Charge Transfer Salts Based on Polyoxometalates and Seleno-Substituted Organic Donors. Synthesis, Structure, and Magnetic Properties of (BEST)$_3$H[PMo$_{12}$O$_{40}$]·CH$_3$CN·CH$_2$Cl$_2$ (BEST = Bis(ethylenediseleno)tetrathiafulvalene)

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Electrochemical oxidation of the tetrathiafulvalene (TTF) type organic donor bis(ethylenediseleno)tetrathiafulvalene (BEST) in the presence of the Keggin polyoxometalate [PMo$_{12}$O$_{40}$]$^{3-}$ affords the radical salt formulated as (BEST)$_3$H[PMo$_{12}$O$_{40}$] (crystal data: triclinic, space group $P\bar{1}$ with a = 13.056(1) Å, b = 13.957(1) Å, c = 22.302(3) Å, α = 97.019(9)°, β = 94.17(1)°, γ = 95.847(9)°, and Z = 2). This is the first salt of a selenium-containing donor with a polyoxometalate cluster. The structure of this organic/inorganic hybrid consists of layers of the organic donors that alternate with polyoxometalate layers in the c direction. The organic molecules, which are completely ionized, form two types of layers with unprecedented packing arrangements and many intra- and interlayer side-on short contacts which give rise to a marked 3D electronic character. The magnetic susceptibility measurements indicate that the BEST$^+$ radicals are strongly antiferromagnetically coupled and that the polyanion has been reduced by one electron to give the mixed-valence anion [PMo$_{12}$O$_{40}$]$^{4-}$. The ESR spectra show the progressive localization of the additional electron which becomes fully trapped on one of the Mo sites of the Keggin unit at low temperatures (T < 7 K).

A recent development of polyoxometalate anions in materials science deals with the use of these soluble metal−oxide clusters as inorganic components of new organic−inorganic hybrid molecular materials based on π-electron donor molecules of the tetrathiafulvalene (TTF) family, which constitute the basic ingredient of the molecular conductors and superconductors.[1]

Most hybrids of this kind are based on the commercially available TTF or bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) (see Chart 1). These donors combined with polyoxometalate clusters of various nuclearities, shapes, and charges have resulted in the preparation of new types of insulating, semiconducting, or even metallic charge transfer salts having unusual structural and/or electronic features.[2] Thus, from the structural point of view, the polyoxoanion has often induced novel packing arrangements in the organic component of the salt. From the electronic point of view, the ability of the polyoxoanion to act as an electron acceptor has led to hybrid

Chart 1. The TTF and ET Type Donors.
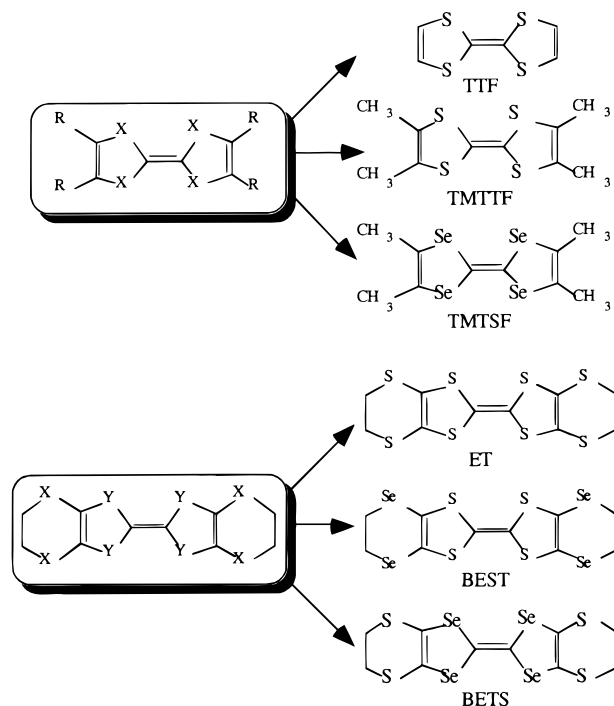
materials in which the extended electron delocalization in the organic component coexists with a restricted electron delocalization within the reduced cluster. Finally, the introduction of localized magnetic moments in the polyanion has produced new hybrid materials in which localized spins and delocalized conducting electrons coexist.[3]

