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Radical salts of the organic donor BET-TTF† with polyoxometalate clusters‡

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The synthesis, structures and physical characterizations of the first radical ion salts of the organic donor BET-TTF **1** with polyoxometalate clusters ($[M_6O_{19}]^{2-}$; M = W^{VI}, Mo^{VI}, **2**) are reported. The 2 : 1 salts $(BET\text{-}TTF^+)_2[M_6O_{19}]^{2-}$ are formed by pairs of the BET-TTF$^+$ radical cations surrounded by polyanions so as to form a 3D packing of anions and cations with short intermolecular contacts between the cation pairs. The synthesis, physical properties and main structural features of the first radical ion salts of the organic donor BET-TTF **1** with the polyoxometalate cluster $[SiW_{12}O_{40}]^{4-}$ **3** are also reported. The 4 : 1 salt $(BET\text{-}TTF^+)_4[SiW_{12}O_{40}]^{4-}$ is formed by a 2D hexagonal packing of anions and by isolated BET-TTF$^+$ pairs. The compounds are insulators and diamagnetic.

A current approach to obtaining new molecular conductors consists of combining organic electron donor molecules with large cluster anions. The so-called polyoxometalates offer interesting structural and electronic characteristics in this context.[1]

(i) These soluble metal–oxides show different sizes, shapes and charges which are maintained in aqueous and non-aqueous solvents as well as in the solid state. These features can induce new packings in the molecular constituents of the conducting part, leading to new band structures and therefore to unusual electrical properties.[1,2]

(ii) They can have a magnetic character when they accommodate magnetic ions or clusters in the structure, or when they act as electron acceptors giving rise to delocalized mixed-valence clusters. These electronic features provide the opportunity to create systems combining magnetic and conducting properties.[3]

The examples so far reported of organic donor–inorganic cluster hybrids are almost exclusively based on the combination of commercially available tetrathiafulvalene (TTF) or bis(ethylenedithio)-TTF (BEDT-TTF or ET) with polyoxometalates having metal nuclearities of six (Lindqvist $[M_6O_{19}]^{2-}$; M = W^{VI}, Mo^{VI}),[2,4] eight (octamolybdate β-$[Mo_8O_{26}]^{4-}$), twelve {Keggin $[XM_{12}O_{40}]^{(8-n)-}$ (X^{n+} = P^V, Si^{IV}, B^{III}, Fe^{3+}, 2H$^+$, Co^{2+}, Cu^{2+}, *etc.*; M = W^{VI}, Mo^{VI}}[5] and eighteen (Wells–Dawson $[P_2W_{18}O_{62}]^{6-}$).[6] With the aim of extending these studies to other organic donors we have combined the molecule bis(ethylenethio)-TTF (in short BET **1**) with Lindqvist **2** (W and Mo derivatives) and Keggin **3** ($[SiW_{12}O_{40}]^{4-}$ anion) polyoxometalates. This organic donor has shown a good ability to form conducting radical salts with simple monoanions[7] such as for example XF_6^- (X = P, As, Sb) or SCN$^-$ with enhanced structural and electronic dimensionalities and also with magnetic anions[8] of the type FeCl$_4^-$. However, in most cases the salts of **1** do not crystallize properly and more than one compound can be formed in the same experiment. Despite this intrinsic difficulty we show herein that radical salts of **1** of sufficient quality for structural and physical characterization can be obtained using polyoxometalate clusters as counterions.

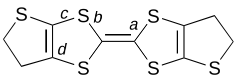
Results and Discussion

The radical salts of BET with the Lindqvist anions $[M_6O_{19}]^{2-}$ (M = W and Mo) 4 and 5

The two salts containing the $[M_6O_{19}]^{2-}$ anions were obtained as single crystals by electrocrystallization. Both salts are isostructural and crystallize in the triclinic system $P\bar{1}$ (see Table 1). The unit cell is displayed in Fig. 1(*a*) and contains two BET crystallographically equivalent molecules and one Lindqvist anion located in the apexes of the unit cell.

