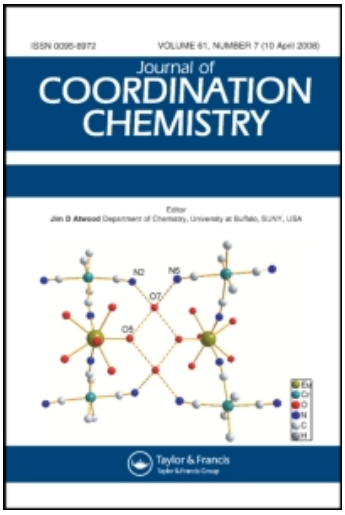

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LIGAND REDISTRIBUTION RATES IN BERYLLIUM AND BORON 1,3-DIKETONATES. STRUCTURE–LABILITY RELATIONSHIPS

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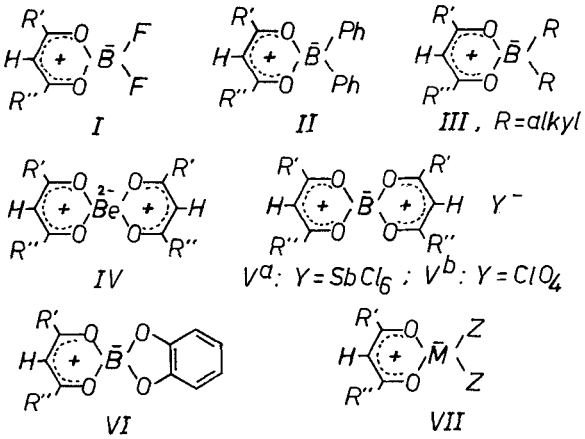
The redistribution of the 1,3-diketonic ligand was investigated in complexes of the types I, II, IV–VI, using samples prepared from ^{14}C-labelled ligands. Ligand lability in the boron complexes studied was found to be proportional to the measured ^{11}B-NMR chemical shift, i.e. inversely proportional to the electron density at the central atom, which is determined by the electronegativities of the ligands Z (formula VII) attached to it: the measured labilities are found to be inversely proportional to the electron-attracting power of the ligands Z, expressed by means of their Taft constants, σ^*. Several other properties of the studied complexes may be related to the same σ^* values: $\pi \rightarrow \pi^*$ transition energies, NMR chemical shifts of the protons of the chelated 1,3-diketone ligand and chemical shifts of the central boron nucleus (^{11}B).

INTRODUCTION

Studies in ligand redistribution[1–4] cleared up the correlation between ligand lability and several fundamental properties of the complex molecule, as the orbital structure of the central atom (the inner orbital–outer orbital concept), its valency and coordination number, the dentarity of the exchanging ligand, etc.

In this work an attempt was made towards further understanding of the relationships between structure and lability of the chelate complexes. All the boron complexes investigated preserve the same set of enumerated fundamental properties. Varied were other structural elements, which influence the electron distribution within the complex molecule: substituents of the chelate ring and of the central atom.



Complexes of the types I–VI were investigated; mostly for practical reasons the 1,3-diketones used were benzoylacetone and dibenzoylmethane. Redistribution experiments on bis-(acetylacetonato)-beryllium were reported earlier.[5]

All these compounds can be represented by formula VII, where $M = Be,B$; R', $R'' = Me,Ph$; $Z = F,Ph$, alkyl or $2Z$ = 1,3-diketone or catechol.

EXPERIMENTAL

Acetylacetone, benzoylacetone and dibenzoylmethane labelled with ^{14}C at their carbonyl groups were prepared by aliphatic acylation procedures,[6] starting from labelled acetic anhydride. Using these labelled ligands, the boron and beryllium complexes II, IV–VI were synthetized by methods used in our laboratory to obtain the inactive compounds.[7–9]

Difluoro-boron 1,3-diketonates I, were prepared as follows: 10 mmoles of 1,3-diketone were dissolved in 25 ml of dry ether and a solution of 1.5 ml boron trifluoride-etherate (cca. 1.5 g, 10 mmoles) in 15 ml of dry ether added. The mixture was refluxed 4–6 hours, then evaporated to dryness. The products were recrystallized from chloroform–petroleum ether.

