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LIGAND FIELD INTERPRETATION OF METAL NMR CHEMICAL SHIFTS IN OCTAHEDRAL d^6 TRANSITION METAL COMPLEXES

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CONTENTS

ABBREVIATIONS

acacH	2,4-pentanedione
CpH	cyclopentadiene
debcH	1,1-diethyl-3-benzoylcarbamide
diars	(*o*-phenylene)bis(dimethylarsine)
dipy	2,2′-dipyridyl
$dmgH_2$	2,3-butanedione dioxime
dmpe	1,2-bis(dimethylphosphino)ethane
dtc	diethyldithiocarbamate
dtp	diethyldithiophosphate
en	1,2-diaminoethane
glyH	glycine

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$malH_2$	malonic acid
oxH_2	oxalic acid
phen	1,10-phenanthroline
ppdH	1-phenyl-1,3-propanedione
tacn	1,4,7-triazacyclononane
tame	1-amino-2,2-bis(methylamino)propane
tfthbdH	4,4,4-trifluoro-1-(2-thienyl)-1,3-butanedione
tmd	1,4-diaminobutane
tmen	2,3-dimethyl-2,3-diaminobutane
tn	1,3-diaminopropane

A. INTRODUCTION

In the rapidly growing field of transition metal NMR spectroscopy several comprehensive reviews have been published [1–7]. In these reviews the material is organized to follow Periodic Table transition metal groups or periods, covering data for different oxidation states of a metal. While such an approach has merit in a general survey of the field, it does not put enough emphasis on the electronic configurations of the transition metals. From the standpoint of the most successful theory of transition metal complexes, the ligand field theory, there is no essential difference between metal complexes of the same electronic configuration. Therefore, if one wants to look for regularities in the spectroscopic behaviour of transition metal complexes, it is more useful to present data for different metals but with the same electronic configuration [8]. Metal NMR chemical shifts, being a direct consequence of the electronic environment of the metal nuclei, are especially suitable for such an approach. Griffith and Orgel [9], in 1956, in their pioneering work on the ligand field interpretation of ^{59}Co NMR chemical shifts in octahedral cobalt(III) complexes stated in the conclusion of their paper, "Finally, we remark that the theory should also be applicable to a wide range of other diamagnetic or feebly paramagnetic transition metal compounds with six *d* electrons ...". Accordingly, an analysis of metal NMR chemical shifts in complexes with the same d^q electronic configuration was advocated from the very beginning.

Among transition metal complexes with the spin-paired d^q electronic configuration, the octahedral d^6 complexes are the most widespread. From the early transition metal complexes of vanadium(−I) to the late transition metal complexes of platinum(IV) a rich chemistry of the d^6 configuration may be followed. Therefore it is not surprising that the main body of transition metal NMR data is on complexes with this configuration [7]. Very valuable data have been collected not only on chemical shifts, but also on metal NMR relaxation and spin–spin coupling constants [1–7]. However, the present review concentrates on metal chemical shifts since they are most directly related to ligand field parameters.

B. INTERPRETATION OF METAL CHEMICAL SHIFTS IN COMPLEXES OF OCTAHEDRAL LIGAND FIELD SYMMETRY

(i) Diamagnetic and paramagnetic shielding

Chemical shifts are usually interpreted in terms of the Ramsey theory of nuclear magnetic shielding [10]. The theory allows division of the shielding into diamagnetic (σ^d) and paramagnetic (σ^p) parts; the former is produced by electrons in the ground state of a molecule and the latter by electronic transition into excited state singlet electronic configurations of a molecule. (The term "paramagnetic" thus refers to the orbital paramagnetism.) It is generally recognized that the Ramsey approach is difficult to apply consistently to the atom in a molecule because of the lack of knowledge on excited state molecular orbitals [11]. Therefore other approaches have been developed, in which local contributions to the nuclear magnetic shielding were explicitly formulated, allowing a more reliable calculation of the major contributions to the shielding [12–14].

Nuclear magnetic shielding of transition metals in their complexes represents a specific case because of the nature of the metal–ligand chemical bond. Since the bond is only partially covalent, metal orbitals are highly localized and the shielding could be considered as mainly of local origin. Ab initio calculations have shown that more than 99% of the shielding is produced by electrons in the metal orbitals [15–17]. Diamagnetic shielding of a metal nucleus is almost completely determined by the metal core electrons and is practically insensitive to the chemical environment in complexes [15–17]. The value of diamagnetic shielding is in fact close to that in a free metal atom. Paramagnetic shielding of a metal nucleus is produced by electrons in metal *d* orbitals almost exclusively [17]. Localization of the paramagnetic shielding is especially augmented by a low energy, metal centred *d–d* electronic transition. Therefore only the local part of the paramagnetic shielding is important and the results of ligand field theory are readily applicable in shielding calculation.

An extremely large range of chemical shifts is observed in octahedral d^6 complexes [1–7]. Since the diamagnetic shielding is not expected to vary significantly from complex to complex, attention has been concentrated on paramagnetic shielding. However, a knowledge of the NMR chemical shifts of the diamagnetically shielded metal nuclei is needed. This shift represents an exact chemical shift reference when the paramagnetic shielding is to be compared. The determination of this shift is difficult. An experimental technique which would enable the direct measurement of the magnetic moment of diamagnetically shielded transition metal nuclei to be made has not been devised. The closest approach is realized by the atomic-beam magnetic resonance (ABMR) method where the direct interaction between nuclear magnetic moment and the magnetic field modified by core electrons could be determined from the hyperfine splitting measurement [18]. Another reliable estimate is afforded by NMR studies of intermetallic compounds [19,20]. A less reliable estimate of the magnetic moment could be achieved from hyperfine coupling in electron–nuclear double magnetic resonance (ENDOR) experiments [21,22] or from studies of the NMR Knight shift in metals [23,24]. An interesting possibility for the determination of the diamagnetically shielded nucleus NMR chemical shift is provided by the highly anisotropic bis(cyclopentadienyl) transition metal complexes [25]. Some of the obtained chemical shifts of diamagnetically shielded transition metal nuclei are presented in Table 1. Among the shifts in Table 1, the cobalt and ruthenium shifts may be considered the most credible.

(ii) Paramagnetic shielding on the basis of ligand field theory

Ligand field interpretation of the paramagnetic shielding strives to express the shielding completely in terms of ligand field parameters. Hence the paramagnetic shielding term calculation involves reduction of the Ramsey general expression to the local contribution caused by a *d–d* electronic transition.

The Ramsey expression for paramagnetic shielding has the form given in eqn. (1):

$$\sigma^{\mathrm{p}}_{\alpha\beta} = -\frac{\mu_0 e^2}{8\pi m^2}\sum_n (E_n - \mathrm{E}_0)^{-1}\Big[\langle 0|\sum_j r_j^{-3} l_{j\alpha}|n\rangle \times \langle n|\sum_j l_{j\beta}|0\rangle + \langle 0|\sum_j l_{j\beta}|n\rangle\langle n|\sum_j r_j^{-3} l_{j\alpha}|n\rangle\Big] \tag{1}$$

Here summation goes over matrix elements between ground $|0\rangle$ and excited $|n\rangle$ states which have energies E_0 and E_n respectively. The angular orbital momentum operator l_j and the coordinate r_j are defined, in the present case, relative to the metal nucleus.

On the basis of the results of the ligand field theory [31–36], the ground state of a low spin d^6 octahedral complex has the electronic configuration $(t_{2g})^6$, while various excited states arise from configurations $(t_{2g})^{6-n}(e_g)^n$, $1 < n < 4$. For instance, the wavefunctions of the ground and the first

TABLE 1

Chemical shifts of diamagnetically shielded transition metal nuclei (δ^d) and magnetogyric ratios of the corresponding chemical shift reference compound (γ_s)

Metal	δ^d (ppm)	Ref.	γ_s (MHz T^{-1})	Ref.
^{55}Mn	-5300 [a]	21	10.553 (MnO_4^-)	21
^{57}Fe	-4500 [a]	22	1.3819 ($[Fe(CN)_6]^{4-}$)	27
^{59}Co	-6700 [b]	25	10.1029 ($[Co(CN)_6]^{3-}$)	28
^{101}Ru	-7600 [c]	26	-2.1975 ($[Ru(CN)_6]^{4-}$)	29
^{103}Rh	-5000 [d]	20	-1.3453 (13.6 MHz)	30

[a] ENDOR. [b] NMR of $CoCp_2^+$. [c] ABMR. [d] NMR of intermetallic compounds.

excited configurations are

$$(t_{2g})^6\colon\ \varphi^0(^1A_{1g})$$

$$(t_{2g})^5(e_g)\colon\ \varphi^1(^3T_{1g}),\ \varphi^1(^3T_{2g}),\ \varphi^1(^1T_{1g}),\ \varphi^1(^1T_{2g})$$

where $\varphi^k(\Gamma_i)$ are appropriate antisymmetrized products of the one-electron functions, t_{2g} and e_g, of O_h symmetry. These one-electron functions contain information on metal–ligand bond covalency and may be expressed as the linear combination of metal and the symmetry-adapted combination (ϕ) of ligand functions:

$$\begin{aligned} t_{2g} &= a_\pi d_{xy} + b_\pi \phi_\pi \\ e_g &= a_\sigma d_{x^2-y^2} + b_\sigma \phi_\sigma \end{aligned} \tag{2}$$

If the ligand field is not very strong, configuration interaction arises, causing formation of new states, the wavefunctions of which are composed of φ functions of the same symmetry:

$$\Psi^n(\Gamma_i) = \sum_k c_k^n \varphi^k(\Gamma_i)$$

On applying the Ramsey expression for paramagnetic shielding (eqn. (1)) to the described electronic configurations of the complexes, it is noted that the orbital angular momentum operator in O_h has $^1T_{1g}$ symmetry and that it couples the ground $^1A_{1g}$ state only with $^1T_{1g}$ excited states [9]. Therefore the paramagnetic shielding expression (eqn. (1)) simplifies to

$$\sigma^{\mathrm{p}} = -\frac{\mu_0 e^2}{4\pi m^2}\sum_n (E_n - E_0)^{-1}\left\langle \Psi^0(^1A_{1g}) \mid L_z \mid \Psi^n(^1T_{1g})\right\rangle \times \left\langle \Psi^n(^1T_{1g}) \mid L_z r^{-3} \mid \Psi^0(^1A_{1g})\right\rangle \tag{3}$$

where $L = \Sigma_j l_j$, and the isotropy of octahedral complexes has been taken into account.

Most octahedral d^6 complexes show behaviour which is close to strong-field behaviour, and the strong-field formulation of the paramagnetic shielding term would be the most appropriate [9,28]. This could be achieved by the introduction of a configuration interaction factor which would take into account the deviation of eqn. (3) from the strong-field conditions. In the strong field, the orbital angular momentum operator couples only the first excited $\varphi^1(^1T_{1g})$ state with the ground $\varphi^0(^1A_{1g})$ state [9]. Therefore the configuration interaction ratio may be defined:

$$\eta_\Sigma = \frac{\sum_n (E_n - E_0)^{-1} \left\langle \Psi^0(^1A_{1g}) \,|\, L_z \,|\, \Psi^n(^1T_{1g}) \right\rangle \left\langle \Psi^n(^1T_{1g}) \,|\, L_z r^{-3} \,|\, \Psi^0(^1A_{1g}) \right\rangle}{(E_1 - E_0)^{-1} \left\langle \varphi^0(^1A_{1g}) \,|\, \mathrm{L}_z \,|\, \varphi^1(^1T_{1g}) \right\rangle \left\langle \varphi^1(^1T_{1g}) \,|\, L_z r^{-3} \,|\, \varphi^0(^1A_{1g}) \right\rangle}$$

or, since $\varphi^0(^1A_{1g})$ and $\varphi^1(^1T_{1g})$ states differ only in that one electron is promoted from a t_{2g} into an e_g orbital

$$\eta_\Sigma = \frac{\sum_n (E_n - E_0)^{-1} \left\langle \Psi^0(^1A_{1g}) \,|\, L_z \,|\, \Psi^n(^1T_{1g}) \right\rangle \left\langle \Psi^n(^1T_{1g}) \,|\, L_z r^{-3} \,|\, \Psi^0(^1A_{1g}) \right\rangle}{\Delta E(^1A_{1g} \rightarrow {}^1T_{1g})^{-1} \langle t_{2g} \,|\, L_z \,|\, e_g \rangle \langle e_g \,|\, L_z r^{-3} \,|\, t_{2g} \rangle} \tag{4}$$

Including the configuration interaction ratio, eqn. (3) may be rewritten in the following form:

$$\sigma^{\mathrm{P}} = -\frac{\mu_0 e^2}{4\pi m^2} \eta_\Sigma \frac{\langle t_{2g} \,|\, L_z \,|\, e_g \rangle \langle e_g \,|\, L_z r^{-3} \,|\, t_{2g} \rangle}{\Delta E(^1A_{1g} \rightarrow {}^1T_{1g})} \tag{5}$$

Further, it may be noted that one-electron functions, t_{2g} and e_g, are not expected to deviate very much from pure d-orbitals. The paramagnetic shielding term expression could reflect this expectation as well. For this purpose the covalency ratio is introduced [37]:

$$\eta_{\sigma\pi} = \frac{\langle t_{2g} \,|\, L_z \,|\, e_g \rangle \langle e_g \,|\, L_z r^{-3} \,|\, t_{2g} \rangle}{\langle d_{xy} \,|\, L_z \,|\, d_{x^2-y^2} \rangle \langle d_{x^2-y^2} \,|\, L_z r^{-3} \,|\, d_{xy} \rangle} \tag{6}$$

Then eqn. (5) transforms to

$$\begin{aligned} \sigma^{\mathrm{P}} &= -\frac{\mu_0 e^2}{4\pi m^2} \eta_\Sigma \eta_{\sigma\pi} \frac{\langle d_{xy} \,|\, L_z \,|\, d_{x^2-y^2} \rangle \langle d_{x^2-y^2} \,|\, L_z r^{-3} \,|\, d_{xy} \rangle}{\Delta E(^1A_{1g} - {}^1T_{1g})} \\ &= -8 \frac{\mu_0 \mu_{\mathrm{B}}^2}{\pi} \langle r_d^{-3} \rangle_{\mathrm{F}} \frac{\eta_\Sigma \eta_{\sigma\pi}}{\Delta E} \end{aligned} \tag{7}$$

where μ_{B} is the Bohr magneton and $\langle r_d^{-3} \rangle_{\mathrm{F}}$ is the d-orbital radial expectation value for a d^6 free ion (atom).

