then, is 6.4 (3) molecules per cell, appreciably less than the eight that would correspond to the reported dihydrate.[5] The water content was determined by thermal gravimetric analysis,[5] which indicated the loss of 1 mol of water between 40 and 85 °C and a second mole between 85 and 120 °C (no error estimate is given). It seems likely that the weakly bound water, O(6), is lost at the lower temperature, and some of this water may have been lost before or during data collection. We note that the density calculated for 6.4 molecules of water per cell is in exact agreement with the measured density of 1.70 g cm⁻³ whereas the value calculated for eight molecules per cell is somewhat higher at 1.725 g cm⁻³.

Registry No. **2**, 71106-46-2; **4**, 71106-47-3; *catena*-bis[μ-(*N*-methylpiperidinium-4-thiolato)]-cadmium(II) perchlorate dihydrate, 71359-32-5; Nb₂Br₆(SC₄H₈)₃, 38531-74-7; Ta₂Br₆(SC₄H₈)₃, 65651-12-9.

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(6) Contribution No. 6266.

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Figure 1. Isotropic shifts of some cation nuclei in [(*n*-C₄H₉)₄N]-[MP(C₆H₅)₃I₃] = Co, Ni) as a function of complex concentrations. The isotropic shift scale is on the left for ¹H and on the right for ¹³C.

A Fourier-Transform NMR Investigation of [(C₄H₉)₄Z][MP(C₆H₅)₃I₃] (Z = N, P; M = Co, Ni)

Sir:

The nature of the interactions within ion couples of the type $(R_4Z)_n^+ML_m^{n-}$ in aprotic solvents has been extensively investigated through ¹H isotropic shift techniques in paramagnetic compounds.[1,2] Detailed models were proposed for the interactions between (*n*-C₄H₉)₄N⁺ (Bu₄N⁺ hereafter) and several paramagnetic anionic complexes.[3–5]

The models were based on the assumption that the observed isotropic shifts (i.e., the difference between the chemical shift of the paramagnetic compound and the chemical shift of the analogous diamagnetic compound) for the protons in the cation were primarily dipolar.[4–6] However, Burkert et al.[7] and Brown and Drago[8] reported evidence of predominant contact contributions on the nitrogen of Bu₄N⁺ through ¹⁴N NMR spectroscopy. An analogous conclusion had been reached by comparing the ³¹P and the ¹H shifts of Bu₄P⁺ in the same kind of complexes.[9]

The dipolar interactions arise from through-space coupling between nuclei and unpaired electrons; the effectiveness of such a mechanism is linked to the magnetic anisotropy of the paramagnetic complex and is strongly dependent on geometrical parameters. The contact shift is present whenever there
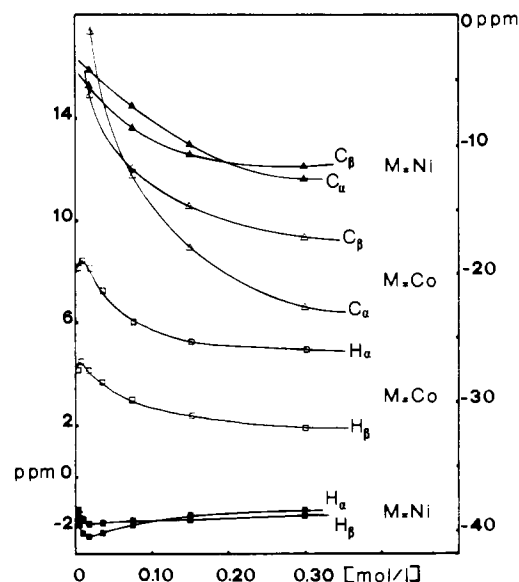
is unpaired spin density on s orbitals of the nucleus under consideration; it is generally believed to be negligible in the absence of true chemical bond. The separation of the above contributions is not straightforward especially in the absence of independent structural and magnetic data.[10,11] An attempt to separate contact and dipolar contributions in ion-pair systems is also reported.[12]

We thought to reinvestigate ion-couple systems through FT NMR techniques which allow for the measurement of NMR parameters of ¹³C in natural abundance as well as the relaxation rates of the various cation nuclei. The relaxation mechanisms contain a contribution due to electron–nucleus coupling occurring through a contact and a dipolar interaction whose separation is often easier to accomplish.[13] Comprehension and comparison of the NMR parameters of the various nuclei may allow a deeper insight into the problem of the nature of the interactions within ion couples.

