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Synthesis and Molecular Structure of $Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}S)(\mu_4,\eta^2\text{-}HC_2C_6H_5)$: An Example of Alkyne Coordination on a Planar Tetrametal Core

Sir:

The versatility in the coordination of alkynes on transition-metal clusters is well documented[1,2] and offers the opportunity to mimic modes of absorption on metal surfaces.[3] The coordination to four-atom clusters was observed almost exclusively for the butterfly structure of the metal core, which was considered a model for the absorption of an alkyne on a [110] plane or on a kink or a step of a metal surface.[4,5] The absorption on a [100] plane could be simulated by the coordination of an alkyne on a square or rectangular M_4 framework, but such compounds are very rare.[6-14] We report the first example of a tetracobalt cluster belonging to this group, in which the alkyne is bonded parallel to the long side of a planar Co_4 rectangle.

In a petroleum ether solution of $Co_3(\mu_3\text{-}S)(CO)_9$,[15] at room temperature, a small amount of freshly sublimed Me_3NO was dissolved under a slow stream of carbon monoxide and, subsequently, a solution of phenylacetylene was added dropwise until the absorption in the infrared spectrum at 2049 cm^{-1} had just disappeared. The new cluster $Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}S)(\mu_4,\eta^2\text{-}HC_2C_6H_5)$ (I) was obtained in ca. 60% yield and characterized by IR, ^1H NMR, and mass spectroscopies and by X-ray diffraction analysis.[16-19] Its structure (Figure 1) consists of a rectangular Co_4 skeleton, to which a quadruply bridging sulfur and a quadruply bridging phenylacetylene are coordinated on opposite sides. The elongation of the rectangle,[20] generally greater than that of the similar complexes $Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}S)_2$ (II),[21] $Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}Se)_2$ (III),[22] $Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}Te)_2$ (IV), and $Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}PC_6H_5)_2$ (V),[23] is not only due to the shortening effect of the CO groups bridging two opposite Co–Co sides but also to the lengthening effect of the acetylene ligand on the other Co–Co sides. Two terminal CO's are bonded to each metal atom up and down the metal plane, approximately in the direction of the diagonal of the rectangle. The four cobalt–sulfur distances lie in the typical range for the $(\mu_3\text{-}S)Co_3$ and $(\mu_4\text{-}S)Co_4$ cores, and the Co–C(alkyne) distances (1.978 (6) and 2.032 (6) Å) are similar to the formally σ and the formally π Co–C(alkyne) distances in the $Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4,\eta^2\text{-}HC_2H)$ butterfly structure.[5] The C(1)–C(2) distance of 1.42 Å corresponds to a value intermediate between those of single and double C–C bonds and is close to the value found in other similar complexes.[6] The high-yield synthesis of complex I is a noteworthy example of a transformation of a trinuclear cluster into a tetranuclear cluster. Such cluster expansion processes are believed to start usually by decarbonylation,[24] which is largely favored by the trimethylamine oxide.

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(16) Complex I was isolated by silica gel TLC by eluting with petroleum ether (other main products: $Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}S)_2$, $[Co_3(CO)_7S]_2S_2$, and $Co_2(CO)_6(HC_2C_6H_5)$) and obtained as air-stable dark crystals by crystallization at −20 °C. IR (cm^{-1}, in *n*-hexane): 2093 (w), 2058 (vs), 2047 (s), 2034 (vs), 2020 (w), 1911 (w, sh), 1902 (m). ^1H NMR (δ, in $CDCl_3$): 6.10 (s, 1 H), 7.28 (m, 5 H). MS: main peaks at *m/e* 650 (M^+) and at *m/e* values corresponding to $(M - n\,CO)^+$ ($n = 1$–10) and to $(Co_2(CO)_{6-n}(HC_2C_6H_5))^+$ ($n = 0$–6).
(17) Red-brown prismatic crystals of the complex were grown from a petroleum ether solution by cooling at −20 °C. X-ray diffraction data were collected at room temperature on a Nicolet R3 diffractometer using graphite-monochromatized Mo Kα radiation (ω-scan technique, scan range (θ) 1–20°). The crystals belong to the triclinic $P\bar{1}$ space group, with $a = 8.376$ (3) Å, $b = 15.565$ (4) Å, $c = 17.002$ (5) Å, $\alpha = 93.73$ (2)°, $\beta = 97.02$ (3)°, $\gamma = 91.36$ (3)°, $V = 2194$ (1) Å^3, $Z = 4$ with two independent molecules per asymmetric unit, $\rho = 1.88$ g cm^{-3}, and $\mu = 29.9$ cm^{-1}; the absorption correction was made according to ref 18. The structure was solved by direct methods and refined with 3109 reflections ($F > 6\sigma(F)$) to final values $R = 0.0521$ and $R_w = 0.0556$ (SHELX76).[19] In the last least-squares cycles the Co and S atoms were anisotropically refined. Some of the hydrogen atoms of the phenyl groups appeared on the difference Fourier maps, but it was preferred to refine the phenyl moiety as rigid groups with the hydrogen atoms in calculated positions. Two further peaks of height 0.6 e Å^{-3} appeared, corresponding to the supposed acetylenic hydrogen atoms of the two independent molecules. They were enclosed at the end of the refinement.
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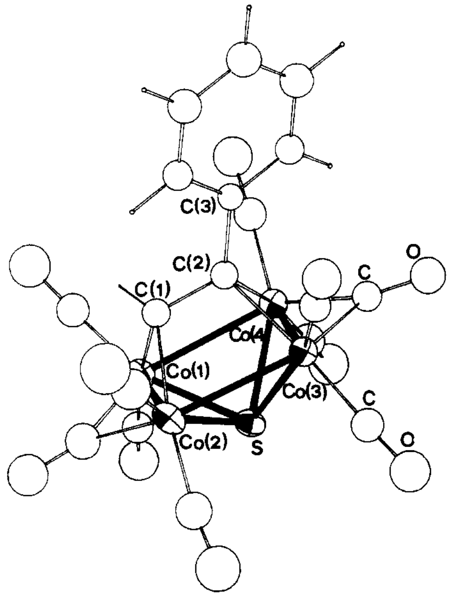

