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Structure-properties relationships in organic molecular conductors based on radical cation salts with octahedral metal complexes as counterions

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Abstract

As a part of our general approach in the study of new hybrid molecular materials combining conducting properties with other physical phenomena, we analyze crystal structures and properties of radical cation salts with the photochromic metal mononitrosyl complexes and magnetic metal oxalates as counterions. A detailed comparative crystallochemical analysis of such materials coupled with calculation of their electronic band structures should allow us to conceive a scenario for the rational search of novel hybrid functional materials. © 2002 Elsevier Science B.V. All rights reserved.

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1. Introduction

Incorporation of photochromic metal mononitrosyl complexes or magnetic metal oxalates in organic matrices has recently been the object of considerable interest. Such hybrid organic-inorganic materials are likely to combine the good conducting properties of the organic component with the specific characteristics of the inorganic network. The potential interplay between different properties in such molecular solids may lead to organic conductors of a novel type. Along this line, we have recently studied radical cation salts of the organic π -donors BEDT-TTF (ET), BEDO-TTF (BEDO), EDT-TTF (EDT), DOET, TTT and TSeT with the $[Fe(CN)_5NO]^{2-}$ (nitroprusside—NP) and $[RuX_5NO]^{2-}$ (X = Br, Cl) anions, as well as those of the $(ET)_4A[M(C_2O_4)_3$]·DMF family, where A = NH₄⁺, K⁺; M = Fe, Cr. In this contribution we analyze the crystal structures and properties of radical cation salts with octahedral metal mononitrosyl complexes and metal oxalates as counterions. The structural comprehension is an extremely important and necessary prerequisite in order to rationally synthesize new

hybrid molecular conductors. A comparative crystallochemical analysis of the β'' -(ET)₄A[Fe(CN)₅NO]₂ and β'' -(ET)₄A[M(C₂O₄)]·Solvent families of organic metals suggests some possible routes to chemically modify these salts with the purpose of changing their physical properties.

2. Results and discussion

The radical cation salts with mononitrosyl complex anions which we have investigated by X-ray diffraction are listed in Table 1. In this contribution only the ET based salts are discussed.

2.1.
$$\beta$$
-(*ET*)₄*A*[*Fe*(*CN*)₅*NO*]₂, *A* = *Na*⁺, *K*⁺, *NH*₄⁺, *Tl*⁺, *Rb*⁺, *Cs*⁺ (*I*)

The crystal structures of several radical cation salts of organic π -donors of the TTF type with the NP anion have been solved to date. The crystal structures are very often disordered so that the CN and NO ligands are statistically distributed over some coordination positions. Moreover, the disorder precluded obtaining accurate M-N and N-O distances. However, it seemed that the (ET)₄A(NP)₂ family was

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 Table 1

 Radical cation salts with the metal mononitrosyl complexes as counterions

	Salt	References
I	$(ET)_4A[Fe(CN)_5NO]_2, A = Na^+, K^+, NH_4^+,$	[1–3]
	Tl^+ , Rb^+ , Cs^+	
II	(BEDO) ₃ [Fe(CN) ₅ NO] _{0.75}	[1,4]
	or (BEDO) ₄ [Fe(CN) ₅ NO]	
III	(EDT) ₃ [Fe(CN) ₅ NO]	[1]
IV	(DOET) ₄ [Fe(CN) ₅ NO] _{1.33} ·(C ₆ H ₅ Cl) _{0.67}	This work, (a)
V	(TTT) ₃ [Fe(CN) ₅ NO]	[5]
VI	(TSeT) ₃ [Fe(CN) ₅ NO]	[5]
VII	κ-(ET) ₄ [RuNOBr ₅]·BN	This work
VIII	δ -(ET) ₄ [RuNOBr ₅] _x	This work
IX	δ -(ET) ₄ [RuNOCl ₅] _{1.33} or (ET) ₃ [RuNOCl ₅]	This work
Х	κ -(ET) ₄ [RuNOCl ₅]·Solv., Solv. = (BN, NB) ^a	This work

(a) Unit cell parameters of **IV**: a = 10.398(2), b = 11.168(2), c = 18.499(4) Å, $\alpha = 103.14(3)$, $\beta = 92.80(3)$, $\gamma = 106.02(3)^{\circ}$, V = 1996.3(7) Å³, space group $P\bar{1}$, Z = 1(293 K).