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(1) Williams, J. M.; Ferraro, J. R.; Thorn, R. J.; Carlson, K. D.; Geiser, U.; Wang, H. H.; Kini, A. M.; Whangbo M. H. In *Organic Superconductors. Synthesis, Structure, Properties and Theory*; Grimes, R. N., Ed.; Prentice Hall: Englewood Cliffs, NJ, 1992.
(2) (a) Triki, S.; Ouahab, L.; Padiou, J.; Grandjean, D. *J. Chem. Soc., Chem. Commun.* **1989**, 1068. (b) Davidson, A.; Boubekeur, K.; Pénicaud, A.; Auban, P.; Lenoir, C.; Batail, P.; Hervé, G. *J. Chem. Soc., Chem. Commun.* **1989**, 1373. (c) Attanasio, D.; Bellitto, C.; Bonamico, M.; Fares, V.; Imperatori, P. *Gazz. Chim. Ital.* **1991**, *121*, 155. (d) Triki, S.; Ouahab, L.; Halet, J. F.; Peña, O.; Padiou, J.; Grandjean, D.; Garrigou-Lagrange, C.; Delhaès, P. *J. Chem. Soc., Dalton Trans.* **1992**, 1217. (e) Gómez-García, C. J.; Coronado, E.; Triki, S.; Ouahab, L.; Delhaès, P. *Adv. Mater.* **1994**, *4*, 283. (f) Bellitto, C.; Bonamico, M.; Fares, V.; Federici, F.; Righini, G.; Kurmoo, M.; Day, P. *Chem. Mater.* **1995**, *7*, 1475 and references therein.

The above features are exemplified by the radical salts obtained by reaction of ET with α-Keggin polyanions with charges between −4 and −6. These salts have the general formula (BEDT-TTF)$_8$[Keggin] and contain Keggin anions[4] that can have an unpaired electron delocalized over the cluster (anion [PMo$_{12}$O$_{40}$]$^{4-}$)[2f] or a paramagnetic metal ion lying in the center[5] or on the surface[6] of the polyanion. In the former case, delocalized electrons coexist in the two mixed-valence sub-systems, while, in the second, a coexistence of localized and itinerant electrons has been found. All these materials show semiconducting behaviors with $\sigma_{RT} \approx 10^{-1}-10^{-2}$ S·cm^{-1} and an activation energy $E_a \approx 100-150$ meV.

As part of our ongoing work with these organic donor/polyoxometalate acceptor molecular materials, we have explored the use of two seleno-substituted ET molecules: bis(ethylene-diseleno)tetrathiafulvalene (BEST) and bis(ethylenedithio)-tetraselenofulvalene (in short, BETS) (see Chart 1). These molecules have attracted much interest in the field of the molecular conductors, as they offer a means of increasing the electrical conductivities thanks to the more extended π orbitals of the selenium, which enhance the donor–donor overlaps.[1] In this paper, we investigate the preparation of hybrid radical salts formed by these organic donors and Keggin polyoxoanions. Here we report the synthesis, structure, and magnetic characterization of the hybrid radical salt (BEST)$_3$H[PMo$_{12}$O$_{40}$]·CH$_3$CN·CH$_2$-Cl$_2$.

Experimental Section

Synthesis. Tetrabutylammonium (NBu$_4$) salts of the polyanions were prepared by the methods reported in the literature.[7] The donor molecules, BEST and BETS, were supplied by Prof. G. C. Papavassiliou (BEST) from the National Hellenic Research Foundation (Athens, Greece) and by Prof. H. Kobayashi (BETS) from the Institute of Molecular Science (Okazaki, Japan). The radical salts were prepared by electrochemical oxidation of the organic donors in the presence of Keggin polyanions of the type XM$_{12}$ (X = 2(H$^+$), B^{III}, Si^{IV}, P^V, Fe^{III}, Co^{II}, Cu^{II}; M = W, Mo) and XZW$_{11}$ (X = P^V and Z = Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}; X= Si^{IV} and Z = Fe^{III}, Cr^{III}). Different mixtures of organic solvents (CH$_3$CN, CH$_2$Cl$_2$, DMF) and low constant currents ($I = 0.6$ μA) were checked in the electrocrystallization. However, crystals of the BEST radical salt were deposited on the electrode only in the presence of the polyanion [PMo$_{12}$O$_{40}$]$^{3-}$. The best results were obtained for 3:7 CH$_3$CN:CH$_2$Cl$_2$ mixtures kept under a constant current of $I = 0.6$ μA for 10 days. Under similar experimental conditions, the BETS

(3) (a) Coronado, E.; Gómez-García, C. J. *Comments Inorg. Chem.*, **1995**, *17*, 255. (b) Coronado, E.; Galán-Mascarós, J. R.; Giménez-Saiz, C.; Gómez-García, C. J. In *Magnetism: A Supramolecular Function*; Kahn, O., Ed.; NATO ASI Series C484; Kluwer Academic Publishers: Dordrecht, The Netherlands, 1996; pp 281−298 and references therein. (c) Coronado, E.; Gómez-García, C. J. *Chem. Rev.* **1998**, *98*, 273.

