 type complexes.[12] Thus, for complexes of type MA_5B (B lying on z axis) one obtains equations (3)—(5) where $a = \Delta E_B/\Delta E_A$.

$$\sigma^p = \frac{1}{3}(\sigma^p_{xx} + \sigma^p_{yy} + \sigma^p_{zz}) = \frac{-B_0}{3}\left(\frac{\eta_{xx}}{\Delta E_{xx}} + \frac{\eta_{yy}}{\Delta E_{yy}} + \frac{\eta_{zz}}{\Delta E_{zz}}\right) \qquad (2)$$

$$\sigma^p_{zz} = -B_0\frac{\eta_A}{\Delta E_A} = \sigma^p_A \qquad (3)$$

$$\sigma^p_{xx} = \sigma^p_{yy} = -B_0\frac{3\eta_A + \eta_B}{3\Delta E_A + \Delta E_B} = \frac{1}{3+a}(3\sigma^p_A + a\sigma^p_B) \qquad (4)$$

$$\sigma^p = \frac{1}{3(3+a)}[(9+a)\sigma^p_A + 2a\sigma^p_B] \qquad (5)$$

Since diamagnetic shielding of the metal nucleus does not vary appreciably from complex to complex,[13,14] the paramagnetic shielding could be replaced by chemical shifts [equation (6)].

$$\delta = \frac{1}{3(3+a)}[(9+a)\delta_A + 2a\delta_B] \qquad (6)$$

Applying the same concept to members of a series $MA_{6-n}B_n$, their metal chemical shifts (δ_n) can be expressed through the chemical shifts of the end members of a series (Table 1). The expressions obtained predict different chemical shifts for the isomers of a complex.

For an easier analysis of the trends, it is convenient to compare chemical shifts predicted by these expressions with those predicted by the first-order approximation, according to which the effects of ligands on metal chemical shifts are additive.[1] Under the additivity assumption, the reduced metal chemical shifts, $(\delta_n - \delta_A)/(\delta_B - \delta_A)$, are simply equal to $n/6$. Therefore, in Table 1 the deviations from additivity of chemical shifts are also given. These deviations are functions of the parameter a, and drop to zero for $a = 1$. Consequently, when the differences in metal chemical shifts between complexes are caused only by different nephelauxetic properties of the ligands, an additivity of the shifts is predicted. When $a \neq 1$, two cases are distinguish-

Table 1. Theoretical expressions for metal n.m.r. chemical shifts (δ), and for their deviations from the additivity of ligand contributions to metal chemical shifts, $[(\delta - \delta_A)/(\delta_B - \delta_A)] - n/6$, in complexes of the type $MA_{6-n}B_n$ as the function of the parameter *a*

n	Complex	δ	$[(\delta - \delta_A)/(\delta_B - \delta_A)] - n/6$
0	MA_6	δ_A	0
1	MA_5B	$\frac{(9 + a)\delta_A + 2a\delta_B}{3(3 + a)}$	$\frac{1}{4}\frac{a - 1}{a + 1}\left[\frac{2(a + 1)}{3 + a}\right]$
2	*cis*-MA_4B_2	$\frac{(9 + 7a)\delta_A + a(5 + 3a)\delta_B}{3(3 + a)(1 + a)}$	$\frac{2}{5}\frac{a - 1}{a + 1}\left[\frac{5(2a + 3)}{6(3 + a)}\right]$
2	*trans*-MA_4B_2	$\frac{(3 + a)\delta_A + 2a\delta_B}{3(1 + a)}$	$\frac{1}{3}\frac{a - 1}{a + 1}$
3	*fac*-MA_3B_3	$\frac{\delta_A + a\delta_B}{1 + a}$	$\frac{1}{2}\frac{a - 1}{a + 1}$
3	*mer*-MA_3B_3	$\frac{(9 + 26a + 13a^2)\delta_A + (13a + 26a^2 + 9a^3)\delta_B}{3(1 + a)(3 + a)(1 + 3a)}$	$\frac{2}{5}\frac{a - 1}{a + 1}\left[\frac{5(9a^2 + 22a + 9)}{12(3 + a)(1 + 3a)}\right]$
4	*trans*-MA_2B_4	$\frac{2\delta_A + (1 + 3a)\delta_B}{3(1 + a)}$	$\frac{1}{3}\frac{a - 1}{a + 1}$
4	*cis*-MA_2B_4	$\frac{(3 + 5a)\delta_B + (7a + 9a^2)\delta_B}{3(1 + a)(1 + 3a)}$	$\frac{2}{5}\frac{a - 1}{a + 1}\left[\frac{5(3a + 2)}{6(1 + 3a)}\right]$
5	MAB_5	$\frac{2\delta_A + (1 + 9a)\delta_B}{3(1 + 3a)}$	$\frac{1}{4}\frac{a - 1}{a + 1}\left[\frac{2(a + 1)}{3a + 1}\right]$
6	MB_6	δ_B	1

