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Metal electron delocalization in 3d complexes estimated by positronium spin-exchange reactions

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Contents

Abstract

The paper is the final account of a series concerning the conversion reactions promoted by ca. 70 complexes of V^{II}, Cr^{II}, Cr^{III}, Mn^{II}, Co^{II} and Ni^{II} ions. The rate constants, k_{CR}, of the reactions, measured at 278, 288, 298 and 308 K, correlate linearly with the metal electron delocalization caused by the ligands as described by the ratio β between the inter-electronic repulsion parameter in 3d complexes, B, and that in the free ions, B_0. The β values were estimated by the empirical equation $\beta = 1 - th$, where t and h are constants characteristic of

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the ion and ligand, respectively. The analysis of the data, limited in a previous review to the experiments carried out at 298 K, is here extended to the other three temperatures in order to ascertain if the t and h values proposed are independent of T, as it is expected. The relationship between the correlations for complexes of the same ion J in high- and low-spin configurations is also taken into consideration. An experimental equation was derived for evaluating k_{CR}^{T} as a function of T and β. The analysis of the data shows that experimental and back-calculated k_{CR}^{T} are in nice agreement with each other, i.e. the mean-square error of the discrepancies between the values of experimental and back-calculated rate constants are 1.3–1.4 times the mean-square error of the experimental data. This supports the statements advanced in order to explain the relationship between k_{CR} and the chemical constitution of 3d complexes. Reciprocally, the statement that the k_{CR} measurements constitute a new method for testing the metal electron delocalization in 3d complexes, gains further support. A short account on the o-Ps into p-Ps conversion reactions, their mechanisms and kinetics is also given.

Keywords: Metal electron delocalization; 3d complexes; Positronium spin-exchange reactions

1. Introduction

The positron, symbol e^+ (or β^+, if originated by radioactive decay), is the anti-electron, i.e. a particle identical to the electron, e^-, except for the sign of its charge, opposite to that of e^- [1]. The ultimate fate of e^+ is to undergo annihilation by interacting with an e^-. Annihilation consists of the transformation of the masses of e^+ and e^- into electromagnetic energy. The modalities of the transformation (lifetimes, angular correlations of emitted quanta, etc.) depend on the chemical environment of e^+. The annihilation modalities may consequently be used as a probe of the electronic structure of the molecules [2,3].

Positrons are generally formed with energies in the order of 10^2 keV by decay of certain radionuclides. After thermalization by collision with the molecules of the medium and before undergoing annihilation, a certain fraction of e^+, depending on the medium, may form bound states with the electrons. The bound states, which resemble the protium atom ^1H, are called positronium atoms, Ps.

As chemical entities, Ps atoms may undergo several types of chemical reactions, which are, oxidation (leading to e^+), addition reactions to double bonds and spin-exchange reactions, which constitute the main point of the present review.

Ps atoms may exist into two spin states: the *ortho*-state, o-Ps, and the *para*-state, p-Ps, depending on the spin orientations of the two particles: parallel in the former and anti-parallel in the latter case. Both types of Ps atoms are unstable, but with different decay modes; this makes it possible to distinguish between the two. Since $m_S(o\text{-Ps}) = 0, \pm 1$ and $m_S(p\text{-Ps}) = 0$, the two types of Ps atoms are formed for statistical reasons in the ratio 3:1. Once formed, o-Ps and p-Ps atoms may be interconverted only in magnetic fields or by collisions with paramagnetic species such as many 3d complexes [3]. It will be shown (1) that the rate constants of the spin-exchange reactions promoted by 3d complexes depend on the delocalization of

the metal electrons caused by the ligands; and (2) that the rate constants of these reactions constitute a new experimental method for ascertaining the electron delocalization in complexes.

Indeed, it was found that the rate constants, k_{CR}, of the conversion reactions, CR, of *o*-Ps into *p*-Ps atoms depend on the density of unpaired metal electrons at the periphery of complexes [3]. In particular the k_{CR}s are linearly dependent on the electron delocalization caused by the ligands, as described by the ratio $\beta = B/B_0$ between the inter-electronic repulsion parameters in the complex, B, and that in the free gaseous ions, B_0; that is:

$$k_{CR} = a - b\beta \quad (1)$$

where a and b are the intercept and slope of the correlation line, both dependent on the coordinating ion J and temperature T. The electron delocalization increases as $\beta \to 0$.

It was also found that for $T =$ constant the intercepts a of the correlation lines of the various ions are proportional to the number n of unpaired electrons [3].

The β ratios were evaluated by means of the following empirical equation (2), already suggested in the literature [4,5]:

$$\beta = 1 - th \quad (2)$$

where h and t are constants depending on the ligands and metal ions, respectively.

Therefore, once the parameters of the correlation line for a certain ion are known, the k_{CR} may be estimated from the corresponding β and, vice versa; the k_{CR} determination allows us to deduce the corresponding β. This reflects a new experimental method for estimating β.

In the present paper the t and h values of six metal ions and 20 ligands deduced from the best fit of the k_{CR}s are presented and compared with those obtained from the UV–vis measurements (Table 1) [6].

The experimental k_{CR} values at 278, 288, 298 and 308 K previously published [3] and presented in Table 2, were used. Initially the t and h values were obtained by trial and error mainly by using the data at 298 K [3]. Here the results at 278, 288 and 308 K are also taken into account. Moreover, the parameters of the correlation lines are also studied as a function of T in order to obtain a more general relationship between k_{CR}^T and β at the various T. The essentials of the β parameters and of the positronium spin-exchange reactions are summarized. Full details on the theory, experimental methods and measurements, on which the present review is based, are given in Refs. [1–3] and the papers quoted therein.

2. The β parameter

The inter-electronic repulsion parameter, B, of 3d electrons in complexes is smaller than that in the free gaseous ions, B_0, due to the expansion of the 3d electron orbitals towards the donor atoms as a consequence of the overlapping of donor and 3d electron orbitals. Therefore the inter-electron repulsion between 3d electrons decreases and B also decreases.

The B values may be derived by UV–vis absorption spectroscopy; e.g. the Cr^{III} octahedral complexes are characterized in the UV–vis region by three absorption bands, whose energies (cm^{-1}) are given by the following equations (3 and 3′) [6]:

$$\bar{\nu}_1 = 10Dq \tag{3}$$

$$\bar{\nu}_{2,3} = 7.5B + 15Dq \pm (225B^2 + 100Dq^2 - 180BDq)^{1/2}/2 \tag{3'}$$

where 10Dq is the splitting of the fivefold degenerate 3d orbitals in a triplet (lower) and a doublet (higher) caused by an octahedral ligand field and B is the inter-electronic repulsion parameter in the complex. Therefore the measurements of $\bar{\nu}_{1-3}$ allows us to obtain B.

Jørgensen [7] suggested that the $B/B_0 = \beta$ ratio may be estimated by the empirical Eq. (2). The t^* and h^* values resulting from the best fit of the UV–vis spectra of several complexes are given in Table 1 [4]. In the first approximation t^* and h^* values were also used to correlate k_{CR} and β. Indeed Eq. (2) seems to work better than it is generally believed [3], at least for its application to Ps correlations.

Another basic hypothesis, which may be controlled a posteriori, is that the β values of complexes formed with mixed ligand arrays, result from linear combina-

Table 1
t and h values to be inserted in Eq. (2) in order to estimate β[a]

Ion	t^*	t	Ligand	h^*	h	Ligand	h^*	h
Co^{II}	0.24	0.24	6 Cl^-	2.0	6.3	6 acetate	–	0.98
Cr^{II}	–	0.13	6 CN^-	2.0	4.0	$edta^{4-}$[e]	–	1.18**
Cr^{III}	0.21	0.21	6 CNS^-	1.8	4.6	2 dien[f]	–	1.56
Mn^{II}	0.07	0.07	3 en[b]	1.5	1.56	3 gly^-[g]	–	1.28**
Ni^{II}	0.12	0.23	3 pn[c]	–	1.56	2 ida^{2-}[h]	–	1.18**
V^{II}	0.08	0.087	6 H_2O	1.0	1.00	6 imH[i]	–	0.97
			6 NH_3	1.4	1.4	6 dmu[j]	–	1.30
			3 ox^{2-}[d]	1.5	1.35	2 ntp^{6-}[k]	–	0.848
			6 urea	1.2	1.33	$edtp^{8-}$[l]	–	1.085
						6 N_3^-	–	3.2

[a] The t^* and h^* values were deduced from best fit UV–vis spectroscopy [4]; while t and h are derived from the correlation lines between k_{CR} and β values. t^* and h^* are given for the sake of comparison, but in the following analysis t and h values are used. The values with ** were calculated by means of the average environment rule (AER). For details see the text.