(4) The Keggin anions that have been combined with BEDT-TTF are of two types: (a) Nonsubstituted polyanions [XM$_{12}$O$_{40}$] (M = W, Mo) with a nonmagnetic heteroatom, X, in the central tetrahedral site (X = 2(H$^+$), Zn^{II}, B^{III}, Si^{IV}, and P^V) or a magnetic one (X = Fe^{III}, Co^{II}, and Cu^{II}). (b) Monosubstituted polyanions [XZ(H$_2$O)M$_{11}$O$_{39}$] (X = Si, P; M = W, Mo) with a magnetic ion, Z, in one of the peripheral octahedral sites (Z = Mn^{II}, Co^{II}, Ni^{II}, Cu^{II}, Fe^{III}, and Cr^{III}).

(5) (a) Gómez-García, C. J.; Ouahab, L.; Giménez-Saiz, C.; Triki, S.; Coronado, E.; Delhaès, P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 223. (b) Gómez-García, C. J.; Giménez-Saiz, C.; Triki, S.; Coronado, E.; Le Magueres, P.; Ouahab, L.; Ducasse, L.; Sourisseau, C.; Delhaès, P. *Inorg. Chem.* **1995**, *34*, 4139.

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(7) (a) Nomiya, K.; Miwa, M.; Kobayashi, R.; Aiso, M. *Bull. Chem. Soc. Jpn.* **1981**, *54*, 2983 and references therein. (b) Sanchez, C.; Livage, J.; Launay, J. P.; Fournier, M.; Jeannin, Y. *J. Am. Chem. Soc.* **1982**, *104*, 3194.

Table 1. Crystallographic Data for the Salt (BEST)$_3$H[PMo$_{12}$O$_{40}$]·CH$_3$CN·CH$_2$Cl$_2$

empirical formula: C$_{33}$H$_{29}$NO$_{40}$Cl$_2$PMo$_{12}$S$_{12}$Se$_{12}$	fw: 3664.96
$a = 13.056(1)$ Å	space group: $P\bar{1}$ (No. 2)
$b = 13.957(1)$ Å	$T = -150$ °C
$c = 22.302(3)$ Å	$\lambda = 0.710\ 73$ Å
$\alpha = 97.019(9)°$	$\rho_{calcd} = 3.045$ g cm^{-3}
$\beta = 94.17(1)°$	$\mu = 77.64$ cm^{-1}
$\gamma = 95.847(9)°$	$R^a = 0.0359$
$V = 3997.6(7)$ Å^3	$R_w{}^b = 0.0874$
$Z = 2$	

$^a R = \sum|F_o| - |F_c|/\sum|F_o|$. $^b R_w = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$.

donor did not give any salt with PMo$_{12}$. However, with the polyanion [SiW$_{12}$O$_{40}$]$^{4-}$, black crystalline powders were obtained with both donors, while the remaining polyanions did not deposit any salt on the electrode.

The IR spectrum of the crystals indicated the presence of the BEST molecules and of the Keggin polyanion. The positions and assignments of the bands are as follows (in cm^{-1}): 1446 (ν_{27}); 1412 and 1398 ($\nu_2 + \delta$CH$_2$); 1340 (ν_3); 1261 (ν_{46}); ≈1170 (ν_{67}); ≈ 1135 (ν_{38}); ≈1120 (ν_{47}); 1057 (P−O); 950 (Mo−O^d); 873 (Mo−O^b−Mo); 794 (Mo−O^c−Mo); 691 (ν_{33}); 620 (ν_{51}); 494 (ν_9). (O^d = terminal oxygen, O^c = bridging oxygen of two octahedra sharing a corner, O^b = bridging oxygen of two octahedra sharing an edge.)

X-ray Crystallography. The X-ray crystal structure of the title compound was determined from a hexagonal plate of size $1.05 \times 0.25 \times 0.03$ mm^3 at low temperature (123(1) K) on an Enraf-Nonius CAD-4 diffractometer. We did not attempt to cut the crystal, because previously examined samples were found to be easily destroyed by cutting. Instead, we took measures during data collection to minimize the effects of the crystal size (vide infra). The orientation matrix for data collection was obtained from least-squares refinement of the setting angles of 25 reflections. The lattice dimensions were verified by axial photography, and final values of the cell constants were determined by a least-squares fit to the setting angles of 25 well-spaced reflections, each measured at four different positions. During data collection, each reflection was measured with a geometry chosen to minimize the effects of absorption and of the crystal size and shape, by keeping the normal to the (001) plane (corresponding to the main face of the crystal) as close as possible to the diffraction plane.[8] Absorption correction was done with a laminar model.[9] Thirteen reflections were used (ψ-scan method),[10] ten of them with a χ angle close to 90°. During data collection three standard reflections were measured every hour and showed no significant decay. The structure was solved by direct methods and developed using full-matrix least-squares refinements and difference Fourier syntheses, which revealed all the atoms of the organic donors, the polyanions, and the solvent molecules, including all but six H atoms of the organic donor molecules. The six missing H atoms were placed at idealized positions with isotropic U values of 1.2 times the equivalent isotropic U's of their respective parent atoms. Important parameters of the crystal structure determination are summarized in Table 1.

