Table I. Typical Determination of the Rate Constant for the Chemical Step in the Reduction of $[Rh(DPE)_2]^+$ (2.0×10^{-4} M) in Wet (0.07 M H_2O) Acetonitrile (0.1 M Et_4NClO_4) Solution at 25.0 °C

scan rate, V s^{-1}	i_p^a/i_p^c	$k_{obsd}\tau$	τ, s	k_{obsd}, s^{-1}
0.020	0.45	1.30	11.0	0.12
0.050	0.63	0.55	4.40	0.13
0.100	0.77	0.28	2.20	0.13
0.200	0.87	0.14	1.10	0.13

Table II. Dependence on the Concentration of Water of the Rate Constants for the Chemical Step in the Reduction of $[M(DPE)_2]^+$ in CH_3CN (0.1 M Et_4NClO_4) Solution at 25.0 °C

M = Rh		M = Ir	
$[H_2O]$, mM	k_{obsd}, s^{-1}	$[H_2O]$, mM	k_{obsd}, s^{-1}
26	0.014	10	1.0
48	0.050	17	2.2
70	0.13	26	4.0
93	0.24	40	8.7
115	0.44	48	13
137	0.78		
160	1.3		

As a matter of fact, CH_3CN is currently reported to act as a proton donor toward some classes of electrochemically generated organic anions.[18] Furthermore, the freshly reduced red solution (see above), upon addition of excess carbon monoxide, quickly turns yellow while 1 mol of DPE precipitates. The infrared spectrum of the solution (bands at 1805 and 1860 cm^{-1}) shows that $[Rh(CO)_2(DPE)]^-$ has formed.[19] Also, the addition of $ClSnPh_3$ to the carbonylated solution allows the d^{10} anion to be isolated.[19] It is noteworthy that the polarogram of the spent yellow catholyte does not exhibit any cathodic wave, thus ruling out the disproportionation by CO of a hypothetical d^9 derivative.[20,22]

In our previous paper[4] we reported and hereby confirm that deliberate addition of increasing amounts of water leads to the stepwise disappearance of the coupled anodic peak, *the cathodic peak being unchanged*, in the cyclic voltammograms of both $[Rh(DPE)_2]^+$ and $[Ir(DPE)_2]^+$. Interestingly, at any selected concentration of water the ratio of peak currents, i_p^a/i_p^c, as a function of the time, τ, required to scan from $E_{1/2}$ to the switching potential, E_λ, fits the Nicholson–Shain working curve for an EC process,[24] thus providing additional evidence for the considered mechanism and allowing the rate constant values for the chemical step to be calculated. This is exemplified in Table I. So far as the dependence of the observed rate constants on the concentration of added water (Table II), the change in order for water at increasing concentrations may be easily rationalized by the presence of more acidic water polymers. D_2O causes the same effect even though no $DRh(DPE)_2$ or $DIr(DPE)_2$ is recovered in preparative electrolyses under these conditions.[1,2] Identical chemical behavior is, however, shown by the one-electron reduction product of $Co(DPE)_2$, viz., $[Co(DPE)_2]^-$, which appears to be quenched mainly by proton abstraction from acetonitrile, as $HCo(DPE)_2$ is formed in CH_3CN with small amounts of D_2O while $DCo(DPE)_2$ is obtained in CD_3CN in the presence of low concentrations of H_2O.

The inconsistency of the D-labeling results could still be solved with the assumption of the likely occurrence of a rapid H/D exchange reaction converting D_2O into H_2O or H_2O into D_2O in CH_3CN or CD_3CN, respectively. As a matter of fact we have found that such an exchange reaction does indeed occur quickly and, for low concentrations of water, quantitatively on the condition that OH^- or OD^-, even in trace amounts, is present.[25]

In line with the EC mechanism, hydroxide ions are produced in the hydride formation already in the early stages of the electrolyses in wet solvents in view of the highly protic nature of water relative to acetonitrile. As a consequence, no sooner do such electrolyses start than the H/D exchange also begins and goes to completion in a very short time.[26]

In conclusion, the labeling experiments that, according to the title authors, should have provided the strongest evidence of the radical nature of the primary reduction product thus lose any meaning.