Labelled complexes used for redistribution experiements were purified by successive recrystallizations till literature melting point and constant

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specific activity were attained. The unlabelled free ligands used in redistribution experiments presented no impurity peaks in their p.m.r. spectra. Spectroscopic grade (Merck) dichloromethane (stabilized against phosgene formation) was used for redistribution, without further purification. Acetonitrile used for redistribution was dried over phosphorus pentoxide and distilled.

Ligand redistribution experiments (Observed maximum errors are indicated in parentheses.) Weighed amounts (0.5%) of labelled complex and unlabelled free ligand were dissolved in 3–9 ml (1.0%) of dichloromethane (acetonitrile for complex salts V) and the solutions kept at 25 ± 2°C. All concentration sets for a given complex were incubated simultaneously. At measured time intervals (1.0%) aliquots of 1 ml were removed and added into 15 ml of petroleum ether (carbon tetrachloride for compounds V). The complex precipitated after stirring. For compound II ($R' = Me$, $R'' = Ph$), chilling to −30° was necessary to obtain a precipitate. The precipitated complex was filtered, washed with petroleum ether and dried in air; no impurities (free ligand was especially followed) could be detected by p.m.r. spectroscopy in complex samples recovered this way. Zero time exchange was monitored and found negligible in each case. A different procedure was used for redistribution of bis-(acetylacetonato)-beryllium.[5]

Specific activities of the complex samples were determined by liquid scintillation spectrometry, using a Packard Tricarb 3375 apparatus. Amounts between 2–5 mg of sample (2.5%) were dissolved in 15 ml of cocktail (toluene–PPO–POPOP) and counted to a standard deviation less than 1.0%. For the complex salts V another cocktail, made from benzonitrile–PPO–POPOP was used.[10] Counting efficiencies found between 20–88% were determined (2.5%) from calibration curves by the AES-Ratio method, using quenched standard ^{14}C samples. The maximum cumulative error of this specific activity determination procedure was checked on 15 samples of bis-(^{14}C-acetylacetonato)-beryllium and found to be 7.5%. Observed errors on kinetic samples were always considerably smaller than this figure.

Kinetic experiments had to be effected on a rather large number of complexes; to keep the amount of experimental work within reasonable limits, the requirements of a rigorous statistics had to be overlooked. Kinetic experiments were run for each complex at three concentration sets at least, but as a rule these experiments were not duplicated. Three samples of different exchange times were taken from each solution. Owing to their very slow redistribution, for several complexes samples had to be taken at low values of the exchange fraction F, a domain of high experimental errors.

UV-Spectra used were recorded in 1,2-dichloroethane solutions during this work, or reported earlier.[9,11–13] P.m.r. spectral data are taken from refs. 12, 14, 15. ^{11}B–N.m.r. spectra were taken from ref. 12, or were recorded with a Perkin Elmer R 10 instrument at a working frequency of 19.2519 MHz, using C.A.T. accumulation where necessary. Boron trifluoride-etherate was used as external standard. Detailed description of these spectra will be published elsewhere.

RESULTS AND DISCUSSION

As shown in the experimental section, ligand redistribution was investigated by preparing complexes I, II, IV–VI, starting from ^{14}C-labelled 1,3-diketone ligands, dissolving the labelled complex in a solution of the unlabelled free ligand and following the activity decrease in the complex, according to the equation

$$*diketMZ_2 + diketH \leftrightarrows diketMZ_2 + *diketH \quad (1)$$

Ligand redistribution rates R* were computed according to the classical McKay approach for isotopic exchange. The rate of exchange by equation (1) will be

$$R^* = -\frac{2.303}{t} \cdot \frac{n.a.b}{n.a + b} \cdot \lg(1 - F) \quad (2)$$

where n is the number of exchangeable diketone units in the complex $diketMz_2$ ($n = 1$ for I, II and VI, $n = 2$ for IV and V), t is the exchange time, a is the concentration of the complex and b is the concentration of the free ligand in the solution. F is the fraction of exchange defined as

$$F = \frac{x_0 - x_t}{x_0 - x_\infty},$$

where x_0, x_t and x_∞ are the specific activities of the complex at $t = 0$, t and ∞ (at equilibrium).

