DALTON

# Synthesis of the cobalt–tellurium 'stellated' octahedral clusters $[Co_6(\mu_3\text{-}Te)_8(PEt_3)_6]^{n+}$ ($n$ = 1 or 2). Molecular structure of $[Co_6(\mu_3\text{-}Te)_8(PEt_3)_6][PF_6]_2$*

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The mono- and di-cationic clusters $[Co_6(\mu_3\text{-}Te)_8(PEt_3)_6][PF_6]_n$ ($n$ = 1 **2** or 2 **3**) have been prepared by oxidation of the uncharged species $[Co_6(\mu_3\text{-}Te)_8(PEt_3)_6]$ **1**. The diamagnetic dicationic cluster has been fully characterized by a crystal structure determination: space group $P2_1/c$, $a$ = 13.303(3), $b$ = 19.043(3), $c$ = 14.401(7) Å, β = 112.30(4)° and $Z$ = 2. The cluster cation, which is isostructural with the other stellated octahedral members of the series $[M_6(\mu_3\text{-}E)_8(PEt_3)_6]^{n+}$ (E = S or Se), is significantly distorted, with Co–Co bond distances ranging from 3.005(2) to 3.265(2) Å. The magnetic behaviour of $[Co_6(\mu_3\text{-}Te)_8(PEt_3)_6][PF_6]_2$ is different from that of a $BF_4^-$ salt previously reported.

For many years our research group has been studying the synthesis, properties and structure of transition-metal chalcogenide clusters such as the members of the series $[M_6(\mu_3\text{-}E)_8(PEt_3)_6]^{n+}$ (M = Fe, E = S or Se, $n$ = 1 or 2; M = Co, E = S, $n$ = 0 or 1).[1,2] Recently we isolated the new representative member $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]^{2+}$ through the chemical oxidation of $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]^+$, but due to the poor quality of the crystals the results of the molecular structure determination could not be published.[3] For this reason, in order to obtain reliable structural parameters of a dicationic cobalt species, we have prepared the telluride derivatives $[Co_6(\mu_3\text{-}Te)_8(PEt_3)_6]^{n+}$ ($n$ = 1 or 2) by oxidation of the corresponding previously reported[4] uncharged species. The dicationic complex, which has been found to be diamagnetic, has now been fully characterized by a crystal structure determination.

While this work was in progress Steigerwald and co-workers[5] reported the magnetic properties of the series $[Co_6(\mu_3\text{-}Te)_8L_6]^{n+}nBF_4^-$ with $n$ = 0–2. In particular $[Co_6(\mu_3\text{-}Te)_8L_6]^{2+}$ was reported to have a room-temperature magnetic moment of 8.2 $\mu_B$ with a slight contraction in the metal–metal separations (< 1%) upon oxidation. The molecular structure of the uncharged cluster $[Co_6(\mu_3\text{-}Te)_8(PEt_3)_6]$ **1** has been published[4] but, as far as we know, no further details on the structures of the charged cations have been reported.

## Experimental

Unless otherwise specified all manipulations were performed under a nitrogen atmosphere using conventional techniques. The cluster $[Co_6(\mu_3\text{-}Te)_8(PEt_3)_6]$ **1** was prepared as previously described.[4] The $^1H$ NMR spectra were recorded at 200.133 MHz on a Bruker 200 AC spectrometer, $^1H\text{-}\{^{31}P\}$ NMR spectra on the same instrument equipped with a 5 mm inverse probe and a BFX-5 amplifier device. Chemical shifts are relative to $SiMe_4$ as external reference. The magnetic susceptibilities of the solid samples were measured on a Faraday balance at 293 K. Since compound **3** was found to be diamagnetic in contrast with the $BF_4^-$ salt,[5] in order to check more carefully the diamagnetism of the compound we have measured the magnetization in the temperature range 3–10 K with a Metronique Ingenierie SQUID susceptometer. No appreciable signal was found.

