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Complex Formation of Silver(I) with Sterically Hindered Pyridine Bases

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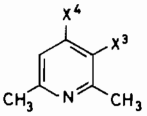
Introduction

Non-coordinating buffer systems are of great interest for kinetic and thermodynamic studies involving metal ions in aqueous solution. Recently we reported [1] on the properties and application of buffer systems for the pH range 3–8 which are based on sterically hindered 2,6-lutidine bases L.



≡ L = 3-X^3-4-X^4-2,6-dimethylpyridine

We found [1] that the proper choice of substituents X^3 and X^4 allows the pK_a of L to vary within the range of 3–8, and due to the shielding effect of the neighbouring methyl groups, complex formation of divalent metal ions with L is very restricted ($K_1 \approx 1.7\ M^{-1}$), independent of the size of the pK_a of L.

It was reported [2] that silver(I) ions coordinate 2,6-lutidine (=L; X^3 = X^4 = H) rather strongly (K_1 = 480 M^{-1}, K_2 = 240 M^{-1}), in contrast to what is found for divalent metals [1]. With silver(I), bis complexes of 2,6-lutidine and 2,4,6-collidine (=L; X^3 = H and X^4 = CH_3) can easily be isolated from aqueous solution [3].

The present study was undertaken to study in detail the effect of steric hindrance on the complex formation of silver(I) (and some more metal ions) with sterically hindered pyridine bases L according to (1):

$$Ag^+ + L \rightleftharpoons [AgL]^+; K_1 \qquad (1)$$

Experimental

$AgNO_3$, $Ba(NO_3)_2$ and $Ce(NO_3)_3 \cdot 6H_2O$ were analytical grade (Merck, Darmstadt). The various 2,6-lutidine bases L (see Table I) were prepared as described previously [1]. The compound 2,6-di-tert.-butyl-4-methylpyridine-3-sulfonic acid was prepared by reaction of SO_3 with 2,6-di-tert.-butyl-4-methylpyridine [4] in liquid SO_2 according to a procedure based on the literature [5]. Its pK_a value was determined by potentiometric titration according to ref. [1].

The mono complex formation of Ag^+, Ba^{2+}, and Ce^{3+} with L ([metal] ≫ [L]) was studied in aqueous solution (I = 0.5 *M* ($NaNO_3$)) at 25 °C by automatic potentiometric titration with a glass electrode.

The evaluation of K_1 from the titration curves has been previously described [1].

Results and Discussion

The K_1 data compiled in Table I allow us to compare the mono complex formation of nickel(II) and

TABLE I. Equilibrium Constants K_1 for Mono Complex Formation according to (1) (25 °C, I = 0.5 *M*).

No.	Ligand L	pK_a[a]	K_1, M^{-1}			
			Ag^+ [d]	Ni^{2+} [e]	Ba^{2+}	Ce^{3+}
1	4-cyanopyridine	1.86[b]	6.5			
2	3-nitro-2,6-lutidine	2.87	13.2	1.7	<0.05	0.7 ± 0.1
3	3-chloropyridine	3.05	23.4			
4	4-cyano-2,6-lutidine	3.68	36.3	1.2		
5	2,6-lutidine-3-sulfonic acid	4.80	89.1	2.3	<0.1	0.7 ± 0.1
6	3-acetyl-2,4,6-collidine	5.91	135	1.8		
7	2,6-lutidine	6.96	324 479[f]	1.6		
8	4-methoxy-2,6-lutidine	8.04	417	1.6	<0.2	–[g]
9	2,6-di-tert.-butyl-4-methylpyridine-3-sulfonic acid	5.05[c]	4.9			

[a] From ref. [1]; limits of error ±0.05 pK_a units. [b] From ref. [6]. [c] This paper. [d] The error is estimated to be 5–10%. [e] From ref. [1]; maximum limits of error ±40%. [f] From ref. [2]. [g] Due to hydrolysis K_1 could not be determined.

