

$\delta\nu(a)$ and $\delta\nu(b)$. However, $\delta\nu(c)$ is always smaller than both $\delta\nu(a)$ and $\delta\nu(b)$.

A significantly different result is obtained if the single-crystal spectrum of VCl_2 at 22°K is studied.¹⁰ In this case, the values of B_{35} and β_{35} are practically independent of the calculation method.¹¹ The deviation $\delta\nu$ is smaller by a factor of about 10^{-2} than in room-temperature solution spectra, although the order of the various $\delta\nu$ values is preserved. Similarly accurate results have been obtained apparently¹² with a number of V^{2+} -doped single crystals at 4.2°K. It is evident that the simple three-parameter ligand field theory may reproduce accurate experimental values of transition energies quite well.

The reason for the strikingly different results of room-temperature solution spectra *vs.* low-temperature single-crystal spectra seems to be obvious. In ligand field theory, transition energies are calculated always at a constant $10Dq$ (*cf.* "vertical" transitions in a Tanabe-Sugano diagram). Since $10Dq = (5/3)Ze^2\langle r^4 \rangle / R^5$, this corresponds to a fixed metal-ligand distance, R . In addition, the states involved in spin-allowed d-d transitions originate always in different configurations $t_{2g}^m e_g^n$ and, consequently, the potential minima of the excited state and ground state do not coincide. The calculated transition energy corresponds, therefore, to the energy of a transition from the zero-point vibrational level of the electronic ground state to an excited vibrational level of the excited state (*cf.* "vertical" transition according to the Franck-Condon principle). This statement is by no means trivial since a problem in ligand field theory is essentially one of a perturbed atom. Neither do interatomic distances appear explicitly in the calculations nor are vibrational interactions considered. Thus any comparison between theoretical and experimental energies should use the Franck-Condon maxima of the absorption bands determined, in principle, at 0°K (*cf.* footnote 11). These energies may be approximated by the centers of gravity of individual bands in spectra measured at cryogenic temperatures. With increasing temperature, however, higher vibrational levels of the ground state become populated and the corresponding band is progressively shifted to lower energy.¹³ Consequently, at room temperature, *e.g.*, significant differences between calculated and observed band energies should be expected.

Of course, all three spin-allowed d-d bands may be observed only in those complexes of vanadium(II) and chromium(III) which involve weak-field ligands. With most medium- and strong-field ligands, the third band is masked by intense ligand or charge-transfer absorption. It is possible that, with these ligands, larger deviations would be encountered than in the examples discussed here.¹⁴

(10) S. S. Kim, S. A. Reed, and J. W. Stout, *Inorg. Chem.*, **9**, 1584 (1970).

(11) The values of the parameters $10Dq$ and B_{35} calculated here are different from those reported by Kim, *et al.*¹⁰ In their original paper, these authors employed the estimated energy of the $0'' \rightarrow 0'$ transition in the calculation. It will be shown below that this procedure is not appropriate.

(12) W. E. Smith, *J. Chem. Soc. A*, 2677 (1969).

(13) J. Lee and A. B. P. Lever, *J. Mol. Spectrosc.*, **26**, 189 (1968).

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Relative Covalencies from Nuclear Magnetic Resonance Contact Shifts in Isostructural Transition Metal Complexes

Sir:

The capability for detailed mapping of the delocalized spin density over a paramagnetic complex, using nmr contact shifts,¹ allows one, in principle, to arrive at some data which can be related to the metal-ligand covalency if the metal-ligand overlap is known.² The lack of these latter overlap data has placed the emphasis more on evaluating trends in covalency^{1,3-6} in a series of isostructural complexes than on characterizing the covalency in individual cases.² Thus proton nmr studies of isostructural complexes, where either the metal ion was varied³⁻⁵ or the oxidation state of a given metal was altered,⁷ have been used to gauge the relative extents of mixing of the metal and various ligand orbitals. There exist in the literature, however, certain ambiguities as to both the exact form of some of the equations used to obtain the spin density and the nature of the proper index (contact shift, hyperfine coupling constant, spin density, or other variable) from which information on the relative metal-ligand covalency may be derived.

