# Cobalt-Assisted Condensation of 2-Butanone Oxime and Acetone: Synthesis and X-ray Structure of the Novel Acetaldiimine Complex $[CoI_2\{((CH_3CH_2)(CH_3)C=NO)_2C(CH_3)_2\}]$

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The synthesis of the first acetaldiimine cobalt complex and its full characterisation are reported. The nitrogen-bonded chelate complex $[CoI_2\{((CH_3CH_2)(CH_3)C=NO)_2C(CH_3)_2\}]$ is obtained in high yield from the reaction of 2-butanone oxime with cobalt iodide dihydrate in acetone, in the presence of trimethyl orthoformate as dehydrating agent. A single-crystal X-ray structure determination, infrared spectroscopy and mass spectrometry analyses confirm the formation of a new ligand in situ from the addition of an acetone molecule to two oximato species. This cobalt-mediated reaction provides an indirect proof for the existence in solution of monodentate *N*-bonded cobalt–ketoxime species.

## Introduction

The chemistry of oxime/oximato transition metal complexes is rich and has shown a great variety of reactivity modes, as demonstrated in the review by Kukushkin et al.[1] Simple oxime complexes[2] (or mono-oximes as opposed to chelating dioximes) are known to form with palladium, nickel[3] or platinum, for which they have been thoroughly studied.[4] These compounds display generally a strict monodentate coordination to the metal by bonding through the nitrogen centre. To date, the analogous cobalt-ketoxime complexes still remain unknown, and only a single cobalt-aldoxime complex has been reported which displays monodentate coordination.[5] Thus, although several hundred complexes of cobalt-dioximes have been identified, the stabilisation and proper description of cobalt mono-ketoxime complexes, especially monodentate ones (either N- or O-bonded), still remains challenging. In the course of our attempts to isolate new cobalt species with simple ketoxime ligands from cobalt halide salts,[6] we have identified an as-yet-unknown reactivity of cobalt allowing the addition of 2-butanone oxime to acetone.

## Results and Discussion

The title compound $[CoI_2\{((CH_3CH_2)(CH_3)C=NO)_2C(CH_3)_2\}]$ (**1**) was prepared from the reaction of $CoI_2{\cdot}2H_2O$ with a solution of $(CH_3CH_2)(CH_3)C=NOH$ in acetone, in the presence of trimethyl orthoformate. The new compound was characterised by infrared spectroscopy, elemental analysis, mass spectrometry and single-crystal X-ray crystallography. A fully labelled representation of the molecular structure of the complex is given in Figure 1. The cobalt(II) atom is surrounded by two iodide and two nitrogen atoms in a distorted tetrahedral environment. The two nitrogen atoms linked to cobalt are part of a novel chelating ligand, which has been formed in situ from two 2-butanone oxime molecules bridged by a $-C(CH_3)_2-$ unit. The six-membered ring formed by the acetaldiimine ligand at cobalt forces the N(1)−Co(2)−N(2) angle to contract to 96.31(13)°, whilst the angle I(1)−Co(1)−I(2) opens to 117.32(2)°, resulting in a distorted tetrahedron around Co. The Co−I distances [Co(1)−I(1) 2.5508(7), Co(1)−I(2) 2.5802(6) Å] are in the range of values reported for $CoI_2$ in a tetrahedral environment.[7] The bond distances in the acetaldiimine ligand are in very good agreement with those of the related compound previously described in the crystallographic literature [1,1-bis(1-phenylethylidenaminooxy)-ethyl]benzene.[8] The six-membered Co(1)−N(1)−O(1)−C(2)−O(2)−N(2) ring adopts a flattened boat conformation at the temperature of measurement. The chair-like conformation for this kind of metal−ligand rings is common,[9] whereas boat forms are rarely observed.[10]

The infrared measurements confirmed the chelating cyclization of the 2-butanone oxime molecules by both the disappearance of the oxime OH stretching vibration at 3214 $cm^{-1}$, and the large shift of the C=N stretching vibration from 1664 $cm^{-1}$ in the free simple oxime to 1620 $cm^{-1}$ in the bound acetaldiimine. From electrospray mass spectrometry experiments on **1**, the parent peak has been found at *m*/*z* = 215; this value corresponds to the ionic fragment $[H(CH_3CH_2)(CH_3)C=NO)_2C(CH_3)_2]^+$, which confirms not only the formation but also the stability of the acetaldiimine ligand.[11] Our attempts to isolate the cobalt chloride and cobalt bromide analogues of **1** have failed, producing sticky