### Preparations

**$[Co_6(\mu_3\text{-}Te)_8(PEt_3)_6]PF_6$ 2.** A solution of $[Fe(C_5H_5)_2]PF_6$ (90 mg, 0.27 mmol) in acetone (15 $cm^3$) was added at room temperature to a solution of $[Co_6(\mu_3\text{-}Te)_8(PEt_3)_6]$ **1**[4] (500 mg, 0.24 mmol) in anhydrous tetrahydrofuran (thf) (25 $cm^3$). Addition of benzene (15 $cm^3$) to the resulting brown solution and further solvent evaporation gave black crystals. These were filtered off and washed with benzene–light petroleum (b.p. 40–70 °C). Yield 85% (Found: C, 19.45; H, 3.95; Co, 15.65. Calc. for $C_{36}H_{90}Co_6F_6P_7Te_8$: C, 19.4; H, 4.05; Co, 15.85%). $^1H$ NMR ($CD_2Cl_2$, 295 K): δ 1.86 (br s, 36 H, $CH_2$) and 0.83 (br s, 54 H, $CH_3$).

**$[Co_6(\mu_3\text{-}Te)_8(PEt_3)_6][PF_6]_2$ 3.** The complex was prepared by the above method using $[Fe(C_5H_5)_2]PF_6$ (220 mg, 0.66 mmol) and $[Co_6(\mu_3\text{-}Te)_8(PEt_3)_6]$ (500 mg, 0.24 mmol). Yield 80% (Found: C, 18.2; H, 3.70; Co, 14.75. Calc. for $C_{36}H_{90}Co_6F_{12}P_8Te_8$: C, 18.2; H, 3.80; Co, 14.9%). $^1H$ NMR ($CD_2Cl_2$, 295 K): δ 1.97 (dq, $^3J_{HH}$ = 7.5,† $^2J_{PH}$ = 7.5, 36 H, $CH_2$) and 1.10 (dt, $^3J_{PH}$ = 16 Hz, 54 H, $CH_3$).

### X-Ray crystallography

Diffraction data were collected at room temperature using an Enraf-Nonius CAD4 automatic diffractometer and graphite-monochromated Mo-Kα radiation (λ 0.710 70 Å). Crystal data and data collection details are given in Table 1. Unit-cell dimensions were determined by least-squares refinements of the angular settings of 25 reflections. Intensity data were collected by the ω–2θ scan method with a range of 0.8 + 0.35 tan θ and a speed ranging from 1.27 to 8.24° $min^{-1}$. The intensities of three standard reflections periodically measured were used to rescale the observed intensities which showed a decay of *ca.* 20%. After correction for background the intensities were assigned a standard deviation σ($I$), calculated[6] using the value of 0.03 for the instability factor $k$. The observed intensities were corrected

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* *Non-SI unit employed:* $\mu_B \approx 9.27 \times 10^{-24}$ J $T^{-1}$.

† The value was determined by recording the $^1H\text{-}\{^{31}P\}$ NMR spectrum.

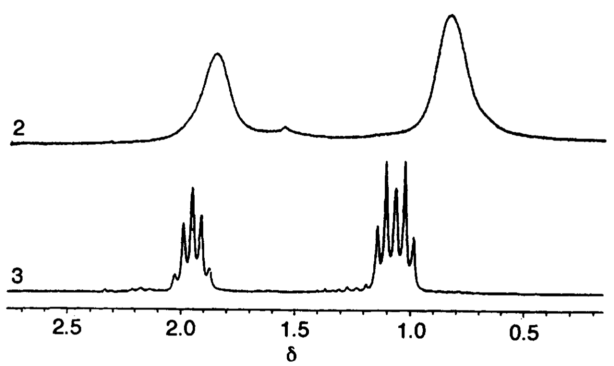

**Fig. 1** Proton NMR spectra of the compounds $[Co_6(\mu_3\text{-}Te)_8(PEt_3)_6]^+$ **2** and $[Co_6(\mu_3\text{-}Te)_8(PEt_3)_6]^{2+}$ **3**