Magnetic Measurements. Variable-temperature susceptibility measurements were carried out in the temperature range 2−300 K at a magnetic field of 0.1 T on polycrystalline samples with a magnetometer (Quantum Design MPMS-XL-5) equipped with a SQUID sensor. The susceptibility data were corrected for the diamagnetic contributions of the BEST molecules (-326×10^{-6} emu·mol^{-1} per BEST molecule, as deduced by using Pascal constant tables) and for the diamagnetic and TIP contributions of the Keggin units (these contributions were calculated from the susceptibility measurement of the NBu$_4$ salt of the corresponding Keggin anion and are similar to those applied in other radical salts of TTF with Keggin polyanions). Variable-temperature

(8) Diffractometer control program: *CAD4-PC 1.5*; Delft Instruments: Delft, The Netherlands, 1994.

(9) The data were processed on a VAXcluster (VMS V5.5-2) with the program XCAD4B (Klaus Harms, Philipps University of Marburg) and with the commercial package *SHELXTL-PLUS*, release 4.21/V; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1990.

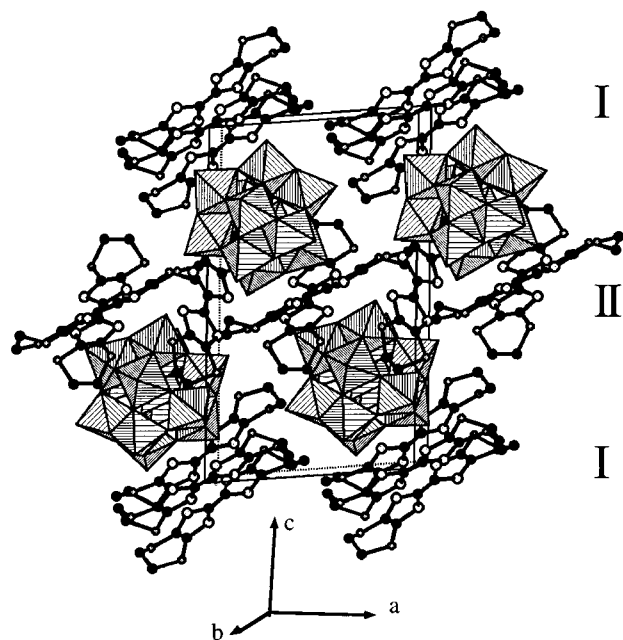(10) North, A. C. T.; Philips, D. C.; Mathews, F. S. *Acta Crystallogr., Sect. A* **1968**, *24*, 351.

Figure 1. Projection of the structure of the title compound in the *ac* plane showing the alternating organic and inorganic layers and the two different types of organic layers (labeled as I and II).

ESR spectra of single crystals were recorded at X-band with a Bruker ER300 spectrometer equipped with a helium cryostat. The field was measured using a diphenylpicrylhydrazyl (DPPH) stable free radical marker.

Results and Discussion

Crystal Structure. The structure of this radical salt can be viewed as layers of the inorganic anions alternating with layers of the organic cations (Figure 1). There are five crystallographically independent BEST molecules, which we call A, B, C, D, and E in the discussion that follows. The unit cell contains two Keggin polyoxoanions and six BEST moieties (two of type A on a set of general positions and one each of the other types, lying on independent centers of symmetry), giving an overall stoichiometry of 3:1. The anions lie on general positions and in the extended structure form a close-packing distribution in the $(00\bar{1})$ plane of the triclinic cell. A noteworthy feature of this structure is the fact that the Keggin polyoxometalates are not disordered, as occurs in most of the previously observed salts containing this anion.[11] The disorder is found when the Keggin anion lies on an inversion center (which necessarily gives rise to the disorder) or when a $\bar{4}$ (S_4) axis (which does not oblige the presence of disorder) passes through its center,[12] which causes the tetrahedral heteroatom X to be surrounded by eight oxygen sites in a cubic arrangement, each with an occupancy factor 0.5. In the present case, however, the anion lies away from the inversion center, and the ordered structure shows the true symmetry, T_d, of this entity.

