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Alkylcobalt chelates with Schiff bases derived from a β -diketone bearing both alkyl and aryl groups ¹

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Abstract

Organocobalt(III) complexes with Schiff bases derived from a β -diketone bearing both an alkyl and an aryl group have been prepared. The template syntheses using benzoylacetone and ethylenediamine as complexing agents provide a route to alkylcobalt chelates with the corresponding tri- and tetradentate Schiff bases. However, if a β -diketone with two aryl groups, e.g. dibenzoylmethane, was employed as the starting ketoenol component, no organometallic products were detected; a new mixed-ligand 'inorganic' chelate of cobalt(II), $[Co{O=C(Ph)CH=C(Ph)O}_2(en)]$, was isolated instead. Its structure as well as that of one of the alkylcobalt complexes with a tridentate Schiff base composed of benzoylacetone and ethylenediamine have been established by X-ray techniques. The current scope of the template synthesis of alkylcobalt complexes with Schiff bases is summarized. \bigcirc 1998 Elsevier Science S.A.

Keywords: Organocobalt complexes; Schiff base complexes; Template synthesis; Crystal structures

1. Introduction

Alkylcobalt chelates with tridentate Schiff bases are of current interest as pH-dependent sources of free radicals [1], since preliminary studies have indicated that they may find application in medicine as well as in synthesis of polymers. Thus, these complexes effectively modify the action of certain antitumor drugs [2,3]. They have also been found to be superior initiators of emulsion polymerization [4]. Therefore attempts to extend the range of such complexes seem to be justified. Furthermore, one-pot synthesis, which was first applied to the preparation of organocobalt complexes by Schrauzer et al. [5] and which is so far the only route to relevant chelates of the tridentate ligands in question [6], presents a rare example of the use of the template method in organometallic chemistry, and, as such, is of a fairly general interest. Nevertheless, and despite our previous studies [6], the scope of the template synthesis of the complexes in question remains unclear. Therefore it is worthy of further investigation. This is particularly true for the synthesis of alkylcobalt chelates with tridentate Schiff bases bearing aromatic groups, which can be readily functionalized via substitution reactions in the starting organic compounds. Attempts to use chelating aromatic diamines or an *N*-aryl-substituted ethylenediamine as reagents failed [6]. We now report the preparation of the desired complexes starting from a mixed aliphatic-aromatic β -diketone.

In symbolic formulae, abbreviations used for Schiff base ligands are to indicate the number of carbonyl components [6].

2. Experimental

2.1. General

Organocobalt complexes were protected from light. Concentration of their solutions was conducted under vacuum, with the bath temperature kept below 40°C. All the template reactions (preparations 1, 2, 5 and 6) were carried out under anaerobic conditions with permanent stirring.

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¹ Dedicated to Professor Jack Halpern in recognition of his great contribution to coordination, organometallic and bioinorganic chemistry, and catalysis.

² Deceased on August 16, 1995.

2.2. Materials

Except for $py \cdot HNO_3$ which was prepared according to the known procedure [7] all materials were commercially available reagent grade chemicals.

2.3. Spectral studies

¹H NMR spectra were recorded at room temperature on a Bruker AMX-400 spectrometer. CD_3OD and TMS were mostly used as solvent and internal standard respectively.

IR spectra were taken on a Specord M-82 spectrometer (Carl Zeiss, Jena) using solid samples, viz KBr pellets (in the wide range of 400–3800 cm⁻¹) and hexachlorobutadiene mulls (in the region of N–H and O–H stretches, namely in the range of 2500–3800 cm⁻¹).

2.4. X-ray structural studies

Crystal and refinement data for complexes [MeCo(bzacen)-(en)]I and [Co $\{O=C(Ph)CH=C(Ph)O\}_2(en)$] are given in Table 1. Both structures were solved by direct methods and refined by the full-matrix least-squares technique. All H atoms were located in the difference Fourier syntheses and

Table |

included in the refinement in the isotropic approximation. All calculations were performed with the SHELXTL PLUS 5 (gamma version) programs on an IBM PC computer. Atomic coordinates and temperature factors for the non-H atoms in the structures are listed in Tables 2 and 3; bond lengths and angles are given in Tables 4 and 5.

2.5. Analyses

Acid-induced decomposition of organocobalt complexes was performed as previously described [7].

2.5.1. Cleavage of alkylcobalt complexes with iodine and detection of resulting alkyl iodides

A solution of the sample under examination containing $\sim 1 \ \mu$ mol of a complex in methanol (1 ml) was added to an ice-cooled methanolic solution of I₂ (4%) and NaI (4%). The reaction mixture was kept at room temperature in a closed vial for 2 h and then cooled again to 0°C. Then, a solution of sodium thiosulfate (pentahydrate, 0.2 g) in ice-water (3 ml) was added. The resulting solution was allowed to react for 5 min and then extracted twice with decalin (2×0.5 ml). The decalinic extract (combined upper layers) was successively washed with water (0.3 ml) and a saturated solution

Crystal and refinement data for complexes $[Co{O=C(Ph)CH=C(Ph)O}_2(en)]$ and [MeCo(bzacen)(en)]I

