

The Non-template Synthesis of Novel non-Symmetrical, Tetradentate Schiff Bases. Their Nickel(II) and Cobalt(III) Complexes

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Novel non-symmetrical, tetradentate Schiff bases have been obtained in a two-step process. In the first step, one mole of ethylene diamine is reacted with one mole of acetylacetone to afford a 1:1 condensation product, which is then reacted with one mole of either salicylaldehyde or 2-hydroxy-acetophenone to yield non-symmetrical diimines. The nickel(II) and cobalt(III) complexes derived from these ligands have been prepared and characterized.

Introduction

Metal complexes of Schiff bases have contributed widely to the inorganic chemistry of chelate systems. Particular attention has been paid to the complexes of tetradentate diimino bases such as bis(acetylacetonate)ethylenediimine (BAE, Fig. 1a) and bis(salicylaldehyde)ethylenediimine (Salen, Fig. 1b). Many cobalt derivatives have been prepared and investigated, with particular emphasis on the reactivity of the metal ions in the transmethylation reactions and the reversible absorption of molecular oxygen. In the complexes containing π -conjugated macrocyclic ligands the reactivity and the redox potential of the central metal are very sensitive to the nature of the chelate ring. However, few works have been devoted to complexes involving non-symmetrical bases such as (acetylacetonate)(salicylaldehyde)ethylenediimine (AESal, Fig. 1d). Generally speaking, the known non-symmetrical diimines have been obtained by a template synthesis and have not been isolated in the free (uncoordinated) state [1–4]. In the present paper, we report on a reliable procedure to obtain non-symmetrical diimines involving ethylene diamine, acetylacetonate, salicylaldehyde (AESal, Fig. 1d) and 2-hydroxy-acetophenone (AEHap, Fig. 1d'). Nickel(II) and cobalt(III) complexes of these two ligands are considered to demonstrate the tetradentate behaviour.

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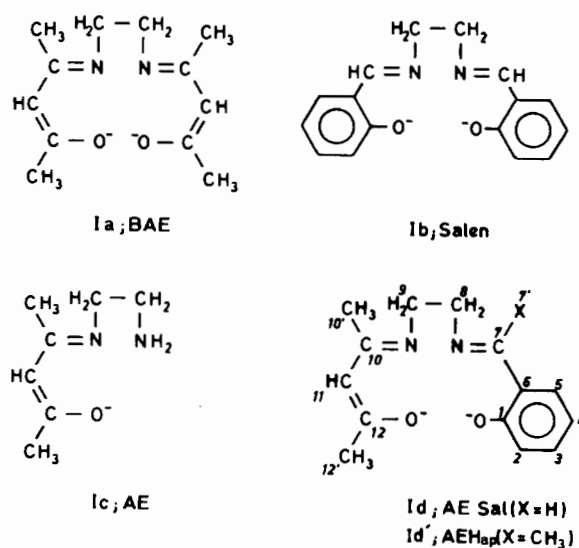
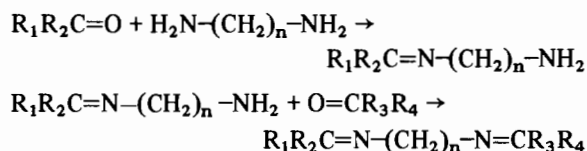


Fig. 1. The ligands.

Results and Discussion

As a possible route to the non-symmetrical Schiff bases, a two-step process may be considered according to the following scheme:



From a literature survey, it is expected that the major difficulty would occur in preparing and isolating the intermediary 1:1 species, $R_1R_2C=N-(CH_2)_n-NH_2$. For instance, it is generally accepted that the reaction between ethylene diamine and acetylacetonate yields the 1:2 compound (BAE), even if equimolecular amounts of both reactants are used. However, a 1:1 condensation product between *o*-acetoacetylphenol and 1,2-propanediamine has been recently

described [5]. We have found that a particular set of experimental conditions allow the 1:1 compound (AE, Fig. 1c) to be prepared and isolated [6]. The second step is straightforward, since the condensation of AE with salicylaldehyde or 2-hydroxy-acetophenone is realized to afford respectively AESal and AEHap. The stability of the AE compound is rather low at room temperature but sufficient to allow further reaction, complexation [6] or condensation. On the contrary the AESal and AEHap compounds are quite stable; their nickel(II), NiL, and cobalt(III), [CoL·2Py]ClO₄ (Py = C₅H₅N) complexes are easily obtained through the use of known methods. Micro-analytical data related to the two ligands and their complexes are consistent with the expected formulations, which were confirmed by the NMR (¹H and ¹³C) data. These data are listed in Tables I and II. We have also reported the data related to the symmetrical bases BAE and Salen.

It is interesting to observe that the ¹³C spectrum of AESal is merely the sum of the BAE and Salen spectra. Therefore the assignments are straightforward. Regarding AEHap, the effects of introducing

a methyl group on the C-7 are restricted to this nucleus and to the C-8 one which are respectively deshielded by ~6 and 10 ppm. When these ligands become coordinated to the nickel(II) and cobalt(III) ions, the chemical shifts of the various carbon nuclei experience modifications which, on the one hand, are more important for the cobalt complexes than for the nickel ones and, on the other hand, mainly concern the BAE moiety. One can note that the carbon nuclei of the pyridine ligands in the [CoL·2Py]ClO₄ complexes stay at the same chemical shifts (125.6 ± 0.2; 139.2 ± 0.2 and 152.5 ± 0.2 ppm) for the three involved ligands. The ¹H NMR data give rise to very similar remarks.

