SHORT PAPER

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Structure of a hexacobalt cluster containing twin pyramidal $Co_3S(CO)_7$ fragments linked by a novel phosphido-thiolato ligand[†]

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The new cluster $[Co_6(\mu_3\text{-}S)_2(CO)_{14}(\mu_4\text{-}\eta^2\text{-}SPC_6H_4OM_e)]$ **1** was isolated from the reaction of $Co_2(CO)_8$ with dimers of *p*-methoxyphenylthionophosphine sulfide, and its structure **1** has been determined by single crystal X-ray diffraction.

Keywords: hexacobalt cluster, $Co_3S(CO)_7$ fragments, phosphido-thiolato ligand

Transition metal complexes containing both phosphorus and sulfur as donating atoms are attractive to biochemists, since phosphorus is the essential element of nucleic acids and sulfur is the important constituent of the nitrogenase and are also interesting to organometallic chemists for since phosphorus and sulfur show many bonding modes to link transition metals in clusters.Complexes containing phosphido-thiolato-bifunctional bridging ligands with linked P and S atoms as bidentate donating atoms are rare. Several kinds of η^2-SPR_2 containing complexes have been reported, *e.g.* : $[M(CO)_2(\eta^5\text{-}C_5H_5)(\eta^2\text{-}SPPh_2)]$,[1]$[M(CO)_2(PPh_3)(\eta^2\text{-}SPPh_2)_2]$ (M=Mo,W);[1] and $[Mo(CO)_2(\eta^5\text{-}C_5H_5)(SPMe_2)]$;[2] ;in which all have a 3-electron donating bidentate phosphato-thioylidene ligand and P is a covalent bonded 1-electron donor and S is a 2-electron donor. There is only one mentioned complex containing a bidentate SPR ligand: $[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(\eta^2\text{-}SPC_6H_4OMe)]$,[3] where SPR was considered as a 4-electron donating phosphino thioylidene ligand and P and S both are 2-electron donors and linked to the different Mo atoms respectively.

Here we report that the reaction of $Co_2(CO)_8$ with the dimer of *p*-meth-oxyphenylthionophosphine sulfide yields a further bridging SPR ligand-containing compound: $[Co_6(\mu_3\text{-}S)_2(CO)_{14}(\mu_4\text{-}\eta^2\text{-}SPC_6H_4OMe)]$ **1**,but in which the μ_4 -SPR is a 6-electron donating ligand. This has established the first known case of a special bidirectional SPR bridging ligand coordinated to four metal atoms.

The similar IR spectral characteristics of cluster **1** and pyramidal Co_3S clusters $[Co_3(CO)_7(\mu_3\text{-}S)(\mu\text{-}\eta^2\text{-}L)(L{=}\eta^2$-bidentate bridged ligands)[4–6] which show only terminal CO absorption bands in the range around 1950–2140cm^{-1} indicate that cluster **1** may be analogous to the Co_3S-skeleton clusters.

The ^{31}P NMR signal will shift to lower field with a paramagnetic deshielding effect for the compounds which have low-lying exited states associated with M–M and M–P bonding systems.[7] The ^{31}P NMR spectrum of cluster **1** was found to exhibit a lower field singlet at δ110.7.This chemical shift value was in the range of many bridging phosphido (μ-PR_2)-containing complexes where the P atom is linked to two metal atoms. This indicates that cluster **1** has a bridging SPR ligand where the P atom is linked to two Co atoms.[7]

The structural features of cluster **1** have been established by X-ray crystal structure determination. The structure (Fig.1) contains two trigonal pyramidal $Co_3S(CO)_7$ units connected to each other through one bridging phosphidothiolato-SPR bidirectional ligand with its phosphido-P atom as 3-electron bridging donor and its thiolato-S atom as 3-electron bridging donor also and linked to the different two of the four Co atoms, respectively toward both left and right directions.

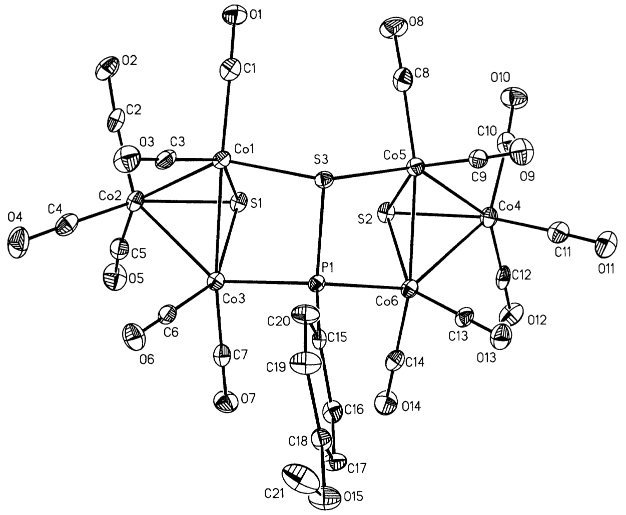

Fig.1 Crystal structure of cluster **1**. Selected bond distances (Å) and angles(°): Co(1)–C0(3) 2.4686(8), Co(1)–Co(2) 2.547(1), Co(2)–Co(3) 2.5438(7), Co(4)–Co(6) 2.5421(7), Co(4)–Co(5) 2.5459(7), Co(5)–Co(6) 2.4690(8), Co(1)–S(1) 2.155(1), Co(2)–S(1) 2.159(1), Co(3)–S(1)2.156(1), Co(4)–S(2) 2.167(1), Co(5)–S(2) 2.170(1), Co(6)–S(2) 2.143(1), Co(1)–S(3) 2.285(1), Co(5)–S(3) 2.295(1), S(3)–P(1) 2.092(1), Co(3)–P(1) 2.225(1), Co(6)–P(1) 2.232(1), Co(1)–Co(3)-Co(2)61.06(3), Co(3)–Co(1)–Co(2) 60.93(2), Co(3)–Co(2)–Co(1) 58.01(2), Co(6)–Co(5)–Co(4) 60.89(2), Co(6)–Co(4)–Co(5) 58.06(2), Co(5)–Co(6)–Co(4) 61.05(2), S(3)–P(1)–C(15) 105.9(1), C(15)–P(1)–Co(3) 111.6(1), C(15)–P(1)–Co(6) 112.1(1), S(3)–P(1)–Co(3) 99.97(5), S(3)–P(1)–Co(6) 99.23(4), Co(3)–P(1)–Co(6) 123.97(4)