able. In the first case ($a < 1$, $\delta_B > \delta_A$), a change in excitation energy is the major cause of the paramagnetic shielding changes. Spectrochemical ordering of ligands is then properly reflected in the metal chemical shifts. For such 'spectrochemical behaviour' of metal chemical shifts, negative deviations from the additivity of chemical shifts are predicted. Further, it is predicted that *trans* isomers should exhibit higher paramagnetic shielding (higher chemical shift) than *cis* isomers, and *mer* isomers higher chemical shifts than *fac* isomers. In the second case ($a > 1$, $\delta_B > \delta_A$), the change in chemical shift from complex to complex is opposite to that expected from the change in excitation energy, but follows the order of nephelauxetic properties of ligands. In this case of 'nephelauxetic behaviour,' a positive deviation from the additivity of chemical shifts is predicted. Also, *trans* isomers should exhibit lower chemical shifts than *cis* isomers, and *mer* isomers lower shifts than *fac* isomers.

Comparing these predictions with the experimental data, I concentrated on the cases in which assignment of chemical shift to the specific isomer is unambiguous, that is to where the pure isomers have been isolated or where n.m.r. spectroscopy of the ligands demonstrates the geometrical configuration. A large number of cases fulfil this requirement, for which the chemical shift of the complexes can be described as obeying the 'spectrochemical behaviour.' They are recognized on the basis that ligands occupying a lower position in the spectrochemical series cause higher metal chemical shifts. Thus, in accordance with the prediction, $\delta_{trans} > \delta_{cis}$ for the isomers of the following complexes: $[V(CO)_4(PF_3)_2]^-$;[15] $[CoL_2(en)_2]^+$ (en = ethylenediamine; L = CN^-, N_3^-, Cl^-, Br^-,[3] OH^-,[16] NCS^-, or NH_3*); $[Co(CN)_2(tn)_2]^+$ (tn = trimethylenediamine);[17] $[CoL_2(NH_3)_4]^+$ (L = CN^-,[2,3] or Cl^-);[3] $[Co(CO_3)_2(NH_3)_2]^-$;[3] $[Co(glyO)_2(L\text{–}L)]^{+/-}$ (glyO = glycinate; L–L = en,[18] tn, or ox^{2-});[2] $[Co(acac)_2(NH_3)_2]^+$ (acac = acetylacetonate);* $[PtCl_4L_2]$ (L = PMe_3, $AsMe_3$, or SMe_2);[19] $[RhX_4L_2]^-$ (X = Cl^- or Br^-; L = SMe_2 or $SOMe_2$);[19] and $[RhX_2(AsMe_3)_4]$ (X = Cl^- or Br^-).[19] Further, $\delta_{mer} > \delta_{fac}$ for the isomers of the following complexes: $[V(CO)_3(PF_3)_3]^-$;[15] $[RuI_3(CO)_3]^-$;[20] $[Co(CN)_3(NH_3)_3]$;[3] $[Co(glyO)_3]$;[2] and $[RhX_3L_3]$ (X = Cl^- or Br^-; L = PMe_3, $AsMe_3$, SMe_2, or SMePh).[19]

Less examples have been reported for complexes whose metal chemical shifts can be classified as obeying the 'nephelauxetic behaviour.' They are recognized on the basis that a ligand occupying a lower position in the spectrochemical series produces lower metal chemical shifts, and at the same time this ligand should occupy a lower position in the nephelauxetic series. The examples are contained in the following series of complexes: $[Co(NO_2)_{6-2n}(en)_n]^{2n-3}$;[1] $[PtCl_{6-n}(OH)_n]^{2-}$;[21] $[PtX_{6-n}(NO_2)_n]^{2-}$ (X = Cl^- or Br^-);[22] and $[PtBr_{6-n}Cl_n]^{2-}$.[23] In accordance with prediction, for the isomers of these complexes, $\delta_{cis} > \delta_{trans}$ and $\delta_{fac} > \delta_{mer}$.

Finally, an ordering of metal chemical shifts contrary to that predicted is observed for the isomers of the complexes $[Co(NO_2)_2L_4]^+$ (L = NH_3,[1,2] tn, or butane-1,4-diamine).[17]

To summarize, metal chemical shifts of 55 pairs of geometrical isomers were considered (all unambiguously assigned chemical shifts for pairs of geometrical isomers reported, to my knowledge) and in all but three cases the sign of the chemical shift difference between isomers was predicted correctly.

