The Dissociation Constants of Diprotonated Chalcogenobispyridines: Transmission of Electronic Effects Across Chalcogen Bridges

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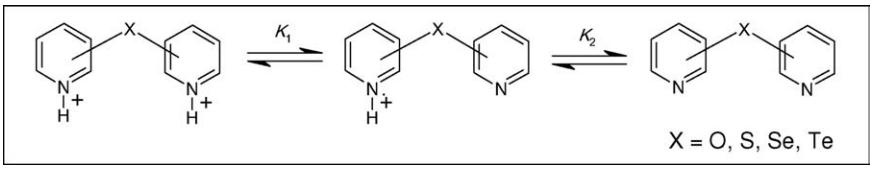

The dissociation constants of the diprotonated chalcogenobispyridines have been determined using potentiometric titrations to establish a method for the measurement of the ability of a bridging ligand to relay electronic effects. The relationship between pK_a and structure of the chalcogenobispyridines results from a balance between inductive, mesomeric, and steric effects. Delocalization of cationic charge onto the bridgehead increases the apparent electronegativity of the bridging atom, thereby relaying a strong base-weakening effect to the site of first deprotonation. Such delocalization was found to be a function of both the substitution site (4-X > 2-X ≫ 3-X) and orbital overlap requirements (S > O ≈ Se > Te).

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INTRODUCTION

Since the pioneering work of Taube [1], there has been great interest in the ability of bridging ligands to facilitate electronic interaction between the valence orbitals of dinuclear metal complexes. The degree of coupling between the metal centres is often quantified by measurement of the comproportionation constant, K_c. This equilibrium constant is a measure of the stability of the mixed-valence state, in which the metal centres at opposite ends of the bridging ligand exist in adjacent oxidation states, as defined below:

$$K_c = [M(n), M(n+1)]^2/([M(n), M(n)] \times [M(n+1), M(n+1)])$$

where M(n) denotes a charged metal ion, n being the charge.

Determination of K_c is non-trivial [2], requiring isolation and purification of the mixed valence dinuclear metal complex, followed by measurement and normalization of the so-called intervalence charge transfer (IVCT) transition in the near-IR region. We were interested in a simpler method for the evaluation of the ability of bridging groups to relay electronic effects between pyridine, bipyridine, and terpyridine capped systems. Our recent studies have focussed upon the synthesis of optimized links between bridge and the chelating group, thereby maximizing electronic overlap. The use of chalcogen atoms as bridging groups allows the study of an array of factors—geometry, orbital overlap, and electronegativity.

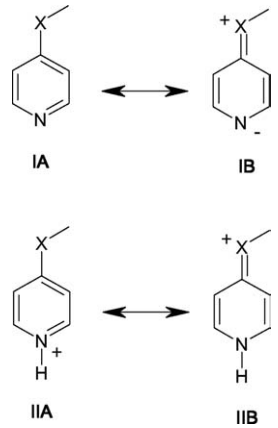
Pyridyl functionalities can be protonated, thereby increasing their electron-withdrawing nature. It was thus of interest to investigate the extent to which the change in protonation state at one end of a pyridyl-capped ligand influences the pK_a of the pyridyl system at the other end of the bridging ligand. Potentiometric titrations have been utilised to determine the protonation/dissociation constants for a wide range of pyridine systems [3]. However, few studies have measured successive pK_a values of bridged bis(pyridyl) systems to examine the degree of interaction between the two sites of protonation [4].

The ability to measure successive pK values allows the determination of the ratio K_1/K_2 which can be seen below to have a related form to the comproportionation constant K_c.

$$K_1/K_2 = [LH^+]^2/[L][LH_2{}^{2+}]$$

where [L] represents the concentration of the neutral bridging ligand, [LH^+] represents the concentration of the monoprotonated ligand, and [LH_2^{2+}] represents the concentration of the diprotonated ligand. As K_c values are specific for the type of complex under study, it was envisaged that determination of the ratio K_1/K_2 can

Scheme 1



serve as a measure of the bridging groups capacity towards electron transfer as well as the suitability of the interface between the bridge and the coordinating group for this application.