The Hamiltonian for the chemically interesting Fermi contact interaction^{8,9} for a complex possessing m spins is

$$\mathcal{H} = A \tilde{S}^m \cdot \tilde{I} \quad (1)$$

where A is the proton-electron hyperfine coupling constant, \tilde{S}^m is the total electron spin, and \tilde{I} is the nuclear spin operator. For cases of "spin-only" magnetic moments, the proton nmr contact shift is given by the conventional equation^{9,10}

$$\frac{\Delta H}{H} = - \frac{Ag\beta S(S+1)}{(\gamma/2\pi)(3kT)} \quad (2)$$

where $S = S^m$. This coupling constant, A , is further related to the effective spin density, ρ , in the one-electron molecular orbital approximation conventionally used to describe the bonding in metal complexes, by the generalized relationship^{11,12}

$$\rho = \frac{2SA}{Q} \quad (3)$$

For aromatic π -spin density, ρ is the spin density in the carbon $2p_z$ orbital,¹¹ while for σ -spin density,¹² ρ is the proton spin density. The Q 's for π - and σ -spin density are -63 and $+1420$ MHz, respectively. However, dif-

(1) D. R. Eaton and W. D. Phillips, *Advan. Magn. Resonance*, **1**, 103 (1965).

(2) J. Owen and J. H. M. Thornley, *Rep. Progr. Phys.*, **29**, 675 (1966).

(3) B. B. Wayland and R. S. Drago, *J. Amer. Chem. Soc.*, **87**, 2372 (1965).

(4) Z. Luz and R. G. Shulman, *J. Chem. Phys.*, **43**, 3750 (1965).

(5) G. N. La Mar, W. D. Horrocks, Jr., and L. C. Allen, *ibid.*, **41**, 2126 (1964).

(6) D. R. Eaton, *J. Amer. Chem. Soc.*, **87**, 3097 (1965); D. R. Eaton and K. L. Chua, *Can. J. Chem.*, **49**, 56 (1971).

(7) G. N. La Mar and E. O. Sherman, to be submitted for publication.

(8) H. M. McConnell and R. E. Robertson, *J. Chem. Phys.*, **29**, 1361 (1958).

(9) R. J. Kurland and B. R. McGarvey, *J. Magn. Resonance*, **2**, 286 (1970).

(10) We will assume here, for the sake of simplicity, that we have "spin-only" magnetic moments, such that eq 2 is applicable. For more complicated systems, the appropriate equation in ref 9 must be used. As we will emphasize here only the relationships among A , ρ , and the covalency, our assumptions are not too restrictive.

(11) H. M. McConnell, *J. Chem. Phys.*, **24**, 764 (1956).

(12) F. Keffer, T. Oguchi, W. O'Sullivan, and J. Yamashita, *Phys. Rev.*, **116**, 1553 (1959).

ferent approaches have been used here, with $2S$ in eq 3 defined either as $2S^m$, the *total* number of spins,^{2,12} or as the number of spins, $2S^u$, involved^{1,6} in the particular delocalization mechanism which gives rise to the observed contact shift.

The necessity of using $2S = 2S^m$ in eq 3 is demonstrated¹² by equating the expectation value for the m -electron Hamiltonian (eq 1) to the expectation value for an effective hyperfine interaction

$$A\langle\tilde{S}^m \cdot \tilde{I}\rangle = \rho\langle\mathcal{H}_{1s}\rangle \quad (4)$$

where \mathcal{H}_{1s} is the usual one-electron hyperfine Hamiltonian¹¹

$$\mathcal{H}_{1s} = QS' \cdot \tilde{I} \quad (5)$$

with $S' = 1/2$. Since

$$\langle\tilde{S}^m \cdot \tilde{I}\rangle = 2S^m\langle\tilde{S}' \cdot \tilde{I}\rangle \quad (6)$$

we get for the effective fraction of an unpaired electron

$$\rho = \frac{2S^m A}{Q} \quad (7)$$

as discussed by Keffer, *et al.*,¹² for a more general case. Thus eq 7 yields the correct fraction of an unpaired spin at a given nucleus in the complex, which may then be related to the covalency in a molecular orbital approximation.

