Cubane-Type Mo_3CoS_4 Molecular Clusters with Three Different Metal Electron Populations: Structure, Reactivity and Their Use in the Synthesis of Hybrid Charge-Transfer Salts

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Abstract: Heterodimetallic cubane-type complexes coordinated to diphosphanes $[Mo_3CoS_4(dmpe)_3Cl_4]^+$ ($[\mathbf{1}]^+$) (dmpe = 1,2-bis(dimethylphosphanyl)ethane), $[Mo_3CoS_4(dmpe)_3Cl_4]$ (**1**) and $[Mo_3CoS_4(dmpe)_3Cl_3(CO)]$ (**2**) with 14, 15 and 16 metal electrons, respectively, have been prepared from the $[Mo_3S_4(dmpe)_3Cl_3]^+$ trinuclear precursor using $[Co_2(CO)_8]$ or $CoCl_2$ as cobalt source. Cluster complexes $[\mathbf{1}]^+$ and **1** are easily interconverted chemically and electrochemically. The Co−Cl distance increases upon electron addition and substitution of the chlorine atom coordinated to cobalt with CO only takes place in presence of a reducing agent to give complex **2**. Structural changes in the intermetallic distances agree with the entering electrons occupying an orbital which is basically Mo−Mo non-bonding and slightly Mo−Co bonding. Magnetic susceptibility measurements for $[\mathbf{1}]^+$ and **1** are consistent with the presence of two and one unpaired electrons, respectively and therefore with an "e" character for the HOMO orbital. Oxidation of **1** with TCNQ results in the formation of a charge transfer salt formulated as $[\mathbf{1}]^+[\mathrm{TCNQ}]^-$ with alternate layers of paramagnetic cluster cations and also paramagnetic organic anions. There is no magnetic interaction between layers and the thermal variation of the magnetic susceptibility has been modelled as a $S = 1/2$ TCNQ antiferromagnetic chain plus a $S = 1$ cluster monomer with zero field splitting.

Keywords: cluster compounds · cobalt · heterodimetallic complexes · magnetism · molybdenum

Introduction

Molecular metal clusters are playing an important role in several scientific areas of current interest such as solid state physics,[1] biochemistry,[2] catalysis[3] and materials science.[4] A well known class of such compounds are the cubane-type transition metal cluster sulfides, which have found important applications as models for active sites of metalloenzymes and for industrial metal sulfide catalysts.[5] This category of coordination compounds include those complexes derived from the cuboidal M_3Q_4 unit (M = Mo, W; Q = S, Se) from which a large number of heterodimetallic $M_3M'Q_4$ cubane type clusters have been obtained by incorporation of a second transition or post transition element, M′.[6–10]

The chemistry of $M_3M'Q_4$ cluster complexes started in 1986 with a report on the synthesis and structure of the $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ aqua ion.[11] Since then the field has seen noticeable advances mainly as aqueous solution chemistry and although characterization has remained a serious problem, the supramolecular approach using cucurbituril has proved to be very useful for the crystallization of these cubane-type aqua clusters.[12–15] These heterodimetallic $M_3M'Q_4$ aqua species crystallize as single cubes or as edged-linked or corner shared double cubes. Although there are numerous structural investigations on these cluster complexes, there are no structural data available on a given single cube $M_3M'Q_4$ system in different oxidation states in spite of the electrochemical reversibility observed upon reduction for most of these complexes.[16,17] This fact can be attributed to the tendency towards dimerization to give edged linked double cubane structures found in $M_3M'Q_4$ aqua spe-

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cies (M′ = Co, Cu) with an odd number of electrons.[8] For example, reaction of $[Mo_3S_4(H_2O)_9]^{4+}$ with cobalt metal in acidic solutions presumably gives the extremely air sensitive 15 electron cluster $[Mo_3CoS_4(H_2O)_{10}]^{4+}$ from which the edged linked $[\{Mo_3CoS_4(H_2O)_9\}_2]^{8+}$ (Co–Co 2.498, Mo–Mo 2.744, Mo–Co 2.64 Å) was recrystallized.[18] Coordination of softer ligands such as CO to the $[Mo_3CoS_4(H_2O)_{10}]^{4+}$ complex affords a much more stable cluster $[Mo_3Co(CO)S_4(H_2O)_9]^{4+}$ with 15 metal electrons although no structural data is available.[7] Curtis et al. have reported the structure of the only organometallic Mo_3CoS_4 cluster $[Mo_3CoS_4Cp_3(CO)]$ (Mo–Mo 2.83–2.84 Å, Mo–Co 2.75 Å) that contains 16 metal electrons.[19]