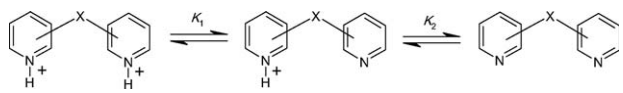
The sulfide and disulfide bridges of 4,4′-thiobispyridine and 4,4′-dipyridyl disulfide were reported in the literature to be particularly effective at mediating metal–metal interactions with K_c values of 158 and 80000, respectively, for their $[(H_3N)_5Ru(\mu\text{-}L)Ru(NH_3)_5]^{n+}$ complexes [5], compared to more traditional π bridging systems, such as 4,4′-bipyridine (K_c 20), 1,2-di(4-pyridyl) ethene (14) and di(4pyridyl)ethyne (14) [1c]. The greater K_c values for 4,4′-thiobispyridine and 4,4′-dipyridyl disulfide most likely result from strong p(π)-d(π) interactions between the pyridyl rings and their sulfur substituents and in the latter case, strong d(π)-d(π) overlap between the sulfur atoms. In this work, we examine the transmission of electronic effects between pyridyl bases via bridging chalcogen atoms through measurement of successive dissociation constants of the diprotonated species.

RESULTS AND DISCUSSION

The chalcogens are π electron donating and σ electron withdrawing substituents relative to the hydrogen atom. Hence chalcogen-substituted pyridines are subject to both a base-weakening inductive effect in all positions, declining in the order 2-X > 3-X > 4-X, plus a powerful base-strengthening mesomeric effect, operable in the 2- and 4- positions only. The pK_a values of the chalcogeno-bispyridines naturally result from a combination of these two opposed influences.

For chalcogenobispyridines in the neutral form (unprotonated), resonance between forms **IA** and **IB** (see Scheme 1) should be slight in the case of X = O, since both the oxygen and the nitrogen atoms in the latter structure bear charges in opposition to their respective electronegativities. A greater degree of **IB** character should be displayed by those systems with bridgeheads of lower electronegativity (e.g., S and Se).

Scheme 2



The 1H-pyridinium systems, however, should possess greater contributions from resonance forms of the type **IIB** (a base-strengthening effect), since the charge distribution is less extreme, particularly for the 4-X derivatives due to the increased distance between the charged centres.

In this study, the first deprotonation occurs in the ''primary'' ring of the diprotonated species (K_1), while the deprotonation of the monoprotonated species occurs in the ''secondary'' ring (K_2) (see Scheme 2). The experimentally determined first and second dissociation constants for the diprotonated chalcogenobispyridines are presented in Table 1 and demonstrated graphically in Figures 1 and 2.

The 2,2′-chalcogenobispyridine series exhibits K_1 values which are characteristic of predominantly inductive influences (see Fig. 1). While mesomeric interaction between the ring π orbitals and the valence orbitals of the bridgehead atom is possible for these diprotonated congeners, steric and coulombic interactions in the proximal region may restrict the adoption of resonance form **IIIB** (see Scheme 3). The monoprotonated forms of 2,2′-oxybispyridine and 2,2′-thiobispyridine are weaker bases (pK_1 2.11 and 2.72, respectively) than the corresponding methylchalcogeno analogs (—OMe 3.28, —SMe

Table 1

First and second dissociation constants for the diprotonated chalcogenobispyridines.

Congener	pK_1	pK_2	ΔpK	K_1/K_2
2,2′-O	2.11(13)	3.66(10)	1.55	35
2,3′-O	3.49(3)	4.54(3)	1.05	11
3,3′-O	3.03(2)	4.526(4)	1.50	32
4,4′-O	3.71(7)	5.77(2)	2.06	115
2,2′-S	2.72(9)	3.54(10)	0.82	7
2,3′-S	3.30(13)	4.33(5)	1.03	11
3,3′-S	2.96(12)	4.33(7)	1.37	23
2,4′-S	2.13(11)	5.27(9)	3.14	1380
3,4′-S	2.60(3)	5.47(2)	2.87	741
4,4′-S	3.27(3)	5.50(2)	2.23	170
2,2′-Se	3.12(9)	3.90(8)	0.78	6
2,3′-Se	3.39(12)	4.58(3)	1.19	15
3,3′-Se	3.09(15)	4.51(5)	1.42	26
2,4′-Se	2.26(8)	5.11(1)	2.85	708
3,4′-Se	2.94(5)	5.42(3)	2.48	302
4,4′-Se	3.56(7)	5.43(4)	1.87	74
2,2′-Te	3.71(6)	5.12(12)	1.41	26
3,3′-Te	3.59(6)	4.91(3)	1.32	21
4,4′-Te	3.85(10)	5.55(2)	1.70	50