Figure 1. ORTEP drawing of one of the two independent $Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4,\eta^2\text{-}HC_2C_6H_5)$ molecules with 36% probability ellipsoids. Selected averaged interatomic distances (Å) and angles (deg) are as follows: Co(1)–Co(2) = 2.451 (1), Co(1)–Co(4) = 2.722 (1), Co(2)–Co(3) = 2.697 (1), Co(3)–Co(4) = 2.449 (1), Co–S = 2.250 (1), Co–C(1) = 1.978 (6), Co–C(2) = 2.032 (6), C(1)–C(2) = 1.404 (11), C(2)–C(3) = 1.519 (9); C(1)–C(2)–C(3) = 120.4 (6).

A subsequent step could be coordination to the "activated" Co_3S system of a second $Co_3S(CO)_9$ molecule, which may act as a source of $Co(CO)_2$ fragments. The chemical form in which the residual dicobalt fragment might be partially recovered in the reaction mixture would be $Co_2(CO)_6HC_2C_6H_5$. The stability of complex I could be the "driving force" of the reaction, considering that it is a 64-electron cluster, electron precise according to the EAN rule. By a similar reaction $Fe_4(CO)_{10}(\mu_4\text{-}PC_6H_5)_2$ was obtained in good yield from $Fe_3(CO)_9(\mu_3\text{-}PC_6H_5)_2$.[25]

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Registry No. I, 116263-38-8; $Co_3(\mu_3\text{-}S)(CO)_9$, 12261-15-3; $Co_4(CO)_8(\mu\text{-}CO)_2(\mu_4\text{-}S)_2$, 57034-21-6; $[Co_3(CO)_7S]_2S_2$, 15927-92-1; $Co_2(CO)_6(HC_2C_6H_5)$, 12154-91-5; phenylacetylene, 536-74-3.

Supplementary Material Available: Tables of fractional atomic coordinates, isotropic and anisotropic thermal parameters, and interatomic distances and angles of the two independent molecules (6 pages); a listing of observed and calculated structure factors (14 pages). Ordering information is given on any current masthead page.

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Luminescence Studies of Copper Phenanthrolines in Aqueous Media: Colloids and DNA Complexes

Sir:

This work demonstrates that charge-transfer (CT) luminescence from copper phenanthrolines can be an extremely useful probe of intermolecular interactions that occur in aqueous media, including binding to DNA. As is well-known, CT absorption occurs in the visible spectra of $[Cu(NN)_2]^+$ complexes, where NN denotes a derivative of 1,10-phenanthroline (phen).[1-4] Although the lowest energy CT excited state is generally quite reactive,[5-8] it tends to be short-lived; for example, in acetonitrile the excited-state lifetime of $[Cu(dmp)_2]^+$, where dmp is 2,9-dimethyl-1,10-phenanthroline, is only 2 ns at room temperature.[9] In donor media the lifetime appears to be limited by an unusual quenching reaction involving nucleophilic attack at the metal center,[9-11] although so far we have been unable to detect the species (exciplex) with an expanded coordination number. Nevertheless, studies of steric effects[12,13] as well as studies of the temperature[9] and pressure[14] dependence of quenching strongly support the proposed quenching mechanism. As we will show below, intermolecular interactions also influence the quenching rate, and the model is readily extended to explain these effects.

Absorption and emission data pertaining to $MeOH/H_2O$ solutions of $[Cu(bcp)_2]^+$, where bcp denotes 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline, are presented in Figure 1 and Table I. As the percentage of water increases, the charge-transfer absorption exhibits hypochromism and undergoes a bathochromic shift. A comparison of the emission yields in CH_2Cl_2 and MeOH reveals that the emission is almost completely quenched in the donor solvent, yet surprisingly intense emission is observed in 6% MeOH. As we shall see, however, the 6% MeOH solution is actually a colloidal suspension. The presence of colloidal particles is difficult to detect by absorbance measurements, although there is a small offset in the absorption spectrum above 650 nm, presumably due to a scattering phenomenon (Figure 1). A more telling observation is that $[Cu(bcp)_2]Cl$ fails to dissolve when directly combined with 6% MeOH. Rather, we obtain stable, emissive solutions by diluting a MeOH solution of the complex into water. (Even with this method, however, turbid solutions are obtained when the final solution is 20–25% MeOH. In 33% MeOH direct dissolution of $[Cu(bcp)_2]Cl$ is possible, but the emission intensity is essentially the same as it is in pure MeOH.) The formation of particulates/aggregates is also indicated by the relatively high degree of emission polarization in 6% MeOH, by the fact that the emission lifetime is anion-dependent (Table I), and by the effect of added polyelectrolyte in 33% MeOH. Polyelectrolytes are known to be capable of inducing aggregation/colloid formation,[15] and in line with this reasoning small

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