The BET molecules present a disorder affecting the sulfur atoms external to the TTF core which are disordered over two different positions. These sites have a multiplicity of 0.5 for C and 0.5 for S. This disorder may be due to the presence of two different orientations of the pure *trans* isomer of the BET molecule (starting material), or maybe to the possible isomeriz-

Table 1 Relevant intramolecular distances of the BET molecule in the salts $BET_2[M_6O_{19}]$ and calculation of its charge Q using the formula of Guionneau *et al.*;[10] $Q = 6.347 - 7.463\{(b+c)-(a+d)\}$



compound	a/Å	b/Å	c/Å	d/Å	Q_{calc}
$BET_2[W_6O_{19}]$	1.38(1)	1.73(1) 1.73(1) 1.72(1) 1.72(1)	1.74(1) 1.72(1) 1.70(1) 1.70(1)	1.33(2) 1.35(2)	0.95
$BET_2[MoO_{19}]$	1.392(5)	1.724(3) 1.730(3) 1.734(3) 1.719(3)	1.726(3) 1.731(4) 1.719(3) 1.717(4)	1.348(5) 1.353(5)	1.07

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† BET-TTF = bis(ethylenethio)tetrathiafulvalene.

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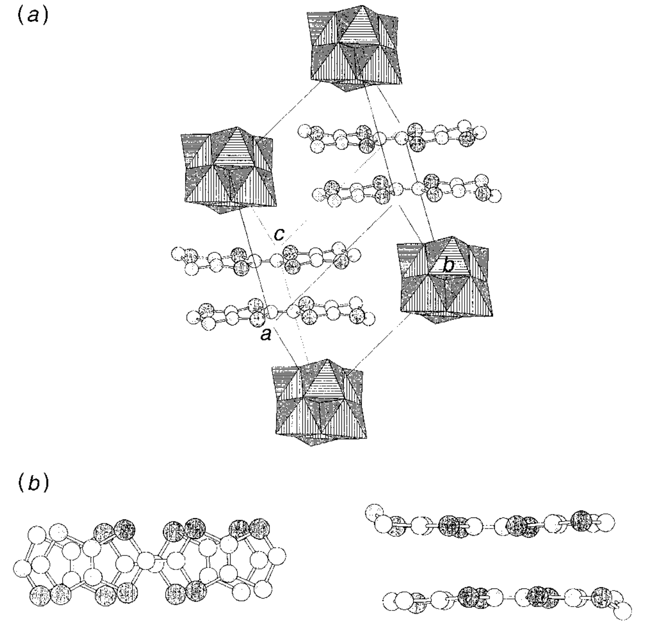

Fig. 1 (*a*) View of the unit cell of the salts **4** and **5**; (*b*) two views of a dimer of BET molecules in **4** and **5**

ation in solution of the *cis–trans* species during the electrooxidation.[9] The BET molecules are associated forming centrosymmetric face to face dimers with short contacts between the central C and S atoms [C(1)—C(1) 3.34 Å, S(2)—S(3) 3.47 Å] although they are not eclipsed [Fig. 1(*b*)]. These dimers are surrounding the polyoxoanions so as to form a compact packing of anions and cations which is reminiscent of that of the NaCl salt. Thus, in the (10$\bar{1}$) plane we observe that anions and dimeric cations are alternating along the directions [101] and [$\bar{1}2\bar{1}$] [Fig. 2(*a*)]. However, due to the tendency of the organic donors to stack, the BET dimers are not completely isolated but show short contacts with the neighbouring dimers. In the above plane the shortest contacts occur in the *b* direction and involves two sulfur atoms (distance d_3 in Fig. 2). Strong interdimer interactions are also observed along the *a* direction [Fig. 2(*b*)].