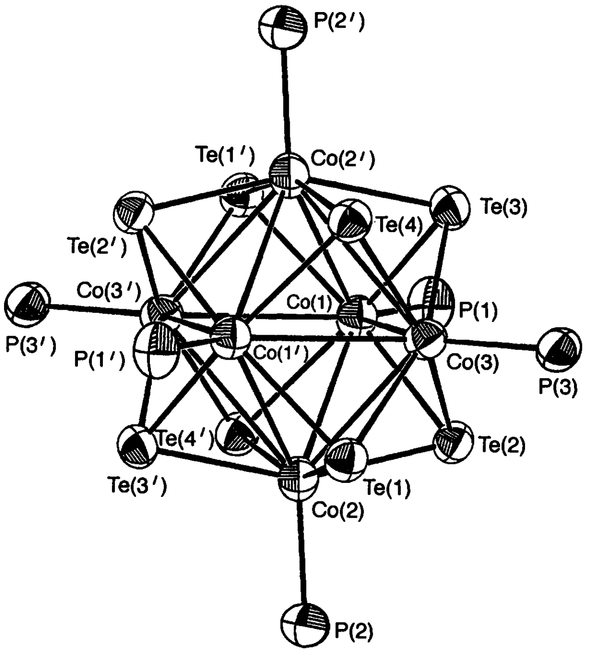

**Fig. 2** Inner core of the cluster cation $[Co_6(\mu_3\text{-}Te)_8(PEt_3)_6]^{2+}$. An ORTEP drawing with 30% probability ellipsoids. Primed atoms are related to the corresponding unprimed atoms by the symmetry operation $-x + 2, -y, -z + 2$

for Lorentz-polarization effects and empirically for absorption using ψ scans.[7]

The structure was solved by the heavy-atom method and refined by full-matrix least squares on $F^2$ with anisotropic thermal parameters only for tellurium, cobalt and phosphorus atoms. Hydrogen atoms were introduced in their calculated positions riding on their carbon atoms, with thermal parameters 20% larger than those of the respective carbon atoms. The function minimized during the refinement was $w(|F_o| - |F_c|)^2$, with $w = 1/[\sigma^2(F_o^2) + (0.063P)^2 + 16.4P]$ where $P = [\max(F_o^2,0) + 2F_c^2]/3$. Atomic scattering factors were taken from ref. 8. An anomalous dispersion correction, real and imaginary parts, was applied.[9] All the calculations were performed on a 486 HP personal computer, using the SHELXL 93[10] and ORTEP[11] programs.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/195.

**Table 1** Crystal data and structure refinement for compound **3**

| | |
|---|---|
| Empirical formula | $C_{36}H_{90}Co_6F_{12}P_8Te_8$ |
| $M$ | 2373.22 |
| Crystal system | Monoclinic |
| Space group | $P2_1/c$ |
| $a$/Å | 13.303(3) |
| $b$/Å | 19.043(3) |
| $c$/Å | 14.401(7) |
| β/° | 112.30(4) |
| $U$/Å$^3$ | 3375(2) |
| $Z$ | 2 |
| $D_c$/Mg m$^{-3}$ | 2.335 |
| μ/mm$^{-1}$ | 5.078 |
| Absorption correction factors | 0.54–1.0 |
| $F(000)$ | 2224 |
| Crystal size/mm | 0.70 × 0.40 × 0.15 |
| θ Range/° for data collection | 2.63–22.05 |
| *hkl* Ranges | − 12 to 12, 0–20, 0–15 |
| Reflections collected | 4474 |
| Independent reflections ($R_{int}$) | 4122 (0.0241) |
| Data, restraints, parameters | 4120, 0, 262 |
| Goodness of fit on $F^2$ | 1.046 |
| Final $R1$, $wR2$ indices [$I > 2\sigma(I)$] | 0.0358, 0.0981 |
| (all data) | 0.0449, 0.1050 |

### Computational details

Density functional theory (DFT) calculations have been performed using version 2.01 of the Amsterdam Density Functional program[12–14] developed by Baerends *et al.* in the local density approximation (LDA). The exchange correlation formula of Volsko *et al.*[15] was used throughout with non-local corrections to the correlation in the form suggested by Stoll *et al.*[16] All the calculations were performed on the model cluster $[Co_6(\mu_3\text{-}Te)_8(PH_3)_6]^{n+}$ ($n$ = 0–2) in the idealized $D_{3d}$ symmetry, following the procedure already applied for other iron[17] and cobalt[18] sulfur clusters. In the present calculations the core orbitals were frozen and relativistic effects for all the atoms except hydrogens were included. Scalar relativistic corrections, *i.e.* Darwin and mass velocity, to the valence electrons were applied. The geometries of the clusters in the various oxidation states were performed using a double-ζ Slater-type orbital (STO) basis set, while more accurate calculations of the energy-level ordering were performed by adding polarization functions on Co, P and Te. The quality of the basis set has been already checked on the uncharged cobalt clusters.[18]