The results of the performed redistribution experiments are shown in Tables I–V.

The actual mechanism of ligand redistribution in metallic 1,3-diketonates can be quite complicated[16] owing to participation of species other than the exchange partners: trace amounts of

TABLE I

Ligand redistribution rates for difluoro-boron 1,3-diketonates (I) in dichloromethane solution.

R'	R''	a	b	R^*	k_1	k_2	S
		moles/l		$10^{-8}\frac{moles}{l.s}$	$10^{-6}.s^{-1}$	$10^{-6}\frac{1}{moles.s}$	$10^{-6}\frac{moles}{l.s}$
CH_3	C_6H_5	0.080 0.128 0.169	0.420 0.345 0.272	0.32±0.08 0.52±0.05 0.69±0.07	0.040±0.001	—	0.040
C_6H_5	C_6H_5	0.053 0.066 0.090	0.243 0.171 0.123	0.06±0.01 0.09±0.02 0.07±0.01	0.011±0.003	—	0.011

TABLE II

Ligand redistribution rates for diphenyl-boron 1,3-diketonates (II) in dichloromethane solution

R'	R''	a	b	R^*	k_1	k_2	S
		moles/l		$10^{-8}\frac{moles}{l.s}$	$10^{-6}.s^{-1}$	$10^{-6}\frac{1}{moles.s}$	$10^{-6}\frac{moles}{l.s}$
CH_3	C_6H_5	0.0347 0.0423	0.1671 0.1074	51.3±7.0 63.3±10.0	14.87±0.09	—	14.9
C_6H_5	C_6H_5	0.0305 0.0430 0.0545	0.195 0.164 0.122	17.6±3.0 25.5±3.0 29.7±3.0	5.7±0.3	—	5.7

TABLE III

Ligand redistribution rates for beryllium 1,3-diketonates (IV) in dichloromethane solution.

R'	R''	a	b	R^*	k_1	k_2	S
		moles/l		$10^{-8}\frac{moles}{l.s}$	$10^{-6}.s^{-1}$	$10^{-6}\frac{1}{moles.s}$	$10^{-6}\frac{moles}{l.s}$
CH_3	CH_3	0.048 0.097 0.097 0.242	2.000 1.000 2.000 5.000	160 160 330 2000	—	16.70±0.30	16.70
CH_3	C_6H_5	0.0427 0.0604 0.0604 0.0790	0.618 0.621 0.433 0.247	7.0±0.6 9.2±0.2 9.3±0.6 12.1±1.5	1.56±0.10	—	1.56
C_6H_5	C_6H_5	0.0450 0.0590 0.0760	0.522 0.375 0.227	2.54±0.18 3.21±0.20 3.50±0.14	0.52±0.06	—	0.52

TABLE IV

Ligand redistribution rates for boronium 1, 3-diketonates (V) in acetonitrile solution

