Inorganica Chimica Acta, *214* (1993) 13–15

Inorganica
Chimica Acta
Preliminary Communication

Dimerization of the stellated octahedral unit $Co_6S_8P_6$: synthesis and X-ray crystal structure of $[Co_{12}(\mu_3\text{-}S)_{14}(\mu_4\text{-}S)_2(PEt_3)_{10}][TCNQ]_2$, where TCNQ = tetracyanoquinodimethane

Franco Cecconi, Carlo A. Ghilardi,
Stefano Midollini and Annabella Orlandini
Istituto per lo Studio della Stereochimica ed Energetica dei Composti di Coordinazione, CNR, via J. Nardi 39, 50132 Florence (Italy)

(Received June 23, 1993)

Abstract

The unprecedented double stellated octahedral cluster $[Co_{12}(\mu_3\text{-}S)_{14}(\mu_4\text{-}S)_2(PEt_3)_{10}][TCNQ]_2$, has been isolated and characterized by an X-ray structure determination. The cation contains two stellated octahedral Co_6S_8 cores linked together through two μ_4-S bridging ligands. The tetracyanoquinodimethane anion exists as the $[TCNQ]_2^{2-}$ dimer, exhibiting the ring-over exocyclic bond type overlap.

Many researchers have stressed the relationships between discrete molecular clusters and solid state structures [1]. Metal chalcogen clusters essentially consist of a core of metallic and chalcogenic atoms, surrounded by ancillary ligands [2]. At least from a speculative point of view a simple way to change from such a discrete structure to a more extended one should be the successive elimination of some terminal groups followed by the formation of chalcogen bridges.

We report here the isolation and X-ray crystal structure of the double stellated octahedron cluster $[Co_{12}(\mu_3\text{-}S)_{14}(\mu_4\text{-}S)_2(PEt_3)_{10}][TCNQ]_2$ which can be considered a first step in the above process.

As previously reported the octahedral cluster $[Co_6(\mu\text{-}S)_8(PEt_3)_6](BPh_4)$ (**1**) [3], can be prepared by the reaction of $[Co(H_2O)_6](BF_4)_2$ and an excess of PEt_3 with H_2S in acetone/ethanol solution, followed by addition of $NaBPh_4$. Now we have found that further evaporation of the mother solution from the synthesis of **1**, allows the precipitation of dark brown crystals together with colorless crystals. The dark crystals were separated by recrystallization from benzene, in which the colorless solid is unsoluble. The ^{1}H NMR spectrum[*] of this material in CD_2Cl_2 essentially showed absorbances at 6.7 and 7.5 ppm due to BPh_4, two signals at 0.35 and 1.65 ppm due to $\mathit{CH_3}CH_2P$ and $CH_3\mathit{CH_2}P$, respectively, of the cluster **1** [4] and a group of broad signals in the region 0.7–2.4 ppm, suggesting the presence also of an unknown compound, **2**. Since such dark crystals appeared unsuitable for a X-ray analysis, we tried to change the anion, by treating them with (PNP)(TCNQ) in CH_2Cl_2/ethanol solution, where PNP = bis(triphenylphosphino)iminium and TCNQ = tetracyanoquinodimethanide. Evaporation of the solvent, separation of the crude material and finally recrystallization of this latter from warm benzene allowed the isolation of a crop of black crystals. The ^{1}H NMR spectrum of these, apart from the anion resonances, was the same as the previous one. A separation, based on the different shape of the crystals, allowed the X-ray determination of the cell constants of two types of compounds, **3** and **4**[**].

The presence of the single cluster $[Co_6(\mu\text{-}S)_8(PEt_3)_6](TCNQ)$ (**3**) was confirmed[†] and a complete X-ray structure determination of **4** was possible. The ^{1}H NMR spectrum of a CD_2Cl_2 solution of a few crystals of **4**, chosen on the basis of the cell constants, only showed the signals at 0.7–2.4 ppm. The X-ray structure determination[††] of **4**, established that the structure consists of cluster cations $[Co_{12}S_{16}P_{10}]^{2+}$ and tetracyanoquinodimethanide ($TCNQ^-$) anions. Figure 1

---

[*] ^{1}H NMR spectra were recorded at 200.13 MHz by a Bruker ACP-200 spectrometer. Chemical shifts are relative to internal Me_4Si, with downfield values reported as positive.