## Results and Discussion

Both complexes **2** and **3** were isolated as black crystals. They are soluble in polar organic solvents such as dichloromethane and nitromethane where they behave respectively as 1 : 1 and 1 : 2 electrolytes. The solid **2** is paramagnetic with $\mu_{eff}$ = 2.42 $\mu_B$ at 295 K which indicates the presence of one unpaired electron for the cluster unit. In contrast **3** is diamagnetic. Consistent with this the $^1H$ NMR spectra of the complexes (Fig. 1) show broad signals (**2**) and well resolved resonances (**3**) respectively. The observed diamagnetism of **3** is in contrast with the magnetic behaviour (8.2 $\mu_B$) reported for the $BF_4^-$ salt.[5] In order to understand this disagreement the electronic structure has been analysed through density functional theory (DFT) calculations, which have been found useful in describing the magnetic properties of iron[17] and cobalt[18] clusters (see below).

### Structure of compound 3

The molecular structure of compound **3** consists of discrete $[Co_6(\mu_3\text{-}Te)_8(PEt_3)_6]^{2+}$ cations and $PF_6^-$ anions. Fig. 2 shows a perspective view of the cation and Table 2 reports selected bond distances and angles. The cation is isostructural with the other members of the series $[M_6(\mu_3\text{-}E)_8(PR_3)_6]^{n+}$ [1,4,19] and

**Table 2** Selected bond lengths (Å) and angles (°)

| | | | |
|---|---|---|---|
| Te(1)–Co(3) | 2.4872(14) | Te(4)–Co(2$^{I}$) | 2.515(2) |
| Te(1)–Co(2) | 2.490(2) | Te(4)–Co(3) | 2.519(2) |
| Te(1)–Co(1$^{I}$) | 2.5142(14) | Te(4)–Co(1$^{I}$) | 2.5200(13) |
| Te(1)–Te(3$^{I}$) | 3.4972(14) | Co(1)–P(1) | 2.217(3) |
| Te(1)–Te(4) | 3.5621(10) | Co(1)–Co(3$^{I}$) | 3.013(2) |
| Te(1)–Te(2) | 3.582(2) | Co(1)–Co(3) | 3.060(2) |
| Te(2)–Co(2) | 2.487(2) | Co(1)–Co(2$^{I}$) | 3.083(2) |
| Te(2)–Co(3) | 2.504(2) | Co(1)–Co(2) | 3.105(2) |
| Te(2)–Co(1) | 2.5172(14) | Co(2)–P(2) | 2.183(3) |
| Te(2)–Te(4$^{I}$) | 3.4783(13) | Co(2)–Co(3) | 3.005(2) |
| Te(2)–Te(3) | 3.5062(9) | Co(2)–Co(3$^{I}$) | 3.265(2) |
| Te(3)–Co(1) | 2.4998(14) | Co(2)–Te(3$^{I}$) | 2.510(2) |
| Te(3)–Co(2$^{I}$) | 2.510(2) | Co(2)–Te(4$^{I}$) | 2.515(2) |
| Te(3)–Co(3) | 2.5156(14) | Co(3)–P(3) | 2.207(3) |
| Te(3)–Te(4) | 3.304(2) | | |
| Co(2)–Te(1)–Co(3) | 74.29(5) | P(1)–Co(1)–Te(4$^{I}$) | 103.51(9) |
| Co(3)–Te(1)–Co(1$^{I}$) | 74.10(4) | Co(1)–Co(2)–Co(3$^{I}$) | 56.40(5) |
| Co(2)–Te(1)–Co(1$^{I}$) | 76.07(5) | Co(1$^{I}$)–Co(2)–Co(3$^{I}$) | 57.55(4) |
| Co(1)–Te(2)–Co(2) | 76.70(4) | Co(3)–Co(2)–Co(1) | 60.08(5) |
| Co(1)–Te(2)–Co(3) | 75.10(5) | Co(3)–Co(2)–Co(1$^{I}$) | 59.32(4) |
| Co(2)–Te(2)–Co(3) | 74.04(5) | Co(3)–Co(2)–Co(3$^{I}$) | 87.95(5) |
| Co(1)–Te(3)–Co(2$^{I}$) | 75.96(5) | Co(1$^{I}$)–Co(2)–Co(1) | 86.27(5) |
| Co(1)–Te(3)–Co(3) | 75.19(5) | P(2)–Co(2)–Te(2) | 98.85(8) |
| Co(2$^{I}$)–Te(3)–Co(3) | 81.04(5) | P(2)–Co(2)–Te(1) | 99.51(8) |
| Co(2$^{I}$)–Te(4)–Co(3) | 80.87(5) | P(2)–Co(2)–Te(3$^{I}$) | 104.58(8) |
| Co(2$^{I}$)–Te(4)–Co(1$^{I}$) | 76.15(4) | P(2)–Co(2)–Te(4$^{I}$) | 102.63(9) |
| Co(3)–Te(4)–Co(1$^{I}$) | 73.46(4) | Co(1)–Co(3)–Co(2) | 61.59(4) |
| Co(3$^{I}$)–Co(1)–Co(2) | 64.48(4) | Co(1)–Co(3)–Co(2$^{I}$) | 58.24(5) |
| Co(3)–Co(1)–Co(2) | 58.34(4) | Co(1$^{I}$)–Co(3)–Co(2$^{I}$) | 59.12(4) |
| Co(3)–Co(1)–Co(3$^{I}$) | 91.69(6) | Co(1$^{I}$)–Co(3)–Co(1) | 88.31(6) |
| Co(3$^{I}$)–Co(1)–Co(2$^{I}$) | 59.06(4) | Co(2)–Co(3)–Co(2$^{I}$) | 92.05(5) |
| Co(3)–Co(1)–Co(2$^{I}$) | 64.21(5) | Co(2)–Co(3)–Co(1$^{I}$) | 61.63(4) |
| Co(2$^{I}$)–Co(1)–Co(2) | 93.73(5) | P(3)–Co(3)–Te(1) | 97.43(8) |
| P(1)–Co(1)–Te(3) | 97.73(9) | P(3)–Co(3)–Te(2) | 99.89(8) |
| P(1)–Co(1)–Te(1$^{I}$) | 96.05(9) | P(3)–Co(3)–Te(3) | 102.36(8) |
| P(1)–Co(1)–Te(2) | 96.05(9) | P(3)–Co(3)–Te(4) | 100.45(8) |