Next, I have considered, in a more quantitative way, the trends in metal chemical shift deviations from additivity. The experimental deviations from additivity were compared with those predicted by the model. To facilitate this the deviations were divided by $|a - 1|/(a + 1)$, after which, according to the model (Table 1, last column), their magnitudes become almost independent of the parameter *a*. The comparison is presented in the Figure. Here, one is necessarily confined to the series of complexes for which metal chemical shifts, and relevant excitation energies, of the end members of the series are available. The chemical shifts generally follow the predicted behaviour, exhibiting positive deviations from additivity in the series obeying 'nephelauxetic behaviour' and negative in the series obeying 'spectrochemical behaviour.' The quantitative agreement is not always good. It is especially bad for *trans* isomers of cobalt(III) complexes whose chemical shifts are closer to the additivity approximation. Such behaviour has been already noted and

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* This work, see Appendix.

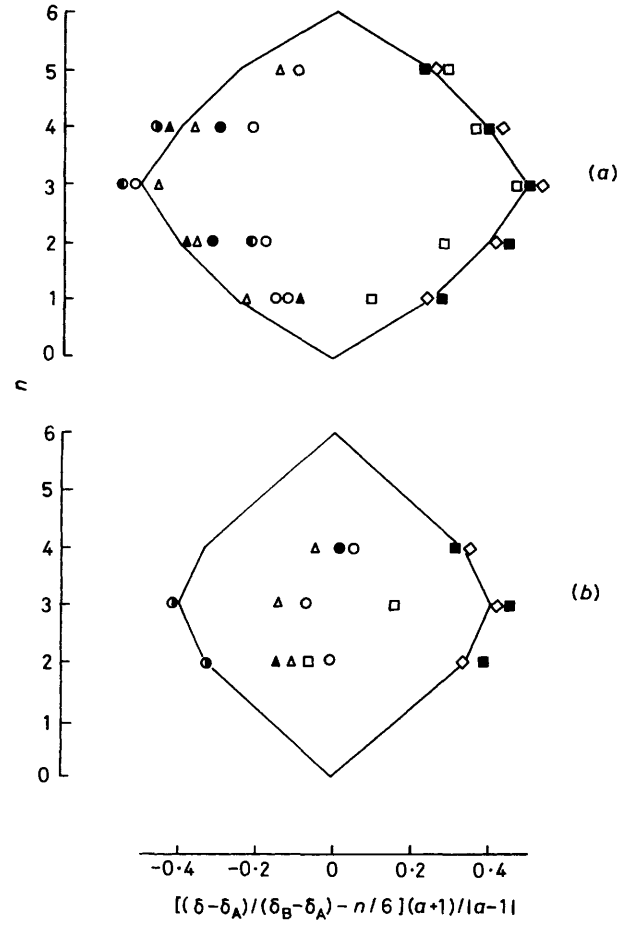

Figure. Deviations from the additivity of ligand contributions to metal chemical shifts, divided by $|a - 1|/(a + 1)$, for *cis* (*a*) and *trans* isomers (*b*) of complexes from the series: $[Co(CN)_{6-n}(NH_3)_n]^{n-3}$,[3] $a = 0.7$ (○); $[Co(CN)_{6-2n}(en)_n]^{2n-3}$,[3] $a = 0.7$ (●); $[CoL_{6-n}L'_n]^{3-n}$ (L = N-bonded glyO$^-$ or en, L' = O-bonded glyO$^-$ or $C_2O_4^{2-}$),[18] $a = 0.7$ (△); $[Co(CO_3)_n(NH_3)_{6-2n}]^{3-2n}$,[3] $a = 0.7$ (▲); $[Co(N_3)_n(NH_3)_{6-n}]^{3-n}$,[3] $a = 0.7$ (◐); $[Pt(OH)_n(NH_3)_{6-n}]^{4-n}$ (T. G. Appleton, J. R. Hall, and S. F. Ralph, *Inorg. Chem.*, 1985, **24**, 4685), $a = 0.7$ (◑); $[PtBr_{6-n}Cl_n]^{2-}$,[23] $a = 1.17$ (◇); $[PtCl_{6-n}(OH)_n]^{2-}$,[21] $a = 1.3$ (■); $[PtBr_{6-n}(NO_2)_n]^{2-}$,[22] $a = 2$ (□). The full lines connect the theoretical values calculated by the expressions in the last column of Table 1 (note that terms in square brackets have values close to 1 for the applied range of a values)

Table 2. Platinum n.m.r. chemical shifts for complexes $[PtBr_nCl_{6-n}]^{2-}$, experimental ($\delta_{\text{exptl.}}$)[23] and calculated by the expressions given in Table 1 ($\delta_{\text{calc.}}$)