In view of the stoichiometry 2:1 of **4** and **5** the organic molecules are expected to be completely ionized (charge +1). This can be confirmed from the correlation between the intramolecular distances of the TTF skeleton and the oxidation degree *Q* proposed by Guionneau *et al.*[10] for the BEDT–TTF molecule (see Table 2) that nicely fits to *Q* values of 0.95 and 1.07 for **4** and **5**, respectively. A further support of this ionic charge is provided by the NIR–VIS spectra which exhibit a very strong and broad band centered at 7700 cm^{-1} which is to be associated with the charge transfer between fully oxidized donors (B band), while the band associated with the electron transfer between partially charged donors (A band) does not appear.[11] The IR spectrum is also typical of fully charged BET ions. In a mixed valence system broad bands associated with the a$_g$ modes are observed in the region 800–1600 cm^{-1} arising from the coupling between delocalized electrons and vibrational modes of the double bonds. In the present case however only sharp bands are observed. The lack of a mixed valence character in the organic part prevents the occurrence of electron delocalization. In fact, the transport properties measured on single crystals (two-probe) indicate that both salts are insulators with low conductivity values [$\sigma_{RT} = 3.2 \times 10^{-6}$ S cm^{-1}] and high activation energies ($E_a = 240$ meV in the range 240–300 K). The temperature dependent magnetic susceptibility indicates that the two compounds are diamagnetic. This result is consistent with the dimerization of the charged BET molecules which have their spins antiferromagnetically coupled giving rise to a $S=0$ ground spin state. Accordingly, only a weak signal is observed in the EPR spectra of both salts. The thermal dependence of the intensity of this signal (proportional to the spin susceptibility) is plotted in Fig. 3. Note that this signal stays roughly constant in the investigated temperature range. Such a behavior can not be attibuted to the exclusive presence of a paramagnetic impurity. The possibility of an excited triplet state thermally accessible