The effect of metal–ligand bond covalency on the paramagnetic shielding could also be expressed in terms of the orbital angular momentum reduction factor [38,39], $k_{\sigma\pi} = \langle t_{2g} | L_z | e_g \rangle / \langle d_{xy} | L_z | d_{x^2-y^2} \rangle$ [49,50]. This factor is connected with the covalency ratio in the following way:

$$\eta_{\sigma\pi} = k_{\sigma\pi} \frac{\langle e_g | L_z r^{-3} | t_{2g} \rangle}{\langle d_{x^2-y^2} | L_z r^{-3} | d_{xy} \rangle} \tag{8}$$

The simplest use of eqn. (7) for the interpretation of metal NMR chemical shifts would be to assume constant values for the configuration interaction (η_Σ) and covalency ($\eta_{\sigma\pi}$) ratios and to look for a linear correlation between the chemical shifts and wavelengths of ${}^1A_{1g} \rightarrow {}^1T_{1g}$ electronic transitions. The first interpretation of ^{59}Co NMR chemical shifts in cobalt(III) complexes [9,29] encouraged such an approach. However, later investigations established large deviations from this simple interpretation [33–45]. Before discussing the nature of the observed deviations, an estimate of the possible variations in η_Σ and $\eta_{\sigma\pi}$ values would be enlightening. For the estimation of η_Σ, first the absence of covalency may be assumed; then expression (4) transforms to

$$\eta_\Sigma = \frac{\sum_n (E_n - E_0)^{-1} \left[\langle \Psi^0({}^1A_{1g}) | L_z | \Psi^n({}^1T_{1g}) \rangle \right]^2}{\Delta E({}^1A_{1g} \rightarrow {}^1T_{1g})^{-1} \left[\langle d_{xy} | L_z | d_{x^2-y^2} \rangle \right]^2} \tag{9}$$

because d orbitals are separable into radial and angular parts. Recently the L_z matrix elements $\langle \Psi^0({}^1A_{1g}) | L_z | \Psi^n({}^1A_{1g}) \rangle$ have been calculated in the intermediate ligand field treatment of the d^6 configuration [46]. It was shown that the matrix element between the ground and the first excited state is the only important one, but that its value differs from the strong ligand field value. Consequently the configuration interaction ratio may be expressed as

$$\eta_\Sigma = \frac{\left[\langle \Psi^0({}^1A_{1g}) | L_z | \Psi^1({}^1T_{1g}) \rangle \right]^2}{\left[\langle d_{xy} | L_z | d_{x^2-y^2} \rangle \right]^2} \tag{10}$$

Its dependence on ligand field strength is presented in Fig. 1. It is seen that η_Σ differs only slightly from unity (the strong-field value). Under the assumed absence of covalency, deviation from the strong-field value is below 10%. Allowing for covalency the deviation is even smaller. Namely, covalency is expected to be more pronounced in the higher excitation states, leading to smaller orbital momentum in these states. This would then

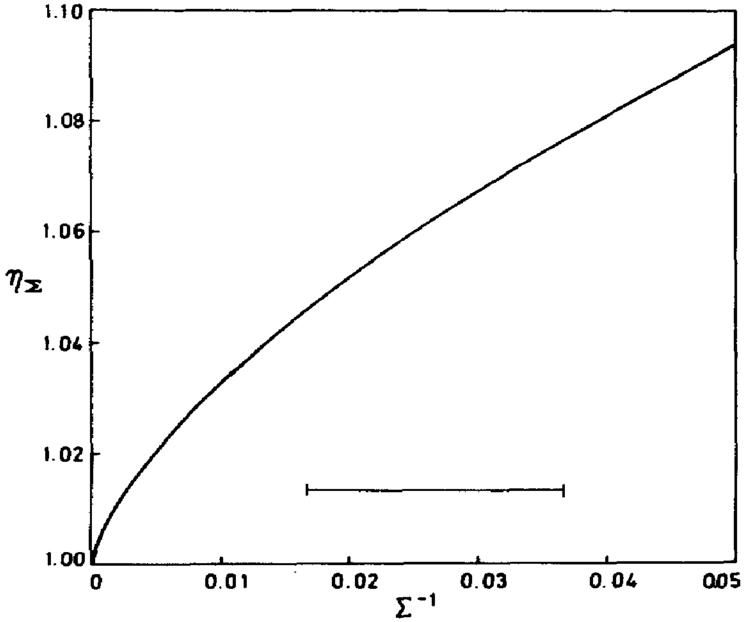

Fig. 1. Configuration interaction ratio (η_Σ) dependence on reciprocal ligand field strength (Σ^{-1}). The experimentally observed range of ligand field strengths in spin-paired d^6 octahedral complexes (———).

diminish the importance of the impact of configuration interaction on the angular orbital momentum between the ground and the first excited state.

For the estimation of $\eta_{\sigma\pi}$, the LCAO expressions of t_{2g} and e_g molecular orbitals (eqn. (2)) may be introduced in expression (6). Assuming little covalency, the following expression is obtained [45]:

$$\eta_{\sigma\pi} \approx a_\sigma^2 a_\pi^2 \frac{\langle r_d^{-3} \rangle_\mathrm{C}}{\langle r_d^{-3} \rangle_\mathrm{F}} \tag{11}$$

where $\langle r_d^{-3} \rangle_\mathrm{C}$ is the radial parameter for the complexed metal *d*-orbitals. For donation of one electron by σ bonding to the metal it was estimated [45] that $\eta_{\sigma\pi} \approx 0.6$. Another estimate of $\eta_{\sigma\pi}$ arises on the basis of the orbital angular momentum reduction factor. Assuming that t_{2g} and e_g molecular orbitals could be replaced by deformed *d*-orbitals it follows from eqn. (8) that $\eta_{\sigma\pi} \approx k_{\sigma\pi}^2 \langle r_d^{-3} \rangle_\mathrm{C} / \langle r_d^{-3} \rangle_\mathrm{F}$. Typically, $k_{\sigma\pi} \approx 0.8$–$0.9$ is quoted for transition metal complexes [47,48]. This would again produce a covalency ratio of about 0.6.

These crude estimates signify a large reduction in $\eta_{\sigma\pi}$ (below unity) and a large impact of the metal–ligand bond covalency on the paramagnetic shielding term. Therefore it seems justified to expect a large variation in $\eta_{\sigma\pi}$, while $\eta_\Sigma \approx 1$ could be assumed.

(iii) Impact of metal–ligand bond covalency on the paramagnetic shielding

General insight into the nature of the metal chemical shift correlation with the transition energies may be obtained by considering data on ^{59}Co NMR chemical shift and $^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ transition energies in cobalt(III) complexes (Table 2a). Correlation of the chemical shifts with the reciprocal values of the transition energies displays a wide spread of data [33–45] (Fig. 2). Some linearity may be noted only if complexes containing ligators of

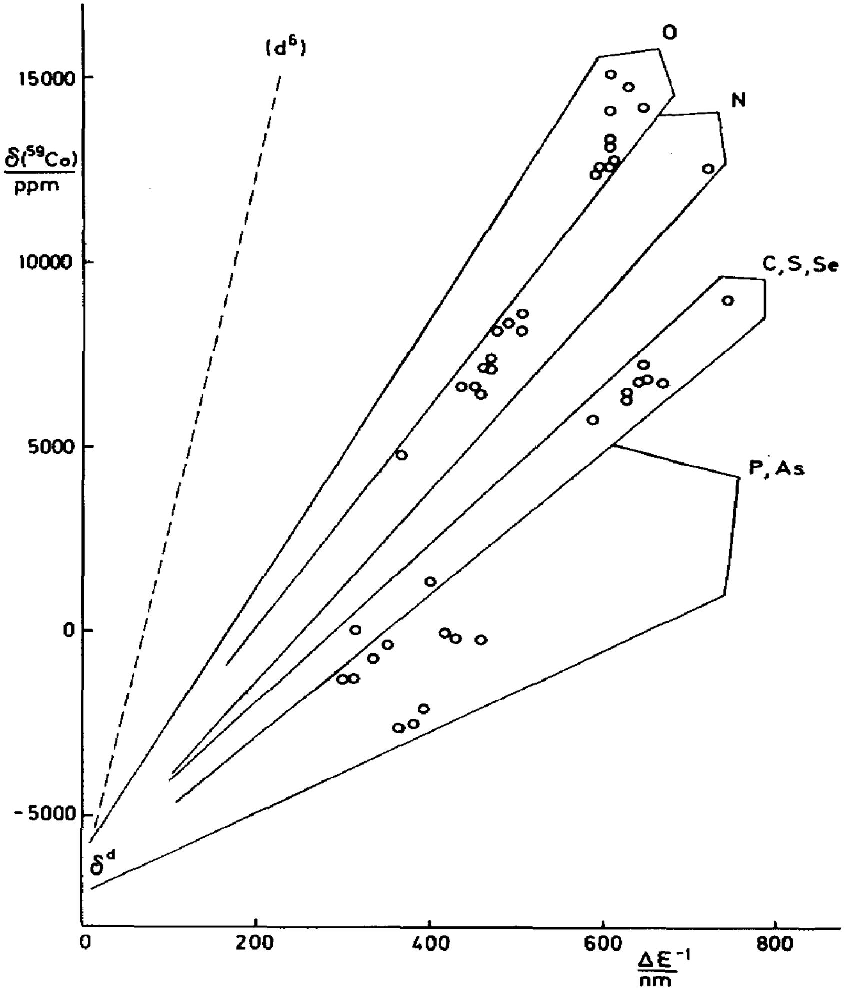

Fig. 2. Correlation between ^{59}Co NMR chemical shifts and $^{1}A_{1g} \rightarrow {}^{1}T_{1g}$ electronic transition wavelengths for cobalt(III) complexes (Table 2a). The correlation has its origin at the chemical shift of the diamagnetically shielded cobalt nucleus ($\delta^{d} = -6820$ ppm, Table 1). In drawing the correlation line which corresponds to completely localized d orbitals of d^6 configuration (— — —) the SCF radial parameter value was used ($\langle r_d^{-3} \rangle_F = 6.65$ a.u. [51].