As previously mentioned, non-symmetrical ligands (such as AESal and AEHap) are expected to allow sharp modulation of the properties of the metal ions. Due to our interest in the cobalt complexes, it is noteworthy that the trend of the electron affinity of the Co(III) ion is consistent with this assumption. Thus, the redox potential (E_{1/2}) (vs. SCE) related to the reaction Co^{III} → Co^{II} in the non symmetrical complexes (CoL2py)⁺ formed by AESal (E_{1/2} =

TABLE I. Analytical Data.

	Colour	C		H		N		Cl		Co	
		calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.	calc.	exp.
AESal	yellow	68.3	68.2	7.32	7.31	11.4	11.3				
AEHap	beige	69.2	67.6	7.7	7.8	11.8	10.9				
[Co(AESal)2py]ClO ₄	deep brown	51.4	51.3	4.7	4.6	10.0	9.9	6.32	6.3	10.9	10.4
[Co(AEHap)2py]ClO ₄	light brown	52.2	52.0	4.9	4.9	9.8	9.6	6.2	6.2	10.3	10.4
										Ni	
Ni AESal	red	55.5	53.8	5.3	5.3	9.2	8.7			19.4	19.3
Ni AEHap	yellow	56.8	55.8	5.7	5.7	8.8	8.7			18.5	17.4

TABLE II a. ¹H Chemical Shifts (ppm) in CDCl₃ (T.M.S. as internal reference).

	H(7)	H(8)	H(9)	H(11)	H(7')	H(10')	H(12')	NH	OH
SALEN	8.44	3.89							13.28
BAE		3.47		4.98		1.13	2.00	11.4	
AESal	8.41	3.73		5.00		1.90	2.15	10.9	13.0
AEHap		3.30		5.04	2.36	1.93	2.00	11.0	11.0
		4.00							
Ni(AESal)		2.84		5.00		1.88	1.95		
		3.65							
Ni(AEHap)		2.93		5.04	2.42	1.93	2.00		
		3.69							
[Co(BAE)2Py]ClO ₄		3.86		5.02		2.11	2.33		
[Co(AESal)2Py]ClO ₄		4.13		5.11		2.20	2.36		
[Co(AEHap)2Py]ClO ₄		4.11		5.09	3.35	2.15	2.40		

TABLE II b. ^{13}C Chemical Shifts (ppm) in CDCl_3 .

	C(1)	C(2)	C(3)	C(4)	C(5)	C(6)	C(7)	C(8)	C(9)	C(10)	C(11)	C(12)	C(10')	C(12')	C(7')
Salen	161.2	117.1	131.6	118.8	132.5	118.9	166.7	59.9	43.3	162.7	95.9	195.3	18.4	28.6	
BAE	161.0	117.0	131.5	118.8	132.6	118.8	167.2	59.9	43.4	162.9	95.9	195.3	18.8	28.8	
AE Sal	162.8	117.4	128.2	118.8	132.4	118.3	173.1	49.9	43.3	162.8	95.8	195.2	18.7	28.7	14.5
AEHap															
Ni(BAE)	165.2	114.5	132.1	121.3	133.3	120.2	161.2	60.0	51.5	164.4	99.7	175.6	21.1	24.3	
Ni(AESal)	164.3	114.5	129.0	122.8	132.1	122.3	168.6	56.0	51.9	164.8	99.8	177.1	21.0	24.3	18.2
Ni(AEHap)															
[Co(BAE)2Py]ClO ₄	165.3	116.4	135.0	123.4	135.8	119.0	169.5	59.3	50.0	171.2	97.7	178.9	22.8	25.8	
[Co(AESal)2Py]ClO ₄	165.6	116.1	130.6	124.3	134.0	122.1	176.5	55.6	50.9	171.4	97.0	179.0	23.4	26.2	20.6
[Co(AEHap)2Py]ClO ₄															

−0.44 V) or AEHap ($E_{1/2} = -0.52$ V) lies between the values characterizing the symmetrical species: $E_{1/2} = -0.59$ V (L = BAE); $E_{1/2} = -0.39$ V (L = Salen) [7]. These data emphasize the usefulness of non-symmetrical ligands in affording a convenient way of varying the properties of complexes. Further work is in progress to study the reactivity (transmethylation and reversible absorption of O_2) of the cobalt centers in these complexes.

Experimental

Preparation of ligands

The preparation of the tridentate Schiff base AE has been described elsewhere [5].

Salicylaldehyde (3 g, 0.03 mol) in chloroform (30 ml) is added to a solution of AE (4 g, 0.03 mol) in CHCl_3 (50 ml). The resulting mixture is refluxed while stirring for 30 minutes and then concentrated under a reduced pressure to yield AESal, which is recrystallized from chloroform hexane. AEHap is obtained in a similar manner using methanol instead of chloroform as solvent.

Preparation of Co(III) complexes

They were prepared according to COSTA's procedure [8] modified by AVERILL and BROMAN [9].

Preparation of Ni(II) complexes

2.46 g (0.01 mol) of the Schiff bases were added to 2.49 g (0.01 mol) of $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ dissolved in 100 ml of methanol. The mixture was refluxed for 15 minutes. The solution was left to cool and was partially evaporated to allow the precipitation of the complexes. Crystals were dried under vacuum.

Measurements

^1H NMR spectra (solution in CHCl_3) were recorded on a Perkin Elmer R12 and ^{13}C data were obtained on a Bruker WH90 spectrometer using CDCl_3 as internal reference and solvent.

The polarograms of Co(III) complexes (10^{-3} M) in pyridine (0.1 M NEt_4ClO_4) were recorded at 0°C with a Tacussel-controlled potential polarograph. All the half-wave reduction potentials were referred to SCE.

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