As regards the packing of the organic molecules, we observe that they do not form stacks with overlapping π orbitals, as is customarily observed in salts of these planar donors, but rather layers with side-on contacts. Two different layers (I and II) parallel to the *ab* plane can be distinguished alternating along
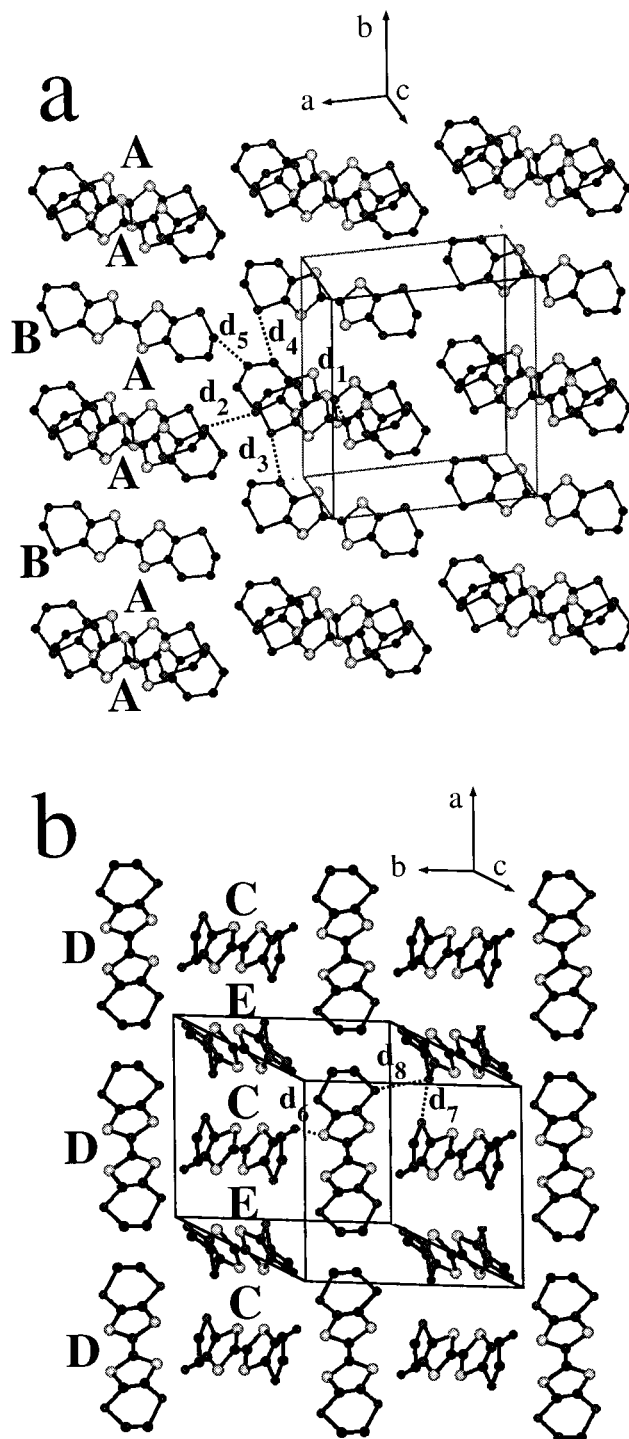
(11) (a) Sergienko, V. S.; Porai-Koshits, M. A.; Yurchenko, E. N. *J. Struct. Chem. (Engl. Transl.)* **1980**, *21*, 87. (b) Fuchs, J.; Thiele, A.; Palm, R. *Angew. Chem., Int. Ed. Engl.* **1982**, *21*, 789. (c) Attanasio, D.; Bonamico, M.; Fares, V.; Imperatori, P.; Buber, L. *J. Chem. Soc., Dalton Trans.* **1990**, 3221.
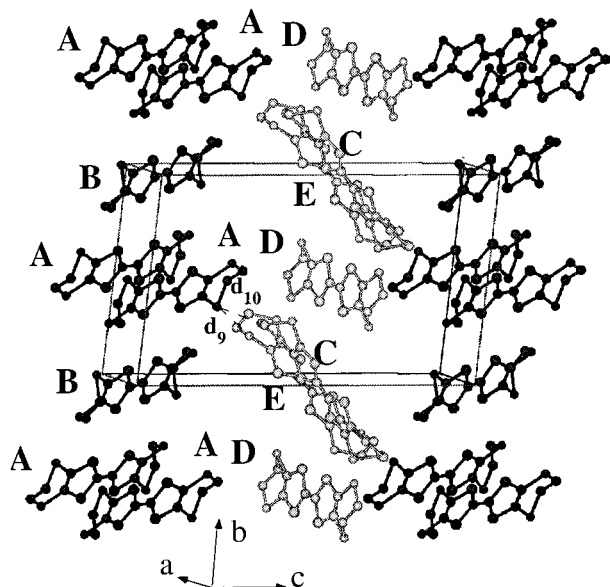(12) Evans, H. T.; Pope, M. T. *Inorg. Chem.* **1984**, *23*, 501.