After this research was completed, a paper appeared[14] dealing with the isotropic shifts of hydrogen and carbon nuclei of Bu₄N⁺ in melted salts of the type (Bu₄N)₂MBr₄ (M = Mn, Co, Ni). By comparison between the ¹H and ¹³C shifts the authors concluded that the dipolar contributions to the overall isotropic shifts were negligible. However, they found their data highly temperature dependent, in such a way that they could not establish the meaning of their observations with respect to dilute solutions.

We wish to report here the isotropic shifts and the relaxation rates of the complexes (Bu₄Z)MPPh₃I₃, where Z = N, P and M = Co, Ni, as well as the ¹H and ¹³C isotropic shifts for the complexes (Bu₄N)₂MX₄, where M = Co, Ni and X = Br, I. Such values are referred to the diamagnetic zinc analogues.

The isotropic shifts for the above complexes are reported in Table I. The values refer to 0.3 M concentration. The sign and magnitudes of the ¹H shifts agree with the values previously reported,[15] if some allowance is made for the different concentrations (see below). In the case of the tetrabromo complexes, the shifts of the protons are upfield for

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Table I. Isotropic Shifts for the Cation $(n\text{-}C_4H_9)_4Z^+$ (Z = N, P) of Some Paramagnetic Complexes and Chemical Shifts Relative to Me_4Si of the Zinc Analogues

$[MI_3PPh_3]^{-\ a}$

		shifts, ppm								
Z	M	α-H	β-H	γ-H	δ-H	α-C	β-C	γ-C	δ-C	Z
N	Co	+4.91	+2.00	+1.39	+0.48	−23.88	−18.12	−13.58	−12.83	−14
N	Ni	−0.92	−1.13	−1.10	−0.58	−14.08	−12.81	−9.54	−8.23	−13
P	Co	+5.13	+1.71	+1.14	+0.33	−25.95	−19.08	−16.53	−11.07	−3.7
P	Ni	−0.72	−1.09	−0.88	−0.45	−18.01	−16.23	−14.39	−7.80	−5.9
N	Zn	−3.23	−1.52	−1.38	−0.97	−59.06	−24.39	−19.90	−13.98	
P	Zn	−2.25	−1.54	−1.52	−0.96	−23.78	−20.37	−18.02	−13.64	

$[MI_4]^{2-\ b}$

		shifts, ppm							
Z	M	α-H	β,γ-H	δ-H	α-C	β-C	γ-C	δ-C	Z
N	Co	+2.33	+0.93	+0.07	−9.42	−10.26	−10.55	−10.04	−18
N	Ni	+0.28	−0.27	−0.22	−7.41	−6.04	−6.38	−6.24	−15
N	Zn	−3.37	−1.55	−1.05	−59.19	−24.73	−20.22	−14.06	

$[MBr_4]^{2-\ b}$

		shifts, ppm							
Z	M	α-H	β,γ-H	δ-H	α-C	β-C	γ-C	δ-C	Z
N	Co	+2.45	+0.93	+0.20	−5.17	−7.22	−8.49	−6.52	−11
N	Ni	−0.55	−0.72	−0.53	−4.11	−6.32	−7.26	−5.76	−11
N	Zn	−3.37	−1.55	−1.05	−59.26	−24.65	−20.18	−14.01	