[b] en = ethylenediamine.

[c] pn = propylenediamine.

[d] ox^{2-} = oxalate.

[e] $edta^{4-}$ = ethylenediaminetetraacetate.

[f] dien = diethylenetriamine.

[g] gly^- = glycinate.

[h] ida^{2-} = iminodiacetate.

[i] imH = imidazole.

[j] dmu = dimethylurea.

[k] $ntpH_6$ = nitrilo-tris (methylene phosphonic) acid.

[l] $edtpH_8$ = ethylenediamine tetra(methylene phosphonic) acid.

tions of the β values of complexes formed with homogeneous arrays of ligands. The rule, referred to as the *average environment* (AER) [8], is extensively applied here. It was originally derived for estimation of mixed complexes because the complex distortion makes its experimental determination from UV–vis spectra rather troublesome. Moreover the rule was extended to include certain multidentate ligands, whose donor groups do not strongly interact among themselves, e.g. the β values of $h(\mathrm{edta}^{4-})$ and $h(3\ \mathrm{gly})$ (edta^{4-} = ethylenediaminetetraacetate; gly = glycinate) were considered equivalent to:

$$h(3\ \mathrm{gly}) = \{h(6\ \mathrm{acetate}) + h(3\ \mathrm{en})\}/2 = 1.26 \tag{4}$$

$$h(\mathrm{edta}^{4-}) = \{2h(6\ \mathrm{acetate}) + h(3\ \mathrm{en})\}/3 = 1.19 \tag{4'}$$

Finally we recall that the h and t constants should be independent of the temperature T.

3. *o*-Ps into *p*-Ps conversion

3.1. Reaction type

All the *o*-Ps into *p*-Ps conversion reactions considered here are diffusion controlled (DC). The rate constants of DC reactions are given by the Smoluchowski equation (5) [3]:

$$k = \frac{R}{1500}(r_{1,\mathrm{R}} + r_{2,\mathrm{R}})\left(\frac{1}{r_{1,\mathrm{D}}} + \frac{1}{r_{2,\mathrm{D}}}\right)\frac{T}{\eta} \tag{5}$$

where $r_{i,\mathrm{R}}$ and $r_{i,\mathrm{D}}$ are the reaction and diffusion radii of the ith reactant; T the absolute temperature; R and η are the gas constant and the viscosity coefficient of the reaction medium; 1500 is a scale factor to be used in order to have k in $\mathrm{dm^3\ mol^{-1}\ s^{-1}}$ if R is in 1 erg $\mathrm{mol^{-1}\ K^{-1}}$ and η in poise.

The following equation (6) relates the viscosity coefficients η to T [9]:

$$\eta = \eta_0 \exp(E_\eta / k_{\mathrm{B}} T) \tag{6}$$

η_0 being a constant characteristic of the medium and k_{B} the Boltzmann constant. By inserting Eq. (6) into Eq. (5) one obtains Eq. (7):

$$\frac{k}{T} = \frac{R}{1500\eta_0}(r_{1,\mathrm{R}} + r_{2,\mathrm{R}})\left(\frac{1}{r_{1,\mathrm{D}}} + \frac{1}{r_{2,\mathrm{D}}}\right)\exp\left(-\frac{E_\eta}{k_{\mathrm{B}} T}\right) \tag{7}$$

Therefore the rate constants of DC reactions, measured in a given medium at various T, must fulfill the following two conditions:

1. k_{CR} must be linearly dependent on T/η and the straight line must have zero intercept (Eq. (5))
2. the activation energy derived from the slope of $\ln(k/T)$ versus $1/T$ must match the activation energy of the viscosity coefficient of the reaction medium.

Table 2
Experimental, k_{exp}, and back-calculated, $\bar{k}_{calc}$, rate constants of CR, in $dm^3\ mol^{-1}\ ns^{-1}$, at various T[a]

Complexes	h_L	β	k_{CR}	278 K	288 K	298 K	308 K
$[V^{II}(H_2O)_6]^{2+}$	1.00	0.913	Exp.	0.38 ± 0.01	0.55 ± 0.02	0.63 ± 0.02	0.91 ± 0.02
			Calc.	*0.41*	*0.55*	*0.72*	*0.91*
$[V^{II}edta]^{2-}$	1.18	0.897	Exp.	0.35 ± 0.02	0.40 ± 0.04	0.72 ± 0.05	0.77 ± 0.07
			Calc.	*0.48*	*0.64*	*0.85*	*1.09*
$[V^{II}dien_2]^{2+}$	1.56	0.864	Exp.	–	–	1.15 ± 0.09	–
			Calc.			*1.11*	
$[V^{II}(NCS)_6]^{4-}$	4.6	0.600	Exp.	2.0 ± 0.2	2.6 ± 0.1	3.5 ± 0.1	4.5 ± 0.1
			Calc.	*1.78*	*2.43*	*3.25*	*4.28*
$[V^{II}(CN)_6]^{4-}$	4.0	0.652	Exp.			2.5 ± 0.2	
			Calc.			*2.83*	
$[V^{II}(imH)_6]^{2+}$	0.97	0.916	Exp.	0.45 ± 0.02	0.62 ± 0.05	0.76 ± 0.03	0.97 ± 0.06
			Calc.	*0.40*	*0.53*	*0.69*	*0.88*
$\bar{\varepsilon}_{exp}$	$\bar{\rho} = 1.6$			0.10	0.06	0.10	0.07
Δ_{calc}				0.13	0.15	0.20	0.20
$[Cr^{II}(H_2O)_6]^{2+}$	1.00	0.870	Exp.	1.21 ± 0.24	1.92 ± 0.18	2.76 ± 0.09	3.39 ± 0.28
			Calc.	*1.47*	*1.99*	*2.66*	*3.46*
$[Cr^{II}edtaH_2O]^{2-}$	1.18	0.847	Exp.	–	–	3.20 ± 0.22	–
			Calc.			*2.88*	
$[Cr^{II}urea_6]^{2+}$	1.33	0.827	Exp.	1.78 ± 0.05	2.35 ± 0.03	3.17 ± 0.05	3.84 ± 0.27
			Calc.	*1.69*	*2.29*	*3.07*	*3.99*
$[Cr^{II}(NCS)_4(H_2O)]^{2-}$	3.40	0.558	Exp.	2.95 ± 0.18	4.32 ± 0.06	5.42 ± 0.06	7.2 ± 0.1
			Calc.	*3.05*	*4.16*	*5.59*	*7.34*
$*[Cr^{II}(CN)_6]^{4-}$	4.00	0.480	Exp.	–	–	3.25 ± 0.10	–
			Calc.			*3.16*	
$[Cr^{II}(imH)_6]^{2+}$	0.97	0.874	Exp.	1.50 ± 0.04	2.08 ± 0.10	2.67 ± 0.06	3.20 ± 0.14
			Calc.	*1.45*	*1.96*	*2.62*	*3.41*
$\bar{\varepsilon}_{exp}$	$\bar{\rho} = 0.93$			0.15	0.11	0.13	0.21
Δ_{calc}				0.15	0.11	0.20	0.15

*ls configuration $S > 1/2$; see Section 4.3

Table 2 (*Continued*)