[**] The yield of **4**, based on the NMR spectrum of the final mixture, was about 5% (referred to the metal).

[†] Determination of the cell constants of **3** (triclinic, space group $P\bar{1}$), $a = 13.231(5)$, $b = 11.884(4)$, $c = 11.789(4)$ Å, $\alpha = 88.40(7)$, $\beta = 113.13(7)$, $\gamma = 98.40(7)°$, has shown that **3** is isomorphous with the corresponding stellated octahedral cluster $[Fe_6(\mu_3\text{-}S)_8(PEt_3)_6]TCNQ$, whose molecular structure has been established by a complete X-ray analysis [5].

[††] Crystal data for $[Co_{12}(\mu_3\text{-}S)_{14}(\mu_4\text{-}S)_2(PEt_3)_{10}][TCNQ]_2$: $M = 2810.2$, monoclinic, space group $C2/c$, $a = 26.538(7)$, $b = 19.374(4)$, $c = 24.338(6)$, $\beta = 105.11(4)°$, $U = 12080.7$ Å^3, $Z = 4$, $D_{calc} = 1.545$ cm^{-1}, monochromatic Mo Kα, $\lambda = 0.7107$ Å, μ(Mo Kα) = 20.38 cm^{-1}. The intensity data were collected within $2\theta < 40°$ on an Enraf Nonius CAD4 diffractometer, using the ω–2θ scan technique at room temperature. The structure was solved by the heavy atom method and refined by full-matrix least-squares procedures, by using the SHELX76 program [6]. At convergence R and R_w factors are 0.057 and 0.058, respectively, for 2368 absorption corrected observed reflections with $I > 3\sigma(I)$.

0020-1693/93/$6.00

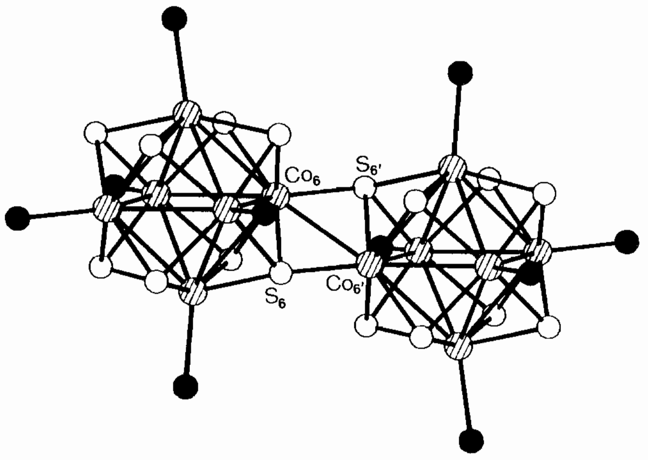

Fig. 1. Perspective view of the cluster unit $[Co_{12}(\mu_3\text{-}S)_{14}(\mu_4\text{-}S)_2(PEt_3)_{10}]^{2-}$; PLUTO [7] drawing (dashed, white and full circles are cobalt, sulfur and phosphorus atoms, respectively). Important selected bond distances (Å): Co6 ..Co6′ 2.639(5), other Co...Co (range) 2.795(5)–2.920(5), Co6–S6′ 2 148(7); other Co–S (range) 2.194(7)–2.263(7); Co–P (range) 2.152(9)–2.164(9).

shows a perspective view of the cluster unit, with selected bond distances.

The cation can be described as a double stellated octahedron cluster; two Co_6S_8 cores, which are related by the $\frac{1}{2}-x$, $\frac{1}{2}-y$, $-z$ symmetry operation, are linked together through two μ_4-S bridging ligands. Each half of the cluster displays the structure already reported for the series $[M_6(\mu_3\text{-}S_8)(PEt_3)_6]^n$ (M = Co, Fe), being built up of an octahedral cobalt framework, whose triangular faces arc triply bridged by sulfur atoms [3, 8]. Five metal atoms are additionally coordinated to a triethylphosphine group, while the sixth cobalt atom has replaced the phosphine with a second cluster unit. The connection of the two cluster units is through two sulfur atoms, which, acting as μ_4-ligands bridge the two halves of the cluster, with a Co...Co separation of 2.639(5) Å. It is noteworthy that the linkage between the two Co_6S_8 cores (Co6...Co6′ 2.639(5), Co6...S6′ 2.148(7) Å) are significantly shorter than the mean distances Co–Co (2.840(11) Å) and Co–S (2.221(4) Å) within each Co_6S_8 unit.