Compound	$[Co{O=C(Ph)CH=C(Ph)O}_2(en)]$	[MeCo(bzacen)(en)]I
Formula	$C_{32}H_{30}C_0N_2O_4$	C ₁₅ H ₂₆ CoIN ₄ O
Molecular weight	565.51	464.23
Crystal system	monoclinic	monoclinic
Space group	Cc	$P2_1/n$
Cell constants		
a (Å)	16.705(3)	12.239(4)
b (Å)	16.883(3)	10.936(3)
c(Å)	10.667(2)	14.192(4)
β(°)	107.01(3)	102.78(2)
$V(\dot{A}^3)$	2877	1852.4
Z	4	4
$D_{\rm calc}$ (g cm ⁻³)	1.306	1.665
Diffractometer	CAD-4	Siemens P3/PC
No. reflections for cell determination	24	24
2θ range (°)	$24 < 2\theta < 25$	$24 < 2\theta < 25$
Temperature (K)	293	153
Radiation	Mo K α ($\lambda = 0.71073$)	Mo K α ($\lambda = 0.71073$)
Scan mode	θ -5/3 θ	θ-2θ
$2\theta_{\max}$ (°)	60	56
Absorption coefficient $\mu(Mo K\alpha) (cm^{-1})$	6.35	26.00
Total no. reflections	4539	4415
No. unique reflections	4308	4212
No. reflections used in refinement	4279	4186
No. observed reflections $(I > 2\sigma(I))$	1536	3532
No. parameters	472	303
Flack absorption structure parameter	-0.04(5)	_
R_1 (on F for observed reflections) ^a	0.0337	0.0369
wR_2 (on F^2 for all reflections) ^b	0.0914	0.0892
Goodness of fit	0.945	1.044

^a $R_1 = \sum |F_0 - |F_c|| / \sum (F_0)$ for observed reflections.

^h $wR_2 = \left\{ \sum \left[w(F_o^2 - F_c^2)^2 \right] / \sum \left[w(F_o^2)^2 \right] \right\}^{0.5}$ for all reflections.

Table 3

Table 2 Fractional atomic coordinates $(\times 10^4)$ and equivalent thermal factors $(\times 10^3 \text{ Å}^2)$ for [Co{O=C(Ph)CH=C(Ph)O}₂(en)]

Atom	x/a	y/b	z/c	Ueq
Co(1)	2923(3)	4798(1)	3988(4)	51(1)
N(1)	3335(8)	5786(8)	2984(12)	69(4)
N(2)	2515(7)	5738(8)	4931(11)	62(4)
O(1)	3354(7)	3921(7)	3024(9)	65(3)
O(2)	4118(6)	4769(7)	5378(8)	61(3)
O(3)	2475(6)	3935(6)	4983(9)	54(3)
O(4)	1808(6)	4786(6)	2631(9)	53(3)
C(1)	3308(15)	6497(9)	3821(15)	113(10)
C(2)	2529(10)	6441(10)	4185(14)	77(5)
C(3)	4638(9)	4202(9)	5554(13)	49(4)
C(4)	4523(9)	3566(7)	4707(15)	54(4)
C(5)	3972(9)	3429(9)	3560(16)	57(4)
C(6)	3998(12)	2694(9)	2774(15)	63(5)
C(7)	3234(11)	2384(9)	2011(16)	67(5)
C(8)	3288(16)	1698(13)	1241(20)	103(7)
C(9)	3993(15)	1372(12)	1156(20)	109(7)
C(10)	4766(17)	1667(11)	1926(26)	115(7)
C(11)	4741(13)	2343(12)	2639(22)	88(6)
C(12)	5328(8)	4287(9)	6703(14)	53(4)
C(13)	5353(11)	4882(11)	7630(17)	62(4)
C(14)	5995(9)	5097(11)	8770(15)	57(3)
C(15)	6719(11)	4646(13)	8932(16)	93(6)
C(16)	6750(11)	4022(13)	8109(19)	89(6)
C(17)	6032(11)	3871(10)	7027(14)	78(5)
C(18)	1276(9)	4242(10)	2404(15)	52(4)
C(19)	1306(9)	3556(10)	3177(15)	62(4)
C(20)	1929(10)	3469(9)	4458(14)	52(4)
C(21)	1862(10)	2753(10)	5210(16)	61(5)
C(22)	1136(14)	2400(12)	5221(22)	81(6)
C(23)	1189(16)	1766(11)	6072(24)	103(7)
C(24)	1874(20)	1403(8)	6712(18)	113(8)
C(25)	2643(14)	1752(10)	6722(15)	85(6)
C(26)	2582(12)	2401(10)	5944(16)	78(5)
C(27)	487(8)	4342(9)	1167(12)	50(3)
C(28)	521(9)	4971(10)	354(14)	58(4)
C(29)	-192(12)	4996(13)	-684(16)	77(5)
C(30)	-859(8)	4555(11)	-989(13)	64(4)
C(31)	-882(11)	3981(11)	-127(15)	78(5)
C(32)	-223(7)	3837(10)	972(14)	65(5)

of sodium sulfate (0.3 ml), and dried with sodium sulfate. To detect alkyl iodides (C1 or C2) in the resulting solution, it was subjected to gas chromatography (GC) analysis using a fused silica capillary column 25 m×0.25 mm (i.d.) with internal surface-bounded 1.5 μ m layer of OV-1701 (Chrompack, USA). The temperature program schedule was 30°C for 12 min, 30–180°C for 6°C min⁻¹, and 180°C for 30 min. Flame-ionization detection was employed and EtBr was used as standard substance.