^a BN: benzonitrile, NB: nitrobenzene.

an excellent system to study and it allowed us to obtain very important results due to the high quality of the single crystals and their low symmetry (space group $P\overline{1}$). It was shown that these salts are isostructural and stable organic metals down to helium temperatures [1,3]. Their structures are characterized by radical cation layers of the β'' -type alternating with layers of the complex anion $[A^+(NP^{2-})_2]^{3-}$. The NP anion is in a general position and ordered so that the NO ligand is unambiguously distinguished from the CN ligands. So, we had the possibility to analyze its geometry. The fact is that up to now a lot of crystallographic studies on NP with different mono-, bi- and tri-valent cations have been carried out using X-ray and neutron diffraction on a wide temperature region from 293 to 11 K. It has been shown that the NP anion is a very stiff molecular module in crystals: it has approximately the same geometry everywhere. However, this changes in the case of the $(ET)_4A(NP)_2$ crystals: the coexistence of the photochromic NP-anion with the conducting radical cation system in the same crystal is such that they affect each other even at room temperature. For instance, not only the geometry parameters of the NP anion change as compared to those of the $Na_2[NP] \cdot 2H_2O$ crystals in the ground state [6] but there are also two crystallographically independent ET molecules with different geometries and different number of short $ET \cdots NP$ type contacts [3]. Since the detailed shape of parts of the Fermi surface of the β'' -(ET)₄A[Fe(CN)₅NO]₂ salts is quite sensitive to either small changes of the transfer integrals (and thus, to the associated geometrical changes) [2] or to the band filling, it is very interesting to try to induce these changes by appropriate chemical modifications.

2.2. κ -(*ET*)₄[*RuNOBr*₅]·*BN* (*VII*) and κ -(*ET*)₄[*RuNOCl*₅]·*Solv*. (*X*)

The crystal structure of **VII** [a = 8.747(2), b = 12.088(1), c = 17.300(2) Å, $\alpha = 95.63(1)$, $\beta = 91.93(2)$, $\gamma = 94.79(2)^{\circ}$, V = 1812.3(5)Å³, $P\overline{1}$, Z = 1] consists of radical cation layers parallel to the *ab* plane alternating with layers of anions and solvent molecules BN. The octahedral anions [RuNOBr₅]²⁻ are located at inversion centers with the Ru– Br bond length of 2.456(9) Å *trans* to the nitrosyl group which is shorter than the average *cis* Ru–Br bond length of 2.520(1) Å. The Ru–N–O group is approximately linear, with an Ru–N–O bond angle of 178(4)° and an Ru–N bond distance of 1.76(2) Å. The conductivity of **VII** at room temperature is 1.2 Ω^1 cm⁻¹ and its temperature dependence has a semiconducting behavior. The salt **X** is isostructural to **VII** according to the X-ray diffraction data and also has semiconducting properties.

2.3. δ -(*ET*)₄[*RuNOCl*₅]_{1.33} (**IX**) and δ -(*ET*)₄[*RuNOBr*₅]_x (**VIII**)

It should be noted that only the average structure has been determined for IX [a = 6.721(1), b = 15.016(2), c =35.386(3) Å, $\alpha = 92.804(8)^{\circ}$, V = 3567.0(8) Å³, I2/c, Z =2]. Evidence for a commensurate (IX) and an incommensurate (VIII) structural modulation was found from the appearance of satellite reflections corresponding to 3a and approximately 2.5a for IX and VIII, respectively. A significant feature of the basic structures at room temperature is the two-dimensional (2D) network of the ET molecules, which is of δ -type. This 2D network is largely responsible for the metallic properties of these organic metals. The Fermi surface of IX is 2D and very similar to those of other δ-phases like δ -(ET)₄Cl₂·4H₂O [7] and δ -(ET)₂Br·3H₂O [8] but, since the ET charge in IX is 2/3+, the cross sectional area of the Brillouin zone for the complete closed portion is now 66.6%. The existence of structural modulations is likely to cause the M - I transitions at around 50 K (IX) and 80 K (VIII).