TABLE 2a

^{59}Co NMR chemical shifts (δ), wavelengths of $^1A_{1g} \rightarrow {}^1T_{1g}$ electronic transition ($1/\Delta E$), covalency ratios ($\eta_{\sigma\pi}$) and nephelauxetic ratios (β_{35}) for cobalt(III) CoL_6 complexes

Complex	δ [a] (ppm)	$1/\Delta E$ (nm)	$\eta_{\sigma\pi}$ [b]	β_{35}	Ref. [c]
CoO_6 type					
$[Co(OH_2)_6]^{3+}$	15050	606	0.58	0.61	46, 46
$[Co(OH)_6(NH_3)_{12}]^{6+}$	14850	625	0.56		52, 52
$[Co(CO_3)_3]^{3-}$	14070	645	0.52	0.49	53, 54
$[Co(mal)_3]^{3-}$	14020	608	0.57	0.50	46, 46
$[Co(debc)_3]$	13300	607	0.53		55, 55
$[Co(ox)_3]^{3-}$	12930	605	0.53	0.49	46, 46
$[Co(tfthbd)_3]$	12800	609	0.52		56, 56
$[Co(acac)_3]$	12630	597	0.52		57, 28
$[CoO_{24}Mo_6H_6]^{3-}$	12550	605	0.52	0.54	46, 46
$[Co(ppd)_3]$	12440	592	0.52		56, 56
CoN_6 type					
$[Co(N_3)_6]^{3-}$	12530	720	0.43	0.42 [d]	53, 58
$[Co(tmd)_3]^{3+}$	8670	501	0.50	0.54	45, 59
$[Co(tn)_3]^{3+}$	8350	488	0.50	0.54	60, 61
$[Co(tmen)_3]^{3+}$	8150	504	0.48	0.52	68, 68
$[Co(NH_3)_6]^{3+}$	8175	475	0.51	0.56	53, 46
$[Co(tame)_2]^{3+}$	7420	469	0.49	0.55	46, 46
$[Co(en)_3]^{3+}$	7145	468	0.48	0.53	53, 46
$[Co(phen)_3]^{3+}$	7080	470	0.47		62, 63
$[Co(dipy)_3]^{3+}$	6620	450	0.48		64, 63
$[Co(NH_2OH)_6]^{3+}$	6620	440	0.49	0.56	57, 65
$[Co(tacn)_2]^{3+}$	6390	459	0.46	0.57	46, 46
$[Co(dmg)_3]$	4880	365	0.51		45, 66
CoS_6, $CoSe_6$ and CoC_6 types					
$[Co(dtp)_3]$	9050	740	0.34	0.36	46, 47
$[Co(S_2CNH_2)_3]$	7320	640	0.36	0.32	40, 67
$[Co(S_2CN(C_2H_5)_2]$	6830	650	0.34		69, 40
$[Co(dtc)_3]$	6790	645	0.34	0.35	69, 67
$[Co(S_2COC_2H_5)_3]$	6250	625	0.33	0.30	44, 44
$[Co(Se_2CN(CH_3)_2)_3]$	6720	667	0.33	0.30	40, 70
$[Co(S_2CS_3)]^{3-}$	6390	625	0.34		45, 71
$[Co(S_2CCH_2C_5H_5)_3]$	5830	590	0.34	0.35	45, 67
$[Co(CNO)_6]^{3-}$	1300	400	0.32	0.41	45, 72
$[Co(CN)_6]^{3-}$	0	311	0.35	0.42	28, 36
CoP_6 and $CoAs_6$ types					
$[Co(P(OCH_3)_3)_6]^{3+}$	−305	350	0.29		42, 42
$[Co(iPrPOCH_2CH_2O)_6]^{3+}$	−724	335	0.29		73, 73
$[Co(P(OCH_2)_3(CH_2)_3)_6]^{3+}$	−1240	300	0.29	0.29	42, 74
$[Co(o\text{-}C_6H_4(PPh_2)_2)_3]^{3+}$	−2120	391	0.19		75, 75
$[Co(Me_2PCH_2CH_2PMe_2)_3]^{3+}$	−2530	380	0.18		75, 75

TABLE 2a (continued)

Complex	δ [a] (ppm)	$1/\Delta E$ (nm)	$\eta_{\sigma\pi}$ [b]	β_{35}	Ref. [c]
$[Co(o\text{-}C_6H_4(PMe)_2)_3]^{3+}$	−2600	362	0.18		75, 75
$[Co(MeAs(o\text{-}C_6H_4AsMe_2)_2)_2]^{3+}$	−30	424	0.25		76, 76
$[Co(diars)_3]^{3+}$	−100	430	0.25		45, 45
$[Co(MeC(CH_2AsMe_2)_3)_2]^{3+}$	−190	462	0.23		76, 76

[a] Chemical shifts relative to the resonance of an aqueous solution of sodium hexacyanocobaltate(III) used as external standard. [b] Calculated according to eqn. (13) with $\delta^d = -6700$ ppm and $\langle r_d^{-3}\rangle_F = 6.67$ a.u., so that $\eta_{\sigma\pi} = [\delta(\text{ppm}) + 6700]\Delta E(\text{nm}^{-1})/61.9$. [c] The first reference is for NMR, the second for optical data. [d] The value $\beta_{35} = 0.38 \pm 0.04$ has been reported [58]; the upper limit is accepted here.

TABLE 2b

^{99}Ru NMR chemical shifts (δ), wavelengths of $^1A_{1g} \rightarrow {}^1T_{1g}$ electronic transition ($1/\Delta E$), covalency ratios ($\eta_{\sigma\pi}$) and nephelauxetic ratios (β_{35}) for ruthenium(II) RuL_6 complexes

Complex	δ (ppm)	$1/\Delta E$ (nm)	$\eta_{\sigma\pi}$ [a]	β_{35}	Ref. [b]
$[Ru(OH_2)_6]^{2+}$	16050	529	0.83	0.79	78, 79
$[Ru(NH_3)_6]^{2+}$	7820	390	0.74	0.73	80, 81
$[Ru(en)_3]^{2+}$	6600	370	0.72	0.71	82, 79
$[Ru(dipy)_3]^{2+}$	4520				80
$[Ru(CN)_6]^{4-}$	0				80
$[Ru(CNCH_3)_6]^{2+}$	−112				29

[a] Calculated applying eqn. (13), with $\delta^d = -7600$ ppm (Table 1) and $\langle r_d^{-3}\rangle_F = 5.6$ a.u. [51].
[b] The first reference is for NMR data, the second for optical data.

similar electronegativities (for instance carbon, sulphur and selenium) are selected [45].

As the origin of the correlation of the chemical shifts with the reciprocal $^1A_{1g} \rightarrow {}^1T_{1g}$ transition energy, the chemical shift of the diamagnetically shielded metal nucleus is used [45]. The question which has been raised is whether it is conceptually correct to postulate constant diamagnetic shielding (and close to that of a free atom) for the correlation of chemical shifts with $1/\Delta E$ [46]. The correlation may suggest that the diamagnetic shielding is reached in the limit $\Delta E \rightarrow \infty$. In this limit of an infinitely strong octahedral ligand field, it is hardly expected that no distortion of the inner electronic shell occurs and that the core shielding of a free atom is appropriate. There is an answer to the question: the experimental data fall in the region where the ligand field strength is insufficient to produce complete distortion even of the valence shell. In this region the core electron diamagnetic shielding is not appreciably disturbed and the free-atom diamagnetic chemical shift is a good reference. Therefore the correlation origin in question should be considered as that reached in the limit $\sigma^{\mathrm{p}} \to 0$ by extrapolation of the correlation observed at reasonable ligand field strengths.

It is important to note that all points in Fig. 2 lie well below the correlation line, which would correspond to a hypothetical case of the completely localized d orbitals of the free-ion d^6 configuration in the strong octahedral ligand field. Thus for this case $\eta_{\sigma\pi} = 1$, and the paramagnetic shielding is given by

$$\sigma^{\mathrm{p}}_{\mathrm{ionic}} = -8\frac{\mu_0\mu_{\mathrm{B}}^2}{\pi}\left\langle r_d^{-3}\right\rangle_{\mathrm{F}}\frac{1}{\Delta E\left({}^1A_{1\mathrm{g}} \to {}^1T_{1\mathrm{g}}\right)} \tag{12}$$

TABLE 2c

Metal NMR chemical shifts (δ), wavelengths of ${}^1A_{1\mathrm{g}} \to {}^1T_{1\mathrm{g}}$ electronic transition ($1/\Delta E$) and nephelauxetic ratios (β_{35}) for some early transition metal d^6 ML_6 complexes

Complex	δ [a] (ppm)	$1/\Delta E$ (nm)	β_{35}	Ref. [b]
V(−I)				
$[\mathrm{V(PF_3)_6}]^-$	−1410			84
$[\mathrm{V(CO)_6}]^-$	−1416	400	0.86 [c]	84, 85
Nb(−I)				
$[\mathrm{Nb(PF_3)_6}]^-$	−1117			84
$[\mathrm{Nb(CO)_6}]^-$	−1170			84
Cr(O)				
$[\mathrm{Cr(CO)_6}]$	−1795	317	0.66	86, 85
Mo(O)				
$[\mathrm{Mo(P(OCH_3)_3)_6}]$	−1359			87
$[\mathrm{Mo(CO)_6}]$	−1875			88
W(O)				
$[\mathrm{W(CO)_6}]$	−3500			89
Mn(I)				
$[\mathrm{Mn(CNCH_3)_6}]^+$	−1292	317	0.54	90, 91
$[\mathrm{Mn(CO)_6}]^+$	−1445			92
Tc(I)				
$[\mathrm{Tc(P(OCH_3)_3)_6}]^+$	−1658			93
$[\mathrm{Tc(dmpe)_3}]^+$	−1854			93
$[\mathrm{Tc(CNCH_3)_6}]^+$	−1908			93
Re(I)				
$[\mathrm{Re(CO)_6}]^+$	−3400			92

[a] Chemical shifts relative to the resonance of MO_4^{n-} ions [94]. [b] The first reference is for chemical shift, the second for the optical data. [c] The Racah parameter of gaseous V(−1), $B = 500\ \mathrm{cm}^{-1}$, is extrapolated from data on V(0)–V(III) [35].

TABLE 2d

Metal NMR chemical shifts (δ), wavelengths of $^1A_{1g} \rightarrow {}^1T_{1g}$ electronic transition ($1/\Delta E$) and nephelauxetic ratios (β_{35}) for iron(II), rhodium(III) and platinum(IV) ML_6 complexes

Complex	δ [a] (ppm)	$1/\Delta E$ (nm)	β_{35}	Ref. [b]
Fe(II)				
$[Fe(dipy)_3]^{2+}$	8770			95
$[Fe(CN)_6]^{4-}$	0	322	0.43	27, 79
Rh(III)				
$[Rh(OH_2)_6]^{3+}$	9990	392	0.71	96, 79
$[Rh(acac)_3]$	8350	385		97
$[RhCl_6]^{3-}$	7975	518	0.48	96, 79
$[RhBr_6]^{3-}$	7080	552	0.39	96, 79
$[Rh(NO_2)_6]^{3-}$	5580	335		98, 99
Pt(IV)				
$[PtF_6]^{2-}$	11180	317	0.51	30, 79
$[Pt(OH)_6]^{2-}$	7150			100
$[PtCl_6]^{2-}$	3850	380		30, 101
$[Pt(en)_3]^{4+}$	2910			30
$[PtBr_6]^{2-}$	1980	435		30, 101
$[Pt(SCN)_6]^{2-}$	390	370		102, 101
$[Pt(CN)_6]^{2-}$	0			30
$[Pt(CH_3)_6]^{2-}$	−314			103
$[PtI_6]^{2-}$	−2200			30

[a] Chemical shift relative to the resonance of the corresponding hexacyano complex except for rhodium chemical shifts for which the frequency $\Xi = 31.6$ MHz is used as standard. [b] The first reference is for chemical shift, the second for optical data.

Interpretation of the chemical shifts considered in terms of the paramagnetic shielding expression (eqn. (7)) would be possible only if some specific value of $\eta_{\sigma\pi}$ is ascribed to each complex. These values of $\eta_{\sigma\pi}$ could be calculated from the slope of the correlation line for each complex relative to the slope for ionic d^6 cases [45]. From eqn. (7) it follows (assuming $\eta_\Sigma \approx 1$) that

$$\eta_{\sigma\pi} = -8\frac{\pi}{\mu_0\mu_B^2}\frac{\Delta E\left({}^1A_{1g} \rightarrow {}^1T_{1g}\right)}{\langle r_d^{-3}\rangle_F}\sigma^p$$

$$= \frac{\sigma^p}{\sigma^p_{\text{ionic}}} = \frac{\delta - \delta^d}{\delta_{\text{ionic}} - \delta^d} \qquad (13)$$

Calculated values of $\eta_{\sigma\pi}$ for cobalt(III) complexes are presented in Table 2. The values are mainly characteristic of the chromophores (CoO_6, 0.52–0.58; CoN_6, 0.43–0.51; CoC_6, CoS_6, $CoSe_6$, 0.32–0.36; CoP_6, $CoAs_6$, 0.18–0.29), being primarily sensitive to the electronegativity of the atoms directly

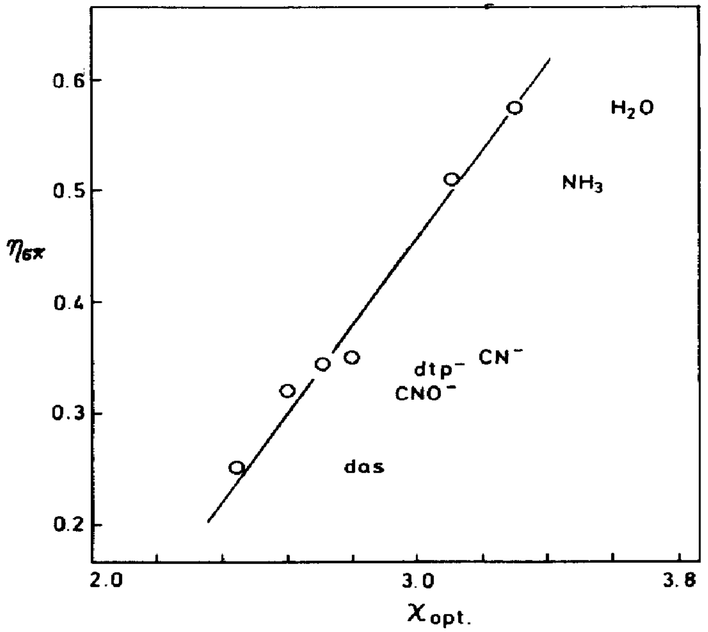

Fig. 3. Correlation between covalency ratio ($\eta_{\sigma\pi}$) and ligand optical electronegativities (χ_{opt}) [77] in cobalt(III) complexes.

bonded to cobalt [45]. The spread of the $\eta_{\sigma\pi}$ values for a chromophore seems to reflect the actual electronegativity of the ligating atom in different ligands. Thus a linear correlation exists between $\eta_{\sigma\pi}$ and ligand optical electronegativities (Fig. 3).