^{a} In $CDCl_3$ (0.3 M, 25 °C). ^{14}N data from Brown and Drago.[8] ^{b} In CH_2Cl_2 (0.3 M, 25 °C). ^1H data from Walker and Drago;[5] ^{14}N data from Brown and Drago.[8]

Table II. Relaxation Parameters (s^{-1}) for the Cation $(n\text{-}C_4H_9)_4Z^+$ (Z = N, P) of $[MI_3PPh_3]^-$ in $CDCl_3$ (0.3 M, 25 °C)

		$^1H\ T_{1p}^{-1}$				$^{13}C\ T_{1p}^{-1}$				$^{13}C\ T_{2p}^{-1}$				
Z	M	α-H	β-H	γ-H	δ-H	α-C	β-C	γ-C	δ-C	α-C	β-C	γ-C	δ-C	$^{31}P\ T_{1p}^{-1}$
N	Co	100	45	37	21	a	a	2.1	1.4	19	9.4	5.9	6.7	
N	Ni	13	7.3	6.8	4.8	a	a	0.6	1.1	30	20	9.0	8.2	
P	Co	66	34	27	23	5.4	2.8	a	a	9.4	6.8	4.6	~2	5.6
P	Ni	14	10	8.0	4.3	2.6	a	a	0.4	36	24	7.1	3.5	1.7

^{a} The differences from the zinc analogue lay within the experimental uncertainty.

cobalt(II) and downfield for nickel(II) complexes, while the shifts in the melted state are upfield in both cases.[14] On the contrary the ^{13}C isotropic shifts are downfield both in solution and in the melted state for both complexes.

The comparison of the signs of the isotropic shifts of ^1H and ^{13}C NMR for the cations of the $MPPh_3I_3$ series rules out the possibility of the dipolar contribution being predominant, since, if the geometrical model of interaction is the same for nickel(II) and cobalt(II) compounds, the proton and carbon shift ratios have to be the same for the two metal complexes. This conclusion is further supported by the observation that ^1H and ^{13}C shifts for the cobalt complex are opposite in sign, contrary to any reasonable geometrical dependence of the shifts. The isotropic shifts of ^{14}N and ^{31}P are also downfield, analogous to the ^{13}C shifts. In the light of the above data, contact shifts are predominant for the heavy nuclei in all the couples of the $MPPh_3I_3$ series, while a relevant dipolar term in the proton isotropic shifts should be present in order to account for their opposite signs in cobalt and nickel complexes.

The observed isotropic shifts are concentration dependent (Figure 1). In particular, the proton shifts for both nickel and cobalt complexes show maxima in absolute values at concentrations around 10^{-2} M. This means that two opposite contributions are operative, presumably corresponding to two differently averaged geometries of the interacting ions. Although such behavior can be accounted for with difficulty, it allows us to justify why the shift patterns in the melted state are different from those in solution.

A further understanding of the nature of the hyperfine coupling between the resonating nuclei and the paramagnetic center can be attempted by analyzing the relaxation rates. The T_i^{-1} enhancements with respect to the zinc analogues (T_{ip}^{-1}) are reported in Table II. The T_2^{-1} data were obtained from line-width measurements through the relationship $T_2^{-1} = \pi(\Delta\nu)$, where $\Delta\nu$ is the signal width at half-peak height. In the case of the ^1H signals the $J\text{-}J$ splitting, whose resolution varies with the concentration of the paramagnetic species, prevented us from obtaining transverse relaxation rates.