It was recently demonstrated that the family of isostrucsalts β'' -(ET)₄A[M(C₂O₄)₃]·Solv. (A = H₃O⁺; tural M = Fe, Cr; Solv. = BN, NB) of monoclinic symmetry (C2/c) exhibit both superconductivity and paramagnetism [9,10]. The only salt ($A = H_3O^+$, M = Fe, Solv. = C_5H_5N) of the same symmetry has been found to have an M - Itransition at 116 K [11]. All salts (A = K⁺, NH₄⁺, H₃O⁺; M = Fe, Cr, Co, Al; Solv. = BN) with orthorhombic symmetry (*Pbcn*) are semiconductors. We have synthesized new isostructural members of the family using DMF as solvent (Table 2). Their single crystals have C2/c symmetry and are stable organic metals down to low temperatures but not superconductors at T > 1.4 K. The electronic structure for our new salt with $A = NH_4^+$, M = Cr, Solv. = DMF and the previously known salt with $A = H_3O^+$, M = Fe, Solv. = BN [9] were calculated. Both salts have very similar Fermi surfaces. We thus suppose that some disorder in the salts with Solv. = DMF is probably one of the reasons for the lack of superconductivity. Furthermore, the terminal ethylene groups in ET exhibit disorder at room temperature which may persist at low temperatures. Thus, we have obtained for the first time new members of the β'' -

Table 2 Unit cell parameters of the β'' -(ET)₄A[M(C₂O₄)₃]·Solv. single crystals (space group *C*2/*c*, *Z* = 4)

MIII	Cr	Fe	Cr	Fe
A	$\mathrm{NH_4}^+$	$\mathrm{NH_4}^+$	\mathbf{K}^+	H_3O^+
Solv.	DMF	DMF	DMF	BN
a (Å)	10.307(1)	10.3143(8)	10.2807(8)	10.232(12)
b (Å)	19.888(2)	20.029(2)	19.880(3)	20.04(3)
c (Å)	34.825(4)	34.823(3)	35.009(2)	34.97(2)
β (°)	92.635(9)	92.613(8)	92.455(9)	93.25(11)
V, (Å ₃)	7131(1)	7186(1)	7149(1)	7157(13)
T (K)	293(2)	293(2)	293(2)	120(2)
Reference	This work	This work	This work	[9]

 $(ET)_4A[M(C_2O_4)_3]$. Solvent family having monoclinic symmetry and metallic properties down to helium temperatures.

3. Conclusion

Several organic conductors based on radical cation salts of ET and its analogs with octahedral mononitrosyl complexes are known to date. They can differ in composition, stoichiometry, type of the conducting radical cation layers in their crystals and, as a result, can also exhibit different physical properties. It is of special interest to compare the families of the (ET)₄A[Fe(CN)₅NO]₂ organic metals and (ET)₄A[M(- $C_2O_4)_3$]·Solv. (A = H₃O⁺, Solv. = BN, NB) organic superconductors. The crystals of both families have β'' -type conducting layers but the (ET)₄ structural building-block has a charge of 3+ for the former but 2+ for the latter. This observation prompts us to try to chemically modify the (ET)₄A[Fe(CN)₅NO]₂ system in several ways. First, doubly charged A^{2+} cations, such as Ba^{2+} , Sr^{2+} or Ca^{2+} , could be used in the synthesis instead of the mono charged cations. The structure of the salt is likely to remain unchanged after this replacement but the electron band filling will change from 5/8 to 3/4, which is a typical one for organic metals and superconductors. Second, the ligands in the coordination sphere of the Fe atom can be varied. It is expected that the replacement of the CN group by NH₃ or H₂O will not

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