A structural specificity of radical cation salts based on BEDT-TTF with $[ReX_6]^{2-}$ (X=Cl or Br) anion

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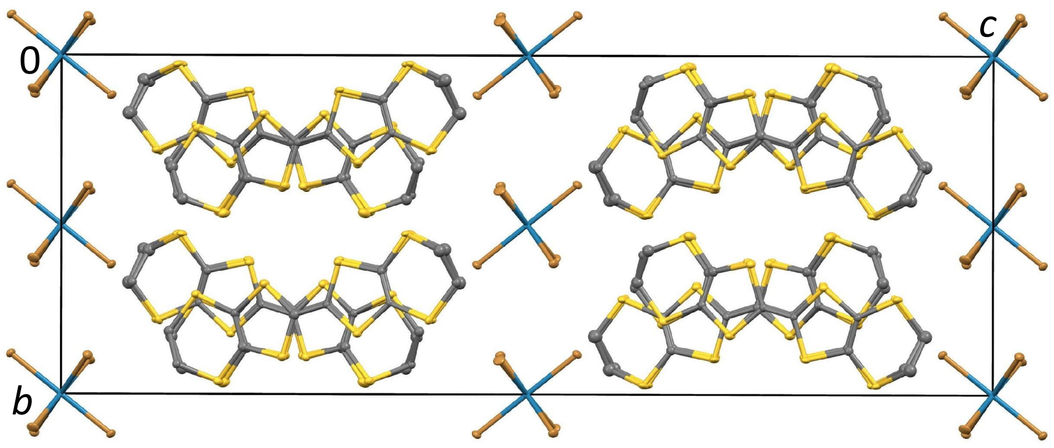
Introduction

Multifunctional materials attract much attention last decades. Motivation of this work was combining conductivity based on organic ET donor with magnetic properties of 5d-ion. This poster shows crystal structures of new radical cation salts of δ-$ET_4[ReCl_6]DMF_2$ (**1**), δ-$ET_4[ReBr_6]DMF_2$ (**2**) and α'-$ET_4[ReBr_6]BN$ (**3**). They were obtained by electrocrystallization with using BN, EtOH and DMF as reaction solvents. All the salts (**1-3**) have layered structures. The **1** and **2** crystals are found to be isostructural and considerably different from early reported δ-$ET_4[ReCl_6]_{2-x}(CB)_x$ [1]. Crystals **3** undergo phase transition with doubling lattice at low temperature.
Crystal data for **1**-**3** are presented in Table 1.

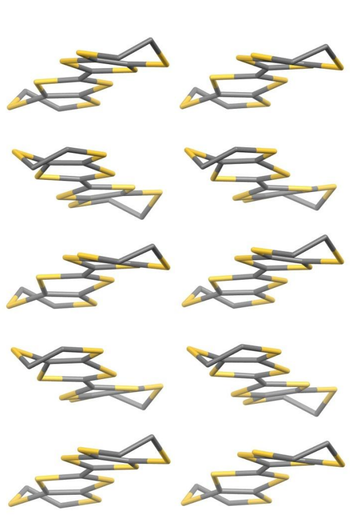
Table 1. Crystal data for new radical cation salts

	1	**2**		**3**	
T, K	295	295	120	295	120
a, Å	15.584(1)	15.5412(4)	15.2162(2)	17.3908(3)	22.1507(3)
b, Å	13.2894(7)	13.2757(3)	13.2152(2)	21.2040(4)	24.1936(3)
c, Å	36.130(2)	36.5543(7)	36.345(1)	22.4890(4)	29.9878(3)
α, °	90	90	90	111.306(2)	78.213(1)
β, °	92.484(5)	91.494(2)	91.169(2)	101.791(2)	81.853(1)
γ, °	90	90	90	102.144(2)	63.222(1)
V, Å^3	7475.6(8)	7539.4(3)	7306.8(3)	7185.4(2)	14021.9(3)
SG, *Z*	*C* 2/*c*, 4	*C* 2/*c*, 4	*C* 2/*c*, 4	*P* -1, 4	*P* -1, 8