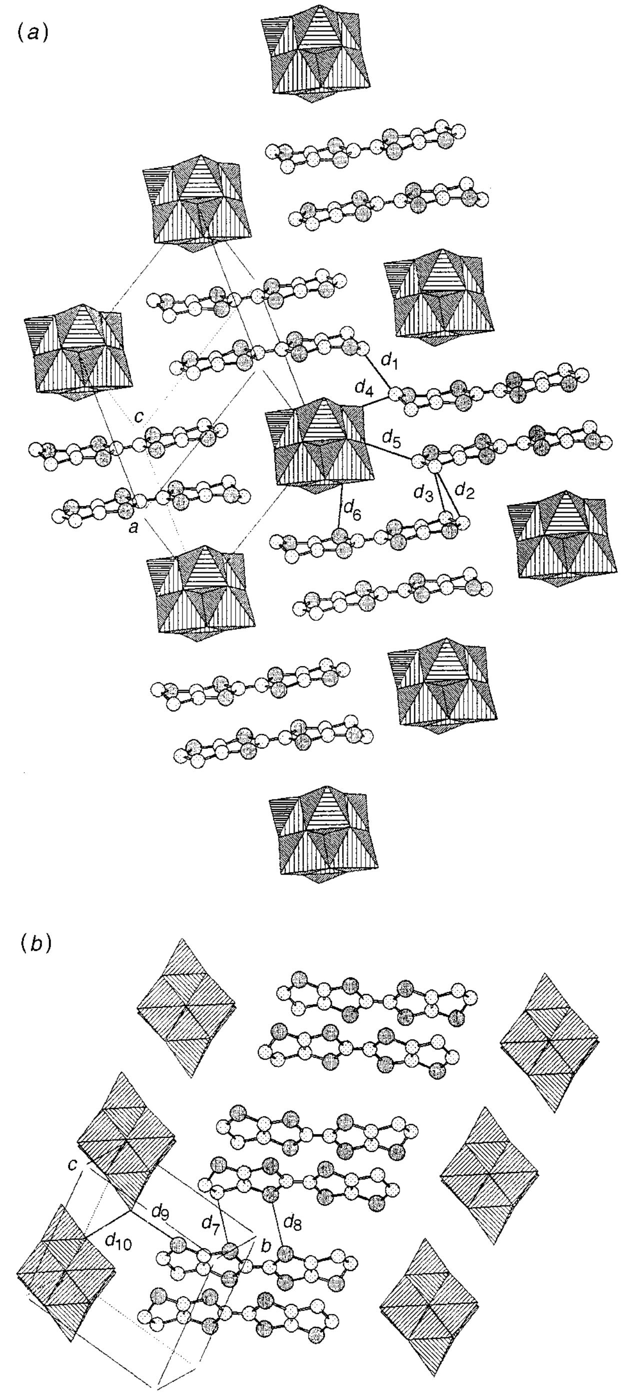

Fig. 2 (*a*) View of the structure of **4** and **5** in the (10$\bar{1}$) plane. Shortest intermolecular distances for **4** (**5**) in Å: d_1 [C(12)—C(12)] = 3.69 (3.67), d_2 [S(6)/C(8)—C(11)] = 3.71 (3.71), d_3 [S(6)/C(8)—C(8)/S(6)] = 3.69 (3.71), d_4 [S(8)/C(10)—O(1)] = 3.18 (3.16), d_5 [C(11)—O(6)] = 3.32 (3.29), d_6 [S(4)—O(8)] = 3.13 (3.12). (*b*) View of the structure in the (012) plane. Shortest intermolecular distances for **4** (**5**) in Å: d_7 [S(7)/C(9)—S(1)] = 3.53 (3.54), d_8 [S(3)—S(3)] = 3.61 (3.62), d_9 [S(5)/C(7)—O(3)] = 3.43 (3.42), d_{10} [O(3)—O(4)] = 3.20 (3.21).

Table 2 Crystallographic data for $C_{20}H_{16}S_{12}W_6O_{19}$ **4**, $C_{20}H_{16}S_{12}Mo_6O_{19}$ **5** and $C_{42}H_{39}NS_{24}SiW_{12}O_{42}$ **6**

chemical formula	$C_{20}H_{16}S_{12}W_6O_{19}$	$C_{20}H_{16}S_{12}Mo_6O_{19}$	$C_{42}H_{39}NS_{24}SiW_{12}O_{42}$
a/Å	8.362(5)	8.352(6)	24.807(5)
b/Å	10.925(6)	10.919(6)	24.194(5)
c/Å	11.664(4)	11.666(5)	14.357(3)
α/degrees	65.28(3)	65.30(4)	90.00
β/degrees	79.11(2)	79.02(3)	90.00
γ/degrees	80.73(3)	80.64(4)	90.00
V/Å^3	946.5(8)	944.7(8)	8616.8(31)
Z	1	1	3
M	2048.21	1520.75	4233.6(3)
space group	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)	$Pnma$ (no. 62)
T/K	293(2)	293(2)	293(2)
λ/Å	0.71073	0.71073	0.71073
D_c/g cm^{-3}	3.593	2.673	3.704
μ(Mo-Kα)/cm^{-1}	18.896	2.672	24.248
$R(F)^a$	0.0363	0.0228	0.0723
$R_w(F)^b$	0.1214	0.0846	0.1937

$^aR=\Sigma[|F_o|-|F_c|]/\Sigma|F_o|$; $^bR_w=[\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w=4F_o^2/[\sigma^2(|F_o|)-(0.07|F_o|^2)]$.

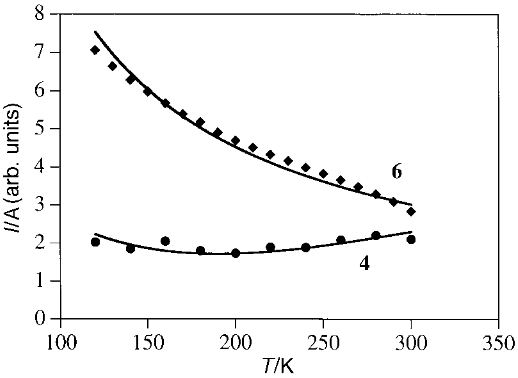

Fig. 3 Thermal dependence of the intensity of the EPR signal for the compounds $BET_2[W_6O_{19}]$ **4** and $BET_4[SiW_{12}O_{40}]$ **6**