Complexes	h_L	β	k_{CR}	278 K	288 K	298 K	308 K
$[Cr^{III}(H_2O)_6]^{3+}$	1.00	0.790	Exp.	0.55 ± 0.05	0.73 ± 0.03	1.01 ± 0.09	1.36 ± 0.06
			Calc.	*0.63*	*0.84*	*1.10*	*1.41*
$[Cr^{III}urea_6]^{3+}$	1.33	0.721	Exp.	1.00 ± 0.10	1.43 ± 0.07	1.74 ± 0.06	2.16 ± 0.04
			Calc.	*0.96*	*1.29*	*1.71*	*2.23*
$[Cr^{III}(NH_3)_6]^{3+}$	1.40	0.706	Exp.	1.06 ± 0.01	1.44 ± 0.07	1.79 ± 0.02	2.06 ± 0.07
			Calc.	*1.03*	*1.39*	*1.84*	*2.40*
$[Cr^{III}ox_3]^{3-}$	1.35	0.716	Exp.	0.98 ± 0.03	1.39 ± 0.05	1.63 ± 0.09	2.06 ± 0.07
			Calc.	*0.99*	*1.33*	*1.75*	*2.29*
$[Cr^{III}en_3]^{3+}$	1.56	0.672	Exp.	1.22 ± 0.09	1.66 ± 0.05	2.09 ± 0.06	2.80 ± 0.08
			Calc.	*1.20*	*1.62*	*2.14*	*2.80*
$[Cr^{III}(CN)_6]^{3-}$	4.00	0.160	Exp.	3.86 ± 0.07	5.40 ± 0.07	6.85 ± 0.12	8.43 ± 0.18
			Calc.	*3.65*	*4.99*	*6.70*	*8.83*
$[Cr^{III}(NCS)_6]^{3-}$	4.6	0.034	Exp.	4.20 ± 0.37	6.15 ± 0.18	8.15 ± 0.17	10.7 ± 0.02
			Calc.	*4.25*	*5.82*	*7.82*	*10.32*
$[Cr^{III}en_2(H_2O)_2]^{3+}$	1.37	0.712	Exp.	0.85 ± 0.02	1.34 ± 0.07	1.80 ± 0.03	2.23 ± 0.07
			Calc.	*1.01*	*1.35*	*1.79*	*2.33*
$[Cr^{III}en_2ox]^{+}$	1.49	0.687	Exp.	1.09 ± 0.02	1.75 ± 0.02	2.21 ± 0.06	2.78 ± 0.06
			Calc.	*1.13*	*1.52*	*2.01*	*2.63*
$[Cr^{III}edtaH_2O]^{-}$	1.19	0.752	Exp.	0.82 ± 0.05	1.17 ± 0.01	1.42 ± 0.02	1.87 ± 0.03
			Calc.	*0.82*	*1.09*	*1.43*	*1.86*
$[Cr^{III}ox_2(H_2O)_2]^{-}$	1.23	0.742	Exp.	0.79 ± 0.04	1.25 ± 0.05	1.53 ± 0.04	1.69 ± 0.04
			Calc.	*0.86*	*1.16*	*1.52*	*1.98*
$[Cr^{III}dien(H_2O)_3]^{3+}$	1.27	0.733	Exp.	0.90 ± 0.03	1.26 ± 0.05	1.72 ± 0.13	2.13 ± 0.03
			Calc.	*0.91*	*1.21*	*1.60*	*2.09*
$[Cr^{III}en_2(NCS)_2]^{+}$	2.55	0.464	Exp.	2.19 ± 0.01	3.56 ± 0.24	4.96 ± 0.13	5.94 ± 0.10
			Calc.	*2.19*	*2.99*	*4.00*	*5.25*
$[Cr^{III}(NH_3)_2(NCS)_4]^{-}$	3.53	0.258	Exp.	2.85 ± 0.24	3.75 ± 0.12	5.07 ± 0.18	6.66 ± 0.11
			Calc.	*3.18*	*4.34*	*5.83*	*7.68*
$[Cr^{III}edta(CN)_2]^{3-}$	2.18	0.542	Exp.	–	–	3.26 ± 0.03	–
			Calc.			*3.30*	
$[Cr^{III}edta(CN)H_2O]^{2-}$	1.68	0.647	Exp.	–	–	2.31 ± 0.05	–
			Calc.			*2.37*	
$[Cr^{III}(H_2O)_5Cl]^{2+}$	1.87	0.607	Exp.	1.24 ± 0.05	1.93 ± 0.11	2.63 ± 0.15	3.39 ± 0.17
			Calc.	*1.51*	*2.04*	*2.72*	*3.57*

Table 2 (*Continued*)

Complexes	h_L	β	k_{CR}	278 K	288 K	298 K	308 K
$[Cr^{III}en_2Cl_2]^+$	3.09	0.351	Exp.	–	–	4.9 ± 0.2	–
			Calc.			*5.00*	
$[Cr^{III}en_2(H_2O)Cl]^{2+}$	2.22	0.534	Exp.	–	–	3.44 ± 0.12	–
			Calc.			*3.37*	
$[Cr^{III}edtp]^{3-}$	1.085	0.772	Exp.	0.65 ± 0.04	0.86 ± 0.04	1.22 ± 0.02	1.50 ± 0.02
			Calc.	*0.72*	*0.96*	*1.26*	*1.63*
$[Cr^{III}(ntp)_2]^{9-}$	0.848	0.822	Exp.	0.52 ± 0.01	0.70 ± 0.05	0.89 ± 0.02	1.18 ± 0.09
			Calc.	*0.48*	*0.63*	*0.81*	*1.04*
$[Cr^{III}(imH)_6]^{3+}$	0.97	0.796	Exp.	0.53 ± 0.05	0.80 ± 0.02	1.10 ± 0.01	1.39 ± 0.05
			Calc.	*0.61*	*0.80*	*1.04*	*1.34*
$[Cr^{III}(H_2O)_4Cl_2]^+$	2.75	0.422	Exp.	–	–	4.5 ± 0.2	–
			Calc.			*4.37*	
$[Cr^{III}(NH_3)_5N_3]^{2+}$	1.70	0.643	Exp.	1.30 ± 0.10	1.73 ± 0.09	2.27 ± 0.09	2.87 ± 0.16
			Calc.	*1.34*	*1.81*	*2.40*	*3.14*
$[Cr^{III}en_2(N_3)_2]^+$	2.09	0.561	Exp.	1.84 ± 0.02	2.48 ± 0.12	3.29 ± 0.07	4.08 ± 0.07
			Calc.	*1.73*	*2.35*	*3.13*	*4.11*
$\frac{\bar{\varepsilon}_{exp}}{\Delta_{calc}}$	$\bar{\rho} = 2.3$			0.11	0.09	0.11	0.10
				0.12	0.23	0.27	0.34
$[Mn^{II}(H_2O)_6]^{2+}$	1.00	0.930	Exp.	0.58 ± 0.03	0.84 ± 0.02	1.06 ± 0.03	1.38 ± 0.02
			Calc.	*0.60*	*0.82*	*1.10*	*1.41*
$[Mn^{II}ida_2]^{2-}$	1.18	0.917	Exp.	0.63 ± 0.03	0.88 ± 0.02	1.26 ± 0.03	1.45 ± 0.03
			Calc.	*0.69*	*0.95*	*1.27*	*1.64*
$[Mn^{II}gly_3]^-$	1.28	0.911	Exp.	0.98 ± 0.03	1.28 ± 0.03	1.59 ± 0.03	1.87 ± 0.08
			Calc.	*0.74*	*1.01*	*1.35*	*1.74*
$[Mn^{II}urea_6]^{2+}$	1.33	0.907	Exp.	0.78 ± 0.02	1.11 ± 0.01	1.39 ± 0.01	1.70 ± 0.06
			Calc.	*0.77*	*1.05*	*1.41*	*1.81*
$[Mn^{II}en_3]^{2+}$	1.56	0.891	Exp.	0.85 ± 0.05	1.20 ± 0.06	1.67 ± 0.05	2.25 ± 0.10
			Calc.	*0.88*	*1.21*	*1.62*	*2.10*
$[Mn^{II}(imH)_6]^{2+}$	0.97	0.932	Exp.	0.58 ± 0.02	0.89 ± 0.01	1.16 ± 0.04	1.56 ± 0.04
			Calc.	*0.58*	*0.80*	*1.07*	*1.37*
$[Mn^{II}dmu_6]^{2+}$	1.30	0.909	Exp.	0.61 ± 0.06	0.99 ± 0.06	1.25 ± 0.06	1.68 ± 0.06
			Calc.	*0.75*	*1.03*	*1.37*	*1.78*
$*[Mn^{II}(CN)_6]^{4-}$	4.0	0.72	Exp.	–	–	2.35 ± 0.18	3.12 ± 0.35
			Calc.			*2.35*	*3.07*

Table 2 (*Continued*)