Symmetry transformation used to generate equivalent atoms: I $-x + 2, -y, -z + 2$.

consists of an octahedron of cobalt atoms with all the triangular faces symmetrically bridged by tellurium atoms. The co-ordination sphere of each metal atom is completed by a terminally bonded phosphine ligand. At variance with the other members of the $[M_6(\mu_3\text{-E})_8(PR_3)_6]^{n+}$ series, the metal framework is more distorted as shown by the spread of the Co–Co distances which vary from 3.005(2) to 3.265(2) Å. On the contrary the Te–Co distances are in the range 2.487(1)–2.520(1) Å. The distortion of the metal core is evidenced by considering the equatorial plane of the cobalt octahedron defined by Co(2), Co(3), Co(2′), Co(3′). This plane, which in a regular octahedron is a square, in the present compound is a rectangle with sides of 3.005(2) and 3.265(2) Å. Since the Co–Te linkages remain fixed to a well established value, it follows that the tellurium atoms Te(3), Te(3′), Te(4), Te(4′) which bridge the longest edges show contact distances significantly shorter than the others (3.30 *vs.* 3.60 Å).

A comparison with the uncharged species $[Co(\mu_3\text{-}Te)_8(PEt_3)_6]$[4,20] shows that, in contrast with the results of Steigerwald and co-workers,[5] the removal of two electrons (96 *vs.* 98) induces a significant contraction of the metal core, the mean Co–Co distance going from 3.230 to 3.085 Å. A similar behaviour upon oxidation has been found for the related $[Fe_6(\mu_3\text{-S})_8(PEt_3)_6]^{n+}$[1a,b] and $[Co_6(\mu_3\text{-S})_8(PEt_3)_6]^{n+}$[1c] family although the amount of contraction is smaller. As has been pointed out,[21] in this family of clusters variation of the number of electrons accompanied by change in the metal–metal separations does not affect significantly the metal–chalcogen distances which are the actual stabilizing factor of the molecular framework.

Moreover the replacement of the sulfur ligand by selenium and then tellurium as well as the expected variation of the Co–E distances causes a significant enlargement of the cluster. In the absence of described dicationic species, the mean Co–Co distance of 3.085 Å of the present compound may be compared with the values of 2.92 and 2.79 Å reported for $[Co_6(\mu_3\text{-}Se)_8(PEt_3)_6]^{+}$*,[22] and $[Co_6(\mu_3\text{-S})_8(PEt_3)_6]^{+}$[1c] respectively.