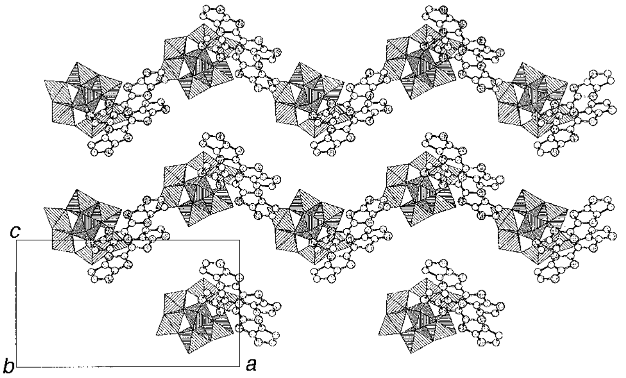

Fig. 4 View of the structure of **6** in the *ac* plane, showing the channels occupied by the disordered BET molecules

can not be excluded. In fact, the data fit to the sum of a paramagnetic contribution, C/T, and a thermally activated contribution, $(C'/T)\exp(-J/kT)$, with a coupling constant J *ca.* 700 cm^{-1} and a 2% paramagnetic contribution.

The radical salt $BET_4[SiW_{12}O_{40}]\cdot CH_3CN\cdot 2H_2O$ 6

The preparation of radical salts of the BET donor with different polyoxometalates having the Keggin structure {series $[XM_{12}O_{40}]$ ($X=P^V$, Si^{IV}, B^{III}, Fe^{3+}, $2H^+$, Co^{2+}, Cu^{2+}, *etc.*; $M=W$, Mo) and $[XM(H_2O)W_{11}O_{39}]$ ($X=P^V$, Si^{IV}; $M=Ni^{2+}$, Co^{2+}, Cu^{2+}, Cr^{3+}, Fe^{3+})} was explored using the electrocrystallization technique. However, only the Si derivative gave single crystals suitable for a crystallographic study. The other polyanions do not gave any solid derivative and only in the cases of PMo_{12} and $PMnW_{11}$ was some powder deposited on the electrode.

Elemental analysis of **6** is consistent with the formula $BET_4[SiW_{12}O_{40}]\cdot CH_3CN\cdot 2H_2O$. Owing to the poor quality of the crystals only limited information about the crystal structure could be extracted by X-ray diffraction experiments. Only the atoms of the Keggin anion as well as those of two of the four BET molecules could be found. The two remaining BET molecules are strongly disordered in the crystal and can not be localized (fragments of the central part of these molecules have been localized in the Fourier maps). Fig. 4 shows a view of the structure in the *ac* plane. As we can see the Keggin anions are forming hexagonal layers in this plane. The two BET molecules are located in between these anions and are associated forming face to face dimers with a geometry which is similar to that found in the Lindqvist salts **4** and **5**, but in this case the dimers are well isolated. The two disordered BET molecules are occupying the hexagonal channels running along the *b* axis created by the polyoxoanions.

Taking into account the stoiquiometry of **6** (4:1) and the charge of the anion $[SiM_{12}O_{40}]$ (-4) the four BET molecules should be completely ionized (charge $+1$). This was confirmed by the absence of the characteristic 'A' band of mixed-valence species in the NIR spectrum. Accordingly the radical-cation salt is an insulator. The magnetic properties indicate a complete coupling of the spins, which is in agreement with the association in dimers of the radical cations. In fact, the EPR spectra show an extremely weak signal which, according to the thermal behavior, has to be attributed to the presence of a small amount of paramagnetic impurity (Fig. 3).

Conclusions

The first radical-cation salts of the electron donor molecule BET with Lindqvist and Keggin polyoxometalate clusters have been prepared. The X-ray crystal structures of these salts show that in both cases the donor molecules are forming non-eclipsed dimers in the solid. However the different size and charge of the two clusters have resulted in a different packing of these dimers with a significant extent of the intermolecular interactions in the Lindqvist derivatives, while quasi-insulated dimers are present in the Keggin derivative. Furthermore, EPR measurements suggest the presence of a thermally activated triplet state in the $[BET^{\cdot +}]_2$ dimers of the Lindqvist salts.