A second ambiguity has arisen as to the proper index of the relative covalency in a series of isostructural complexes, which has been variously taken as either the spin density,^{5,6} ρ , or the coupling constant,³ A . This problem may be resolved by considering the spin containing MO in a complex, which can be written as²

$$\Psi_A = N(d - \lambda\phi_L) \quad (8)$$

with $N = (1 - 2\lambda D + \lambda^2)^{-1/2}$, where d and ϕ_L are the appropriate 3d and ligand orbitals, λ is the mixing coefficient, and D is the d - ϕ_L overlap.¹³ If the d orbital is singly occupied, the net transfer of spin density to the ligand, or the covalency (in the limit of small λ and D ¹⁴), is given by λ^2 . Therefore, the covalency for a more general MO described by eq 8 can be obtained if the probability of the d orbital containing an unpaired electron is known.¹⁵ For a series of octahedral, O_h , complexes, where the delocalization mechanism in all complexes involves either the σ or π systems (but not both), the relative covalencies can be obtained from the relative spin densities (eq 7) by taking into consideration the spin occupation probability of the subset of the d orbitals (e_g for σ , and t_{2g} for π bonding) according to

$$\lambda^2 \propto \frac{\rho v}{u} \quad (9)$$

where v is the degeneracy of the subset of d orbitals (2 for e_g and 3 for t_{2g}) and u is the number of unpaired spins in that subset; u need not be integral.¹⁶ If all d orbitals of a subset are singly occupied [for example, Cr(III) for t_{2g} and Ni(II) for e_g], the spin density is a direct measure of the covalency. This rule has been

(13) The chemically more interesting bonding orbital, $\Psi_B = N'(\phi_L + \epsilon d)$, can be obtained if Ψ_A is known, by virtue of the orthogonality and normalization of Ψ_A and Ψ_B , with $\epsilon = \lambda - D$.

(14) We assume here that $\lambda \ll 1$ and $D \ll 1$.

(15) See ref 2, in particular, pp 687-688.

(16) C. J. Ballhausen, "Introduction to Ligand Field Theory," McGraw-Hill, New York, N. Y., 1962, pp 69-74.

used^{2,17} in principle in the analysis of the nmr contact shifts in terms of covalency of the transition metal fluoride crystals. Therefore, the relative spin densities are indices of relative covalency only when properly normalized to the spin occupation probability¹⁸ according to eq 9. Since A and ρ are related by S^m , while ρ and λ^2 are related by S^u , both of which may differ between the complexes being compared, neither A nor ρ need be a valid index of the covalency. It is also obvious here that the calculated relative covalencies for a series of complexes containing spins in both the e_g and t_{2g} orbitals will depend on the assumed delocalization mechanism¹⁹ (σ or π), which cannot always be unambiguously characterized, particularly for small ligands exhibiting a single resonance.

The relative effects of different S^m and S^u on calculated covalencies are illustrated for the fictitious hexahydrides of the first-row divalent transition metal ions, $M^{II}H_6^{4-}$, which are analyzed on the basis of spin-only magnetic moments¹⁰ and the weak-field limit¹⁶ in O_h symmetry. The relative coupling constants, spin densities, and covalencies [normalized to Ni(II)], for the case where all complexes exhibit identical contact shifts, are given in Table I.²⁰ The advantage of using the fic-

TABLE I
RELATIVE COUPLING CONSTANTS, SPIN DENSITIES, AND
COVALENCIES FOR $M^{II}H_6^{4-}$ COMPLEXES EXHIBITING
IDENTICAL CONTACT SHIFTS^a

	Cr	Mn	Fe	Co	Ni	Cu
$2S^m$	4	5	4	3	2	1
$2S^u$	1	2	2	$9/5$	2	1
Rel A^b	$1/3A$	$8/35A$	$1/3A$	$8/15A$	A	$8/3A$
Rel ρ^c	$2/3\rho$	$4/7\rho$	$2/3\rho$	$4/5\rho$	ρ	$4/3\rho$
Rel covalency ^d	$4/3\rho$	$4/7\rho$	$2/3\rho$	$8/5\rho$	ρ	$8/3\rho$

^a Coupling constants, spin densities, and covalencies all compared to Ni(II) complex. ^b Calculated from eq 2. ^c Calculated from eq 7. ^d Calculated from eq 9, with $v = 2$ (e_g).

