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STABILIZATION OF NEGATIVE CHARGE BY THE COBALTICINIUM NUCLEUS

III*. THE EFFECT OF SUBSTITUENTS ON THE ACIDITIES OF HYDROXY-COBALTICINIUM AND -RHODICINIUM SALTS

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Summary

The acidity constant, K_a, has been determined spectrophotometrically for 13 substituted hydroxycobalticinium and hydroxyrhodicinium salts. The acidity is increased with increasing electronegativity of the substituent but is decreased with rhodium(III) replacing cobalt(III) or with the addition of five methyl groups on the second cyclopentadienyl ring. An attempt has been made to relate acidities to Hammett's substituent constants. The pK_a of the unsubstituted hydroxycobalticinium ion is estimated to be 3.38 ± 0.08. The pK_as of 10 hydroxycobalticinium salts show a linear correlation with ν(CO) of the deprotonated cyclopentadienone analogues. Values of pK_{a1} and pK_{a2} of cyclopentadienyl(tetraethyl-*p*-hydroquinone)cobalt have been found to be —2.42 ± 0.10 and 1.15 ± 0.06.

Introduction

The assessment of the electronic effects in metallocenes has been the focus of considerable research and the subject of two reviews [1—2], but most work concerned with these phenomena has been on ferrocene compounds. The effects exhibited by the cobalticinium group have received relatively little attention due to the paucity of derivatives available. Previous investigations into the properties of the cobalticinium group [3—8] have shown that it is

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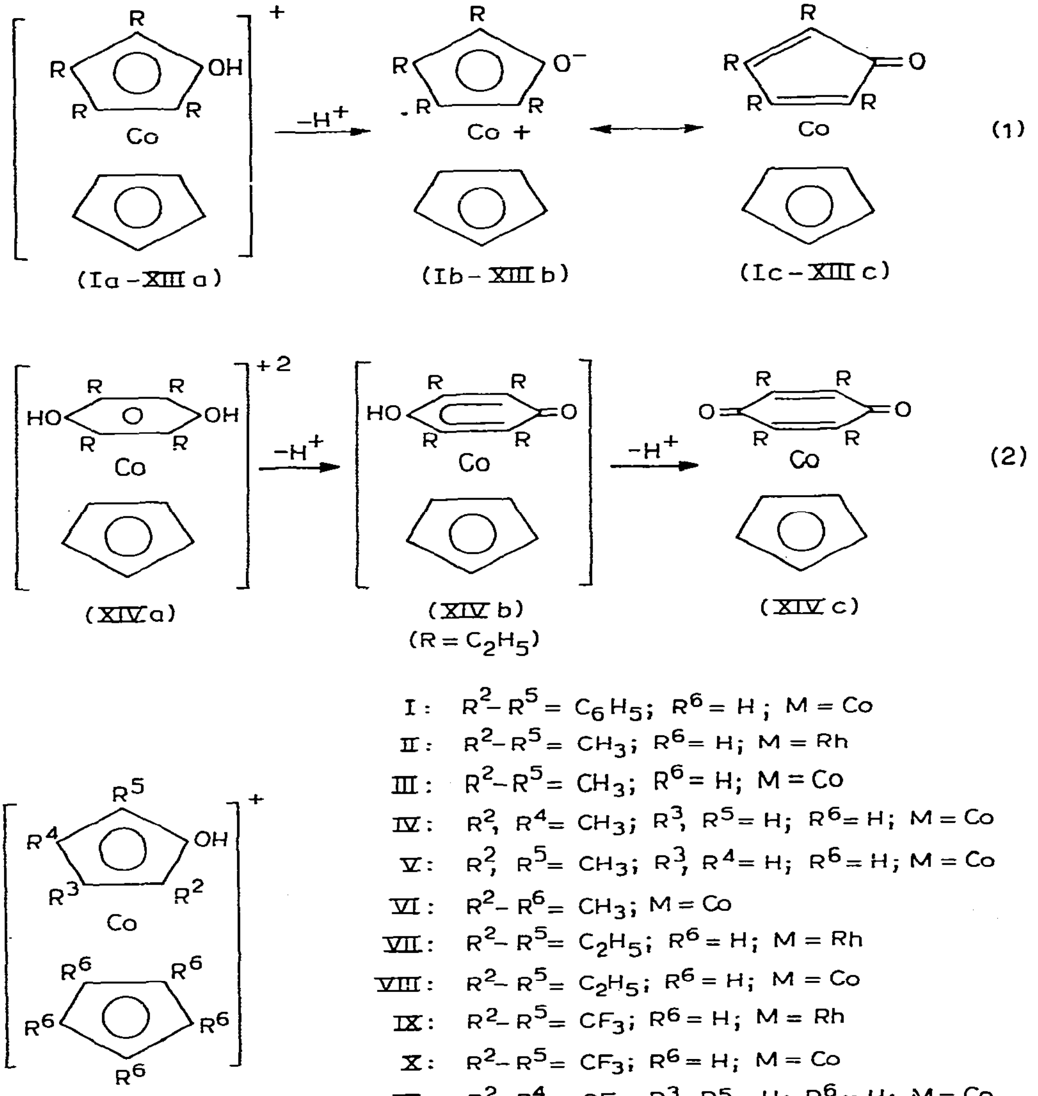
* For Part II, see Ref. 7.