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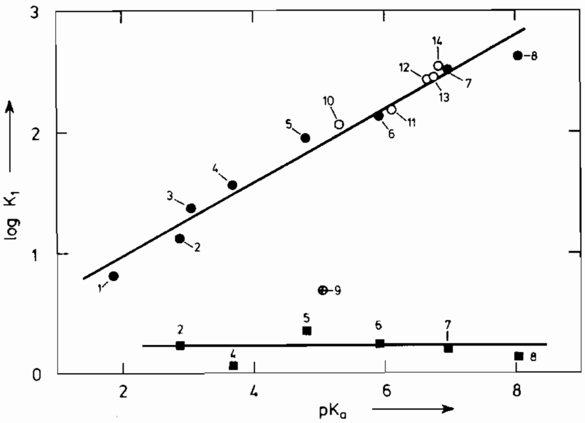

Fig. 1. Logarithmic plot of equilibrium constant K_1 for mono complex formation of silver(I) and nickel(II) with 2,6-lutidine bases and pyridine bases *versus* pK_a (Ag^+: ●, ○, ⊕; Ni^{2+}: ■; the numbers 1–9 refer to those of the ligands L in Table I; 10: L = pyridine, 11: L = 4-picoline, 12: L = 3,4-lutidine, 13: L = 2,3-lutidine, 14: L = 2,4-lutidine; the K_1 data for nos. 10–14 were taken from ref. [9]).

silver(I) with sterically hindered pyridine bases L differing in their pK_a values. The complex formation of nickel(II) is very restricted and virtually independent of pK_a (mean value: K_1 = 1.7 M^{-1}; see also Fig. 1). For silver(I), however, strong complex formation is observed and the K_1 values obtained obviously follow the basicity of the donor nitrogen in L as characterized by its pK_a value (see Fig. 1). The surprising finding is that silver(I) is able to coordinate 2,6-lutidine bases, despite the steric hindrance imposed by the two adjacent methyl groups.

The complex formation of Ce^{3+} ions and especially Ba^{2+} ions is even more restricted than that of Ni^{2+} ions (see Table I). For monovalent cations such as Cs^+, K^+, and Tl^+ the coordination of the various bases L can hardly be detected. These findings and similar earlier findings for Mg^{2+}, Ca^{2+}, and Zn^{2+} ions [1] indicate that the strong complex formation of Ag^+ ions cannot simply be related to the parameter 'softness' (as based on charge and ionic radius).

Further support for the unique coordination properties of silver(I) is presented in Fig. 1. The data points representing complex formation with Ag^+ ions refer to 2,6-lutidine bases on the one hand (filled circles) and to pyridine bases not carrying methyl groups in 2- and 6-position on the other hand (open circles). All of the data fit the same line (slope: 0.30 ± 0.02). This means that a 2,6-lutidine base and a pyridine base of the same pK_a are coordinated by Ag^+ ions to the same extent, *i.e.*, Ag^+ ions do not recognize the steric hindrance of the 2,6-lutidine base. As shown by data point no. 9 in Fig. 1 (symbol ⊕; L = 2,6-di-tert.-butyl-4-methylpyridine-3-sulfonic acid; pK_a = 5.05), only two bulky tert.-butyl groups instead of the two methyl groups in 2,6-lutidine are able to reduce K_1 considerably, though not even as much as in the system Ni^{2+}/2,6-lutidine-3-sulfonic acid (pK_a = 4.80).

The results presented for complex formation according to (1) are in line with those obtained by Hancock *et al.* [7] on complex formation in the system $Ag^+/R-NH_2$ (R = Me, Et, i-Pr, tert.-Bu, cyclo-Pe, cyclo-Hex) in the sense that Ag^+ ions appear to be very little susceptible to steric hindrance. Silver(I) is obviously able to form linear complex species $[L-Ag-L]^+$ even with sterically demanding ligands L such as 2,6-lutidine bases, which fail to be similarly coordinated by mono-, di- or trivalent cations. This interesting behaviour of silver(I) may well be related to the low hydration number of Ag^+ ions, reported to be in the range 2–4 [8].

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