110 K that are too large. These results are in qualitative agreement with Smedarchina et al.'s golden rule tunneling calculation for tetraphenylporphyrin.[13]

Considering the simplicity of the tunneling model, the barrier parameters cannot be taken too literally. Reasonable fits can be obtained for barrier heights of 4400–5700 cm⁻¹, depending on the classical pre-exponential factor. The porphine isomer with the inner hydrogens on adjacent nitrogens has a calculated energy of 1670–1960 cm⁻¹ above the energy of the isomer with hydrogens on opposite nitrogens. The calculated rate for the mono-deuteriated porphine is very close to the rate for the di-deuteriated porphine, which is consistent with experimental results for tetraphenylporphyrin.[10]

Registry No. Porphine, 101-60-0; deuterium, 7782-39-0.

Nephelauxetic Effect in Paramagnetic Shielding of Transition-Metal Nuclei in Octahedral d⁶ Complexes

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Abstract: For transition metals, using reliable d electron radial wave functions, it was calculated that the d electron radial parameters, B_{Racah} and $\langle r_d^{-3} \rangle$, are equally influenced by change in the d-orbital occupancy. On this basis, introduction of the first power of the nephelauxetic ratio into the paramagnetic shielding term of octahedral d⁶-complex transition-metal nuclei is justified. Interpretations of rhodium NMR chemical shifts in rhodium(III) complexes were analyzed.

In the recent interpretation of metal NMR chemical shifts in octahedral d⁶ transition metal complexes,[1] the paramagnetic shielding term (σ^P) has been expressed by the ligand field parameters in the following way:

$$\sigma^P = -8 \frac{\mu_0 \mu_B^2}{\pi} \langle r_d^{-3} \rangle_F \frac{\beta_{35}}{\Delta E} \tag{1}$$

(where μ_0 is the vacuum permeability, μ_B the Bohr magneton, $\langle r_d^{-3} \rangle_F$ the free-ion(atom) expectation value of d electron inverse cube distance, β_{35} the nephelauxetic ratio, and ΔE the energy of the $^1A_{1g} \leftarrow ^1T_{1g}$ electronic transition). Some arguments for incorporation of the nephelauxetic ratio into the paramagnetic shielding term, based on molecular orbital analysis of the covalency effects, have been put forward.[2] However, the general validity of the proposed relationship has been questioned by Bramley et al.,[3] since they would rather expect the third power of the nephelauxetic parameter to be incorporated in the paramagnetic shielding term. They suggested that rhodium chemical shifts in rhodium(III) complexes are in accordance with that expectation. Therefore, I undertook further investigation of the theoretical foundation of eq 1, the results of which are presented here.

Results

Ramsey's theory of nuclear paramagnetic shielding, applied to a metal with d⁶ configuration in a strong octahedral ligand field,[4,5] leads, in the molecular orbital formulation,[2,6] to the expression:

$$\sigma^P = -\frac{\mu_0 e^2}{4\pi m^2} \frac{\langle e_g | \sum_k l_{z,k} | t_{2g} \rangle \langle t_{2g} | \sum_k l_{z,k} r_k^{-3} | e_g \rangle}{\Delta E(^1A_{1g} \leftarrow ^1T_{1g})} \tag{2}$$

(where l_z is orbital angular momentum operator). Molecular orbitals $e_g(t_{2g}^5 e_g;^1T_{1g})$ and $t_{2g}(t_{2g}^6;^1A_{1g})$, which in the ionic limit are reduced to the metal $d_{x^2-y^2}$ and d_{xy} orbitals, respectively, contain information on the metal–ligand bond covalency. As a measure of the impact of covalency on the paramagnetic shielding term, the following ratio may be introduced:[2,7]

$$\eta_{\sigma\pi} = \frac{\langle e_g | \sum_k l_{z,k} | t_{2g} \rangle \langle t_{2g} | \sum_k l_{z,k} r_k^{-3} | e_g \rangle}{\langle d_{x^2-y^2} | \sum_k l_{z,k} | d_{xy} \rangle \langle d_{xy} | \sum_k l_{z,k} r_k^{-3} | d_{x^2-y^2} \rangle} \tag{3}$$

which allows eq 2 to be put into the form:

$$\sigma^P = -8 \frac{\mu_0 \mu_B^2}{\pi} \langle r_d^{-3} \rangle_F \frac{\eta_{\sigma\pi}}{\Delta E} \tag{4}$$

The theoretical foundation of eq 1 depends on whether the covalency ratio $\eta_{\sigma\pi}$ in eq 4 could be replaced by the nephelauxetic ratio β_{35}.