Figure 2. (a) View of the type I organic layer in the *ab* plane. (b) View of the type II organic layer in the *ab* plane. The shorter intermolecular distances are indicated and labeled according to the text.

the *c* direction (Figure 1). Layer I is formed by chains running in the *b* direction composed of A−A dimers and isolated B molecules. In this layer, the axes of all the molecules (defined by the central C=C bond) and the molecular planes are almost parallel (Figure 2a). Layer II, formed by C, D, and E molecules, shows two kinds of chains running in the *a* direction (Figure 2b). One of these chains is made of aligned D molecules, whereas the other chain contains alternating C and E molecules stacked in a W mode (Figure 2 b). Both C and E molecules are almost perpendicular to the D molecules of the neighboring chains.

Figure 3. View of the two types of organic layers in the *bc* plane showing the shortest interlayer distances (see text).

Despite the lack of π stacking in these layers, numerous short contacts between BEST molecules are observed both within the layers and between the layers; the contacts mainly involve the Se atoms. Thus, in layer I short distances are observed within the A−A dimers (d1(C2−C2) = 3.24 Å), between the dimers (d2(Se4−Se4) = 3.57 Å), and between A and B molecules (d3-(Se1−Se6) = 3.40 Å; d4(Se3−Se5) = 3.52 Å; d5(C9−C14) = 3.42 Å) (Figure 2 a). In layer II, the shortest contacts between C and D molecules (d6(Se7−S9) = 3.40 Å), between C and E (d7(Se8−Se11) = 3.57 Å), and between D and E (d8(Se10−Se11) = 3.84 Å) are also shorter than the sum of the van der Waals radii of the corresponding atoms (Figure 2 b). Strong interlayer interactions are also observed between A and E molecules (d9(Se1−Se11) = 3.96 Å) and between A and C molecules (d10(Se1−C20) = 3.40 Å) (Figure 3). Finally, short contacts are found between the organic BEST and the Keggin polyanion (shortest Se−O, S−O, and C−O distances of 2.95, 2.96, and 3.02 Å, respectively).

It is interesting to estimate the ionic charges on the BEST molecules from the known correlations between the intramolecular distances of the central TTF skeleton and the oxidation degree, recently proposed by Guionneau et al.[13] As we can see in Table 2, this correlation indicates that all the BEST molecules are completely ionized (oxidation degree very close to +1). The IR spectrum supports this result. In fact, the positions of the observed bands are very close to those found for other completely ionized ET^+ radical cations[14] (see Experimental Section).

With ET and $[PW_{12}O_{40}]^{3-}$ two 3:1 salts are known: ET_3-$[PW_{12}O_{40}]$[15] and $(ET)_3[PW_{12}O_{40}]\cdot THF$.[16] The first of these salts presents chains of ET molecules formed by orthogonally

Table 2. Intramolecular Bond Distances and Calculated Degrees of Ionicity (*Q*) for All the BEST Molecules in the Salt $(BEST)_3H[PMo_{12}O_{40}]\cdot CH_3CN\cdot CH_2Cl_2$
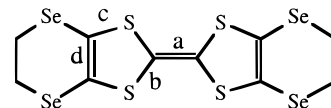
molecule	*a* (Å)	*b* (Å)	*c* (Å)	*d* (Å)	Q^a
A	1.389(10)	1.719(8)	1.726(8)	1.345(11)	1.04
		1.708(8)	1.731(7)	1.353(11)	
		1.715(8)	1.726(7)		
		1.740(7)	1.731(8)		
B	1.389(15)	1.726(7)	1.724(8)	1.355(11)	1.06
		1.711(8)	1.744(7)		
C	1.380(15)	1.715(8)	1.731(7)	1.348(10)	0.96
		1.725(7)	1.729(7)		
D	1.360(14)	1.730(7)	1.719(7)	1.344(10)	0.74
		1.727(8)	1.734(7)		
E	1.387(15)	1.715(8)	1.734(8)	1.354(11)	1.05
		1.722(8)	1.731(8)		

^{a} $Q = 6.347 - 7.463\delta$, with $\delta = (b + c) - (a + d)$.

alternating dimers and isolated molecules. For the second salt, there are no definite structural results.

Magnetic Properties. Magnetic susceptibility data in the temperature range 2−40 K show a Curie law with a constant *C* = 0.378 emu·mol^{-1}, which corresponds to one unpaired electron per mole. The ESR study indicates that the unpaired electron resides on the Keggin anion, while the electrons of the $BEST^+$ radicals are completely paired even at room temperature. Thus, the spectra, recorded on a single crystal at fixed orientations, show at room temperature a very weak and narrow signal at *g* values between 2.0059 and 2.0089 and line widths of 4.8−5.2 G, depending on the crystal orientation, which can be attributed to paramagnetic impurities of the $BEST^+$ radicals. Below 125 K, an isotropic and broad signal centered at 3400 G dominates the spectrum (signal I in Figure 4a). This signal splits below *T* ≈ 10 K into two signals (named II and III in Figure 4 a). Signal II slightly decreases its intensity and shifts toward lower fields when the temperature is decreased, while signal III increases in intensity and shifts toward higher fields. A detailed inspection of the low-temperature spectra allows one to observe well-resolved hyperfine lines on signals II (*g* = 2.01) and III (*g* = 1.95) at *T* < 8 K. In particular, at *T* = 6.7 K, we can clearly distinguish up to two sextuplets on each signal with hyperfine couplings of ca. 20 G, centered at *g* = 2.01 (signal II) and *g* = 1.95 (signal III) (Figure 4b). Below this temperature, the hyperfine components are more difficult to detect and even disappear.