titious hexahydrides for demonstrative purposes is that only σ bonding need be considered. The necessity of using eq 9 is clearly indicated by the comparison of the Ni(II) and C(II) complexes,²¹ in the former, each e_g orbital is singly occupied, so that $u = v = 2$ and $\lambda^2 \propto \rho$, while in the latter, each e_g orbital contains, on the average, only half a spin, with $v = 2$, $u = 1$, and $\lambda^2 \propto 2\rho$. Inspection of Table I reveals that, in general, neither A nor ρ is proportional to the relative covalency. In particular, although the relative covalencies decrease with A for Cu(II) through Mn(II), comparison of Co(II) and Cr(II) yields $A_{Co} > A_{Cr}$, though $\lambda^2_{Cr} > \lambda^2_{Co}$. The smooth decrease in covalency previously proposed³ on the basis of decreasing A from Cu(II) to Mn(II) in a series of tetrakis-hexamethylphosphoramidate complexes, in fact, leads to relative covalencies in the order $Cu > Ni > Co > Fe < Mn$, when analyzed according to eq 9,

(17) M. Bose, *Progr. Nucl. Magn. Resonance Spectrosc.*, **4**, 335 (1969).

(18) The relationship between spin density and spin occupation probability was recognized in ref 4, where it was shown that, although A varied in some hexaaquo complexes of divalent and trivalent metal ions, the extent of spin delocalization was approximately proportional to the number of t_{2g} spins, indicating comparable covalencies.

(19) If two mechanisms contribute involving both subsets of orbitals, as is likely in the hexaammine complexes, where A changes sign on varying the metal (B. B. Wayland and W. L. Rice, *Inorg. Chem.*, **5**, 54 (1966)), the relative covalencies cannot be unambiguously determined for either interaction.

(20) The shifts for all complexes were set equal for convenience. Any arbitrary choice will lead to similar conclusions.

(21) Any distortion expected (ref 16, chapter 8) for the Cu(II) complexes in O_h symmetry is ignored.

with only spins in the t_2 orbitals participating in the delocalization.²²

Thus the relative A is a direct index of relative covalency only if all complexes being compared have all of their spins in the same orbital subset [*i.e.*, Ni(II) and Cu(II)]. The relative spin density, ρ , is an index of the relative covalency only among members of a series of complexes where the spin occupation probability of the orbital subset is constant [*i.e.*, Mn(II), Fe(II), and Ni(II) in Table I]. In all other cases, eq 9 must be used. Though this analysis is given only for σ bonding in O_h symmetry, a similar analysis can easily be carried out for π bonding or for other symmetries. However, it may be difficult to determine the spin occupation probabilities of the d electrons in low-symmetry fields.²³ This latter problem is not serious as long as the distortion is not too severe and the covalencies being compared differ significantly.

(22) If the e spins also participate significantly in the delocalization, the relative covalencies of the Mn(II) and Fe(II) complexes cannot be unambiguously determined.

(23) See ref 16, pp 99-106.

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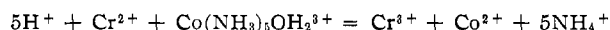
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On the Role of Coordinated Water as a Bridging Ligand in Oxidation-Reduction Reactions

Sir:

The role that water coordinated to the oxidant plays in oxidation-reduction reactions has been much discussed.¹⁻⁴ The general observation has been that reductants that utilize the inner-sphere mechanism react with such oxidants by a rate law that features a strong term inverse in $[H^+]$. This observation has led to the postulate that inner-sphere reactants will exhibit a large rate ratio for the inverse $[H^+]$ path to the path that is independent of $[H^+]$. In an attempt to obtain detailed information about the nature of the reaction of Cr(II) with $Co(NH_3)_5OH_2^{3+}$, we were led to reexamine⁵ the rate of this oxidation-reduction reaction



In this report we present the results of these studies and examine the ramifications of those results on redox reactions involving water coordinated to the oxidant.

The reduction of $[Co(NH_3)_5OH_2](ClO_4)_3$ by Cr(II) was carried out in ClO_4^- medium at $I = 1.0 M$ and 25° . Solutions were prepared from doubly distilled water and distilled $HClO_4$. The $[H^+]$ was varied over a range of 0.096-0.79 M , with the ionic medium held constant with $LiClO_4$. Individual rate constants were computed with a nonlinear least-squares program.