Registry No. $[Rh(DPE)_2]^+$, 47895-57-8; $[Ir(DPE)_2]^+$, 29871-99-6.

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[16] In a subsequent paper, which appeared while this reply was submitted for publication, Eisenberg et al.[17] report that in benzonitrile the primary source of hydrogen for rhodium hydride formation is the electrolyte, tetrabutylammonium perchlorate, and not the solvent, since 1-butene and tributylamine are formed. The authors themselves, while claiming once more the ECE character of the overall process, acknowledge that "the formation of Hofmann degradation products from the reaction of electrochemically generated anionic intermediates with tetraalkylammonium salts is not uncommon".

[17] J. A. Sofranko, R. Eisenberg, and J. A. Kampmeier, *J. Am. Chem. Soc.*, **102**, 1163 (1980).

[18] See, for example A. J. Bellamy, *J. Chem. Soc., Chem. Commun.*, 944 (1975); K. P. Butin, M. T. Ismail, and O. A. Reutov, *J. Organomet. Chem.*, **175**, 157 (1979).

[19] G. Pilloni, G. Zotti, and M. Martelli, *Inorg. Chim. Acta*, **13**, 213 (1975).

[20] All the chemical reactions reported for $Rh(DPE)_2$ may be easily be accommodated on the basis of $[Rh(DPE)_2]^-$ formation. In particular, the quoted[2] radical products formation could be accounted for by an oxidative addition reaction of the organic halide to the d^{10} complex, $[Rh(DPE)_2]^-$, followed by dissociative reduction of the resulting organometallic derivative. Related behavior has already been found, for instance, in $[Ni(CH_3)(P(CH_3)_3)_4]^+$, which undergoes reductive elimination to give $[Ni(P(CH_3)_3)_4]^+$.[21]

[21] A. Gleizes, M. Dartinguenave, Y. Dartinguenave, and H. F. Klein, *J. Am. Chem. Soc.*, **99**, 5187 (1977).

[22] As far as the alleged d^9 species is concerned, Mulazzani et al. have produced it by pulse radiolysis in methanol.[23] This transient species has a half-life that appears beyond the reach of cyclic voltammetry, and its fate is oxidation by the solvent back to $[Rh(DPE)_2]^+$ without formation of a metal–hydrogen bond.

[23] Q. G. Mu'azzani, P. G. Fuochi, G. Pilloni, and E. Vecchi, *Int. J. Radiat. Phys. Chem.*, **10**, 275 (1977).

[24] R. S. Nicholson and I. Shain, *Anal. Chem.*, **36**, 706 (1964).

[25] The conversion of D_2O and vice versa in acetonitrile has been evidenced by IR measurements in 0.05-cm CaF_2 liquid cells with compensation of the bands of D_2O (2700, 2600, and 1200 cm^{-1}) and H_2O (3640, 3540, and 1630 cm^{-1}) of the solutions (1 mol % or less of water) before and after addition of tetraethylammonium hydroxide ($\geq 2 \times 10^{-5}$ M).

[26] A typical electrolysis performed on a 2×10^{-3} M solution of $[Rh(DPE)_2]^+$ in CH_3CN in the presence of D_2O (≈ 1 mol %) has shown that full conversion of D_2O into H_2O has already taken place after 1% of the exhaustive amount of charge had been allowed to pass.

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Proton Relaxation Enhancement in Paramagnetic Dinuclear Transition-Metal Complexes

Sir:

The magnetic interactions in dinuclear metal complexes have been intensively investigated, mainly through magnetic susceptibility measurements and EPR spectroscopy.[1-10] Far less

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[1] Kokoszka, G. F.; Duerst, R. W. *Coord. Chem. Rev.* **1970**, *5*, 209.