The observed thermal evolution of the ESR spectra can be correlated with the dynamics of the unpaired electron in the one-electron-reduced polyanion. In fact, in these mixed-valence clusters, the delocalized "blue" electron undergoes a progressive localization as the temperature is lowered. This thermally activated electron hopping has been studied in solutions and in dilute polycrystalline samples.[2f,17] In our case, the observation

(13) Guionneau, P.; Kepert, C. J.; Bravic, G.; Chasseau, D.; Truter, M. R.; Kurmoo, M.; Day, P. *Synth. Met.* **1997**, *86*, 1973. Although this method is applied only for ET molecules, it may be also applied for the BEST molecules, due to the similarity in the bond distances of the central skeleton (the only ones considered) of both, ET and BEST molecules.

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(15) Ouahab, L.; Triki, S.; Grandjean, D.; Bencharif, M.; Garrigou-Lagrange, C.; Delhaès, P. In *Lower Dimensional Systems and Molecular Electronics*; Metzger, R. M., Day, P., Papavassiliou, G. C., Eds.; NATO ASI Series B248; Plenum Press: New York, 1991; p 185.

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(17) (a) Prados, R. A.; Pope, M. T. *Inorg. Chem.* **1976**, *15*, 2547. (b) Sánchez, C.; Livage, J.; Launay, J. P.; Fournier, M.; Jeannin, Y. *J. Am. Chem. Soc.* **1982**, *104*, 3194. (c) Barrows, J. N.; Pope, M. T. In *Electron Transfer in Biology and the Solid State. Inorganic Compounds with Unusual Properties*; Johnson, M. K., et al., Eds.; Advances in Chemistry Series 226; American Chemical Society: Washington, DC, 1990; p 403.

of a single signal down to 10 K indicates that above this temperature the electron is fully delocalized over the 12 Mo^{VI} ions of the cluster. At lower temperatures, the progressive electron localization leads to the appearance of more than one signal, since the 12 Mo atoms are no longer equivalent on the ESR time scale. The occurrence of sextuplet splittings at 6.7 K clearly indicates that at this temperature the unpaired electron is trapped on a single molybdenum site. In fact, these six-line splittings arise from the coupling of the electron spin with the nuclear spin $I = {}^5/_2$ of the molybdenum isotopes ^{95}Mo and ^{97}Mo (natural abundances of 15.9% and 9.6%, respectively). The presence of more than one hyperfine structure in this spectrum is due to the different orientations of the MoO_6 octahedral sites of the Keggin anions with respect to the magnetic field direction.

We can conclude that the Keggin polyanion is reduced by one electron and that therefore its charge should be -4. The reduction of the $[PMo_{12}]^{3-}$ anion has been observed in all the reported radical salts with TTF type donors. For the ET type molecules, the reduction must be accomplished at the cathode of the electrochemical cell, as the donor character of these molecules is not strong enough to reduce this anion.[2f]

As a result, the title radical salt should be formulated as $(BEST)_3H[PMo_{12}O_{40}]\cdot CH_3CN\cdot CH_2Cl_2$, where a proton needs to be introduced in order to compensate the anionic charge, as in other related radical salts.[18]

Conclusions

In this work, we have investigated for the first time the possibility of combining Keggin polyoxometalates with organic donor derivatives of ET with Se substituting S atoms (in the internal TTF skeleton or in the peripheral rings). As a result, the radical salt formulated as $(BEST)_3H[PMo_{12}O_{40}]\cdot CH_3CN\cdot CH_2Cl_2$ has been obtained, which is formed by the mixed-valence polyoxometalate $[PMo_{12}O_{40}]^{4-}$ and fully ionized organic radical cations $BEST^+$. The first point deserving attention concerns the strong differences observed, both in the chemistry and in the structure of the final solid, when we pass from the ET donor to the corresponding seleno-substituted molecules. Thus, whereas ET has been successfully combined with many different polyanions possessing the Keggin structure to give extensive series of crystalline radical salts, the polyoxometalate salts with seleno-substituted donors have been much more difficult to obtain. From the structural point of view we have seen that a small modification in the ET molecule (substitution of S by Se in the periphery) has led to drastic changes in the composition of the resulting radical salt (from a stoichiometry of 8:1 to 3:1) and, therefore, in its structure and electronic properties. Thus, for the 3:1 salt, the lack of a mixed-valence character in the organic part prevents electron delocalization and the compound is an insulator. Attempts to obtain the 8:1 salt are now in progress.