highly electron withdrawing, both destabilizing positive charge on the α-position of a side chain and stabilizing negative charge. This effect arises from the relative proximity of the cobalt(III) center to the charge and the opportunity for resonance interaction between the cobalticinium group and lone pairs of electrons α to the cyclopentadienyl ring.

The ability of the cobalticinium group to stabilize negative charge is displayed in the case of the substituted hydroxycobalticinium ions, the acidities of which are enhanced relative to that of phenol. Upon deprotonation, the zwitterion (b) is able to resonate with the cyclopentadienone complex (c), the oxidation state of cobalt in the latter being reduced from +3 to +1 (Scheme 1,



I: R^2–R^5 = C_6H_5; R^6 = H; M = Co

II: R^2–R^5 = CH_3; R^6 = H; M = Rh

III: R^2–R^5 = CH_3; R^6 = H; M = Co

IV: R^2, R^4 = CH_3; R^3, R^5 = H; R^6 = H; M = Co

V: R^2, R^5 = CH_3; R^3, R^4 = H; R^6 = H; M = Co

VI: R^2–R^6 = CH_3; M = Co

VII: R^2–R^5 = C_2H_5; R^6 = H; M = Rh

VIII: R^2–R^5 = C_2H_5; R^6 = H; M = Co

IX: R^2–R^5 = CF_3; R^6 = H; M = Rh

X: R^2–R^5 = CF_3; R^6 = H; M = Co

XI: R^2, R^4 = CF_3; R^3, R^5 = H; R^6 = H; M = Co

XII: R^2, R^5 = CF_3; R^3, R^4 = H; R^6 = H; M = Co

XIII: R^2–R^5 = CF_3; R^6 = CH_3; M = Co

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eq. 1). In a previous paper [7] it was shown that hydroxycobalticinium and hydroxyrhodicinium salts act as moderately strong acids. Herein we examine the acidities of a wider range of hydroxy-cobalticinium and -rhodicinium salts (Ia—XIIIa), paying particular attention to the effects which the substituents and the metal center exert. In addition, we report the first measure of the acidity of a cyclopentadienyl(tetra-substituted-*p*-hydroquinone)cobalt complex (XIV; eq. 2).

Results and discussion

The UV spectra of hydroxymetallocinium salts differ from those of the cyclopentadienone complexes (Table 1). The change in spectrum was originally attributed to the solvation of the carbonyl group of the latter [9], but it was later shown that the actual cause is direct protonation of the carbonyl group to form the hydroxymetallocinium ion [5]. Complete protonation diminishes the shoulder absorption between 400—500 nm in the cobalt compounds (300—400 nm in the rhodium compounds) relative to that for the