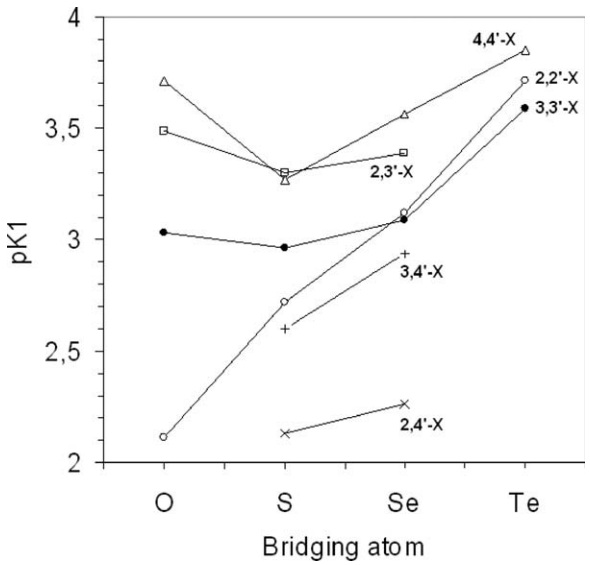


Figure 1. pK_1 data for the chalcogenobispyridines (key: ○ 2,2′-X, □ 2,3′-X, × 2,4′-X, • 3,3′-X, + 3,4′-X, △ 4,4′-X).

3.62), suggesting a significant inductive influence from the cationic charge in the secondary ring through the C-chalcogen bonds. The similarity between the pK_1 values of 2,2′-selenobispyridine (3.12) and 2-methylselenopyridine (3.62) may arise from poorer orbital overlap between the ring and bridgehead and the tighter C-X-C angle.

The protonated 3′-pyridyl rings of the 2,3′-chalcogenobispyridines cannot interact mesomerically with the bridging atom. Subsequently, the 2-pyridyl ring tends to

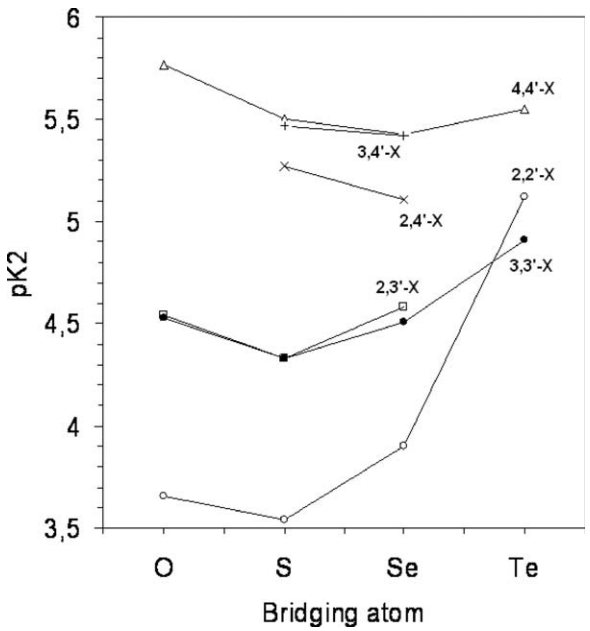
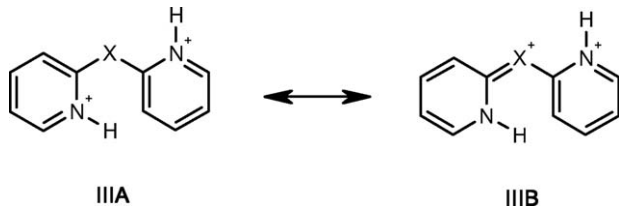


Figure 2. pK_2 data for the chalcogenobispyridines (key: ○ 2,2′-X, □ 2,3′-X, × 2,4′-X, • 3,3′-X, + 3,4′-X, △ 4,4′-X).

Scheme 3



lie coplanar with the C-X-C plane, due to lack of competition, as indicated by our earlier conformational studies [6]. The resultant delocalisation of cationic charge from the primary ring onto the bridgehead dramatically increases the base strength of that ring. Thus, the monoprotonated forms of 2,3′-chalcogenobispyridines (O, S, Se) are stronger bases than their 3,3′-equivalents, despite the proximity of their protonation sites to the electronegative bridging atom (see Fig. 1).