Complexes	h_L	β	k_{CR}	278 K	288 K	298 K	308 K
$\bar{\varepsilon}_{exp}$	$\bar{\rho} = 2.1$			0.14	0.04	0.07	0.14
$\bar{\Delta}_{calc}$				0.11	0.11	0.10	0.14
*ls configuration; $S = 1/2$, see Section 4.3							
$[Co^{II}(H_2O)_6]^{2+}$	1.00	0.760	Exp.	1.30 ± 0.06	1.74 ± 0.03	2.21 ± 0.07	2.71 ± 0.10
			Calc.	*1.14*	*1.48*	*1.89*	*2.37*
$[Co^{II}ntp_2]^{10-}$	0.848	0.797	Exp.	0.97 ± 0.03	1.35 ± 0.06	1.79 ± 0.06	2.36 ± 0.08
			Calc.	*0.98*	*1.26*	*1.58*	*1.96*
$[Co^{II}edtp]^{6-}$	1.085	0.746	Exp.	1.01 ± 0.08	1.43 ± 0.06	1.87 ± 0.05	2.30 ± 0.01
			Calc.	*1.20*	*1.57*	*2.00*	*2.52*
$[Co^{II}edtaH_2O]^{2-}$	1.18	0.717	Exp.	1.38 ± 0.04	1.85 ± 0.02	2.41 ± 0.05	3.02 ± 0.10
			Calc.	*1.33*	*1.74*	*2.24*	*2.84*
$[Co^{II}urea_6]^{2+}$	1.33	0.681	Exp.	1.58 ± 0.02	2.00 ± 0.03	2.54 ± 0.08	3.13 ± 0.09
			Calc.	*1.48*	*1.96*	*2.53*	*3.24*
$[Co^{II}gly_3]^{-}$	1.28	0.693	Exp.	1.51 ± 0.04	2.06 ± 0.05	2.47 ± 0.02	2.86 ± 0.03
			Calc.	*1.43*	*1.89*	*2.44*	*3.10*
$[Co^{II}dien_2]^{2+}$	1.56	0.626	Exp.	1.58 ± 0.06	2.20 ± 0.03	2.66 ± 0.03	3.27 ± 0.07
			Calc.	*1.72*	*2.29*	*2.99*	*3.84*
$*[Co^{II}(CN)_5H_2O]^{3-}$	3.50	0.160	Exp.	3.49 ± 0.18	4.82 ± 0.09	6.74 ± 0.10	8.95 ± 0.35
			Calc.	*3.72*	*5.10*	*6.81*	*8.98*
$[Co^{II}imH_6]^{2+}$	0.97	0.767	Exp.	0.96 ± 0.08	1.27 ± 0.03	1.63 ± 0.03	2.18 ± 0.10
			Calc.	*1.11*	*1.44*	*1.83*	*2.29*
$[Co^{II}dmu_6]^{2+}$	1.30	0.688	Exp.	1.50 ± 0.04	2.17 ± 0.08	2.61 ± 0.09	3.13 ± 0.07
			Calc.	*1.45*	*1.92*	*2.48*	*3.16*
$\bar{\varepsilon}_{exp}$	$\bar{\rho} = 1.3$			0.08	0.16	0.14	0.29
$\bar{\Delta}_{calc}$				0.14	0.23	0.18	0.25
*ls configuration $S = 1/2$; see Section 4.3							
$[Ni^{II}ntp_2]^{10-}$	0.848	0.805	Exp.	1.47 ± 0.13	1.85 ± 0.10	2.38 ± 0.07	2.99 ± 0.16
			Calc.	*1.54*	*2.03*	*2.61*	*3.27*
$[Ni^{II}edtaH_2O]^{2-}$	1.18	0.729	Exp.	1.87 ± 0.08	2.61 ± 0.12	3.15 ± 0.15	3.96 ± 0.05
			Calc.	*1.67*	*2.21*	*2.88*	*3.64*
$[Ni^{II}(H_2O)_6]^{2+}$	1.00	0.770	Exp.	1.44 ± 0.02	1.99 ± 0.05	2.58 ± 0.03	3.27 ± 0.10
			Calc.	*1.60*	*2.11*	*2.73*	*3.44*

Table 2 (*Continued*)

Complexes	h_L	β	k_{CR}	278 K	288 K	298 K	308 K
$[Ni^{II}urea]^{2+}$	1.33	0.694	Exp.	1.82 ± 0.01	2.37 ± 0.06	2.96 ± 0.06	3.70 ± 0.07
			Calc.	*1.73*	*2.30*	*3.00*	*3.81*
$[Ni^{II}(NCS)_2H_2OedtaH_2]^{2-}$	2.42	0.443	Exp.	2.23 ± 0.08	3.02 ± 0.06	3.84 ± 0.17	4.65 ± 0.06
			Calc.	*2.17*	*2.93*	*3.87*	*5.01*
$[Ni^{II}(NCS)_2H_2Ogly]^{-}$	2.32	0.466	Exp.	1.92 ± 0.01	2.95 ± 0.04	3.81 ± 0.08	4.59 ± 0.03
			Calc.	*2.13*	*2.87*	*3.79*	*4.90*
$[Ni^{II}dien_2]^{2+}$	1.57	0.639	Exp.	1.80 ± 0.03	2.45 ± 0.07	3.12 ± 0.07	4.03 ± 0.12
			Calc.	*1.83*	*2.44*	*3.19*	*4.07*
$[Ni^{II}(dmu)_6]^{2+}$	1.30	0.700	Exp.	1.59 ± 0.16	2.26 ± 0.12	3.00 ± 0.15	3.83 ± 0.27
			Calc.	*1.72*	*2.29*	*2.98*	*3.78*
$[Ni^{II}(imH)_6]^{2+}$	0.97	0.777	Exp.	1.45 ± 0.04	1.82 ± 0.02	2.71 ± 0.04	3.55 ± 0.11
			Calc.	*1.59*	*2.10*	*2.71*	*3.41*
$[Ni^{II}edtp]^{6-}$	1.085	0.750	Exp.	1.56 ± 0.05	2.22 ± 0.06	2.89 ± 0.12	3.57 ± 0.17
			Calc.	*1.63*	*2.16*	*2.80*	*3.54*
$[Ni^{II}gly_3]^{-}$	1.28	0.706	Exp.	2.01 ± 0.06	2.57 ± 0.02	3.16 ± 0.08	3.86 ± 0.09
			Calc.	*1.71*	*2.27*	*2.96*	*3.75*
$\bar{\varepsilon}_{exp}$	$\bar{\rho} = 1.5$			0.08	0.16	0.10	0.13
$\bar{\Delta}_{calc}$				0.18	0.19	0.14	0.21

[a] The β values were calculated with t and h constants of Table 1; the h, and then β values of mixed complexes were estimated by means of the average environment rule (AER). The $\bar{k}_{calc}$ were evaluated by using Eq. (13), eventually corrected for the spin configuration of the complexes. $\bar{\varepsilon}_{exp}$ and $\bar{\Delta}_{calc}$ are, respectively, the mean-square experimental error and the mean-square difference between experimental and back-calculated rate constants for each set of complexes at various T. ρ^T is the mean of the ratio between $\bar{\Delta}^T_{calc}$ and $\bar{\varepsilon}^T_{exp}$ at each T and $\bar{\rho}$ is the mean of ρ^T. For details see the text.

All the reactions here considered are DC, i.e. their rate constants satisfy the two conditions above. However, the rate constants of many Ps reactions, even if they satisfy the conditions above, may be larger or smaller than those (ca. 5 $dm^3\ mol^{-1}\ ns^{-1}$ in H_2O) estimated by introducing the reactant and diffusion radii equal to the crystal radii, i.e. equal to radii estimated by bond lengths and angles in the Smoluchowski equation [10,11]. This is by no means typical of positronium reactions, indeed Hart and Anbar had ascertained the same behavior in numerous reactions of hydrated electrons, e^-_{aq}, particularly in those occurring by tunneling [12]. The conclusion advanced was that the reactants cannot be considered as hard spheres with radii equal to the crystal radii, if the reactions are ruled by quantum-mechanical processes such as the reduction by tunneling or spin–spin coupling, as happens for CR.

3.2. Mechanisms and probability factors of CR

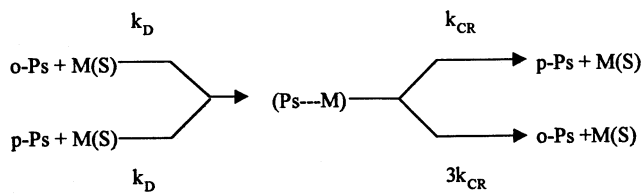
Depending on the value of the spin S of the paramagnetic species, the o-Ps into p-Ps conversion and vice versa may occur by two mechanisms: the *spin-flip* ($S = 1/2$) and the *catalyzed spin-exchange* ($S > 1/2$).