The T_{ip}^{-1} enhancements are related to the properties of the paramagnetic center through the Solomon–Bloembergen–Morgan equations[16] (1) and (2) where r is the electron–nucleus

$$T_{1p}^{-1} = \frac{S(S + 1)\gamma_I^2 g^2 \beta^2}{15r^6}\left(6\tau_c + \frac{14\tau_c}{1 + \omega_s^2\tau_c^2}\right) +$$
$$\frac{1}{3}\left(\frac{A}{\hbar}\right)^2 S(S + 1)\left(\frac{2\tau_e}{1 + \omega_s^2\tau_e^2}\right) \quad (1)$$

$$T_{2p}^{-1} = \frac{S(S + 1)\gamma_I^2 g^2 \beta^2}{15r^6}\left(7\tau_c + \frac{13\tau_c}{1 + \omega_s^2\tau_c^2}\right) +$$
$$\frac{1}{3}\left(\frac{A}{\hbar}\right)^2 S(S + 1)\left(\tau_e + \frac{\tau_e}{1 + \omega_s^2\tau_e^2}\right) \quad (2)$$

distance, $A/\hbar$ is the Fermi contact hyperfine coupling, τ_e is

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Table III. Isotropic Shifts of the $(n\text{-}C_4H_9)Z^+$ Cation As Compared to the Square Roots of the ^{13}C Transverse Relaxation Rates T_{2p}^{-1}, in $[(n\text{-}C_4H_9)_4Z][MP(C_6H_5)_3I_3]$ Complexes[a]

Z	M	C	$\Delta\nu(i)/$ $\Delta\nu(\alpha)$	$T_{2p}^{-1/2}(i)/$ $T_{2p}^{-1/2}(\alpha)$
N	Co	α	1	1
N	Co	β	0.76	0.70
N	Co	γ	0.57	0.56
N	Co	δ	0.54	0.59
N	Ni	α	1	1
N	Ni	β	0.91	0.82
N	Ni	γ	0.68	0.55
N	Ni	δ	0.58	0.52
P	Co	α	1	1
P	Co	β	0.86	0.85
P	Co	γ	0.80	0.70
P	Co	δ	0.65	0.46
P	Ni	α	1	1
P	Ni	β	0.90	0.82
P	Ni	γ	0.80	0.44
P	Ni	δ	0.43	0.31

[a] The values are relative to those experienced by the α-carbons.

the electronic relaxation time, and τ_c is a correlation time which is related to τ_e and to the rotational time of the couple through the relation $\tau_c^{-1} = \tau_e^{-1} + \tau_r^{-1}$. The first term of eq 1 and 2 is dipolar in origin, as it depends on the sixth power of the metal–nucleus distance, and the second arises from unpaired spin density on s orbitals of the nucleus. If the coupling is entirely dipolar in origin, according to the above equations, a T_1/T_2 ratio ranging between 1 and 1.14 is expected. From T_1^{-1} and T_2^{-1} data in Table II for ^{13}C it appears that T_2^{-1} is generally much larger than T_1^{-1}. This difference may only originate from the contact term, whose contribution on T_2^{-1} is therefore the dominant one. If the ^{13}C isotropic shifts are dominated by contact contributions also, they should be related to the square root of the transverse relaxation rates T_{2p}^{-1}. As shown in Table III the ratios between the isotropic shifts for the various carbon atoms are close to the ratios between the square roots of the T_{2p}^{-1} values, especially for the Bu_4N^+ compounds. The discrepancy presumably gives an idea of the extent of dipolar contributions.

A larger contact term on T_2^{-1} with respect to T_1^{-1} implies that the τ_e values involved are larger than 3×10^{-12} s, which is the reciprocal of the electron resonance frequency for our spectrometer. Electronic relaxation times of the order of 10^{-11} s are not unexpected for tetrahedral cobalt(II) complexes, while tetrahedral nickel(II) generally experiences shorter relaxation times;[1,17] however, deviations from regular tetrahedral symmetry may lead to an increase of such values.