TABLE 1

ULTRAVIOLET SPECTRA OF SUBSTITUTED HYDROXYCOBALTICINIUM AND HYDROXYRHODICINIUM SALTS

Compound	λ_{max} (ϵ)				Solvent
Ia	232 (sh) (27700)	332 (18650)			50% EtOH/ 6 *M* HCl
Ic	238 (sh) (24650)	330 (15500)			50% EtOH/ H_2O
IIa	249 (46300)				1 *M* HCl
IIc	252 (33840)	325 (2900)			H_2O
IIIa	283 (27150)	337 (970)	400 (sh) (350)		1 *M* HCl
IIIc	285 (21000)	335 (1630)	400 (760)		H_2O
IVa	277 (28700)	325 (1200)	385 (360)		1 *M* HCl
IVc	282 (23200)	352 (2300)	400 (700)		H_2O
Va	274 (25400)	337 (1520)	400 (sh) (380)		1 *M* HCl
Vc	278 (19900)	352 (2500)	400 (714)		H_2O
VIa	294 (31100)	347 (1180)	400 (sh) (450)		1 *M* HCl
VIc	297 (24600)	365 (2100)	405 (900)		pH 8 buffer
VIIa	250 (45300)				1 *M* HCl
VIIc	248 (34750)	325 (3110)			H_2O
VIIIa	282 (27800)	335 (1010)	400 (sh) (360)		1 *M* HCl
VIIIc	285 (21300)	355 (1700)	400 (710)		H_2O
IXa	243 (37000)	298 (2440)			96% H_2SO_4
IXc	246 (19200)	334 (3340)			5% H_2SO_4
Xa	243 (8330)	278 (23800)	345 (2080)	410 (sh) (530)	96% H_2SO_4
Xc	240 (11200)	283 (12700)	358 (3490)	415 (1110)	5% H_2SO_4
XIa	275 (22000)	337 (948)	405 (sh) (500)		10.8 *M* HCl
XIc	276 (14800)	348 (3110)	420 (900)		H_2O
XIIa	276 (23000)	340 (2230)	400 (sh) (610)		10.8 *M* HCl
XIIc	277 (15500)	353 (3610)	417 (1010)		H_2O
XIIIa	212 (sh) (10100)	254 (6830)	300 (38000)	367 (1420)	96% H_2SO_4
XIIIc	262 (9910)	313 (11800)	395 (3630)		5% H_2SO_4
XIVa	238 (15600)	310 (14300)	379 (3460)		10.8 *M* HCl
XIVb	247 (15400)	304 (11000)	392 (4300)		1.2 *M* HCl
XIVc	248 (15800)	302 (10000)	402 (5980)		H_2O

deprotonated species. The variations in spectra in these regions in solutions of intermediate acidity provide the opportunity for determining the acidity constants for the compounds.

The pK_a values for compounds Ia—XIVa are given in Table 2. The substituted hydroxymetallocinium salts have acidities 10^4 to 10^{15} times that of phenol (pK_a = 9.99) and the analogous neutral compound hydroxyferrocene (pK_a 10.17) [10] due to the strong field, inductive, and resonance effects of the metallocinium group. The substitution of rhodium(III) for cobalt(III) as the metal center lowers the acidity to a variable extent; VIIa is 0.05 powers of 10 less acidic than VIIIa, but IXa is 0.5 power less acidic than Xa. The combination of the larger ionic radius (with consequent reduction of the field effect of the positive charge) and the greater electron-donating ability of the rhodium(III) ion are responsible for this difference.

The nature of the substituent has a far greater influence on the acidity than does the metal center; compound Xa is more than 10^8 times more acidic than VIIIa. Although the types of substituents studied are insufficiently varied to allow any final conclusions to be made, some important facts can be seen in a Hammett correlation. Using $2\sigma_m$ for a 2,4-disubstituted compound and $4\sigma_m$ for a 2,3,4,5-tetrasubstituted compound, a plot of σ_m vs. $\log K_a$ (Fig. 1) shows a slope ρ of +4.84. The coefficient of correlation is 0.995. Values of σ_m were used in assessing this homoannular substitutent effect because direct resonance between the substituent and the reaction center is more difficult on a five-membered ring than on a six-membered ring. The value of ρ obtained is more than twice the value of +2.11 for monosubstituted phenols and reflects significant electron withdrawal by the cobalt(III) center. However, the true quantitative