It may be concluded that experimental $\eta_{\sigma\pi}$ values reflect metal–ligand bond covalency, in agreement with expectation. It is also obvious (Fig. 2) that metal–ligand bond covalency has an impact on the paramagnetic shielding, comparable to that of the excitation energy. Hence, if the paramagnetic shielding is to be expressed by ligand field parameters, the bond covalency must be properly taken into account.

(iv) Nephelauxetic effect on the paramagnetic shielding

An insight into metal–ligand bond covalency could also be achieved on the basis of the nephelauxetic ratio [36]. Therefore some correspondence between the covalency ratio $\eta_{\sigma\pi}$ and the nephelauxetic ratio β_{35} may be expected. Indeed, it was established that these ratios are affected by covalency to the same extent [43,44]. Data on cobalt(III) and ruthenium(II) complexes illustrating this fact are presented in Fig. 4 ($\eta_{\sigma\pi}$ is calculated only for these two metals because of the reliability of δ^{d}).

It is perhaps unexpected that two quite different parameters, the paramagnetic shielding and the interelectronic repulsion energy, are equally

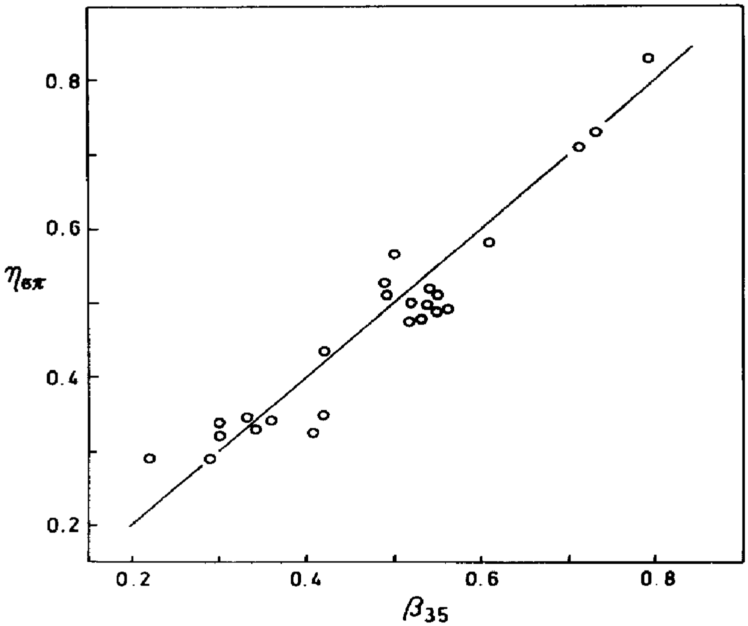

Fig. 4. Correlation between covalency ratios ($\eta_{\sigma\pi}$) and nephelauxetic ratios (β_{35}) in cobalt(III) and ruthenium(II) complexes (Tables 2a and 2b).

reduced by bond covalency. The underlying reasons for such behaviour are very interesting. An insight into them was provided by analysis of the covalency ratio and the nephelauxetic ratio in an LCAO molecular orbital approximation [37]. Thus, approximate expressions for the ratios are [37,45]

$$\begin{aligned} \eta_{\sigma\pi} &= a_\sigma^2 a_\pi^2 \frac{\langle r_d^{-3} \rangle_{\mathrm{C}}}{\langle r_d^{-3} \rangle_{\mathrm{F}}} \\ \beta_{35} &= a_\sigma^2 a_\pi^2 \frac{B_{\mathrm{C}}}{B_{\mathrm{F}}} \end{aligned} \tag{14}$$

which show the same impact of the "symmetry restricted covalency" ($a_\sigma^2 a_\pi^2$) on both ratios. The ratios of the *d* electron inverse cube distance in complexes and in a free ion (atom), $\langle r_d^{-3} \rangle_{\mathrm{C}} / \langle r_d^{-3} \rangle_{\mathrm{F}}$, and the Racah parameter in the complex and in the free ion (atom), $B_{\mathrm{C}}/B_{\mathrm{F}}$, could be considered a measure of the "central field covalency". It is not easy to see why the central field covalency would affect almost equally the *d* electron inverse cube distance and the interelectronic repulsion energy. Nevertheless, calculation of the ratios using "double-zeta" *d*-electron wavefunctions demonstrated their almost equal reduction upon addition of electrons to the metal ion [37] (Fig. 5). Such behaviour could be understood by considering the importance of the radial parameters to the electron energy in multielectron atoms [37].

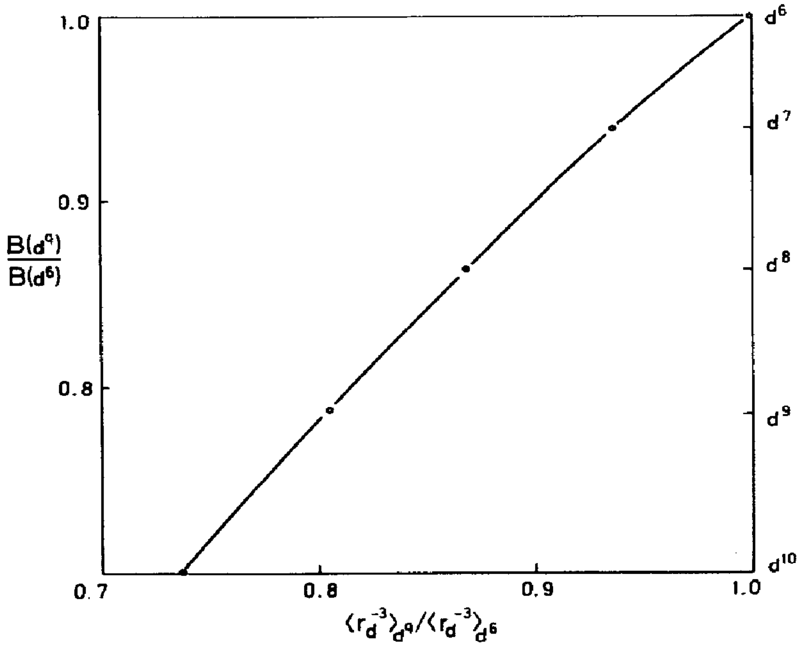

Fig. 5. Comparison of the reduction of central field covalency ratios $B(d^q)/B(d^6)$ and $\langle r_d^{-3}\rangle_{d^q}/\langle r_d^{-3}\rangle_{d^6}$ upon addition of electrons to Ni^{4+} [37].

From the aforesaid, it may be concluded that the similarity of the covalency ratios, $\eta_{\sigma\pi}$ and β_{35}, observed in cobalt(III) and ruthenium(II) complexes, should be of general validity in d^6 complexes. On this basis, $\eta_{\sigma\pi}$ could be replaced by β_{35} in eqn. (7):

$$\sigma^{\mathrm{P}} = -8\frac{\mu_0\mu_{\mathrm{B}}^2}{\pi}\langle r_d^{-3}\rangle_{\mathrm{F}}\frac{\beta_{35}}{\Delta E} \tag{15}$$

which allows interpretation of the metal chemical shifts completely in terms of the ligand field parameters. Correlation of the metal chemical shifts with $\beta_{35}/\Delta E$ proved to be successful for cobalt(III) [43,46], ruthenium(II) [82], and rhodium(III) complexes [37]. Analysis of the correlation for cobalt(III) complexes established a better correlation for ortho-axial complexes than for non-ortho-axial complexes [46] (Fig. 6). This is due to a lowering of the ligand field symmetry below octahedral under the action of D_3 molecular symmetry.

By using the full potential of eqn. (15); the metal chemical shifts in d^6 octahedral complexes could be interpreted in a unique way [83]. Correlation of the chemical shifts with the calculated paramagnetic shielding should produce a single correlation line for various metals, providing that the chemical shift references have similar paramagnetic shielding. When referenced to the corresponding hexacyano complexes (or for early transition

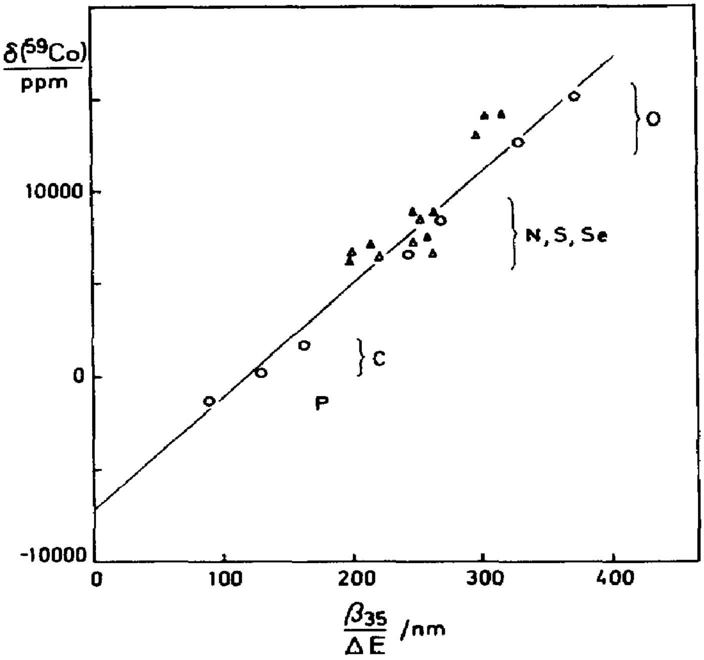

Fig. 6. Correlation of ^{59}Co NMR chemical shifts with $^1A_{1g} \rightarrow {}^1T_{1g}$ electronic transition wavelength ($1/\Delta E$) multiplied by nephelauxetic ratio β_{35} for ortho-axial (○) and non-ortho-axial (△) cobalt(III) complexes.

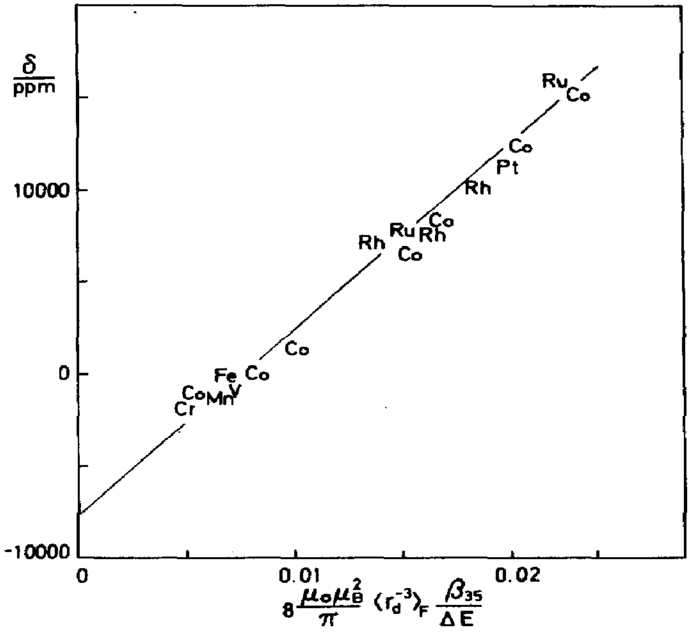

Fig. 7. Octahedral complex NMR chemical shift correlation with ligand field parameter expressed paramagnetic shielding (data for ortho-axial complexes in Tables 2a–2d are used). The unit slope of the correlation line should be noted.

metals to the chemical shift of the MO_4^{n-} ion) the metal chemical shift seems to fulfil this requirement and a single correlation line is obtained in terms of eqn. (15) (Fig. 7). A correlation of the same quality is obtained when the chemical shift of the diamagnetically shielded nuclei is taken as reference [83].

The success of eqn. (15) is of considerable importance. It advances the application of both the Ramsey theory of nuclear magnetic shielding and ligand field theory for the interpretation of transition metal NMR chemical shifts. It also affords independent information on the nephelauxetic effect in transition metal complexes. For a number of complexes, for which only the $^1A_{1g} \rightarrow {}^1T_{1g}$ *d–d* transition is measurable, insight into the nephelauxetic properties is now available through determination of $\eta_{\sigma\pi}$ (Tables 2a and 2b).

(v) *Medium effects on the paramagnetic shielding*

Variations of up to several hundred parts per million in metal chemical shifts, dependent upon the medium (solvent, phase, temperature, pressure), have been observed [1–7]. The ligand field interpretation of the paramagnetic shielding requires that these variations arise as a consequence of corresponding changes in the ligand field parameters.