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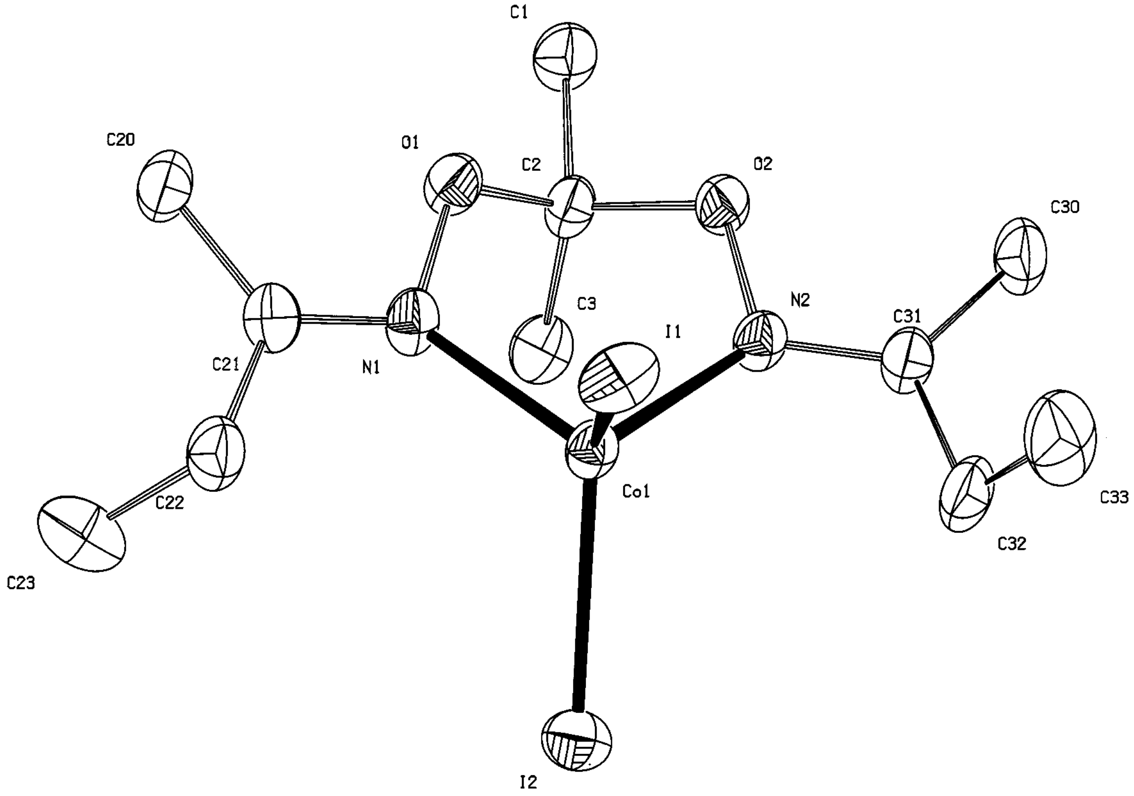

Figure 1. Ortep view at 50% probability level of the molecular structure of **1**; selected bond lengths [Å] and bond angles [°]: Co(1)−I(1) 2.5508(7), Co(1)−I(2) 2.5802(6), Co(1)−N(1) 2.029(3), Co(1)−N(2) 2.035(3), N(1)−C(21) 1.281(5), N(2)−C(31) 1.286(5), O(1)−N(1) 1.422(4), O(2)−N(2) 1.421(4); I(1)−Co(1)−I(2) 117.32(2), I(1)−Co(1)−N(1) 105.46, I(1)−Co(1)−N(2) 109.68(10), I(2)−Co(1)−N(1) 114.61(10), I(2)−Co(1)−N(2) 111.34(10), N1−Co(1)−N(2) 96.31(13), N(1)−O(1)−C(2) 113.9(3), N(2)−O(2)−C(2) 114.2(3), Co(1)−N(1)−O(1) 115.83(18), Co(1)−N(2)−O(2) 119.3(2), O(1)−C(2)−O(2) 110.6(4)

oils which are difficult to characterise. The van der Waals volume of the iodide ions, which is considerable larger than those of the smaller halide analogues, possibly permits the crystallisation of the complex. The tetrahedral geometry around cobalt is confirmed by Vis-NIR spectroscopy (typical broad band split in three, centred around 7000 cm$^{-1}$ and a more intense band around 15000 cm$^{-1}$).