One may compare these two ratios by expressing relevant molecular orbitals as a linear combination of the corresponding atomic orbitals and, under the assumption of a small admixing of ligand into metal orbitals, obtain for $\eta_{\sigma\pi}$:[2]

$$\eta_{\sigma\pi} = a_\sigma^2 a_\pi^2 (\langle r_d^{-3} \rangle_C / \langle r_d^{-3} \rangle_F)$$

or for the nephelauxetic ratio:[8,9]

$$\beta_{35} = a_\sigma^2 a_\pi^2 (B_C / B_F)$$

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(7) Note also that:

$$\eta_{\sigma\pi} = k_{\sigma\pi} \frac{\langle t_{2g} | \sum_k l_{z,k} r_k^{-3} | e_g \rangle}{\langle d_{xy} | \sum_k l_{z,k} r_k^{-3} | d_{x^2-y^2} \rangle} \sim k_{\sigma\pi}^2 \frac{\langle r_d^{-3} \rangle_C}{\langle r_d^{-3} \rangle_F}$$

where $k_{\sigma\pi}$ is the orbital angular momentum reduction factor: Stevans, K. W. H. *Proc. R. Soc. London, Ser. A* **1953**, *219*, 542.
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Table I. Ratio of Racah Parameters $B(d^q)/B(d^6) = (B)$ and of d Electron Radial Parameters $\langle r_d^{-3}\rangle_{d^q}/\langle r_d^{-3}\rangle_{d^3} = (r^{-3})$ and $\langle r_d^{-1}\rangle_{d^q}/\langle r_d^{-3}\rangle_{d^6} = (r^{-1})$, for Selected d^q Configurations, Calculated Using "Double-ζ" Radial Wave Functions of Richardson and Co-workers

	Mn			Fe			Co			Ni		
d^q	(B)	(r^{-3})	(r^{-1})	(B)	(r^{-3})	(r^{-1})	(B)	(r^{-3})	(r^{-1})	(B)	(r^{-3})	(r^{-1})
d^7	0.892	0.891	0.922	0.912	0.910	0.940	0.927	0.923	0.956	0.944	0.934	0.961
d^8				0.820	0.828	0.910	0.858	0.850	0.906	0.881	0.869	0.921
d^9							0.773	0.782	0.848	0.800	0.804	0.876
d^{10}										0.738	0.740	0.827

The expressions show that the impact of symmetry restricted covalency, $a_\sigma^2 a_\pi^2$ (where a_σ and a_π are the population coefficients of $d_{x^2-y^2}$ and d_{xy} metal orbitals, respectively), is the same in both ratios. The central field covalency is contained in the ratio of radial parameters $\langle r_d^{-3}\rangle_C/\langle r_d^{-3}\rangle_F$ and B_C/B_F, where B is the Racah parameter and C denotes parameters of complexed metal and F of a free metal ion (atom). In the applied LCAO approximation, parameters of a complexed metal are to be calculated for the d^q configuration using free ion (atom) wave functions which correspond to the self-consistent charge on the metal in a complex.[8] The parameters of a free ion (atom) are to be calculated for the free ion (atom) d^6 configuration. Therefore, the central field covalency ratios may be denoted also as $\langle r_d^{-3}\rangle_{d^q}/\langle r_d^{-3}\rangle_{d^6}$ and $B(d^q)/B(d^6)$. The question is whether these ratios are of approximately the same value for the d^q configurations of interest.