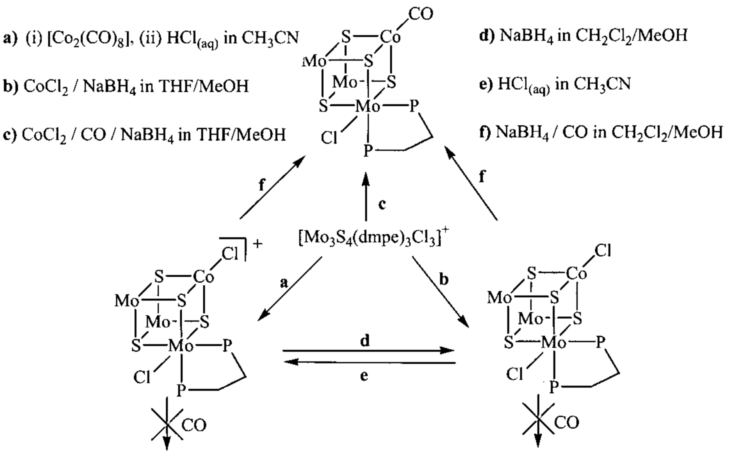
Here we report the synthesis and structure of a series of $[Mo_3CoS_4]^{n+}$ ($n = 3$–5) complexes with three different metal electron populations: $[Mo_3CoS_4(dmpe)_3Cl_4]^+$ ($[\mathbf{1}]^+$) (dmpe = 1,2-bis(dimethylphosphanyl)ethane) with 14 electrons, $[Mo_3CoS_4(dmpe)_3Cl_4]$ (**1**) with 15 electrons and $[Mo_3CoS_4(dmpe)_3Cl_3(CO)]$ (**2**) with 16 metal electrons. The cobalt site reactivity of these clusters towards CO has been investigated due to its relevance in hydrodesulfurization catalysis. The structural and magnetic consequences of electron addition and removal are analyzed under the framework of the present theoretical bonding schemes. Taking advantage of the electroactive and magnetic character of these clusters we have also explored the possibility of using them as inorganic component of hybrid molecular materials based on the electron acceptor 7,7,8,8-tetracyanoquinodimethane (TCNQ).

Abstract in Spanish: *Se han sintetizado los complejos heterodimetálicos coordinados a difosfinas con estructura de cubano de fórmula* $[Mo_3CoS_4(dmpe)_3Cl_4]^+$ *(*$[\mathbf{1}]^+$*) (dmpe = 1,2-bis(dimetilfosfino)etano),* $[Mo_3CoS_4(dmpe)_3Cl_4]$ *(**1**) y* $[Mo_3CoS_4(dmpe)_3Cl_3(CO)]$ *(**2**) con 14, 15 y 16 electrones metálicos, respectivamente, a partir del cluster trinuclear* $[Mo_3S_4(dmpe)_3Cl_3]^+$ *y utilizando como fuente de cobalto* $Co_2(CO)_8$ *ó* $CoCl_2$*. Los complejos cluster* $[\mathbf{1}]^+$ *y **1** pueden interconvertirse con facilidad tanto química como electroquímicamente. La distancia Co–Cl aumenta al añadir electrones y la sustitución del átomo de cloro por carbonilo únicamente ocurre en presencia de un reductor para dar el complejo **2**. Los cambios estructurales en las distancias intermetálicas concuerdan con la ocupación por parte de los electrones adicionales de un orbital fundamentalmente no enlazante Mo–Mo y ligeramente enlazante Mo–Co. Las medidas de susceptibilidad magnética de* $[\mathbf{1}]^+$ *y **1** son consistentes con la presencia de dos y un electrones desapareados, respectivamente, y por lo tanto con un carácter "e" para el orbital HOMO. La oxidación de **1** con TCNQ da lugar a una sal de transferencia de carga formulada como* $[\mathbf{1}]^+[TCNQ]^-$ *con capas alternas de clústeres paramagnéticos catiónicos y aniones orgánicos también paramagnéticos. No hay interacciones magnéticas entre las capas y la variación de la susceptibilidad magnética con la temperatura se ajusta a una cadena antiferromagnética de TCNQ con S = 1/2 más un monómero cluster con S = 1 y desdoblamiento a campo cero.*

Results and Discussion

Synthesis and reactivity: Several synthetic entries to the cuboidal complexes $Mo_3M'S_4$ (M′ = transition metal) have been reported both in aqueous and organic media.[9,10] In all cases two kinds of driving forces are invoked as responsible for the incorporation of the heterometal into the $Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3$ incomplete cubane-type cluster, one is the affinity of the metal for the bridging sulfur atoms and the other is the reducing ability of the heterometal.[16] This last driving force can be replaced by a external reducing agent such as borohydride. Recently we have reported the synthesis of a series of heterodimetallic cubane-type complexes $[M_3Q_4Cu]$ of molybdenum and tungsten with Q = S and Se through a [3+1] building block strategy using the molecular clusters $[M_3Q_4(diphosphane)_3X_3]^+$ as starting materials.[17,20] This synthetic strategy can be extended to other transition metals such as nickel, palladium and cobalt.[21]