For thin layer chromatography (TLC) identification of organocobalt complexes, 'Silufol' plates (Kavalier, Czech Republic) were used in combination with 0.1 M solution of NaOAc in MeOH-H₂O 4:1 (A), CH₂Cl₂-py mixture 19:1 (B) or CHCl₃ (C) as eluents.

High performance liquid chromatography (HPLC) analyses were carried out on a 5000S HPLC System (Bio-Rad, USA) using a stainless steel column 150×4 mm (i.d.)

Fractional atomic coordinates ($\times10^4)$ and equivalent thermal factors ($\times10^3$ Å^2) for [MeCo(bzacen)(en)]I

Atom	x/a	y/b	zlc	$U_{\rm eq}$
I(1)	7730(1)	4438(1)	4024(1)	24(1)
Co(1)	11054(1)	4350(1)	2701(1)	16(1)
O(1)	11487(2)	5011(2)	1600(2)	21(1)
N(1)	10544(2)	2840(2)	2105(2)	19(1)
N(2)	10610(2)	3704(3)	3849(2)	21(1)
N(3)	9510(3)	5221(3)	2199(2)	24(1)
N(4)	11504(3)	5951(3)	3316(2)	21(1)
C(1)	12570(3)	3692(3)	3176(3)	24(1)
C(2)	11633(3)	4349(3)	884(2)	17(1)
C(3)	11323(3)	3142(3)	715(2)	20(1)
C(4)	10729(3)	2427(3)	1285(2)	19(1)
C(5)	9877(3)	2152(4)	2669(3)	26(1)
C(6)	10405(3)	2369(3)	3728(2)	25(1)
C(7)	9737(3)	6553(4)	2274(3)	29(1)
C(8)	10519(3)	6773(3)	3244(3)	28(1)
C(9)	10302(3)	1199(3)	875(3)	27(1)
C(10)	12142(3)	5022(3)	169(2)	19(1)
C(11)	12877(3)	4460(3)	-325(3)	27(1)
C(12)	13325(4)	5131(4)	-990(3)	34(1)
C(13)	13050(3)	6345(4)	1161(3)	29(1)
C(14)	12319(3)	6913(3)	-673(2)	25(1)
C(15)	11874(3)	6253(3)	-12(2)	20(1)

packed with Diasorb 130 T C16. The eluent was a 97:3 (vol./ vol.) mixture of methanol with 0.01 M aqueous acetic acid adjusted to pH 7.0 with ethylenediamine; the flow rate was 1 ml min⁻¹; the detection wavelength was 313 nm.

Capillary electrophoresis (CE) analyses were taken on CE System BioFocus 3000 (Bio-Rad, USA) using a fused silica capillary 24 cm \times 0.25 mm (i.d.) with internal linear polyacrylamide cladding; capillary and sample carousel were thermostated at 20 and 4°C respectively; the detection wavelength was 310 nm; the buffer was an 80:20 (vol./vol.) mixture of methanol with 0.025 M aqueous acetic acid adjusted to pH 7.25 with ethylenediamine.

2.6. Preparations

2.6.1. [MeCo(bzacen)(en*)]I³ and [EtCo(bzacen)(en)]Br

The preparations were generally carried out by analogy with those of [MeCo(7-Me-salen)(en*)]I and [EtCo(7-Me-salen)(en)]Br [6]. Benzoylacetone (2.43 g, 15 mmol), ethylenediamine (1.01 ml, 15 mmol) and CoCl₂·6H₂O (1.78 g, 7.5 mmol) were successively dissolved in MeOH (55 ml). The resulting dark red solution was cooled to 10– 15°C, and then NaOH (1.6 g, ~40 mmol) was gradually added to it. To the resulting orange suspension, the corresponding alkyl halide RX (MeI, 0.8 ml, or EtBr, 1.4 ml; 15 mmol) and a 2% solution of PdCl₂ in 1 M aqueous KCI (0.15 ml) were added. Then, the temperature of the water bath was raised to 22–25°C. Then ~1/10 of a solution of

³ In this formula en* means both ethylenediamine (en) and its *N*-methylated homologue (N-Me-en). Partial methylation of the ethylenediamine ligand in the course of similar template syntheses was detected earlier [6].