The global equation for the reaction leading to the acetaldiimine can be written as:

$$2\ RR'C{=}N{-}OH + (CH_3)_2C{=}O \rightleftarrows H_2O + RR'C{=}N{-}O{-}C(CH_3)_2{-}O{-}N{=}CR'R$$

The use of trimethyl orthoformate, which reacts readily with water molecules to form methanol and methyl formate,[12] displaces the above equilibrium to the right toward the formation of the adduct. Experiments with 2-butanone oxime and acetone (four equivalents) refluxed at 80 °C for three hours in either an acidic (pH = 3), neutral, or basic (pH = 12) medium, in the absence of the cobalt salt, do not show any changes in the infrared and $^1$H NMR spectra of the mixture. Similar attempts conducted in the presence of trimethyl orthoformate also failed to yield the acetaldiimine, showing the need for cobalt in order to perform the condensation of the oxime and acetone.

Oximes, being weak oxygen acids, can react with bases and undergo deprotonation. Literature reports state that the nitrogen coordination of oxime ligands to a metal centre leads to a large increase in their acidic character, and the formation of oximato ligands is favourable upon coordination. It has also been shown that oximes behave as nucleophiles towards other unsaturated species such as olefins, arenes or ketones involving nucleophilic addition by either the O or the N atom.[1] From these data the following hypothesis can be proposed concerning the global mechanism of formation of the ligand and the complex: (i) the 2-butanone oxime molecules could coordinate to the cobalt centre giving a strong acidic character at their OH hydrogen atoms, (ii) the electrophilic attack of an acetone molecule towards the activated oxygens in the coordination sphere of the metal could then take place, the formation of the adduct being favoured by the progressive consumption of water by reaction with trimethyl orthoformate (without this reactant no compound has been isolated). Following this idea, the formation of the complex should be favoured in alkaline medium and disfavoured in acidic medium. Indeed, the synthesis conducted with addition of 0.1 mL of 1 M NaOH solution in water leads to **1** precipitating quickly as a fine powder, whereas from an acidic medium (addition of 0.1 mL of HCl in water at pH = 2), compound **1** could not be isolated. It is worthwhile to note that conventional acetal formation is acid-catalysed and does not proceed under alkaline conditions, contrary to this metal-mediated reaction. The qualitative observations reported above support the formation in solution of intermediary N-bonded monodentate cobalt-ketoxime species, explaining the OH acidic activation towards the oximato species. However, these N-bonded monodentate cobalt-ketoxime complexes still have to be isolated.

Only a few other examples of the metal-assisted addition of oximes to compounds containing double or triple bonds are described in the literature.[13,14] Amongst these the most notable one was described by Kukushkin et al.:[15] from the reaction of the platinum(II) complex $[PtCl_2((CH_3)_2C{=}NOH)_2]$ with *m*-chloroperoxybenzoic acid in acetone the *N*,*O*-chelating complex $[PtCl_2\{OC(CH_3)_2ON{=}C(CH_3)_2\}_2]$ was obtained which contains two five-membered Pt−N−O−C−O rings. The most likely explanation for the formation of the product was proposed to be the coordination of acetone molecules at vacant sites on platinum, followed by ring closure with neighbouring N-coordinated monodentate oxime ligands. Here, the isolated platinum bis(ketoxime) species is the starting product, and, similarly, a cobalt-ketoxime compound is assumed to be an intermediate in the formation of **1**.

In conclusion, this work describes a novel template reaction of acetone with two ketoxime molecules, forming a symmetric chelating diimine ligand with an acetal backbone. Applications of this template reactivity in syntheses of new diimine ligands can be of interest in comparison to the "organic" routes reported so far,[16] and might be further explored.