Ligand		Anion	a	b	R^*	k_1	k_2	S
R'	R''	Y^-	moles/l		$10^{-8}\frac{\text{moles}}{\text{l}\,.\,\text{s}}$	$10^{-6}\,.\,\text{s}^{-1}$	$10^{-6}\frac{1}{\text{moles}\,.\,\text{s}}$	$10^{-6}\frac{\text{moles}}{\text{l}\,.\,\text{s}}$
CH_3	C_6H_5	$SbCl_6$	0.0208	0.309	2.90±0.10	0.89±0.01	1.63±0.05	2.52
			0.0315	0.216	3.90±0.23			
			0.0419	0.113	4.50±0.23			
		ClO_4	0.0256	0.639	1.63±0.05	0.60±0.02	0.06 ± 0.03	0.66
			0.0354	0.263	2.22±0.30			
			0.0470	0.376	2.90±0.08			
C_6H_5	C_6H_5	$SbCl_6$	0.0127	0.1494	0.75±0.07	0.36±0.06	1.61 ± 0.30	1.97
			0.0193	0.1235	1.04±0.08			
			0.0259	0.0930	1.30±0.24			
		ClO_4	0.0123	0.2242	0.24±0.10	0.15±0.02	—	0.15
			0.0193	0.1513	0.31±0.07			
			0.0246	0.0933	0.31±0.03			

TABLE V

Ligand redistribution rates for 2,2-spiro-1′,3′-diketonato-1,3,2-benzodioxaboroles (VI) in dichloromethane solution.

R'	R''	a	b	R^*	k_1	k_2	S
		moles/l		$10^{-8}\frac{\text{moles}}{\text{l}\,.\,\text{s}}$	$10^{-6}\,.\,\text{s}^{-1}$	$10^{-6}\frac{1}{\text{moles}\,.\,\text{s}}$	$10^{-6}\frac{\text{moles}}{\text{l}\,.\,\text{s}}$
CH_3	C_6H_5	0.0425	0.335	273±25	61±5	—	61
		0.0481	0.197	283±15			
		0.0613	0.268	397±26			
		0.0787	0.219	445±18			
C_6H_5	C_6H_5	0.024	0.225	51.0±1.0	20±1	—	20
		0.032	0.166	62.5±0.8			
		0.039	0.114	77.0±0.2			

water or H_3O^+ in the exchange system may be especially important. However in many cases the actual mechanism can be satisfactorily approximated by a relatively simple equation:[5,17-19]

$$R^* = k_1\,.\,a + k_2\,.\,a\,.\,b.$$

Since the elucidation of the reaction mechanisms in all detail was beyond the scope of this work, this simple approach was used to calculate redistribution rate constants. Actually in most cases even k_2 seemed unimportant, the best approximation being realized by a monomolecular equation, $R^* = k_1\,.\,a$. This equation was used for all cases in Tables I–V, where no k_2 is indicated. The value[5] of k_2 for bis-(acetylacetonato)-beryllium (Table III), was calculated according to a purely bimolecular equation: $R^* = k_2\,.\,a\,.\,b$. For characterization of ligand lability in the investigated complexes the redistribution rate S in molar solution both for the complex ($a = 1$) and the free ligand ($b = 1$) was used. Numerically we have $S = k_1 + k_2$. Owing to this simplistic view about the redistribution mechanism and to the statistical unorthodoxy of the kinetic experiments (discussed in the experi-

mental section) the calculated rate constants (k_1, k_2) are subject to considerable uncertainty. But as S values differ from complex to complex by orders of magnitude, they are certainly significant for the discussion below.

A crucial observation concerning the influence of the molecular structure of the complex on ligand lability is the proportionality between ligand labilities expressed as lgS and ^{11}B–NMR chemical shifts of the central atom as shown in Fig. 1. The