**Table 3** Bond distances computed for $[Co_6(\mu_3\text{-Te})_8(PH_3)_6]^{n+}$ ($n$ = 0–2) in $D_{3d}$ symmetry

| | Distance/Å | | | |
|---|---|---|---|---|
| $n$ | Co–Co | Te–Te | Co–Te | Co–P |
| 0 | 3.05 | 3.58 | 2.55 | 2.19 |
| 1 | 3.01 | 3.56 | 2.55 | 2.22 |
| 2 | 2.99 | 3.55 | 2.55 | 2.25 |

### Density functional calculations

Relevant geometrical parameters obtained from the geometry optimization of $[Co_6(\mu_3\text{-Te})_8(PH_3)_6]^{n+}$ ($n$ = 0–2) are collected in Table 3. The computed Co–Co bond distance in $[Co_6(\mu_3\text{-}Te)_8(PH_3)_6]$, slightly shorter than that computed by neglecting relativistic effects (3.08 Å), is still in fairly good agreement with the experimental value (3.23 Å).[4] Also the computed Te–Te, Co–Te and Co–P distances compare well with the values experimentally measured. The DFT electronic structure of $[Co_6(\mu_3\text{-E})_8(PH_3)_6]$ (E = S, Se or Te) has been described in some detail in ref. 18 and the magnetic properties of the mono- and di-cations have been related to the nature of the gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO – LUMO) for the sulfide derivatives. The electronic structure computed for $[Co_6(\mu_3\text{-Te})_8(PH_3)_6]^{n+}$ ($n$ = 0–2) closely resembles that obtained for the sulfides.[18] In particular, a HOMO – LUMO gap of 0.6 eV (*ca.* $0.96 \times 10^{-19}$ J) is computed which is almost unchanged upon oxidation of the clusters. The ground state of the uncharged cluster is a singlet corresponding to full occupancy of all of the one-electron energy levels up to the gap. The HOMOs are a set of three quasi-degenerate orbitals ($6a_{2g}{}^2 19e_g{}^4$) which correspond to a $t_{1g}{}^6$ configuration of idealized $O_h$ symmetry. Upon oxidation of the cluster a number of multiplets arises and an accurate calculation of the multiplet structure is not possible. Following the Aufbau principle, in the monocharged species, however, a $S = \frac{1}{2}$ state corresponding to a ($6a_{2g}{}^2 19e_g{}^3$) configuration is obtained and for the doubly charged species the triplet state ($6a_{2g}{}^2 19e_g{}^2$) is expected as the ground state. The near degeneracy of the $19e_g$ and $6a_{2g}$ orbitals is removed with a gap of 0.1 eV in the latter species. Although the Aufbau principle allowed us to rationalize the magnetic structure of the iron[17] and cobalt[18] clusters, in the present case the observed diamagnetism cannot be reproduced on these simple grounds. It must be noted, however, that the structure of the doubly charged cluster is largely distorted from idealized $D_{3d}$ symmetry, therefore removal of the degeneracy of the $e_g$ orbitals can be anticipated, which can account for the observed diamagnetism of the $[Co_6(\mu_3\text{-Te})_8(PEt_3)_6]^{2+}$ cluster.

## Conclusion

Concerning the disagreement of the magnetic behaviour of compound **3** with that of the $BF_4^-$ salt,[5] while the above calculations can justify diamagnetism as a consequence of the observed structural distortion, they are not consistent with a ground state having more than two unpaired electrons. Such a

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* $[Co_6(\mu_3\text{-Se})_8(PEt_3)_6]BPh_4$: space group $P1$, $a = 26.656(9)$, $b = 13.138(7)$, $c = 11.920(6)$ Å, $\alpha = 104.6(1)$, $\beta = 91.3(1)$, $\gamma = 91.2(1)°$, $Z = 2$.

ground state could be stabilized only with a HOMO − LUMO gap drastically reduced as a consequence of an important structural change. On the other hand, whereas the work of Steigerwald and co-workers[5] appears to be extremely precise as to the magnetic characterization, the synthetic and stuctural details are very thin. For these reasons in our opinion it is not possible to establish whether the compound reported was a different species. Anyway we would like to point out the complexity of the magnetic behaviour of these systems which cannot be accounted for by simple models. In this context it is worthy of note that the detailed temperature dependence of the magnetic susceptibility is also a function of the nature of the counter ions, as observed in the iron–sulfur cluster analogue.[1d,17]

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