The spin-flip mechanism is sketched out in Eq. (8), where ↑ and ↑ denote the electron and positron spins, respectively:

$$o\text{-Ps}\ (\uparrow\uparrow) + \mathrm{M}\ (\downarrow) \underset{3k_{CR}}{\overset{k_D}{\rightleftarrows}} (\mathrm{M}\cdots\mathrm{Ps}) \underset{k_D}{\overset{k_{CR}}{\rightleftarrows}} \mathrm{M}\ (\uparrow) + p\text{-Ps}\ (\uparrow\downarrow) \tag{8}$$

k_D is the rate constant of formation of the collisional complex (M···Ps); k_{CR} and $3k_{CR}$ are the rate constants of o-Ps into p-Ps conversion and vice versa. Indeed, the collisional complex has three paths to o-Ps and only one path to p-Ps atom, because $m_S(o\text{-Ps}) = 0, \pm 1$ and $m_S(p\text{-Ps}) = 0$. Therefore the conversion probability of o-Ps into p-Ps per collision is 1/4. The rate constant, $k_{SE,}$ of the Ps *spin-exchange reactions*, that is the overall rate of conversion of o-Ps into p-Ps and vice versa, is $k_{SE} = k_{CR} + 3k_{CR}$. According to a long-standing agreement since the early times of Ps chemistry, the k_{CR} are presented here rather than k_{SE}.

If the reaction is of the DC type and $S > 1/2$, it cannot occur by spin flip because of the consequent spin pairing of 3d electrons requiring 1.5–3.0 eV [13]. For these cases Ferrell proposed [14] the mechanisms called *catalyzed spin-exchange*, sketched out in Eq. 8′:



(8′)

We argue as Green and Lee [15] did following Porter and Wright [16] that: since $m_S(o\text{-Ps}) = 0, \pm 1$, the spin of the collisional pair (Ps···M) between o-Ps and M(S) with $S > 1/2$, may be $(S-1)$, $(S+1)$ or S. Only in the third case, occurring in one

out of three collisions, will the *o*-Ps into *p*-Ps conversion reaction occur without violating the spin conservation law and only in 1/4 of these collisions will *p*-Ps formation result (see above).

In conclusion, the conversion reaction probability is 1/4 according to spin flip and 1/12 according to the catalyzed exchange.

All the paramagnetic complexes considered here have $S > 1/2$, excluding the $[Mn^{II}(CN)_6]^{4-}$ and $[Co^{II}(CN)_5H_2O]^{3-}$ low spin, ls, complexes, for which $S = 1/2$. Therefore, the spin flip mechanism is effective only in these two cases. They are discussed separately in the following together with that of the $[Cr^{II}(CN)_6]^{4-}$ complex ($S = 1$), also of ls type. All the other complexes considered are of the high spin, hs, type [13].

3.3. Rate constants k_{CR} of Ps conversion reactions promoted by 3d complexes

The occurrence of SE reactions does not depend only on the statistical factor discussed above, but also on the spin–spin coupling during the M and Ps contact time in the collisional complex. In the early stages of Ps chemistry and occasionally since then this factor was tentatively correlated with the number n of unpaired electrons [17], but without success however. Recently it was suggested that k_{CR} should not directly depend on n, but rather on the electron spin density at the periphery of the complexes, where the collisions between the complex species and Ps atoms occur [18]. In turn, the spin density, i.e. the electron density, should depend on both:

1. the ligand capability to delocalize the unpaired metal electrons;
2. and the tendency of metal ions to spread out their electrons towards the donor atoms and finally towards the periphery of the complexes.

In conclusion, it was argued that the k_{CR} of complexes of the ion J with the same electron configuration should be linearly correlated with β (Eq. (9)):

$$k^T_{CR,Jl} = a^T_J - b^T_J \beta_{Jl} \tag{9}$$

where $k^T_{CR,Jl}$ is the rate constant of CR promoted by the complex of the ion J with the ligand l at the temperature T; β_{Jl} is the electron delocalization in the complex; a^T_J and b^T_J are the intercept and slope of the correlation line, respectively, at the temperature T.

As a consequence, $k^T_{CR}$is expected to be proportional to n only for $\beta = 0$, i.e. only the intercepts a^T_j of the correlation lines should be directly proportional to the number n of unpaired metal electrons.

At first, the k_{CR} values were correlated with the β values calculated with Eq. (2) and the t^* and h^* values of Table 1 derived by the best fit of the UV–vis absorption data [4]. However, it was immediately recognized that better correlations could be obtained if the h^* values of Cl^-, CN^- and NCS^- ligands (2.0; 2.0 and 1.8, respectively) were substituted by 6.3; 4.0 and 4.6 (Table 1) [3,18,19]. The h^*(6 urea) and h^*(3 ox^{2-}) constants were also slightly modified to 1.33 and 1.35, respectively, instead of 1.20 and 1.50. The new h values are shown in Table 1. In order to explain the discrepancies between h^* and h, it was tentatively suggested

Table 3
Intercepts, a_J^T, slopes, b_J^T ($dm^3\ mol^{-1}\ ns^{-1}$), and correlation coefficients, r, of the correlation lines, at various T, between k_{CR}^T (in $dm^3\ mol^{-1}\ ns^{-1}$) and β for hs complexes of the ion J[a]

Ion	Parameter	278 K	288 K	298 K	308 K
Cr^{III}	a_J	4.38 ± 0.09	6.25 ± 0.16	8.22 ± 0.17	10.54 ± 0.24
$n=3$	b_J	4.82 ± 0.13	6.86 ± 0.25	9.03 ± 0.28	11.65 ± 0.36
	r	-0.9938	-0.9881	-0.9894	-0.9914
V^{II}	a_J	5.10 ± 0.31	6.59 ± 0.57	8.17 ± 0.56	11.47 ± 0.70
$n=3$	b_J	5.18 ± 0.37	6.68 ± 0.67	8.21 ± 0.69	11.65 ± 0.83
	r	-0.9949	-0.9900	-0.9862	-0.9950
Co^{II}	a_J	4.03 ± 0.16	5.70 ± 0.21	7.90 ± 0.25	10.56 ± 0.38
$n=3$	b_J	3.78 ± 0.23	5.45 ± 0.30	7.85 ± 0.37	10.89 ± 0.55
	r	-0.9850	-0.9882	-0.9913	-0.9896
Mn^{II}	a_J	7.32 ± 3.43	9.42 ± 3.26	13.67 ± 3.35	18.02 ± 4.30
$n=5$	b_J	7.22 ± 3.76	9.19 ± 3.56	13.49 ± 3.67	17.86 ± 4.71
	r	-0.6521	-0.7556	-0.8547	-0.8615
Ni^{II}	a_J	2.90 ± 0.30	4.38 ± 0.35	5.48 ± 0.27	6.44 ± 0.34
$n=2$	b_J	1.70 ± 0.44	2.96 ± 0.51	3.56 ± 0.40	3.86 ± 0.50
	r	-0.7893	-0.8871	-0.9479	-0.9322
Cr^{II}	a_J	5.73 ± 0.59	8.43 ± 0.29	11.00 ± 0.43	14.15 ± 0.21
$n=4$	b_J	4.94 ± 0.74	7.37 ± 0.36	9.43 ± 0.56	12.45 ± 0.27
	r	-0.9781	-0.9976	-0.9929	-0.9995
χ^T	Exp.[b]	1.47 ± 0.04	2.02 ± 0.06	2.72 ± 0.02	3.57 ± 0.06
	Calc.[c]	*1.47 ± 0.01*	*2.02 ± 0.01*	*2.71 ± 0.01*	*3.58 ± 0.03*

[a] n_J is the number of its unpaired electrons. χ^T, in $dm^3\ mol^{-1}\ ns^{-1}$ (number of electron)$^{-1}$, is the slope of the correlation line of a_J^T vs. n_J at any given T. The extrapolations were carried out without any constraint both for $a_J^T$and b_J^T. Details in the text.

[b] χ_{exp}^T are the experimental slopes of a_J^T vs. n_J.

[c] χ_{calc}^T are the slopes of a_J^T vs. n_J back-calculated by means of Eq. (11′)).

that the UV–vis measurements probe the metal electron delocalization to donor atoms, while the k_{CR} test that at the periphery of the complexes (see below). The point will be reconsidered later on.

The intercepts a_J^T and slopes b_J^T of the correlation lines between k_{CR}^T and β for complexes of the various ions are given in Table 3 as a function of T.

As anticipated at $T =$ constant the intercepts a_J^T of the correlation lines are proportional to the number n_J of unpaired electrons of the ion J (see Table 3 and Fig. 1), i.e.:

$$a_J^T = n_J \chi^T \tag{10}$$

By extrapolating the experimental a_J^T of Table 3 versus n_J using the least mean-squares method with the obvious constraint that the straight line must pass through the Cartesian axes origin, the χ^T values shown in Table 3 (items χ_{exp}^T) were obtained.