By using Slater orbitals one would conclude that they are not, because it follows that $B = 389\langle r_d^{-1}\rangle$,[10] and $B(d^q)/B(d^6) = \langle r_d^{-1}\rangle_{d^q}/\langle r_d^{-1}\rangle_{d^6}$; hence the expectation that the third power of the nephelauxetic ratio should be incorporated into the paramagnetic shielding term.[3] However, a single Slater orbital cannot describe accurately d orbitals, as has been shown by Watson.[11] Moreover, the shape of the d orbital is changing with ionization in a way which cannot be taken into account by changing the orbital exponent of a single Slater-type orbital. Namely, in Watson SCF wave functions, which are composed of four Slater-type orbitals, both orbital exponents and participation of individual Slater-type orbitals change with the degree of ionization. This could have dramatic effect on central field covalency ratios considered here.

Richardson and co-workers[12] devised simplified 3d wave functions, composed of two Slater-type orbitals, which are almost as accurate as Watson functions in a comparative calculations.[13] I have, therefore, calculated the considered ratios for different d^q configurations of manganese, iron, cobalt, and nickel using "double-zeta (ζ)" 3d radial functions given by Richardson and co-workers for the different ionization states of these metals. The results obtained are compared in Table I and Figure 1.

As it is seen, $B(d^q)/B(d^6)$ and $\langle r_d^{-3}\rangle_{d^q}/\langle r_d^{-3}\rangle_{d^6}$ follow each other very closely in their reduction with the increasing number of d electrons, never differing more than 2%. Contrary to that, $\langle r_d^{-1}\rangle_{d^q}/\langle r_d^{-1}\rangle_{d^6}$ is not reduced enough to be comparable with $B(d^q)/B(d^6)$. Reasons for this behavior may be found when one considers the importance of the expectation values of B, $\langle r^{-1}\rangle$, and $\langle r^{-3}\rangle$ for the electron SCF energy in multielectron atoms. The most important parameter is $\langle r^{-1}\rangle$ since it is directly related to the electron–nucleus attraction energy. The requirement of the energy minimization would keep the value of $\langle r^{-1}\rangle$ as high as possible. The second in importance is B since it expresses the interelectron repulsion energy, and the requirement of the energy minimization would tend to diminish its value. The least important for the electron energy is $\langle r^{-3}\rangle$, since it is connected with weaker, magnetic, interactions. Therefore, it may be expected generally that upon addition of an electron to a multielectron atom $\langle r^{-1}\rangle$ would be reduced less than B. However, this could be accomplished only if different regions of the orbital wave function are of different importance for $\langle r^{-1}\rangle$ and B. The analysis of the d^6 configuration 3d "double-ζ" wave functions shows that the radial parameters of the "outer" Slater-type function contribute about
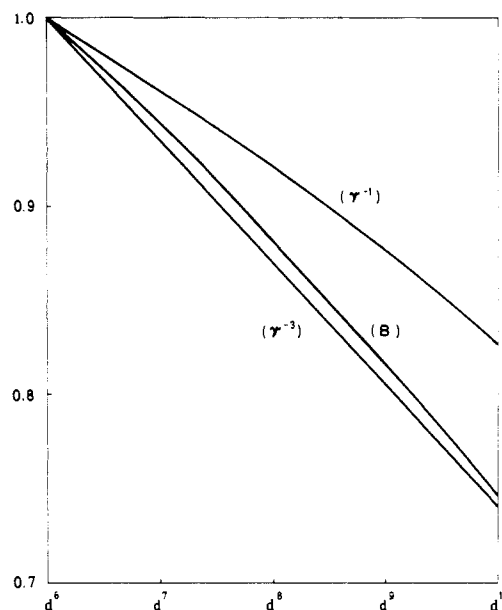
Figure 1. Comparison of the reduction of the central field covalency ratios $(B(d^q)/B(d^6) = (B)$, $\langle r_d^{-3}\rangle_{d^q}/\langle r_d^{-3}\rangle_{d^6} = (r^{-3})$, $\langle r_d^{-1}\rangle_{d^q}/\langle r_d^{-1}\rangle_{d^6} = (r^{-1}))$ with the increasing number of d electrons for Ni.