The low pK_1 values for 2,4′-thio- (2.13) and 2,4′-selenobispyridine (2.26) imply a very strong interaction between the protonated centres. A greater contribution from the resonance structure **IIIB** for these congeners significantly increases the apparent electronegativity of the chalcogen atom, thereby decreasing the base strength in the primary 2-pyridyl ring. The proximity of the bridgehead to the site of the first deprotonation amplifies this effect. The 3,4′- and 4,4′-chalcogenobispyridines display a similar effect, although it is tempered by increasing distance between the protonation site and the bridgehead. The lower electronegativities of S (2.58) and Se (2.55) also help to increase the contribution from these charge-transferring resonance forms.

When the chalcogen atom is unable to interact resonantly with the ring π system (as in the case of 3-pyridyl substituents), it is the polarisability of the bridging atom which controls the degree of interaction. The greater polarisability of S and Se permits a better relay of the inductive influence of the protonated 3′-pyridyl ring in 3,3′-thio- and 3,3′-selenobispyridine, resulting in pK_1 values equivalent to that of 3,3′-oxybispyridine.

Reduced overlap between the Se valence orbitals and the π system of pyridine results in lower populations of the base-weakening resonance forms of the secondary ring (e.g., **IIIB**) and hence, all isomers of selenobispyridine are stronger bases than their thio equivalents. The similarity between the pK_1 values for the symmetrical isomers of tellurobispyridine reflects both the low electronegativity of Te (2.1) and the poor overlap between its valence orbitals and those of the ring π system.

The pK_2 values reflect the influence of neutral chalcogenopyridyl substituents upon the pK values of the monoprotonated systems. As can be seen from Figure 2, the pK_2 values are clustered into three distinct regions—allowing identification of the site of first protonation in

each unsymmetrical congener. For example, the similarity between the pK_2 values for 2,3′- and 3,3′-oxybispyridine suggests the site of first protonation to be the 3-pyridyl substituent. This near-equivalence also suggests that the neutral primary rings induce relatively small inductive effects, compared to their protonated analogs. Contributions from resonance forms of the type **IB** for these neutral substituents is greater in the cases of the thio- and selenobispyridines which, in most cases, possess lower pK_2 values than their oxybispyridine equivalents.

The ability of the bridging atom to transmit electronic effects is dependent upon the nature of its attachment to the pyridine moiety. A strong mesomeric interaction between the ring and the bridge is necessary for the efficient transfer of cationic charge to the bridge, from where its influence can be relayed to other electroactive centres. In this respect, substitution in the 4-position of the pyridine ring is more favored since it allows the greatest degree of charge polarisation. The ΔpK values ($pK_2 - pK_1$) and K_1/K_2 values listed in Table 1 give an indication of those systems displaying a strong electronic interaction between redox centres ($\Delta pK > 1.80$; 2,4′-X, 3,4′-X, and 4,4′-X), while those systems controlled mostly by inductive effects possessed ΔpK values less than 1.5 (2,2′-X, 2,3′-X, 3,3′-X). However, it must be borne in mind that the unsymmetrical isomers have an inherent ΔpK due to the differing sites of substitution. The K_1/K_2 value obtained for 4,4′-thiobispyridine (170) compares well with the value obtained through IVCT measurements (158) [5], giving support for this model.

EXPERIMENTAL

All compounds were synthesized using methods previously reported [7]. Potentiometric titrations were performed with a Metrohm 665 automated burette and a Metrohm 605 digital pH meter fitted with a Metrohm combined glass electrode. All measurements were fully automated under control of an IBM clone computer. Titrations were performed at 25.0 ± 0.1°C in constant ionic strength aqueous solutions (I = 0.5, KCl) under nitrogen. Solutions of each chalcogenobispyridine (with concentrations in the range 1–4 × 10^{-3} mo1 dm^{-3}) were adjusted to low pH then titrated with 98 increments (of 1.0 × 10^5 dm^{-3}) of NaOH (0.3 mol dm^{-3}). Equilibrium constants were calculated from potentiometric data with a TURBO BASIC version of the program TITFIT [8]. The fitted pK values are given in Table 1 and displayed graphically in Figures 1 and 2.

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