A medium effect on *d–d* electronic transition energies is observable and amounts to hundreds of reciprocal centimetres. The nephelauxetic ratio is much less affected [36(a)]. Therefore, according to eqn. (15), a linear correlation between metal chemical shifts and the $^1A_{1g} \rightarrow {}^1T_{1g}$ electronic transition energy for a single complex in different media may be expected. Moreover, the slope of such a correlation should vary directly with the

TABLE 3

Dependence of metal NMR chemical shifts on $^1A_{1g} \rightarrow {}^1T_{1g}$ electronic transition wavelength for some cobalt(III) complexes with temperature change ($\Delta\delta/\Delta\lambda$) and dependence calculated on the basis of eqn. (15) ($(8\mu_0\mu_B^2/\pi)\langle r_d^{-3}\rangle_F\,\beta_{35}$)

Complex	$\Delta\delta/\Delta\lambda$ [a] (cm^{-1})	β_{35}	$8\frac{\mu_0\mu_B^2}{\pi}\langle r_d^{-3}\rangle\,\beta_{35}$ (cm^{-1})
$[Co(NH_3)_6]^{3+}$	330 ± 20 [b]	0.56	350
$[Co(ox)_3]^{3-}$	310 ± 30 [b]	0.49	310
$[Co(en)_3]^{3+}$	280 ± 20 [b]	0.53	330
$[Co(CN)_6]^{3-}$	230 ± 20 [c]	0.42	260
$[Co(S_2CNH_2)_3]$	200 ± 10 [c]	0.32	200
$[Co(S_2COC_2H_5)_3]$	180 ± 20 [c]	0.30	190

[a] Calculated from $\Delta\gamma/\Delta\lambda$ values given in ref. 44. [b] From aqueous solution in the temperature range 0–90 °C. [c] From chloroform solution in the temperature range 0–60 °C.

TABLE 4

The medium effect on ^{59}Co NMR chemical shift (δ) and wavelength of $^1A_{1g} \rightarrow {}^1T_{1g}$ electronic transition energy of the hexacyanocobaltate(III) complex

Temperature (°C)	Solvent	Pressure (kg m^{-2})	δ (ppm)	$1/\Delta E$ (nm)	Ref.
1	H_2O	– [a]	–32	310.5	104 [b]
25	H_2O	– [a]	0	311	105 [b]
40	H_2O	– [a]	24	312.5	104
80	H_2O	– [a]	84	314.5	104
25	HCOOH	– [a]	–72	309	105
25	CH_3OH	– [a]	84	312	105
33.5	C_2H_5OH	– [a]	132	–	5 [c]
33.5	1-Pentanol	– [a]	154	–	5
33.5	3-Pentanol	– [a]	195	–	5
25	CH_3CN	– [a]	265	318	105
25	Me_2SO	– [a]	282	321	105
20.3	H_2O	9000	–15.8	–	106 [b]

[a] Atmospheric pressure. [b] $K_3[Co(CN)_6]$ salt. [c] $(n\text{-}Bu_4N)_3[Co(CN)_6]$ salt.

TABLE 5

Metal NMR chemical shift temperature coefficients ($\Delta\delta/\Delta T$) for octahedral d^6 complexes

Complex	$\Delta\delta/\delta T$ (ppm K^{-1})	Temperature (°C)	Solvent	Ref.
$[Co(OH_2)_6]^{3+}$	2.6	–20–80	H_2O	109
$[Co(acac)_3]$	3.1	–20–60	$CDCl_3$	110
	2.97	–60–60	$CHCl_3$	28
	2.4	–20–60	$CHCl_3$	109
	2.43	–20–40	$CHCl_3$	104
	2.3	–60–100	Toluene	28
$[RhCl_6]^{3-}$	2.3	3–35	H_2O	111
$[Rh(OH_2)_6]^{3+}$	2.0	3–35	H_2O	111
$[Co(ox)_3]^{3-}$	1.83	20–80	H_2O	104
$[Co(NH_3)_6]^{3+}$	1.68	75	H_2O	106
	1.42	10	H_2O	106
$[Co(en)_3]^{3+}$	1.5	20–80	H_2O	104
$[Co(tn)_3]^{3+}$	1.5	20–80	H_2O	104
$[Co(S_2CNH_2)_3]$	1.5	20–40	$CHCl_3$	104
$[Co(CN)_6]^{3-}$	1.38	0–80	H_2O	106
$[Co(S_2COC_2H_5)_3]$	1.2	20–70	$CHCl_3$	104
$[PtCl_6]^{2-}$	1.1		H_2O	30
$[Mn(CNCH_3)_6]^+$	0.707	–35–25	CH_3CN	112
$[Pt(CN)_6]^{2-}$	0.51		H_2O	30
$[Ru(CN)_6]^{4-}$	0.48	30–80	D_2O	29
$[V(CO)_6]^-$	0.31	–80–50	TMF	113
$[Mo(CO)_6]$	0.29	40	TMF	87
$[Nb(CO)_6]^-$	0.18		THF	114

nephelauxetic ratio. Determination of $\Delta\delta/\Delta\lambda$ with change in temperature for a few cobalt(III) complexes proved this to be the case [44]. The slopes observed are in good agreement with those predicted from eqn. (15) (Table 3). The medium effects are perhaps best documented for the hexacyanocobaltate(III) ion (Table 4) and the data obtained agree well with the data from eqn. (15). Hence the medium effect is properly interpreted in terms of ligand field parameter changes. This then leaves the medium effect on the latter parameters to be explained.

The solvent effect on the transition energy has been explained as a consequence of second-sphere hydrogen bonding [5,105,107,108]. Increasing pressure strengthens the ligand field due to a shortening of the metal–ligand bond [106]. The effect of temperature on chemical shifts has attracted much attention and chemical shift temperature coefficients have been reported for a number of complexes (Table 5). The effect is explained in terms of a lowering of the excitation energy, owing to increasing occupancy of the higher vibrational levels with a rise in temperature [9,106,113]. The theory also explains the correlation between the temperature coefficients and the paramagnetic shielding [113], which is generally observable (Tables 2 and 5).

C. INTERPRETATION OF METAL NMR CHEMICAL SHIFTS IN COMPLEXES OF LOWER LIGAND FIELD SYMMETRY

(i) Paramagnetic shielding in complexes of lower ligand field symmetry

A lowering of the ligand field symmetry produces anisotropy of the electronic properties of a complex, and the paramagnetic shielding tensor principal components (eqn. (1)) would as a rule be unequal. For example, in complexes of D_{4h} ligand field symmetry, the first excited singlet state of ${}^1T_{1g}$ symmetry in O_h descends to ${}^1A_{2g}+{}^1E_g'+{}^1E_g''$ symmetries. Therefore new wavefunctions of the ground and the first excited singlet configurations are obtained:

$$\begin{aligned}
&(b_{2g})^2(e_g')^2(e_g'')^2: && \varphi^0({}^1A_{1g})\\
&(b_{2g})(e_g')^2(e_g'')^2(b_{1g}): && \varphi^1({}^1A_{2g})\\
&(b_{2g})^2(e_g')(e_g'')^2\left(-\tfrac{1}{2}b_{1g}+\frac{\sqrt{3}}{2}a_{1g}\right): && \varphi^1({}^1E_g')\\
&(b_{2g})^2(e_g')^2(e_g'')\left(-\tfrac{1}{2}b_{1g}-\frac{\sqrt{3}}{2}a_{1g}\right): && \varphi^1({}^1E_g'')
\end{aligned}$$

Here $\varphi^k(\Gamma_i)$ are appropriate antisymmetrized products of the following one-electron functions:

$$b_{2g} = a_\pi d_{xy} + b_\pi \phi_\pi \qquad b_{1g} = a_\sigma d_{x^2-y^2} + b_\sigma \phi_\sigma$$

$$e'_g = a'_\pi d_{xz} + b'_\pi \phi'_\pi \qquad a_{1g} = a'_\sigma d_{z^2} + b'_\sigma \phi'_\sigma$$

$$e''_g = a''_\pi d_{yz} + b''_\pi \phi''_\pi$$

The orbital angular momentum operator also descends in symmetry, so that the L_x component has symmetry ${}^1E''_g$, L_y symmetry ${}^1E'_g$ and L_z component symmetry ${}^1A_{2g}$. Applying eqn. (1) and disregarding the effect of configurational interaction, which was shown to be small, the paramagnetic shielding along the principal axes in D_{4h} symmetry is obtained [39,115]:

$$\begin{aligned}
\sigma^{\mathrm{P}}_{zz} &= -\frac{\mu_0 e^2}{4\pi m^2} \frac{\left\langle \varphi^0\left({}^1A_{1g}\right) | L_z | \varphi^1\left({}^1A_{2g}\right)\right\rangle \left\langle \varphi^1\left({}^1A_{2g}\right) | L_z r^{-3} | \varphi^0\left({}^1A_{1g}\right)\right\rangle}{\Delta E\left({}^1A_{1g} \rightarrow {}^1A_{2g}\right)} \\
&= -\frac{\mu_0 e^2}{4\pi m^2} \frac{\left\langle b_{2g} | L_z | b_{1g}\right\rangle \left\langle b_{1g} | L_z r^{-3} | b_{2g}\right\rangle}{\Delta E\left({}^1A_{1g} \rightarrow {}^1A_{2g}\right)} \\
\sigma^{\mathrm{P}}_{xx} = \sigma^{\mathrm{P}}_{yy} &= -\frac{\mu_0 e^2}{4\pi m^2} \frac{\left\langle \varphi^0\left({}^1A_{1g}\right) | L_z | \varphi^1\left({}^1E_g\right)\right\rangle \left\langle \varphi^1\left({}^1E_g\right) | L_z r^{-3} | \varphi^0\left({}^1A_{1g}\right)\right\rangle}{\Delta E\left({}^1A_{1g} \rightarrow {}^1E_g\right)} \\
&= -\frac{\mu_0 e^2}{4\pi m^2} \frac{\left\langle e'_g | L_y | -\tfrac{1}{2} b_{1g} + \frac{\sqrt{3}}{2} a_{1g}\right\rangle \left\langle -\tfrac{1}{2} b_{1g} + \frac{\sqrt{3}}{2} a_{1g} | L_y r^{-3} | e'_g\right\rangle}{\Delta E\left({}^1A_{1g} \rightarrow {}^1E_g\right)}
\end{aligned} \tag{16}$$

The covalency ratios must be defined for each component:

$$\begin{aligned}
\eta_{\sigma\pi}\left({}^1A_{2g}\right) &= \frac{\langle b_{2g} | L_z | b_{1g}\rangle \langle b_{1g} | L_z r^{-3} | b_{2g}\rangle}{\langle d_{xy} | L_z | d_{x^2-y^2}\rangle \langle d_{x^2-y^2} | L_z r^{-3} | d_{xy}\rangle} \\
\eta_{\sigma\pi}\left({}^1E_g\right) &= \frac{\left\langle e'_g | L_y | -\tfrac{1}{2} b_{1g} + \frac{\sqrt{3}}{2} a_{1g}\right\rangle \left\langle -\tfrac{1}{2} b_{1g} + \frac{\sqrt{3}}{2} a_{1g} | L_y r^{-3} | e'_g\right\rangle}{\langle d_{yz} | L_x | d_{x^2-z^2}\rangle \langle d_{y^2-z^2} | L_y r^{-3} | d_{yz}\rangle}
\end{aligned} \tag{17}$$

from which eqn. (16) may be rewritten as

$$\begin{aligned}
\sigma^{\mathrm{P}}_{zz} &= -8 \frac{\mu_0 \mu_{\mathrm{B}}^2}{\pi} \langle r_d^{-3} \rangle_{\mathrm{F}} \frac{\eta_{\sigma\pi}\left({}^1A_{2g}\right)}{\Delta E\left({}^1A_{2g}\right)} \\
\sigma^{\mathrm{P}}_{xx} = \sigma^{\mathrm{P}}_{yy} &= -8 \frac{\mu_0 \mu_{\mathrm{B}}^2}{\pi} \langle r_d^{-3} \rangle_{\mathrm{F}} \frac{\eta_{\sigma\pi}\left({}^1E_g\right)}{\Delta E\left({}^1E_g\right)}
\end{aligned} \tag{18}$$

In solution, the average paramagnetic shielding is observed:

$$\sigma^{\mathrm{P}} = \tfrac{1}{3}\left(\sigma^{\mathrm{P}}_{xx} + \sigma^{\mathrm{P}}_{yy} + \sigma^{\mathrm{P}}_{zz}\right)$$

$$= -8\frac{\mu_0\mu_{\mathrm{B}}^2}{\pi}\langle r_d^{-3}\rangle_{\mathrm{F}}\left[\frac{1}{3}\frac{\eta_{\sigma\pi}\left({}^1A_{2\mathrm{g}}\right)}{\Delta E\left({}^1A_{2\mathrm{g}}\right)} + \frac{2}{3}\frac{\eta_{\sigma\pi}\left({}^1E_{\mathrm{g}}\right)}{\Delta E\left({}^1E_{\mathrm{g}}\right)}\right] \qquad (19)$$

By analogous procedures the paramagnetic shielding expression can also be obtained for other symmetries [115]. The final expressions for some common lower ligand field symmetry complexes are as follows:

For MA_5B

$$\sigma^{\mathrm{P}}(C_{4\mathrm{v}}) = -8\frac{\mu_0\mu_{\mathrm{B}}^2}{\pi}\langle r_d^{-3}\rangle_{\mathrm{F}}\left[\frac{1}{3}\frac{\eta_{\sigma\pi}\left({}^1A_2\right)}{\Delta E\left({}^1A_2\right)} + \frac{2}{3}\frac{\eta_{\sigma\pi}\left({}^1E\right)}{\Delta E\left({}^1E\right)}\right]$$