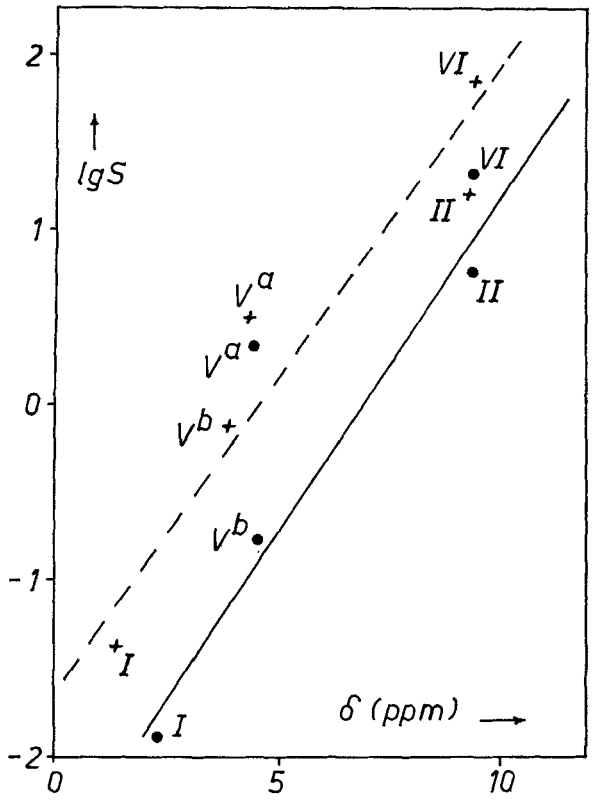


FIGURE 1 Dependance of ligand labilities S for boron 1,3-diketonates from the ^{11}B chemical shift of the central atom.
+ – $R' = Me$, $R'' = Ph$; ● – R^1, $R'' = Ph$.

chemical shift is an experimental measure of the electron density at the respective nucleus; our data are δ values, i.e. to low fields from the standard, which means that they are inversely proportional to the respective electron densities. Consequently, ligand lability is inversely proportional to the electron density at the central atom. The redistributing 1,3-diketone ligand being the same, these differences in electron density (and ligand lability) have to be attributed to the substituents Z (formula VII) of the central atom, and namely to their inductive effect. Indeed, an approximate proportionality is obtained when plotting the observed labilities (lgS) against the electron attracting power of the substituents Z expressed as their Taft constants,[20] σ^* (Fig. 2). An item remains to be

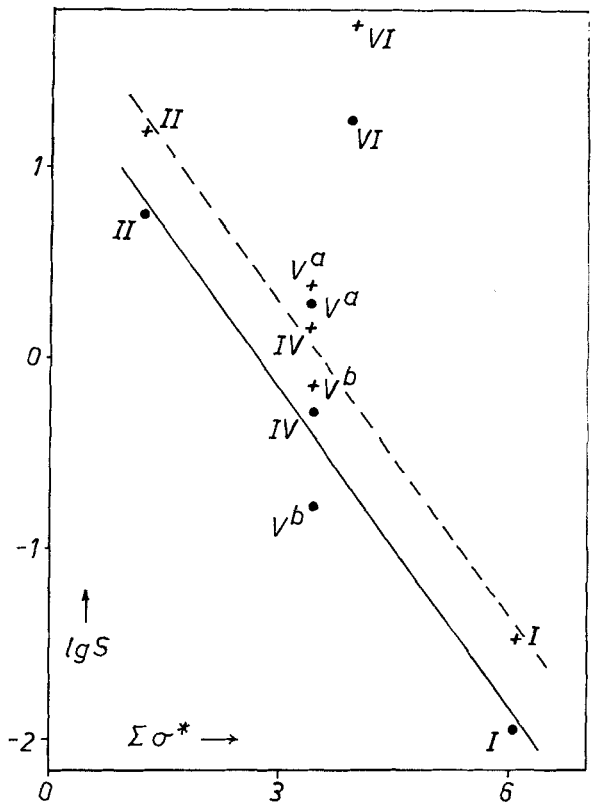


FIGURE 2 Dependance of ligand labilities S from the electron-attracting power of the substituents Z of the central atom.
+ – $R' = Me$, $R'' = Ph$; ● – R', $R'' = Ph$.

clarified at this point: there are no available Taft constants for our bidentate substituents $2Z$ and there seems no easy way to determine them experimentally. The values in Fig. 2–5 are rough estimates, using constants for similar atom groups: two $COCH_3$ groups for an 1,3-diketone and a OC_6H_5 plus a OCH_3 group for catechol. The important abberations observed for the catechol complexes VI from the supposed proportionality plotted in Fig. 2 show that the estimated σ^* value for catechol is seriously in error, or that other than inductive effects influence greatly the electron density at the central atom.