The reaction of $[Mo_3S_4(dmpe)_3Cl_3]^+$ with $CoCl_2$ in the presence of an excess of sodium borhydride in THF/CH_3OH mixtures gives the neutral 15 metal electron cluster $[Mo_3CoS_4(dmpe)_3Cl_4]$ (**1**) which precipitates from the reaction mixture in 30% yield. When the reaction is done under a CO atmosphere, the also neutral 16 metal electron cluster $[Mo_3CoS_4(dmpe)_3Cl_3(CO)]$ (**2**) is obtained in similar yields instead. The 15 electron cluster does not dimerize to give an edged linked double cube structure as observed for the $[Mo_3CoS_4]^{4+}$ aqua ion. The neutral complexes **1** and **2** are easily ionized in the electrospray mass spectrometer (ESMS) conditions (typically 30 V) showing the presence of abundant signals due to the molecular peaks attributed to the cations $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$. On the other hand, the reaction of $[Co_2(CO)_8]$ with $[Mo_3S_4Cl_3(dmpe)_3]^+$ in CH_3CN has been monitored by ESMS and the final reaction product consists of a mixture of compounds **1** and **2**. Although their $[\mathbf{1}]^+$ and $[\mathbf{2}]^+$ peaks appear at 1067 and 1060 amu, respectively, their signals overlap due to their wide isotope pattern at natural abundance of 20 amu. In spite of this, the product mixture could be unambiguously identified by inducing the fragmentation of the products at higher voltages with the identification of the $[\mathbf{1}-\text{dmpe}]^+$, $[\mathbf{2}-\text{CO}]^+$ and $[\mathbf{2}-\text{CO}-\text{dmpe}]^+$ signals. All attempts to separate complexes **1** and **2** have been unsuccessful. However, treatment of the reaction mixture containing these two complexes or reaction in air of the pure compounds **1** or **2** with a diluted aqueous solution of HCl in CH_3CN and further precipitation with $NaBPh_4$ gives $[\mathbf{1}][BPh_4]$ as analytically pure compound. This is the only case reported up to date of a Mo_3CoS_4 complex with 14 metal electrons, the other known examples are found for iron as heterometal, namely $[Mo_3FeS_4(H_2O)_{10}]^{4+}$ and $[Mo_3FeS_4Cp'_3(SH)]$.[16,19] The high stability in air observed for $[\mathbf{1}]^+$ contrasts with the sensitivity found for the $[Mo_3FeS_4]^{4+}$ aqua ion which gets easily oxidized to give Fe^{2+} and $[Mo_3S_4(H_2O)_9]^{4+}$. The 14 electron cation $[\mathbf{1}]^+$ is reduced with an excess of $NaBH_4$ in CH_2Cl_2/CH_3OH solutions to afford the neutral **1** complex which precipitates from the reaction mixture. When the reduction is done in the presence of CO, the neutral **2** complex precipitates instead. Neither complex $[\mathbf{1}]^+$ or **1** does react with CO in CH_2Cl_2. A summary of the reactions involving these Mo_3CoS_4 cluster species is presented in Scheme 1.



Scheme 1.

The reversibility of the $[\mathbf{1}]^+/\mathbf{1}$ redox interconversion is also seen in the cyclic voltammogram of these complexes (Figure 1) where a reversible wave associated to the $[\mathbf{1}]^+ \leftrightarrow \mathbf{1}$ couple is observed at a half wave potential of −0.10 V (vs Ag/AgCl). A second reduction process appears at −0.91 V which is completely irreversible, a fact that we attribute to the decoordination of the chloride ligand upon reduction. The electrochemical behaviour can be summarized as follows:

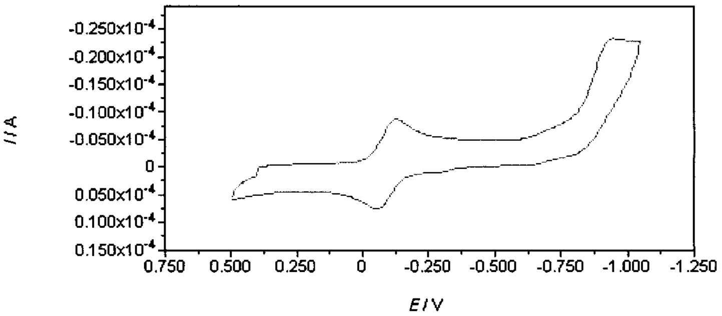


Figure 1. Cyclic voltammogram for the compound [1][BPh_4] in CH_2Cl_2 at a scan rate of 100 $mV\,s^{-1}$.

$$[Mo_3CoS_4Cl_4(dmpe)_3]^+ \overset{e}{\rightleftharpoons} [Mo_3CoS_4Cl_4(dmpe)_3] \xrightarrow{e} [Mo_3CoS_4Cl_4(dmpe)_3] + Cl^-$$

The reduction wave on the electrochemical precursor $[Mo_3S_4(dmpe)_3Cl_3]^+$ is observed at −0.69 V and has been attributed to a bielectronic reduction associated to the process $Mo_3^{IV} \leftrightarrow Mo^{IV}Mo_2^{III}$. The cobalt insertion into the incomplete trinuclear cube results in an anodic shift of the first reduction potential of 0.59 V. A similar behaviour is observed upon copper incorporation although the anodic shift in this case is smaller (0.30 V). In contrast, the 14 electron $[Mo_3FeS_4]^{4+}$ aqua cluster is 0.45 V more difficult to reduce than the trinuclear aqua precursor. Differences in the electrochemical behaviour have been attributed to changes in the oxidation state of the molybdenum atoms upon insertion of the heterometal.[16]