For *cis*-MA_4B_2

$$\sigma^{\mathrm{P}}(C_{2\mathrm{v}}) = -8\frac{\mu_0\mu_{\mathrm{B}}^2}{\pi}\langle r_d^{-3}\rangle_{\mathrm{F}}\left[\frac{1}{3}\frac{\eta_{\sigma\pi}\left({}^1B_1\right)}{\Delta E\left({}^1B_1\right)} + \frac{2}{3}\frac{\eta_{\sigma\pi}\left({}^1A_2, {}^1B_2\right)}{\Delta E\left({}^1A_2, {}^1B_2\right)}\right]$$

For *mer*-MA_3B_3

$$\sigma^{\mathrm{P}}(C_{2\mathrm{v}}) = -8\frac{\mu_0\mu_{\mathrm{B}}^2}{\pi}\langle r_d^{-3}\rangle_{\mathrm{F}}\left[\frac{1}{3}\frac{\eta_{\sigma\pi}\left({}^1B_1\right)}{\Delta E\left({}^1B_1\right)} + \frac{1}{3}\frac{\eta_{\sigma\pi}\left({}^1A_2\right)}{\Delta E\left({}^1A_2\right)} + \frac{1}{3}\frac{\eta_{\sigma\pi}\left({}^1B_2\right)}{\Delta E\left({}^1B_2\right)}\right] \qquad (20)$$

For *fac*-MA_3B_3

$$\sigma^{\mathrm{P}}(C_{3\mathrm{v}}) = -8\frac{\mu_0\mu_{\mathrm{B}}^2}{\pi}\langle r_d^{-3}\rangle_{\mathrm{F}}\frac{\eta_{\sigma\pi}\left({}^1A_2, {}^1E\right)}{\Delta E\left({}^1A_2, {}^1E\right)}$$

For *trans*-MA_4B_2-type complexes the paramagnetic shielding expression is given by eqn. (19).

In some cases, anisotropic metal chemical shifts have been measured in the solid complexes (Table 6). These data are in agreement with the prediction based on the ligand field symmetry in that shielding components involving ${}^1E$ terms (δ_{xx} and δ_{yy} in $C_{4\mathrm{v}}$ and $D_{4\mathrm{h}}$ symmetries) are similar. Also, it may be noted that the shielding component involving the ${}^1A_2$ term (δ_{zz} in $C_{4\mathrm{v}}$ and $D_{4\mathrm{h}}$ symmetries) is only slightly influenced by ligands lying on the z axis, which would be expected if there were no ligand mutual interaction. For a few complexes from Table 6, anisotropic optical transitions have been determined from the circularly polarized electronic spectra of single crystals [119]. This allows calculation of the anisotropic covalency

TABLE 6

Metal NMR chemical shift tensor principal components (δ_{xx}, δ_{yy}, δ_{zz}) in some lower ligand field symmetry complexes of manganese(I) and cobalt(III)

Ligand field symmetry	Complex	δ_{xx}	δ_{yy}	δ_{zz} [a]	Ref.
C_{4v}	$[Mn(CO)_5Cl]$	0.5	0.6	1.9	116
	$[Mn(CO)_5Br]$	0.6	0.7	1.9	116
	$[Mn(CO)_5I]$	1.0	1.0	2.0	116
	$[Co(NH_3)_5(OH_2)](ClO_4)_3$	10.1	10.1	7.1	117
	$[Co(NH_3)_5(CN)]Cl_2$	6.0	5.9	8.2	118
D_{4h}	*trans*-$[Co(en)_2Cl_2]Cl \cdot HCl \cdot H_2O$	10.6	10.9	6.1	118
	trans-$[Co(en)_2(NO_2)_2]NO_2$	6.2	6.5	6.1	118
C_{2v}	$[Co(NH_3)_4CO_3]Br$	9.9	10.4	8.9	118

[a] $\delta(^{55}Mn)$ in parts per thousand from MnO^{4-}; $\delta(^{59}Co)$ in parts per thousand from $[Co(CN)_6]^{3-}$.

ratios by applying eqns. (18)–(20). The covalency ratios (Table 7) involving the $^1A_{1g} \rightarrow {}^1A_{2g}$ transition in bis(ethylenediamine)cobalt(III) complexes are practically the same as the covalency ratio of the tris(ethylenediamine) cobalt(III) complex (Table 2a). This would be expected if there were no ligand mutual interaction, since the transition is influenced only by the ethylenediamine ligands [120].

The application of eqn. (20) for the interpretation of chemical shifts in solution in terms of optical parameters is difficult. Most lower symmetry complexes exhibit an asymmetric first *d–d* absorption band which, however, does not usually allow determination of the principal transition energies. When this is possible, eqn. (20) can be used [115,121]. A specific case is represented by complexes of *fac*-MA_3B_3 type (C_{3v} symmetry) (Table 8) which are isotropic owing to the accidental degeneracy of A and E terms.

TABLE 7

Anisotropic optical transition energies [118,119] and calculated anisotropic covalency ratios ($\eta_{\sigma\pi}$) for some cobalt(III) lower ligand field symmetry complexes

Complex	Transition energy (cm^{-1})	Covalency ratio
$[Co(en)_2Cl_2]Cl \cdot HCl \cdot H_2O$	$\Delta E(^1A_{1g} \rightarrow {}^1A_{2g}) = 22700$	$\eta_{\sigma\pi}(^1A_{2g}) = 0.47$
	$\Delta E(^1A_{1g} \rightarrow {}^1E_g) = 16000$	$\eta_{\sigma\pi}(^1E_g) = 0.45$
$[Co(en)_2(NO_2)_2]NO_2$	$\Delta E(^1A_{1g} \rightarrow {}^1A_{2g}) = 22000$	$\eta_{\sigma\pi}(^1A_{2g}) = 0.46$
	$\Delta E(^1A_{1g} \rightarrow {}^1E_g) = 23000$	$\eta_{\sigma\pi}(^1E_g) = 0.49$
$[Co(NH_3)_5(OH_2)](ClO_4)_3$	$\Delta E(^1A_{1g} \rightarrow {}^1E_g) = 20900$	$\eta_{\sigma\pi}(^1A_2) = 0.47$
	$\Delta E(^1A_1 \rightarrow {}^1E) = 19700$	$\eta_{\sigma\pi}(^1E) = 0.54$

TABLE 8

Metal NMR chemical shift (δ, ${}^1A_1 \rightarrow {}^1A_2$, ${}^1E$ (σ_1) and ${}^1A_1 \rightarrow {}^1A_1$, ${}^1E$ (σ_2) electronic transition energies, and nephelauxetic ratios (β_{35}) of some C_{3v} ligand field symmetry complexes

Complex	δ (ppm)	$\sigma_1/10^3$ (cm^{-1})	$\sigma_2/10^3$ (cm^{-1})	β_{35} [a]	Ref. [b]
fac-$[Co(CN)_3(CNMe)_3]$	−136	32.40	39.22	0.42	122, 122
fac-$[Co(CN)_3(NH_3)_3]$	3314	26.32	34.50	0.52	123, 124
fac-$[Co(NH_3)_3(OH_2)_3]$	10780	18.95	27.50	0.59	125, 126
fac-$[CoCl_3(NH_3)_3]$	10500	15.60	22.0	0.48	122, 126
fac-$[RhCl_3(OH_2)_3]$	8753	21.1	26.7	0.53	111, 127

[a] Calculated using the Schäffer intermediate ligand field strength formula [46]. [b] The first reference is for the metal chemical shifts, the second for the optical data.

Their solution spectra could be used in much the same way as those of the octahedral ligand field symmetry complexes. The interpretation of their metal chemical shifts in terms of eqn. (15) is as successful as for octahedral ligand field complexes (Fig. 8).

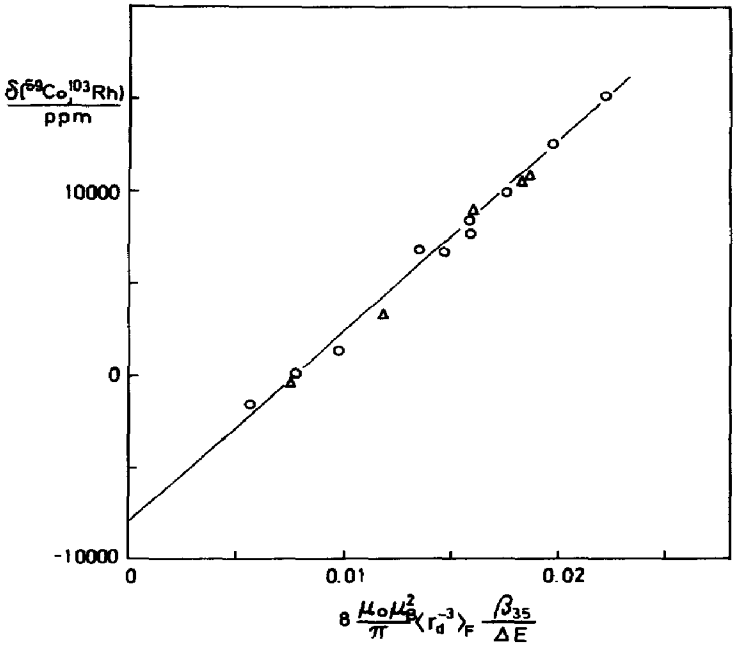

Fig. 8. Correlation of metal NMR chemical shifts with ligand field parameter expressed paramagnetic shielding for C_{3v} ligand field symmetry complexes (△) of cobalt(III) and rhodium(III) in comparison with the corresponding correlation for O_h ligand field symmetry complexes (○).

(ii) *Effect of geometrical isomerism on metal chemical shifts*

The interpretation of metal chemical shifts in complexes of lower than octahedral ligand field symmetry involves understanding the effect of geometrical isomerism on these shifts. The effect is very pronounced, and differences in chemical shifts as large as 500 ppm have been observed between various geometrical isomers.

The effect was considered to be stereochemical, as a consequence of different geometrical arrangements of ligands, which themselves are essentially of constant properties and mutually non-interacting. However, it could also be considered a consequence of a ligand mutual interaction, which is known to be highly specific and different in *cis* and *trans* complexes. The former possibility is of greater interest since it would lead to some general regularity. An investigation into the effect of geometrical configuration on metal chemical shifts in mixed-ligand complexes of $MA_{6-n}B_n$ type has shown this to be the case [128].

The essence of the calculation of the stereochemical effect can be seen in the example of *trans*-MA_4B_2-type complexes. These complexes possess D_{4h} symmetry and the paramagnetic shielding along the principal axes is given in eqn. (16). The shielding along any of the axes involves molecular orbitals formed between metal and ligands in the plane perpendicular to the axis (Fig. 9). Ligand bonding properties are considered to be the same as in MA_6

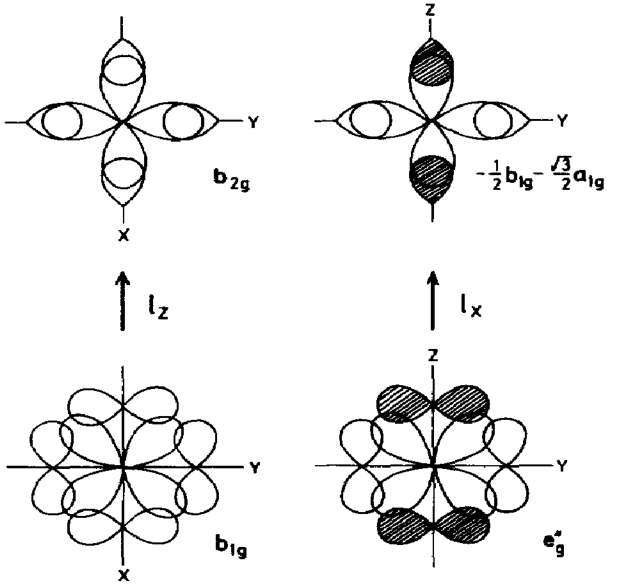

Fig. 9. Molecular orbitals and orbital angular momentum operators involved in the paramagnetic shielding along z and x axes of D_{4h} ligand field symmetry complexes.

or MB_6 complexes. Therefore it follows that $\sigma_{zz}^{P} = \sigma_{A}^{P}$. The shielding along x and y axes is influenced by A and B ligands. The influence goes both through the excitation energy and through the covalency ratio. Since ligands are considered mutually non-interacting, it is rightly supposed that ligand contributions to the excitation energy or to the covalency ratio are additive. Hence the paramagnetic shielding is given by

$$\sigma_{xx}^{P} = \sigma_{yy}^{P} = -8\frac{\mu_0\mu_B^2}{\pi}\langle r_d^{-3}\rangle_F \frac{2\eta_A + 2\eta_B}{2\Delta E_A + 2\Delta E_B}$$

$$= \frac{1}{1+a}(\sigma_A + a\sigma_B), \tag{21}$$

where $a = \Delta E_B/\Delta E_A$. In solution, an average value is measured, so that the chemical shift of the *trans*-MA_4B_2 complex could be expressed through the chemical shifts of MA_6 and MB_6 complexes [128]:

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

The same procedure is applicable to all members of the $MA_{6-n}B_n$ series of complexes [128]. The expressions obtained (Table 9) predict different chemical shifts for the isomeric pairs of complexes. For an easier analysis of the trends in the stereochemical effect, it was convenient to follow the deviation of the reduced chemical shifts from additivity: $(\delta_n - \delta_A)/(\delta_B - \delta_A) - n/6$. Analysis has shown that complexes whose metal chemical shifts are mainly governed by the spectrochemical ligand properties ($a < 1$, $\delta_B > \delta_A$) should exhibit negative chemical shift deviations from additivity and higher chemical shifts for *trans* than for *cis* isomers. Complexes whose metal chemical shifts are mainly governed by the nephelauxetic ligand properties ($a > 1$, $\delta_B > \delta_A$) should exhibit positive chemical shift deviations from additivity and a lower chemical shift for *trans* than for *cis* isomers. An illustration of the predicted behaviour is presented in Fig. 10. Quantitative agreement is obtained when the ligands in a complex are very similar, e.g. $PtCl_{6-n}Br_n$, but only qualitative when ligands are more different. Generally, qualitative agreement is obtained and the great majority of complexes exhibit "spectrochemical" or "nephelauxetic" behaviour [128]. As an illustration of this statement, the chemical shifts of two series of isomeric pairs of complexes are presented in Table 10, together with the chemical shift order predicted from the equations in Table 9. The excellent agreement underlines the importance of the stereochemical effect on metal chemical shifts of geometrical isomers.