Several other physical properties of the studied complexes can be plotted against the same σ^* values of the substituents Z, giving approximate proportionality relations.[12] One such property is the extra electronic delocalization in the chelate ring, created by complexation. This extra delocalization is measured as the difference Λ between the wavelengths of the UV maxima attributed to the

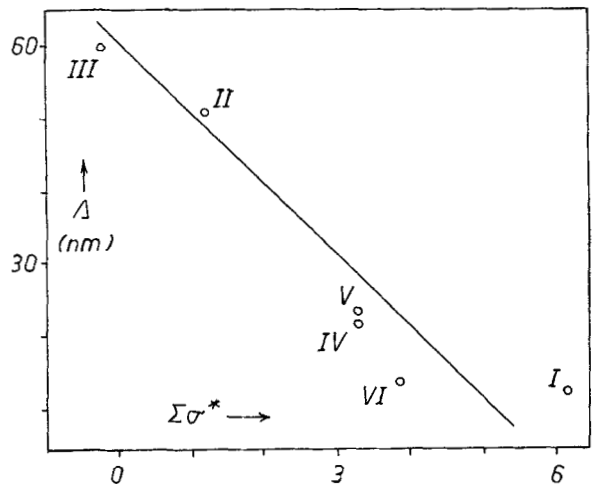


FIGURE 3 Extra electron delocalizations in the chelate ring produced by complexation, as a function of the electron-attracting power of the substituents Z of the central atom. R', R'' = *Me*.

$\pi \rightarrow \pi^*$ transition in the complex and in the chelated free 1,3-ketoenol ligand, see Fig. 3. Acetylacetonates were considered rather than benzoylacetonates or dibenzoylmethanates, because R', $R'' =$ *Ph* groups influence the wavelengths in question by conjugation, in a way which was found to differ from complex to complex.[9] Another property to be related to the electron-attracting power of the Z groups is the extra deshielding of the 1,3-diketone ligand protons produced by complexation. This is measured as the chemical shift difference Δ between the complex and the chelated free 1,3-ketoenol ligand, for the proton directly attached to the chelate ring, see Fig. 4. Acetylacetonates were considered, because $R', R'' =$ *Ph* substituents influence greatly the chemical shift of the proton attached to the chelate ring, due to their magnetic anistropy, and the magnitude of this effect may vary from complex to complex.[14] Boronium 1,3-diketonate salts, V, are not included in this figure, because the formal positive charge of the complex cation produce a strong deshielding of the proton attached to the chelate ring.[14] Finally an approximative proportionality is observed by plotting ^{11}B–NMR chemical shifts against σ^* values of the substituents Z (Fig. 5), which is not unexpected, being a consequence of Fig. 1 and 2, and proves our former assumption, that electron density at the central atom is determined by the inductive effect of the substituents Z. Note that the catechol complex constitutes again an exception.

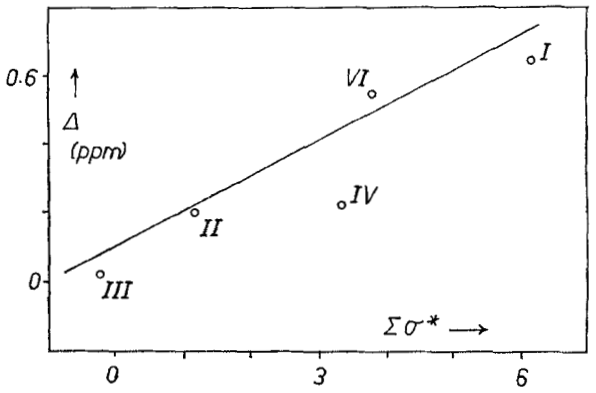


FIGURE 4 Extra deshieldings of the proton attached to the chelate ring, produced by complexation, as a function of the electron-attracting power of the substituents Z of the central atom. R', $R'' =$ *Me*.