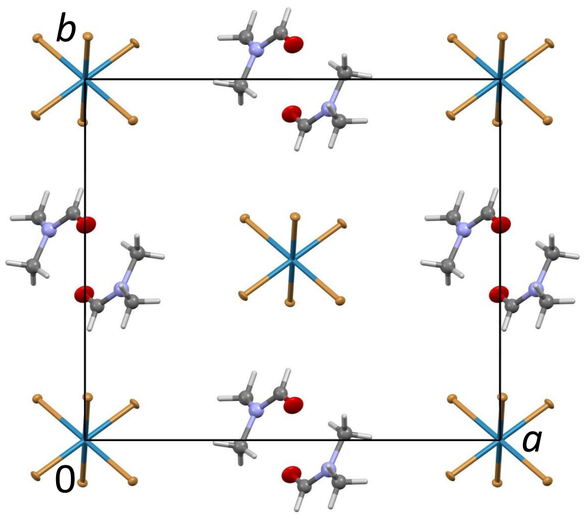
δ-$ET_4[ReBr_6]DMF_2$ (2)



Projection of structure **2** at 120K along *a*-direction. DMF molecules and H-atoms are omitted for clarity.

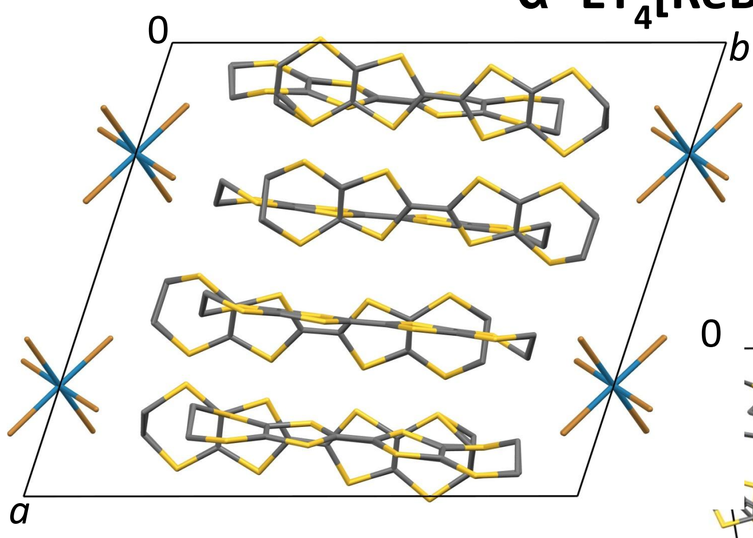


Cation layer of structure **2** at 120K. Each molecule turns along axis normal to the molecule.

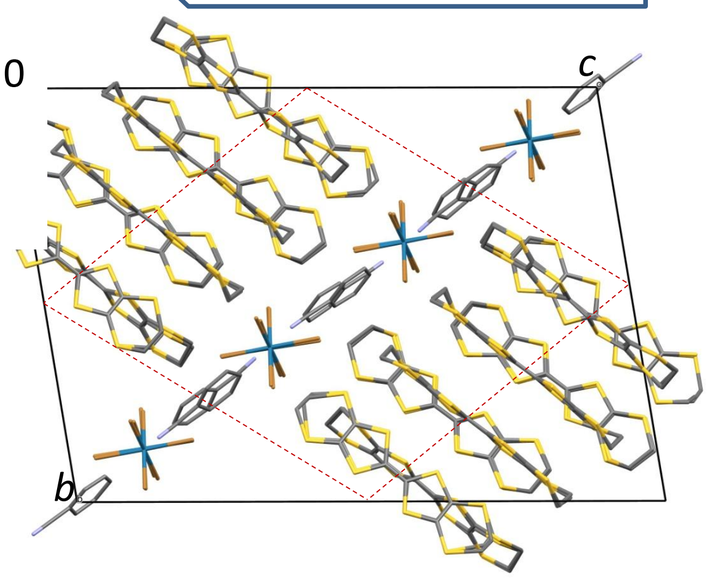


Projection of anion layer of **2** at 120K along *c*-direction. Anion and solvent are well ordered.

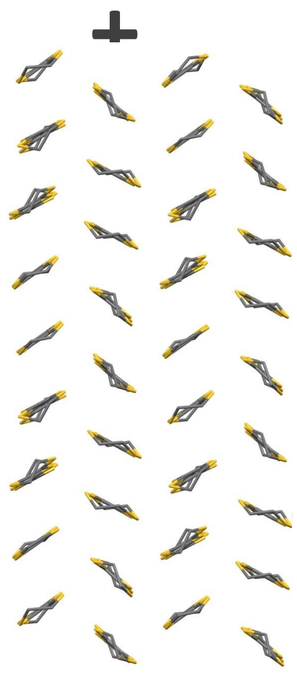
α'-$ET_4[ReBr_6]BN$ (3)



Projection of structure **3** at RT along *c*-direction. BN molecules and H-atoms are omitted for clarity.