4. The final refinement of the correlations

Analysis of the experimental data summarized above was restrained mainly to results obtained at 298 K [3]; the h and t values used for calculating β (Table 1) were also chiefly derived from experiments carried out at this temperature [3]. The present objectives are:

1. to see if the t and h values derived from the k_{CR} at 298 K (Table 2) may also satisfactorily be used at other temperatures, as expected;
2. to find the dependence a_J^T and b_J^T on T;
3. to test the relationship between the correlation parameters for low spin, ls, and high spin, hs, complexes of the same ion and meantime to check the ratio between the reaction statistical factors for complexes with $S = 1/2$ and $S > 1/2$ (3:1) (Section 3.2);
4. to compare the experimental k_{CR}^T with those $\bar{k}_{CR}^T$ calculated by using the a_J^T and b_J^T values obtained by extrapolating the experimental a_J^T and b_J^T versus T (see below Eqs. (11) and (12))
5. to analyze the discrepancies Δ between the experimental, k_{CR}, and evaluated, $\bar{k}_{CR}$, rate constants in order to compare them with the experimental errors, ε_{exp}, of the k_{CR} measurements.

4.1. Reliability of t and h values

The β values of the various complexes are given in Table 2, while the t and h values used are shown in Table 1. The reliability of the hypothesis that t, h and then β are independent of T, may be checked by means of the correlation coefficients r of the straight lines extrapolating k_{CR} versus β at various T. There is no evidence (Table 3) that the r values depend on T, with the exclusion, perhaps, of Mn^{II}

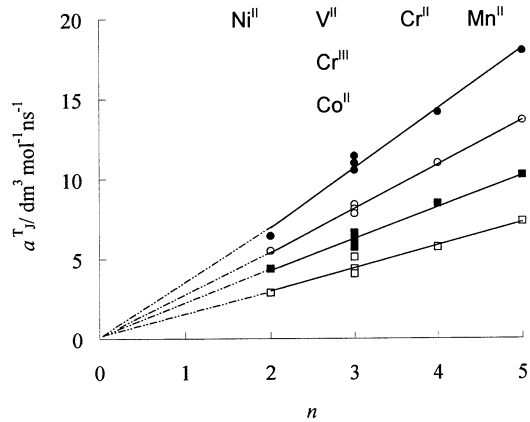


Fig. 1. Intercepts a^T of the various correlation lines versus the number n of unpaired electrons ($5 \geq n > 1$) of the named ions in the hs configuration: □ 278; ■ 288; ○ 298; ● 308 K. Data from Table 3.

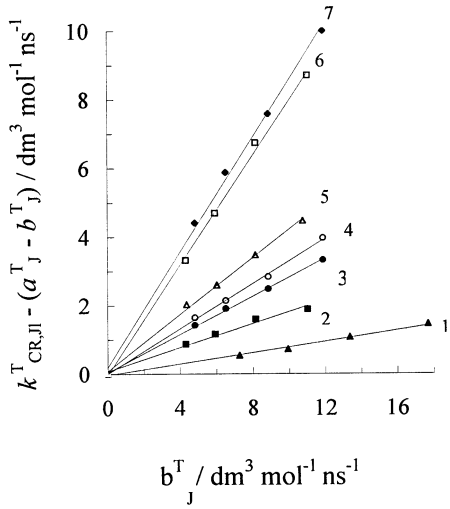


Fig. 2. Plots of Eq. (9′) for various complexes. The plots support the statement that the products t_J by h_l, suggested here, and therefore β, do not depend on T: 1 $[Mn^{II}(ida)_2]^{2-}$; 2 $[Co^{II}(imH)_6]^{2+}$; 3 $[Cr^{III}urea_6]^{3+}$; 4 $[Cr^{III}en_3]^{3+}$; 5 $[V^{II}(NCS)_6]^{4-}$; 6 $[Co^{II}(CN)_5H_2O]^{3-}$; 7 $[Cr^{III}(CN)_6]^{3-}$. k^T_{CR} from Table 2; a^T_J and b^T_J from Table 4.

complexes (r values are worse at 278 and 288 K) possibly because of the small k_{CR} values at 278 and 288 K.

The statement may also be checked by writing Eq. (9) as shown below (Eq. (9′)):

$$k^T_{CR,J,l} - (a^T_J - b^T_J) = b^T_J t_J h_l \tag{9′}$$

A plot of the left-hand side of Eq. (9′) versus b^T_J for any given complex Jl at various T, should be a straight line passing through the Cartesian origin, provided that the product t_J by h_l is independent of T. As an example some plots of this type are shown in Fig. 2; the plots support the statement, at least, within the T interval checked and the experimental error. Later on it will be shown that the parameter t is also independent of the spin configuration of the complexes.

4.2. Intercepts and slopes of the correlation lines between k_{CR} and β as a function of T

The Smoluchowski equation (7), which applies to k^T_{CR} values, may also be extended to b^T_J and a^T_J and therefore to χ^T. For χ^T, one obtains Eq. (11):

$$\frac{\chi^T}{T} = \alpha_0 \exp(-E_a/k_B T) \tag{11}$$

where E_a is the activation energy of χ^T and α_0 is a constant given in dm^3 mol^{-1} ns^{-1} (number of electron)$^{-1}$. The activation energy E_a of χ^T, obtained from the

slope of the straight line extrapolating $\ln(\chi^T/T)$ versus $1/T$, is 2243 ± 11 mol K^{-1}, corresponding to $E_a = 0.194 \pm 0.001$ eV. E_a is practically equal to the activation energy E_η of the viscosity coefficient of the reaction medium, water in the present case ($E_\eta = 0.184 \pm 0.004$) [3]. The intercept, $\ln \alpha_0$, of the straight line is 2.826 ± 0.039 (1.4%), i.e. $\alpha_0 = 16.86 \pm 0.66$ dm^3 mol^{-1} ns^{-1} (number of electron)$^{-1}$.

The χ^T values back-calculated with the following equation:

$$\chi^T = 16.87T \exp(-2243/T) \quad (11')$$

are equal (see χ^T_{calc} in Table 3) to the measured ones within the experimental error, i.e. within ± 0.01 dm^3 mol^{-1} ns^{-1} (number of electron)$^{-1}$.

In order to obtain b_J^T, since a_J^T at T = constant is given by $n_J\chi^T$, the experimental $k^T_{CR,Jl}$ were extrapolated versus β with the constraint that the straight lines must pass through the points $P(0,n_J\chi^T)$, i.e. the intercept a_J^T of the correlation line was constrained to the value $n_J\chi^T$. The χ^T values were calculated by means of Eq. (11′) and the parameters α_0 and E_a quoted above (see also Table 3). The estimated b_J^T values are shown in Table 4 (items $b^T_{J,exp}$).

The $b^T_{J,exp}$ of each ion J may be extrapolated versus T by means of Eq. (12), also derived from Eq. (7):

Table 4
Slopes b_J^T (same units as in Table 3) of the straight lines extrapolating $k^T_{CR,Jl}$ vs. β for hs complexes of the ion J with the ligand l as a function of T[a]

Ion	Parameters of the extrapolating line		278 K	288 K	298 K	308 K
Cr^{III}	$a_J^T = n_J\chi^T$		4.41	6.04_5	8.12	10.72
$n_J = 3$	b_J^T	Exp.[b]	4.83 ± 0.04	6.52 ± 0.08	8.86 ± 0.09	11.88 ± 0.12
		Calc.[c]	4.78 ± 0.01	6.59 ± 0.03	8.80 ± 0.005	11.78 ± 0.010
V^{II}	$a_J^T = n_J\chi^T$		4.41	6.04_5	8.12	10.72
$n_J = 3$	b_J^T	Exp.[b]	4.37 ± 0.09	6.03 ± 0.11	8.15 ± 0.10	10.75 ± 0.14
		Calc.[c]	4.37 ± 0.03	6.02 ± 0.03	8.13 ± 0.05	10.77 ± 0.08
Co^{II}	$a_J^T = n_J\chi^T$		4.41	6.04_5	8.12	10.72
$n_J = 3$	b_J^T	Exp.[b]	4.32 ± 0.07	5.93 ± 0.08	8.16 ± 0.09	11.02 ± 0.13
		Calc.[c]	4.30 ± 0.01	6.00 ± 0.01	8.20 ± 0.01	10.99 ± 0.02
Mn^{II}	$a_J^T = n_J\chi^T$		7.35	10.08	13.55	17.85
$n_J = 5$	b_J^T	Exp.[b]	7.26 ± 0.05	9.92 ± 0.05	13.36 ± 0.05	17.67 ± 0.06
		Calc.[c]	7.26 ± 0.01	9.96 ± 0.01	13.39 ± 0.01	17.68 ± 0.01
Ni^{II}	$a_J^T = n_J\chi^T$		2.94	4.03	5.42	7.14
$n_J = 2$	b_J^T	Exp.[b]	1.76 ± 0.07	$2.45 \pm .09$	3.48 ± 0.06	4.85 ± 0.10
		Calc.[c]	1.74 ± 0.01	2.49 ± 0.01	3.49 ± 0.01	4.80 ± 0.02
Cr^{II}	$a_J^T = n_J\chi^T$		5.88	8.06	10.84	14.28
$n_J = 4$	b_J^T	Exp.[b]	5.13 ± 0.10	6.91 ± 0.07	9.24 ± 0.11	12.62 ± 0.04
		Calc.[c]	5.07 ± 0.01	6.98 ± 0.02	9.40 ± 0.02	12.44 ± 0.05

[a] The constraints that the intercepts must be $n_J\chi_0^T$ are imposed. n_J and χ_0^T in Table 3 (details in the text).