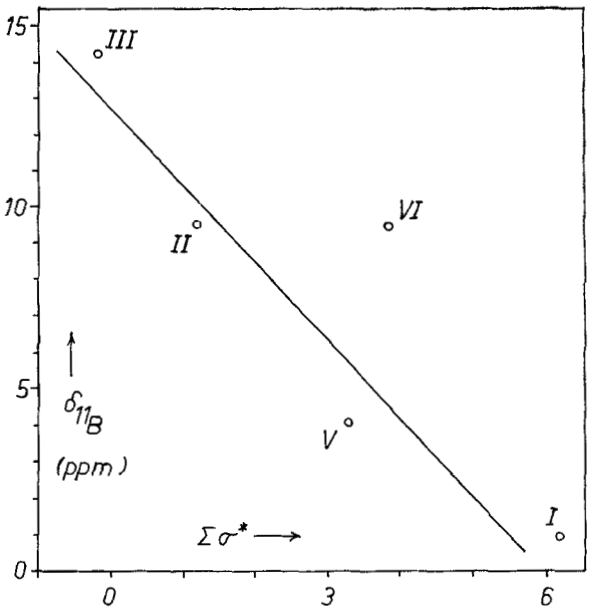
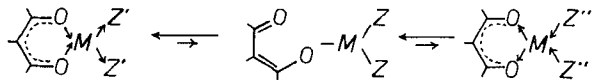


FIGURE 5 ^{11}B-NMR chemical shifts of the central boron atom as a function of the electron-attracting power of its substituents Z. R', $R'' =$ *Me*.

A rationalization of all these observed correlations between structure and properties can be attempted.

(i) As shown in Fig. 5, the electron density at the central atom appears to be directly proportional to the electron-attracting power of its substituents, Z. Thus, strongly electron-attracting substituents (Z') will produce an increased electron density at the central atom at the expense of the chelate ring (as in formula VIII), producing an increase of the $\pi \rightarrow \pi^*$ transition energy (Fig. 3) in the chelate ring and a deshielding of the protons attached to it (Fig. 4). On the contrary, electron-repelling substituents (Z'') will decrease the electron density at the central atom in favour of the chelate



VIII *IX* *X*

ring, as in *X*. The increase of electron density at the central atom through electron attracting Z' substituents will produce a reinforcement of the coordinative O–M bonds; thus in the one-end dissociation equilibrium VIII $\rightleftharpoons$ IX recombination to VIII will be favoured, which corresponds to low lability values (S), in accordance with experimental data. Similarly, electron-repelling substituents Z'' will energetically favour the one-end dissociated form IX (against the chelated one X), thus giving high redistribution rates *S*, again in agreement with experimental data. One-end dissociation was recognized as the crucial first step towards redistribution of chelating ligands by several investigators, see for example refs. 16–19, 21, 22.

(ii) Progressive replacement of methyl by phenyl groups in the R', R'' positions of the 1,3-diketone causes a continuous decrease of the lability of this ligand, as shown for example in Table III. Several factors can be considered to explain this. First there is a mass effect: the decreasing mobility in solution of the exchanging 1,3-diketone. On the other hand, conjugation with the phenyl groups will increase the delocalization of the positive charge of the chelate ring and consequently stabilize the negative charge at the central atom, thus slowing down one-end dissociation, and consequently decreasing the lability. This is consistent with the observation (of limited value because of the approximative character of the mechanistic assumptions), that for certain complexes (IV, V), progressive substitution of methyl by phenyl produce an alteration of the redistribution kinetics towards a monomolecular expression; a slow one-end dissociation may become the rate-determining step, which will give a monomolecular kinetic expression.

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