Table 5

Table 4 Selected bond lengths (Å) and angles (°) for $[Co{O=C(Ph)CH=C-(Ph)O}_2(en)]$

Bond lengths			
Co(1) - O(4)	1.996(10)	O(4)-C(18)	1.25(2)
Co(1)-O(1)	2.050(11)	C(1) - C(2)	1.47(2)
Co(1)-O(3)	2.067(11)	C(3) - C(4)	1.38(2)
Co(1) - N(2)	2.096(12)	C(3)-C(12)	1.42(2)
Co(1)-O(2)	2.110(10)	C(4) - C(5)	1.32(2)
Co(1)-N(1)	2.199(13)	C(5) - C(6)	1.51(2)
N(1)-C(1)	1.50(2)	C(18)-C(19)	1.41(2)
N(2) - C(2)	1.43(2)	C(18)-C(27)	1.58(2)
O(1)-C(5)	1.32(2)	C(19)-C(20)	1.46(2)
O(2)-C(3)	1.27(2)	C(20)-C(21)	1.47(2)
O(3)-C(20)	1.21(2)		
Bond angles			
O(4)-Co(1)-O(1)	91.0(4)	O(2)-C(3)-C(4)	122.1(13)
O(4)-Co(1)-O(3)	88.0(4)	O(2)-C(3)-C(12)	113.5(14)
O(1)-Co(1)-O(3)	88.9(2)	C(4)-C(3)-C(12)	124.4(14)
O(4)-Co(1)-N(2)	89.5(4)	C(5)-C(4)-C(3)	132.0(14)
O(1)-Co(1)-N(2)	177.0(5)	C(4)-C(5)-O(1)	123(2)
O(3)-Co(1)-N(2)	94.1(5)	C(4)-C(5)-C(6)	122(2)
O(4)-Co(1)-O(2)	177.4(4)	O(1)-C(5)-C(6)	115.1(14)
O(1)-Co(1)-O(2)	86.4(4)	C(7)-C(6)-C(5)	117(2)
O(3)Co(1)O(2)	91.9(4)	C(11)-C(6)-C(5)	125(2)
N(2)-Co(1)-O(2)	93.1(4)	C(17)-C(12)-C(3)	127(2)
O(4)-Co(1)-N(1)	90.8(4)	C(13)-C(12)-C(3)	122.0(13)
O(1)-Co(1)-N(1)	95.6(5)	O(4)-C(18)-C(19)	125.9(14)
O(3)-Co(1)-N(1)	175.4(5)	O(4)-C(18)-C(27)	117.1(13)
N(2)-Co(1)-N(1)	81.5(2)	C(19)-C(18)-C(27)	117.0(13)
O(2)-Co(1)-N(1)	89.6(5)	C(20)-C(19)-C(18)	121.4(13)
C(1)-N(1)-Co(1)	104.3(10)	O(3)-C(20)-C(19)	126.9(14)
C(2)-N(2)-Co(1)	107.5(9)	O(3)-C(20)-C(21)	116.6(14)
C(5)-O(1)-Co(1)	125.6(10)	C(19)-C(20)-C(21)	116.4(14)
C(3)-O(2)-Co(1)	126.0(10)	C(22)-C(21)-C(20)	125(2)
C(20)O(3)Co(1)	123.9(9)	C(26)-C(21)-C(20)	118(2)
C(18)-O(4)-Co(1)	127.4(10)	C(32)-C(27)-C(18)	120.9(13)
C(2)-C(1)-N(1)	107(2)	C(28)-C(27)-C(18)	115.4(12)
N(2)-C(2)-C(1)	111.1(13)		

NaBH₄ (in toto, 0.4 g, ~10 mmol) in methanolic solution of NaOH (0.4 g (~10 mmol) in 10 ml) was added. The remaining NaBH₄ solution was continuously added during 4 h at such a rate that gas evolution was maintained throughout. Then stirring under anaerobic conditions was prolonged by 1 h.

The resulting brown suspension was filtered, and the solid residue was extracted with methanol with a few drops of concentrated ammonia solution added, until the solvent remained colourless. The (red) filtrate combined with these washings was concentrated under vacuum to a volume of 20 ml. Then the corresponding halide salt, NaI or NaBr (0.8 g), and ice-water (20 ml) were successively added. The resulting suspension was reduced in volume in the same manner as above. Crystallization of the product(s) was allowed to go to the end at 0°C. The precipitate was separated by filtration, washed with a small amount of cold water with a drop of ethylenediamine added, and dried first by suction and finally under vacuum over CaCl₂.