As far as the reactivity of these complexes is concerned, it is worth mentioning that a narrow range of heterodimetallic $Mo_3M'S_4$ cubes react with CO, namely M' = Co, Ni and Pd. An understanding of this reactivity is relevant to the role of these complexes as models for hydroprocessing catalysis because the CO uptake is often taken as a measure of the hydrodesulfurization activity (HDS) of an heterogeneous catalyst.[22] In our case, cluster **1** or its cation $[\mathbf{1}]^+$ do not react with CO in CH_2Cl_2, and a reducing agent, such as borohydride in THF/methanol mixtures, is required for the reaction to take place. Although it has been suggested that 15 Mo_3CoS_4 and 16 $Mo_3M'S_4$ (M' = Ni, Cu, Pd) metal electron clusters bind CO, our findings prove that among the $[Mo_3CoS_4(dmpe)_3Cl_4]^{+,0,-}$ derivatives only the 16 electron species react with CO. The absence of reactivity for the 14 and 15 metal electron clusters may be due to the spin forbidden character of these reactions. In our opinion the reactivity of the 15 electron cluster $[Mo_3CoS_4(H_2O)_{10}]^{4+}$ to give the corresponding CO derivative for which only spectroscopic evidence is provided, can be reformulated as a reduction to the 16 metal electron cube followed by CO addition to afford the $[Mo_3CoS_4(H_2O)_9(CO)]^{3+}$ complex also with 16 metal electrons.[7,23] Additionally we have observed that the Co−Cl distance increases upon electron addition. Based on these findings we predict that only 16 metal electron complexes, such as $[Mo_3CoS_4(dmpe)_3Cl_3(CO)]$, are good candidates as HDS catalysis models.

Molecular and electronic structures: One of the basic aspects in inorganic chemistry remains the development of theoretical bonding schemes that could be supported by experimental evidences. On this regard structural and spectroscopic consequences of electron addition and removal can be physically observed, and this experimental data can be used to corroborate theoretical descriptions of the bonding. This approach has been employed to validate the qualitative MO bond diagram proposed by Harris for the $Mo_2M'_2S_4$ cubanes or that developed by Dahl and Curtis on the homologous homometallic M_4S_4 complexes.[24–26]

The X-ray crystal structure determination of the tetraphenylborate salt of $[\mathbf{1}]^+$ (Figure 2) together with that of **1** and **2** have been carried out in order to get an insight on the structural changes upon differences in electron populations. Table 1 contains a list of the most important averaged bond lengths for these complexes. The Mo−Mo distances for [**1**][BPh_4], **1**, and **2** are 2.782(7), 2.8079(12), and 2.8028(14) Å, respectively, and the Mo−Co bond lengths are 2.760(14) for $[\mathbf{1}]^+$, 2.7069(16) for **1** and 2.6729(17) Å for **2**. These observations agree with the entering electrons occupying an orbital which is basically Mo−Mo non-bonding and slightly Mo−Co bonding.

MO theoretical predictions on $Mo_3M'S_4$ clusters indicate that in these clusters with 14 to 16 metal electrons, 12 metal electrons will occupy the cluster bonding orbitals (1e, $1a_1$

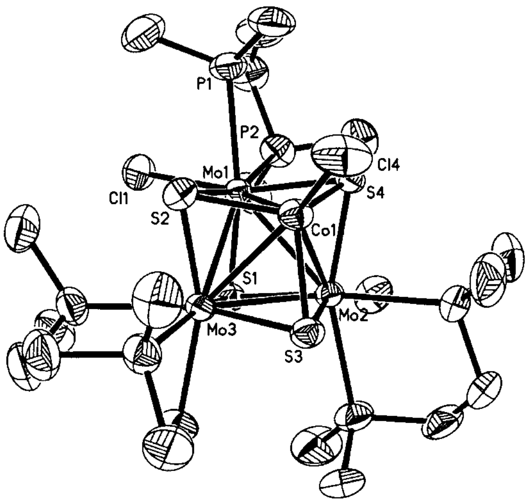


Figure 2. ORTEP representation (50% probability ellipsoids) of the cation $[Mo_3CoS_4(dmpe)_3Cl_4]^+$, $[\mathbf{1}]^+$.