Upon dimerization the geometry of the octahedral core presents only minor variation with respect to the monomeric cluster; however we can note that the Co...Co separations in the triangular face bridged by the μ_4-S ligand appear significantly larger (2.888(16) Å) than all the others (2.824(7) Å). The average value of the Co–P (2.159(2) Å) and Co–S (2.221(4) Å) bond distances fall well within the range of values reported in the literature [2, 3, 8].

Dimerization of a single cluster unit by the formation of sulfur bridges through the loss of terminal ligands is known. Single and double cubane like clusters have been reported, for which a sort of interconversion between the single and double cluster (depending on the nature of the solvent, of the anion and the reaction conditions) has been ascertained [9]. However, as far as we know, the title compound represents the first example of sulfur stellated octahedron type cluster dimerization. A different bridging mode has been previously reported for the organometallic cluster $[Rh_{12}(CO)_{20}(\mu_3\text{-}CO)_8(\mu_2\text{-}CO)_2]^{2-}$; its structure consists of two octahedral units linked by two carbonyl groups bridging only the intercluster Rh–Rh connection [10].

The tetracyanoquinomethanide anion exists as the $(TCNQ)_2{}^{2-}$ dimer, the interplanar separation between the least-square planes of the x, y, z molecule and that referred by the symmetry operation $\frac{1}{2}-x$, $\frac{1}{2}-y$, $1-z$ being c. 3.3 Å; the latter value accords well with the separation reported for dimeric described TCNQ anions [11]. The dimer exhibits the ring-over-exocyclic bond type overlap with each TCNQ molecule slightly boat-shaped.

We arc working to isolate a sufficient amount of the title complex for magnetic and EPR characterization.

Acknowledgement

This work has been partially supported by Progetto Finalizzato-Chimica Fine II (CNR), Rome.

References

1 S.C Lee and R H. Holm, *Angew Chem , Int Ed Engl., 29* (1990) 840, Z. Nomikou, B. Schubert, R. Hoffmann and M.L Steigerwald, *Inorg Chem , 31* (1992) 220, and refs. therein.

2 D. Fenske, J. Ohmer, J. Hachgenei and K. Merzweiler, *Angew. Chem , Int Ed Engl , 27* (1988) 1277; A Bencini and S. Midollini, *Coord Chem Rev , 120* (1922) 87

3 F. Cecconi, C.A. Ghilardi, S. Midollini, A Orlandini and P. Zanello, *Polyhedron, 12* (1986) 2021

4 A. Bencini, S Midollini and C Zanchini, *Inorg Chem , 31* (1992) 2132.

5 F Cecconi, C.A. Ghilardi, S. Midollini and A Orlandini, to be published

6 G M. Sheldrick, *SHELX76 System of Computing Programs*, University of Cambridge, UK, 1976

7 *PLUTO*, Cambridge Crystallographic Data Center, University Chemical Laboratory, Lensfield Road, Cambridge, UK, copyright 1989.

8 F Cecconi, C A. Ghilardi and S Midollini, *J Chem Soc , Chem Commun ,* (1981) 640; F. Cecconi, C.A. Ghilardi, S.

Midollini, A. Orlandini and P. Zanello, *J. Chem. Soc., Dalton Trans*, (1987) 831.

9 T. Shibahara, H. Akashi and H. Kuroya, *J Am Chem. Soc.*, *110* (1988) 3313; T. Murata, H. Gao, Y. Mizobe, F. Nakano, S. Motomura, T. Tanase, S. Yano and M. Hidai, *J. Am Chem. Soc.*, *114* (1992) 8287.

10 V.G. Albano and P.L. Bellon, *J Organomet. Chem*, *19* (1969) 405.

11 L. Ballester, M.C. Barral, A. Gutierrez, R. Jimenez-Aparicio, J.M. Martinez-Muyo, M.F. Perpinan, M.A. Monge and C. Ruiz-Valero, *J Chem. Soc, Chem Commun.*, (1991) 1396, and refs therein.