There is as yet a small group of complexes in which the metal chemical shifts exhibit another kind of behaviour with respect to geometrical isomer-

TABLE 9

Theoretical expressions for stereochemically dependent metal NMR chemical shift (δ_n) in $MA_{6-n}B_n$ complexes as a function of the electronic transition energy ratio ($a = \Delta E_B / \Delta E_A$)

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

TABLE 10

Metal NMR chemical shifts (δ) of geometrical isomers of $Co(en)_2L_2$ and $PtCl_4L_2$ complexes

Complex	δ_c [a] (ppm)	δ_t [a] (ppm)	Ref.	Predicted [b]
$[Co(en)_2(CN)_2]^+$	4379	4727	53	$\delta_c < \delta_t$
$[Co(en)_2(NO_2)_2]^+$	6660	6580	60	$\delta_c > \delta_t$
$[Co(en)_2(NH_3)_2]^{3+}$	7468	7470	128	$\delta_c < \delta_t$
$[Co(en)_2(NCS)_2]^+$	7952	8010	128	$\delta_c < \delta_t$
$[Co(en)_2(N_3)_2]^+$	8763	9092	53	$\delta_c < \delta_t$
$[Co(en)_2Br_2]^+$	8764	8982	53	$\delta_c < \delta_t$
$[Co(en)_2Cl_2]^+$	8974	9333	53	$\delta_c < \delta_t$
$[Co(en)_2(OH)_2]^+$	9358	9388	123	$\delta_c < \delta_t$
$[PtCl_4(PMe_3)_2]$	1249	1965	30	$\delta_c < \delta_t$
$[PtCl_4(AsMe_3)_2]$	1454	1830	30	$\delta_c < \delta_t$
$[PtCl_4(SMe_2)_2]$	2116	2178	30	$\delta_c < \delta_t$
$[PtCl_4Br_2]^{2-}$	3283	3271	129	$\delta_c > \delta_t$
$[PtCl_4(NO_2)_2]^{2-}$	4716	4349	144	$\delta_c > \delta_t$
$[PtCl_4(OH_2)_2]$	4862	4983	100	$\delta_c > \delta_t$
$[PtCl_4(OH)_2]^{2-}$	4716	4349	100	$\delta_c > \delta_t$

[a] Relative to the chemical shift of the corresponding hexacyano ion in aqueous solution. [b] Applying the equations in Table 9.

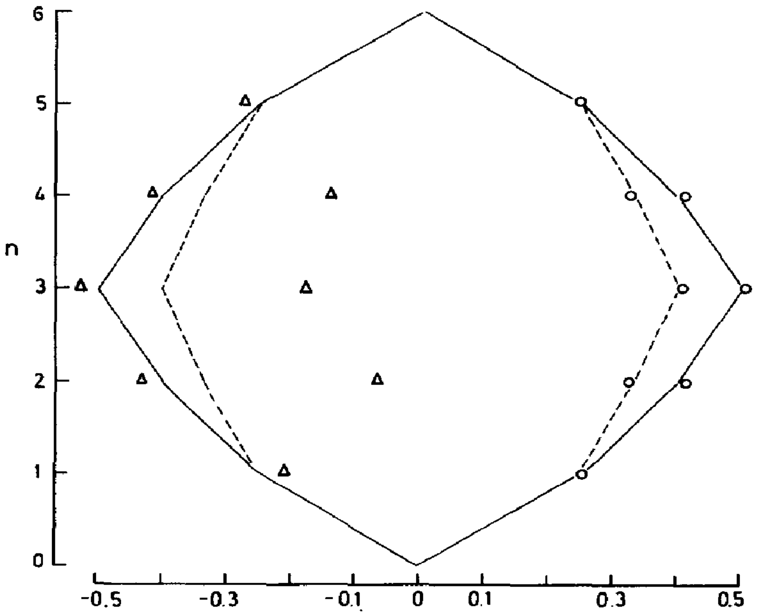

Fig. 10. Reduced metal NMR chemical shift deviations from additivity of ligand contributions to metal chemical shifts, $[(\delta_n - \delta_A)/(\delta_B - \delta_A) - n/6](a+1)/(a-1)$, for $n = 1$–6. The full line connects the theoretical points for *cis* isomers and the broken line connects the points for *trans* isomers. Experimental points are those for $[Co(ox)_x(gly)_y(en)_z]^{3-y-2x}$ (△) and those for $[PtBr_{6-n}Cl_n]^{2-}$ (○) complexes [60,129].

ism. Thus in the complexes $Mo(CO)_{6-n}(P(OMe)_3)_n$ [87], $W(CO)_{6-n}(P(OMe)_3)_n$ [87], $Co(P(OMe)_3)_{6-n}(P(OCH_2)_3CC_2H_5)_n$ [73], $Co(NO_2)_{6-n}(NH_3)_n$ [123], $RhCl_{6-n}(OH_2)_n$ [111] and $PtCl_{6-n}(OH_2)_n$ [100] the chemical shift deviation from additivity is negative, but *cis* isomers exhibit higher chemical shifts than *trans* isomers. These are examples of the influence of ligand mutual interaction on chemical shifts [128]. In the first four series the bulkyness of the phosphites or of nitro groups causes strong repulsion of the *cis* oriented ligands. This weakens the ligand field strength and causes the observed behaviour. In the last two series, the aqua ligand is suspected to be the cause of the observed behaviour, since the corresponding hydroxo complexes exhibit "normal", nephelauxetic-type behaviour (see Table 10).

D. CONCEPTS ON LIGAND AND METAL CONTRIBUTIONS TO METAL CHEMICAL SHIFTS

(i) Magnetochemical series of ligands

Ligand contributions to shielding are considered in terms of the magnetochemical series of ligands [44]. The series is obtained when ligands are ordered according to increasing magnetic shielding of the metal nucleus. This magnetochemical series is closely comparable to the ligand field strength series [130]. Thus the ligand field strength, $\Sigma = \Delta/B$, is, to a good approximation, inversely proportional to $\beta_{35}/\Delta E(^1A_{1g} \rightarrow {}^1T_{1g})$, and consequently $\sigma^{\mathrm{P}} \approx \Sigma^{-1}$.

The spectrochemical series and the magnetochemical series are not independent of metal, while the spectrochemical and nephelauxetic series of ligands [36] are mainly independent of metal ion. Ligand positions in the magnetochemical series are influenced by ligand position in both the spectrochemical and nephelauxetic series, which makes this position in many cases dependent on the metal ion. For instance, the spectrochemical series of some often-encountered ligands is $\mathrm{CO} > \mathrm{P(OR)_3} > \mathrm{CN^-} > \mathrm{diars} > \mathrm{en} > \mathrm{NH_3} > \mathrm{ox^{2-}} > \mathrm{dtc^-} > \mathrm{F^-} > \mathrm{N_3^-} > \mathrm{dtp^-} > \mathrm{Cl^-} > \mathrm{Br^-} > \mathrm{I^-}$, while for the same ligands the nephelauxetic series is $\mathrm{diars} \approx \mathrm{I^-} < \mathrm{P(OR)_3} < \mathrm{dtc^-} < \mathrm{dtp^-} < \mathrm{N_3^-} < \mathrm{Br^-} < \mathrm{Cl^-} < \mathrm{CN^-} \approx \mathrm{CO} < \mathrm{ox^{2-}} < \mathrm{en} < \mathrm{NH_3} < \mathrm{F^-}$.

A ligand which is to precede another in the magnetochemical series must occupy a higher position in the spectrochemical series and a lower position in the nephelauxetic series. With this in mind the following orders arise:

$$\begin{array}{l}
000036\mathrm{CO} > \mathrm{CN^-} > \mathrm{en} > \mathrm{NH_3} > \mathrm{OH_2} > \mathrm{F^-} \\
\mathrm{diars} > \mathrm{dtc^-} > \mathrm{dtp^-} > \mathrm{Br^-} \\
\mathrm{P(OR)_3} > \mathrm{dtc^-} > \mathrm{N_3^-} \\
\mathrm{diars} > \mathrm{en} \\
\mathrm{dtp^-} > \mathrm{Cl^-} \\
\mathrm{dtc^-} > \mathrm{F^-}
\end{array} \tag{22}$$

TABLE 11

Magnetochemical series of ligands

Metal	Ligand order in the series	Ref.
V(−I)	$\mathrm{CO} \approx \mathrm{PF_3} > \mathrm{P(OMe)_3} > \mathrm{CN^-} > \mathrm{NH_3}$; $\mathrm{I^-} > \mathrm{Br^-} > \mathrm{Cl^-}$	84, 131, 132
M(0)	$\mathrm{CO} > \mathrm{P(OMe)_3} > \mathrm{CN^-} > \mathrm{I^-} > \mathrm{Br^-} > \mathrm{Cl^-}$; $\mathrm{dtc^-} > \mathrm{dtp^-}$	87, 88, 133, 134
Mn(I)	$\mathrm{P(OMe)_3} > \mathrm{CO} > \mathrm{I^-} > \mathrm{Br^-} > \mathrm{Cl^-}$; $\mathrm{CO} > \mathrm{CNMe}$	15, 90, 92, 132
Tc(I)	$\mathrm{CO} > \mathrm{CNMe} > \mathrm{P(OMe)_3} > \mathrm{Br^-}$	93, 135
Ru(II)	$\mathrm{CO} > \mathrm{CNMe} > \mathrm{CN^-} > \mathrm{dipy} > \mathrm{en} > \mathrm{NH_3} > \mathrm{OH_2}$; $\mathrm{I^-} > \mathrm{Cl^-}$	29, 78, 80, 82
Co(III)	$\mathrm{P(OMe)_3} > \mathrm{diars} > \mathrm{CN^-} > \mathrm{dipy} > \mathrm{dtc^-} > \mathrm{en} > \mathrm{NO_2^-} > \mathrm{NH_3} > \mathrm{I^-} > \mathrm{Br^-} \approx \mathrm{acac^-} > \mathrm{Cl^-} > \mathrm{OH_2} > \mathrm{F^-}$	28, 39–46, 53, 56, 57, 60–64, 73, 75, 76, 136, 137
Rh(III)	$\mathrm{CNR^-} > \mathrm{I^-} > \mathrm{NO_2^-} > \mathrm{Br^-} > \mathrm{Cl^-} > \mathrm{acac^-} > \mathrm{OH_2}$	30, 96–98
Pt(IV)	$\mathrm{I^-} > \mathrm{CH_3} > \mathrm{CN^-} > \mathrm{Br^-} > \mathrm{en} > \mathrm{NH_3} > \mathrm{Cl^-} > \mathrm{NO_2^-} > \mathrm{OH_2} > \mathrm{F^-}$	30, 102, 103, 139

This may be compared with the magnetochemical series established so far (Table 11). General statements on the ligand order in the magnetochemical series given above (eqn. (22)) are never violated.

For most ligands containing first period ligating atoms, the magnetochemical series is independent of metal ion [138]. The most variable ligand in the magnetochemical series is the iodine ligand. It may be the most shielding ligand when bound to a metal which induces high nephelauxetism, e.g. platinum(IV). In the other extreme, it may be found almost as deshielding as the aqua ligand, for instance in cobalt(III) complexes.

The relative order of the halogeno ligands in the magnetochemical series must be considered uncertain because of their similar order in the spectrochemical and nephelauxetic series. However, all d^6 metals studied so far induce high enough nephelauxetism for metal shielding of so-called "normal halogen dependence" [30] to be observed: $I^- > Br^- > Cl^- > F^-$.