and 2e), and the weakly antibonding ($2a_1$) orbital and two to four electrons will partially or fully occupy the also weakly antibonding HOMO (3e) orbital.[27] Therefore there are some minor discrepancies regarding the metal–metal bonding character of the HOMO orbital which experimentally is found to be weakly bonding instead of weakly antibonding. On the other hand we observed that this HOMO orbital is slightly antibonding with regard to the metal-halogen bonds. Addition of one electron to the $[\mathbf{1}]^+$ cation (Mo–Cl, 2.473(4); Co–Cl, 2.1639(16) Å) produces an increase of 0.06 Å in the Mo–Cl distance and a 0.08 Å increase on the Co–Cl distance. Further support to this MO Scheme is provided by the magnetic susceptibility measurements in the temperature range 2–300 K that show an effective magnetic moment of 2.88 μ_B for $[\mathbf{1}]^+$ and 2.17 μ_B for **1** at room temperature, consistent with the presence of two and one unpaired electrons, respectively, and, therefore, with an "e" character for the HOMO orbital. Both complexes follow a Curie–Weiss magnetic behaviour. The high magnetic moment of **1**, as compared to the expected value (1.7–1.8 μ_B), has been attributed to the presence of paramagnetic impurities, namely Co^{II} and $[\mathbf{1}]^+$ traces, also observed in the low temperature EPR spectra. As theoretically predicted, compound **2** is diamagnetic. These ground spin states are confirmed by the X-band EPR measurements: $[\mathbf{1}]^+$ and **2** are EPR silent, in agreement with the integer ground spin state of $[\mathbf{1}]^+$, $S=1$, and with the diamagnetic nature of **2**, $S=0$. In turn, **1** exhibits an anisotropic signal centered at $g \approx 2.05$ with a paramagnetic behaviour in the temperature range 30–300 K, which is consistent with the $S=\frac{1}{2}$ ground spin state. Furthermore, this signal shows a hyperfine structure ($A=90$ G) with eight signals clearly observed at intermediate temperatures. Both, the splitting pattern and the hyperfine coupling constant are typical of the $^{59}Co^{2+}$ ion ($I=\frac{7}{2}$).[28,29] This observation clearly evidences that the unpaired electron density is mainly located around the cobalt ion. The result obtained for this 15 electron cluster contrasts with that reported for the 17 electron cluster $[Mo_3CuS_4(H_2O)_{10}]^{4+}$ for which the unpaired electron seems to be mainly located on one of the Mo atoms and not on the heteroatom.[30]

Table 1. Crystallographic data for $[Mo_3CoS_4(dmpe)_3Cl_4]$ (**1**), $[Mo_3CoS_4(dmpe)_3Cl_3(CO)]\cdot 0.5\,CH_2Cl_2$ ($\mathbf{2}\cdot 0.5\,CH_2Cl_2$), $[Mo_3CoS_4(dmpe)_3Cl_4]BPh_4$ ($[\mathbf{1}][BPh_4]$) and $[Mo_3CoS_4(dmpe)_3Cl_4]TCNQ\cdot CH_2Cl_2$ ($[\mathbf{1}][TCNQ]\cdot CH_2Cl_2$).

Compound	**1**	$\mathbf{2}\cdot 0.5\,CH_2Cl_2$	$[\mathbf{1}][BPh_4]$	$[\mathbf{1}][TCNQ]\cdot CH_2Cl_2$
empirical formula	$C_{18}H_{48}Cl_4CoMo_3P_6S_4$	$C_{19.50}H_{49}Cl_4CoMo_3OP_6S_4$	$C_{42}H_{68}BCl_4CoMo_3P_6S_4$	$C_{31}H_{54}Cl_6CoMo_3N_4P_6S_4$
formula weight	1067.17	1102.20	1386.38	1356.29
crystal system	cubic	rhombohedral	monoclinic	monoclinic
a [Å]	16.5291(15)	15.7420(10)	17.953(5)	10.539(3)
b [Å]			16.907(4)	26.902(7)
c [Å]		29.308(3)	20.735(5)	18.865(4)
β [°]			114.146(6)	103.190(7)
V [Å^3]	4515.9(7)	6289.8(9)	5743(3)	5208(2)
T [K]	293(2)	293(2)	293(2)	293(2)
space group	$P2(1)3$	$R3c$	$P2(1)/n$	$P2(1)/n$
Z	6	6	4	4
$\mu(Mo_{K\alpha})$ [mm^{-1}]	2.730	1.965	1.452	1.700
refls coll	25851	11247	32550	29599
ϕ data range coll [°]	1.74–24.99	2.04–24.99	1.62–25.00	1.34–25.00
unique refls/R_{int}	2664	2454	10116	9161
R(int)	0.0723	0.0558	0.0665	0.1242
GoF on F^2	1.238	1.142	0.968	0.981
$R1$[a]	0.0425	0.0498	0.0437	0.0553
$wR2$[b]	0.1280	0.1214	0.0801	0.1085
$R1$[a] (all data)	0.0506	0.0582	0.0867	0.1327
$wR2$[b] (all data)	0.1323	0.1258	0.0919	0.1449
residual ρ [e A^{-3}]	0.855 and −0.474	1.035 and −0.722	0.548 and −0.420	0.629 and −0.759

[a] $R1=\Sigma||F_0|-|F_c||/\Sigma F_0$. [b] $wR2=[\Sigma[w(F_0^2-F_c^2)^2]/\Sigma[w(F_0^2)^2]]^{1/2}$.