TABLE 2

ACIDITIES OF SUBSTITUTED HYDROXY-COBALTICINIUM AND -RHODICINIUM SALTS

Compound	pK_a (Ia—XIVa)	ν(CO) [a] (Ic—XIIIc) (cm^{-1})
I	2.62 ± 0.03 [b]	1591
	2.24 ± 0.10 [c]	
	2.42 ± 0.10 [d]	
II	4.43 ± 0.04	
III	4.36 ± 0.03	1580
	4.30 ± 0.07 [e]	
IV	3.87 ± 0.03	1581
V	4.13 ± 0.03	1563
VI	5.90 ± 0.03	1542
VII	4.50 ± 0.04	
VIII	4.45 ± 0.03	1563
IX	−4.44 ± 0.04	
X	−4.97 ± 0.06	1683
XI	−1.49 ± 0.06	1639
XII	0.23 ± 0.03	1632
XIII	−1.89 ± 0.04	1635
XIV	−2.42 ± 0.10	
	1.15 ± 0.06	

[a] Spectra in KBr. [b] 50% ethanol solution. [c] Ref. 5; 50% ethanol solution. [d] Ref. 7; 50% dioxane solution; [e] Ref. 7.

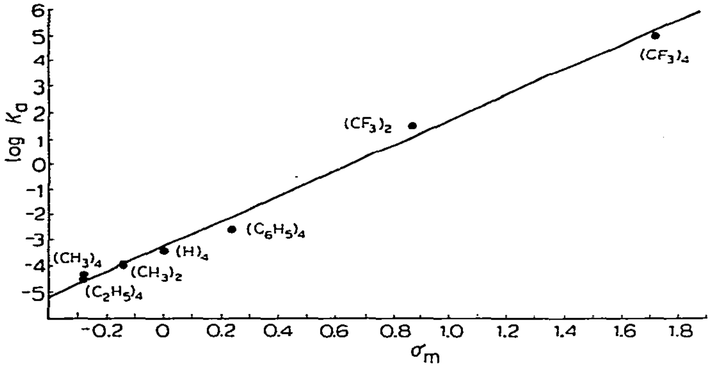


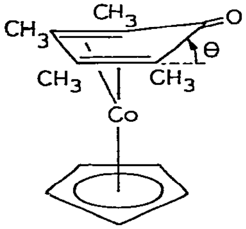
Fig. 1. σ_m vs. log K_a for hydroxycobalticinium salts.

measure of substituent effects on the acidities of hydroxymetallocinium ions, as well as the applicability of σ_m over other substituent constants, will require the use of other classes of substituents.

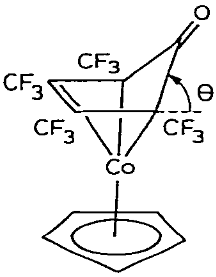
Interannular substituent effects were studied using two compounds, VIa and XIIIa, where the second cyclopentadienyl ring is substituted with five methyl groups. The collective influence of the multiple substitution is great; compound VIa is over 30 times less acidic than IIIa and XIIIa is more than 1000 times less acidic than Xa. Each methyl group in the 1′-position lowers the pK_a by 0.31 in VIa and by 0.62 in XIIIa. A parallel effect in the ferrocene system is seen in the case of ferrocenoic acid, which is 1.4 times more acidic than 1′-ethylferrocenoic acid [11]. Little and Eisenthal found that the pK_as of heteroannularly substituted ferrocenoic acids correlated with σ_p to give $\rho = +0.74$ [12]. The inductive effect of the pentamethylcyclopentadienyl ring has been shown to be sufficient to stabilize low-spin manganese(II) in decamethylmanganocene [13].

Variations in acidity caused by isomerism and disubstitution were studied using IVa—Va and XIa—XIIa. The acidities of the 2,5-disubstituted compounds Va and XIIa are lower than those of the asymmetric disubstituted isomers IVa and XIa. Given the difference in the electronegativities of the two sets of substituents, it seems likely that substitution of the 2- and 5-positions leads to lower solvation of the reaction center with consequent lowering of the acidity relative to the isomer where only one of these positions is substituted. Another possible explanation is that electron withdrawal takes place most effectively from the 3-position and electron donation is favored in the 2-position.

By extrapolation of the acidities of IIIa and IVa to that for an unsubstituted species, which has thus far eluded synthesis, an estimated pK_a of 3.38 ± 0.08 is arrived at. The pK_a extrapolated from the acidities of Xa and XIa is 2.01 ± 0.10. The difference of 1.37 pK units between the two extrapolated values may be due to non-cumulative substituent effects. Crystallographic structure determinations show that the cyclopentadienone ring is not planar but is distorted, with the carbonyl group elevated above the C(2)—C(5) plane. The degree of distortion is strongly dependent on the substituent and has been found to be 9° in IIIc [14] and 21° in Xc [15]. The bonding between the cyclopentadienone ring and the metal has been postulated to be an η^4 structure in IIIc (XV) and an η^2,σ^2 structure in Xc (XVI) [15]. Changes in the metal center, or in homoannular or heteroannular substituents, change the bonding, and thus the acidity, less in compounds with lower acidities while such changes have a greater impact on both bonding and acidity in compounds of generally higher acidity.