The crude products obtained in yields of 1.80 and 1.70 g (≈ 53 and 52%) respectively were recrystallized at room

Bond lengths			
Co(1) - N(1)	1.897(3)	N(2)-C(6)	1.485(5)
Co(1)-O(1)	1.901(2)	N(3)-C(7)	1.483(5)
Co(1)-N(2)	1.959(3)	N(4) - C(8)	1.489(5)
Co(1)-C(1)	1.965(4)	C(2)-C(3)	1.380(4)
Co(1)-N(4)	1.979(3)	C(2) - C(10)	1.496(4)
Co(1)-N(3)	2.095(3)	C(3) - C(4)	1.433(5)
O(1) - C(2)	1.292(4)	C(4) - C(9)	1.510(5)
N(1) - C(4)	1.314(4)	C(5) - C(6)	1.518(5)
N(1)-C(5)	1.470(4)	C(7)–C(8)	1.511(5)
Bond angles			
N(1)-Co(1)-O(1)	95.04(11)	C(5)-N(1)-Co(1)	111.7(2)
N(1)-Co(1)-N(2)	86.14(12)	C(6)-N(2)-Co(1)	109.2(2)
O(1)-Co(1)-N(2)	178.79(11)	C(7)-N(3)-Co(1)	106.3(2)
N(1)-Co(1)-C(1)	91.50(14)	C(8) - N(4) - Co(1)	111.2(2)
O(1)-Co(1)-C(1)	90.41(13)	O(1)-C(2)-C(3)	126.3(3)
N(2)-Co(1)-C(1)	89.86(14)	O(1) - C(2) - C(10)	114.1(3)
N(1)-Co(1)-N(4)	177.07(12)	C(3)-C(2)-C(10)	119.5(3)
O(1)-Co(1)-N(4)	85.72(11)	C(2)-C(3)-C(4)	125.4(3)
N(2)-Co(1)-N(4)	93.09(12)	N(1)-C(4)-C(3)	121.4(3)
C(1)-Co(1)-N(4)	91.3(2)	N(1)-C(4)-C(9)	122.3(3)
N(1)-Co(1)-N(3)	93.51(13)	C(3)-C(4)-C(9)	116.3(3)
O(1)-Co(1)-N(3)	86.67(12)	N(1)-C(5)-C(6)	107.0(3)
N(2)-Co(1)-N(3)	92.96(13)	N(2)-C(6)-C(5)	107.0(3)
C(1)-Co(1)-N(3)	174.41(14)	N(3)-C(7)-C(8)	107.0(3)
N(4)-Co(1)-N(3)	83.70(13)	N(4)-C(8)-C(7)	107.9(3)
C(2)-O(1)-Co(1)	123.1(2)	C(15)-C(10)-C(2)	118.9(3)
C(4) - N(1) - C(5)	122.1(3)	C(11)-C(10)-C(2)	122.3(3)
C(4) = N(1) = Co(1)	126.2(2)		

temperature from MeOH with NaX (X=I and Br respectively) and a few drops of ethylenediamine added.

[EtCo(bzacen)(en)]Br: brown powder. Anal. Found: C, 44.53; H, 6.81; N, 13.13; Co, 13.68. Calc. for $C_{16}H_{28}$ -N₄OBrCo: C, 44.64; H, 6.56; N, 13.02; Co, 13.70%. TLC (eluent A): $R_f = 0.46$.

2.6.2. $[MeCo(bzacen)(py)_2]I$

py · HNO₃ (200 mg, 1.2 mmol), [MeCo(bzacen)(en^{*})]I (250 mg, ≤0.6 mmol) and NaI (100 mg) were successively introduced in MeOH (20 ml) under stirring which was then continued for 2 h. Next, precipitated en · 2HI was filtered off. Py (0.35 ml) and MeOH (10 ml) were added to the filtrate. 1 h later, the resulting solution was concentrated under vacuum to ~ 5 ml. The product was allowed to crystallize at 0°C, then it was separated by filtration, washed with ice water and dried over NaOH under vacuum. Yield, 250 mg (≥76%); red crystals. *Anal.* Found: C, 49.41; H, 5.16; N, 9.98; Co, 10.33. Calc. for C₂₃H₂₈N₄OICo: C, 49.12; H, 5.02; N, 9.97; Co, 10.49%. TLC (eluent A): $R_f = 0.55$.

2.6.3. [MeCo(bzacen)(en)]I

[MeCo(bzacen)(py)₂]I (200 mg, 0.35 mmol), en (35 ml, 0.52 mmol) and NaI (100 mg) were successively dissolved in MeOH (15 ml). The resulting precipitate was separated by filtration, washed with ice water and dried under vacuum over CaCl₂. Yield, 100 mg (60%); orange powder.

Anal. Found: C, 39.13; H, 5.70; N, 12.13. Calc. for $C_{15}H_{26}$ -N₄OICo: C, 38.79; H, 5.65; N, 12.07%. TLC (eluent A): $R_f = 0.45$.

2.6.4. [EtCo(bzac₂en)(py)]

The template reaction was carried out as for the synthesis of [EtCo(bzacen)(en)]Br, but the ratio of cobalt(II) salt, benzoylacetone and ethylenediamine was changed to 1:2:1 (7.5:15:7.5 mmol). The product was washed with ice water and dried under vacuum over CaCl₂. Yield, 270 mg (8%, as calculated for the tentative formula EtCo(bzac₂en)); black powder.

Then this crude product was dissolved in CH₂Cl₂ (30 ml) and py (0.08 ml, 1.0 mmol) was added. The resulting red solution was concentrated under vacuum to ~5 ml. The product was allowed to crystallize at 0°C, then it was separated by filtration, washed with ice water and dried over NaOH under vacuum. Yield, 0.24 g; red powder. TLC (eluent B): $R_f = 0.30$.