[b] The experimental b_J^T values obtained under the conditions given above.

[c] The backcalculated b_J^T values were obtained by means of Eq. (12) with the γ_{0J} and $E_{b,J}$ given in Table 5.

Table 5
The parameters $\gamma_{0,J}$ and $E_{bJ}$of Eq. (12), obtained by linear extrapolation of $\ln(b_J^T/T)$ vs. $1/T$, are given together with the correlation coefficients, r, of the straight lines[a]

	r	$\ln \gamma_{0,J}$	$\gamma_{0,J}$	E_{bJ}/k_B (K)	$E_{b,J}$ (eV)
Cr^{III}	0.9996	4.1422	62.94	2281 ± 45	0.197 ± 0.000
V^{II}	1.0000	4.0448	57.10	2279 ± 9	0.197 ± 0.001
Co^{II}	0.9998	4.4096	82.24	2385 ± 27	0.206 ± 0.002
Mn^{II}	1.0000	4.4376	84.57	2247 ± 8	0.194 ± 0.001
Ni^{II}	0.9994	4.3126	74.63	2610 ± 66	0.225 ± 0.006
Cr^{II}	0.9990	4.1478	63.29	2266 ± 73	0.196 ± 0.006
		$\ln \alpha_0$	α_0	E_a/k_B (K)	E_a (eV)
χ	1.0000	2.8257	16.87	2243 ± 11	0.194 ± 0.001

[a] The $r_{2;0.01}$ and $r_{2;0.001}$ for two degrees of freedom at 0.01 and 0.001 levels of risk are 0.9900. The analogous parameters α_0 and E_a of Eq. (11) are given in the last line.

$$b_J^T = \gamma_0 T \exp(-E_{bJ}/k_B T) \tag{12}$$

Table 5 shows the parameters γ_0 and E_{bJ} of Eq. (12) obtained by extrapolating $\ln(b_{J,\mathrm{exp}}^T/T)$ (Table 4) versus $1/T$ by means of the least-squares method. With the exception, perhaps, of the Ni^{II} ion, the E_{bJ} activation energies are compatible with the activation energy of the viscosity coefficient of the reaction medium, water in the present case (0.184 ± 0.005 eV). The discrepancy presented by Ni^{II} may be due both to the small variations of the k_{CR} of Ni^{II} complexes with β and to their experimental error.

Table 4 shows the slopes $b_{J,\mathrm{calc}}^T$, calculated using Eq. (12) and the pertinent γ_{0J} and E_{bJ} values of Table 5. They agree rather well with experimental values.

4.3. Correlations between k_{CR} and β for high- and low-spin complexes

We assume that t is dependent on the ion valence, but independent of the spin configuration of the complexes, and that, in order to adapt the correlation lines of hs to ls complexes, the intercepts a and slopes b of the hs correlation lines must be:

1. multiplied by $\bar{n}_J/n_J$, where $\bar{n}_J$ and n_J are the number of unpaired electrons of the ion J in ls and hs configurations, respectively;
2. and, if $S = 1/2$ in ls configuration, a and b must also be multiplied by 3 in order to take into account the different reaction probabilities for $S = 1/2$ and $S > 1/2$ (1/4: 1/12, respectively) (see Section 3.2).

The $[Cr^{II}(CN)_6]^{4-}$, $[Mn^{II}(CN)_6]^{4-}$, and $[Co^{II}(CN)_5H_2O]^{3-}$ complexes (see Table 6) may illustrate the different cases offered by the normalization of the k_{CR} values of the ls complexes to the k_{CR} values predicted by the correlation lines for hs complexes with the same β. Calling F the normalization factor, one has:

1. $[Cr^{II}(CN)_6]^{4-}$: Since $n_J = 4$ and $\bar{n}_J = 2$, F is 2. This is the simplest case.
2. $[Mn^{II}(CN)_6]^{4-}$: Since $n_J = 5$ and $\bar{n}_J = 1$, F is 5/3; the factor 5 accounts for the different number of unpaired electrons in hs and ls configurations (5:1), while

1/3 takes into account the different reaction probabilities for $S > 1/2$ and $S = 1/2$ (Section 3.2).

3. $[Co^{II}(CN)_5H_2O]^{3-}$: Since $n_J = 3$, $\bar{n}_J = 1$ and the ratio of the reaction probabilities in hs and ls configurations for $S = 1/2$ is 1/3, the normalization factor F is 1. The case is analogous to the previous one, but here the two parts of the normalization factor fortuitously compensate each other.

Reciprocally, the parameters a and b of the correlation lines for ls complexes may be obtained by multiplying those of the hs configurations (Table 4) by $\bar{n}_J/n_J$ and also by 3 if $\bar{n}_J = 1$. Table 2 shows that the experimental k_{CR} values of the ls complexes are in agreement with their estimates, suggested here.

4.4. Comparison between experimental and back-calculated rate constants

The back-calculated $\bar{k}^T_{CR,J}$ values for complexes of the ions mentioned in the hs configurations may be obtained by means of the following equation (13) derived by combining Eqs. (1), (2), (10) and (11) and Eq. (12):

$$\bar{k}^T_{CR,J} = n_J \alpha_0 T \exp(-E_a/k_B T) - \gamma_{0J} T[\exp(-E_{bJ}/k_B T)](1 - th) \quad (13)$$

n_J being the number of unpaired electrons of the ion J in the hs configuration. For low spin complexes see Section 4.3.

By using the α_0, E_a, γ_{0J}, E_{bJ}values of Table 5 and the t and h values of Table 1, the $\bar{k}^T_{CR,Jl}$ values shown in Table 2 (in italic) were derived.

The mean-square difference $\bar{\Delta}^T_J$ between calculated and experimental rate constants are reported in Table 2 for the complexes of each ion J at various T. The mean-square, $\bar{\varepsilon}^T_{exp}$, of the experimental errors, and the mean values, $\bar{\rho}_J$, of $\rho = \bar{\Delta}^T_J / \varepsilon^T_{exp}$ are also inserted in Table 2.

It may be seen that $\bar{\rho}_J$ is no larger than 1.9. Thus, by assuming that:

$$\bar{\Delta} = (\bar{\varepsilon}^2_{exp} + \bar{\varepsilon}^2_{calc})^{1/2} \quad (14)$$

where $\bar{\varepsilon}_{calc}$ is the mean-square error of the rate constants $\bar{k}^T_{CR,Jl}$ estimated by Eq. (13), one obtains:

Table 6
High- and low-spin configurations of Cr^{II} (d^4), Mn^{II} (d^5) and Co^{II} (d^7) ions together with the corresponding S values. β values are also shown together with the factors F which normalize the k_{CR} of ls configurations (Table 2) to those of the complexes in hs configurations[a]

Complex	ls	hs	β	F
$[Cr^{II}(CN)_6]^{4-}$	t^4_{2g}; $S = 1$	$t^3_{2g}e^1_g$; $S = 2$	0.480	2
$[Mn^{II}(CN)_6]^{4-}$	t^5_{2g}; $S = 1/2$	$t^3_{2g}e^2_g$; $S = 5/2$	0.720	5/3
$[Co^{II}(CN)_5H_2O]^{3-}$	$t^6_{2g}e^1_g$; $S = 1/2$	$t^5_{2g}e^2_g$; $S = 3/2$	0.160	1

[a] Slopes and intercepts of the hs correlation lines are given in Table 4.The normalized k_{CR} are in nice agreement with those of the hypothetical complexes of the same ions J with the same β (Table 2).