16% to the total value of $\langle r_d^{-1}\rangle$, but only about 6% to the total value of B or $\langle r_d^{-3}\rangle$. Therefore, a diminishing of the inner and enlarging and expanding of the outer parts of the orbital are observed upon addition of electrons, resulting in the higher reduction of B and $\langle r_d^{-3}\rangle$ than that of $\langle r_d^{-1}\rangle$.

The relativistic 4d and 5d functions, obtained by the multiconfiguration Dirac–Fock method, give the analogous result, as it is seen from the following data on ruthenium and osmium:

	$B(d^7s)/B(d^6s^2)$	$\langle r_d^{-3}\rangle_{d^7s}/\langle r_d^{-3}\rangle_{d^6s^2}$
Ru	0.909	0.916
Os	0.943	0.928

which have been calculated from radial parameters given by Büttgenbach.[14] Again two ratios coincide within 2%.

Therefore, it may be concluded that for the metal complexes of a strong ligand field, in the LCAO approximation of a small ligand in metal orbital admixing, the approximate equivalency of $\eta_{\sigma\pi}$ and β_{35} is proved, and hence eq 1 is well founded.

Finally, a short analysis of interpretation of the rhodium chemical shifts in rhodium(III) complexes is necessary. Bramley et al.[3] suggested that the paramagnetic shielding term in these complexes is proprotional to $\beta_{35}^3/\Delta E$. However, as presented in Figure 2, an approximately linear dependence of chemical shifts is obtained only when they are correlated with $\beta_{35}/\Delta E$. Besides, the reliable estimation of the rhodium nuclear magnetic moment[15] shows that the core electron diamagnetically shielded rhodium chemical shift is around −5000 ppm. This value is an acceptable

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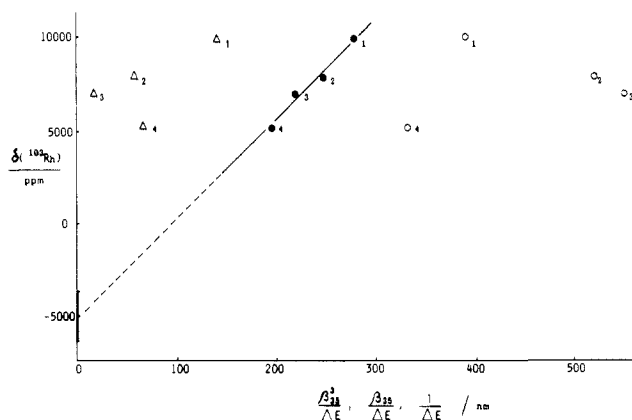(17) Schmidtke, H. Z. Phys. Chem. (Frankfurt) 1964, 40, 96.

Figure 2. Correlation of the rhodium chemical shift of rhodium(III) complexes {1, $[Rh(OH_2)_6]^{3+}$; 2, $[RhCl_6]^{3-}$; 3, $[RhBr_6]^{3-}$; 4, $[Rh(NO_2)_6]^{3-}$} with the ligand field parameters ($1/\Delta E$ (O), $\beta_{35}/\Delta E$ (●), and $\beta_{35}^3/\Delta E$ (▲)). Relevant spectroscopic data for complexes 1–3 have been collected in ref 1b. For the hexanitrorhodate(III) complex, the chemical shift[16] and excitation energy[17] have been reported, while for the nephelauxetic parameter (not experimentally available) the value of the tris(ethylene-diamine)rhodium(III) complex[9] is applied based on the evidence that in cobalt(III) complexes the nephelauxetic effect of nitro and ethylenediamine ligands is the same.[2]

origin only for the correlation of the chemical shifts with $\beta_{35}/\Delta E$. Hence, interpretation of the metal chemical shifts in terms of eq 1 is supported also by data on rhodium(III) complexes.