2.6.5. $[Co{O=C(Ph)CH=C(Ph)O}_{2}(en)]$

Dibenzoylmethane (3.36 g, 15 mmol) and en (1.01 ml, 15 mmol) were dissolved in MeOH (55 ml), and the solution was kept for 1 h until it turned distinctly yellow. Then $CoCl_2 \cdot 6H_2O$ (1.78 g, 7.5 mmol) was introduced. To the resulting dark red solution, NaOH (1.6 g, 40 mmol) was gradually added with cooling by water bath. The resulting bright brick suspension was stirred at ambient temperature for 10 min and then filtered. The precipitate was washed with water and dried over CaCl₂. Yield, 2.3 g (56%); light orange powder. *Anal.* Found: C, 67.83; H, 5.33; Co, 10.30. Calc. for $C_{32}H_{30}N_2O_4Co: C, 67.95; H, 5.35; Co, 10.43\%$. TLC (eluent C): $R_f = 0.45$.

3. Results and discussion

The template syntheses (Scheme 1) using benzoylacetone and ethylenediamine as complexing agents, and generally following known procedures [6] produced the anticipated alkylcobalt(III) complexes with the tetra- and tridentate Schiff bases, Ia (I: $R^1 = Me$, $R^2 = Ph$, $R^3 = H$, $Z = (CH_2)_2$) and IIa (II: $R^1 = Me$, $R^2 = Ph$, $R^3 = H$, $Z = (CH_2)_2$, X = Br, I). They were characterized by satisfactory elemental analyses, adequate ¹H NMR (Table 6) and IR spectra, GC identification of volatile organic products of acid-induced decomposition (hydrocarbons resulting from coupling–disproportionation of the alkyl ligand) and cleavage by iodine (the corresponding alkyl iodides RI), and typical behaviour upon TLC on SiO₂ and ligand substitution reactions (cf. Refs. [6,7]). Furthermore, the detailed structure of an alkylcobalt chelate with the tridentate ligand was established by X-ray analysis and will be discussed later.

Thus, the main result of this study is the first preparation of organocobalt chelates including Schiff base ligands derived from a mixed aliphatic-aromatic β -diketone of the type AlkCOCHR'COAr. Only the complexes derived from either purely aliphatic β -diketones such as acetylacetone, or aromatic o-hydroxyaldehydes and -ketones had been known before. However, the yields of IIa and especially Ia are lower than those of the related complexes derived from acetylacetone which were synthesized earlier [4,6]. This is probably due to the increasing hydrolytic lability of Schiff base ligands along with the weakening of their donor ability [6]. Failure of our attempt to prepare alkylcobalt complexes starting from dibenzoylmethane, a β -diketone with two aryl groups, can be similarly explained; a new mixed-ligand 'inorganic' chelate of cobalt(II), viz $[Co{PhC(O)CH=C(Ph)O}_{2}(en)]$ (IV), has been isolated instead. Its structure was established by X-ray analysis.

3.1. Crystal structure of [Co{O=C(Ph)CH=C(Ph)-CO}₂(en)] (IV)

R

R4

The crystal is built from the isolated neutral molecules of the complex, $[Co(en)(L)_2]$ (IV) where ligand L is in a deprotonated enolate form (O=C(Ph)CH=C(Ph)O⁻), which is most typical of coordinated β -diketones (Fig. 1).

References



Z is a 2- or 3-links saturated hydrocarbon bridge. Red/Cat = NaBH₄/Pd or H₂/Ni. RX is prim- or sec-alkyl bromide or iodide. The ~ symbol means either that R^2 = Alk, and R^3 = H or Alk, or that R^2 , R^3 represent the fragment of annelated o-arylene.

R¹ R² R³



Scheme 1. Template synthesis of alkylcobalt chelates with Schiff bases.

Table 6

RCo Complex Tridentate ligand c-pyb b γ-H CH₃Co CH₃CH₂ $CH_3C=0$ =CH $C_6H_5C=0$ **β-**Η α-H [MeCo(acacen)(en)]I 2.08, s 1.96. s [MeCo(acacen)(py)₂]I 2.34, s 2.10. s 5.10, s 8.53, dd 7.51, td 7.98, td 2.19, s o: 7.62, dd; [MeCo(bzacen)(en)]I 5.49, s $m, p: 7.32 \text{ m}^{d}$ 2.44, s 5.84, s o: 7.63, dd; 8.63, dd $[MeCo(bzacen)(py)_2]I$ 7.56, td 7.98, td m, p: 7.28 m^d [EtCo(acacen)(en)]Br e 0.60, t 1.94, s 4.98, s [EtCo(bzacen)(en)]Br 0.66, t 5.50, s o: 7.65, dd; m, p: 7.27 m^d $[EtCo(bzac_2en)(py)]^{1}$ -0.15, t 5.82, s o: 7.89; dd; 8.94, br g m, p: 7.38

Signals ^a of methyl, vinyl and aromatic protons in ¹H NMR spectra of alkylcobalt(III) chelates with Schiff bases derived from ethylenediamine and acetyl- or benzoylacetone

^a Spectra were generally registered in Cd₃OD. Intensities of the signals are consistent with their assignments, δ (ppm vs. TMS).