Development of hybrid charge transfer salts based on Mo_3CoS_4 clusters: In view of the easiness of **1** to be oxidized and the paramagnetic nature and stability of the resulting cation, these molecular clusters may be used as inorganic component for the preparation of hybrid molecular materials. This class of materials represent a very active focus of research in the field of functional molecular materials since it can provide examples of multifunctionality.[31] A first attempt has been done using the organic acceptor TCNQ which has been widely used for the preparation of conducting charge-transfer salts.[32] The oxidation of **1** with TCNQ has resulted in the formation of an organic/inorganic salt formulated as $[\mathbf{1}]^+[\mathrm{TCNQ}]^-$ in which both the cluster cation and the organic anion are paramagnetic. This compound represents the first charge transfer salt based on heterodimetallic $Mo_3M'S_4$ cuboidal clusters. The packing of the salt shows alternate layers of cluster cations and TCNQ anions (Figure 3). There is one crystallographically independent TCNQ anion which forms a ladder chain with each step made out by two TCNQ units slightly dimerized (interplanar spacing 3.45 Å). The overlap within the dimer is of the symmetrical ring-*exo* double bond type characteristic of conducting TCNQ.

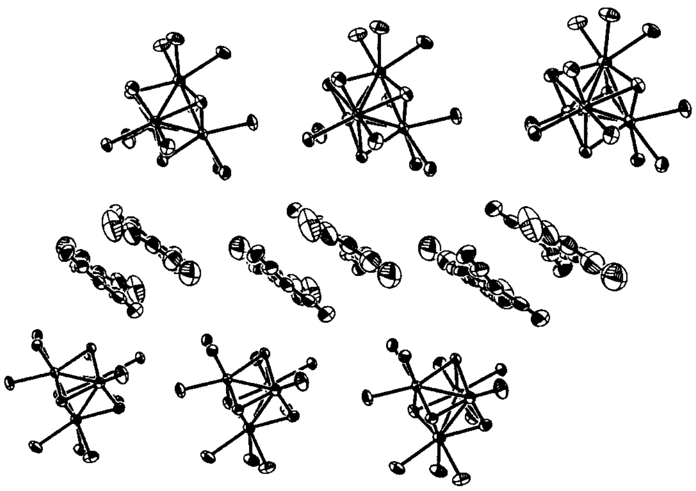


Figure 3. Alternate cation and anion chains in [**1**][TCNQ]. Carbon atoms on the phosphane ligands have been omitted for clarity. The "*a*" axis is horizontal.

However, due to the lack of mixed valence in the TCNQ stacks, the compound is an insulator. Further investigations to produce partial charge transfer salts are in progress. The thermal variation of the χ_mT product of this salt (Figure 4) shows a continuous decrease when cooling the sample to reach a plateau of 1.1 emu K mol^{-1} at $\approx$50 K; this suggests the presence of antiferromagnetic interactions in the $S=\frac{1}{2}$ TCNQ chain. Below ~50 K only the contribution of the $S=1$ from the $[\mathbf{1}]^+$ cations is observed. At temperatures below ~10 K the χ_mT product decreases sharply, which indicates the presence of intermonomer antiferromagnetic interactions and/or zero field splitting (ZFS) in the $S=1$ cation. Accordingly, we have fit the thermal variation of the χ_mT product with a model including a regular $S=\frac{1}{2}$ antiferromagnetic chain[33] plus a $S=1$ monomer with a ZFS.[34] This model reproduces very satisfactorily the χ_mT product in the whole temperature range with the following set of parameters: $g_{\mathrm{chain}}=2$ (fixed value to reduce the number of adjustable parameters), $J_{\mathrm{chain}}=-140(3)\ \mathrm{cm}^{-1}$, $g_{\mathrm{cation}}=2.039(1)$ and $|D|=3.97(4)\ \mathrm{cm}^{-1}$ (solid line in Figure 3). Note that the D value includes possible intermonomer antiferromagnetic interactions and, therefore, it is overestimated.

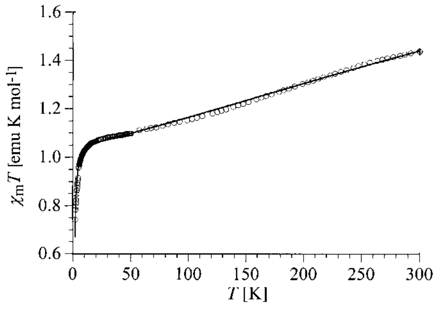


Figure 4. Thermal variation of the χ_mT product for the [**1**][TCNQ] complex. The solid line is reproduced using a ZFS model.