Complex ion	$\delta_{\text{exptl.}}$[a]	$\delta_{\text{calc.}}$[b]
$[PtBr_6]^{2-}$	−1 879.4	−1 879.4
$[PtBr_5Cl]^{2-}$	−1 529.0	−1 528
cis-$[PtBr_4Cl_2]^{2-}$	−1 191.0	−1 190
trans-$[PtBr_4Cl_2]^{2-}$	−1 205.7	−1 204
fac-$[PtBr_3Cl_3]^{2-}$	−864.4	−866
mer-$[PtBr_3Cl_3]^{2-}$	−878.5	−878
trans-$[PtBr_2Cl_4]^{2-}$	−578.2	−577
cis-$[PtBr_2Cl_4]^{2-}$	−565.7	−566
$[PtBrCl_5]^{2-}$	−277.1	−278
$[PtCl_6]^{2-}$	0	0

[a] Ref. 23. [b] Calculated with $a = \Delta E_{Cl}/\Delta E_{Br} = 26.40/22.50 = 1.17$; excitation energies taken from D. L. Swithart and W. R. Mason, *Inorg. Chem.*, 1970, **9**, 1749.

Table 3. Cobalt-59 n.m.r. chemical shifts (δ) and linewidths (Δν) for the isomers of some cobalt(III) complexes

Complex	δ/p.p.m.	Δν/kHz	Synthesis
cis-$[Co(en)_2(NH_3)_2]Cl_3$	7 468	0.2	*a*
trans-$[Co(en)_2(NH_3)_2]Cl_3$	7 470	0.3	*a*
cis-$[Co(NCS)_2(en)_2]Cl$	7 950[b]	4[b]	*c*
trans-$[Co(NCS)_2(en)_2]Cl$	8 010[b]	8[b]	*c*
cis-$[Co(acac)_2(NH_3)_2]I$	10 740	1.0	*d*
trans-$[Co(acac)_2(NH_3)_2]I$	10 850	2.5	*d*

[a] J. C. Bailar and J. B. Work, *J. Am. Chem. Soc.*, 1945, **67**, 176. [b] In dimethyl sulphoxide. [c] M. M. Chamberlain and J. C. Bailar, *J. Am. Chem. Soc.*, 1959, **81**, 6412. [d] R. D. Archer and B. P. Cotsoradis, *Inorg. Chem.*, 1965, **4**, 1584.

explained by deviations of the excitation energies from those predicted by the rule of average environment.[2] The model predicts very precisely the chemical shifts of both *cis* and *trans* isomers of mixed-ligand complexes containing similar ligands, *e.g.* $[PtBr_nCl_{6-n}]^{2-}$ complexes (Table 2), as expected for a model based on the rule of average environment. In this context it is interesting that rhodium chemical shifts for all members of the series $[RhBr_nCl_{6-n}]^{2-}$ in solution have been observed, and tentative assignments made of chemical shifts of geometrical isomers, according to which $\delta_{trans} > \delta_{cis}$.[24] However, these assignments are not compatible with the present model, and in view of the aforesaid the opposite assignment ($\delta_{cis} > \delta_{trans}$) should be the correct one.

The model cannot be applied to complexes containing sterically demanding ligands. In such complexes, *cis* positioning of a sterically demanding ligand, as well as progressive introduction of sterically demanding ligands, weakens the ligand field. As a consequence, large negative deviations of metal chemical shifts from additivity and $\delta_{cis} > \delta_{trans}$ are observed. Thus for most nitro-complexes of cobalt(III) the observed deviations of metal chemical shifts from additivity are negative and very large,[2] well beyond those predicted by the model. A similar effect seems to be caused by $P(OMe)_3$ in the complexes $[Mo(CO)_{6-n}\{P(OMe)_3\}_n]$.[25]

It is very probable that other examples will be found to which the presented model cannot be applied. However, these examples should be confined to complexes suspected of involving extensive mutual ligand interactions. Therefore, it may be concluded that this model for chemical shift calculation, based upon the application of the rule of average environment to the spectrochemical and nephelauxetic properties of complexes, does afford a rationalization of the experimentally observed trends in the metal chemical shifts of geometrical isomers and will be useful in the assignment of chemical shifts for geometrical isomers of mixed-ligand octahedral d^6 complexes.

Appendix

Metal n.m.r. data for some geometrical isomers of cobalt(III) complexes used in this work have not been published previously, and are given in Table 3. In fact, for isomers of $[Co(en)_2(NH_3)_2]^{3+}$ contradictory results were published. In one paper[26] $\delta_{trans} > \delta_{cis}$, in another[1] $\delta_{cis} > \delta_{trans}$ was reported; the chemical shifts were also quite different.

The ^{59}Co n.m.r. data were determined with a Bruker SXP-100 Pulse FFT spectrometer operating at 21.5 MHz. Aqueous, *ca.* 0.2 mol dm^{-3} solutions were used, except for thiocyanato complexes which were dissolved to saturation in dimethyl sulphoxide.

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