(ii) *Intrinsic shielding sensitivities of metals*

Metal contributions to shielding have been considered in terms of metal intrinsic shielding sensitivities. The metal shielding sensitivities have been deduced by comparison of the chemical shifts of different metals in isoelectronic and isostructural complexes [1,60,80,140]. However, the approach encountered difficulties [6], which is understandable if the nature of the magnetochemical series of ligands is considered. For instance, by comparison of iodo with cyano ligand in pentacyanocobalt(III) and pentacyanoplatinum(IV) complexes [136,141]

$$\delta[\mathrm{Co(CN)_5I}]^{3-} - \delta[\mathrm{Co(CN)_6}]^{3-} = 780 \text{ ppm}$$

$$\delta[\mathrm{Pt(CN)_5I}]^{2-} - \delta[\mathrm{Pt(CN)_6}]^{2-} = -348 \text{ ppm}$$

Thus mutually opposite trends are observed, while substitution of ethylenediamine with the cyano ligand (Table 2) yields

$$\delta[\mathrm{Co(en)_3}]^{3+} - \delta[\mathrm{Co(CN)_6}]^{3-} = 7130 \text{ ppm}$$

$$\delta[\mathrm{Pt(en)_3}]^{4+} - \delta[\mathrm{Pt(CN)_6}]^{2-} = 2910 \text{ ppm}$$

thereby providing a shift in the same sense for both metals. The cause of such behaviour is the very different position of the iodine ligand in the magnetochemical series of cobalt and platinum complexes. Hence it is clear that there is great variability, depending on the complexes chosen for comparison.

A more fundamental approach would be the approach based on eqn. (15). Accordingly the intrinsic shielding sensitivity would depend on the metal

TABLE 12

Self-consistent field values of *d* electron inverse cube distance ($<r_d^{-3}>_{d^6}$) for some transition metal atoms and ions in d^6 electronic configuration

Metal ion (atom)	$\langle r_d^{-3}\rangle_F$ (a.u.)	Ref.
Cr	2.43	51
Mn^+	3.68	51
Fe^{2+}	5.08	51
Co^{3+}	6.65	51
Ni^{4+}	8.54	51
Nb^-	2.73	143
Mo	3.94	143
Tc^+	4.41	143
Ru^{2+}	5.57 [a]	18
Rh^{3+}	7 [c]	18
Re^+	7.23 [b]	18
Os^+	9.18 [a]	18
Ir^{3+}	11.43 [a]	143
Pt^{4+}	13 [c]	18

[a] This is the value for the d^6s^2 configuration. [b] This is the value for the d^6s configuration. [c] Extrapolated from the value for the d^7s^2 configuration of rhodium (6.55) and from the value for the d^8s^2 configuration of platinum (12.01).

radial parameter $\langle r_d^{-3}\rangle_F$ (Table 12) and metal spectrochemical and nephelauxetic properties. The energy of the $^1A_{1g} \rightarrow {}^1T_{1g}$ electronic transition could be factorized into metal and ligand contributions, $\Delta E = ml$ [138,142], so that the metal intrinsic spectrochemical sensitivity depends on the $1/m$ factor. Hence, disregarding for a moment the influence of nephelauxetism, the intrinsic sensitivity would vary as $\langle r_d^{-3}\rangle_F/m$. It is interesting that this ratio does not vary much because $\langle r_d^{-3}\rangle_F$ and m are roughly proportional (Fig. 11). Therefore the influence of the large variations in metal intrinsic spectrochemical sensitivity on the chemical shifts is buffered by the corresponding change in the radial parameter.

The nephelauxetic ratio has been also factorized into metal and ligand contributions: $\beta_{35} = 1 - h$ (ligand) $\times$ k (metal) [36]. However, such factorization of β_{35} does not allow factorization of the paramagnetic shielding term into metal and ligand nephelauxetic contributions. Unlike the excitation energy, the nephelauxetic ratio is not a proportional quantity for different metals. Therefore it is difficult to define a metal nephelauxetic shielding sensitivity. Yet from the factorization of β_{35} it is known that nephelauxetism varies considerably for d^6 metals, and the following order according to decreasing nephelauxetic ratio has been found [36]: ruthenium(II) >

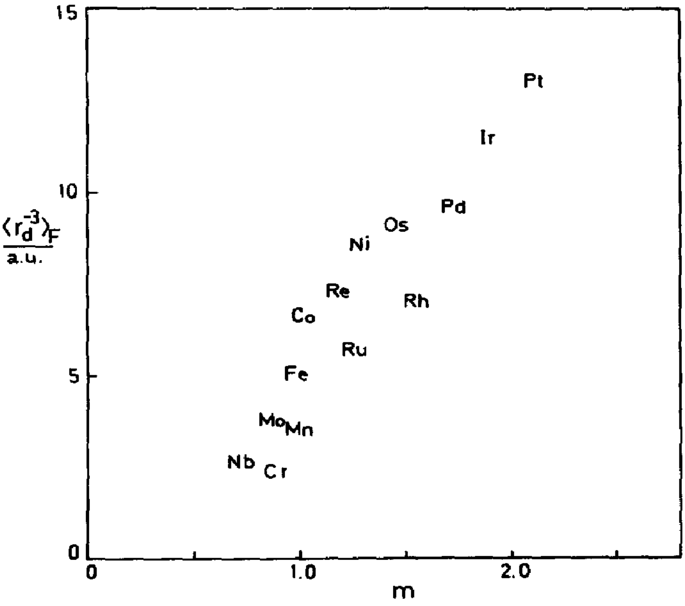

Fig. 11. Free-ion (atom) d-electron inverse cube distance ($\langle r_d^{-3}\rangle_F$, Table 12) correlation with metal complex excitation energy parameter m [142] for d^6 transition metals.

rhodium(III) ≈ iridium(III) > cobalt(III) > platinum(IV) > palladium(IV) > nickel(IV).

An insight into overall metal intrinsic sensitivity could be acquired by comparison of the chemical shifts of complexes of the same nephelauxetic properties. Thus on the basis of eqn. (7), for two complexes of the same nephelauxetic properties but different spectrochemical properties, it follows that

$$\sigma_2^P - \sigma_1^P - \delta_2 = 8\frac{\mu_0\mu_B^2}{\pi}\frac{\langle r_d^{-3}\rangle_F}{m}\eta_{\sigma\pi}\left(\frac{1}{l_1} - \frac{1}{l_2}\right) \tag{23}$$

It is seen that metal contributions to this chemical shift difference depend on the factor $(\langle r_d^{-3}\rangle_F/m)\eta_{\sigma\pi}$, and eqn. (23) could well be applied to the difference in metal chemical shifts obtained upon substitution of cyano with chloro ligand. Large variations in this chemical shift difference are observed, depending on the metal ion: for cobalt(III), ruthenium(II) and platinum(IV), $\delta_{Cl^-} - \delta_{CN^-}$ equals 2000 ppm, 2200 ppm and 600 ppm respectively. The decrease in the sensitivity is in the order ruthenium(III) > cobalt(III) > platinum(IV) and follows strictly the decrease in the nephelauxetic ratio.

(iii) Metal chemical shift parameterization

Concepts on metal and ligand contributions to the chemical shifts ultimately led to chemical shift parameterization [53,125,138]. According to the paramagnetic shielding term expression (eqn. (7)), the specific influences of the metal–ligand bond on the shielding are contained in the covalency ratio $\eta_{\sigma\pi}$ and in the ${}^1A_{1g} \rightarrow {}^1T_{1g}$ electronic transition energy ΔE. Therefore the parameterization of these two quantities into metal-only and ligand-only contributions is the best approach to paramagnetic term parameterization [138]. Since $\eta_{\sigma\pi}$ and ΔE reflect the nephelauxetic and spectrochemical properties of a complex, the parameterization could be expected to follow the parameterization of the spectrochemical and nephelauxetic series [36]. A very good approximation for the excitation energy is to write $\Delta E = ml$. However, the covalency ratio has been parameterized [138] in a different way from the nephelauxetic ratio because the parameterization of the latter ratio [36] is not precise enough (for instance, it predicts negative values for β_{35} in most platinum(IV) complexes). Relying on the evidence that $\eta_{\sigma\pi}$ is linearly related to ligand electronegativities [45], then $\eta_{\sigma\pi}$ is proportional to the difference between ligand and metal electronegativity parameters: $\eta_{\sigma\pi} = a(\chi_L - \chi_M)$ [138]. Consequently, the paramagnetic shielding term is

$$\sigma^{\mathrm{p}} = -8\frac{\mu_0\mu_{\mathrm{B}}^2}{\pi}\langle r_d^{-3}\rangle_{\mathrm{F}}\frac{a(\chi_{\mathrm{L}} - \chi_{\mathrm{M}})}{ml} \tag{24}$$

Chemical shift parameterization requires the diamagnetically shielded metal nucleus chemical shift to be the additional parameter:

$$\begin{aligned}\delta &= \delta^{\mathrm{d}} + 8\frac{\mu_0\mu_{\mathrm{B}}^2}{\pi}\langle r_d^{-3}\rangle_{\mathrm{F}}\frac{a(\chi_{\mathrm{L}} - \chi_{\mathrm{M}})}{ml}\\ &= A + B\frac{\chi_{\mathrm{L}} - \chi_{\mathrm{M}}}{l}\end{aligned} \tag{25}$$

Parameterization with the use of five parameters may not seem a great achievement. However, the parameterization of ΔE is done independently of the chemical shifts, on the basis of experimental excitation energies [138,142]. Furthermore, ligand electronegativity parameters, χ_L, are known for many ligands, being determined from the charge transfer electronic spectra of metal complexes [77].

A good example of the power of the parameterization method is provided by platinum(IV) complexes. For most of them, ligand field parameters cannot be experimentally determined and an interpretation of metal chemical shifts in terms of eqn. (15) is not possible. However, using the parameters for the excitation energy calculation, and the ligand and the metal optical electronegativities, excellent agreement of the platinum chemical shifts with eqn. (25) is obtained (Fig. 12).

E. CONCLUDING REMARKS

The ligand field interpretation of metal NMR chemical shifts in octahedral d^6 complexes may be considered successful. At the present level of

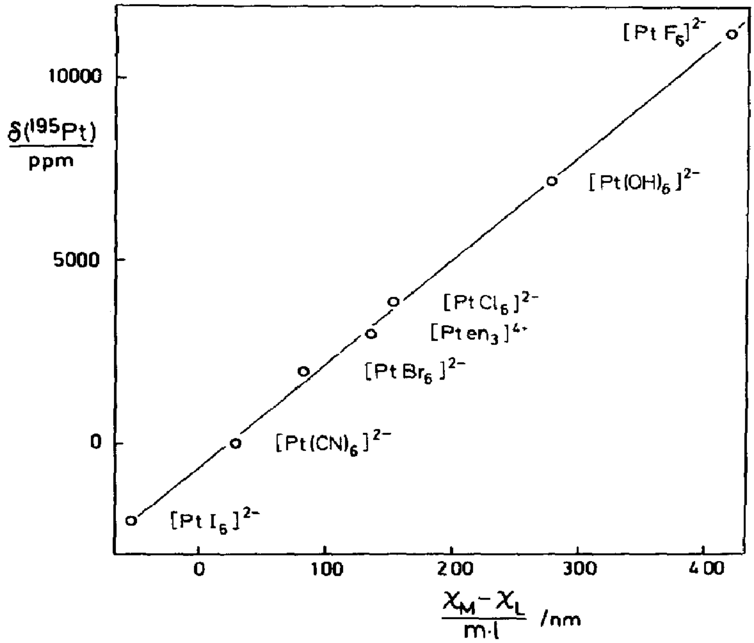

Fig. 12. ^{195}Pt NMR chemical shift correlation with parameterized paramagnetic shielding term. Metal (χ_M) and ligand (χ_L) optical electronegativities given by Jörgensen [77] and *d*-electron excitation energy parameters given by Shimura [142] are used.

sophistication it provides a correct qualitative and in many cases a quantitative account of the metal chemical shift.

For the further developement of the field it is important to determine metal NMR data for many complexes for which the necessary optical data are known (e.g. iron(II), rhodium(III) and iridium(III) complexes) as well as to determine the optical data for complexes for which metal NMR chemical shifts have been measured, e.g. early transition metal complexes. An effort must be made to prepare octahedral d^6 complexes of metals in unusual oxidation states (e.g. vanadium(– I), niobium(– I), nickel(IV)) with a greater variety of ligands.

The ligand field interpretation of metal chemical shifts has not yet presented a proper treatment of the effect of spin–orbit interaction on the shifts. An approximate treatment of the effect on the paramagnetic shielding has been given within the Ramsey theory of shielding, and the estimated contribution to the shielding was found to be small [41]. However, in the presence of spin–orbit coupling, the non-relativistic theory is inaccurate. The relativistic analogue to the Ramsey theory has been presented [145] but its application is rather difficult since no relativistic molecular orbital calculations have been reported to transition metal shielding in complexes. It has been argued that the effect of relativity is large for inner-core electrons and probably small in the paramagnetic shielding [146]. Such an expectation is supported by the interpretation of the platinum chemical shifts in a way analogous to those of the lighter transition metals [138] (see Fig. 12). Nevertheless, proper calculation of the effect is needed.

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