^b The cis-R-ligand, which was proved [6] unexchangeable in the NMR time-scale.

^c Probably covered by the peak of residual protons of the solvent (CD₃OH, $\delta \approx 4.98$ ppm).

^d ABB'XX' system.

^e In D₂O, with DSS as internal standard.

¹ In CD₂Cl₂ without standard (CHDCl₂, $\delta \approx 3.50$ ppm).

^g This signal is apparently covered by signals of *m*- and *p*-H of phenyl group.



Fig. 1. Molecular structure of the $[Co{O=C(Ph)CH=C(Ph)O}_2(en)]$ complex.

The cobalt atom has a distorted *cis*-octahedral environment, the N(2), O(1), O(2) and O(4) atoms form the best 'equatorial' plane (the mean atomic deviation being 0.02 Å), whereas the O(3) and N(1) atoms occupy the 'axial' positions, their displacements from the 'equatorial' plane being equal to -2.09(1) and 2.16(1) Å.

Each of the three ligands in the complex (en, L_1 , and L_2) is bidentate and forms either the six-membered (L_1 and L_2) or five-membered chelate cycle (en). All chelate rings are non-planar. Six-membered rings are folded along the O···O lines, the dihedral angles Co(1)O(1)O(2)/C(3)C(4)C(5) and Co(1)O(3)O(4)/C(18)C(19)C(20) being equal to 23(2) and 24(2)°, respectively. The C(1) and C(2) atoms in the five-membered ring are displaced to the opposite sides of the Co(1)N(1)N(2) plane by 0.40(3) and 0.35(2) Å respectively. The 'axial' chelate rings, those of en and L₂, are almost orthogonal to the 'equatorial' plane, the dihedral angles O(1)O(2)O(4)N(2)/Co(1)O(3)O(4) and O(1)O(2)O(4)N(2)/Co(1)N(1)N(2) being equal to 87.4(3) and 89.2(4)°, respectively.

Two phenyl rings in each of the L ligands have different orientations relative to the chelate cycles: the dihedral angles formed by the C(6)–C(11) and the C(21)–C(26) planes with the mean planes of the corresponding chelate rings are 28.2(7) and $30.2(7)^\circ$, respectively, whereas the planes of the other two phenyl rings C(12)–C(17) and C(27)–C(32) form much smaller dihedral angles with the chelate rings, namely 7.7(9) and 6.0(9)°.

The geometrical parameters of complex IV are generally close to those observed in the molecule of $[Co(acac)-(Et_2NCH_2CH_2NEt_2)]$ (V) [8], which has a similar structure to the *cis*-octahedral environment of the Co atom. Thus, both molecules exhibit the inequality of the Co–N(eq.) and Co– N(ax.) bond distances, the axial bonds Co(1)-N(1)(2.10(1) and 2.20(1) Å in IV and V, respectively) being significantly shorter than the corresponding equatorial distances Co(1)-N(2) (2.20(1) and 2.32(1) Å in IV and V). At the same time the N(1)–C(1) bonds involving the 'axial' N atoms (1.50(2) and 1.54(1) Å in IV and V) are noticeably longer than the N(2)–C(2) bonds involving the 'equatorial' N atoms (1.43(2) and 1.41(2) Å in IV and V, respectively). It is noteworthy that the Co–N bonds in both molecules are significantly longer than the standard value for the Co(II)– $NH_2C_{sp}3$ bond for an octahedrally coordinated Co(II) ion which, according to Ref. [9], is equal to 1.965 Å. The Co–O bonds (2.00–2.11 Å in IV, 2.03–2.08 Å in V), in contrast, are typical for the octahedral bis(diketonate) complexes of Co(II), e.g. the analogous distances in [Co(acac)₂-(imidazole)₂], [Co{O=C(Ph)CH=C(Me)O}₂(imidazole)₂] [10] and [Co{O=C(Ph)CH=C(Ph)O}₂(py)₂] [11] span the range of 2.02–2.08 Å.

Three of the four 'active' H-atoms in the crystal of **IV** do not take part in H-bonding; the only short intermolecular $N(1)-H(1)\cdots O(3A)$ (x, 1-y, z-0.5) contact suggests a rather weak H-bond (N(1) $\cdots O(3A)$ (x, 1-y, z-0.5) 3.14(1), $H(1N1)\cdots O(3A)$ (x, 1-y, z-0.5) 2.35(6) Å, $N(1)-H(1N1)\cdots O(3A)$ (x, 1-y, z-0.5) $170(5)^{\circ}$).

The new series of alkylcobalt chelates with the tridentate Schiff base composed of benzoylacetone and ethylenediamine (IIa) exhibit a reactivity pattern similar to that of related complexes derived from purely aliphatic β -diketones or aromatic *o*-hydroxyketones. This is particularly true for acid-induced reactions of decomposition and ligand substitution.