In the reported salts the donor molecules have been found to be completely ionized and not surprisingly they are insulators with very low conductivity values. Compared with the equivalent BEDT–TTF radical salts we notice that a similar 2:1 insulating salt formed by $[BEDT\text{–}TTF^{\cdot +}]_2$ dimers has

Table 3 Atomic coordinates and isotropic or equivalent isotropic thermal parameters for the salt $\mathrm{BET_2[W_6O_{19}]}$

atom	x	y	z	U^a/Å^2	atom	x	y	z	U^a/Å^2
W(1)	0.15295(5)	0.33787(4)	−0.06422(4)	0.0274(1)	C(3)	0.451(1)	0.179(1)	0.614(1)	0.031(2)
W(2)	−0.23398(5)	0.38887(4)	0.04408(4)	0.0293(1)	C(4)	0.555(1)	0.194(1)	0.509(1)	0.034(2)
W(3)	0.05657(5)	0.37228(4)	0.20745(4)	0.0275(1)	C(5)	0.130(1)	0.764(1)	0.343(1)	0.032(2)
O(1)	0.262(1)	0.2156(7)	−0.1099(7)	0.040(2)	C(6)	0.236(1)	0.780(1)	0.236(1)	0.035(2)
O(2)	0.099(1)	0.2794(8)	0.3598(7)	0.042(2)	C(7)^b	0.4558(6)	0.0281(5)	0.7392(5)	0.045(1)
O(3)	−0.400(1)	0.3056(10)	0.0770(9)	0.051(2)	C(8)^b	0.6883(7)	0.0581(6)	0.5139(6)	0.052(1)
O(4)	−0.3089(9)	0.5414(7)	0.0887(7)	0.033(2)	C(9)^b	−0.0158(5)	0.9004(4)	0.3318(4)	0.0281(8)
O(5)	−0.0668(9)	0.2821(7)	−0.0183(7)	0.032(2)	C(10)^b	0.214(1)	0.9252(7)	0.1132(8)	0.078(2)
O(6)	0.1671(9)	0.2662(7)	0.1130(7)	0.029(2)	C(11)	0.618(2)	−0.036(1)	0.667(2)	0.051(3)
O(7)	−0.075(1)	0.5284(7)	0.2196(7)	0.033(2)	C(12)	0.023(2)	0.962(1)	0.166(2)	0.063(5)
O(8)	0.232(1)	0.4833(7)	0.1315(7)	0.034(2)	H(1)^a	0.478(3)	0.034(1)	0.816(4)	0.050
O(9)	−0.1413(9)	0.3062(7)	0.2004(7)	0.033(2)	H(2)^a	0.359(3)	−0.019(1)	0.757(4)	0.050
O(10)	0.0000	0.5000	0.0000	0.024(2)	H(3)^a	0.672(3)	0.021(1)	0.455(4)	0.050
S(1)	0.3157(3)	0.3193(2)	0.6116(2)	0.0315(5)	H(4)^a	0.802(3)	0.076(1)	0.502(4)	0.050
S(2)	0.5486(3)	0.3477(3)	0.3815(3)	0.0356(6)	H(5)^a	−0.126(3)	0.874(1)	0.367(4)	0.050
S(3)	0.1489(3)	0.6155(2)	0.4717(2)	0.0312(5)	H(6)^a	0.012(3)	0.960(1)	0.366(4)	0.050
S(4)	0.3809(3)	0.6501(3)	0.2409(2)	0.0334(5)	H(7)^a	0.226(3)	0.915(1)	0.033(4)	0.050
S(5)^b	0.4558(6)	0.0281(5)	0.7392(5)	0.045(1)	H(8)^a	0.287(3)	0.989(1)	0.107(4)	0.050
S(6)^b	0.6883(7)	0.0581(6)	0.5139(6)	0.052(1)	H(9)	0.592(2)	−0.121(1)	0.671(2)	0.050
S(7)^b	−0.0158(5)	0.9004(4)	0.3318(4)	0.0281(8)	H(10)	0.708(2)	−0.057(1)	0.716(2)	0.050
S(8)^b	0.214(1)	0.9252(7)	0.1132(8)	0.078(2)	H(11)	−0.049(2)	0.924(1)	0.136(2)	0.050
C(1)	0.386(1)	0.4193(9)	0.4556(9)	0.028(2)	H(12)	−0.002(2)	1.059(1)	0.130(2)	0.050
C(2)	0.311(1)	0.5477(9)	0.396(1)	0.028(2)					

$^a U_{\mathrm{eq}} = (4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$; H atoms with fixed U. ^{b}Atoms with multiplicity of 0.5.