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numerous are the reports on the NMR spectra,[11-15] one limiting circumstance being often the low solubility of the dinuclear complexes themselves. However, there is some interest in the field bound also to the possibility of investigation of pairs of metal ions, which are present in some naturally occurring chemical systems.

One of the most important parameters determining the possibility of recording NMR spectra of paramagnetic compounds is the electronic spin–lattice relaxation time, which often determines the correlation time in the NMR experiment.[16,17] The shorter the electronic relaxation time the sharper the NMR line is expected to be. Concerning octahedral complexes, it is well-known that cobalt(II) complexes yield rather sharp ^{1}H NMR lines, whereas much broader spectra are detected for nickel(II) and copper(II) complexes, which are characterized by longer electronic relaxation times.

In dinuclear complexes one proton can be under the influence of two paramagnetic centers. It is of interest to determine the conditions under which it can be expected that NMR spectra are easily obtained and how they are related to the nature of the two metal ions. The simplest case that can arise is that when the magnetic coupling between the two ions is negligible. It seems reasonable to suggest that the relaxation rate T_{1M}^{-1} of a proton should be determined by the sum of the two independent contributions of the two metal ions, since it is expected that the T_{1M} values are mainly determined by dipolar interactions. Therefore, for a dinuclear (M–M′)L$_n$ complex, the relaxation rate $T_{1M}(\text{M–M}')_i^{-1}$ of a given proton i should be given by the relationship

$$T_{1M}(\text{M–M}')_i^{-1} = T_{1M}(\text{M})_i^{-1} + T_{1M}(\text{M}')_i^{-1} \qquad (1)$$

where $T_{1M}(\text{M})_i^{-1}$ and $T_{1M}(\text{M}')_i^{-1}$ are the relaxation rates of the proton i when it experiences the influence of the paramagnetic metal ion M or M′ alone, respectively.

In order to check the above statement, we measured the T_1 values of protons of the dinuclear MM′(PMK)$_3^{4+}$ cations (M, M′ = Co, Ni, Cu, Zn; PMK = 2-pyridyl methyl ketazine) (**1**).

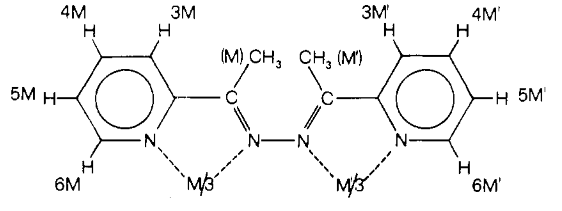

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Table I. T_{1M} Values (ms) of MM′(PMK)$_3^{4+}$ Complexes in D$_2$O at 24 °C[a]

compd		M				M′			
M	M′	3-H	4-H	5-H	CH$_3$	3-H	4-H	5-H	CH$_3$
Co	Zn	30	138	44	16	155	690	376	33
Co	Co	26 (25)[b]	103 (109)[b]	42 (39)[b]	10 (11)[b]	26 (25)[b]	103 (109)[b]	42 (39)[b]	10 (11)[b]
Co	Cu	24	93	35	10	8	61	16	8
Co	Ni	19	50	28	5	6	19	5	3
Cu	Zn	(8)[b]	(69)[b]	(17)[b]	(11)[b]	(120)[b]	(285)[b]	(171)[b]	(27)[b]
Ni	Zn	(6)[b]	(20)[b]	(5)[b]	(3)[b]	(52)[b]	(78)[b]	(77)[b]	(7)[b]

[a] Estimated error ±10%. The reported values are obtained by the relationship $T_{1M}^{-1} = T_{1(\text{exptl})}^{-1} - T_{1(\text{exptl})}^{-1}(\text{Zn–Zn})$. T_1(Zn–Zn) values (ms): CH$_3$, 280; 3-H, 536; 4-H, 550; 5-H, 524.
[b] Calculated by relation 1 (see the text).