(XV; θ 9°)



(XVI; θ 21°)

The value for the pK_a of the unsubstituted hydroxycobalticinium ion of 3.38, extrapolated from the pK_a of IIIa and IVa, is more reliable due to the relative closeness of these two acidities. As the pK_a values of 2,6- and 2,4-dinitrophenol are 3.71 and 4.09, respectively, the combined field, inductive, and resonance effect of the cobalticinium ion qualitatively appears to be somewhat more than that exerted by two nitro groups.

The carbonyl stretching frequencies, ν(CO), of the deprotonated cyclopentadienecyclopentadienonecobalt complexes show a good correlation with the pK_a values of the hydroxycobalticinium salts. Increased electronegativity in the substituent will lead to higher frequencies, but substituents which are electron donating will polarize the carbon—oxygen double bond and the tendency toward formation of the zwitterion (b) (eq. 1) will become apparent in lower values of ν(CO). A plot of ν(CO) vs. pK_a for 10 cobalt compounds (Fig. 2) reveals a straight line with the equation pK_a = —0.0789 ν(CO) + 128.09. The coefficient of correlation is 0.983.

Although the syntheses and electronic spectra of tetra-substituted-*p*-quinone complexes have been reported [9,17—21], no study has been done previously on the acidity of the protonated moiety. ^{13}C NMR data compiled by Bodnar and Englemann [22] showed that the structure of the duroquinone derivative in $CDCl_3$ was that of the η^4 compound (c) (Scheme 1, eq. 2) but changed to the η^6 complex (a) in D_2SO_4. Fairhurst and White [23] have isolated the monoprotonated and diprotonated derivatives of $(C_5Me_5)Co[(MeC_2Me)_2(CO)_2]$. The spectrum of XIVc in water shows a maximum at 402 nm (ϵ 6000). The molar extinction coefficient is reduced to ϵ 4300 as the acid strength approaches 1 *M* HCl, then remains constant until the HCl concentration exceeds 3.5 *M*. The maximum in 10.8 *M* HCl is shifted to 379 nm (ϵ 3500). A clear separation thus exists between the monoprotonated and diprotonated forms with monoprotonation occurring in 1 *M* HCl. A spectrophotometric examination of the proteolytic equilibrium of XIVa-b-c reveals two acidity constants for this species: pK_{a1} = —2.42 ± 0.10 and pK_{a2} = 1.15 ± 0.06. The acidity of XIVa-b is 10^{12}—

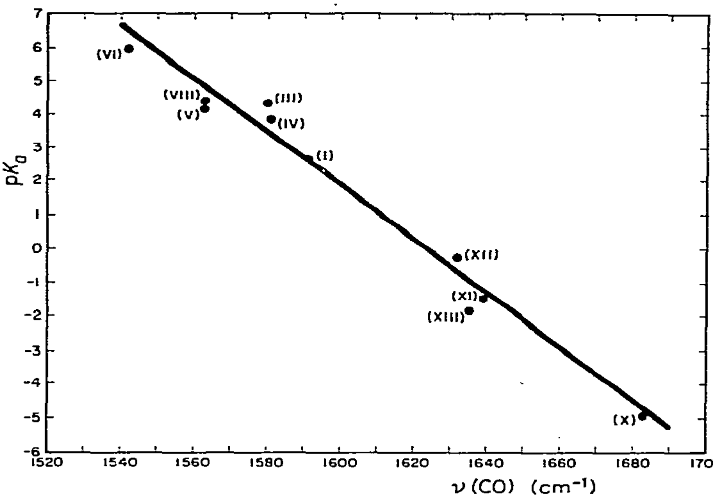


Fig. 2. ν(CO) (cm^{-1}) vs. pK_a for 10 cyclopentadienecyclopentadienonecobalt complexes.

