A novel trinuclear cobalt complex comprising moieties derived from single and double C–S bond cleavage of diethyldithiocarbamate

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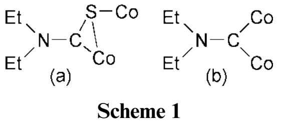
A trinuclear cobalt complex, [$Co_3(\mu_3\text{-}S)(\mu\text{-}CNEt_2)(\mu\text{-}SCNEt_2)_2(PPh_3)_2Cl]\cdot 2CH_3CN$, comprising moieties derived from single and double C–S bond cleavage of diethyldithiocarbamate was isolated and characterized by X-ray structural analysis.

Owing to the importance of fossil fuels in studies on hydrodesulfurization, metal-mediated C–S bond cleavage has attracted considerable interest for several years.[1] Many such studies have been carried out in transition metal complexes,[2] especially those with low oxidation state metals and metal–metal multiple bonds.[3] Our earlier work shows that the low oxidation state cobalt phosphine complex $Co(PPh_3)_3Cl$ is a good starting material for studies on C–S bond cleavage and a series of complexes comprising moieties resulting from C–S bond cleavage have been isolated and characterized.[4] Dialkyldithiocarbamates (R_2dtc) are well known for their ability to stabilize metal centers, especially high oxidation state metal centers,[5] thus they are good models for the study of metal-mediated C–S bond cleavage which usually follows an oxidative addition process.[6] To date, many studies on the mono C–S bond cleavage of R_2dtc have been reported,[7] but studies on double C–S bond cleavage and its intermediates are scarce.[8] As part of our systematic work, we recently began to explore the reactions of $Co(PPh_3)_3Cl$ with R_2dtc, hoping to observe the double C–S bond cleavage by trapping the intermediates. Herein we report a trinuclear cobalt complex, [$Co_3(\mu_3\text{-}S)(\mu\text{-}CNEt_2)(\mu\text{-}SCNEt_2)_2(PPh_3)_2Cl]\cdot 2CH_3CN$ (**1**), which contains moieties derived from both the single and double C–S bond cleavage of Et_2dtc.

The reaction of $CoCl_2$, PPh_3 and (Et_2dtc)Na in CH_3CN in the presence of zinc powder results in the formation of **1**.† Both ^1H and ^{31}P NMR spectra are very broad, indicating the paramagnetic nature of the complex. The single peak in the ^{31}P NMR illustrates that only one kind of phosphorus is present in **1**, and the peaks at 430, 619, and 1435 cm^{-1} in the IR indicate the presence of Co–S, Co–C and C=N bonds, respectively. X-Ray crystal structural analysis ‡ confirms **1** is a neutral trinuclear cobalt complex comprising one μ_3-bridged S, two thiocarboxamido, and one aminomethylidyne moieties, which come from the single and double C–S bond cleavage of Et_2dtc.

As shown in Fig. 1, the triangle plane formed by the three cobalt atoms is capped by a μ_3-S atom with an average Co–S distance of 2.289 Å. Each thiocarboxamido ligand adopts a chelating-bridging mode linking two cobalt atoms (Co(2,3), Co(1,3)) (Scheme 1a) with average Co–Co, Co–S, and Co–C distances being 2.724, 2.474 and 1.828 Å, respectively, while the aminomethylidyne ligand acts as a bridge connecting two cobalt atoms (Scheme 1b) with average Co–C distance of 1.828 Å and a very short Co–Co distance of 2.415(2) Å. Thus, there are two types of cobalt coordination environment: Co(1) and Co(2) are coordinated by two sulfur atoms, two carbon atoms and one phosphorus atom in a highly distorted S_2C_2P square pyramidal geometry in which two S and two C atoms form the equatorial plane; Co(3) is coordinated by three sulfur atoms and a chlorine atom in a distorted tetrahedral geometry. The Co–C distances range from 1.823(8) to 1.833(8) Å, in the range of transition metal-stabilized carbenes,[9] while the N–C bonds for carboxamido carbon (1.319(9) Å) and aminomethylidyne carbon (1.323(9) Å) show a high degree of double bond character,[10] in agreement with the IR data. Thereby, both thiocarboxamido and aminomethylidyne ligands may adopt a mono-anion configuration, resulting in an average oxidation state of +2 for the cobalt atoms and a paramagnetic character for **1**. It has been well documented that the reaction of $CoCl_2$, PPh_3 and Zn powder results in the formation of $Co(PPh_3)_3Cl$,[4] which is the starting material in our reaction. Hence the C–S bond cleavage of Et_2dtc and the formation of **1** also follows an oxidative addition process.[6]