Table II. Calculated and Estimated $r_{\text{H}_i(\text{M})}/r_{\text{CH}_3(\text{Co})}$ Distance Ratios for the (Co–Zn)(PMK)$_3^{4+}$ Complex

	Co				Zn			
	CH$_3$	3-H	4-H	5-H	CH$_3$	3-H	4-H	5-H
calcd	1.00	1.11	1.43	1.18	1.13	1.46	1.87	1.69
estd	1.00	1.08	1.26	1.12	1.08	1.39	1.75	1.73

We have previously reported the ^{1}H spectra of these complexes[13] and found that the isotropic shifts of the pairs could be understood by using the simple relationship

$$\frac{\Delta H_i}{H}(\text{M–M}') = \frac{\Delta H_i}{H}(\text{M}) + \frac{\Delta H_i}{H}(\text{M}') \qquad (2)$$

The individual contributions $\Delta H_i/H(\text{M})$ and $\Delta H_i/H(\text{M}')$ were obtained from the analysis of the spectra of the M–Zn and M′–Zn derivatives.

A similar analysis of the T_{1M} values is reported here, but due to the overlap of the signals and instrumental problems, only the T_{1M} values of the Co–Zn, Co–Co, Co–Cu, and Co–Ni complexes could be obtained.

The relaxation rate measurements were carried out on a Varian CFT 20 spectrometer operating at 80 MHz, with use of the inversion recovery method. The calculated T_{1M} values, as obtained by subtracting the appropriate diamagnetic contribution to the experimental T_1 values, are shown in Table I. In order to exclude effects due to intermolecular association, we carried out the measurements on D$_2$O solutions at various concentrations; however, negligible differences in the obtained results were found, when solutions of concentration lower than 10^{-1} M were considered.

An approximate analysis of the T_{1M}^{-1} values for the Co–Zn derivative can be attempted with use of the Solomon–Bloembergen–Morgan equation[18,19]

$$T_{1M}^{-1} = \frac{2}{15}\,\frac{\gamma_I^2 g^2 S(S+1)\beta^2}{r^6}\left(\frac{3\tau_c}{1+\omega_I^2\tau_c^2} + \frac{7\tau_c}{1+\omega_S^2\tau_c^2}\right) + \frac{2}{3}S(S+1)\frac{A^2}{\hbar^2}\left(\frac{\tau_e}{1+\omega_S^2\tau_e^2}\right) \qquad (3)$$

although it may be expected that it is only a rough approximation for high-spin cobalt(II) complexes, since it was derived for species having an isotropic g tensor. Since the dipole–dipole interaction between the electron spin and the nuclear spin is expected to dominate in eq 3, the ratio of the T_{1M} values of two protons should equal the sixth power of the ratio of the distances of the protons themselves from the paramagnetic center. Although no crystal structure of **1** is available, it is possible to estimate reliable values for these distances from

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molecular models. In Table II the calculated and estimated ratios are compared. The agreement can be considered satisfactory, taking into account the expected approximation of eq 3 for the cobalt(II) ion and the experimental errors.

On passing from the Co–Zn to the Co–Co complex, we observe a relaxation rate enhancement for all the protons, as expected from the presence of two noninteracting paramagnetic metal ions. Using eq 1 it is possible to calculate the T_{1M} values for the Co–Co species, by using the T_{1M} values obtained for the Co–Zn species. In a manner similar to our previous analysis of the isotropic shifts, we have used the T_{1M} value of the proton i closest to cobalt in the Co–Zn species for $T_{1M}(\mathrm{Co})_i$ and the T_{1M} value of the proton closest to zinc for $T_{1M}(\mathrm{Zn})_i$. As an example the T_{1M}^{-1} value of the methyl group in the Co–Co species may be calculated as follows: $T_{1M}^{-1}(\mathrm{Co{-}Co})_{\mathrm{CH_3}} = 0.0625 + 0.0303 = 0.0928$ ms^{-1}, where 0.0625 ms^{-1} and 0.0303 ms^{-1} are the T_{1M}^{-1} values of the methyl groups closest to the cobalt and to the zinc in the Co–Zn species. Therefore the calculated $T_{1M}(\mathrm{Co{-}Co})_{\mathrm{CH_3}}$ is 11 ms. The calculated values are shown in Table I. It is apparent that they are equal to the observed ones within the error, thus giving support to the use of eq 1.