10^{11} times greater than that of hydroquinone ($pK_{a1} = 10$, $pK_{a2} = 12$) and the electron-withdrawing effect of the benzenecyclopentadienylcobalt group is 10^7 times that of the cobalticinium group. Similar effects are observed in the benzenecyclopentadienyliron(II) group; the pK_a of carboxybenzenecyclopentadienyliron(II) is 3.05 [24] vs. 6.11 for ferrocenoic acid [12]. The opportunity for resonance with the benzoquinone structure, the electroneutrality of the benzene ring as opposed to the negative charge of the cyclopentadienyl ring, and the increased field effect of the cobalt(III) center may account for the high acidity of XIVa-c, but a quantitative measure of the effect exerted by this group awaits the syntheses of other substituted benzenecyclopentadienylcobalt complexes.

Experimental

Ultraviolet spectra were recorded on a Cary 15 UV spectrophotometer. Infrared spectra were measured as a 1% suspension of the compounds in KBr on a Perkin—Elmer 283 spectrophotometer. Samples of compounds Ic and IIIc [7], IVc, Vc, XIc, and XIIc [16], IIc, IXc, and Xc [17], VIIc, VIIIc, and XIVc [18], and VIc and XIIIc [25] were obtained from the sources cited.

Determination of pK_a of Ia

A solution 5.00×10^{-3} *M* in Ic (dissolved in ethanol) was prepared. 1 ml aliquots were diluted with 4 ml of ethanol and with 5 ml of the following: buffers of pH 7 (all Ic), 2.4, 1.9, 1.7, and 1.4 and with 12 *M* HCl (all Ia). Spectra were recorded between 550 and 400 nm for all solutions. The relative amounts of Ia and Ic in each of the four intermediate solutions were calculated. A solution 2.00×10^{-4} *M* in 4-aminoazobenzene in ethanol was prepared and solutions similar to those above were prepared. Spectra between 700—325 nm were recorded for all solutions and log (BH^+)/(B) was calculated for the intermediate buffer solutions. From these data, values of H_0 for the buffers in 50% ethanol were calculated and the pK_a of Ia determined.

Determination of pK_a of IIa—VIIIa and XIa—XIIa

10 ml solutions 1.00×10^{-3} *M* in the cobalt compounds and 5.00×10^{-4} *M* in the rhodium compounds in water were prepared. 1 ml aliquots were diluted to 10 ml with water (fully deprotonated; VIc in pH 8 buffer), 12 *M* HCl (fully protonated), and buffer or HCl solutions of sufficient pH to give spectra whose absorbances were intermediate between the two extremes when recorded between 575—325 nm. The percentages of protonated and deprotonated species in each intermediate solution were calculated and the pK_a of each compound determined.

Determination of pK_a of IXa, Xa, and XIIIa

10 ml solutions 5.00×10^{-4} *M* in IXc, Xc, and XIIIc in 96% H_2SO_4 were prepared. 1 ml aliquots were diluted to 10 ml with water (fully deprotonated), 96% H_2SO_4 (fully protonated), and H_2SO_4 solutions of sufficient strength to yield spectra with absorbances between the two extremes between 575—325 nm. Weighed aliquots of the intermediate solutions were titrated with standard NaOH solution and the weight percentage of H_2SO_4 in each was calculated. Using an H_0 scale for H_2SO_4 solutions [26], the pK_as of the compounds was determined as above.

Determination of pK_{a1} and pK_{a2} of XIVa-b

A 10 ml solution 2.00×10^{-5} *M* in XIVc in water was prepared. 1 ml aliquots were diluted to 10 ml with the following: water (all XIVc) 0.05 *M*, 0.1 *M*, and 0.2 *M* HCl solutions and with 1 *M* HCl. Spectra were recorded between 575—325 nm for all solutions; the spectrum in 1 *M* HCl was chosen to be that of the monoprotonated form. From the relative amounts of XIVb and XIVc present in each solution, pK_{a2} was calculated. To 1 ml aliquots of the stock solution were added 1 *M* HCl (all XIVb), 4, 5, and 6 ml of 12 *M* HCl (solutions diluted 10 ml), and 12 *M* HCl (all XIVa). Spectra were recorded between 575—325 nm. With $[H^+]$ based on the H_0 scale [26], pK_{a1} was determined as above.

Acknowledgements

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