Table 4 Atomic coordinates and isotropic or equivalent isotropic thermal parameters for the salt $\mathrm{BET_2[Mo_6O_{19}]}$

atom	x	y	z	U^a/Å^2	atom	x	y	z	U^a/Å^2
Mo(1)	0.15585(4)	0.33745(3)	−0.06201(3)	0.03034(7)	C(2)	0.3134(4)	0.5484(3)	0.3947(3)	0.0289(6)
Mo(2)	−0.23197(4)	0.38691(3)	0.04392(3)	0.03308(8)	C(3)	0.4487(4)	0.1792(3)	0.6153(3)	0.0314(6)
Mo(3)	0.05504(4)	0.37431(3)	0.20835(3)	0.03162(8)	C(4)	0.5567(4)	0.1929(4)	0.5099(3)	0.0333(7)
O(1)	0.2616(4)	0.2174(3)	−0.1097(2)	0.0414(6)	C(5)	0.1279(4)	0.7670(3)	0.3410(3)	0.0324(7)
O(2)	0.0954(4)	0.2787(3)	0.3583(2)	0.0437(7)	C(6)	0.2348(5)	0.7822(3)	0.2342(3)	0.0338(7)
O(3)	−0.3979(4)	0.3043(3)	0.0747(3)	0.0498(7)	C(7)^b	0.4562(2)	0.0280(2)	0.7409(2)	0.0502(4)
O(4)	−0.3100(3)	0.5403(3)	0.0910(2)	0.0350(5)	C(8)^b	0.690(1)	0.056(1)	0.513(1)	0.0476(4)
O(5)	−0.0667(3)	0.2834(2)	−0.0232(2)	0.0347(5)	C(9)^b	−0.014(1)	0.9002(9)	0.329(1)	0.0346(3)
O(6)	0.1649(3)	0.2625(2)	0.1135(2)	0.0324(5)	C(10)^b	0.216(2)	0.928(1)	0.110(1)	0.0674(6)
O(7)	−0.0775(3)	0.5247(2)	0.2214(2)	0.0350(5)	C(11)	0.6183(6)	−0.0395(4)	0.6682(5)	0.055(1)
O(8)	0.2362(3)	0.4809(3)	0.1310(2)	0.0359(5)	C(12)	0.0224(2)	0.9645(2)	0.1649(2)	0.060(1)
O(9)	−0.1427(3)	0.3042(2)	0.2016(2)	0.0342(5)	H(1)^b	0.4799(2)	0.0342(2)	0.8165(2)	0.050
O(10)	0.0000	0.5000	0.0000	0.0253(6)	H(4)^b	0.672(1)	0.019(1)	0.454(1)	0.050
S(1)	0.3154(1)	0.31878(8)	0.61201(8)	0.0322(2)	H(5)^b	0.013(1)	0.9591(9)	0.364(1)	0.050
S(2)	0.5490(1)	0.3475(1)	0.38096(8)	0.0361(2)	H(6)^b	−0.124(1)	0.8740(9)	0.363(1)	0.050
S(3)	0.1486(1)	0.61678(8)	0.47129(8)	0.0323(2)	H(7)^b	0.227(2)	0.917(1)	0.030(1)	0.050
S(4)	0.3807(1)	0.65015(9)	0.23974(8)	0.0340(2)	H(8)^b	0.290(2)	0.991(1)	0.103(1)	0.050
S(5)^b	0.4562(2)	0.0280(2)	0.7409(2)	0.0502(4)	H(9)	0.5887(6)	−0.1231(4)	0.6709(5)	0.050
S(6)^b	0.6903(2)	0.0571(2)	0.5136(2)	0.0476(4)	H(10)	0.7077(6)	−0.0633(4)	0.7181(5)	0.050
S(7)^b	−0.0152(2)	0.9025(2)	0.3304(2)	0.0346(3)	H(11)	−0.0496(2)	0.9261(2)	0.1352(2)	0.050
S(8)^b	0.2135(2)	0.9290(2)	0.1114(2)	0.0674(6)	H(12)	−0.0032(2)	1.0619(2)	0.1300(2)	0.050
C(1)	0.3857(4)	0.4181(3)	0.4563(3)	0.0291(6)					