Equation 1 can also be applied to the Co–Cu and Co–Ni derivatives to estimate the T_{1M} values of the Cu–Zn and Ni–Zn derivatives, which cannot be obtained directly because of the overlap and/or broadness of the signals. The calculated values are reported in Table I. It would appear that in these compounds the ligand protons experience greater relaxation enhancements than the Co–Zn analogues. In particular, the T_{1M} values for the nickel(II) derivatives are significantly shorter.

The differences in the T_{1M} values for the M–Zn species reflect the differences in the electronic spin–lattice relaxation times of the individual metal ions. With use again of eq 3, the assumption $\omega_I^2\tau_c^2 \ll 1$, and the distance ratios reported in Table II, the following τ_c values can be estimated: Co(II), 7×10^{-13} s; Ni(II), 1.2×10^{-11} s; Cu(II), 2.1×10^{-11} s.[20] The short τ_c value characterized for the cobalt(II) ion reflects the short spin–lattice relaxation time expected for this ion in an octahedral environment, while the values observed for the copper(II) and nickel(II) derivatives are close to the limit expected for the rotational correlation time. In fact, on purely electronic grounds, the spin–lattice relaxation time of copper(II) would be expected to be longer than that of nickel(II). The fact that the relaxation enhancement of the nickel(II) ion is larger than that of copper(II) is a consequence of the larger magnetic moment of the former.

The data we reported show that the possibility of observing the ^{1}H NMR spectra of paramagnetic dinuclear metal complexes is bound to the electronic spin–lattice relaxation time of individual metal ions. In any case the proton T_{1M}^{-1} values in a dinuclear complex formed by two paramagnetic metal ions M and M′ seem to be given to a good approximation by the sum of the T_{1M}^{-1} values of the M–Zn and M′–Zn species. When one of the two paramagnetic ions, let us say M, is characterized by a much shorter electronic relaxation time than the other one, the T_{1M} values observed for the protons of the dinuclear M–M′ complex are close to, although somewhat shorter than, those observed for complexes in which the proton relaxation enhancements are determined by the metal ion M alone. As a consequence, the presence of the metal M is sufficient to produce a substantial narrowing of the signals of the protons closer to the metal ion characterized by a longer electronic spin–lattice relaxation time, thus allowing one to record ^{1}H NMR spectra even in the case of copper(II) and manganese(II) complexes.[21]

When the exchange interaction between the two paramagnetic metal ions cannot be neglected, the T_{1M} values are expected to depend on the sign and on the actual value of the exchange coupling constant *J*. To a first approximation one can say that for antiferromagnetic coupling the T_{1M} values of the pair will be longer than required by relationship 1, while the reverse will be true for ferromagnetic coupling.

Registry No. $\mathrm{CoZn(PMK)_3^{4+}}$, 68200-93-1; $\mathrm{CoCo(PMK)_3^{4+}}$, 53158-63-7; $\mathrm{CoCu(PMK)_3^{4+}}$, 68200-96-4; $\mathrm{CoNi(PMK)_3^{4+}}$, 68200-95-3; $\mathrm{CuZn(PMK)_3^{4+}}$, 68200-97-5; $\mathrm{NiZn(PMK)_3^{4+}}$, 68200-94-2.

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(20) Estimated error ±20%.

(21) Unpublished results of this laboratory.