Experimental Section

Physical measurements: ^{31}P NMR spectra were recorded on Varian 300 MHz spectrometer, using CD_2Cl_2 as a solvent and are referenced to external 85 % H_3PO_4. IR spectra were recorded on a Perkin-Elmer System 2000 FTIR using KBr pellets. Cyclic voltammetry experiments were performed with a Echochemie Pgstat 20 electrochemical analyzer. All measurements were carried out with a conventional three-electrode configuration consisting of platinum working and auxiliary electrodes and a Ag/AgCl reference electrode containing aqueous 3 M KCl The solvent used in all experiments was CH_2Cl_2 (Merck HPLC grade). The supporting electrolyte was 0.1 M tetrabutylammonium hexafluorophosphate. $E_{1/2}$ values were determined as $\frac{1}{2}(E_a + E_c)$, where E_a and E_c are the anodic and cathodic peak potentials, respectively. All potentials reported were not corrected for the junction potential. Magnetic susceptibility measurements were performed on a SQUID instrument. Electrospray mass spectra were recorded on a Micromass Quattro LC instrument using dichloromethane as solvent.

Synthesis: All reactions were carried out under a nitrogen atmosphere using standard Schlenk techniques. The molecular triangular cluster $[Mo_3S_4(dmpe)_3Cl_3][PF_6]$ was prepared according to literature methods.[35] The tetraphenylborate salt was prepared by addition of an excess of $NaBPh_4$ to methanol solutions of $[Mo_3S_4(dmpe)_3Cl_3][PF_6]$ that precipitate the desired compound. The remaining reactants were obtained from commercial sources and used as received. Solvents for synthesis were dried and degassed by standard methods before use.

$[Mo_3CoS_4(dmpe)_3Cl_4]$ (1): $[Mo_3S_4(dmpe)_3Cl_3][BPh_4]$ (0.1 g, 0.07 mmol) and $CoCl_2$ (13 mg, 0.1 mmol) were dissolved in a solution THF/MeOH 8:1 (20 mL). $NaBH_4$ (8 mg, 0.2 mmol) was added and the reaction mixture was stirred for 1 h at room temperature. The solution turns brown after 30 min. Addition of Et_2O (30 mL) caused the complete precipitation of a brown solid which was washed with THF (3×2 mL) and Et_2O, redissolved in CH_2Cl_2 and filtered in order to eliminate the inorganic salts from $NaBH_4$. Finally Et_2O was layered on this solution to afford brown cubic crystals of the titled compound (30 mg, 30 %). Elemental analysis calcd (%) for $C_{18}H_{48}P_6Cl_4S_4CoMo_3$: C 20.26, H 4.53, S 12.02; found: C 20.45, H 4.70, S 12.22; ESI-MS (65 V): *m*/*z* (CH_2Cl_2): 1067 $[M]^+$, 917 $[M-\mathrm{dmpe}]^+$.

$[Mo_3CoS_4(dmpe)_3Cl_3(CO)]$ (2): $[Mo_3S_4(dmpe)Cl_3]BPh_4$ (0.1 g, 0.07 mmol) and $CoCl_2$ (26 mg, 0.2 mmol) were dissolved in a solution THF/MeOH 8:1 (20 mL). $NaBH_4$ (16 mg, 0.4 mmol) was added under a CO (1 atm) atmosphere and the reaction mixture was stirred for 1 h at room temperature. The solution turns brown after 30 min. Addition of Et_2O (30 mL) caused the complete precipitation of a brown solid which was washed with THF (3×2 mL) and Et_2O, redissolved in CH_2Cl_2 and filtered in order to eliminate the inorganic salts from $NaBH_4$. Finally Et_2O was layered on this solution to afford brown cubic crystals of the titled compound (20 mg, 26 %). Elemental analysis calcd (%) for $C_{19}H_{48}OP_6Cl_3S_4CoMo_3$: C 21.53, H 4.57, O 1.51, S 12.10; found: C 21.56, H 4.70, O 1.39, S 12.20; IR: $\tilde{\nu}_{\max} = 1923\ \mathrm{cm}^{-1}$ (C=O); ^{31}P NMR (121.47 MHz, 25 °C): $\delta=25.4$ (d, 3P, $^1J_{P-P}=12$ Hz), 16.8 (d, 3P, $^1J_{P-P}=12$ Hz); ESI-MS (65 V): *m*/*z* (CH_2Cl_2): 1060 $[M]^+$, 1032 $[M-\mathrm{CO}]^+$, 882 $[M-\mathrm{CO}-\mathrm{dmpe}]^+$.

$[Mo_3CoS_4(dmpe)_3Cl_4][BPh_4]$, [1][BPh$_4$]: $[Co_2(CO)_8]$ (0.040 g, 0.12 mmol) was added under nitrogen to a green solution of $[Mo_3S_4(dmpe)_3Cl_3][PF_6]$

(0.1 g, 0.09 mmol) in CH_3CN and the mixture was heated under reflux for 3 h. The colour of solution turns dark brown after 1 h. After filtration through Kieselgur, the resulting solution (which contains a mixture of cationic compounds identified by mass spectrometry as [**2**]$^+$ and [**1**]$^+$) was treated with 0.1 M HCl (3 mL) and stirred in air at room temperature for 10 min. No colour changes was observed at this step. The mixture was taken to dryness, redissolved in CH_3OH, filtered and to this filtrate, $NaBPh_4$ (15 mg) was added to precipitate the titled compound which was washed with CH_3OH (3×2 mL) and Et_2O. Finally, recrystallization from CH_2Cl_2/Et_2O gave brown needle crystals suitable for X-ray analysis (39 mg, 37%). Elemental analysis calcd (%) for $C_{42}H_{68}BP_6Cl_4S_4CoMo_3$: C 36.38, H 4.94, S 9.25; found: C 36.55, H 4.78, S 9.27; ESI-MS (65 V): m/z (CH_2Cl_2): 1067 $[M]^+$, 917 $[M-\text{dmpe}]^+$.