In the analysis of the metal NMR chemical shifts there remain the question as to whether there is any higher energy contribution to the magnetic shielding, besides that from d–d spin-allowed transitions. In the view of the good linearity, and the correct slope value, of the correlation of the chemical shifts with $\beta_{35}/\Delta E$,[1,3] these contributions should be very small or, very unlikely, invariant on complex composition.

Appendix

For "double-zeta" 3d radial wave functions:

$$R_{3d} = c_1 \frac{(2\zeta_1)^{7/2}}{(6!)^{1/2}} r^2 e^{-\zeta_1 r} + c_2 \frac{(2\zeta_2)^{7/2}}{(6!)^{1/2}} r^2 e^{-\zeta_2 r}$$

the following expression for the Racah parameter B is obtained:

$$B = c_1^4 B(\zeta_1) + c_2^4 B(\zeta_2) + c_3^4 B(\zeta_3) + 2c_1^2 c_2^2 B(\zeta_1,\zeta_2) + 2c_1^2 c_3^2 B(\zeta_1,\zeta_3) + 2c_2^2 c_3^2 B(\zeta_2,\zeta_3)$$

where:

$$c_3^2 = 2c_1 c_2 \frac{(\zeta_1 \zeta_2)^{7/2}}{\zeta_3^7}$$

$$\zeta_3 = (\zeta_1 + \zeta_2)/2$$

$$B(\zeta_i) = 389.15\zeta_i$$

$$B(\zeta_i,\zeta_j) =$$
$$4180\zeta_i a^2 \left\{ 1 - \frac{25a^2}{3}[1 - (1 + a^{-1})^{-2}] + \frac{50}{3}a(1 + a^{-1})^{-3} + \frac{1}{3}(1 + a^{-1})^{-4}[72 + 88(1 + a)^{-1} + 95(1 + a)^{-2} + 90(1 + a)^{-5}] \right\}$$

$$a = \zeta_i/\zeta_j$$

Electron Transfer via Dithiaspiroalkane Linkages. Nature of Long-Range Through-Bond Electronic Coupling in Disulfoxide Radical Cations and Bis(metal) Complexes and Implications for the Characterization of the SO Bond

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Abstract: Electron transfer in bis(ruthenium pentaammine) complexes III–V of the single-, double-, and triple-ring dithiaspiroalkanes is known to be surprisingly facile. The mechanism of donor–acceptor interaction with these rigid nonconjugated bridges is thus of considerable interest. The electronic structure of the series of disulfoxides VI and VII for which photoelectron spectroscopic data are available has been studied in order to investigate this. Ab initio SCF calculations using a variety of basis sets have been carried out, and the ionization potentials (IP's) at Koopmans' theorem, ΔSCF, and projected broken-symmetry levels of approximation, obtained. Calculations were also performed for the related dithiaspiroalkanes, for the single-ring sulfide X and monosulfide IX, for dimethyl sulfoxide, and for ethylene sulfoxide, at the experimental or interpolated geometries. The use of a polarized (3-21G*) rather than an unpolarized (3-21G) basis for IX and the double-ring disulfoxide VI resulted in comparatively small changes in calculated IP's and orbital character. Thus, orbital assignments obtained without the inclusion of 3d functions are judged to be justified. The SO bond is then considered as an essentially semipolar link ($>S^{\delta+}$—$O^{\delta-}$) rather than as one involving hypervalent S ($>S$=O). The observed near constancy of the first IP of dithiaspiroalkanes and their mono- and disulfoxide derivatives is shown to be accidental. The trends in the experimental IP's are well reproduced by calculations, and the nature of the through-bond interaction is related to orbital type. An SO bond lying out of the plane of the thiaspiroalkane ring is necessary for nonzero interaction. Implications for electron transfer in metal complexes and relationships with transfer through rigid hydrocarbon chains are discussed. Through-space effects are equally important in the radical cation of the double-ring molecule VI.

The concept of through-space and through-bond interactions was first introduced by Hoffmann and co-workers nearly 20 years

ago, in interpreting the results of their extended Hückel molecular orbital[1,2] calculations on diradical systems in terms of these types