Table 7
Slopes and correlation coefficients of the straight lines extrapolating $\bar{k}^T_{CR,Jl}$ vs. $k^T_{CR,Jl}$ at 278, 288, 298 and 308 K (see Fig. 3(a–d))[a]

T (K)	Slopes	r	v
278	1.012 ± 0.011	0.987	56
288	0.973 ± 0.011	1.000	56
298	0.986 ± 0.008	0.991	66
308	1.013 ± 0.009	0.992	56

[a] The correlation coefficients r for 66 and 56 degrees of freedom (v) at 0.001 level of risk are: $r_{66;0.001} < r_{56;0.001} = 0.41$.

$$\frac{\bar{\Delta}}{\bar{\varepsilon}_{exp}} = \left(1 + \frac{\bar{\varepsilon}^2_{calc}}{\bar{\varepsilon}^2_{exp}}\right)^{1/2} = \bar{\rho} \tag{15}$$

where $\bar{\varepsilon}_{calc}$ is the mean square error of the calculated $\bar{k}^T_{CR,Jl}$. Since $\rho \leq 1.9$ (see Table 2), it follows that $\bar{\varepsilon}_{calc}$ is not larger than 1.6 times $\bar{\varepsilon}_{exp}$.

Finally, slopes and correlation coefficients of the straight lines extrapolating $\bar{k}^T_{CR,Jl}$ versus $k^T_{CR,Jl}$ at various T with the constraint that the straight lines must pass through the origin (see Table 7 and Fig. 3(a–d)) are practically equal to 1.

5. Conclusions

The main achievements from the data reviewed here [3] may be summarized as follows: the rate constants, $k^T_{CR,Jl}$ of the conversion reactions promoted at the temperature T by the complexes of the 3d ion J with the ligands l, may be estimated by Eq. (9). The a^T_J and b^T_J values may be calculated by means of Eqs. (11′) and (12) within 278 and 308 K, but the T interval may probably be enlarged on both sides by at least 5 K.

The electron delocalization β_{Jl}, given by the B/B_0 ratio between the inter-electronic repulsion parameters in complex, B, and that in the free ions, B_0, may be estimated by means of the an empirical equation (Eq. (2)), already suggested in the literature.

The constants t and h, presented in Table 1, were obtained by assuming the following conditions: $h(6\ H_2O) = 1$ and $\beta = 0$ as h attains the value $1/t$ [3]. While the first condition is also common to that used in the best fit of UV–vis absorption spectra [7], the second is new for t and h values derived from k_{CR} measurements [3]. The constants t and h of Table 1 give the best results as far as the correlation between k_{CR} and β values are concerned.

The differences between h and h^* values (Table 1) may be ascribed to the fact that the UV–vis spectra probe the electron delocalization towards the donor atoms, while k_{CR} should test that at the periphery of the complexes. However, one cannot disregard the consequences of the different mathematical constraint applied to the product t by h in the two cases [3].

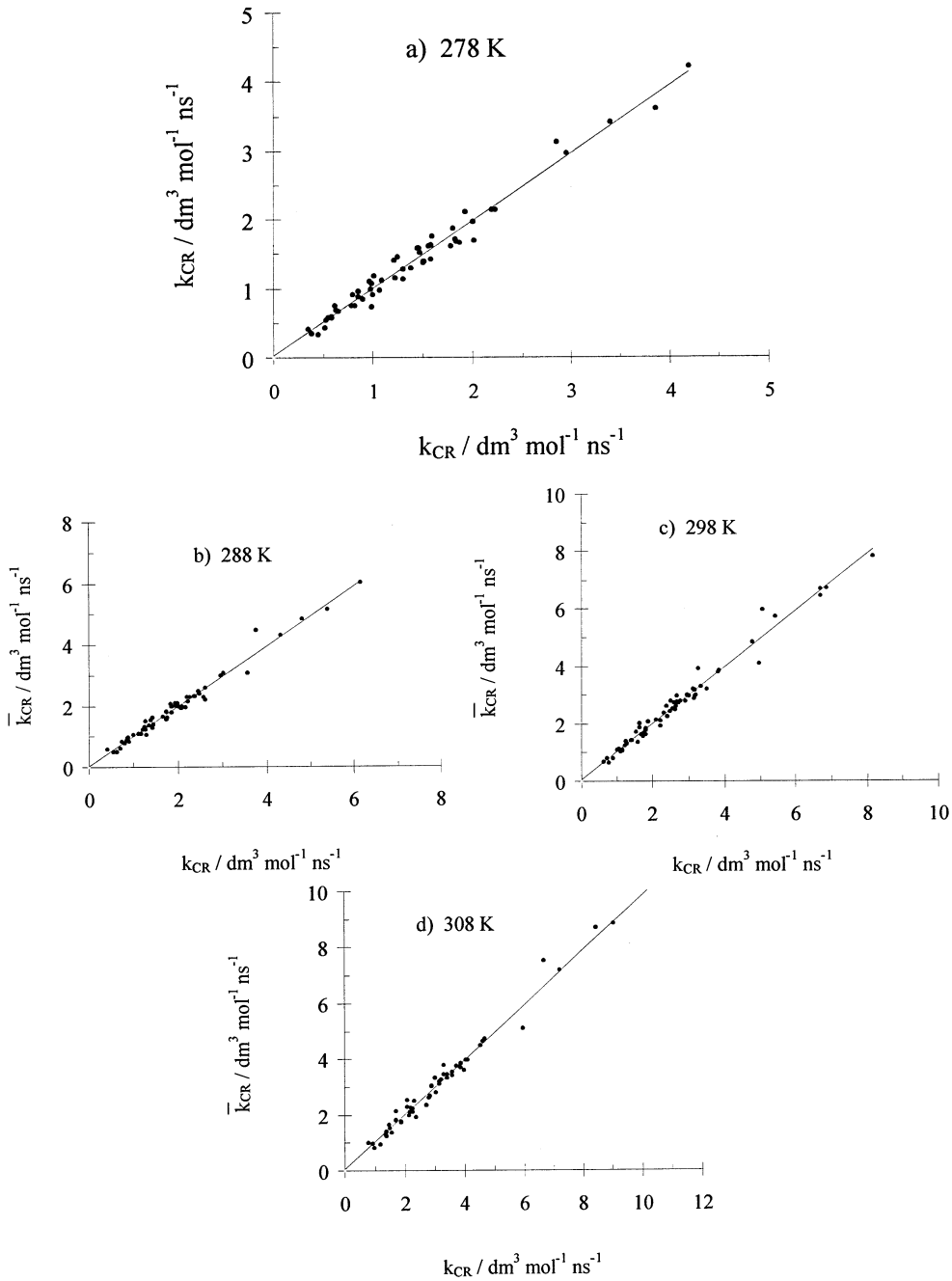


Fig. 3. Plots of $\bar{k}_{CR}$ vs. k_{CR} at various T: (a) 278; (b) 288; (c) 298; (d) 308 K. The slopes of the extrapolating straight lines are given in Table 7 together with their correlation coefficients r and the degrees of freedom v.

The t, h, a_J^T and b_J^T values proposed in Tables 1 and 4 constitute a congruent system of data, from which k_{CR}^T may be evaluated, once the β values are known. Vice versa, the β values of the complexes may be estimated by means of the corresponding k_{CR}^T values and Eq. (9′).

Eq. (13) valid for complexes of the ion J in the hs configuration may be adapted to complexes in the ls configuration by multiplying both terms on the right side of Eq. (9′) by $\bar{n}_J/n_J$, where $\bar{n}_J$ and n_J are the number unpaired electrons of the ion in ls and hs configurations respectively, and, eventually, by 3, if $\bar{n}_J = 1$.

In conclusion, four main points may be stated:

1. Eq. (2) seems to work better than previously believed;
2. the explanation advanced to justify the dependence of the *o*-Ps into *p*-Ps conversion rate constants on the chemical constitution of the paramagnetic 3d complexes causing the spin exchange, should be regarded as a new successful outcome of ligand field theory;
3. the t value of Eq. (2) does not depend on the spin configuration;
4. a new experimental method is suggested for determining the electron delocalization in 3d complexes caused by ligands.

From a more general point of view, one may say that the chemistry of exotic atoms is not esoteric, i.e. an isolated branch of the chemistry, but, on the contrary, it involves the core of many fundamental chemical problems. Moreover the positronium chemistry of 3d complexes, including the redox reactions which were not considered here [3], is by no means the lone point of impact between positronium and chemistry; other examples are surface chemistry, radiation chemistry, polymer chemistry, solid state chemistry, micelle chemistry and even biological chemistry, since micelles are the simplest model of cellular structures [2]. The apparent novelty and strangeness of this research is a product both of the present fragmentation of the sciences and also of the difficulty to dominate nearby fields of chemistry.

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