[Mo_3CoS_4(dmpe)$_3Cl_4$][TCNQ], [1][TCNQ]: TCNQ (0.012 g, 0.06 mmol) under nitrogen was added to a brown solution of **1** (0.045 g, 0.04 mmol) in CH_2Cl_2 and the mixture was stirred for 30 min. The colour of solution turns green immediately. The resulting solution was filtered and Et_2O was layered to give needle green crystals suitable for X-ray analysis which were washed with toluene and Et_2O (50 mg, 93%). Elemental analysis calcd (%) for $C_{42}H_{68}BP_6Cl_4S_4CoMo_3$: C 28.34, H 4.12, N 4.41, S 10.09; found: C 28.40, H 4.18, N 4.48, S 9.27; IR: $\tilde{\nu}_{\max}$ 2051 cm^{-1} ($C\equiv N$); ESI-MS (65 V): m/z (CH_2Cl_2): 1067 $[M]^+$, 917 $[M-\text{dmpe}]^+$.

X-ray data collection and structure refinement: The crystals are air stable and were mounted on the tip of a glass fiber with the use of epoxy cement. X-ray diffraction experiments was carried out on a Bruker SMART CCD diffractometer using $Mo_{K\alpha}$ radiation ($\lambda = 0.71073$ Å) at room temperature. The data were collected with a frame width of 0.3° in ω and a counting time of 15, 20, 25 and 20 s per frame for compounds **1**, **2**, [**1**][BPh_4], and [**1**][TCNQ], respectively at a crystal to detector distance of 4 cm. The diffraction frames were integrated using the SAINT package and corrected for absorption with SADABS.[36,37] The structure was solved by direct methods and refined by the full-matrix method based on F^2 using the SHELXTL software package.[38] The crystal parameters and basic information relating data collection and structure refinement for compounds **1**, **2**, [**1**][BPh_4], and [**1**][TCNQ] are summarized in Table 2.

The neutral compounds **1** and **2** crystallize in the chiral groups $P2(1)3$ and $R3c$ with absolute structure parameters being refined as 0.02(7) and 0.07(6). All the non-hydrogen atoms were refined anisotropically; the positions of all hydrogen atoms in the clusters and the counteranions were generated geometrically, assigned isotropic thermal parameters and allowed to ride on their respective parent carbon atoms. The last Fourier map in compounds **1** and [**1**][TCNQ] showed a half and one dichloromethane molecule, respectively which were refined isotropically. The hydrogen atoms in this solvent were not included in the refinement.

CCDC-217717 (**1**), -217715 (**2**·0.5 CH_2Cl_2), - 217716 ([**1**][BPh_4]), and -217718 ([**1**][TCNQ]·CH_2Cl_2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336033; or deposit@ccdc.cam.uk).

Conclusion

The first complete family of $Mo_3M'S_4$ heterodimetallic clusters with single cube structures and three different metal electron counts has been synthesized using Co as heterometal and diphosphanes as outer ligands. This circumstance has allowed us to investigate the influence of the metal electron populations on the reactivity of these complexes, in particular the CO uptake due to its relevance in HDS catalysis. Only the 16 metal electron cluster "[Mo_3CoS_4(dmpe)$_3Cl_4$]$^-$" reacts with CO to give the substitution product [Mo_3CoS_4(dmpe)$_3Cl_3$(CO)]. Structural and magnetic investigations on these complexes have been used to validate the MO bond diagram proposed by Harris for the $Mo_3M'S_4$ cubanes. In addition, the easiness of electrochemical interconversion among these clusters together with their magnetic character has been explored aimed to the preparation of hybrid materials that combine electric and magnetic properties.

Table 2. Selected averaged bond lengths [Å] for compounds [**1**][BPh_4], **1**, **2**·0.5 CH_2Cl_2, and [**1**][TCNQ]·CH_2Cl_2.[a]

	[**1**][BPh_4]	**1**	**2**·0.5 CH_2Cl_2	[**1**][TCNQ]·CH_2Cl_2
Mo–Mo	2.782[7]	2.8079(12)	2.8028(14)	2.786[4]
Mo–Co	2.760[14]	2.7069(16)	2.6729(17)	2.768[12]
Mo–Cl	2.473[4]	2.530(2)	2.542(2)	2.481[6]
Co–S	2.251[1]	2.214(2)	2.186(3)	2.252[3]
Co–Cl	2.1639(16)	2.240(4)		2.156(3)

[a] Averaged values are given in brackets.

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