TABLE I
RATE CONSTANTS FOR THE REDUCTION OF $Co(NH_3)_5OH_2^{3+}$ BY Cr^{2+} AS A FUNCTION OF $[H^+]$ AT 25.1°

$[H^+]$, M	$10^3[Cr^{2+}]_0$, M	$10^3[Co(III)]_0$, M	k_{obsd} , $M^{-1} sec^{-1}$	k_{calcd}^a , $M^{-1} sec^{-1}$
0.794	7.13	2.58	3.39 ± 0.03	3.22
0.654	17.8	2.09	4.06 ± 0.04	4.12
0.560	7.13	2.58	4.83 ± 0.03	4.85
0.494	7.13	2.09	5.43 ± 0.02	5.59
0.438	3.56	2.09	6.53 ± 0.04	6.39
0.411	3.56	2.58	7.51 ± 0.16	6.86
0.386	14.3	2.09	6.72 ± 0.21	7.35
0.271	3.56	2.58	10.9 ± 0.1	10.8
0.202	3.56	2.58	14.9 ± 0.1	14.8
0.131	3.56	2.58	23.3 ± 0.2	23.0
0.114	3.58	2.60	27.1 ± 0.3	26.1
0.0965	3.56	2.58	31.6 ± 2.5	31.7

^a Calculated using the expression $k_{calcd} = c[H^+]^{-1} \exp(-d/[H^+])$, where c and d were obtained by nonlinear weighted least-squares analysis of these data. Weights were obtained from the standard deviations of the individual data points.

The individual points are listed in Table I. We have chosen two ways to fit these data. The first is

$$k_{obsd} = a + b[H^+]^{-1} \quad (1)$$

Least-squares analysis of this equation yields the values $a = -0.72 \pm 0.14 M^{-1} sec^{-1}$ and $b = 3.12 \pm 0.05 sec^{-1}$. The second equation tested was a single-term rate law with a medium effect given by a Harned-type equation⁶

$$k_{obsd} = c[H^+]^{-1} e^{-d/[H^+]} \quad (2)$$

The values of the parameters for this equation obtained by nonlinear least-squares analysis are $c = 3.13 \pm 0.05 sec^{-1}$ and $d = 0.25 \pm 0.05 M^{-1}$. The fit of the observed rate constants to eq 2 is illustrated by comparison of column 5 and column 4 of Table I. Although the value for d is somewhat large for medium effects,^{7,8} we believe that eq 2 is a considerably more satisfactory way to represent the variation in observed rate constant with a change in ionic medium. Certainly the negative value for a makes eq 1 unlikely. We conclude that the $[H^+]$ -independent term reported earlier is most likely a medium effect also. For instance, it has been reported by Butler and Taube⁹ that the change from Na^+ to Li^+ has a significant effect on the measured H^+ dependence of several oxidation-reduction reactions involving Cr(II) and Co(III).

If it is accepted that the hydrogen ion independent term in the Cr(II) reduction of $Co(NH_3)_5OH_2^{3+}$ is too small to measure directly, a self-consistent picture of oxidation-reduction reactions involving oxidants with coordinated water emerges. We present the hypothesis that the hydrogen ion independent path for all reactions of Cr^{2+} (and perhaps other reductants) with oxidants containing coordinated water as the only bridging ligand proceeds by an outer-sphere mechanism. This hypothesis is based on three lines of evidence. (1) The only experimentally relevant data in favor of an inner-sphere path for reduction of a water-containing oxidant is that of Kruse and Taube,¹⁰ who observed that 1.01 ± 0.01 water mole-

(1) A. Zwickel and H. Taube, *Discuss. Faraday Soc.*, **No. 29**, 42 (1960).

(2) N. Sutin, *Accounts Chem. Res.*, **1**, 225 (1968).

(3) D. W. Carlyle and J. H. Espenson, *J. Amer. Chem. Soc.*, **90**, 2272 (1968).

(4) M. P. Liteplo and J. F. Endicott, *ibid.*, **91**, 3982 (1969).

(5) A. Zwickel and H. Taube, *ibid.*, **81**, 1288 (1959).

(6) H. S. Harned and B. B. Owen, "The Physical Chemistry of Electrolytic Solutions," Reinhold, New York, N. Y., 1958, p 585 ff.

(7) T. W. Newton and F. B. Baker, *J. Phys. Chem.*, **67**, 1425 (1963).

(8) T. W. Newton and F. B. Baker, *Inorg. Chem.*, **4**, 1166 (1965).

(9) R. D. Butler and H. Taube, *J. Amer. Chem. Soc.*, **87**, 5597 (1965).

(10) W. Kruse and H. Taube, *ibid.*, **82**, 526 (1960).