Scheme 1

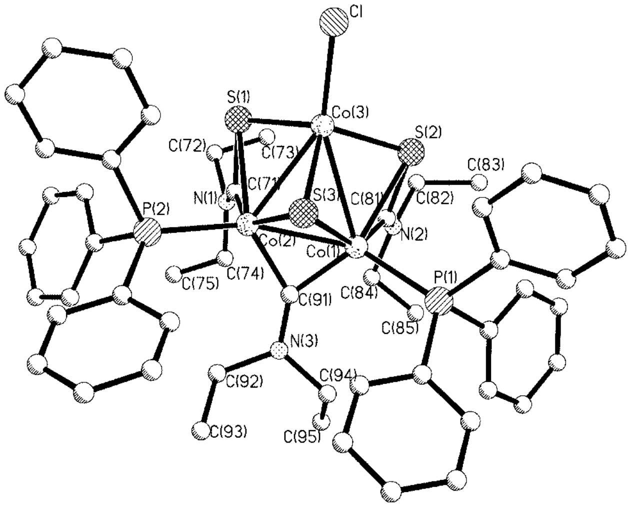


Fig. 1 Structure of **1**. Selected bond lengths (Å): Co(1)–Co(2) 2.415(2), Co(1)–Co(3) 2.715(2), Co(2)–Co(3) 2.732(2), Co(1)–C(81) 1.823(8), Co(1)–C(91) 1.823(8), Co(1)–S(2) 2.510(2), Co(1)–S(3) 2.285(2), Co(1)–P(1) 2.253(2), Co(2)–C(91) 1.833(8), Co(2)–C(71) 1.833(8), Co(2)–S(1) 2.520(3), Co(2)–S(3) 2.286(2), Co(2)–P(2) 2.246(3), Co(3)–Cl 2.227(2), Co(3)–S(1) 2.417(3), Co(3)–S(2) 2.449(2), Co(3)–S(3) 2.298(2), S(1)–C(71) 1.737(8), S(2)–C(81) 1.736(8), N(1)–C(71) 1.319(9), N(2)–C(81) 1.316(9), N(3)–C(91) 1.323(9).

In conclusion, we have successfully isolated a trinuclear cobalt complex which traps a variety of moieties derived from C–S bond cleavage in Et_2dtc, including two thiocarboxamido moieties from single S–C bond cleavage, one aminomethylidyne moiety from double S–C bond cleavage and one S^{2-}. The other three S atoms derived from C–S bond cleavage are not trapped in the complex and further work is underway to determine their

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exact form. Although C–S bond cleavage of R_2dtc has been reported,[7] for cobalt complexes it has only been observed in carbonyl systems.[9,10] Herein we report the first reaction involving both single and double C–S bond cleavage of R_2dtc in a cobalt–phosphine system. Complex **1** is the first high oxidation state cobalt complex containing bridging thiocarboxamido and aminomethylidyne ligands. To the best of our knowledge, the only other example reported to contain these ligands was an iron carbonyl complex in which the oxidation state of Fe was only +1.[11]

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Notes and references

[†] Synthesis of $[Co_3(\mu_3\text{-}S)(\mu\text{-}CNEt_2)(\mu\text{-}SCNEt_2)_2(PPh_3)_2Cl]\cdot 2CH_3CN$. Under a N_2 atmosphere, anhydrous $CoCl_2$ (129 mg, 1 mmol), PPh_3 (787 mg, 3 mmol) and Zn (0.25 g) was added to dried CH_3CN (25 ml) and the mixture was stirred for 3 hours to give a light yellow-green slurry. To the above mixture, $(Et_2dtc)Na\cdot 3H_3O$ (225 mg, 1 mmol) was added and stirred for 24 h at room temperature. After filtration, the brown-black mother liquor was stored at 0 °C, and black cubic crystals of **1** were obtained after three weeks. Yield: 43%. Found: C, 56.47; H, 5.42; N, 5.75; S, 8.10. Calc. for $C_{55}H_{66}ClCo_3N_5P_2S_3$: C, 56.58; H, 5.70; N, 6.00; S, 8.24%. ^{1}H NMR (500 MHz, $CDCl_3$): δ 7.24–7.66 (m, Ph), 3.78–3.92 (br, m, $-CH_2-$), 3.29–3.41 (br, m, $-CH_2-$), 1.11–1.456 (br, m, $-CH_3$); ^{31}P NMR (500 MHz, $CDCl_3$): δ 28.27 (s). IR (KBr, cm^{-1}): 3051 (m), 2974 (m), 2931 (m), 2872 (m), 1967 (w), 1900 (w), 1819 (w), 1435 (s), 744 (m), 696 (s), 619 (m), 517 (s), 430 (m).

[‡] Crystal data: $C_{55}H_{66}ClCo_3N_5P_2S_3$: $M_r = 1167.49$, orthorhombic, space group *Pbca*, $a = 15.471(4)$, $b = 25.898(9)$, $c = 28.726(6)$ Å, $V = 11510(5)$ Å^3, $Z = 8$, $\mu = 1.105$ mm^{-1}, $T = 293$ K, 42994 reflections collected for $2.84 < 2\theta < 50.1$, 10055 independent reflections. $R1 = 0.081$, $wR2 = 0.135$ for reflections with $I > 2\sigma(I)$. Data collection was by means of a Siemens SMART CCD diffractometer with full-matrix refinement on F^2 using SHELXL-97.[12] CCDC reference number 167932. See http://www.rsc.org/suppdata/dt/b1/b107017g/ for crystallographic data in CIF or other electronic format.

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