It is obvious that a position isomerism may occur in $[N_2O]$ or $[N_2O_2]$ ligands bearing two different substituents. For example, in our case, two forms of the tridentate ligand, which can be symbolically designated as bzacen and acbzen, are a priori possible. While neither the free tridentate ligand in question is known nor had its metal complexes been reported before this work, structures of the related tetradentate Schiff base [12] and of a number of its chelates (see e.g. Refs. [13,14]) have been studied. In all of them, the phenyl and methyl groups occupy the positions adjacent to the enol(ate) and azomethine functions, respectively. Our HPLC or CE

(for neutral or cationic complexes, Ia or IIa, respectively), and ¹H NMR data for both the types of complexes indicate that a single isomer is formed in every case. An X-ray structural study of the methylcobalt complex with the tridentate ligand IIa1 (IIa: R = Me, X = I) has shown that the latter corresponds to the bzacen form, with the phenyl and methyl groups being in the same positions as above.

3.2. Crystal structure of [MeCo(bzacen)(en)]I(IIa1)

The structure of the cation in the crystal of IIa1 is shown in Fig. 2. As might be expected, the tridentate bzacen ligand occupies three meridional sites in the coordination octahedron of the cobalt atom. The six-membered chelate cycle Co(1)O(1)C(2)C(3)C(4)N(1) exhibits substantial deviations from planarity, the dihedral angle formed by the Co(1)O(1)N(1) and N(1)C(4)C(3)C(2)O(1) planes being equal to $13.5(2)^\circ$. The N(2) atom lies almost exactly in the former plane (its deviation is equal to 0.01 Å), whereas the N(4) atom is displaced from this plane by 0.091(4) Å. Both five-membered chelate rings are not planar either; the torsion angles N(1)C(5)C(6)N(2) and N(3)C(7)C(8)-N(4) are equal to 46.8(4) and $53.5(4)^\circ$, respectively.

Three Co–N(NH₂) bond lengths in the coordination octahedron of the cobalt atom show significant variation obviously associated with different nature of the *trans* substituents. Thus, the shortest Co(1)–N(2) bond (1.959(3) Å) involves the NH₂ group in the *trans* position to the oxygen atom, the longest Co(1)–N(3) bond (2.095(3) Å) is in the *trans* position relative to the metal– carbon σ bond (Co(1)–C(1) 1.965(4) Å) whereas the Co(1)–N(4) bond length with the N(1) atom as a *trans* partner has an intermediate value of 1.979(3) Å. This bond lengths distribution pattern in the coordination sphere of the



Fig. 2. Structure of the [MeCo(bzacen)(en)] + cation.

cobalt atom in this cation is in general quite close to that observed in the previously studied alkylcobalt complexes with tridentate Schiff bases derived from an aromatic ohydroxyketone, namely [MeCo(7-Me-salen-N-Me)(N-Meen)]I (VI) [6] and [EtCo(7-Me-salen)(en)]Br (VII) [15,16]. In all the three complexes the Co-N bonds in the $N(4)H_2$ -Co(1)-N(1) triad (the atomic identifiers in all cases refer to Fig. 2) coincide almost exactly in length. The (Co(1)-N(1)) and Co(1)-N(4) bond lengths are equal to 1.890(4) and 1.970(4) in VI and 1.896(7) and 1.973(7) Å in IV, respectively). The Co-N(2) bond in VI is probably slightly longer (1.974(4)) than in IIa1 and VII (1.959(3)) and 1.964(7) Å respectively), which may be caused by the influence of the N-Me substituent in the 7-Me-salen-N-Me ligand. The same is true for the Co(1)-N(3) bond in VI (2.146(4) Å) which is significantly longer than the analogous bond in IIa1 (2.095(3) Å) and even somewhat longer than the relevant bond in VII (2.128(7) Å) which may be attributed to a steric hindrance induced by the methyl substituent in the diamine ligand of complex VI [6]. The strong *trans* influence of the alkyl group σ bonded to the metal atom [17,18] is clearly manifested in all three complexes.

The cations [MeCo(bzacen)(en)]⁺ and anions I⁻ in the crystal of I are linked via I⁻…HN hydrogen bonds into dimeric centrosymmetric aggregates, with each of them involving two cations, two anions and four symmetry independent H bonds. Distances I⁻…H, I⁻…N (Å) and I⁻…H-N angle (°) for H bonds are as follows: 2.74(6), 3.677(3), and 162(4) for I(1)…H(21)–N(2); 2.86(4), 3.707(3), and 167(3) for I(1)…H(42A)–N(4A) (2-x, 1-y, 1-z); 3.01(5), 3.832(3), and 170(3) for I(1)…H(31)–N(3); 3.02(5), 3.828(3), and 151(4) for I(1)…H(22A)–N(2A) (2-x, 1-y, 1-z).

4. Conclusion

Finally, taking into account the results of this work, the current scope of the template synthesis of organocobalt chelates with Schiff bases can be summarized by Scheme 1.

5. Supplementary material

Detailed digital data that resulted from X-ray studies including tables of H atoms coordinates have been deposited with the Cambridge Crystallographic Center.

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