## Experimental Section

Acetone was distilled, dried and degassed over molecular sieves under an argon atmosphere. Other reactants and solvents were used as received from commercial sources. Vis-NIR spectra were obtained on a Perkin−Elmer Lambda 900 spectrophotometer using the diffuse reflectance technique with MgO as a reference. Infrared spectra were obtained on a Perkin−Elmer Paragon 1000 FTIR spectrophotometer equipped with a Golden Gate ATR device, using the reflectance technique (4000−500 $cm^{-1}$, res. 4 $cm^{-1}$). NMR measurements were performed at 300.13 MHz on a Bruker 300 DPX spectrometer. Mass spectrometry and elemental analyses were performed in the analytical service department of the Gorlaeus laboratories.

**IR of 2-Butanone Oxime:** Selected bands ($cm^{-1}$): $\tilde{\nu}$ = 923 vs/br, 975 vs; 1072 s, 1096 s, CC stretching; 1368 s, 1458 s, CH bending; 1664 m, C=N stretching; 2880 m, 2972 m, sh, CH stretching; 3214 s, br, OH stretching.

**Synthesis of $[Co\{((CH_3CH_2)(CH_3)C{=}NO)_2C(CH_3)_2\}I_2]$ (1):** $CoI_2\cdot 2H_2O$ (0.65 g, 1.9 mmol) in an Erlenmeyer flask was covered by 2.5 mL of trimethyl orthoformate and then dissolved in 10 mL of dry acetone to give a bright deep green solution. An excess of 2-butanone oxime (0.60 g, 7.3 mmol) in 15 mL of dry acetone was prepared. The two solutions were boiled and mixed, the mixture was boiled for 5−6 minutes to reduce the volume to approximately 10 mL. After 24 h standing in air, almost all the residual solvent was evaporated and bright green needles were formed. The crystals were washed with a minimum of acetone, and quickly with 2 × 1 mL of diethyl ether, then with pentane, resulting in 0.78 g of complex (yield 80%) as single crystals suitable for X-ray diffraction measurements. $C_{11}H_{22}CoI_2N_2O_2$ (527.04): calcd. C 25.07, H 4.21, N 5.32, Co 11.18; found C 24.94, H 3.96, N 5.32, Co 11.42. − IR ($cm^{-1}$): $\tilde{\nu}$ = 891 vs, 933 vs; 1148 s, CO stretching; 1366 s, 1377 s, 1456 s, CH bending; 1620 s, C=N stretching; 2972 m, sh, CH stretching. Vis-NIR (solid state, $cm^{-1}$): $\tilde{\nu}$ = 6900, 7400, 9600, 14900, 28000.

**X-ray Crystal Structure Analysis of 1:** $C_{11}H_{22}CoI_2N_2O_2$, $M$ = 527.04, dark green needles (0.21 × 0.09 × 0.09 $mm^3$), monoclinic, $P2_1/c$ (no. 14), $a$ = 10.9678(3), $b$ = 12.0102(4), $c$ = 15.7274(4) Å, $\beta$ = 119.924(2)°, $V$ = 1795.52(10) $Å^3$, $Z$ = 4, $D_c$ = 1.950 $g\cdot cm^{-3}$, $F(000)$ = 1004, $\mu(Mo\text{-}K_\alpha)$ = 4.392 $mm^{-1}$, 11288 reflections measured, 4509 independent, $R_{int}$ = 0.036. Data were collected on a Nonius Kappa CCD area detector with rotating anode, $\lambda(Mo\text{-}K_\alpha)$ = 0.71073 Å, $T$ = 150 K, using a graphite monochromator. Absorption corrections based on multiple measured equivalent reflections were applied. The structure was solved by Patterson techniques (DIRDIF-99[17]) and refined using full-matrix least-squares on $F^2$ (SHELXL-97[18]). All non-hydrogen atoms were refined with anisotropic displacement parameters, hydrogen atoms were located at calculated positions and refined riding on their carrier atoms. Refinement converged at $R1$ = 0.0331 [for 3929 reflections with $F_o > 4\sigma(F_o)$], $wR2$ value of 0.0740 ($S$ = 1.193). Geometric calculations and molecular graphics were performed with PLATON.[19] One of the butane moieties is disordered due to an exchange of the methyl, C(30), and ethyl, C(32)−C(33), groups (major site occupancy 80% is shown in Figure 1).

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited at the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-144112. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax:+44-1223/336-033; E-mail: deposit@ccdc.cam.ac.uk].

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