If a τ_e of 10^{-11} s is introduced in the contact term of eq 2, the order of magnitude of $A/\hbar$ can be estimated to range between 10^5 and 10^6 s^{-1}, which is a relatively small value for carbon nuclei but large enough to yield a sizable contact contribution to T_1^{-1}; this result does not allow the use of the ^{13}C T_1^{-1} values for structural purposes on the basis of the dipolar part of eq 1. A comparison between the carbon T_1^{-1} values and those of their attached hydrogens shows that the former are about 1 order of magnitude smaller than the latter in almost every case. This suggests that the proton longitudinal relaxation rates are not dominated by the contact term, since larger $A/\hbar$ values for protons would be required with respect to those of the corresponding carbon atom. Furthermore the dipolar term is usually larger for protons than for carbons, the other factors being the same, owing to the larger γ_N values

experienced by hydrogen nuclei. Nevertheless, if the ^1H longitudinal relaxation rates are used to calculate the distances from the paramagnetic center, the ratios between the distances are smaller than 1.3. This is inconsistent with any reasonable geometry of the ionic couple. This result should not be surprising since, in the presence of electron-spin delocalization along the aliphatic chain, a further dipolar contribution may arise from unpaired spin density on non-s orbitals;[18,19] even small delocalization effects may significantly contribute to the overall relaxation, owing to the much shorter r values involved. The effect of this contribution would be to considerably quench the actual distance ratios. Again, this is a confirmation of unpaired spin density being delocalized onto the cation.

All the evidence obtained in this research indicates a large predominance of the contact term in the hyperfine coupling experienced by ^{13}C nuclei of Bu_4Z^+. Such unpaired spin density on the ligand is likely to be present also in s orbitals of hydrogens, although it appears that dipolar contributions may be indeed relevant in the hydrogen isotropic shifts, as previously suggested.[12]

It should be noted that the magnitude of both the estimated Fermi contact coupling constants on the carbon atoms and the observed isotropic shifts for ^1H and ^{13}C nuclei are definitely smaller than those experienced by the same nuclei when bound in a covalent fashion to the paramagnetic center.[20,21] Such small values cannot be attributed, as previously shown,[22] to the presence of free ions in equilibria with couples or clusters of ions, especially at the relatively high concentrations used in the present work. Therefore the mechanisms of unpaired spin transfer should be rather inefficient. Marginal overlaps among molecular orbitals of the interacting ions would provide a mechanism for the observed contact contributions to the NMR parameters. This mechanism would be similar to that proposed to account for exchange effects displayed by paramagnetic centers in the solid state and responsible for weak magnetic interactions.[23] The detailed anion–cation interaction could be of the type previously suggested, i.e., through the interaction between α-CH_2 and the iodide atom.[8] Both spin-transfer and spin-polarization mechanisms could be operative.[14]

Since the magnitude of the shifts and, in some cases, even the signs are concentration dependent, as outlined by comparison between melted and solution data, it is reasonable to assume the existence in solution of clusters of ions.

All the compounds were prepared as previously reported[5,24-26] and satisfactorily analyzed for C, H, and N. The NMR spectra were registered on a Varian CFT20. The ^1H and ^{13}C chemical shifts have been measured with respect to internal Me_4Si; ^{31}P shifts have been measured with respect to external H_3PO_4 and corrected for bulk susceptibility shifts. T_1 measurements have been performed by using the inversion recovery method.

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An *E* and *C* Analysis of Donor Numbers and Soret Band Shifts in Adducts of Zinc Tetraphenylporphine

Sir:

Previous papers have been concerned[1,2] with establishing the *E* and *C* equation as a viable means of correlating and predicting σ-bond strengths (−Δ*H*). Two terms are needed to

$$-\Delta H = E_A E_B + C_A C_B$$

fit the data, and these relate to qualitative ideas about covalent (*C*) and electrostatic (*E*) bonding. The approach has been used in conjuction with spectroscopic and electrochemical measurements to probe intermolecular interactions.[3] With these objectives, the main concern had involved enthalpy determination and interpretation.