Focusing now on the structure and properties of the novel radical salt reported in this work, the following points have to be emphasized:

(i) With respect to the structure, the most attractive aspect concerns the unprecedented packing of the organic molecules, which, instead of forming stacks in order to maximize the intermolecular contacts through the π molecular orbitals, are packed, forming layers with side-on intermolecular contacts. Numerous short intermolecular distances involving the Se atoms
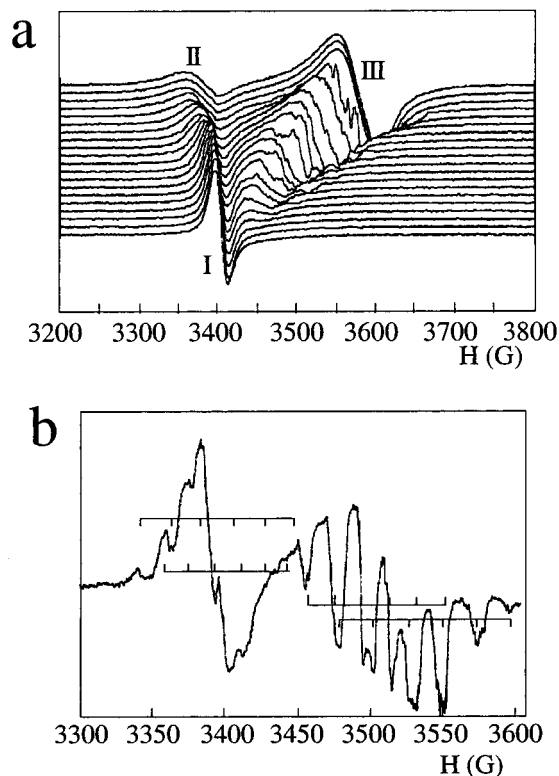
(18) Ouahab, L.; Bencharif, M.; Mhanni, A.; Pelloquin, D.; Halet, J. F.; Peña, O.; Padiou, J.; Grandjean, D.; Garrigou-Lagrange, C.; Amiell, J.; Delhaès, P. *Chem. Mater.* **1992**, *4*, 666.

Figure 4. (a) Thermal variation of the ESR spectra of the radical salt $(BEST)_3H[PMo_{12}O_{40}]\cdot CH_3CN\cdot CH_2Cl_2$. Every three spectra represent a decrease of $\sim$1 K from 10 K (front) to 4.2 K (back). (b) ESR spectrum of the title compound at 6.7 K showing the two sextuplets observed in the signals II and III as a consequence of the electron localization on a single Mo site (see text).

are observed both within and between the layers, giving rise to a 3D organic network in which all the unpaired spins of the $BEST^+$ radicals are strongly antiferromagnetically coupled. A second aspect of interest concerns the large number of crystallographically independent organic molecules. Five different types of BEST's are present in the structure, while in the related ET salts the maximum number is 3.

(ii) As far as the polyoxometalates are concerned, the most original result deals with the possibility of following through ESR the electronic localization−delocalization process in the one-electron-reduced Keggin polyoxometalate $[PMo_{12}O_{40}]^{4-}$. In the solid state, it has previously been very difficult to observe the hyperfine spectra of this mixed-valence cluster due to dipolar broadening of the lines. At best, only weak satellite peaks were observed at low temperatures. For example, for the related radical salt $[ET]_8[PMo_{12}O_{40}]$ only a close examination of the spectra at the lowest temperature (4.3 K) revealed fine structures; they were so weak that a second-derivative spectrum was needed in order to make them more pronounced.[2f] In the present case, thanks to the larger size of the organic molecules and to the complete pairing of their spins, the reduced polyoxometalates are well isolated, from the magnetic point of view, allowing a clear observation of the hyperfine components in the low-temperature single-crystal spectra. A comparison of the ESR results reported in this work to those previously reported in acetonitrile solutions containing the $[PMo_{12}O_{40}]^{4-}$ polyanion[17] indicates that the thermally activated electron hopping appears to be much easier in this solid than in the solutions. Thus, in solution, the hyperfine components were clearly detectable below 60 K, while in the present case, evidence of the electron

localization (splitting of the ESR signal or hyperfine splittings) has been observed only below 10 K.

Supporting Information Available: ORTEP drawings with labeling schemes and tables giving complete X-ray data collection and structure refinement details, atomic coordinates, bond distances and angles, and thermal parameters for the title compound (14 pages). Ordering information is given on any current masthead page.

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