$^a U_{\mathrm{eq}} = (4/3)\ [a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\gamma)B(1,2) + ac(\cos\beta)B(1,3) + bc(\cos\alpha)B(2,3)]$; H atoms with fixed U. ^{b}Atoms with multiplicity of 0.5.

been found with the Lindqvist anions, although in this last case the structure is formed by alternating layers of the organic donor and the anions,[12] as is customarily observed in the BEDT–TTF salts. With the Keggin anions the differences between the BEDT–TTF salts and the BET ones are more pronounced. Thus, while the former donor forms a wide 8:1 family of semiconducting salts in which mixed-valence layers of the organic donor alternate with anion layers,[5a] the latter salts exhibit a dimeric association of fully charged radical cations. The lack of mixed valence states in the reported BET salts may be then attributed to the larger tendency of these donors to form $[\mathrm{BET}^{\cdot+}]_2$ dimers. The preparation of related BET salts having higher electron delocalization and, eventually, a magnetic component is now being explored. With this aim we are using Lindqvist and Keggin anions of different charges containing magnetic centers.

Experimental

Synthesis

All the radical salts were obtained on a platinum wire electrode by anodic oxidation of the organic donor **1** in a U-shaped electrocrystallization cell under low constant current (1.2 μA) in the presence of the tetrabutylammonium ($\mathrm{TBA^+}$) salts of the polyanions as supporting electrolyte. The $\mathrm{TBA^+}$ salts of **2** were prepared by metathesis from the $\mathrm{Na^+}$ salts,[13] and recrystallized from acetone or DMF. The $\mathrm{TBA^+}$ salt of **3** was prepared by metathesis from the acid (commercial grade), and recrystallized from acetonitrile. The solvents were not previously dried. All the crystals were collected, washed with $\mathrm{CH_3CN}$, $\mathrm{CH_2Cl_2}$ and/or DMF (to remove any portion of neutral BET crystals or of the $\mathrm{TBA^+}$ salts of the polyanions), and air-dried. Good quality black prismatic crystals of

$BET_2[M_6O_{19}]$ (M = W **4**, Mo **5**) were obtained in DMF, and shiny black needle-like crystals of $BET_4[SiW_{12}O_{40}]$ **6**, were obtained from CH_3CN–CH_2Cl_2 (2 : 3). The stoichiometries of **4** and **5** were only determined from the X-ray structure. For **6** the stoichiometry was determined from elemental analysis which indicated that the correct formula for **6** is $BET_4[SiW_{12}O_{40}]\cdot CH_3CN\cdot 2H_2O$ (Found: C, 11.81; H, 0.94; N, 0.39; S, 16,91%. Calc.: C, 11.92; H, 0.97; N, 0.33; S, 18.18%).

X-Ray crystallography

Crystals of the three salts, which are stable in air, were mounted on an Enraf-Nonius CAD4 diffractometer equipped with a graphite crystal, incident beam monochromator. Preliminary examination and data collection were performed with Mo-Kα radiation. Cell constants and an orientation matrix for data collection were obtained from least-squares refinement, using the setting angles of 25 reflections. Lorentz, polarization and a semi-empirical absorption correction (ψ-scan method)[14] were applied to the intensity data. Other important features of the crystals are summarized in Table 2 with atomic coordinates and thermal parameters for **4** and **5** listed in Tables 3 and 4. The X-ray crystal structures were determined for **4** and **5** (M = Mo, W), which are isostructural as expected, and were solved by direct methods and developed with successive full-matrix least-squares refinements and difference Fourier syntheses, which showed all the atoms of organic donors and polyanions. In contrast, the structure of **6** could not be fully determined and only the atoms of polyanions and two BET molecules could be found. This was owing to the presence of disorder affecting the position of the other two BET molecules in the formula, and to the poor quality of the crystals, which prevented the assigment of peaks with $\Delta\rho < 2.53$ e Å^{-3}. Full crystallographic details, excluding structure factors, have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1998, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/68.

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