We notice that the average bond length of 2.4688Å for Co(1)–Co(3) and Co(4)–Co(6), bridged by the SPR ligand, is shorter than the average bond length of the other Co–Co of 2.5488Å.The tendency is the same as that in the 48-electron clusters of $Co_3(\mu_3\text{-}S)(CO)_7(\mu\text{-}\eta^2\text{-}L)$(where L=bridging 3-electron bidentate ligands).[4] It indicates that the shortering of the Co–Co bonds bridged by L is because of a compression effect by the bridge in the 48-electron clusters. Thus the 96-electron cluster **1** naturally is considered to be a doublet of a 48-electron $Co_3(\mu_3\text{-}S)(CO)_7(\mu\text{-}\eta^2\text{-}L)$ complex.

The S–P distance of 2.002(1)Å shown in$[(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_4(SPC_6H_4OMe)]$[3] was closer to a P=S double bond (normal P=S distance in the range 1.91–1.98Å, P-S distance in the range 2.07–2.14Å)[8] but the S–P distance of 2.092(1)Å found in cluster **1** is closer to a P–S single bond.

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[†] This is a Short Paper, there is therefore no corresponding material in *J Chem. Research (M).*

Thus the four P–S single bonds of the ligand precursor are imagined to be cleaved to yield the S=P-C_6H_4OMe fragment as ligand in the Mo_2 complex,[3] but the two P=S double bonds and two of the four P–S single bonds of the ligand precursor are to be cleaved to yield the S and S-PC_6H_4OMe fragments as essential constituents to build the cluster **1**.

Experimental

All reactions were performed under a pure dinitrogen atmosphere using standard Schlenk and vacuum-line techniques. Column chromatography was carried out using silica gel of 100–200 mesh. $Co_2(CO)_8$ was purchased from OSSO Laboratory of Lanzhou Institute of Chemical Physics, Lanzhou, China. $[(MeOC_6H_4PS_2)_2]$ was prepared by the literature method.[9] IR spectra were recorded on a Nicolet 170 SX spectrometer.^{1}H and ^{31}P NMR spectra on a Bruker AM-500MHz instrument. MS spectra(FAB) on a ZAB-HS instrument. Analyses (C,H) were conducted on a Perkin-Elmer 2400 analyser.

Preparation of $[Co_6(\mu_3\text{-}S)_2(CO)_{14}(\mu_4\text{-}\eta^2\text{-}SPC_6H_4OMe)]$ **1**: -$Co_2(CO)_8$ (400mg, 17mmol) and dimers of *p*-methoxyphenylthionophine sulfide (850mg,2.34mmol) were dissolved in THF (35ml). The solution was stirred at 30–32°C for 10 hrs and then evacuated to dryness. The resulting residue was dissolved in CH_2Cl_2 and chromatographed on a silica gel column. The separation and crystallisation yield 39mg (10.2%) of **1** from a dark-red eluent [petroleum ether: benzene (v/v) = 3:1] Anal. Calc. (found) for $C_{21}H_7O_{15}PS_3Co_6$: C, 25.71(25.91); H, 0.71(0.69).IR(CH_2Cl_2) γ (CO)cm^{-1}: 2095w, 2070vs, 2051vs, 2022m. ^{1}H NMR($CDCl_3$) δ 7. 13, 6.98 (d, 4H, C_6H_4), 3.86(s, 3H, OCH_3).^{31} P NMR($CDCl_3$) δ 110.6 (s, SPC_6H_4OMe). MS(FAB): Calc. of parention. $m/z = 980.03$. Found (m/z) : 980-nx28(n=5-14).

Crystal data for **1**: A violet block-shaped crystal of cluster **1** [$C_{21}H_7O_{15}PS_3Co_8$,Mr = 980.03] was grown from a C_6H_{14}–CH_2Cl_2 solution and were measured on a Rigaku Raxis Rapid IP area detector using graphite monochromated MoKα radiation ($\lambda = 0.71073$Å). Crystal data for **1**: monoclinic, P2(1)/C. a =13.703(1) Å, b = 16.617 (1)Å, c = 15.289(1) Å. $\alpha = 90°$, $\beta = 113.918$ (4)°, $\gamma = 90°$. $Z = 4$, V = 3182.3(4) Å^3, Dc = 2.045g cm^3, μ = 33.69cm^{-1}, θ range: 2.45° –27.48°, and $F(000) = 1912$. 7179 observed unique reflections [$I \geq 2\sigma(I)$] were collected at 173(2)K for **1** and the refinement converged to $R = 0.0313$, $Rw = 0.0337$. Minimun and maximum final electron densities were –0.648 and 0.513eÅ^3. The calculations were performed using the SHELXS-97 program packages. The non hydrogen atoms were refined anisotropically and hydrogen atoms isotropically.

Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). Any request to the CCDC for this material should quote the full literature citation and the reference number 182501.

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