Projection of structure **3** at 120K along *a*-direction. Red lines represent RT cell. H-atoms are omitted for clarity.



Charge distribution in cation layers of **3** at RT (left figure) and 120K (right figure)

8 independent ET form conducting layer at RT, while 16 independent ET already in the layer at low temperature.

At 120K charge ordering is not so strong as at RT.

Conclusion

Studied crystals are semiconductors. Crystals **1** and **2** have δ-type packing of ET cations and more or less uniformed charge distribution in layer. However all crystals were twins and precision of the charge calculation is very low.

Phase transition with doubling cell was found in crystals **3**. During phase transition charge distribution becomes less ordered at 120K.

A summary of known radical cation salts based on ET with octahedral complex anions of 5d-metals is collected in Table 2. Relationship between crystal structure and conducting properties is also noted.

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[1] Kazakova A.V., Yagubskii E.B., Kushch L.A., Buravov L.I., Tolstikova A.O., Khasanov S.S., Shibaeva R.P., Abstracts ICSM-2014, P3.033.

Table 2. Crystal data for known radical cation salts with octahedral anions of 5d-metals.

κ-$(ET)_4[OsNOCl_5]\cdot BN$	8.741	11.90	17.18	95.31	92.65	95.13	1770.6	*P* -1, 1	I, XASCEA *)
α'-$(ET)_4[OsNOCl_5]\cdot NB$	9.628	11.16	18.06	101.5	91.93	110.9	1765.3	*P* -1, 1	I, XASBUP
δ-$(ET)_4[OsNOCl_5]_{1.33}$	15.03	6.728	35.21	90	92.98	90	3556.3	*I* 2/*c*, 2	M-I, XASCAW
β''-$(ET)_3[OsNOCl_5]$	7.667	9.866	17.97	91.15	93.64	102.4	1324.2	*P* -1, 1	δ, TAXGEG
β-$(ET)_2[OsNOCl_5]$	8.725	10.35	11.10	110.4	98.43	103.8	881.8	*P*-1(*P*1), 1	I, XASCIE
β-$(ET)_2[IrCl_6]$	8.721	10.26	11.09	111.0	98.31	103.3	872.3	*P* -1, 1	I, RIHFAP
β-$(ET)_2[ReCl_6]$	8.728	10.34	11.13	110.9	98.37	103.4	884.7	*P* -1, 1	I
α'-$(ET)_4(ReCl_6)(BN)$	9.455	11.31	18.19	101.9	92.74	110.5	1767.3	*P* -1, 1	I, RIHFET
α'-$(ET)_4(ReCl_6)(DCE)_2$	9.056	11.09	36.23	90	95.37	90	3623.3	*P* $2_1/c$, 2	I, Ph.Tr.
α'-$(ET)_4(ReCl_6)(DCE)_2$ (120K)	14.26	21.09	36.22	85.28	86.73	81.33	10717	*P* -1, 6	Incom.
δ-$(ET)_4(ReCl_6)_{2-x}(CB)_x$	35.36	6.617	14.78	90	92.12	90	3456.1	*C* 2/*c*, 2	M-I, Ph. Tr.
δ-$(ET)_4(ReCl_6)_{2-x}(CB)_x$ (120K)	35.58	19.97	14.87	90	92.01	90	10565	*P* $2_1/c$, 6	I
δ-$(ET)_4(ReCl_6)(DMF)_2$	15.58	13.29	36.13	90	92.48	90	7475.6	*C* 2/*c*, 8	I
δ-$(ET)_4(ReBr_6)(DMF)_2$	15.54	13.28	36.55	90	91.49	90	7539.4	*C* 2/*c*, 8	I
α'-$(ET)_4(ReBr_6)(BN)$	17.39	21.20	22.49	111.3	101.8	102.1	7185.4	*P* -1, 8	I, Ph. Tr.
α'-$(ET)_4(ReBr_6)(BN)$ (120K)	22.15	24.19	29.99	78.21	81.85	63.22	14022	*P* -1, 16	I
1D-$(ET)(ReCl_4(ox))$	18.34	10.84	11.13	90	99.97	90	2179.4	*C* 2/*c*, 4	I, COBCAZ
α-$(ET)_4(ReCl_4(ox))BN$	11.85	32.91	36.42	90	96.74	90	14108	*P* $2_1/c$, 8	M-I, COBCED

*) M - metal, I - semiconductor, Ph.Tr. -phase transition, XASCEA et al. – CCDC ref. code