The data used in the *E* and *C* approach makes it a viable indicator of σ-bond strengths, and these parameters should be used to replace commonly used, invalid measures of this effect. For example, when investigators attempt to gain insights about the σ-bond contributions to some measured property by correlating or plotting it against p*K*_B and donor number[4] values, they are making an error. These scales are not general indicators of sigma σ-bond strength because the former contains an entropy contribution and both provide only single scale basicity orders that include solvation energy contributions.[5] We have not described in detail how the *E* and *C* approach should be used to determine if trends in measured quantities (other than enthalpies in poorly solvating solvents) are being dominated by σ-bond interactions. This is a probable cause of the continued appearance in the literature of plots of spectroscopic and thermodynamic data obtained in nonaqueous solvents with donor numbers and p*K*_B and also of some incorrect applications of the *E* and *C* parameters. Accordingly, we decided to prepare this paper describing the philosophy and procedure for this type of application of *E* and *C*.

One can *attempt* to interpret any spectral or reactivity parameter with the *E* and *C* model by writing

$$\Delta\chi = "E_A"E_B + "C_A"C_B \tag{1}$$

or

$$\Delta\chi + W = "E_A"E_B + "C_A"C_B \tag{2}$$

for the case where an acid is held constant and a series of bases is studied. The quotation marks imply that conversion units for converting E_B from (kcal mol⁻¹)^{1/2} are included in "E_A" along with the response to the quantity measured induced in the acid by the base. Equation 1 differs from eq 2 in that the latter permits incorporation of systems in which there is constant contribution to the measured parameter in all systems studied.[2]

In addition to converting the units, the quantities E_A and C_A can also include weighting factors that permit a different contribution of the two terms ($E_A E_B$ and $C_A C_B$) to the measured property than is involved in the enthalpy correlation. When Δχ is a free energy, a successful correlation implies that the entropy term changes in a linear fashion with Δ*H*. The magnitudes of the "E_A" and "C_A" parameters accommodate this linear contribution as has been demonstrated for a linearly varying promotion energy.[6] Thus a successful correlation of the measured property with eq 1 implies that σ-bond strength considerations dominate the trends in the measured properties. If there are several systems that miss the attempted correlation by more than the experimental error these systems can be examined for some common property (π bonding, steric effect, etc.) that might account for the deviation.[3] Independent experiments can be designed to probe these effects.[3] If the average deviation is greater than the average error, some factor other than σ-bond strength is making an important contribution to the measured quantity. A large deviation would imply dominance by some other effect.

In the course of evaluating various correlations in the literature, the routine application of correlation coefficients is a common and often misleading practice. For example, if the *E* and *C* model were applied to a data base that contained systems with some systematic exceptions, a lower correlation coefficient for an *E* and *C* fit than for some "other parameter" fit would not signal a rejection of *E* and *C*. The "other parameter" fit might mask this systematic contribution to the measured property if the data base used to derive these "other parameters" has some contribution from this variable causing the systematic deviation built into it. The application of the correlation coefficient criterion should be limited to cases in which random misses with no systematic pattern exist for all the fits being compared. In such applications, the data base must be carefully selected to give nearly equal weight to the different classes of systems that manifest the potential variables to different extents. Even then a case in which a high correlation coefficient is obtained from, for example, a data base of 15 systems with a nearly perfect fit and three with substantial, unexplained, random misses is bothersome in terms of predicting the behavior of new systems. Finally, the correlation coefficent gives no indication of the order of magnitude for the range over which the variables have been studied.

The use of the *E* and *C* equation and a critical discussion of the correlation coefficient will be illustrated by first analyzing the data referred to as donor numbers[4] (DN), i.e., enthalpies associated with the reaction of solutions of SbCl₅ with bases in 1,2-dichloroethane. Various investigators continue to use these parameters to estimate donor–acceptor interactions, and they report successful correlations of spectral and reactivity data. Since it was previously demonstrated[5] that there are extensive contributions to the donor numbers from solvation effects, we were interested in determining why such correlations exist and *what they mean.* In an attempt to obtain a better understanding of the relationship of donor numbers to bond strengths and to understand the limitations of a donor number correlation, an *E* and *C* analysis of this data was undertaken. Reported donor number values were substituted

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